Orientation in Aromatic Disubstitution

When electrophilic substitution takes place into a benzene ring which already contains one substituent (S), the second substituent (E) may enter the ring in any of the remaining positions (2,3,4,5,6). Thus the possible disubstitution products are :

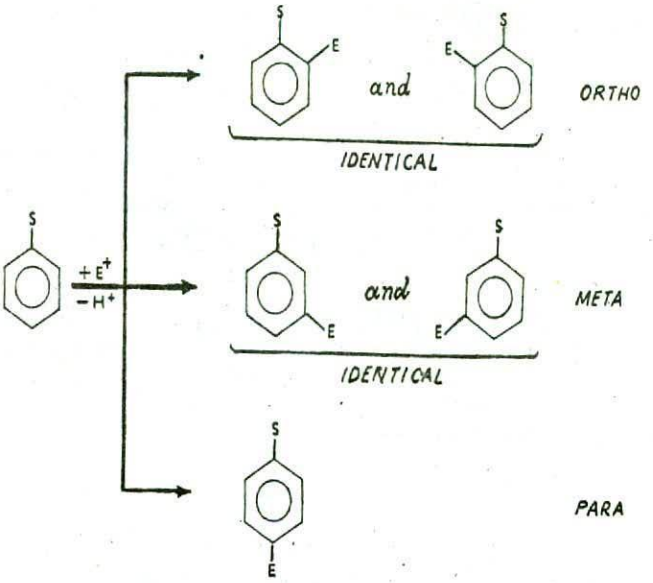


Fig. 36.1. A substituted benzene C_6H_5—S can give only three disubstituted products : *ortho*, *meta* and *para*.

On purely statistical basis one would expect the ratio of *ortho*, *meta* and *para* products as
ORTHO = 2/5 (40%), since *two* out of *five* products can be ortho
META = 2/5 (40%), since *two* out of *five* products can be meta
PARA = 1/5 (20%) since *one* out of *five* products can be para.
But in actual practice this proportion is never observed.

SEPARATION OF ISOMERS

The quantities of each disubstitution product formed (ortho, meta and para) can be found by their preparation and estimation. The differences in melting point, boiling point, and solubility of the isomers enabled the separation of the isomers by fractional crystallisation and fractional distillation.

Table. Melting and Boiling points of some Isomers

Disubstituted Isomer compound		*Ortho*	*Meta*	*Para*
Xylenes, $C_6H_4(CH_3)_2$	mp	−28°C	−54°C	13°C
	bp	144°	139°	138°
Cresols, $C_6H_4(OH)_2$	mp	30	−11	37
	bp	191·5	202·8	202·6
Dibromobenzenes, $C_6H_4Br_2$	mp	6·7	−6·5	89
	bp	224	219·4	218

It will be observed from the table that differences in melting and boiling points of the isomers may not be large enough to make the separation easy. The modern technique of various forms of chromatography, especially gas-liquid chromatography, has now made it possible to separate and estimate small quantities of material. Therefore, the proportions of the ortho, meta and para forms can be found accurately.

DETERMINATION OF ORIENTATION

Having effected the separation of the isomeric disubstituted derivatives of benzene, next there is the problem of their identification. In other words, we have got to assign positions to the two substituents in each of these derivatives on the benzene ring. *The arrangement of substituents on the benzene ring* is often referred to as **Orientation.** This term is often used for the process of determining the positions to substituents (*Orient*=to determine position of) on the benzene ring.

(3) **The Physical Methods.** The isomeric disubstituted benzene could be easily identified today by the physical methods.

(*a*) *Dipole Moments.* For compounds of the type $C_6H_4X_2$, orientation can be accomplished by the measurement of dipole moments. The *p*-isomer has a zero moment, and the dipole moment of the *o*-isomer is larger than that of the *m*-isomer.

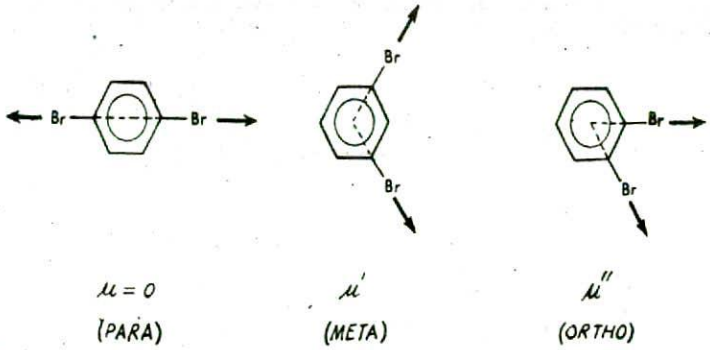


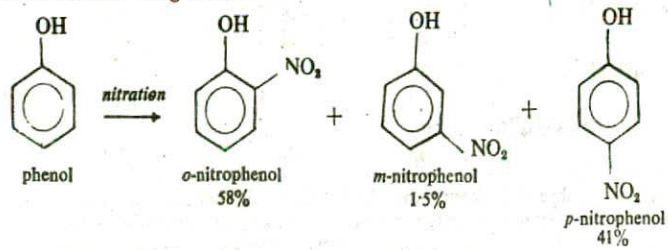
Fig. 36·2. Value of magnetic moments of para isomer μ=0; while that of *meta* isomer is lower than of *ortho* isomer *i.e.*, $\mu' > \mu''$.

) Although NMR spectra and IR spectra of substituted benzenes are often difficult to interpret, both may provide evidence about the number of adjacent hydrogen atoms on a benzene ring. This indirectly affords evidence upon which orientation can be based.

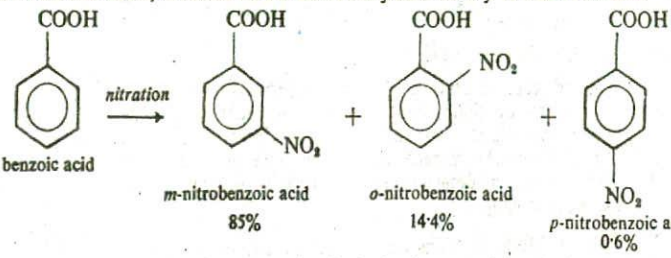
DIRECTIVE INFLUENCE OF SUBSTITUENTS

As already discussed in the introductory paragraph of the chapter, on purely statistical consideratior the proportion of *ortho*, *meta* and *para* disubstituted benzene derivatives should be 40%, 40%, and 20% respectively. But in actual practice this propostion is never observed.

Thus when phenol is nitrated, the main products obtained are ortho and para, very little of the meta isome being formed.



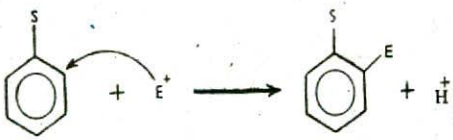
On the other hand, nitration of benzoic acid yields mainly the meta isomer.



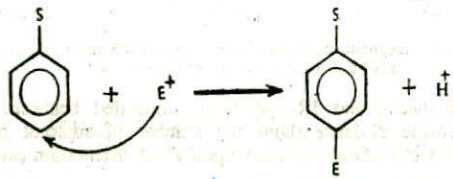
From these and many other aromatic disubstitution reactions, it has been conclusively proved that :

The position taken up by the second substituent on the ring depends primarily on the nature of the first substituent group (S) present on the ring.

As a result of extensive experimentation and disregarding the negligible quantities of isomers produced, t has been established that there are two classes of substituents (S) present in aromatic rings :



O-DISUBSTITUTION PRODUCT



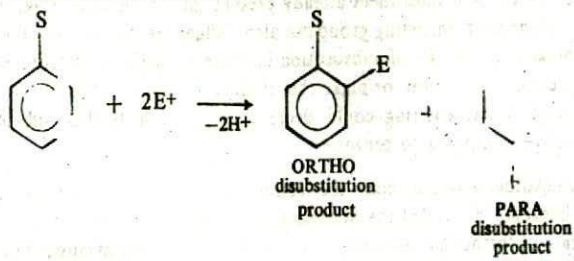
P-DISUBSTITUTION PRODUCT

(*a*) *Ortho and Para Directors* These direct the new substituent to enter the ring primarily in *ortho* and *para* positions to themselves;

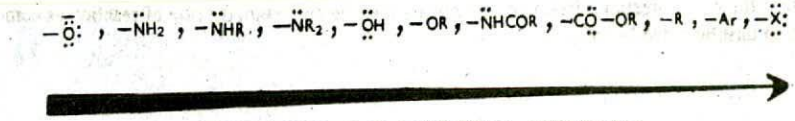
(*b*) *Meta Directors* : These direct the new substituents to enter the ring primarily in the meta position to themselves

Ortho and Para Directors. These substituents follow the general electrophilic substitution reactions simultaneously.

The overall reaction is often written as

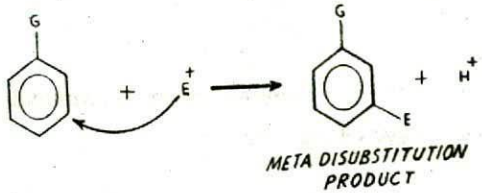


In the above reaction the substituent 'S' already present on the ring, which determines the course of second substitution, may represent any one of the following groups.

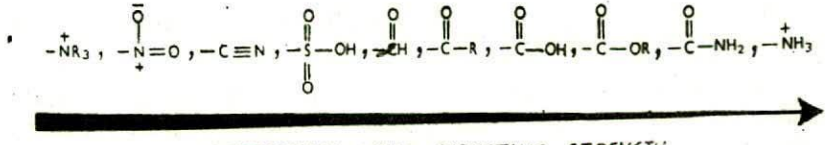


Evidently, the above groups are characterised by the presence of either a negative charge on the atom bonded to the ring, called the *key atom*, or the presence of one or more unshared pairs of electrons on it. Such groups or substituents on the ring, would therefore exercise an 'electron-donating influence' on the aromatic ring.

Meta Directors. These substituents permit the electrophilic substitution to follow the reaction as represented below.



The substituent or group G, already present, may be any one of the groups tabulated below.



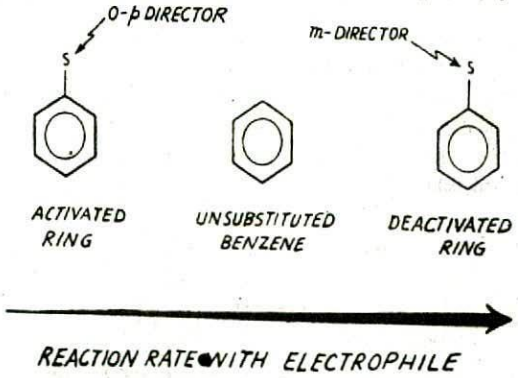
The substituents are characterised by either the presence of a positive charge on the *key atom*, or the *key atom* is attached to an electronegative atom by a multiple bond. Such a substituent would, therefore, be expected to exercise an 'electron-withdrawing influence' on the ring system.

ACTIVATING AND DEACTIVATING INFLUENCE OF SUBSTITUENTS

The nature of a substituent already present in the benzene ring, not only determines the position of the next incoming group but also influences the rate of the second substitution reaction compared to the rate of substitution in benzene itself. A substituent might increase the rate of the second substitution or make the ring more reactive relative to benzene. Another group if present in benzene ring could decrease the rate of further substitution or make the ring less reactive compared to benzene.

The sustituents which cause the compound C_6H_5—S to undergo second substitution faster than benzene, are called the **Activating Substituents**. On the contrary, substituents which retard the rate of further substitution are referred to as the **Deactivating Substituents**.

It has been found experimentally that in general ortho-para directing substituents activate the benzene ring and thus enhance the rate of reaction with electrophiles. On the contrary the meta directing substituents deactivate the ring and retard the rate of reaction as compared to unsubstituted benzene.



We may conclude by making the generalisation :

Ortho-Para Directing substituents are RING ACTIVATORS, while Meta Directing substituents are RING DEACTIVATORS.

Only one noticeable exception to the above general rule has been observed experimentally. In a halogen substituted benzene (C_6H_5X), the substituent X is found to be *ortho* and *para* director and yet deactivates the aromatic ring with re to benzene.

Table. Activating and Deactivating Effects of Substituents.

Activating Substituents			*Deactivating Substituents*		
Ortho, Para Directing			*Meta Directing*		*Ortho, Para Directing*
$-\ddot{O}^-$	$-NH_2$	$-\ddot{N}HR$	$-\overset{+}{N}R_3$	$-NO_2$	$-F$
$-\ddot{N}R_2$	$-\ddot{O}H$	$-\ddot{O}R$	$-C\equiv N$	$-SO_3H$	$-Cl$
$-NHCOR$	$-CO-R$	$-R$	$-\overset{O}{\overset{\|}{C}}-H$	$-\overset{O}{\overset{\|}{C}}-R$	$-Br$
$-Ar$			$-\overset{O}{\overset{\|}{C}}-OH$	$-\overset{O}{\overset{\|}{C}}-OR$	$-I$
			$-\overset{O}{\overset{\|}{C}}-NH_2$	$-\overset{+}{N}H_3$	

INTERPRETATION OF DIRECTIVE AND ACTIVATING EFFECTS

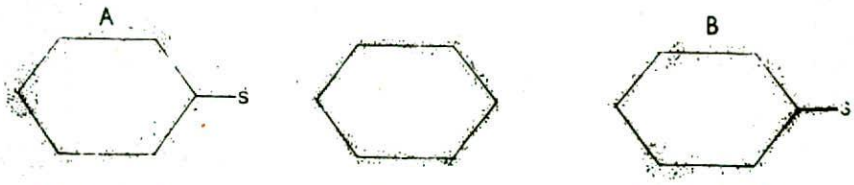
The directive effects as also the activating and deactivating effects of substituents on the benzene ring can be accounted for in terms of the mechanism of aromatic substitution and electron displacement effects discussed earlier. There are two types of mechanism of electrophilic disubstitution which are generally accepted :

(*a*) *One based on Charge Distributions* ;

(*b*) *The other based on Stability considerations of Wheland Intermediate Carbonium ions i.e., σ-complexes.*

Of these two approaches, the second one is the more satisfying one.

(1) **Charge Distribution Theory.** According to this theory the nature of the substituent (S) already present in the ring determines the orientation of the disubstituted product. If the substituent is ortho and para directing, the incoming electrophile (E^+) enters the ring in these positions. On the contrary if it is meta directing, the fresh entrant occupies the meta position. Therefore, to interpret such reactions we presume that electron-donating groups, which are ortho-para directing, increase electron density in ortho and para positions on the ring. The electron-withdrawing groups, on the other hand, are meta directing and increase electron density in the meta position on the ring.



C_6H_5—S, when S is electron-donating | Benzene | C_6H_5—S, when S is electron-withdrawing

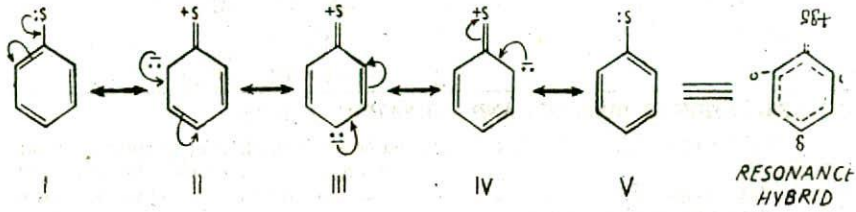
Fig. 36·3. π electron densities in ortho and para positions in monosubstituted benzene represented by A are much greater in ortho-para positions compared to benzene. In B the electron densities are greater in meta position.

The uneven distribution of electrons caused by the substituents of two types, leads to charge separation and polarisation of the σ carbon skeleton of the ring systems. It is also evident from the illustration (Fig. 36·3) that the overall electron density of the ring increases by the presence of *o-p* directing substituents and decreases by the presence of *meta* directing groups. This would explain the activation of the ring in the former case (A) to electrophilic attack, and deactivation of the ring in the second case (B).

The charge distribution in a monosubstituted benzene, C_6H_5S, depends on two factors (*i*) *the resonance* or *mesomeric effect* (*M*) ; and (*ii*) *the inductive effect* (*I*). Sometimes these two effects are additive, while they oppose each other occasionally. It may be noted that the resonance effect (*M*) generally plays a significant role in determining the position of electrophilic attack and often outdoes the weaker inductive effect (*I*). The two electronic effects also determine whether the electron density of the ring is increased or decreased relative to benzene, and hence also help in predicting the activating and deactivating influence of the substituent *S* on the ring system. The following cases arise depending on the nature of the substituent *S*.

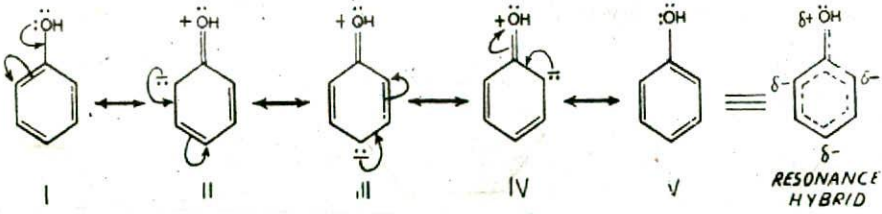
(A) WHEN THE SUBSTITUENT IS ELECTRON-DONATING

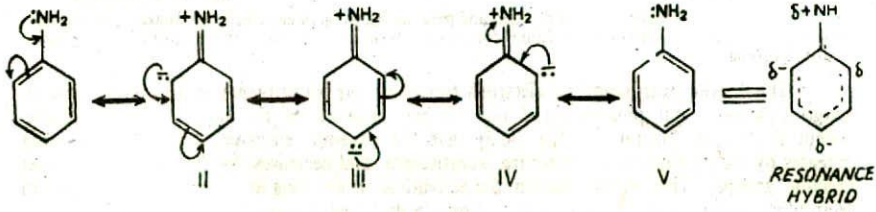
We have already seen that when the substituent —S̈ present in the ring, has one or more lone pairs of electrons on the atom adjacent to the ring, it interacts with π electron system



the ring. This gives rise to the above five resonance forms. The structure of the monosubstituted benzene, C_6H_5—S̈, is, in fact, represented by the resonance hybrid. It may be noted that in the hybrid structure the overall electron density of the benzene ring is enhanced compared to unsubstituted benzene ring, and more so at the *o-p* positions of the ring. Therefore the presence of an electron-donating group such as —S̈ causes further electrophilic substitution in *o-p* positions and also activitates the ring to electrophilic attack.

Let us take the example of phenol, C_6H_5—Ö—H, and aniline, C_6H_5—N̈H_2, which have available electron pair on the key atoms of the substituents. Thus phenol and aniline exhibit resonance and can be represented as hybrid of the following five canonical forms.





The overall electron density of the ring in each hybrid is increased and the benzene ring system as a whole is activated to electrophilic attack. Of course, the electrophile (E^+) would attack the ring preferentially at *o-p* positions where the electron density relatively is greater as compared to the meta positions.

In case of benzene derivatives such as phenol and aniline, where the substituent is electron donating to the ring by resonance, the inductive effect of the substituent opposes this displacement of electrons. For example, in phenol the key atom 'O' of the substituent —ÖH being more electronegative than carbon, exercises a strong (—I) effect and tends to withdraw electrons from the ring. Thus here the mesomeric or resonance effect and inductive effect oppose each other, but the resonance effect predominates. The overall displacement of electrons no doubt is slightly decreased but the net result is again the increase of electron density of the ring, and more so in *o-p* positions.

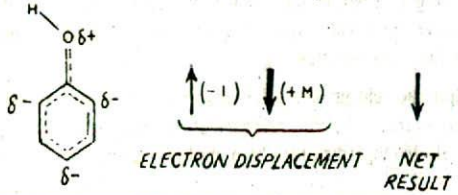


Fig. 36·4. Net result of the resonance and inductive effects of the electron donating —OH substituent is the increase of electron density in the ring more pronounced

From the above considerations, we conclude that for all electron donating substituents as —ÖH, —ÖR, —$\ddot{N}H_2$ etc., the overall density of the benzene ring is enhanced with distinct charge separation (δ-) in the *o-p* positions. Thus the electrophile (E^+) would attack the ring at these positions of the ring which as a whole is greatly activated to such an attack.

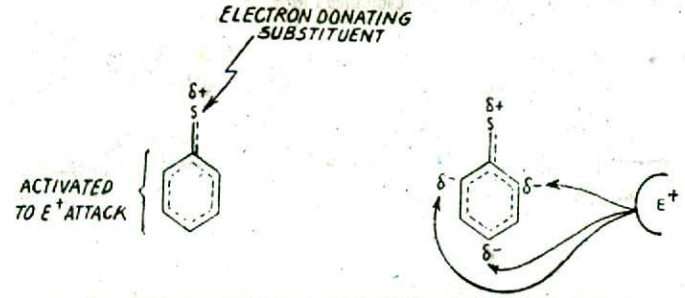
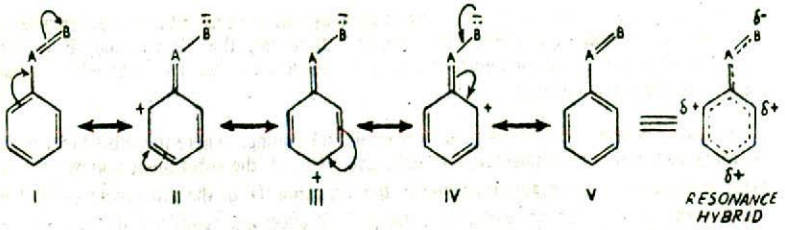


Fig. 36·5. Electron donating groups enhance overall electron density of benzene ring which is activated to electrophilic attack. Such groups direct electrophilic substitution at *o-p* positions which are relatively electron rich.

Thus all groups which are electron donating : —NH_2, —NHR, —NR_2, —OH, —OR, etc., are ortho-para directing and facilitate electrophilic substitution in the benzene ring.

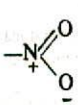
(B) WHEN THE SUBSTITUENT HAS AT LEAST ONE STRONGLY ELECTRONEGATIVE ATOM AND A MULTIPLE BOND IN CONJUGATION WITH BENZENE RING

Let A=B represent the group or substituent in which B is more electronegative than A. The highly electronegative atom pulls the electron pair of the multiple bond which in turn withdraws electrons from benzene ring (—M effect), giving rise to the following five canonical forms

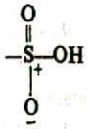


The structure of the benzene derivative C_6H_5—A=B is, in fact, represented by the resonance hybrid shown above. Evidently electrons are withdrawn by the substituent group from the ring, and more so from the *o-p* positions where the electron density declines. In other words, the electron density of the ring as a whole falls and that deactivates it to electrophile attack. Also, the meta positions have relatively more electron density and, therefore, electrophilic substitution takes place at the meta positions.

The nitro and sulphonic acid groups offer examples of the type of electron withdrawing substituents which are characterised by the presence of a strongly electronegative atom (N, S) attached to another more electronegative atom by a multiple bond.

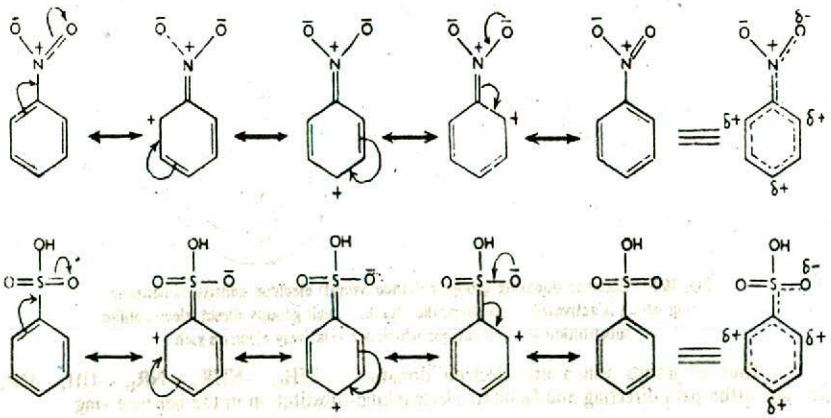


Nitro group



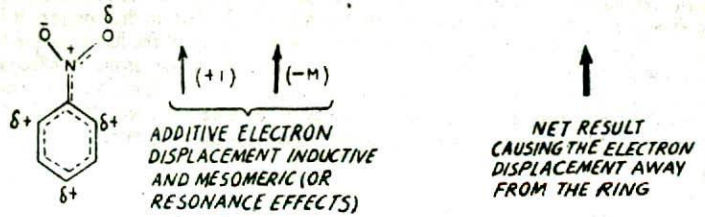
Sulphonic acid group

Nitrobenzene and benzenesulphonic acid, which contain respectively —NO_2 and —SO_3H groups, are able to exist as the following resonance forms.



