AROMATIC HYDROCARBON

Main Source

Bituminous coal when subjected to destructive distillation in the absence of air [1000°-1200°C] the chief constituent obtained is coal tar.

Fractional distillation of coal tar : Diferent fractions are :

	Fraction	Temperature	Main constutuents
(a)	Light oil	80-170°C	Benzene, toluene, xylene etc.
(b)	Middle oil (carbolic oil)	170°-230°C	Nephthalene,
			Phenol etc.
(c)	Heavy oil	230°-270°C	Cresols, naphthalene
(d)	Green oil	270°-360°C	Anthracene
(e)	Pitch	Residue	Carbon

Benzene



Obviously, each orbital formed in the partial overlapping is attracted by two carbon nucleus hence less stable.



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Delocalized p-orbital



Methods of Preparation of Benzene

Isolation From 'Light Oil Fraction - Industrial method

In 'light oil' at least 60-65% benzene is present. Alkaline impurities (aniline, pyridine, quinolene, etc.) are removed by washing 'light oil' with cold and conc. H_2SO_4 . The acidic impurities are removed by washing with dilute NaOH solution. After that, NaOH is removed washing with water. Three fractions are obtained at different temperature ranges by fractional distillation of the neutral sample of oil.

[i] 90% Benzol (90's benzol). 80-110°

[ii] 50% Benzol (50's benzol). 110-140°

[iii] Solvent naphtha - 140°-170°

The 90% benzol contains abount 70% benzene 24% toluene and remaining xylenes. Fractional distillation gives benzene at 80°, toluene at 110° and a mixture of all the three xylenes at 137-145°. Crystals are formed on colling benzene from which pure benzene can be obtained by melting the crystals.

Electrophilic Aromatic Substitution Reaction

Introduction

Aromatic hydrocarbons are known generally as arenes. An aryl groups is one derived from an arene by removal of a hydrogen atom and its symbol is Ar–. Thus, arenes are designated ArH just as alkanes are designated RH.

The most characteristic reactions of benzenoid arenes are the substitution reactions that occur when they react with electrophilic reagents. These reactions are of the general type shown below.



The electrophilic are either a positive ion (E^*) or some other electron-deficient speices with a large partial positive charge. For example, benzene can be brominated when it reacts with bromine in the presence of FeBr₃. Bromine and FeBr₃ react react to produce positive bromine ions, Br^{*}. These positive bromine ions act as electrophiles and attack the benzene ring, replacing one of the hydrogen atoms in a reaction that is called an electrophilic aromatic substitution (EAS).

Electrophilic aromatic substitutions allow the direct introduction of a wide variety of groups into an aromatic ring, and because of this they provide synthetic routes to many important compounds. The five electrophilic aromatic substitutions that we shall study in this chapter are outlined in figure.



AROMATIC HYDROCARBON



Electrophilic Aromatic Substitution Reactions

(1) A General Mechanism For Electrophilic Aromatic Substitution

Benzene is susceptible to electrophilic attack primarily because of its exposed π -electrons. In this respect benzene resembles an alkene, for in the reaction of an alkene with an electrophilic the site of attack is the exposed π -bond.

We sae in however, that benzene differs from an alkene in a very significant way. Benzene's closed shell of six six π electrons gives it a special stability. So although benzene is susceptible to electrophilic attack, it undergoes substitution reactions rather that addition reactions. Substitution reactions alow the aromatic sextet of π electrons to be regenerated after attack by the electrophile was occurred. We can see hwo this happens of we examine a general mechanism for electrophilic aromatic substitution.

Once the electrophilic, E⁺ is generated in the reaction. it ethers into some kind of a weak interaction with the π cloud of benzene ring leading to the formation of a π -complex. This π -complex is a donor-acceptor type of a complex, benzene being the donor and electrophille, the acceptor. These adducts are known as charge transfer complex. In the complex that benzene forms with bromine, it has been shown that the halogen molecule is located centrally and at right angles to the plane of the benzene ring.



In step 1 the electrophile takes two electrons of the six-electron π system to form a σ bond to one carbon atom of the benzen ring. Formation of this bond interrupts the cyclic system of π -electrons, because in the formation of the arenium ion the carbon that forms a bond to the electrophile becomes sp³ hybridized and therefore, no longer has an available π -orbital. Now only five carbon atoms of the ring are still sp² hybridized and still have p-orbitals. A calculated electrostatic potential map for the arenium ion formed by electrophilic addition of bromine to benzene indicated that positive charge is distributed in the arenium ion ring (figure) just as was shown in the contributing resonance structure.



In step 2 a proton is removed from the carbon atom of the arenium ion that bears the electrophile. The two electrons that bonded this proton to carbon becomes a part of the π system. The carbon atom that bears the electrophile becomes sp² hybridized again and a benzene derivative with six fully delocalized π electrons is formed. We can represent step 2 with any one of the resonance structures for the arenium ion.



(The proton is removed by any of the bases present, for example, by the anion derived from the electrophile). Kekul'e structure are more appropriate for writing mechanisms such as electrophilic aromatic substitution because they permit the use of resonance theory, it can be described however, using the modern formula for benzene in the following way.



Where K_1 and K_2 is the rate constant of the forward and backward reaction in step-I, K_2 is the rate constant of the step-II. There is firm experimental evidence that the arenium ion is a true intermediate in electrophilic substitution reactions. It is not a transition state. This means that in a free energy (figure shown below) the arenium ion lies in an energy valley between two transition states.

The free energy of activation, $\Delta G_{(1)}^{\#}$, for the reaction leading from benzene and the electrophile, E⁺, to the arenium

ion has been shown to be much greater than the free energy of activation, $\Delta G_{(2)}^{\#}$, leading from the arenium ion to

the final product. This is consistent with what we would expect. The reaction leading from benzen and an electrophile to the arenium ion is high endothermic, because the benzene ring loses its resonance energy. The reaction leading from the arenium ion to the substituted benzene, by contrast, is highly exothermic because in it the benzene ring regains its resonance energy.



Reaction coordinate —

Of the above two steps, 1 the formation of the arenium ion - is usually the ratedetermining step in electrophilic aromatic substitution.

Step 2, sthe removal of a proton, occurs rapidly relative to step 1 and has no effect on the overall rate of reaction.



Isotope Effect

The next question which comes up is hwo do we ascertain the presence of two discrete steps in the mechanism and also that the formation of σ -complex is the rate determining step. Answer to this question can be obtained from the study of kinetic isotope effect. If the rate of a reaction depends on a step while involves breaking of a C-H bond, then a kinetic isotope effect (K_0/K_0) to 6 to 7 is expected. Absence of any significant isotope effect in aromatic electrophilic substitution (except sulphonation) suggests that the proton is lost in the fast step subsequent to rds. We see that the isotope effect study has provided two pieces of important information regarding the mechanism. Firstly, it has shown that the reaction takes in two steps and secondly, that the first step is slower than the second step.

(2) **Nitration**

Nitration reaction is generally carried out with a mixture of concentrated nitric acid and sulphuric acid. The reagents which cause nitration are called nitrating agents.

The various nitrating agents which are commonly employed are :

- (a) N₂O₅ in CCl₄ in the presence of P₂O₅ is used when anhydrous conditions are required.
- (b) Ethyl nitrate (C,H,ONO,) is used to carry out nitration in alkaline medium.
- (c) In the case of polycyclic hydrocarbons N_2O_4 and nitronium salts such as $NO_2^+BF_4^-$, $NO_2^+PF_6^-$, $NO_2^+SO_3^-$, can be

used. The electrophile involved in nitration is nitronium ion (NO_2^{\oplus}) .

Mechanism

Generation of electrophile from nitrating agent.

(a) In a mixture of nitric acid and sulphuric acid, an acid base reaction takes place in which nitric acid acts as the base.

$$HO-NO_{2} + H_{2}SO_{4} \longrightarrow H - O - NO_{2} + HSO_{4}^{\Theta}$$

Base H

$$\begin{array}{c} H \xrightarrow{\Phi_{0}} NO_{2} \longrightarrow NO_{2}^{\oplus} + H_{2}O \\ H \end{array}$$

$$H_{2}O + H_{2}SO_{4} \longrightarrow H_{3}O^{\oplus} + HSO_{4}^{\Theta}$$
$$HNO_{3} + 2H_{2}SO_{4} \longrightarrow NO_{2}^{\oplus} + H_{3}O^{\oplus} + 2HSO_{4}^{\Theta}$$

 N_2O_5 in CCl₄ when used, results in a spontaneous dissociation reaction.

$$N_2O_5 \Longrightarrow NO_2^{\oplus} + NO_3^{-}$$

With concentrated HNO3 alone (c)

$$2HNO_3 \Longrightarrow NO_2^{\oplus} + NO_3^{-} + H_2O$$

The electrophile generated in this case is obtained by the behaviour of one nitric acid as the base and other molecules as the acid, but the equilibrium lies in the reactant side.



