R. A. Shoymardonov

ORGANIK KIMYO

II QISM

O‘zbekiston Respublikasi Oliy va o‘rta maxsus ta’lim vazirligi 5440400 - kimyo ta’lim yo‘nalishi talabalari uchun o‘quv qo‘llanmasi sifatida tavsiya etgan.

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Taqrizchilar

A.M.Yo'ldoshev - O'zbekiston Milliy universiteti organik kimyo kafedrasi dotsenti

O.M.Yoriyev - Buxoro davlat universiteti umumiy kimyo kafedrasi mudiri, kimyo fanlari doktori

S.Q.Qosimov - Buxoro gaz sanoati kolleji o'qituvchisi, kimyo fanlari nomzodi, dotsent

O'quv qo'llanmasi 5440400 – kimyo ta'lim yo'nalishi o'quv dasturi asosida yozilgan bo'lib, unda halqali (alitsiklik, aromatik, geterotsiklik) organik birikmalarning nomlanishi, izomeriyasi, olinish usullari, xossalari va muhim vakillari bayon qilingan. Har bir mavzuning oxirida talabalarning mustaqil yechishi uchun savol va mashqlar berilgan.

Kitobdan organik kimyo fani o'qitiladigan boshqa oliy o'quv yurtlari talabalari, kimyo o'qituvchilari, akademik litsey, kasb-hunar kollejlari va maktab o'quvchilari ham foydalanishlari mumkin.

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SO‘ZBOSHI

Organik kimyo - 5440400 – kimyo ta'lim yo‘nalishi talabalari o‘rganadigan asosiy fanlardan biridir. O‘quv dasturi talablariga to‘liq javob beradigan, o‘zbek tilida nashr qilingan darslik va o‘quv qo‘llanmalarining yetarli emasligi bu fanni o‘qitish va reyting nazoratlarini o‘tkazishda qiyinchilik tug‘diradi. Bu o‘quv qo‘llanma ana shu qiyinchiliklarni ma‘lum darajada bartaraf qilish maqsadida yozildi.

Qo‘llanmaning har bir mavzusida tayanch iboralar ajratib ko‘rsatilgan, uning oxirida savol va mashqlar keltirilgan.

O‘quv qo‘llanma qo‘lyozmasi bilan tanishib, qimmatli fikr va mulohazalarini bildirganliklari uchun O‘zbekiston Milliy universiteti organik kimyo kafedrasi dotsenti A.M.Yo'ldoshevga, Bu-xoro davlat universiteti umumiy kimyo kafedrasi mudiri, kimyo fanlari doktori O.M.Yoriyevga, Buxoro gaz sanoati kolleji o‘qituvchisi, kimyo fanlari nomzodi, dotsent S.Q.Qosimovga, BuxDU organik va fizkolloid kimyo kafedrasi mudiri, kimyo fanlari doktori, professor B.B.Umarovga, katta o‘qituvchi B.X.Ibotovga, o‘qituvchi S.F.Abdurahmonovga, BuxDU o‘zbek tilshunosligi kafedrasi mudiri M.Abuzalovaga samimiy minnatdorchilik bildiraman.

O‘quv qo‘llanma haqidagi barcha fikr va mulohazalar samimiyat bilan qabul qilinadi.

Muallif

KARBOTSIKLIK BIRIKMALAR

Karbotsiklik (izotsiklik) birikmalar molekulasida faqat uglerod atomlaridan iborat bitta yoki bir nechta halqa saqlagan organik birikmalardir. Karbotsiklik birikmalar o‘z navbatida alitsiklik va aromatik birikmalarga bo‘linadi.

I.Alitsiklik birikmalar

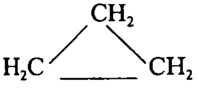
Alitsiklik birikmalarning sinflanishi, nomlanishi, izomeriyasi, olinish usullari, fizikaviy va kimyoviy xossalari, muhim vakillari.

Alitsiklik birikmalar xossalari bilan alifatik qator birikmalarga o‘xshash bo‘lgan halqali birikmalardir.

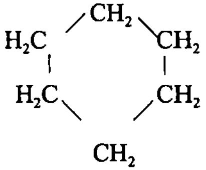
Sinflanishi, nomlanishi va izomeriyasi

Alitsiklik birikmalar halqasidagi uglerod atomlarining soniga qarab uch-, to‘rt-, besh- va hokazo (halqasida 34 ta uglerod atomi bor keton olingan) a‘zoli bo‘ladi. Uch va to‘rt a‘zoli sikllar kichik, besh, olti va yetti a‘zolilar odatdagi, sakkiz-o‘n bir o‘rta, o‘n bittadan ko‘p a‘zolilar esa **makrotsikllar** deyiladi. Alitsikllar to‘yingan (sikloalkanlar C_nH_{2n}) va to‘yinmagan (sikloalkenlar C_nH_{2n-2}, sikloalkadiyenlar C_nH_{2n-4}, sikloalkatriyenlar C_nH_{2n-6} va hokazo), shuningdek, bir -, ikki -, uch – va hokazo halqali bo‘lishi mumkin. Poliatsiklik birikmalar ikkita qo‘shni halqa uchun umumiy bo‘lgan uglerod atomlarining soniga qarab turli sinflarga bo‘linadi.

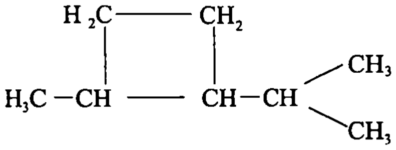
Ratsional nomenklaturada to‘yingan alitsiklik uglevodorodlar **polimetilenlar** deb aytiladi va ular halqadagi metilen guruhlarining soniga (tri, tetra, penta, geksa va hokazo) qarab nomlanadi. Agar halqada o‘rinbosar bo‘lsa, uning nomi asosiy halqa nomidan oldin aytiladi:



trimetilen

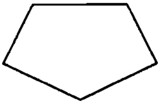


geksametilen

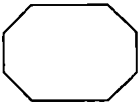


α - metil-β-izopropil-tetrametilen

Sistematik nomenklaturaga binoan to'yingan monotsiklik uglevodorodlar **sikloalkanlar** deyiladi. Ularning nomi siklo - old qo'shimchasi va tegishli alkan nomidan hosil qilinadi:

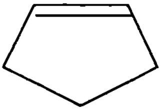


siklopentan

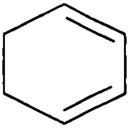


siklooktan

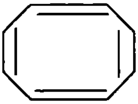
To'yinmagan monotsiklik uglevodorodlarning nomlari tegishli sikloalkan nomidagi – an qo'shimchasini – yen, - diyen va hokazoga almashtirish bilan hosil qilinadi. Qo'sh bog'larning holati iloji boricha eng kichik raqamlar bilan belgilanadi:



siklopenten

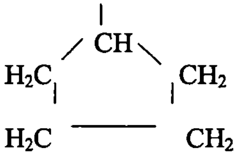


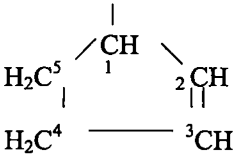
1,3 -siklogeksadiyen

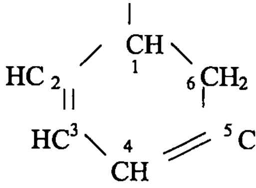


1,3,5,7 -siklooktatetrayen

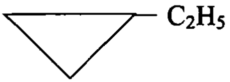
Sikloalkanlarning bir valentli radikallari –il, to'yinmagan monotsiklik uglevodorodlarning bir valentli radikallari esa –yenil, -diyenil va hokazo qo'shimchalarga ega:

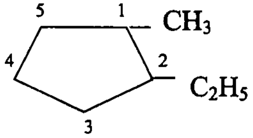

siklopentil

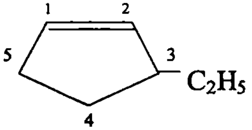

2-siklopenten-1-il

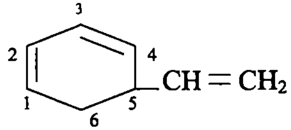

2,4-siklogeksadiyen-1-il

Almashingan alitsikllar quyidagicha raqamlanadi va nomlanadi:


etilsiklopropan

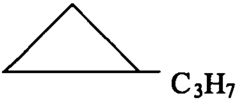

1-metil-2-etil-siklopentan

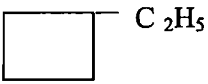

3-etilsiklopenten

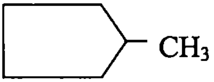

5-vinil-1,3-siklogeksadiyen

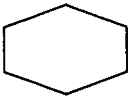
Alitsiklik uglevodorodlarning gomologlari va hosilalari uchun strukturaviy izomeriyaning quyidagi turlari xos:

1. Halqaning katta-kichikligiga bog'liq izomeriya:

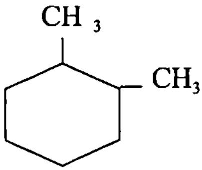

propilsiklopropan


etilsiklobutan

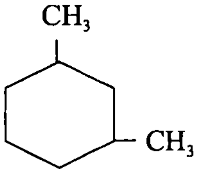

metilsiklopentan


siklogeksan

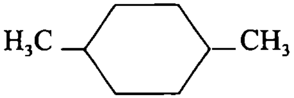
2. Halqadagi o'rinbosarlarning holati bilan bog'liq izomeriya:



1,2-dimetil-
siklogeksan

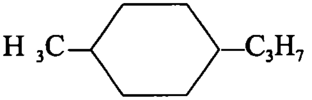


1,3 -dimetil-
siklogeksan

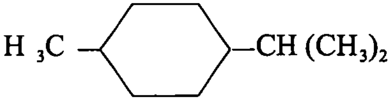


1,4-dimetil-
siklogeksan

3. Yon zanjirlar izomeriyasi:

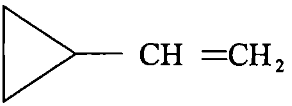


1-metil-4-propil-
siklogeksan

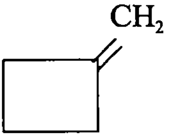


1 -metil-4-izopropil-
siklogeksan

4. Qo'sh bog'ning holati bilan bog'liq izomeriya:

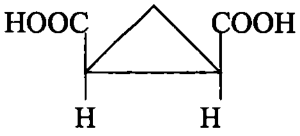


vinilsiklopropan

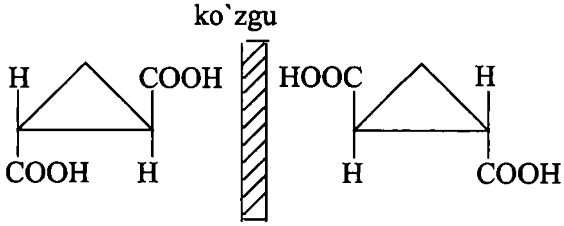


metilensiklobutan

Monoalmashingan, shuningdek, 1,1-dialmashingan sikloalkanlar stereoizomer hosil qila olmaydi. Halqasida ikkita bir xil asimmetrik uglerod atomi bor alitsiklik birikmalar uchta konfiguratsion izomer holida uchraydi:

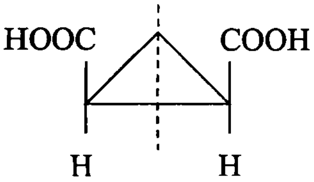


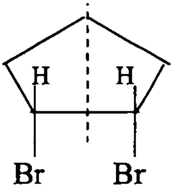
(1R , 2S) – siklo-
propan 1,2-dikarbonlar
kislota (sis-izomer)



(1R , 2R) va (1S , 2S) - siklo-
propan-1,2-dikarbon kislotalar
(trans-izomerlar)

Sis-izomerlarda ham ikkita asimmetrik uglerod atomi borligiga qaramasdan ular disimmetrik birikmalar hisoblanmaydi va ikkita enantiomer holida mavjud bo‘la olmaydi. Sis-izomerlar tuzilishiga qarasangiz, molekulalarning birinchi yarmi ikkinchi yarmining ko‘zgudagi aksi ekanligini ko‘rasiz:

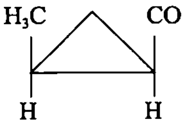


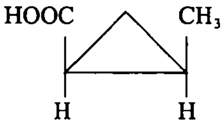


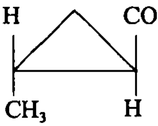
Shu bois sis-izomerlar mezo-birikmalar bo‘lib, optik faol emas.

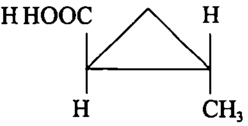
Trans-izomerlar esa disimmetrik birikmalardir. Ular ikkita enantiomer holida mavjud bo‘ladi. Bu enantiomerlarning har biri individual holda optik faol bo‘lib, ularni ajratib olish mumkin.

Molekulasida ikkita turli xil asimmetrik uglerod atomi bor alitsiklik birikmalar (masalan, 2-metilsiklopropankarbon kislota) to‘rtta konfiguratsion izomerlar holida mavjud bo‘ladi:


(1R,2S)-
I

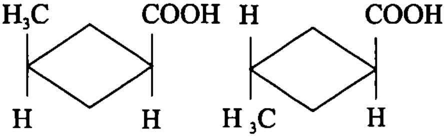

(1S,2R)-
II

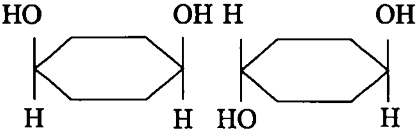

(1R,2R)-
III


(1S,2S)-
IV

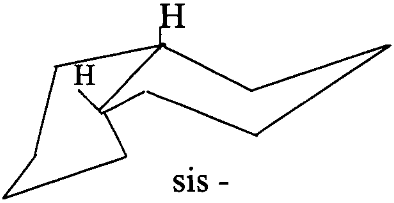
I va II sis-, III va IV esa trans-2- metilsiklopropankarbon kislotalardir. I va II, shuningdek, III va IV bir-biriga enantiomer, I bilan III va IV, shuningdek, II bilan III va IV bir-biriga diasteromerlardir.

Ikkita bir xil yoki turli xil o‘rinbosarlari bor 1,3-dialmashingan siklobutanlar, 1,4-dialmashingan siklogeksanlar, 1,5 – dialmashingan sikllooktanlar singari alitsiklik birikmalar molekulasida asimmetrik uglerod atomi yo‘qligi bois, ularning sis-izomerlari ham, trans - izomerlari ham enantiomerlar holida mavjud bo‘la olmaydi. Unday sis- va trans - izomerlar bir- biriga diastereomerlar hisoblanadi

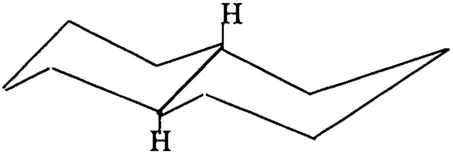

sis - trans -
3-metilsiklobutankarbon kislota


sis - trans -
siklogeksandiol -1,4

Sis- va trans - dekalinlar (bitsiklo-[4,4,0] dekanlar) ham molekulasida asimmetrik uglerod atomi yo‘q diastereomerlarga misol bo‘la oladi:



sis -



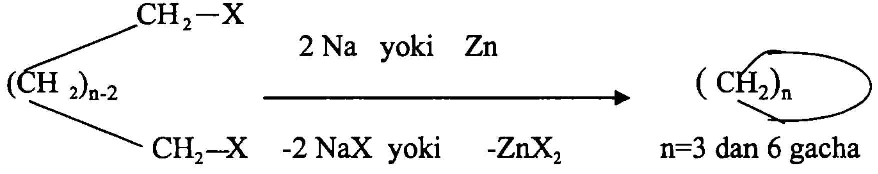
trans -

Olinish usullari

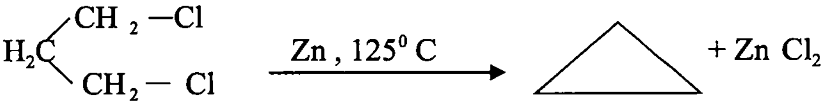
Ba‘zi neftlar tarkibida ko‘p miqdorda (Boku neftida 80% gacha) sikloalkanlar (siklopentan, siklogeksan va ularning gomologlari), oz miqdorda bu uglevodorodlarning karbon kislotalari (naften kislotalar) uchraydi. Shu bois sanoat uchun zarur siklogeksan va metilsiklogeksan neftdan fraksiyalab haydash usuli bilan olinadi. Sikloalkanlarning sintetik olinish usullari umumiy va maxsus usullarga bo‘linadi.

Umumiy usullar

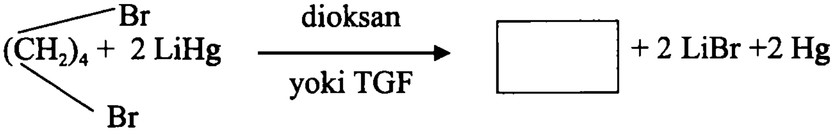
1. Digalogenalkanlarni natriy (Freynd, 1882-yil) yoki rux (G. G. Gustavson, 1887-yil) bilan degalogenlash:



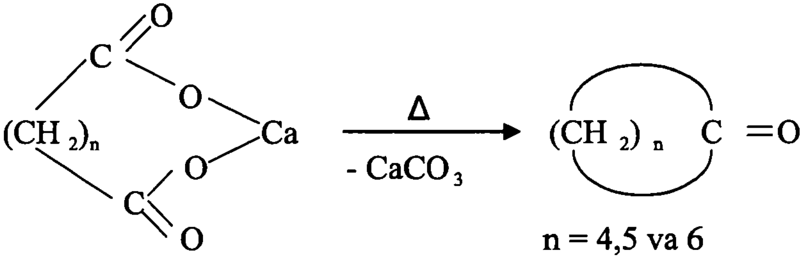
Siklopropan texnikada 1,3-dixlorpropanni degalogenlash bilan olinadi:



2. Siklobutan va siklopentanni olish uchun 1,4 – va 1,5- dibromalkanga litiy amalgamasi ta'sir ettiriladi (Konner,Uilson,1967-y):



3. Besh, olti va yetti a'zoli alitsikllar dikarbon kislotalar kalsiyli va bariyli tuzlarini piroliz qilish bilan olinadi (Vislitsenus, 1893 – y.):

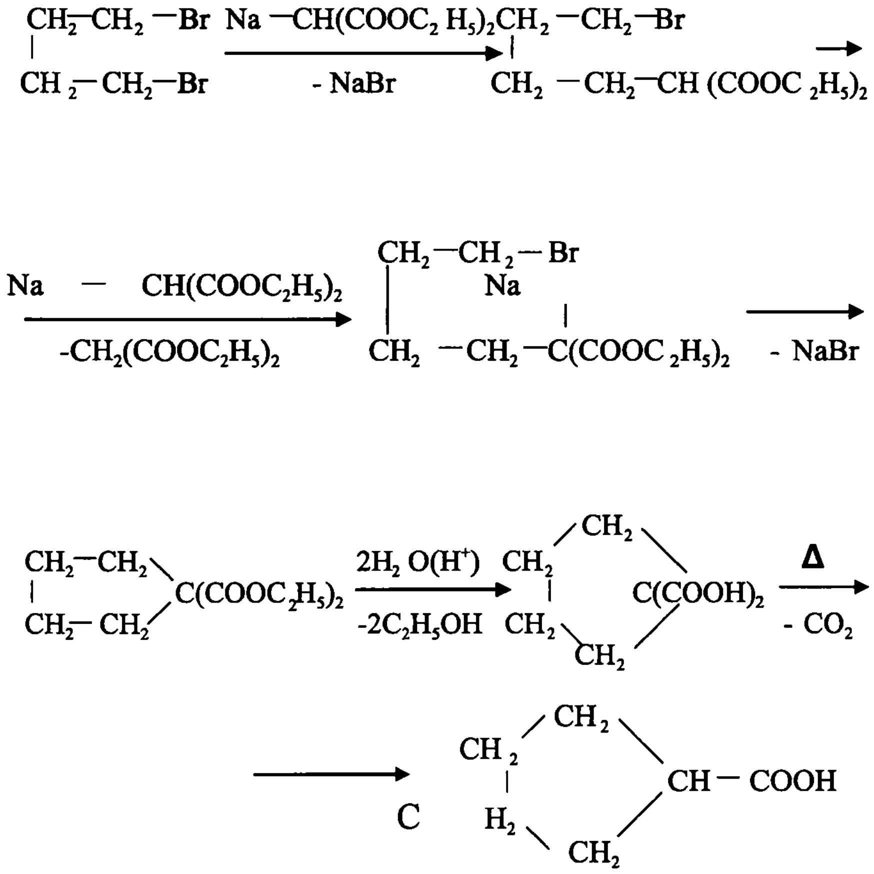


n = 4,5 va 6

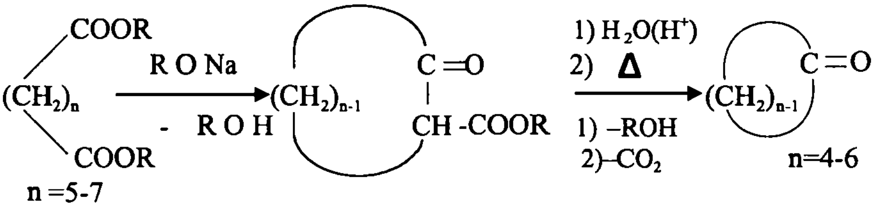
Hosil bo‘lgan halqali keton tegishli uglevodorodgacha qaytariladi.

Rujichka 1928–yilda dikarbon kislotalarning toriyli va seriyli tuzlarini piroliz qilib, katta (30 va undan ortiq uglerodi bor) sikllarni ham sintez qildi.

4. Uch-, to‘rt-, besh- va olti - a‘zoli sikllarni olish uchun natriymalon efiriga tegishli ravishda 1,2-, 1,3-, 1,4- va 1,5- digalogenalkan ta‘sir ettiriladi (Perkin, 1883- y.):



5. Besh-, olti- va yetti a'zoli halqali ketonlar tegishli dikarbon kislotalar murakkab efirlarining alkogolyatlar ta'sirida boradigan kondensatsiyasi (Dikman, 1901- y.) natijasida hosil bo'ladi:

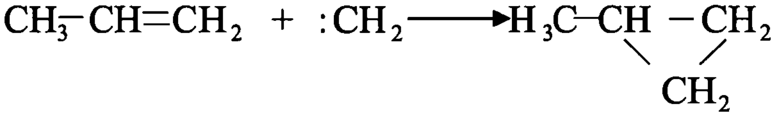


Maxsus usullar

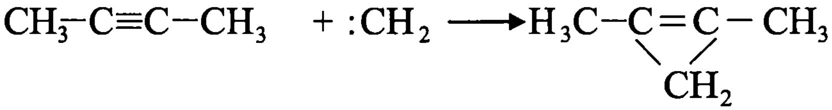
Siklopropanlarning olinishi

1. Alken yoki alkinlarga karbenlarning birikishi (siklobirikish):

a) $CH_2N_2 \longrightarrow :CH_2 + N_2$

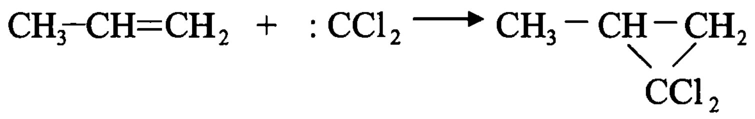


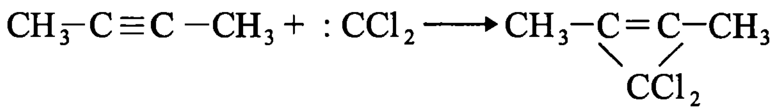
$CH_3-CH{=}CH_2 + :CH_2 \longrightarrow H_3C-\underset{\diagdown\ \ \diagup}{CH-CH_2}$ CH_2



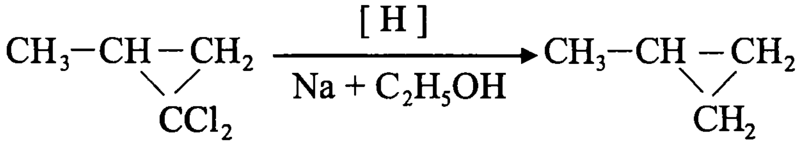
$CH_3-C{\equiv}C-CH_3 + :CH_2 \longrightarrow H_3C-C{=}C-CH_3$ (halqa: CH_2)

b) $CHCl_3 + R-ONa \longrightarrow NaCl + R-OH + :CCl_2$
dixlorkarben

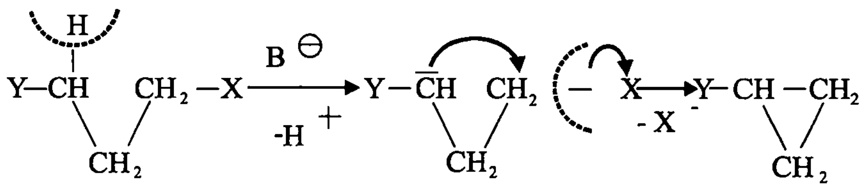




Yuqori unum bilan hosil bo'ladigan galogenalkilsiklopropan va galogenalkilsiklopropenlar qaytarilganda alkilsiklopropanlarga aylanadi:



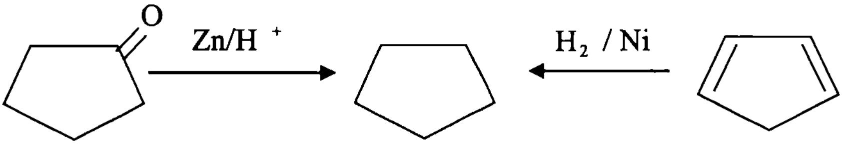
2. Elektrofil guruhlari bor β-almashingan birikmalarni degalogenlash:



$X = Cl, Br$
$Y = COR, COOR, C{\equiv}N, NO_2$

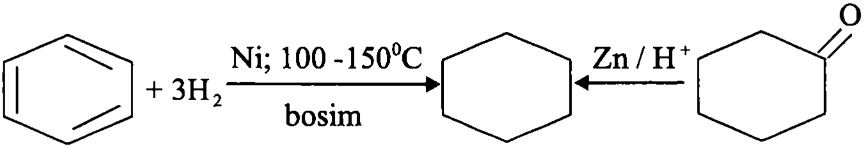
Siklopentanning olinishi

Sintetik siklopentan uning kislorod saqlagan yoki to'yinmagan hosilalaridan olinadi:



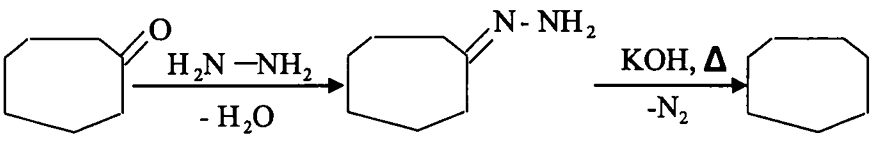
Siklogeksanning olinishi

Siklogeksan va uning gomologlari tegishli aromatik uglevodorodlarni katalitik gidrogenlash yoki siklogeksanonlarni qaytarish bilan olinadi:



Siklogeptanning olinishi

Siklogeptan siklogeptanonni Kijner usulida qaytarish bilan olinadi:



Fizikaviy xossalari

Sikloalkanlar gomologik qatorining birinchi va ikkinchi vakili (siklopropan va siklobutan) –gaz , 5 tadan 10 tagacha uglerodi bor birikmalar- suyuqlik, yuqori sikloalkanlar esa qattiq moddalardir. Sikloalkanlarning solishtirma og'irligi tegishli alkanlarnikiga nisbatan katta, qaynash va suyuqlanish harorati esa yuqoridir (1-jadval):

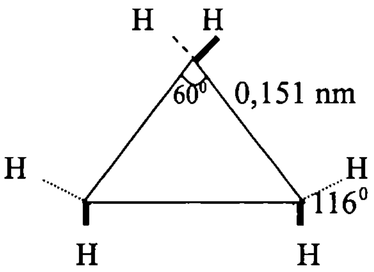
1-jadval

Sikloalkanlarning fizikaviy doimiyliklari

Nomi	Suyuqlanish harorati ^{0}C	Qaynash harorati ^{0}C	Zichligi D_4^{20}
Siklopropan	-126,9	-33	0,688(qaynash haroratida)
Siklobutan	- 80	13	0,7038
Metilsiklopropan	177,2	0,7	0,6912
Siklopentan	94,4	49,3	0,7460
Metilsiklobutan	-149,3	36,8	0,6931
Etilsiklopropan	-149,4	34,5	0,6770
Siklogeksan	6,5	80,7	0,7781
Metilsiklopentan	-142,2	71,9	0,7488
Etilsiklobutan	-142	71,5	0,7450
Propilsiklopropan	--	68,5	0,7120 (16,7 ^{0})

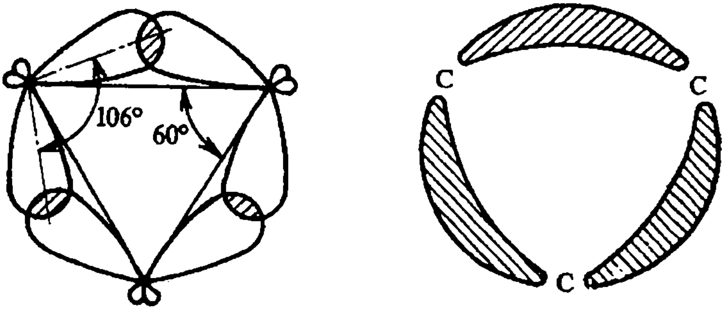
Tuzilishi

Siklopropan teng tomonli uchburchak tuzilishiga ega yagona tekis karbotsikl bo‘lib, halqasi oson uziladi:



Siklopropan halqasi beqarorligining sabablaridan biri qo‘shni uglerod atomlari bilan bog‘langan vodorodlaming tekislikning ustida va ostida energetik jihatdan noqulay bo‘lgan to‘silgan holatda joylashganligidir.

Siklopropan C - C bog‘larining hosil bo‘lishida sof sp^2 – yoki sof sp^3 – gibridlanmagan atom orbitallar bir-birini birlashtiruvchi to‘g‘ri chiziq yo‘nalishida emas, balki undan tashqarida qisman qoplaydi. Buning natijasida o‘z tabiati va mustahkamligiga ko‘ra σ- va π - bog‘lar oralig‘idagi holatni egallagan, qisman to‘yinmagan xarakterga ega, egik «banan bog‘lari» hosil bo‘ladi va bog‘lar orasidagi burchaklar 106^0 C gacha kattalashib, kuchlanishga ega (1-rasm):



1-rasm. Siklopropanning tuzilishi (a) va «Banan bog‘lari» (b)

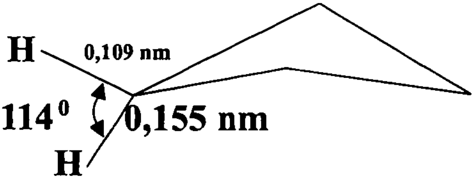
Siklopropanning bitta metilen guruhi uchun hisoblangan yonish issiqligi va zahira energiyasi siklogeksanning yonish issiqligi va zahira energiyasiga nisbatan eng katta (2-jadval). Shu bois siklopropanning C – C bog‘lari siklogeksanning C – C bog‘lariga nisbatan oson uziladi.

2 – jadval

Sikloalkanlarning yonish issiqligi

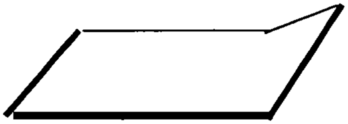
Sikloalkan	Bitta metilen guruhi uchun hisoblangan yonish issiqligi, kJ/mol	Siklogeksanga nisbatan ortiqcha energiya, kJ / mol.
Siklopropan	698,0	38.5
Siklobutan	686.7	27.2
Siklopentan	666.4	5.5
Siklogeksan	659.5	0.0
Siklogeptan	663.3	3.8
Siklooktan	664.5	5.0
Siklononan	664.4	5.5
Siklodekan	664.5	4.6

Siklobutanda vodorod atomlari o'rtasida ichki molekulyar o'zaro itarilish kuchlari borligidan halqadagi to'rtta uglerod atomi bir tekislikda yotmaydi. Siklobutan halqasining notekis tuzilganligi rentgenografiya, elektronografiya, diyelkometriya, YAMR-spektroskopiya va boshqa usullar yordamida aniqlangan:

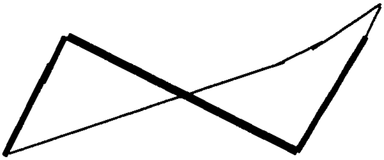


Siklobutanning valent burchaklari kamroq kuchlangan bo'lib, atom orbitallari bir-birini to'liqroq qoplaydi. Shuning uchun ham u siklopropanga nisbatan barqarorroq bo'ladi.

Siklopentan molekulasi tekis tuzilganda edi, barcha vodorod atomlari to'silgan holatda joylashardi. Bunday konformer energetik noqulay bo'lgani sababli siklopentan va uning hosilalari notekis tuzilgan. Vodorod atomlari orasida itarilish kuchlari borligi tufayli siklopentandagi C – C bog'lar (0,155 nm) alkanlardagi C –C bog'larga nisbatan biroz uzunroq, bog'lanmagan uglerod atomlari orasidagi masofa (0,244 nm) esa, normal alkanlardagi (0,255 nm) ga nisbatan qisqa. Almashingan siklopentanlar konvert va yarim kreslo yoki tvist konformatsiyalarda mavjud bo'lishi mumkin:

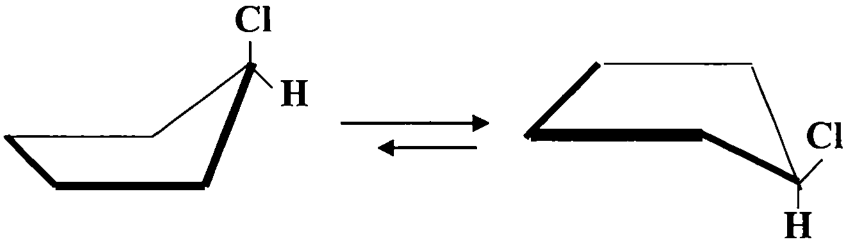


konvert

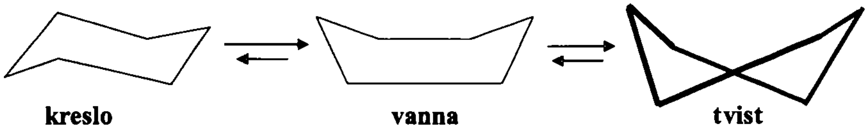


yarim kreslo yoki tvist

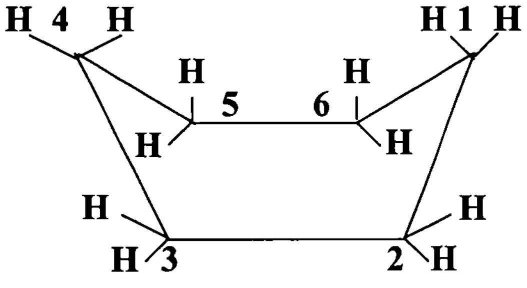
Konvert konformatsiyada bitta uglerod atomi qolgan to‘rtta uglerod atomi hosil qilgan tekislikdan tashqarida joylashgan. Yarim kreslo yoki tvist konformatsiyada esa ikkita qo‘shni uglerod atomidan bittasi qolgan uchta uglerod atomi yotgan tekislikning ustida, ikkinchisi esa ostida joylashgan. Bu ikkala konformatsiyadan qaysi birining energetik qulayroq bo‘lishi o‘rinbosarlarga bog‘liq. Masalan, xlortsiklopentanda xlor psevdoekvatorial holatni egallagan konformer energetik qulayroq:



Siklogeksan molekulasi tekis tuzilganda edi, uning barcha vodorod atomlari energetik noqulay to‘silgan holatda joylashgan, uglerod atomlari orasidagi burchaklar esa, 120^0 ga teng bo'lar edi. Tabiiyki, bunday sikl beqaror bo'ladi. Haqiqatda olti a'zoli sikl eng barqaror hisoblanadi. Tadqiqotlar siklogeksanni kreslo, vanna va tvist shakllarda mavjudligini ko'rsatdi:

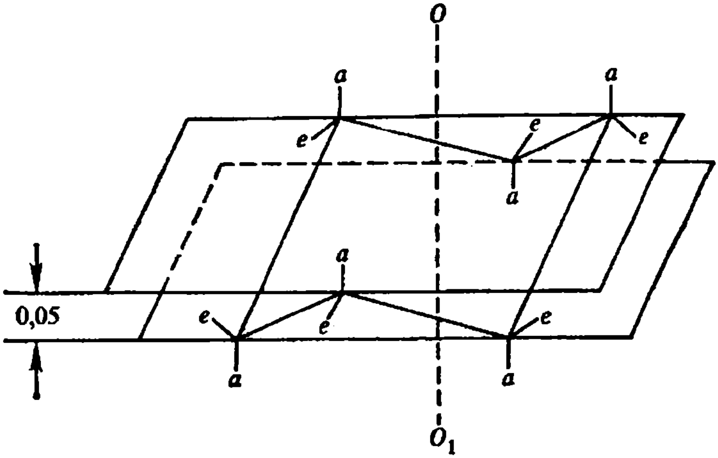


Bu konformerlardagi valent burchaklari 109^{0}28^1 ga teng. Demak, ularda kuchlanish yo'q. Vanna konformatsiyasida to'rtta (2,3,5,6) uglerod atomlari bir tekislikda, ikkitasi (1 va 4) esa boshqa tekislikda joylashgan:



Vanna va tvist shakllarida 1- va 4 – uglerod atomlari bilan bog'langan vodorodlar orasida Van-der-Vaals itarish kuchlari bor. Shu bois kreslo shakliga nisbatan vannada 29,8 kJ / mol, tvist shaklida esa 22,2 kJ / mol energiya ko'p. Buning natijasida vanna shakli harakatchan bo'lib, tvist shakliga o'tadi. Chunki, tvist shaklida to'liq to'silgan konformatsiyalar yo'qligidan, u vannaga nisbatan energetik birmuncha qulay (6,7 kJ / mol kam energiya saqlaydi).

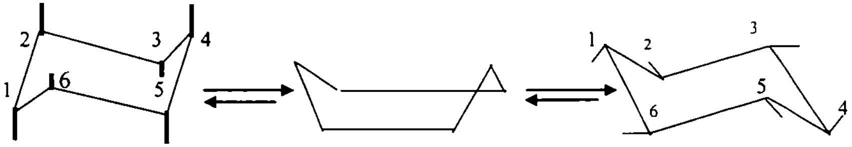
Kreslo konformatsiyasida qo'shni uglerod atomlari bilan bog'langan vodorod atomlari bir-biriga nisbatan tormozlangan holatda joylashganligi sababli, xona haroratida siklogeksan molekulalarining 99,9 % shu konformatsiyada mavjud bo'ladi. Boshqacha aytganda, kreslo shaklidagi mingta molekulaga vanna shaklidagi bitta molekula to'g'ri keladi. Kreslo konformatsiyasida uglerod atomlari uchtadan ikkita parallel tekislikda joylashgan bo'lib, tekisliklar orasidagi masofa 0,05 nm ga teng (2-rasm):



2- rasm. Siklogeksanning kreslo konformatsiyasi

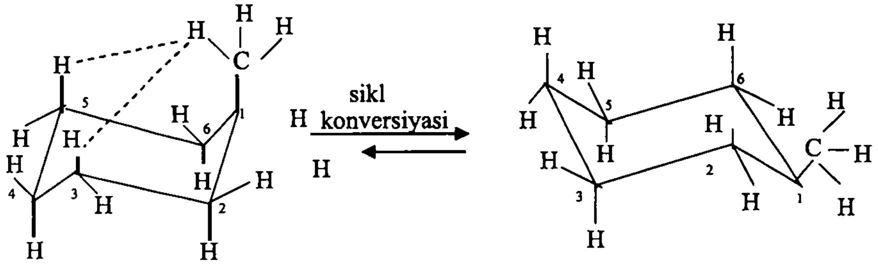
Kreslo konformatsiyasida siklogeksan molekulasidagi 12 ta C – H bog'ining 6 tasi bir-biriga va uchinchi tartibli simmetriya o'qiga parallel bo'lib, halqadan yuqoriga va pastga yo'nalgan. Bu bog'lar aksial (ɑ) bog'lar deyiladi. Qolgan 6 tasi halqaning yon tomonlariga yo'nalgan bo'lib, ekvatorial (e) bog'lar deyiladi.

Siklogeksan molekulasi bir-biriga ekvivalent bo'lgan ikkita kreslosimon konformatsiya holida mavjud bo'lishi mumkin. Kresloning bir konformatsiyasidan boshqasiga o'tganda (bunday o'tish vanna konformatsiyasi orqali amalga oshadi) aksial vodorod atomlari ekvatorial vodorod atomlariga, ekvatorial vodorod atomlari esa aksial vodorod atomlariga aylanadi:



Bunday aylanish kreslo shaklining konversiyasi deyiladi va u juda tez (sekundiga 10^6 aylanish) amalga oshadi. Inversiya jarayonida kimyoviy bog'lar uzilmaydi va yangidan hosil bo'lmaydi, faqatgina konformatsiya o'zgaradi, xolos.

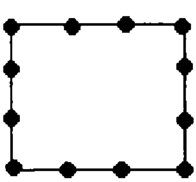
Monoalmashingan siklogeksanlar (masalan, metiltsiklogeksan) ning ikkita kreslosimon konformatsiyasi teng qiymatli emas. Chunki metil guruhi ularning birida aksial, ikkinchisida esa ekvatorial holatni egallaydi:



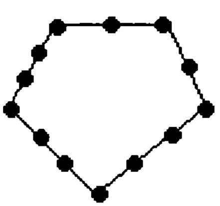
a – metilsiklogeksan e - metilsiklogeksan

a–Metilsiklogeksanda metil guruh bilan 3- va 5- holatlardagi aksial vodorod atomlari yaqinlashgani bois, ular orasida fazoviy (1,3-diaksial) ta‘sirlashuv ro‘y beradi. e-Metilsiklogeksanda esa bunday ta‘sirlashuv yo‘q. Shuning uchun ham bu konformatsiyalar orasidagi energetik farq 6,7 kJ/ mol ga teng bo‘lib, 25^0 C da metilsiklogeksan molekulalarining 95 % i ekvatorial konformatsiyada, faqat 5 % igina aksial konformatsiyada mavjud bo‘ladi. Siklogeksan, metilsiklogeksan va boshqa almashingan siklogeksanlarning konformatsiyalari molekulalarning yagona shakli mavjud bo‘lmaydigan geometrik shakllaridir.

Siklododekan notekis to‘rtburchak, siklotridekan esa notekis beshburchak shakliga ega:



siklododekan



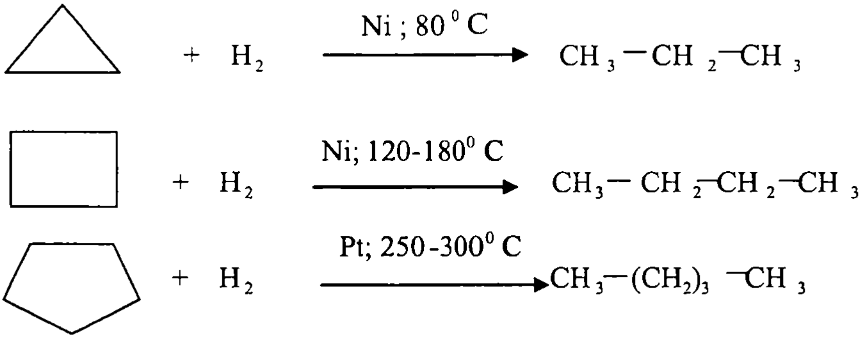
siklotridekan

12 tadan ko‘p a‘zoli alitsikllar katta konformatsion harakatchanlikka ega. C – C bog‘lar atrofida aylanishning deyarli erkinligi natijasida bu makrotsikllarda sis-trans-izomerlar mavjud bo‘la olmaydi, bularda ma‘lum konformatsiyalarni aniqlash ham qiyin.

Kimyoviy xossalari

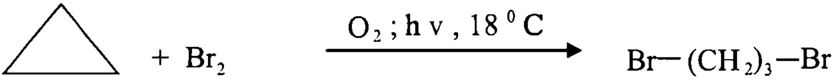
Sikloalkanlar uchun asosan halqaning ochilishi, halqaning torayishi va kengayishi, shuningdek, vodorod atomlarining almashinishi bilan boradigan reaksiyalar xos.

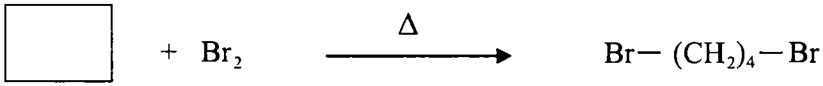
Katalitik gidrogenoliz. Vodorodning katalitik birikishi alitsiklning barqarorligiga qarab turli sharoitda boradi:



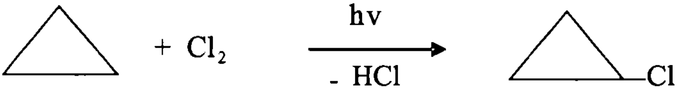
Siklogeksandan boshlab sikloalkanlar gidrogenoliz reaksiyasiga kirishmaydi.

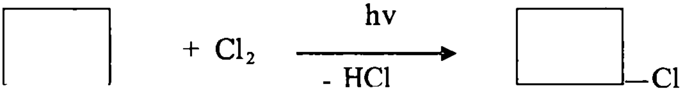
Galogenlarning ta‘siri. Brom siklopropanga kislorod va nur ishtirokida, siklobutanga esa qizdirilganda birikadi:



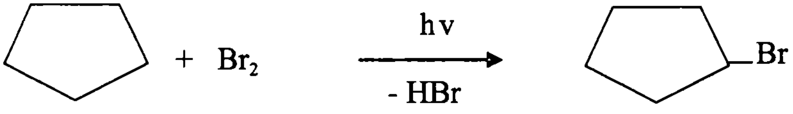


Siklopropan va siklobutanni xlorlaganda vodorod atomlari almashinadi:

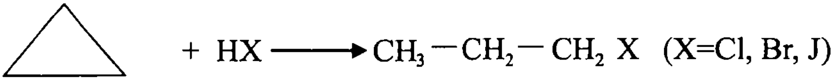


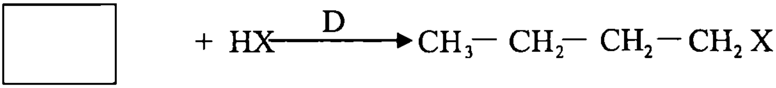


Siklopentan va yuqori sikloalkanlarni galogenlaganda, faqat vodorod atomlari almashinadi:

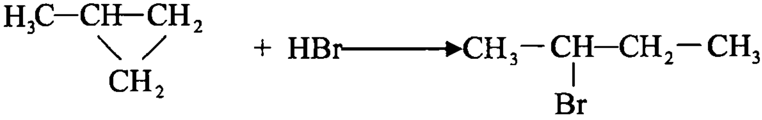


Gidrogalogenlash. Siklopropan vodorod galogenidlarni oson, siklobutan esa qiyin biriktiradi:





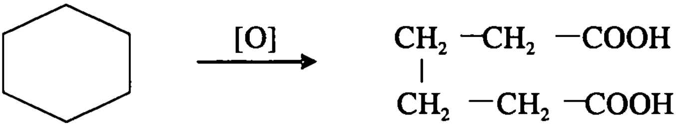
Vodorod galogenidlar siklopropanning gomologlariga V.V. Markovnikov qoidasiga muvofiq ionli mexanizmda birikadi:



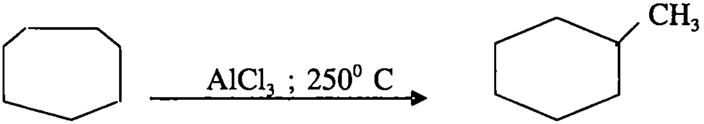
$$H_3C-\underset{\diagdown\ \diagup\atop CH_2}{CH-CH_2} + HBr \longrightarrow CH_3-\underset{Br}{\underset{|}{CH}}-CH_2-CH_3$$

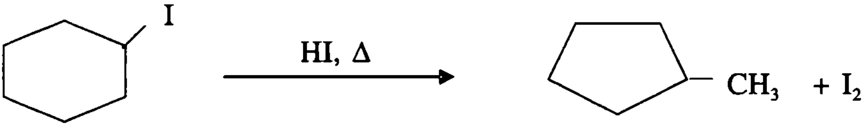
Siklopentan, siklogeksan va yuqori sikloalkanlar vodorod galogenidlarni biriktirmaydi.

Oksidlanishi. Sikloalkanlarning oksidlanish reaksiyalari halqaning tuzilishi va oksidlovchining tabiatiga qarab turli yo'nalishda boradi. Sikloalkanlar, hatto siklopropan va siklobutan ham oksidlovchilar ta'siriga chidamli. Kuchli oksidlovchilar bilan yuqori haroratda oksidlanganda halqa uzilib, tegishli dikarbon kislotalar hosil bo'ladi:

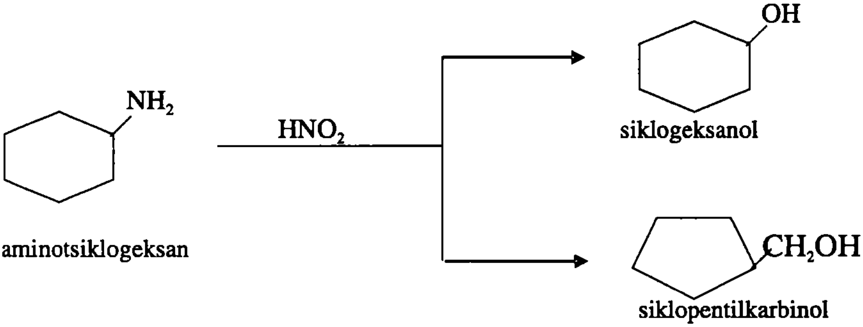


Alitsikllarning torayishi va kengayishi. $AlCl_3$ yoki HI bilan qizdirilganda sikl torayadi:

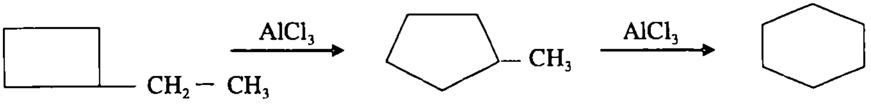




Nitrit kislota ta‘sirida ham sikl torayadi:



Siklning kengayishi $AlCl_3$ ishtirokida sovuqda boradi:



Muhim vakillari

Siklopropan – 34⁰ C da qaynaydigan rangsiz gaz bo'lib, tibbiyotda umumiy anesteziya uchun narkotik modda sifatida ishlatiladi.

Siklobutan – 12.5⁰ C da qaynaydigan rangsiz gaz bo'lib, organik sintezda qo'llaniladi.

Siklopentan – 49,5⁰ C da qaynaydigan rangsiz suyuqlik bo'lib, laboratoriyada siklopentadiyenni gidrogenlash bilan olinadi. U organik sintezda ishlatidadi.

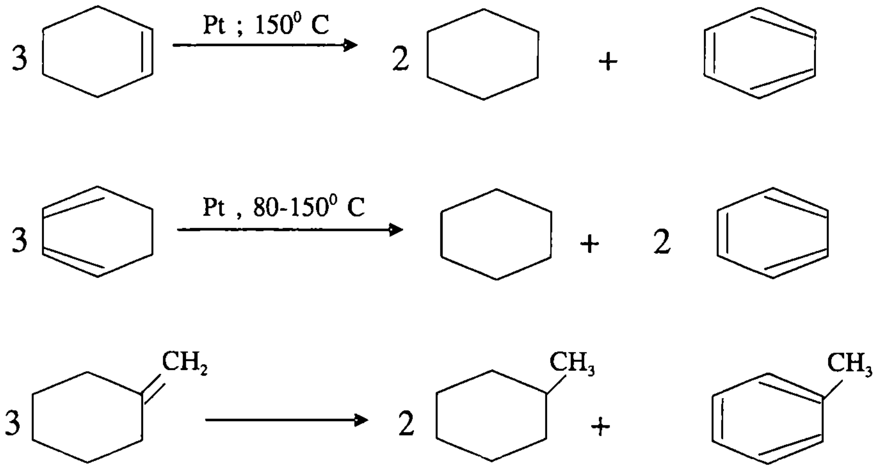
Siklopenten – 44,2⁰ C da qaynaydigan rangsiz suyuqlik bo'lib, siklopentanolni degidratlash yo'li bilan olinadi. U organik sintezda siklopentan hosilalarini olishda ishlatiladi.

Siklopentadiyen – 41⁰ C da qaynaydigan, o'ziga xos hidli suyuqlik bo'lib, organik sintezda insektitsid, ferrotsen va boshqa metallotsenlarni olishda ishlatiladi.

Siklogeksan – 80,7⁰ C da qaynaydigan rangsiz suyuqlik bo'lib, benzolni katalitik gidrogenlab olinadi. U erituvchi sifatida, kaprolaktam va adipin kislotani olishda xom ashyo sifatida ishlatiladi.

Siklogeksen – 83⁰ C da qaynaydigan, o'tkir hidli rangsiz suyuqlikdir. U siklogeksanolni degidratlash bilan olinadi. Siklogeksen alkenlarga xos reaksiyalarga kirishadi.

Siklogeksen, siklogeksadiyen va ularning gomologlari platina yoki palladiy ishtirokida qizdirilganda vodorod atomlarini qayta taqsimlash (disproportsionirlash) xossasiga ega:



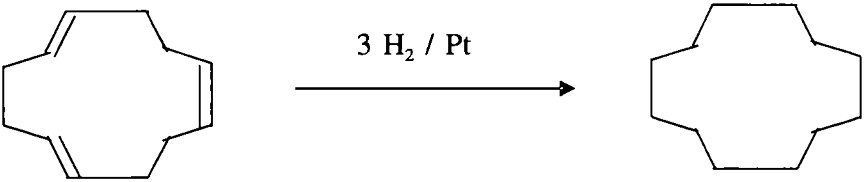
Siklogeksan, benzol va ularning gomologlaridan siklogeksen, siklogeksadiyen va ularning gomologlarini olib bo'lmaydi. Shuning uchun ham N.D. Zelinskiy 1911- yilda bunday reaksiyalarni qaytmas kataliz deb atadi.

Siklogeptan 119⁰ C da qaynaydigan, suvda erimaydigan, o'ziga xos hidli, rangsiz suyuqlikdir. Siklogeptan va uning gomologlari kimyoviy xossalari bilan alkanlarni eslatadi. U organik sintezda ishlatiladi.

Siklooktan 145⁰ C da qaynaydigan, kamfora hidli, rangsiz suyuqlik bo'lib, siklooktatetrayenni katalitik gidrogenlash bilan olinadi. U organik sintezda ishlatiladi.

Siklooktatetrayen 142⁰ C da qaynaydigan, oson polimerlanadigan, sariq rangli suyuqlikdir. U atsetilendan olinadi.

Siklododekan siklododekatriyen – 1,5,9 ni katalitik gidrogenlash bilan olinadi:



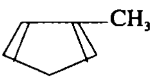
Siklododekan poliamidlar sintezida xom ashyo sifatida ishlatiladi.

Dekalinlar. Naftalinni katalitik gidrogenlaganda sis-va trans –dekalinlar aralashmasi hosil bo'ladi. Sis-dekalin 194,6⁰ C trans-dekalin esa 185,5⁰ C da qaynaydigan, o'ziga xos hidli, suvda erimaydigan, rangsiz suyuqliklardir. Dekalinlar kimyoviy xossalari bilan siklogeksanga o'xshaydi. Sis- va trans- dekalinlar aralashmasi erituvchi sifatida ishlatiladi.

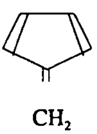
Savol va mashqlar

1. Birikmalarni nomlang:

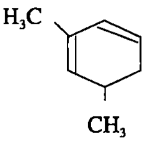
a)



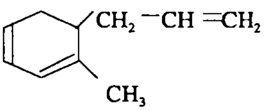
b)



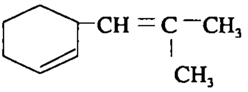
d)



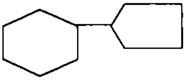
e)



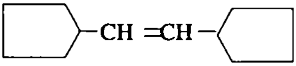
f)



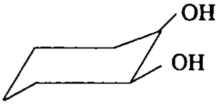
g)



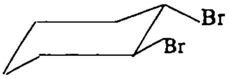
h)



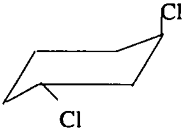
i)



j)



k)



2. Birikmalarning tuzilish formulalarini yozing:

a) 2,6 – ditsiklopropilgeksan; b) 1,2 – ditsiklopentiletan;

d) 2-metil-3-siklopenten-1-ol; e) metoksitsiklobutan;

f) 1-metil-4-izopropilidensiklogeksen (terpinolen);

g) spiro [2,6] nonan; h) bitsiklo [5,3,1] undekan;

i) sis-1,2-siklopentandiol; j) trans-1,4-dixlorsiklogeksan.

3. C_7H_{16} tarkibli sikloalkanlar nechta strukturaviy izomer holida uchrashi mumkin? Ularning tuzilish formulalarini yozing va nomlang.

4. Metilsiklogeksadien izomerlarining tuzilish formulalarini yozing va ularni nomlang.

5. Quyidagi birikmalarning qaysilari enantiomerlar holida mavjud bo‘la olmaydi?

a) 1,1-dibromsiklobutan; b) trans-1,2-dibromsiklopropan;

d) sis-1,2-dixlorsiklopentan; e) sis-1,4-dibromsiklogeksan;

f) trans-1,4-dibromsiklogeksan, g) trans-1,3-dibromsiklo-butan;

h) trans-1,2-dixlorsiklopentan.

6. Quyidagi birikmalarga rux ta‘sir ettirganda qanday sikloalkanlar hosil bo‘ladi?

a) 1,4-dibrompentanga; b) 1,3-dibrombutanga;

d) 1,3-dibrompentanga; e) 1,4-dibrom-2,3-dimetilbutanga;

f) 1,4-dibrom-2-metilpentanga .

7. a) siklopentan; b) siklogeptan olish uchun qanday kislotalarning kalsiyli tuzlari piroliz qilinadi?

8. Sintezlar sxemasini tuzing :

a) atsetilen   siklopropan
b) atsetilen   siklogeksan
d) atsetilen   siklopentan
e) 1-brom-3-xlorpropan   siklopropan karbon kislota
f)siklopropan karbon kislota   siklopropen
g)natriy etilat   siklopentan

10. Quyidagi trienlarning termik sikllanishidan qanday birikmalar hosil bo'ladi?

a) (2E, 4Z, 6E)-2.4.6-oktatrien;
b) (2E, 4Z, 6Z)-2,4,6-oktatrien.

11. Sintezlar sxemasini tuzing:

a) 1,3-dibrompropan   siklobutankarbon kislota
b) 1,3-dibrompropan   1,3-siklogeksandikarbon kislota
d) 1,7-dibromgeptan   siklooktan

12. Reaksiyalarni davom ettiring :

a) 1,3-siklopentadiyen + 2 Br_2 •••
b) 1,3-siklopentadiyen + HBr   •••
d) 3-siklopentadiyen + malein angidrid   •••

13. a) siklopentanni ; b) 1,3,5,7- siklooktatetrayenni kuchli oksidlovchi bilan oksidlanganda qanday birikmalar hosil bo'ladi?

14. Siklodekanni transannulyar sikllanishidan hosil bo'ladigan birikmani nomlang.

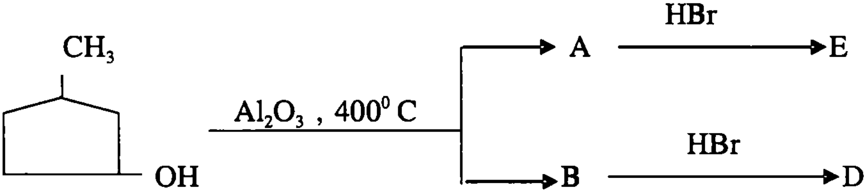
15. Atsetilen, siklogeksan va noorganik moddalardan metiltsiklogeksilkarbinolni sintez qilish sxemasini tuzing. Bu spirtni oksidlaganda qanday birikma hosil bo'ladi?

16. Siklogeksanon bilan: a) sianid kislota; b) gidroksilamin; d) PCl_5; e) etilmagniy bromid orasida boradigan reaksiyalar tenglamalarini yozing.

17. Quyidagi birikmalarni platina yoki palladiy ishtirokida qizdirganda (qaytmas kataliz) qanday uglevodorodlar hosil bo'ladi?

a) 1-metil-4-izopropil-1-siklogeksenni;
b) 1-etil-1-siklogeksenni;
d) 1,2-dimetil-1,3-siklogeksadiyenni.

18. Quyidagi sxema bo‘yicha boradigan reaksiyalar tenglamalarini tuzing:

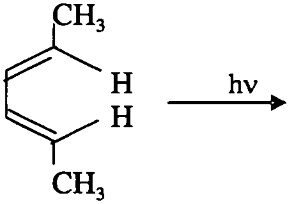


19. Malein angidridni biriktiradigan, palladiy ishtirokida qizdirganda ikki atom vodorodni ajratib, toluolga aylanadigan C_7H_{10} tarkibli optik faol moddaning tuzilishini aniqlang.

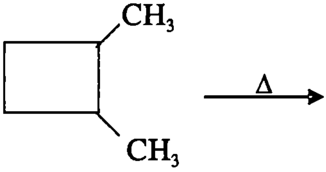
20. Metiltsiklopropan bilan: a) bromid kislota; b) triftorsirka kislota orasida boradigan reaksiyalar tenglamalarini yozing. Siklogeksan bu kislotalarni biriktiradimi?

21. Quyidagi elektrotsiklik reaksiyalar natijasida qanday birikmalar hosil bo‘ladi?

a)



b)



AROMATIK BIRIKMALAR

Aromatik birikmalar molekulasida bir yoki bir necha benzol yadrosini saqlagan karbotsiklik birikmalarning katta guruhidir. Dastlabki vakillari tabiiy smola va balzamlardan ajratib olingani va xushbo'y bo'lgani uchun ularga «Aromatik birikmalar» deb nom berilgan. Lekin ko'p aromatik birikmalar xushbo'y bo'lmasa ham, bu tarixiy atama fanda saqlanib qoldi.

Aromatik uglevodorodlarga arenlar deyiladi. Arenlar molekulasidagi sikllarning soniga qarab, mono – va politsiklik arenlarga bo'linadi.

II. Benzol qatori uglevodorodlari

Benzolning tuziiishi, Xyukkelning aromatiklik qoidasi, nobenzoid aromatik birikmalar, antiaromatik annulen va ionlar, benzolning valent izomerlari.

Benzol qatori uglevodorodlarining nomlanishi, izomeriyasi, olinish usullari, fizikaviy xossalari va spektral tavsifi, kimyoviy xossalari. Elektrofil almashinish reaksiyalari uchun yo'naltirish (oriyentatsiya) qoidalari.

Muhim vakillari. Savol va mashqlar.

Aromatik uglevodorodlarning bosh vakili benzoldir. Uni 1825- yilda Faradey yoritgich gazdan ajratdi. 1834-yilda E. Mitcherlix benzolni benzoy kislota tuzini qizdirib oldi va uning elementar tarkibi – C_6H_6 ni aniqladi. 1845-yilda A. Gofman benzolni toshko'mir smolasidan ajratdi. Keyinchalik Yu. Libix bu moddaga benzol deb nom berdi.

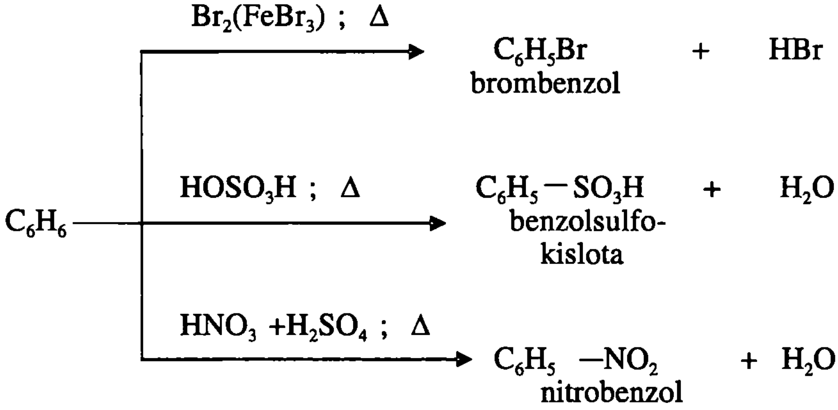
Benzolning tuzilishi

Benzolning tuzilishini o'rganish uzoq yillar davomida organik kimyoning markaziy muammolaridan biri edi. Benzol kashf qilingandan boshlab olimlarning ko'p avlodi bu murakkab va qiziqarli muammo ustida tadqiqot olib bordi.

Benzol tarkibi (C_6H_6) ga qaraganda, u xuddi atsetilen (C_2H_2) singari to‘yinmagan bo‘lishi kerak. Lekin u barqarorligi, birikish va oksidlanish reaksiyalariga qiyin kirishishi bilan to‘yinmagan birikmalardan keskin farq qiladi.

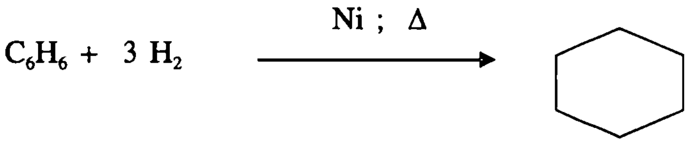
Benzol odatdagi sharoitda bromli suvni rangsizlantirmaydi, kaliy permanganat eritmasi ta‘sirida oksidlanmaydi, sulfat kislota bilan reaksiyaga kirishmaydi.

U faqat maxsus sharoit (qizdirish, katalizator) bo‘lgandagina brom, sulfat va nitrat kislotalari bilan almashinish reaksiyalariga kirishadi:



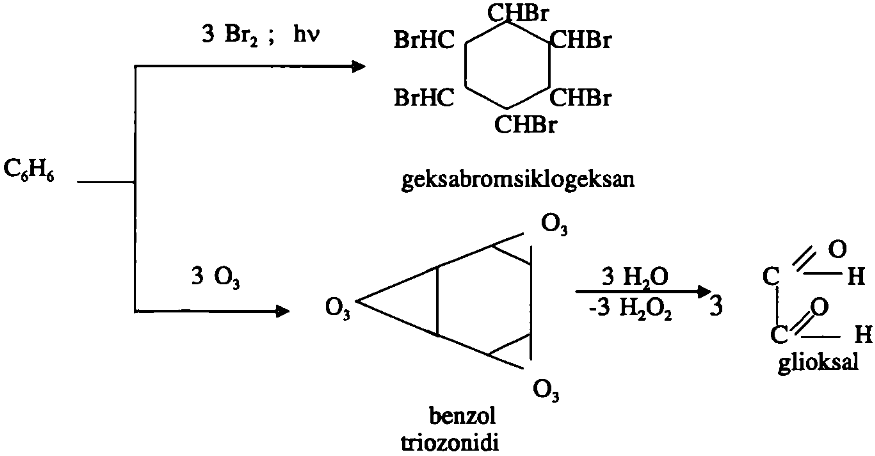
Benzolning birikish va oksidlanish reaksiyalariga qiyin, almashinish reaksiyalariga esa nisbatan oson kirishishi, barqarorligi va boshqa o‘ziga xos xususiyatlari uning «aromatik» xossalari yoki tabiati deb yuritiladi.

Benzolning «aromatik» tabiati, molekulasining elektron tuzilishidan kelib chiqadi. Katalitik gidrogenlanganda siklogeksanning hosil bo'lishi, benzolning halqali tuzilishidan dalolat beradi. (Sabat'e):

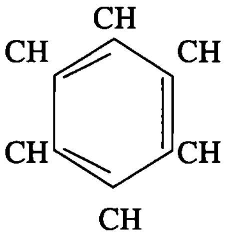


Tarixiy jihatdan benzolning halqali tuzilishini ko'p bosqichli sintezlar yordamida A. Bayer va R. Vilshtetterlar isbotladilar.

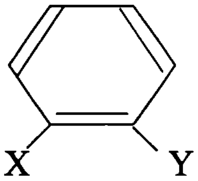
Monoalmashingan benzol hosilalari (brombenzol, nitrobenzol va hokazo) ning faqat bitta izomeri borligi, boshqa izomerlari olinmaganligi benzol molekulasidagi oltita vodorod atomining teng qiymatli ekanligini ko'rsatadi. Shu bilan bir qatorda benzol to'yinmagan birikmalar uchun xos bo'lgan ayrim reaksiyalarga ham kirishadi:



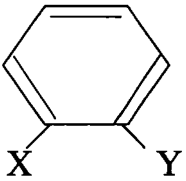
Benzol katalitik gidrogenlash, bromlash va ozonlash reaksiyalarida uchta qo'sh bog'i bor to'yinmagan uglevodorod xossalarini namoyon qiladi. Shularga o'xshash eksperimental dalillarga asoslanib, A. Kekule 1865- yilda benzolni uchta qo'sh bog'i bor olti a'zoli halqa tuzilishiga ega degan fikrni maydonga tashladi va uni teng tomonli oltiburchak bilan tasvirladi:



Lekin tez orada Kekule formulasining talabga to'liq javob bermasligi aniqlandi. Chunki agar bu formula to'g'ri bo'lganda edi, benzolning nosimmetrik 1,2-dialmashingan hosilalari ikkita (I va II) izomer shaklida mavjud bo'lishi kerak edi:

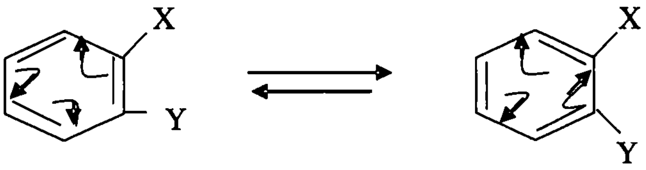


I

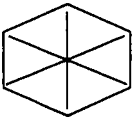


II

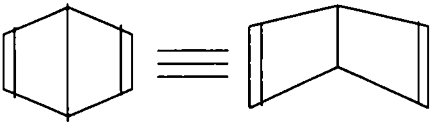
Ikkala izomer qo'sh bog'larning holati bilan farq qilishi lozim. Lekin haqiqatda bitta o – izomer mavjud. Kekule bu noaniqlikni tushuntirish uchun halqadagi qo‘sh bog‘lar o‘rnini to‘xtovsiz o‘zgartirib turadi, boshqacha aytganda qo‘sh bog‘lar ostillyatsiyasi sodir bo‘lib, bu ikkala izomer bir-biriga tez o‘tib turadi degan fikrni ilgari surdi:



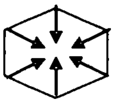
Benzol tuzilishini ifodalash uchun XIX asrning ikkinchi yarmida boshqa olimlar ham qator formulalarni taklif qildilar. Masalan:



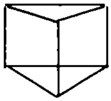
Klaus formulasi
(1867- y.)



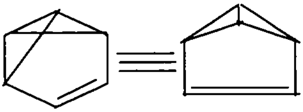
Dyuar benzoli yoki bitsiklo [2,2,0] – geksadiyen – 2,5 (1867- y.)



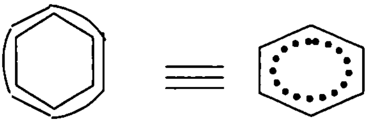
Armstrong (1887-y.)
va Bayer (1888-y.)
formulasi



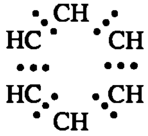
Ladenburg
benzoli
(prizman) (1869-y.)



Xyukkel benzoli
(benzvalen)



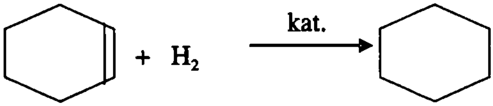
Tile formulasi (1889-y.)



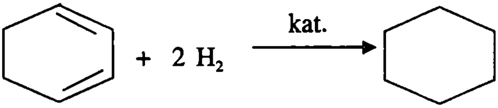
Tomson, Kermak va Robinsonlarning uch elektronli bog` tutgan formulasi

Bu formulalarning birortasi ham benzol xossalarini to'liq tushuntira olmadi. Endi benzol halqasi nega barqaror degan savolga javob beraylik.

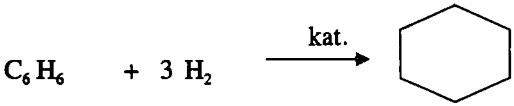
Kekule formulasiga ko'ra benzol siklogeksatriyendir. Lekin uning tajribada topilgan gidrogenlanish, yonish va hosil bo'lish issiqligi nazariy hisoblangan 150,8-159,2 kJ/mol kam. 1 mol to'yinmagan modda gidrogenlanganida ajraladigan issiqlik miqdori gidrogenlanish issiqligi deyilishi va uning miqdori ko'p hollarda bitta qo'sh bog' uchun hisoblaganda 117,3-125,7 kJ/mol ga teng bo'lishini eslatmoqchimiz. Masalan:



Δ H = - 119,8 kJ



Δ H = - 232,1 kJ kutilgan issiqlik miqdori 2•(-119,8)= - 239,6 kJ



Δ H = - 208,6 kJ kutilgan issiqlik miqdori 3•(-119,8)= - 359,4 kJ

Demak, siklogeksatriyenning gidrogenlanish issiqligi 119,8x3=359,4 kJ bo‘lishi kerak. Haqiqatda esa benzolniki 359,4 – 208,6=150,8 kJ kam. Benzolning yonish reaksiyasining issiqlik effekti quyidagicha:

$$2\ C_6H_6(gaz)+3O_2(gaz)\ 12CO_2(gaz)+6H_2O(suyuq)\ \Delta H=-3305,9\ kJ$$

Bog‘laming o‘rtacha energiyasi bo‘yicha nazariy hisoblanganda bu qiymat 3465,1 kJ/mol bo‘lib, farqi 3465,1-3305,9=159,2 kJ . Endi benzolning bog‘ energiyalari yig‘indisini hisoblaymiz.

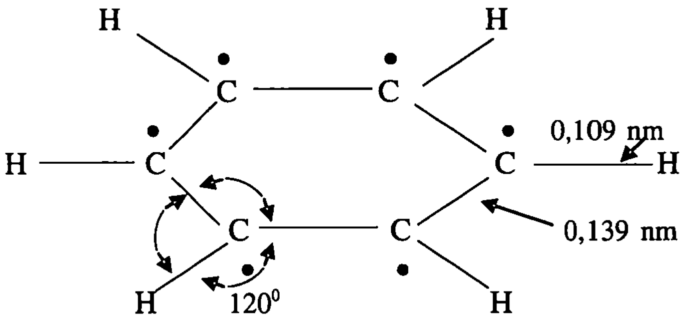
Kekule formulasi bo‘yicha benzolda uchta C - C oddiy bog‘, uchta C=C qo‘sh bog‘, oltita oddiy C - H bog‘ bor. Bog‘larning energiyasi asosida hisoblasak:

$$3 \times 339,5 + 3 \times 615,9 + 6 \times 414,8 = 5354,9\ kJ / mol$$

Tajribada topilgan qiymat 5505,7 kj/mol. Farqi 5505,7 – 5354,9 = 150,8 kJ / mol. Yuqoridagi uch xil usul bilan topilgan, 150,8 kJ/mol benzolning rezonans (delokallanish yoki barqarorlik) energiyasi deb yuritiladi.

Demak, benzol molekulasining hosil bo‘lishida 150,8 kJ / mol energiya ko‘p ajraladi ya‘ni benzolning hosil bo‘lishi energetik jihatdan qulay. Benzol molekulasini parchalashda kimyoviy bog‘larni uzish uchun talab qilinadigan energiyadan tashqari yana 150,8 kJ energiya sarf qilish kerak. Shuning uchun ham benzol barqaror moddadir.

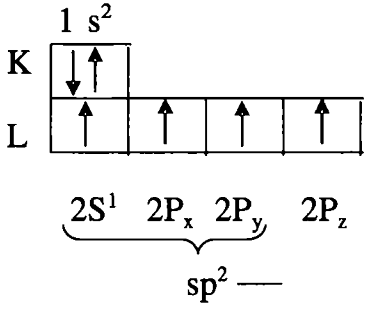
Rentgenostruktur tahlil usuli yordamida benzoldagi yadrolar orasidagi masofaning bir xilligi aniqlandi. Demak, undagi barcha C – C va C – H bog‘lari teng qiymatlidir:

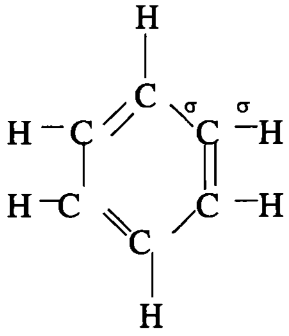


C - C bog'lar uzunligining 0,139 nm ga tengligi, benzol molekulasida na haqiqiy C˜ =C qo'sh bog', na haqiqiy C˜ C oddiy bog'lar borligini ko'rsatadi. Benzolning dipol momenti nolga teng. Demak, uning molekulasi qutbsiz. Chunki unda elektronlar buluti tekis tarqalgan.

Valentlikning elektron nazariyasi kvant mexanikasi nuqtayi nazaridan qaytadan ko'rib chiqilgach, benzolning haqiqiy tuzilishi muammosini to'g'ri hal qilish imkoniyati tug'ildi. Valentlikning kvant nazariyasi esa 30-yillarda asosan L. Poling va E. Xyukkelning ishlari natijasida yaratildi.

Benzol molekulasida 6 ta uglerod atomining tashqi qavatidagi jami 24 ta elektronlardan 6 ta C - C va 6 ta C˜ - H σ - bog'larni hosil qilish uchun 18 tasi sarf bo'ladi. Benzolning uglerod atomlari sp^2 – gibridlangan:





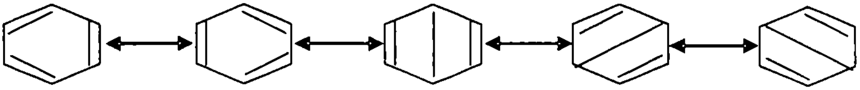
qolgan 6 ta gibridlanmagan Pz - elektron 6 ta uglerod atomi maydonida harakat qiladi.

Shu oltita Pz - elektronning tabiati qanday? – degan savol tug'iladi. Kvant kimyosi bu muammoni yechish uchun ikki xil uslubdan foydalanadi.

1. Valent bog'lar (lokallashgan juftlar, rezonans strukturalar, valent sxemalar) uslubi.

2. Molekulyar orbitallar uslubi (MOU)

Poling tomonidan rivojlantirilgan valent bog'lar uslubiga ko'ra 6 ta Pz – elektronlar yadroning uglerod atomlariga taqsimlanadi va benzolni quyidagi rezonans strukturalarning gibridi deb qarash mumkin:



39 % 39 % 7 % 7 % 7 %

I II III IV V

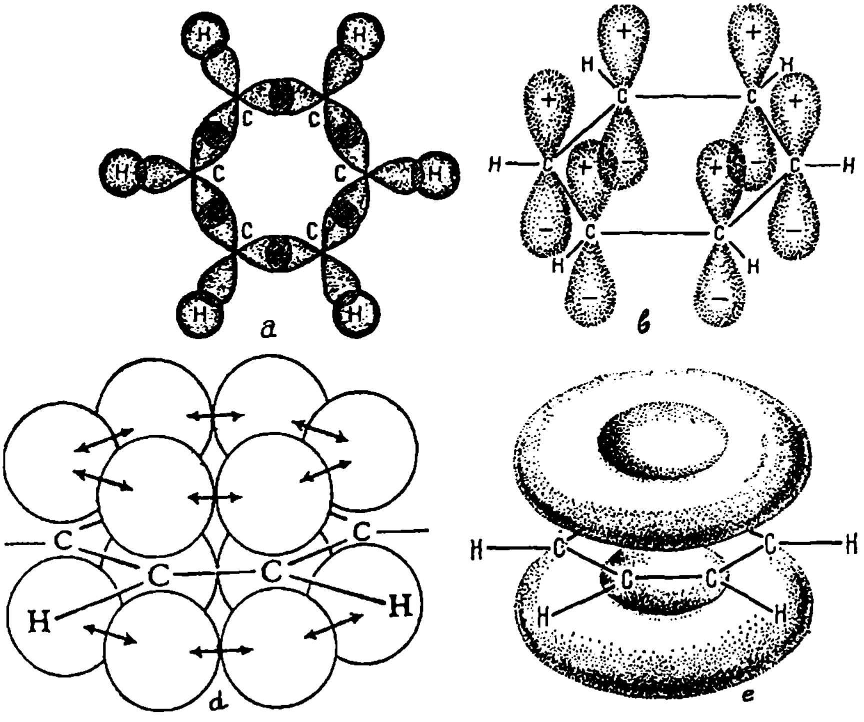
I – V rezonans yoki kanonik strukturalar alohida olinganda real emas, mustaqil mavjud bo'la olmaydi. Benzol molekulasining energiyasi bu strukturalarning energiyasidan kam.

Shunday qilib, benzol molekulasining haqiqiy holati I – V rezonans strukturalarning oralig'ida bo'ladi.

Rezonans strukturalar benzoldagi C – C bog'larni qo'sh bog'ga yaqinlashish darajasini hisoblash imkonini beradi. Benzoldagi har bir C–C bog' Kekulening ikkita strukturasidan bittasida va Dyuaming uchta strukturasidan bittasida qo'sh bog' hisoblanadi. Demak, benzolning har bir bog'i 46% (39%+7%)

ga qo‘sh bog‘dir. Etanda bog‘ tartibini 1 ga, etilenda 2 ga, atsetilenda 3 ga teng deb olsak, benzoldagi uglerod-uglerod bog‘ining tartibi 1,46 ga teng bo‘ladi.

E. Xyukkel tomonidan ishlab chiqilgan molekulyar orbitallar uslubiga ko‘ra benzoldagi 6 ta gibridlanmagan. Pz – elektron (Pz - AO) molekulaning yassi tuzilgan σ- skeletiga perpendikulyar, bir-biriga esa parallel joylashgan. Ularning o‘zaro qoplanishidan yagona π - elektronli bulut hosil bo‘ladi. Molekula σ - skeleti tekisligining ustida va ostida bulut zichligi katta bo‘ladi.

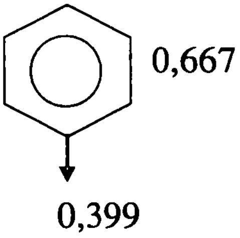


3-rasm. Benzol molekulasining tuzilishi.

a) σ - bog‘lari b) delokallashgan π - molekulyar orbitallari d) π - bog‘ni hosil qiluvchi p-orbitallarning qoplanishi e) halqa tekisligining ustida va ostida joylashgan π - bulut.

Demak, benzolda 6 π - elektrondan tashkil topgan barqaror, yopiq tizim hosil bo'ladi. Uning barqarorligi va yopiqligi barcha π- elektronlaming bog'lovchi molekulyar orbitallarda joylashganligidan kelib chiqadi. Yangi elektronlarni qabul qilish ham , bor elektronlarni berishi ham energiya sarfini talab qiladi.

MOU dan foydalanib, benzoldagi bog'lar tartibi va uglerod atomlarining bog'langanlik darajasini ko'rsatuvchi erkin valentlik indeksi (molekulyar diagrammasi) aniqlangan:

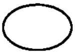


0,399 – uglerod atomining erkin valentlik indeksi. Benzoldagi 6 ta uglerod atomining barchasi bir xil erkin valentlik indeksiga ega.

0,667 - π-elektronlar hosil qiluvchi bog' tartibi. Benzol molekulasidagi barcha σ - bog'lar tartibi 1 ga, π - bog'lar tartibi esa 0,667 ga teng. Demak, benzoldagi C – C bog' tartibi esa, 1,667 ga to'g'ri keladi.

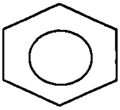
Benzolning valent bog'lar nazariyasidan foydalanib, hisoblangan bog' tartibining qiymati MOU ga asosan chiqarilgan qiymatdan farq qilsa-da, ularning o'zgarish xususiyati deyarli bir xil.

Benzol tuzilishi quyidagi formulalar bilan ham tasvirlanadi:

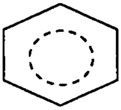


yoki

6 π -elektronli yopiq aromatik sekstetni bildiradi.



yoki

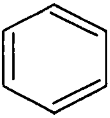


Kekule, Dyuar, Ladenburg, Klaus, Xyukkel formulalari singari bu formulalar ham benzol molekulasining haqiqiy holatini va ayniqsa uning turli-tuman xossalarini tushuntirib bera olmaydi.

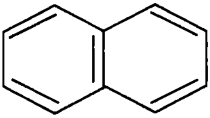
Xyukkelning aromatiklik qoidasi

1931-yilda Xyukkel kvant-mexanikaviy hisoblashlar asosida o‘zining quyidagi qoidasini maydonga tashladi.

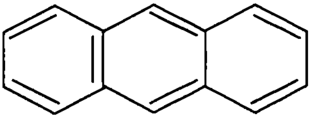
Birikma yassi tuzilishga ega bo‘lib, (4n+2)- π elektronli halqa saqlagandagina aromatik xossalarni namoyon qila oladi (n=0.1.2.3 va hokazo). Bu qoidaga asosan 2,6,10,14,18,22,26 va hokazo π - elektron saqlagan tizimlar aromatik hisoblanadi. Masalan:



(n=1; 4•1+2=6)

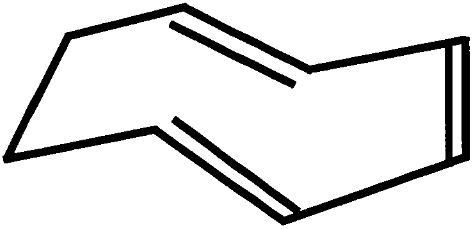


naftalin
(n=2 ; 4•2+2=10)

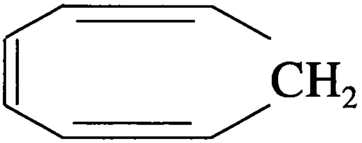


antratsen
(n=3; 4•3+2=14)

Aromatik bo‘lishi uchun halqali birikma molekulasi yassi bo‘lishi shart, chunki shunday bo‘lgandagina π - bog‘larni hosil qiluvchi p-elektronlar orbitallari parallel bo‘ladi va bir-birini qop-laydi. Aks holda tutashish buziladi, p- elektronlar bir-birini qop-lay olmaydi va tizim aromatik xossalarini yo'qotadi. Masalan: siklooktatetrayen molekulasi yassi bo'lmaganligi bois uning p – elektronlari tutashish hosil qila olmaydi va birikma aromatik xossalarga ega bo'la olmaydi:



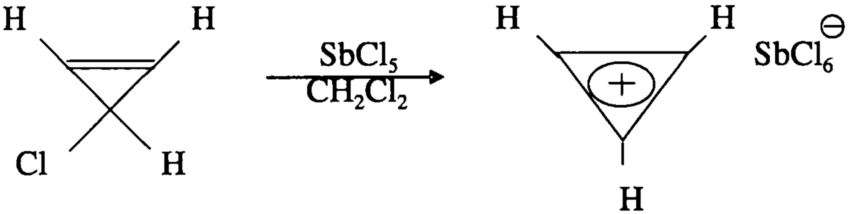
Aromatik halqada π, π- tutashishda uzilish bo'lganda ham aromatiklik yo'qoladi. Masalan:



Nobenzoid aromatik birikmalar

Xyukkelning aromatiklik qoidasiga javob beradigan nobenzoid aromatik ion va birikmalar ham bor.