It may be noted that resonance causes the decrease of electron density in th ring of nitrobenzene and benzenesulphonic acid, and specifically at the *o-p* positions.

In the two examples discussed above, the resonance effect (—M) and the inductive effect act in the same direction. They reinforce each other and the great drain of electrons from the benzene ring makes it distinctly less susceptible to electrophilic attack.



In other words the displacement of electrons away from the ring deactivates it. Since positive charge appears in *o-p* positions, there is no scope of electrophilic attack at these positions. The meta positions are relatively unaffected by the substituents and have higher electron density compared to *o-p* positions, and are therefore attacked.

From the above considerations we are able to make a general conclusion that the electron withdrawing substituents of the type —A=B, decrease the electron density in the benzene ring and thereby act as *deactivators* and *meta directors*.

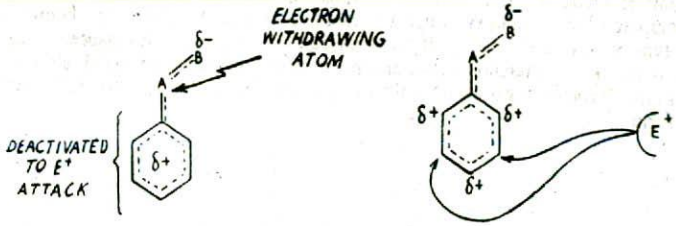
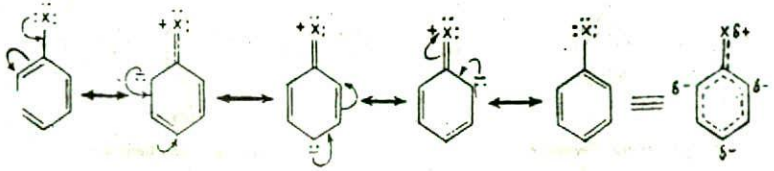


Fig. 36·7. Resonance hybrid illustrating the deactivation of ring and electrophile attacking at the meta positions.

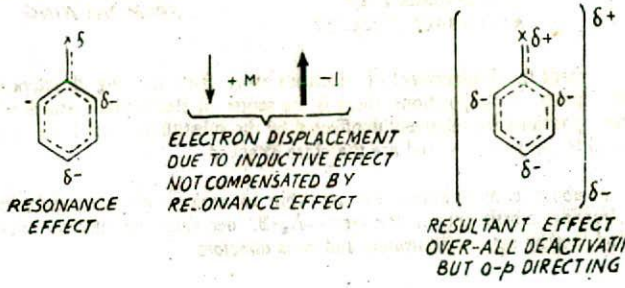
We can carry out similar analysis for the other electron withdrawing substituents of this class such as —COOR, —COR, —CHO, —SO_2Cl, —C≡N etc. to establish that these are deactivating but meta directors.

Anomalous Behaviour of Halogen Substituent. We have studied above that the *o-p* directing substituents are generally ring activators. However, in case of halogen substituents it has been experimentally observed that they direct the new entrant to the ortho-para positions but deactivate the benzene ring. This anomalous behaviour of the halogen substituent (X) can be rationalised by invoking both resonance and inductive effects.

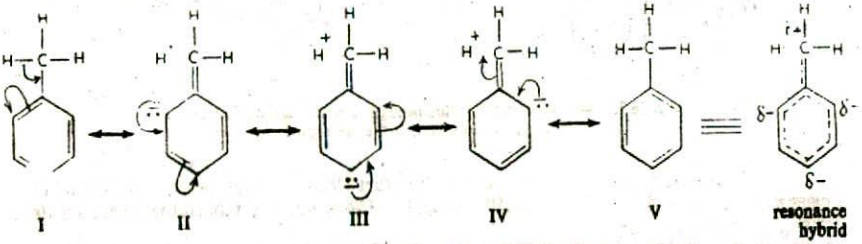
A halogen-substituted benzene (C_6H_5— X) by virtue of the presence of unshared electron pair on the halogen, exhibits resonance. Thus it can be represented by the resonance hybrid of the following canonical forms.



Th resonance hybrid structure enables the halogen substituent to act as *o-p* director. It is also expected to activate the ring to electrophilic attack, but on the contrary it is a ring deactivator. This is attributed to the very high electronegativities of the halogens due to which they withdraw electrons so as to deactivate the benzene ring. While the resonance effect accounts for the ability of halogen to donate electrons to *o-p* positions, the combinat on of the two effects makes the halogenated benzene deactivated. This is so because in respect of the displacement of electrons the(+M) effect is not sufficient to compensate for the (—I) effect, which deactivates the ring.

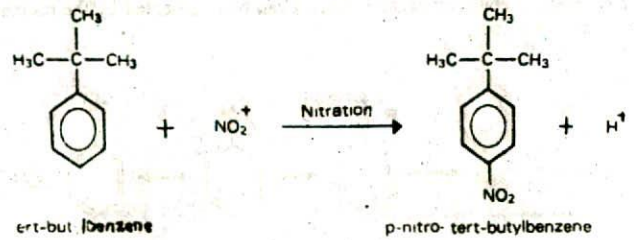


Alkyl Groups and Orientation. Methyl and other alkyl groups do not possess an unshared pair of electrons. Yet they are *o-p* directors and ring activators. Apart from their electron pumping effect, the alkyl groups attached to a conjugate system are known to exhibit a special type of resonance called **Hyperconjugative** or 'no bond' resonance. This type of resonance required the interaction of σ electrons instead of usual unshared electron pair on the key atom. Hyperconjugation in toluene (C_6H_5—CH_3) gives rise to the following five canonical forms.



As clear from the structure of the resonance hybrid, electron density of the ring is enhanced which is accompanied by appearance of δ- charge in *o-p* positions. Hence the alkyl group activates the ring and ortho-para positions are preferred spots for electrophilic substitution.

The electrophilic substitution of *tert*-butylbenzene yields almost exclusively the para isomer. This is so because the electrophile approach to the ortho position is well nigh impossible on account of the steric influence of the substituent —$C(CH_3)_3$.



Thus for an alkyl group to take part in hyperconjugation, there must be at least one H-atom on the carbon joined to the ring carbon. The relative ability of alkyl groups to be involved in hyperconjugation ie in the order

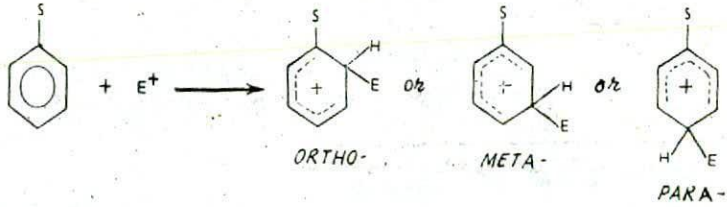
methyl > *primary* > *secondary* > *tertiary*

This will also be the order of rate of electrophilic substitution in C_6H_5—R.

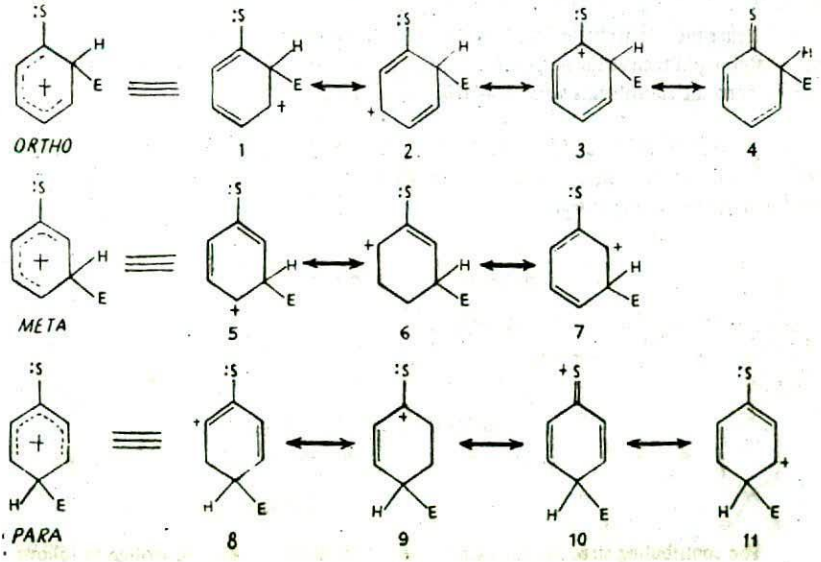
(2) **Orientation Based on Stability of Carbonium Ion** (σ-Complex). This method of predicting the position of an incoming group in second substitution reaction consists of examining all possible forms of Wheland intermediates for the reaction at each position of the ring. The substituent (S) already present interacts with the charge of carbonium ion and determines which intermediate is energetically favoured. By selecting the intermediates which contribute towards greater stabilisation, we are able to tell the probable position of attack and know as to which isomer is ultimately obtained.

Let us examine this approach for the two types of substituents.

(A) WHEN THE SUBSTITUENT ALREADY PRESENT IS ELECTRON-DONATING. Let us consider an electrophilic attack on substituted benzene, C_6H_5—S, where 'S' is an electron donating substituent. The electrophile (E^+) may attack at any of the three positions to form σ-complex or carbonium ions.



To ascertain as to which of these three will be stable, we proceed to draw the possible Wheland structures for each of the carbonium ions.



There are four possible resonance forms of Wheland carbonium ions in ortho and para substitution. In one of these (no: 4 for ortho ; no: 10 for para), the positive charge is placed on the substituent S. No such structure with a positive charge on the substituent S is possible for meta substitution. Thus there are a smaller number of contributing structures for meta substitution (*three only*). Their resonance hybrid is, therefore, less stabilised than the intermediate formed by electrophilic attack at the *o-p* positions. Since the intermediate obtained by the attack at *o-p* positions is more stable than that for *m-* attack, the transition state of *o-p* positions is at a lower energy level than the transition state for *m-* attack.

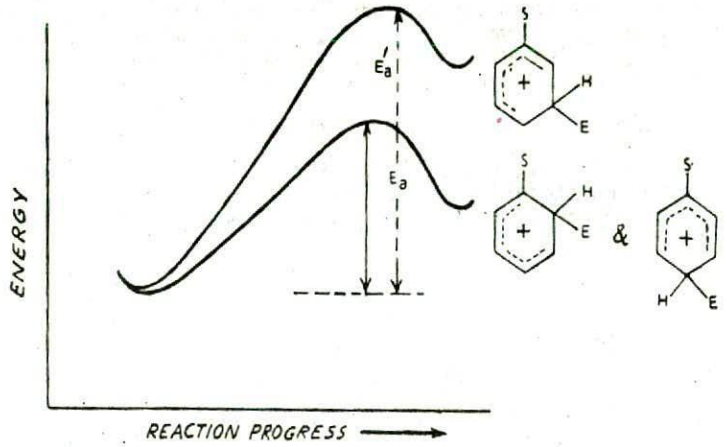
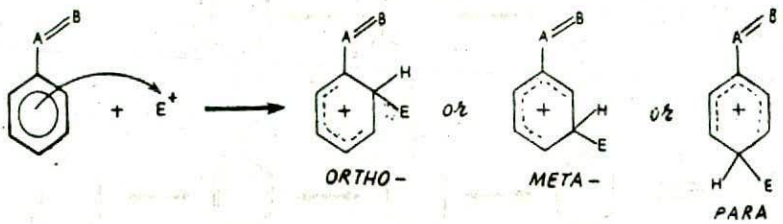


Fig. 36·8. Energies of activation for the formation of different intermediates. E_a for *o- and p*-positions is less than E_a' for *m*-substituted intermediate.

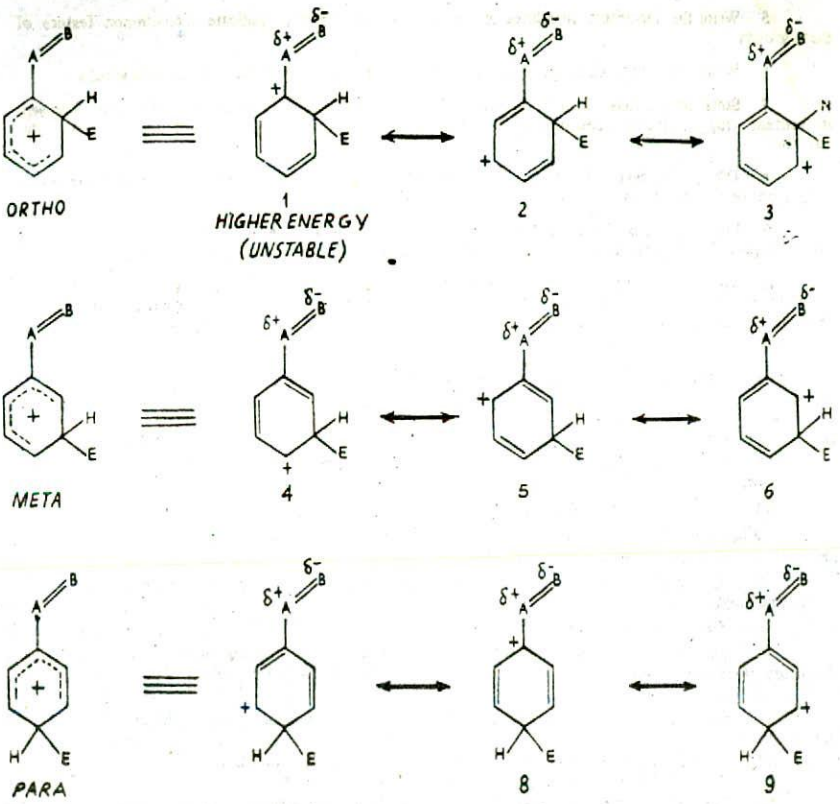
Hence the electrophile attack at the *o-* or *p*-position involving less activation energy (E_a) is more rapid than at the *m-* position. Similar conclusions will be derived for any of the electron donating substituents such as $-\ddot{N}H_2$ $-\ddot{O}H$ etc.

(B) WHEN THE SUBSTITUENT ALREADY PRESENT IS ELECTRON-WITHDRAWING (—A=B). Electrophilic attack on the substituted benzene, C_6H_5—A=B, could give three carbonium ions or σ-complexes.



Carbonium ions

The contributing structure for each of these carbonium ions may be written as follows.



higher energy (*unstable*)

In structure 1 and 8 for the ortho and para carboniums respectively, a positive charge appears on a ring carbon to which the electron-withdrawing substituent is attached. These structures are relatively unstable owing to adjacency of two positive charges (repulsive interactions lead to higher energy and lesser stability). These do not contribute appreciably to the stability of their resonance hybrids. In the Wheland intermediates resulting from meta attack, all the three contributing structures are fairly stable, since there is no such charge proximity. Owing to the greater stability of the intermediate carbonium ion from meta substitution product (three contributing structures), the meta attack is more favourable than the attack at either ortho or para position (two stuctures).

QUESTIONS

1. What do you understand by aromatic substitution ? Proceed to show that all conditions of such a reaction being identical electrophilic disubstitution of benzene will form ortho, meta and para isomers in the ratio 2 : 2 : 1.

2. Discuss briefly the methods of isolation of ortho, para and meta isomers from a mixture obtained by disubstitution of benzene.

3. What do you understand by 'Orientation' of a benzene derivative ? Describe the various methods hitherto used for orientation of unknown disubstituted benzene. Which of these you consider the best ?

4. Explain the meaning of the term : "Directive influence' of the substituent present in benzene ring on the course of further substitution.

5. Write the electronic structures of six *o-p*-directing groups ? Indicate the common feature of these groups.

6. Write four meta directing groups ? How do they differ from the *o-p*-directing groups ?

7. State in a concise fashion the activating and deactivating influence of a substituent S present in benzene ring on further substitution. Name a substituent which is *o-p*-directing and yet deactivates the ring.

8. Discuss in detail the theories put forward to explain the directive and activating effects of a substituent on disubstitution.

9. With the help of 'Charge Separation Theory', show that all groups which are electron-donating are ortho-para directing and ring activating. Mention exception, if any, to this generalisation.

10. Discuss the theory of Orientation based on the 'stability of the intermediate carbonium ion' to interpret the ortho-para and meta directing influence of substituent already present in benzene ring. How is this theory helpful in interpreting the ease of distribution depending on the nature of the previous substituent ?

11. Explain (*i*) $-NO_2$ group is activating and *o-* and *p-* directing towards aromatic nucleophilic substitution.

(*ii*) Halogen when present in benzene is deactivating but *o-* and *p-* directing towards electrophilic substitution. *(Udaipur BSc II, 1980)*

12. Classify the following as o, p- orienting and m-orienting substituents:—
Methyl, Nitro, Cyano, Methoxyl. *(Kerala BSc II, 1980)*

13. Account for the following:

When nitrobenzene is heated with conc H_2SO_4 and conc HNO_3, we get m-dinitrobenzene while anisole on similar treatment gives a mixture of *o-* and *p*-nitro compounds. *(Calicut BSc III, 1980)*

14. Give electronic explanation of the directive influence of the following atoms or groups when present in benzene ring:

(*i*) —OH, (*ii*) —Br, (*iii*) —CHO. *(Delhi BSc III, 1980)*

15. What is meant by directing influence of a group or atom in the benzene nucleus ? Explain using the theory of electrophilic substitution why —CHO is meta-directing and —OH is ortho- and para-directing. *(Bombay BSc II, 1980)*

16. Explain: Chlorine is deactivating, yet it is ortho and para-directing in electrophilic aromatic substitution reactions. *(Punjab BSc II, 1980)*

17. Illustrate the directive influence of the following groups in the benzene nucleus:—
(*i*) —COOH (*ii*) $-NO_2$ (*iii*) —Br (*iv*) $-CH_3$. *(Annamali BSc, 1980)*

18. Explain why the hydroxy group (—OH) acts as an ortho-para director when it is present on a benzene ring undergoing an electrophilic attack. *(Punjab BSc Chem Engg, 1981)*

19. Give reasons: Methyl group in toluene is an activator and ortho and para director in further substitution in the ring. *(Gulbarga BSc II, 1981)*

20. Write a short explanatory note on isomerism in benzene disubstitution products and the orienting influence of various groups. *(Kerala BSc, 1982)*

21. Which of the following groups are ortho and para or meta directing ? Give reasons:

(*i*) —OH; (*ii*) $-NH_2$; (*iii*) $-\overset{\overset{O}{\|}}{C}-OH$; (*iv*) $-NO_2$. *(Guru Nanak Dev BSc II, 1982)*

22. On the basis of modern electronic theory discuss the directive effect of —OH, —Cl, $-NO_2$, and —COOH groups during electrophilic aromatic substitution. *(Jiwaji BSc III, 1987)*

23. Explain why methoxy group ($-OCH_3$) acts as an ortho-para director. *(Panjab BSc, 1988)*

24. Explain why methoxy group ($-OCH_3$) acts as an ortho-para director towards electrophilic aromatic substitution. *(Panjab BSc, 1994)*

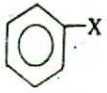
25. On the basis of modern electronic theory discuss the directive effect of –OH, –Cl, $-NO_2$, and –COOH groups during electrophilic aromatic substitution. *(Baingalore BSc, 1993; Kalyani BSc, 1994)*

Chapter **37**

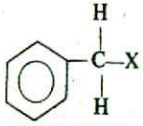
Aromatic Halogen Compounds

The halogen derivatives of aromatic hydrocarbons may be divided into two classes.

(*a*) **Aryl halides** (Ar—X), in which the halogen atom is attached directly to a carbon of the aromatic ring.



aryl halide
(*halogen bonded to benzene ring*)



arylalkyl halide
(*halogen bonded to side-chain*)

(*b*) **Arylalkyl halides** or **Aralkyl halides** (Ar—CH_2—X), in which the halogen atom is attached to a carbon of the side-chain.

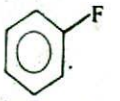
Strictly speaking the arylalkyl halides are 'alkyl halides' and differ considerably in their chemical reactivity from the aryl halides.

ARYL HALIDES

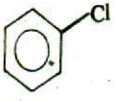
Aryl halides are named according to the IUPAC system as substitution products of the parent aromatic hydrocarbons (halohydrocarbons). If more than one halogen is present, the name of the halogen is preceded by the prefix *di-*, *tri-*, *tetra-*, etc to signify the number present. The position of halogens is indicated by the use of numbers or appropriate prefixes - *ortho*, *meta*, *para*.

Simple halides are also assigned the common names after the names of the groups present in their molecule *e.g.*, C_6H_5Cl would be phenyl chloride.

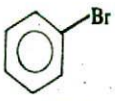
Monohalo Derivatives



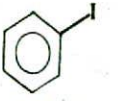
fluorobenzene,
phenyl fluoride



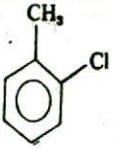
chlorobenzene,
phenyl chloride



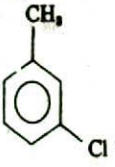
bromobenzene,
phenyl bromide



iodobenzene,
phenyl iodide



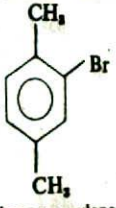
2-chlorotoluene,
o-chlorotoluene



3-chlorotoluene,
m-chlorotoluene

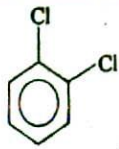


4-chlorotolune,
p-chlorotoluene

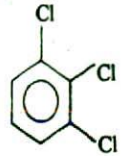


2-bromo-*p*-xylene

***Di*-and *Trihalo Derivatives* :**



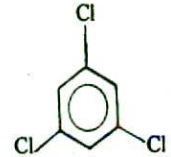
1, 2-dichlorobenzene, *o*-dichlorobenzene



1, 3-dichlorobenzene, *m*-dichlorobenzene



1, 4-dichlorobenzene, *p*-dichlorobenzene



1, 3, 5-trichlorobenzene *sym*-trichlorobenzene

STRUCTURE

The structure of aryl halides is basically the same as that of benzene, except that the halogen bonded to a carbon of the ring has a *p* orbital containing a lone pair of electrons. This

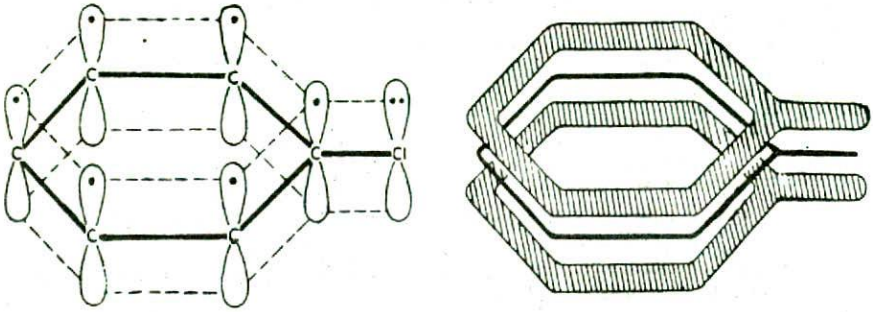
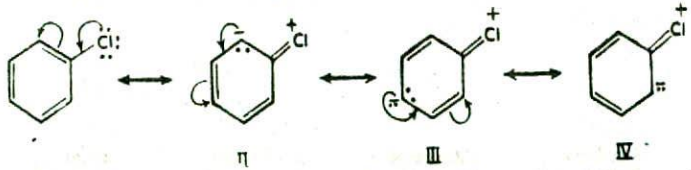


Fig. 37-1. Orbital structure of halobenezene *e.g.*, C_6H_5—Cl

p-orbital of halogen interacts with the π orbital enveloping the ring, to form an extended π orbital. The extended orbital envelopes the six carbons of the ring as also the halogen. In other words, the six electrons of the ring carbons (one belonging to each carbon) and two electrons of the halogen are now associated with all the seven atoms. This delocalisation of electrons lends some double bond character to the carbon-halogen bond.