(b)

(3) Sulphonation

Sulphonation is another synthetically important reaction. It is often accomplish with concentrated sulphuric acid or fuming sulphuric acid containing excess of SO₃ or chlorosulphonic acid, ClSO₂OH.

It is believed that the electrophile varies with the reagent, thought in all cases SO₃, is involved either free or along with a carrier, like in $H_2SO_4(SO_3 + H_3O^+)$ or $H_2S_2O_7$. Sulphur trioxide is generated form sulphuric acid as follows $2H_2SO_4 \implies HSO_4^- + H_3O^+ + SO_3$. The mechanism of sulphonation of benzene is given below :



Sulphonations is different from other aromatic electrophilic substitution reactions, Firstly, it is reversible and secondly, it shows some amount of isotope effect which is totally absent in other cases. Let us have a look at the potential energy diagram, Fig. of sulphonation reaction to understand these anomalies.



Reaction coordinate ----

We see that once the σ^- complexed benzenium intermediate is formed ; the energy barriers on either side of the intermediate are roughly of the same magnitude. This means that the intermediate can cross over to the product and can also come back to the reactant. This accounts for a reversible nature. Now, if we have the deuterated substrate, then the potntial energy diagram gets slightly modified (dotted curve). The barrier to step II becomes higher as it now involves the cleavage of C–D bond. The barrier for step I. The barrier for step I, on the other hand, remains the same as it pertains to σ - complex foramtion. The rate of its reverting back to reactants is higher than its crossover to the product. Therefore, there is a net decrease in the overall rate of sulphonation for deuterated substrate-it shows a kinetic isotope effect. The loss of proton (Step II) is the slowest step (rds). The equilibrium in step III lies to the left as aryl sulphonic acids are strong acids.

In the case of other electrophilic substitutions, in contrast, energy barrier for the first step is much higher than that for the second step even for a deuterated substrate.

(4) Halogenation

Halogenation of an aromatic ring is a synthetically important reaction. It takes place in the presence of varied reaction condition depending on the reactivity of the aromatic ring. For very reactive aromatic compounds in polar solvents, the molecular halogens themselves may acts as electrophiles. In the case of nonpolar solvents, halogenation is catalysed by a Lewis acid like AlCl₃ or FeCl₃, Reactivity of halogens has the following order,

$$I_2 < Br_2 < Cl_2$$

Let us take chlorination as a representative reaction to understant the mechanism of halogenation. Chlorine, in the presence of AlCl₃ or FeCl₃ forms a complex, Cl_2 –AlCl₃. This complex can itself be the reactive electrophile or it may dissociate to give Cl⁺.



Step 1:
$$Cl - Cl + AlCl_{3} \implies AlCl_{3} \implies Cl - Cl - AlCl_{3}$$

Step 2: $H + Cl - Cl - AlCl_{3} \implies H + AlCl_{4} \implies$

However, there is no significant evidence for the involvement of Cl^+ as an electrophile and it is likely that the complex itself attacks the substrate. In the $Cl_2 - AlCl_3$ complex, role of the Lewis acid is to polarize the halogen molecule and weaken the Cl–Cl bond. This lowers the activation energy for the formation of σ -complex.



Schematic potential energy diagram for chlorination of benzene with $Cl_2(-)$ and $Cl_2AlCl_3(--)$ as an electrophile

Bromination follows a similar mechanism. As said above, lodine is weakest of the three halogens and even in the presence of a Lewis acid, It can halogenate reactive aromatics only. Therefore, in most other cases iodine-monochloride is used in the presence of Lewis acid, ZnCl₂.

Halogenation may be effected by hypohalous acids, $\stackrel{\delta^-}{HO} - \stackrel{\delta^+}{X}$, also. This is markedly slower than with molecular Halogens as HO⁻ is a poorer leaving group from $\stackrel{\delta^-}{HO} - \stackrel{\delta^+}{X}$, than, X⁻ is from $\stackrel{\delta^+}{X} - \stackrel{\delta^-}{X}$. The reaction is speeded in the presence of X⁻, however, as HO–X is then converted into the more reactive X₂, e.g. :

$$^{\Theta}$$
OCl + Cl $^{\Theta}$ + 2H $^{\oplus}$ \longrightarrow Cl₂ + H₂O

In the presence of strong acid, however, HO–Hal becomes a very powerful halogenating agent due to the formation of a highly polarized complex :

$$H\ddot{O} - X + H^{\oplus} \longrightarrow H_2 \overset{\oplus}{\bigcirc} X \longrightarrow H_2 O - X^{\oplus}$$

The evidence is that this species is the effective electrophile under these conditions and does not support the further conversion of complex into Hal^{\oplus}, i.e. unlike the case, with H₂O^{\oplus}-NO₂. F₂ reacts vigorously with benzene, but C–C bond breaking occurs and the reactions is of no preparative significance.



(5) Fridel-Crafts Alkylation

Alkyl halides react with benzene in presence of aluminium chloride to yield alkyl benzenes. Alkylation of benzenw with alkyl halides in the presence of aluminium chloride was discovered by Charles Friedel and James. M. Crafts in 1877.

A general equation for a friedel-Crafts alkylation reaction is the following.

$$+ R - X \xrightarrow{AlCl_3} R + HX$$

Alkyl halides by themselves are insufficiently electrophilic to react with benzene. $AlCl_3$ serves as a Lewis acid catalyst to enhance the electrophilicity of the alkylating agent. The mechanism for the reaction (shown in the following steps, with isopropyl chloride as R–X) starts with the formation of carbocation (step I). The carbocation then acts as an electrophile (step II) and attacks the benzene ring to form an arenium ion. The arenium ion (Step III) then loses a proton to generate isopropyl benzen. Some times carbocation rearrange to a more stable carbocation.

Mechanism for the Reaction



With R-X is a primary halide, a simple carbocation probably does not form. Instead, the AlCl₃ forms a complex with the alkyl halide and this complex acts as the electrophile. In the complex the carbon halogen bond is nearly broken and one in which the carbon atom has a considerable +ve charge.

$R - CH_2 - CH_2 - CH_3$

These complexes are so carbocation like that they also undergo typical carbocation rearrangements.

Friedel-Crafts alkylations are not restricted to the use of alkyl halides and $AlCl_3$. Many other pairs of reagents that form carbocations (or carbocation like species) may be used as well. These possibilities include the use of a mixture of an alkene and an acid.



A mixture of an alcohol an acid may also be used.





(6) Friedel-crafts Acylation

The group is called an acyl group and a reaction whereby an acyl group is introduced into a compound is called an acylation reaction.

The Friedel-Crafts acylation reaction is an effective means of introducing an acyl group into an aromatic ring. The reaction is often carried out by treating the aromatic compound with an acyl halide.



Acly chlorides (also called acid chlorides) are early prepared by treating carboxylic acids with thionyl chloride $(SOCl_2)$ or phosphorous pentachloride (PCl_2) .



Fridel-Crafts acylations can also be carried cut using carboxylic acid anhydrides. eg.



Mechanism of the Reaction

In most Fridel-Crafts acylation reactions the electrophile appears to be an acylium ion formed from an acyl halid ein the following way.





In the last step, $AlCl_3$ (a Lesis acid) forms a complex with the ketone (a Lewis base). After the reaction is over, treating the complex with water liberates the ketone.



Limitations of Friedel - Crafts Reactions

Several restrictions limit the usefulness of Friedel-Crafts reactions.

(a) When the carbocation formed from an alkyl halide, alkene, or alcohol can rearrange to a more stable carbocation, it usually does so and the major product obtained from the reaction is usually the one from the more stable carbocation. When benzene is alkylated with butyl bromide, for example, some of the developing butyl cations rearrange by a hydride shift-some developing 1° carbocations (see following reactions) become more stable 2° carbocations. The benzene reacts with both kinds of carbocations to form bot butylbenzene and sec-butylbenzene.



(b) An aromatic ring less reactive than that of halobenzene don't undergo Friedal Craft's reaction. Aromatic ring containing $-NH_2$, -NHR, $-NR_2$, groups does not undergo friedal craf's alkylation due to formation of anilinum complex which is meta direction and has more electron withdrawing power than halogen in benzene ring.



(c) Friedel-Crafts reactions do not occur when powerful electron-withdrawing groups are present on the aromatic ring or when the ring bears an -NH₂, -NHR or -NR₂ group. This applies to bot alkylations and acylations.