Siklopropeniliy kationi – ikkita π - elektron saqlagan, aromatik xossalarni namoyon qiladigan, oddiy aromatik ion bo‘lib, quyidagicha olinadi:

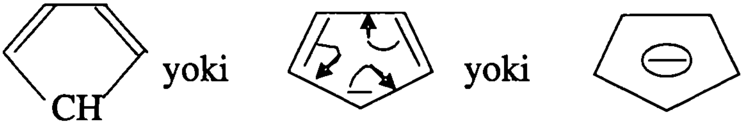


(n=0; 4•0+2=2)

Siklopropeniliy kationining birinchi hosilasi-trifenilsiklopropeniliy kationi 1957 - yilda R. Breslou tomonidan olindi.

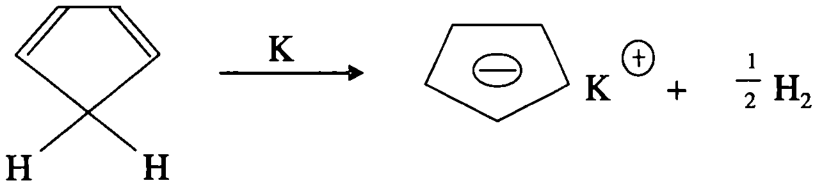
Bu birikma barqaror bo‘lib, birikish va halqaning uzilishi bilan boradigan reaksiyalarga kirishmaydi.

Siklopentadiyenil anioni – olti- π - elektronli yopiq bulut saqlagan aromatik ion bo‘lib, uning tuzilishini quyidagicha tasvirlash mumkin:



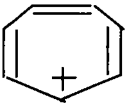
(n=1; 4•1+2=6)

Siklopentadiyenil anioni ishqoriy va ishqoriy-er metallarining tuzlari holida mavjud bo‘ladi. Bu tuzlarni olish uchun siklopentadiyenga metallar (masalan,natriy yoki kaliy) ta‘sir ettiriladi:

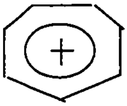


Siklopentadiyenil anioni aromatik xossalarga ega bo‘lib, elektrofil reagentlar bilan reaksiyaga oson kirishadi:

Siklogeptatriyeniliy (tropiliy) kationi – 1891-yilda olingan bo‘lib, uning tuzilishi 1954- yilda aniqlanildi:

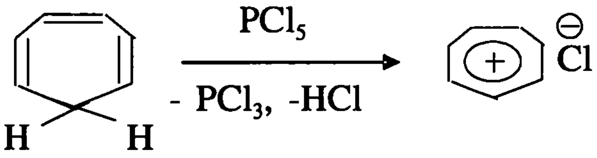


yoki

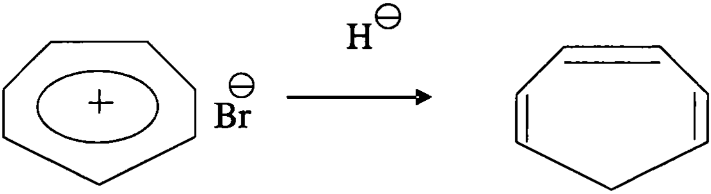


(n=1; 4· 1+2=6)

1,3,5 – siklogeptatriyen (propiliden) dan gidrid ionining ajralishi natijasida tropiliy tuzlari hosil bo‘ladi:

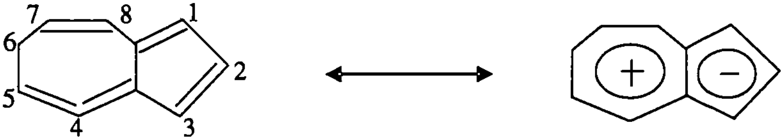


Tropiliy tuzlari (masalan, xloridlari, bromidlari, yodidlari) kristall moddalar bo‘lib, ularda tropiliy kationi galogen bilan ionli bog‘langan. Benzol qatori birikmalaridan farqli o‘laroq, tropiliy kationi elektrofil reagentlar bilan reaksiyaga kirishmaydi (masalan, nitrolanmaydi, sulfolanmaydi). Tropiliy kationi nukleofil reagentlar bilan reaksiyaga kirishadi. Masalan, u gidrid-ionining donori hisoblangan litiyalyuminiy yoki natriyborgidrid ta‘sirida siklogeptatriyenga aylanadi:

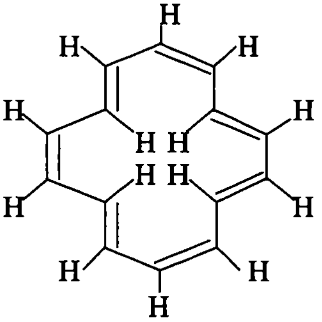


Azulen - to‘q ko‘k rangli kristall modda bo‘lib, aromatik xossalarni yaqqol namoyon qiladi.

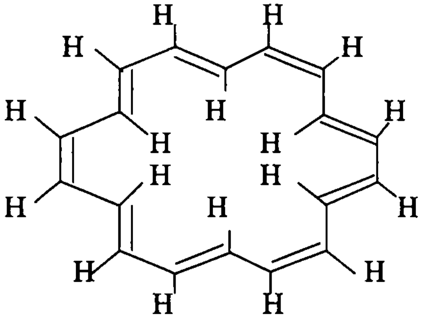
10 ta π - elektron saqlagan azulen molekulasida tropiliy kationi va siklopentadiyenil anioni yadrolari kondensirlangan:



14 π - va 18 π elektronli annulenlar ham aromatik xossalarga ega. Lekin sikl ichidagi vodorod atomlarining itarilishi molekulani notekis qilib, barqarorligini kamaytiradi:



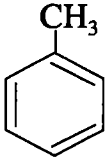
[14] – annulen



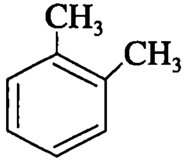
[18] – annulen

Nomlanishi

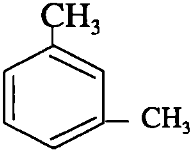
enzol qatori uglevodorodlarini trivial, ratsional va sistematik nomenklaturalarda nomlash mumkin:



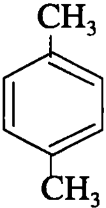
toluol ,
metil-
benzol



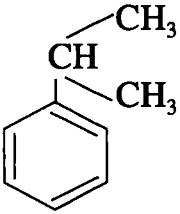
o – ksilol ,
o-dimetilbenzol,
1,2-dimetilbenzol



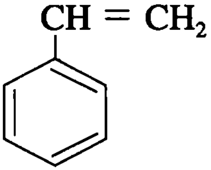
m – ksilol ,
m-dimetilbenzol,
1,3-dimetilbenzol



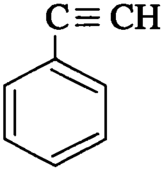
p – ksilol ,
p-dimetilbenzol,
1,4-dimetilbenzol



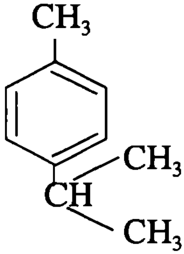
kumol,
izopropilbenzol



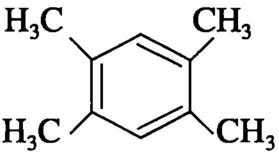
stirol,
vinilbenzol,
feniletilen



etinilbenzol,
fenilatsetilen

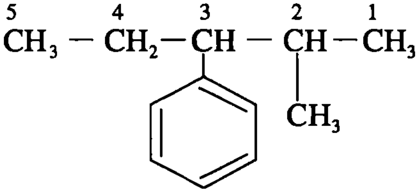


simol,
1-metil – 4- izopropilbenzol

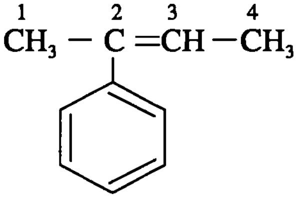


durol,
1,2,4,5 – tetra -
metilbenzol

Yon zanjiri murakkab tuzilgan benzol qatori uglevodorodlari atsiklik uglevodorodlarning hosilasi deb qaraladi:

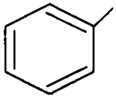


2-metil-3-fenilpentan

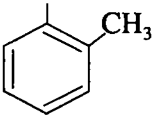


2-fenil-2-buten

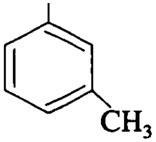
Bir valentli radikallarga arillar , ikki valentli aromatik radikallar esa arilenlar deyiladi:



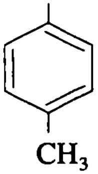
fenil



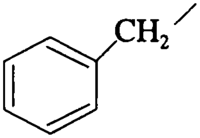
o – tolil



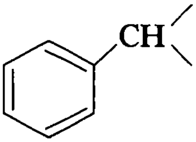
m – tolil



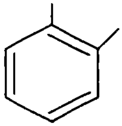
p – tolil



benzil



benziliden



o – fenilen

Izomeriyasi

Benzolning bir xil o'rinbosar saqlagan bir, besh – va olti almashingan hosilalarining bittadan, ikki, uch va to'rt almashingan hosilalarining esa uchtadan izomeri bor.

Agar benzolning ikkita bir xil o'rinbosari bor hosilasi molekulasiga uchinchi (boshqa xil) o'rinbosar kiritilsa o – izomerdan ikkita, m – izomerdan uchta, p – izomerdan esa bitta uch almashingan izomer hosil bo'ladi (Kerner qoidasi):

Halqasida uchta har xil o'rinbosari bor benzol hosilasi o'nta izomer holida uchraydi.

Olinish usullari

Aromatik uglevodorodlarning asosiy tabiiy manbayi toshko'mir va neftdir.

Toshko'mirni quruq haydash. Toshko'mirni koks pechlarida havoni kiritmasdan 1000-1200°C da qizdirganda koks, toshko'mir smolasi, ammiakli suv, koks gazlari hosil bo'ladi.

Koks – metallurgiya sanoatida rudalardan metallarni ajratib olishda qaytaruvchi sifatida ishlatiladi.

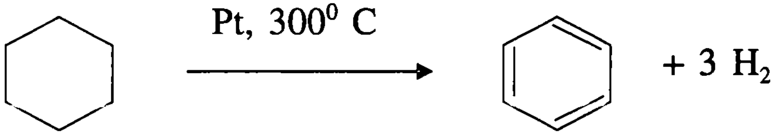
Toshko'mir smolasidan benzol, toluol, ksilollar, fenol, krezollar, naftalin, piridin, tiofen, xinolin, difenil, atsenaften, flyuoren, antratsen, fenantren singari 160 dan ortiq kimyoviy mahsulot ajratib olinadi.

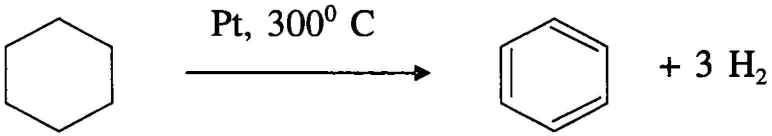
Koks gazlaridan ham benzol, toluol, ksilollar, fenollar, naftalin, piridin asoslari, ammiak va boshqa mahsulotlar olinadi. Hozirgi kunda toshko'mirni quruq haydash bilan olinadigan benzolning qariyb 90% i koks gazlaridan, qolgani esa toshko'mir smolasidan ajratiladi. Koks gazlari tarkibidagi ammiakni oksidlab, nitrat kislota, ammiak va sulfat kislotadan esa ammoniy sulfati olinadi.

Neftdan olish. Ayrim neftlarda 60% gacha aromatik uglevodorodlar bo'lib, ular oddiy haydash yoki piroliz, shuningdek, katalitik kreking usuli bilan ajratib olinadi.

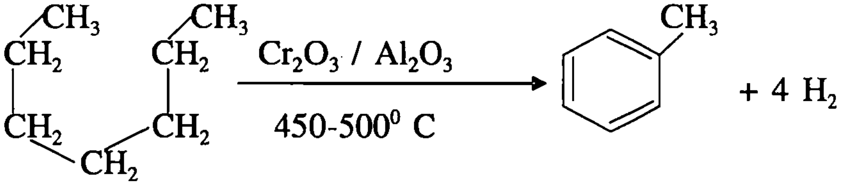
Sintetik usullar

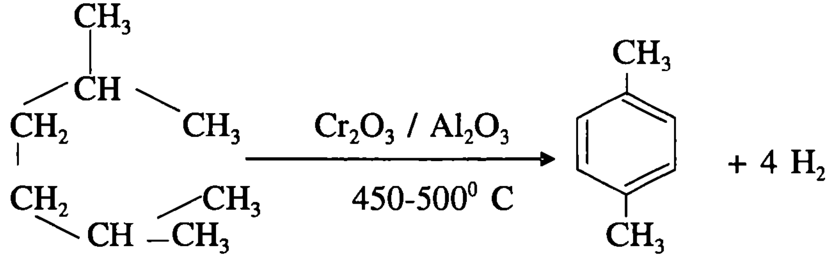
1. Gidroaromatik uglevodorodlarni katalitik degidrogenlash:





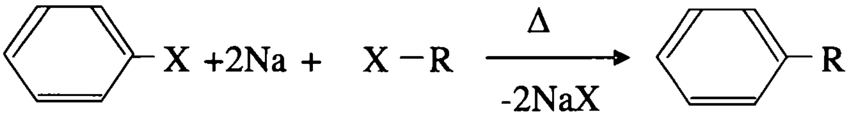
2. Alkanlarni degidrotsikllash yoki aromatlash (R. L. Moldavskiy, B. A. Plate):





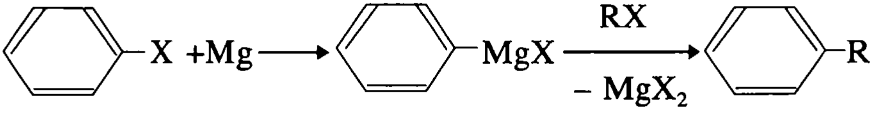
3. Vyurs – Fittig reaksiyasi (1863 – y.):

Galogenbenzol va galogenalkanlarga natriyni ta'sir ettirib, alkilbenzollar olinadi:

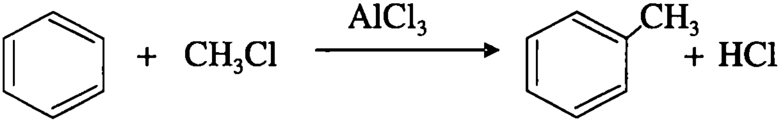


Bu reaksiyada qo'shimcha mahsulotlar sifatida bifenil va alkanlar hosil bo'ladi, lekin ularni alkilarenlardan oson ajratish mumkin.

4. Vyurs – Grinyar reaksiyasi. Fenilmagniygalogenidlarga galogenalkanlarni ta'sir ettirganda benzol gomologlari hosil bo'ladi:

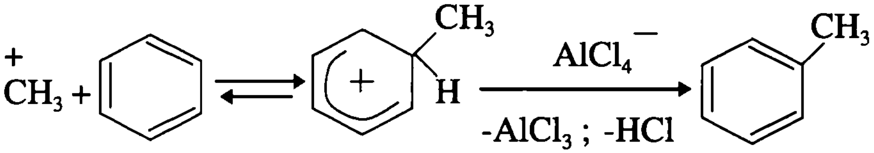


5. Fridel – Krafts reaksiyasi (1877 – y.). Arenlar alyuminiy xlorid ishtirokida galogenalkanlar bilan alkillash reaksiyasiga kirishadi:

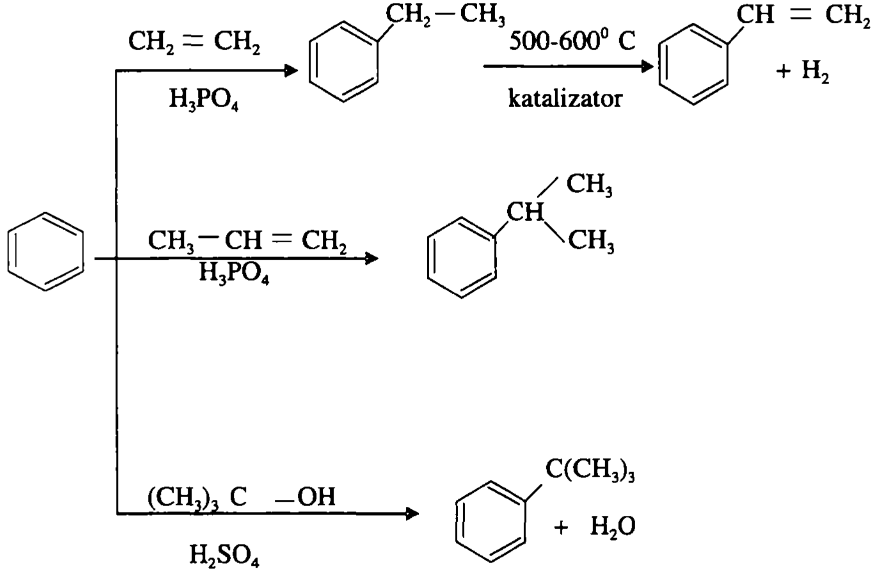


Bu S_E reaksiyada $\overset{+}{C}H_3$ elektrofil reagentdir:

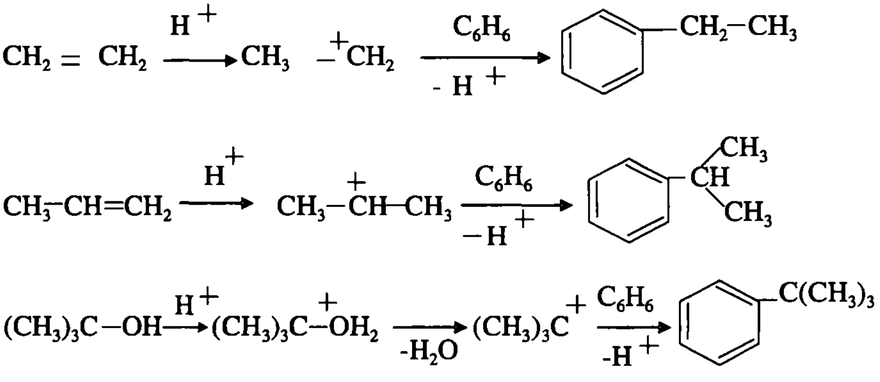
$$CH_3Cl + AlCl_3 \rightleftharpoons \overset{-}{AlCl_4} + \overset{+}{C}H_3$$



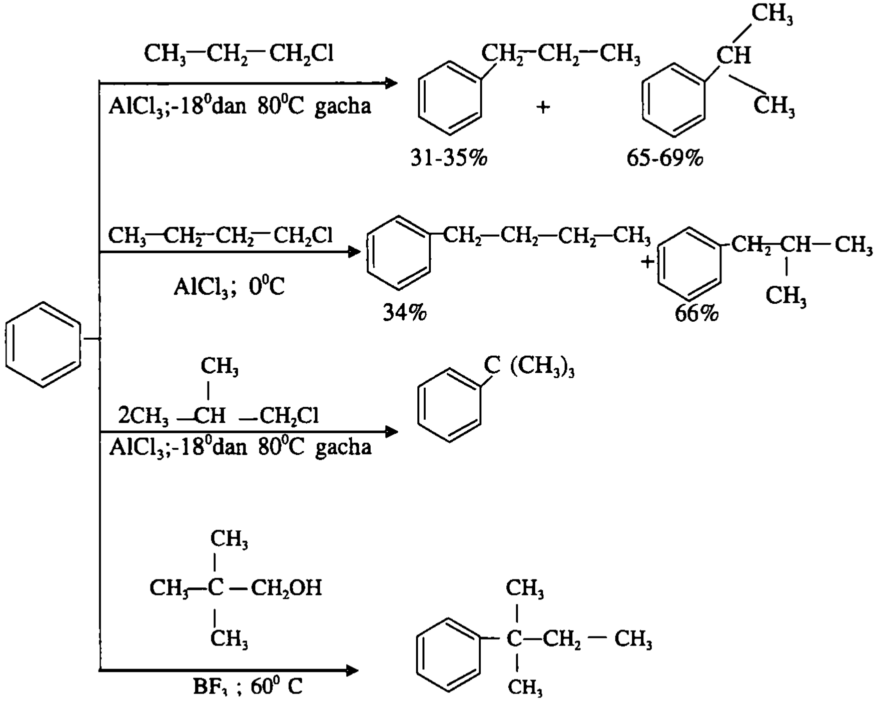
Fredel – Krafts bo‘yicha alkillashda katalizator sifatida $AlCl_3$ o‘rnida $AlBr_3$, $FeCl_3$, $SnCl_4$, $ZnCl_2$ alkillovchi reagentlar sifatida esa H_3PO_4 , H_2SO_4 yoki HF ishtirokida alken va spirtlar ham ishlatiladi:



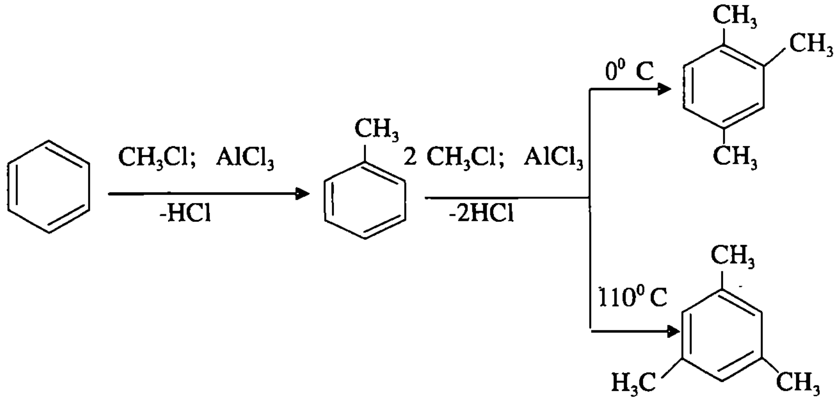
Bu reaksiyalarda ham alken va spirtga kislota protonining birikishidan hosil bo'ladigan karbokation, aromatik halqaga hujum qiladi:



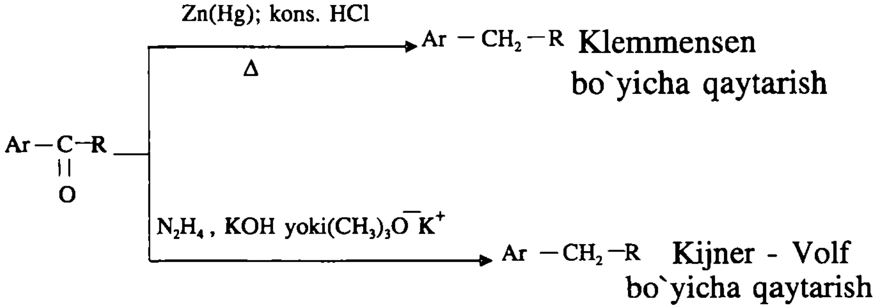
Fridel – Krafts reaksiyalarida hosil bo'ladigan birlamchi karbokationlar o'zlariga nisbatan barqaror bo'lgan ikkilamchi yoki uchlamchi karbokationlarga qayta guruhlanadi, keyin ikkilamchi va uchlamchi karbokationlar aromatik halqani alkillaydi. Buni quyidagi reaksiyalar mahsulotlarining unumidan bilsa bo‘ladi:



Benzol toluol va ksilollarga nisbatan qiyin alkillanadi. Alkillash reaksiyalarida ko‘pincha di va trialkilbenzollar ham hosil bo‘ladi:



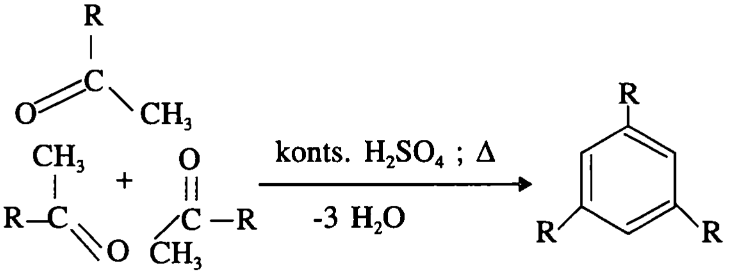
6.Alkilarilketonlarni qaytarish:



7.Aromatik kislotalar tuzlaridan olish:

$$C_6H_5-COONa + NaOH \xrightarrow{\Delta} C_6H_6 + Na_2CO_3$$

8. R - CO - CH_3 tipidagi ketonlardan sintez qilish:



R = CH_3 atseton, R = CH_3 mezitilen ,
R = C_6H_5 atsetofenon R = C_6H_5 1,3,5 – trifenilbenzol

9. «Qaytmas kataliz» reaksiyasi bilan siklogeksen, siklogeksadiyen va ularning gomologlaridan olish (30- bet).

Fizikaviy xossalari va tavsifi

Benzol va uning gomologlari suvda erimaydigan, organik erituvchilarda esa yaxshi eriydigan, o'ziga xos hidli suyuqlikdir. (3-jadval) Benzol qatori arenlarining fizikaviy doimiyliklari.

Nomi	Suyuqlanish harorati, ^{0} C	Qaynash harorati, ^{0} C	D_4^{20}
Benzol	5,5	80,1	0,8790
Toluol	-95	110,6	0,8669
Etilbenzol	-94,9	136,2	0,8670
o-Ksilol	-29	144,4	0,8802
m- Ksilol	-53,6	139,1	0,8641
p- Ksilol	13,2	138,4	0,8610
Kumol	-96,9	152,4	0,8618
Mezitilen	-52,7	164,7	0,8651
Vinil benzol	-30,6	145,2	0,9090
Fenilatsetilen	-44,8	142,4	0,9295

Benzol va alkilbenzollarning ultrabinafsha spektrlarida 170-210 nm sohada intensiv , 240-270 nm sohada esa intensivligi kam yutilish bo'ladi.

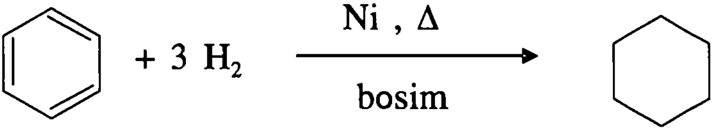
Benzol va uning IQ - spektrida C$\overset{\cdots}{=}$C bog'larning valent tebranishlari 1500 - 1600 sm^{-1}, C - H bog'larning valent tebranishlari 3000-3050 sm^{-1},C - H bog'larning deformatsion tebranishlari esa 700 – 900 sm^{-1} sohada kuzatiladi.

PMR – spektrlarida benzol halqasi protonlarining signallari kuchsiz maydonda (δ = 6,5-8,5 m.h) kuzatiladi.

Benzol va uning gomologlari mass-spektrlarida molekulyar ion intensiv pik beradi. Alkilbenzolning mass-spektrlarida maksimal pik tropiliy ioni C_7H_7+ (m/b=77,65,53,50 va 39) bo'lgan ionlarning fragmentlari ham xarakterli hisoblanadi.

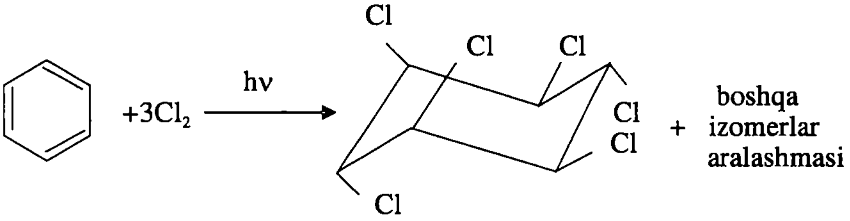
Kimyoviy xossalari

Gidrogenlash. Benzol halqasi alken qo'sh bog'i va alkin uch bog'iga nisbatan qiyin gidrogenlanadi. Benzol va uning hosilalarini siklogeksan hosilalarigacha gidroganlash Reney nikeli ishtirokida, 1200-150°C haroratda va 1-1,5•10^7 Pa (100-150 atm) bosimda boradi:



Benzol halqasining katalitik gidrogenlanishini birinchi va ikkinchi bosqichda to'xtatib, qisman gidrogenlangan siklogeksen va siklogeksadiyenlarni ajratib olishning iloji yo'q, chunki ular aromatik birikmaga nisbatan katta tezlikda gidrogenlanadi.

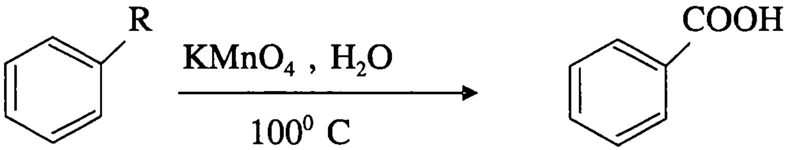
Xlorning birikishi. Benzolga xlorning radikal birikishidan geksaxlortsiklogeksan hosil bo'ladi. Bu birikmaning sakkizta fazoviy izomeri bo'lib, ulardan bittasi geksaxlorandir:



Izomerlar aralashmasida 18 % gacha geksaxloran (lindan, gammeksan) bo‘ladi. U odam va hayvonlar uchun juda zaharli bo‘lgani sababli, hozirgi kunda ishlab chiqarilmaydi.

Oksidlash. Benzol halqasi ko‘pchilik oksidlovchilar ta‘siriga chidamli, lekin alkilbenzollarning alkil guruhlari $Na_2Cr_2O_7+H_2SO_4$, CrO_3+CH_3COOH, $KMnO_4$, 20-40% li HNO_3 kabi oksidlovchilar ta‘sirida oson oksidlanib, aromatik karbon kislotalarni hosil qiladi.

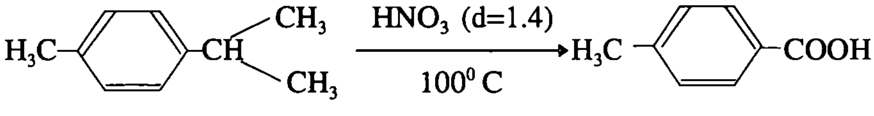
Alkilbenzollar yon zanjirini karboksilgacha oksidlash uchun kaliy permanganatning suvdagi eritmasi ko‘p qo‘llaniladi:



benzoy kislota (60-80%)

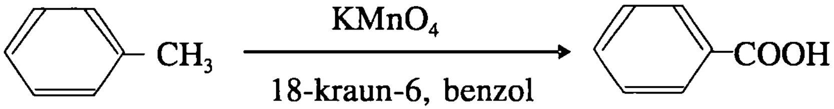
$R=CH_3$, C_2H_5 , izo- C_3H_7 , n - C_3H_7 va hokazo.

Suyultirilgan nitrat kislota alkilbenzollarning yon zanjirini tanlab oksidlaydi:



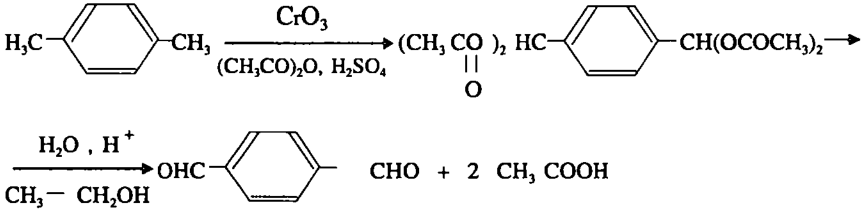
p – toluil kislota
(50%)

Qattiq kaliy permanganatning benzolda 18 – kraun–6-poliefir ishtirokida qisman erishidan hosil bo‘ladigan eritmadan alkilbenzollarni oksidlashda keng qo‘llaniladi:



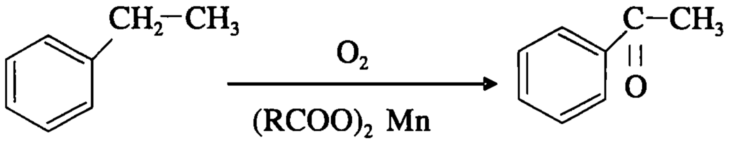
(100%)

Xrom oksidi va sirka angidridi aralashmasi arenlar metil guruhini aldegid guruhigacha oksidlashda eng yaxshi reagentdir:

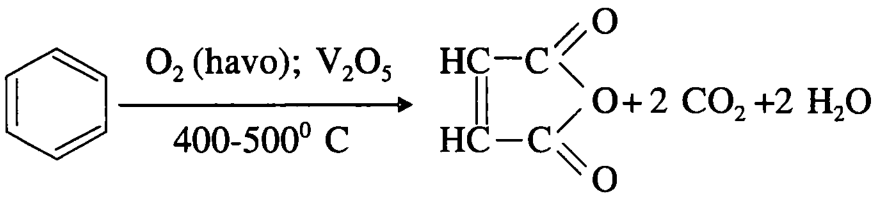


tereftal
aldegidi (52%)

Etilbenzol havo kislorodi va marganets tuzlari katalizatorligida oksidlansa, atsetofenon hosil bo‘ladi:



Benzol halqasini oksidlash uchun qattiq sharoit talab qilinadi. Masalan, benzolni V_2O_5 katalizatorligida havo kislorodi bilan yuqori haroratda oksidlab, malein angidridi olinadi:



Almashinish reaksiyalari. Aromatik almashinish reaksiyalari uchga bo'linadi:

1. Elektrofil aromatik almashinish:

$$Ar-H + E^+ \longrightarrow Ar-H + H^+$$

2. Nukleofil aromatik almashinish:

$$Ar-H + :Nu^- \longrightarrow Ar-Nu + :H^-$$

3. Radikal aromatik almashinish:

$$Ar-H + R^{\bullet} \longrightarrow Ar-R + H^{\bullet}$$

Aromatik birikmalar uchun elektrofil almashinish reaksiyalari eng xarakterli bo'lib, ularning mexanizmlari va organik sintezda qo'llanilishi har tomonlama o'rganilgan.

Elektrofil reagentlarni oddiylik uchun E^+ bilan belgilasakda, ularda zaryadning bo'lishi shart emas, zaryadlanmagan elektronodefitsitli elektrofillar (masalan, SO_3, $Hg(OCOCH_3)_2$ va hokazo) ham bor.

Elektrofillar shartli ravishda kuchli (nitroniy ioni NO^{2+}, Cl_2 yoki Br_2 ning $FeCl_3$, $AlBr_3$, FCl_3, $SbSl_5$ va boshqa Lyuis kislotalari bilan komplekslari, H_2OCl^+, H_2OBr^+, RSO_2, HSO_3^+, $H_2S_2O_7$); o'rtacha kuchdagi (alkilgalogenidlar yoki atsilgalogenidlarning Lyuis kislotalari bilan komplekslari $RCl \bullet AlCl_3$) va kuchsiz (diazoniy $ArN{\equiv}N$, iminiy $CH_2 = NH_2$ va nitrozoniy NO^+ kationlari, CO_2) elektrofillarga bo'linadi.

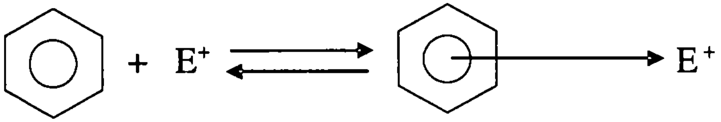
Kuchli elektrofillar halqasida elektrodonor o'rinbosari bor benzol hosilalari bilan ham, shuningdek, elektronoaktseptor o'rinbosarlarni saqlagan benzol qatori birikmalari bilan ham reaksiyaga kirisha oladi.

O'rtacha kuchdagi elektrofillar halqasida elektronodonor (faollashtiruvchi) o'rinbosar va halqa faolligini bir muncha kamaytiradigan galogen atomlarini saqlagan benzol hosilalari bilan reaksiyaga kirishadi, lekin $-NO_2$, $-SO_3H$, -COR, - CN kabi kuchli elektronoaktseptor o'rinbosarlarni saqlagan benzol hosilalari bilan reaksiyaga kirishmaydi.

Kuchsiz elektrofillar esa faqat juda kuchli elektronodonor o‘rinbosarlar (-OH, -OR, $-NH_2$, $-NR_2$,-O- va hokazo) ni saqlagan benzol hosilalari bilangina reaksiyaga kirisha oladi.

Elektrofil aromatik almashinish mexanizmi

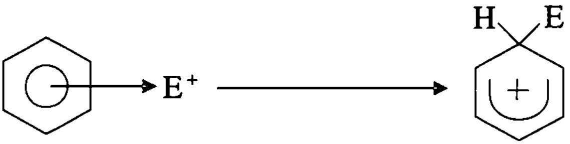
Aromatik qatorda elektrofil almashinish reaksiyalari (S_EAr) bir necha bosqichda boradi. Dastlab, elektrofil reagent aromatik birikmaning delokallashgan π - orbitallari bilan o‘zaro ta‘sirlashib, π - kompleksni hosil qiladi:



π - kompleks

π- kompleksda E ⁺ yadroning biror atomi bilan ham haqiqiy kimyoviy bog‘ hosil qilmaydi. E ⁺ ni yadrodagi oltita elektronning umumiy manfiy zaryadi tortib turadi.

π- kompleks ma‘lum miqdor energiyani yutib, σ- kompleksga o‘tadi:

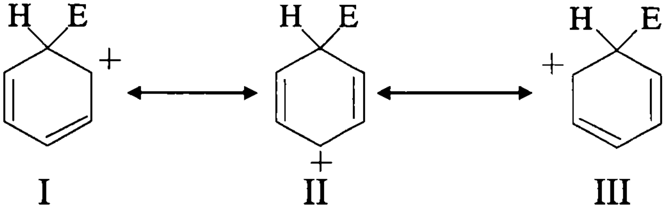


σ - kompleks

σ- Kompleksda E + bilan yadroning bitta uglerod atomi o‘rtasida haqiqiy C¯ E kovalent bog‘i vujudga keladi. Bu bog‘

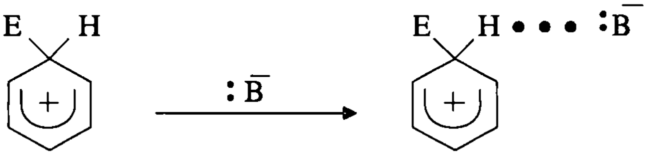
aromatik yadrodagi oltita umumiy elektronning bir jufti hisobidan hosil bo'ladi va buning natijasida aromatik holat (umumiy 6π - elektronli tizim) buziladi.

σ- Kompleksda musbat zaryad beshta uglerod atomida delokallashgan, oltinchi uglerod atomi esa sp^3 – gibridlangan holatda bo'lib, tutashishda ishtirok qilmaydi. σ- kompleksda elektronlar zichligining taqsimlanishini quyidagi uchta rezonans struktura bilan ham tasvirlash mumkin:

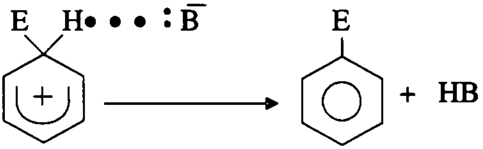


I , II va III strukturalar bir- biridan qo'sh bog'larning va musbat zaryadning holati bilangina farq qiladi. Musbat zaryad bitta uglerod atomida lokallashgan emas, balki butun molekulada taqsimlangan (E ga nisbatan orto – va para- holatlarda ko'proq) bo'ladi. Musbat zaryadning rezonans tufayli butun molekulada taqsimlanganligi σ- kompleksning lokallashgan musbat zaryadli ionga nisbatan barqaror bo'lishiga olib keladi.

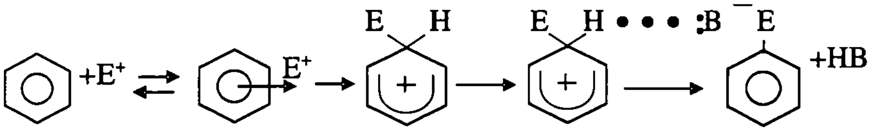
Navbatdagi bosqichda σ - kompleksdan uzoqlashayotgan proton bilan reaksiya muhitidagi anion-asos orasida o'tish holati hosil bo'ladi:



Nihoyat o'tish holatidan proton ajralib chiqadi va aromatik birikma hosil bo'ladi:



Endi elektrofil almashinish jarayonini bitta sxema bilan tasvirlaymiz:



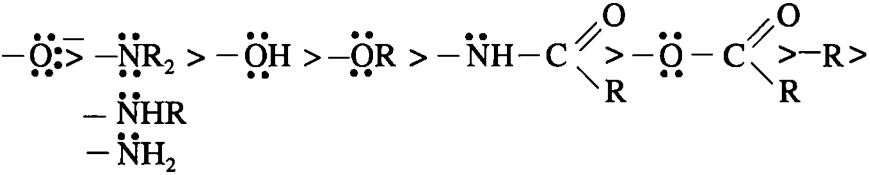
π-kompleks σ-kompleks o`tish holati

Benzol va alkilbenzollarning galogenlash, nitrolash, sulfolash, alkillash, atsillash reaksiyalari ham yuqoridagi mexanizm bo‘yicha boradi. Ular bilan keyingi mavzularda tanishamiz.

Elektrofil almashinish reaksiyalarida yo‘naltirish (orientatsiya) qoidalari

Benzol yadrosiga o‘rinbosar kiritilganda π - elektronlar bulutining simmetriyasi buziladi va elektronlar buluti o‘rinbosar xarakteriga qarab ma‘lum bir tomonga siljiydi. Benzol halqasi faolligini oshirish yoki kamaytirish va yangi elektrofil o‘rinbosarni yo‘naltirish ta‘siriga ko‘ra o‘rinbosarlar uch guruhga bo‘linadi.

1. Aromatik halqaning faolligini oshirib, orto- va para- holatlarga yo‘naltiruvchi o‘rinbosarlar (orto-va para- orientantlar) guruhida



$$-\ddot{\underset{\cdot\cdot}{O}}:^{-} > -\underset{\cdot\cdot}{\ddot{N}}R_2 > -\underset{\cdot\cdot}{\ddot{O}}H > -\underset{\cdot\cdot}{\ddot{O}}R > -\ddot{N}H-C(=O)R > -\underset{\cdot\cdot}{\ddot{O}}-C(=O)R > -R >$$

$$-\ddot{N}HR$$

$$-\ddot{N}H_2$$

$> -C_6H_5 > -CH_2COOH$ kiradi.

Aromatik halqani faollash ta'sirining kuchsizlanib borishi tartibida joylashtirilgan bu o'rinbosarlardan

$$-\underset{\cdot\cdot}{\ddot{O}}:^{-},\ -\ddot{N}R_2,\ -\ddot{N}HR,\ -\ddot{N}H_2 \quad \text{va} \ -\underset{\cdot\cdot}{\ddot{O}}H \quad \text{kuchli}$$

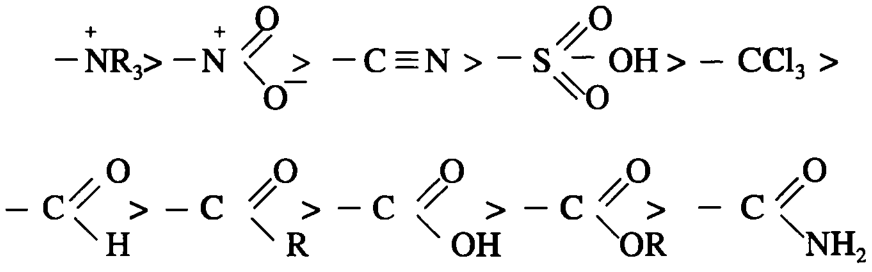
faollashtiradigan, OR, NHCOR, OCOR o'rtacha faollashtiradigan, R(alkillar), C_6H_5(arillar) va CH_2COOH esa kuchsiz faollashtiradigan o'rinbosarlardir. Bu o'rinbosarlar aromatik yadroning barcha holatlarini (ayniqsa orto- va para- holatlarini) benzolning o'zidagiga nisbatan faollashtiradi va yangi elektrofil reagentni asosan orto- va para- holatlariga yo'naltiradi.

2. Aromatik halqaning faolligini kamaytirib, ta'sirining kuchsizlanib borish tartibida galogenlarni quyidagicha joylashtirish mumkin:

$$-\underset{\cdot\cdot}{\ddot{F}}: \ > \ -\underset{\cdot\cdot}{\ddot{Cl}}: \ > \ -\underset{\cdot\cdot}{\ddot{Br}}: \ > \ -\underset{\cdot\cdot}{\ddot{I}}:$$

Bu o'rinbosarlar yadroning barcha holatlarini (ayniqsa meta - holati) faolligini benzol yadrosidagiga nisbatan kamaytiradi va elektrofil reagentni asosan orto- va para- holatlarga yo'naltiradi.

3. Aromatik halqa faolligini kamaytirib, meta - holatga yo'naltiruvchi o'rinbosarlar (meta- orientantlar). Halqa faolligini kamaytirish ta'sirining kuchsizlanib borishi tartibida bu guruh o'rinbosarlarini quyidagicha joylashtirish mumkin:



$$-\overset{+}{N}R_3 > -\overset{+}{N}{\scriptstyle\left\langle{}^{O}_{O^-}\right.} > -C\equiv N > -S{\scriptstyle\left\langle{}^{\,O}_{\,O}\right.}\!\!-OH > -CCl_3 >$$

$$-C{\scriptstyle\left\langle{}^{O}_{H}\right.} > -C{\scriptstyle\left\langle{}^{O}_{R}\right.} > -C{\scriptstyle\left\langle{}^{O}_{OH}\right.} > -C{\scriptstyle\left\langle{}^{O}_{OR}\right.} > -C{\scriptstyle\left\langle{}^{O}_{NH_2}\right.}$$

Bu o‘rinbosarlar yadroning barcha holatlari (ayniqsa) orto- va para- holatlari faolligini benzolga nisbatan kamaytiradi va yangi elektrofil reagentni asosan meta- holatga yo‘naltiradi.

Elektrofil almashinish reaksiyalarining yo‘nalishi va tezligi birinchidan, statik omillar (reaksiyaga kirishmagan molekuladagi elektron zichligining taqsimlanishi)ga, ikkinchidan dinamik omillar (reaksiya vaqtida elektron zichligining qayta taqsimlanish) ga bog‘liq.

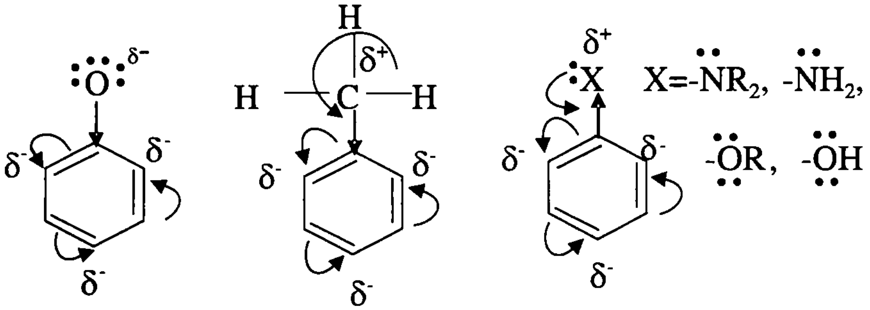
Reaksiya jarayonida elektrofil reagentlar ta‘sirida molekulada elektron siljishlar sodir bo‘ladi. Bu siljishlarda yadrodagi o‘rinbosar ham ishtirok etadi.

O‘rinbosarning aromatik yadro bilan ta‘sirlashuvi elektron (induktsion va mezomer) effektlar orqali amalga oshadi.

I guruh o‘rinbosarlaridan kislorod anioni $(-\ddot{\underset{\bullet\bullet}{O}}\!:)$musbat induktsion va ρ, π- tutashish turidagi musbat mezomer effektlarni, azot va kislorod atomida umumlashmagan eletron jufti bor o‘rinbosarlar

$$-\ddot{N}R_2, -\ddot{N}H_2, -\underset{\bullet\bullet}{\ddot{O}}R, -\underset{\bullet\bullet}{\ddot{O}}H, \ \ddot{N}H\text{-CO-R}, -\underset{\bullet\bullet}{\ddot{O}}\text{-CO-R}$$

va boshqalar) musbat mezomer va manfiy induktsion effektlarni, metil guruhi esa musbat induktsion va musbat mezomer (δ, π - tutashish) effektlarni namoyon qiladi va aromatik yadroning elektron zichligini (ayniqsa, orto- va para- holatlarda) benzol yadrosidagi zichlikka nisbatan oshirib, elektrofil reagentlar bilan reaksiyaga kirishishini osonlashtiradi:

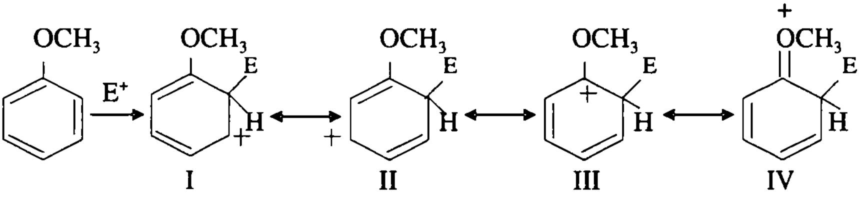


+J ;+M (P,π-)   +J ;+M (σ,π-)   +M (P,π-) > -J

Reaksiya jarayonida elektron zichligi qayta taqsimlanadi. Monoalmashingan benzol va elektrofil reagentlardan σ -kompleks hosil bo'lganda, aromatik halqada musbat zaryad paydo bo'ladi. Musbat zaryadning delokallanishiga olib keladigan o'rinbosarlar σ -kompleksni barqaror qiladi, elektrofil almashinish reaksiyasini osonlashtiradi.

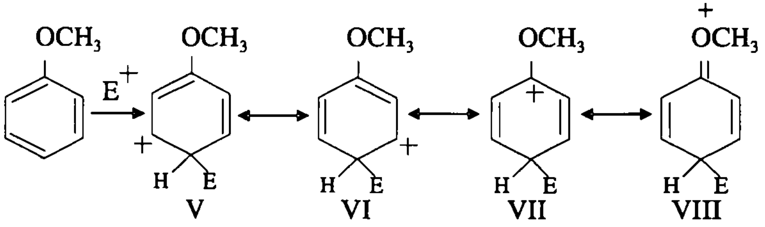
Endi +M effekt namoyon qiladigan o'rinbosar tutgan monoalmashingan benzol (masalan, anizol) molekulasiga elektrofil reagent hujum qilganda hosil bo'ladigan σ -komplekslarning tuzilishini ko'rib chiqamiz va ularning barqarorligini taqqoslaymiz.

Elektrofil reagent E+ orto - holatga hujum qilganda hosil bo'ladigan σ -kompleks tuzilishini I – IV rezonans strukturalar bilan tasvirlash mumkin:



I va II ikkilamchi, III esa uchlamchi karbokation bo'lib, undagi musbat zaryad – OCH_3 guruhi kislorodining umumlashmagan elektronlar jufti hisobiga qo'shimcha barqarorlashgan.

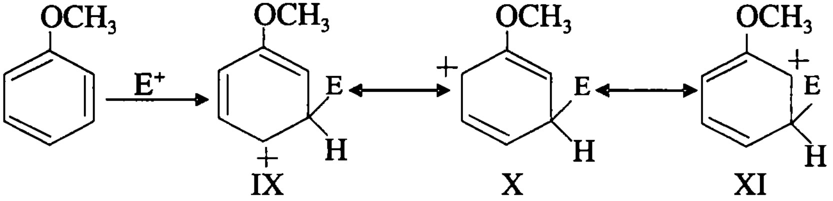
E+ para- holatga hujum qilganda hosil bo'ladigan *δ* -kompleksning rezonans strukturalari quyidagilar:



V va VI ikkilamchi, VII esa qo‘shni $-OCH_3$ guruhi ta‘sirida barqarorlashgan uchlamchi karbokation hisoblanadi.

- OCH_3 guruhi ta‘sirida siklogeksadiyenil kationining barqarorlashgani anizolning orto- va para- almashinishini osonlashtiradi hamda elektrofil reagent E+ ni shu holatga yo‘naltiradi.

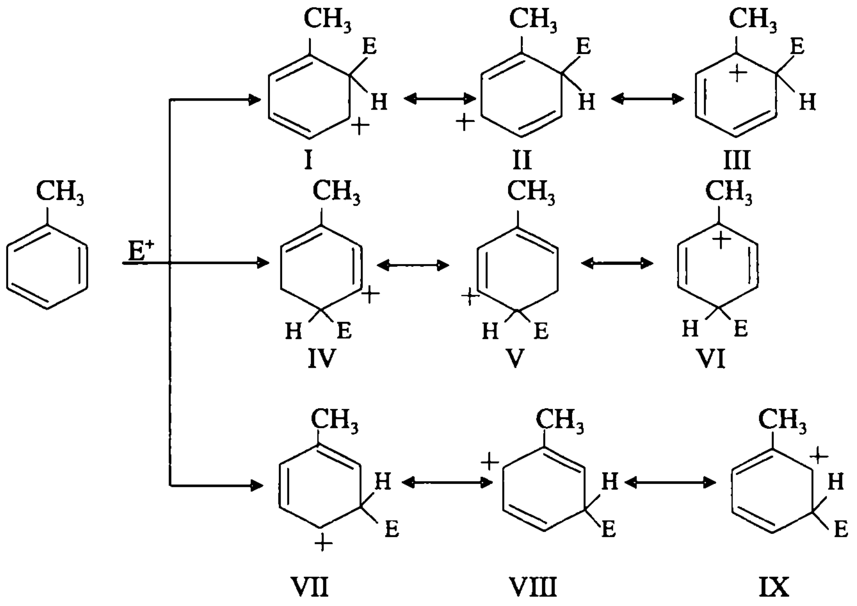
E+ anizolning meta- holatiga hujum qilganida hosil bo‘ladigan δ - kompleksning tuzilishini IX – XI rezonans strukturalar bilan tasvirlash mumkin:



IX – XI formulalarda $-OCH_3$ guruhi bilan bevosita bog‘langan uglerod atomi musbat zaryadlanmaganligi sababli, ularning birortasi ham barqaror emas. Aksincha, $-OCH_3$ guruhining –J – effekti ularni siklogeksadiyenil kationiga nisbatan beqaror qiladi.

Aromatik halqada-OCH_3 o‘rnida $-NR_2$, $-NH_2$, -OH, -NH -CO-R, -O-CO-R kabi boshqa + M – effektni namoyon qiladigan o‘rinbosar bo‘lganda ham yuqoridagiga o‘xshash holat kuzatiladi.

Toluolga elektrofil reagent hujum qilganda hosil bo‘ladigan σ - komplekslar quyidagicha tuzilishga ega bo‘lishi mumkin:

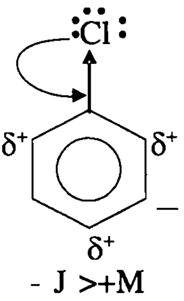


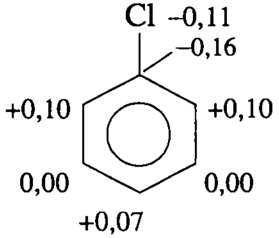
Orto- va para- almashinganda hosil bo'ladigan I, II, IV va V rezonans strukturalar ikkilamchi karbokationlar , III va VI esa metil guruhi bilan giperkonyugatsiya (p,π- tutashish) hisobiga barqarorlashgan uchlamchi karbokationlardir. Bundan tashqari I va VI rezonans strukturalarini metil guruhining +J – effekti ham barqaror qiladi.

Meta- almashinganda hosil bo'ladigan VII-IX rezonans strukturalarning uchalasi ham ikkilamchi karbokationlar bo'lib, ularni metil guruhining +J-effekti orto- va para- holatlaridagi singari unchalik barqaror qilmaydi. Shuning uchun ham toluolning meta- holati almashinish reaksiyalarida benzolga nisbatan faol, lekin toluolning orto- va para- holatlariga nisbatan faolligi kam.

II-guruh o'rinbosarlari (-F, -Cl, -Br, -J) ning elektromanfiyligi katta bo'lganligidan, ular aromatik yadro faolligini kamaytiradi. Galogen benzollarning statik holatida elektron zichligining taqsimlanishiga galogenlarning –J – effekti ta'sir ko'rsatadi.

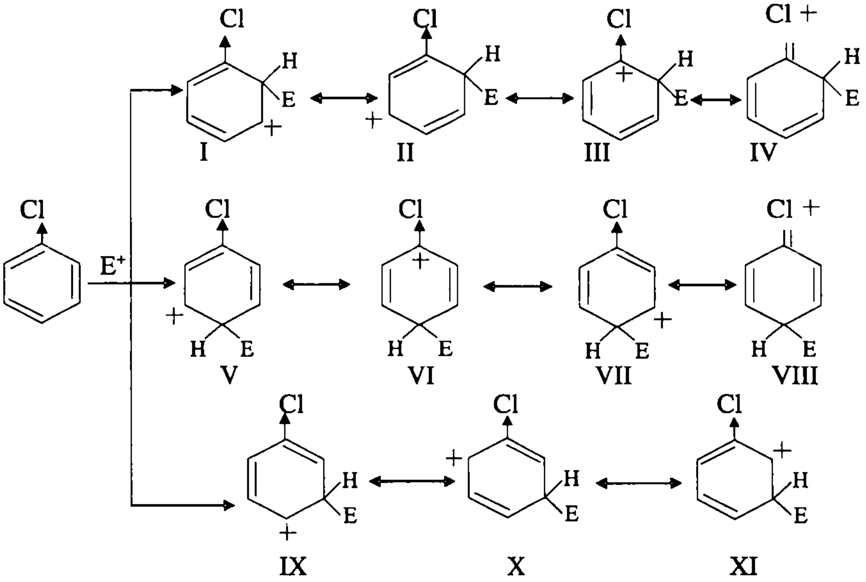
Shu bois reaksiyaga kirishmagan galogenbenzol molekulasida aromatik halqaning orto- va para- holatlarida qisman musbat zaryad hosil bo'ladi:





Demak, reaksiyaga kirishmagan xlorbenzol molekulasida elektron zichligining taqsimlanishi orto- va para- elektrofil almashinish uchun qulay emas. Lekin reaksiya vaqtida xlorning +M (p, π- tutashish)- effekti hal qiluvchi ahamiyatga ega bo'ladi. Tutashish tufayli galogenning umumlashmagan elektron jufti δ- kompleks (+) – zaryadning delokallanishida ishtirok etadi.

Xlorbenzolning orto- va para- va meta- holatlariga elektrofil reagentlar hujum qilganda hosil bo'ladigan δ - komplekslarning rezonans strukturalarini taqqoslaylik:



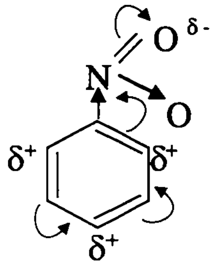
I-III va V-VI strukturalar benzolga E^{+} hujum qilganda hosil bo'ladigan σ - kompleksga nisbatan beqaror, chunki ularda $C^{+}Cl^{\delta-}$ bog'i dipolining musbat qutbi bilan karbokation markazi orasida elektrostatik ta'sirlashuv bor. III va VI strukturalarda musbat zaryad xlor bilan bog'langan uglerod atomida lokallashgan. Xlor bu atomdan elektronlarni kuchli tortganligi sababli bu strukturalar ayniqsa beqarordir.

IV va VIII strukturalar α - xloralmashingan kation tuzilishiga ega bo'lib, xlor atomidagi musbat zaryad tufayli barqarorlashgan. Shuning uchun ham bu strukturalarning orto – va paraalmashinishida hosil bo'ladigan α - komplekslarning real strukturasiga qo'shadigan hissasi katta.

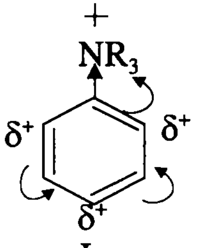
X va XI strukturalar esa eng beqarordir, chunki ularda $C^{\delta+}Cl^{\delta-}$ dipolining musbat qutbi bilan karbokation markazi orasida kuchli elektrostatik ta'sirlashuv mavjud.

Shunday qilib, elektrofil reagent xlorbenzolning meta- holatiga hujum qilganda beqaror σ - kopmleks, orto – va para-holatlariga hujum qilganda esa nisbatan barqaror σ - kopmleks hosil bo‘ladi. Shu bois galogenlar benzol halqasi faolligini kamaytirsa ham, elektrofil reagentlarni orto – va para - holatlarga yo‘naltiradi.

III guruh o‘rinbosarlarining aromatik yadro bilan ta‘sirlashuvi –I- va –M – effektlar hisobiga amalga oshadi:

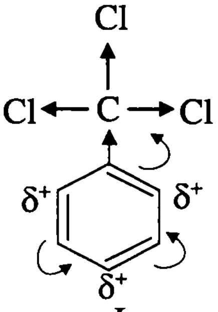


- I ; -M (π,π-)



-J

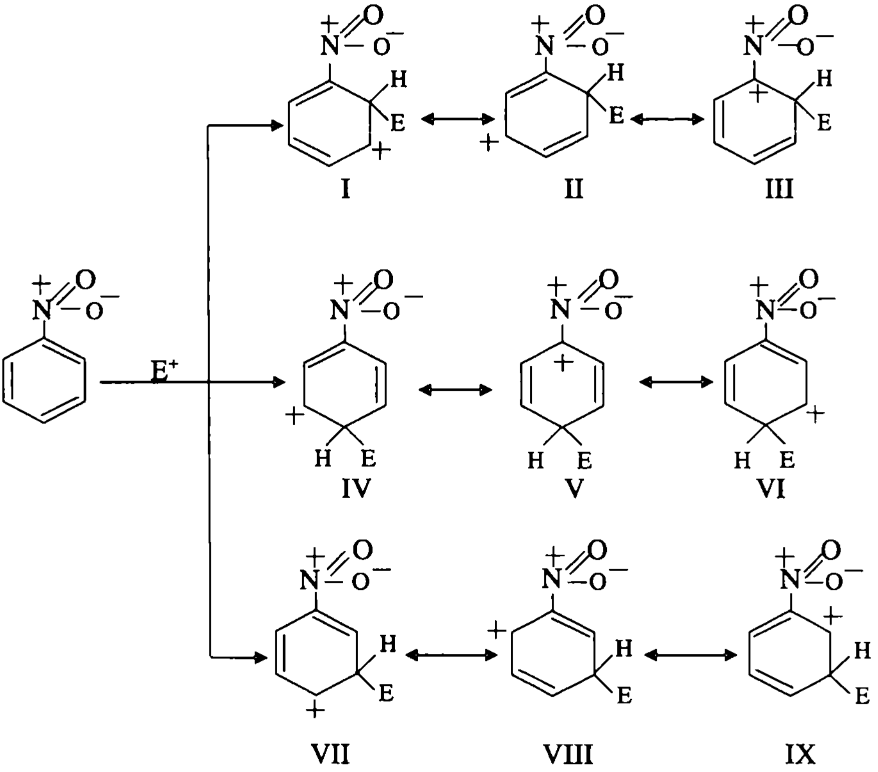
trialkil-
fenilammoniy



-J

trixlormetil-
benzol

Nitrobenzol molekulasiga elektrofil reagent hujum qilganda hosil bo‘ladigan δ - komplekslarning tuzilishini ko‘rib chiqamiz va ularning barqarorligini taqqoslaymiz:



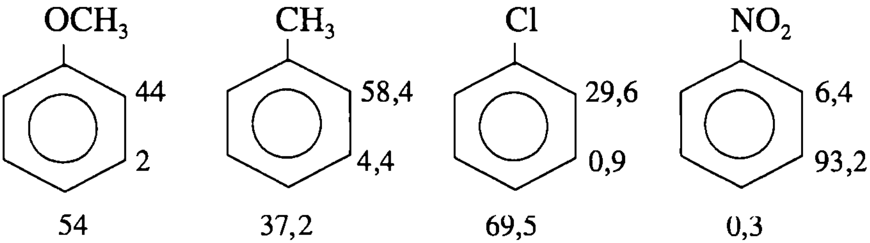
Barcha I – IX rezonans strukturalarida $C^{\delta+}$ $NO_2^{\delta-}$ bog'i dipolining musbat qutbi bilan karbokation markazi orasida kuchli elektrostatik itarilish ro'y beradi. Shu bois nitrobenzol barcha holatlarining faolligi benzolga nisbatan kamaygan.

III va V strukturalar eng barqaror bo'lib, mavjudligi real emas. Chunki ularda qo'shni uglerod va azot atomlari musbat zaryadlangan. Demak, orto- va para- almashinishda faqat ikkitadan (I, II va IV, VI) strukturalar mavjud bo'lishi mumkin. Lekin bu strukturalarda ham musbat zaryad ikkita uglerod atomi orasida taqsimlanganligidan ular VII – IX strukturalarga nisbatan beqarordir.

Meta–almashinishda hosil bo'ladigan VIII va IX strukturalarda ikkita musbat zaryad bitta uglerod atomi bilan ajratilganligi uchun bular I-VI strukturalarga nisbatan barqarordir.

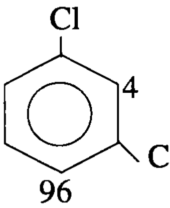
Shunday qilib, elektrofil zarracha nitrobenzolning meta - holatiga hujum qilgandagina barqaror σ - kompleks hosil bo‘ladi. σ-Kompleks qanchalik barqaror bo‘lsa, u shunchalik oson hosil bo‘lishini oldingi mavzulardan bilasiz. Shu boisdan ham nitrobenzolga elektrofil reagentlar ta‘sir ettirilganda asosan uning meta- almashingan izomerlari hosil bo‘ladi.

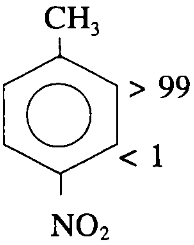
Elektrofil almashinish reaksiyalari uchun yo‘naltirish qoidalari nisbiy xarakterga ega bo‘lib, faqatgina reaksiyaning asosiy yo‘nalishini ko‘rsatadi, xolos. Odatda, almashinish reaksiyalarida hosil bo‘lish imkoniyati bor barcha izomerlar aralashmasi hosil bo‘ladi, lekin ularning nisbati yo‘naltirish qoidalariga asosan bo‘ladi. Masalan, monoalmashingan benzollarni nitrolashda quyidagi natijalar (izomerlar unumi foiz hisobida halqaning tegishli holatlarida keltirilgan) olingan:

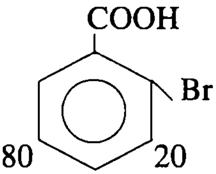


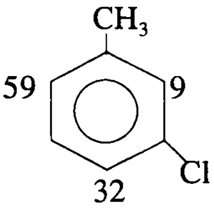
Dialmashingan benzollarning elektrofil almashinish reaksiyalarida kelishilgan va kelishilmagan yo‘naltirish bo‘lishi mumkin.

Kelishilgan yo‘naltirishda aromatik halqadagi ikkala o‘rinbosar uchinchisini asosan bir xil holatga yo‘naltiradi. Bir-biriga nisbatan meta -holatda joylashgan ikkita orto- va para-oriyentant yoki ikkita metaoriyentant, shuningdek, bir-biriga nisbatan orto- va para- holatda bitta orto – va para- oriyentant bo‘lganda kelishilgan yo‘naltirish kuzatiladi. Masalan, dialmashingan benzollarni nitrolab, quyidagi natijalar (izomerlar unumi foiz hisobida halqaning tegishli holatlarida keltirilgan) olingan:









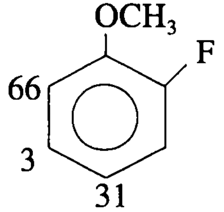
Aromatik halqadagi ikkita o‘rinbosarning yo‘naltirish ta‘siri turlicha bo‘lganda, ularni uch sinfga bo‘lish maqsadga muvofiqdir.

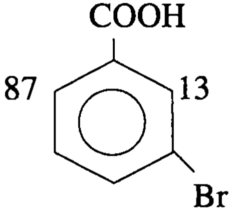
1) kuchli faollashtirilgan orto- va para- oriyentantlar (NR_2; NHR; NH_2; OH; OR);

2) alkil guruhlari va galogenlar;

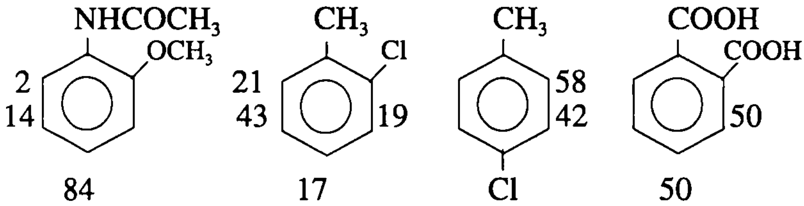
3) halqa faolligini kamaytiradigan meta- orientantlar

Ikkita o‘rinbosar turli sinflarga mansub bo‘lganda, doimo faollashtiradigan o‘rinbosarning ya‘ni, orto- va para – oriyentantning yo‘naltirish effekti meta- oriyentantga nisbatan katta bo‘ladi. Masalan, nitrolashda:





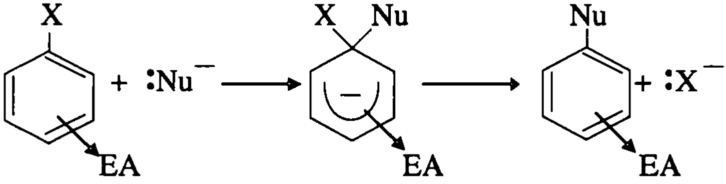
Kelishilmagan yo‘naltirishda yadrodagi bitta sinfga mansub bo‘lgan ikkita o‘rinbosar uchinchisini boshqa –boshqa holatlarga yo‘naltiradi. Masalan, quyidagi dialmashingan benzollarni nitrolaganda izomer mahsulotlarining murakkab aralashmasi hosil bo‘ladi:



Nukleofil aromatik almashinish reaksiyalari

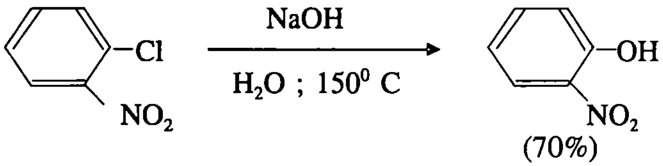
Nukleofil almashinish aromatik uglevodorodlar uchun xarakterli emas. Almashingan benzol nukleofil reagentlar bilan reaksiyaga kirishmaydi. Benzol halqasida elektron zichligini oshiruvchi elektrodonor o‘rinbosarlar bo‘lsa, nukleofil almashinish yanada qiyinlashadi. Halqasida π - elektronlarni tortib, zichlikni kamaytiradigan elektronoaktseptor o‘rinbosarlarni saqlagan aromatik birikmalargina nukleofil almashinish reaksiyalariga kirishadi. Aromatik substratning tabiatiga qarab nukleofil almashinish turli mexanizmlarda borishi mumkin.

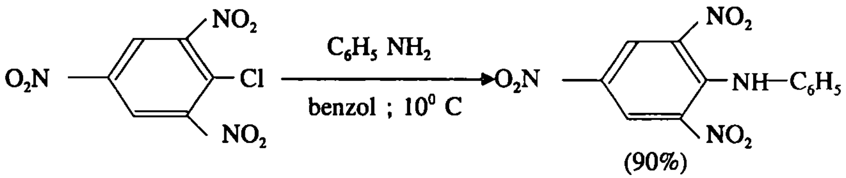
Nukleofil reagentning birikishini osonlashtiruvchi bitta, ikkita yoki uchta kuchli elektronoaktseptor o‘rinbosari (EA) bor birikmalar birikish – ajralish bimolekulyar mexanizmida reaksiyaga kirishadi. Anionli σ - kompleks (Meyzengeymer kompleksi) ning hosil bo‘lish bosqichi orqali boradigan bu jarayon faollashtirilgan aromatik nukleofil almashinish reaksiyalari deb yuritiladi va S_NAr bilan belgilanadi (Bannet, 1958-y.):



Bunda X – ajralib chiquvchi (nukleofug) guruh
EA= $N^+ \equiv N$, $-NO_2$, $-NO$, $-CN$, RSO_2 va hokazo
$:Nu = OH^-$, OR^-, SR^- RNH_2, R_2NH, NH_2NH_2 va boshqalar

Turli nukleofil agentlar ta'sirida boradigan S_NAr reaksiyalariga misollar keltiramiz:

1.


2.


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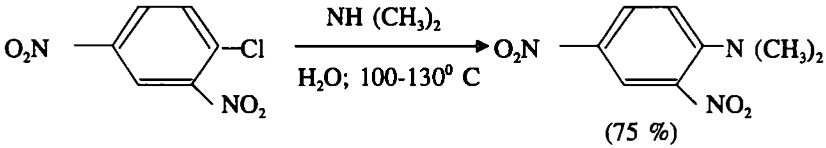

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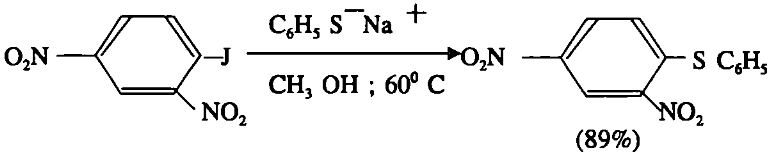
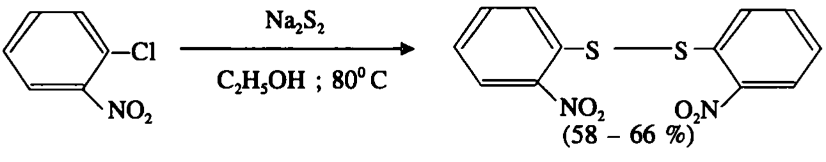
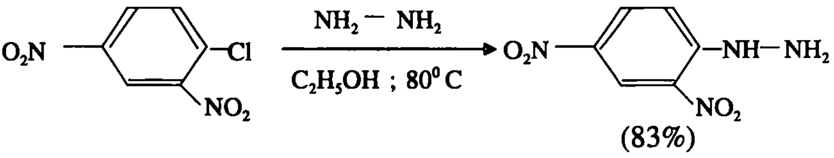


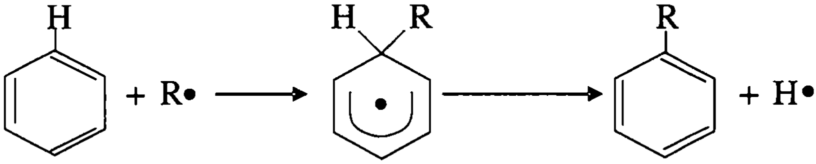
5.


6,


Kuchli elektronoakseptor o'rinbosari yo'q (faollashmagan) aromatik birikmalar kuchli nukleofillar bilan ajralish-birikish (arin) mexanizmida reaksiyaga kirishadi (arilgalogenidlarning kimyoviy xossalariga qarang).

Aromatik yadroda radikal almashinish

Bu reaksiyalar quyidagi mexanizm bilan boradi:



Radikalli σ - komplekslar beqaror bo'lib, ularni sof holda ajratib olishning iloji yo'q.

Muhim vakillari

Benzol - o'ziga xos hidli, suvda deyarli erimaydigan, rangsiz suyuqlik bo'lib, toshko'mirni quruq haydash va neftni qayta ishlash bilan olinadi. U etilbenzol, stirol, izopropilbenzol, xlorbenzol, nitrobenzol, sulfobenzol, siklogeksan, malein angidridi, feniletil spirti va boshqa birikmalarni olishda, shuningdek, erituvchi sifatida keng qo'llaniladi.

Toluol – suvdan yengil rangsiz suyuqlik bo'lib, toshko'mirni quruq haydash va geptanni degidrotsikllash bilan olinadi. U benzoy kislota, benzaldegid, benzil xloridi, nitrotoluollar olishda, portlovchi moddalar, bo'yoqlar, sintetik yuvish vositalari, dorivor moddalar, kaprolaktam ishlab chiqarishda, shuningdek, erituvchi sifatida qo'llaniladi.

Ksilollar - Toshko'mirni quruq haydash va oktanlarni degidrotsikllash bilan o-, m- va p- ksilollar aralashmasi olinadi.

Izomerlar aralashmasini past haroratda kristallash, keyin fraktsiyalab haydash bilan sof ksilollarga ajratiladi.

Ksilollar aralashmasi erituvchi va yuqori oktanli benzinlarning komponenti sifatida, nitroksilollar, bo'yoqlar va portlovchi moddalar ishlab chiqarishda qo'llaniladi. o – Ksiloldan ftal (1,2-benzoldikarbon) kislota, p- ksiloldan esa tereftal (1,4-benzoldikarbon) kislota olinadi.

Etilbenzol – rangsiz suyuqlik bo'lib, stirol olishda qo'llaniladi.

Izopropilbenzol (kumol) – rangsiz suyuqlik bo'lib, benzolni propen bilan alkillab olinadi. Kumolni oksidlab fenol va atseton olinadi.

Stirol (vinilbenzol) – suvda erimaydigan, xushbo'y, rangsiz suyuqlik bo'lib, etilbenzolni katalizator ishtirokida degidrogenlab olinadi. U polistirol va butadiyenstirolli kauchuk olishda ishlatiladi.

Savol va mashqlar

1. Quyidagi arenlarni tuzilish formulalarini yozing:
a) 1,2- dimetil-3-propilbenzol;
b) 1-vinil-4-propilbenzol;
d) allilbenzol;
e) o- butiltoluol;
f) p- etilstirol .
2. Quyidagi radikallarning tuzilish formulalarini yozing:
a) p- tollil;
b) o- fenilen;
d) mezitil;
e) o- kumenil;
f) 2-metil-5- propilfenil.

3. Metilpropilbutilbenzolning barcha izomerlari tuzilish formulalarini yozing va ularni nomlang.

4. a) toluol; b) p – ksilol; d) o- ksilol va etilbenzol qanday

alkanlarning degidrotsikllanishidan hosil bo‘ladi?

5. a) 1,3,5 –trimetilbenzol; b) geksametilbenzol qanday alkinlarning siklotrimerlanishidan hosil bo‘ladi? Bu reaksiyalar qanday sharoitda kechadi?

6. Vyurs – Fittig reaksiyasidan foydalanib, quyidagi arenlarni hosil qiling:

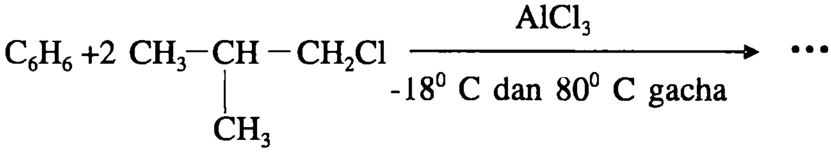
a) 1-izopropil-4-uchlamchibutilbenzol;
b) 1-metil-4- ikkilamchibutilbenzol
d) 1,4-dietilbenzol.

7. Quyidagi reaksiyalarni oxirigacha yetkazing va mahsulotlarni nomlang:

a) $C_6H_6 +$ 1 – xlorpropan $\xrightarrow[-18^0\ C \text{ dan } 80^0\ C \text{ gacha}]{AlCl_3} \cdots$

b) $C_6H_6 +$ 1 – xlorbutan $\xrightarrow[0^0\ C]{AlCl_3} \cdots$

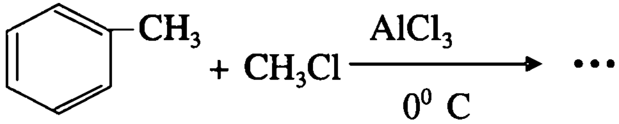
d)

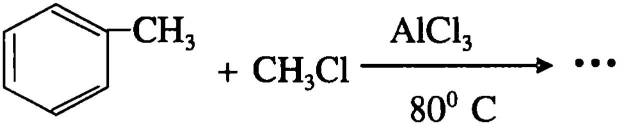


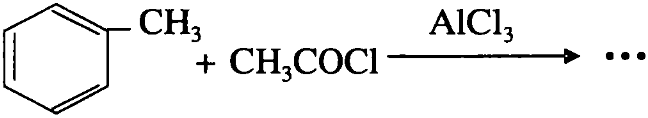
$$C_6H_6 + 2\ CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2Cl \xrightarrow[-18^0\ C \text{ dan } 80^0\ C \text{ gacha}]{AlCl_3} \cdots$$

e) $C_6H_6 +$ neopentil spirti $\xrightarrow[60^0\ C]{BF_3} \cdots$

8. Reaksiyalarni oxirigacha yetkazing:

a)


b)


d)


9. $KMnO_4$ bilan oksidlaganda benzoy kislotani hosil qiladigan C_8H_{10} tarkibli alkilbenzolning tuzilishini aniqlang.

10. Oksidlanganda benzoy kislota, kumush oksidning ammiakdagi eritmasi ta'sirida esa cho'kma hosil qiladigan, bromli suvni rangsizlantiradigan C_8H_{10} tarkibli uglevodorodlarning tuzilishini aniqlang.

11. Stirol bilan quyidagi reagentlar orasida boradigan reaksiyalar tenglamalarini yozing :

a) H_2, Ni, 20^0 C, 2-3 atm
b) H_2, Ni , 125^0 C, 110 atm
d) H_2O_2, HCOOH
e) $KMnO_4$, Δ.

III. KONDENSIRLANMAGAN KO‘P YADROLI AROMATIK BIRIKMALAR

Difenil. Olinishi, xossalari, difenil hosilalarining atropoizomeriyasi.

Difenilmetan. Olinishi va xossalari.

Trifenilmetan. Olinishi va xossalari.

Barqaror trifenilmetan erkin radikallari va ionlari.

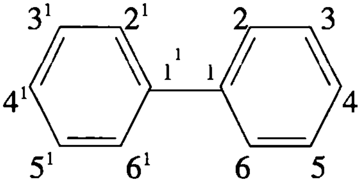
Trifenilmetan bo‘yoqlari.

Savol va mashqlar.

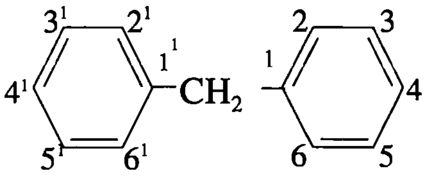
Molekulasida ikki va undan ortiq benzol halqasini tutgan birikmalarga ko‘p yadroli aromatik birikmalar deyiladi.

Halqalarining bog‘lanish xarakteriga qarab ular kondensirlangan(tutashmas) va kondensirlangan (tutash) benzol halqali ko‘p yadroli aromatik birikmalarga bo‘linadi.

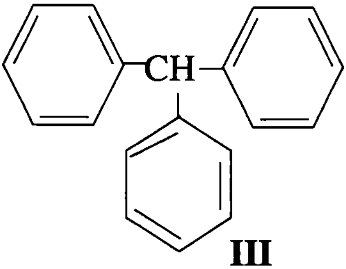
Difenil (I), difenilmetan (II), trifenilmetan (III), difeniletilen (IV) va hokazo uglevodorodlar hamda ularning hosilalari tutashmas benzol halqali ko‘p yadroli aromatik birikmalardir:



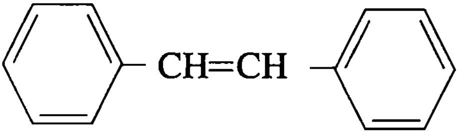
I



II



III

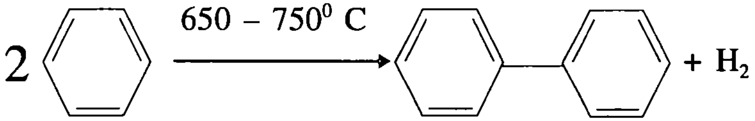


IV

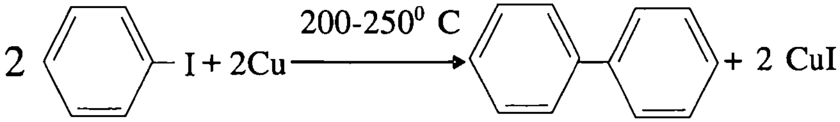
Difenil. Difenil hosilalarining atropoizomeriyasi.

Difenil – 71° C da suyuqlanib, 254° C da qaynaydigan o‘ziga xos hidli, suvda erimaydigan rangsiz kristall modda. U quyidagi usullar bilan olinadi:

1. Benzolni piroliz qilib olish (Bertlo, 1867- y.):



2. Yodbenzolni mis kukuni ishtirokida qizdirish (Ulman reaksiyasi, 1903- y.).



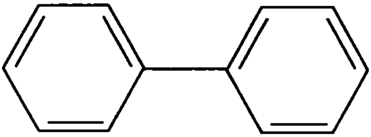
3. Benzolni palladiy tuzlari ishtirokida dimerlash:

$$2\ C_6H_6 + PdX_2 \longrightarrow C_6H_5-C_6H_5 + Pd + 2\ HX$$

4. Fenildiazoniy tuzining ishqordagi eritmasiga benzolni ta‘sir ettirish (Gomberg – Baxman reaksiyasi, 1924 - y.):

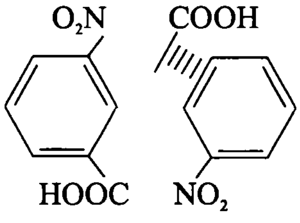
$$\left[C_6H_5-N\equiv N\right]^{+}X^{-} \xrightarrow[-NaX]{NaOH} C_6H_5-\ddot{N}=\ddot{N}-OH \xrightarrow[-N_2,\,-{}^{\bullet}OH]{} C_6H_5^{\bullet} \xrightarrow{C_6H_6} C_6H_5-C_6H_5$$

Difenil molekulasi yassi tuzilishga ega bo‘lib, ikkala halqa bir tekislikda joylashgan:

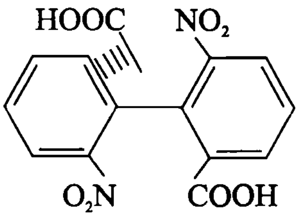


Difenil molekulasidagi ikkala halqa C - C (1-1^{I}) bog‘ atrofida erkin aylana oladi. Lekin 2-, 2^{I}-, 6- va 6^{I}- holatlarda hajmi katta o‘rinbosarlari bor difenil hosilalarida, masalan 6,6^{I} – dinitrodifenildikarbon – 2,2^{I}- kislotada 1-1^{I} bog‘ atrofida erkin aylanish yo‘q. Chunki fazoviy to‘siq tufayli bir halqadagi nitroguruh ikkinchi halqadagi nitroguruh yoki karboksil guruhi qarshisiga kela olmaydi. Boshqacha aytganda, o – va o^{I} - holatlaridagi nitro- va karboksil guruhlari 1-1^{I} bog‘ atrofida erkin aylanishga xalaqit beradi.

Natijada halqalar bir tekislikda emas, balki bir-biriga perpendikulyar tekisliklarda joylashib, molekula xiral bo‘lib qoladi va ikkita enantiomer (V-VI) holida mavjud bo‘ladi:



V

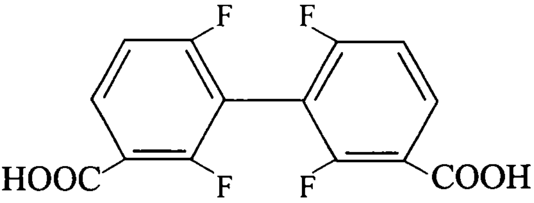


VI

Oddiy bog‘ atrofida erkin aylanishning yo‘qligidan kelib chiqadigan fazoviy izomeriyaning bu turiga atropoizomeriya (grekcha «tropos» - aylanish, a -inkor) deyiladi.

Difenil qatorining optik faol atropoizomerlari molekulalaridagi o‘ziga xos fazoviy sharoit tufayli barqarorlashgan konformerlardir.