The electronic structure of aryl halides could be represented by the following canonical forms. Thus aryl halides are to be regarded as resonance hybrid of the four contributing forms



II III IV

shown above. For this reason the C—X bonds of aryl halides are shorter and stronger than those of the alkyl halides. The actual double bond character as in chlorobenzene is only about

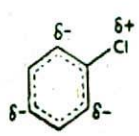


Fig. 37·2. Resonance hybrid of aryl chloride

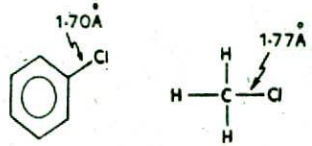


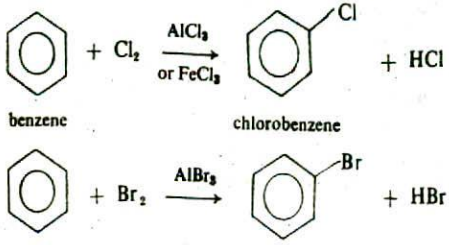
Fig. 37·3. Hybrid C—Cl bond in aryl chloride is shorter and stronger than C – Cl bond in methyl chloride

5 per cent and the forms II, III and IV contribute only a small part to the ground state of aryl halides.

METHODS OF PREPARATION

Aryl halides may be prepared from aromatic hydrocarbons or their derivatives by the following methods.

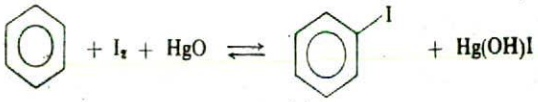
(1) **Direct Halogenation.** (*a*) *Aryl chlorides* and *Aryl bromides* are generally prepared by the direct halogenation of aromatic hydrocarbons in the presence of a Lewis-acid catalyst, such as $AlCl_3$, $AlBr_3$, or $FeCl_3$.



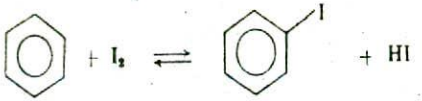
If excess of halogen is used, dihalo derivatives are formed.

(*b*) *Aryl iodides* are obtained in good yield is presence of reagents like HgO, HNO_3, HIO_3 which remove the HI produced in the reaction.

(*i*)

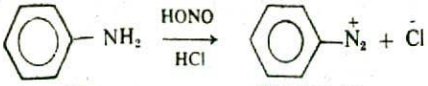


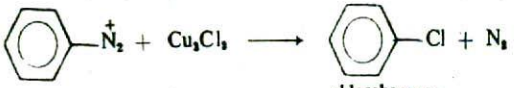
(*ii*)

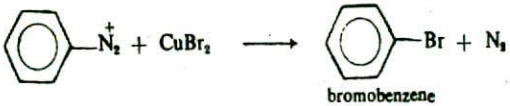


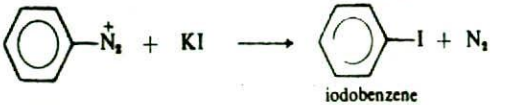
$$4HI + 2HNO_3 \longrightarrow 2I_2 + N_2O_3 + 3H_2O$$

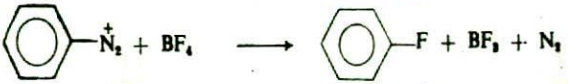
(2) **Decomposition of Diazonium Salts.** Aryl halides are prepared most satisfactorily by the decomposition of diazonium salts in the presence of appropriate metal halides. The dia onium salt ($C_6H_5N_2^+X^-$) required for the reaction is obtained from the corresponding aromatic amine.





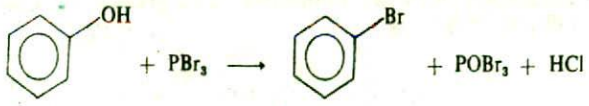






This method is particularly useful for the preparation of iodo and fluoro compounds which cannot be obtained easily by other methods.

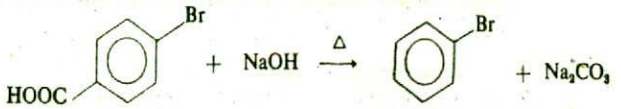
(3) **Substitution of —OH of Phenol by a Halide.** When a phenol is treated with halogenating agents, such as PBr_3 or $SOCl_2$, an aryl halide is produced.



phenol bromobenzene

Since the yield of the halide is generally poor, it is not a useful synthetic procedure.

(4) **Decarboxylation of Halogenated acids.** The sodium salt of an aromatic halogenated acid when heated with sodalime yields the corresponding aryl halide.



p-bromobenzoic acid bromobenzene

PHYSICAL PROPERTIES

(1) Aryl halides are colourless oily liquids or relatively low melting solids, having odour characteristic of aromatic compounds.

(2) Because of their low polarity, they are insoluble in water but soluble in all common organic solvents such as ethanol and diethyl ether.

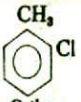
(3) They have density greater than one.

(4) Their boiling points, melting points and densities rise gradually as we pass from fluoro to iodo compounds.

Halobenzene	*bp* °C	*mp* °C	*density* (*g*/*ml at* 20°)
Fluorobenzene, C_6H_5F	85	—42	1·031
Chlorobenzene, C_6H_5Cl	132	—45	1·112
Bromobenzene, C_6H_5Br	156	—31	1·495
Iodobenzene, C_6H_5I	188	—30	1·838

(5) The boiling points of *o*-, *m*-, and *p*-isomers are so close that these are difficult to separate by distillation. However, the melting point of a *p*-isomer is much higher than that of an *o*- or *m*-isomer. This is so because the more symmetrical *p*-isomer fits more easily into a crystal lattice and the stronger intracrystalline forces result in a higher melting point.

Table. Physical Constants of *Ortho*, *Meta* and *Para* Isomers

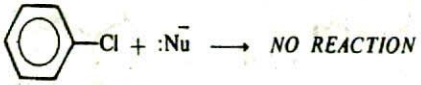
Dichlorobenzenes	*bp* °C	*mp* °C	*Chlorotoluenes*	*bp* °C	*mp* °C
 Ortho	179	—17	 Ortho	158	—27
 Meta	172	—26	 Meta	162	—48
 Para	175	—53	 Para	162	8

(6) Many derivatives of aromatic hydrocarbons show physiological activity and are used as insecticides (DDT).

CHEMICAL PROPERTIES

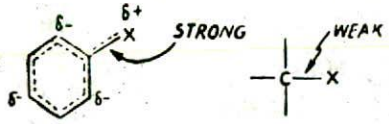
(1) Nucleophilic Substitution of Aromatic halogen. Halogens attached to an aromatic ring do not ordinarily undergo displacement (S_N1 or S_N2). Thus unlike alkyl halides, aryl halides do not react with nucleophilic reagents under normal laboratory conditions.

$$\underset{\text{methyl chloride}}{CH_3—Cl} + :\bar{N}u \longrightarrow \underset{\text{product}}{CH_3—Nu} + \bar{C}l$$



chlorobenzene

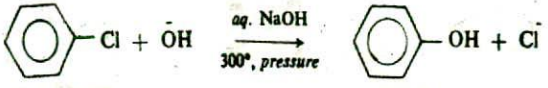
The low reactivity of aromatic halogen to nucleophiles is attributed to the facts : (1) the halogen has a positive charge on it; and (2) aryl halides could be represented as resonance hybrid whereby C—X bond in them possesses a double bond character and is stronger than C—X bond in alkyl halides.



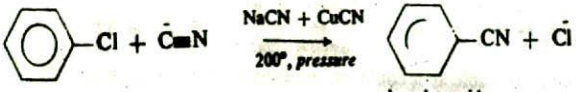
ARYL HALIDE ALKYL HALIDE

For these reasons, the substitution of halogen in aryl halides by S_N1 mechanism is considerably more difficult than with alkyl halides. S_N2 reactions are not possible because the usual backside approach of the nucleophile required for such a reaction is blocked by the aromatic ring in aryl halides.

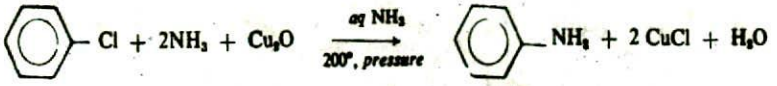
As stated above, simple aryl halides are ordinarily inert to most nucleophiles *e.g.*, hydroxide, cyanide ion, or with ammonia. However, at sufficiently high temperatures and pressure several nucleophilic substitutions can be carried out.



chlorobenzene phenol



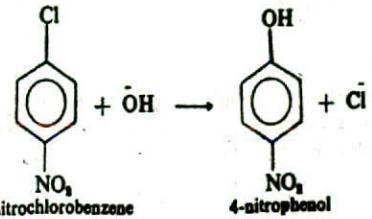
phenyl cyanide



aniline

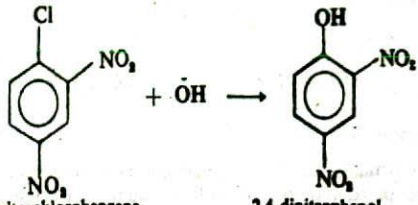
These reactions are used for the manufacture of the above derivatives. Because of the high temperature and pressure required, they are unsuitable as laboratory methods of preparation.

Aryl halides undergo nucleophilic displacement with increasing readiness if a strongly electron attracting group (NO_2) is present in the 2-position (*ortho*) or in 4-position (*para*).



(55% yield)

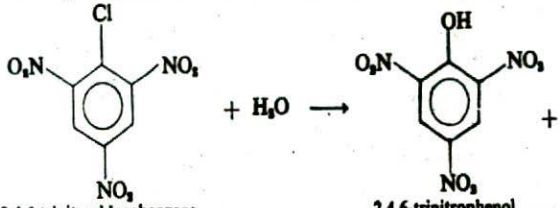
4-nitrochlorobenzene 4-nitrophenol



(76% yield)

2,4-dinitrochlorobenzene 2,4-dinitrophenol

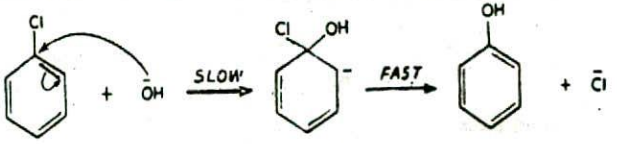
When three nitro groups are placed in 2, 4 and 6-positions to a halogen, the reactivity of the latter is greatly increased and is comparable to that of alkyl halides.



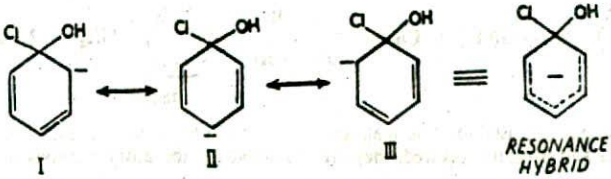
(93% yield)

2,4,6-trinitrochlorobenzene (picryl chloride) 2,4,6-trinitrophenol (picric acid)

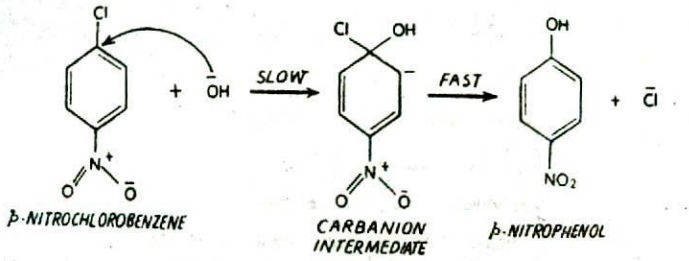
MECHANISM. The preparation of phenol from chlorobenzene illustrates the reaction mechanism of the nucleophilic substitution of aryl halides. The reaction is believed to take place in two steps. In the first step a carbanion is formed by the nucleophilic attack of ÖH on the carbon carrying the chlorine. This is a slow and rate determining step. In the second step which is fast, the halogen leaves the carbanion and phenol is produced.



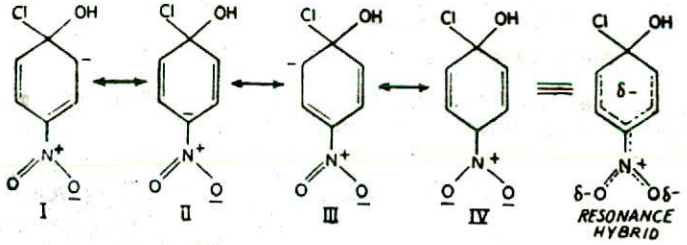
● The carbanion is stable as it could be represented as the resonance hybrid of the following three canonical forms.



It will be noticed that the carbanion has small negative charges in ortho and para positions. An electron-attracting group, such as —NO_2 group if present in ortho or para position to chlorine, spreads the negative charge to the oxygen atoms through resonance.

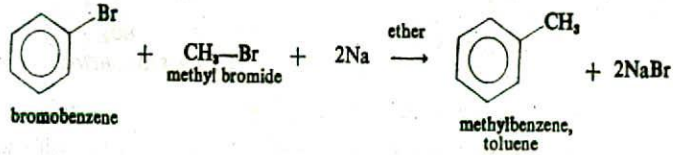


Thus the carbanion here is more stable than in case of hydrolysis of chlorobenzene because of greater dispersion of the negative charge brought about by the presence of $-NO_2$ group in para position.



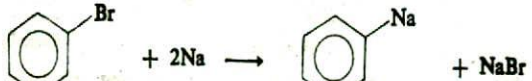
Hence the nucleophilic substitution with ortho or para nitrochlorobenzene is facilitated.

(2) **Wurtz-Fittig Reaction.** Aryl halides and alkyl halides undergo coupling reaction in the presence of sodium in ether to form alkylated aromatic hydrocarbons (arenes). This reaction is often referred to as *Wurtz-Fittig Reaction* since it is an extension of Wurtz Reaction discovered by Fittig (1863).



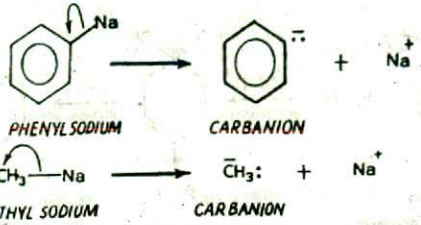
Although it is possible to get also diaryl by coupling of two aryl groups and butane by coupling of two ethyl groups, arene is obtained in a much higher yield.

MECHANISM. The sodium can react with either the aryl halide or the alkyl halide to form arylsodium or alkylsodium.

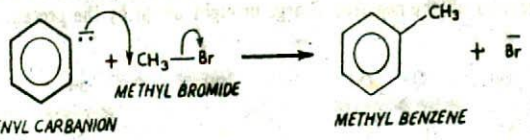


$$\underset{\text{alkyl bromide}}{CH_3—Br} + 2Na \longrightarrow \underset{\text{alkylsodium}}{R—Na} + NaBr$$

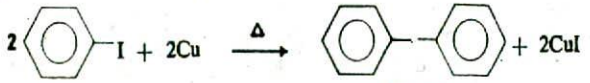
The C—Na bond has considerable ionic character so that we could write phenylsodium and alkylsodium as



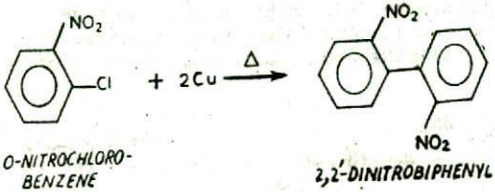
The carbanion of phenylsodium has larger amount of resonance stabilisation than does the carbanion of alkylsodium and is formed mainly. It is a relatively strong nucleophile and displaces the halogen of alkyl halide to form arene.



(3) **Ullmann Reaction.** Ullmann found that aryl halides when refluxed with copper powder, undergo coupling reaction to form biaryls. Thus,



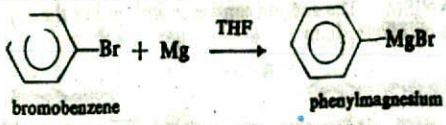
Aryl chlorides and bromides usually do not give this reaction unless the halogen is activated by a suitable substituent (NO_2) in the ortho or para position.



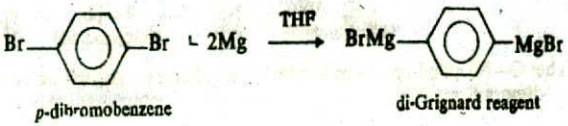
Ullmann reaction may be regarded as a modification of Fittig reaction

(4) **Formation of Organometallic Compounds.** Aryl halides react readily with the more active metals to give organometallic compounds.

(*a*) **Grignard Reagents.** Aryl halides react with magnesium in tetrahydrofuran (in place of ether) to form the corresponding Alkylmagnesium halides.

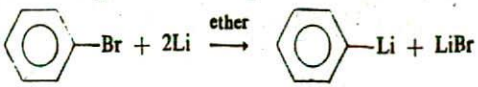


If there are two halogen atoms on benzene ring (not ortho), *mono-* or *di-*Grignard formation occurs.



The order of reactivity is ArI > ArBr > ArCl. Because of the expense of the iodides and low reactivity of chlorides, aryl bromides are generally taken as a good compromise in Laboratory synthesis. Arylmagnesium bromides so obtained are used for the preparation of many useful products including primary, secondary and tertiary alcohols.

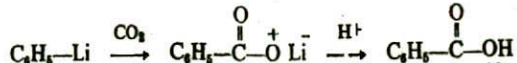
(*b*) **Aryllithiums** (Ar—Li). Aryl chlorides and aryl bromides react with metallic lithium in dry ether to form aryllithium organometallic compounds.



bromobenzene phenyllithium

Chlorobenzene does not form Grignard reagent in ether solution, but it yields phenyllithium readily.

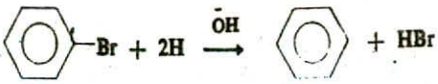
Aryllithiums undergo most of the reactions of Grignard reagent and may be used in synthesis in a similar manner. For example,



phenyllithium benzoic acid

When aryl chloride is more easily obtained than aryl bromide, aryllithium is a valuable substitute for Grignard reagent.

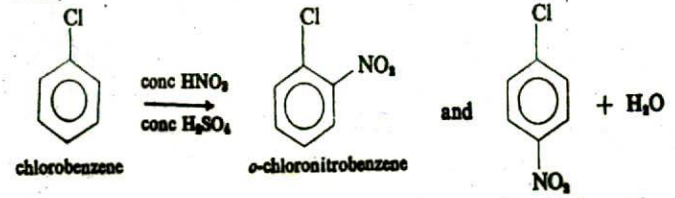
(5) **Reduction.** Aryl halides when reduced by means of nickel-aluminium alloy in presence of alkali, yield the parent hydrocarbon.



bromobenzene benzene

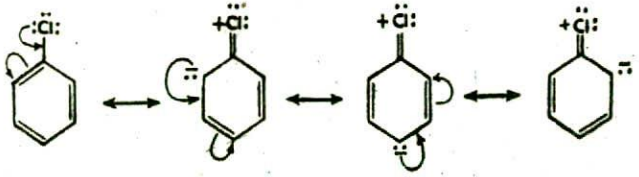
The reduction cannot be brought about with the usual reducing agents including hydrogen in the presence of metals (*e.g.*, platinum), unless the halogen is rendered labile by the presence of NO_2 group in an ortho or para position.

(6) **Electrophilic Substitution in Benzene Ring.** Aryl halides undergo substitution in the benzene ring with electrophilic reagents to form ortho and para derivatives as the major product. Thus,



chlorobenzene *o*-chloronitrobenzene *p*-chloronitrobenzene

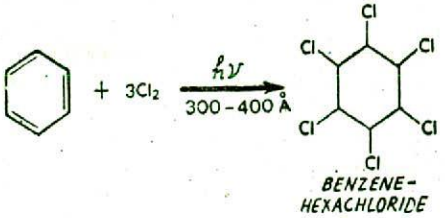
However, it may be noted that such electrophilic substitution reactions do not take place very readily. In the above reaction, the chlorine is not a good donor of electrons by resonance.



This is so because of the high electronegativity of the chlorine atom, and because of the poor 2*p* (C)—3*p* (Cl) overlap (see Fig. 37·1). Thus the inductive effect of chlorine wins over the resonance effect, and the chlorine atom deactivates the benzene ring, but not very much.

ADDITION HALOGEN COMPOUNDS

In the presence of sunlight or of ultraviolet light, chlorine and bromine (but not iodine), add to benzene to give crystalline hexachlorides and hexabromides, $C_6H_6Cl_6$ and $C_6H_6Br_6$.

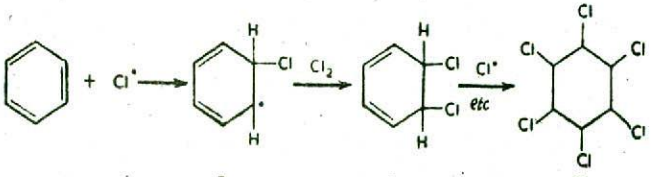


BENZENE-HEXACHLORIDE

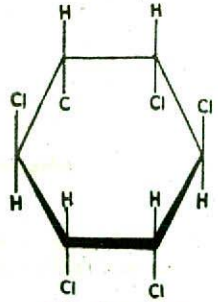
These addition reactions occur by a free radical mechanism.

$$Cl{-}Cl \xrightarrow{h\nu} Cl\cdot + Cl\cdot$$

The chlorine atom reacts with a benzene molecule to form a free radical (I). By reaction of this free radical with a chlorine molecule, a dichloride is produced (II), and also another chlorine atom. The latter carries on chain reaction. A continuation of the process finally gives the hexachloride (III).



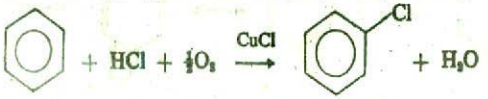
Benzene Hexachloride, 1,2,3,4,5,6-hexachlorocyclohexane, can theoretically exist in nine stereoisomeric forms due to different arrangements of H and Cl on opposite sides of the plane of benzene ring. Seven of these have been isolated from the mixture obtained by the above procedure. They are called α, β, γ, δ, ε, η and θ. The mixture of stereoisomeric hexachlorides is valuable because of its insecticidal properties. It is known by the commercial name BHC (benzene hexachloride) or 666, derived from its formula $C_6H_6Cl_6$. The insecticidal properties are due to γ-isomer which is called **Gammexane** or **Lindane**. It is very stable and acts more quickly than DDT. γ-BHC has been shown to have the configuration given in Fig. 37·4. Its molecule is smaller than those of the other stereoisomers and hence can penetrate more raadily for antiseptic action.