These to not undergo Friedel-Crafts reactions



(d) Aryl and vinylic haldies cannot be used as the halide component because they do not florm carbocations readily.



(e) Polyalkylations often occur - Alkyl groups are electron releasing groups, and once one is introduced into the benzene ring it activated the towards fruther substitution.



Polyacylations are not a problem in Friedel-Crafts acylations however. The acyl group (RCO–) by itself is an electron-withdrawing group, and when it forms a complex with AlCl₃ in the last step of the reaction, it is made even more electron withdrawing. This strongly inhibits further substitution and makes monoacylation easy.



Aromatic Hydrocarbon





AROMATIC HYDROCARBON

(f) Decarboxylation of Aromatic acids

$$\bigcirc$$
 -COONa + NaOH $\xrightarrow{\Delta, CaO}$ \bigcirc + Na₂CO₃

(g) Wurtz–Fitting reaction

$$\bigcirc Br + 2Na + Br - R \xrightarrow{dry ether} \bigcirc R + 2NaBr$$

(h) Deoxygenation of Phenols

$$\underbrace{\bigcirc}_{O} - OH \xrightarrow{Zn}_{A} \underbrace{\bigcirc}_{O}; \underbrace{\bigcirc}_{O} - OH \xrightarrow{Zn}_{A} \underbrace{\bigcirc}_{O} - OH$$

(i) Reduction of Diazonium salts

$$\bigcirc -N_2Cl + H_3PO_2 + H_2O \longrightarrow \bigcirc + N_2Cl + H_3PO_3 + HCl$$

(j) Desulphonation of sulphonic acids

$$\bigcirc$$
 $-SO_3 + H_2O_{steam} \xrightarrow{400-420 \text{ K}} \bigcirc$ $+ H_2SO_4$

Mechanisms of the above reactions have been given in further section.

- 1. All meta-directing groups are deactivating groups;
- 2. All ortho, para-direc ting groups except for the halogen are activating groups.
- 3. The halogens are deactivating groups

The activating substituents make the benzene ring more reactive towards electrophilic substitution, the deactivating substituents make the benzene ring less reactive towards electrophilic substitution.

All the strong activating substituents donate electrons into the ring by resonance and withdraw electrons inductively. The fact that are strong activators indicate that electron donation into the ring by resonance (which increases electron-density hence, nucleophilicity) is much greater than electron withdrawl frm the ring by the inductive effect (which decreases electron-density hence nucleophilicity). Strongly activating substituents are :



The moderately activating substituents also donate into the ring by resonance and withdraw electrons from the ring inductively. However they donate electrons into the ring by resonance less effectively than do not strongly activating substituents. These substituents are less effective at resonance donatin since, they can donate electrons by resonance in two competing directions-into the ring and away from the ring and thus net resonance effect is diminished and still electron donation by resonance is more than the electron withdrawl by induction and thus, these substituents are activators though moderately.





(substituents donates electrons by resonance into the benzene ring)



(substituents donates electrons aways from the benzene ring)

Alkyl, aryl and CH=CHR groups weakly activating substituents. Two of the three groups (aryl and CH = CHR) can donate electrons into the ring by resonance and can also withdraw from the ring by resonance. The fact that they are weak activators indicates that they are slightly more electron-donating than they are electron-withdrawing. An alkyl substituent is weak electron donor because of hyperconjugation.



The halogen are weakly deactivating substituents. They donate electrons into the ring by resonance and withdraw electrons inductively. Since, they have been found deactivators, we can conclude that they withdraw electrons inductively more strongly than they donate electrons by resonance.



The moderately deactivating substituents all have carbonyl groups directly attached to the benzene ring. They withdraw electron both inductively and by resonance.





The strongly deactivating substituents are powerful electron withdrawers. With the exception of $-\overset{\oplus}{NH_3}, -\overset{\oplus}{NH_2R}, -\overset{\oplus}{NHR_2}$ and $-\overset{\oplus}{NR_5}$ and they withdraw electrons both inductively and by resonance. The ammonium ions have no resonance effect, but the positive charge on the nitrogen atom causes them to strongly withdraw electron inductively.



Treatment of areanes with group I metal (like sodium, lithium) and methanol (or ethanol) in liquid reduces arenes to non-conjugated dienes.



Alkyl substituted arenes give, 1, 4-cyclohexadienes in which the alkyl group is a substituent on the double bond.



Metal ammonia-alcohol reduction of aromatic ring is known as Birch reductin and is one type of a more general class of react6ions called dissolving metal reduction.





When oxidised using $KMnO_4/OH^-$, $Na_2Cr_2O_7/H^+$, $KMnO_4/H^+$ the entire side chain, with at least one H at α -C, regardless of length is oxidised to –COOH.





The conversion of alkyl benzenes to benzoic acid with strong oxidations suggest that benzene ring is more stable than the side chains, this is correct so long as the side-chain contains at least one benzylic C–H bond. The first step in the mechanism is the removal of hydrogen from the benzylic carbon. If the side-chain has no C–H bond at the α -carbon (w.r.t. benzene nucleus), then benzene ring is cleaved.



(e) Combustion

$$2C_6H_6 + 15O_2 \xrightarrow{\Delta} 12CO_2 + 6H_2$$

(f) Side-chain halogenation



This provides a source of preparing other derivatives from benzene and toluene.



(NBS is N-bromo succinimide)



Relative Reactivity of Substituted Benzene

Ortho para directors Strongly activating	Meta directors Moderately deactivating
-O°, -'NH ₂ ,-'NR ₂ , -ÖH,-ÖR	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Moderately activating	Strongly deactivating
О О — ::::::::::::::::::::::::::::::::::	$-\overset{\oplus}{\mathrm{NH}}_{3},-\overset{\oplus}{\mathrm{NR}}_{3},-\mathrm{NO}_{2},-\mathrm{C}\equiv\mathrm{N},-\mathrm{CF}_{3},-\mathrm{CCl}_{3}$
Weakly activating CH3,CH ₂ CH ₃ ,R	
Weakly deactivating	
- <u>F</u> :,- <u>C</u> :,- <u>B</u> r:, - I:	

Directing Influence As Decided By Electron Density

• –OH group is ortho and para-directing since it increase electron-density at ortho and para-positions for electrophilic attacks; electron-density at meta-position is decreased hence, electrophilic attack at this position is least.





•-NO, group is electron- withdrawing group. It deactivates ortho and para-position for electrophilic attack and thus electrophile can ocupy meta-position. I to V are resonance and VI is resonance hybrid.



In this case nucleophilic attack at electron-rich ortho and para-sites is favoured.



Anamalous Behaviour Of Halogen Substituent

-X(F, Cl, Br, I) is o⁻, p-directing but is deactivating group.



This deactivating nature is attributed to high electronegativity of the halogen atom due to which they withdraw electrons; resonance effect explains its electron-donating behavivour.









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Alkyl groups and Orientation

Alkyl groups ($-CH_3$, $-CH_2CH_3$, etc.) have complete octet and are without and are without one-pair of electrons; but they are ring activators and o–, p-directors. They not only show electron-pumping effect, but also when attached to conjugated system show hyperconjugated effect (no-bond resonance). This type of resonance requires the interaction of σ -electrons instead of usual lone-pair of electrons. It toluene, hyperconjugation is show below :



Thus, hyperconjugation helps in increasing-density at o-and p-sites in case of alkyl groups.

There must be at least one H-atom on the carbon of the alkyl joined to the ring carbon to take part in hyperconjugation and relative ability of alkyl groups for this effect is



In this case, only p-isomer is obtained. It is due to steric influence of the substituents– $C(CH_3)_3$ and due to its unability to show hyperconjugation.

Orientation and Synthesis

By using the nature of directing group (subtituent), it is possible to prepare variety of products.

To prepare meta-bromonitrobenzene from benzene, we have to first carry out nitration and then bromination, and to prepare o-and p-dereivatives, sequence will be bromination and then nitration.





Orientation in Disubstituted benzene

When two substitution are present, orientatiion of the third coming S_E is complicated.

 $-CH_3$ group is o-, p-directing and $-NO_2$ group is m-directing, thus in p-nitrotoluene, new electrophile can be in a position shown by arrow :



Similarly we can decide the position of the new electrophile in other disubstituted compounds.



Problems may arise in the following cases :



Both are ortho, para-directing and none one of the vacant positions are ortho-and para, w.r.t. each. In such cases we follows : (a) Strongly activating groups generally win over deactivating or weakly activating groups.





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(b) If the subtitution are meta to each for other, S_{μ} in between vacant sites takes place rarely.