Atropoizomeriyaning namoyon bo‘lishi difenil molekulasidagi o- va o^{I}- o‘rinbosarlarning o‘lchamiga ham bog‘liq. Van-der-vaals radiuslari yig‘indisi 0,290 nm gacha o- , o^{I}- holatlaridagi o‘rinbosarlar $1\text{-}1^{I}$ bog‘ atrofida erkin aylanishga xalaqit bera olmaydi. Natijada difenilning bunday hosilalari (masalan, VII birikma) notekis tuzilishga ega bo‘la olmaydi va atropoizomerlar holida uchramaydi:



VII

VII birikmada ikkita orto- ftor atomlarining radiuslari yig‘indisi 0,139 • 2=0,278 nm ga teng.

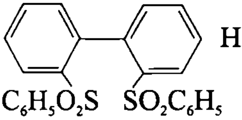
$6,6^1$ – dinitrodifenildikarbon – $2,2^1$- kislotada ikkita nitroguruh radiuslari yig‘indisi 0,192•2=0,384 nm, ikkita karboksil guruhiniki 0,156•2=0,312 nm, nitro- va karboksil guruhlari radiuslari yig‘indisi esa 0,192+0,156=0,348 nm ga teng. Shuning uchun ham bu birikma optik faol enantiomerlar (V va VI) holida

Atom yoki guruh	radius, nm	Atom yoki guruh	radius, nm
H	0,094	CH_3	0,173
F	0,139	Cl	0,189
OH	0,145	NO_2	0,192
COOH	0,156	Br	0,211
NH_2	0,156	I	0,220

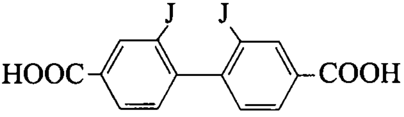
mavjud bo'ladi.

Turli atom va guruhlarning radiuslari quyida keltirilgan:

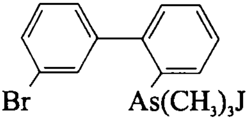
Difenil qatorining optik faol atropoizomerlari orto- holatlarida to'rtta yoki uchta hajmli o'rinbosar saqlashi shart emas. Atropoizomeriyaning namoyon bo'lishi uchun (VIII va IX) ba'zan hatto bitta (X) juda katta hajmli o- o'rinbosar ham yetarli:



VIII

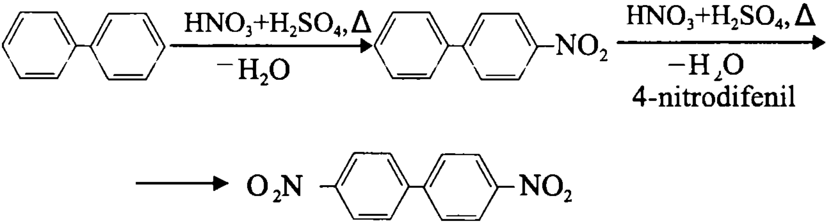


IX



X

Difenil kimyoviy xossalari bilan benzolga o'xshaydi. U nitrolash, galogenlash va boshqa elektrofil almashinish reaksiyalariga oson kirishadi. Bu reaksiyalar asosan 4-va 4^1- holatlarda boradi:

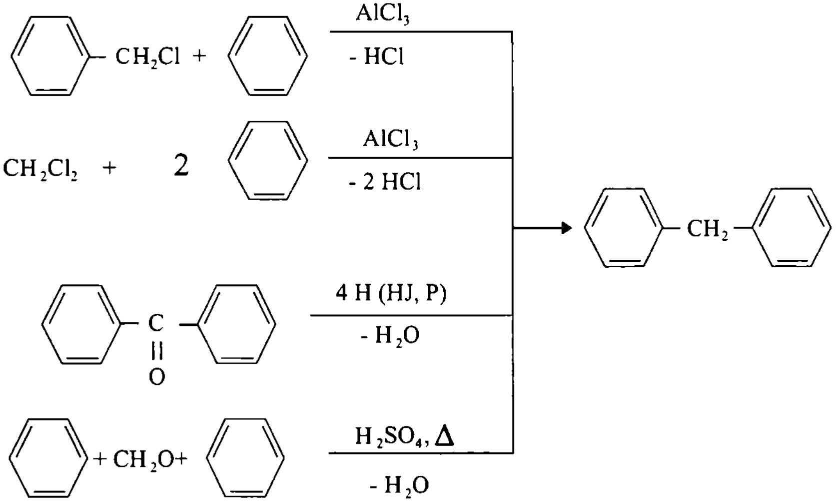


$4,4^1$- dinitrodifenil

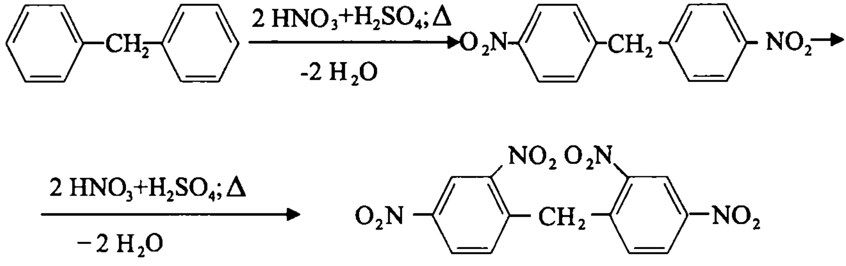
Difenil bilan difenil efirning aralashmasi (dauterm) kimyoviy reaktorlar va boshqa qurilmalarni isitishda yuqori haroratga chidamli issiq o'tkazuvchi sifatida, benzindan esa bo'yoqlar ishlab chiqarishda qo'llaniladi.

Difenilmetan

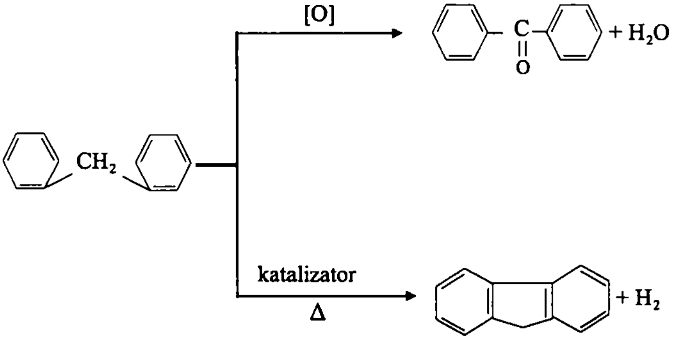
Difenilmetan – 27^0 C da suyuqlanadigan, apelsin hidli rangsiz kristall modda. U benzolni benzil xloridi yoki dixlormetan bilan Fridel-Krafts bo‘yicha alkillash, benzofenonni qaytarish va benzolning formaldegid bilan kondensatsiyasi asosida olinadi:



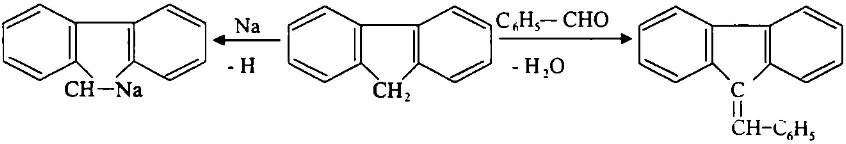
Difenilmetan kimyoviy xossalari bilan benzolni eslatadi. Oson boradigan elektrofil almashinish reaksiyalarida asosan $4, 4^I$ – dialmashingan va $2,4, 2^I, 4^I$ – to‘rtalmashingan difenilmetanlar hosil bo‘ladi:



Difenilmetanning oksidlanishidan benzofenon, kondensatsiyasidan esa fluoren hosil bo'ladi:



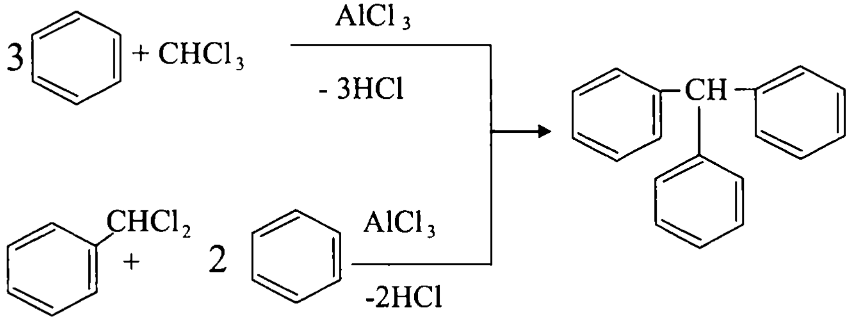
Fluoren-kristall modda. U ikkita benzol yadrosi ta'sirida harakatchan bo'lib qolgan CH_2 guruhi vodorodlari hisobiga reaksiyalarga kirishadi:



Difenilmetan lak-bo'yoq sanoati erituvchilariga qo'shiladi, shuningdek, sovunlarga hid berishda ishlatiladi.

Trifenilmetan

Trifenilmetan – 92,5° C da suyuqlanib, 360° C da qaynaydigan rangsiz kristall modda. U Fridel-Krafts reaksiyasi bilan benzol va xloroform yoki benzil xloridan olinadi:



Trifenilmetanning harakatchan vodorodi metallarga va galogenlarga oson almashinadi:

$$(C_6H_5)_3C{-}H \xrightarrow[-\,H]{Na} (C_6H_5)_3\,\overset{\overline{\bullet\bullet}}{C}-Na^{+}$$

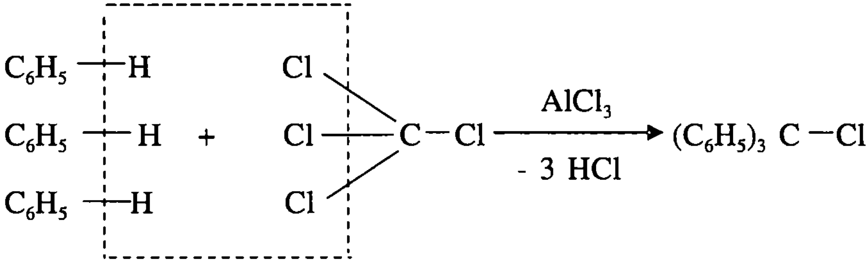
$$(C_6H_5)_3C{-}H \xrightarrow[-\,NH_3]{KNH_2} (C_6H_5)_3\overset{\overline{\bullet\bullet}}{C}-K^{+}$$

kaliy trifenilmetilidi

$$(C_6H_5)_3C{-}H \xrightarrow[-\,HBr]{Br_2} (C_6H_5)_3\,C{-}Br$$

trifenilbrommetan

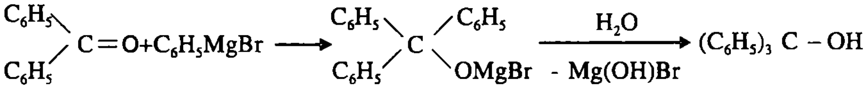
Fridel-Krafts reaksiyasiga benzol bilan tetraxlormetan kiritilsa, trifenilxlormetan hosil bo‘ladi:



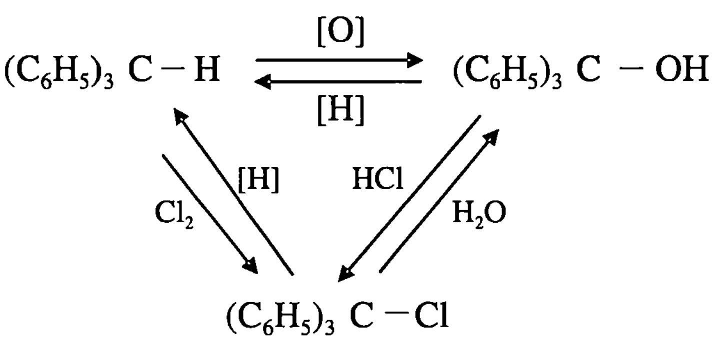
Trifenilxlormetan – 113⁰ C da suyuqlanadigan kristall modda bo'lib, suv ta'sirida trifenilkarbinolni hosil qiladi :

$$(C_6H_5)_3C-Cl + H_2O \longrightarrow (C_6H_5)_3C-OH + HCl$$

Trifenilkarbinol – 162,5⁰ C da suyuqlanadigan, rangsiz kristall modda. U quyidagicha olinadi:



Trifenilmetan, trifenilxlormetan va trifenilkarbinol bir-biriga oson o'tadi:



Bu reaksiyalar trifenilmetan guruhining H, OH va Cl bilan hosil qilgan bog'lari mustahkam emasligidan dalolat beradi.

Barqaror trifenilmetil erkin radikallari va ionlari

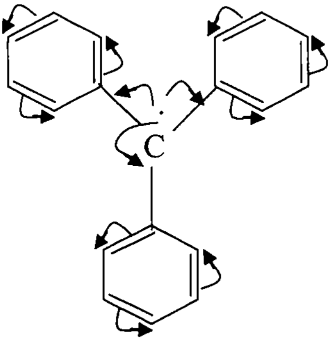
Trifenilmetil guruhi bilan bog'langan atom va guruhlarning bunday harakatchanligiga sabab C– X (X=H, Cl, Br, OH va hokazo) bog'ining dissotsialanishidan hosil bo'ladigan trifenilmetil erkin radikallari yoki ionlarining nisbatan barqarorligidir:

$$(C_6H_5)_3\,C:X \rightleftharpoons (C_6H_5)_3\,C\bullet + X\bullet$$

$$(C_6H_5)_3\,C-X \rightleftharpoons (C_6H_5)_3C^{+} + X^{-}$$

$$(C_6H_5)_3\,C-X \rightleftharpoons (C_6H_5)_3\,C^{-}: + X^{+}$$

Markaziy uglerod atomidagi toq elektron (ionlarda zaryad) ning uchta benzol halqasi π - elektron tizimi bilan tutashish hosil qilib, delokallanishi bu erkin radikal va ionlarni barqaror bo'lishiga olib keladi:



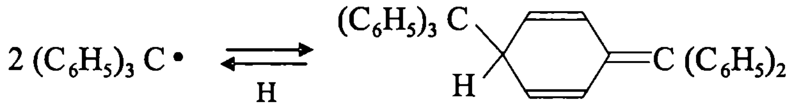
Trifenilxlormetanning benzoldagi eritmasiga CO_2 yoki N_2 atmosferasida kumush, rux yoki simob ta'sir ettirilganda sariq rangli trifenilmetil erkin radikali va uning rangsiz dimeri aralashmasi hosil bo'ladi:

$$2\,(C_6H_5)_3\,C-Cl+2Ag \xrightarrow[-2\,AgCl]{80^0\,C} (C_6H_5)_3\,C\bullet \rightleftarrows \text{dimer}$$

1900 -yilda trifenilmetil radikalining hosil bo'lganligini isbotlagan Gomberg dimerni geksafeniletan tuzilishiga ega deb hisobladi:

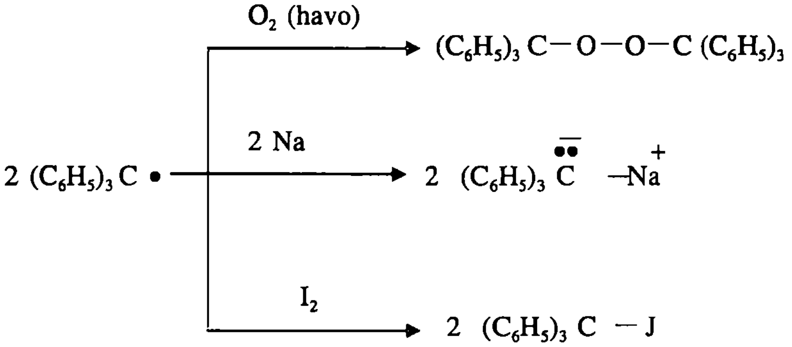
$$2\,(C_6H_5)_3\,C\bullet \rightleftarrows (C_6H_5)_3\,C-C\,(C_6H_5)_3$$

Keyingi tadqiqotlar (Lankamp, 1968 - y., Gutri, 1969 - y.) dimerni 1-difenilmetilen-4-trifenilmetiltsiklogeksadien-2,5 tuzilishiga ega ekanligini ko'rsatdi:



Hozirgacha sintez qilinmagan geksafeniletan individual birikma sifatida mavjud bo'la olmasligi aniqlandi.

Trifenilmetil radikali kislorod bilan reaksiyaga kirishganda rangsiz trifenilmetil peroksidi, natriy bilan qizil g'isht rangli natriy trifenilmetilidi, yod bilan esa trifenilyodmetan hosil bo'ladi:



$$2\,(C_6H_5)_3C\bullet \xrightarrow{O_2\ (havo)} (C_6H_5)_3C-O-O-C(C_6H_5)_3$$

$$2\,(C_6H_5)_3C\bullet \xrightarrow{2\,Na} 2\,(C_6H_5)_3\overset{\bullet\bullet}{\bar{C}}-\overset{+}{Na}$$

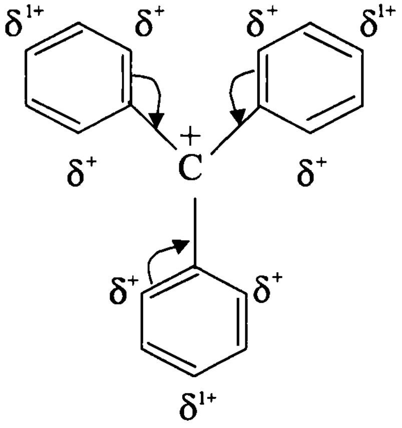
$$2\,(C_6H_5)_3C\bullet \xrightarrow{I_2} 2\,(C_6H_5)_3C-J$$

Trifenilxlormetan suyuq SO_2 va $AlCl_3$ ishtirokida yoki trifenilkarbinolni kons. H_2SO_4 da ionlanishidan qizil-sarg'ish rangli trifenilmetilkation hosil bo'ladi:

$$(C_6H_5)_3C-Cl+AlCl_3 \rightleftarrows (C_6H_5)_3\overset{+}{C}\ Al\overset{-}{Cl_4}$$

$$(C_6H_5)_3C-OH+H_2SO_4 \rightleftarrows (C_6H_5)_3\overset{+}{C}\ HSO_4^- + H_2O$$

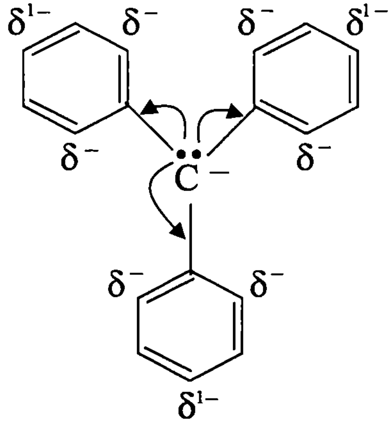
Katta tutashish tizimiga egaligi va musbat zaryadining delokallashgani trifenilmetilkationni barqaror qiladi:



Trifenilmetan suyuq ammiak eritmasida natriy amidi bilan reaksiyaga kirishib, qizil rangli trifenilmetanid-ionni hosil qiladi.

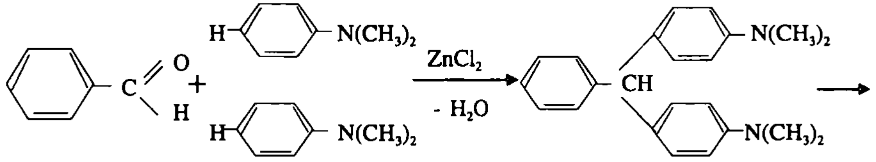
Trifenilmetanid-ionda markaziy uglerod atomi sp² – gibridlangan holatida bo'lib, elektron jufti delokallashgan:

$$(C_6H_5)_3\,CH + NaNH_2 \rightleftharpoons (C_6H_5)_3\,\overset{-}{C}\colon \overset{+}{Na} + NH_3$$

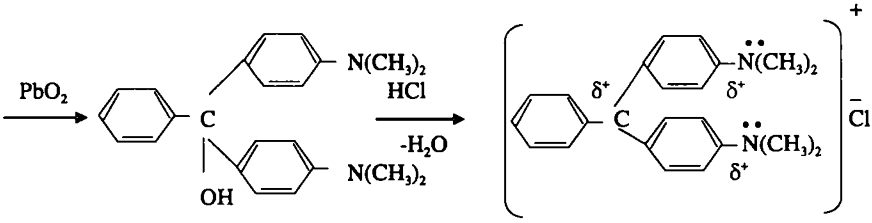


Trifenilmetan bo'yoqlari. Trifenilmetanning benzol halqalarida, $-NH_2$, $-N(CH_3)_2$, $-N(C_2H_5)_2$ yoki $-OH$ guruhlari bor hosilalari rangsiz moddalar bo'lib, bo'yoqlarning leykobirikmalari yoki leykoasoslari (yunoncha leukos –oq) deyiladi. Ularning oksidlanishidan rangsiz karbinollar (karbinol asoslar) hosil bo'ladi. Karbinol asoslarning kislotalar bilan hosil qilgan rangli tuzlari esa bo'yoqlardir.

Ipak, jun va paxtani bo'yashda ishlatiladigan malaxit yashili bo'yog'i benzaldegid va dimetilanilindan quyidagicha olinadi:



leykobirikma



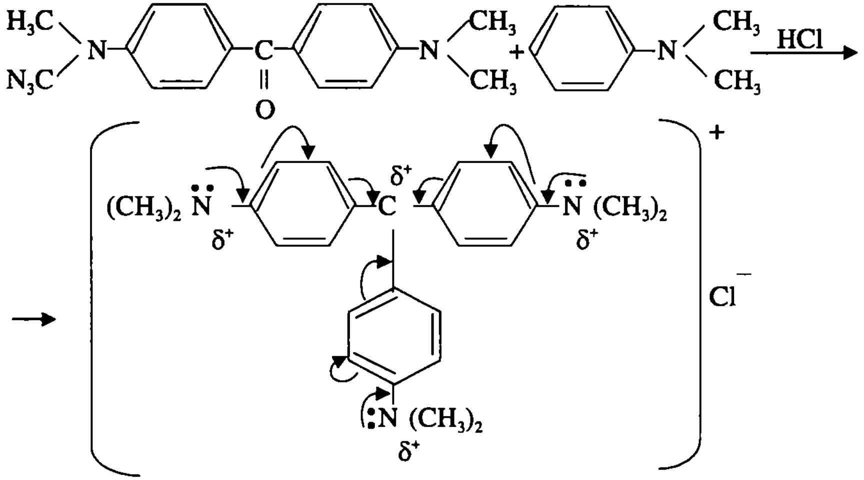
karbinol asosi

rangli tuz (bo`yoq)

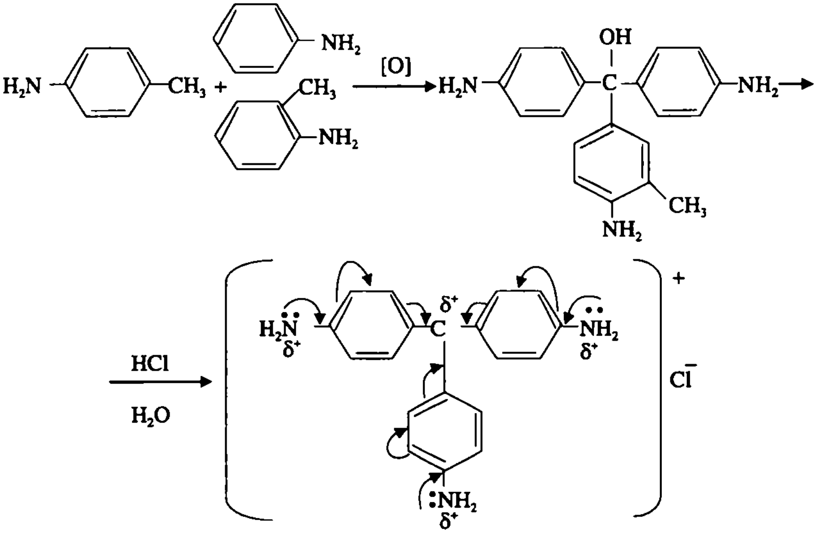
Bu bo'yoqlarda musbat zaryadli kation rang tashuvchi hisoblanadi. Musbat zaryadli uglerod va azot atomlari orasida taqsimlanganligi bois tutashish tizimi bor bu kation barqarordir. Bo'yoqga ko'proq kislota qo'shib, $-N(CH_3)_2$ guruhlari tutashish-dan chiqarilsa, rang yo'qoladi. Bo'yoqga ishqor qo'shganda sekin neytrallanish reaksiyasi borib, rangsiz karbinol ajraladi.

Malaxit yashilining to'rtta metil guruhi o'rnida to'rtta etil guruhi bor gomologi **brillyant yashili** deyiladi. U bo'yoq, shuningdek, tibbiyotda antiseptik sifatida ishlatiladi.

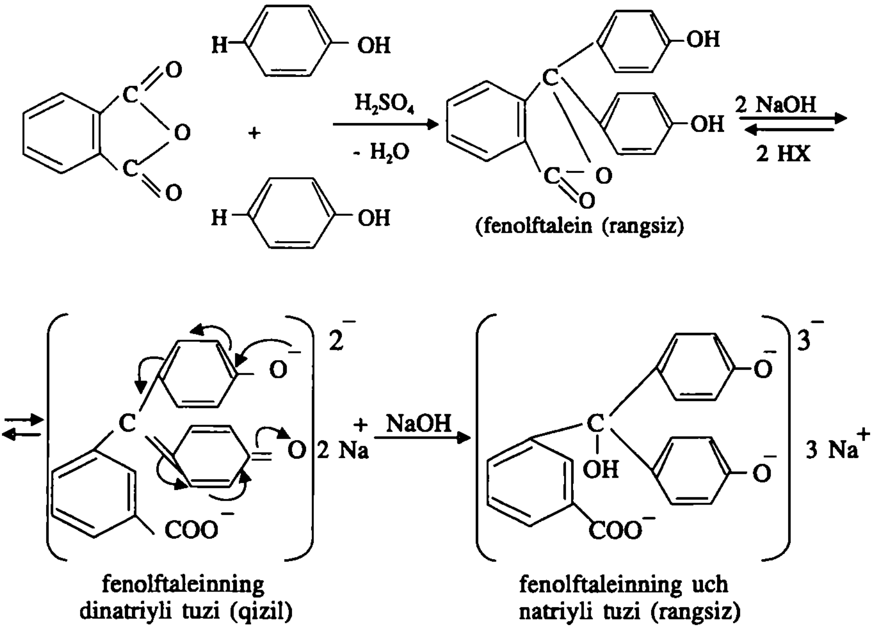
Kristall binafsha bo'yog'i Mixler ketoni (n, n^1, N, N^1 –tetrametildiaminobenzofenon) dan olinadi:



Trifenilmetan bo'yoqlaridan sanoat miqyosida birinchi marta olingani fuksindir. U o- va p- toluidinlar bilan anilin aralashmasini oksidlab olinadi:



Molekulasida gidroksid guruhlarini tutgan anionli trifenilmetan bo‘yoqlariga fenolftalein misol bo‘la oladi. Uni olishda ftal angidridining fenol bilan kondensatsiyasi kons. H_2SO_4 ishtirokida olib boriladi (Bayer, 1871 -y.)



Fenolftaleinning dinatriyli tuzida anion rang tashuvchi hisoblanadi. Ortiqcha ishqor ta'sirida uch zaryadli karbinol asosi hosil bo'ladi va qizil rang yo'qoladi.

Savol va mashqlar

1. Quyidagi birikmalarning tuzilish formulalarni yozing:

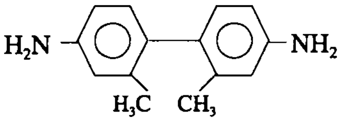
a) 3,4' – diaminodifenil;

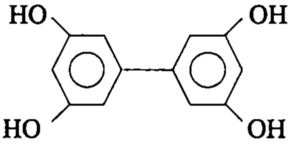
b) 4,4' – dibrom-2,2' –dinitrodifenil;

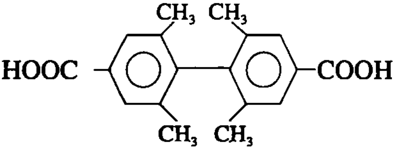
d) 2,4,2',4' –tetragidroksidifenilmetan;

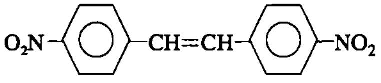
e) tri-(n-nitrofenil) metil erkin radikali

2. Quyidagi birikmalarni nomlang:

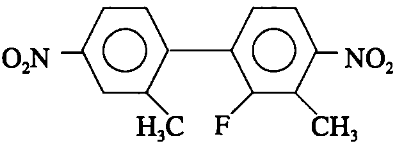
a) 

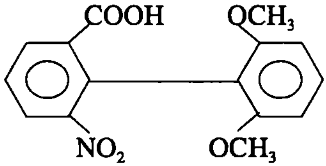
b) 

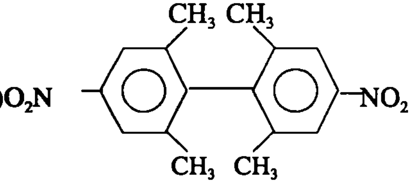
d) 

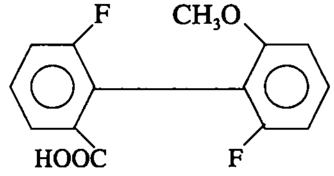
e) 

3. Quyidagi birikmalarning qaysilari optik antipodlar holida mavjud bo'ladi?

a) 

b) 

d) 

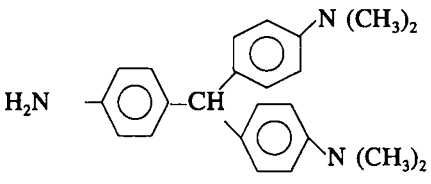
e) 

4. Istalgan reagentlardan foydalanib, quyidagi sintezlarni amalga oshiring:

a) p – bromtoluol → $4,4^{I}$-diaminodifenil

b) benzaldegid → difenilkarbinol

d) nitrobenzaldegid →



e) benzol → α,α^{I} – dixlordifenilmetan

5. Quyidagi aylanishlarni amalga oshiring:

a) gidrazobenzol → difenil

b) toluol → 4-gidroksidifenilmetan

d) toluol → $3,3^{I}$-dimetilbenzidin (o-tolidin)

6. Istalgan reagentlardan foydalanib, quyidagi sintezlarni amalga oshiring :

a) benzol → 4-nitro-4-aminodifenil

b) benzol → 4-brom-4^{I}-nitrodifenil

7. Brombenzol, benzoy kislotaning etil efiri va boshqa reagentlardan foydalanib, trifenilxlormetanni sintez qiling.

8. Benzol, sirkaetil efiri va boshqa reagentlardan foydalanib difenilmetilkarbinolni sintez qilish sxemasini yozing.

9. Quyidagi sintez sxemasini yozing:

Gidrazobenzol → qizil kongo

10. Trifenilmetanga:

a) Br_2 (CCl_4 , yorug'lik);

b) $KMnO_4$ (H_2O);

d) CH_3Na;

e) HNO_3 (H_2SO_4) ni ta'sir ettirganda boradigan reaksiyalar tenglamalarini yozing.

IV. KONDENSIRLANGAN HALQALI KO‘P YADROLI AROMATIK BIRIKMALAR

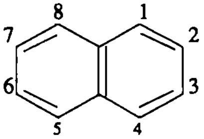
Sinflanishi, nomlanishi.

Naftalin. Tuzilishi, izomeriyasi, olinishi, xossaslari, ishlatilishi.

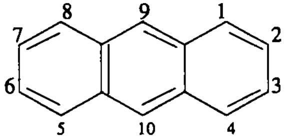
Antratsen. Tuzilishi, izomeriyasi, olinishi, xossalari, ishlatilishi.

Fenantren. Olinishi, xossalari, ishlatilishi. Polibenzollar (piren, perilen, koronen). Kanserogen moddalar haqida tushuncha.

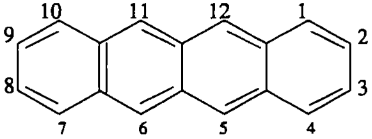
Naftalin (I), antratsen (II), naftatsen (III), fenantren (IV), piren (V), koronen (VI) va hokazo arenlar hamda ularning hosilalari kondensirlangan benzol halqali ko‘p yadroli aromatik birikmalardir:



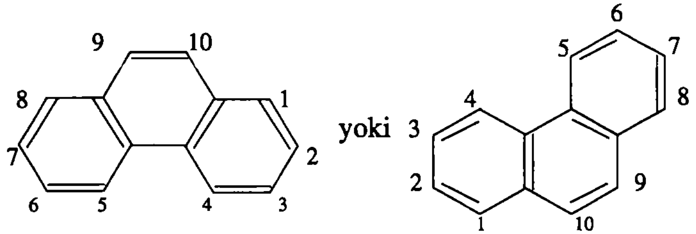
I



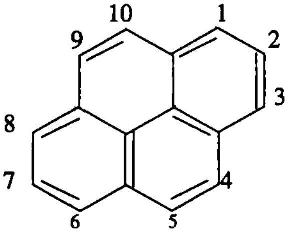
II



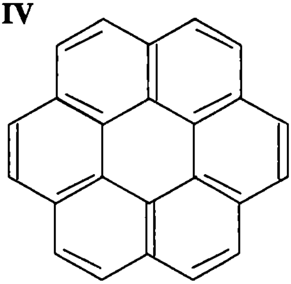
III



IV



V

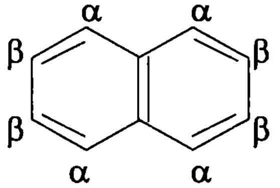


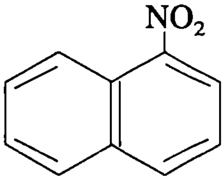
VI

Naftalin, antratsen va naftatsenda benzol halqalari o'zaro chiziqsimon – fenantren, piren va koronenda angulyar tutashgan.

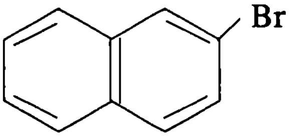
Nomlanishi

Ratsional nomenklaturada naftalin yadrosidagi o'rinbosarlarning holati α - va β bilan belgilanadi:



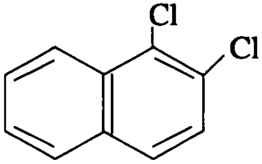


α - nitronaftalin

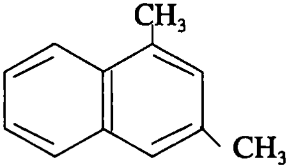


β - bromnaftalin

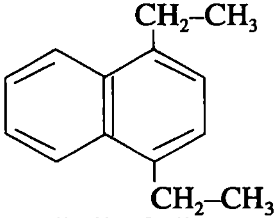
Bordi-yu, naftalin halqalarining bittasida ikkita o'rinbosar bo'lsa, ularning holati o -, m -, p- bilan belgilanadi:



o-dixlornaftalin

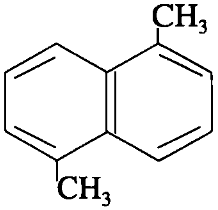


m-dimetilnaftalin

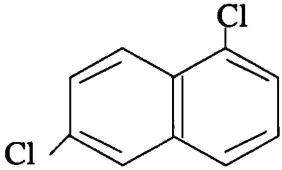


p-dietilnaftalin

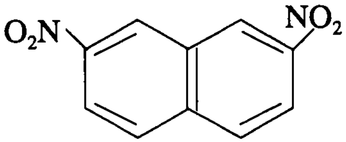
Ikkita o'rinbosar naftalinning ikkita halqasida joylashgan bo'lsa, 1,5 -holatlar ana, 1,6 – epi, 1,7- kata, 1,8-peri, 2,6-amfi, 2,7- holatlar esa – pros deyiladi:



ana- dimetil-
naftalin

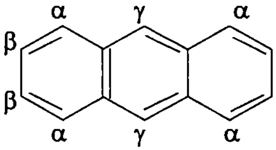


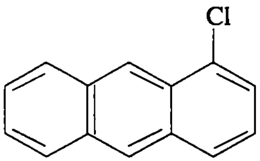
epi – dixlor-
naftalin



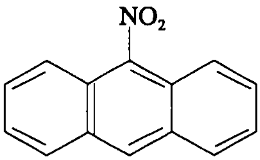
pros- dinitro-
naftalin

Antratsen halqasidagi o‘rinbosarlarning holati α-, β-, γ- bilan belgilanadi:





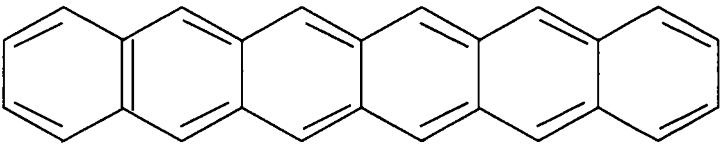
α - xlorantratsen



γ- nitroantratsen

Sistematik nomenklaturaga binoan tutash benzol halqali ko‘p yadroli arenlarning nomlari – en- qo‘shimchasiga ega (naftalin bundan mustasno).

Besh va undan ortiq benzol yadrolari chiziqsimon tutashgan aromatik uglevodorodlar (atsenlar) ning nomlari grek sonlari va – atsen- qo‘shimchasidan hosil qilinadi:



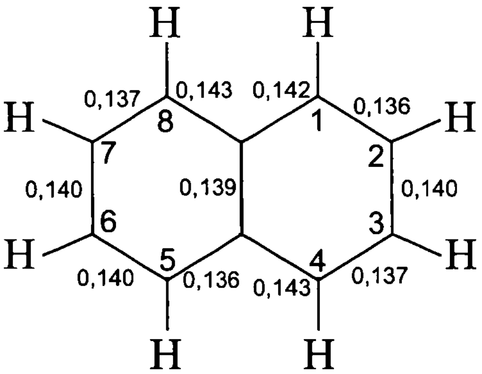
geksatsen

Naftalin

Tuzilishi. Naftalinning elementar tarkibi ($C_{10}H_8$) ni 1835-yilda A. A Voskresenskiy aniqladi. Uning tuzilishini aniqlashda Erlenmeyer, ayniqsa Grebening xizmati katta.

Naftalin molekulasi ikkita umumiy o – uglerod atomlariga ega bo‘lgan ikkita benzol halqasidan tuzilgan. Uning molekulasi yassi tuzilishga ega. Xyukkelning aromatiklik qoidasiga asosan naftalindagi 10 ta π - elektron bog‘lovchi molekulyar orbitallarda joylashgan. Naftalinning tajribada topilgan mezomeriya energiyasi 61 kkal/molga teng. Agar bitta π- elektron uchun hisoblaganda (61:10), bu qiymat taxminan benzoldagidek (36:6) bo‘ladi. Shunga qaramasdan naftalin benzolga nisbatan ancha beqaror, uning reaksiyaga kirishish qobiliyati esa kuchliroqdir. Chunki naftalin halqalaridan bittasining aromatikligini buzish uchun kamroq (25 kkal), ikkinchisining aromatikligini buzish uchun esa ko‘proq (36 kkal) energiya sarflash kerak. Shu bois naftalin faqat almashingan benzol hosil bo‘lish bosqichigacha ya‘ni bitta halqaning aromatikligi buzilguncha benzolga nisbatan oson oksidlanadi va qaytariladi. Okidlanish va qaytarilish reaksiyalarining ikkinchi bosqichi esa benzol singari qiyin boradi.

Rentgenostruktur tahlil naftalin C – C bog‘larining uzunligi (nm da) bir xil emasligini ko‘rsatdi:

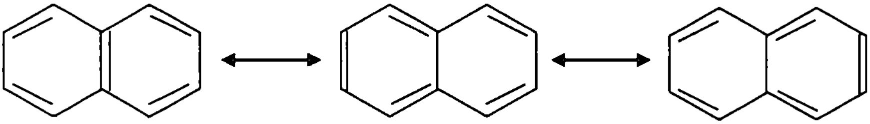


Naftalin molekulasidagi π -elektronlar buluti benzoldagi singari simmetrik tarqalgan emas. Shu bois bog'larning tengligi buzilgan . 1-2, 3-4, 5-6, 7-8 C – C bog'larning elekron zichligi esa benzolning C –C bog'lari elektron zichligidan kichik.

Naftalinning α - holatlari β- holatlariga nisbatan faol. Shu boisdan birikish va elektrofil almashinish reaksiyalari β- holatlariga nisbatan α - holatlarda oson boradi.

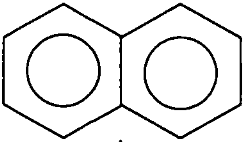
Naftalin molekulasidagi 10 ta π - elektron delokallashib, ikkala halqa uchun ham energetik jihatdan qulay bo'lgan molekulyar orbitalni hosil qiladi. 10 π - elektronli yopiq, bir butun bulut bitta halqa uchun emas, balki ikkala halqa uchun umumiydir.

Valent bog'lar uslubiga ko'ra naftalin I – III rezonans strukturalarning gibridi deb qaraladi:

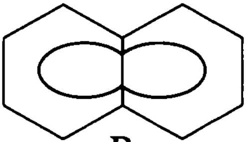


I II III

Naftalinning bir butun (ikkala halqa uchun umumiy) π- elektronlar buluti borligini ko'rsatadigan tuzilishini A formula bilan emas, balki B formula bilan tasvirlash to'g'ridir:



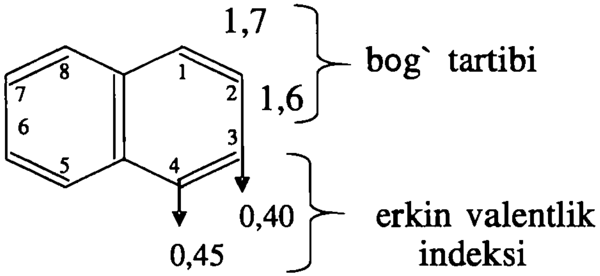
A



B

A formula bilan tasvirlash noto'g'ri, chunki naftalinda ikkita mustaqil benzol tizimi yo'q.

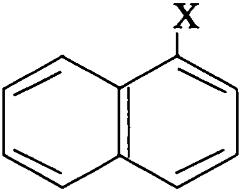
Naftalinning molekulyar diagrammasi quyidagicha:



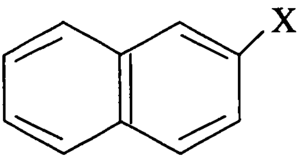
Naftalinda bog' tartibi har xil. Naftalin molekulasidagi α- va β- uglerod atomlarini bog'lab turadigan 1-2, 3-4, 5-6, va 7-8 C-C bog'lar C=C qo'sh bog'iga yaqin.

Naftalinda erkin valentlik indeksi ham bir xil emas. α - uglerod atomlarining erkin valentlik indeksi β-atomlar va benzol uglerod atomlari erkin valentlik indeksiga nisbatan yuqori.

Izomeriyasi. Naftalindagi α - va β- uglerod atomlarining kimyoviy tabiati bir xil emasligi bois naftalinning monoalmashingan hosilalari ikki xil (α- va β-) holida uchraydi:



α - izomer

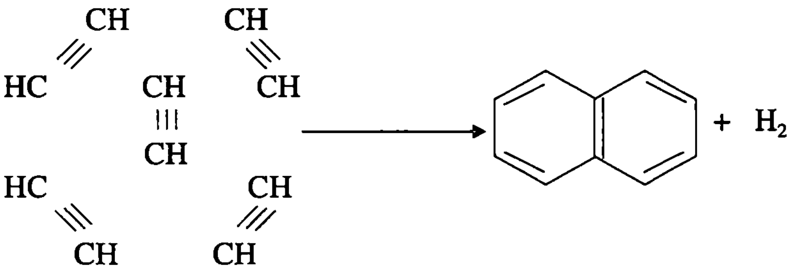


β - izomer

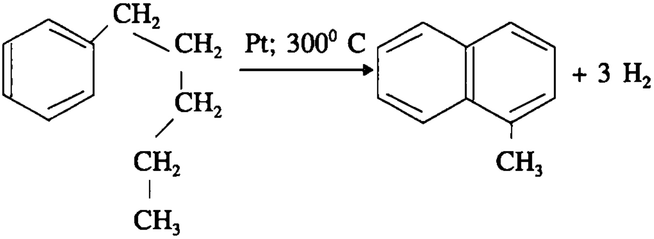
Naftalinning ikkita bir xil o'rinbosar saqlagan dialmashingan hosilalari 10 xil (1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 2,3-, 2,6- va 2,7-) izomer holida uchraydi.

Olinishi. Naftalinning asosiy manbayi toshko'mir smolasidir. Smolada ~5% naftalin bor. Uni neftning pirolizi mahsulotlaridan ham olinadi. Naftalin va uning hosilalarini sintetik usullar bilan ham olish mumkin:

1. Atsetilen 400⁰ C da pista ko'mir ustidan o'tkazilganda benzol bilan bir qatorda naftalin ham hosil bo'ladi. (N. D. Zelinskiy, B.A. Kazanskiy):

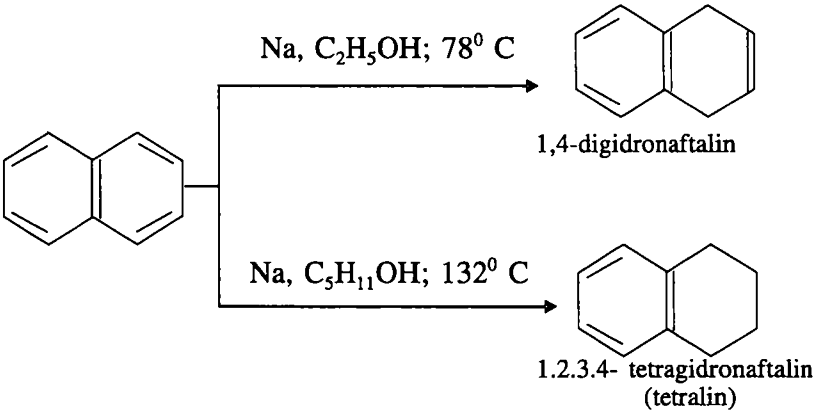


2. Yon zanjirida to'rtta va undan ortiq uglerod atomlari bor benzol gomologlarini degidrosikllanishidan:

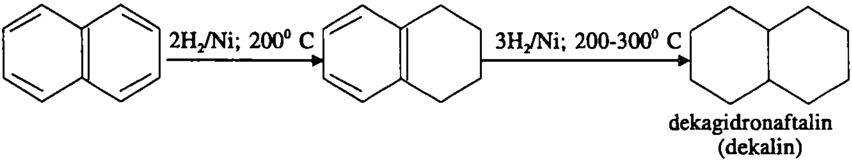


Fizikaviy va kimyoviy xossalari. Naftalin 80°C da suyuqlanadigan o'ziga xos hidli kristall modda bo'lib, hatto xona haroratida ham uchuvchandir. U sublimatlanadi va suv bug'i bilan haydaladi.

a) birikish reaksiyalari. Benzoldan farqli o'laroq naftalinni kimyoviy qaytaruvchilar bilan qaytarish mumkin:



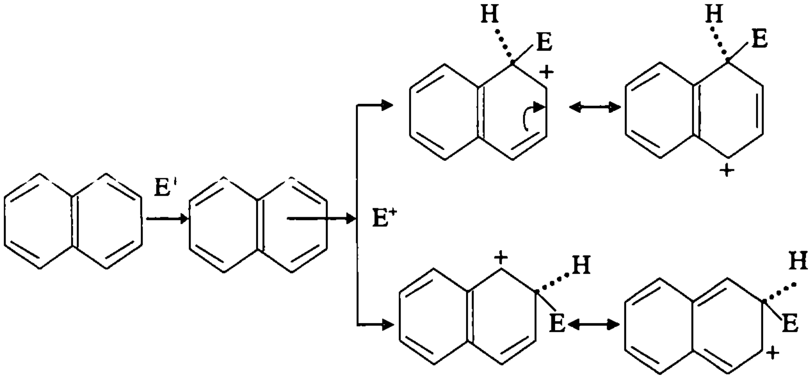
Tetralinni benzolning hosilasi deb qarash mumkin. Shu bois u benzolning boshqa hosilalari singari qiyin (katalizator ishtirokida) gidrogenlanadi:



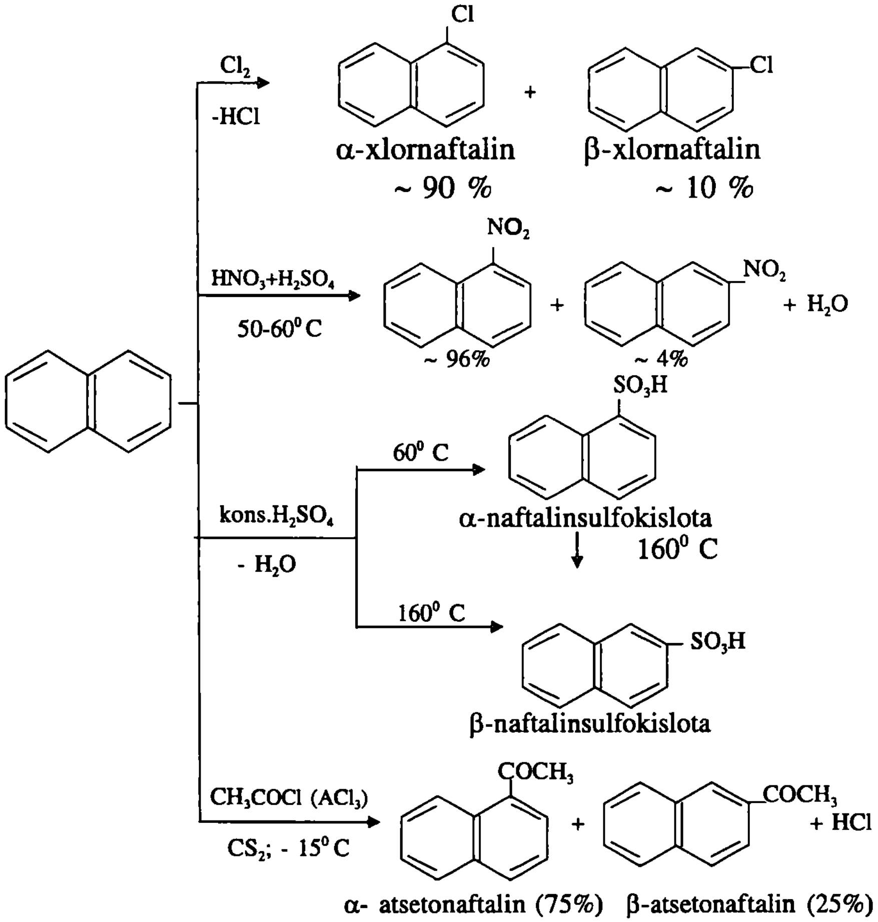
Tetralin va dekalin sanoat miqyosida ishlab chiqariladi. Ular avtomobil yoqilg'ilariga qo'shiladi va yaxshi erituvchi hisoblanadi.

Naftalin xlorni ham benzolga nisbatan oson biriktiradi.

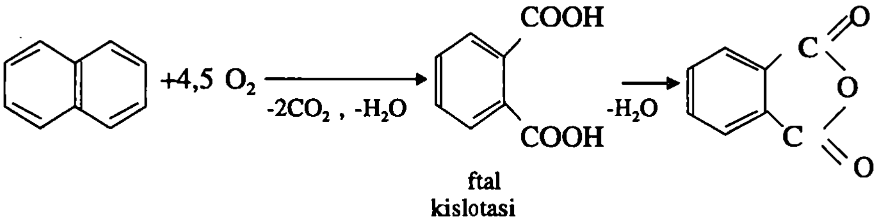
b) elektrofil almashinish reaksiyalari. Naftalin elektrofil almashinish reaksiyalariga benzol va uning gomologlariga nisbatan oson kirishadi. Chunki u benzol va uning gomologlariga nisbatan kuchli elektrodonor xossalarga egaligi bois π- komplekslarni oson hosil qiladi. Bu reaksiyalarda elektrofil reagent ko'pincha α- holatni egallaydi. Chunki α- holatda boradigan almashinishda hosil bo'ladigan σ - kompleks, β - holatda boradigan almashinishda hosil bo'ladigan σ - kompleksga nisbatan barqaror:



Naftalinning elektrofil almashinish reaksiyalari quyidagicha boradi:



v) Oksidlanishi. Naftalin turli oksidlovchilar ta'sirida oksidlanadi. Havo naftalin aralashmasini V_2O_5 katalizatori ustida 350-450° C da oksidlab, sanoatda ftal angidridi olinadi:

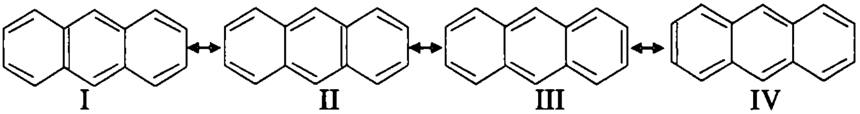


Ishlatilishi. Naftalin asosan ftal angidridini ishlab chiqarish uchun sarflanadi. U insektitsidlar va repelentlar, 2-naftol, sintetik oshlovchi moddalar, tetralin, dekalin, xlornaftalinlar va hokazolarni olishda ham ishlatiladi. Naftalinning gomologlari va ayrim hosilalari ham amaliy ahamiyatga ega.

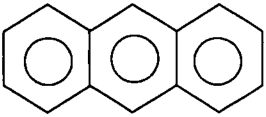
Antratsen

Tuzilishi. Antratsen yassi tuzilishga ega. Uning molekulasidagi 14 π-elektronlar bog'lovchi molekulyar orbitallarda joylashgan bo'lib, umumiy bir butun 14 π-elektronlar bulutini hosil qiladi. Antratsenning mezomeriya energiyasi 84 kkal/mol ga teng. Antratsenda bog'larning teng qiymatliligi naftalinga nisbatan ko'proq buzilgan. 9- va 10- (mezo - holatdagi) uglerod atomlarining nisbiy to'yinmaganligi α- (1-, 4-, 5-, 8-,) va β- (2-, 3-, 6-, 7-,) – uglerod atomlarining nisbiy to'yinmaganligidan katta. C_1 va C_2 uglerod atomlari orasidagi bog' tartibi, C_2 va C_3 orasidagi bog' tartibidan katta (antratsenning molekulyar diagrammasiga qarang).

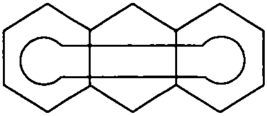
Valent bog'lar uslubiga ko'ra antratsenni I – IV rezonans strukturalarning gibridi deb qarash mumkin:



Antratsenning bir butun 14 π-elektronlar buluti borligini ko'rsatadigan tuzilish formulasini A formula bilan emas, B formula bilan tasvirlash to'g'ridir:

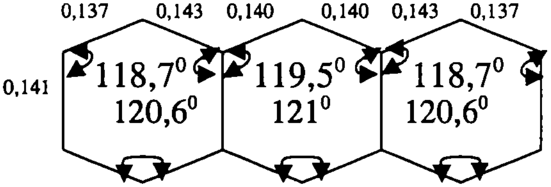


A

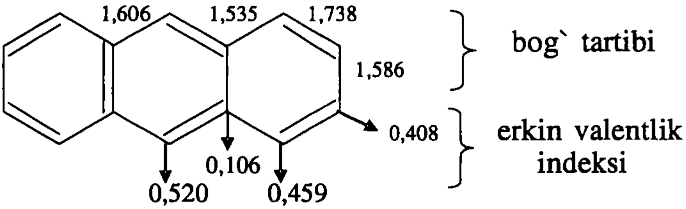


B

Rentgenostruktur tahlil antratsenda bog'lar uzunligining tengligi buzilganligini va aromatik halqalarning oltiburchaklari deformatsiyaga uchraganligini ko'rsatdi:



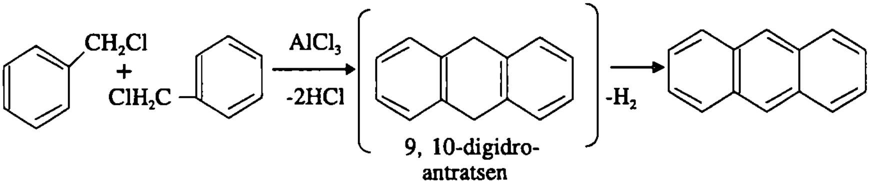
Antratsenning molekulyar diagrammasi quyidagicha:

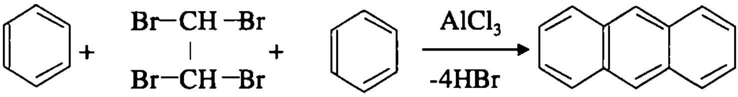


Izomeriyasi. Antratsendagi α- (1-, 4-, 5-, 8-,) va β- (2-, 3-, 6-, 7-,) va γ- (9-, 10-) uglerod atomlarining kimyoviy tabiati bir xil emasligi bois antratsenning monoalmashingan hosilalari uch xil (α-, β-, va γ-) izomer holida uchraydi.

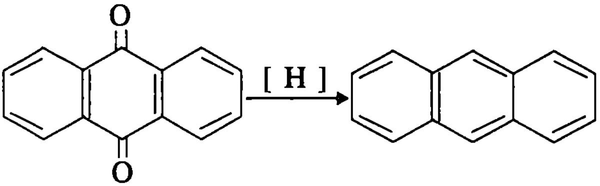
Olinishi. Dyuma va Loran 1832-yilda antratsenni toshko'mir smolasidan ajratib oldilar. Smolada 0,25-0,5 % antratsen bo'ladi. Antratsen va uning gomologlari quyidagi sintetik usullar bilan olinadi.

1. Benzol, uning gomologlari, aralkilgalogenlar va poligalogenalkanlarni Fridel-Krafts bo'yicha alkillash:



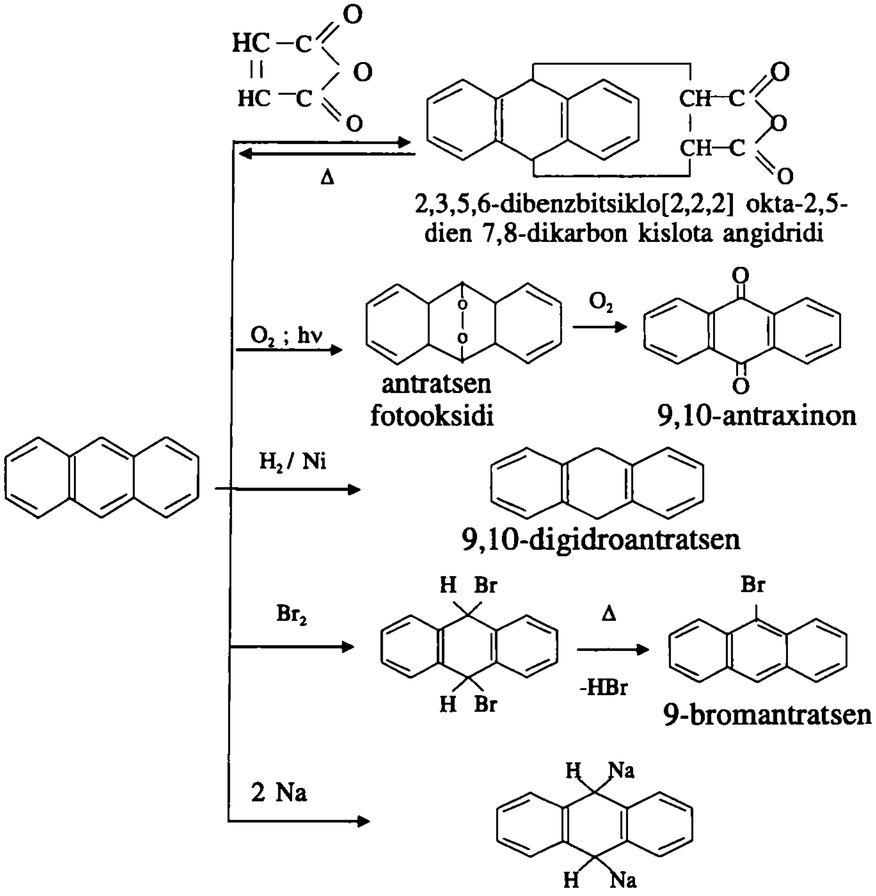


2. 9, 10-antraxinon va uning hosilalarini qaytarish:

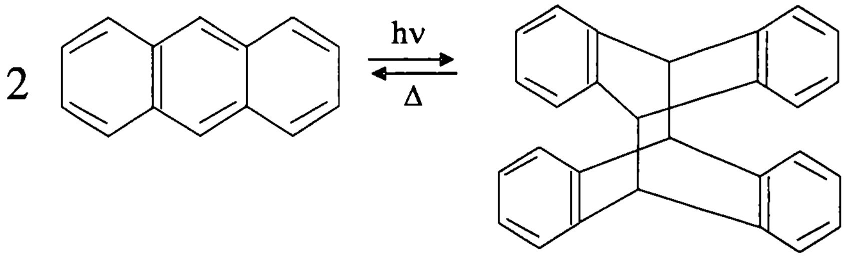


Fizikaviy va kimyoviy xossalari. Antratsen va uning gomologlari yuqori haroratlarda suyuqlanadigan (antratsen 217°C da suyuqlanib, 351°C da qaynaydi), rangsiz yoki och sariq rangli kristall moddalardir.

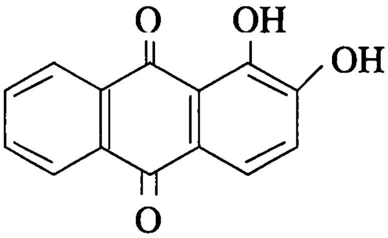
Antratsen naftalinga nisbatan birikish reaksiyalariga oson kirishadi. Unga malein angidridi va boshqa dienofillar, kislorod, natriy, brom, xlor va vodorodning birikish ikkita benzol halqasi ta'sirida faollashgan 9- va 10- (mezo-) holatlar hisobiga boradi:



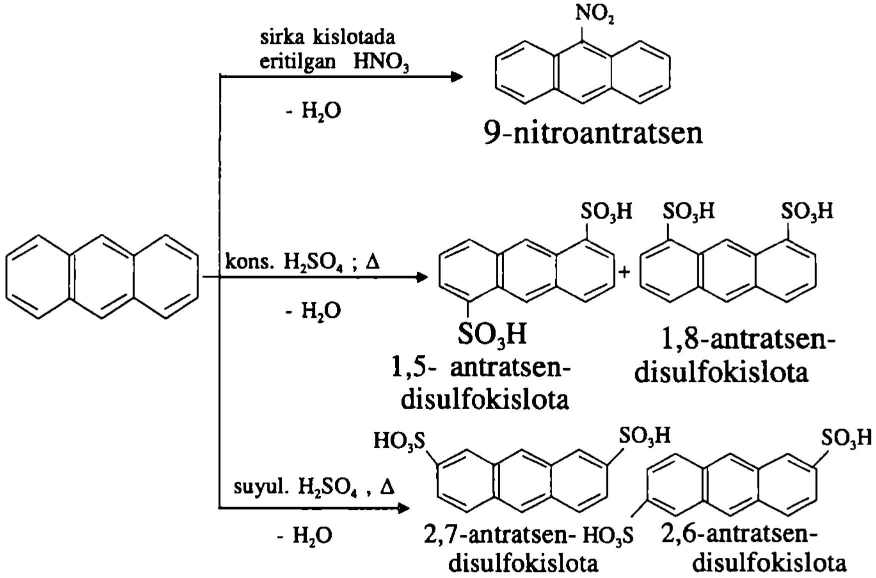
Antratsen nur ta'sirida fotokimyoviy siklobirikish reaksiyasiga kirishadi va dimerlanib diantratsenga aylanadi. Hosil bo'lgan dimer qorong'ida yana antratsenga o'tadi:



Antraxinon va uning hosilalari muhim organik birikmalardir. Masalan, 1,2-digidroksiantraxinon (alizarin) muhim bo'yoq hisoblanadi:



Antratsen nitrolash va sulfolash reaksiyalariga oson kirishadi:

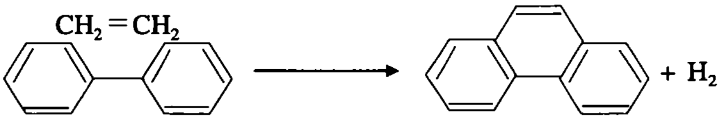


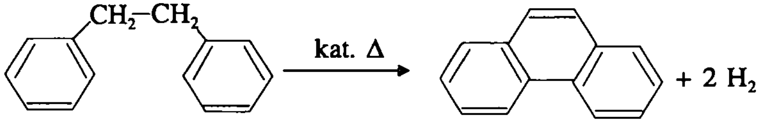
Fenantren

Izomeriyasi. Fenantrenning monoalmashingan hosilalari beshta (1-, 2-, 3-, 4- va 9-) izomer holida uchraydi.

Olinishi. Antratsenga izomer bo‘lgan fenantren toshko‘mir smolasidan ajratib olinadi. Difenil bilan etilen aralashmasi cho‘g‘langan nay orqali o‘tkazilganda fenantren hosil bo‘ladi.

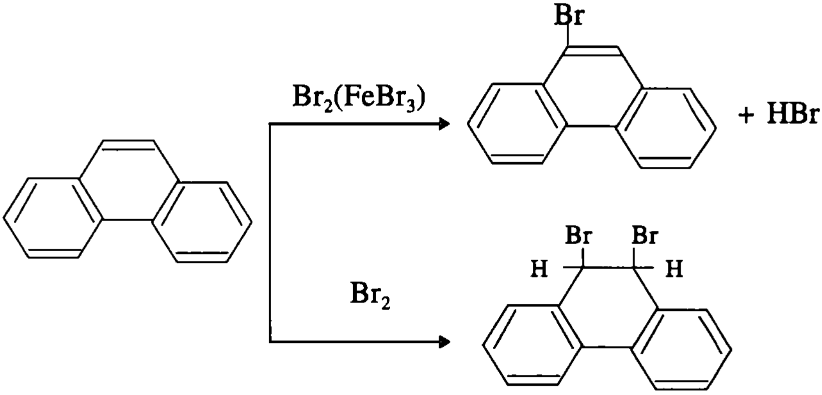
Fenantren va uning gomologlari $0,0^1$- dialkildifenillar yoki 1,2 difeniletan hosilalarini degidrotsikllash bilan ham sintez qilinadi:



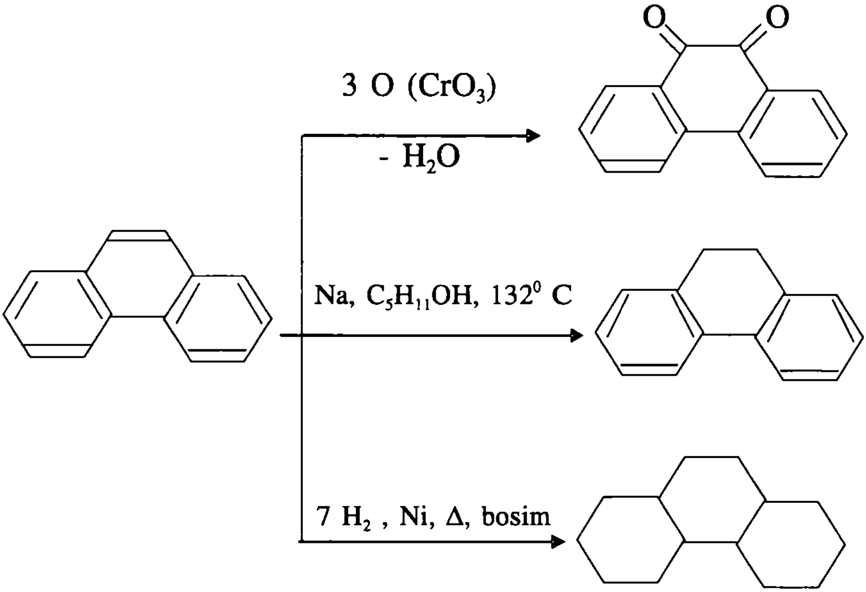


Fizikaviy va kimyoviy xossalari. Fenantren va uning gomologlari rangsiz kristall moddalardir. Fenantren antratsenga nisbatan yaxshi eruvchan va u past harorat (100^0C) da suyuqlanadi. Fenantren ham yassi tuzilishga ega bo'lib, uning mezomeriya energiyasi 92 kkal/molga teng. Fenantren molekulasi antratsen molekulasiga nisbatan birmuncha barqaror, reaksiyaga kirishish qobiliyati esa kuchsizroq.

Fenantren elektrofil reagentlar bilan reaksiyaga oson kirishadi. Uning 9- va 10- holatlari almashinish va birikish reaksiyalariga faol:



Fenantrenni oksidlaganda 9,10- fenantrexinon, gidrogenlaganda esa 9,10- digidrofenantren (yuqori bosim va haroratda katalitik gidrogenlaganda pergidrofenantren) hosil bo'ladi:



pergidrofenantren

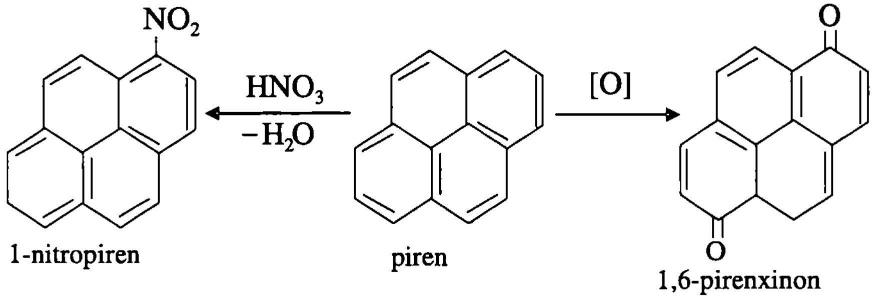
Ishlatilishi. Fenantren organik sintezda (masalan, bo'yoqlar sintezida qo'llaniladigan 9,10- fenantrexinonni olishda) xomashyo sifatida ishlatiladi.

Qisman yoki to'liq gidrogenlangan fenantren skeletini saqlagan birikmalar hayvonot va o'simliklar dunyosida keng tarqalgan. Fenantren skeleti steroid spirtlari, o't kislotalari, jinsiy gormonlar, morfin guruhi alkaloidlari va boshqa biologik faol birikmalar molekulasi tarkibiga kiradi.

Polibenzollar

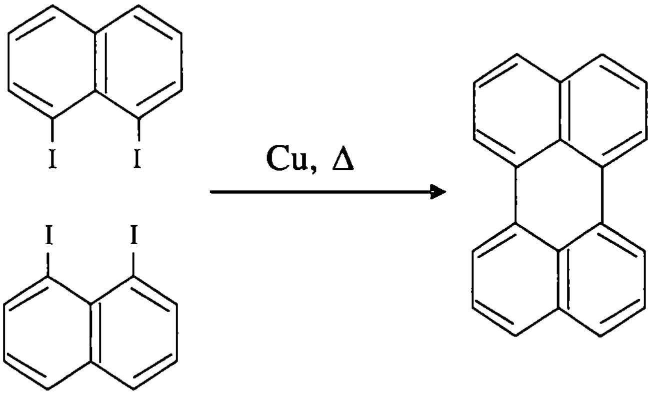
Benzol halqalari angulyar tutashgan ko'p yadroli arenlardan piren, perilen va koronen toshko'mir smolasida uchraydi.

Piren – 156⁰ C da suyuqlanadigan, rangsiz, kristall modda. U elektrofil almashinish va oksidlanish reaksiyalariga oson kirishadi:



Piren organik bo‘yoqlar sintez qilishda xomashyo sifatida ishlatiladi.

Perilen – 274⁰ C da suyuqlanadigan kristall modda. 1,8 – diyodnaftalindan olinishi uning tuzilishini isbotlaydi:



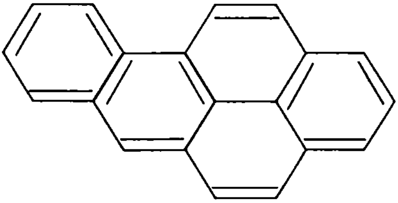
Perilen kimyoviy xossalari bilan naftalinni eslatadi. U elektrofil reagentlar bilan reaksiyalarga oson kirishadi, oson oksidlanadi. Perilennnig hosilalari muhim organik bo‘yoqlar hisoblanadi.

Koronen – 438⁰ C da suyuqlanadigan, och sariq rangli, termik va kimyoviy barqaror modda. U gidrogenlash, sulfolash, nitrolash, galogenlash reaksiyalariga kirishadi.

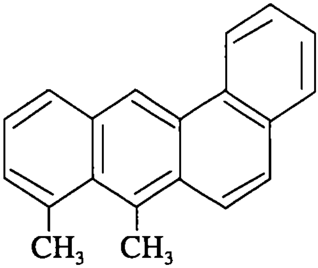
Kanserogen moddalar

Toshko‘mir smolasining yuqori haroratlarda qaynaydigan ayrim fraktsiyalarida besh, olti va undan ortiq yadroli aromatik birikmalar uchraydi. Ularning ko‘pchiligi ekzema va terining rak kasalligini keltirib chiqaradi. Bunday moddalarga kanserogenlar (lotincha canser- rak) deyiladi.

1,2– benzpiren, 5,10– dimetil– 1,2– benzantratsen, metilxolantren, shuningdek, *β*- naftilamin, benzidin, n– dimetilaminoazobenzol kabi moddalar kanserogenlardir:



1,2 – benzpiren



5,10-dimetil-1,2-benzantratsen

Shu bois toshko‘mir smolasi, gudron, bitum, asfalt bilan ishlaganda texnika xavfsizligiga qat‘iy rioya qilish, maxsus kiyim va qo‘lqoplarda ishlash lozim.

Savol va mashqlar

1. Quyidagi birikmalarning tuzilish formulalarini yozing:

a) *β* - bromnaftalin;

b) *α* - etilnaftalin;

d) 2 – bromnaftalin-4-karbon kislota;

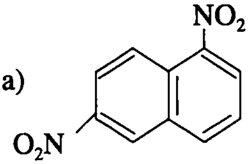
e) 2 – naftilamin-4,8-disulfokislota;

f) 2 – metil-1,4-naftoxinon;

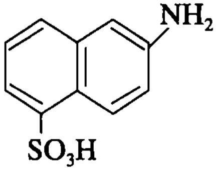
g) pergidrofenantren.

2. Quyidagi birikmalarni nomlang:

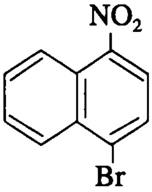
a)



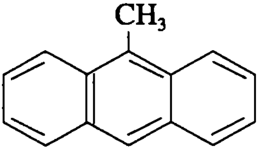
b)



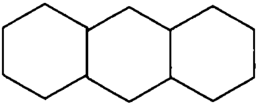
d)



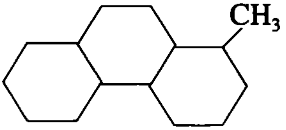
e)



f)



g)



3. Barcha izomer dixlornaftalinlarning tuzilish formulalarini yozing.

4. Barcha izomer bromfenantrenlarning tuzilish formulalarini yozing.

5. Naftalin va boshqa reagentlardan foydalanib, quyidagi birikmalarni sintez qiling:

a) β-bromnaftalin; b) 5-brom-1-nitronaftalin;

d) α-yodnaftalin; e) α-naftoy kislota (naftalin-1 - karbon kislota);

6. Quyidagi reaksiyalarda qanday mahsulotlar hosil bo‘ladi?

a) 1,2,3,4-tetragidronaftalin $\xrightarrow{Pd/\ C,\ \Delta}$

b) 1,3-dimetildekalin $\xrightarrow{S\ ,\ \Delta}$

d) 9,10-digidrofenantren $\xrightarrow{Se,\ \Delta}$

7. Quyidagi reaksiyalarda qanday mahsulotlar hosil bo'ladi?

a) 1-metilnaftalin + $Br_2 \xrightarrow[\text{[CCl}_4\text{]}]{\text{qorong`ida}}$

b) 1-nitronaftalin + $HNO_3 \xrightarrow[0^0\text{ C}]{H_2SO_4}$

d) 2-naftalinsulfokislota + $HNO_3 \xrightarrow{H_2SO_4}$

8. Benzol, naftalin va antratsenning aromatik xossalarini taqqosiang. Ularning birikish, elektrofil almashinish va oksidlanish reaksiyalari qanday sharoitda boradi?

9. Quyidagi xinonlar qanday birikmalarning oksidlanishidan hosil bo'ladi?

a) 2-metil-1,4-naftoxinon; b) 2,6-naftoxinon;
d) 9,10-antraxinon; e) 9,10-fenantrenxinon.

10. Naftalin va boshqa reagentlardan foydalanib quyidagi birikmalarni sintez qiling:

a) antratsenni; d) 9,10-antraxinonni;
b) fenantrenni; e) 4,8-dibrom-1,5-diyodnaftalinni.

V. BENZOL QATORINING GALOGENLI HOSILALARI

Benzol qatori galogenli hosilalarining nomlanishi, olinish usullari va fizikaviy xossalari.

Galogenarenlar nukleofil almashinish reaksiyalarining ajralish- birikish mexanizmi. Degidrobenzol.

Faollangan aril galogenidlar nukleofil almashinish reaksiyalarining birikish-ajralish bimolekulyar mexanizmi. S_N2Ar reaksiyalarida elektronoaktseptor guruhlarning roli. Galogenarenlarning elektrofil almashinish reaksiyalari. Aralkilgalogenidlarning nukleofil almashinish reaksiyalari.

Benzol qatori galogenli hosilalarining muhim vakillari.

Savol va mashqlar

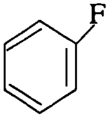
Benzol qatorining galogenli hosilalari tuzilishi, xossalari va olinish usullariga qarab ikki guruhga bo'linadi:

1) Yadrosida galogen tutgan birikmalar (arilgalogenidlar yoki galogenarenlar);

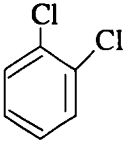
2) Yon zanjirida galogen tutgan birikmalar (arilalkilgalogenidlar)

Nomlanishi

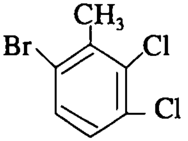
Arilgalogenidlarning nomlari galogen nomiga benzol (ba'zan toluol) so'zini yoki boshqa monoalmashingan aren nomini qo'shish bilan hosil qilinadi. Galogen atomining halqadagi holati o-, m-, p- (ratsional nomenklaturada) yoki raqam bilan (sistematik nomenklaturada) belgilanadi. Arilalkilgalogenidlarning nomi aromatik radikal va galogen nomidan hosil qilinadi.



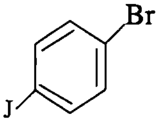
ftorbenzol



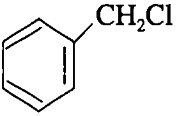
1,2-dixlorbenzol
(o-dixlorbenzol)



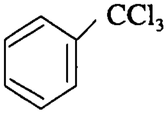
1-brom-2-metil-3,4-
dixlorbenzol



1-brom-4-yodbenzol



benzil xlorid



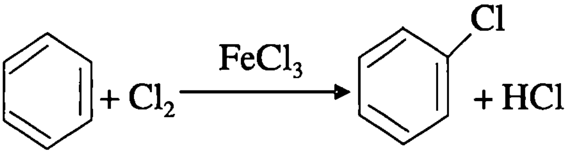
benzotrixlorid

Olinish usullari

Arilgalogenidlarning olinishi

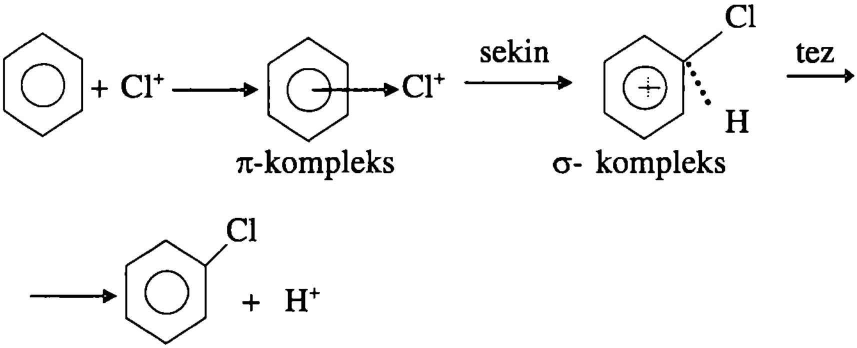
1. Benzol va uning gomologlarini to‘g‘ridan-to‘g‘ri galogenlash xlor-, brom- va yodarenlar olinishning asosiy usulidir.

Katalizatorlar (Fe, $FeCl_3$, $AlCl_3$, $SbCl_3$, $SbCl_5$, J_2) ishtirokida benzol juda oson xlorlanadi:



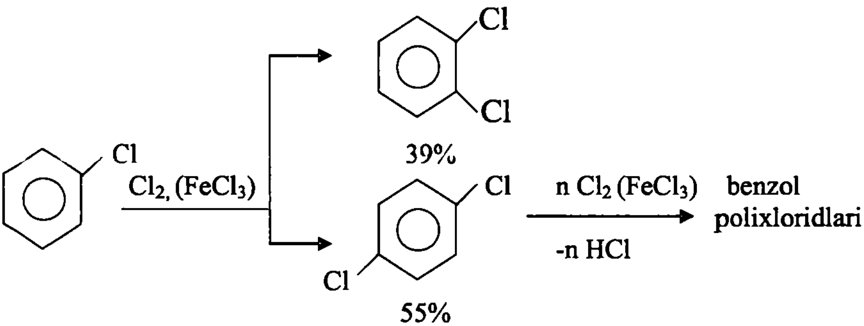
Reaksiya S_E2 aromat. mexanizm bo‘yicha boradi :

$FeCl_3 + :\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{Cl}}: \longrightarrow FeCl_4^{-} + Cl^{+}$ yoki $Cl^{\delta+}—Cl^{\delta-}\cdots FeCl_3$

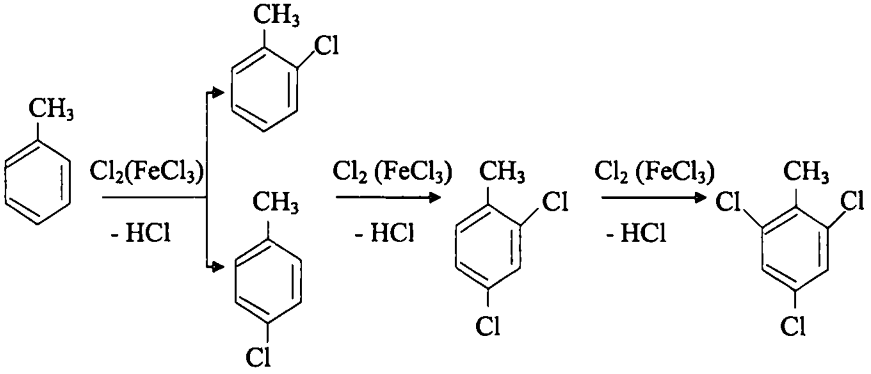


$FeCl_4^{-} + H^{+} \longrightarrow HCl + FeCl_3$

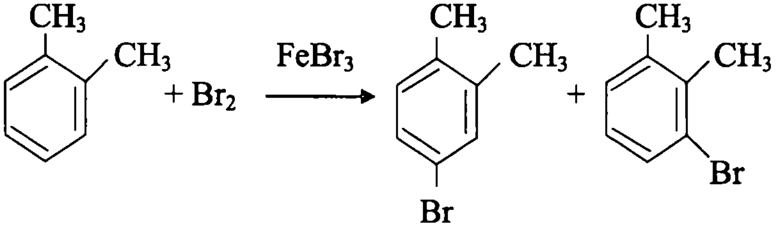
Xlorbenzol benzolga nisbatan qiyin xlorlanadi. Harorat oshganda polixlorli hosilalar hosil bo'ladi.