37·4. Gammexane

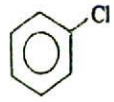
CHLOROBENZENE, *Phenyl Chloride*, C_6H_5Cl

It is prepared by passing chlorine through benzene in the presence of a catalyst ($AlCl_3$, $FeCl_3$, I_2). Chlorobenzene is produced industrially by passing a mixture of benzene vapour, air and hydrogen chloride over a copper(I)chloride catalyst (*Raschig Process*).



benzene chlorobenzene

Properties. Chlorobenzene is a colourless, pleasant smelling liquid; *bp* 132°C. It is insoluble in water, ethanol and ether. It is heavier than water, density 1·112 g/ml at 20°C. It is steam-volatile. It gives all the reactions characteristic of aryl halides.



chlorobenzene

$$+ \; aq.NaOH \xrightarrow[pressure]{300^\circ} \underset{\text{phenol}}{C_6H_5{-}OH} + NaCl$$

$$+ \; CuCN \xrightarrow[pressure]{200^\circ} \underset{\text{phenyl cyanide}}{C_6H_5{-}CN} + CuCl$$

$$+ \; aqNH_3 \xrightarrow[pressure]{200^\circ} \underset{\text{aniline}}{C_6H_5{-}NH_2} + HCl$$

$$+ \; CH_3Cl + 2Na \longrightarrow \underset{\text{toluene}}{C_6H_5{-}CH_3} + 2NaCl$$

$$+ \; Mg \xrightarrow{THF} \underset{\text{phenylmagnesium chloride}}{C_6H_5{-}MgCl}$$

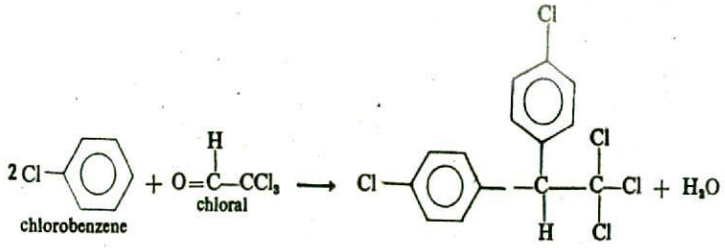
$$+ \; Li \xrightarrow{\text{ether}} \underset{\text{phenyllithium}}{C_6H_5{-}Li} + LiCl$$

$$+ \; 2H \xrightarrow[NaOH]{Ni-Al} \underset{\text{benzene}}{C_6H_6} + HCl$$

$$+ \text{ conc. } HNO_3 \xrightarrow{(H_2SO_4)} \underset{\text{o- and p-nitrochloro-benzene}}{Cl{-}C_6H_4{-}NO_2} + H_2O$$

Uses. Chlorobenzene is used in the manufacture of phenols, aniline and DDT.

DDT, *2, 2-di (p-chlorophenyl) -1, 1, 1-trichloroethane.* The initials DDT come from the compound's commercial name Dichlorodiphenyl-trichloroethane. It is prepared by heating chlorobenzene with chloral (trichloroacetaldehyde) in presence of concentrated sulphuric acid. Two molecules of chlorobenzene condense with one molecule of chloral to from DDT.

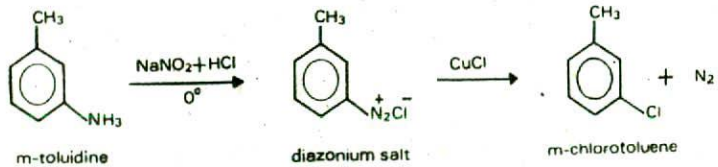


DDT

DDT is a solid, mp 109-110°C. It has a high and rather specific toxicity for various insects such as the common house fly and mosquito. Wide scale use of DDT as an insecticide began in 1946, both as a measure against malaria and for control of agricultural pests. Soon it was discovered that DDT is not readily metabolised and destroyed by environmental destructive forces. It is found to exist for months and years, not only in the soil but in plant and animal life as well where it produces unforeseen ecological effects. Thus the effect in birds could be devastating since DDT causes poor egg formation. In view of such ecological problems, the use of DDT has been substantially reduced in the mid-1960's and it is currently being replaced by safer insecticides.

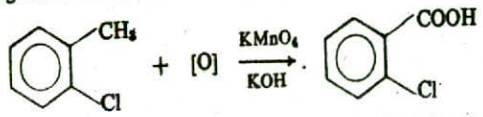
CHLOROTOLUENES, *Tolyl chloride*, $CH_3—C_6H_4—Cl$

o- and *p*-chlorotoluenes are prepared by chlorinating toluene in the presence of $FeCl_3$ or iodine as catylyst. *m*-chlorotoluene is obtained from the corresponding toluidine by Sandmeyer's reaction. Thus,

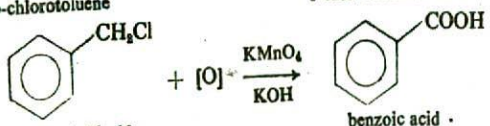


m-toluidine diazonium salt m-chlorotoluene

Properties. Chlorotoluenes are heavy, colourless liquids bp : *ortho* 158°; *meta* 162°; *para* 162°. In chemical behaviour they closely resemble chlorobenzene. On oxidation with alkaline potassium permanganate, they form the corresponding chlorobenzoic acids. This reaction is often employed to distinguish chlorotoluenes from the isomeric benzyl chloride. Thus,



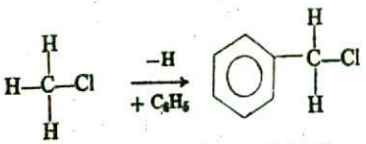
o-chlorotoluene *o*-chlorobenzoic acid



benzyl chloride benzoic acid

ARALKYL HALIDES

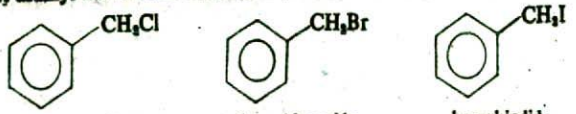
These compounds, in fact, could be regarded as aryl-substituted alkyl halides.



methyl chloride benzyl chloride

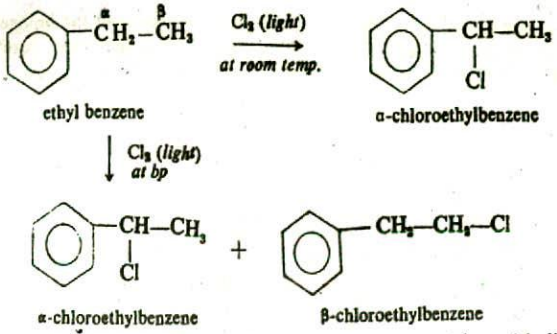
They have halogen atoms present in the side-chain and are also often referred to as **Side-chain Halogen Derivatives.**

The simplest aralkyl halides are those derived from toluene.



benzyl chloride benzyl bromide benzyl iodide

Benzyl chloride and benzyl bromide can be obtained by direct halogenation of toluene in sunlight. Benzyl iodide is prepared by boiling under reflux benzyl chloride and potassium iodide in ethanol. Chloro and bromo derivatives of homologues of benzene with longer side-chains are obtained by halogenation with Cl_2 or Br_2 in the presence of light, when the halogen enters the α-position. However, halogenation at the boiling point also yields derivatives with halogen in other positions.



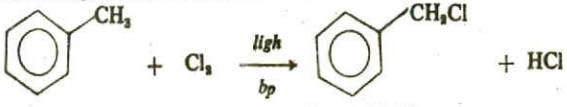
Benzyl halides are liquids at room temperature except benzyl iodide which is a solid. The aralkyl halides having halogen on the α-carbon are lachrymators (tear producers).

In their chemical behaviour, they resemble with simple alkyl halides, undergoing the same nucleophilic substitution reactions and forming Grignard reagents. Here we will discuss in detail benzyl chloride as a typical representative of the class.

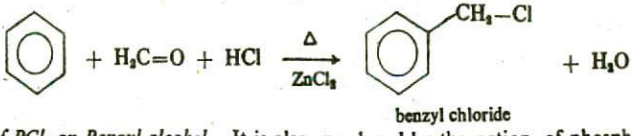
BENZYL CHLORIDE, $C_6H_5CH_2Cl$

It is isomeric with the three chlorotoluenes but differs from them widely in many respects.

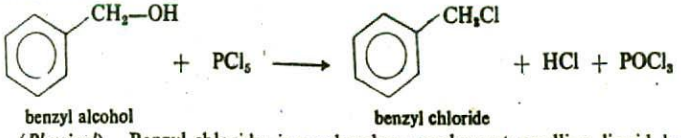
Preparation. (1) *Direct Chlorination of Toluene.* Benzyl chloride is prepared by passing chlorine into boiling toluene in light till the theoretical increase in weight is reached.



(2) *Chloromethylation of Benzene.* It may be prepared by heating benzene with formalin (HCHO) and hydrochloric acid in the presence of anhydrous zinc chloride.

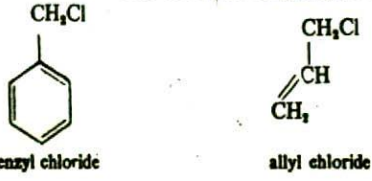


(3) *Action of PCl_5 on Benzyl alcohol.* It is also produced by the action of phosphorus pentachloride on benzyl alcohol.

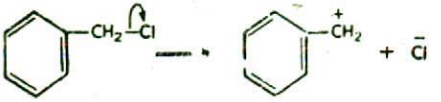


Properties. (*Physical*). Benzyl chloride is a colourless unpleasant smelling liquid, bp 179°C. It is insoluble in water, but is miscible with most organic solvents. Its vapours have an irritating action on eyes and nose, causing flow of tears.

(*Chemical*). (1) *Nucleophilic Substitution Reactions.* An examination of the Kekule structure of benzyl chloride shows a remarkable electronic similarity to that of allyl chloride.

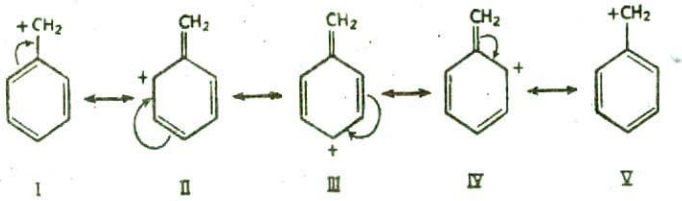


Thus benzyl chloride gives nucleophilic substitution reactions at the halogen as readily as allyl chloride, and even more readily than ethyl chloride. This increased reactivity of the chlorine in benzyl chloride is due to the fact that the residual carbonium ion $C_6H_5CH_2^+$ is resonance stabilised.



BENZYL CHLORIDE CARBONIUM ION

The carbonium ion is stable as it exists in the following five canonical forms.



I II III IV V

As shown in Fig. 37·5 benzyl carbonium ion can be stabilised by resonance since the benzyl carbon atom has a vacant *p*-orbital which can overlap with six *p*-orbitals of the ring carbons. This permits the six π electrons to become associated with all the seven carbons in an extended π orbital.

As predicted by the structure of benzyl chloride, it undergoes nucleophilic displacement reactions (S_N1) easily just like allyl chloride. For example,

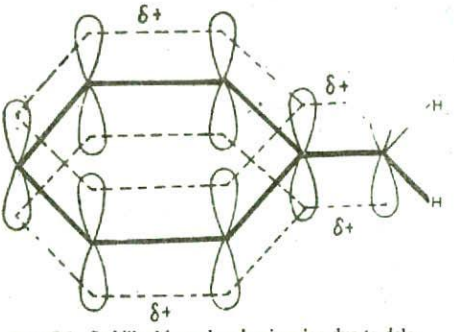
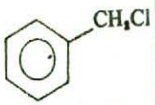


Fig. 37·5. Stabilised benzyl carbonium ion due to delocalisation of electrons and dispersal of positive charge over all seven carbons.



benzyl chloride

$$+ \text{ aq. KOH} \longrightarrow C_6H_5{-}CH_2OH + KCl$$
benzyl alcohol

$$+ \text{ aq. KCN} \longrightarrow C_6H_5{-}CH_2CN + KCl$$
benzyl cyanide

$$+ \text{ alc. } NH_3 \longrightarrow C_6H_5{-}CH_2NH_2 + HCl$$
benzylamine

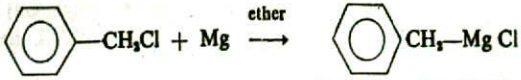
$$+ CH_3COOAg \longrightarrow C_6H_5{-}CH_2OOCCH_3 + AgCl$$
benzyl acetate

(2) *Wurtz Reaction.* Upon treatment with sodium metal it gives dibenzyl, thus behaving like alkyl halide.



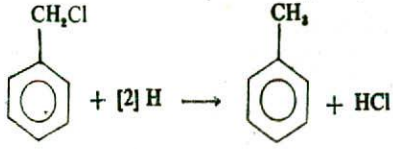
benzyl chloride dibenzyl

(3) *Formation of Grignard Reagent.* It forms a Grignard reagent readily when reacted with magnesium in ether.



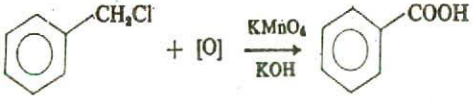
benzylmagnesium chloride

(4). *Reduction.* When reduced with Zn-Cu couple it yields toluene.



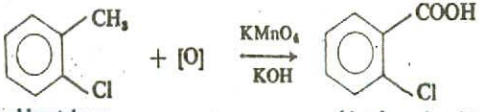
benzyl chloride toluene

(5) *Oxidation.* When oxidised with dilute nitric acid or alkaline potassium permanganate, the —CH_2Cl group is oxidised to —COOH group. Benzoic acid is the product.



benzyl chloride benzoic acid

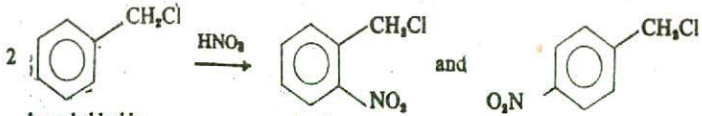
This reaction can be used for distinguishing benzyl chloride from the isomeric chlorotoluenes.



o-chlorotoluene *o*-chlorobenzoic acid

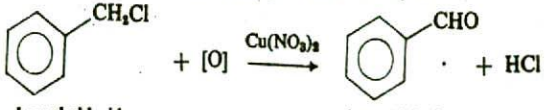
The product obtained from *o*-chlorotoluene contains the chlorine atom, while that from benzyl chloride does not.

(6) *Substitution in Benzene Ring.* Benzyl chloride can be nitrated and sulphonated in the benzene ring to yield *o*- and *p*- nitro and sulphonic acid derivatives.



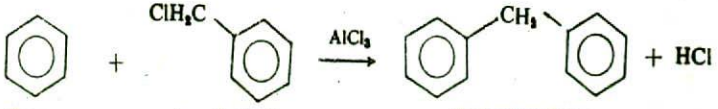
benzyl chloride *o*-nitrobenzyl chloride *o*-nitrobenzyl chloride

On mild oxidation with cupric nitrate, it gives benzaldehyde.



benzyl chloride benzaldehyde

(7) *Friedel-Crafts Reaction.* Benzyl chloride also responds to Friedel-Crafts reaction like the alkyl halides.

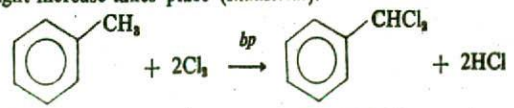


benzene benzyl chloride diphenyl methane

Uses. Benzyl chloride is used for the introduction of benzyl group (*benzylation*) in organic compounds. It is the starting material for the manufacture of benzyl alcohol, benzylamine and benzaldehyde.

BENZAL CHLORIDE, *Benzilidene Chloride*, $C_6H_5—CHCl_2$

Benzal chloride may be prepared: (1) By passing chlorine into boiling toluene until the required weight increase takes place (*Industrial*).



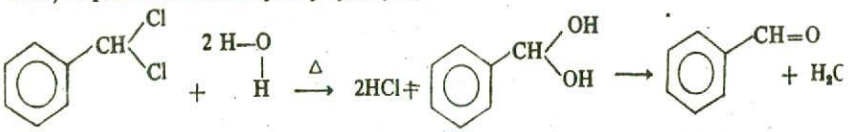
toluene benzal chloride

(2) By the action of phosphorus pentachloride on benzaldehyde.



benzaldehyde benzal chloride

Properties. Benzal chloride is a colourless liquid, bp 207°C. It lacks the lachrymatory property that benzyl chloride possesses. When heated with calcium hydroxide solution (lime water) it produces benzaldehyde by hydrolysis.

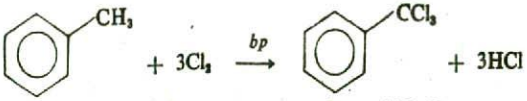


benzal chloride water (*unstable*) benzaldehyde

Thus benzal chloride is used for industrial preparation of benzaldehyde.

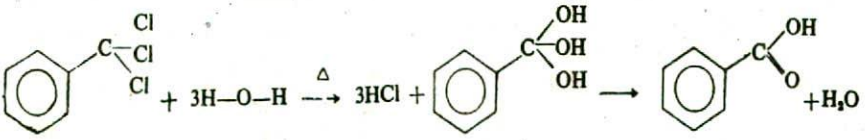
BENZOTRICRHLOIDE, *Phenylchloroform*, $C_6H_5—CCl_3$

It is prepared by passing chlorine into boiling toluene till no further increase in weight takes place.



toluene benzotrichloride

Properties. Benzotrichloride is a colourless liquid, bp 214°C. Since the halogen atoms are attached to an electron-donating phenyl group, these are more reactive than in chloroform. Thus w en boiled with calcium hydroxide solution, it is hydrolysed to yield benzoic acid.



(*unstable*) benzoic acid

This reaction is used for the industrial production of benzoic acid

Aryl halides	*Aralkyl halides*
1. Colourless liquids; insoluble in water, soluble in organic solvents. Agreeable aromatic odour; not lachrymatory.	1. Relatively high boiling colourless liquids or solids; insoluble in water, soluble in organic solvents. Pungent smelling and lachrymatory.
2. Nucleophilic substitution reactions of halogen atom do not take place under ordinary laboratory condition. The replacement of halogen by OH, CN, NH_2 can be carried under high energetic conditions (high temp., pressure, catalyst).	2. Nucleophilic substitution reactions given as readily as by alkyl halides, under ordinary conditions.
3. Couple with alkyl halides in presence of sodium in ether to form alkylated aromatic hydrocarbons—*Wurtz-Fittig Reaction.*	3. Couple with alkyl halides in the presence of sodium in ether, giving aryl-substituted alkanes—*Wurtz Reaction.*
4. Aryl iodides when refluxed with copper powder, undergo coupling to form biaryls—*Ullmann Reaction.*	4. Do not give Ullmann Reaction.
5. Aryl chlorides do not react with magnesium in ether to from Grignard Reagents. Aryl bromides and aryl iodides do so.	5. Form Grignard Reagents in ether.
6. When reduced with nickel-aluminium alloy in presence of alkali, yield the parent hydrocarbon.	6. On reduction with Zn-Cu couple, they yield the parent hydrocarbon.
7. On oxidation with alkaline permanganate the halogen remains attached to the benzene ring.	7. On similar oxidation, the halogen is knocked out from the molecule.
8. Do not give Friedel-Crafts reaction.	8. Undergo Friedel-Crafts reaction.
9. Undergo electrophilic substitution reactions in the aromatic ring but not very readily.	9. Undergo electrophilic substitution (halogenation) readily in the side-chain.

QUESTIONS

1. Give the main types of aromatic halogen compounds. Write the structural formulae of two important members of each class and assign to them systematic names.

2. Discuss the orbital structure of chlorobenzene. How do you account for double bond character of C—Cl bond ?

3. Describe the general methods of preparation of Aryl halides. How can you obtain iodobenzene and fluorobenzene through the formation of diazonium salts ?

4. The melting points of chlorotoluenes are in the order *para* > *ortho* or *meta*. Explain.

5. How do you explain that aryl halides, unlike alkyl halides, do not undergo 'Nucleophilic substitution' under ordinary laboratory conditions.

6. "The halogen in chlorobenzene becomes more reactive if we introduce a NO_2 group in the ortho or para position in the benzene ring." Comment.

7. Discuss the mechanism of formation of phenol from chlorobenzene by reaction with aqueous NaOH at high temperature and pressure.

8. What is Wurtz-Fittig Reaction ? Discuss its mechanism taking example of the preparation of methylbenzene from bromobenzene and methyl bromide.

9. **List the general reactions of aryl halides. How can you distinguish *o*-chlorotoluene from benzyl chloride.**

10. **Write short notes on the preparation, properties and uses of (*a*) Gammexane, (*b*) DDT. Why the use of DDT is going under prohibition now a days ?**

11. **Describe the methods of preparation and reactions of chlorotoluenes.**

12. **Give a general account of aralkyl halides and their chemical behaviour. How is it that the reactions of benzyl chloride are analogous to those of allyl chloride ?**

13. **Give the preparation and properties of benzyl chloride, pointing out as to where does it differ from aryl halides.**

14. **Write notes on : Benzal chloride ; and Benzotrichloride.**

15. Write the mechanism of nucleophilic substitution in Aryl halides. ***(Kurukshetra BSc III, 1980)***

16. How will you convert toluene into benzyl chloride and benzyl bromide ? Give equations. ***(Kerala BSc II, 1980)***

17. Give the mechanism when Bromobenzene reacts with nitric acid in the presence of sulphuric acid. ***(Panjab BSc Chem Engg, 1981)***

18. (*a*) Explain the mechanism of nuclear halogenation.

(*b*) What is the product formed when:—

(*i*) Chlorobenzene reacts with chloral in the presence of conc H_2SO_4.

(*ii*) Nitrobenzene is reduced under different conditions. *(Gorakhpur BSc II, 1981)*

19. Give methods for introducing halogens in the nucleus and the side-chain of toluene. Discuss the mechanism involved in both types of halogenation. *(Rajasthan BSc III, 1981)*

20. Discuss the mechanism of chlorination of benzene in presence of $FeCl_3$. *(Baroda BSc III, 1982)*

21. What are the conditions for nuclear and side-chain substitution, when chlorine reacts with toluene ? Give characteristics of two types of halogen compounds. How will you prepare *m*-chlorotoluene ? *(Delhi BSc, 1993)*

22. Write the structural formulae of all possible isomers of aromatic compounds having the molecular formula C_7H_7Cl. *(Manipur BSc, 1994)*

23. Describe the preparation and properties of chlorobenzene. *(Agra BSc, 1993)*

24. Explain : Low reactivity of aryl halides and vinyl halides. *(Andhra BSc, 1993; Saugar BSc, 1994)*

25. How will you synthesise biphenyl from chlorobenzene ? *(Goa BSc, 1993)*

26. How will you synthesise DDT from chlorobenzene ? *(Baroda BSc, 1994)*

27. How will you synthesise phenylacetic acid from toluene ?

Hint. Use the following steps : (*i*) Cl_2/UV, (*ii*) Mg/ether, (*iii*) CO_2, and (*iv*) H_2O/H^+

28. How will you distinguish between benzyl bromide and *p*-bromotoluene ? *(Madras BSc, 1994; Panjab BSc, 1994)*

Hint. Benzyl bromide forms a precipitate of AgBr with alcoholic $AgNO_3$ solution. *p*-Bromotoluene does not react.

29. Compound (A), C_8H_9Br, is optically active. When treated with alcoholic silver nitrate solution, (A) precipitated AgBr immediately, and on oxidation (A) gave benzoic acid. What is the structure of (A) ?

Answer. (A) is 1-Bromo-1-phenylethane.

30. Three isomers (A), (B), and (C) of formula C_8H_9Cl gave the following compounds on oxidation :

(A) *gives* benzoic acid (B) *gives* phthalic acid (C) *gives p*-chlorobenzoic acid

(A) is optically active. Both (A) and (B), but not (C), give a white precipitate when warmed with an alcoholic silver nitrate solution. Deduce the structures of (A), (B), and (C).