Halogen Compound

Aryl Halides

Source/Preparation

Direct halogenation



Low temperature and the presence of a halogen carrier favour nuclear substitution. The chlorides or bromides of Al, Fe, Sb may use used :

$$Fe \xrightarrow{Cl_{2}} FeCl_{2} \xrightarrow{FeCl_{4}} + Cl^{+}$$

$$fe \xrightarrow{Cl_{2}} FeCl_{4} + Cl^{+}$$

$$fe \xrightarrow{Cl_{4}} + Cl^{\oplus} \xrightarrow{G} \xrightarrow{Cl_{4}} + Cl^{+}$$

$$fe \xrightarrow{Cl_{4}} + H^{+} \xrightarrow{Cl_{4}} + H^{+}$$

$$FeCl_{4} + H^{+} \xrightarrow{FeCl_{4}} + HCl$$

Iron is most commonly used being converted to Lewis acid FeCl₃ as shown above.

It is agian S_E reaction and without halogen-carrier (Lewis acid) Cl^+ (halogena) is not formed and hence, reaction is not possible :





A methoxy group is so strongly activating that anisole quickly bromines in water without a catalyst :



Direction iodination is not possible since, iodine is least reactive and HI formed makes reaction reversible. In presence of oxidising agensts like HNO₃ or HIO₃, iodination of benzene is possible and HI formed is converted to I₂

$$1/2 I_2 + HNO_3 + \bigcirc \qquad \textcircled{O} \longrightarrow O \longrightarrow I + H_2O + NO_2$$

5 HI + HIO₃ \longrightarrow 3 I₂ + 3 H₂O

Iodination probably involves an electrophilic aromatic substitution with iodonium (I^+) acting as the electrophile. I+ is formed from iodine by oxidation with HNO₃.

$$H^{+} + HNO_{3} + 1/2 I_{2} \longrightarrow I^{+} + NO_{2} + H_{2}O$$

$$OH \qquad \qquad OH \qquad OH \qquad \qquad OH$$

Diazonium salts are converted to halogen compounds

$$\begin{array}{c} Br \\ N_{2} + \bigcirc & \underbrace{CuBr/HCl} \\ (Sandmeyer) \\ & \bigcirc & \underbrace{CuBr/HCl} \\ & \bigcirc & + N_{2} \\ & \bigcirc & + N_{2} \\ & + N_{2} \\ & \bigcirc \\ & + N_{2} \\ & \bigcirc \\ & + KCl \\ & \underbrace{A} \\ & \bigcirc \\ & \bigcirc \\ & + KCl \\ &$$

Diazonium salts are obtained by diazotisation of amino compounds and this provides a better route to convert amino compounds into halogen compounds :





Side - Chain Derivatives



Side-chain halogenation involves free radical mechanism due to lower bond energy of the benzyl C-H bond:



Benzyl radical is stablised by resonance due to delocalisaton of odd electrons into ring :



NBS can also be used for bromination of side-chain alkyl group :



In presence of an activating group -OH or -NH₂, side chain halogenation is difficult :



Properties

Physical

- **Example 1** Less polar, insoluble in water but soluble in organic solvents like ethanol and ether.
- **20** They show physiological activity and are used as insecticides. Examples are :





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Chemical

(a) Low reactivity of Aryl halide for S_N reaction

C-X bond in aryl halide is stable due to delocalisation of electrons by resonance. Also (C-X) bond possesses a double bond character like vinyl chloride and is stronger than C-X bond in alkyl halide.



Hence, S_N reaction is not possible in benzene nucleus under ordinary conditions. However, under high temperature and pressure, S_N reaction is made possible.

$$(\bigcirc -Cl \qquad + OH^{-} \xrightarrow{570 \text{ K, pressure}} (\bigcirc -OH + Cl^{-} + CN^{-} \xrightarrow{CuCN} (\bigcirc -CN + Cl^{-} + NH_3 + Cu_2O \xrightarrow{aq. NH_3} (\bigcirc -NH_2 + CuCl + H_2O)$$

If the benzene ring has (1) one or more substituents that strongly withdraw electrons from the ring by resonance, and (Z) a good leaving group (such as halogens), nucleophilic aromatic substitution reactions can occur without using extreme conditions. These electron-withdrawing groups must be positioned ortho or para to the leaving group. The greater the number of electron-withdrawing substituents, the easier it will be to carryout the nucleophilic aromatic substitution reactions.

$$\begin{array}{c} \bigcap_{Q} \left(\begin{array}{c} +z \\ \end{array} \right) \\ \bigoplus_{G} \left(\begin{array}{c} +z \\ \end{array} \right) \\ \bigoplus_{G} \left(\begin{array}{c} +z \\ \end{array} \right) \\ \bigoplus_{G} \left(\begin{array}{c} -N \\ \end{array} \right) \\ \bigoplus_{G} \left(\begin{array}{c} +z \\ \end{array} \right) \\ \bigoplus_{G} \left(\begin{array}{c} -N \\ \end{array} \right) \\ \bigoplus_{G} \left(\begin{array}{c} +z \\ \end{array} \right) \\ = \left(\begin{array}{c} +z \\ \end{array} \right) \\ \bigoplus_{G} \left(\begin{array}{c} +z \\ \end{array} \right) \\ = \left(\begin{array}{c} +z \\ \end{array} \right) \\ \bigoplus_{G} \left(\begin{array}{c} +z \\ \end{array} \right) \\ = \left(\begin{array}{c} +z \end{array} \right) \\ = \left(\begin{array}{c}$$

Add. 41-42A, Ashok Park Main, New Rohtak Road, New Delhi-110035 +91-9350679141 Nucleophilic aromatic substitution takes place by a two-step reaction known as an S_N Ar reaction byfollowing mechanism :



(b) Elimination - Addition Through Benzyne Internate

An aryl halide can undergo a nucleophilic substitution reaction in the presence of a very strong base such as NH_2^{Θ} .

When chlorobenzene-that has the carbon to which chlorine is attached isotropically labelled with ${}^{14}C$ – is treated with amide ion in liquid ammonia, aniline is obtained as a product. Half of the product has the amino group attached to the isotopically labelled carbon (*) as expected, but the other half has the amino group attached to the carbon adjacent to the labelled carbon.



The mechanisms that accounts for the experimental observations involves formation of a benzene intermediate which has two equivalent carbon atoms to which amino group can be attached. Benzyne has an extra π -bond between two adjacent carbon atoms of benzene and can be formed as :

Step -I : Strong base NH_2^{Θ} removes a proton from the position ortho to halogen :



Step -II : Anion formed in step I eliminates the halide ion, thereby forming benzyne :





The incoming nucleophile can attack either of the carbons of the "triple bond" of benzyne. Protonation of the resulting anion form the substitutin product. The overall reaction is an elimination-addition reaction; benzyne is formed in an elimination reaction and immediately undergoes an addition reaction.



Substitution at the carbon (*) that was attached to the leaving group is called direct substitution. Substitution at the adjacent carbon is called cine substitution.



(c) Wurtz -Fitting Reaction

$$\underbrace{\bigcirc}_{\text{aryl halide}} \text{Cl} + \text{CH}_{3}\text{Cl} + 2\text{Na} \xrightarrow{\text{ether}} \bigodot \rightarrow \text{CH}_{3}$$

$$\underbrace{\bigcirc}_{\text{alkyl halide}} \text{Cl} + \underbrace{\bigcirc}_{\text{Cl}} \text{Cl} + 2\text{Na} \xrightarrow{\text{ether}} \bigodot \rightarrow \text{CH}_{2} \xrightarrow{\text{Cl}} \bigcirc$$

aryl halide (side chain) $(x - C) + 2Na \rightarrow 0$

If only aryl halide is involved, diphenyl is formed (Fitting reaction)

(d) Ullman synthesis

$$2 \bigcirc -I + 2Cu \longrightarrow \bigcirc -\bigcirc \bigcirc$$

(e) Reaction with Chloral DDT is formed when chloral react with chlorobenzene in presence of concentrated H₂SO₄.

$$2 \underbrace{\bigcirc} - Cl + H - C = O \xrightarrow[CCl_3]{\text{conc. } H_2SO_4} Cl - \underbrace{\bigcirc}_{H} C - C - C - Cl$$

$$(CCl_3) \xrightarrow{Cl_3} Cl - \underbrace{\bigcirc}_{H} Cl$$

$$(2, 2-di (p-chlorophenyl)-1, 1)$$

$$(1-trichloroethane(DDT))$$

DDT is causing ecological problems, its use as insecticides is being banned.