Toluol yadrosi katalizatorlar ishtirokida benzoldan ham oson xlorlanadi:

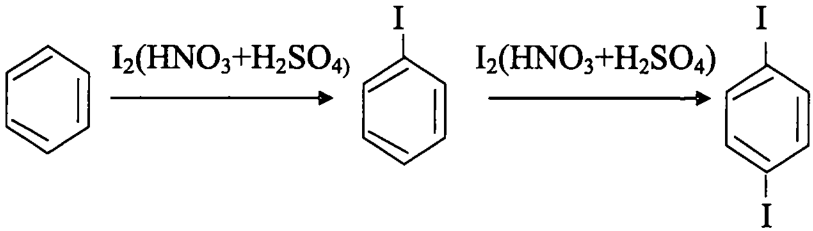


Arenlar yadrosini bromlash xlorlashga nisbatan qiyinroq boradi:

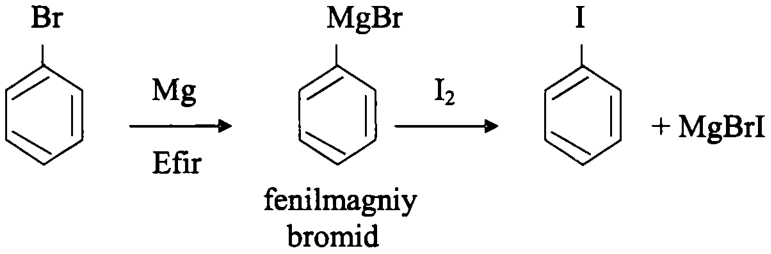


Iod arenlar bilan to‘g‘ridan – to‘g‘ri reaksiyaga kirishmaydi. Shu bois arenlarni iodlash oksidlovchilar (HgO, HIO_3, HNO_3 + H_2SO_4, H_2O_2) ishtirokida olib boriladi. Oksidlovchilar iod molekulasini iod kationiga aylantiradi, I^+ esa nisbatan kuchli elektrofildir:

$$I_2 \xrightarrow{HNO_3 + H_2SO_4} \overset{+}{I} + H\overset{-}{SO_4}$$

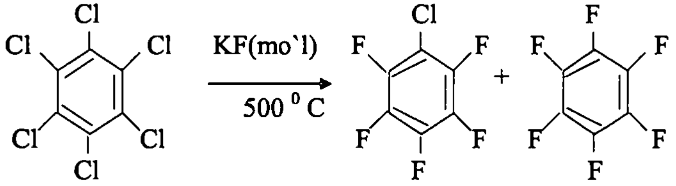


Benzol halqasi faollashgan arenlarni iod xloridi ICl bilan iodlash mumkin. Iodbenzol brombenzoldan quyidagicha olinadi:



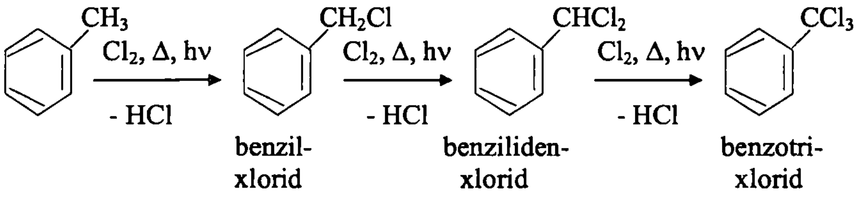
Ftorarenlarni olish uchun xlorarenlarga yuqori harorat va bosimda KF ta'sir ettiriladi:

$$Ar{-}Cl + KF \xrightarrow[\text{bosim}]{\text{yuqori } \Delta,} Ar{-}F + KCl$$



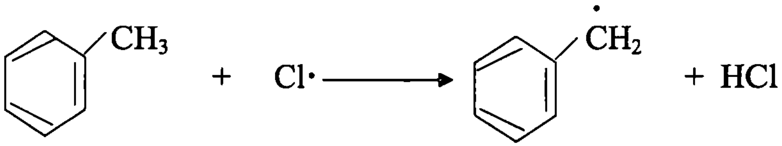
Alkilarenlar yon zanjirini galogenlash

1. Alkilarenlar yon zanjirini galogenlash katalizatorsiz yuqori harorat va UB – nur ta'sirida boradi:

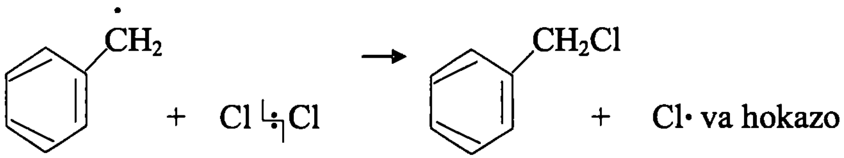


Reaksiya S_R mexanizmi bo'yicha boradi.

$$Cl \lfloor\!\vdots\!\rceil Cl \xrightarrow{\Delta,\, h\nu} 2Cl\cdot$$

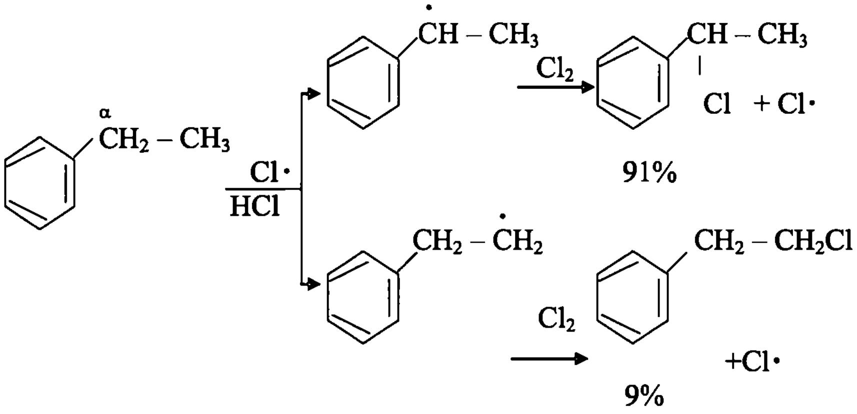


benzil radikali



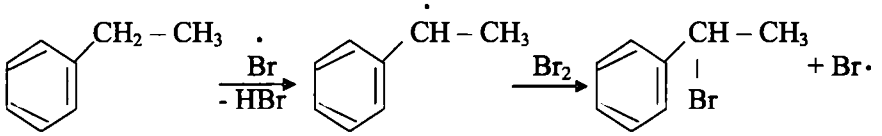
Etilbenzol galogenlanganda yon zang'irning α - uglerodi bilan bog'langan vodorod atomlari galogenga oson almashinadi:

$$\mathrm{Cl}\ \lfloor\!\cdot\!\rceil\ \mathrm{Cl} \xrightarrow{\Delta,\ h\nu} 2\mathrm{Cl}\cdot$$

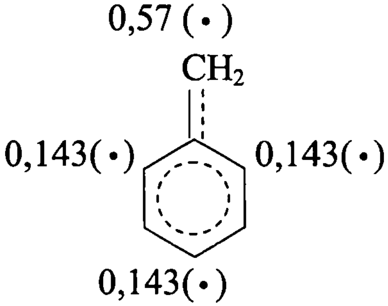


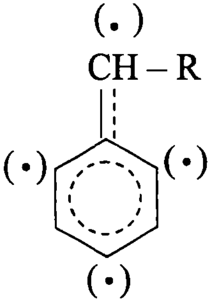
Bromning selektivligi katta bo‘lganligi uchun etilbenzol bromlanganda bitta mahsulot hosil bo‘ladi:

$$\mathrm{Br:Br} \xrightarrow{\Delta,\ h\nu} 2\mathrm{Br}\cdot$$



Benzil erkin radikallarining toq elektronlari tutashishi tufayli halqalar delokallashgan. Shu bois ular barqaror va oson hosil bo‘ladi:





2. Xlormetillash (Blan reaksiyasi). $ZnCl_2$ ishtirokida arenlar formaldegid va vodorod xloridi bilan reaksiyaga kirishganida yadro vodorodi xlormetil $-CH_2Cl$ guruhiga almashinadi:

$$C_6H_6 + CH_2O + HCl \xrightarrow{ZnCl_2} C_6H_5CH_2Cl + H_2O$$

3. Toluol va CCl_4 dan olish (Yu.A.Oldekon):

$$C_6H_5CH_3 + CCl_4 \xrightarrow{225-235^0\,C} C_6H_5CH_2Cl + CHCl_3$$

4. Alkilarenlar yon zanjirini ftorlash uchun tegishli xloridlarga SbF_3, AgF ta'sir ettiriladi:

$$C_6H_5CCl_3 + SbF_3 \xrightarrow{\Delta} \underset{\text{benzotriftorid}}{C_6H_5CF_3} + SbCl_3$$

Fizikaviy xossalari

Benzol qatorining galogenli hosilalari – suvda erimaydigan og'ir suyuqlik yoki kristall moddalardir. Arilgalogenidlar kuchsiz aromatik hidga, arilalkilgalogenidlar esa ko'zdan yosh oqizuvchi o'ziga xos hidga ega. (4- jadval).

4- jadval

Benzol qatori galogenli hosilalarining fizikaviy doimiyliklari

Nomi	Suyuqlanish harorati C^0	Qaynash harorati C^0	Zichligi
Ftorbenzol	- 39,2	85,2	1,024
Xlorbenzol	- 45,2	132,2	1,106
Brombenzol	- 30,6	156,2	1,495
Iodbenzol	- 31,6	185,5	1,831
Benzil xloridi	- 43,0	179	1,1026 (18^0 C)
Benzil bromidi	- 4,0	198	1,4380 (22^0 C)
Benziliden xlorid	- 16,0	207	1,2557 (14^0 C)
Benzotrixlorid	- 22,0	214,0	1,3803

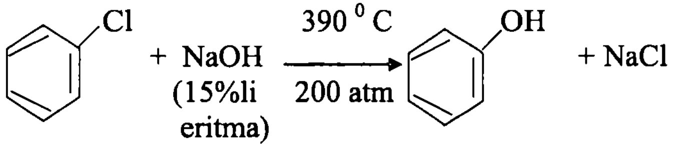
Kimyoviy xossalari

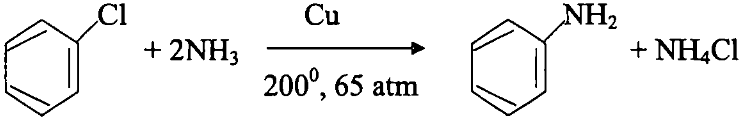
A. Nukleofil almashinish reaksiyalari

Galogenning umumlashmagan elektron jufti yadroning π - elektronlari bilan P, π - tutashish hosil qilganligi tufayli arilgalogenlarning uglerod – galogen bog'i galogenalkanlar uglerod – galogen bog'idan qisqa va mustahkam, galogen esa inert.

Shu bois galogenalkanlar reaksiyaga kirishadigan sharoitlarda arilgalogenidlar o'yuvchi natriy, ammiak, kumush tuzlari, natriy alkogolyatlari, sianid kislota tuzlari yoki natriy sulfidi singari nukleofil reagentlar bilan reaksiyaga kirishmaydi.

Xlor- va brombenzollar o'yuvchi ishqorlar bilan 300^0 C va undan yuqori haroratda, ammiak bilan esa 200^0 C da, mis yoki bir valentli mis tuzlari katalizatorligida reaksiyaga kirishadi. Masalan, fenol va anilin sanoat miqyosida xlorbenzoldan quyidagicha olinadi:



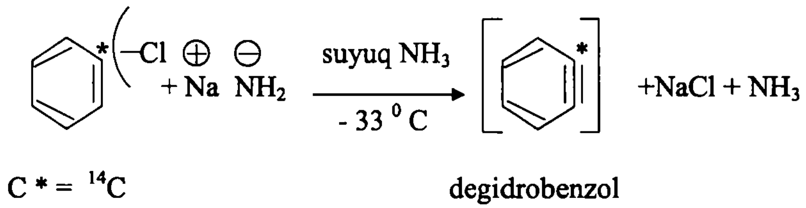


Iodarenlar boshqa galogenlarga nisbatan reaksiyalarga oson kirishadi:

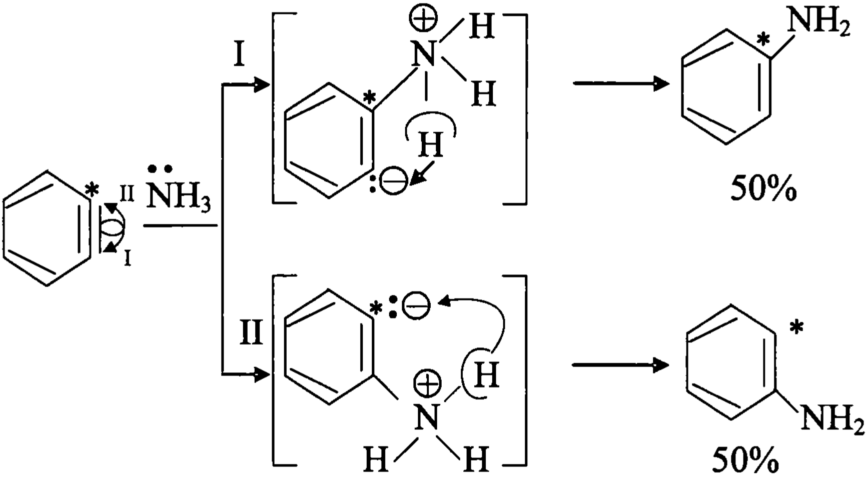
Arilgalogenidlarning nukleofil almashinish reaksiyalari turli mexanizmlarda boradi.

Ajralish – birikish – (arin) - mexanizmi. Faollashmagan (o- va p- holatlarda elektronoaktseptor guruhlari yo'q) arilgalogenidlar kuchli nukleofil reagentlar bilan ikki bosqichli ajralish – birikish (arin mexanizmi bo'yicha) reaksiyasiga kirishadi.

I (ajralish) bosqichida kuchli nukleofil reagent ta'sirida arilgalogeniddan vodorod galogenid ajralib, reaksiyaga kirishish qobiliyati juda kuchli bo'lgan oraliq mahsulot (intermediat) – degidrobenzol (benzin) hosil boladi.

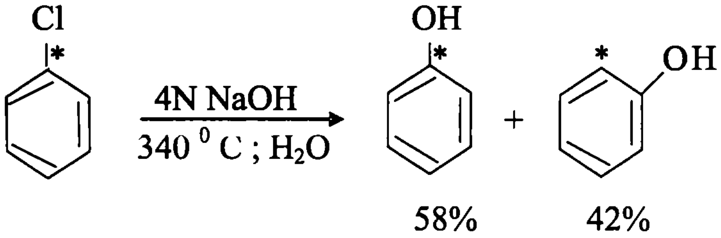


II (birikish) bosqichida degidrobenzolga nukleofil reagent birikadi:

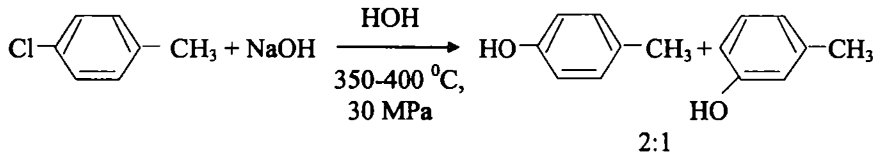


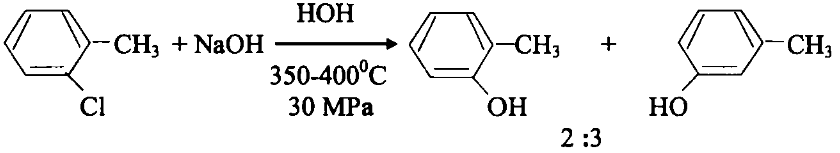
Quyidagi misollar arin mexanizmini isbotlaydi:

a) sanoatda xlorbenzoldan fenol olish jarayoni ham degidrobenzol bosqichi orqali boradi:

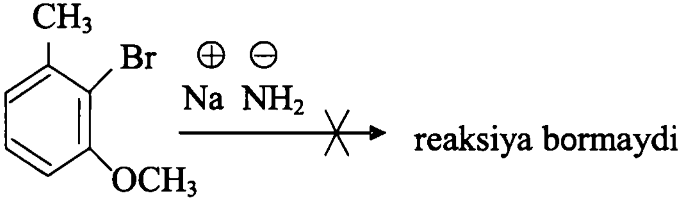


b) p- Xlortoluolni o‘yuvchi natriyning suvdagi 15 % li eritmasi bilan bosim ostida qizdirganda para- va meta- krezollarning 2:1 nisbatdagi aralashmasi hosil bo‘ladi. Shunday sharoitda o-xlortoluoldan esa orto- va meta – krezollarning 2:3 nisbatdagi aralashmasi hosil bo‘ladi:



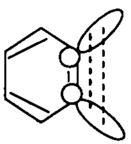


d) 2,6- dialmashingan galogen benzollardan degidrobenzol hosil bo‘la olmaydi. Shu bois 2 – brom – 3 – metoksitoluolning bromi aminoguruhga almashinmaydi:



Demak galogenga nisbatan orto – holatlarda ajraladigan vodorod bo‘lmasa degidrobenzol hosil bo‘lmaydi.

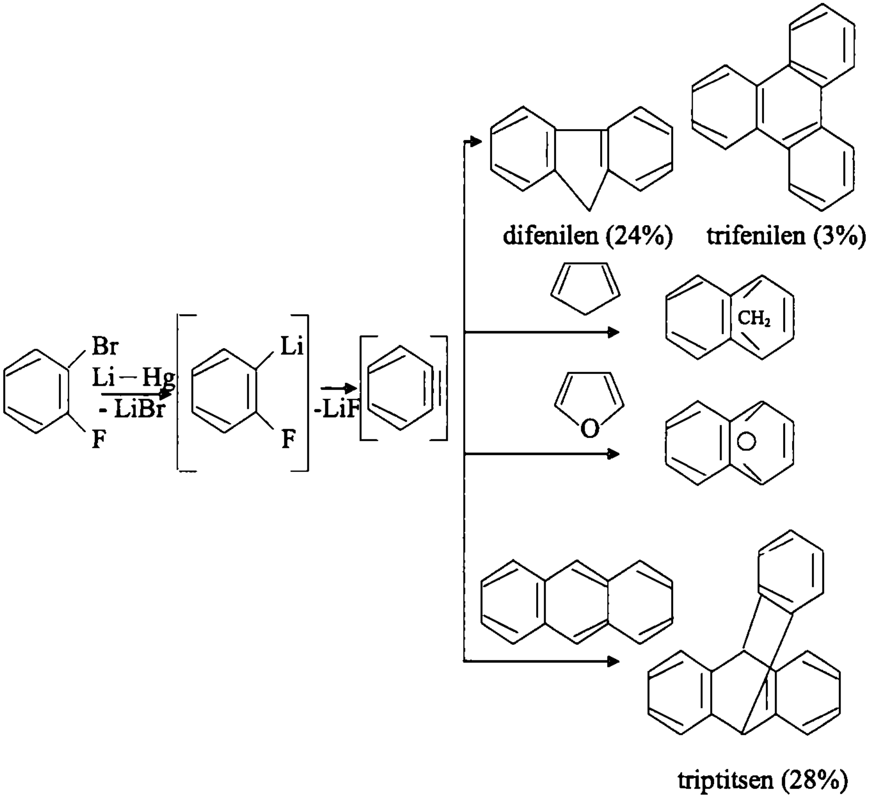
Degidrobenzol “uch bog‘i” ning ikkinchi “π - bog‘i” ikkita qo‘shni uglerod atomlari sp² – orbitalining yon tomonida qoplanishidan hosil bo‘ladi. Bu sp² – orbitallar bir – biridan uzoqda joylashganligi sababli ularning qoplanish sohasi kichik. Shu bois hosil bo‘ladigan ikkinchi ”π - bog“ odatdagi π - bog‘dan taxminan ikki marta kuchsiz.



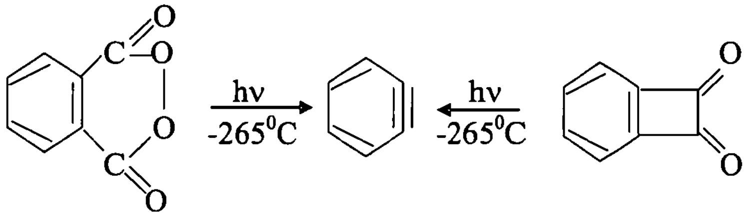
Degidrobenzol ”uch bog‘i” ning ikkinchi “π - bog‘i “ hosil bo‘lishida sp² – orbitallarning qoplanish sohasi

Degidrobenzol birikish reaksiyalariga “uch bog‘i” ning ikkinchi “π - bog‘i “ hisobiga kirishadi.

1 – brom – 2 – ftorbenzolga litiy amalgamasini ta‘sir ettirganda hosil bo‘ladigan degidrobenzol dimer (difenilen) va trimer (trifenilen) ga aylanadi. Agar shu reaksiya siklopentadien – 1,3 va furan kabi faol diyenlar bilan yoki antratsen ishtirokida olib borilsa, hosil bo‘ladigan degidrobenzol faol diyenofil sifatida Dil‘s – Alder reaksiyalariga kirishadi:



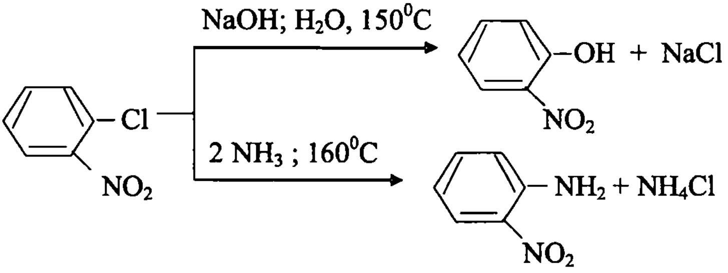
1973 – yilda ftaloilperoksid yoki benztsiklobuten – 1,2 – dion qattiq argon matritsasida -265_0C da fotoliz qilinganida degidrobenzol individual birikma sifatida hosil bo‘lishi aniqlandi. U -230^0 C da furanga oson birikadi.

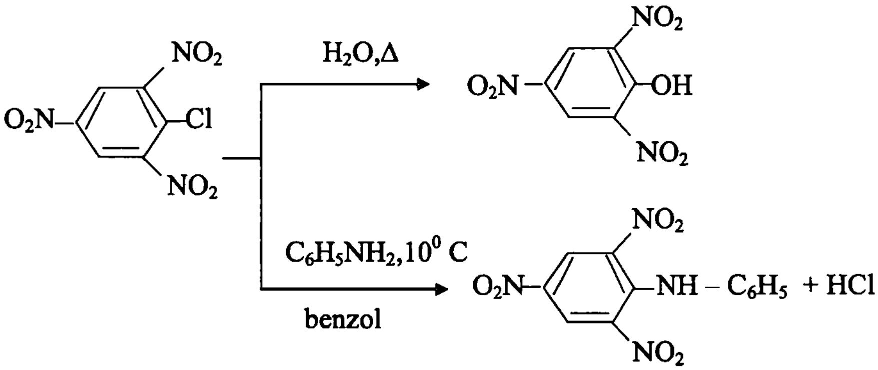


Birikish – ajralish bimolekulyar mexanizmi (S_N2 Ar)

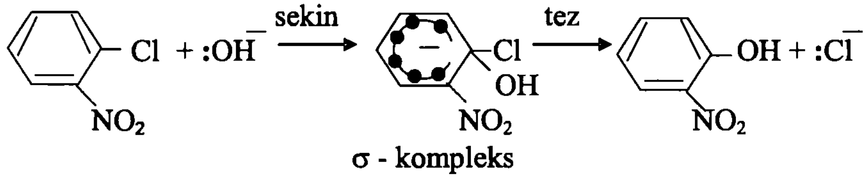
Yadrosida galogenga nisbatan orto- va para- holatlarda joylashgan bitta, ikkita yoki uchta kuchli elektronoakseptor o'rinbosarlar ($-NO_2$, -NO, $-N^+_2$, -COOH, -CHO, -CN, $-SO_3H$ va hokazo) bor arilgalogenidlar faollangan arilgalogenidlar deyiladi.

Faollangan arilgalogenidlarning galogen atomi harakatchan bo'lib, nukleofil almashinish reaksiyalariga oson kirishadi:





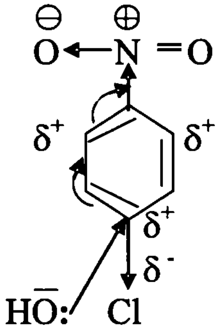
Bu reaksiyalar S_N2 Ar mexanizmida boradi:



I (birikish) bosqichida hosil bo'ladigan manfiy zaryadli *σ* - kompleks (karbanion) aromatik qatorda boradigan elektrofil almashinish reaksiyalarida hosil bo'ladigan *σ* - kompleks (karbkation) ning anionli analogidir. Karbanionda 6 ta elektron 5 ta uglerod atomi maydonida boladi. Manfiy zaryadli *σ* - komplekslarga nisbatan beqaror bo'lsa-da, ba'zan ularni reaksion massadan ajratib olish mumkin.

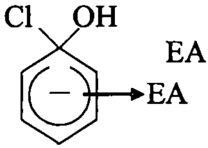
S_N2 Ar reaksiyalarida elektronoakseptor guruhlarning roli

Reaksiyaga kirishmagan molekulada galogen (xlor) va elektronoakseptor (NO_2) guruh ta'sirida benzol halqasi *π* - elektron zichligining simmetriyasi buziladi (statik omil):



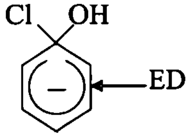
Nitroguruhning – M – effekti va xlorning – I – effekti tufayli xlor bilan bog'langan uglerod atomida qisman musbat zaryadning miqdori oshadi. Natijada bu atomning elektrofilligi oshadi va u hujum qiluvchi anion bilan oson reaksiyaga kirishadi.

O'rinbosarning tabiatiga qarab reaksiya vaqtida hosil bo'ladigan manfiy zaryadli π - kompleks (karbanion) ning barqarorligi o'zgaradi (dinamik ta'sir) . Elektronlarni tortuvchi elektronoakseptor guruhlar (EA) karbaninon manfiy zaryadini neytrallaydi, uni barqaror qiladi va nukleofil almashinish reaksiyasini tezlashtiradi:



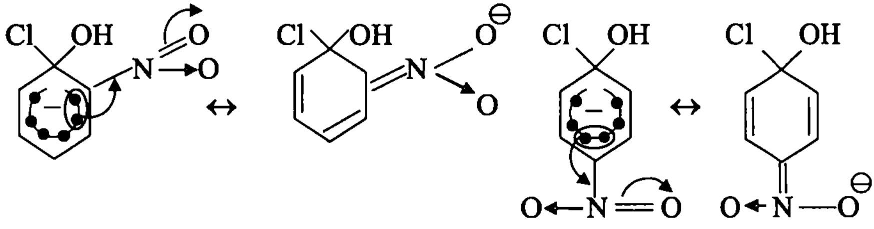
EA = NO_2, NO, COOH, CN, SO_3H, CHO va hokazo

Elektronlarni beruvchi elektronodonor guruhlar (ED) karbaninon manfiy zaryadini oshirib, uni barqaror qiladi va nukleofil almashinish reaksiyasini sekinlashtiradi:



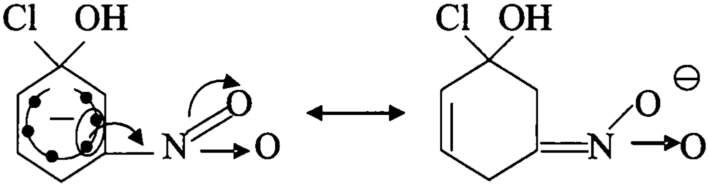
ED = NH_2, NHR, NR_2, OH, OR, OCOR va hokazo

Elektronoakseptor o'rinbosarlar galogenga nisbatan orto–va para – holatlariga kiritilgandagina galogenning harakatchanligi keskin ortadi. Tutashish tufayli manfiy σ- kompleks barqarorlashadi:



Orto – va para – holatlardagi nitroguruh yoki boshqa elektrono-aktseptor o'rinbosar σ - kompleks manfiy zaryadini aromatik yadrodan tortib, uni barqaror qiladi. Demak nitroguruh tutashish tufayli σ - kompleks manfiy zaryadini delokallanishida ishtirok etadi.

Nitroguruh meta – holatda bo'lganida σ - kompleks manfiy zaryadini delokallanishida ishtirok qila olmaydi:



Halqada ikkinchi bog`ni joylashtirib bo`lmaydi.

B. Elektrofil almashinish reaksiyalari

Galogen atomlari benzol yadrosining elektron zichligini kamaytirib, orto – va para – holatlarga yo'naltiradi (51-53 – betlar). Shu bois arilgalogenidlar elektrofil almashinish reaksiyalariga benzolga nisbatan qiyin kirishadi.

V. Metallorganik birikmalarning olinishi

Grinyar reaktivlari arilbromid yoki ariliodid bilan magniydan oson hosil bo'ladi:

$$C_6H_5Br + Mg \xrightarrow{\text{efir}} \underset{\text{fenilmagniybromid}}{C_6H_5MgBr}$$

Arilmagniyxloridlar quyidagicha olinadi:

$$ArCl + Mg \xrightarrow{\text{TGF}} ArMgCl$$

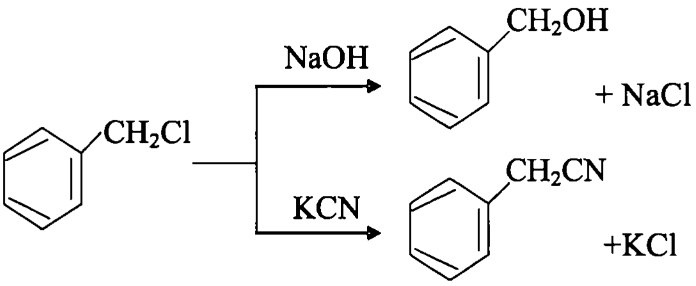
Litiyning arilli hosilalari xlor – yoki bromarenlarga litiyni to'g'ridan – to'g'ri ta'sir ettirish bilan olinadi:

$$C_6H_5Cl + 2Li \xrightarrow{efir} C_6H_5Li + LiCl$$

fenillitiy

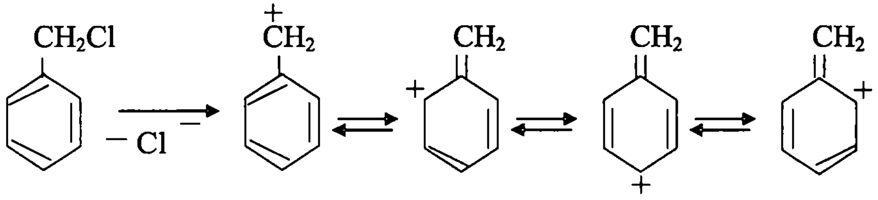
Aralkilgalogenidlarning nukleofil almashinish reaksiyalari

Yon zanjiridagi galogen nukleofil almashinish reaksiyalariga oson kirishadi:



Benzil galogenidlar galogenalkanlarga nisbatan ham faol bo'lib reaksiyaga kirishishi qobiliyati jihatidan allil galogenidlarga o'xshaydi. Benzil galogenidlardagi uglerod – galogen bog'i arilgalogenidlardagi uglerod – galogen bog'i singari mustahkam emas. Masalan, C – Br bog'ining dissotsilanish energiyasi brombenzolda 71 kkal/mol, etilbromidda 65 kkal/mol, benzilbromidda 51 kkal/mol, allilbromidda 46 kkal/mol ga teng.

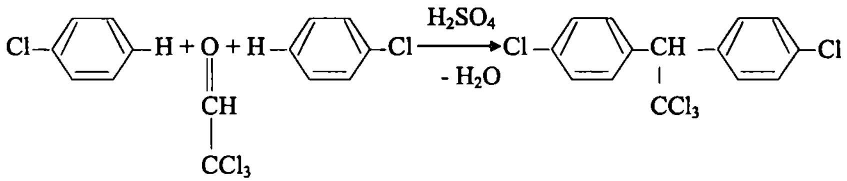
Benzilgalogenidlarning S_N1 – reaksiyalariga oson kirishish qobiliyati hosil bo'ladigan benzil kationining barqarorligi bilan tushuntiriladi. Bu kationda musbat zaryad orto – va para – holatlarda delokallashgani bois u barqaror va oson hosil bo'ladi:



Muhim vakillari

Xlorbenzol - 132^0 C da qaynaydigan o'ziga xos hidli suyuqlik. U sanoatda benzolni temir ishtirokida xlorlash bilan olinadi. Xlorbenzol erituvchi sifatida, organik sintezda (fenol, anilin, nitroxlorbenzollar, bo'yoqlar olishda) xomashyo sifatida ishlatiladi.

4,4^I – Dixlordifeniltrixlormetilmetan (DDT) - 108–109^0 C da suyuqlanadigan, organik erituvchilarda yaxshi eriydigan, rangsiz kristall modda. U kontsenrlangan sulfat kislota ishtirokida xlorbenzol va trixlorsirka aldegid (xloral) dan olinadi:



DDT kuchli ta'sir qiluvchi insektitsid bo'lib, uzoq yillar davomida zararli hasharotlarga qarshi kurashishda keng qo'llanilgan. U tuproqda, o'simliklarda, hayvonlar organizmida, sut mahsulotlarida to'planib, surunkali zararlanishga olib keladi. Shu bois DDT hozirgi kunda keng qo'llanilmaydi.

Benzil xloridi – 179^0 C da qaynaydigan, o'tkir hidli suyuqlik. U benzoy kislotaning murakkab efirlarini va benzil spirtini olishda ishlatiladi.

Savol va mashqlar

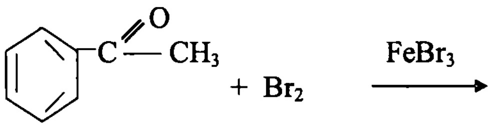
1. Quyidagi birikmalarning tuzilish formulalarini yozing:

a) p – brombenzilxlorid b) m – iodbenzolsulfokislota

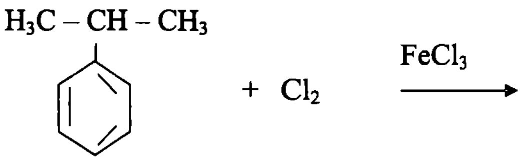
d) p – brombenzilidenxlorid e) 1 – brom – 2 feniletan

2. Quyidagi reaksiyalarni oxirigacha yetkasing:

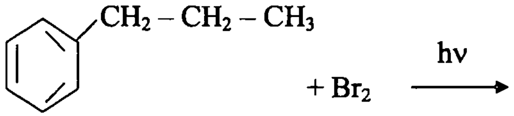
a)



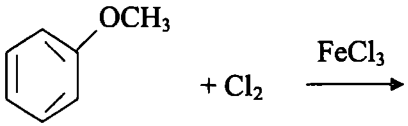
b)



d)

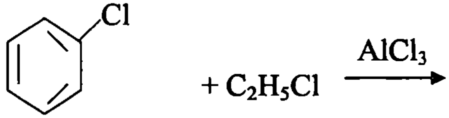


e)

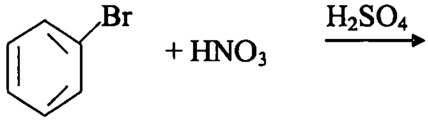


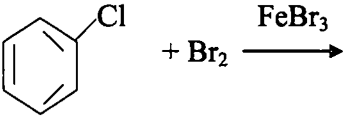
3) Quyidagi elektrofil almashinish reaksiyalarini oxirigacha yetkazing:

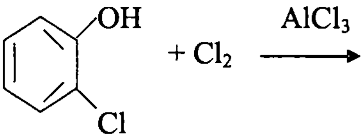
a)



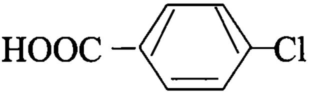
b)

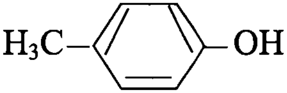


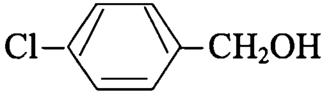
d) 

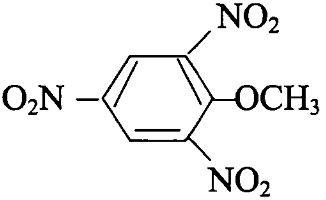
e) 

4) Benzol va boshqa reagentlardan foydalanib quyidagi birikmalarni sintez qiling:

a) 

b) 

d) 

e) 

5. Quyidagi birikmalarni sintez qilish sxemalarini tuzing:

a) p – nitroxlorbenzolni; b) m – nitroxlorbenzolni;
d) m – xlorbenzotrixloridni; e) 2,5 - dixlornitrobenzolni.

6. Quyidagi birikmalarni sintez qilish sxemasini tuzing:

a) o-nitroxlorbenzolni; b) o-nitroxlorbenzolni;
d) p-xlorbenzotrixloridni; e) 2,5-dixlornitrobenzolni

7. Quyidagi reaksiyalar oraliq va oxirgi mahsulotlari tuzilish formulalarini yozing:

a) $$C_6H_6 \xrightarrow{Br_2;FeBr_3} A \xrightarrow[efir]{Mg} B \xrightarrow{CO_2} D \xrightarrow[HOH]{HCl} E \xrightarrow{Br_2;FeBr_3} F$$

b) $$C_6H_6 \xrightarrow[AlCl_3]{CH_3Cl} A \xrightarrow{Cl_2;\,FeCl_3} B \xrightarrow{KMnO_4,\,\Delta} D \xrightarrow{Cl_2;\,FeCl_3} E$$

8. Quyidagi reaksiyalar oraliq va oxirgi mahsulotlari tuzilish formulalarini yozing:

a) $$C_6H_6 \xrightarrow[FeBr_3]{Br_2} A \xrightarrow[H_2SO_4]{HNO_3} B \xrightarrow[AlCl_3]{CH_3Cl} D \xrightarrow[efir]{Mg} E \xrightarrow{CO_2} F \xrightarrow[HOH]{HCl} G$$

b) $$C_6H_6 \xrightarrow[FeCl_3]{Cl_2} A \xrightarrow[H_2SO_4]{HNO_3} B \xrightarrow[FeCl_3]{Cl_2} D \xrightarrow[1\ mol]{NaOH + H_2O} E$$

9. Quyidagi birikmalarning gidroliz reakstiyalari sxemalarini yozing:

a) p-bromtoluolning; b) 2.4-dinitrobrombenzolning;

d) 1- brom -1- fenilpropanning,

Qaysi birikmaning gidrolizi oson boradi?

10. S_E2 Ar reaksiyalarda galogen orto- va para- orientant bo‘la turib, nega benzol yadrosi faolligini kamaytiradi?

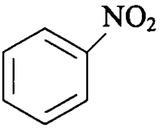
VI. BENZOL QATORI NITROBIRIKMALARI

Benzol qatori nitrobirikmalarining nomlanishi, olinish usullari, fizikaviy va kimyoviy xossalari, muhim vakillari. Savol va mashqlar

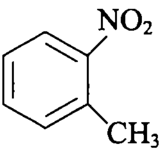
Benzol qatori nitrobirikmalari benzol yadrosida yoki yon zanjirida nitroguruh saqlagan birikmalardir.

Nomlanishi

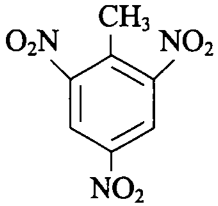
Benzol qatori nitrobirikmalarining nomlari benzol yoki uning monoalmashingan hosilasi nomiga **nitro** old qo'shimchasini qo'shish bilan hosil qilinadi. Zarur bo'lganda benzol yadrosi bilan bog'langan o'rinbosarlarning holati *o*-, *м*-, *p*- bilan (ratsional nomenklaturada) yoki raqam bilan (sistematik nomenklaturada) belgilanadi :



nitrobenzol

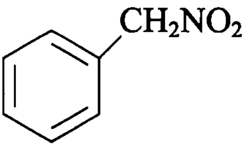


o – nitrotoluol



2,4,6 – trinitrotoluol

Ba'zan benzol halqasini uglerod skeletidagi o'rinbosar deb qaraladi va uni fenil old qo'shimchasi bilan belgilanadi:



fenilnitrometan

Nitroguruh benzol halqasi uglerodi bilan bevosita bog'langan aromatik nitrobirikmalar katta amaliy ahamiyatga ega. Ular bo'yoqlar, portlovchi va xushbo'y moddalar, erituvchilar va boshqa organik birikmalarni ishlab chiqarishda keng ishlatiladi.

Olinish usullari

Aromatik nitrobirikmalar olishning asosiy usuli – nitrolashdir:

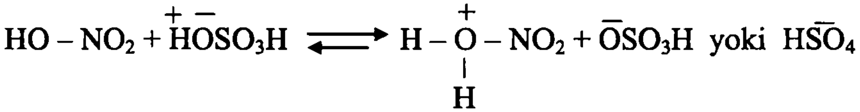
$$ArH + {}^{+}NO_2 \longrightarrow ArNO_2 + H^{+}$$

Aromatik birikma vodorodini nitroguruh bilan to'g'ridan – to'g'ri almashtirish nitrolovchi reagentlar yordamida amalga oshiriladi. Nitrolovchi reagentlar sifatida turli kontsentratsiyali nitrat kislota, nitrolovchi aralashma (konsentrlangan nitrat va sulfat kislotalarning aralashmasi), sulfat kislota ishtirokida ishqoriy metallarning nitratlari va azot oksidlari qo'llaniladi.

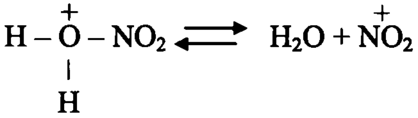
Aromatik birikmalarning laboratoriyada va sanoatda nitrolash uchun ko'pincha nitrolovchi aralashmadan foydalaniladi.

Nitrolovchi aralashma bilan aromatik birikmalarni nitrolash elektrofil almashinish reaksiyasi bo'lib, uning mexanizmi har tomonlama o'rganilgan.

Bu reaksiyada nitroniy kationi NO_2^{+} elektrofil reagent bo'lib, u nitrat va sulfat kislotalardan quyidagicha hosil bo'ladi:



$$HO-NO_2 + \overset{+}{H}\overset{-}{O}SO_3H \rightleftarrows H-\underset{\underset{H}{|}}{\overset{+}{O}}-NO_2 + \overset{-}{O}SO_3H \text{ yoki } HS\overset{-}{O}_4$$



$$H-\underset{\underset{H}{|}}{\overset{+}{O}}-NO_2 \rightleftarrows H_2O + \overset{+}{N}O_2$$

$$H_2O + H_2SO_4 \rightleftarrows H_3\overset{+}{O} + \overline{O}SO_3H \text{ yoki } HS\overline{O}_4$$

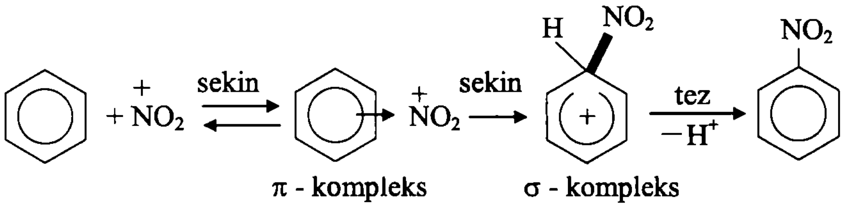
$$HNO_3 + 2H_2SO_4 \qquad \overset{+}{N}O_2 + H_3\overset{+}{O} + 2\overline{O}SO_3H \text{ yoki } 2HS\overline{O}_4$$

Bu reaksiyada kuchli sulfat kislota – kislota , unga nisbatan kuchsiz nitrat kislota esa asos rolini o‘ynaydi.

Nitroniyning ayrim barqaror tuzlari (masalan nitroniy perxlorat $[NO_2]^+ClO^-_4$, nitroniy tetraftorborat $[NO_2]^+BF^-_4$) ham nitrolovchi agentlar hisoblanadi. Ular nitrometan yoki sirka kislota muhitida aromatik birikmalarni hatto xona haroratida ham yaxshi nitrolaydi (G. Ola):

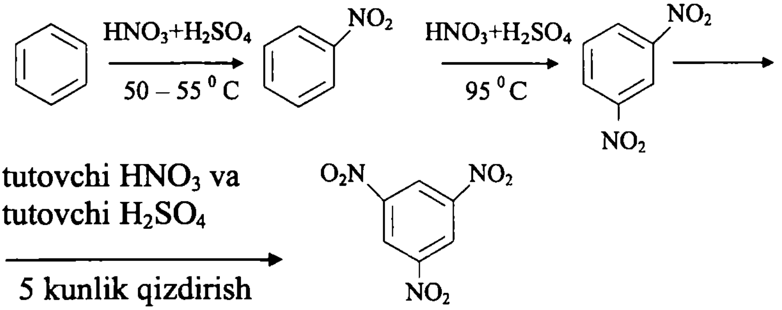
$$ArH + [NO_2]^+BF_4 \rightleftarrows Ar - NO_2 + BF_3 + HF$$

Nitrolash S_E2 mexanizmi bo`yicha boradi:

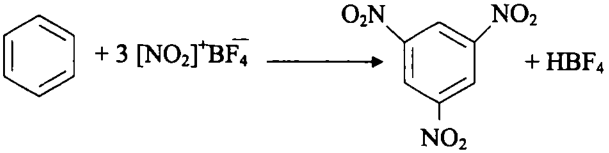


$$H^+ + HS\overline{O}_4 \longrightarrow H_2SO_4$$

Nitroguruh benzol halqasi elektron zichligini kamaytirgani bois (53-54–betlar) ikkinchi nitroguruhni kiritish yuqori haroratda kontsentrlangan kislotalar ishtirokida amalga oshiririladi. Uchinchi nitroguruhni esa juda qiyinchilik bilan meta – holatga kiritish mumkin. To‘rtinchi nitroguruhni esa to‘g‘ridan – to‘g‘ri kiritib bo‘lmaydi.



Benzolni nitroniy tetraftorborat bilan nitrolaganda 1,3,5 – trinitrobenzol hosil bo`ladi:



Benzolning gomologlari uning o‘ziga nisbatan oson nitrolanadi.

Fenilnitrometan toluolni suyultirilgan nitrat kislota bilan 100-150⁰ C da nitrolab oiinadi :

$$C_6H_5 - CH_3 + HONO_2 \longrightarrow C_6H_5 - CH_2NO_2 + H_2O$$

Benzil xloridga kumush nitritni ta‘sir ettirib ham fenil nitrometanni olish mumkin :

$$C_6H_5 - CH_2Cl + AgNO_2 \longrightarrow C_6H_5 - CH_2NO_2 + AgCl$$

Fizikaviy xossalari

Benzol qatorining nitrobirikmalari suyuq , ko‘pchiligi sariq kristall moddalar bo‘lib, suvda erimaydi, organik erituvchilarda esa yaxshi eriydi.

(5-jadval)

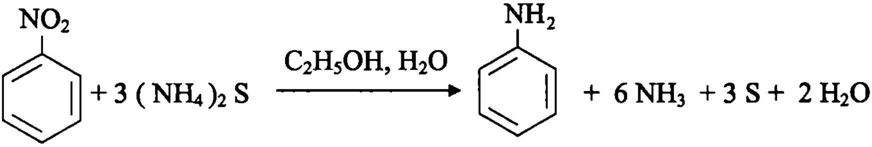
Benzol qatori nitrobirikmalarining fizikaviy doimiyliklari

Nomi	Suyuqlanish harorati ^{0}C	Qaynash harorati, ^{0}C	Zichligi α^{20}_4 ,	Dipol momenti, benzolda, 20^{0}C
Nitrobenzol	5.7	210.9	1.2030	3.97
1,2 – dinitrobenzol	118	319 (773 mm sim. ust. bosimda)	1.565	5.98
1.3 – dinitrobenzol	89.57	303 (770 mm sim. ust. boslmda)	1.571	3.78
1,4 - dinitrobenzol	173.5	299	1.625	0.00
2 – nitrotoluol	- 4.1	222.3	1.1630	3.69
3 – nitrotoluol	+ 15.5	231.0	1.1571	4.17
2,4,6 – trinitrotoluol	80.7	240 (portlaydi)	1.654	1.15 (15^0 C da)

Kimyoviy xossalari

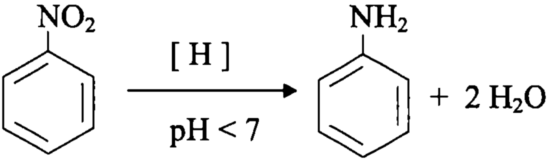
Nitroarenlar qaytarilish, elektrofil almashinish, hamda nukleofil almashinish reaksiyalariga kirishadi.

Nitroguruhning qaytarilishi. N.N. Zinin 1842–yilda nitrobenzolni suv-spirtli eritmada ammoniy sulfidi bilan qaytarib, anilinni sintez qildi :



Nitroarenlarning qaytarilishida reaksiya muhitining ta'siri katta.

Nitroarenlar kislotali muhitda birdaniga aromatik aminlargacha qaytariladi :



Kislotali muhitda qaytaruvchilar sifatida temir, qalay yoki rux va xlorid kislota ishlatiladi.

Sanoatda nitroarenlar temir qirindilari (arzonligi uchun) bilan xlorid kislota yoki Reney nikeli ishtirokida molekulyar vodorod bilan qaytariladi :

$$4\,C_6H_5NO_2 + 9\,Fe + H_2O \xrightarrow{HCl} C_6H_5NH_2 + 3\,Fe_3O_4$$

$$C_6H_5NO_2 + 3\,H_2 \xrightarrow{\sim 350\,^0C;\ 1.5\ atm.} C_6H_5NH_2 + 2\,H_2O$$

Ishqoriy muhitda qaytaruvchilar sifatida natriy gidroksidi ishtirokida ammoniy sulfidi va rux, shuningdek natriy sulfidi ishlatiladi.

Qaytaruvchi reagentlar neytral va ishqoriy eritmalarda nitrobenzolni kislotali eritmalardagi singari faol qaytarmaydi.

Masalan, rux mo'l xlorid kislota ishtirokida nitrobenzolni anilingacha, ammoniy xloridning ta'sirida esa

N- fenilgidroksilamingacha qaytaradi :

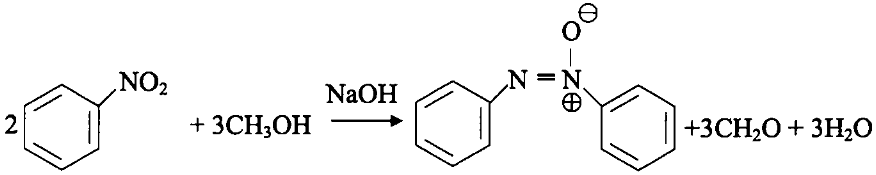
$$C_6H_5NO_2 + 3\,Zn + 6\,HCl \xrightarrow{H_2O} C_6H_5NH_2 + 3\,ZnCl_2 + 2\,H_2O$$

$$C_6H_5NO_2 + 2\,Zn + 4\,NH_4\,Cl \xrightarrow{H_2O} C_6H_5NHOH + 2\,Zn(NH_3)_2\,Cl_2 + H_2O$$

Nitrobenzolni to'g'ridan–to'g'ri qaytarish bilan nitrozobenzolni olib bo'lmaydi, chunki u behad oson qaytariladi. Shu bois nitrozobenzol N – fenilgidroksilaminni oksidlash bilan olinadi :

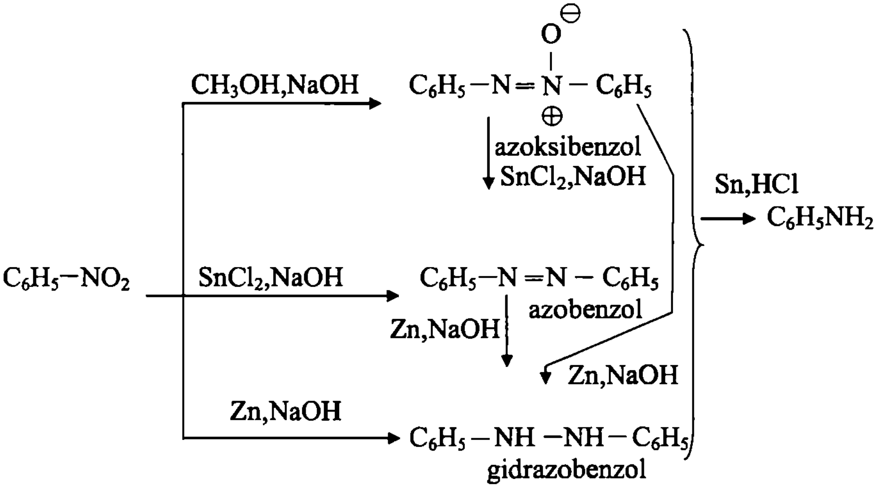
$$C_6H_5 - NHOH \xrightarrow[0^0C]{K_2Cr_2O_7 + H_2SO_4} C_6H_5 - N = O$$

Nitrobenzolni o'yuvchi natriy ishtirokida metanol bilan qaytarganda azoksibenzol hosil bo'ladi :

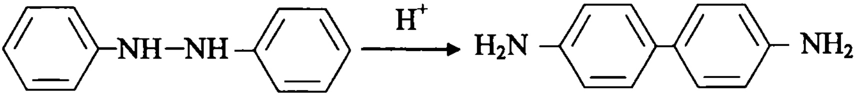


Ishqoriy muhitda metanol rux va xlorid kislota singari kuchli qaytaruvchi reagent emasligi bois nitrobenzolni anilingacha emas, balki azoksibenzolgacha qaytaradi.

Metanolga nisbatan kuchli qaytaruvchilar ($SnCl_2$, Zn) ishqor ishtirokida nitrobenzolni azobenzol va gidrazobenzolga aylantiradi. Azobenzol va gidrazobenzolni azoksibenzoldan ham olish mumkin:

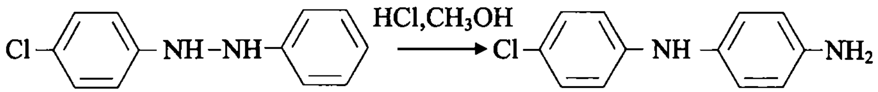


Ma'dan kislotalar ta'sirida gidrazobenzolning benzidinga aylanishi benzidin qayta guruhlanishi deyiladi:



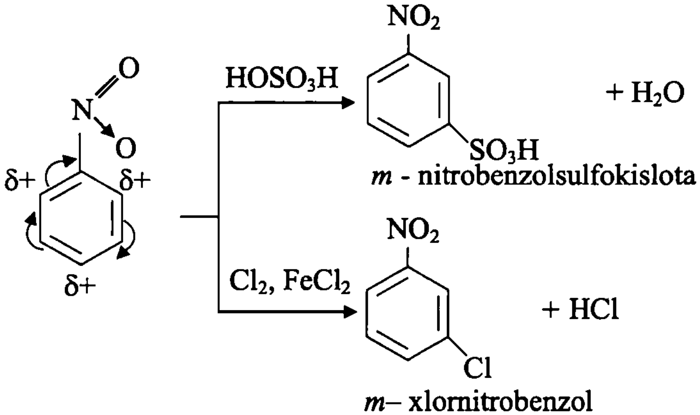
benzidin

Agar gidrazobenzol yadrolaridan birining para – holati o'rinbosar bilan band bo'lsa, semidin qayta guruhlanishi boradi. Masalan p – xlorgidrazobenzol vodorod xlorid ta'sirda 4 – amino – 4 – xlordifenilaminga qayta guruhlanadi:

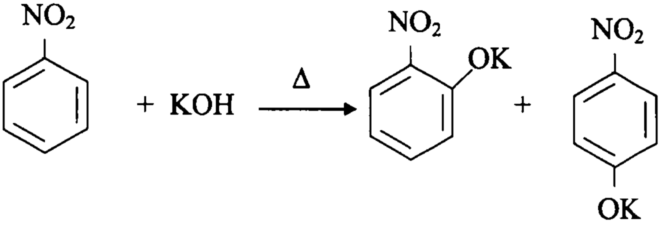


Elektrofil almashinish reaksiyalari. Nitroguruh kuchli elektronoaktseptor o'rinbosar bo'lib, - I – va – M – effektlar ta'sirida yadroning elektron zichligini (ayniqsa orto – va para – holatlarda) benzolning o'zidagiga nisbatan kamaytiradi, elektrofil almashinish reaksiyalarining borisini qiyinlashtiradi (71-72 – betlar).

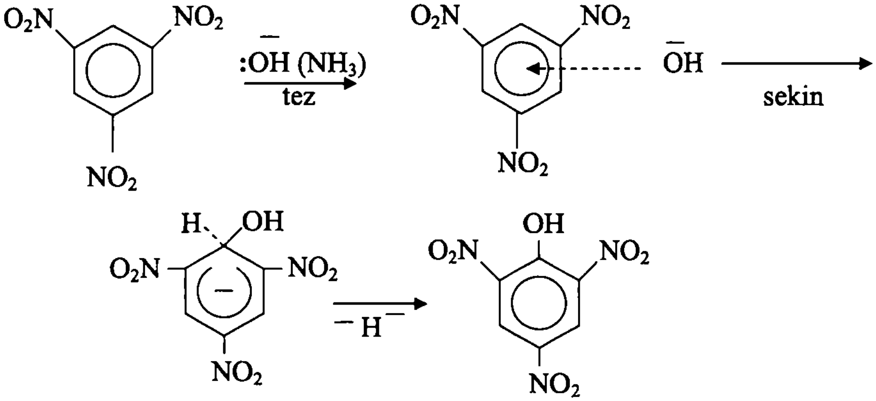
Shu bois nitrobenzolni sulfolash yuqori haroratda oleum ta'sirida, xlorlash esa katalizator ishtirokida boradi. Nitroguruh elektrofil o'rinbosarlarni asosan meta-holatga yo'naltiradi.



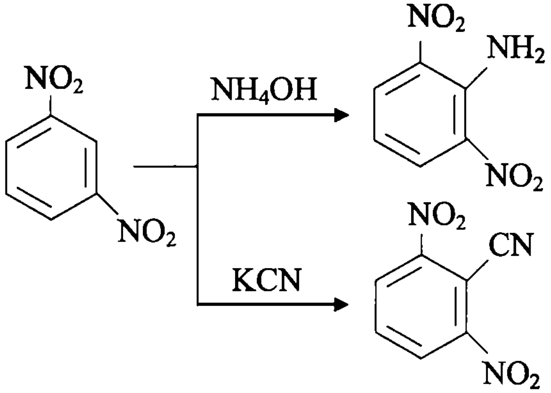
Nukleofil almashinish reaksiyalari. Mononitroarenlar kuchsiz elektronoakseptorlar bo'lib, faqat kuchli nukleofillar bilangina reaksiyaga kirishadi. Nitroguruh nukleofil reagentlarni *o*- va *p*- holatlarga yo'naltiradi. Nitrobenzolni kukun holidagi KOH bilan qizdirilganda *o*- va *p*- nitrokaliy fenolyatlar hosil bo'ladi.



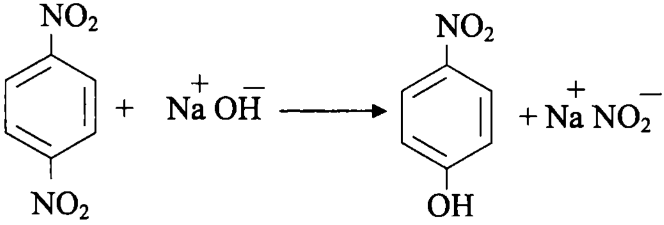
1,3,5 – trinitrobenzol ammiakning suvdagi eritmasida ishqorlar bilan S_N2- mexanizmda reaksiyaga kirishadi.



m – Dinitrobenzolni aminlash va sianlash reaksiyalarida tegishli ravishda 2,6 – dinitroanilin va 2,6 – dinitrobenzonitril hosil bo'ladi:



Dinitroarenlardagi *o* – yoki *p* – holatlarda joylashgan nitroguruhlar bir – birini faollashtiradi. *p* – dinitrobenzolga o‘yuvchi natriyni ta‘sir ettirganda nitroguruh OH ga almashinadi:



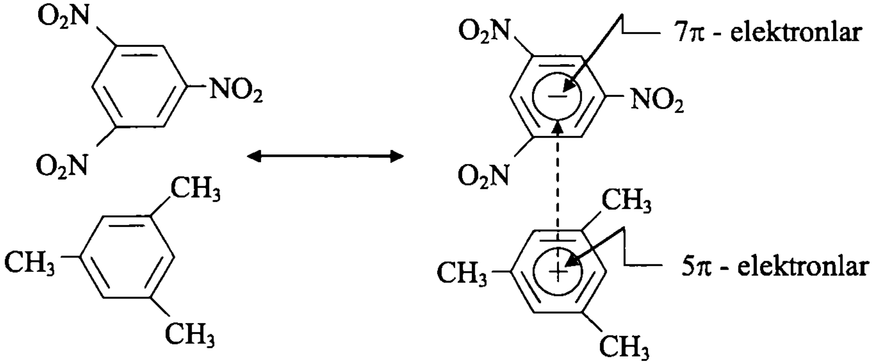
Zaryadi ko‘chgan komplekslar

Polinitrobirikmalar 1,3,5 – trinitrobenzol , geksametilbenzol, naftalin, antratsen, benzpiren , stilben singari elektron zichligi katta bo‘lgan aromatik uglevodorodlar bilan zaryadi ko‘chgan kompleks (π - kompleks)larni hosil qiladi.

Bu komplekslar odatda yaxshi kristallanadigan, rangli qattiq moddalar bo‘lib, aniq suyuqlanish haroratiga ega. Masalan, trinitrobenzolning naftalin bilan kompleksi 153°C da suyuqlanadigan sariq, antratsen bilan kompleksi 164°C da suyuqlanadugan qizil kristall moddalardir.

Pikrin kislota ham aromatik uglevodorodlar bilan yaxchi kristallanadigan komplekslarni hosil qiladi. Bu komplekslardan shu uglevodorodlarni ajratish, tozalash va identifikatsiyalashda foydalaniladi. Pikrin kislotaning komplekslari ko'pincha uglevodorodlarning "pikratlari" deb aytiladi. Pikratlari deb aytish noto'g'ri, chunki, birinchidan bunday komplekslar tuzlar emas, ikkinchidan, shularga o'xshash komplekslarning trinitrobenzol bilan aromatik uglevodorodlardan ham olingani, komplekslarning hosil bo'lishida asosiy rolni gidroksil emas, balki nitroguruhlar o'ynashidan dalolat beradi.

Zaryadi ko'chgan komplekslarda aromatik halqalar parallel tekisliklarda joylashadi va elektronlar aktseptori (polinitrobirikma) bilan elektron donori (aromatik uglevodorod) orasidagi tortilish kuchlarining ta'siri natijasida bog' hosil bo'ladi:

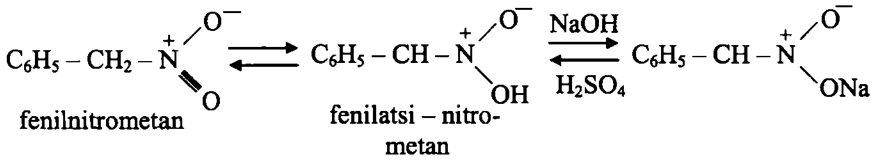


Yon zanjirida nitroguruhi bor nitrobirikmalarning xarakterli xossalari

Yon zanjirida nitroguruhi bor aromatik nitrobirikmalar suvda yomon eriydigan suyuqlik yoki qattiq moddalardir. Ular turli usullar bilan tegishli aminlargacha qaytariladi:

$$C_6H_5-CH_2NO_2 \xrightarrow{[H]} C_6H_5-CH_2NH_2+2H_2O$$

Benzol yadrosida nitroguruhi bor nitrobirikmalardan farqli o‘laroq yon zanjirida nitroguruh saqlagan birikmalar kuchli CH – kislotalar bo‘lib, ishqorlar bilan atsi – nitrobirikma tuzlarini hosil qiladi. Atsi – nitrobirikma tuzlariga kislotalarni ta‘sir ettirganda atsi – nitrobirikmalar ajraladi:



$$C_6H_5-CH_2-\overset{+}{N}{\begin{smallmatrix}O^-\\ O\end{smallmatrix}} \rightleftarrows C_6H_5-CH-\overset{+}{N}{\begin{smallmatrix}O^-\\ OH\end{smallmatrix}} \underset{H_2SO_4}{\overset{NaOH}{\rightleftarrows}} C_6H_5-CH-\overset{+}{N}{\begin{smallmatrix}O^-\\ ONa\end{smallmatrix}}$$

Fenilatsi – nitrometan sariq kristall modda bo‘lib, vaqt o‘tishi bilan yana suyuq fenilnitrometanga tautomerlanadi.

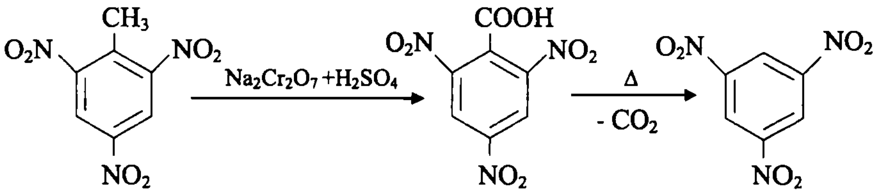
Muhim vakillari

Nitrobenzol – 210⁰ C da qaynaydigan, suvda erimaydigan, achchiq bodom hidli, rangsiz, zaharli suyuqlikdir. U ko‘p miqdorda benzolni nitrolash bilan olinadi. Nitrobenzol asosan anilin ishlab chiqarishda, shuningdek, organik sintezda qo‘llaniladi.

Nitrotoluollar. *o* – Nitrotoluol – 222⁰ C da qaynaydigan, och sariq rangli suyuqlik. *p* – Nitrotoluol esa 52⁰ C da eriydigan och sariq rangli kristall modda. Nitrotoluollar toluolni 30 – 40⁰C da nitrolash bilan olinadi. *o*– va *p* – nitrotoluollar amaliy ahamiyatga ega. Nitrotoluollarni qaytarib bo‘yoqlar sintezi uchun zarur toluidinlar, metal guruhini oksidlab nitrobenzaldegidlar va nitrobenzoy kislotalar olinadi.

1,3,5 – Trinitrobenzol (TNB) – juda kuchli portlovchi modda. Uni benzolni nitrolash bilan olish qiyin.

TNB 2,4,6 – tinitrotoluoldan sintez qilinadi:



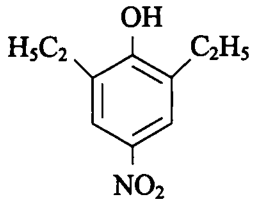
2,4,6 – trinitrotoluol 80,6°C da suyuqlanadigan, sarg'ish rangli kristall modda. U nitrotoluolni 100 % li nitrat va sulfat kislotalar aralashmasi bilan nitrolab olinadi. Trinitrotoluol (trotil, tol) – keng tarqalgan, muhim portlovchi moddadir.

Savol va mashqlar

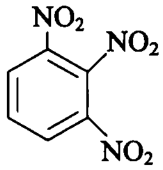
1. Quyidagi birikmalarning tuzilish formulalarini yozing:
a) 2,4 – dinitrofenol; b) m – etilnitrobenzol
d) 3 – brom – 4 – nitrobenzoy kislota e) m – nitroanilin
f) metilfenilnitrometan g) dimetilbenzilnitrometan

2. Quyidagi birikmalarni nomlang:

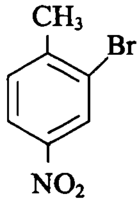
a)



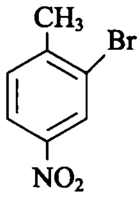
b)



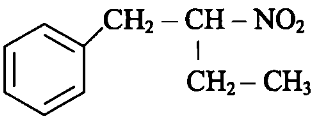
d)



e)



f)



3. $C_6H_5NO_2$ tarkibli izomer aromatik nitrobirikmalar tuzilish formulalarini yozing va ularni nomlang.

4. a) etilbenzol; b) izopropilbenzol; d) brombenzol; e) *m* – dixlorbenzol nitrolanganda qanday birikmalar hosil boladi?

5. Benzoldan quyidagi birikmalami sintez qiling:

a) *p* – nitroanilin; b) 2,4 – dinitrofenol;
d) *p* – nitrovinilbenzol; e) *p* – aminofenol;
f) *o* – bromnitrobenzol; g) 4 – nitro – 2 – xlortoluol.

6. Quyidagi sxemalar bo‘yicha boradigan reaksiyalardagi oraliq va oxirgi moddalar tuzilish formulalarini yozing :

a) $C_6H_6 \xrightarrow[H_2SO_4]{HNO_3} A \xrightarrow[H_2SO_4]{HNO_3} B \xrightarrow{Cl_2,\ (FeCl_3)} D$

b) $C_6H_6 \xrightarrow[H_2SO_4]{HNO_3} A \xrightarrow[AlCl_3]{C_2H_5Cl} B \xrightarrow{Cl_2, h\nu} D \xrightarrow[HOH]{NaOH} E$

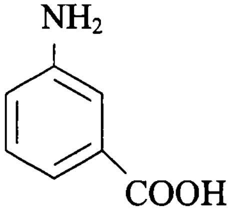
d) $C_6H_6 \xrightarrow[AlCl_3]{CH_3Cl} A \xrightarrow[\Delta,\ \text{bosim}]{\text{suyul. } HNO_3} B \xrightarrow{[H]} D$

7. Quyidagi kimyoviy aylanishlarni amalga oshiring:

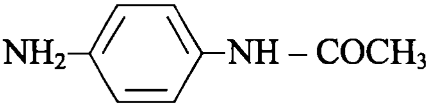
a) nitrobenzol ⟶ benzidin
b) nitrobenzol ⟶ *p* – nitroatsetanilid
d) xlorbenzol ⟶ *p* – xloranilin

8. Quyidagi kimyoviy aylanishlarni amalga oshiring:

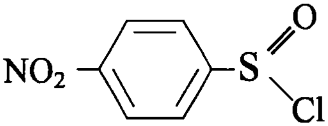
a) nitrobenzol $\longrightarrow$



b) nitrobenzol $\longrightarrow$



d) toluol $\longrightarrow$



9. Nukleofil almashinish reaksiyalarini oxiriga yetkazing:

a) o – xlornitrobenzol $\xrightarrow[\Delta]{2NH_3}$

b) p - dinitrobenzol $\xrightarrow[NaOH + HOH,\ \Delta]{:\bar{O}H}$

d) o – xlornitrobenzol $\xrightarrow[Na_2CO_3]{HOH,\ \Delta}$

10. p – Xlornitrobenzol bilan quyidagi birikmalar reaksiyaga kirishganda qanday moddalar hosil bo'ladi?

a) 130^0 C da Na_2CO_3 ning suvdagi eritmasi;
b) $2NH_3$ (160^0 C da)
d) CH_3OH + KOH (suv ishtirokida)

VII. BENZOL QATORI SULFOKISLOTALARI

Benzol qatori sulfokislotalarining tuzilishi, nomlanishi, olinish usullari, xossalari, hosilalari (xlorangidridlari, murakkab efirlari, amidlari, xloramidlari) va muhim vakillari.

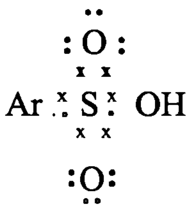
Diarilsulfonlar, arensulfin kislotalar va diarilsulfidlar haqida tushuncha.

Savol va mashqlar.

Benzol qatori sulfokislotalari halqasida yoki yon zanjirida bir yoki bir necha sulfoguruh SO_3H saqlagan birikmalardir.

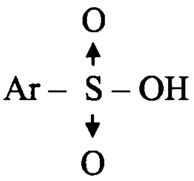
Tuzilishi

Oktet formulasiga ko‘ra sulfoguruhda ikkita kovalent va ikkita semipolyar bog‘ bor. Semipolyar bog‘lar faqat oltingugurt atomining elektronlari ishtirokida hosil bo‘ladi (I,II). Lekin sulfokislotalar uchun oltita kovalent (ikkita oddiy va ikkita qo‘sh) bog‘ga ega formula (III) ham ishlatilishi mumkin. Chunki oltingugurt atomlari bo‘sh 3d orbitallarga ega bo‘lib, ularda ham elektronlar joylashishi mumkin.



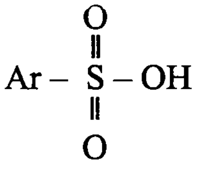
$$\begin{array}{c} :\ddot{O}: \\ \times\times \\ Ar \overset{\times}{\underset{\cdot}{\cdot}} S \overset{\times}{\underset{\cdot}{\cdot}} OH \\ \times\times \\ :\underset{\cdot\cdot}{O}: \end{array}$$

I



$$Ar-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-OH$$

II



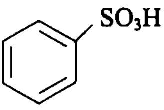
$$Ar-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$$

III

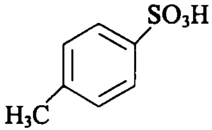
Oltingugurt atomining haqiqiy holati II va III formulalar oralig‘idagi bir holatdir.

Nomlanishi

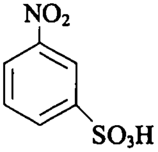
Benzol qatori sulfokislotalarining nomlari aromatik birikma nomiga **sulfokislota** (sistematik nomenklaturada sulfon kislota) so'zini qo'shish bilan hosil qilinadi:



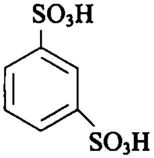
benzolsulfokislota
(benzolsulfon kislota)



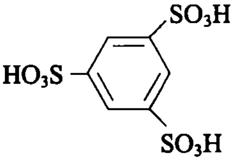
p – toluolsulfokislota
(*p* – toluolsulfon kislota)



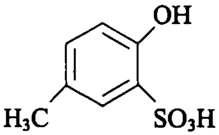
m – nitrobenzolsulfokislota



m– benzoldisulfokislota
(1,3 – benzoldisulfon kislota)



simm – benzoltri - sulfokislota



2 – gidroksi – 5 – metilbenzolsulfokislota

Olinish usullari

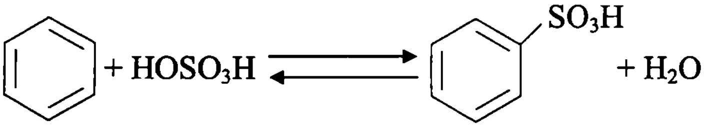
Benzol qatori sulfokislotalari arenlar yoki ularning hosilalarini sulfolash bilan olinadi:

$$Ar-H + HOSO_3H \overset{\Delta}{\rightleftarrows} Ar-SO_3H + H_2O$$

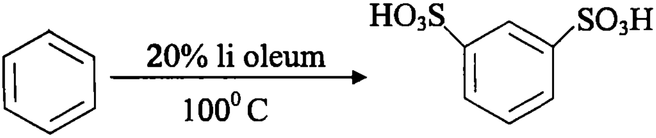
Bu reaksiyada ajralib chiqadigan suv sekinlik bilan sulfat kislota konsentrasiyasini pasaytirib, uning sulfolash ta'sirini kuchsizlantiradi. Sulfolashning o'ziga xos tomoni reaksiyaning qaytarligidir. Reaksiya jarayonida sulfolash bilan bir vaqtda sulfoguruhning gidrolizi – desulfolash reaksiyasi ham boradi.

Sulfolovchi reagentlar sifatida 98 – 100 % li sulfat kislota (monogidrat), 92 – 94 % li sulfat kislota (kuporos moyi) , 20% dan 60% gacha sulfat angidridi bor oleum, SO_3 ning SO_2 va metilen xlorididagi eritmalari, xlorsulfon kislota (sulfat kislotaning monoxlorangidridi) $ClSO_3H$ ishlatiladi.

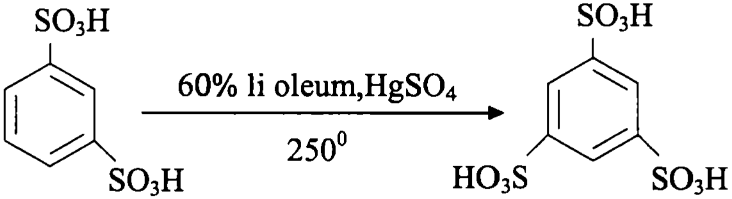
Arenlar konsentrlangan sulfat kislota yoki oleum ta'sirida oson sulfolanadi. Masalan, benzolni 92 – 94 % li sulfat kislota bilan 40–50°C da qizdirganda 90 – 96 % unum bilan benzolsulfokislota hosil bo'ladi:



Sulfoguruh halqaga ikkinchi sulfoguruhning kiritilish tezligini 10^4 marta kamaytiradi. Shu bois m – benzoldisulfokislotalarni olish uchun benzol mo'l olingan 20% li oleum bilan 100^0 C da yoki 60% li oleum bilan 60 – 80^0 C da qizdiriladi:



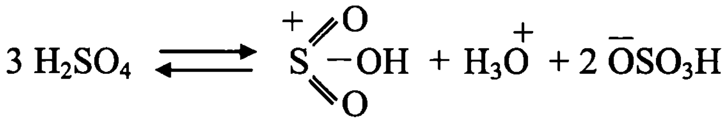
m– Benzoldisulfokislotani 1,3,5 – trisulfokislotagacha sulfolash simob sulfati ishtirokida 60% li oleum bilan 250⁰ C da amalga oshiriladi:



Sulfolash mexanizmi borasida yagona fikr yo'q, chunki u nitrolash va galogenlash mexanizmlaridek yaxshi o'rganilmagan.

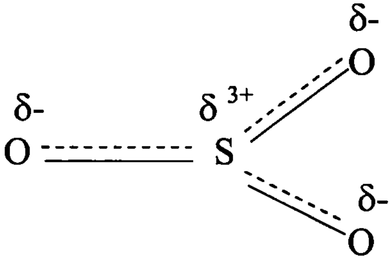
Sulfolovchi reagent sifatida 100% li yoki konsenrlangan sulfat kislota ishlatilganda molekulalarning ozaro ta'sirlashuvidan faol elektrofil zarrachalar – sulfat angidridi va gidrosulfoniy kationi hosil bo'ladi:

$$2H_2SO_4 \rightleftarrows SO_3 + H_3\overset{+}{O} + \overset{-}{O}SO_3H$$

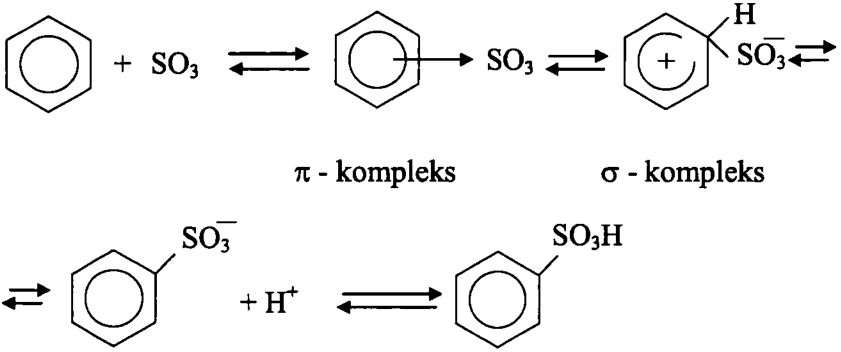


$$3\,H_2SO_4 \rightleftarrows \overset{+}{S}(=O)_2{-}OH + H_3\overset{+}{O} + 2\,\overset{-}{O}SO_3H$$

Tutovchi sulfat kislota bilan sulfolaganda asosiy sulfolovchi agent SO_3 dir. Reaksiyaga kirishish qobiliyati sulfat kislotaga nisbatan kuchli bo'lgan SO_3 molekulasida oltingugurt atomi qisman musbat zaryadlangan:

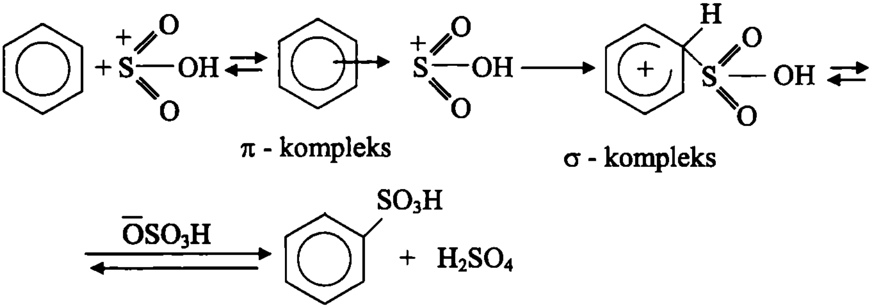


Benzolni SO_3 bilan sulfolash mexanizmi quyidagicha:

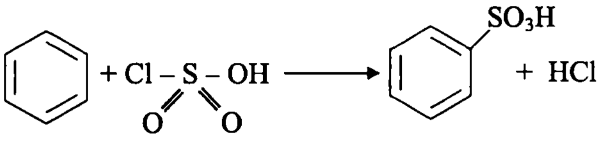


SO_3 bilan sulfolashda hosil bo'lgan *σ* - kompleks boshqa S_E2 – reaksiyalaridagidek *σ* - kompleks-kation emas, balki biqutbli iondir.

Benzolni gidrosulfoniy kationi bilan sulfolash quyidagi mexanizm bo'yicha boradi:



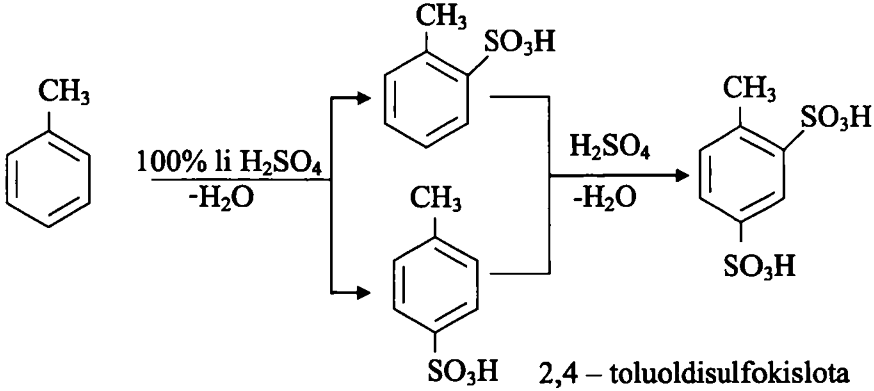
Sulfat angidridi va vodorod xloridining olinadigan xlorsulfon kislota arenlarni samarali sulfolovchi reagent hisoblanadi:



Arenlar tionil xloridi ishtirokida xona haroratida sulfolanadi (Bredli,1960–y):

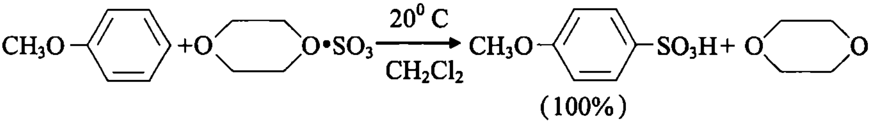
$$Ar-H + H_2SO_4 + SOCl_2 \longrightarrow Ar-SO_3H + SO_2 + HCl$$

Toluol benzolga nisbatan oson sulfolanadi:



2,4 – toluoldisulfokislota

Yadrosida elektronodonor o'rinbosarlar saqlagan aromatik birikmalarni sulfolashda sulfat angidridining piridin yoki dioksan bilan kompleksidan foydalaniladi:



Xossalari

Benzol qatori sulfokislotalari suvda yaxshi eriydigan, rangsiz, gigroskopik kristall moddalardir. Ular suvdagi eritmalarida to'la ionlangan bo'ladi:

$$Ar-SO_3H + H_2O \rightleftarrows Ar-SO_3^- + H_3O^+$$

Tuzlar hosil qilishi. Arensulfokislotalar kuchli kislotalar (benzolsulfo-kislota uchun pKa $\approx$ 0,4) bo'lib, ishqoriy va ishqoriy – yer metallar gidroksidlari bilan tuz (sulfonat) lar hosil qiladi:

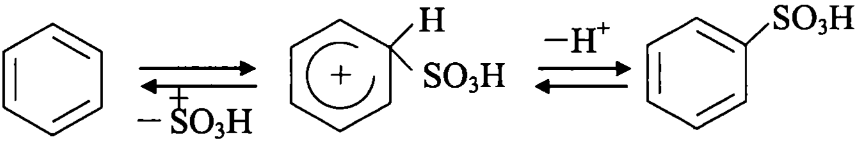
$$C_6H_5-SO_3H + NaOH \longrightarrow C_6H_5-SO_3Na + H_2O$$

Tegishli sulfatlardan farqli o‘laroq kaltsiy, bariy, va qo‘rg‘oshin (II) sulfonatlari suvda yaxshi eriydi.

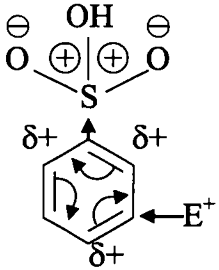
Desulfolanishi (gidrolizi). Arensulfokislotalarning gidrolizi arenlarni sulfat kislota bilan sulfolash reaksiyasiga teskari bo‘lgan reaksiyadir:

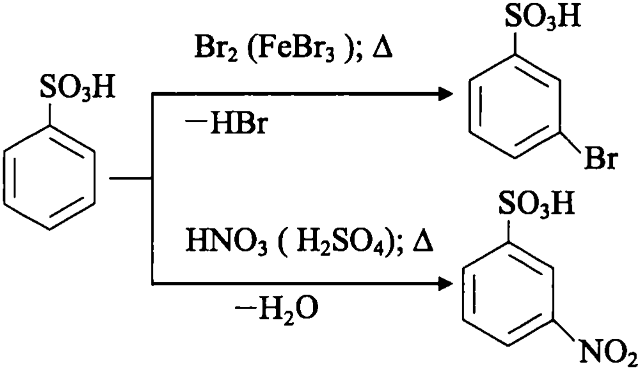
$$Ar-SO_3H + H_2O \xrightarrow{H^+,\ \Delta} Ar-H + H_2SO_4$$

Bu reaksiyada sulfoguruh protonga elektrofil almashinadi. Sulfat kislota bilan sulfolaganda ham, arensulfokislotalarning gidrolizida ham bir xil σ - kompleks hosil bo‘ladi. σ - Kompleksdan gidrosulfoniy kationi ajralganda aromatik uglevodorod, proton ajralganda esa arensulfokislota hosil bo‘ladi:

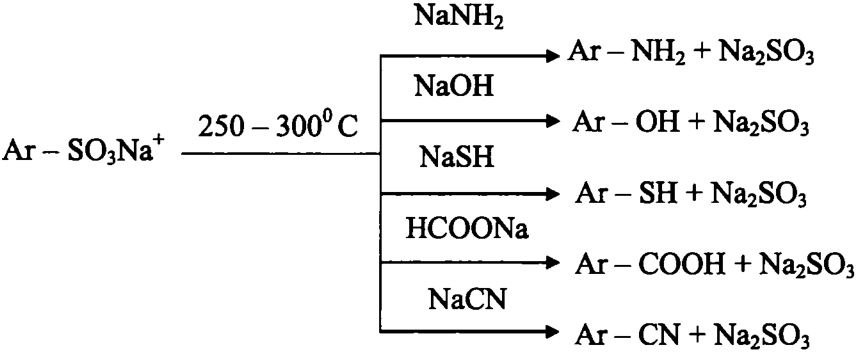


Elektrofil almashinish reaksiyalari. Sulfoguruh aromatik yadro elektron buluti zichligini kamaytiradi va elektrofil almashinishni qiyinlashtirib, o‘rinbosarni **meta** – holatga yo‘naltiradi:





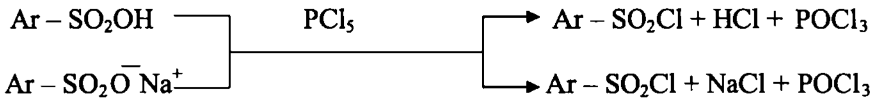
Nukleofil almashinish reaksiyalari. Sulfokislotalarda aromatik yadroning qisman musbat zaryadlanganligi nukleofil reagent hujumini va sulfoguruhning sulfit – ion holida ajralishini osonlashtiradi:



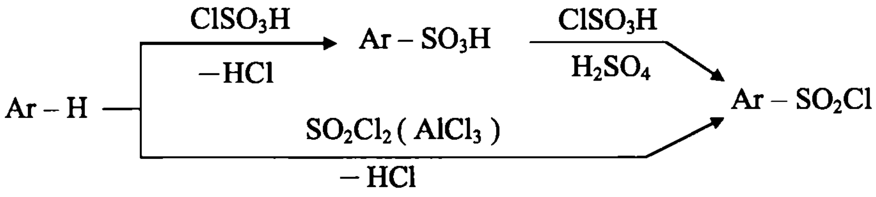
Arensulfokislotalarning hosilalari

Arensulfokislotalar karbon kislotalar singari galogenangidridlar, amidlar va murakkab efirlarni hosil qiladi. Bu hosilalarning olinishi karbon kislotalar hosilalarining olinishiga o‘xshaydi.

Arensulfoxloridlar arensulfokislotalar yoki ularning natriyli tuzlari va fosfor pentaxloriddan olinadi:



Arenlarga mo‘l xlorsulfon kislota yoki $AlCl_3$ ishtirokida sulfuril xlorid ta‘sir etganda ham arensulfoxloridlar hosil bo‘ladi:



Arensulfoxloridlar elektrofil xossalarni yaqqol namoyon qiladi va turli nukleofillar bilan reaksiyalarga oson kirishadi. Ularni qaytarganda arentiollar (tiofenollar) hosil bo‘ladi:

$$C_6H_5-SO_2Cl \xrightarrow[Zn+HCl]{[H]} \underset{\substack{\text{merkaptobenzol} \\ \text{(tiofenol)}}}{C_6H_5-SH} + HCl + 2H_2O$$

Arensulfoxloridlar arensulfokislotalarning murakkab efirlari, amidlari, gidrazidlari va boshqa hosilalarini sintez qilishda ishlatiladi:

Arensulfokislotalarning murakkab efirlari arensulfokislotaning qattiq natriyli tuzini dimetil – yoki dietilsulfat bilan qizdirish, shuningdek, sulfoxloridga spirt yoki alkogolyatni ta'sir ettirish bilan olinadi:

$$Ar-SO_2-ONa + (CH_3)_2SO_4 \xrightarrow[-CH_3NaSO_4]{150-160\,^0C} Ar-SO_2-OCH_3$$

$$Ar-SO_2Cl + ROH \longrightarrow Ar-SO_2-OR + HCl$$

Arensulfokislotalarning murakkab efirlari suyuqlik yoki qattiq moddalardir. Ular spirtlar, fenollar, karbon kislotalar va aminlarni yaxshi alkillovchi agentlar sifatida ishlatiladi:

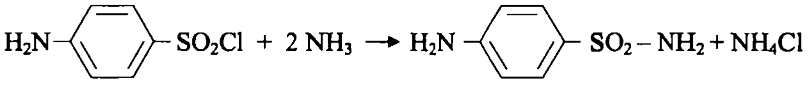
$$Ar-SO_2-OCH_3 + ROH \longrightarrow Ar-SO_2-OH + ROCH_3$$

Arensulfokislotalar murakkab efirlarini ishqorlar ta'sirida gidroliz qilinganda O – alkil bog'i uziladi:

$$Ar-SO_2-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-R + :\overline{O}H \longrightarrow Ar-SO_3^{\overline{\ \ }} + R-OH$$

Arensulfokislotalarning ***amidlari*** (arensulfamidlar) ni olish uchun arensulfoxloridlarga ammiak, birlamchi yoki ikkilamchi amin ta'sir ettiriladi:

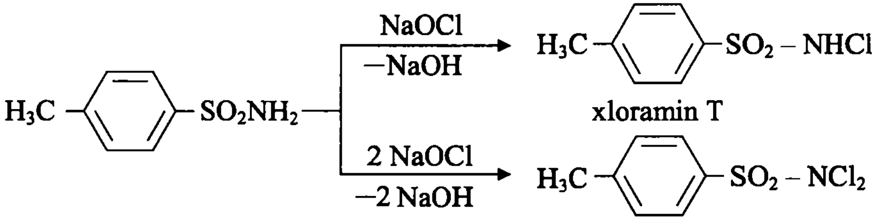
$$Ar-SO_2Cl + 2\,NH_3 \longrightarrow Ar-SO_2-NH_2 + NH_4Cl$$



oq streptotsid

Arensulfamidlar rangsiz kristall moddalardir. Ular karbon kislotalarning amidlariga nisbatan sekin gidrolizlanadi.