Answer. (A) *is* 1-chloro-1-phenylethane

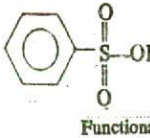
(B) *is o*-methylbenzyl chloride

(C) *is p*-chloroethylbenzene

Chapter 38

Aromatic Sulphonic Acids

They are the derivatives of aromatic hydrocarbons in which one or more hydrogen atoms of the benzene ring have been replaced by the function $-SO_3H$, called the *Sulphonic acid group*. The simplest member of the class, benzenesulphonic acid may be written as

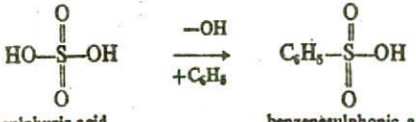


Functional group

or $C_6H_5-SO_3-OH$ or $C_6H_5-SO_3H$

In other words, aromatic sulphonic acids are compounds in which one or more sulphonic acid groups ($-SO_3H$) are attached directly to the aromatic ring through the sulphur atom. They contain C—S bond.

Aromatic sulphonic acids could well be regarded as derived from sulphuric acid by substitution of aryl group for —OH group.



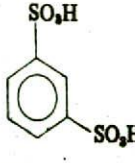
sulphuric acid benzenesulphonic acid

Thus aromatic sulphonic acids are strong acids like sulphuric acid and give many similar reactions.

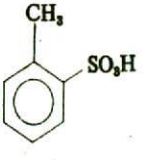
Nomenclature. They are named by attaching the suffix *-sulphonic acid* to the name of the parent hydrocarbon. The position of the sulphonic acid groups is indicated by numbers or letters when necessary. For illustration,



benzenesulphonic acid



benzene-*m*-disulphonic acid, benzene-1, 3-disulphonic acid

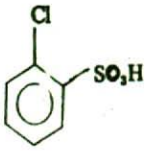


o-toluenesulphonic acid



P-toluenesulphonic acid

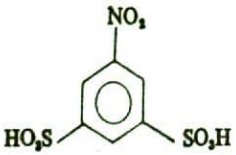
Similarly, derivatives of aromatic sulphonic acids are named by appending the suffix *-sulphonic acid* to the name of the orginal compound. Thus :



o-chlorobenzenesulphonic acid, 2-chlorobenzenesulphonic acid



p-aminobenzenesulphonic acid (*sulphanilic acid*)

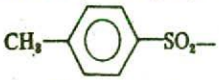


5-nitro-1, 3-benzenedisulphonic acid

The $-SO_2-$ group is called *sulphonyl group*, being analogous to carbonyl group —CO— of the carboxylic acids. The groups obtained after removal of —OH group from sulphonic acids are named accordingly.



benzenesulphonyl



p-toluenesulphonyl (*tosyl*)

Sulphonic acids form derivatives at the $—SO_2—OH$ group which are analogous to the corresponding carboxylic acid derivatives. Their nomenclature is also similar. Thus,



pot. benzenesulphonate



ethyl benzenesulphonate



benzenesulphonyl chloride



benzenesulphonamide



pot. *p*-toluenesulphonate



ethyl *p*-toluenesulphonate (*ethyl tosylate*)



p-toluenesulphonylchloride (*tosyl chloride*)

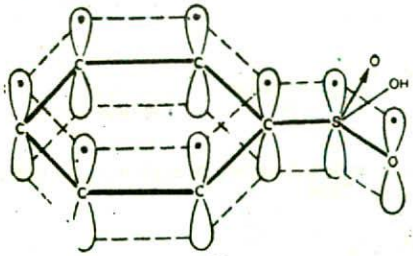


p-toluenesulphonamide

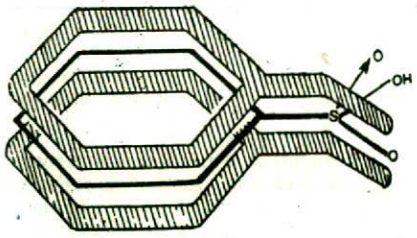
The more important aromatic sulphonic acids and their derivatives are often assigned the *Common Names* (given in brackets).

STRUCTURE

The molecular structure of aromatic sulphonic acids is similar to that of nitrobenzene. The *p* orbitals in one of the π bonds of $-SO_2H$ group are aligned with *p* orbitals of the benzene ring. Hence these interact to form extended π orbital enveloping the benzene ring and one of the double bonds (S=O) in the sulphonic acid group. This interaction is also made possible by the shortness of C—S bond.



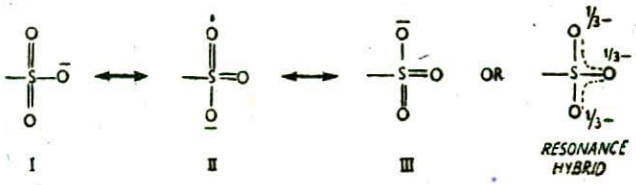
Atomic Orbital model



Electron Cloud model

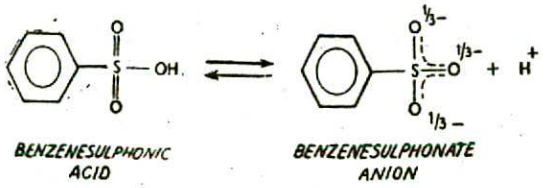
Fig. 38·1. Structure of Benzenesulphonic acid

The sulphonate anion is resonance stabilised and is regarded as a hybrid of the following three canonical forms.



I II III

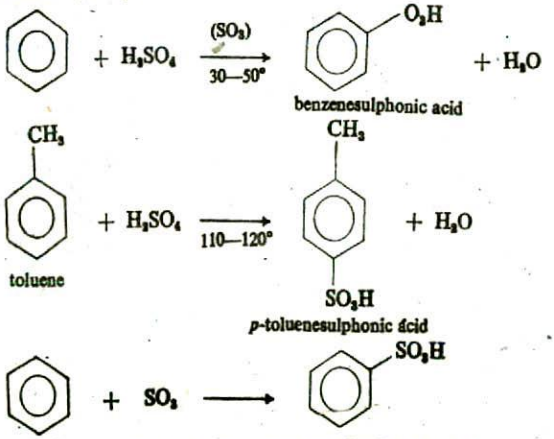
Since the structure I is the major contributor, benzenesulphonic acid is generally represented as



BENZENESULPHONIC ACID BENZENESULPHONATE ANION

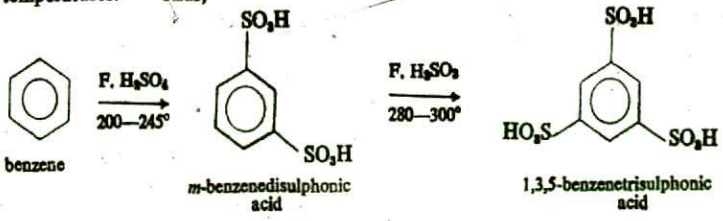
PREPARATION

(1) **Direct Sulphonation.** Aromatic sulphonic acids are almost always prepared by direct sulphonation of appropriate aromatic hydrocarbon. This can be accomplished by treatement of the hydrocarbon with concentrated sulphuric acid (SO_3 dissolved in sulphuric acid), or liquid sulphur dioxide (1947).

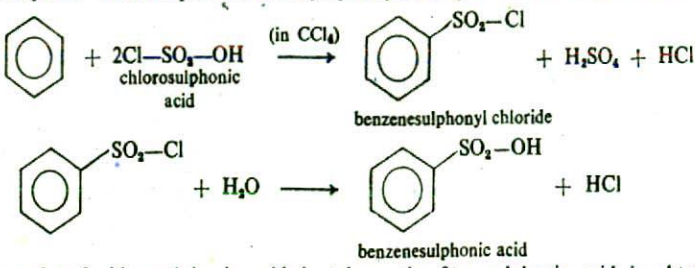


With sulphur trioxide, the product is free from excess of sulphuric acid.

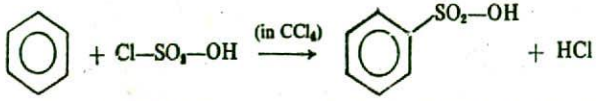
Di- and trisulphonic acids can be prepared by the action of fuming sulphuric acid at elevated temperatures. Thus,



(2) **Action with Chlorosulphonic acid.** In this method the aromatic hydrocarbon is treated with chlorosulphonic acid (2 moles) at room temperature, to form the respective arylsulphonyl chloride in good yield. This compound is readily hydrolysed to give the free sulphonic acid.

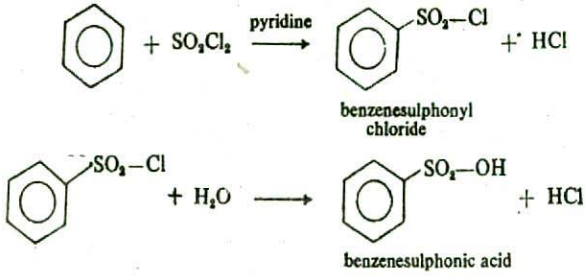


If one mole of chlorosulphonic acid is taken, the free sulphonic acid is obtained straightway.



Here no water is produced and the HCl gas escapes from the solution, leaving pure sulphonic acid.

(3) **Action with Sulphuryl chloride.** Aromatic sulphonic acids may also be prepared by the action of sulphuryl chloride on aromatic hydrocarbons in the presence of pyridine.



Isolation of Sulphonic acids The isolation of free sulponic acids from the reaction mixture is usually difficult because they are highly soluble in water and nonvolatile. This may be done in two ways.

(1) By *'Salting out* The reaction mixture is run into a saturated solution of sodium chloride which throws out crystalline sodium benzenesulphonate.

$$\underset{\text{benzenesulphonic acid}}{C_6H_5SO_2OH} + NaCl \longrightarrow \underset{\text{sod. benzenesulphonate}}{C_6H_5SO_2ONa} + HCl$$

2) *By forming soluble Barium or Lead Sulphonate.* The reaction mixture is diluted and ntralised with barium hydroxide or lead carbonate. The excess of sulphuric acid, if any, is emoved as insoluble barium sulphate or lead sulphate and filtered. The soluble barium or ead sulphonate goes in the filtrate and is treated with calculated amount of sulphuric acid. The resulting solution is filtered and evaporated to dryness under reduced pressure to recover the free sulphonic acid.

$$\underset{\substack{\text{benzenesulphonic}\\\text{acid}}}{2C_6H_5SO_3H} + Ba(OH)_2 \longrightarrow \underset{\substack{\text{barium sulphonate}\\(soluble)}}{(C_6H_5SO_3)_2Ba} \quad 2H_2O$$

$$(C_6H_5SO_3)_2Ba \quad H_2SO_4 \longrightarrow \underset{\substack{\text{benzenesulphonic}\\\text{acid}}}{2C_6H_5SO_3H} + \underset{(insoluble)}{BaSO_4}$$

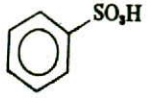
PHYSICAL PROPERTIES

(1) Aromatic sulphonic acids are white crystalline solids.

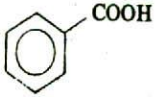
(2) They are extremely soluble in water and this causes them to be deliquescent in moist air. They are insoluble in organic solvents like benzene, carbon tetrachloride, etc.

(3) They are relatively nonvolatile, although some can be distilled at low pressure without decomposition. Thus benzenesulphonic acid boils at 135-137°C at a pressure below 0·01 mm of Hg.

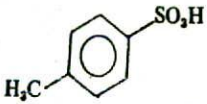
(4) Their melting points are lower than those of the corresponding carboxylic acids.



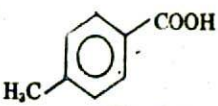
benzenesulphonic acid, *mp* 50-51°



benzoic acid, *mp* 122°



p-tlouenesulphonic acid, *mp* 106°



p-toluic acid, *mp* 180°

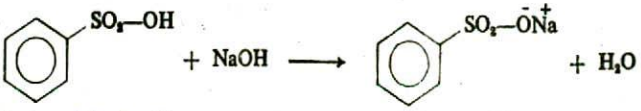
(5) They are strong acids (intermediate between HCl and H_2SO_4) and are completely ionised in aqueous solutions.

(6) The absorptions in the infrared region due to $-SO_3H$ group occur below 1,500 cm^{-1}. Hence these absorptions are seldom used in the structure determination of organic substances.

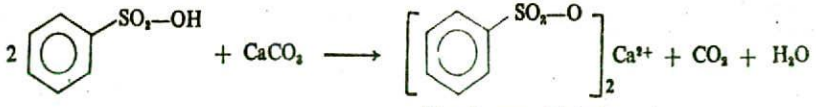
CHEMICAL PROPERTIES

REACTIONS AS ACIDS :

(1) **Salt Formation.** Aromatic sulphonic acids are of strongly acid nature. Their acid strengths are about the same as of sulphuric acid. Thus they form stable salts, called **Sulphonates,** with inorganic bases *i.e.*, metals, oxides, hydroxides and carbonates.



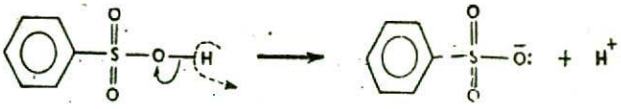
benzenesulphonic acid — sod. benzenesulphonate.



calcium benzenesulphonate

The salts of sulphonic acids are soluble in water and can easily be isolated. Since on account of their extreme water-solubility sulphonic acids cannot be easily separated, their salts are generally used in place of free acids in reactions.

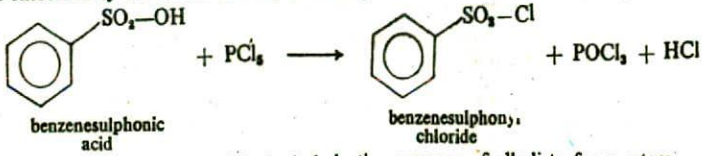
The strong acidic character of sulphonic acids is due to the ready formation of the resonance stabilised sulphonate anion.



SULPHONATE ANION
(RESONANCE STABILISED)

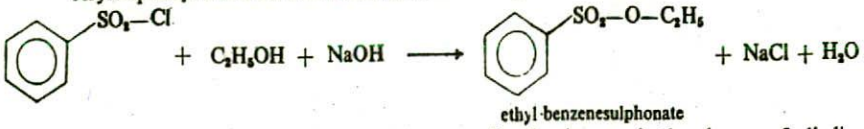
Electronegative groups increase the acidity, particularly where they are present in *ortho* or *para* positions.

(2) **Formation of Sulphonyl chlorides and Esters.** Arylsulphonic acids are converted into sulphonyl chlorides by the action af PCl_5 or $SOCl_2$.



benzenesulphonic acid — benzenesulphonyl chloride

Arylsulphonyl chlorides react with alcohols in the presence of alkali to form esters.



ethyl benzenesulphonate

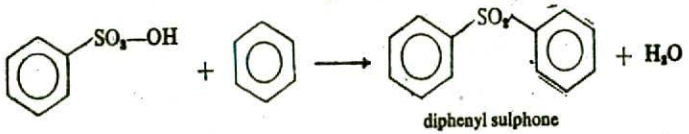
The sulphonic esters cannot be prepared by direct esterification because in the absence of alkali, the sulphonic ester produced alkylates the alcohol to from ether.

$$\underset{\text{sulphonic acid}}{Ar{-}SO_2{-}OH} + C_2H_5OH \longrightarrow \underset{\text{ethyl sulphonate (ester)}}{Ar{-}SO_2{-}OC_2H_5}$$

$$Ar{-}SO_2{-}OC_2H_5 + \underset{\text{ethyl alcohol}}{C_2H_5{-}O{-}H} \longrightarrow Ar{-}SO_2{-}OH + \underset{\text{diethyl ether}}{C_2H_5{-}O{-}C_2H_5}$$

The sulphonyl chlorides behave like the acid chlorides of carboxylic acids. They react with ammonia to give *sulphonamides* which have definite melting points and are used for ideniti-fying sulphonic acids.

(3) **Formation af Sulphones.** Arylsulphonic acids react with hydrocarbons to form *sulphones* which are neutral compounds.

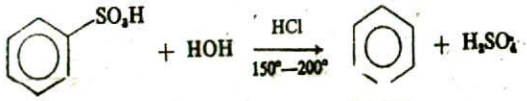


diphenyl sulphone

Sulphones are formed as secondary products during sulphonation of hydrocarbons.

REACTIONS IN WHICH $-SO_3H$ GROUP IS REPLACED

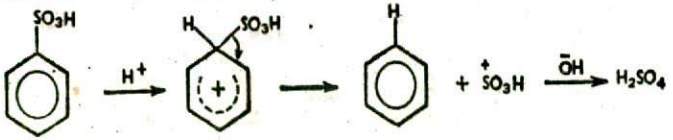
(4) **Desulphonation.** When arylsulphonic acids are heated with aqueous hydrochloric acid, the $-SO_3H$ group is replaced by H atom to form the parent hydrocarbon.



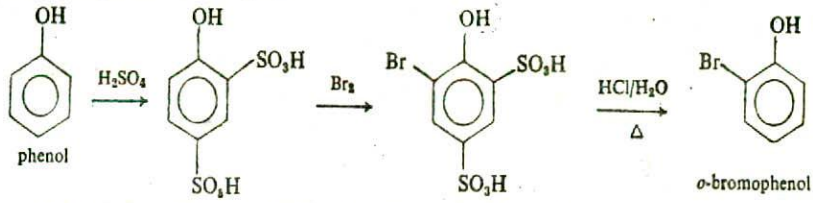
benzenesulphonic acid — benzene

This knocking out of sulphonic acid group from benzene ring is called *Desulphonation*. The strength of the acid and the temperature required to effect desulphonation depend on the nature of the aromatic ring.

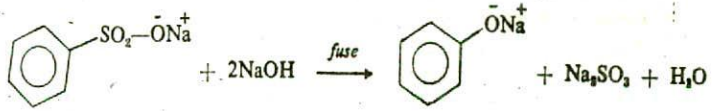
MECHANISM. Sulphonation is a reversible process and the mechanism of desulpho-nation is essentially the reverse of the formation of arylsulphonic acids.



Desulphonation has proved to be useful in the synthesis of a pure isomer which is otherwise difficult to make by direct methods. For example, direct bromination of phenol at 0—5°C gives chiefly *p*-bromophenol. To get the pure isomer, *o*-bromophenol, the following procedure involving desulphonation is adopted.

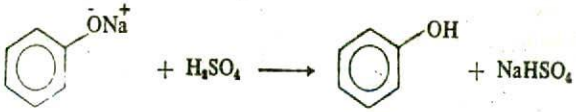


(5) **Formation of Phenols.** When the sodium salt of an arylsulphonic acid is fused with solid NaOH or KOH, the sulphonate group is replaced to give the sodium or potassium salt of a phenol.



sod benzenesulphonate sod phenoxide

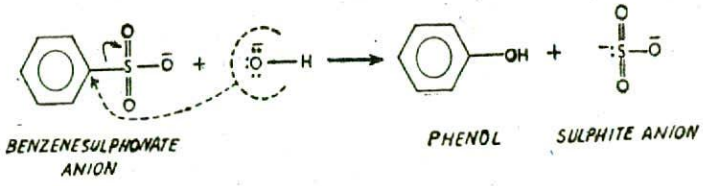
The sodium phenoxide on acidification yields phenol.

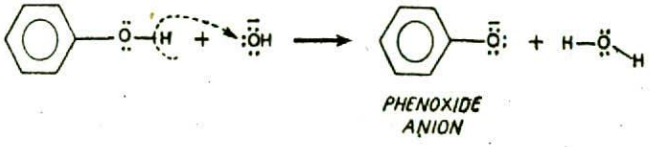


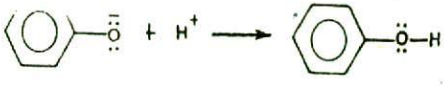
phenol

Yields are good and this is an important general method for preparing phenols.

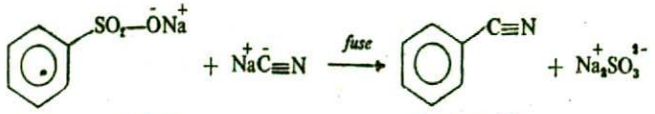
MECHANISM. It is a nucleophilic replacement of the sulphonate group by $\bar{O}H$ anion. Thus :







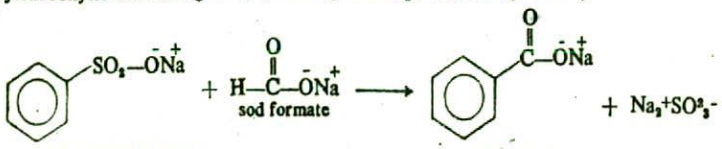
(6) **Formation of Nitriles.** When sodium sulphonates are fused with sodium cyanide, the sulphonate anion is replaced by cyanide anion to form a nitrile.



sod benenzesulphonate phenyl cyanide

This is a nucleophilic replacement by the cyanide ion.

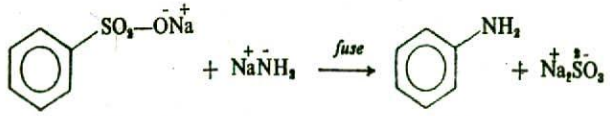
(7) **Formation of Carboxylic acids.** Heating a sodium sulphonate with sodium formate, ves an arylcarboxylic acid straightway (Nucleophilic replacement by COO^-).



sod benzenesulphonate sod benzoate

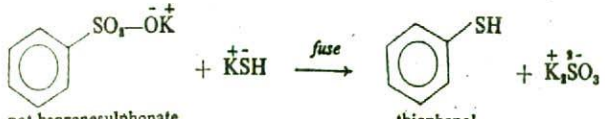
ı acidification free carboxylic acid is formed.

(8) **Formation of Amines.** When sodium sulphonates are fused with sodamide, aromatic ıines are obtained. (Nucleophilic replacement by $-NH_2$).



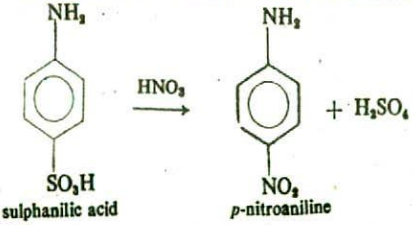
sod benzenesulphonate aniline

(9) **Formation of Thiophenols.** On heating potassium sulphonates with potassium hydro- ɑ sulphide, thiophenols are formed. (Nucleophilic replacement by —SH).



pot benzenesulphonate thiophenol

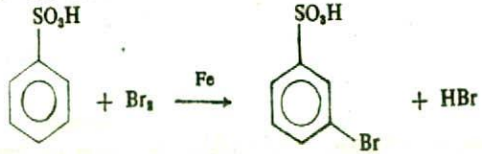
(10) **Formation of Nitro derivatives.** The sulphonic acid group is often readily replaced by ıitro group. It provides a method of preparing nitro derivatives of compounds that are easily ıidised by nitric acid, because sulphonic acid derivatives are resistant to oxidation. For example,



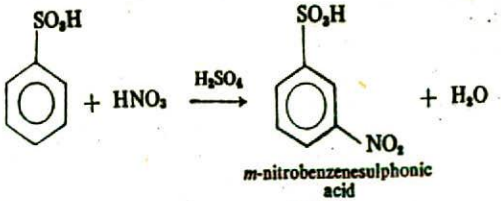
sulphanilic acid *p*-nitroaniline

EACTIONS OF THE BENZENE RING

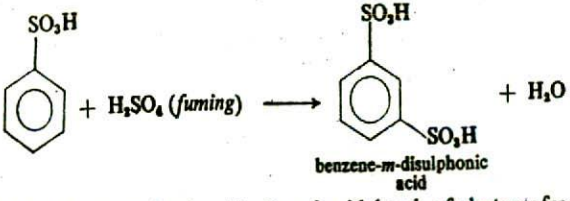
The aromatic ring of sulphonic acids can be halogenated, nitrated or sulphonated in the ual manner. However, the reactions require more drastic conditions than those for the corres- ıding benzene substitutions. The new substituent is directed to the meta position.



benzenesulphonic acid *m*-bromobenzenesulphonic acid

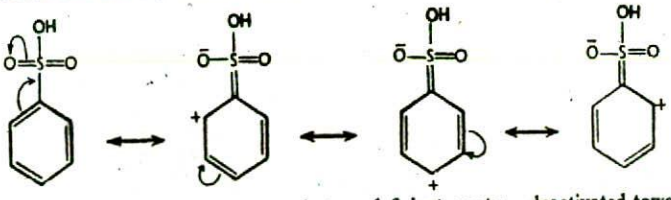


m-nitrobenzenesulphonic acid



benzene-*m*-disulphonic acid

MECHANISM. In arylsulphonic acids, there is withdrawl of electrons from the benzene ring due to inductive and mesomeric effects.