Nitration





Chlorination



Sulphonation



• Chlorine is not a good donor of electrons by resonance due to its high electronegativity. Thus, the inductive effect of the Cl atom overcomes the resonance effect, and thus, it deactivates the benzene ring.

(g) Substitution on benzyl carbons (SN) : The greater reactivities of benzylic halides result from the stabilities of the carbocation intermediates that are formed when they react.



Tertiary cumyl chloride ionises to a carbocation with four important resonacne structure :



(resonance -stablised)

Because of the possibilitie of resonance, ortho and para substituent group on the benzene ring that activate electrophilic aromatic substitution further accelerate S_N 1 reaction at the benzylic position. Thus p-methoxy tert-cumyl chloride (I) undergoes hydrolysis about 3400 times faster than tert-cumyl chloride II.





Add. 41-42A, Ashok Park Main, New Rohtak Road, New Delhi-110035 +91-9350679141 Benzylic halides undergoes ${\rm S}_{\rm _N}$ reactions like aliphatic halides.



This provides a path of converting toluence into so many other compounds benzyl chloride.

Aromatic Nitro Compounds



Source

Direct nitration

Nitratig agent is

(a) conc. $HNO_3 + conc. H_2SO_4 \text{ or } (b)$ acetyl nitrate (N2O5 in acetic anhydride)

 $-NO_2$ is deactivating group, hence, further nitration takes plac with furning HNO_3 and H_2SO_4 mixture. Intermediate is o-complex (arenium carbocation) stablished by resonance.





 $-CH_3$ and $-OCH_3$ groups are activating groups hence, nitration of toluene and methoxy benzene (anisole) is easier than that of benzene.



From Diazonium salts

$$H_3C \longrightarrow N_2^+Cl^- \longrightarrow H_3C \longrightarrow H_3C \longrightarrow N_2^+ + HCl + NO_2$$

Oxidation Amino compounds : (using trifluroperbenzoic acid)





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Properties

- 80 Nitro-compounds are yellow crystalline solids (nitrobenzene is yellow liquid)
- Steam-volatile, denser than water in which they are in soluble
- 80 Nitro group is attacked by Grignard reagent, nitro-substituted aryl halides cannot be used for the preparation of these reagents.

$$O_2N \longrightarrow Br \xrightarrow{Mg/ether} No$$
 reaction

There is also partial positive charge on the ortho and para-positions. Thus, $-NO_2$ activates the benzene nucleus for nucleophilic substitutions at the ortho and para-positions.



Electrophilic substitutions (SE)



Further nitration to form trinitrobenzene takes place under drasitic conditions. Presence of electron-releasing group activates benzene nucleus for S_E . Toluene can be nitrated only once but nitro group introduced retards a second nitration on the same ring.

fuming HNO₃/H₂SO



80 -NO, group also deactivatives benzene nucleus alkyl for alkylation by Fridel-Crafts reaction.



Nucleophilic Substitution Reactions

Substitution of hydrogen by a nucleophile does not ocur in benzene itself, but the presence of one nitro group is sufficient to activate the o- and p-positions.



Aromatic Sulphonic Acids

They are derivatives of aromatic hydrocarbons in which one or more hydrogen of the benzene ring have been replaced by the function – SO₃H, called the sulphonic grouop.





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Source

Direct sulphonation



In the sulphonation, electrophile is SO₃ formed as :

$$2H_{2}SO_{4} \Longrightarrow SO_{3} + H_{3}O^{+} + HSO_{4}^{-}$$

Although it appears neutral, sulphur carries positives charge due to resonance :



Properties

Colourless crystalline deliquescent solid. Very soluble in water and solution is strongly acidic.

$$\bigcirc$$
 $\operatorname{SO}_3H + H_2O \Longrightarrow \bigcirc$ $\operatorname{SO}_3^- + H_3O^+$

They are stronger acid than carboxylic acid.

$$\bigcup_{i=1}^{SO_3H} (K_a = \text{very large}) \qquad \bigcup_{i=1}^{COOH} (ka = 6.3 \times 10^{-5})$$



Formation of diphenyl sulphone



Desulphonation

The knocking out of sulphonic acid group from benzene nucleus is called desulphonation.



 $SO_3H + OH^-$ (from water) $\longrightarrow H_2SO_4$

The desulphonation is very useful for preparation of certain isomers which are otherwise not obtained in pure state.

Reactions of sodium salt of benzene sulphonic acid

(conversioin into other derivatives)

NO



Source

Nitrobenzene can be reduced under different media to produce aniline and releated compounds. (a)

$$O - NO_2 \xrightarrow{Sn/HCl} O - NH_2 + H_2O$$

$$O - NO_2 \xrightarrow{NO_2} + TiCl_3 + HCl \longrightarrow TiCl_4 + H_2O O$$

$$O - NH_2 + H_2O O - NH_2 + H_2O O O - NH_2 + H_2O O - NH_2 + H_2O O O - NH_2 + H_2O - NH_2 +$$

(b)

$$\bigcup_{NO_2}^{NO_2} + 3 \text{ NH}_4 \text{Hs} \longrightarrow \bigcup_{NO_2}^{NH_2} + 3 \text{ NH}_3 + 3\text{S} + 2\text{H}_2\text{O}$$

 NH_4 HS is suitable reagent where only one $-NO_2$ (in stages) is to be reduced.





Action of NH_4HS and $SnCl_2/HCl$ is specific. NH_4HS reduces $-NO_2$ para to $-CH_3$ while $SnCl_2/HCl$ reduces $-NO_2$ ortho to $-CH_3$.

$$\bigcup_{NO_2}^{CHO} \xrightarrow[or]{or}_{NH} O_{NH}$$

Alkaline Fe^{2+} does not reduce – CHO into – $CH_2OH.SnCl_2/HCl$ can also be used here.

(c)
$$(C_1 + NH_3 \xrightarrow{Cu_2O} (NH_3 + HCl)$$

C-Cl bond is stable, hence ammonolysis of aryl halide takes place under high temperature and pressure. However electron withdrawing group in benzene nucleus makes C-Cl bond highly reactive.

$$O_2N - O_2N -$$

$$\bigcirc -\text{OH+NH}_3 \xrightarrow{\text{ZnCl}_2} \bigcirc -\text{NH}_2 + \text{H}_2\text{O}$$

(d) $(O) \rightarrow O$ $(O) \rightarrow O$

When the migrating group is aryl, the rate of the Hofmann degradation reaction is increased by the presence of electron releasing substituens in the aromatic ring.

$$G \longrightarrow CONH_2 \longrightarrow NH_2$$

 $G := -OCH > -H > -CI > -NH$

(e)
$$(O)$$
-COOH $\xrightarrow{N_3H, D (Schmidt)}$ (O) -NH₂+CO₂+N₂
conc. H₂SO₄

(f)
$$(N_3H, \Delta (\text{Schmidt}))$$
 (O) $-\text{COOH} \xrightarrow{N_3H, \Delta (\text{Schmidt})}$ (O) $-\text{NH}_2 + \text{CO}_2 + \text{N}_2$

(g)
$$(\bigcirc -N = N - (\bigcirc) \xrightarrow{H_2, Ni} (\bigcirc -NH - NH - (\bigcirc) \xrightarrow{H_2, Ni} (\bigcirc -NH - NH - (\bigcirc) \xrightarrow{H_2, Ni} (\bigcirc -NH_2) (\bigcirc -NH_2)$$

(h)
$$\bigcirc$$
 + NH₂OH
hydroxylamine \longrightarrow \bigcirc NH₂+H₂O





This is called **Hofmann-Martius rearrangement** and alkyl group preferentially migrates to p-position and if it is occupied, then to o-position.

(j)
$$()$$
 -NC $\xrightarrow{\text{reduction}}$ $()$ -NHCH₃
(N-methyl aniline)

(k)
$$(NH_2 \xrightarrow{RX} OH^- NHR \xrightarrow{RX} OH^- NHR \xrightarrow{RX} OH^- NHR \xrightarrow{RX} R$$



Some other methods are very similar to that used for aliphatic amines.

Properties

Physical

• Colourless liquid/solids, but due to air oxidation, they turn brown.



- Slightly soluble in water (polar solvent) but highly soluble in benzen and other organic solvents.
- High b.p. due to intermolecular H-bonding-N, N-dimethyl aniline hs lower b.p. due to lack of H-bonding but molecular weight is also important affecting b.p.



• Para-substituted aniline, being the most symmetric, have the highest melting points. Thus p-toluidine is solid at room temperature while o-toluidines are liquids.