Arensulfamidlar natriy gipoxlorit bilan reaksiyaga kirishganda amid guruhining vodorod atomlari xlorga almashinadi va arensulfokislotalarning xloramidlari (xloraminlar) hosil bo'ladi:



xloramin T

dixloramin T

Benzolsulfodixloramid (dixloramin B) $C_6H_5SO_2NCl_2$ xloramin T ning natriyli tuzi $p-CH_3-C_6H_4SO_2N^- ClNa^+$ $*3H_2O$ va boshqa xloramidlar samarali antiseptiklar sifatida ishlatiladi. Xloraminlarning ta'siri ular gidrolizlanganda gipoxlorit kislotaning hosil bo'lishiga asoslangan.

Muhim vakillari

Benzolsulfokislota –suvda va spirtda yaxshi eriydigan, 171-172°C da suyuqlanadigan kristall modda. Uning natriyli tuzi fenol olishda ishlatiladi.

p-**Toluolsulfokislota** – 104° C da suyuqlanadigan, suvda juda yaxshi eriydigan, rangsiz kristall modda. U toluolni sulfolash yoki *p*-toluolsulfoxloridni gidrolizlash bilan olinadi. Ko'p organik erituvchilarda eriganligi bois u organik reaksiyalarda kislotali katalizator sifatida ishlatiladi.

p-**Toluolsulfoxlorid** (tozilxlorid) tozil guruhini kiritishda qo'llaniladi.

Benzolsulfoxlorid – 251,5° C da qaynaydigan og'ir suyuqlik. U turli organik birikma va dori preparatlarini sintez qilishda ishlatiladi.

Alkil-p-toluolsulfonatlar (tozilatlar) – $p-CH_3-C_6H_4SO_2OR$- suvda erimaydigan kristall moddalar. Ular ishqor ishtirokida tozilxlorid va alkanollardan olinadi. Tozilatlar alkillovchi reagentlar sifatida ishlatiladi.

p-**Toluolsulfamid** $p–CH_3-C_6H_4SO_2NH_2$ – 138°C da suyuqlanadigan, suvda kam eriydigan, rangsiz kristall modda. U xloraminlar olishda ishlatiladi.

Yon zanjirida 12 tadan 16 tagacha uglerod atomi bor alkilbenzolsulfokislotalarning natriyli tuzlari sirt-faol moddalar va sintetik yuvish vositalari sifatida ishlatiladi. Ularni sintez qilish uchun benzol n-alkanlar aralashmasini radikal xlorlab olinadigan xloralkanlar aralashmasi bilan alkillanadi.

Diarilsulfonlar, arensulfin kislotalar, diarilsulfidlar

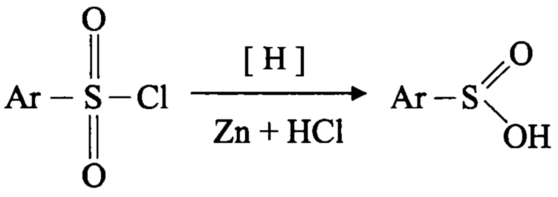
Arensulfoxloridlar alyuminiy xloridi ishtirokida aromatik uglevodorodlar bilan reaksiyaga kirishganda diarilsulfonlar hosil bo'ladi :

$$C_6H_5\text{-}SO_2Cl + C_6H_6 \xrightarrow{AlCl_3} C_6H_5-SO_2-C_6H_5 + HCl$$

difenilsulfon

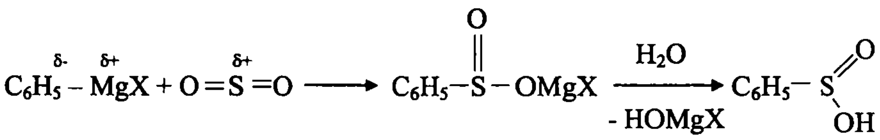
Diarilsulfonlar – kimyoviy inert va termik barqaror birikmalardir. Sulfon guruhi kuchli elektronoaktseptor xossalarga ega metaoriyentant bo'lib, elektrofil almashinish reaksiyalarida benzol halqalari faolligini pasaytiradi.

Arensulfoxloridni rux bilan kislotali muhitda qaytarilsa **arensulfin kislotalar** hosil bo'ladi :



$$Ar-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Cl \xrightarrow[Zn + HCl]{[H]} Ar-S(=O)-OH$$

Arensulfin kislotalarni metallorganik birikmalarga SO_2 ni ta'sir ettirib ham olinadi :



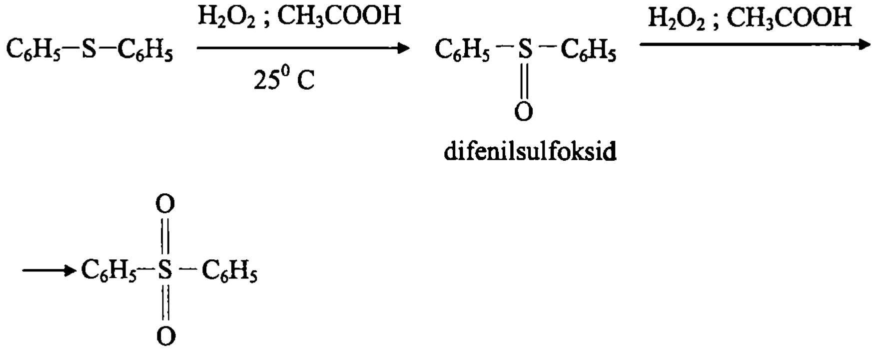
$$\overset{\delta-}{C_6H_5}-\overset{\delta+}{MgX} + O=\overset{\delta+}{S}=O \longrightarrow C_6H_5-\overset{\overset{O}{\|}}{S}-OMgX \xrightarrow[-\ HOMgX]{H_2O} C_6H_5-S(=O)-OH$$

Arensulfin kislotalar karbonil birikmalarga va azometinlarga birikish xossasi bilan natriy gidrosulfitiga o‘xshaydi.

Arenlar Lyuis kislotalari ishtirokida oltingugurt galogenidlari bilan reaksiyaga kirishganida **diarilsulfidlar** hosil bo‘ladi :

$$2\,Ar-H + S_2Cl_2 \xrightarrow{AlCl_3} Ar-S-Ar + S + 2\,HCl$$

Difenilsulfidni sirka kislotada ekvimolekulyar miqdordagi vodorod peroksidi bilan oksidlaganda difenilsulfoksid, vodorod peroksidi mo‘l olinganda esa difenilsulfon hosil bo‘ladi :



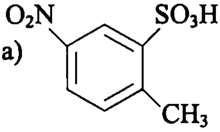
$$C_6H_5-S-C_6H_5 \xrightarrow[25^0\,C]{H_2O_2\,;\,CH_3COOH} C_6H_5-\underset{\underset{O}{\|}}{S}-C_6H_5 \xrightarrow{H_2O_2\,;\,CH_3COOH} C_6H_5-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-C_6H_5$$

difenilsulfoksid

Savol va mashqlar

1. Quyidagi birikmalarning tuzilish formulalarini yozing :
a) 3 – etilbenzolsulfokislota ;
b) natriy *m* – brombenzolsulfonat ;
d) metal – *p* – toluolsulfonat (metiltozilat) ;
e) nitrobenzoldisulfokislota -3.5 ;
f) bariy *m* – xlorbenzolsulfonati ;
g) 2 – metil – 5 – xlorbenzolsulfamid

2. Quyidagi birikmalarni nomlang :

a)


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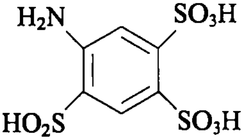

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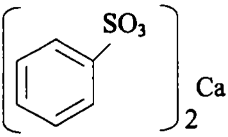

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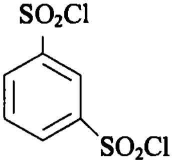
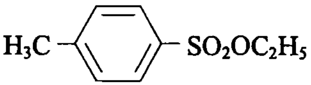
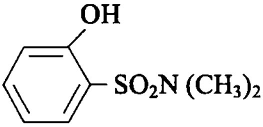


f)


g)


3. Quyidagi reaksiyalarni oxirigacha yetkazing:

a) $m\text{ –fenolbenzolsulfokislota} \xrightarrow[\Delta]{\text{kons. } H_2SO_4}$

b) $\text{fenol} \xrightarrow{\text{mo'l } HOSO_2Cl}$

d) $p\text{ – krezol} \xrightarrow{\text{kons. } H_2SO_4}$

e) $m\text{ – xlortoluol} \xrightarrow{SO_3}$

4. Benzoldan quyidagi birikmalarni sintez qiling:

a) *p* – toluolsulfokislota ; b) *p* – xlorbenzolsulfokislota : d) 2 – meta – 5 – nitrobenzolsulfokislota; e) *p* – toluolsulfoxlorid;
f) 3 – brom – 5 – nitrobenzolsulfokislota;

5. Quyidagi sxemalarni to'ldiring:

a) $C_6H_6 \xrightarrow{\text{konts. } H_2SO_4} A \xrightarrow{H_2SO_4, SO_3} B \xrightarrow{2\,NaOH} D$

b) $C_6H_5OH \xrightarrow[\text{orto – izomer}]{\text{konts.}H_2SO_4} A \xrightarrow[H_2SO_4]{HNO_3} B \xrightarrow[HOH]{KOH} D \xrightarrow{KCN} E \xrightarrow[H^+]{2\,HOH} F$

d) $C_6H_6 \xrightarrow[H^+]{CH_2{=}CH_2} A \xrightarrow[\text{para-izomer}]{H_2SO_4} B \xrightarrow[FeBr_3]{Br_2} D$

g) $C_6H_5{-}CH_3 \xrightarrow[\text{para-izomer}]{H_2SO_4} A \xrightarrow[AlCl_3]{CH_3Cl} B \xrightarrow{2\,KMnO_4} D \xrightarrow{HOSO_2Cl} E$

6. Quyidagi birikmalarni oson sulfolanish tartibida joylashtiring:

a) etilbenzol; b) xlorbenzol; d) benzol; e) *m*-benzoldisulfokislota;

7. Kimyoviy aylanishlarni amalga oshiring:

a) benzol ⟶ *p*-toluolsulfokislotaning monoxloramidi
b) benzol ⟶ benzolsulfodixloramid $C_6H_5 - SO_2 - NCl_2$
d) *p*-xlornitrobenzol ⟶ 2- gidroksidi-3.5-dinitrobenzolsulfokislota
e) benzolsulfokislota ⟶ *m* – krezol

8. Quyidagi reaksiyalarni oxirigacha yetkazing:

a) xlorbenzol + 100% li $H_2SO_4 \xrightarrow{100^0\,C}$

b) *p*- nitrotoluol + 20% li oleum $\xrightarrow{60\,^0C}$

d) nitrobenzol + 60 % li oleum $\xrightarrow{80\text{-}100^0C}$

e) 2.4 – dimetilbenzolsulfokislota + o'ta qizigan suv bug'i $\xrightarrow{H^+}$

9. Sulfolash reaksiyalari aromatik qatorda boradigan boshqa elektrofil almashinish reaksiyalaridan qanday farq qiladi?

10. Xlorsulfon kislota bilan reaksiyaga kirishganida $C_7H_8SO_2Cl$ ni, sulfat kislota ishtirokida suv bug'i bilan haydaganda C_7H_8 ni, KOH bilan 300-350^{0}C gacha qizdirilganda esa para-gidroksitoluolni hosil qiladigan $C_7H_8O_3S$ tarkibli moddaning tuzilishini aniqlang. Tegishli reaksiyalar tenglamalarini yozing.

VIII. FENOLLAR

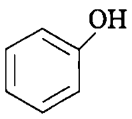
Fenollarning sinflanishi va nomlanishi. Bir atomli fenollarning olinish usullari, fizikaviy xossalari, spektral tavsifi ,kimyoviy xossalari (kislotalik xossalari, oddiy va murakkab efirlarining olinishi, elektrofil almashinish reaksiyalari,gidroksil guruhining nukleofil almashinishi, gidrogenlash, oksidlash va boshqa reaksiyalari,barqaror aroksil reaksiyalar),muhim vakillari.

Ikki va uch atomli fenollar. Xinonlar. Savol va mashqlar.

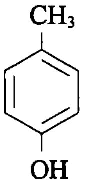
Molekulasida aromatik yadro bilan bevosita bog'langan bir yoki bir necha gidroksil guruhi bor organik birikmalarga fenollar deyiladi. Gidroksil guruhining soniga qarab fenollar bir-, ikki-, uch- va ko'p atomli bo'ladi.

Nomlanishi

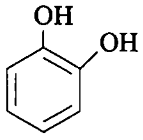
Fenollarning trivial nomlari ko'p ishlatiladi. Sistematik nomenklaturada fenollarning nomi tegishli arenlar nomi va – ol qo'shimchasidan hosil qilinadi. Raqamlash gidroksil guruhi bilan bog'langan uglerod atomidan boshlanadi. Ba'zan gidroksil guruhining borligi gidroksi-(oksi) old qo'shimchasi bilan belgilanadi :



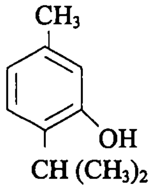
fenol
(gidroksibenzol)



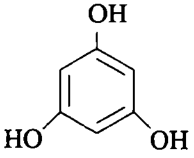
p – krezol
(*p*– metilfenol,
4 - metilfenol)



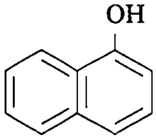
pirokatexin
(benzendiol – 1,2 ;)
1,2 – digidroksi - benzol)



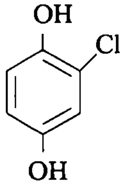
timol
(2 – izopropil - 5 - metilfenol)



floroglyutsin
(benzentriol – 1,3,5;
1,3,5 – trigidroksi -
benzol)



α - naftol
(naftol – 1)



xlorgidroxinon
(2 – xlor – 1,4 – digid -
roksibenzol)

Bir atomli fenollar

Olinish usullari

Fenol va uning gomologlari toshko‘mir smolasidan, shuningdek, sintetik usullar bilan olinadi. Fenollarni sintez qilishda aromatik yadrodagi sulfoguruh, galogenlar, aminoguruh, diazoguruh va ba‘zan vodorod atomlari gidroksil guruhiga almashtiriladi.

1. Arensulfokislotalar tuzlarini ishqor bilan qizdirish :

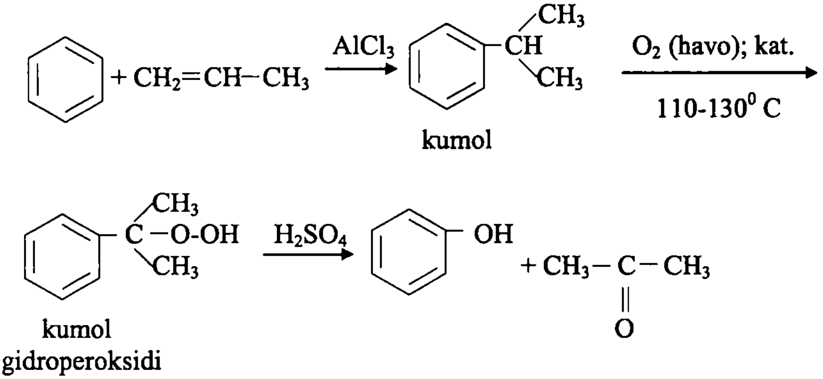
$$C_6H_5 - SO_3Na + 2\ NaOH \xrightarrow{320^0\,C} C_6H_5 - ONa + Na_2SO_3 + H_2O$$

$$2\ C_6H_5 - ONa + SO_2 + H_2O \longrightarrow 2\ C_6H_5OH + Na_2SO_3$$

2. Galogenli hosilalarni gidrolizlash :

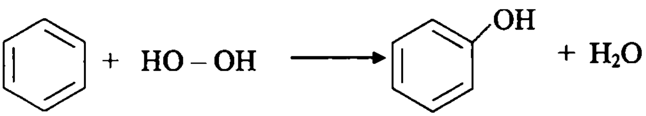
$$C_6H_5{-}Cl + \underset{\substack{10\ \%\ li \\ eritma}}{NaOH} \xrightarrow{300\text{-}350^0\,C;\ 196\ MPa} C_6H_5OH + NaCl$$

3. Kumol (izopropilbenzol)dan olish (P.G.Sergeyev, B.D.Krujalov, P.Y.Udris, M.E.Nemsev, 1949–y). Xomashyo sifatida benzol va propilen ishlatiladi :



Reaksiya natijasida ikkita muhim mahsulot (fenol va atseton) hosil bo'ladi.

4. To'g'ridan – to'g'ri gidroksillash Fe (II), Cu (II) yoki Ti (III) tuzlari katalizatorligida arenlarga vodorod peroksidini ta'sir ettirganda vodorod atomi gidroksil guruhiga almashinadi:

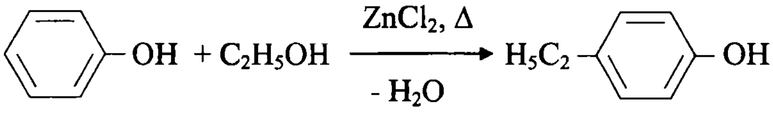


5. Aminoguruhni diazoniy tuzlari orqali gidroksilga almashtirish :

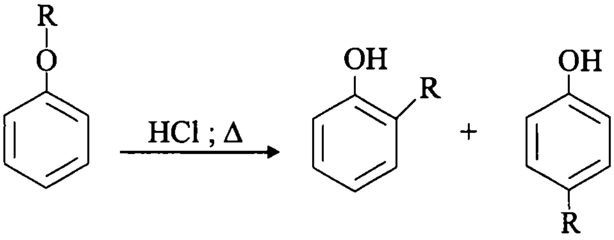
$$C_6H_5\,NH_2 \xrightarrow[-NaCl;\ -\,2\,H_2O]{NaNO_2\ +2HCl} \left[C_6H_5-N_2\right]^+ Cl^- \xrightarrow[-N_2\ ;\ -HCl]{H_2O\ ,\ \Delta} C_6H_5\,OH$$

6. Fenol gomologlarini yuqoridagi usullar bilan benzol gomologlarining sulfo-, galogenli- yoki aminohosilalaridan olish mumkin. Lekin fenol yadrosiga alkil guruhini kiritish usullari ham

bor. Fenollarni alkillash benzol va uning gomologlarini alkillashga nisbatan oson boradi. Katalizator sifatida rux xloridni, alkillovchi reagent sifatida esa spirtlarni qo'lllash mumkin :



Fenollar efirlarini kislotalar ishtirokida qizdirilganda ham fenollarning alkillanishi sodir bo'ladi :



Fizikaviy xossalari va spektral tavsifi

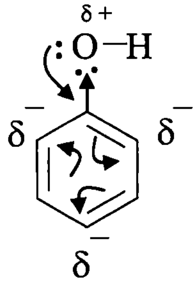
Fenollar o'ziga xos hidli, suvda qiyin eriydigan, suv bug'i bilan haydaladigan, kristall moddalardir. Ular zaharli bo'lib, teriga tegsa kuydiradi (yara paydo qiladi).

Fenollarning IQ – spektrlarida O–H guruhining valent tebranishlari 3200-3600 sm^{-1} sohada kuzatiladi.

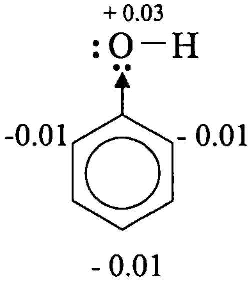
PMR – spektrlarida OH guruhi protoni signali δ = 4.5-7.5 (CCl_4 dagi eritmasi) sohalarda kuzatiladi.

Kimyoviy xossalari

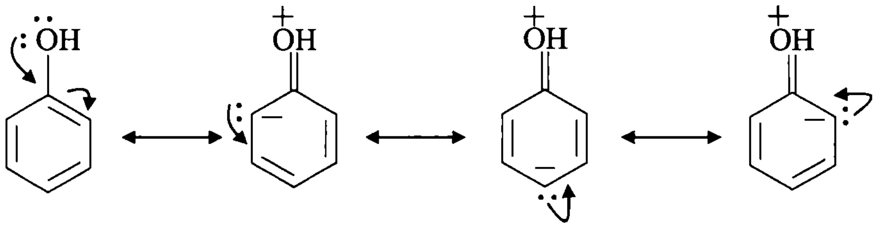
Fenolning π - elektron tizimiga 8 ta (benzol halqasining 6 ta, kislorod atomidan 2 ta) elektron kiradi. Gidroksil guruhining musbat mezomer effekti ta'sirida halqaning *o*- va *p*- holatlarida elektron zichligi ortadi, kislorod atomida esa kamayadi:



$+M(P, \pi) > -J$



Fenollardagi C – O bog'i sof σ - bog' emas. U p, π - tutashish tufayli muayyan miqdordagi π- elektron zichligiga ham ega bo'ladi. Buni fenolning rezonans strukturalari yordamida quyidagicha tasvirlash mumkin :



Shu bois fenollarning benzol halqasidan kislorod atomining ajralishi bilan boradigan reaksiyalarni amalga oshirish juda qiyin.

Fenollarning ko'p sonli reaksiyalari gidroksil guruhining elektronodonor ta'siri tufayli faollashgan benzol halqasida boradi. Gidroksil guruhi hisobidan esa fenollar kuchsiz kislota xossalarini namoyon qiladi hamda alkillash va atsillash reaksiyalariga kirishadi.

1.Kislotalilik xususiyatlari. Fenollar alkanollarga nisbatan kuchli, lekin karbon kislotalar va hatto karbonat kislotadan ham kuchsiz OH – kislotalardir.

Fenollar ishqoriy metallar va ishqorlarning suvdagi eritmalari bilan reaksiyaga kirishib, fenolyatlarni hosil qiladi :

$$2\,Ar{-}OH + 2\,Na \longrightarrow 2\,[ArO]^{-}Na^{+} + H_2$$

$$Ar{-}OH + NaOH \rightleftarrows [ArO]^{-}Na^{+} + H_2O$$

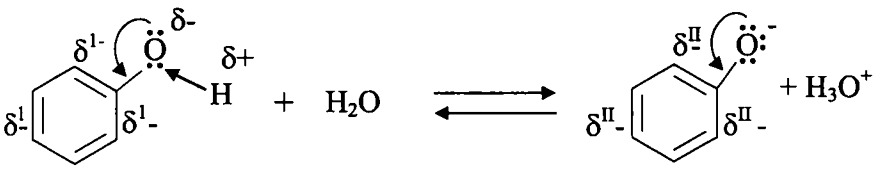
Fenollar natriy karbonatdan CO_2 ni siqib chiqara olmaydi. Karbonat kislota esa fenolyatlar eritmalaridan fenollarni siqib chiqaradi :

$$[ArO]^{-}Na^{+} + CO_2 + H_2O \longrightarrow ArOH + NaHCO_3$$

Aromatik yadro bilan bog'langan elektronoaktseptor o'rinbosarlar fenol gidroksil guruhi kislotaliligini oshiradi. Ba'zi fenollarning pKa qiymatlari quyida keltirilgan:

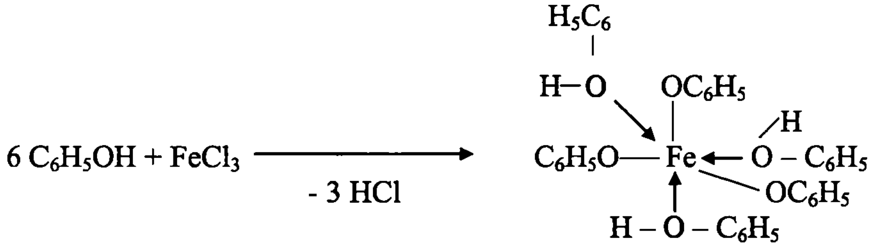
Fenollar	pKa
Fenol	9.98
2- nitrofenol	7.23
3-nitrofenol	8.40
4-nitrofenol	7.15
2,4- nitrofenol	4.03
2,4,6 – trinitrofenol	0.20

Fenollar kislotalik xossalarining alkanollarnikiga nisbatan kuchliligi ikki xil omilga bog'liq. Birinchidan, gidroksil guruhining musbat mezomer effekti tufayli fenollar kislorodida elektron zichligi kamayadi. Buning natijasida fenollar gidroksilining protoni alkanollar gidroksilidagi protonga nisbatan harakatchan bo'lib qoladi. Ikkinchidan, fenolyat anioninig hosil bo'lishi alkogolyat anionining hosil bo'lishiga qaraganda energetik qulay, chunki fenolyat anionda tutashish tufayli manfiy zaryad delokallashgan. Alkogolyat – anionda esa bunday tutashish imkoniyati yoq.



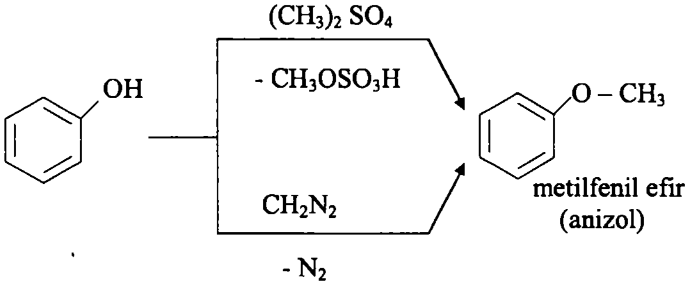
$(\delta^{II}\text{-}>>\delta^{I}\text{-})$

2. $FeCl_3$ ning ta'siri. Fenol suvdagi yoki spirtdagi suyultirilgan eritmalarda $FeCl_3$ bilan binafsha rangli kompleks tuz beradi:

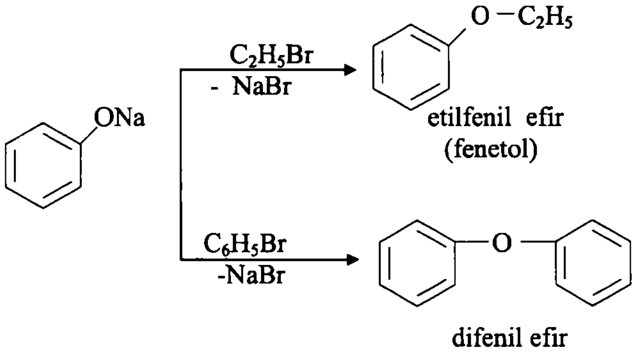


Bu fenolga xos sifat reaksiyasidir.

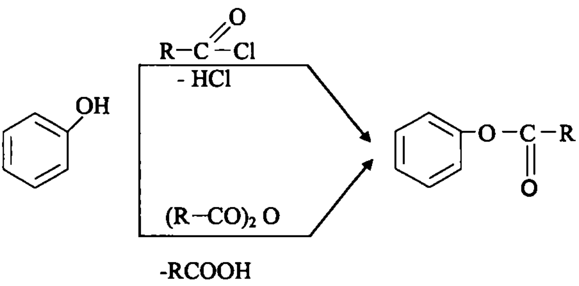
3.Oddiy efirlarining olinishi. Fenollar dimetilsulfat yoki diazometan bilan reaksiyaga kirishganda metilfenil efirlar hosil bo'ladi:



Oddiy efirlar fenolyatlardan ham oson hosil bo'ladi :

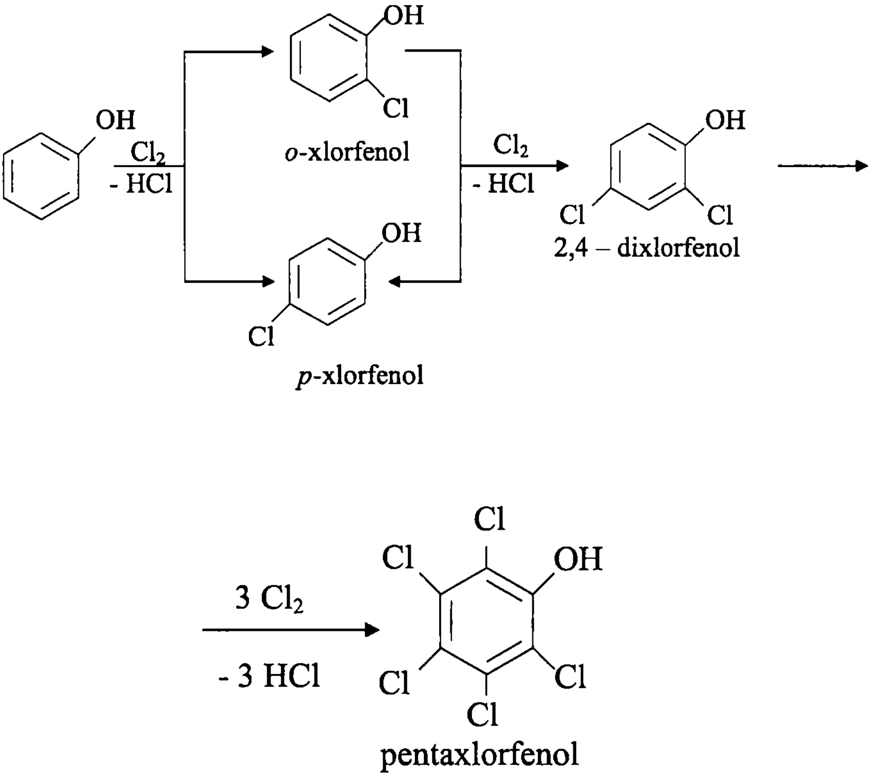


4. Murakkab efirlarining olinishi. Fenollar sulfat kislota ishtirokida karbon kislotalar bilan eterifikatsiya reaksiyasiga kirishganda hosil bo'ladigan murakkab efirlarning unumi juda kam bo'ladi. Shu bois fenollarning murakkab efirlarini olish uchun fenollar yoki fenolyatlarga karbon kislotalarning angidridlari yoki galogenangidridlar ta'sir ettiriladi :

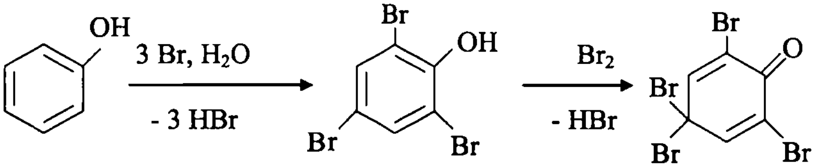


5. Elektrofil reagentlarning ta'siri. Fenollar elektrofil reagentlar bilan benzol va uning gomologlariga nisbatan reaksiyalarga oson kirishadi.

a) fenollarning galogenlanishi katalizatorsiz ham oson boradi:



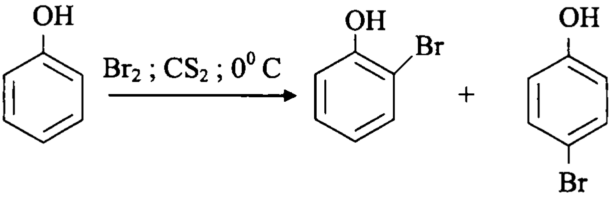
Fenolni bromlash sezgir reaksiya bo'lib, u juda suyultirilgan suvli eritmalarda ham oson boradi. Bromli suv mo'l olinganda oxirgi mahsulot sifatida 2,4,4,6 – tetrabromtsiklogeksadiyenon hosil bo'ladi:



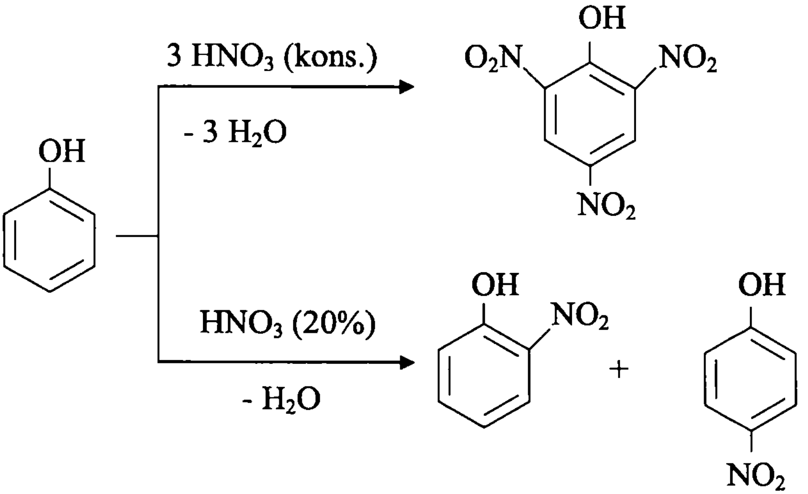
2,4,6 – tribrom-fenol

2,4,4,6 – tetrabrom - siklogeksadiyen - - 2,5 – on – 1

2- yoki 4- bromfenollarni sintez qilish uchun bromlash 0° C da uglerod sulfidida olib boriladi :



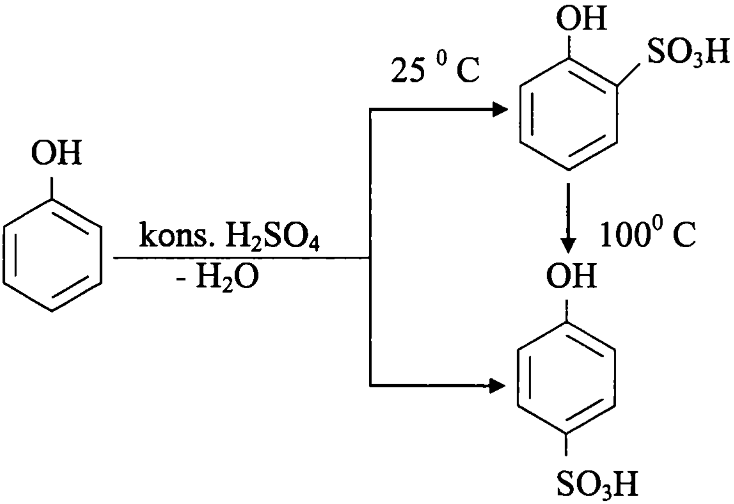
b). Fenolni konsentrlangan nitrat kislota yoki nitrolovchi aralashma bilan nitrolaganda 2,4,6 – **trinitrofenol** (pikrin kislota) hosil bo‘ladi. Mononitrofenollarni olish uchun nitrolashni past haroratda suyultirilgan nitrat kislota ta‘sirida o‘tkaziladi :



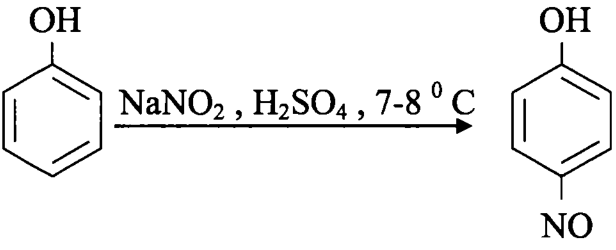
o- nitrofenol *p*- nitrofenol

d). Fenolni **sulfolash** juda oson boradi va haroratga qarab o- yoki p- izomerlar hosil bo‘ladi .

o- Fenolsulfokislota 100⁰ C da p- fenolsulfokislotaga qayta guruhlanadi :

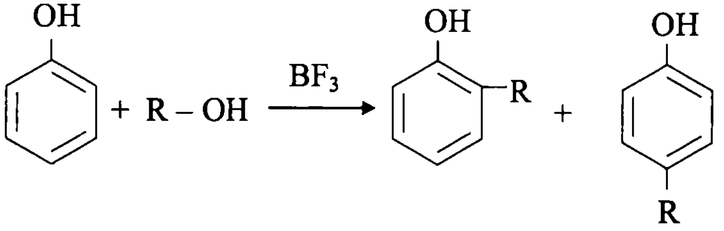


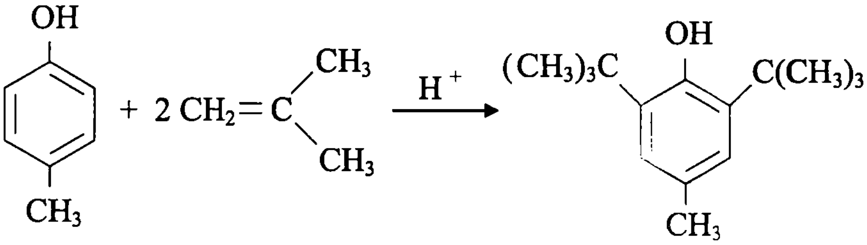
e). Fenollar nitrit kislota bilan **nitrozirlash** reaksiyasiga kirishib, nitrozofenollarni hosil qiladi :



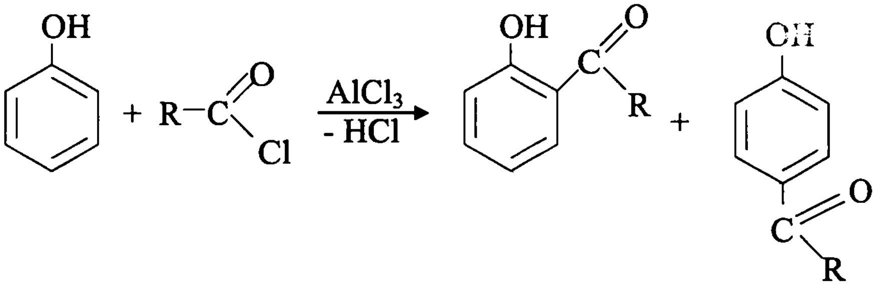
p-nitrozofenol

f). Fenollar H_2SO_4 , H_3PO_4 yoki Lyuis kislotalari ishtirokida alkanollar va alkenlar bilan alkillash reaksiyalariga kirishadi :

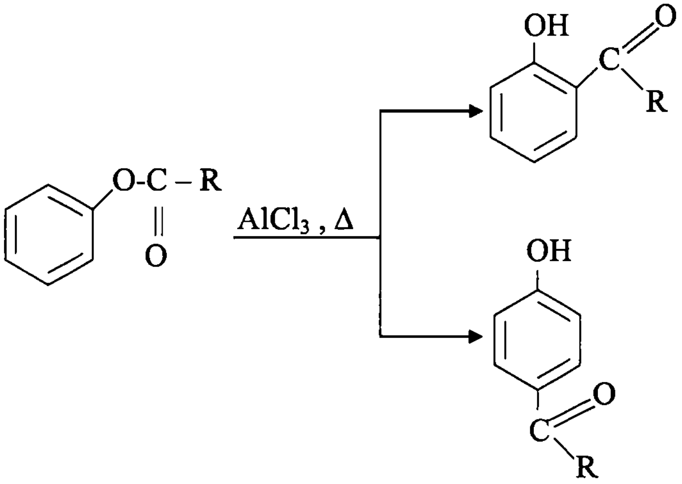




g). Fenollar atsilxloridlar yoki karbon kislotalar angidridlari bilan Lyuis kislotalari ishtirokida atsillash reaksiyalariga oson kirishadi :



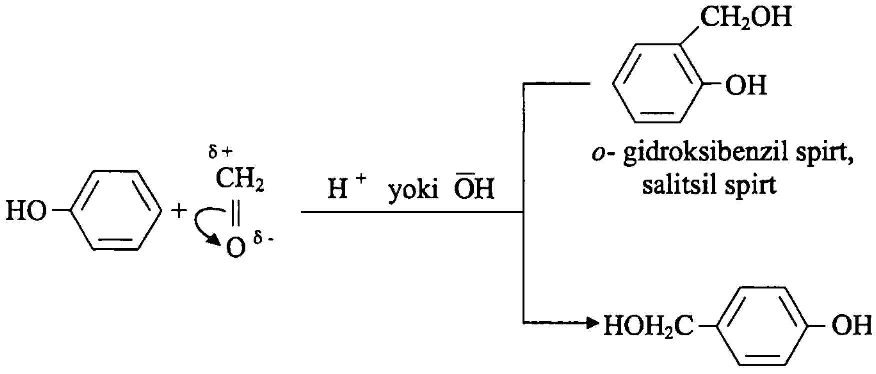
o- va *p*- atsilfenol (*o*-va *p*- gidroksifenilketon) lar fenollar murakkab efirlarining alyuminiy xloridi ishtirokida qayta guruhlanishi (Fris-qayta guruhlanishi, 1908-y) bilan ham olinadi :



60⁰ C da ko‘proq para-, 160⁰C da esa orto- atsilfenollar hosil bo‘ladi.

h). Fenollar elektrofil almashinish reaksiyalarida juda faol bo‘lgani bois kislotalar yoki asoslar ishtirokida kuchsiz elektrofillar- aldegid va ketonlar bilan ham reaksiyaga kirishadi.

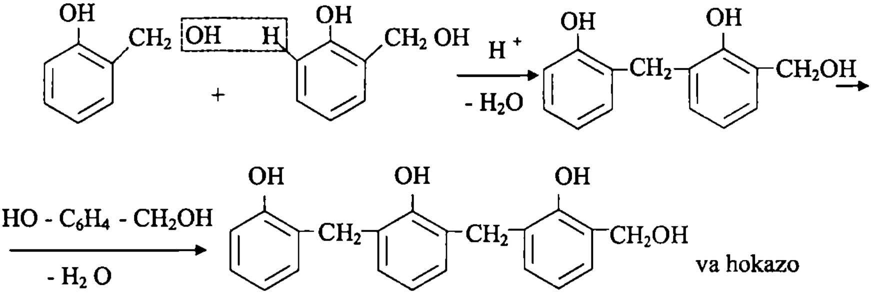
Ishqoriy yoki kislotali katalizatorlar ishtirokida fenolning formaldegid bilan kondensatlanishidan fenolospirtlar (gidroksimetilfenollar) hosil bo‘ladi:



o- gidroksibenzil spirt, salitsil spirt

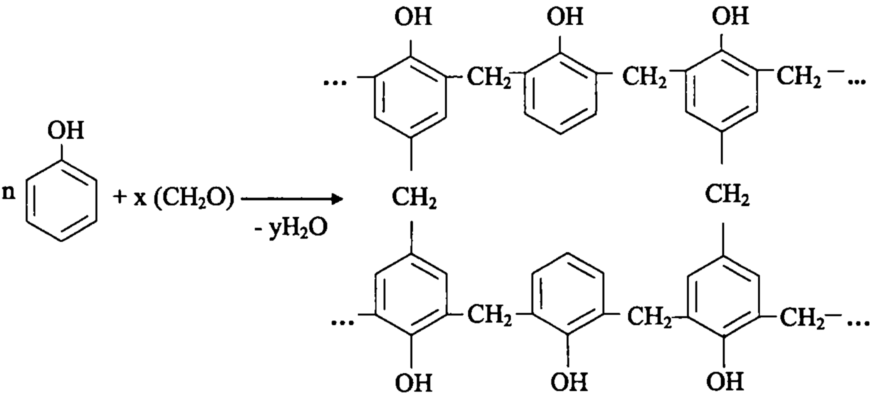
p – gidroksibenzil spirt

So‘ngra fenolspirtlar fenol molekulasining kimyoviy faol vodorod atomlari yoki fenolspirtning boshqa molekulasi bilan polikondensatlanish reaksiyasiga kirishib, chiziqsimon fenol-formaldegid polimerini hosil qiladi:



7:6 nisbatda olingan fenol va formaldegiddan kislotali muhitda hosil bo‘ladigan bu termoplastik polimerlar **novolaklar** deb yuritiladi.

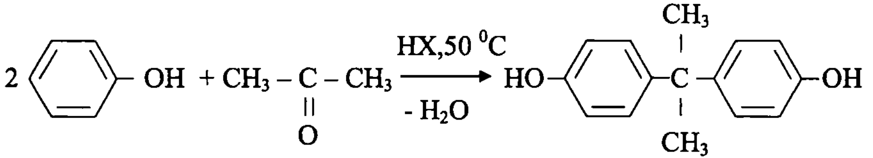
Fenolning mo‘l olingan formaldegid bilan ishqoriy muhitda polikondensatlanishidan tarmoqlangan termoreaktiv polimer hosil bo‘ladi:



bakelit S

Fenolformaldegid polimerlar (smolalar) katta amaliy ahamiyatga ega. Ular korroziyaga chidamli laklar, trubalar, mashinalarning detallari, uy – ro'zg'or buyumlari, tekstolit, steklotekstolit va hokazolarni ishlab chiqarishda keng qo'llaniladi.

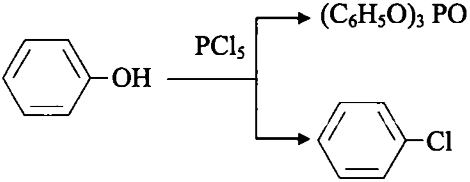
Fenol alifatik ketonlar bilan reaksiyaga kirishganda p,p^1 –di-gidroksifenilalkanlar hosil bo'ladi:



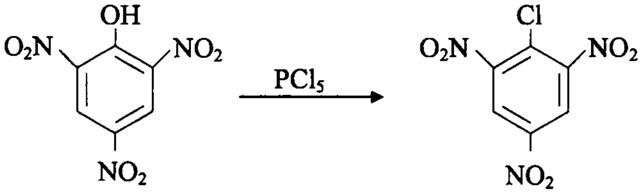
$4,4^1$ – digidroksidifenilpropan

$4,4^1$ – digidroksidifenilpropan epoksid polimerlar ishlab chiqarishda qo'llaniladi.

6. Gidroksil guruhining nukleofil almashininshi. Fenol PCl_5 bilan reaksiyaga kirishganda asosiy mahsulot sifatida trifenilfosfat va oz miqdorda xlorbenzol hosil bo'ladi:

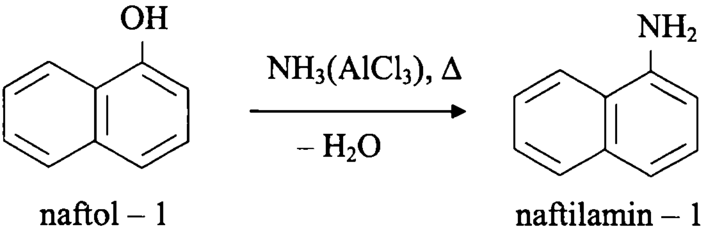


o – va *p* – holatlarda elektronoaktseptor o'rinbosarlari bor fenollarning gidroksil guruhi xlorga oson almashinadi:

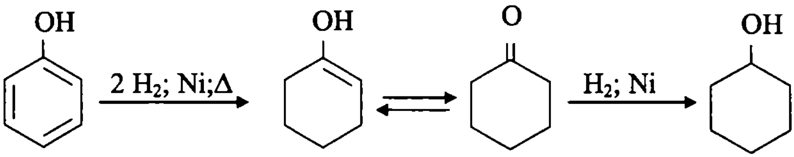


pikril xlorid

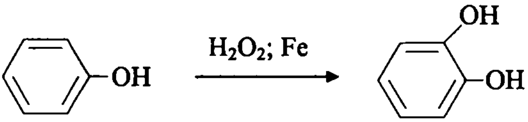
Fenollarni ammiak va alyuminiy xloridi bilan 400 °C gacha qizdirganda aminlar hosil bo'ladi:



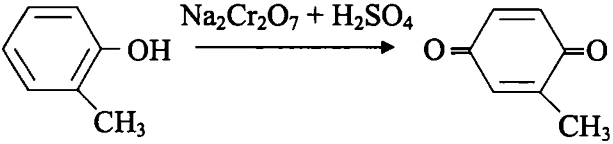
7. Gidrogenlash. Fenolni katalitik gidrogenlaganda siklogeksanol (oraliq mahsulot sifatida siklogeksanon) hosil bo'ladi:



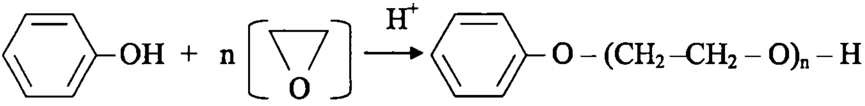
8. Oksidlanishi. Fenollar hatto havo kislorodi ta'sirida ham oson oksidlanib, rangini o'zgartiradi. Oksidlovchining tabiati va reaksiya sharoitiga qarab turli mahsulotlar hosil bo'ladi. Masalan, fenolni temir katalizatori ishtirokida vodorod peroksidi bilan oksidlaganda kam unum bilan pirokatexin hosil bo'ladi:



Fenollami xromli aralashma bilan oksidlaganda xinonlar hosil bo'ladi:



9. Fenol etilen oksidi bilan kondensatlanib, polietilenglikolning fenil efirini hosil qiladi:

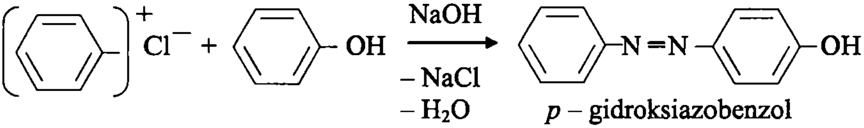


Fenol molekulasida alkil guruhi bor bunday efirlar sirt – faol xossalarga ega. Masalan, oktilfenolning polietilen efirlari

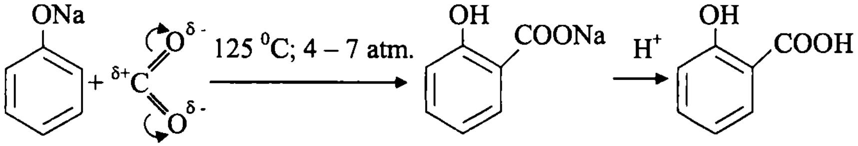
$$C_8H_{17} - C_6H_4 - O - CH_2 - CH_2 - [O - CH_2 - CH_2]_{x-1} - OH \quad (x=7,10)$$

to'qimachilik materiallarini tozalashda qo'llaniladi.

10. Fenollar kuchsiz ishqoriy muhitda diazoniy tuzlari bilan azobirikish reaksiyasiga kirishib, **gidroksiazoarenlarni** hosil qiladi:

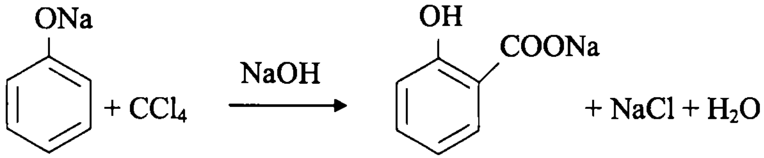


11. Natriy fenolyatini CO_2 bilan qizdirganda halqa protoni karboksil guruhiga almashinadi (Kolbe reaksiyasi):

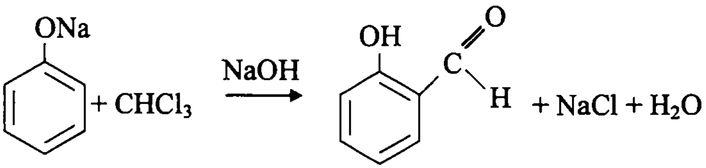


natriy salitsilat salitsil kislota

Mo'l ishqor ishtirokida natriy fenolyatiga tetraxlormetanni ta'sir ettirganda ham natriy salitsilati hosil bo'ladi:



12. Natriy fenolyatiga ishqor ishtirokida xloroformni ta'sir ettirganda halqa vodorodi aldegid guruhiga almashinadi (Reymer – Timan reaksiyasi):



salitsil aldegidi

Muhim vakillari

Fenol (benzen yoki karbol kislota) +43°C da suyuqlanadigan, suvda yomon eriydigan kristall modda. Dunyo miqyosida har yili 1,5 – 2 mln. tonna fenol ishlab chiqariladi. Shu miqdor fenolning 90 foizi sintetik usullar bilan, 10 foizi esa toshko‘mir smolasidan olinadi.

Fenol organik sintezning muhim mahsulotidir. U fenolformaldegid smolalari, polimerlar, bo‘yoqlar, dori preparatlari, portlovchi moddalar, pestitsidlar, kaprolaktam, polimerlar stabilizatorlari, yuvish vositalari, antiseptik moddalar, pikrin kislota va boshqa kimyoviy mahsulotlarni olishda ishlatiladi.

o-, ***m- va p-*** **krezollar** (*o*-, *m*- va *p*- metilfenollar) toshko‘mir, torf va yonuvchi slanetslarni quruq haydash mahsulotlaridan, shuningdek, sintetik usullar bilan toluoldan olinadi. *o*-, *m*- va *p*- krezollarning olingan aralashmasini tarkibiy qismlarga ajratish yoki ajratmasdan ishlatish mumkin.

Toza krezollardan bo‘yoqlar, dori preparatlari, antioksidantlar, antiseptik moddalar, krezollar aralashmasidan esa krezolformaldegid smolalari olinadi.

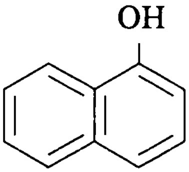
Ksilenollar (dimetilfenollar) ning oltita izomeri bor. Toshko‘mir , qo‘ng‘ir ko‘mir va yonuvchi slanetsni quruq haydash mahsulotlaridan ksilenollar aralashmasi olinadi. Aralashmani tarkibiy qismlarga ajratish qiyin. Shu bois toza ksilenollar aralashmasi olinadi.

Ksilenollar aralashmasidan sintetik smolalar ishlab chiqariladi.

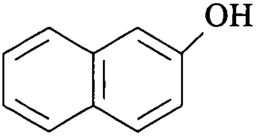
Timol (2-izopropil-5-fenilfenol) $+51^0$ C da suyuqlanadigan kristall modda. Efir moylarida bo‘ladi. Stomatologiyada antiseptik sifatida ishlatiladi.

$4,4^1$ - Digidroksidifenilpropan 156 – 157^0C da suyuqlanadigan kristall modda bo‘lib, fenol va atsetondan olinadi. U turli sintetik smolalar, antioksidantlar va gerbetsidlarni olishda ishlatiladi.

Naftollar. Naftolning ikkita (α- va β-) izomeri bor :



α - naftol



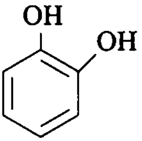
β- naftol

α - Naftol 96^0 C da , β- naftol esa 123^0 C da suyuqlanadigan, o'ziga xos hidli kristall moddalar bo'lib, naftolinsulfokislotalarni ishqor bilan 280-320^0 C da qizdirib olinadi.

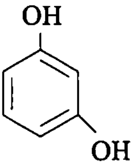
Naftollar fenollar kirishadigan reaksiyalarga kirishadi. Ulardan bo'yoqlar sintez qilinadi.

Ikki atomli fenollar

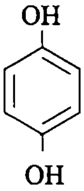
Ikki atomli fenollar (digidroksibenzollar) uchta izomer holida uchraydi:



pirokatexin
(1,2 – benzendiol,
1,2 – digidroksibenzol)



rezorsin
(1,3 – benzendiol,
1,3 – digidroksibenzol)

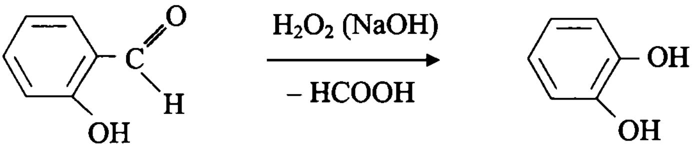


gidroxinon
(1,4 – benzendiol,
1,4 – digidroksibenzol)

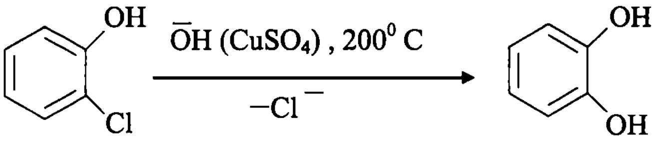
Pirokatexin – 105^0 C da suyuqlanadigan, suvda yaxshi eriydigan, fenol hidli, rangsiz modda. Pirokatexin va uning hosilalari o'simliklarda uchraydi. U lignin, oshlovchi moddalar va tabiiy smolalar tarkibiga kiradi. Birinchi marta katex daraxti smolasini haydab olingani uchun pirokatexin deb nomlangan.

Pirokatexin sanoatda toshko'mir smolasidan ajratiladi va quyidagi sintetik usullar bilan olinadi.

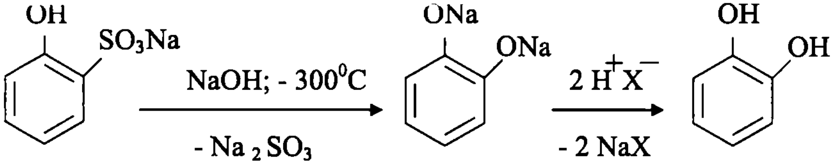
1) Salitsil aldegidiga vodorod peroksidi va o'yuvchi natriyni ta'sir ettirish (Dakin reaksiyasi, 1909- y.) bilan:



2) 2- xlorfenol (yoki 1,2 – dixlorbenzol) ni $CuSO_4$ ishtirokida o'yuvchi natriyning suvdagi 20 % li eritmasi bilan qizdirish :



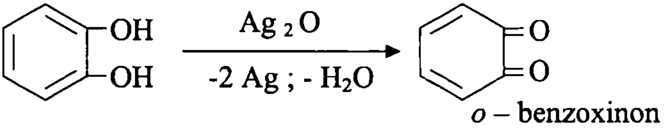
3) *o* – fenolsulfokislota tuzini ishqor bilan qizdirish :



Ikki atomli fenollar bir atomli fenollarga nisbatan kuchli kislotalardir. Ular bitta yoki ikkala gidroksil guruhi hisobidan reaksiyaga kirisha oladi.

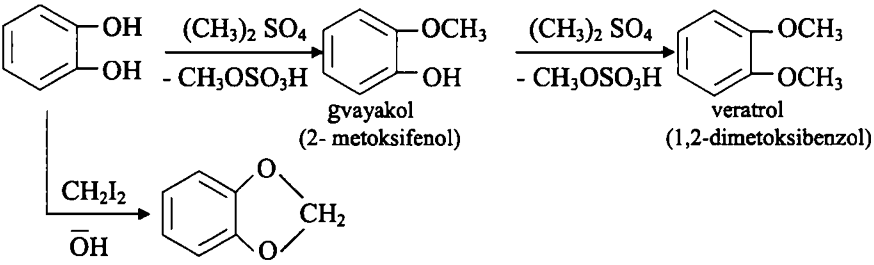
Ikki atomli fenollar oson oksidlanadi va kuchli qaytaruvchilar hisoblanadi.

Pirokatexinni dietilefirda kumush oksidi bilan oksidlaganda *o*- benzoxinon hosil bo‘ladi:



Pirokatexin $FeCl_3$ bilan yashil rang beradi, natriy karbonat va ammiak qo‘shganda u qizil rangga o‘tadi.

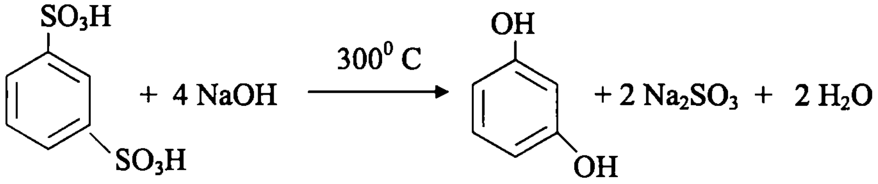
Pirokatexin oson alkillanib, oddiy (jumladan, halqali) efirlarni hosil qiladi :



Pirokatexinning aromatik halqasi elektrofil almashinish (xlorlash, nitrolash va boshqa) reaksiyalariga oson kirishadi.

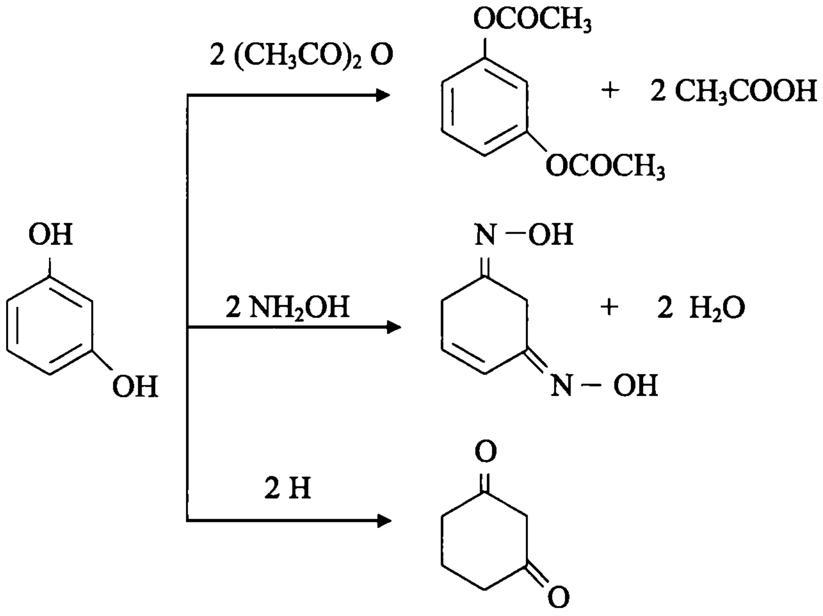
Pirokatexin fotografiyada kuchli qaytaruvchi sifatida, turli sintezlarda uning oddiy efirlari (gvayakol va veratrol) esa xushbo‘y moddalar va dori preparatlarini ishlab chiqarishda qo‘llaniladi.

Rezorsin 118^{0}C da suyuqlanadigan, suvda yaxshi eriydigan rangsiz kristall modda. U benzol – 1,3 – disulfokislotani ishqor bilan qizdirib olinadi:

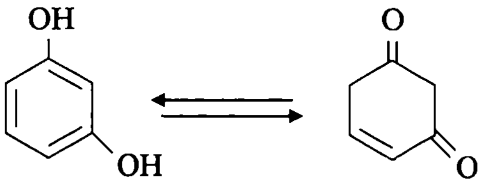


Aromatik yadroda ikki va undan ortiq gidroksil guruhining borligi (ayniqsa m- holatda) elektrofil almashinish reaksiyalarida halqani behad faollashtiradi. Shu bois rezorsin elektrofil reagentlar bilan juda oson (ayniqsa ishqoriy muhitda) reaksiyaga kirishadi.

Rezorsin sirka angidridi bilan reaksiyaga kirishganida diatsetat, gidroksilamin bilan siklogeksen-4-dion-1,3 dioksimi, katalitik gidrogenlanganda yoki natriy amalgamasi bilan qaytarganda esa siklogeksandion – 1,3 hosil bo‘ladi:



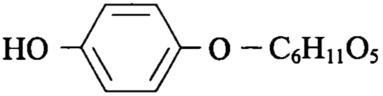
Bu reaksiyalar rezorsinda keto – enol tautomeriya borligini ko‘rsatadi:



siklogeksen – 4- dion – 1,3

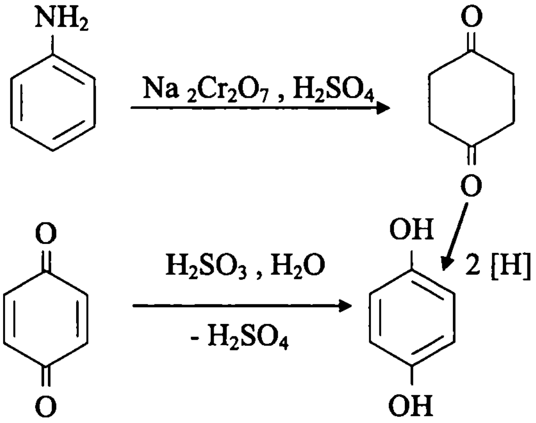
Rezorsinning oson boradigan alkillash, atsiliash va nitrolash reaksiyalari mahsulotlari bo‘yoqlar, antiseptik moddalar, antioksidantlar, portlovchi moddalar olishda ishlatiladi.

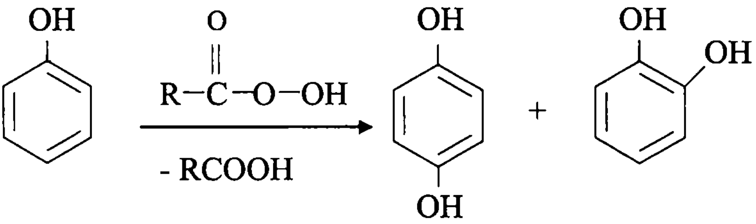
Gidroxinon 170°C da suyuqlanadigan, suvda eriydigan, rangsiz kristall modda. U arbutin glyukozidi holida o‘simliklarda bo‘ladi:



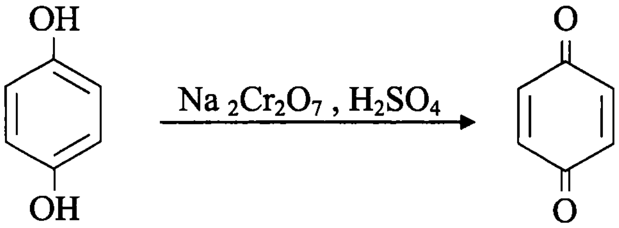
arbutin

Gidroxinon quyidagi usullar bilan olinadi:

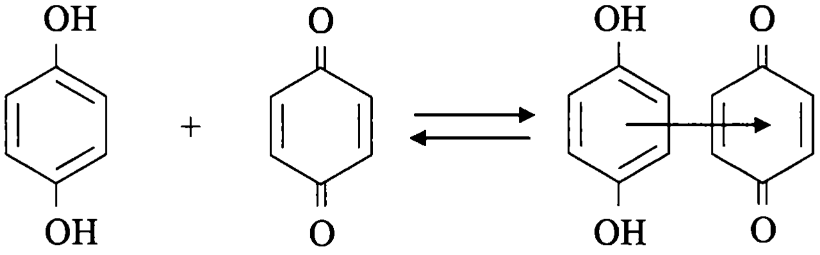




Gidroxinon 1,4-benzoxinongacha oson oksidlanadi:



Gidroxinon hatto $FeCl_3$ eritmasi bilan ham *p*- benzoxinongacha oksidlanadi. Uning suvdagi eritmasidan xingidronning qora-binafsha kristallari cho'kmaga tushadi:



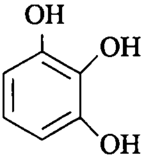
xingidron

Xingidron elektronodonor gidroxinon bilan elektronoakseptor *p*- benzoxinon orasidagi zaryadi ko'chgan kompleksi (*p*- xinonning gidroxinon bilan molekulyar birikmasi) dir.

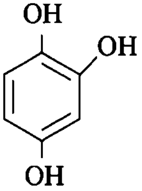
Gidroxinon fotografiyada ochiltirgich, kauchuklar va oziq-ovqat mahsulotlari uchun antioksidant, polimerlanish ingibitori, bo'yoqlar sintez qilishda xomashyo sifatida ishlatiladi.

Uch atomli fenollar

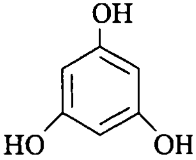
Uch atomli fenolning uchta izomeri bor:



pirogallol
(1,2,3-benzentriol,
1,2,3-trigidroksi-
benzol)



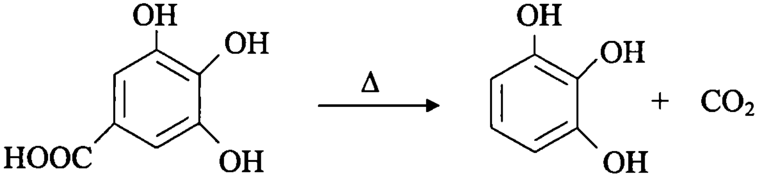
gidroksigidroxinon
(1,2,4--benzentriol,
1,2,4- trigidroksi-
benzol)



floroglyutsin
(1,3,5--benzentriol,
1,3,5- trigidroksi-
benzol)

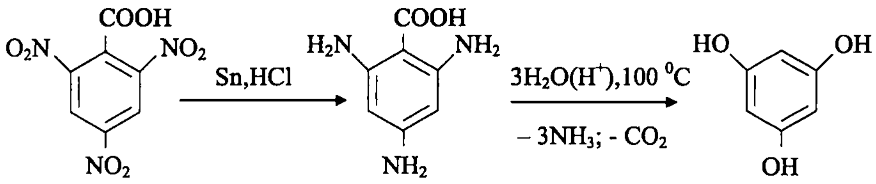
Pirogallol 133^0 C da suyuqlanadigan, suvda yaxshi eriydigan, rangsiz kristall modda. U $FeCl_3$ bilan qizil rang beradi.

Piragallol o'simliklarda uchraydigan gall kislotani qizdirish bilan olinadi (K. Sheele , 1786 – y.):

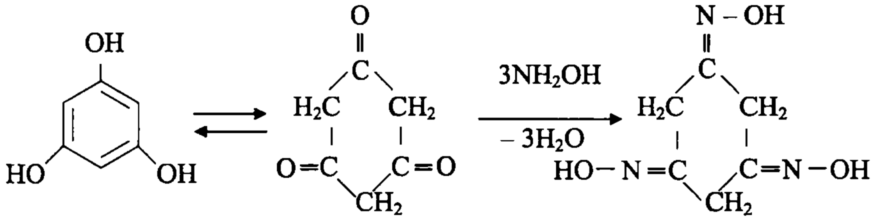


Pirogallol kuchli qaytaruvchi bo'lib, ishqoriy eritmada kislorod bilan reaksiyaga juda tez kirishadi. Shu bois u gazlarda kislorodni aniqlashda ishlatiladi. Piragallol tibbiyotda va bo'yoqlar olishda ham qo'llaniladi.

Floroglyutsin 218^{0}C da suyuqlanadigan kristall modda bo'lib, $FeCl_3$ bilan to'q binafsha rang beradi. U 2,4,6-trinitrobenzoy kislotadan olinadi:



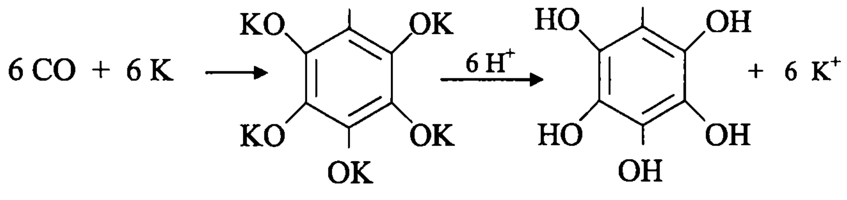
Floroglyutsin ikki xil tautomer holida uchraydi. Uchta C=O guruhi borligi bois gidroksilamin bilan trioksim beradi:



enol shakli keton shakli

Floroglyutsin pentozalar, furfurol va lignin aniqlashda reaktiv sifatida ishlatiladi.

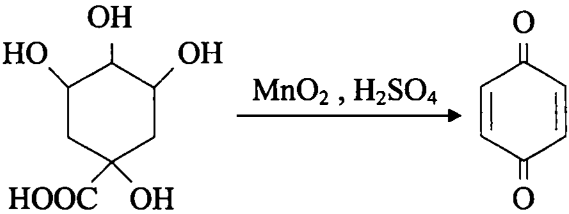
Geksagidroksibenzol. Poligidroksibenzollardan geksagidroksibenzol kaliy metali va CO dan olinadi:



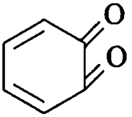
Xinonlar

Xinonlar – to'yinmagan alitsiklik diketonlar bo'lib, ularning yadrosi aromatik xossalarni namoyon qilmaydi.

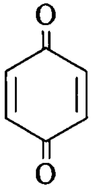
Aromatik birikmalardan oson hosil bo'lishi va ularga oson aylanishini inobatga olib, xinonlar aromatik qator birikmalari bilan o'rganiladi. Ularning birinchi vakili *p*- benzoxinonni 1838- yilda A.A. Voskresenskiy xinna (1,3,4,5-tetragidroksitsiklogeksankarbon) kislotasini oksidlab olgani uchun bu sinf birikmalari **xinonlar** deb nomlanadi:



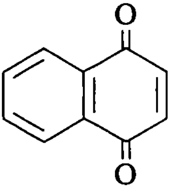
Xinonlar molekulasidagi sikllar soni va karbonil guruhlarining holatiga qarab sinflanadi. Muhim vakillarining tuzilishi va nomlanishi quyidagicha:



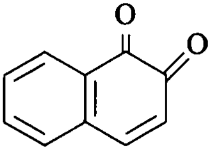
o-benzoxinon,
1,2-benzoxinon



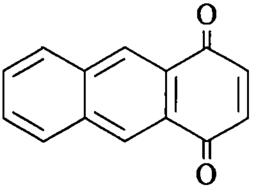
p-benzoxinon,
1,4-benzoxinon



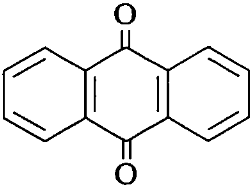
1,4-naftoxinon



1,2-naftoxinon



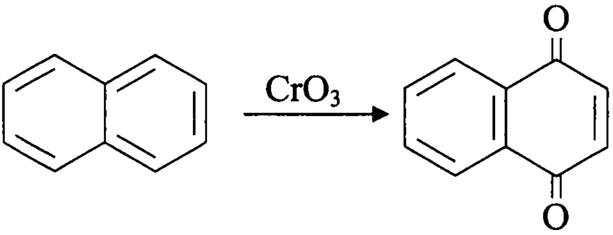
1,4-antraxinon



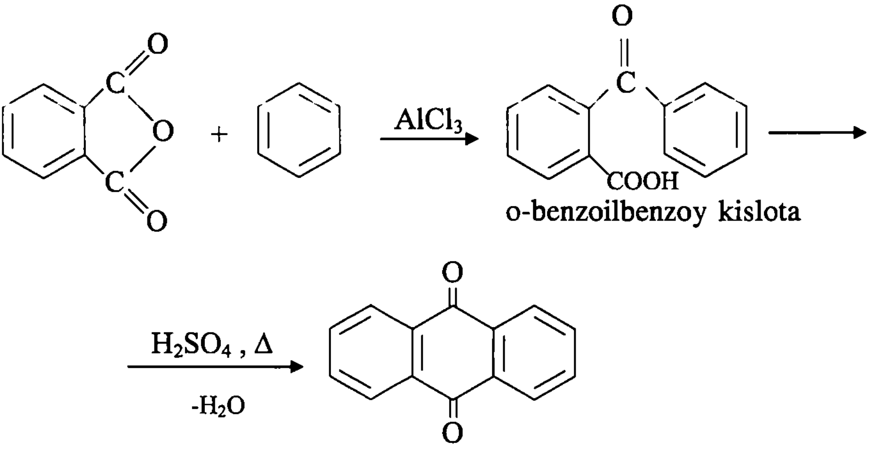
9,10-antraxinon

o- Benzoxinon pirokatexinni kumush oksidi bilan oksidlab, *p*- benzoxinon esa gidroxinonni xromli aralashma bilan oksidlab olinadi.

Naftalinni CrO_3 bilan oksidlaganda 1,4-naftoxinon hosil bo'ladi:

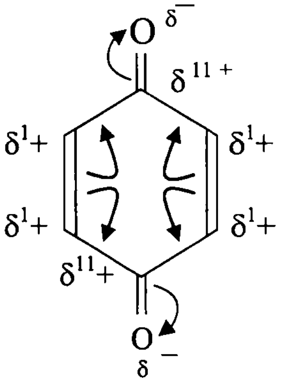


9,10- Antraxinon antratsenni oksidlaganda hosil bo'ladi. Sanoatda u malein angidridi va benzoldan quyidagi sxema bo'yicha olinadi:

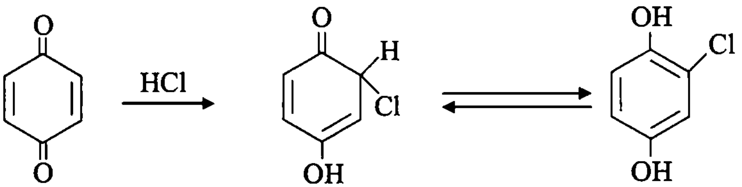


p- Benzoxinonlar sariq, *o*- benzoxinonlar qizil, naftoxinonlar va fenantroxinonlar esa ochiq sariq rangli kristall moddalardir.

Xinon molekulasidagi C – C bog‘larining uzunligi bir xil emas. Karbonil guruhlarining elektronoaktseptor ta‘sirida uglerod atomlari qisman musbat zaryadlanadi va elektronoaktseptor xossalarni namoyon qiladi:

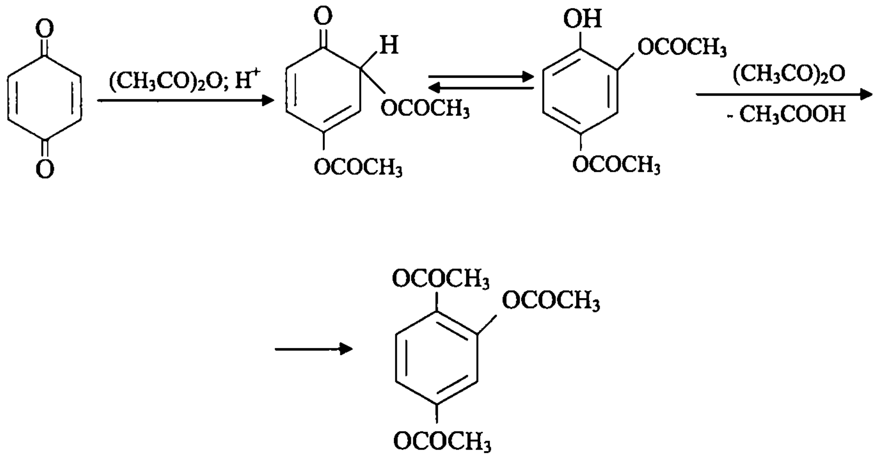


Xinonlar ochiq zanjirli *α*, *β*- to‘yinmagan ketonlarga nisbatan reaksiyaga kirishish qobiliyati kuchli moddalar bo‘lib , ko‘p birikmalar bilan 1,4-birikish reaksiyalariga kirishadi. Hosil bo‘lgan birikish mahsulotlari aromatik birikmalarga izomerlanadi:

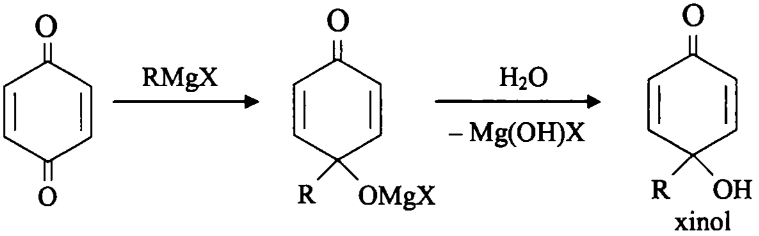


2 – xlorgidroxinon, 2 – xlor - -1,4 – digidroksibenzol

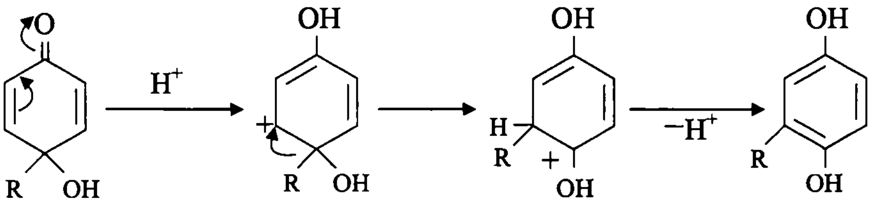
1,4-Benzoxinon sirka angidridi bilan reaksiyaga kirishganda gidroksigidroxinon triatsetati hosil bo‘ladi:



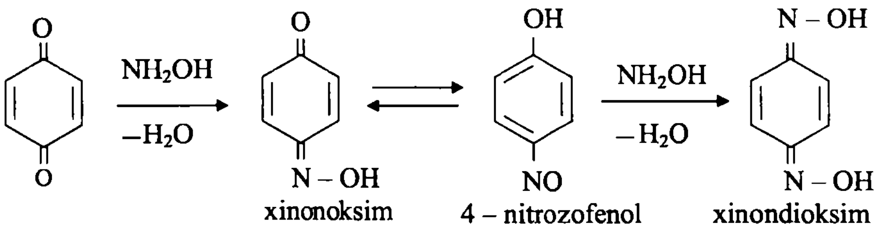
Xinonlarga Grinyar reaktivining birikishidan xinollar hosil bo‘ladi:



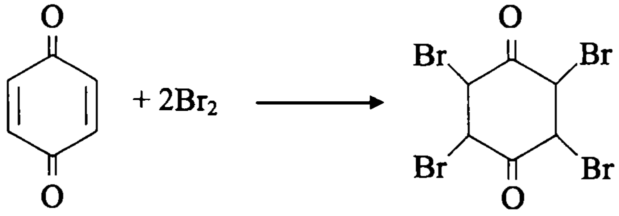
Xinonlar alkilgidroxinonlarga oson qayta guruhlanadi (diyenon – fenol qayta guruhlanishi):



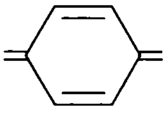
1,4 – Benzoxinon gidroksilamin bilan mono – va dioksim hosil qiladi. Monooksim 4 – nitrozofenol (*p* – nitrozofenol) bilan tautomer muvozanatda bo‘ladi:



Mono – va dioksim hosil qilishi, shuningdek ikkita qo‘sh bog‘iga bromni biriktirishi p – benzoxinon tuzilishini isbotlaydi:



Xinon molekulasida qo‘sh bog‘lar tizimi xinoid guruhlanishi deyiladi:



m – Xinonlarning mavjud emasligi benzolning tuzilishiga muvofiq keladi.

1,4 – Benzoxinonpolimerlanish ingibitori sifatida, xloranil (tetraxlor – 1,4 – benzoxinon) degidrogenlovchi agent sifatida, 9,10 – antraxinon esa bo‘yoqlarni sintez qilishda ishlatiladi.

Savollar va mashqlar

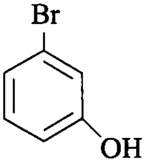
1. Quyidagi birikmalarning tuzilish formulalarini yozing:

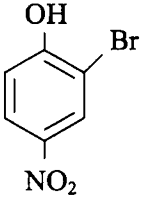
a) 4 –*p*– geksilrezorsin; b) 2,5 – dimetil – 1 – gidroksibenzol

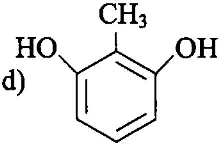
d) fenoldisulfokislota – 1,4 ; e) *p* – metoksifenol ;

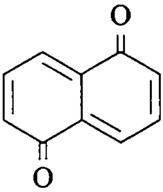
f) 2,6 – naftoxinon; g) 1,2 – antraxinon.

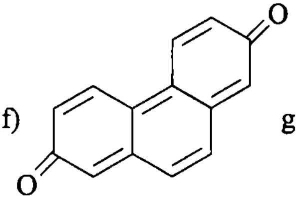
2. Quyidagi birikmalarni nomlang:

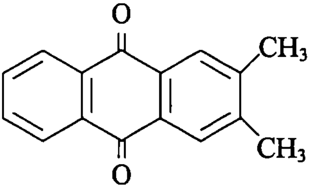
a)


b)


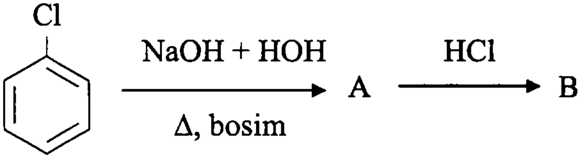
d)


e)


f)


g)


3. Quyidagi reaksiyalarni amalga oshiring:

a)


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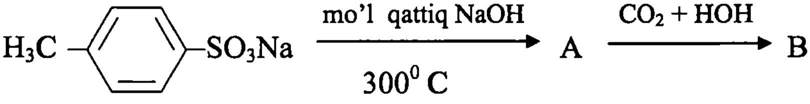
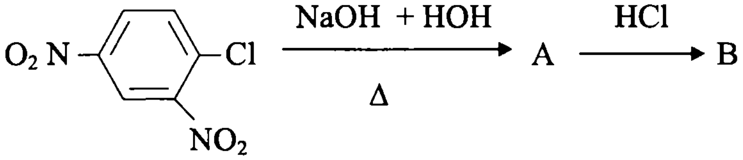
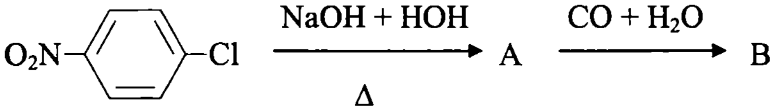
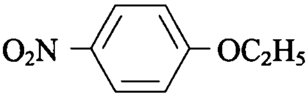
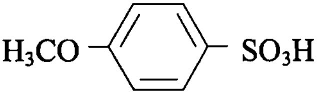


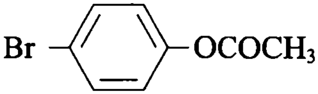
d) 

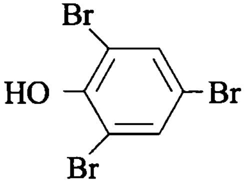
e) 

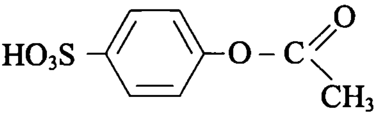
4. Benzoldan quyidagi birikmalarni sintez qilish sxemalarini keltiring:

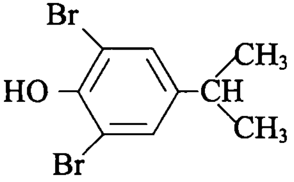
a) 

b) 

d) 

e) 

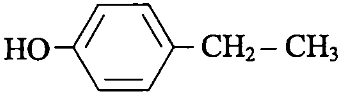
f) 

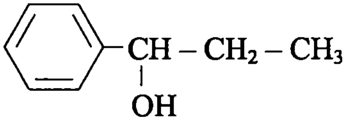
g) 

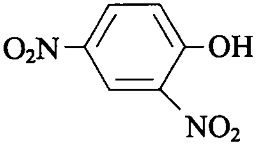
5. Quyidagi sintezlar sxemasini tuzing:

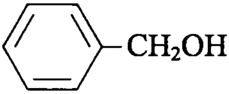
a) Toluol → *o*- krezol;
b) Toluol → floroglyusin
d) izopropilbenzol → 2,6-dibrom-4-izopropilfenol
e) fenilmagniy bromid → fenol

6. Quyidagi birikmalarning qaysilari FeCl$_3$ bilan rang beradi?

a) 

b) 

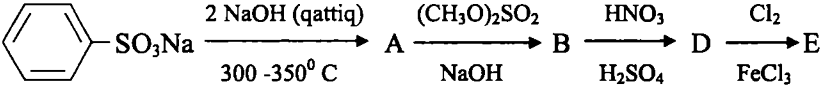
d) 

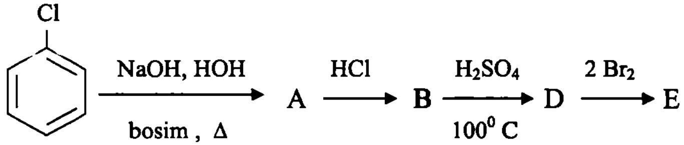
e) 

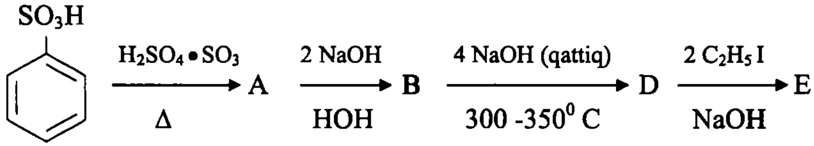
7. Quyidagi birikmalarni kislotalik xossalarining kuchayib borishi tartibida joylashtiring:

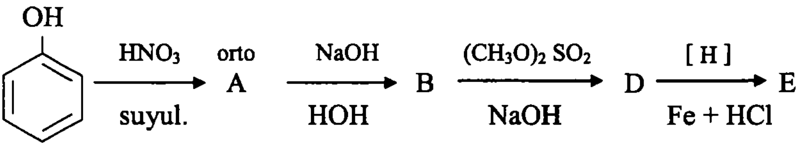
a) pikrin kislota; b) fenol; d) *o* – krezol;
e) *p*- nitrofenol; f) 3,4 – dinitrofenol;

8. Quyidagi sxemalardagi oraliq va oxirgi mahsulotlar tuzilish formulalarini yozing:

a) 

b) 

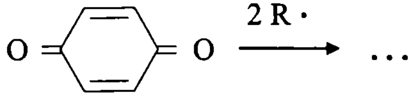
d) 

e) 

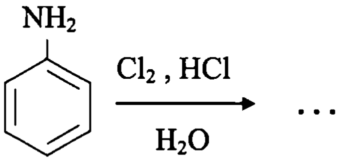
9. Elektronodonor va elektronoakseptor o‘rinbosarlar fenollarning kislotaligiga qanday ta‘sir ko‘rsatishini misollar bilan tushuntiring.