Thus the benzene ring becomes an electron-deficient centre, deactivated towards attack by electrophilic reagents (Br^+, NO_2^+, SO_3). The positions 2 and 4 become positive by the mesomeric effect shown above. Therefore the sites of electrophilic attack are positions 3 and 5 (*meta*). The mechanism of halogenation, nitration and sulphonation of aromatic rings in sulphonic acid is similar to electrophilic substitution of benzene which we have already considered.

USES OF SULPHONIC ACIDS

The free arylsulphonic acids find very little use. On account of their weak oxidising action compared to sulphonic acid, they are frequently used as acid catalysts.

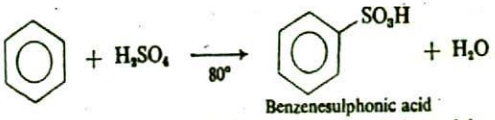
Sodium sulphonates are used for making phenols by fusion with NaOH. The sodium sulphonate ($-SO_3Na$) in direct or substantive dyes confers solubility on the dyestuff. Sodium salts of alkylated arylsulphonic acids are important synthetic detergents.

INDIVIDUAL MEMBERS AND DERIVATIVES

BENZENESULPHONIC ACID, $C_6H_5-SO_3-OH$

It is a typical and most important member of the class. It was first prepared by Mitscherlich in 1834. It is found in the waste products of metabolism.

Preparation. Benzenesulphonic acid is readily prepared by heating benzene with concentrated sulphuric acid at 80°.



Benzenesulphonic acid

A mixture of benzene and concentrated sulphuric acid (1:2) is heated in round-bottom flask fitted with a reflux condenser. The resulting mixture is poured into a solution of NaCl when sodium benzenesulphonate separates. This is used as such for most purposes. If pure benzenesulphonate is required, the sulphonating mixture is neutralised with lead carbonate.

The precipitate of lead sulphate formed by excess of H_2SO_4 is filtered. The filtrate containing lead benzenesulphonate is decomposed with calculated amount of dilute sulphuric acid, filtered and filtrate concentrated to crystallisation.

Properties. (*Physical*). Benzenesulphonic acid crystallises from white leaflets containing $1\frac{1}{2}$ H_2O. The anhydrous compound melts at 50—51°. It is very hygroscopic and forms a syrupy liquid when exposed to moist air. It is highly soluble in water and the solution is strongly acidic (about as strong as sulphuric acid).

(*Chemical*). In benzenesulphonic acid the $-SO_3H$ group is not tightly attached to the benzene ring and can be replaced by other atoms. The sulponic acid group exibits analogous behaviour to that of —COOH group and forms similar derivatives.

Reactions of $-SO_2-OH$ *similar to* $-CO-OH$:

$C_6H_5-SO_2-OH$ (benzenesulphonic acid)

$+ NaOH \xrightarrow{(H_2O)} C_6H_5-SO_2-\overset{-}{O}\overset{+}{Na} + H_2O$ (sod benzenesulphonate)

$+ PCl_5 \longrightarrow C_6H_5-SO_2-Cl + POCl_3 + HCl$ (benzenesulphonyl chloride)

$+ C_6H_6 \longrightarrow C_6H_5-SO_2-C_6H_5 + H_2O$ (diphenyl sulphone)

Reactions in which $-SO_3H$ *group is replaced* :

$C_6H_5-SO_3H + H-O-H \xrightarrow[150-200]{HCl} C_6H_6 + H_2SO_4$

$C_6H_5-S\overset{-}{O}_3\overset{+}{Na}$ (sod benzenesulphonate)

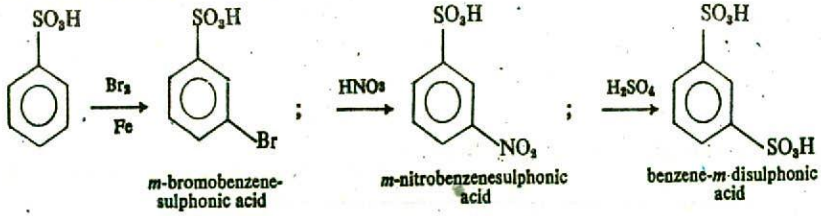
$+ 2NaOH \xrightarrow{fuse} C_6H_5-O\overset{-}{\overset{+}{Na}} \xrightarrow{H_2SO_4} C_6H_5-OH$ (sod phenoxide; phenol)

$+ NaCN \xrightarrow{fuse} C_6H_5-CN + Na_2SO_3$ (phenyl cyanide)

$+ NaNH_2 \xrightarrow{fuse} C_6H_5-NH_2 + Na_2SO_3$ (aniline)

$+ KSH \xrightarrow{fuse} C_6H_5-SH + K_2SO_3$ (thiophenol)

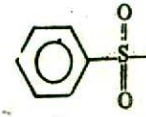
It can be halogenated, nitrated and sulphonated in the benzene ring under more drastic conditions than benzene itself. The new substituent goes to the meta position.



m-bromobenzenesulphonic acid; *m*-nitrobenzenesulphonic acid; benzene-*m*-disulphonic acid

Uses. Benzenesulphonic acid is the starting material for the preparation of many benzene derivatives. It is an important intermediate in the manufacture of certain dyes and drugs. It is used as a catalyst in the preparation of alkenes and ethers.

Benzenesulphonyl Chloride,



or $C_6H_5-SO_2-Cl$ or $C_6H_5SO_2Cl$

It is the acid chloride of benzenesulphonic acid and may be considered as a typical aromatic sulphonyl chloride.

Preparation. (1) It is obtained by the action of PCl_5 on benzenesulphonic acid or its sodium salt.

$$\underset{\text{benzenesulphonic acid}}{C_6H_5{-}SO_2{-}OH} + PCl_5 \longrightarrow \underset{\substack{\text{benzenesulphonyl}\\ \text{chloride}}}{C_6H_5{-}SO_2{-}Cl} + POCl_3 + HCl$$

$$\underset{\text{sod benzenesulphonate}}{C_6H_5{-}SO_2{-}\overset{-}{O}\overset{+}{N}a} + PCl_5 \longrightarrow C_6H_5{-}SO_2{-}Cl + POCl_3 + NaCl$$

(2) It is best prepared by the action of excess chlorosulphonic acid on benzene.

$$C_6H_6 + 2\ \underset{\substack{\text{chlorosulphonic}\\ \text{acid}}}{Cl{-}SO_2{-}OH} \longrightarrow C_6H_5{-}SO_2{-}Cl + HCl + H_2SO_4$$

(3) It may also be obtained by the action of sulphuryl chloride on benzene in the presence of anhydrous aluminium chloride

$$C_6H_6 + \underset{\text{sulphuryl chloride}}{Cl{-}SO_2{-}Cl} \xrightarrow{AlCl_3} C_6H_5{-}SO_2{-}Cl + HCl$$

Properties (*Physical*). Benzenesulphonyl chloride is a colourless liquid, bp 250°C. It has a characteristic disagreeable odour and is lachrymatory. It is insoluble in water but soluble in an organic solvent like ether.

(*Chemical*). In general its behaviour is analogous to the acid chlorides of arylcarboxylic acids, although it is not as reactive.

(1) *Hydrolysis.* It is decomposed slowly by cold water. The hydrolysis is faster in alkali, when the salt is formed.

$$\underset{\substack{\text{benzenesulphonyl}\\ \text{chloride}}}{C_6H_5{-}SO_2{-}Cl} + H{-}OH \longrightarrow \underset{\text{benzenesulphonic acid}}{C_6H_5{-}SO_2{-}OH} + HCl$$

(2) *Formation of Esters.* If reacts with alcohols and phenols in the presence of an alkali to form esters *i.e.*, alkyl benzenesulphonates.

$$C_6H_5{-}SO_2{-}Cl + \underset{\text{alcohol}}{H{-}O{-}R} \xrightarrow{(NaOH)} \underset{\text{Alkyl benzenesulphonate}}{C_6H_5{-}SO_2{-}O{-}R} + HCl$$

$$C_6H_5{-}SO_2{-}Cl + H{-}O{-}C_6H_5 \xrightarrow{NaOH} \underset{\text{phenyl benzenesulphonate}}{C_6H_5{-}SO_2{-}O{-}C_6H_5} + HCl$$

(3) *Formation of Amide.* It reacts with concentrated ammonia to form benzenesuphonamide, mp 150°C.

$$C_6H_5{-}SO_2{-}Cl + NH_3 \longrightarrow \underset{\text{benzenesulphonamide}}{C_6H_5{-}SO_2{-}NH_2} + \overset{+}{H} + \overset{-}{Cl}$$

(4) *Formation of N-substituted amides* It reacts with primary and secondary amines to from N-alkyl and *N, N*-dialkylsulphonamides espectively.

$$C_6H_5{-}SO_2{-}Cl + \underset{\text{1° amine}}{H{-}\overset{H}{\overset{|}{N}}{-}R} \longrightarrow \underset{\substack{\textit{N}\text{-alkylsulphonamide}\\ (\textit{soluble in alkali})}}{C_6H_5{-}SO_2{-}\overset{H}{\overset{|}{N}}{-}R} + H^+ + Cl^-$$

$$C_6H_5SO_2{-}Cl + \underset{\text{2° amine}}{H{-}\overset{R}{\overset{|}{N}}{-}R} \longrightarrow \underset{\substack{\textit{N, N}\text{-dialkylsulphonamide}\\ (\textit{insoluble in alkali})}}{C_6H_5{-}SO_2{-}\overset{R}{\overset{|}{N}}{-}R} + H^+ + Cl^-$$

This reaction forms the basis of Hinsberg's method for the separation and identification of 1°, 2° and 3° amines.

(5) *Reduction.* While benzenesulphonic acid is resistant to reduction, the sulphonyl chloride is reduced to thiophenol in two stages.

(*i*) With a mild reducing agent such as zinc dust and water, benzenesulphonic acid is formed.

$$C_6H_5{-}SO_2{-}Cl + 2H \xrightarrow{Zn/H_2O} \underset{\text{benzenesulphinic acid}}{C_6H_5{-}\overset{\overset{O}{\|}}{S}{-}OH} + HCl$$

(*iii*) With a stronger reducing agent such as zinc and hydrochloric acid, or lithiumaluminium hydride, thiophenol is formed.

$$C_6H_5{-}SO_2{-}Cl + 6H \xrightarrow{LiAlH_4} \underset{\text{thiophenol}}{C_6H_5{-}SH} + HCl + 2H_2O$$

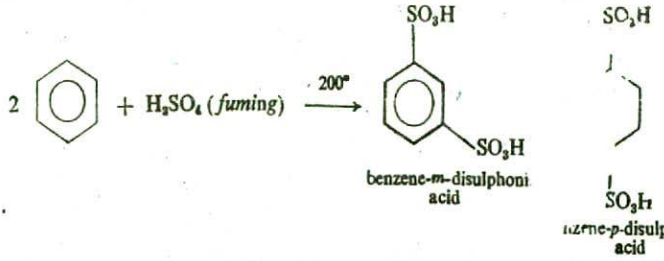
(6) *Friedel-Crafts Reaction.* Benzenesulphonyl chloride undergoes Friedel-Crafts reaction with aromatic compounds in the presence of anhydrous aluminium chloride to give diphenyl sulphone.

$$C_6H_6 + Cl{-}SO_2{-}C_6H_5 \xrightarrow{AlCl_3} \underset{\text{diphenyl sulphone}}{C_6H_5{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}C_6H_5} + HCl$$

Uses. Benzenesulphonyl chloride is used to introduce benzenesulphonyl group ($C_6H_5{-}SO_2{-}$) in aromatic molecules. It is used for the preparation of benzamide, substituted amides, benzenesulphonate esters. It is also used as Hinsberg reagent for isolation of 1°, 2°, 3° amines from mixtures.

BENZENEDISULPHONIC ACIDS, $C_6H_4(SO_3H)_2$

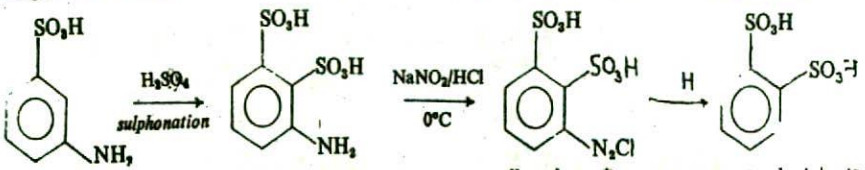
When benzene is heated with excess of fuming sulphuric acid at 200°C, it yields benzene-*m*-disulphonic acid alongwith a small amount of benzene-*p*-disulphonic acid.



benzene-*m*-disulphonic acid

benzene-*p*-disulphonic acid

The yield of the *p*-isomer is increased to about 30 per cent in the presence of mercuric sulphate as catalyst. Benzene-*o*-disulphonic acid may be prepared by the following scheme

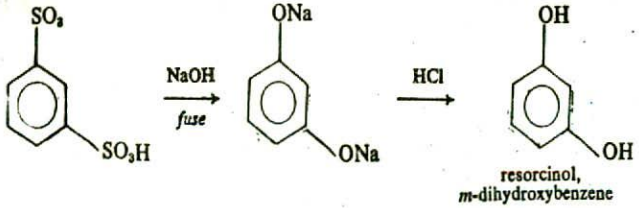


m-aminobenzenesulphonic acid

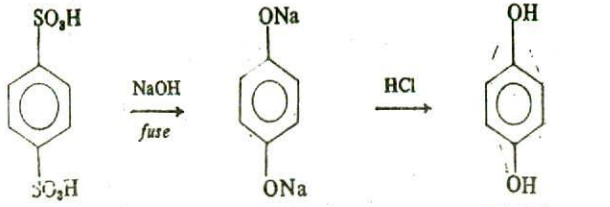
diazonium salt

benzene-*o*-disulphonic acid

When fused with potassium hydroxide benzene-*m*-disulphonic acid (also *p*-isomer) yield *resorcinol*. The *o*-isomer forms calechol.



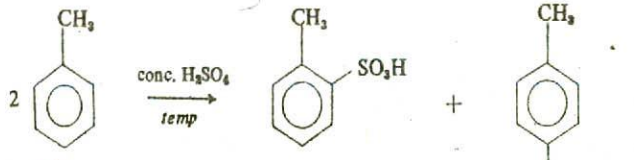
resorcinol,
m-dihydroxybenzene



catechol,
o-dihydroxybenzene

TOLUENESULPHONIC ACIDS, $CH_3—C_6H_4—SO_3H$

Toluene on sulphonation with concentrated sulphuric acid forms *o*- and *p*-toluenesulphonic acid.



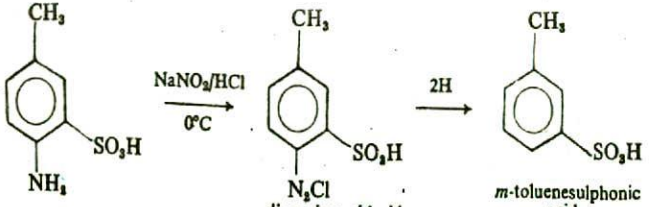
toluene

o-toluenesulphonic acid (50%)

p-toluenesulphonic acid (45%)

If the reaction is carried at 110—120°C the *p*-isomer predominates in the product, while at room temperature the product is mainly the *o*-isomer.

The *m*-toluenesulphonic acid may be obtained from *p*-toluidine-*m*-sulphonic acid by replacing $—NH_2$ group by H atom.



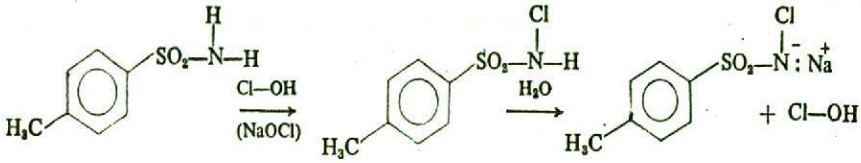
diazonium chloride

m-toluenesulphonic acid

Both *o*- and *p*-toluenesulphonic acids are white crystalline solids, the *o*- melting at 67·5° and *p*- at 106°, the *m*-isomer is a colourless oil.

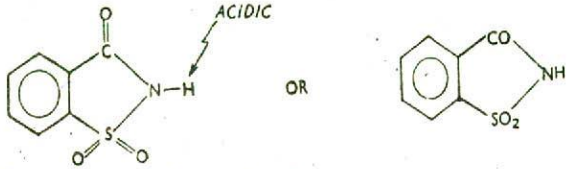
o-Toluenesulphonic acid is used in the preparation of saccharin. *p*-Toluenesulphonic acid is needed in the synthesis of *Chloramine T*.

Chloramine T. It is the sodium salt of *N*-chloro-*p*-toluenesulphonamide. It is made by the action of sodium hypochlorite (NaOCl) on *p*-toluenesulphonamide.

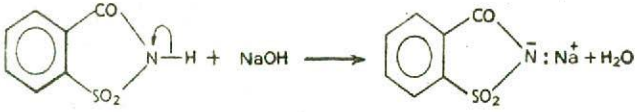


Chloramine T is a stable solid when dry, but is slowly hydrolysed in water with the formation of hypochlorous acid. It, therefore, possess the antiseptic properties of hypochlorite solutions and has the advantage of being more stable.

Saccharin, *o-Sulphobenzoic acid.* It is the cyclic imide of *o*-sulphobenzoic acid.

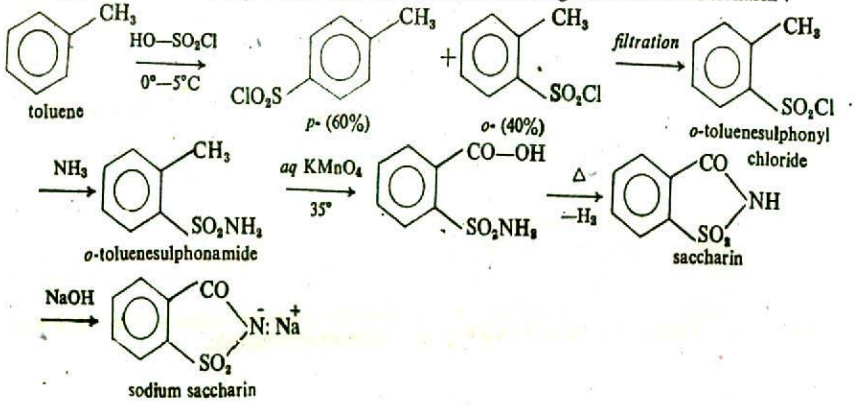


Here nitrogen is attached to carbonyl group on one side and a sulphonyl group ($>SO_2$) on the other. Both these groups being strongly electron-withdrawing, the hydrogen atom attached to the nitrogen atom is fairly strongly acidic ($K_a = 10^{-2}$). It loses a proton under the action of alkali to form a soluble salt.



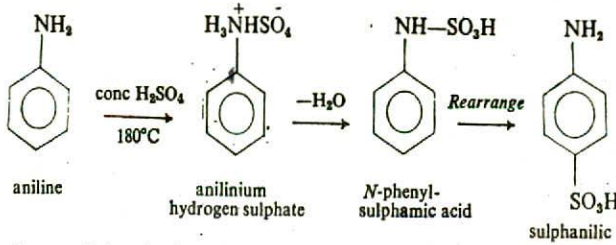
Saccharin is a colourless crystalline solid, mp 224°C. It is some 300 to 500 times as sweet as table sugar. It is almost insoluble in water. As a sweetening agent it is sold as sodium salt (*soluble saccharin*) which is very soluble. For most tastes a ½ grain (0·03 gram) tablet replaces a heaping tea spoon (10 grams) of sucrose. However, unlike carbohydrates, saccharin has no food value and is excreted unchanged in urine. It is used only by diabetic and obese persons who are not allowed sugar in their diet. Saccharin has long been used as a substitute for sugar in tooth pastes and mouth washes, as also in cheap drinks.

Saccharin is manufactured from toluene by the following steps : (*i*) Toluene is treated with excess of chlorosulphonic acid when a mixture of *o*-toluenesulphonyl chloride (*liquid*) and *p*-toluenesulphonyl chloride is obtained ; (*iii*) The *o*-isomer is separated by filtration and treated with ammonia to form *o*-toluenesulphonamide ; (*iii*) *o*-toluenesulphonamide is oxidised with aqueous $KMnO_4$ at 35° when CH_3 is oxidised to COOH; (*iv*) The acid resulting from step (*iii*) on heating gives saccharin ; (*iv*) This is then treated with alkali to get the 'soluble saccharin'.



SULPHANILIC ACID, *p-Aminobenzenesulphonic acid*

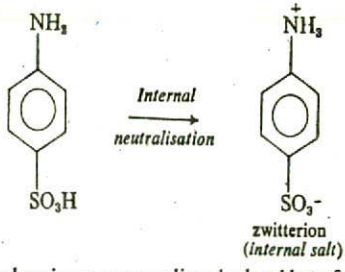
It is prepared by sulphonation of aniline with concentrated sulphuric acid at 180°, in high yield. It is believed that *N*-phenylsulphamic acid is produced as an intermediate in the sulphonation.



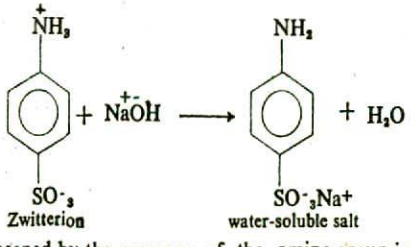
It may be noted that the intermediate sulphamic acid undergoes rearrangement involving sulphonation on the ring and desulphonation on the nitrogen.

Properties and Uses. Sulphanilic acid is a white crystalline solid, *mp* 280° with decomposition. It is almost insoluble in cold water and many organic solvents.

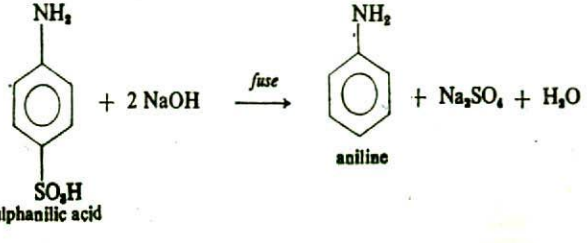
These unusual properties arise from the salt-like character of the molecule. The sulphanilic acid molecule has an acid group ($-SO_3H$) and a basic group ($-NH_2$) existing side by side. These groups interact to form an internal salt or a dipolar ion, called the *Zwitterion.*

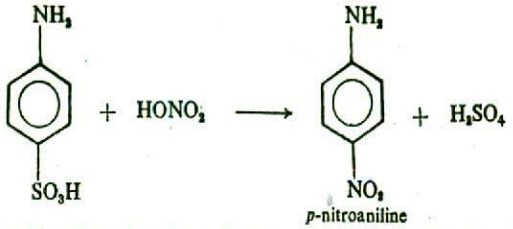


Sulphanilic acid dissolves in aqueous sodium hydroxide to form water-soluble salt because a base can extract a proton from the $-H_3N^+$ group of the Zwitterion.



The SO_3H is loosened by the presence of the amino group in para position and can be replaced by $-H$ or $-NO_2$ group.





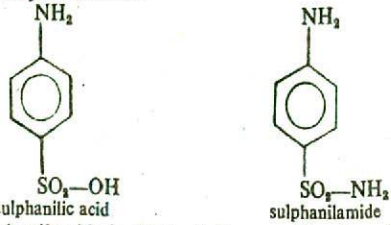
p-nitroaniline

Both sulphanilic acid and *p*-nitroaniline can be diazotised and coupled with phenols to form dyes.