Relations of the -NH₂ group

(a) Methylation (Alkylation)

$$\underbrace{\bigcirc} \text{-NH}_2 + \text{CH}_3 \text{I} \xrightarrow{\text{OH}^-} \underbrace{\bigcirc} \text{-NHCH}_3 \xrightarrow{\text{OH}^-} \underbrace{\bigcirc} \text{-N-CH}_3 \xrightarrow{\text{CH}_3 \text{I}} \underbrace{\bigcirc} \text{-N-CH}_3 \xrightarrow{\text{CH}_3 \text{I}} \xrightarrow{\text{CH}_3 \text{I}} \text{-N-CH}_3 \xrightarrow{\text{CH}_3 \text{I}} \xrightarrow{\text{CH}_3$$

(b) Arylation

Arylation of aniline with C₆H₅Cl is difficult.

$$\bigcirc -\mathrm{NH}_{2} + \bigodot -\mathrm{Cl} \xrightarrow{473\mathrm{K}, \text{ pressure}} \bigcirc -\mathrm{NH}_{2} - \bigotimes \xrightarrow{\text{diphenyl amine}} \xrightarrow{\text{diphenyl amine}} \xrightarrow{\text{diphenyl amine}} \xrightarrow{413\mathrm{K}} \xrightarrow{\mathrm{pressure}} -\mathrm{NH}_{2} - \operatorname{NH}_{2} - \operatorname{NH}_{3} - \operatorname{Cl} \xrightarrow{413\mathrm{K}} \xrightarrow{\mathrm{pressure}} -\mathrm{NH}_{4} - \operatorname{Cl} \xrightarrow{\mathrm{Cl}} \xrightarrow$$

(c) Acylation

Arylation of aniline with C₆H₅Cl is difficult.

$$\bigcirc$$
 -NH₂+CH₃COCl \longrightarrow \bigcirc -NHCOCH₃
N-acetyl aniline
(acetanilide)

Acetyl group deactivates $-NH_2$ group, whenever aniline is subjected to nitration, acetylation is necessary to protect the ring from being oxidised.

(d) Sulphonylation



 2° amine also reacts but the product is insoluble in alkali. This provides a method (called Hinsberg method) of separation of mixture of 1° , 2° and 3° amines.

(e) Carbyl Amine Reaction

Only 1° amines give this reaction when unpleasant smell of isocyanides is obtained on heating a mixture of alcoholic KOH, CHCl, and 1° amine.

$$\bigcirc -\mathrm{NH}_2 + \mathrm{CHCl}_3 + 3 \mathrm{KOH} \longrightarrow \bigcirc -\mathrm{NC} + 3\mathrm{KCl} + 3\mathrm{H}_2\mathrm{O}$$



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(f) Formation of Schiff base

$$\textcircled{O}-NH_2+OHC-\textcircled{O}\longrightarrow\textcircled{O}-N=HC-\textcircled{O}\longrightarrow\textcircled{H_2O}$$

These Schiff bases are easily hydrolysed to the free maines and so their formation offers a mean of 'protecting' an amino group (during nitration).

(g) Oxidation



(h) Reaction with HNO_2

1° amines form diazonium salts at low temperature (273-278K). A reaction in which - NH, group is converted into

diazo group $\begin{pmatrix} \oplus \\ -N \end{pmatrix}$ is called diazotisation. Diazonium salts are stable in cold aqueous solution.

$$NaNO_{2} + HCl \xrightarrow{273K} HNO_{2} + NaCl$$

$$O - NH_{2} + HCl \xrightarrow{273K} O - NH_{3}^{+}Cl^{-}$$

$$O - NH_{3}^{+} + HNO_{2} \xrightarrow{273K} O - NH_{3}^{\oplus} NCl^{-}$$
benzene diazonium chloride

Aniline can be converted into so many other compounds through the formation of diazonium salts.

$$\bigcirc -N_{2}^{+}+Cl^{-} \xrightarrow{H,O, \Lambda} \bigodot \bigcirc -OH+N_{2}+HCl$$

$$\xrightarrow{H,PO_{2}+H,O} \bigodot +H_{3}PO_{3}+HCl$$

$$\xrightarrow{CuCl+HCl} \bigodot \bigcirc -Cl+N_{2}$$

$$\xrightarrow{CuBr+HBr} \bigodot \bigcirc -Cl+N_{2}$$

$$\xrightarrow{Cu,\Lambda} \bigodot \bigcirc -Cl+N_{2}$$

$$\xrightarrow{Cu,\Lambda} \bigodot \bigcirc -Cl+N_{2}$$



More reacious are given in sec. 16.8 (diazonium salts)

2º amines form nitrosamine (yellow oily liquid) which is stable at room temperature. However on reaction with HCl in ether and alcohol – NO group nigrates to para-position (Fischer-Hepp)

$$\bigotimes_{\substack{I \\ CH_3}} NH+HNO_2 \longrightarrow \bigotimes_{\substack{I \\ CH_3}} N-NO \xrightarrow{HCl,ether/C_2H_3OH} ON-\bigotimes_{p-nitroso-N-methyl aniline} ON$$

3° amines form p-nitroso derivatives



(strongly p-activating)





Hydrolysis of p-nitrosos derivative gives 2° amines

$$\begin{array}{c} H_{3}C \\ H_{3}C \end{array} \\ N \longrightarrow O \\ H_{3}C \end{array} \\ N \longrightarrow O \\ N O + H_{2}O \xrightarrow{NaOH} O \\ P-nitrosophenol \end{array} \\ \begin{array}{c} H_{3}C \\ H_{3}C \\ 2^{\circ} \text{ amine} \end{array} \\ \end{array} \\ \begin{array}{c} H_{3}C \\ 2^{\circ} \text{ amine} \end{array} \\ \end{array}$$

This provides a path of the preparation of 2° amines

$$\bigcirc -\mathrm{NH}_2 + \mathrm{K} \xrightarrow{\Delta} \bigcirc -\mathrm{NH}^-\mathrm{K}^+ + 1/2 \mathrm{H}_2$$

This represent acidic nature of aniline. Hypochlorous acid also reacts with aniline in which active H is replaced :

$$\bigcirc -\mathrm{NH}_2 + \mathrm{HOCl} \longrightarrow \bigotimes_{\text{N-Chloroaniline}} -\mathrm{NHCl} + \mathrm{H}_2\mathrm{O}$$



Electrophilic substitution in benzene nucleus

-NH₂ group is o, -p directing and activating group.



Hence, -NH₂ group activatives benzene nucleus for ortho and para-electrophilic attack.



(resonance stablised σ -complex)

(a) Bromination



 $-NH_2$ group is greatly activating group hence reacton takes place rapidly. However if ring is deactivated by acetylation, o-and p-isomers are obtained.



(b) Nitration

Direct nitration of aniline with nitric acid gives a complex mixture of mono-,di-and tri-nitro compounds and oxidation products. If –NH, group is protected by acetylation and then nitrated, p-isomer is the main product.





AROMATIC HYDROCARBON

Like antranilic acid, sulphanilic acid also exists as Zwitter ion due to inernal neutralisation.



Distinction between Aliphatic and Aromatic Amines

S. No.	Test		CH ₃ NH ₂
1.	Diazotisation	Diazonium salt is formed	– NH is replaced by – OH
	(reaction with HNO_2)	$\sqrt{N_2^+}$	
		which forms azo dye with	
2.	S _E	can be halogenated,	
3.	Basic nature	sulphonated, nitrated. less basic than CH ₃ NH ₂ ,NH ₃	no more basic than NH ₃

Phenolic compounds

Phenols are the compounds of the general formula ArOH, where, Ar is phenyl or substitued phenyl. Phenols differs from alcohols in having the –OH group attached directly toan aromatic ring.





Diazonium salts are obtained from aniline and its derivatives by a process called diazotisation.



Alkali Fusion of Benzene Sulphonic Acid salts



Hydrolysis of Aryl Halides

Halogen atom attached to benzene nucleus does not give S_N^2 reaction since C–X bond is stable due to resonance. However, in presence of electron withdrawing group in o- and p-positions, S_N reaction is favoured and phenolic compounds are formed.

no reaction
$$\bigcirc \frac{\text{NaOH}}{\text{high, temp, pressure}} \bigcirc (\text{Dow's process})$$



$$\bigcup_{NO_2}^{Cl} \bigcup_{\substack{(i) \text{ NaOH} \\ (ii) \text{ HCl}}} \bigcup_{NO_2}^{OH} \bigcup_{NO_2}^{NO_2}$$

Distillation of Phenolic Acids



Oxidation of Grignard Reagent





Middle Oil of Coil - Tar Distillation

Middle oil of coal-tar distillation has naphthalene and phenolic compounds. Phenolic compounds are isolated in following step :

Step-I : Middle oil is washed with H_2SO_4 . It dissolves basic impurities like pyridine (base).