10. Quyidagi reaksiyalarni oxirigacha yetkazing:

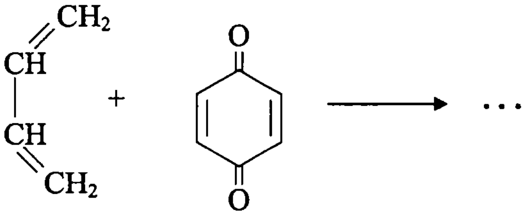
a)



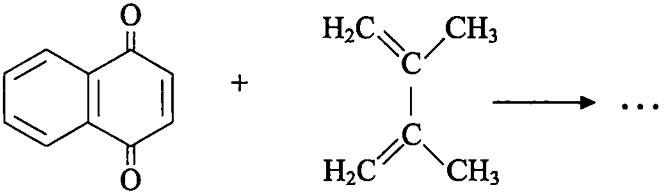
b)



d)



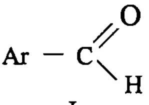
e)



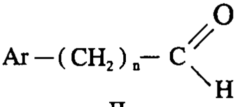
IX. AROMATIK ALDEGID VA KETONLAR

Aromatik aldegid va ketonlarning sinflanishi, nomlanishi, olinish usullari, fizikaviy va kimyoviy xossalari, muhim vakillari. Savol va mashqlar.

Aromatik aldegidlarda aldegid guruhi aromatik halqa bilan (I) yoki yon zanjir uglerodi bilan (II) bog'langan:



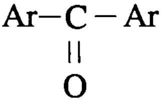
I



II

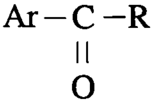
n = 1, 2 va hokazo

Aromatik ketonlar sof aromatik va alkilarilketonlarga bo'linadi. Sof aromatik ketonlar (III) da karbonil guruhi ikkita aromatik radikal bilan, alkilarilketonlar (IV) da esa aromatik va alifatik radikallar bilan bog'langan bo'ladi:



$$Ar-\underset{\underset{O}{\|}}{C}-Ar$$

III

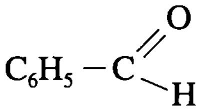


$$Ar-\underset{\underset{O}{\|}}{C}-R$$

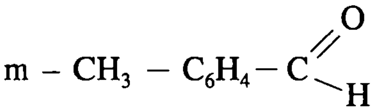
IV

Nomlanishi

Aromatik aldegidlarning trivial nomlari, ular oksidlanganda hosil bo'ladigan tegishli aromatik kislotalarning nomlaridan olingan:



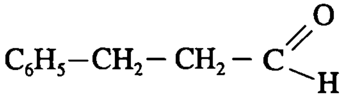
benzoy aldegidi



m – toluil aldegidi

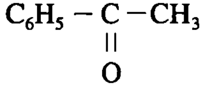
Sistematik nomenklaturaga ko'ra aldegid guruhi halqa bilan bevosita bog'langan vakillari **arenkarbaldegidlar** deb yuritiladi va ularning nomi tegishli aromatik halqa nomiga karbaldegid so'zini qo'shish bilan hosil qilinadi. Masalan, benzoy aldegidini benzenkarbaldegid deb nomlash mumkin.

Aldegid guruhining yon zanjir uglerodi bilan bog'langan vakillari ochiq zanjirli aldegidlarning hosilalaridek nomlanadi:



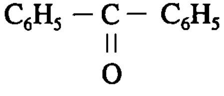
β - fenilpropion aldegidi ,
3 – fenilpropanal

Aromatik ketonlarning nomlari karbonil bilan bog'langan radikallar nomidan hosil qilinadi:



$$C_6H_5-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$$

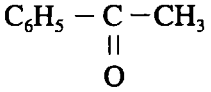
metilfenilketon,
atsetofenon



$$C_6H_5-\underset{\displaystyle O}{\underset{\|}{C}}-C_6H_5$$

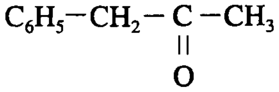
difenilketon,
benzofenon

Sistematik nomenklaturaga ko‘ra nomlashda aromatik radikal va tegishli atsiklik uglevodorod nomiga – on qo‘shimchasi qo‘shiladi:



$$C_6H_5-\underset{\underset{O}{\|}}{C}-CH_3$$

feniletanon



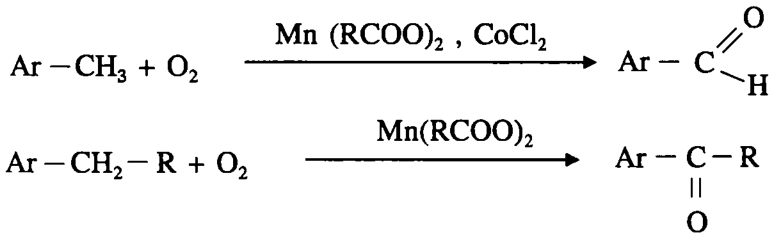
$$C_6H_5-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

1 – fenilpropanon -2

Olinish usullari

1. Alkilarenlar, diarilmetanlar va aromatik spirtlarni oksidlab olish:

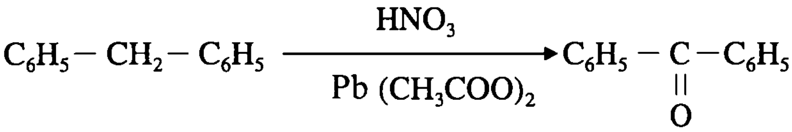
a). Alkilarenlarni katalizatorlar (V_2O_5 , CrO_3 yoki kobalt va marganets tuzlari) ishtirokida havo kislorodi bilan oksidlash:



$$Ar-CH_3 + O_2 \xrightarrow{Mn(RCOO)_2\ ,\ CoCl_2} Ar-C\begin{matrix}/\!\!/O\\ \diagdown H\end{matrix}$$

$$Ar-CH_2-R + O_2 \xrightarrow{Mn(RCOO)_2} Ar-\underset{\underset{O}{\|}}{C}-R$$

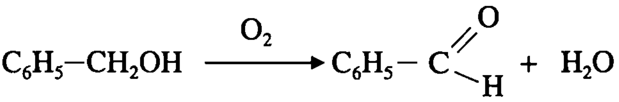
b). Difenilmetanni suyultirilgan nitrat kislota ta‘sirida oksidlab, sanoatda benzofenon olinadi:



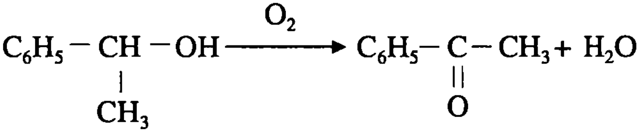
$$C_6H_5-CH_2-C_6H_5 \xrightarrow[Pb(CH_3COO)_2]{HNO_3} C_6H_5-\underset{\underset{O}{\parallel}}{C}-C_6H_5$$

Diarilmetanlarni anorganik oksidlovchilar ($KMnO_4$, MnO_2 , CrO_3) bilan oksidlaganda ham diarilketonlar hosil bo‘ladi.

d). Aromatik spirtlarni oksidlash:

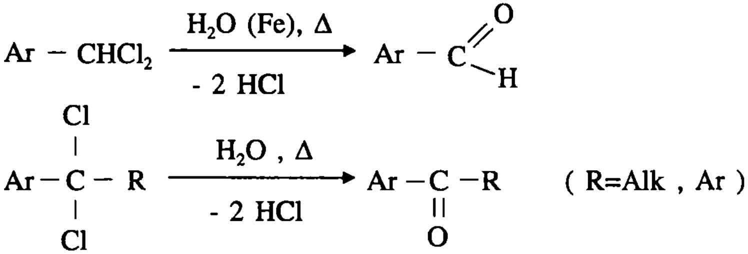


$$C_6H_5-CH_2OH \xrightarrow{O_2} C_6H_5-C\overset{\displaystyle /\!/ O}{\underset{\displaystyle \diagdown H}{}} + H_2O$$



$$C_6H_5-\underset{\underset{CH_3}{|}}{CH}-OH \xrightarrow{O_2} C_6H_5-\underset{\underset{O}{\parallel}}{C}-CH_3 + H_2O$$

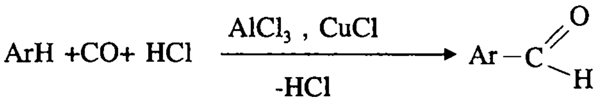
Digalogenalkilarenlarni gidrolizlash:



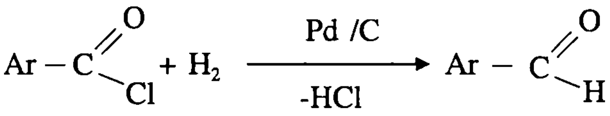
$$Ar-CHCl_2 \xrightarrow[-\,2\,HCl]{H_2O\,(Fe),\,\Delta} Ar-C\overset{\displaystyle /\!/ O}{\underset{\displaystyle \diagdown H}{}}$$

$$Ar-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-R \xrightarrow[-\,2\,HCl]{H_2O\,,\,\Delta} Ar-\underset{\underset{O}{\parallel}}{C}-R \qquad (R=Alk\,,\,Ar)$$

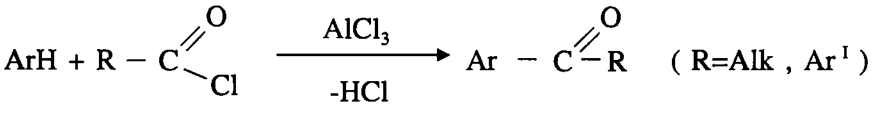
3. Arenlarni CO va HCl aralashmasi bilan $AlCl_3$ va $CuCl_2$ ishtirokida formillash (Gatterman-Kox reaksiyasi, 1897 – y.):



4. Arenkarbon kislotalar xlorangidridlarini palladiy katalizatori ishtirokida vodorod bilan qaytarish:



5. Arenlarni $AlCl_3$ yoki Lyuisning boshqa kislotalari ishtirokida atsilxloridlar bilan Fridel – Krafts usulida atsillash:



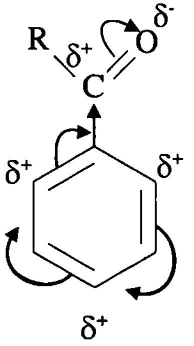
Fizikaviy xossalari

Aromatik aldegidlar - suvda erimaydigan, achchiq bodom hidli suyuqliklar.

Aromatik ketonlar - suvda erimaydigan, suyuqlik yoki qattiq moddalar bo‘lib, ko‘pchiligi yoqimli hidga ega.

Kimyoviy xossalari

Aromatik aldegid va ketonlar molekulasidagi elektronoaktseptor karbonil guruhi benzol halqasi bilan π, π - tutashish hosil qilib, orto- va para- holatlar elektron buluti zichligini kamaytiradi. Aldegid va karbonil guruhlari -J -va -M- effektlarni namoyon qiladigan o‘rinbosarlardir:



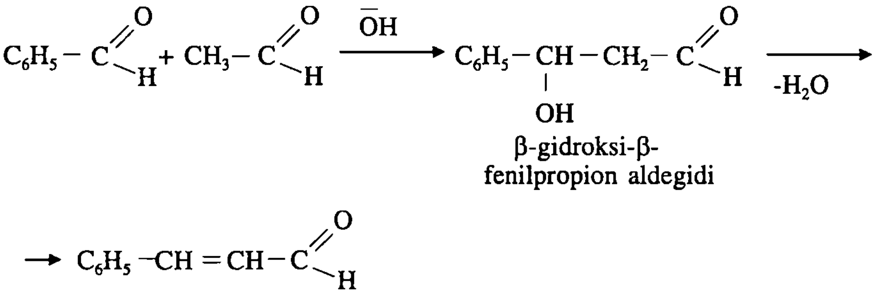
R=H, alkil

$-J$; $-M(\pi, \pi -)$

Aromatik aldegid va ketonlar to‘yingan alifatik qator aldegid va ketonlari uchun xos bo‘lgan ko‘pchilik reaksiyalarga kirishadi. Lekin aromatik aldegid va ketonlarda (ayniqsa, diarilketonlarda) karbonil uglerodidagi musbat zaryad alifatik aldegid va ketonlardagiga nisbatan kamaygan. Shu bois ularning nukleofil reagentlar bilan reaksiyaga kirishish qobiliyati ancha pasaygan. Alifatik aldegidlardan farqli o‘laroq aromatik aldegidlar aldol kondensatsiyasi reaksiyasiga kirishmaydi. Chunki ularda aldegid guruhi faol metil yoki metilen guruhi bilan bog‘lanmagan.

Aromatik aldegid va ketonlar uchun xos reaksiyalar bilan tanishamiz:

1. Aromatik aldegidlar alifatik aldegidlar bilan aldol va kroton kondensatsiyasiga kirishadi:

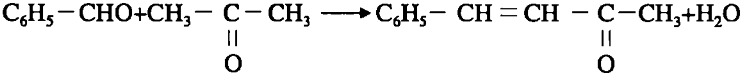


$$C_6H_5-CHO + CH_3-CHO \xrightarrow{\bar{O}H} C_6H_5-CH(OH)-CH_2-CHO \xrightarrow[-H_2O]{} C_6H_5-CH=CH-CHO$$

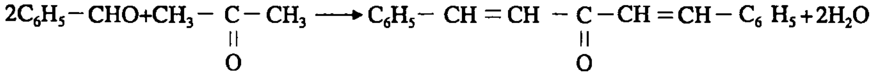
β-gidroksi-β-fenilpropion aldegidi

dolchin aldegidi

Benzaldegid atseton bilan suyultirilgan ishqor ishtirokida kroton kondensatsiyasiga oson kirishadi. Reagentlarning nisbatiga qarab benzalatseton yoki dibenzalatseton hosil bo'ladi:

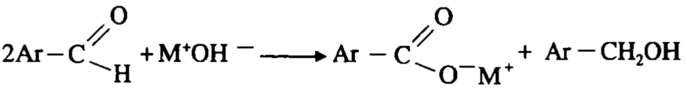


$$C_6H_5-CHO+CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow C_6H_5-CH=CH-\underset{\underset{O}{\|}}{C}-CH_3+H_2O$$



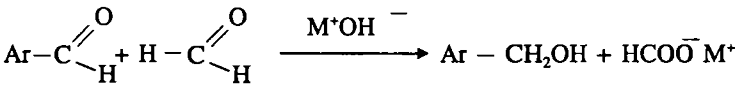
$$2C_6H_5-CHO+CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow C_6H_5-CH=CH-\underset{\underset{O}{\|}}{C}-CH=CH-C_6H_5+2H_2O$$

2. Aromatik aldegidlar ishqoriy yoki ishqoriy yer metallarining gidroksidlari ishtirokida arenkarbon kislota tuzi va arilmetanolga aylanadi (Kannitstsaro reaksiyasi, 1853 - y.):



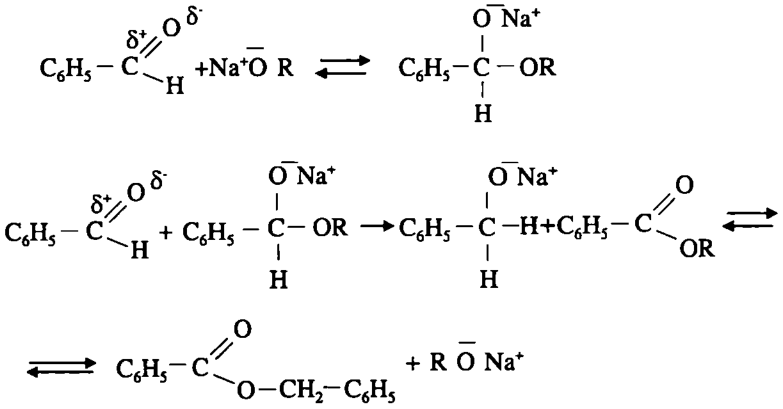
Kannitstsaro reaksiyasida aromatik aldegidning bir molekulasi qaytariladi, boshqasi esa oksidlanadi.

Formaldegid va trialkilsirka aldegid R_3C - CHO ham Kannitstsaro reaksiyasiga kirishadi:

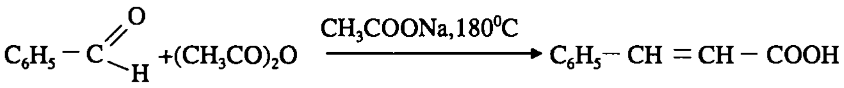


Formaldegid bu reaksiyada qaytaruvchi rolini o'ynaydi.

3. Aromatik aldegidlarga alkagolyatlarni ta'sir ettirganda murakkab efirlar hosil bo'ladi (L.Klyauzen, 1887):

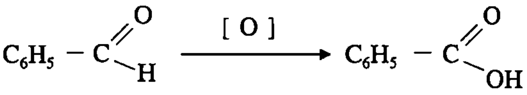


4. Aromatik aldegidlar asoslar (natriy atsetat, natriy propionat va hokazo) ishtirokida kislotalarning angidridlari bilan kondensatsiya reaksiyasiga kirishib, α, β-to‘yinmagan aromatik kislotalarni hosil qiladi (Perkin kondensatsiyasi):



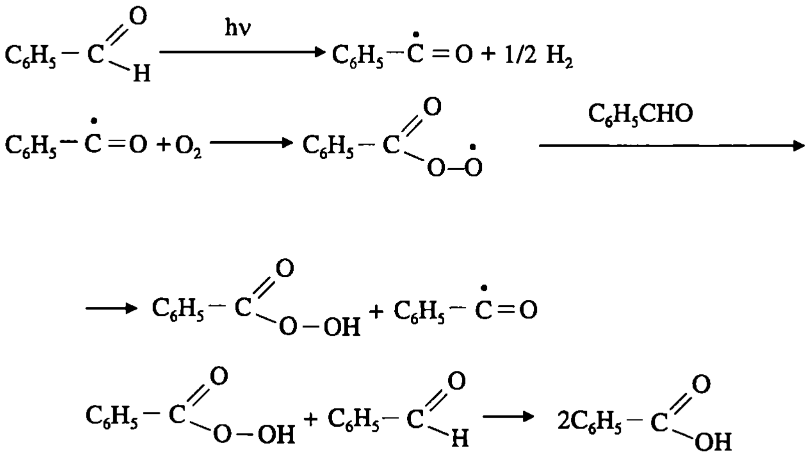
$$C_6H_5-CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa,\,180^0C} C_6H_5-CH=CH-COOH$$

5. Aromatik aldegidlar havo kislorodi ta‘sirida o‘z-o‘zidan juda oson oksidlanadi (autooksidlanish):



$$C_6H_5-CHO \xrightarrow{[\,O\,]} C_6H_5-COOH$$

Oksidlanish zanjirli radikal mexanizmida barqaror benzoil radikalining hosil bo‘lishi bilan boradi:



$$C_6H_5-CHO \xrightarrow{h\nu} C_6H_5-\dot{C}=O + 1/2\ H_2$$

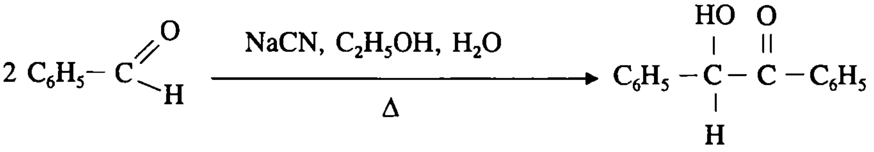
$$C_6H_5-\dot{C}=O + O_2 \longrightarrow C_6H_5-C(=O)-O-\dot{O} \xrightarrow{C_6H_5CHO}$$

$$\longrightarrow C_6H_5-C(=O)-O-OH + C_6H_5-\dot{C}=O$$

$$C_6H_5-C(=O)-O-OH + C_6H_5-CHO \longrightarrow 2C_6H_5-COOH$$

Yorug'lik yoki ayrim metallar (masalan, temir) ning tuzlari autooksidlanishni tezlashtiradi. Aromatik aldegidlarni uzoq muddat saqlaganda, autooksidlanishining oldini olish maqsadida ularga ingibitorlar yoki antioksidantlar (gidroxinon, alkilpirokatexinlar va boshqalar) qo'shiladi.

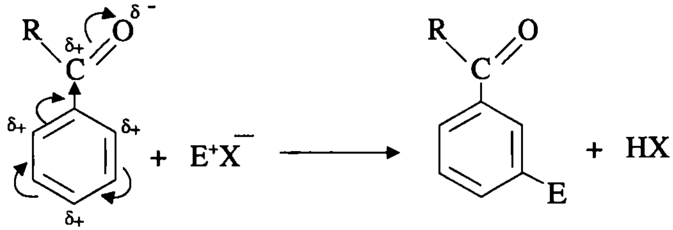
6. Natriy yoki kaliy sianidi katalizatorligida benzaldegid dimerlanib, benzoin deb nomlanadigan α-gidroksiketonni hosil qiladi (benzoin kondensatsiyasi):



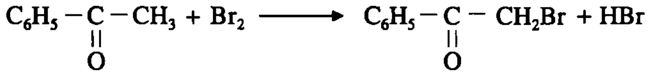
$$2\,C_6H_5-CHO \xrightarrow[\Delta]{NaCN,\ C_2H_5OH,\ H_2O} C_6H_5-CH(OH)-C(=O)-C_6H_5$$

benzoin

7. Aromatik aldegid va ketonlar aren halqasida boradigan elektrofil almashinish reaksiyalariga arenlarga nisbatan qiyin kirishadi. Elektrofil almashinish asosan meta – holatda boradi:

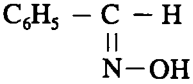


8. Aromatik ketonlarning karbonil guruhi alifatik ketonlardagi singari faol emas. Masalan, atsetofenon va benzofenon natriy gidrosulfiti bilan reaksiyaga kirishmaydi. Lekin, alkilarilketonlardagi metil va metilen guruhlarining vodorod atomlari harakatchan bo'lib, oson almashinadi:



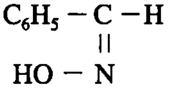
$$C_6H_5-\underset{\underset{O}{\|}}{C}-CH_3 + Br_2 \longrightarrow C_6H_5-\underset{\underset{O}{\|}}{C}-CH_2Br + HBr$$

9. Aromatik aldegid va ketonlar gidroksilamin bilan reaksiyaga kirishib, sin – va anti – izomerlar holida mavjud bo'ladigan aldoksim va ketoksimlarni hosil qiladi:



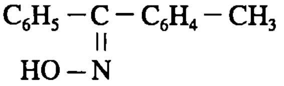
$$C_6H_5-\underset{\underset{N-OH}{\|}}{C}-H$$

sin – benzaldoksim



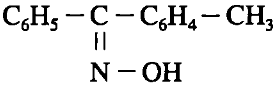
$$C_6H_5-\underset{\underset{HO-N}{\|}}{C}-H$$

anti – benzaldoksim



$$C_6H_5-\underset{\underset{HO-N}{\|}}{C}-C_6H_4-CH_3$$

sin – fenil-o-tolilketoksim



$$C_6H_5-\underset{\underset{N-OH}{\|}}{C}-C_6H_4-CH_3$$

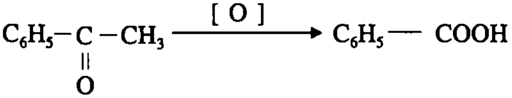
anti – fenil-o-tolilketoksim

Sin – izomerlarda gidroksil guruhi va nisbatan murakkab bo'lmagan atom yoki radikal *sis* – holatda joylashadi. *Anti*-izomerlar barqarorroq bo'ladi.

Geometrik *sin*- va *anti* – izomerlar xossalari jihatidan o'zaro farq qiladi. Ular bir – biriga aylana oladi.

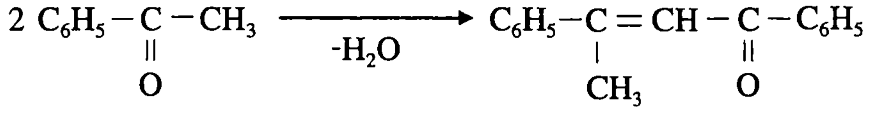
10. Yon zanjirida aldegid guruhi bor aromatik aldegidlar kimyoviy xossalari bilan alifatik aldegidlardan farq qilmaydi.

11. Alkilarilketonlar oson oksidlanib, aromatik kislotalarni hosil qiladi:

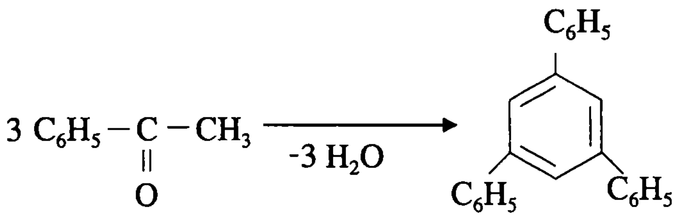


$$C_6H_5-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{[O]} C_6H_5-COOH$$

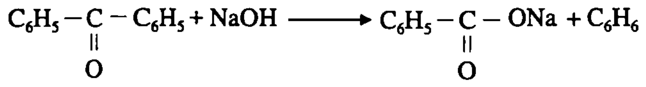
12. Atsetofenon metil guruhining harakatchan α- vodorodlari hisobidan kroton kondensatsiyasiga kirishganda *dipnon* va *trifenilbenzol* hosil bo'ladi:



$$2\,C_6H_5-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[-H_2O]{} C_6H_5-\underset{\underset{CH_3}{|}}{C}=CH-\underset{\underset{O}{\|}}{C}-C_6H_5$$



13. Sof aromatik ketonlar yuqori haroratda kontsentrlangan ishqor ta'sirida parchalanadi:



$$C_6H_5-\underset{\underset{O}{\|}}{C}-C_6H_5+NaOH \longrightarrow C_6H_5-\underset{\underset{O}{\|}}{C}-ONa+C_6H_6$$

Muhim vakillari

Benzaldegid 179°C da qaynaydigan, achchiq bodom hidli, rangsiz suyuqlik. Sanoatda u toluolni to'g'ridan – to'g'ri oksidlash yoki benzalxlorid $C_6H_5CHCl_2$ gacha xlorlab, so'ngra kislotali gidroliz qilish bilan olinadi. Benzaldegid benzoil xlorid, trifenilmetan bo'yoqlari va boshqa birikmalarni sintez qilishda dastlabki modda sifatida ishlatiladi.

Dolchin aldegidi (3-fenilpropenal) 252°C da qaynaydigan suyuqlik bo‘lib, atir-upachilikda ishlatiladi.

Atsetofenon 20°C da eriydigan, yoqimli hidli, rangsiz modda. U sanoatda benzolni atsetillash yoki etilbenzolni oksidlash bilan olinadi. Organik sintezda va atir – upachilik sanoatida ishlatiladi.

Benzofenon 49°C da suyuqlanadigan rangsiz kristall modda. U sanoatda difenilmetanni oksidlab olinadi va organik sintezda qo‘llaniladi.

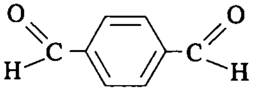
Savol va mashqlar

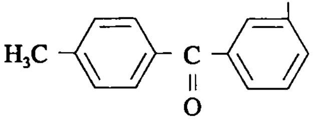
1. Birikmalarning tuzilish formulalarini yozing:

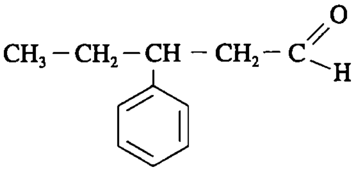
a) 2 - fenilpropanal;
b) fenilatseton;
d) 2-metil –2- fenilpropanal;
e) *o* – gidroksibenzaldegid (salitsil aldegid);
f) α - metildolchin aldegid;
g) 4 – formilbenzol - sulfokislota.

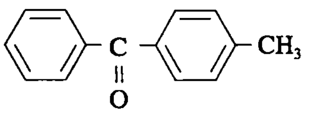
2. Birikmalarni nomlang:

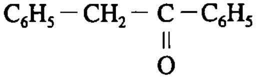
a) $C_6H_5-CO-CH_2-CH_2-CH_3$

b)


d)


e)


f)


g)

$C_6H_5-CH_2-\underset{\underset{O}{\|}}{C}-C_6H_5$

3. C_8H_8O tarkibli izomer aromatik aldegid hamda ketonlarning tuzilish formulalarini yozing va ularni nomlang.

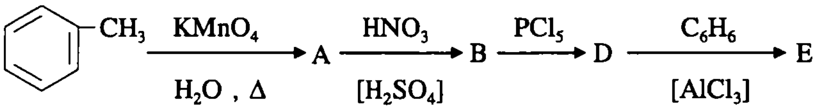
4. Quyidagi spirtlar oksidlanganda hosil bo'ladigan birikmalarni nomlang:

a) metilbenzilkarbinol; b) *m* – gidroksibenzil spirt

d) propilfenilkarbinol e) *p* – brombenzil spirt.

5. Reaksiyalar tenglamalarini yozing. Hosil bo'ladigan oraliq va oxirgi mahsulotlarni nomlang.

$$a)\ C_6H_6 \xrightarrow[{[FeCl_3]}]{Cl_2} A \xrightarrow[efir]{Mg} B \xrightarrow{1)\ CO_2;\ 2)\ H_3O^+} D \xrightarrow{SOCl_2} E \xrightarrow[{[AlCl_3]}]{C_6H_6} F$$

b) 

$$-CH_3 \xrightarrow[H_2O\ ,\ \Delta]{KMnO_4} A \xrightarrow[{[H_2SO_4]}]{HNO_3} B \xrightarrow{PCl_5} D \xrightarrow[{[AlCl_3]}]{C_6H_6} E$$

6. Benzaldegid bilan quyidagi birikmalar orasida boradigan reaksiyalar sxemalarini yozing. Hosil bo'ladigan organik moddalarni nomlang:

a) gidrazin; b) $NaHSO_3$;

d) gidroksilamin; e) $LiAlH_4$;

f) H_2 , Ni , Δ , bosim.

7. Benzaldegid bilan quyidagi birikmalar orasida boradigan reaksiyalar sxemalarini yozing . Hosil bo'ladigan organik moddalarni nomlang:

a) Br_2, $FeBr_3$; b) $(C_2H_5CO)_2$, C_2H_5– COONa, Δ.

d) HNO_3, H_2SO_4 , Δ; e) nitrometan;

f) malon kislota dinitrili. g) metiletilketon.

8. C_9H_8O tarkibli modda bromli suvni rangsizlantiradi, kumush ko'zgu reaksiyasini beradi, kaliy permanganati bilan oksidlanganda benzoy kislota hosil bo'ladi. C_9H_8O moddaning tuzilishini aniqlang.

9. Quyidagi aromatik aldegidlar kaliy sianidi ishtirokida benzoin kondensatsiyasiga kirishganda qanday birikmalar hosil bo'ladi ?

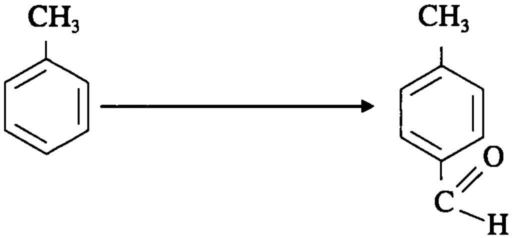
a) *m* – xlorbenzaldegid;

d) *p* – toluil aldegid va n–nitrobenzaldegid aralashmasi.

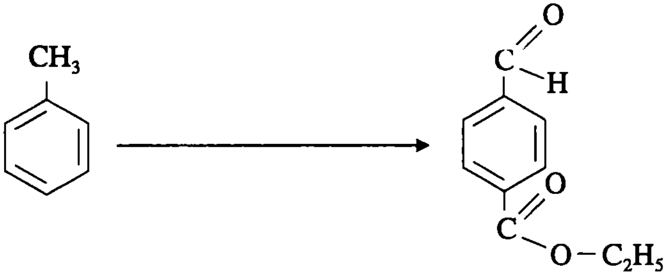
b) *p*- metoksibenzaldegid va *p* – xlorbenzaldegid aralashmasi;

10. Quyidagi sintezlar sxemalarini tuzing:

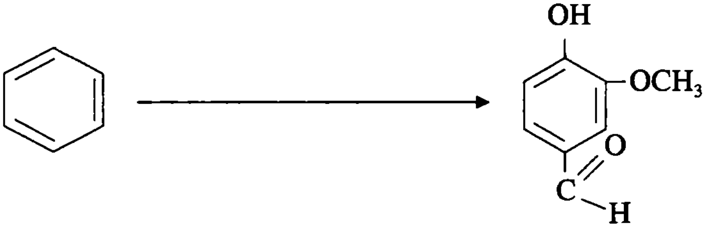
a)



b)



d)



X. AROMATIK KARBON KISLOTALAR

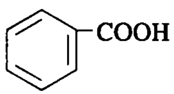
Aromatik karbon kislotalarning sinflanishi va nomlanishi. Arenmonokarbon kislotalarning olinish usullari, fizikaviy xossalari va tuzilishi, kimyoviy xossalari, muhim vakillari. Aromatik gidroksi – va aminokislotalar, oshlovchi moddalar. Ftal va tereftal kislotalarning olinishi, xossalari, muhim birikmalari. Savol va mashqlar.

Aromatik karbon kislotalar molekulasida bir yoki bir necha karboksil guruhi benzol halqasi yoki yon zanjir uglerodi bilan bog'langan bo'ladi.

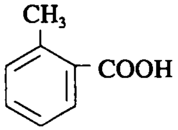
Sinflanishi va nomlanishi

Aromatik karbon kislotalar molekulasidagi karboksil guruhining soniga qarab arenmonokarbon, arendikarbon va arenpolikarbon kislotalarga bo'linadi. Yon zanjiri to'yingan va to'yinmagan, shuningdek, almashingan aromatik (galogenbenzoy, nitrobenzoy, sulfobenzoy, gidroksibenzoy, aminobenzoy) kislotalar bo'ladi.

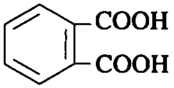
Karboksil guruhi benzol halqasi bilan bevosita bog'langan aromatik kislotalarning trivial, shuningdek, tegishli aren nomi va karbon kislota so'zlaridan hosil qilinadigan nomlari ishlatiladi:



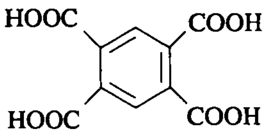
benzoy kislota,
benzolkarbon kislota.



o – toluil kislota,
o – toluolkarbon kislota

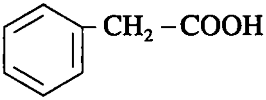


ftal kislota,
1,2 – benzoldikarbon
kislota

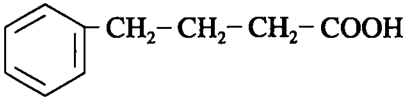


piromellit kislota,
1,2,4,5 – benzoltetrakarbon
kislota

Yon zanjirida karboksil guruhi bor aromatik kislotalarning trivial va sistematik nomlari tegishli alifatik kislotalarning trivial va sistematik nomlaridan hosil qilinadi:



α - fenilsirka kislota,
2 – feniletan kislota



γ - fenilmoy kislota,
4 – fenilbutan kislota

ARENMONOKARBON KISLOTALAR

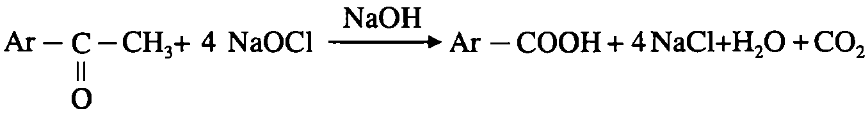
OLINISH USULLARI

Alifatik monokarbon kislotalarning barcha umumiy olinish usullari bilan arenmonokarbon kislotalarni ham olish mumkin. Ko‘p qo‘llaniladigan maxsus usullar bilan tanishamiz.

1. Alkilarenlarni $KMnO_4$, CrO_3 yoki Co va Mn tuzlari ishtirokida kislorod bilan oksidlash:

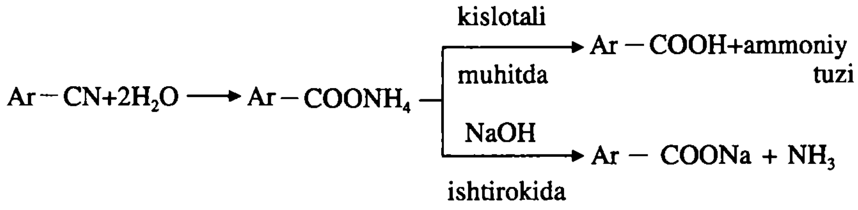
$$Ar - CH_3 \xrightarrow{[\,O\,]} Ar - COOH + H_2O$$

2. Metilarilketonlarni gipoxloritlar bilan oksidlash:



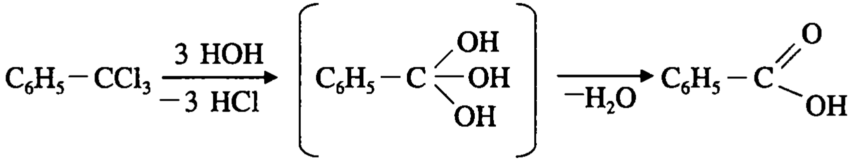
$$Ar - \underset{\underset{O}{\|}}{C} - CH_3 + 4\ NaOCl \xrightarrow{NaOH} Ar - COOH + 4NaCl + H_2O + CO_2$$

3. Aromatik nitrillarni gidroliz qilish:

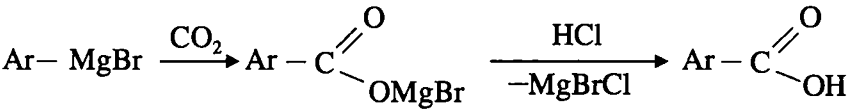


$$\begin{tikzcd} & & Ar - COOH + \text{ammoniy tuzi} \\ Ar - CN + 2H_2O \arrow[r] & Ar - COONH_4 \arrow[ur, "\text{kislotali}", "\text{muhitda}"'] \arrow[dr, "NaOH", "\text{ishtirokida}"'] & \\ & & Ar - COONa + NH_3 \end{tikzcd}$$

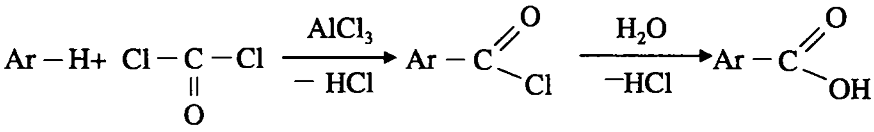
4.Galogenlari bitta uglerod atomi bilan bog‘langan aromatik trigalogenli hosilalarni gidrolizlab olish:



5. Aromatik metallorganik birikmalar va CO_2 dan olish:



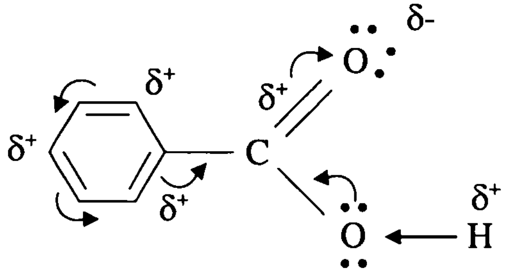
6. Fridel – Krafts reaksiyasi bilan arenlar va fosgendan sintez qilish:



Fizikaviy xossalari va tuzilishi

Arenmonokarbon kislotalar suvda yomon eriydigan (benzoy kislota qaynoq suvda yaxshi eriydi), rangsiz kristall moddalardir. Ular tegishli (molekulasida shuncha uglerod atomi bor) alifatik qator kislotalariga nisbatan yuqori haroratda suyuqlanadi va qaynaydi.

Karboksil guruhi aren halqasi bilan bevosita bog'langan arenmonokarbon kislotalarda tutashish tizimi bor:

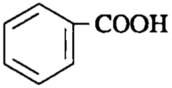
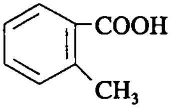
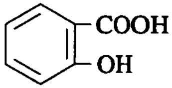
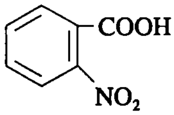
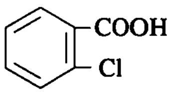
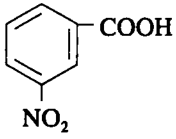


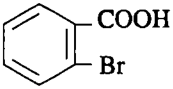
Kimyoviy xossalari

Aromatik kislotalar alifatik qator kislotalari uchun xos bo'lgan barcha asosiy reaksiyalarga kirishadi.

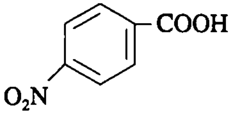
Kislota xossalari. Arenmonokarbon kislotalar alifatik analoglariga nisbatan kuchli kislotalardir. Masalan, benzoy kislotaning pK qiymati 4,20 ga, sirka kislotaning pK qiymati esa 4,75 ga teng.

Almashingan benzoy kislotalarning kuchi halqadagi o'rinbosarlarning tabiatiga va uning karboksiliga nisbatan joylashgan holatiga bog'liq. Taqqoslash uchun ba'zi almashingan benzoy kislotalarning pK qiymatlarini keltiramiz:

Kislota	pK	Kislota	pK
	4,20		4,08
	2,98		2,17
	2,94		3,45

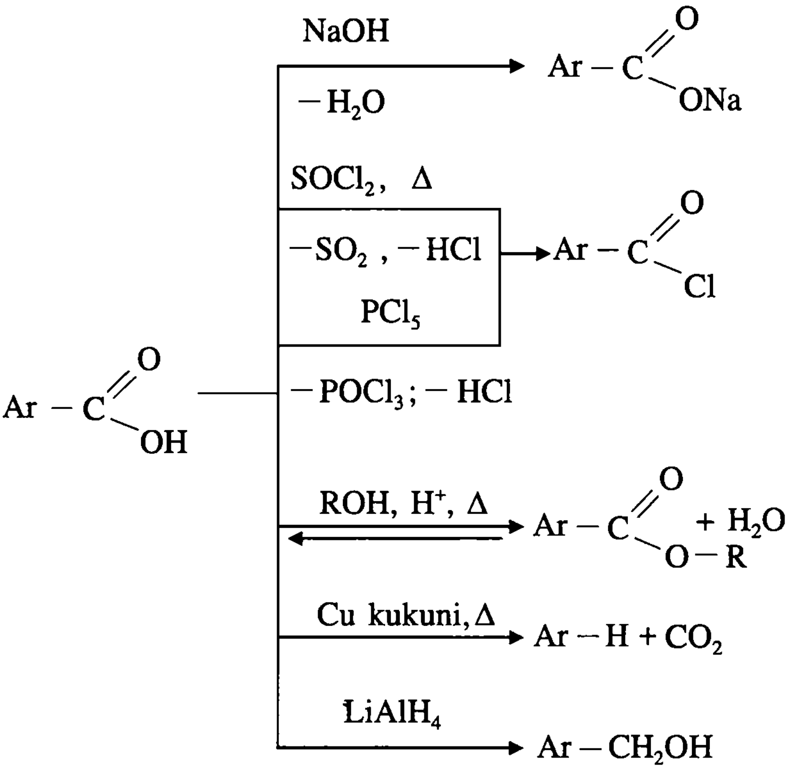


2,85

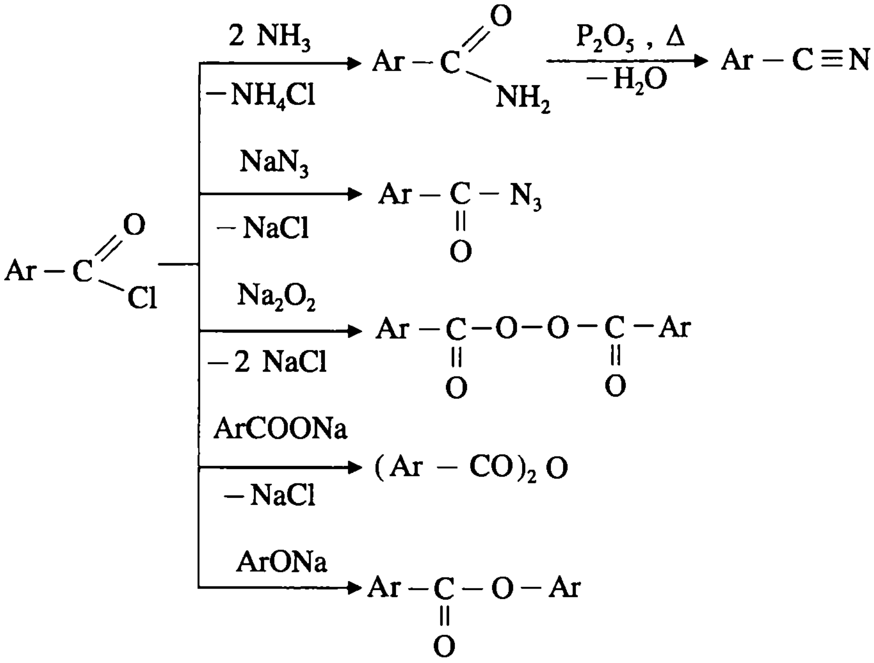


3,43

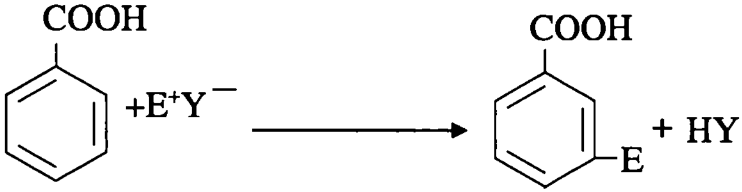
Karboksil guruhi reaksiyalari. Arenmonokarbon kislotalar karboksil guruhi hisobidan tuzlar, murakkab efirlar, galogenangidridlar, aromatik spirtlar va hokazo birikmalarni hosil qiladi:



Galogenangidridlardan arenmonokarbon kislotalarning boshqa hosilalarini olish mumkin:



Aromatik halqa reaksiyalari. Arenmonokarbon kislotalar elektrofil reagentlar bilan elektrofil almashinish (galogenlash, nitrolash, sulfolash) reaksiyalariga kirishadi. Karboksil guruhi elektrofil o‘rinbosarlarni *m* – holatga yo‘naltiradi:



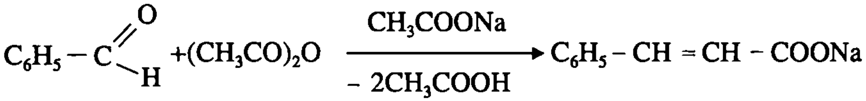
$E^+ = \overset{+}{N}O_2$, $\overset{+}{S}O_3H$, $\overset{+}{C}l^+$, $\overset{+}{B}r^+$ va boshqa elektrofillar.

Muhim vakillari

Benzoy kislota –122°C da suyuqlanadigan, kuchli antiseptik ta'sirga ega bo'lgan rangsiz kristall erkin holida ba'zi smolalar (ayniqsa, benzoy smolasi) da uchraydi, benzil efiri holida esa peruan balzami tarkibiga kiradi. Benzoy kislota sanoatda toluolni oksidlash bilan olinadi. U bo'yoqlar, xushbo'y va dorivor moddalarni olishda dastlabki modda sifatida, natriy benzoati esa oziq - ovqat mahsulotlarini konservalashda qo'llaniladi. Benzoy kislotaning muhim hosilasi – **benzoil xlorididir**. U o'ziga xos hidli, kuchli lakrimator ta'siriga ega suyuqlik bo'lib, benzoillovchi agent sifatida qo'llaniladi. Benzoil xloridi va natriy peroksididan olinadigan **benzoil peroksidi** polimerlanish initsiatori sifatida ishlatiladi.

Fenilsirka kislota –77°C da suyuqlanadigan rangsiz kristall modda bo'lib, benzil sianidini gidrolizlash bilan olinadi. Fenilsirka kislota metilen guruhining harakatchan vodorodlari hisobidan turli kondensatsiya reaksiyalariga kirishadi. Bu kislota va uning efirlari xushbo'y va dorivor moddalarni olishda qo'llaniladi.

Dolchin kislota – (trans- 3- fenilpropen kislota) –133°C da suyuqlanadigan, rangsiz kristall modda. U benzaldegid va sirka angidridini natriy atsetati ishtirokida qizdirib olinadi (U. Perkin reaksiyasi, 1868 – y):



$$C_6H_5-CHO + (CH_3CO)_2O \xrightarrow[-\ 2CH_3COOH]{CH_3COONa} C_6H_5-CH=CH-COONa$$

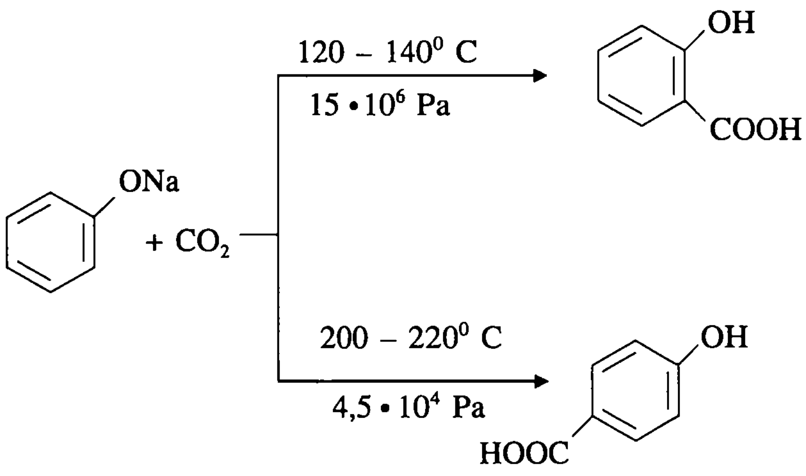
Dolchin kislotadan xushbo'y va dorivor moddalar olinadi.

Almashingan arenmonokarbon kislotalar

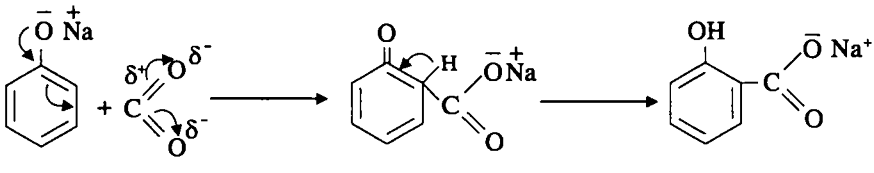
Almashingan arenmonokarbon kislotalardan aromatik gidroksikislotalar va aminokislotalar bilan tanishamiz.

Aromatik gidroksikislotalar

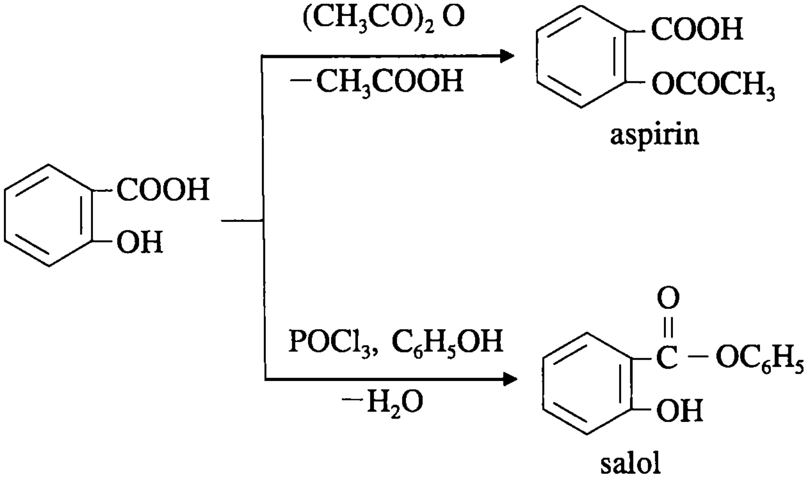
Aromatik monogidroksikarbon kislotalardan **o – gidroksibenzoy (salitsil)** kislota katta ahamiyatga ega. U natriy fenolyatiga uglerod (IV)-oksidini ta'sir ettirib olinadi (Kolbe reaksiyasi). Reaksiyani nisbatan yuqori harorat va kichik bosimda o'tgazilganda ***p*** – gidroksibenzoy kislota hosil bo'ladi:



Kolbe reaksiyasi elektrofil almashinish mexanizmida boradi:



Salitsil kislota molekulasidagi gidroksil guruhi hisobidan atsil xloridlari yoki kislota angidridlari bilan, karboksil hisobidan esa fenollar yoki spirtlar bilan murakkab efirlar hosil qiladi:

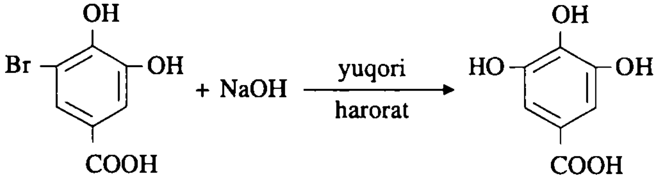


Aspirin va salol tibbiyotda keng ishlatiladigan dorilardir.

p – gidroksibenzoy kislota va uning efirlari yuqori antiseptik xossalarga egaligi bois oziq - ovqat mahsulotlarini konservalashda qo'llaniladi.

m – sulfobenzoy kislotadan ishqor qo'shib qizdirish bilan olinadigan *m* - gidroksibenzoy kislota bo'yoqlar tayyorlashda qo'llaniladi.

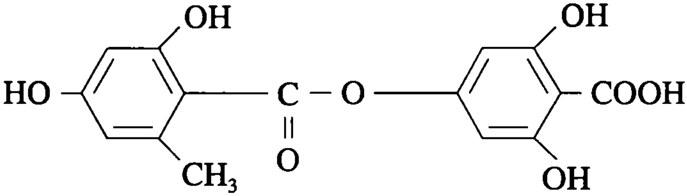
Trigidroksikarbon kislotalardan **gall** kislota (3,4,5 – trigidroksibenzoy kislota) o'simliklar dunyosida keng tarqalgan. U tabiiy oshlovchi moddalar (choy bargi, dub po'stlog'i, anor daraxtining ildizi va hokazo) tarkibida bo'ladi. Gall kislota laboratoriyada protokatex kislotaning galogenli hosilalarini ishqor qo'shib qizdirish bilan olinadi:



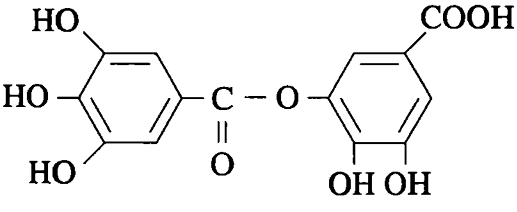
Gall kislota – kristall modda. U kuchli qaytaruvchi xossasiga ega bo'lib, qadimdan qora siyoh va bo'yoqlar olishda qo'llanilgan. Uning vismutli asosli tuzi **dermatol** nomi bilan kuchli antiseptik sifatida ishlatiladi.

Aromatik poligidroksikislotalaming ikki molekulasidan (birining karboksil guruhi boshqasining fenol gidroksili hisobidan) hosil bo'ladigan murakkab efirlarga **depsidlar** deyiladi. Ularga lekanor va

m – digall kislotalar misol bo'ladi:



lekanor kislota



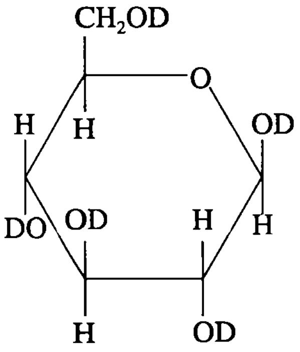
m – digall kislota

Oshlovchi moddalar depsidlarning hosilalari bo‘lib, ba‘zi o‘simliklar to‘qimalaridan (masalan, dub po‘stlog‘idan) ajratib olinadi. Ular gidrolizlanadigan va gidrolizlanmaydigan oshlovchi moddalarga bo‘linadi.

Gidrolizlanadigan oshlovchi moddalar - gall va *m* – digall kislota-larning hosilalaridir.

Tanninlar va boshqa oshlovchi ekstraktlar charm va mo‘yna ishlab chiqarishda, to‘qimalarni xurushli bo‘yashda katta ahamiyatga ega.

Turli o‘simliklardan, hatto bitta o‘simlikdan ajratiladigan tanninlar ham glyukozaning digall va gall kislotalar bilan hosil qilgan murakkab efirlari aralashmasi bo‘lib, quyidagi umumiy formulaga ega:



D= gall yoki digall kislota qoldig`i yoki H

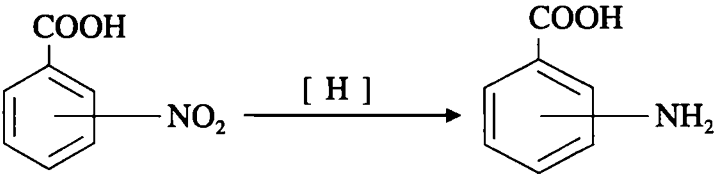
Tanninlar gidroliz qilinganda glyukoza, digall kislota va oz miqdorda gall kislota hosil bo‘ladi.

E. Fisher glyukoza va digall kislotadan tannin xossalariga ega pentaefirni olishga muvaffaq bo‘ldi. Formaldegid bilan fenolsulfokislotalarning kondensatsiyasi asosida sintetik oshlovchi moddalar olindi.

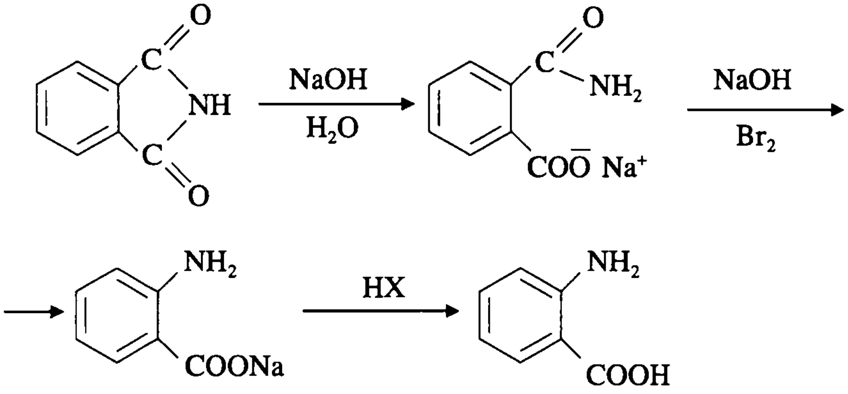
Aromatik tabiat, kislotali xossalar va katta molekulyar massaga ega bo‘lishi barcha tabiiy va sintetik oshlovchi moddalar uchun umumiy xususiyat hisoblanadi. Shu xususiyat tufayli oshlovchi moddalar xom terilarni oshlashda qo‘llaniladi. Oshlash jarayonida oshlovchi modda va teri oqsillari molekulalari orasida kimyoviy bog‘ hosil bo‘ladi. Natijada fermentlar va gidrolizlovchi agentlar ta‘siriga chidamli, suv va gazni qiyin o‘tkazadigan, termik va kimyoviy jihatdan barqaror qavat hosil bo‘ladi.

Aromatik aminokislotalar

Aromatik aminokislotalar benzol halqasida yoki yon zanjirida amino va karboksil guruhlari bor birikmalardir. Amino va karboksil guruhlari benzol halqasida joylashgan aminokislotalar (ayniqsa, orto- va para-aminobenzoy kislotalar) katta ahamiyatga ega. ***o-***, ***m-*** va ***p-*** aminobenzoy kislotalar tegishli nitrobenzoy kislotalarni qaytarish bilan olinadi:



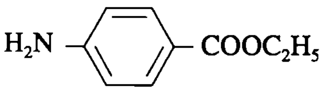
o– aminobenzoy (antranil) kislota ftalimidni Gofman usulida parchalash bilan olinadi:



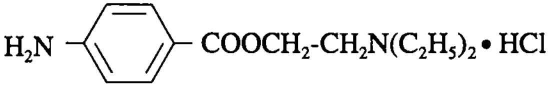
Antranil kislota – suvda yaxshi eriydigan, kristall modda. U turli bo‘yoqlar, jumladan indigoni (110- bet) olishda ko‘p miqdorda ishlatiladi.

m – aminobenzoy kislota ham bo‘yoqlar ishlab chiqarishda qo‘llaniladi

p – aminobenzoy kislota suvda eriydigan vitaminlar guruhiga kiradi. Uning anestezin (p – aminobenzoy kislotaning etil efiri) va novokain (dietilaminoetil efir xlorgidrati) singari hosilalari og‘riqni qoldiruvchi ta‘sirga ega bo‘lgani bois tibbiyotda ishlatiladi:



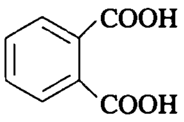
anestezin



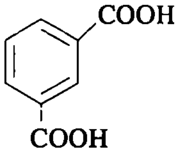
novokain

Arendikarbon kislotalar

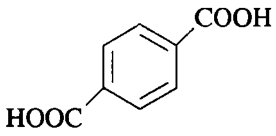
Bu kislotalarning uchta izomeri mavjud:



ftal kislota



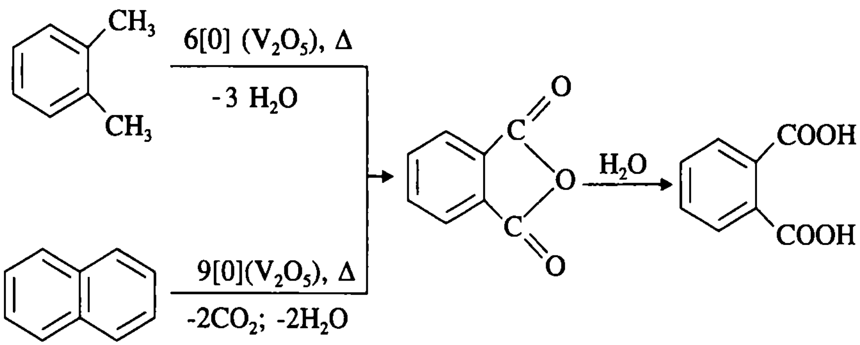
izoftal kislota



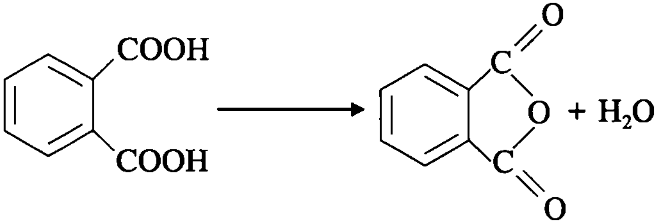
tereftal kislota

Arendikarbon kislotalar arenmonokarbon kislotalarga nisbatan kuchli kislotalardir.

Ftal kislota – 200^{0}C da suyuqlanadigan, suvda kam eriydigan, rangsiz kristall modda. U sanoatda o- ksilol yoki naftalinni havo kislorodi bilan 400 – 450^{0} C da, katalizator (V_2O_5) ishtirokida oksidlab olinadi. Reaksiya sharoitida oldin ftal angidrid hosil bo‘ladi, so‘ngra u suvni oson biriktirib ftal kislotaga aylanadi:

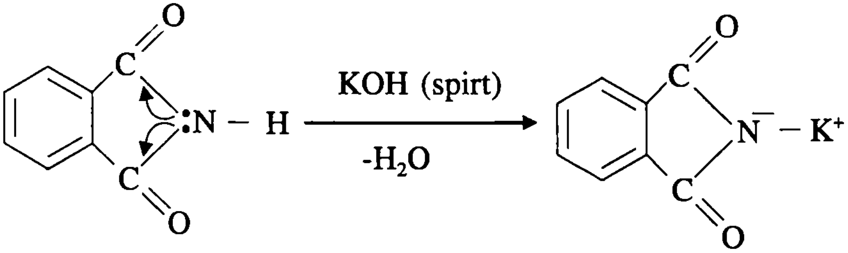


Ftal kislota suyuqlanish haroratida (200°C da) angidridga aylanadi:



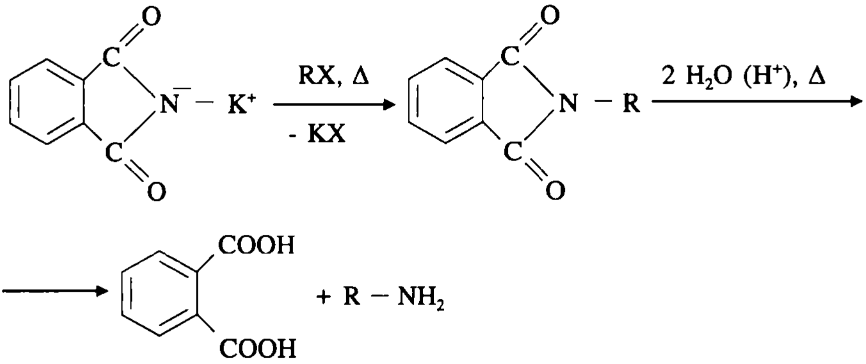
Ftal angidridi 130–131° C da suyuqlanadigan rangsiz kristall modda bo‘lib, organik sintezda keng ishlatiladi.

Ftalimid azotining umumlashmagan elektron jufti karbonil guruhlari bilan tutashishda bo‘lgani bois >N–H vodorodi harakatchan va u metallarga oson almashinadi:

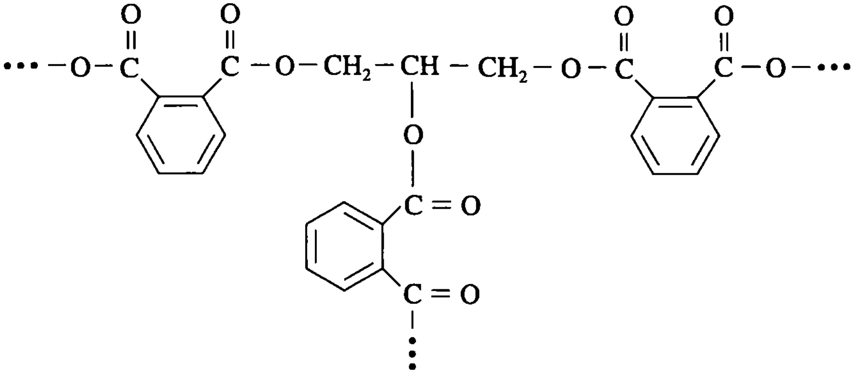


kaliy ftalimidi

Kaliy ftalimidi Gabriel sintezi bilan birlamchi alifatik aminlarni olishda ishlatiladi:

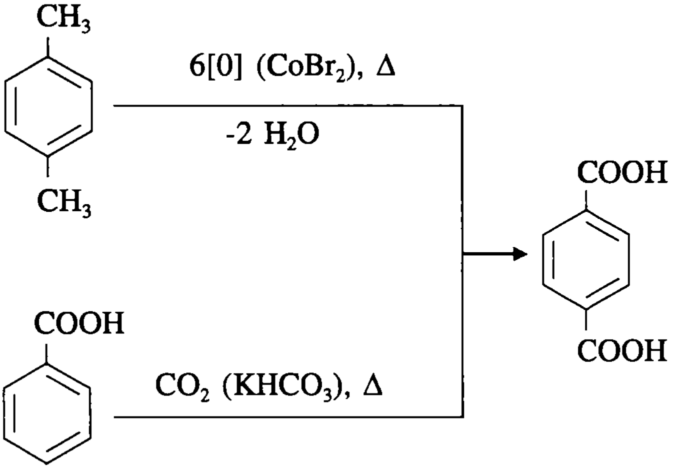


Ftal kislotaning dimetil, dietil va dibutil efirlari repelentlar sifatida ishlatiladi. Ftal angidridini glitserin bilan polikondensatsiyalab makromolekulyar birikmalar – **gliftal smolalar** olinadi:

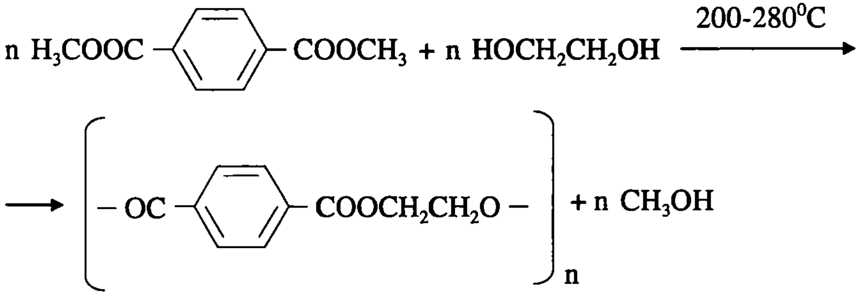


Gliftal smolalar texnikada plyonka va laklar sifatida qo‘llaniladi.

Tereftal kislota – suvda va organik erituvchilarda kam eriydigan rangsiz kristall modda. U sanoatda p- ksilolni havo kislorodi bilan 130 – 160^0 C va 0,5 –1 • 10^6 Pa bosimda kobalt (II) bromid ishtirokida oksidlash yoki benzoy kislotani uglerod (IV)- oksidi bilan kaliy gidrokarbonat ishtirokida 340^0C da karboksillash bilan olinadi:



Tereftal kislotaning dimetil efiri va etilenglikoldan polietilentereftalat olinadi:



Bu polimer **lavsan** sun'iy tolasini ishlab chiqarishda qo'llaniladi.

Savol va mashqlar

1. Quyidagi birikmalarning tuzilish formulalarini yozing:

a) 3-fenilbutan kislota; b) m - xlorbenzoy kislotaning metil efiri;

d) p- atsetoaminobenzoy kislota

e) dolchin kislotaning etil efiri; f) p- nitrodolchin kislota;

g) izoftal kislotaning diamidi;

h) β- fenilpropion kislotaning etil efiri;

i) 3,5 – dinitrobenzoil xlorid.

2. Halqasida va yon zanjirida karboksil guruhi bor $C_9H_{10}O_2$ tarkibli barcha aromatik kislotalarning tuzilish formulalarini yozing va ularni nomlang.

3. CO, H_2, benzol va boshqa reagentlardan o – xlorbenzoy kislotasini sintez qiling.

4. Benzol, diazometan va boshqa reagentlardan fenilsirka kislotasini sintez qiling.

5. Quyidagi sintez sxemasini tuzing:

Toluol $\longrightarrow$ 2,4,6 – trinitrobenzoy kislota

6. Anilin, sirka angidridi va boshqa reagentlardan p- nitrobenzoy kislotasini sintez qiling.

7. Quyidagi sintezlar sxemasini tuzing:

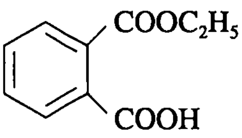
a) p- metilbenzoy kislotasi $\longrightarrow$ 2-nitro-5-xlortoluol;

b) benzoy kislotasi $\longrightarrow$ benzilatsetat

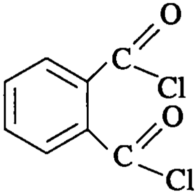
8. Benzoy, salitsil, p- gidroksibenzoy va 2,6-digidroksibenzoy kislotalarning pKa qiymatlari tegishli ravishda 4,20; 2,98; 4,58; 1,30 ga teng. Bu qiymatlarning bir-biridan farq qilish sabablarini tushuntiring.

9. Ftal kislota va boshqa reagentlardan quyidagi birikmalarni sintez qiling:

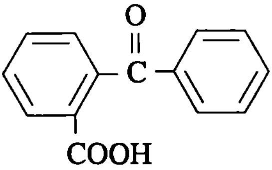
a)



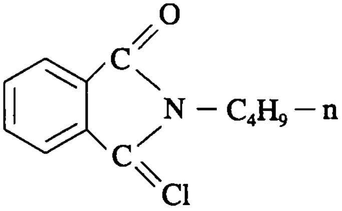
b)



d)



e)



10. Quyidagi sintezlar sxemasini tuzing:

a) ftal kislotasi ⟶ lavsan;

b) naftalin ⟶ gliftal smola.

XI. AROMATIK AMINLAR (ARILAMINLAR)

Arilaminlarning sinflanishi, nomlanishi, izomeriyasi, olinish usullari, fizikaviy xossalari va spektral tavsifi, kimyoviy xossalari, muhim vakillari. Savol va mashqlar.

Sinflanishi

Aromatik aminlar azot bilan bog'langan radikallarning soniga qarab birlamchi (I), ikkilamchi (II, III) va uchlamchi (IV,V,VI) bo'ladi:

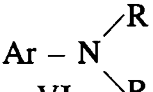
$Ar - NH_2$ I

$(Ar)_2NH$ II

$Ar - NH - R$ III

$(Ar)_3N$ IV

$(Ar)_2NR$ V



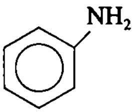
$Ar - N\begin{matrix} \diagup R \\ \diagdown R \end{matrix}$

VI

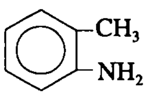
Aromatik aminlar sof aromatik va alkilaromatik aminlarga bo'linadi. Sof aromatik aminlar (I,II, IV) da azot atomi faqat aromatik radikallar bilan, alkilaromatik aminlar (III, V, VI) da esa aromatik va alifatik radikallar bilan bog'langan.

Nomlanishi va izomeriyasi

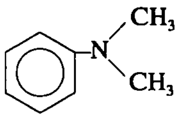
Aromatik aminlarning trivial nomlari keng qo'llaniladi:



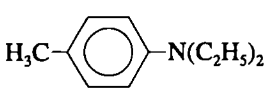
anilin



o-toluidin

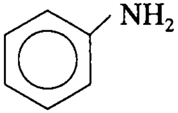


N, N-dimetil-anilin

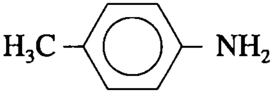


N,N-dietil – p-toluidin

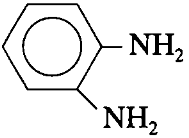
Sistematik nomenklaturaga binoan arilaminlarning nomlari amino-old qo‘shimchasi va aromatik uglevodorod nomidan yoki radikal nomiga amin (diamin) so‘zini qo‘shish bilan hosil qilinadi:



aminobenzol,
fenilamin



4 - aminotoluol



o - fenilendiamin

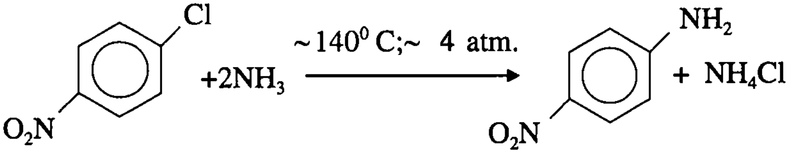
C_7H_9N tarkibli arilamin 5 ta izomer (benzilamin, **N**-metilanilin, *o* - *m* - va *p* - toluidinlar) holida uchraydi.

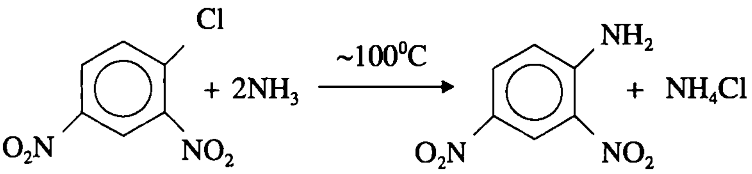
Olinish usullari

1. Nitroarenlarni qaytarish (152-153- betlar).

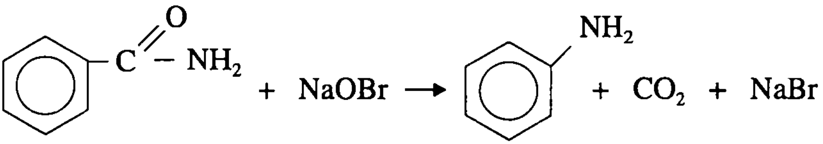
2. Galogenarenlarni aminlash. Galogenarenlar ammiak va aminlar bilan yuqori harorat va bosimda, katalizatorlar (mis va uning birikmalari) ishtirokida reaksiyaga kirishadi (135 - bet).

Agar galogenaren molekulasida galogenga nisbatan *o* – va p – holatlarda joylashgan kuchli elektronoaktseptor guruhlar (NO_2,CN, COR) bo‘lsa, galogen atomining nukleofil almashinishi osonlashadi:





3. Gofman reaksiyasi bilan amidlardan olish:



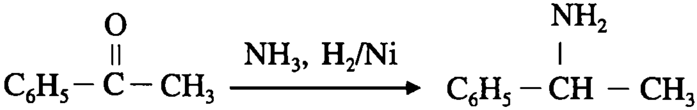
4. Aromatik nitrillarni qaytarish:

$$C_6H_5 - CH_2Cl \xrightarrow[-NaCl]{NaCN} C_6H_5 - CH_2CN \xrightarrow{H_2/Ni;140^0C} C_6H_5\text{–}CH_2CH_2NH_2$$

β – feniletilamin

5. Aromatik aldegid va ketonlarni ammiak ishtirokida katalitik qaytarish:

$$C_6H_5 - CHO \xrightarrow{NH_3,\ H_2/Ni} C_6H_5 - CH_2NH_2$$



$$C_6H_5 - \overset{\overset{\displaystyle O}{||}}{C} - CH_3 \xrightarrow{NH_3,\ H_2/Ni} C_6H_5 - \overset{\overset{\displaystyle NH_2}{|}}{CH} - CH_3$$

α - feniletilamin

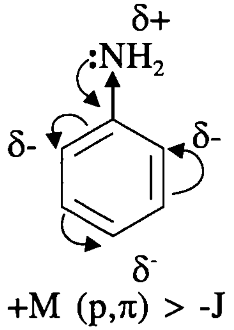
Fizikaviy xossalari va spektral tavsifi

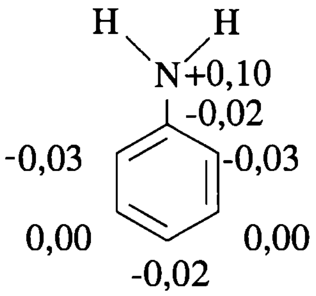
Arilaminlar o'ziga xos hidli, rangsiz suyuqlik yoki qattiq moddalar bo'lib, suvda yomon eriydi. Molekulasida aminoguruh sonining oshishi bilan ularning eruvchanligi yaxshilanadi. Di va triaminlar suvda yaxshi eriydi.

Anilinning IQ- spektrida C N bog'ining valent tebranishlari 1180-1360 sm^{-1},N–H bog'ining valent tebranishlari esa 3200–3500 sm^{-1} sohalarda kuzatiladi. PMR– spektrida N–H protonining signallari δ = 1 - 5 m.h. da rezonanslashadi.

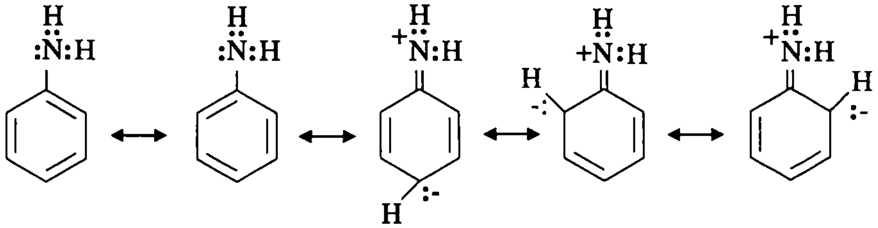
Kimyoviy xossalari

Aromatik aminlardagi aminoguruh +M - va –I – (+M > -I) effektlarni namoyon qilib, aromatik yadro elektron zichligini oshiradi:



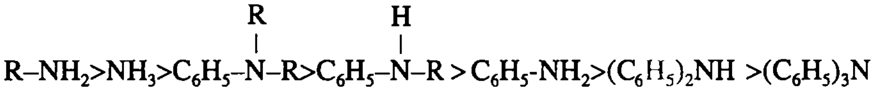


Buni anilinning rezonans strukturalari yordamida quyidagicha tasvirlash mumkin:



Asosligi. Arilaminlarda azot atomining erkin elektron jufti elektronga moyil benzol halqasi bilan p, π - tutashish hosil qiladi. Bunday tutashish tufayli erkin elektron jufti delokallashadi va kislotalar bilan reaksiyaga kirishganda uning protonni biriktirib olish qobiliyati pasayadi. Shu bois anilin metilaminga nisbatan qariyb million marta kuchsiz asos bo‘lib, uning suvdagi eritmalari kuchsiz (karbonat, sianid, sulfid) kislotalar bilan tuzlar hosil qilmaydi, lakmus va fenolftalein rangini o‘zgartirmaydi.

Aminlaming asos xossalari quyidagi tartibda kuchsizlanib boradi:



$$R{-}NH_2 > NH_3 > C_6H_5{-}\overset{R}{\overset{|}{N}}{-}R > C_6H_5{-}\overset{H}{\overset{|}{N}}{-}R > C_6H_5{-}NH_2 > (C_6H_5)_2NH > (C_6H_5)_3N$$

Trifenilamin asos xossalariga deyarli ega emas.

Arilaminlar kislotalar bilan tuzlar hosil qiladi:

$$C_6H_5 - NH_2 + HCl \rightleftharpoons [C_6H_5 - NH_3]^+ Cl^-$$

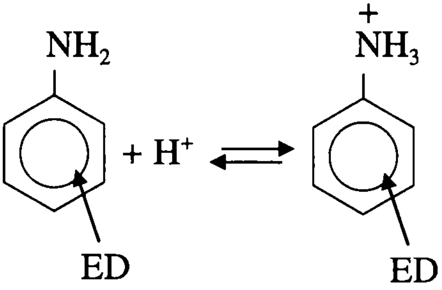
aniliniy xloridi

$$C_6H_5 - N(CH_3)_2 + CH_3COOH \rightleftharpoons [C_6H_5 - NH(CH_3)_2]^+ \overset{-}{O}OCCH_3$$

N,N-dimetilaniliniy atsetati

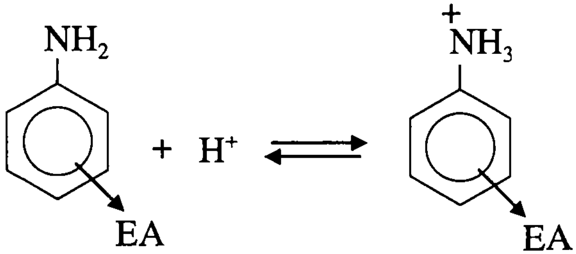
Aromatik yadrodagi o‘rinbosarlarning tabiati va joylashishi ham arilaminlarning asos xossalariga ta‘sir qiladi.

Amino guruhga nisbatan meta- yoki para- holatda joylashgan elektronodonor (ED) o‘rinbosarlar ($-NH_2$, $-OCH_3$, $-CH_3$) elektronlarni beradi, aniliniy kationining musbat zaryadini kamaytiradi, kationni aminga nisbatan barqaror qiladi, anilinning asos xossalarini kuchaytiradi:



Aminoguruhga nisbatan orto-holatda joylashgan elektronodonor o'rinbosarlar esa protonlanishni fazoviy qiyinlashtiradi (orto- effekt) va anilin asosligini kuchsizlantiradi.

Elektronoaktseptor (EA) o'rinbosarlar(-$\overset{+}{N}H_3$, -NO_2, -$\overset{-}{S}O_3$, COOH, galogenlar) elektronlarni tortadi, aniliniy kationining musbat zaryadini kuchaytiradi, kationni aminga nisbatan beqaror qiladi, anilin asos xossalarini kuchsizlantiradi:



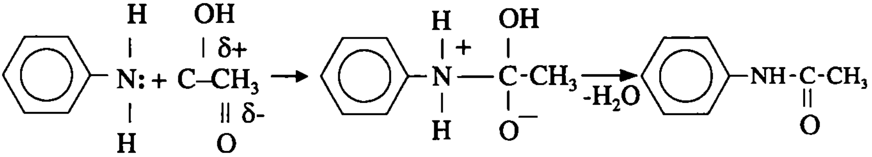
EA o'rinbosar amino guruhga nisbatan orto- holatda joylashganda, uning ta'siri yanada sezilarli bo'ladi.