Sulphanilic acid is a valuable dye intermediate. Its substituted amides form numerous sulphanilamide drugs.

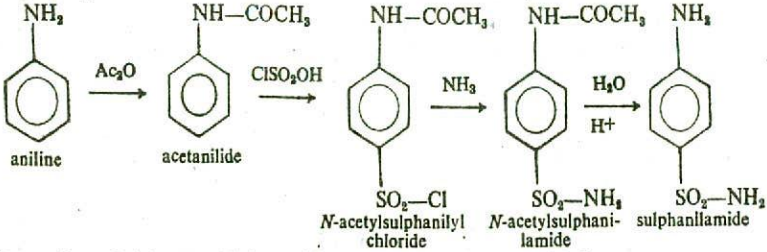
Sulphanilamide, *p-Aminobenzenesulphonamide*

It is the amide of sulphanilic acid.



sulphanilic acid sulphanilamide

Preparation. Sulphanilamide is obtained from aniline by : (1) acetylation with acetic anhydride, AC_2O, (to protect NH_2 from chlorosulphonic acid) when acetanilide is formed ; (2) reaction with excess chlorosulphonic acid to form *N*-acetylsulphanilyl chloride ; (3) reaction with ammonia to get *N*-acetylsulphanilamide ; (4) regeneration of NH_2 group by hydrolysis of acetyl group by aqueous acid.

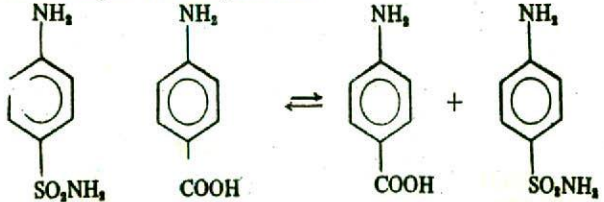


aniline acetanilide *N*-acetylsulphanilyl chloride *N*-acetylsulphanilamide sulphanilamide

Properties. Sulphanilamide is a white crystalline solid, mp 166·5°C.

Sulphanilamide and its derivatives have a remarkable action in curing diseases caused by bacterial infections, such as pneumonia, meningitus, dysentery, typhoid etc. These compounds have been used as valuable medicinal drugs for long.

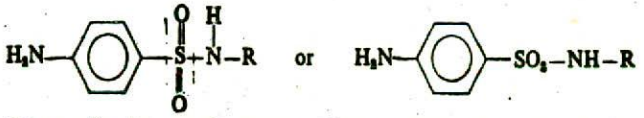
Bacteriostatic Action. *p*-Aminobenzoic acid is produced in our body by the hydrolysis of proteins. It is an intermediate necessary for the growth of certain bacterial enzymes which cause disease. The enzyme forms a complex with *p*-aminobenzoic acid in one of the metabolic reactions for its growth. When sulphanilamide which is stucturally similar is added in excess, the enzyme (•) forms complex with it in preference.



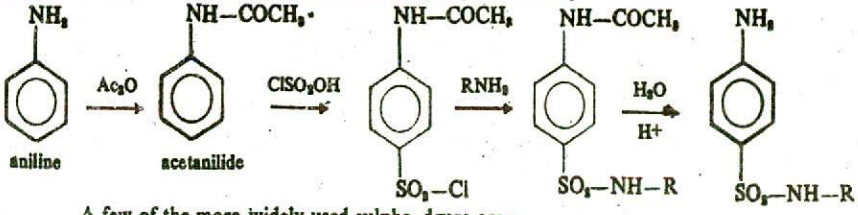
sulphanilamide (excess)

Thus the complex formation of the enzyme with *p*-aminobenzoic acid becomes static and the bacterial growth stops. Because of this bacteriostatic action of sulphanilamide and its derivatives (*Sulpha drugs*), these compounds act as valuable antibacterial agents and stop infection.

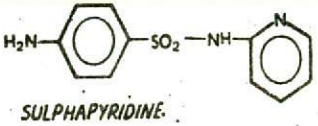
Sulpha Drugs. The sulpha' drugs which have been of great medicinal value can be represented by the general structure.



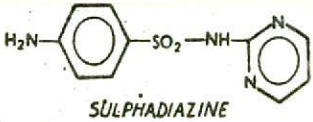
Where R is usually a heterocyclic group. They are made from aniline by the same procedure as used for sulphanilamide, taking RNH_2 in place of NH_3.



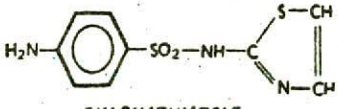
A few of the more widely used sulpha drugs are :



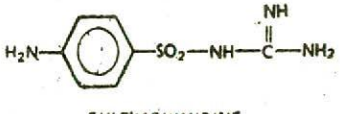
SULPHAPYRIDINE



SULPHADIAZINE



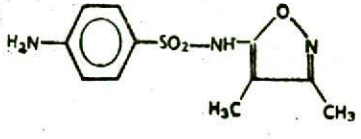
SULPHATHIAZOLE



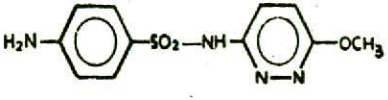
SULPHAGUINIDINE

Sulphapyridine has a specific curative effect for pneumonia. Sulphaguanidine is useful in the treatment of intestinal infections. Sulphadiazine and sulphathiazole are effective general antimicrobial agents.

Although the sulpha drugs have been replaced to some extent by more powerful and less toxic antibiotics (penicillin, aureomycin), certain drugs of this class are still in use. The following two sulpha drugs have been introduced recently and are very effective even in very small dozes.



5-SULPHANILAMIDE-3,4-DIMETHYLISOXAZOLE

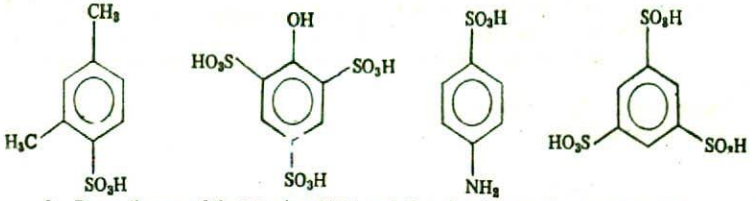


3-SULPHANILAMIDE-6-METHOXYPYRIDAZINE

The medicinal effect of the sulpha drugs has been attributed to the generation of free sulphanilamide by cleavage of the molecule at the N—C bond.

QUESTIONS

1. What are arenesulphonic acids? Write the structural formula of benzenesulphonic acid and mark out the functional group.
2. How are aromatic sulphonic acids assigned systematic names. Assign such names to the following.



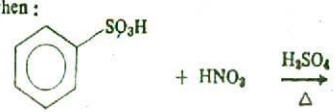
3. Draw diagram of the 'atomic orbital model' and 'electron cloud model' of benzenesulphonic acid. Write the canonical forms of the sulphonate anion as also the 'resonance hybrid' form.

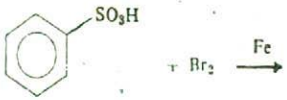
4. Give the general methods of introducing sulphonic acid group in aromatic rings. In what way the use of chlorosulphonic acid is superior to direct sulphonation by concentrated sulphuric acid ? Discuss the isolation of pure benzenesulphonic acid from the sulphonating mixture.

5. Describe the general reactions of aromatic sulphonic acids with special reference to (*a*) Desulphonation ; (*b*) Esterification ; (*c*) formation of phenols ; and (*d*) formation of nitriles. Give an outline of the mechanism of desulphonation taking example of benzenesulphonic acid.

6. How are phenols prepared from arylsulphonic acids ? Give the mechanism of the reactions involved.

7. What happens when :





Give the mechanism of these reactions.

8. Describe the preparation of pure benzenesulphonic acid and list its reactions in the form of equations. How can you convert it into benzene-*m*-disulphonic acid ?

9. Give the preparation, properties and uses of benzenesulphonyl chloride.

10. How are toluenesulphonic acids obtained ? Write notes on : (*a*) Saccharin ; and (*b*) Chloramin *T*.

11. Outline steps involved in the conversion of *p*-toluenesulphonamide ; (*b*) ethyl *p*-toluenesulphonate ; (*c*) *p*-cresol ; (*d*) *o*-bromotoluene.

12. Explain why ? : (*a*) Benzenesulphonic acid is stronger than benzoic acid ; (*b*) benzenesulphonyl chloride reacts much more slowly than benzoyl chloride ; (*c*) arylsulphonamides are stronger acids than arylcarbonylamides.

13. What are Sulpha drugs ? How are they prepared from aniline ?

14. Give two methods for the preparation of benzenesulphonic acid. *(Tripura BSc, 1993)*

15. Discuss the mechanism of sulphonation of benzene. *(Kalyani BSc Hons, 1993)*

16. How will you synthesise chloramine-T from toluene ? *(Nehu BSc Hons, 1994)*

Answer. Use the following steps : (*i*) $ClSO_3H$, (*ii*) NH_3, and (*iii*) NaOCl/NaOH.

17. Describe the laboratory preparation of benzenesulphonic acid. How will you obtain from it : (*a*) Phenol, (*b*) Aniline, and (*c*) Benzene sulphonamide. *(Manipur BSc, 1994)*

18. Describe the preparation and properties of benzenesulphonic acid. *(Bundelkhand BSc, 1994)*

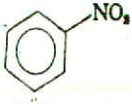
19. Give the preparation and uses of : (*a*) Saccharin, and (*b*) Chloramine-T.

(Karnataka BSc, 1993; Kanpur BSc, 1993; Vikram BSc, 1994)

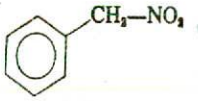
Chapter **39**

Aromatic Nitro Compounds

The aromatic nitro compounds are the substitution products of aromatic hydrocarbons in which one or more H atoms have been replaced by the nitro group ($-NO_2$). As in the case of the halogen compounds, these could be divided into two classes : (*a*) those in which the nitro group is attached to the aromatic nucleus ; and (*b*) those in which it is in the side-chain.



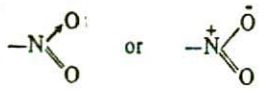
nitrobenzene
(*nuclear nitro compound*)



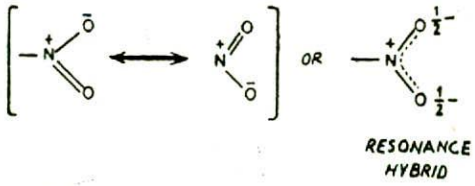
phenylnitromethane
(*side-chain nitro compound*)

The nuclear nitro compounds are by far more important because they can be conveniently prepared from the aromatic hydrocarbons by direct nitration. They have been used for over a century as intremediates for the production of other valuable substances, notably dyes and pharmaceuticals. Their use as explosives is too well-known.

The function $-NO_2$ may be represented as



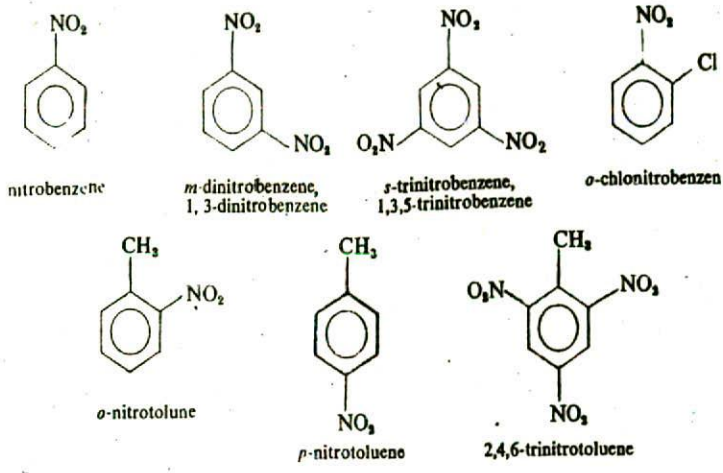
Bond length and dipole measurements show that the two nitrogen-oxygen distances are equ (1·2 Å). Therefore, the structure of $-NO_2$ groups is best regarded as a resonance hybrid of th following two canonical forms (I and II).



I II

NOMENCLATURE

The aromatic nitro compounds are named as nitro-substitution products of the parent hydrocarbon. The word nitro is inserted in front of the name of the hydrocarbon, and where necessary the position is indicated by prefixing *o*-, *m*- or *p*-, or a numeral.



STRUCTURE

The structure of aromatic nitro compounds will be illustrated by discussing the structure of nitrobenzene It is basically the same as that of benzene excepting that the unused *p* orbitals

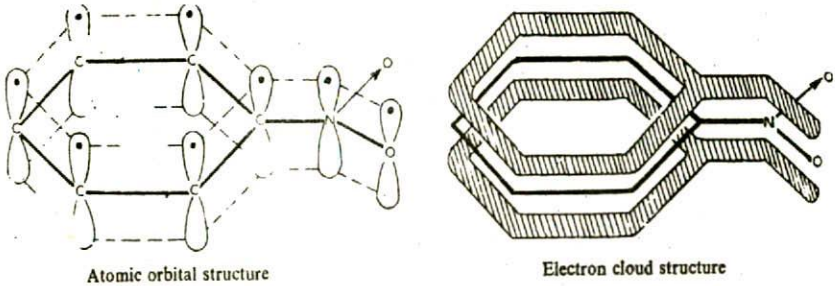
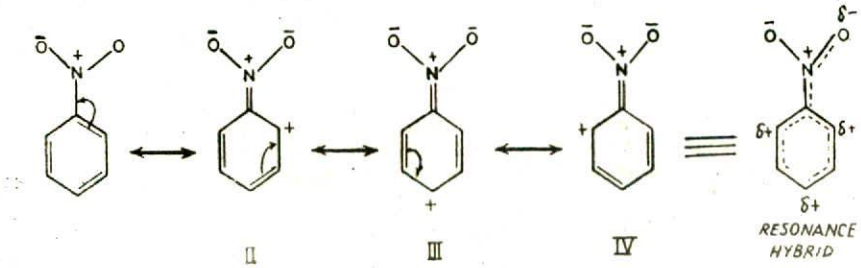


Fig. 39·1. The structure of Nitrobenzene.

of the ring carbons can interact with the unused *p* orbitals of N and O atoms of the nitr group as indicated above. This is made possible because these *p* orbitals are aligned and hence they can interact to give a larger delocalised π orbital encompassing the six ring carbons as also the N and O of the nitro group.

The electronic structure of nitrobenzene can be represented as a resonance hybrid of the following four canonical forms.



METHODS OF PREPARATION

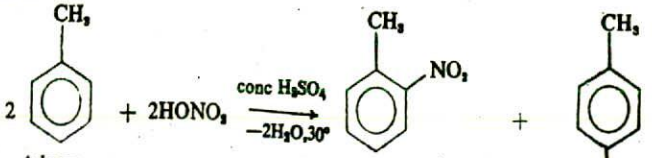
Aromatic nitro compounds are generally prepared by the following methods.

(1) **Direct Nitration.** The most common method for introducing nitro group in an aromatic ring is by the action of a mixture of nitric acid and sulphuric acid on the appropriate hydrocarbon. The extent of nitration is controlled by varying the strength of the nitrating mixture and temperature of the reaction. For example,



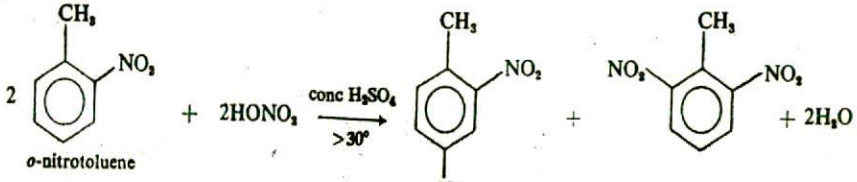
nitrobenzene — *m*-dinitrobenzene

Nitration of toluene takes place at a lower temperature to yield ortho and para nitro derivatives.



toluene — *o*-nitrotoluene — *p*-nitrotoluene

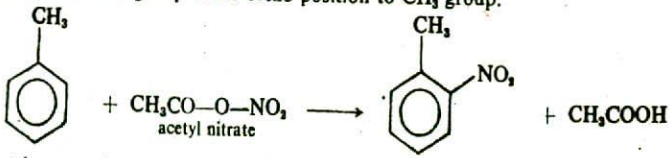
By raising the the temperature of the reaction mixture, dinitrotolouenes are produced. Thus,



o-nitrotoluene — 2,4-dinitrotoluene — 2,6-dinitrotoluene

Since all aromatic nitro compounds are insoluble in water, they are isolated from the reaction mixture by pouring it into water. The insoluble product is then removed from water by filtration. The ortho and para isomers can usually be separated from each other by crystallisation, steam distillation or chromatography.

(2) **Action of Acetyl Nitrate.** In certain cases, acetyl nitrate is used with advantage, since it introduces only one nitro group in the ortho position to CH_3 group.

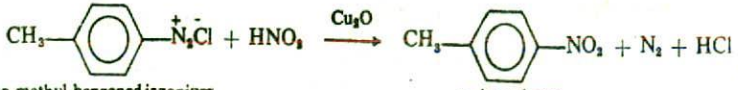


toluene — *o*-nitrotoluene

The use of acetyl nitrate is somewhat dangerous, since it tends to explode when heated. It is prepared by reaction between acetic anhydride and nitrogen pentoxide.

$$\underset{\text{acetic anhydride}}{CH_3{-}CO{-}O{-}CO{-}CH_3} + N_2O_5 \longrightarrow 2\,\underset{\text{acetyl nitrate}}{CH_3{-}CO{-}O{-}NO_2} + O_2$$

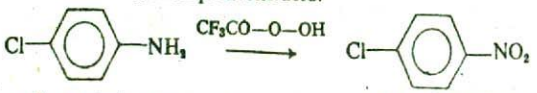
(3) **From Diazonium Salts.** Aromatic nitro compounds are also produced by the action of nitrous acid on diazonium salts in the presence of cuprous oxide.



p-methyl-benzenediazonium chloride — *p*-nitrotoluene

This method is used when direct nitration cannot give the desired nitro compound.

(4) **Oxidation of Amino Compounds.** When an aromatic amino compound is available, the $-NH_2$ can be oxidised with trifluoroperacetic acid.



p-chloroaminobenzene — *p*-chloronitrobenzene

This method is of limited application since amines themselves are obtained from nitro compounds.

PHYSICAL PROPERTIES

(1) A few aromatic nitro compounds such as nitrobenzene and nitrotoluenes are pale yellow liquids having pleasant sweetish odours. Others are almost colourless, crystalline solids having no odour.

(2) In general they are steam-volatile and toxic compounds.

(3) They are heavier than water and almost insoluble in it, but dissolve readily in organic solvents such as benzene, ethanol and ether.

Aromatic nitro compounds dissolve, without decomposition in cold concentrated sulphuric acid, towards which they behave as bases giving ionic solutions.

$$Ar{-}NO_2 + \underset{\text{(cold)}}{H_2SO_4} \rightleftharpoons Ar{-}\overset{+}{N}O_2H + \overset{-}{H}SO_4$$

(4) Introduction of a nitro group into the aromatic ring raises the melting and boiling points considerably. Thus nitrobenzene boils at 80°C and nitrobenzene at 211°C. This is explained by the electrostatic attraction between the highly polar nature of the nitro group. It, therefore, necessitates a larger amount of energy (as heat) in order to separate them. For the same reason, *mono-*, *di-* and *tri-* nitro derivatives have progressively higher melting and boiling points.

Table. Melting and Boiling points of Nitro Compounds

Name	*Formula*		*mp* °C	*bp* °C
Nitrobenzene	$C_6H_5(NO_2)$		5·7	211
o-Dinitrobenzene	$C_6H_4(NO_2)_2$	1, 2–	118	318
m-Dinitrobenzene	$C_6H_4(NO_2)_2$	1, 3–	90	302
p-Dinitrobenzene	$C_6H_4(NO_2)_2$	1, 4–	173	298
s-Trinitrobenzene	$C_6H_3(NO_2)_3$	1, 3, 5–	122	—
o-Nitrotoluene	$CH_3{-}C_6H_4(NO_2)$	1, 2–	3	222
m-Nitrotoluene	$CH_3{-}C_6H_4(NO_2)$	1, 3–	16	233
p-Nitrotoluene	$CH_3{-}C_6H_4(NO_2)$	1, 4–	52	238
2, 4-Dinitrotoluene	$CH_3{-}C_6H_3(NO_2)_2$	1, 2, 4–	70	—
2, 4, 6-Trinitrotoluene	$CH_3{-}C_6H_2(NO_2)_3$	1, 2, 4, 6–	80	—

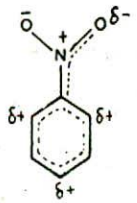
(5) They are powerful explosives, especially the polynitro compounds. Thus when heated strongly, they detonate with explosive violence and, therefore, cannot be distilled under atmospheric pressure.

CHEMICAL PROPERTIES

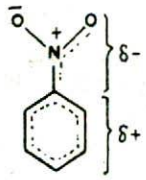
The reactions of the aromatic nitro compounds are : (*i*) those of aromatic ring ; and (*ii*) those of the nitro group or groups.

A. REACTIONS OF BENZENE RING

We have already seen that aromatic nitro compounds are resonance hybrids. Thus nitrobenzene can be represented as

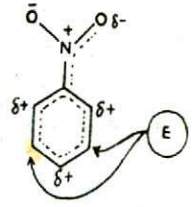


resonance hybrid

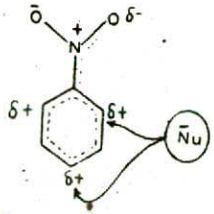


benzene ring develops overall positive charge due to withdrawl of electrons by NO_2 group

The electron withdrawl by NO_2 as a result of resonance and inductive effect from the benzene ring deactivates it to the attack of electrophiles. Further, a partial positive charge develops on the ortho and para positions. Thus an electrophile seeking to attach at the most negative positions, will avoid the *ortho* and *para* positions and will attach at the *meta* position (which bears no positive charge).



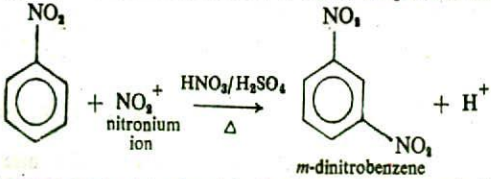
An electrophile (E+) attacks at the most negative meta-positions.



Nucleophile ($\bar{N}u$) attacks at the positively charged ortho and para positions.

It may also be noted that the presence of the electron withdrawing $-NO_2$ group activates the ring for the attack of nucleophiles at the ortho and para positions which bear positive charge. This marks the nucleophilic substitution possible in ortho and para positions in the benzene ring of nitrobenzene.

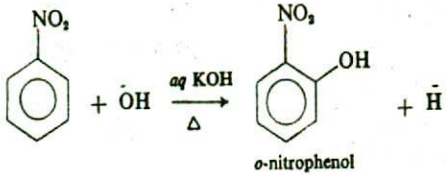
(1) **Electrophilic substitution.** As already observed, the $-NO_2$ group in nitrobenzene exerts deactivating and *meta*-directive effects on electrophilic substitution in the benzene ring. Thus the second $-NO_2$ group can be introduced in it at higher temperature and in *meta* position



m-dinitrobenzene

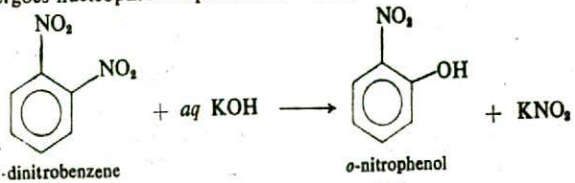
The third nitro group can be introduced in the ring under extremely forcing conditions.