Step-II: Excessive cooling separates naphthalene (a low melting solid)

Step-III : Filtrate of step II is treated with aqueous NaOH when phenols dissolves as phenoxides.

Carbon dioxide is then blown through the solution to liberate phenols.

$$\bigcirc -\text{OH} + \text{NaOH} \longrightarrow \bigcirc -\text{ONa} + \text{H}_2\text{O} \xrightarrow{\text{CO}_2,\text{H}_2\text{O}} \bigotimes \bigcirc -\text{OH} + \text{Na}_2\text{CO}_2$$

Step-IV : Drude phenol (of step III) is subjected to fractional distillation.

 $\begin{array}{c|c} Crude & \underbrace{fractional} \\ phenols & \underbrace{distillation} \\ \hline \\ 484 - 508K \\ \hline \\ \\ xylo(hydroxy xylenes) \\ \hline \\ \end{array}$

Properties

Physical

Similest phenols are liquids or low-melting solids.

They are capable of forming intermolecular H-bonding among themselves and with water. Thus,

- thy have high b.p.
- they are soluble in water.



(intermolecular H-bonding among phenol molecules)



(crossed intermolecular H-bonding between water and phenol molecules)

Due to intermolecular H-bonding and high dipole moment, m.p. and b.p. of phenol are much higher than that of hydrocarbon of comparable molecular weights.

Solute	mol. wt.	b.p.	m.p.
phenol	$94 \mathrm{g} \mathrm{mol}^{-1}$	455 K	314 K
toluene	$92 g mol^{-1}$	384 K	178 K



Isomer	b.p. at 760 mm	Solubility g/100 g	
o-nitrophenol	373 K	0.2	volatile in steam
p-nitrophenol	decomposes	1.69	non-volatile in steam
m-nitrophenol	467 K	1.35	non-volatile in steam

Comparison of properties of nitrophenols

Form the above table, it is clear that o-nitrophenol has much lower b.p. and much lower solubility in water than its isomer and is only steam-volatile.

-m and p-isomer have high b.p. because of intermolecular H-bonding and high solubility in water is againdue to crossed intermolecular H-bonding with H₂O.

o-isomer has intramolecular H-bonding due to which association with different molecules decreases hence, b.p. is low giving volatile character to it and also H-bonding with H_2O molecules is not possible which makes it water soluble to a very small extent.

-Steam distillation depends upon a substance having an appreciable vapour pressure at the b.p. of water, by lowering the v.p., intermolecular hydrogen bonding inhibits steam distillation of the m-and p-isomer.



intermolecular hydrogen bonding in p-nitrophenol molecules



Acidity of Phenols And Effect of Substituents On It





eakter acid



Phenols are converted into their salts by aqueous NaOH, but not by aqueou bicarbonates. The salts are converted to free phenols by aqueous mineral acids (HCl, etc.,) carboxylic acid or carbonic acids. Phenol is more acidic than alcohols but less than carboxylic acid. Enhanced acidity of phenol is due to (a) polar effect (b) resonance effect.





Add. 41-42A, Ashok Park Main, New Rohtak Road, New Delhi-110035 +91-9350679141 C_6H_5 - (phenyl) group is electron-withdrawing and phenoxide ion is more resonance stabilised than phenol, hence following equilibrium is displaced towards the right where stable phenoxide ionis formed.



Alkoxides are stabilised neither by resonance nor by the polar effect of benzene rings or double bonds.



• electron-attracting substituents like -X, or $-NO_2$ increase the acidity of phenols are electron-releasing substituents like $-CH_3$ decrease acidity.



 K_a (acidity constant) and p K_a of different substituted phenola are given in table. The marked lower acidity in case of meta-isomer is explained by the fact that m-nitrophenoxide ion is stablised by inductive effect only and no resonance effect operates with $-NO_2$ group.



• Reactions in which phenol is a source of active H are :





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Formation of Complexes with FeCl₃

Phenols form coloured iron complexes when related with neutral FeCl₃ solution. The formation of iron complexes is attributed to the existence of keto-enol tautomerism in phenols. Phenol predominantly exists in enolic form, hence colour formation is used to identify phenols.



Other Reaction of –OH Groups



This is called Williumson's synthesis. The phenoxide ionis a nucleophile and will replace halogen of the alkylhalide.







Electrophilic Substitution In Benzene Nucleus

-OH group is o- and p-directing and activating group for SE reactions.





In presence of NaOH, phenoxide ion is formed which is mroe reactive than phenol towards electrophilic aromatic substitution.



At room temperature, ortho-isomer while at 373 K the para-isomer is the main product. **Nitration**

-OH group is activating group, hence, nitration is possible with dil. HNO₃.

 $HNO_3 + HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$



 HNO_3 is oxidising agent and may lead to cleavage of benzene ring hence, further nitration is done carefully. However ring can be deactivated by sulphonation and then nitration will give picric acid in better yield.





Nitrosation

 $HNO_2 + H_2SO_4 \rightleftharpoons NO^+ HSO_4^- + H_2O$



Nitrosophenol ca be oxidised to $-NO_2$ by HNO₃; this provides a path of preparing nitrophenol.



Alkylation (Friedel-Crafts Reaction)



$$\underbrace{\bigcirc}_{\text{OH}} - \text{OH} + \text{CH}_{3} - \underbrace{\stackrel{\text{CH}_{3}}{\text{C}}_{\text{OH}} - \text{OH}}_{\text{CH}_{3}} \underbrace{\stackrel{\text{70\% H}_{2}\text{SO}_{4}}{\text{AlCl}_{3}} \rightarrow \text{H}_{3}\text{C} - \underbrace{\stackrel{\text{CH}_{3}}{\text{C}}_{\text{CH}_{3}}}_{\text{CH}_{3}} - \text{OH} + \text{H}_{2}\text{O}$$

Acylation (Friedel-Crafts Reaction)



Intermediate of this reaction is $CH_3 \overset{\oplus}{C} = O$ (acylium ion).

Fries rearrangement

When esters or phenols are heated with $AlCl_3$ the acyl group migrates from the phenolic oxygen to an ortho or paraposition of the ring thus, yielding a ketone. This reaction is called the Fries rearrangement and appears to involve generation of an acylium ion, RCO^+ , which then attack the ring as in ordinary Friedel-Cracft acylation.





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Claisen rearrangement



This is the arrangement of allyl ethers to allyl phenols. Allyl group migrates to ortho-position. If ortho-position is already occupied, para-isomer is obtained.



In this Claisen rearrangement, carbon which gets attached to benzene nucleus is vinylic and no allylic.

Coupling reactions (Azo dye formation)

Phenol reacts with aryl diazonium salts in presence of alkali at low temperature of form form azo dyes.







Kolbe reaction (Carbonation)

Treatment of the ssalt of a phenol with CO_2 under pressure brings about substitution of the carboxyl group, –COOH, for hydrogen of the ring. This is called Kolbe reaction.



This provides a path of conversion of phenol into hydroxy carboxylic acids. It seems likely that CO_2 attaches itself initially to phenoxide oxygen rather than to the ring.



At high temperature (525 – 575 K), p-isomers is obtained.



H-atom attached to the ortho-positoin combines with phenoxide oxygen. Salicyclic acidis used to prepare aspirin, salol and picric acid :





Gattermann Reaction (Formylation)



This reaction is used to prepare aldehyde when activating groups like -OH, -NH, are present.

$$HCN + HCl \rightleftharpoons Cl - CH = NH \xrightarrow{ZnCl_2} CH = NH + ZnCl_3$$



Condensation Reaction

(a) Condensation of phenol with HCHO in presence of acid of acid forms bakelite.



(b) Condensation of phenol with phthalic acid in presence of concentration H_2SO_4 forms phenolphthalein (an indicator) which gives pink colour with NaOH (phthalein test of dibasic acid)







Sandymeyer Reaction

Nucleophiles such as CN^- , Cl^- etc., replace the diazonium group if appropriate cuprous salt is added to the solution containing diazonium salt.

$$O - N_2^+, Cl^- \xrightarrow{CuCl, HCl} O - Cl^- + N_2$$
$$O - N_2^+, Cl^- \xrightarrow{CuBr, HCN} O - Br + N_2$$
$$O - N_2^+, Cl^- \xrightarrow{CuCN, HCN} O - CN + N_2$$

Sandmeyer reaction involves : $CuCl + Cl \rightarrow CuCl_2$ -



Diazo coupling often takes place in basic solutions since due to deprotponation of the phenolic –OH group or benzene sulphonic acid and carboxylic groups, activate the aromatic ring for S_E reaction. Common azo dyes have sulphonate/carboxylate groups to enhance solubility of the azo dye in water and to help bind the dye to the polar surface of common fibres such as cotton and wool.