Amino guruh ishtirokidagi reaksiyalar

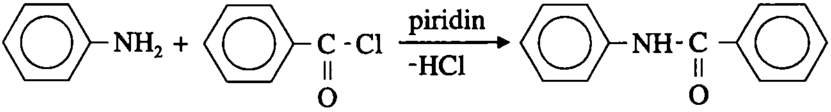
Alkillash. Anilin va metanol bug'lari degidratlovchi katalizator (Al_2O_3) ustidan o'tkazilganda ham N-metil- va N,N-dimetilanilinlar hosil bo'ladi:

$$C_6H_5\text{-}NH_2 + CH_3OH \xrightarrow{Al_2O_3,\ \Delta} C_6H_5\text{-}NH\text{-}CH_3 + H_2O$$

Atsillash. Arilaminlarni atsillash (formillash, atsetillash va benzoillash) reaksiyalarida atsillovchi reagentlar sifatida chumoli, sirka va benzoy kislotalar yoki ularning xlorangidridlari ishlatiladi:



atsetanilid

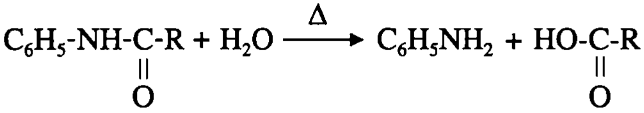


benzanilid

Atsillash reaksiyalarining teziigi arilaminlarning asosligi va atsillovchi reagentning faolligiga bog‘liq. Reagentlaming faolligi qatorda quyidagi tartibda oshib boradi:

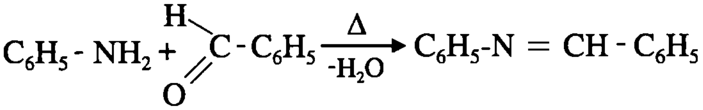
Karbon kislota < karbon kislota angidridi < karbon kislota xlorangidridi

Anilidlar kislotali va ishqoriy muhitda qizdirilganda gidrolizlanadi:

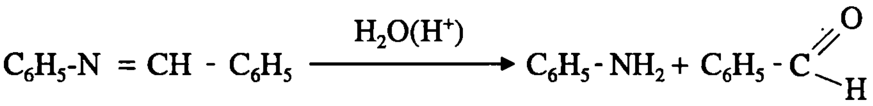


$$C_6H_5\text{-NH-}\underset{\underset{O}{\|}}{C}\text{-R} + H_2O \xrightarrow{\Delta} C_6H_5NH_2 + \text{HO-}\underset{\underset{O}{\|}}{C}\text{-R}$$

Azometinlar olish. Arilaminlar aromatik aldegidlar bilan reaksiyaga kirishganda azometinlar (Shiff asoslari) hosil bo‘ladi:



Azometinlar suyultirilgan kislotalar ta‘sirida amin va aldegidga parchalanadi:



Izonitrillarning hosil bo‘lishi. Birlamchi aromatik aminlarni xloroform va ishqorning spirtdagi eritmasi bilan qizdirilganda badbo‘y izonitrillar hosil bo‘ladi (izonitril reaksiyasi, A.Gofman, 1868):

$$C_6H_5\text{-}NH_2 + CHCl_3 + 3\ KOH \xrightarrow{\Delta} C_6H_5\text{-}\overset{+}{N} \equiv \overset{-}{C}: + 3\ H_2O + 3\ KCl$$

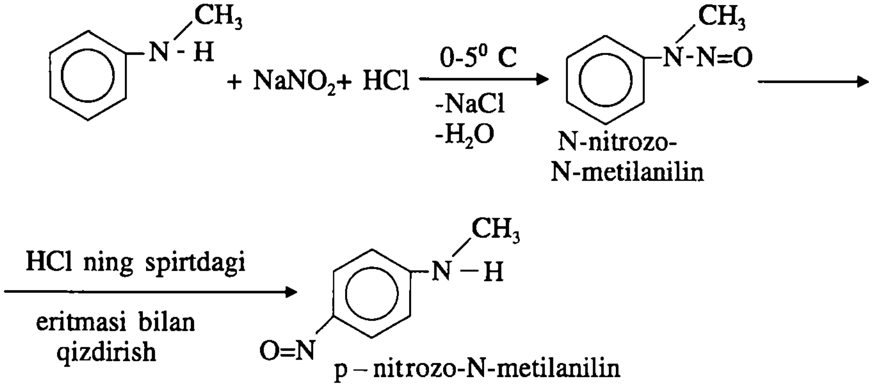
Bu reaksiyadan birlamchi aminlarni sifat jihatidan aniqlashda (ajraladigan izonitrillarning hididan) foydalaniladi.

Nitrit kislotaning ta‘siri. Birlamchi, ikkilamchi va uchlamchi aromatik aminlar nitrit kislota bilan turlicha reaksiyaga kirishadi.

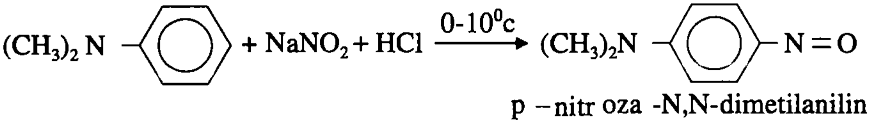
Birlamchi aromatik aminlar nitrit kislota bilan diazotirlash reaksiyasiga kirishib, arendiazoniy tuzlarini hosil qiladi:

$$Ar - NH_2 + NaNO_2 + 2\ HX \xrightarrow{0\text{-}5^0\ C} [Ar - \overset{+}{N_2}]\ \overset{-}{X} + NaX + 2\ H_2O$$

Ikkilamchi alkilaromatik aminlar nitrit kislota ta‘sirida N-nitrozoaminlarni hosil qiladi. Mineral kislotalar bilan qizdirilganda N-nitrozoaminlarning nitrozo guruhi yadroning *p*-holatiga o‘tadi (Fisher-Xepp qayta guruhlanishi):



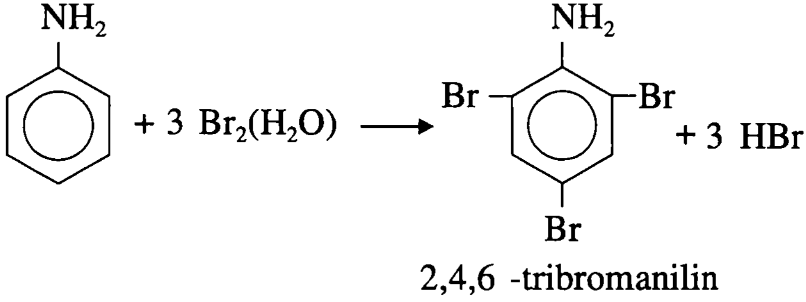
Uchlamchi dialkilaromatik aminlar nitrit kislota ta'sirida *p* - nitrozobirikmalarni hosil qiladi:



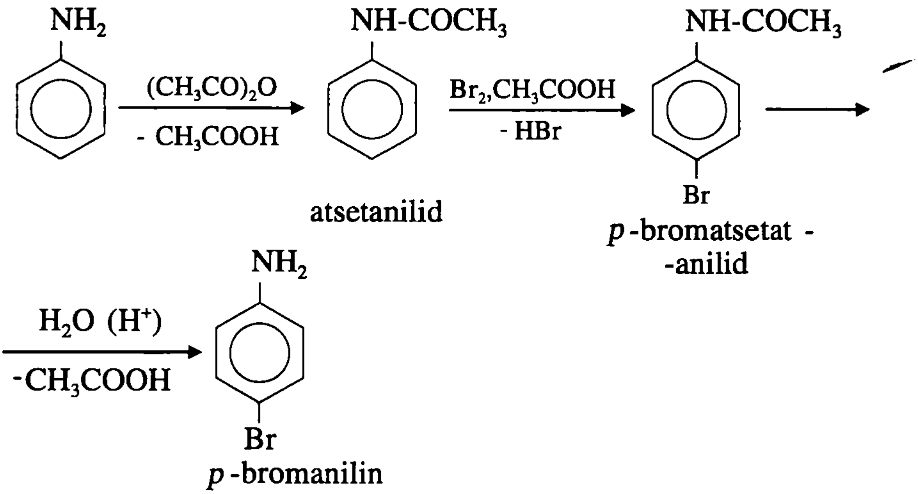
Aromatik aminlar halqasida boradigan elektrofil almashinish reaksiyalari

$-NH_2$, -NHR va $-NR_2$ guruhlari aromatik halqa faolligini keskin oshirib, elektrofil o'rinbosarlarni **orto-** va **para-** holatlarga yo'naltiradi.

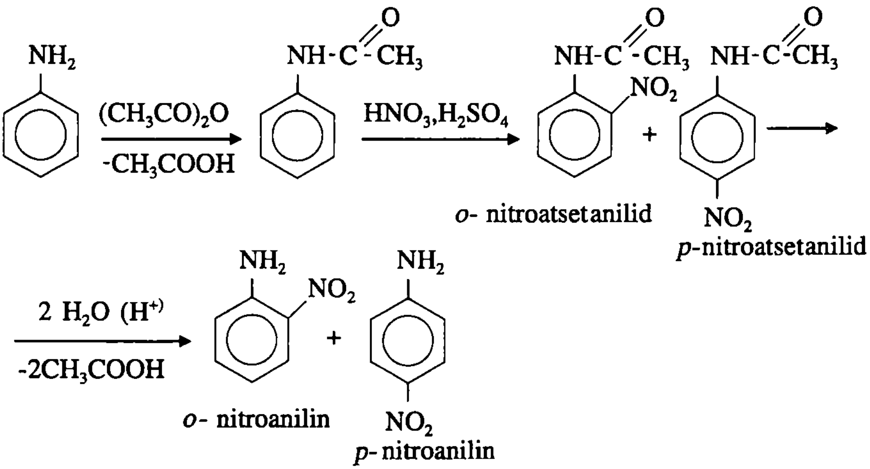
Galogenlash. Aromatik aminlami galogenlash nihoyatda tez boradi. Anilinga hatto bromli yoki xlorli suv ta'sir ettirilganda ham galogen atomlari halqaning barcha **orto-** va **para-** holatlarini egallaydi:



Monogalogenalmashingan arilaminlarni olish uchun oldin amino guruhni atsetillash bilan himoya qilinadi. So'ngra amid guruhini gidrolizlab, kerakli amin olinadi:



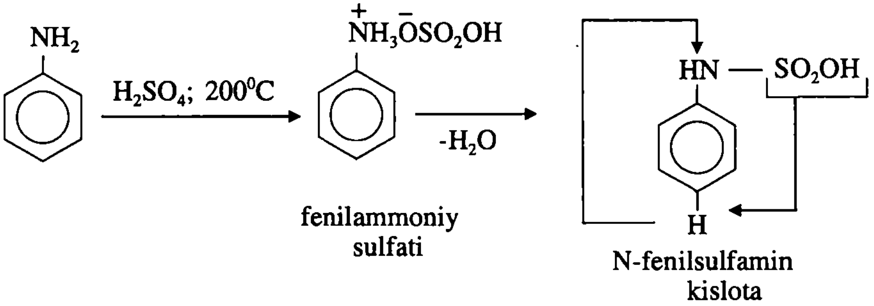
Nitrollash. Halqasi oksidlanishga juda sezgir aromatik aminlarni nitrat kislota bilan bevosita nitrolab bo'lmaydi. Anilin nitrat kislota bilan reaksiyaga kirishganda smolasimon oksidlanish mahsulotlari va azot oksidlari hosil bo'ladi. Bu oksidlar esa anilinning oksidlanmasdan qolgan qismini diazotirlaydi. Shu bois anilin oldin atsetillanadi, so'ngra hosil bo'lgan anilid nitrolanadi:

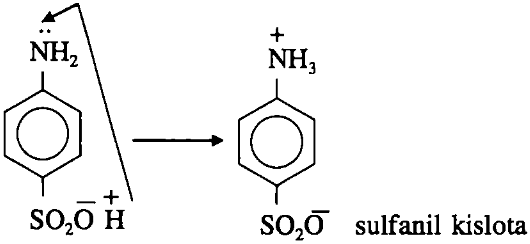


Bu reaksiyada asosan para izomerlar hosil bo'ladi.

Atsetillashdan bunday foydalanish ko'pincha amino guruhni himoyalash deb ataladi. Haqiqatda bu usul bilan butun molekula oksidlanishidan himoya qilinadi.

Sulfolash. Anilinni mo'l olingan suyultirilgan sulfat kislota bilan sulfolaganda *o*- va *p*- anilinsulfokislotalarning aralashmasi hosil bo'ladi. Uni ekvimolekulyar miqdordagi konsentrlangan sulfat kislota bilan sulfolaganda esa fenilammoniy sulfati hosil bo'ladi. 200^{0}C gacha qizdirilganda bu tuz dastlab N-fenilsulfamin kislotaga aylanadi. So'ngra u *p*-anilinsulfokislota (sulfanil kislotaga) qayta guruhlanadi (sulfanil qayta guruhlanishi):





Sulfanil kislota biqutbli ion holida mavjud bo‘ladi.

Muhim vakillari

Anilin (arabcha an-nil-indigo) – 184,4⁰ C da qaynaydigan, o‘ziga xos hidli, rangsiz suyuqlik bo‘lib, suvda oz eriydi.

Anilinni birinchi marta 1826 - yilda O.Unferdorben indigoni ohak bilan haydab oldi. 1842 - yilda N.N.Zinin nitrobenzolni $(NH_4)_2S$ ta‘sirida qaytarib anilin oldi. Hozirgi vaqtda dunyoda bir million tonnadan ziyod anilin ishlab chiqariladi. U sanoat miqyosida asosan quyidagi usullar bilan olinadi.

1. Nitrobenzolni 250-350⁰ C da NiS / Al_2O_3 yoki Cu / SiO_2 ustida vodorod bilan katalitik qaytarish:

$$C_6H_5NO_2 + 3\ H_2 \longrightarrow C_6H_5NH_2 + 2\ H_2O + 443{,}8\ kJ/mol$$

2. 300-600⁰ C va 1 MPa dan yuqori bosimda fenolni katalizator (Al_2O_3 yoki alyumosilikat) ishtirokida ammonolizlash:

$$C_6H_5OH + NH_3 \longrightarrow C_6H_5NH_2 + H_2O$$

Anilin bo'yoqlar, vulkanlash tezlashtirgichlari, poliuretanlar, dori vositalari , pestitsidlar, antioksidantlar va hokazolarni ishlab chiqarishda qo'llaniladi.

N,N-dimetilanilin – 194°C da qaynaydigan, o'ziga xos hidli, rangsiz suyuqlik bo'lib, suvda kam eriydi. U anilinni metanol bilan sulfat kislota ishtirokida alkillab olinadi.

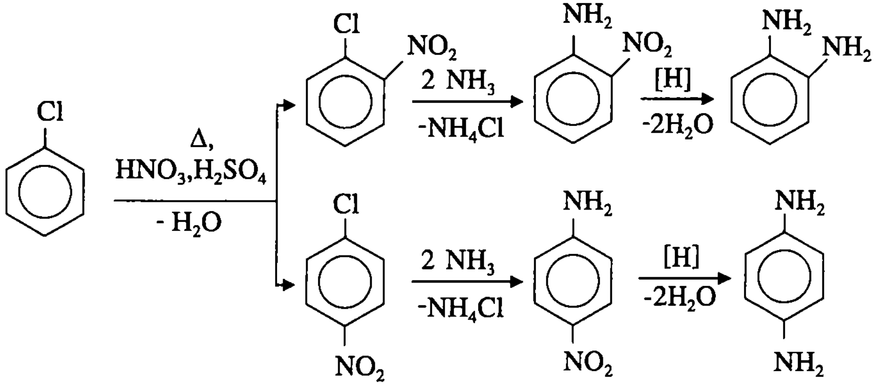
N,N- dimetilanilin bo'yoqlar va portlovchi moddalar ishlab chiqarishda qo'llaniladi.

β-naftilamin -113°C da suyuqlanadigan, rangsiz kristall modda. U β-naftolni ammiak va sulfit angidridi bilan 130-150°C da suv muhitida qizdirib olinadi (X.Buxerer, 1903-1904-y.): β-naftilamin bo'yoqlar sintezida qo'llaniladi. Kanserogen xossalarga egaligi sababli hozirgi vaqtda u keng miqyosda ishlab chiqarilmaydi.

o-Fenilendiamin –102°C da suyuqlanadigan, rangsiz kristall modda bo'lib, geterotsiklik birikmalar sintezida ishlatiladi.

***p*-Fenilendiamin** -147°C da suyuqlanadigan, rangsiz kristall modda bo'lib, azin bo'yoqlari sintezida ishlatiladi.

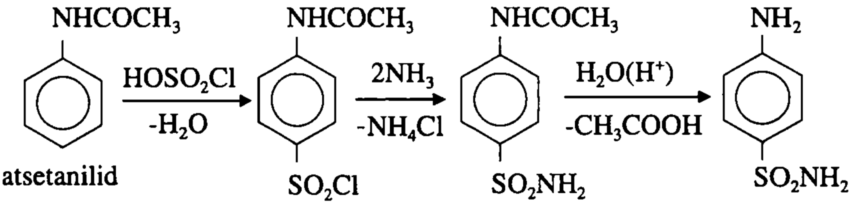
o- va ***p*-** fenilendiaminlar quyidagi sxema bo'yicha sintez qilinadi:



p-Toluidin -45°C da suyuqlanadigan kristall modda, ***o-*** va ***-m-* toluidinlar** esa suyuqliklardir. Toluidinlar bo‘yoqlar sintezida qo‘llaniladi.

Sulfanil kislota- 290°C da suyuqlanadigan,suvda oz eriydigan, rangsiz kristall modda bo‘lib, anilin va sulfat kislotadan olinadi. U azobo‘yoqlar ishlab chiqarishda qo‘llaniladi.

Sulfanil kislotaning amidi (oq streptotsid) tibbiyotda samarali antibakterial vosita sifatida ishlatiladi. Oq streptotsidni quyidagi sxema bo‘yicha sintez qilish mumkin:



atsetanilid

atsetanilid
p-sulfoxlorid

atsetanilid
p-sulfamidi

sulfanilamid
(oq streptotsid)

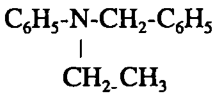
Sulfanilamidning sulfidin, disulfan, norsulfazol, sulfadimezin kabi bir necha hosilalari ham turli yuqumli kasalliklarni davolashda qo‘llaniladi.

Savol va mashqlar

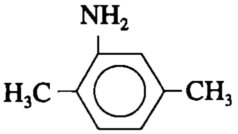
1.Quyidagi birikmalarning tuzilish formulalarini yozing:

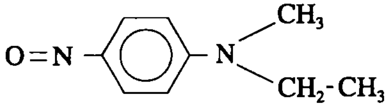
a) fenilbenzilamin; b) 4-amino-1,2-dimetilbenzol;
d) N-izopropilanilin; e) $4,4^1$-dimetildifenilamin;
f) γ -**m**-tolilpropilamin; g) 5-amino-2-fenilgeksan;

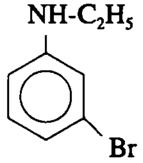
2. Birikmalarni nomlang:

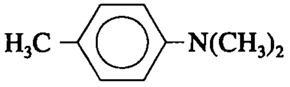
a) 

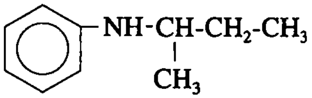
$C_6H_5\text{-}\underset{CH_2\text{-}CH_3}{\underset{|}{N}}\text{-}CH_2\text{-}C_6H_5$

b) 

d) 

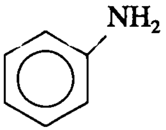
e) 

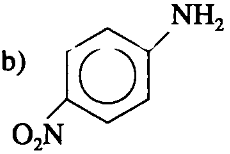
f) 

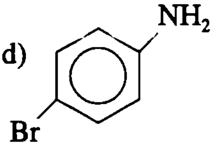
g) 

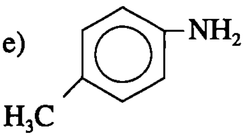
3. $C_9H_{13}N$ tarkibli izomer aromatik aminlarning tuzilish formulalarini yozing va ularni nomlang. Sof arilaminlar va alkilarilaminlarni ko‘rsating.

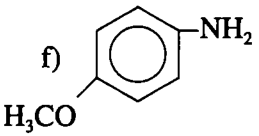
4. Quyidagi birikmalarni asos xossalarining kuchsizlanib borishi tartibida joylashtiring:

a) 

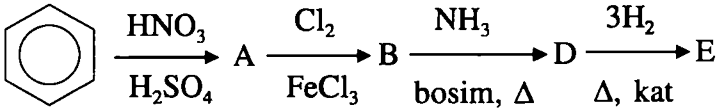
b) 

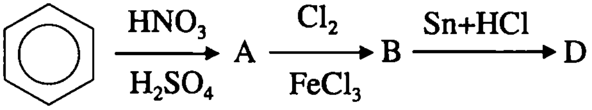
d) 

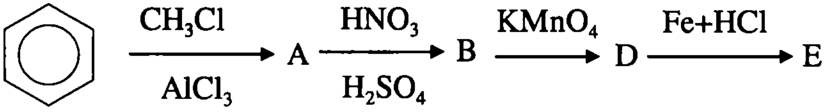
e) 

f) 

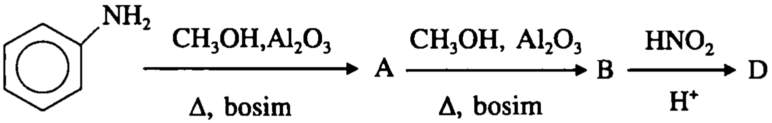
5. Quyidagi sxemalarda oraliq va oxirgi mahsulotlarning tuzilish formulalarini yozing:

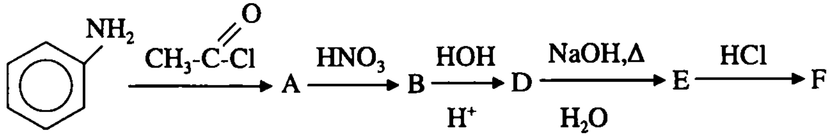
a)


b)


d)


6. Quyidagi sxemalarda oraliq va oxirgi mahsulotlarning tuzilish formulalarini yozing:

a)


b)


7. Quyidagi sintezlar sxemalarini tuzing:

a) benzol ⟶ *p* –aminoatsetanilid;
b) toluol ⟶ *m* – bromanilin;
d) toluol ⟶ *o.* o^1- diaminodifenil;
e) benzol ⟶ *p* – xloratsetanilid.

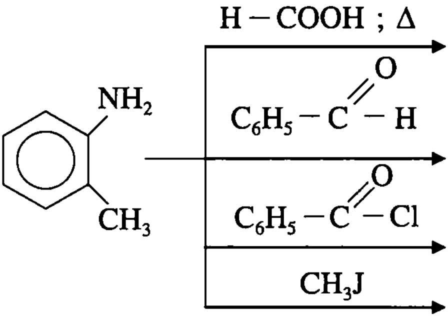
8. Anilin va boshqa reaktivlardan quyidagi birikmalarning sintez qilish sxemalarini tuzing:

a) *p* –dixlorbenzol; b) 3,4,5 – triiodnitrobenzol;
d) *p* –aminoatsetanilid; e) 3,5 –dinitroxlorbenzol.

9. Anilinning quyidagi reagentlar bilan oksidlash reaksiyalari sxemalarini yozing:

a) natriy bixromat va suyultirilgan sulfat kislota;
b) kaliy permanganat;
d) Karo kislotasi (H_2SO_5).

10. Quyidagi reaksiyalar natijasida hosil bo‘ladigan organik birikmalarning tuzilish formulalarini yozing:



XII. AROMATIK DIAZO – VA AZOBIRIKMALAR

Aromatik diazobirikmaiar. Nomlanishi, tuzilishi. Arendiazoniy tuzlarining olinishi, diazotirlash reaksiyasi mexanizmi. Arendiazoniy tuzlarining azot ajralishi va ajralmasligi bilan boradigan reaksiyalari. Azobirikish reaksiyasi va uning mexanizmi. Azobirikmalar. Nomlanishi, olinishi va xossalari. Azobo'yoqlar. Savol va mashqlar.

Aromatik diazobirikmalar

Arildiazoniy tuzlari (I), diazogidratlar (II), diazotatlar (III), diazotsianidlar (IV) va boshqa shularga o'xshash birikmalar aromatik diazobirikmalar deyiladi:

$[Ar-N\equiv N]^+X^-$
($X^- = Cl^-, Br^-, NO_3^-, HSO_4^-, BF_4^-, ClO_4^-$
va boshqa anionlar)
I

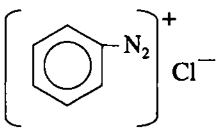
$Ar-N=N-OH$
II

$Ar-N=N-O^-\ M^+$ (M=metall)
III

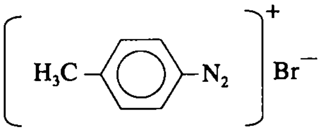
$Ar-N=N-CN$
IV

Nomlanishi

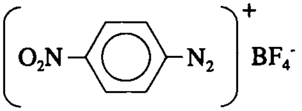
Aromatik diazobirikmalar quyidagicha nomlanadi:



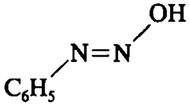
fenildiazoniy xloridi



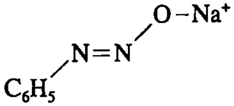
p - tolildiazoniy bromidi



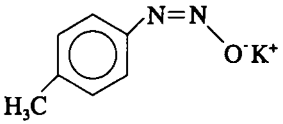
p-nitrofenildiazoniy borftoridi



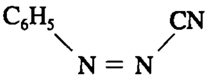
benzol-anti - diazogidroksid



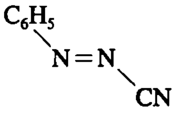
natriy benzol-antidiazotati



kaliy p-toluol-sin-diazotati



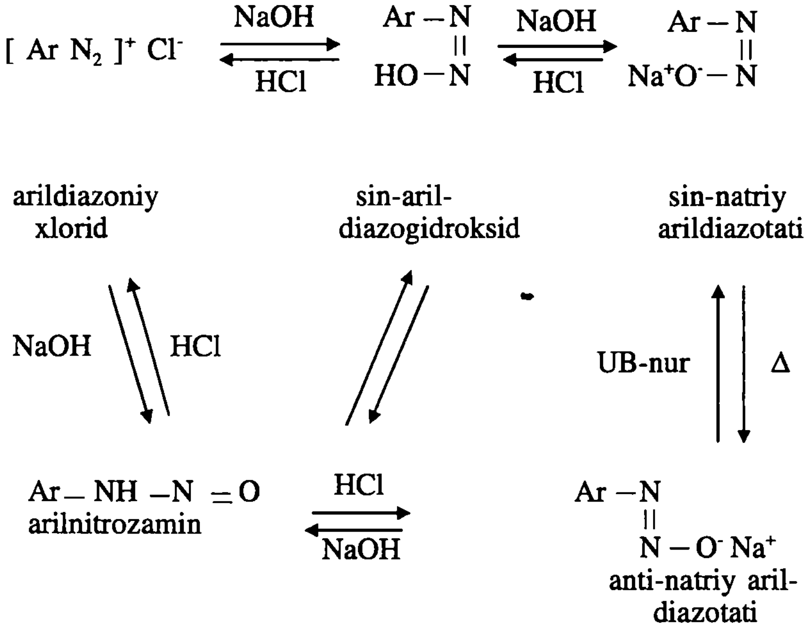
sin-fenildiazotsianid



anti-fenildiazotsianid

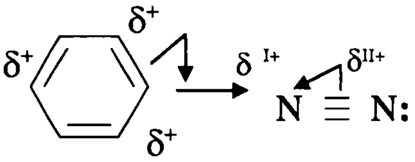
Tuzilishi

Diazobirikmalar suvdagi eritmalarida bir-biriga aylana oladigan bir necha izomer shakllarda mavjud bo‘ladi:



Diazobirikmalar kislotali muhitda diazoniy tuzlari shaklida bo‘ladi.

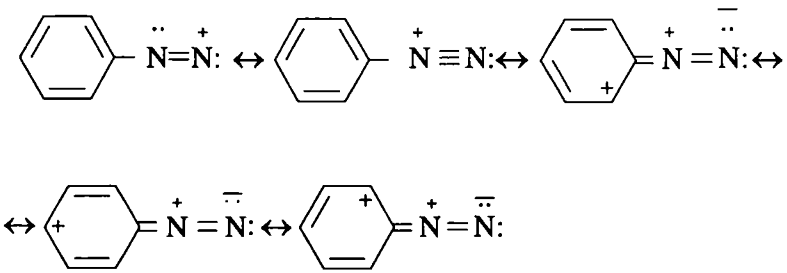
Fenildiazoniy kationida benzolning π -elektronlari bilan diazoniy guruhining uch bog‘i orasida o‘zaro kuchli ta‘sirlashuv amalga oshadi:

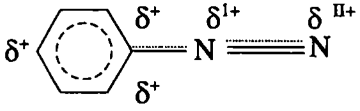


$\delta^{1+} > \delta^{II+}$

Diazoniy guruhining musbat zaryadi asosan azot atomlari orasida taqsimlangan, lekin u benzol yadrosining π-elektronlari hisobiga qisman kompensatsiyalanadi.

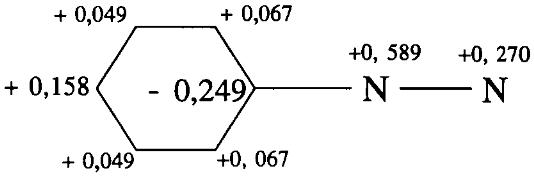
Buni fenildiazoniy kationining rezonans strukturalari va mezoformulasi ko‘rinishida tasvirlash mumkin:



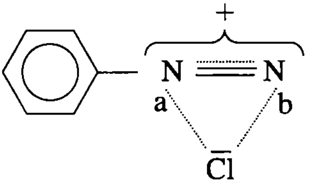


$\delta^{1+} > \delta^{II+}$

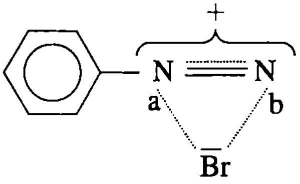
fenildiazoniy kationi atomlarida zaryadlar quyidagicha taqsimlangan:



Diazoniy tuzlarida anion ikkala azot atomidan qariyb bir xil (chetki atomga sal yaqinroq) joylashgan:



a=0,324 nm
b=0,322 nm



a=0,346 nm
b=0,331 nm

Aromatik diazobirikmalardan arendiazoniy tuzlari katta amaliy ahamiyatga ega.

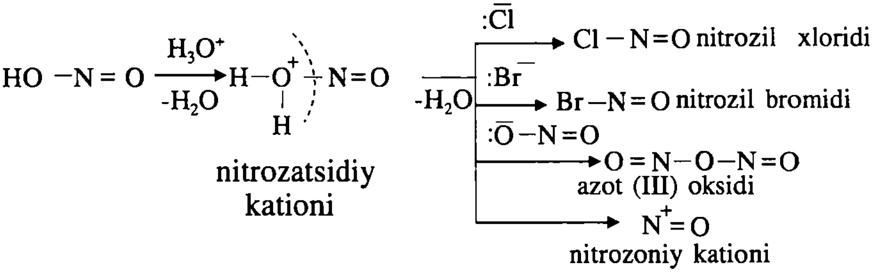
Olinishi

Arildiazoniy tuzlari birlamchi arilaminlarni nitrit kislota bilan ma'dan (xlorid, sulfat, bromid va boshqa) kislotalar muhitida diazotirlab olinadi (Griss, 1858 - y.):

$$\mathrm{Ar\,NH_2 + NaNO_2 + 2HX} \xrightarrow[\mathrm{-NaX,-2\,H_2O}]{\mathrm{0\ dan{+}5^0C\ gacha}} \mathrm{[\,Ar\,N_2]^+X^-}$$

Nitrit kislotani reaksiya jarayonida natriy nitriti va ma'dan kislotadan hosil qilinadi. Kuchli kislotali muhitda nitrit kislotaning suvdagi eritmasida bir necha bevosita diazotirlovchi faol elektrofil reagentlar hosil bo'ladi:

$H^+X^- + H_2O \rightleftarrows H_3O^+ + X^-$ $X^- = Cl^-$, O^-SO_3H, Br^- va boshqalar

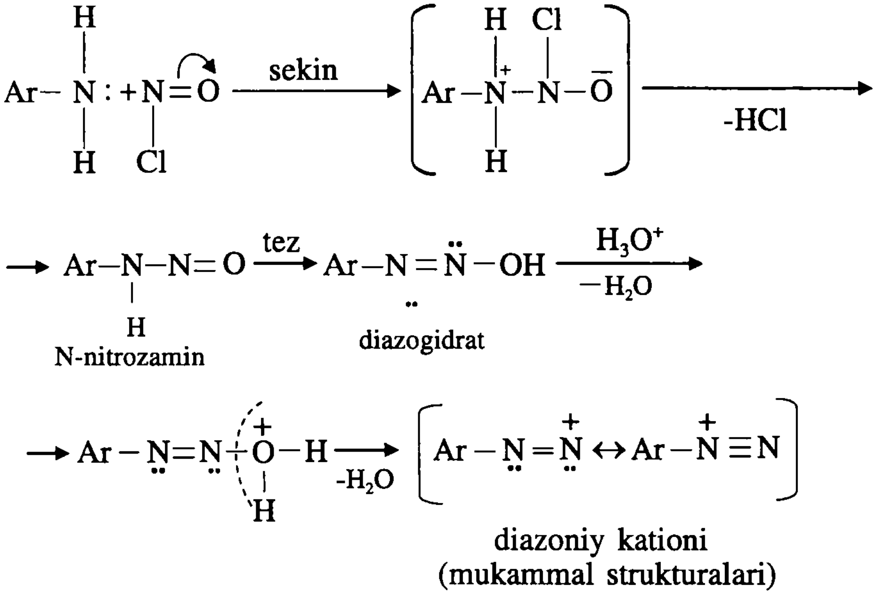


Diazotirlashni xlorid kislotada olib borilganda asosiy elektrofil reagent nitrozil xloridi, suyultirilgan sulfat kislotada nitroatsidiy kationi, suvli muhitda esa azot (III) oksididir.

Faol reagent hisoblangan nitrozoniy kationi faqat konsentrlangan sulfat kislota muhitidagina mavjud bo'ladi:

$$HNO_2 + 2\,H_2SO_4 \rightleftarrows \overset{+}{N}O + H_3\overset{+}{O} + 2\,\overset{-}{O}SO_3H$$

Diazotirlash reaksiyasining mexanizmi to'liq o'rganilgan. Reaksiya elektrofil reagentlarning erkin elektron jufti bor azot atomiga hujumi bilan boshlanadi. Birlamchi arilaminlarni nitrozil xloridi bilan diazo-tirlash quyidagi sxema bo'yicha boradi:



Reaksiyaning birinchi bosqichida hosil bo‘ladigan N-nitrozamin faqat –70⁰ C da barqaror bo‘lib, diazogidratga tez aylanadi. Diazogidratning gidroksil guruhi kislotali muhitda protonlanadi. Protonlangan diazogidratdan suv ajralib, diazoniy kationi hosil bo‘ladi. Diazotirlash reaksiyasi kuchli kislotali muhitda sovitish bilan olib boriladi. Mo‘l olingan kislota natriy nitritidan nitrit kislotani ajratish, faol nitrozirlovchi agentni hosil qilish va qo‘shimcha reaksiya (diazoaminobirikmalar hosil bo‘lishi)ning oldini olish uchun kerak. Bundan tashqari mo‘l ma‘dan kislota diazoniy tuzlari barqarorligini oshiradi.

Ma‘dan kislotaning konsentratsiyasi diazotirlanadigan aminning asosligiga mos kelishi kerak. Asosligi yuqori va o‘rtacha bo‘lgan aminlar (anilin va uning gomologlari, naftilaminlar, benzidin, mononitroanilinlar, aminlarning sulfohosilalari va boshqalar)ni suvli muhitda diazotirlashda 1 mol amindan 2,5-3 mol ma‘dan kislota olinadi. Asosligi past bo'lgan aminlar faqat faol diazotirlovchi agentlar bilangina reaksiyaga kirishishi mumkin. Shu bois ular konsentrlangan sulfat kislotada diazotirlanadi. Diazobirikmalar va reaksion aralashmadagi nitrit kislota termik beqaror bo'lib, harorat oshganda parchalanadi. Shu bois diazotirlash reaksiyasi past haroratda (odatda 0 dan +5^{0}C gacha) o'tkaziladi.

Reaksion aralashmada ma'dan kislotaning meyoridan kamligi va reaksiya haroratining oshishi qo'shimcha reaksiyalarning borishi uchun sharoit yaratadi.

Reaksiya harorati oshganda, diazoniy tuzlari va nitrit kislota parchalanadi:

$$[Ar-N_2]^+X^- + H_2O \longrightarrow Ar-OH + N_2 + HX$$

$$2\ HNO_2 \longrightarrow NO_2 + NO + H_2O$$

Nitrit kislotaning parchalanishi diazotirlovchi reagentning yetishmasligiga va reaksiyaning oxirigacha bormasligiga olib keiadi.

Xossalari

Arildiazoniy tuzlari suvda eriydigan, quruq holida oson portlab parchalanadigan, rangsiz kristall moddalardir. Shu bois ularni suvdagi eritmalaridan ajratmasdan keyingi reaksiyalar uchun ishlatiladi.

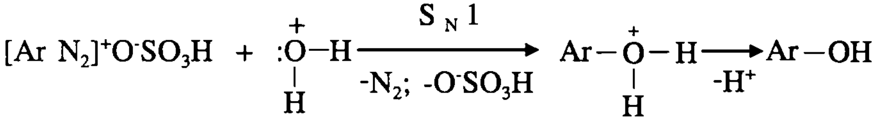
$[Ar\ N_2]^+BF_4^-$ tipidagi tuzlar nisbatan barqaror bo'lib, ularni oylab saqlash mumkin.

Arildiazoniy tuzlari – reaksiyaga kirishish qobiliyati kuchli bo'lgan birikmalardir. Ular kirishadigan reaksiyalar azotning ajralishi va ajralmasligi bilan boradi.

Azot ajralishi bilan boradigan reaksiyalar

Bu reaksiyalarda diazoguruh turli atom va guruhlar (F, Cl, Br, J, CN, OH, H, Ar, NO_2, OR, SH, SR, NCS, NCO, PO_3H_2, AsO_3H_2 va hokazo) ga almashinadi.

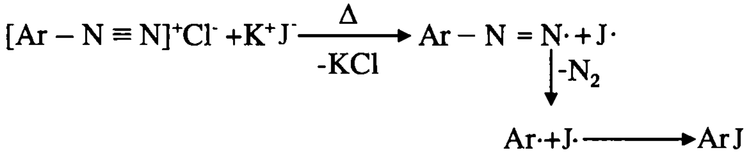
1. Arildiazoniy tuzlarining kislotali eritmalari qaynatilganda azot ajraladi va fenollar hosil bo‘ladi:



$$[Ar\,N_2]^+O^-SO_3H + :\overset{+}{\underset{H}{O}}-H \xrightarrow[-N_2;\ -O^-SO_3H]{S_N1} Ar-\overset{+}{\underset{H}{O}}-H \xrightarrow[-H^+]{} Ar-OH$$

Fenollar arildiazoniy gidrosulfatlari va tetraftorboratlaridan olinadi. Arildiazoniy galogenidlaridan olinganda esa, qo‘shimcha mahsulotlar sifatida arilgalogenidlar ham hosil bo‘ladi.

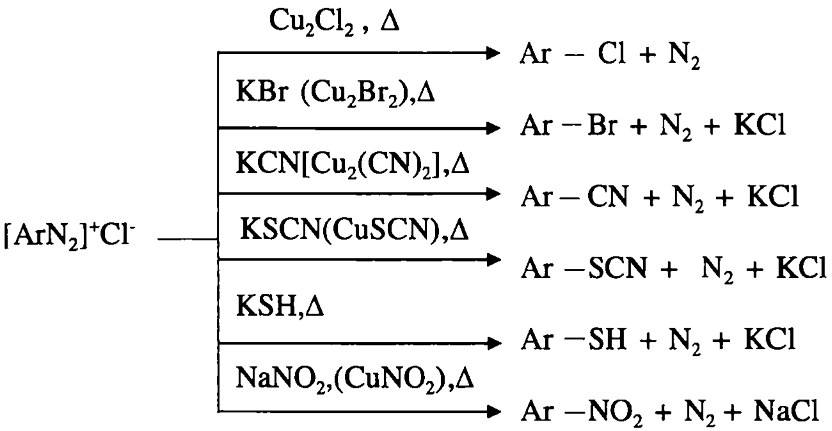
2. Arildiazoniy xloridlariga natriy yoki kaliy yodidini ta‘sir ettirilganda, arilyodidlar hosil bo‘ladi. Bu reaksiya aromatik yadroga yodni kiritishning qulay usuli bo‘lib, erkin radikalli mexanizmda boradi:



$$[Ar-N\equiv N]^+Cl^- + K^+J^- \xrightarrow[-KCl]{\Delta} Ar-N=N\cdot + J\cdot$$

$$\xrightarrow{-N_2}\ Ar\cdot + J\cdot \longrightarrow ArJ$$

3. Diazoguruhning xlor, brom, CN, NO_2, SCN va boshqa guruhlarga almashinishi katalizatorlar - bir valentli mis tuzlari ishtirokida boradi. (Zandmeyer reaksiyasi, 1884 - y.):



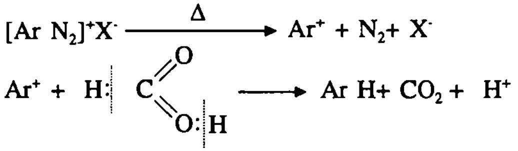
Bu reaksiyalar mis kukuni katalizatorligida ham boradi (Gatterman reaksiyasi).

4. Arildiazoniy tuzlariga HBF_4 yoki $NaBF_4$ ta'sir ettirilganda arildiazoniy tetraftorborat cho'kmaga tushadi. Cho'kma qizdirilganda arilftorid, azot va bor ftoridiga parchalanadi (Shiman reaksiyasi):

$$[Ar\ N_2]^+Cl^- \xrightarrow[-HCl]{HBF_4} \downarrow [Ar\ N_2]^+BF_4^- \xrightarrow[-N_2\ ;\ -BF_3]{\Delta} ArF$$

Shiman reaksiyasi aromatik halqaga ftor kiritishning qulay usulidar.

5.Turli qaytaruvchilar (masalan, chumoli kislota) ta'sirida diazoguruh vodorodga almashinadi:



$$[Ar\ N_2]^+X^- \xrightarrow{\Delta} Ar^+ + N_2 + X^-$$

$$Ar^+ + H{:}C(=O)O{:}H \longrightarrow Ar\,H + CO_2 + H^+$$

Gipofosfit kislota ta'sirida ham diazoguruh vodorodga oson almashinadi:

$$[Ar\ N_2]^+X^- + H_3PO_2 + H_2O \longrightarrow Ar - H + H_3PO_3 + HX + N_2$$

6. Arildiazoniy va simob galogenidlardan olinadigan qo'sh tuzlarning mis kukuni ishtirokida parchalanishidan simoborganik birikmalar hosil bo'ladi (A.N.Nesmeyanov, 1929-y.):

$$[C_6H_5N_2]^+Cl^- + HgCl_2 \longrightarrow C_6H_5N_2Cl \cdot HgCl_2$$

$$C_6H_5N_2Cl \cdot HgCl_2 + 2\ Cu \xrightarrow{\Delta} \underset{\text{fenilsimob xloridi}}{C_6H_5\ HgCl} + N_2 + 2\ CuCl$$

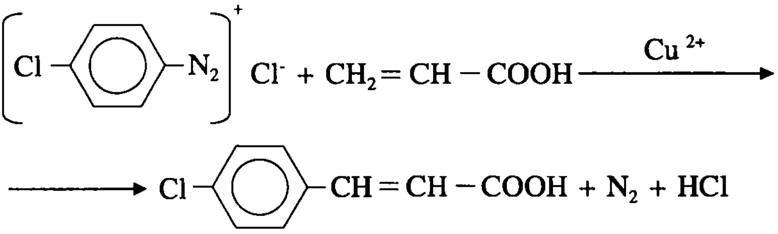
A.N.Nesmeyanov usuli bilan qalay-, vismut-, surma- va titanorganik birikmalar olindi, shuningdek, diazoniy tuzlari bilan erkin metallar orasidagi reaksiyalar amalga oshirildi.

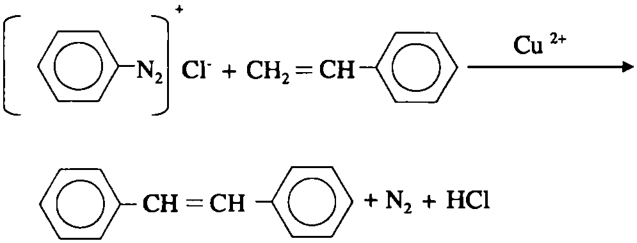
7. Kuchsiz ishqoriy muhitda arildiazoniy tuzlarini arenlar yoki ularning hosilalari bilan qizdirilganda, diazoguruh arilga almashinadi:

$$[Ar\ N_2]^+\ X^- + Ar^I\ H \xrightarrow[CH_3COONa]{H_2O} Ar - Ar^I + \text{boshqa mahsulotlar}$$

8. Arildiazoniy tuzlari mis tuzlari ishtirokida faol qo‘sh bog‘i bor birikmalar bilan arillash reaksiyasiga kirishadi:

(X. Meerveyn, 1939 - y.):



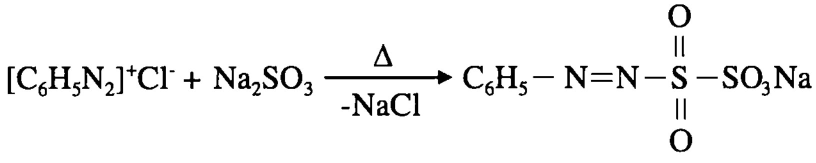


Azot ajralmasligi bilan boradigan reaksiyalar

Arildiazoniy tuzlari yumshoq sharoitda ($SnCl_2$ ning xlorid kislotadagi eritmasi yoki sirka kislotada rux bilan) qaytarilganda arilgidrazinlarning tuzlari hosil bo‘ladi:

$$[Ar\ N_2]^+ Cl^- + 2\ SnCl_2 + 4\ HCl \longrightarrow [Ar - NH - NH_3]^+ Cl^- + 2\ SnCl_4$$

Fenilgidrazin sanoat miqyosida quyidagicha olinadi:



$$[C_6H_5N_2]^+Cl^- + Na_2SO_3 \xrightarrow[-NaCl]{\Delta} C_6H_5-N=N-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-SO_3Na$$

natriy fenildiazosulfonati

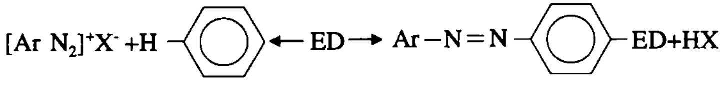
$$\xrightarrow[-H_2SO_4]{H_2SO_3;\ H_2O} \underset{\text{natriy fenilgidrazin sulfonati}}{C_6H_5-NH-NH-SO_3Na} \xrightarrow[-NaHSO_4]{H_2SO_4\ ;\ H_2O}$$

$$\longrightarrow [C_6H_5-NH-NH_3]^+\ O^-\ SO_3H$$

Arilgidrazinlar ba'zi bo'yoq va dori vositalarini olishda, shuningdek, aldegid va ketonlar uchun reagentlar sifatida ishlatiladi.

Azobirikish reaksiyalari

Halqasida kuchli elektronodonor guruh (ED) tutgan aromatik birikmalar (fenollar va arilaminlar) diazoniy tuzlari bilan **azobirikish** reaksiyasiga kirishib, azobirikmalarni hosil qiladi. Bu reaksiyada fenol yoki amin aromatik halqasining vodorodi Ar– N = N – guruhiga almashinadi:



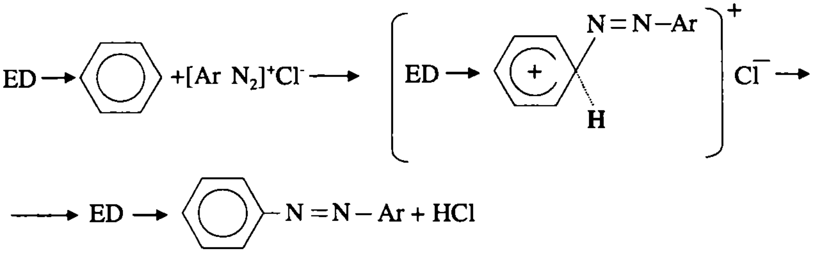
ED= $-O^-$, $-OH$, $-OR$, $-NH_2$, $-NHR$, $-NR_2$

Diazoniy tuzlari kuchsiz elektrofillar bo'lgani bois, kuchli +M-effekt namoyon qiladigan o'rinbosarlari bor fenollar va aminlar bilan reaksiyaga kirishadi:

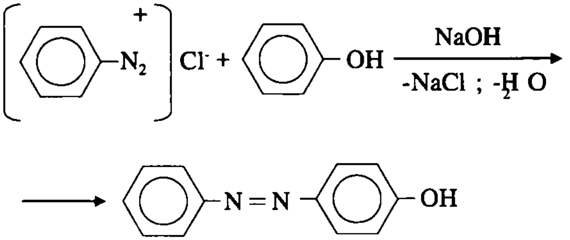
Azobirikish reaksiyalarida almashinish odatda elektronodonor guruhga nisbatan ***para*** – holatda, agar u band bo'lsa, ***orto*** – holatda boradi.

Azobirikish o'z mexanizmiga ko'ra aromatik yadroda boradigan elektrofil almashinish reaksiyalariga kiradi. Diazoniy kationi Ar N_2^+

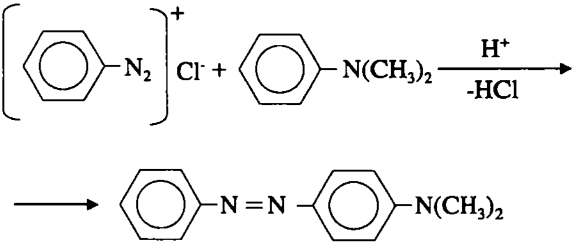
esa musbat zaryadi tufayli elektrofil zarracha rolini o'ynaydi:



Azobirikish reaksiyalari fenollar bilan kuchsiz ishqoriy muhitda , arilaminlar bilan esa kuchsiz kislotali muhitda boradi:



p - gidroksiazobenzol

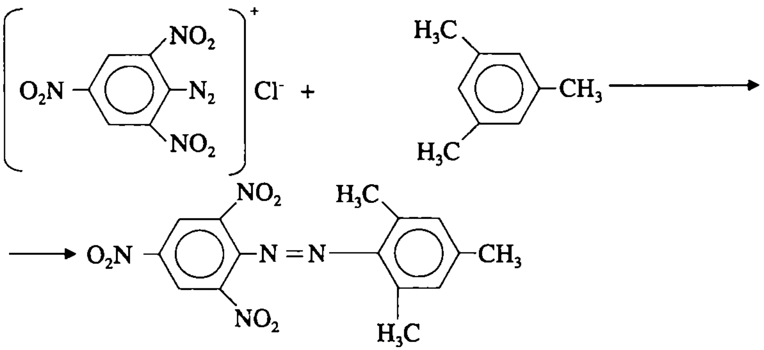


p- dimetilaminoazobenzol

Azobirikish reaksiyalariga kirishadigan fenollar va arilaminlar **azokomponentlar** yoki **azotashkil etuvchilar**, diazoniy tuzlari esa **diazokomponentlar** yoki **diazotashkil etuvchilar** deyiladi.

Azokomponentlar yadrosida elektron zichligi qanchalik katta bo'lsa, azobirikish reaksiyalariga ular shunchalik faol qatnashadi. Shu bois ko'p atomli fenollar, poliaminlar, aminofenollar reaksiyaga juda oson kirishadi.

Aromatik yadrosida diazokation musbat zaryadini oshiradigan elektronoaktseptor o'rinbosarlari bor diazokomponentlar azobirikish reaksiyalarida juda faoldir. Shu bois diazotirlangan pikramid, hatto, mezitilen uglevodorodi bilan ham azobirikish reaksiyasiga kirishadi:



Azobirikish reaksiyalarida muhitning roli katta. Fenollarning azobirikishi kuchsiz ishqoriy muhitda (pH 9 dan 10 gacha) boradi. Bu muhitda fenoldan fenolyat hosil bo'ladi. Fenolyat – ionning to'liq manfiy zaryadga ega kislorod atomi –O- , fenol gidroksiliga nisbatan aromatik halqa elektron zichligini ko'proq oshiradi va uni kuchli faollashtiradi. Shu bois fenolyat-ion azobirikish reaksiyasiga fenolga nisbatan oson kirishadi. Fenollarning azobirikish reaksiyalari kuchli ishqoriy muhitda bormaydi. Chunki kuchli ishqoriy eritmalarda diazoniy tuzlari azobirikish reaksiyalariga kirisha olmaydigan arildiazotatlarga aylanadi.

Aminlarning azobirikish reaksiyalari kuchli kislotali muhitda bormaydi. Chunki kuchli kislotali eritmalarda aminlar arilammoniy tuzlarini hosil qiladi. Bu tuzlarning musbat zaryadli ioni kuchli - J- effekt namoyon qilib, halqadan elektron zichligini tortadi, halqa faolligini behad pasaytiradi.

Diazoniy tuzlari birlamchi va ikkilamchi aromatik aminlar bilan neytral va kuchsiz kislotali eritmalarda azobirikish reaksiyasiga kirishib, 1,3 – diariltriazenlarni hosil qiladi. Masalan, fenildiazoniy xloridi va anilindan natriy atsetati ishtirokida diazoaminobenzol (1,3 – difeniltriazen) hosil bo'ladi:

$$[C_6H_5N_2]^+ Cl^- + C_6H_5NH_2 \xrightarrow[-HCl]{CH_3COONa} C_6H_5-N=N-NH-C_6H_5$$

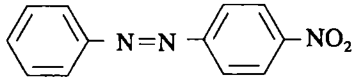
Azobirikmalar

Azobirikish reaksiyalari natijasida hosil bo'ladigan organik moddalar azobirikmalar sinfiga kiritiladi.

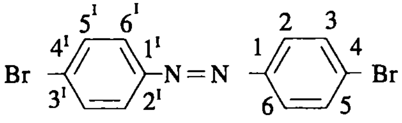
Azobirikmalar molekulasida azoguruh – N=N – ikkita aromatik radikal bilan bog'langan.

Nomlanishi

Unchalik murakkab bo'lmagan azobirikmalar azobenzolning hosilalari deb qaraladi:



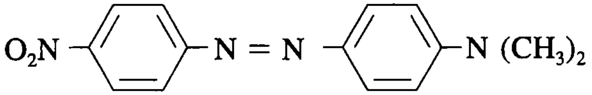
p - nitroazobenzol



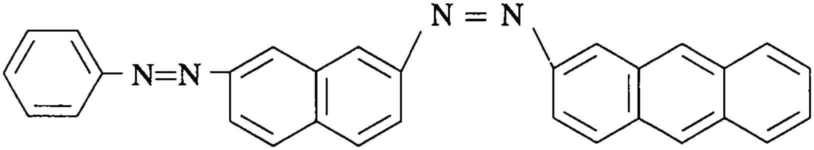
4,4I – dibromazobenzol

Nisbatan murakkab azobirikmalarni nomlashda arilazoguruh

Ar–N=N o‘rinbosar deb qaraladi:



p- (*p* - nitrofenilazo) –N,N – dimetilanilin



2-(7-fenilazo-2-naftilazo) antratsen.

Olinishi

1. Aromatik diazobirikmalarning asosiy olinish usuli azobirikishdir.

2. Birlamchi arilaminlarga aromatik nitrozobirikmalarni ta‘sir ettirish:

$$Ar{-}N{=}O + Ar^{I}\,NH_2 \xrightarrow{\text{asos}} Ar{-}N{=}N{-}Ar^{I} + H_2O$$

3. Nitro va nitrozobirikmalarni qaytarish:

$$Ar{-}NO_2 \xrightarrow{[H]} Ar{-}N{=}N{-}Ar + H_2O$$

$$Ar{-}N{=}O \xrightarrow{[H]} Ar{-}N{=}N{-}Ar + H_2O$$

4. Birlamchi arilaminlarni oksidlash:

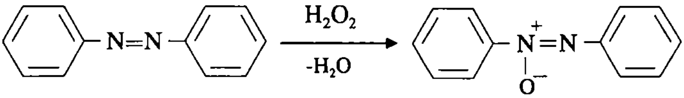
$$Ar{-}NH_2 \xrightarrow{[O]} Ar{-}N{=}N{-}Ar + H_2O$$

Xossalari

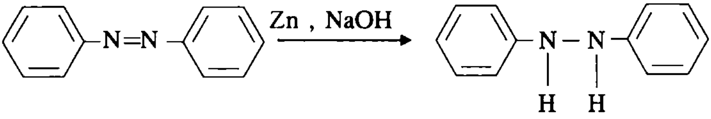
Aromatik azobirikmalarning oddiy vakili azobenzoldir. U 68°C da suyuqlanadigan, suvda erimaydigan, etanol, efir, benzol va xloroformda eriydigan, qizil pushti rangli kristall.

Azobirikmalar molekulasining tuzilishiga qarab sariq, qizil pushti, qizil, ko‘k, hatto yashil rangda bo‘lishi mumkin.

Azobirikmalarni yumshoq sharoitda, masalan, vodorod peroksidi bilan oksidlaganda azobirikmalar, rux va o‘yuvchi natriy bilan qaytarganda esa gidrazobirikmalar hosil bo‘ladi:



azoksibenzol



gidrazobenzol

Kuchli qaytaruvchilar, masalan, qalay (II) – xlorid ta‘sirida azobirikmalar ikkita aminga parchalanadi:

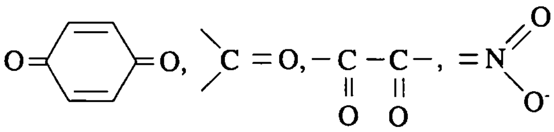
$$Ar-N{=}N-Ar^I \xrightarrow{SnCl_2,\ H^+} Ar-NH_2+H_2N-Ar^I$$

Bu reaksiyadan azobirikmalar tuzilishini aniqlashda foydalaniladi.

Azobo‘yoqlar

Azobo‘yoqlar juda keng tarqalgan va arzon sintetik bo‘yoqlar bo‘lib, azobenzolning hosilalaridir. Sanoatda qo‘llaniladigan bo‘yoqlarning taxminan yarmi azobo‘yoqlardir. Ular o‘simlik, hayvon va sintetik to‘qimalarni, plastmassa, rezina, yog‘och, teri va oziq-ovqat mahsulotlarini bo‘yashda, laklar va poligrafiya bo‘yoqlari tayyorlashda, shuningdek, indikatorlar sifatida ishlatiladi.

Rangli organik moddalar molekulasida **xromofor** (grekcha chroma- rang, phoros- tashuvchi) guruhlar (– N=N–, – N=O



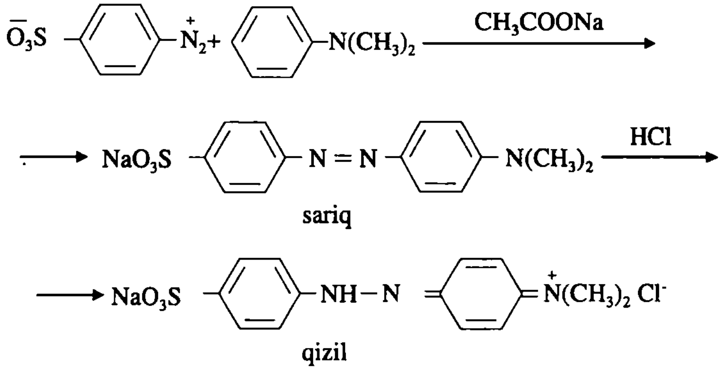
va hokazo) bo`ladi.

Lekin faqat xromofor guruhi bor rangli moddalar bo‘yoq bo‘la olmaydi. Masalan, qizil pushti rangli azobenzolda azoguruh bo‘lgan bilan u boshqa predmetlarni, masalan, to‘qimalarni bo‘yash xususiyatiga ega emas.

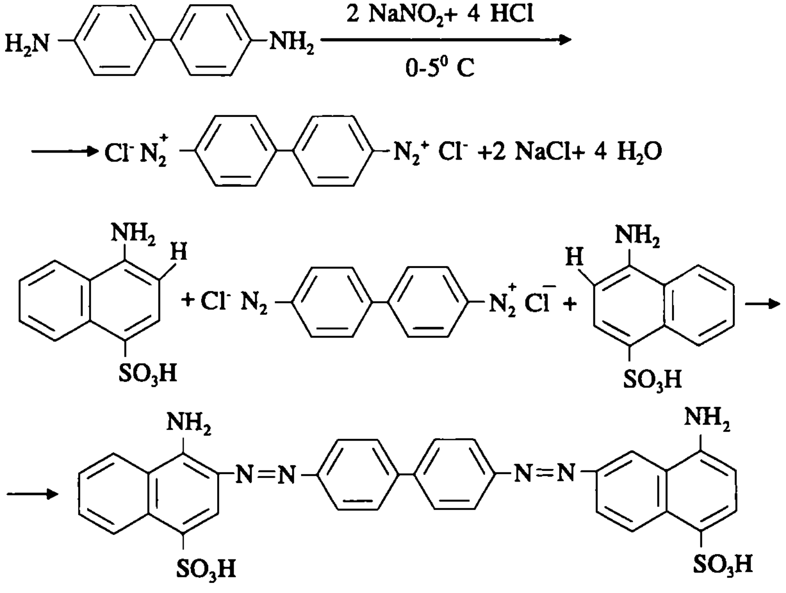
Rangli organik modda bo‘yoq bo‘lishi uchun uning molekulasida xromofor guruhdan tashqari **auksoxrom** (grekcha auxsano – ko‘paytiraman) guruhlar ham bo‘lishi kerak.

Auksoxromlar (-NH_2, - $N(CH_3)_2$, - OH, -SO_3H, -COOH va hokazo) moddalarga xromoforlarsiz rang bera olmaydi, lekin xromoforlar bo‘lganda rangni kuchaytiradi va o‘zgartiradi.

Azobo‘yoqlar molekulasidagi azoguruhning soniga qarab mono-, bis- va poliazobo‘yoqlarga bo‘linadi. *p*- dimetilaminoazobenzol, natriy dimetilaminoazobenzol sulfonati (geliantin, metiloranj) monoazobo‘yoqlardir. Diazosulfanilkislota va dimetilanilindan olinadigan metiloranj kislota – asosli indikator sifatida keng ishlatiladi. U ishqoriy muhitda sariq (benzoidli shakli), kislotali muhitda esa qizil (xinoidli shakli) rangga bo‘yaladi:

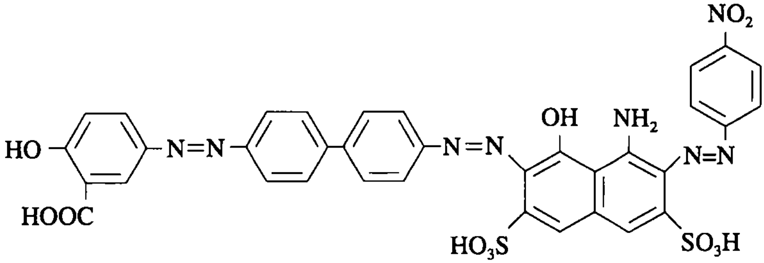


Bis – azobo'yoqlarga misol qilib qizil ***kongoni*** ko'rsatish mumkin. Uni olishda diazotirlangan benzidin 2 mol naftion kislota bilan azobirikish reaksiyasiga kiritiladi:

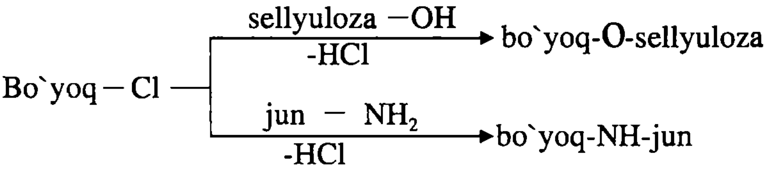


Qizil kongo kislota-asosli indikator xossalariga ega bo'lib, kislota qo'shganda ko'karadi.

Poliazobo'yoqlarga quyidagi yashil rangli bo'yoq misol bo'la oladi:



Faol azobo‘yoqlar bo‘yaladigan material (masalan, paxta va jun tolalari) bilan mustahkam kovalent bog‘larni hosil qiladi. Masalan, harakatchan xlor atomlari bor faol bo‘yoqlar paxta bilan gidroksil, jun bilan esa aminoguruh hisobiga reaksiyaga kirishadi:



$$\text{Bo`yoq}-\text{Cl}\xrightarrow[-\text{HCl}]{\text{sellyuloza}-\text{OH}}\text{bo`yoq-O-sellyuloza}$$

$$\text{Bo`yoq}-\text{Cl}\xrightarrow[-\text{HCl}]{\text{jun}-\text{NH}_2}\text{bo`yoq-NH-jun}$$

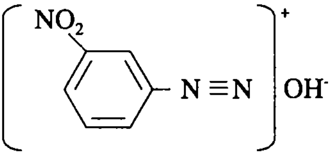
Faol azobo‘yoqlar bilan bo‘yalgan materiallar ochiq rangli bo‘lib, yuvilishga, ishqalanishga va yorug‘lik ta’siriga chidamlidir.

Savol va mashqlar

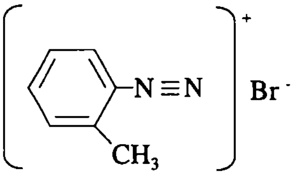
1. Quyidagi birikmalarning tuzilish formulalarini yozing:
a) o-xlorfenildiazoniy xlorid;
b) *p*-metoksifenildiazoniy yodid;
d) *p*-sulfofenildiazoniy gidrosulfat;
e) 4-(*p*-dimetilaminofenilazo) benzosulfokislota;
f) 1-(*o*-tolilazo-1)-2-oksi-4-metilbenzol.

2. Quyidagi birikmalarni nomlang:

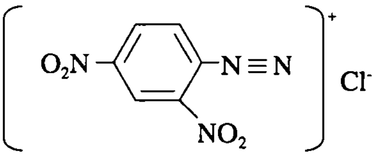
a)



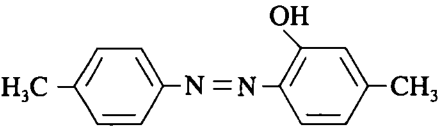
b)



d)



e)



3. Quyidagi diazoniy tuzlarini fenol bilan reaksiyaga kirishish qobiliyatining o‘sib borishi tartibida joylashtiring:

a) fenildiazoniy xloridi; b) *p* - nitrofenildiazoniy xloridi;
d) *m* - tolildiazoniy xloridi; e) *p* - sulfofenildiazoniy xloridi.

4. Quyidagi aminlarning diazotirlash reaksiyalari sxemalarini yozing:

a) sulfanil kislota; b) *p*- metoksianilin;
d) 2,4-dinitroanilin; e) 2,4,6-trinitroanilin;
f) *p* - toluidin; g) *o* - karboksianilin.

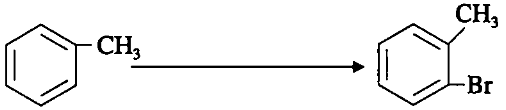
Bu aminlarning qaysilari « to‘g‘ri » va qaysilari « teskari » usul bilan diazotirlanadi?

5. *p* - tolildiazoniy xlorid va boshqa reagentlardan foydalanib , quyidagi birikmalarni sintez qiling:

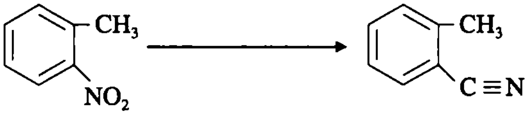
a) *p*- iodtoluol; b) *p*-toluilnitril; d) *p*-ftortoluol;
e) 2,4-dioksi-4^1-metilazobenzol; f) 4-metil-4^1-(N, N-dimetilamino) azobenzol.

6. Diazobirikmalar reaksiyalaridan foydalanib, quyidagi sintezlar sxemalarini tuzing:

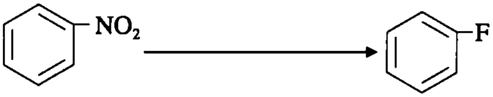
a)



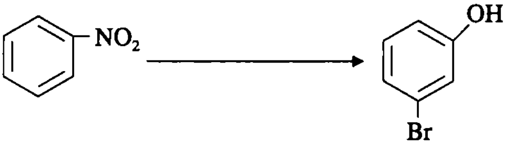
b)



d)

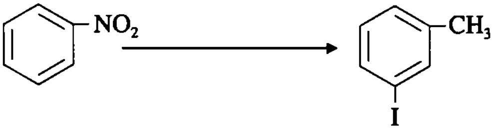


e)



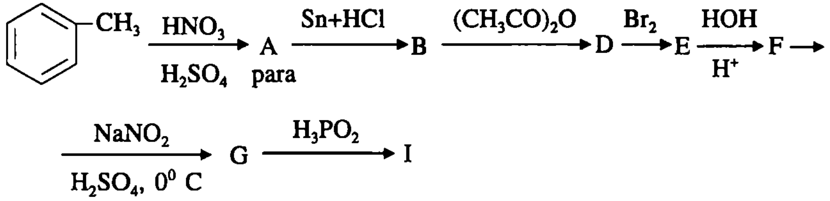
f)

g)

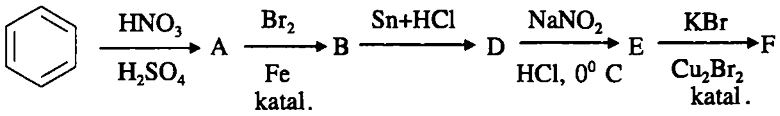


7. Diazobirikmalar reaksiyalaridan foydalanib, quyidagi sxemalardagi oraliq va oxirgi mahsulotlarning tuzilish formulalarini yozing:

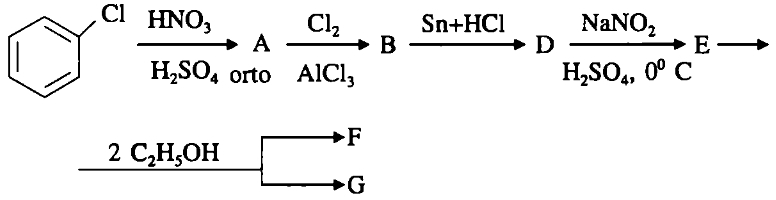
a)



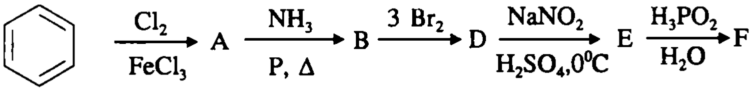
b)



d)



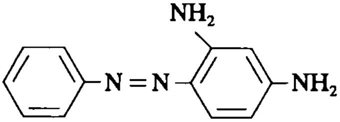
e)



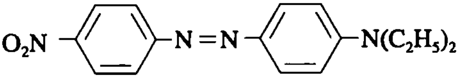
8. Azobirikish reaksiyalarida ko‘p ishlatiladigan diazo- va azokomponentlarga misollar keltiring.

9. Quyidagi azobo‘yoqlarning olinish sxemalarini yozing. Bu bo‘yoqlardagi diazo- va azotashkil etuvchilarni ko‘rsating:

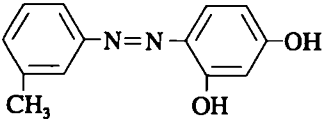
a)



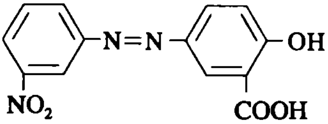
b)



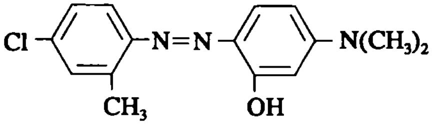
d)



e)

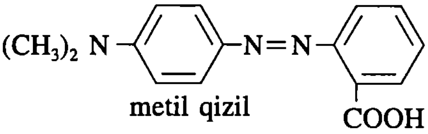


f)



10. Benzol va boshqa reagentlardan foydalanib, quyidagi bo‘yoqlarni sintez qilish sxemalarini yozing:

a) qizil kongo

b) 

metil qizil

Bu bo‘yoqlarning kislota-asosli indikatorlar sifatida ishlatilishini tushuntiring.

GETEROTSIKLIK BIRIKMALAR

XIII. BIR GETEROATOMLI BESH A‘ZOLI GETEROTSIKLIK BIRIKMALAR

Geterotsiklik birikmalar haqida umumiy tushunchalar, ularning sinflanishi va nomlanishi. Bir geteroatomli besh a‘zoli geterotsikllarning tuzilishi. Furan, tiofen, pirrol va ularning hosilalari. Savol va mashqlar.

Geterotsiklik birikmalar haqida tushunchalar

Molekulasida uglerod va boshqa element atomlaridan tuzilgan halqa (sikl) lari bor yopiq zanjirli birikmalarga geterotsiklik birikmalar deyiladi. Halqa tarkibiga kirgan ugleroddan boshqa element (kislorod, azot, oltingugurt, fosfor, vismut, kremniy, germaniy, qalay, qo‘rg‘oshin, simob va hokazo) atomlari **geteroatomlar** (grekcha geteros – boshqa, har xil, turli) deb yuritiladi.

Ko‘pchilik geterotsiklik birikmalar katta amaliy ahamiyatga ega. Ular bo‘yoq sanoatida, qishloq xo‘jaligida, biologiyada, tibbiyotda va boshqa sohalarda keng ishlatiiadi. Qon gemini, yashil o‘simliklarning xlorofili, nuklein kislotalar, alkaloidlar, dori vositalari, bo‘yoqlar, insektitsidlar va boshqa katta ahamiyatga ega birikmalar molekulasida u yoki bu geterotsiklni saqlaydi. Shu bois geterotsiklik birikmalar kimyosi juda tez sur‘atlar bilan rivojlanmoqda.

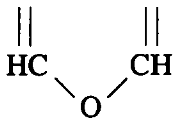
Sinflanishi

Geterotsiklik birikmalar juda turli - tumandir. Kamida ikki valentli har bir element atomi nazariy jihatdan olganda sikl hosil qilishda qatnasha oladi. Geterotsikllar to‘yingan va to‘yinmagan, uch, to‘rt, besh, olti va hokazo a‘zoli , oddiy va kondersirlangan, bir, ikki, uch va hokazo geteroatomli bo‘lishi mumkin.

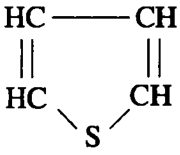
Geterotsiklik birikmalarning muhim guruhlari va ularga kiradigan vakillariga misollar keltiramiz:

Besh a'zoli geterotsikllar:

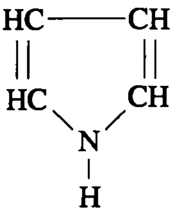
A. Bir geteroatomli :



furan

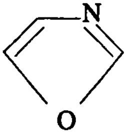


tiofen

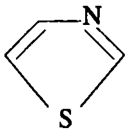


pirrol

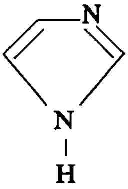
B. Ikki geteroatomli :



oksazol

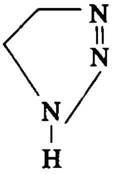


tiazol

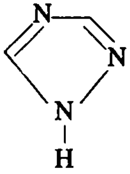


imidazol

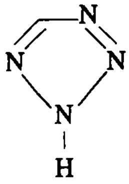
D. Uch va undan ortiq geteroatomli :



1,2,3-triazol



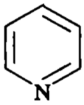
1,2,4-triazol



1,2,3,5-tetrazol

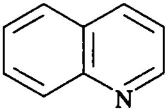
Olti a`zoli geterotsikllar :

A. Bir geteroatomli :



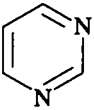
piridin

B. Benzol yadrosi bilan kondensirlangan bir geteroatomli :



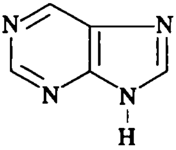
xinolin
(α , β-benzopiridin)

D. Ikki geteroatomli :



pirimidin (1,3-diazin)

Bitsiklik geterotsikllar :



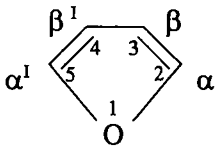
purin
(imidazopirimidin)

Nomlanishi

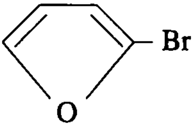
Odatda geterotsiklik birikmalarning yuqorida keltirilgan trivial nomlari keng ishlatiladi .

Bir geteroatomli geterotsiklik birikmalarni ratsional nomenklaturaga ko'ra nomlashda ham tegishli geterotsikllarning trivial nomlari asos qilib olinadi.

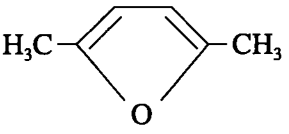
Besh a'zoli geterotsikllarda o'rinbosarlarning holati raqam yoki α, α^1, β, β^1 harflari bilan belgilanadi:



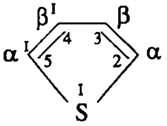
furan



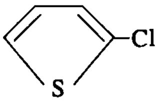
α-bromfuran
yoki 2-bromfuran



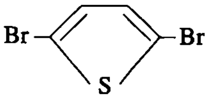
α, α^1-dimetilfuran
yoki 2,5-dimetilfuran



tiofen

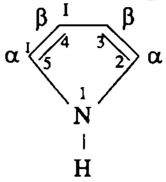


α - xlortiofen
yoki 2 – xlortiofen

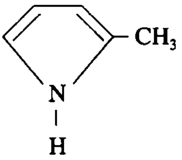


α, α^I – dibromtiofen
yoki 2,5 – dibromtiofen

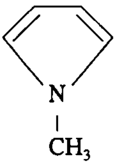
Azot atomi bilan bog`langan o`rinbosarlar oldiga N harfi qo`yiladi:



pirrol

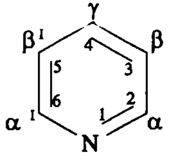


α - metilpirrol
yoki 2 – metilpirrol

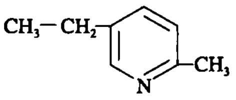


N – metilpirrol

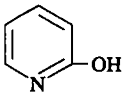
Piridin yadrosidagi uglerod atomlari α, α^I, β, β^I, γ, xinolindagi atomlar esa α, β, γ va o, m, p, a (ana) harflari bilan belgilanadi :



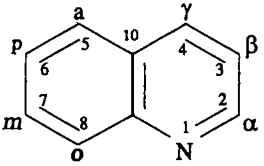
piridin



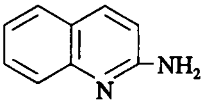
α-metil-β^I–etilpiridin
yoki 2–metil–5-etilpiridin



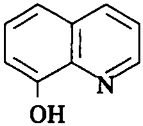
α-gidroksipiridin
yoki 2-gidroksipiridin



xinolin



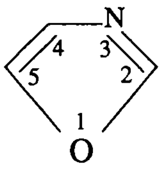
α - aminoxinolin
yoki 2-aminoxinolin



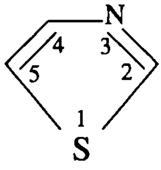
o- gidroksixinolin
yoki 8-gidroksixinolin

Agar geterotsiklik birikmalarda bir necha har xil geteroatom bo‘lsa, raqamlash kislorod atomidan boshlanadi, so‘ngra oltingugurt va azot atomlariga o‘tiladi. Geterotsikllarda NH va uchlamchi azot bo‘lganda 1 raqami bilan NH belgilanadi.

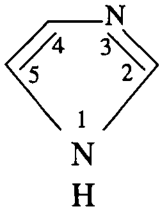
Demak, ikki va undan ortiq har xil geteroatomlari bor geterotsikllar O, S, NH, N tartibiga rioya qilingan holda raqamlanadi:



oksazol



tiazol



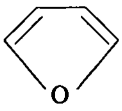
imidazol

IUPAC (sof va amaliy kimyo xalqaro ittifoqi) 1957- yilda geterotsiklik birikmalarning nomenklaturasini ishlab chiqdi .

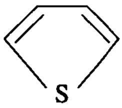
Besh va olti a‘zoli geterosikllar trivial nomlar bilan ataladi.

Bir geteroatomli besh a‘zoli geterotsikllarning tuzilishi

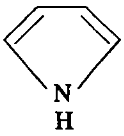
Bir geteroatomli besh a‘zoli geterotsiklik birikmalarning eng oddiy vakillari furan (I), tiofen (II) va pirroldir (III):



I



II



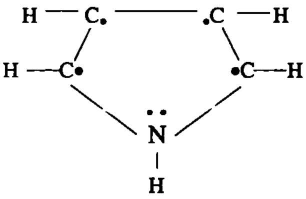
III

Bu formulalarga qaraganda furan dien va oddiy efir, tiofen dien va sulfid, pirrol esa dien va amin xossalariga ega bo‘lishi kerak. Haqiqatda esa ular kutilgan xossalarni namoyon qilmaydi. Tiofen sulfidlardan farqli o‘laroq, odatdagi sharoitda oksidlanmaydi, pirrol esa aminlarining aksicha asos xossalariga deyarli ega emas. Bu geterotsikllar xuddi benzol kabi birikish reaksiyalariga qaraganda nitrolash, sulfolash, galogenlash va boshqa elektrofil almashinish reaksiyalariga oson kirishadi.

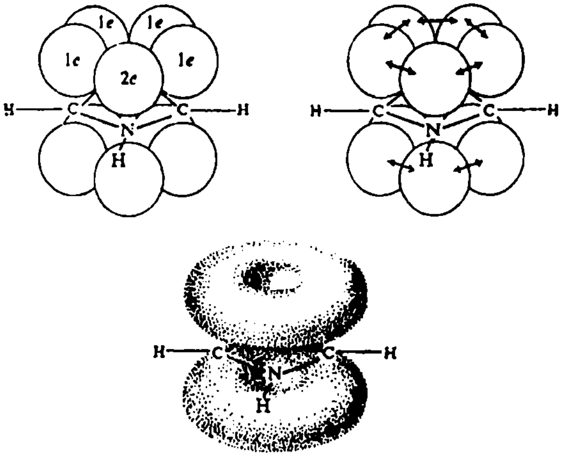
Furan, tiofen va pirrolning aromatik xossalari ular molekulasining o'ziga xos elektron tuzilishi bilan tushuntiriladi. Shu bois ulardan birining , masalan pirrolning elektron tuzilishini qarab chiqamiz.

Pirrol molekulasi tekis tuzilishga ega bo'lib, halqadagi uglerod atomlari ham sp^2 – gibridlangan. Har qaysi uglerod atomi uchta sp^2 – gibrid orbitalidan ikkitasini uglerod-uglerod va bittasini uglerod-vodorod σ - bog'larini hosil qilish uchun sarflaydi. Xuddi , shuningdek, azot atomining uchta sp^2 - orbitalidan ikkitasi azot-uglerod , bittasi esa azot-vodorod σ - bog'ining hosil bo'lishi uchun sarflanadi.

Halqadagi har bir uglerod atomida bittadan, azot atomida esa ikkita (jami oltita) sof p- elektron qoladi:

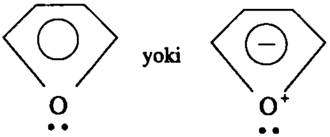


Bu p – elektronlarning bulutlari halqa tekisligining ustiga va ostiga qarab yo'naladi va bir-birini qoplaydi. Natijada benzol molekulasidagi singari molekula tekisligiga perpendikulyar bo'lgan umumiy olti π - elektronli bulut, boshqacha aytganda, yopiq π - elektronli aromatik sekstet hosil bo'ladi (4 - rasm):

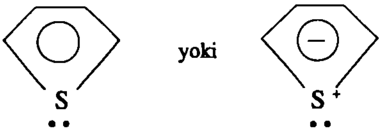


4-rasm. Pirrolning tuzilishi.

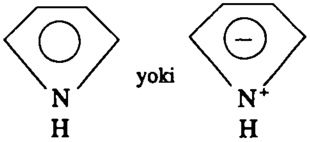
π - elektronlarning bunday delokallashishi geterotsiklni barqaror qiladi. Furan va tiofenning tuzilishi ham pirrolga o'xshaydi. Ularda ham ikkita qo'sh bog'ning to'rtta elektroni va geteroatomning ikkita umumlashmagan p – elektroni hisobidan yopiq π- elektronli sekstet hosil bo'ladi. Demak, yuqorida keltirilgan I , II va III formulalar furan, tiofen va pirrolning haqiqiy tuzilishini tasvirlay olmaydi. Ularning tuzilishini quyidagicha tasvirlasa to'g'ri bo'ladi:



furan



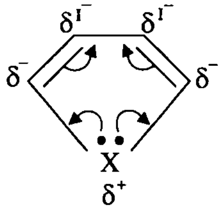
tiofen



pirrol

Furan, tiofen va pirrolda geteroatom p –elektronlarining halqa π - elektronlari bilan o'zaro mezomer ta'sirlashuvga kirishish qobiliyati geteroatomning elektromanfiyligiga bog'liq. Geteroatomning elektromanfiyligi qanchalik kichik bo'lsa, uning halqa π - elektronlari bilan mezomer ta'sirlashuvi shunchalik kuchli bo'ladi. Shuning uchun ham bunday mezomer ta'sirlashuv tiofenda eng kuchli, furanda esa eng kuchsizdir. Shu bois tiofenning mezomeriya (rezonans, delokallashish yoki barqarorlik) energiyasi (130,2 kJ/ mol) benzolnikiga (150,8 kJ/ mol) yaqin va barcha besh a'zoli geterotsikllardan o'z xossalari bilan benzolga eng yaqin turadigani ham tiofendir. Aksincha, furanning mezomeriya energiyasi (92,4 kJ/ mol) benzolnikidan ancha kam. Shuning uchun ham u ba'zi reaksiyalarda aromatik birikmalardan ko'ra alifatik dien xossalarini ko'proq namoyon qiladi. Pirrolning mezomeriya energiyasi 109,2 kJ/ mol ga teng. Benzoldan farqli o'laroq , bu geterotsikllar dipol momentiga ega. Furanning dipol momenti 0,70 D ga, tiofenniki 0,55 D ga, pirrolniki esa 1,80 D ga teng. Geteroatom dipolning musbat qutbi, geteroatom p-elektronlarini o'ziga tortgan geterotsiklning uglevodorod qismi esa manfiy qutbidir.

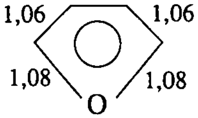
Pirrolda dipolning musbat qutbi azot atomida emas, balki N-H guruhining elektromanfiyligi kichik bo'lgan vodorod atomida to'plangan. Shuning uchun pirrolning dipol momenti katta bo'lib, undagi N H guruh vodorodi ishqorlar ta'sirida metallga almashina oladi. Benzoldan farqli o'laroq, geterotsiklik birikmalarda elektron bulutining zichligi bir tekisda tarqalmagan. Bir geteroatomli besh a'zoli geterotsikllarda elektron bulutining zichligi geteroatomdan halqaga tomon siljigan bo'lib, α - holatda joylashgan uglerod atomlarida ko'proq to'plangan. Shu bois furan, tiofen va pirrol halqalari benzolga nisbatan oshirilgan elektron zichligiga ega va ular elektrofil almashinish reaksiyalariga oson kirishadi. Geteroatomga nisbatan α - holatda joylashgan uglerod atomlarida elektron zichligi katta bo'lganidan elektrofil reagentlarning hujumi birinchi navbatda shu atomlarga qaratiladi, boshqacha aytganda, elektrofil almashinish reaksiyalari α - uglerod atomlarida eng oson boradi:

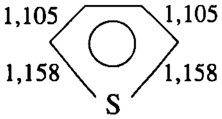


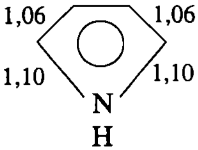
X= O, S , NH

$\delta^- > \delta^I$

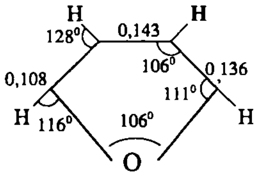
Furan, tiofen va pirrolda π-elektron zichligi quyidagicha taqsimlangan:

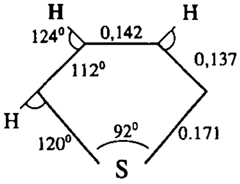


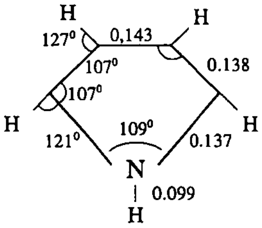




Geteroatom umumlashmagan elektron jufti bilan halqa π - elektronlari orasidagi p, π- tutashish bog'laming uzunligiga ta'sir qiladi. Shu bois furan, tiofen va pirrol bog'lari odatdagi C – C, C – O, C – C, C – N bog'laridan qisqa, C = C qo'sh bog'iga nisbatan esa uzun:



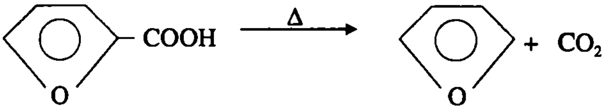




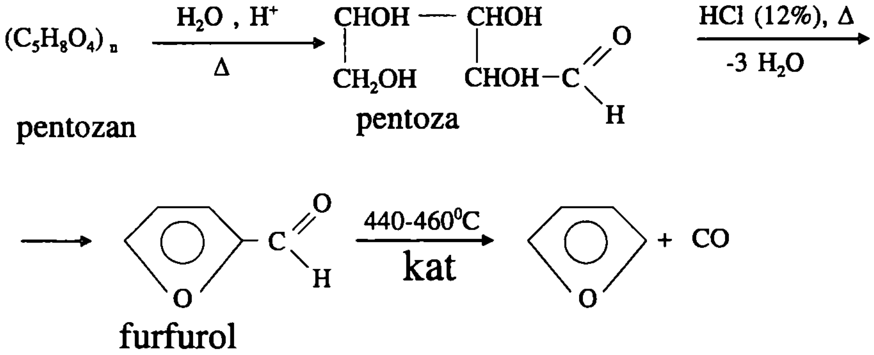
Furan va uning hosilalari

Furan xloroform hidli, rangsiz, harakatchan suyuqlikdir. U 31°C da qaynaydi, suvda erimaydi, havoda oksidlanib qorayadi.