Acyl chlorides can be reduced to aldehyde by treating them with lithium tri-ter-butoxy aluminium hydride, LiAlH($OC(CH_1)$, at 195 K.



The reduction is brought by the transfer of a hydride ion from the aluminum atom to the carbonyl carbon of the acyl chloride. Subsequent hydrolysis frees the aldehyde.

Reimer-Tiemann reaction is used to prepare phenolic aldehydes

$$\underbrace{\bigcirc}_{\text{OH}}^{\text{OH}} + \text{CHCl}_3 + 3\text{KOH} (aq) \xrightarrow{\Delta} \underbrace{\bigcirc}_{\substack{\text{OH}\\(\text{and } p-)}}^{\text{OH}} + 3\text{KCl} + 2\text{H}_2\text{O}$$



Friedel-Crafts Acylation



This reaction cannot be used on strongly deactivated aromatic systems.

Gattermann-Koch Reaction



Thus, HCl (reactant) and HCl (product) are different. H of HCl (reactant) and CO appear in the form of –CHO in the benzene nucleus. It is confirmed by the fact that using isotopic DCI instead of HCl, would form –CDO and no –CHO. This reaction also succeeds only with benzene and acitvated benzene derivative.

Gattermann-Aldehyde Synthesis

$$\bigcirc + \text{HCN} + \text{HCl} + \text{H}_2\text{O} \xrightarrow{\text{AlCl}_3} \bigcirc + \text{NH}_4\text{Cl}$$

Stephan Reaction

$$\bigcirc \xrightarrow{\text{CN}} \xrightarrow{\text{SnCl}_2/\text{HCl}} \bigcirc \xrightarrow{\text{CH} = \text{NH}} \bigcirc \xrightarrow{\text{CH} = \text{NH}, \text{HCl}} \bigcirc \xrightarrow{\text{CH} = \text{NH}, \text{HCl}} \xrightarrow{\text{CH} = \text{NH}$$

Grignard Reagent

$$\bigcirc^{\text{MgBr}} \overset{\text{O}}{\longrightarrow} \overset{\text{CHO}}{\longrightarrow} \bigcirc^{\text{CHO}}$$

Oxidation of Benzyl Chloride

Using Diazonium Salts

$$\bigcirc - \overset{\textcircled{\sc benzaldoxime}}{\mbox{NCI} + CH_2 = NOH} \longrightarrow \bigodot - \overset{\sc benzaldoxime}{\mbox{benzaldoxime}} \longrightarrow \bigodot - CHO$$



Properties

Physical

 C_6H_5 CHO is a colourless liquid with smellof bitter slmond, spari9ngly soluble in water but readily in ehtanol and ether.

 $C_6H_5COCH_3$ is crystalline solid and is steam volatile, soluble readily in ethanol and ether but sparingly soluble in water. It produces natural type of sleep when administered orally.

Ortho-quinones, particularly ortho-benzoquinone are less stable than their para-quinone isomers. It is due to the fact that in ortho-isomer, the C = O bond dipoles are nearly aligned and these have a repulsive destabilising interaction. In para-isomers, these dipoles are farther apart.



Chemical

Aromatic carbonyl compounds with following structure

Conjugation of the carbonyl carbon with the aryl ring reduces the electrophilic reactivity of the carbonyl carbon atom due to delocalisation of π -electrons. Hence, aromatic aldehydes and ketones are less reactive than aliphatic classes.

Benzaldehyde, like aliphatic aldehydes, reduces Tollen's reagent (silver-mirror test). However, it does not reduce Fehling's solution. (a distinction from aliphatic class).

They slow elimination and addition reaction of aliphatic classes.

$$>C = O + H_2NG \longrightarrow >C = NG + H_2O$$

$$\rangle C = O + HCN \longrightarrow C < CN^{OH}$$

However, acetophenone does not form bisulphite complex, probably due to steric hindrance.

no reaction
$$4$$
 NaHSO₃ 4 O-CHO $-$ CH 4 $-$

Benzaldehyde can react with hydrazine to form benzylideneazine.

$$\bigcirc -\text{CHO} + \text{H}_2\text{O} - \text{NH}_2 + \text{OHC} - \bigcirc \rightarrow \bigcirc -\text{CH} = \text{N} - \text{N} = \text{HC} - \bigcirc \text{benzylideneazine}$$

Oxidation





Reduction



Cannizzaro Reaction

$$2 \bigcirc + N_{a}OH \longrightarrow \bigcirc + \bigcirc + \bigcirc$$

- It is given by those aldehydes which do not have H at α -carbon, and also by HCHO.
- It is a disproportionation reaction.
- Benzoin condensation

When benzaldehyde is heated with aqueous ethanolic NaCN or KCN, it dimerises to form an a hydroxy ketone ketone called benzoin, and reaction is called benzoin condensation.

It involves self condensation of an aromatic aldehyde in the presence of CN⁻ as catalyst.

$$\underbrace{\bigcirc}_{C,H_{0}O} \xrightarrow{H}_{C,H_{0}O} \underbrace{\bigcirc}_{C,H_{0}OH} \xrightarrow{H}_{O} \xrightarrow{H}_{C,H_{0}OH} \xrightarrow{H}_{O} \xrightarrow{H}_{$$

It resembles Aldol condensation of aliphatic aldehyde in which α -H condenses, but –CHO group is free.

$$\begin{array}{c} H & O \\ I & H \\ CH_3C + H - CH_2CH \xrightarrow{NaOH} CH_3CHCH_2CHO \\ O & OH \end{array}$$

Perkin Reaction

It is the condensation reaction in which aromatic aldehyde is heated with an anhydride of an aliphatic acid in the presence of sodium salt of the same acid form α , β -unsaturated acid.

$$\bigcirc -\text{CHO} + \text{CH}_{3}\text{C} - \text{O} - \text{CCH}_{3} \xrightarrow{\text{CH}_{3}\text{COONa}} \checkmark \bigcirc -\text{CH} = \text{CHCOOH} + \text{CH}_{3}\text{COOH}$$

acetic anhydride

However, with cylic anhydride (succinic anhydride), β , γ -unsaturated acid is formed.

$$\bigcirc -\text{CHO} + \bigcup_{\text{CH}_2\text{CO}}^{\text{CH}_2\text{CO}} \circ \xrightarrow{\text{CH}_2\text{COONa}} \checkmark \bigcirc -\text{CH} = \text{CHCH}_2\text{COOH}$$



Witting Reaction

It converts the carbonyl group of a ketone or aldehyde into a new double bond on reaction with phosphorus ylides.

$$\begin{array}{c} R \\ R \\ R \\ R \\ C = O + \overset{\bigoplus}{P} h_3 - \overset{\bigoplus}{C} H_2 \\ \underset{\text{phosphorus}}{\text{phosphorus}} \\ \text{ylide} \\ \end{array} \\ \begin{array}{c} R \\ R \\ C = CH_2 + Ph_3P = O \\ R \\ \end{array}$$

$$\bigcirc -C = O + Ph_{3}^{\textcircled{p}} - C \Leftrightarrow \bigcirc \bigcirc H$$

Mixture of cis and trans-isomers often result when geometric isomerism is possible.

$$\bigcirc -\text{CHO} + \text{H}_{2}\text{N} - \bigotimes \bigcirc -\text{CH} = \text{N} - \bigotimes \bigcirc \text{CH} = \text{N} - \bigotimes \bigcirc \text{Schiff's base}$$
$$\bigcirc -\text{CHO} + \text{CH}_{2} = \text{CHLi} \xrightarrow{(i) \text{ ether}} \bigotimes \bigcirc -\text{CHCH} = \text{CH}_{2}$$
$$1 - \text{phenyl-2-propen-1-ol}$$
$$\bigcirc -\text{CHO} + \text{CH}_{3}\text{CH}_{2}\text{NH}_{2} \xrightarrow{\text{NaBH}_{3}\text{CN}} \bigotimes \bigcirc -\text{CH}_{2}\text{NHCH}_{2}\text{CH}_{3}$$
$$\text{N-ethylbenzylamine}$$

Reactions of Benzene Nucleus

$$\begin{array}{c} H - C - O^{0} \\ & & H - C - O^{0} \\ & & & H - C - O^{0} \\ & & & & H - C - O^{0} \\ & & & & & H - C - O^{0} \\ & & & & & & H - C - O^{0} \\ & & & & & & & \\ \end{array}$$



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