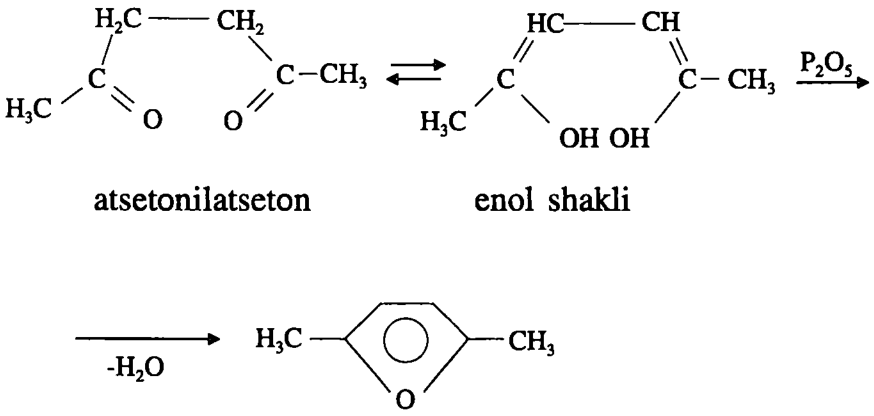
Olinish usullari. 1. Piroshilliq (furan-2-karbon) kislotani mis katalizatori ishtirokida dekarboksillash bilan olish:



2. Furfurol 440 – 460°C da, katalizator (rux va temir xromitlari, marganets, xrom va rux oksidlari aralashmasi) ishtirokida dekarbonillanib furanga aylanadi. Furfurol olish uchun tarkibida pentozan bo'lgan xom ashyo (yog'och, kepak, somon, kungaboqar po'chog'i, makkajo'xori so'tasi va boshqa qishloq xo'jaligi chiqindilari) suyultirilgan H_2SO_4 yoki H_3PO_4 ishtirokida qizdiriladi

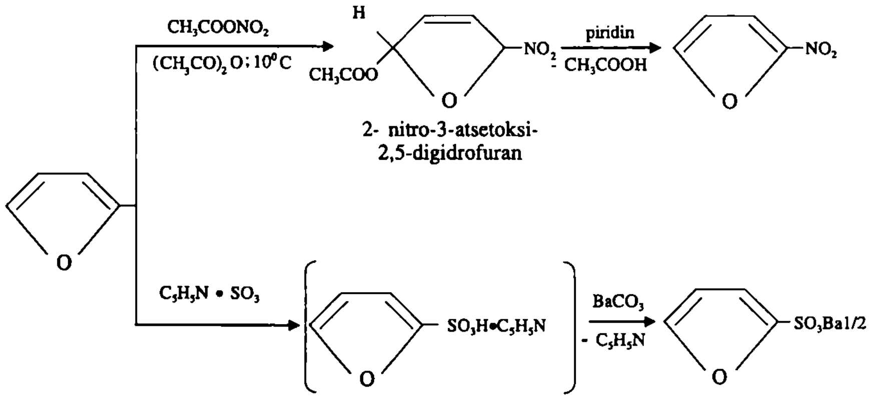


3. Furan gomologlari 1,4 – diketonlarni $ZnCl_2$, P_2O_5 yoki H_2SO_4 ishtirokida degidratlash bilan olinadi:

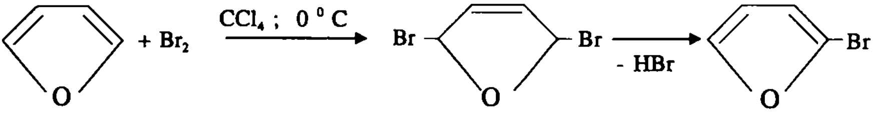


Kimyoviy xossalari. Furan elektrofil almashinish va birikish reaksiyalariga, shuningdek, halqaning ochilishi hamda kislorodning almashinishi bilan boradigan reaksiyalarga kirisha oladi.

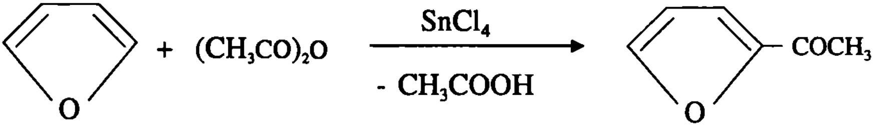
Furan halqasi ishqorlar ta'siriga chidamli, ma'dan kislotalar ta'sirida esa oson parchalanadi. Shuning uchun ham furanni nitrolashda nitrat kislota o'rniga atsetilnitrat, sulfolashda esa sulfat kislota o'rniga piridinsulfotrioksid ishlatiladi:



Furanni galogenlash nitrolash singari oraliq birikish mahsulot-larining hosil bo'lishi orqali boradi:

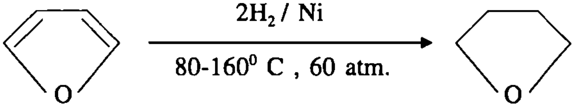


Furanni atsetillash $SnCl_4$, $ZnCl_2$, BF_3, I_2, HI, $HClO_4$ yoki Mg $(ClO_4)_2$ ishtirokida oson boradi



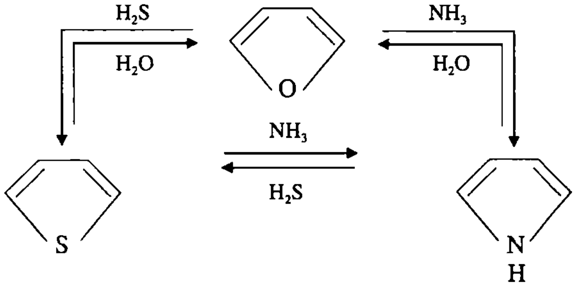
2 - atsetilfuran

Uni katalitik gidrogenlaganda tetragidrofuran (TGF) hosil bo‘ladi:



TGF - alifatik oddiy efir xossalariga ega. Furandan farqli o‘laroq, u aromatik xossalarni namoyon qilmaydi.

Furan 400 – 450⁰ C da Al_2O_3 ishtirokida vodorod sulfid bilan reaksiyaga kirishib tiofen, ammiak bilan esa pirrol hosil qiladi. Bu reaksiyalarda halqadagi kislorod oltingugurt va azotga almashadi.Furan, tiofen va pirrolning yuqori haroratda Al_2O_3 ishtirokida bir-biriga aylanishi quyidagicha sxema bo‘yicha boradi (Yu. K. Yuryev reaksiyasi)



Furfurol. U sanoatda yog‘och, kepak va tarkibida pentozan bo‘lgan qishloq xo‘jaligi chiqindilarini kislotali gidroliz qilib olinadi (220 - bet).

Furfurol - yangi yopilgan non hidli suvda yomon eriydigan rangsiz suyuqlik. 162⁰ C da qaynaydi, havoda oson oksidlanadi va qora smolaga aylanadi. U furanning eng muhim hosilasi bo‘lib, kimyoviy xossalari jihatdan benzoy aldegidga o‘xshaydi.

Furan birikmalarining amaliy ahamiyati. Furan birikmalari neftni qayta ishlash va oziq-ovqat sanoatida keng qo'llaniladi.

TGF sellyuloza efirlari, sintetik smolalar, sintetik kauchuklar va polivinilxloridning inert erituvchisi sifatida, shuningdek, naylon va kapron ishlab chiqarishda qo'llaniladi.

Furan birikmalari bilan malein angidridi yoki butadien –1,3 dan samarali ta'sir qiladigan repellentlar (zararli hasharotlarga qarshi ishlatiladigan vositalar) olinadi.

Ayrim furan birikmalarining simobli va bisulfitli hosilalari begona o'tlarga qarshi kurashda ishlatiladi.

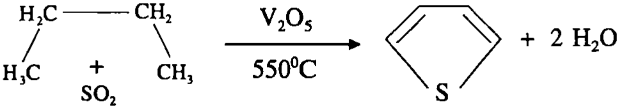
Furan qatorining bir necha nitrohosilalari - kuchli bakteritsid ta'siriga ega.

Furfurol surkov moylarini to'yinmagan va aromatik tabiatli qo'shimchalardan tozalashda, baliqlar jigaridan A vitaminini ekstraktsiya qilishda, erituvchi sifatida, shuningdek, furan qatori birikmalari, adipin kislota, geksametilendiamin va boshqa moddalarni olishda xom ashyo sifatida ishlatiladi.

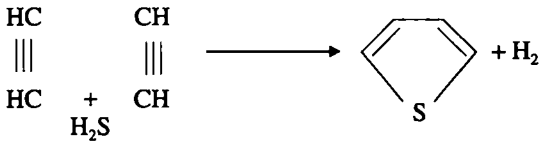
Tiofen va uning hosilalari

Tiofen 84⁰C da qaynaydigan, benzol hidli, suvda erimaydigan rangsiz suyuqlik.

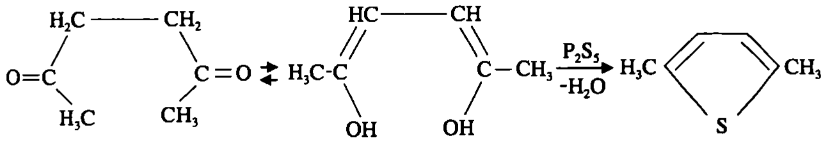
Olinish usullari. 1. Sanoatda tiofen butan va sulfit angidrid bug'ini katalizator (Cr_2O_3 , Mo_2O_3 , V_2O_5) to'ldirilgan va 550⁰C gacha qizdirilgan naydan o'tkazish bilan olinadi:



2. Atsetilen bilan vodorod sulfid 400 – 450⁰C gacha qizdirilgan alyuminiy oksid ustidan o'tkazilganda tiofen hosil bo'ladi (A. E. Chichibabin):



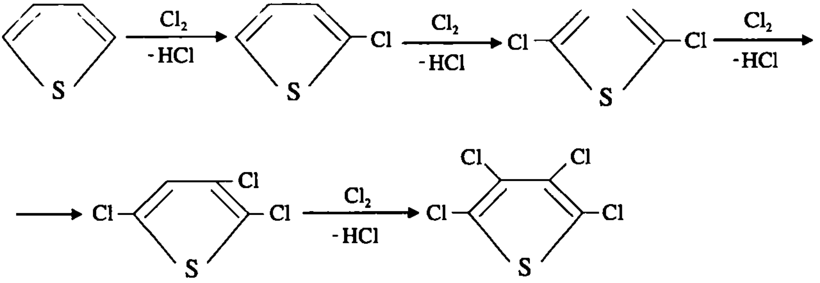
3. Tiofen va uning gomologlarini sintez qilish uchun 1,4 – dikarbonil birikmalar P_2S_5 bilan qizdiriladi:



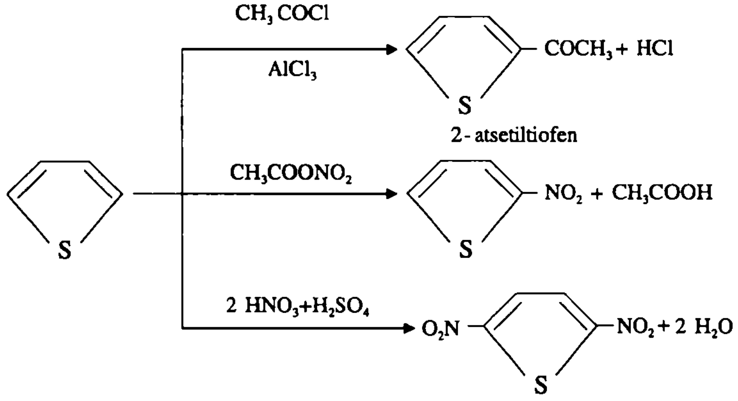
2,5 –dimetiltiofen

Kimyoviy xossalari. Tiofen furandan farqli o‘laroq havoda o‘zgarmaydigan, kislotalar va oksidlovchilar ta‘siriga chidamli, xossalari jihatdan benzolga eng yaqin barqaror aromatik birikmadir. U elektrofil almashinish reaksiyalariga kirishish xususiyati jihatdan furan bilan benzol oralig‘idagi holatni egallaydi. Tiofen bu reaksiyalarga benzolga nisbatan bir necha marta tez kirishadi. U oson galogenlanadi.

Qo‘llaniladigan xlorning miqdoriga qarab, mono-, di-, tri-, va tetraxlortiofenlar aralashmasi hosil bo‘ladi:



Tiofen $SnCl_4$, $AlCl_3$ yoki VF_3 katalizatorligida kislotalarning angidridlari yoki xlorangidridlari bilan Fridel – Krafts bo‘yicha atsillash, nitrolovchi aralashma yoki atsetilnitrat bilan esa nitrolash reaksiyalariga kirishadi:



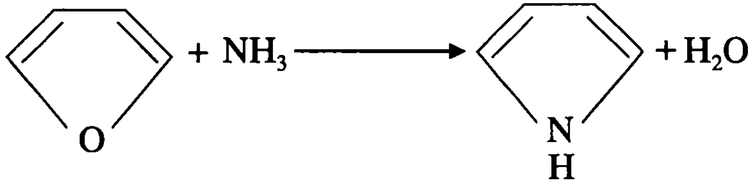
Tiofen hosilalari tioindigo va boshqa bo'yoqlar, plastifikatorlar, analitik reagentlar, insektitsidlar ishlab chiqarishda qo'llaniladi.

Pirrol va uning hosilalari

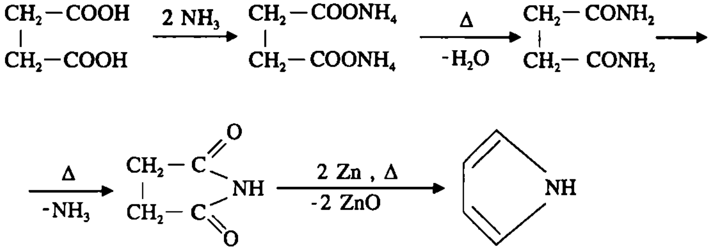
Pirrol 130°C da qaynaydigan, suvda erimaydigan, rangsiz suyuqlik. U havoda tez oksidlanib, smolaga aylanadi. Pirrol toshko'mir smolasi va suyak moyi (suyakni quruq haydab olinadi) tarkibida bo'ladi.

Xlorid kislota bilan ho'llangan archa cho'pini pirrol bug'i qizil rangga bo'yagani uchun, unga pirrol (grekcha *pir* – olov demakdir) deb nom berilgan.

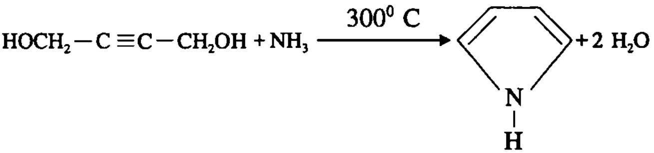
Olinish usullari. 1. Sanoatda pirrol furan va ammiak bug'larini 400° C gacha qizdirilgan alyuminiy oksidi ustidan o'tkazish (Yu. K. Yuryev reaksiyasi) bilan olinadi:



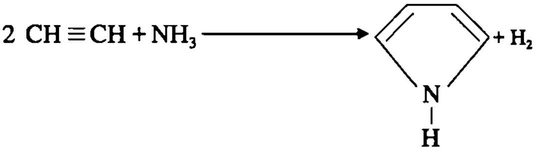
2. Qahrabo kislota va ammiakdan olish :



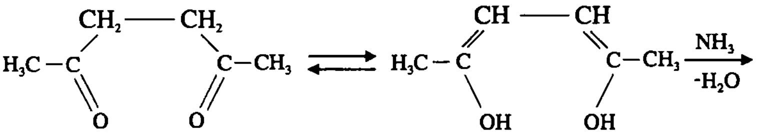
3. Katalizator (alyuminiy va toriy oksidlari aralashmasi) ishtirokida butin – 2 – diol – 1,4 va ammiakdan olish :



4. Atsetilen va ammiakni qizdirilgan Fe_2O_3 ustidan o`tkazish bilan olish :



5. Pirrol gomologlari 1,4 – diketonlarni ammiak bilan qizdirib (Paal – Knorr sintezi) olinadi :



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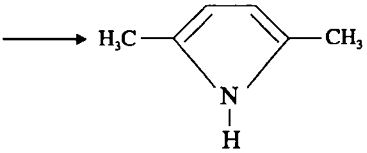
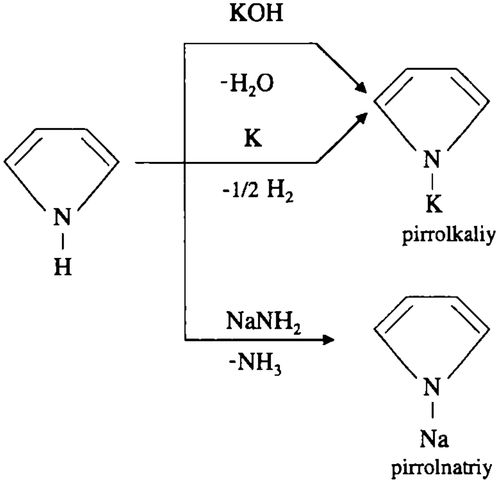
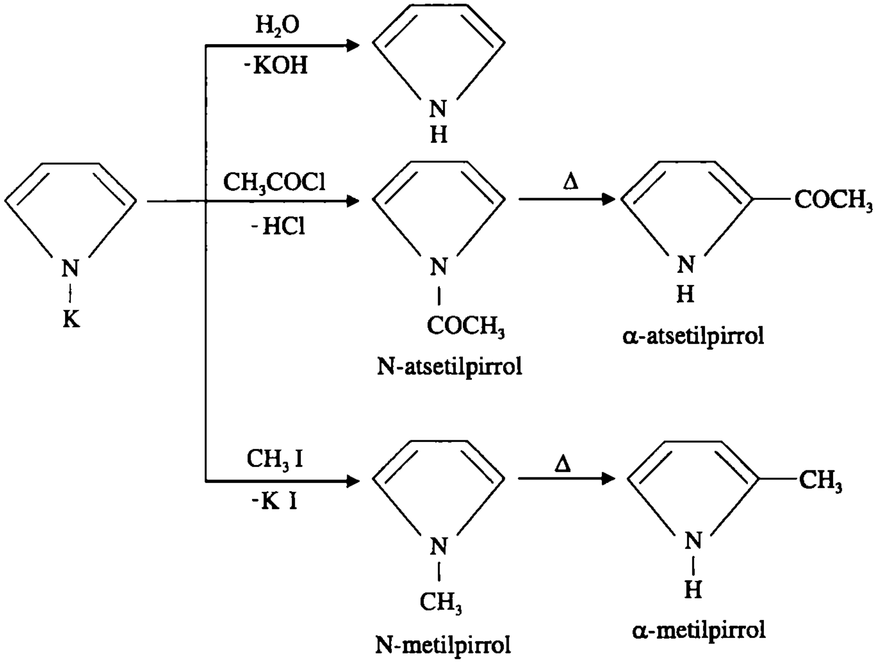


2,5-dimetiltiofen

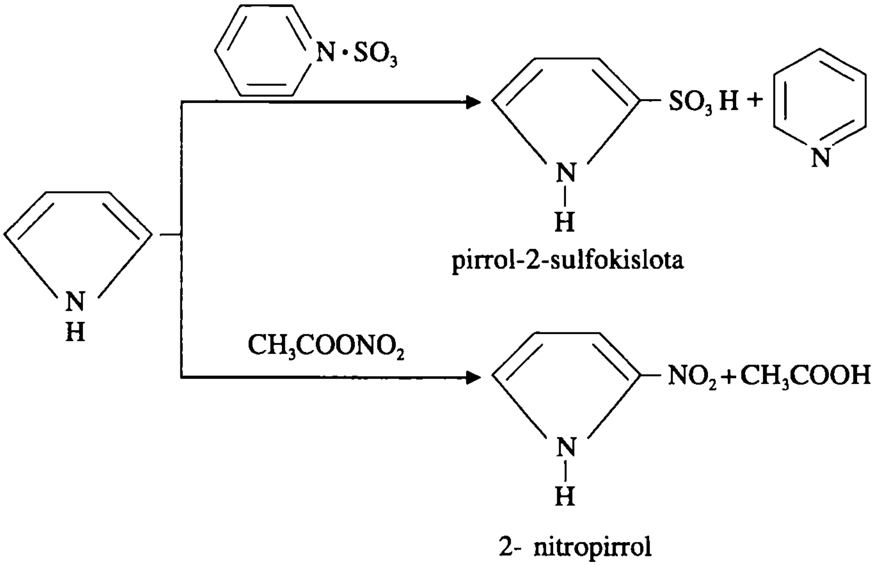
Kimyoviy xossalari. Pirrol asos xossalariga deyarli ega emas. Uning imino guruhi vodorodi juda kuchsiz kislota xossalariga ega bo'lib, kaliy, natriy, litiy singari metallarga almashinadi va pirrolning tuzlari hosil bo'ladi:



Pirrolkaliy qattiq modda bo'lib, suv bilan reaksiyaga kirishganida pirrol, galogenalkanlar bilan – N- aikilpirrollar, kislota xlorangidridlari ta'sirida esa N – atsilpirrollarni hosil qiladi. Agar reaksiyalar qizdirish bilan olib borilsa, N – atsil – va N – alkilpirrollar qayta guruhlanadi, ya'ni alkil va atsil guruhlari azot atomidan α - uglerod atomiga o'tadi:



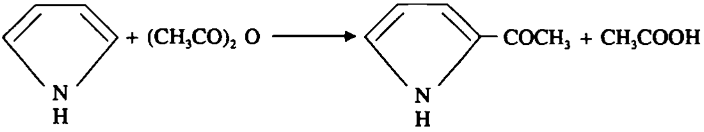
Pirrol va uning hosilalari aromatik xossalarni yaqqol namoyon qiladi. U o‘z xossalari bilan fenolga o‘xshaydi. Elektrofil almashinish (sulfolash, nitrolash, galogenlash, azobirikish va hokazo) reaksiyalariga oson kirishadi. Pirrol furan singari kislotalar ta‘siriga juda sezgir («atsidofob») bo‘lgani uchun uni odatdagi sulfolovchi va nitrolovchi reagentlar bilan sulfolab yoki nitrolab bo‘lmaydi. Sulfolovchi agent sifatida N– piridinsulfotrioksid yoki dioksansulfotrioksid (A. P. Terentev) ishlatiladi. Atsidofob geterotsiklik birikmalarni sulfolashda qo‘llaniladigan N-piridinsulfotrioksid va dioksansulfotrioksid neytral moddalar bo‘lib, reaksiya vaqtida dastlabki komponentlarga parchalanadi va sulfolaydi. Pirrolni nitrolashda atsetilnitrat (nitrat kislota bilan sirka angidridning aralashmasi) ishlatiladi:



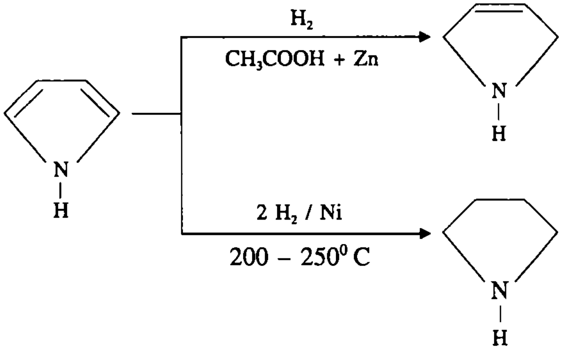
Pirrolni galogenlashda , masalan , iodlashda dastlab 2-iodpirrol, so'ngra esa 2,3,4,5 – tetraiodpirrol hosil bo'ladi:

2,3,4,5 – tetraiodpirrol barqaror, sariq kristall modda bo'lib, tibbiyotda *iodol* nomi bilan antiseptik sifatida ishlatiladi.

Pirrolni atsetillash juda oson va katalizatorsiz boradi:



Pirrol furanga nisbatan qiyin qaytariladi. U qaynoq spirtda natriy bilan qaytarilmaydi. Uni rux kukuni va sirka kislota bilan gidrogen-langanda 3 – pirrolin (2,5 – digidropirrol), Ni yoki Pt katalizatori ishtirokida vodorod bilan qaytarganda esa pirrolidin hosil bo'ladi:



3 – pirolin 90^0 C da, pirrolidin esa 87 – 88^0 C da qaynaydigan suyuqlikdir.

3 – pirrolinning hosil bo'lishi pirrolning qisman diyenli xarakterga ega ekanligini ko'rsatadi.

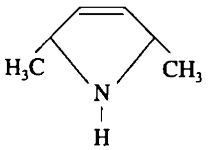
Pirrolidin molekulasidagi azot atomida erkin elektron jufti borligi uchun u aminlar singari asos xossalariga ega. Pirrolidin pirrolga nisbatan 10^{14} marta kuchli asos hisoblanadi.

Savol va mashqlar

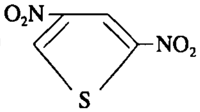
1. Quyidagi birikmalarning tuzilish formulalarini yozing:
a) α , β^1 – dimetilfuran; b) 2,4 – dimetiltiofen;
d) metil- α - furilketon ; e) 5,7 –dimetil-3-etilindol;
f) β - uchlamchi butiltetragidrotiofen;
g) pirrolidin - α -karbon kislota;
h) 3 – (2-aminoetil) indol; i) piroshilliq kislotaning metil efiri.
j) 5 – nitroindol-2- karbon kislota;

2.Quyidagi birikmalarni ratsional nomenklaturaga binoan nomlang:

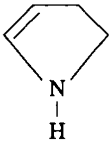
a)



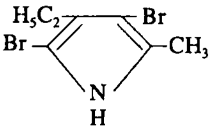
b)



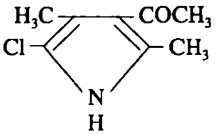
d)



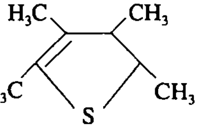
e)



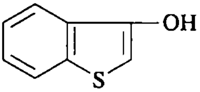
f)



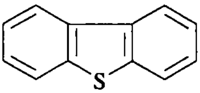
g)



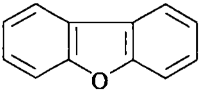
h)



i)



j)



3. Quyidagi sintezlar sxemalarini tuzing:

a) anilin ⟶ 3 - metilindol

b) atsetosirkaefir ⟶ 2,5 - dimetiltiofen

d) o – nitrotoluol ⟶ 6,6 – dibromindigo

4. Quyidagi sintezlar sxemalarini tuzing:

a) etanol ⟶ furan

b) metanol ⟶ tetragidrofuran

d) anilin ⟶ ko‘k indigo

5. Quyidagi birikmalarni elektrofil almashinish reaksiyalariga oson kirishish xossasining kuchayib borishi tartibida joylashtiring:

a) mezitilen; b) anilin; d) benzol; e) furan;

f) benzoy kislota; g) pirrol; h) tiofen.

6. Quyidagi reaksiyalar tenglamalarini yozing. Oraliq va oxirgi mahsulotlarni nomlang:

$$\text{pirrol} \xrightarrow[\text{efir}]{CH_3MgI} A \xrightarrow{CH_3COCl} B \xrightarrow{NH_2OH} D \xrightarrow[\text{TGF}]{LiAlH_4} E$$

7. Pirrolning atsidofob xossalarini tushuntiring.

8. Furan va tiofenning aromatik xossalari qanday reaksiyalarda namoyon bo'ladi?

9. Furfurolning aromatik yadrosi va aldegid guruhi hisobidan boradigan reaksiyaiarga misollar keltiring.

10. Furan, tiofen, pirrol va ularning hosilalari qanday maqsadlarda ishlatiladi?

XIV. IKKI VA UNDAN ORTIQ GETEROATOMLI BESH A‘ZOLI GETEROTSIKLLAR (AZOLLAR)

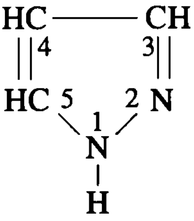
Pirazol va imidazol. Ularning tuzilishi, olinishi, xossalari va hosilalari.

Triazollar, tetrazollar.

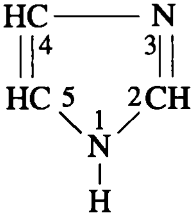
Oksazol, tiazol va ularning hosilalari.

Savol va mashqlar.

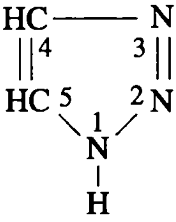
Bu azollardan quyidagilar katta ahamiyatga ega :



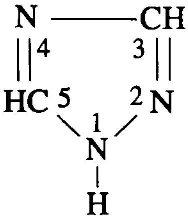
pirazol
(1,2-diazol)



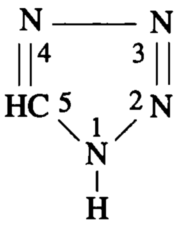
imidazol
(1,3-diazol)



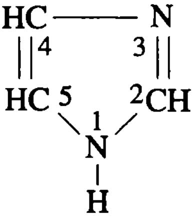
1, 2, 3 – triazol



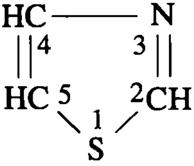
1, 2, 4 – triazol



tetrazol



oksazol



tiazol

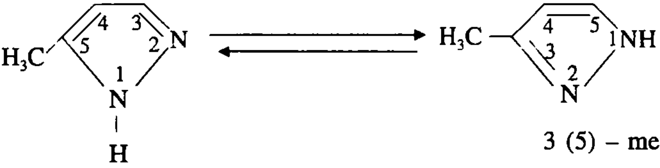
Pirazol va imidazolning tuzilishi

Pirazol va imidazolda uchta uglerod atomining bittadan uchta elektroni hamda ikkita azot atomining uchta elektroni hisobidan yopiq π - elektronli sekstet hosil bo'ladi. Shu bois bu geterotsikllar aromatik xossalarni namoyon qiladi.

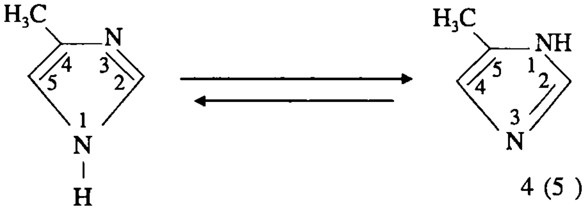
Pirazol va imidazolning tuzilish formulalariga qaraganda, ular halqasidagi azot atomlaridan bittasi piridinning azot atomiga, ikkinchisi esa pirrolning azot atomiga o'xshaydi.

Bunday tuzilishda 3- va 5- almashingan pirazollar, shuningdek, 4- va 5- almashingan imidazollar mavjud bo'lishi kerak. Lekin pirazol va imidazoldagi harakatchan vodorod atomi bir azot atomidan boshqasiga tez o'tib turganligi sababli bunday izomerlar hosil bo'lmaydi.

Pirazol va imidazol molekulalaridagi har ikkala azot atomi teng qiymatli. Shuning uchun ham pirazoldagi 3- va 5 - , imidazoldagi 4- va 5- holatlar amalda bir-biridan farq qilmaydi. Shu bois pirazolning 3- va 5- uglerod atomlaridagi almashinish 3 (5) – yoki 5 (3) – almashinish, imidazolning 4- va 5- holatlaridagi almashinish esa 4(5)- yoki 5(4)- almashinish deb belgilanadi:



3 (5) – metilpirazol



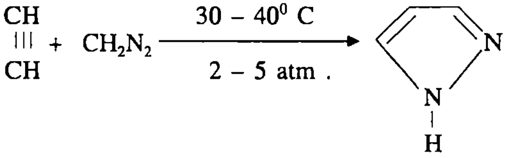
4 (5) – metilimidazol

Pirazol va imidazol halqalarining aromatik xarakteri ularning oksidlovchilar ta'siriga chidamliligida, birikish reaksiyalariga moyil emasligida, shuningdek, elektrofil almashinish reaksiyalariga oson kirishishida namoyon bo‘ladi. Pirazolda ham, imidazolda ham elektrofil almashinish halqaning 4 - holatida boradi.

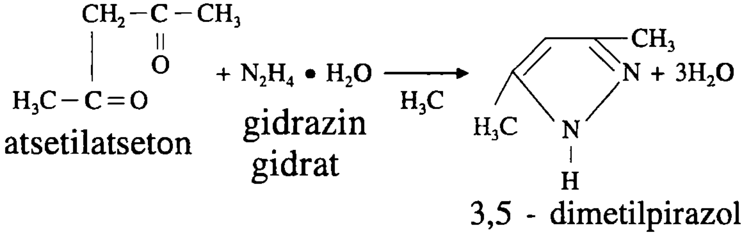
Pirazol va uning hosilalari. Pirazol 69°C da suyuqlanadigan, suvda, spirtda, efirda va benzolda yaxshi eriydigan piridin hidli kristall modda. Pirazol va uning hosilalari tabiatda topilmagan.

Pirazollar quyidagi reaksiyalar bilan olinadi:

1. Alkinlarga diazometan birikkanda pirazollar hosil bo‘ladi



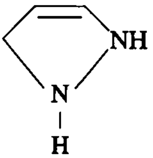
2. Pirazol gomologlari 1,3 – dikarbonil birikmalar va gidrazin yoki uning hosilalaridan sintez qilinadi:



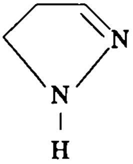
Pirazol kuchsiz asos va kuchsiz kislota xossalarini namoyon qiladi. Uning azot bilan bog‘langan vodorod atomi ishqoriy metallarga, magniy va kumushga oson almashinadi.

Pirazolni sulfolash juda qattiq sharoitda boradi. 3 – metilpirazolni 20% li oleumda 6 soat davomida 100° C gacha qizdirganda sulfoguruh 4 – holatga kiradi : Pirazolni nitrolash ham qattiq sharoitda boradi.

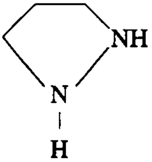
Pirazolni qisman qaytarganda pirazolinlar, to‘liq qaytarganda esa pirazolidin hosil bo‘ladi:



3 –pirazolin



2 –pirazolin



pirazolidin

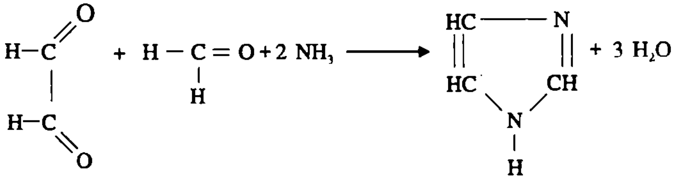
Pirazolinlar reaksiyaga kirishish qobiliyati kuchli birikmalardir.

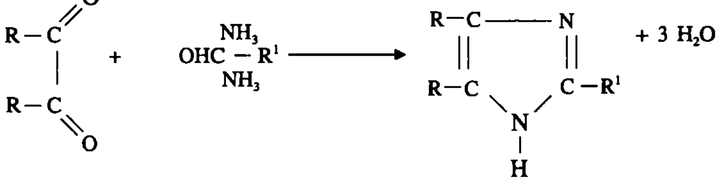
Pirazol hosilalari dori preparatlari (piramidon, analgin, arisul), bo'yoqlar, insektitsidlar sifatida va boshqa maqsadlarda ishlatiladi.

Imidazol va uning hosilalari. Imidazol 90°C da suyuqlanadigan kristall modda, suvda yaxshi, qutbsiz organik erituvchilarda yomon eriydi.

Pirazoldan farqli o'laroq imidazol o'zining hosilalari (gistidin va gistamin aminokislotalari, alkaloidlar, purin birikmalari) holida o'simlik va hayvonot dunyosida keng tarqalgan bo'lib, muhim biologik rol o'ynaydi.

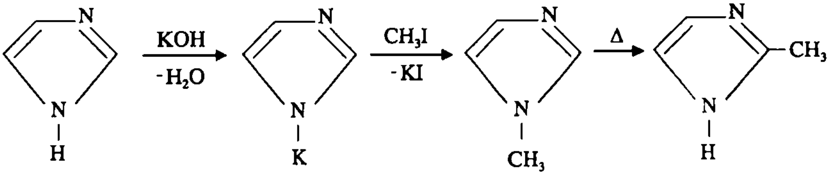
Imidazol glioksil, ammiak va formaldegiddan, uning gomologlari esa 1,2 – dioksobirikmalar, aldegidlar va ammiakdan olinadi:





Imidazol ammiakka nisbatan kuchsiz, lekin piridinga nisbatan kuchli asosdir. U kuchli kislotalar bilan reaksiyaga kirishib, gidrolizlanmaydigan qattiq tuzlarni hosil qiladi.

Shu bilan bir qatorda imidazol kislotali xossalarni ham namoyon qiladi. Uning N – H guruhi vodorodi metallarga oson almashinadi. Imidazolning metalli hosilalari esa galogenalkanlar bilan reaksiyaga kirishib, N – alkilimidazol hosii qiladi. N - alkilimidazol qizdirilganda 2 – alkilimidazolga qayta guruhlanadi:

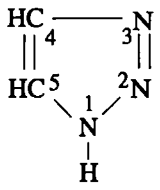


Imidazol kaliy N-metil-imidazol 2-metil - imidazol

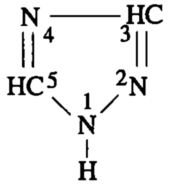
Imidazol aromatik birikmalar singari elektrofil almashinish reaksiyalariga kirishadi. Uni bromlaganda 4 (5) – bromimidazol, nitrolovchi aralashma ta'sirida 4 (5) – nitroimidazol, tutovchi sulfat kislota bilan sulfolaganda esa 4 (5) –imidazolsulfokislota hosil bo'ladi.

Imidazol hosilalari - katta amaliy ahamiyatga ega. Uning hosilalari dibazol, priskol, nirvanol (difenin) kabi muhim dorilar hisoblanadi. Imidazol qiyin sovunlanadigan kislota efirlari va amidlarining gidrolizlanish reaksiyalarida katalizator sifatida qo'llaniladi.

Triazollar. Halqasidagi uchta azot atomining joylashishiga qarab 1, 2, 3 – triazol (I) va 1, 2, 4 – triazol (II) farqlanadi:

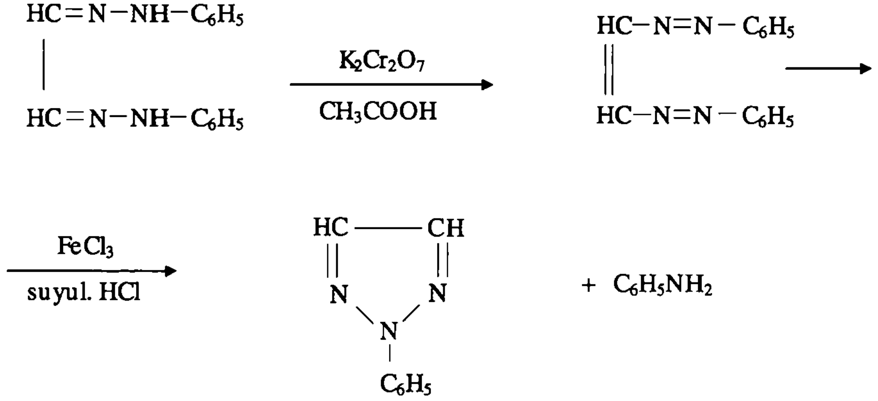


I



II

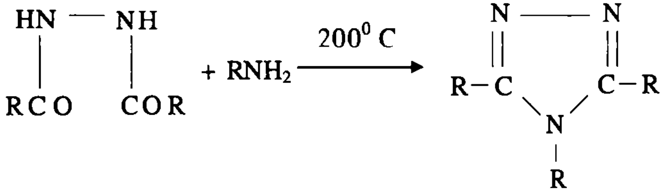
1, 2, 3 – triazollar ozazonlarni sirka kislota va kaliy bixromat bilan oksidlaganda oson hosil bo'ladi:



1,2,3 – triazollar juda kuchsiz asoslar bo‘lib, barqaror xlorgidratlar va boshqa tuzlarni hosil qilmaydi, ularning uglerod atomlari elektrofil reagentlarga nisbatan inert. Shu bilan bir qatorda 1,2,3 – triazollar kuchsiz kislota xossalarini namoyon qiladi. Bu geterotsikllar azot atomlari hisobidan N – alkillash, N – atsillash reaksiyalariga kirishadi, N – oksidlarni hosil qiladi.

1,2,3 – triazol halqasi behad barqaror bo‘lib, uning ko‘p hosilalari parchalanmasdan haydaladi.

1,2,4 – triazollar diatsilgidrazinlar va ammiak yoki aminlardan oiinadi:



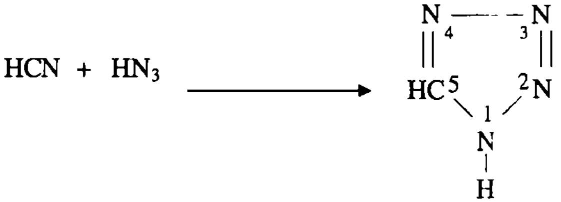
1,2,4 – triazol aromatik xossalarni namoyon qiladi. Uning halqasi litiy alyumogidrid, kaliy permanganat, peroksidlar singari kuchli reagentlar ta'siriga inert. Elektrofil almashinish halqaning uglerod atomlarida juda qiyin boradi. Sulfolash, Fridel – Krafts bo‘yicha alkillash va atsillash reaksiyalari hozirgacha ma‘lum emas. 1,2,4–triazolni nitrolash faqat halqada elektronodonor o‘rinbosar bo‘lgandagina boradi. 1,2,4 – triazolning nukleofil almashinish reaksiyalari ham sekin boradi.

Aminotriazollar tibbiyotda, sanoatda va fotografiyada qo'llaniladi. Amizol (3 – amino - 1,2,4 - triazol) samarali gerbitsid, 1,2,4 – triazolning ba'zi hosilalari esa korroziyaga qarshi vosita sifatida ishlatiladi.

Tetrazollar. Tetrazollar aromatik birikmalar bo'lib, ularning delokallashish energiyasi (231,8 – 265 kj/mol) boshqa besh a'zoli geterotsikllarning delokallashish energiyasidan katta.

Tetrazolning azot atomlari umumlashmagan elektron juftlari hisobidan turli reaksiyalarga kirishadi. Tetrazol halqasi - qizdirishga, kislota, ishqor, oksidlovchi va qaytaruvchilar ta'siriga ancha chidamli.

Tetrazolning o'zi vodorod sianid va HN_3 dan olinadi:



Tetrazollar ishqoriy metallar bilan tuzlar hosil qiladigan kuchsiz kislotalardir. Shu bilan bir qatorda tetrazollar asosli xossalarni namoyon qilib, ba'zi kislotalar bilan tuzlarni hosil qiladi.

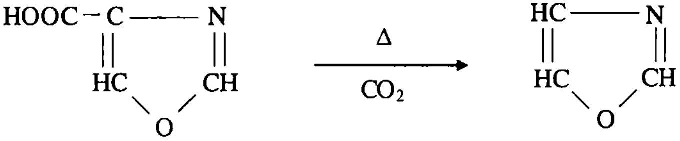
Tetrazollarning uglerod atomida boradigan elektrofil almashinish reaksiyalaridan faqat bittasi (1-feniltetrazolni bromlab 1 – fenil-5- bromtetrazol olingan) amalga oshirilgan. 1- feniltetrazolni nitrolaganda 1 – (r - nitrofenil)- tetrazol hosil bo'ladi. Xlor esa 1 – feniltetrazol bilan reaksiyaga kirishmaydi.

Tetrazol hosilalari tibbiyotda keng qo'llaniladi. Ulardan kordiazol (korazol) – pentametilentetrazol markaziy asab tizimi va yurak faoliyatining samarali stimulyatori hisoblanadi :

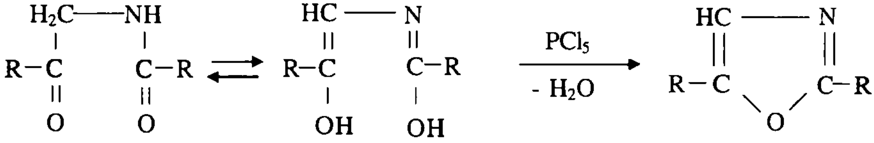
5– aminotetrazol va uning atsilli hosilalari polivinil-xlorinli bo'yoqlarni quyosh nuri, qizdirish yoki shamol ta'sirida rangsizlanishidan himoya qiladi. Tetrazol hosilalari fotografiyada

, misni korroziyadan himoya qilishda, portlovchi aralashmalar initsiatori sifatida va boshqa maqsadlarda ishlatiladi.

Oksazol va uning hosilalari. Oksazol 69 – 70°C da qaynaydigan, piridin hidli suyuqlik bo'lib, oksazol-4-karbon kislotani dekarboksillash bilan olinadi:



α - atsilketonlar H_2SO_4 yoki PCl_5 ishtirokida xona haroratida juda tez sikllanib, oksazollarni hosil qiladi (Robinson- Gabriel sintezi):



Oksazolda C = C va N =C bog'larning ikkitadan to'rtta π - elektroni hamda kislorod atomining umumlashmagan p – elektronlar juftidan iborat halqali 6 π - elektronli tizim borligidan u aromatik xossalarga ega.

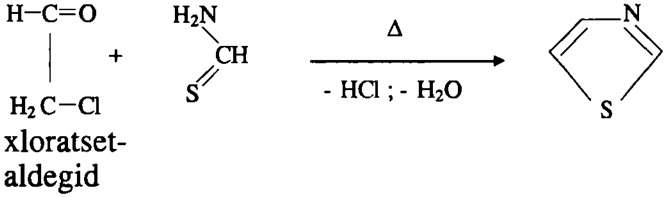
Oksazollar juda kuchsiz asoslar bo'lib, ishqoriy muhitda barqaror.

Elektrofil almashinish reaksiyalari oksazol uchun xarakterli emas.

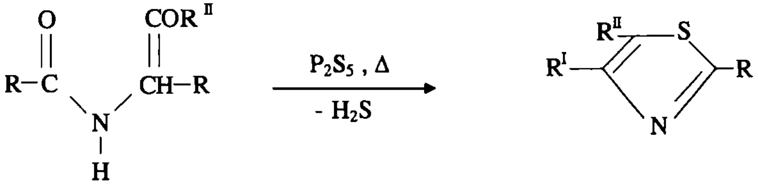
Oksazollar va ularning hosilalari α - aminokislotalar, polipeptidlar va biopolimerlar (polilizin, poliornitin, poliglutamin kislota) ni sintez qilishda, turli dorilar sifatida, oksazolli bo'yoqlar ishlab chiqarishda qo'llaniladi.

Tiazol va uning hosilalari. Tiazol 117°C da qaynaydigan, piridin hidli suyuqlik. Tiazol yadrosi B_1 vitamini, penitsillin, karboksilaza fermenti singari muhim tabiiy biologik faol moddalar tarkibiga kiradi.

Tiazol va uning gomologlarini sintez qilish uchun xlorketon yoki α - xloraldegidlarga tioamidlar ta'sir ettiriladi (Ganch, 1888-y.):

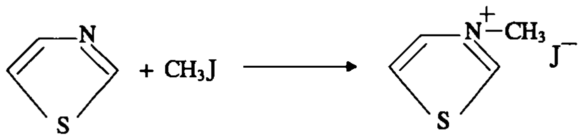


Almashingan tiazollar α - atsilaminokarbonil birikmalar va P_2S_5 dan olinadi:



Tiazol aromatik xossalarni yaqqol namoyon qiladi, kimyoviy xossalari jihatidan piridinga o'xshaydi.

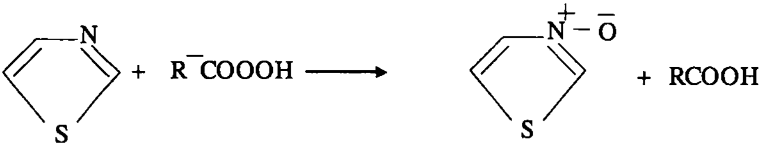
Tiazol kuchsiz asos bo'lsa-da, kislotalar bilan barqaror tuzlarni hosil qiladi. Tiazollar faol alkillovchi moddalar bilan reaksiyaga kirishganda tiazoliy tuzlari hosil bo'ladi:



Tiazolning o'zini bevosita nitrolash, sulfolash va galogenlash reaksiyalari qiyin boradi.

Tiazol elektrofil almashinish reaksiyalariga qiyin kirishishi jihatdan piridinni eslatadi.

Perkislotalar bilan reaksiyaga kirishib, N – oksid hosil qilishi bilan ham tiazol piridinga o'xshaydi:



tiazol N – oksidi

Tiazol hosilalari dorivor moddalar tayyorlashda qo'llaniladi. Ulardan biri kuchli bakteritsid ta'siriga ega bo'lgan sulfamid preparat – sulfatiazol (norsulfazol) dir.

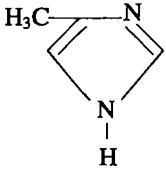
Tiazol halqasini saqlagan boshqa sulfamid preparatlar ham tibbiyotda ishlatiladi.

Benzotiazollardan rangli va infraqizil fotografiyada qo'llaniladigan bo'yoq olinadi.

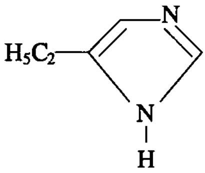
Savol va mashqlar

1. Quyidagi birikmalarni nomlang:

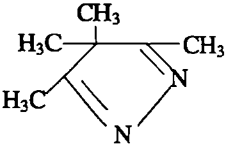
a)



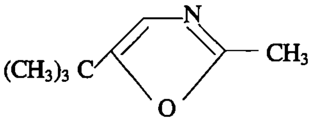
b)



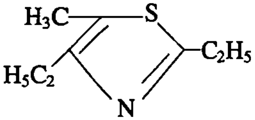
d)



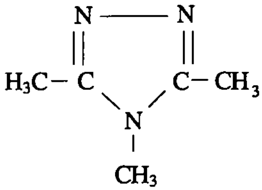
e)



f)



g)



2. Quyidagi birikmalarning tuzilish formulalarini yozing:

a) 4 (5) – imidazolsulfokislota;

b) 1,2 – dimetil – 1,2,4 – triazol;
d) 3 – metil-5-fenilpirazol
e) 2 – metil – 4 – feniloksazol

3. Pirazol va uning hosilalari qanday usullar bilan olinadi?

4. Imidazol va uning hosilalari qanday usullar bilan olinadi?

5. Oksazol va tiazol qanday olinadi?

6. Pirazollar va imidazollar uchun xos bo‘lgan reaksiyalarga misollar keltiring.

7. 1,2,3 – va 1,2,4 – triazollar qanday olinadi va ular uchun qanday reaksiyalar xos?

8. Pirazol va imidazol hosilalari qaerlarda ishlatiladi?

9. Oksazol va tiazol kirishadigan reaksiyalarga misollar keltiring.

10. Oksazol va tiazol hosilalari qaerlarda ishlatiladi?

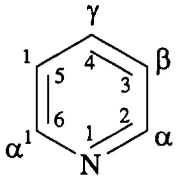
XV. BIR GETEROATOMLI OLTI A‘ZOLI GETEROTSIKLLAR

Piridin. Olinish usullari, tuzilishi, kimyoviy xossalari va muhim birikmalari.

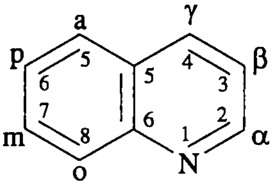
Xinolin. Muhim reaksiyalari va hosilalari.

Savol va mashqlar.

Bu geterotsikllardan piridin bilan batafsil, xinolin va piranlar bilan esa qisqacha tanishamiz:



piridin



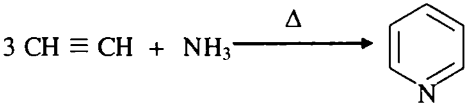
xinolin

Piridinni benzolning bitta CH guruhi azot atomi bilan almashingan analogi deb qarash mumkin. Piridin 115^{0}C da qaynaydigan o‘ziga xos yoqimsiz hidli suyuqlik bo‘lib, suvda va ko‘pchilik organik erituvchilarda yaxshi eriydi. Piridin gomologlarining trivial nomlari ko‘p ishlatiladi. Monometilpiridinlar pikolinlar, dimetilpiridinlar lutidinlar, trimetilpiridinlar kollodinlar deb ataladi. Piridin oz miqdorda toshko‘mir smolasida va suyak moyi tarkibida bo‘ladi.

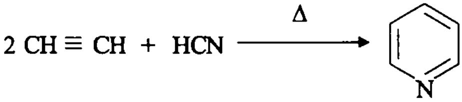
Olinish usullari

1. Piridin va uning gomologlari toshko‘mir smolasidan ajratib olinadi. Toshko‘mir smolasida piridin miqdori juda oz (0,1 % ga yaqin) bo‘lgani sababli bu usul sanoat talabini to‘liq qondira olmadi.

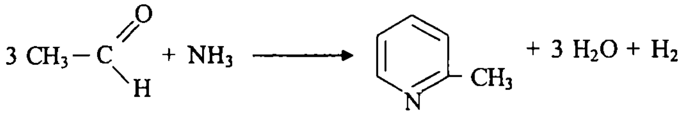
2. Sintetik piridin olish uchun atsetilen va ammiak katalitik kondensatsiya reaksiyasiga kiritiladi:



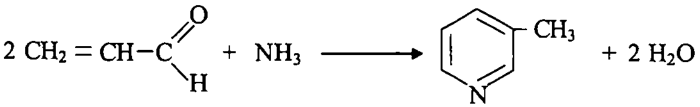
Atsetilenning sianid kislota bilan kondensatsiyasi yuqori haroratda boradi:



3. Piridin gomologlarini sintez qilish uchun aldegidlar ammiak bilan katalizator (Al_2O_3) ishtirokida qizdiriladi:



α - metilpiridin
(α - pikolin)



β - metilpiridin
(β- pikolin)

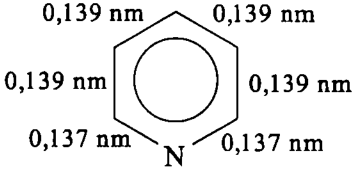
Tuzilishi va kimyoviy xossalari

Piridin ham furan, tiofen va pirrol singari aromatik sekstetga ega bo'lib, xossalari jihatidan benzolga o'xshaydi. Aromatik sekstet hosil bo'lishida uglerod atomlari, shuningdek, azot atomi ham bittadan elektron beradi. Pirroldan farqli o'laroq, piridindagi azot atomining erkin elektron jufti yadro π - elektronlarining aromatik sekstetini ($4n+2$, $n=1$) hosil qilishida ishtirok etmaydi. Shunga ko'ra piridin azotdagi erkin elektron jufti hisobiga kuchsiz (lekin pirrolga nisbatan kuchli) asos xossalarini namoyon qiladi. Piridinning dipol momenti 2,11 D ga, rezonans energiya esa 23 kkal/ molga teng. Azot uglerodga nisbatan elektromanfiy element bo'lgani uchun yadroning elektron zichligini o'ziga tortadi, shu boisdan pirroldan farqli o'laroq, piridinda dipolning manfiy qutbi azot atomi hisoblanadi.

Piridin yadrosi kaliy bixromat va nitrat kislota singari kuchli oksidlovchilar ta'siriga chidamli, termik barqaror bo'lib, aromatik xossalarni yaqqol namoyon qiladi.

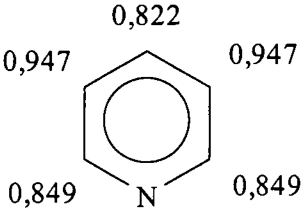
Piridin molekulasida π - elektronlar zichligining taqsimlanishi va yadrolar orasidagi masofalarning kattaligini aniqlash uning benzol bilan strukturaviy o'xshashligini ko'rsatadi. Piridin halqasi deyarli to'g'ri oltiburchak bo'lib, C – C bog'larning uzunligi benzol C – C bog'larining uzunligiga yaqin, C – N bog'ining uzunligi esa aminlardagiga nisbatan qisqa:

$$H_3C\overset{0,146\ \text{nm}}{\overline{\qquad\qquad}}NH_2$$

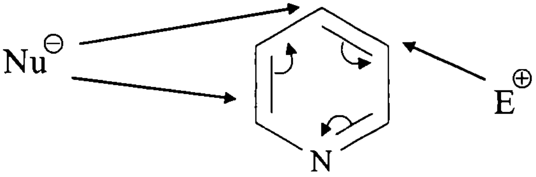


Elektron zichliklarining yig'indisi molekuladagi π-elektronlarning umumiy soniga teng, ya'ni $0,822+0,947+0,947+0,849+1,586=6$.

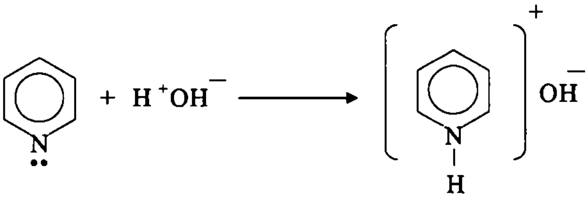
Azot yadroning elektron zichligini o'ziga tortadi va natijada uglerod atomlaridagi elektronlar zichligi benzol molekulasidagi tegishli elektronlar zichligidan, ya'ni 1 dan kamayadi:



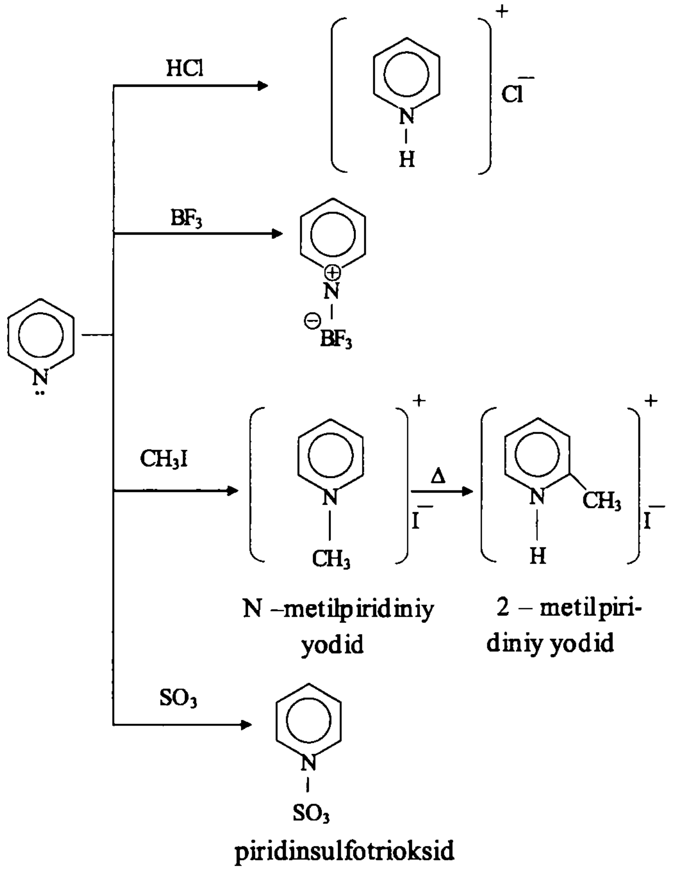
Shuning uchun ham piridinning elektrofil almashinish reaksiyalariga kirishish qobiliyati benzolga nisbatan kuchsiz. Piridindagi 3 – va 5 – uglerod atomlarida (β - va β^1 - holatlarda) π - elektronlarning zichligi birmuncha katta bo'lganidan elektrofil almashinish reaksiyalarida reagentlarning hujumi birinchi navbatda shu atomlarga qaratiladi. 2 -, 4 – va 6 – uglerod atomlarida (α -, α^1 – va γ - holatlarda) esa elektronlar zichligi kichik, shuning uchun ham ular nukleofil almashinish reaksiyalariga kirishish qobiliyatiga ega:



Piridin suv bilan ammoniy gidroksidga o'xshash birikma hosil qiladi, shuning uchun piridinning suvdagi eritmasi qizil lakmusni ko'kartiradi:



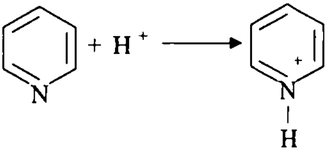
Piridin azot atomining umumlashmagan elektron jufti hisobiga kuchli kislotalar bilan reaksiyaga kirishib, oson kristallanadigan tuzlar, aprotonli kislotalar, masalan, bor va alyuminiy trigalogenidlar bilan kompleks birikmalar, galogenalkanlar bilan alkilpiridiniy tuzlari, sulfat angidridni biriktirib, piridin sulfotrioksid kompleksini hosil qiladi:



Piridin bunday reaksiyalarda uchiamchi amin xossalarini namoyon qiladi.

Elektrofil almashinish reaksiyalari. Piridin elektrofil almashinish reaksiyalariga benzolga nisbatan juda qiyin kirishadi. Buning asosiy sababi piridin azotining yadrodagi umumiy π - elektronlar zichligini kamaytirganidadir. Bundan tashqari elektrofil almashinish (nitrolash, sulfolash) kislotali muhitda olib boriladi.

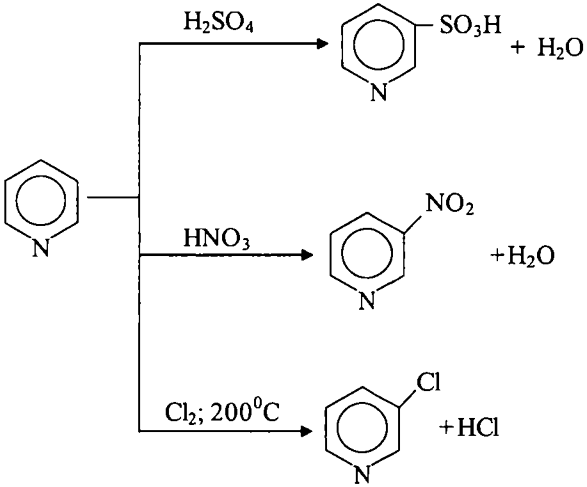
Kislotali muhitda piridin tuz hosil qiladi va undagi azot atomi ammoniy azotiga o‘xshash musbat zaryadli bo‘lib qoladi, boshqacha aytganda, bunday muhitda piridin kation hoiida bo‘ladi:



Azotdagi musbat zaryad yadroning umumiy elektron zichligini yanada kamaytirib, elektrofil zarrachalarning hujumini qiyinlashtiradi.

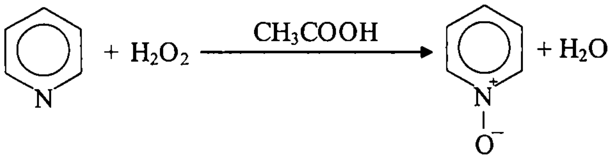
Piridinni 220-230⁰ C da tutovchi sulfat kislota bilan simob sulfat ishtirokida sulfolab, 40 % li unum bilan piridin- 3- sulfokislota olish mumkin. Piridin 300-350⁰ C da simob katalizator ishtirokisiz sulfolanganda ham piridin – 3 sulfokislota hosil bo‘ladi, lekin reaksiyaning unumi kam bo‘ladi. Nitrolash uchun esa 300⁰C da temir katalizatorligida piridinning 100% li sulfat kislotadagi eritmasiga kaliy nitratning nitrat kislotadagi eritmasi ta‘sir ettiriladi va kam unum bilan 3 – nitropiridin hosil bo‘ladi:

Piridinni galogenlash ham yuqori haroratda olib boriladi:



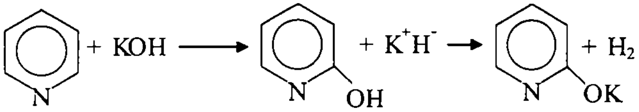
Piridin Fridel – Krafts reaksiyasiga mutlaqo kirishmaydi.

Piridin peroksikislotalar yoki sirka kislota eritmasida vodorod peroksid bilan oksidlanganda piridin – N – oksid hosil bo‘ladi:

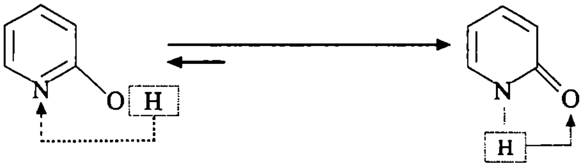


Piridin – N – oksid piridinga nisbatan elektrofil almashinish reaksiyalariga oson kirishadi.

Nukleofil almashinish reaksiyalari. Piridin 300- 400^{0}C da quruq o‘yuvchi kaliy bilan qizdirilganda 2 – gidroksipiridin (α-gidroksipiridin) hosil bo‘ladi (A. E. Chichibabin):



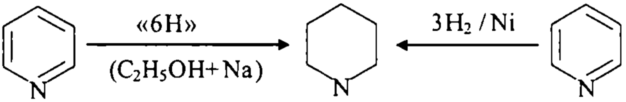
2 – gidroksipiridinning tautomer shakli 2 – piridondir:



laktim shakli laktam shakli

Bu laktim – laktam tautomeriyada muvozanat o‘ngga kuchli siljigandir.

Qaytarilishi. Piridin benzolga nisbatan oson qaytariladi. U ajralib chiqish paytidagi vodorod (piridinning spirtdagi eritmasiga natriy ta‘sir ettirish) bilan qaytarilganda (bunday sharoitda benzol qaytarilmaydi) yoki katalitik gidrogenlanganda piperidinga aylanadi:



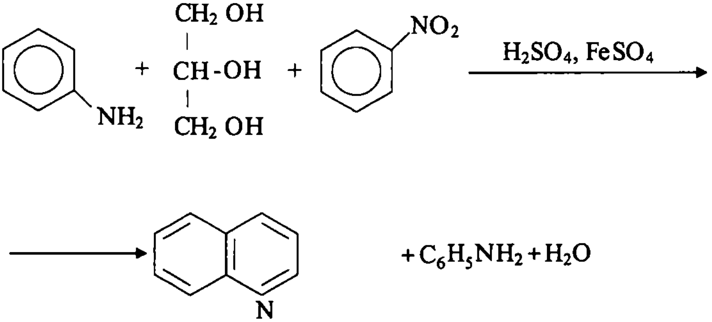
Piperidin suvda eruvchan, rangsiz suyuqlik, 105,6^{0}C da qaynaydi, ikkilamchi alifatik amin xossalariga ega U piridinga nisbatan ancha kuchli asos hisoblanadi Piperidin halqasi sovuqda kaliy permanganat (kislotali muhitda), xromat angidrid, nitrat kislota singari oksidlovchilar ta'siriga chidamli, lekin qizdirilganda oksidlanish muhitiga qarab asta-sekin turli aminokislotalargacha oksidlanadi. U ikkilamchi alifatik aminlardek nitrozamin, N- alkil va N – atsilli hosilalar beradi. Piridin va piperidin ko'pgina organik reaksiyalarda asosli katalizator sifatida keng qo'llaniladi.

Xinolin va uning hosilalari

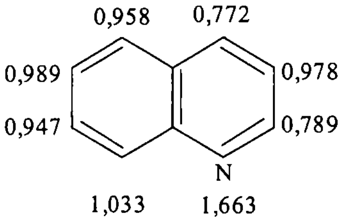
Xinolin 238^0 C da qaynaydigan, o'ziga xos o'tkir hidli, kuchsiz uchlamchi asosdir. Xinolinda benzol va piridin halqalari kondensirlangan, shuning uchun uni boshqacha qilib, α, β - benzopiridin deb aytish mumkin.

Xinolin va uning gomologlari toshko'mir smolasidan, shuningdek, sintetik usullar bilan olinadi.

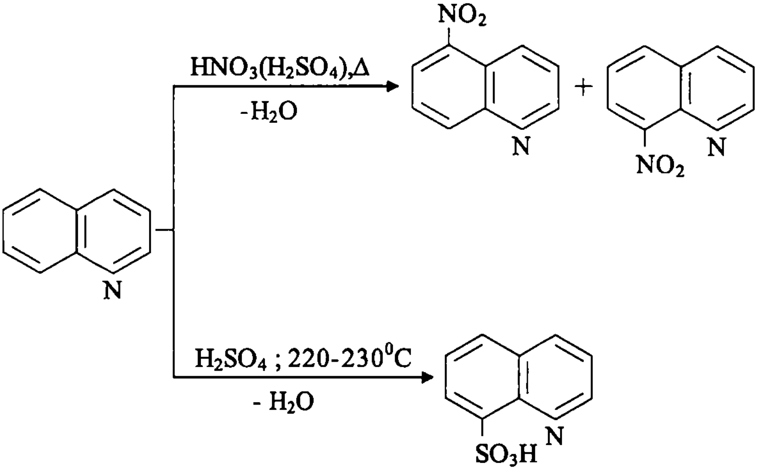
Z. Skraup sintezi (1880-y) bilan xinolin olishda anilin glitserin, konsentrlangan sulfat kislota, nitrobenzol va temir (II) – sulfat ishtirokida qizdiriladi:



Xinolin molekulasida elektron zichligi quyidagicha taqsimlangan:

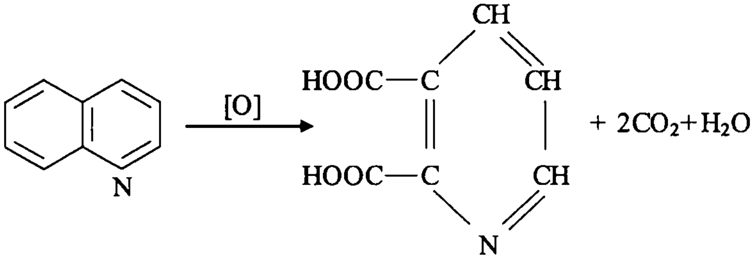


Benzol yadrosida elektron zichligi piridin yadrosidagiga nisbatan yuqori bo'lgani uchun elektrofil reagentlarning hujumi, birinchi navbatda, molekulaning benzol qismiga, nukleofil zarrachalarning hujumi esa piridin qismiga qaratiiadi : Masalan, nitrolovchi aralashma ta'sirida 5 – va 8 – nitroxinolinlar, sulfolaganda esa 8 –xinolinsulfokislota hosil bo'ladi:

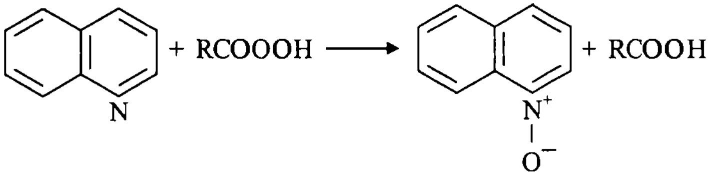


Sulfolash 300⁰ C dan yuqori haroratda olib borilganda 6-xinolinsulfokislota hosil bo'ladi.

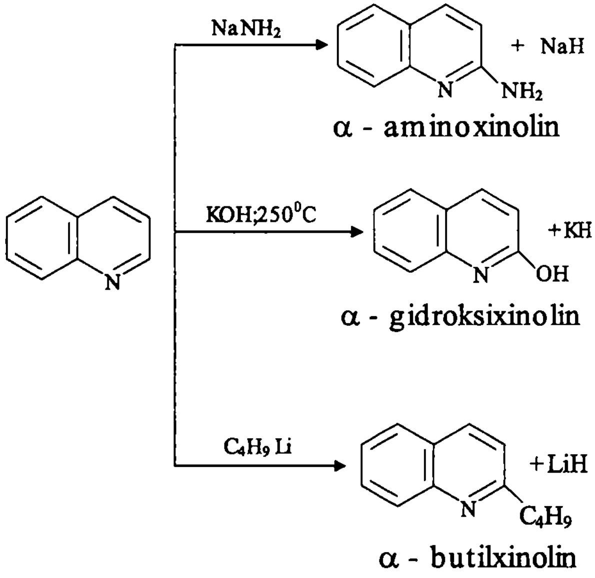
Xinolin kaliy permanganat bilan oksidlanganda benzol halqasi parchalanib, α,β - piridinkarbon kislota (xinolin kislota) hosil bo'ladi:



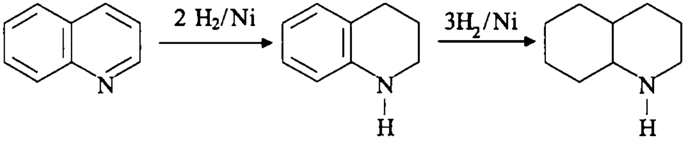
Perkislotalar yoki vodorod peroksidi bilan reaksiyaga kirishganida xinolin – N – oksidini hosil qiladi:



Nukleofil almashinish reaksiyalarida piridin yadrosining α - holati eng faol hisoblanadi:



Xinolin qaytarilganda oldin piridin, so'ngra benzol halqasi gidrogenlanadi:



tetragidroxinolin dekagidroxinolin

Tetragidroxinolin ko'p xossalari bilan piperidinga, dekagidroxinolin esa ikkilamchi alifatik aminlarga o'xshaydi. Xinolin yadrosi ba'zi alkaloidlar, dorilar molekulasi tarkibiga kiradi.

Savol va mashqlar

1.Quyidagi birikmalarning tuzilish formulalarini yozing:

a) 2,6 – dimetilpiridin ; b) 3 – brom-1-metilpiperidin ;

d) N, α , α^1 – trimetil piperidin; e) 6 – metil–8-aminoxinolin f)5,8-diokso-5,8-digidroxinolin ; g) N-metilpiridiniy yodid .

2. Barcha izomer dimetilpiridinlarning tuzilish formulalarini yozing va ularni nomlang.

3. Monometilxinolinlarning barcha izomerlari tuzilish formulalarini yozing va ularni nomlang.

4. Nega piridin asos xossalariga ega-yu, pirrol ega emas ?

5. Nega piridin halqasi kislotalar ta'siriga chidamli-yu, pirrol halqasi chidamli emas ?

6. Istalgan reagentlardan foydalanib, quyidagi sintezlarni amalga oshiring:

a) β - pikolin $\longrightarrow$ vitamin PP (nikotinamid)

b) γ - pikolin $\longrightarrow$ izonikotin kislota gidrazidi

7. Piridin molekulasining elektron tuzilishini tushuntiring.

8. Quyidagi reaksiyalar tenglamalarini yozing. Oraliq va oxirgi mahsulotlarni nomlang:

$$\alpha\text{ - pikolin} \xrightarrow{[O]} A \xrightarrow{SOCl_2} B \xrightarrow{NH_3} D.$$

9. Quyidagi birikmalarni oson nitrolanishi tartibida joylashtiring:

a) benzol; b) toluol; v) tiofen

g) piridin; d) m – dinitrobenzol.

10. Piridin, piperidin, xinolin va ularning hosilalari qanday maqsadlarda ishlatiladi?

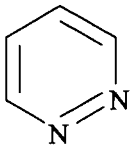
XVI. BIR NECHA GETEROATOMLI OLTI A'ZOLI GETEROTSIKLLAR

Diazinlar. Pirimidinning olinishi, xossalari va muhim hosilalari.

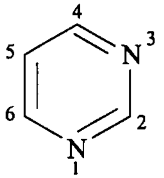
Purin va uning hosilalari.

Savollar.

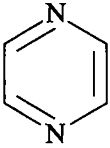
Halqasida ikkita azot atomi bor olti a'zoli geterotsikllarga diazinlar deb ataladi:



piridazin
(1,2 – diazin)



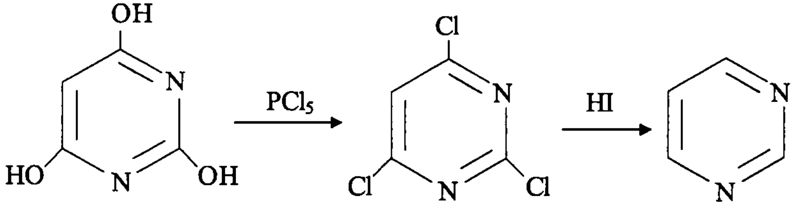
pirimidin
(1,3 – diazin)



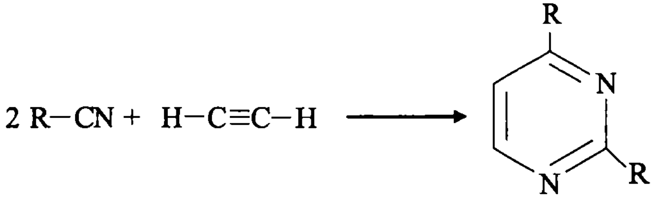
pirazin
(1,4 - diazin)

Diazinlardan pirimidin va uning hosilalari katta ahamiyatga ega. Pirimidin yadrosi nuklein kislotalar, kofermentlar, vitaminlar, alkaloidlar, dorivor preparatlar molekulalari tarkibiga kiradi.

Pirimidin suvda eriydigan, rangsiz kristall modda bo'lib, 21^{0}C da suyuqlanadi, 124^{0}C da qaynaydi. U barbitur kislotadan olinadi:

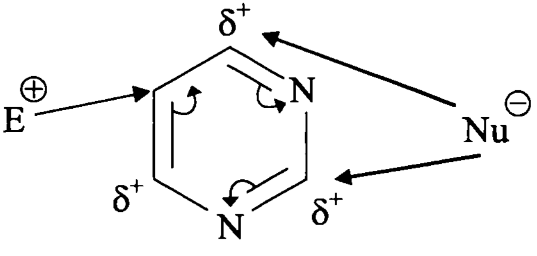


Pirimidin gomologlari nitrillar bilan atsetilendan sintez qilinadi:



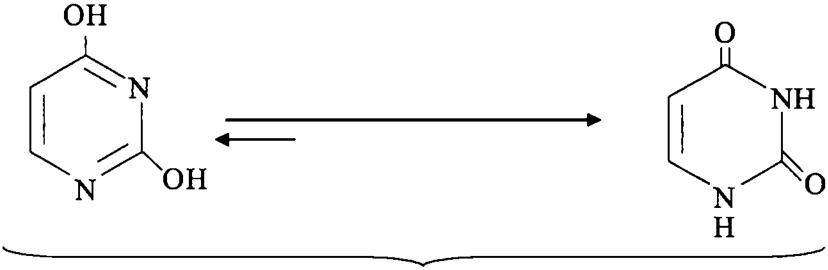
Pirimidin va uning gomologlarining suvdagi eritmalari neytral muhitga ega, lekin kislotalar bilan tuzlar hosil qiladi.

Pirimidin kimyoviy xossalariga ko‘ra piridinga o‘xshaydi, lekin elektrofil almashinish reaksiyalariga piridindan qiyin kirishadi. Pirimidinning 2 - , 4 – va 6 – holatlarida elektron zichligi ancha kam, 5 – holatida esa ko‘proq. Shuning uchun ham nukleofil reagentlarning hujumi 2 - , 4 – va 6 – uglerod atomlariga, elektrofil reagentlar hujumi esa 5 – uglerod atomiga qaratiladi:

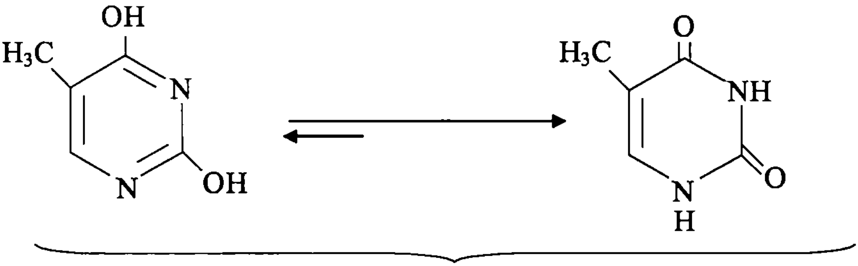


Ribonuklein kislotalar (RNK) gidrolizining oxirgi mahsulotlari – uratsil, timin, sitozin, adenin, guanin, β - D-2- dezoksiriboza va fosfat kislota hisoblanadi.

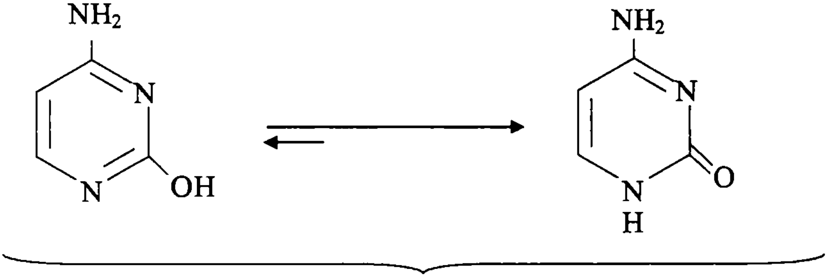
Uratsil, timin va sitozin pirimidinli asoslar deyiiadi:



uratsil



timin

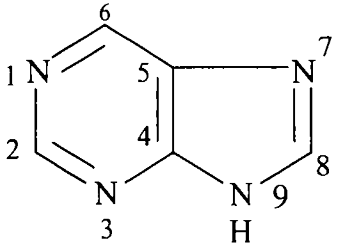


sitozin

Uratsil, timin va sitozin asosan laktam shaklida mavjud. Ularning laktim shakllari esa faqat eritmalarda juda oz miqdorda bo'ladi, xolos.

Uratsil, timin va sitozin suvda eriydigan, qutbsiz erituvchilarda esa erimaydigan, 300^0 C dan yuqori haroratda suyuqlanadigan moddalar bo'lib, sintetik usullar bilan ham olinadi.

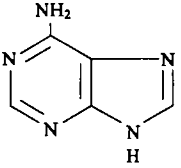
Purin va uning hosilalari. Purin molekulasida pirimidin va imidazol halqalari o'zaro tutashgan:



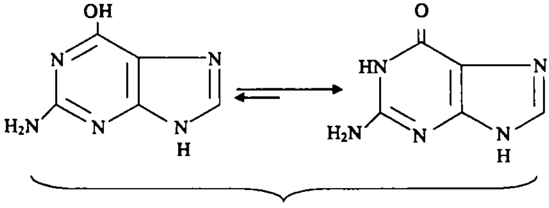
Purinda qo‘sh bog‘larning sakkizta π - elektroni va 9 – holatdagi azot atomining umumlashmagan elektron jufti aromatik detset (4n + 2, n=2) hosil qiladi. Uglerod va azot π - elektronlarning bunday mezomer ta‘sirlashuvi natijasida bog‘larning uzunligi o‘zgaradi. Shu bois purinda haqiqiy oddiy va qo‘sh bog‘lar yo‘q.

Purin 217^0 C da suyuqlanadigan, suvda yaxshi eriydigan, oksidlovchilar ta‘siriga chidamli asosdir.

RNK va DNK tarkibida bo‘ladigan purinli asoslar – adenin va guanin purinning eng muhim hosilalaridir:



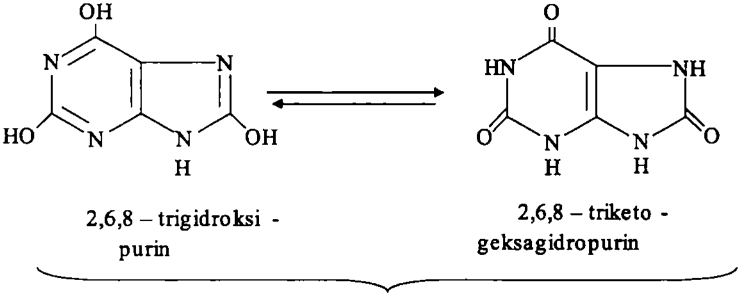
adenin



guanin

Adenin - (6 - aminopurin) $360–365^0$C da suyuqlanadigan, suvda kam eriydigan, rangsiz kristall modda. U sanoatda formamid va $POCl_3$ dan olinadi. Organik va mikrobiologik sintezda dastlabki modda, tibbiyotda donor qonining konservanti sifatida ishlatiladi.

Guanin - (2 – amino-6-gidroksipurin) 365^{0}C da suyuqlanadigan, rangsiz kristall modda. U qushlar chiqindisida, baliqlar va sudralib yuruvchilar tangachalarida bo‘ladi. Sintetik guanin 2,6,8 – trixlorpurindan yoki boshqa usullar bilan olinadi. Guaninning okso (laktam) shakli barqaror. Purinning muhim hosilalaridan biri *siydik kislotadir:*



2,6,8 – trigidroksi - purin

2,6,8 – triketo - geksagidropurin

siydik kislota

Siydik kislota rangsiz kristall modda, suvda yomon eriydi.

U tirik organizmlarda azot almashinuvining oxirgi mahsuloti hisoblanadi va siydik bilan organizmdan chiqariladi. Qush va sudralib yuruvchilar chiqindisining asosiy qismi, ilonlar chiqindisining esa 90 % i siydik kislotadan iborat. Siydik kislota - tautomer birikma bo‘lib, uning triokso shakli nisbatan barqaror. Siydik kislota purinning turli hosilalarini sintez qilishda dastlabki modda sifatida ishlatiladi.

Savollar

1. Pirimidinning olinishi, tuzilishi va xossalarini tushuntiring.

2. RNK va DNK gidroliz qilinganda hosil bo‘ladigan pirimidinli va purinli asoslarning tuzilish formulalarini yozing. Ulardan qaysi biri tautomer shakllarda mavjud emas?

3. Purinning tuzilishi, xossalari va muhim hosilalarini bayon qiling.

4. Adenin va siydik kislota qanday maqsadlarda ishlatiladi?

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Mundarija

Shoymardonov R.A.

ORGANIK KIMYO

Oliy o‘quv yurtlari kimyo ta‘lim yo‘nalishi
talabalari uchun o‘quv qo‘llanma

«Yangiyul Poligraph Service» MChJ
Toshkent – 2008

Muharrir – A.Zolotaryova
Texnik muharrir – B.Azimov
Dizayner –V.Kuznetsov

Original maketdan bosishga ruxsat etildi 28.07.08.
Arial garniturasi. Bichimi 60x90 1/16.
Ofset usulida bosildi. Bosma tabog‘i 22,0.
Nusxasi 500. Buyurtma № 39.

Bahosi shartnoma asosida.

«Yangiyul Poligraph Service» MChJ bosmaxonasida bosildi.
Manzili: Yangiyo‘l shahri, Samarqand ko‘chasi, 44.

Qaydlar uchun

Qaydlar uchun

Qaydlar uchun

Qaydlar uchun