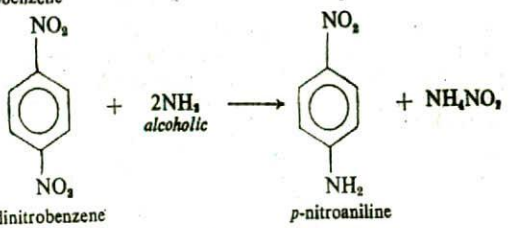
(2) **Nucleophilic substitution.** The ortho and para positions of benzene ring are activated and bear a positive charge, due to the presence of $-NO_2$ group in the ring. Thus when nitrobenzene is heated with aqueous potassium hydroxide in the presence of air, *o*-nitrophenol is produced.



$$2\bar{H} + O_2 \longrightarrow 2\,\bar{O}H$$

When a second $-NO_2$ group is present in the benzene ring of nitrobenzene in the *ortho-* or *para-* position, it undergoes nucleophilic displacement. Thus,





B. REACTIONS OF THE NITRO GROUPS

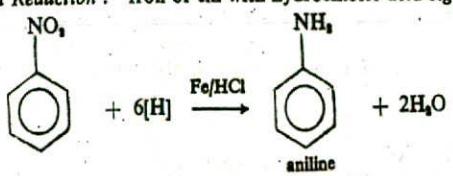
The nitro groups, being made of nitrogen and oxygen only, show no other reactions except those of reduction.

Reduction of Aromatic Nitro Compounds

(1) **Conversion to 1° Amines.** Aromatic nitro groups ($-NO_2$) on reduction with powerful reducing agents are converted to primary amino groups ($-NH_2$). Thus aromatic primary amines are produced.

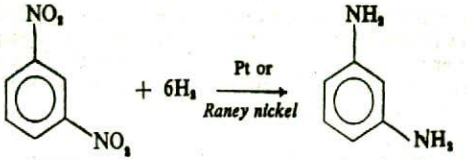
$$Ar{-}NO_2 \xrightarrow[\text{reducing agent}]{\text{Powerful}} Ar{-}NH_2 \quad (1^\circ \text{ amine})$$

(*a*) *Metal-Acid Reduction* : Iron or tin with hydrochloric acid *e.g.*,



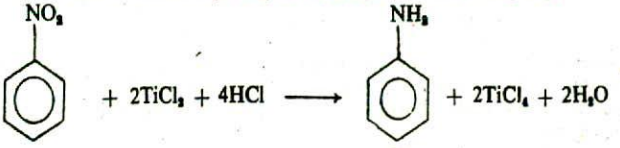
The reduction of nitrobenzene with iron and hydrochloric acid is used for the industrial production of aniline.

(*b*) *Catalytic Hydrogenation.* Hydrogen in the presence of a metal catalyst platinum or Raney nickel.



m-dinitrobenzene *m*-phenylenediamine

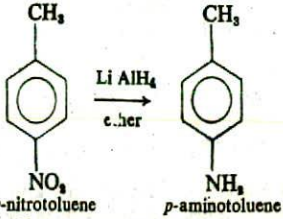
(*c*) *With Stannous chloride* ($SnCl_2$) *or Titanous chloride* ($TiCl_3$) *e.g.*,



aniline

This is used for the quantitative estimation of $-NO_2$ group.

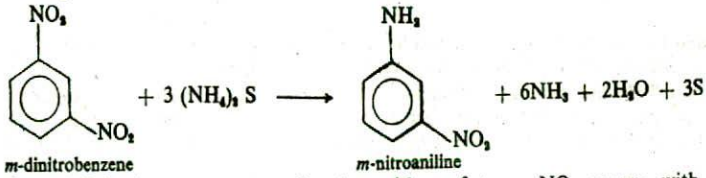
(*d*) *With* $LiAlH_4$ *e.g.*,



p-nitrotoluene *p*-aminotoluene

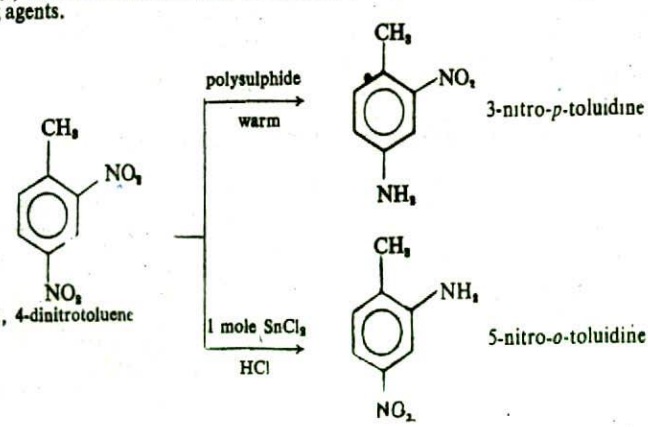
(2) **Selective Reduction.** If two or more nitro groups are present in the aromatic ring, it is possible to reduce one of them without the others. Such selective reductions may be carried by proper choice of a weak reducing agent. For example,

(*a*) *m*-dinitrobenzene is converted into *m*-nitroaniline when reduced with sodium or ammonium sulphides.

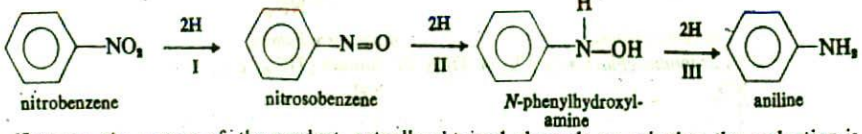


m-dinitrobenzene *m*-nitroaniline

(*b*) 2, 4-dinitrobenzene may be reduced at either of two $-NO_2$ groups with suitable reducing agents.



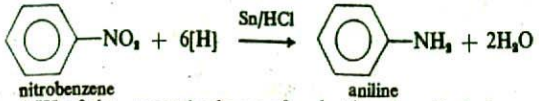
(3) **Reduction of Nitrobenzene under different conditions.** The reduction of aromatic nitro compounds is a complex process. In fact, it involves the formation of many intermediate and side-products before the final stage — the production of an aromatic 1° amine — is reached. For example, the electrochemical studies of the reduction of nitrobenzene indicate that the reduction proceeds by the following three steps.



nitrobenzene — nitrosobenzene — *N*-phenylhydroxylamine — aniline

However, the nature of the product actually obtained depends on whether the reduction is carried in acid, neutral or alkaline medium as also on the reagent employed. It is noteworthy that all the products obtained under different conditions can be reduced to aniline using more vigorous reducing agents.

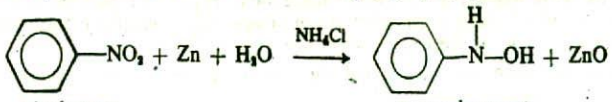
(*a*) **Reduction in Acid Medium.** The reduction of nitrobenzene with a metal and mineral acid (Sn/HCl; Fe/HCl) gives aniline.



nitrobenzene — aniline

Here the step II and III of the general scheme of reduction described above, are skipped over and the end product, aniline, is obtained straightway. This is so because the intermediate compounds (nitrosobenzene and *N*-phenylhydroxylamine) are transitory and are reduced as soon as they are formed.

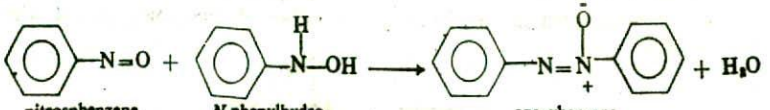
(*b*) **Reduction in Neutral Medium.** When reduced with zinc dust in presence of aqueous ammonium chloride, nitrobenzene is converted into *N*-phenylhydroxylamine.



nitrobenzene — *N*-phenylhydroxylamine

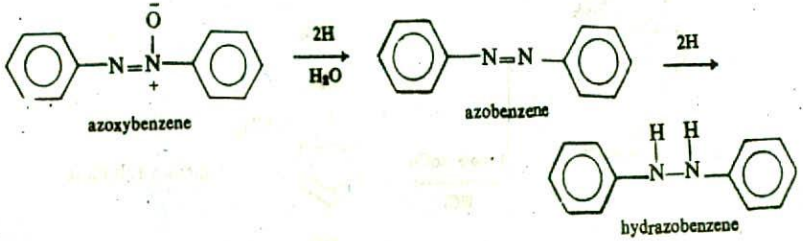
Here, step I is skipped over since nitrosobenzene is transitory and is not isolated. The product, *N*-phenylhydroxylamine, obtained from step II is the stable end product.

(*c*) **Reduction in Alkaline Medium.** The various theoretical steps listed earlier in the general scheme of reduction of nitrobenzene, are the same here also. But the nisrosobenzene from step I reacts with *N*-phenylhydroxylamine from step II to produce azoxybenzene.



nitrosnbenzene (from step I) — *N*-phenylhydroxylamine (from step II) — azoxybenzene

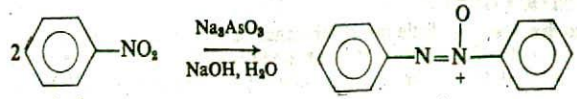
The azoxybenzene, in turn, may be reduced to form azobenzene and hydrazobenzene.



azoxybenzene — azobenzene — hydrazobenzene

The formation of most of the above reduction products can be achieved experimentally by the appopriate choice of the reducing agents and conditions.

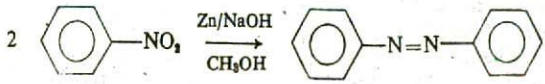
(*i*) *Azoxybenzene* is produced by direct reduction in alkaline medium with sodium arsenite.



nitrobenzene azoxybenzene

Azoxybenzene on further reduction with iron and heat, yields azobenzene.

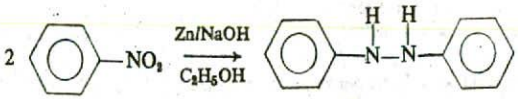
(*ii*) *Azobenzene* is formed by reduction of nitrobenzene with zinc and methanolic sodium hydroxide.



nitrobenzene azobenzene

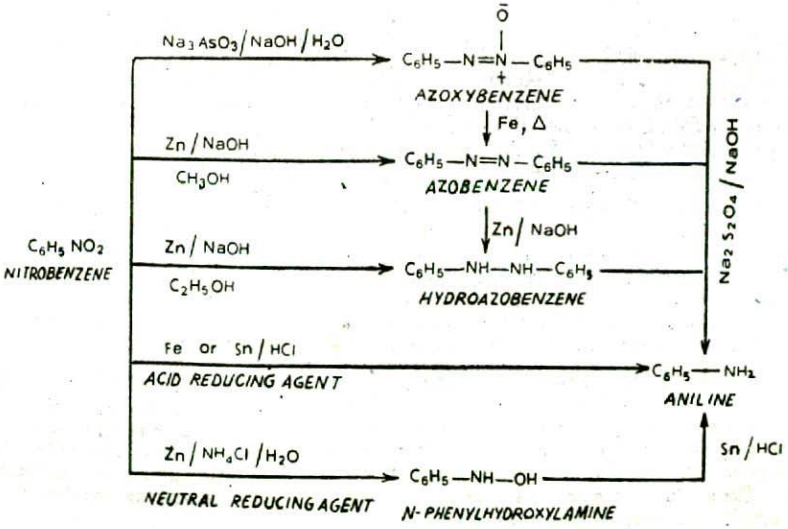
When reduced with Zn and NaOH, azobenzene is converted into hydrazobenzene.

(*iii*) With zinc and sodium hydroxide, nitrobenzene is reduced straightway to *hydrazobenzene.*



nitrobenzene hydrazobenzene

All the products obtained by reduction of nitrobenzene in alkaline medium, upon further reduction with sodium hydrosulphate, $Na_2S_2O_4$ and sodium hydroxide, lead to the formation of aniline.



(*d*) **Electrolytic Reduction.** When nitrobenzene is reduced by electrolysis in dil. sulphuric acid solution, the reaction is interrupted after stage II. The *N*-phenylhydroxylamine as soon as it is produced, undergoes an intramolecular rearrangement to yield *p*-aminophenol.



N-phenyl hydroxylamine (from step II) — *p*-aminophenol

TESTS FOR NITRO GROUP

(1) **Azo-dye Test.** A little given substance is suspended in water and reduced with tin and hydrochloric acid. The solution thus obtained is cooled and a little sodium nitrite solution added. A red precipitate of the azo-dye shows the presence of $-NO_2$ group in the original substance.

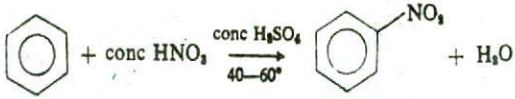
(2) **Fehling Solution Test.** The given substance is boiled with zinc dust and ethanol, and filtered. The filtrate is then heated with Fehling solution. A red precipitate appears which indicates the presence of $-NO_2$ group. In this reaction the nitro compound is first reduced to arylhydroxylamine which reduces the Fehling solution to red copper (I) oxide.

(3) **IR Spectra.** Aromatic nitro groups exhibit strong infrared absorption in the 1550—1510 ; 1365—1335 and 860 cm^{-1} regions. These are often observed by C–H, C—C and C=C bond absorptions. Since most organic compounds contain either, or both, of these types of bond, the nitro-group infrared bands are not commonly used toid entify these groups, but only as confirmatory proof.

NITROBENZENE, $C_6H_5—NO_2$

It is the most important aromatic nitro compound and was first prepared by Mitscherlich in 1834. Because of its odour, nitrobenzene was called *'Oil of Mirabane'* or *'Artificial Oil of Bitter almonds'*.

Laboratory Preparation. Nitrobenzene is prepared in the laboratory by the action of a mixture of conc. HNO_3 and conc. H_2SO_4 on benzene at 40—60° C.



nitrobenzene

To 60 ml of concentrated nitric acid in a round-bottom flask is added 120 ml concentrated sulphuric acid, shaking and cooling the flask under a stream of running water. 70 ml of benzene is then added in small portions from a tap-funnel. The flask is shaken after each addition and the temperature of the contents is not allowed to rise above 50°C at this stage, by immersing the flask in cold water if necessary. This is important as at a higher temperature *m*-dinitrobenzene is formed. When all the benzene has been added, the mixture is heated in a water-bath at 60° C for 30 minutes to complete the reaction.

The contents of the flask are then allowed to cool and transferred to a separating funnel. The lower layer is drawn off and discarded. The nitrobenzene left is shaken successively with small portions of water, sodium carbonate solution, and then water, to remove any acid. The lower layer of nitrobenzene is drawn off after washing each time and retained. This is then dried by standing over a few lumps of fused anhydrous calcium chloride. When the liquid clears, it is decanted and nitrobenzene distilled using an air-condenser. The fraction passing between 207° and 211° C is collected. It consists of almost pure nitrobenzene.

Commercial Preparation. On a large scale also, nitrobenzene is prepared by the action of a mixture of nitric acid and sulphuric acid on benzene. The working details remain the same as in the laboratory process except that here the nitration is carried in a pan provided with a mechanical stirrer and cold-water pipe. At the end, the spent acids are withdrawn and the nitrobenzene layer given the necessary washing with water, sodium carbonate solution, and again water. The product is exposed to a current of steam until free from benzene, and then dried over anhydrous calcium chloride.

Properties. (*Physical.*) Nitrobenzene is a pale yellow oily liquid, bp 210°C ; Sp. Gr., 1·087, having odour of bitter almonds. Its colour darkens somewhat with age. It is insoluble

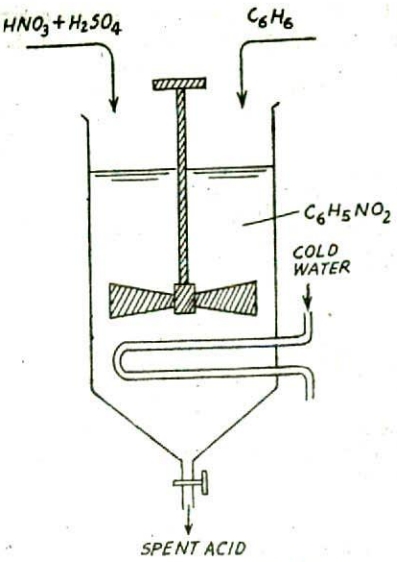


Fig. 39·2. Manufacture of Nitrobenzene.

in water but dissolves readily in ethanol and ether. It is volatile in steam. It is highly toxic and dangerous since its vapours are absorbed readily through skin, particularly from solutions.

(*Chemical*). The chemical reactions of nitrobenzene are those of the nitro group and a phenyl group. The hybrid structure of nitrobenzene is shown in Fig. 39·3.

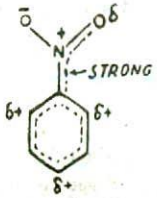


Fig. 39·3. Due to delocalisation of electrons (shown by dotted rule), the C—N bond becomes strong and benzene ring stable.

(1) The NO_2 group is tightly attached to the phenyl group and cannot be replaced by other atoms or groups. Thus aqueous NaOH or ethanolic NH_3 has no action on nitrobenzene.

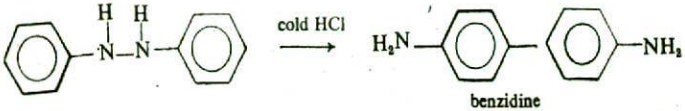
(2) When reduced with tin and hydrochloric acid, it is converted to aniline.

$$C_6H_5{-}NO_2 + 6\,[H] \xrightarrow{Sn/HCl} \underset{\text{aniline in ethanol}}{C_6H_5{-}NH_2} + 2H_2O$$

On reduction with zinc and alkali, it yields hydrazobenzene.

$$2\,C_6H_5{-}NO_2 + 6[H] \xrightarrow[C_2H_5OH]{Zn/NaOH} \underset{\text{hydrazobenzene}}{C_6H_5{-}NH{-}NH{-}C_6H_5}$$

Hydrazobenzene is technically important because it undergoes a molecular rearrangement to benzidine when treated with cold conc HCl.



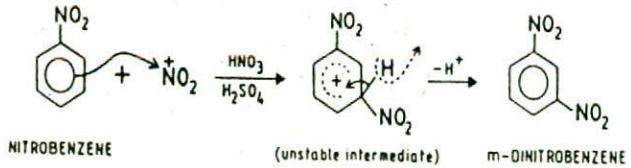
benzidine

With a neutral reducing agent such as zinc and aqueous ammonium chloride, it gives *N*-phenylhydroxylamine

$$C_6H_5{-}NO_2 + 4[H] \xrightarrow[H_2O]{Zn/NH_4Cl} \underset{\text{amine}}{\underset{N\text{-phenylhydroxyl-}}{C_6H_5{-}NH{-}OH}}$$

The reduction of nitrobenzene has already been discussed in greater detail before.

(3) As suggested by the hybrid structure stated above, nitrobenzene undergoes electrophilic substitution in meta position which carries no positive charge. Thus it can be nitrated, sulphonated and chlorinated to form meta substitution product.



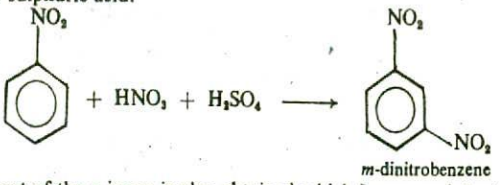
Uses. Nitrobenzene is used : (1) mainly for the manufacture of aniline and aniline dyes ; (2) as high-boiling industrial solvent ; (3) for the preparation of benzidine ; and (4) as an oxidising agent in organic synthesis.

At one time, nitrobenzene was used in large quantities as a cheap flavouring agent for scenting soaps and as a solvent for shoe polishes. Because of its high toxicity, these practices are now prohibited in most countries.

m-DINITROBENZENE

Of the three isomeric dinitrobenzenes (*o*-, *m*-, *p*-), the meta derivative is by far the most important.

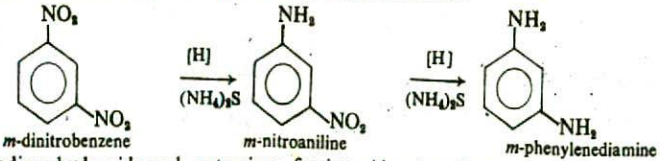
Preparation. It is prepraed by vigorous nitration of nitrobenzéne with a mixture of fuming nitric acid and sulphuric acid.



m-dinitrobenzene

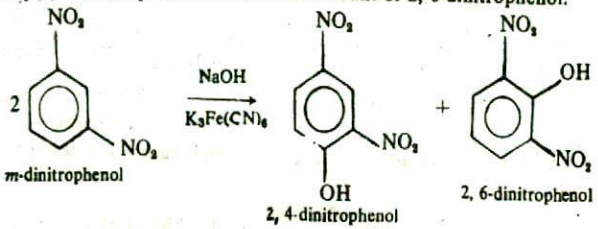
About 7 per cent of the *o*-ismer is also obtained which is removed during crystallisation.

Properties. *m*-Dinitrobenzene forms pale yellow crystals, mp 90 C. It is insoluble in water but is volatile in steam. It is very toxic. When reduced with ethanolic ammonium sulphide, it is first converted to *m*-nitroaniline and then to *m*-phenylenediamine.



m-dinitrobenzene *m*-nitroaniline *m*-phenylenediamine

With sodium hydroxide and potassium ferricyanide, it undergoes nucleophilic substitution yielding mainly 2, 4-dinitrophenol and a small amount of 2, 6-dinitrophenol.

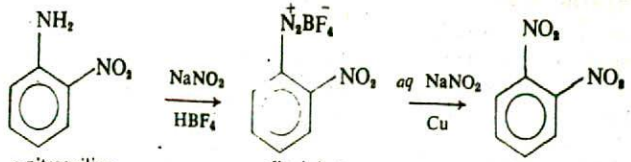


m-dinitrophenol 2, 4-dinitrophenol 2, 6-dinitrophenol

m-Dinitrobenzene is used in the production of the explosive *Roburite* and *Securite*, and for synthesising *m*-phenylenediamine.

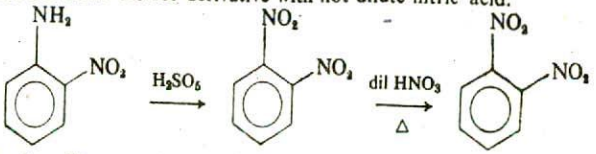
o-DINITROBENZENE

Preparation. (1) It may be obtained from *o*-nitroaniline by replacing the $-NH_2$ group by $-NO_2$, by diazotisation and treatment with sodium nitrite in the presence of copper powder.



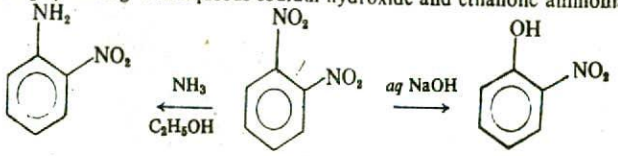
o-nitroaniline — diazonium fluoroborate — *o*-dinitrobenzene

(2) It can also be prepared by oxidation of *o*-nitroaniline with Caro's acid (H_2SO_5), and then to oxidise the mono-nitroso derivative with hot dilute nitric acid.



o-nitroaniline — *o*-nitronitrosobenzene — *o*-dinitrobenezene

Properties. *o*-Dinitrobenzene is a colourless solid, mp 118° C. It resembles the *m*-isomer in reduction. It differs from the latter in that one of the $-NO_2$ groups can be replaced by $-OH$ or $-NH_2$ by boiling with aqueous sodium hydroxide and ethanolic ammonia respectively

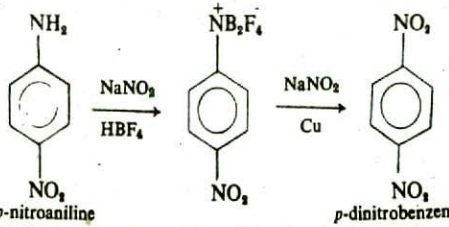


o-nitroaniline — *o*-dinitrobenzene — *o*-nitrophenol

p-DINITROBENZENE

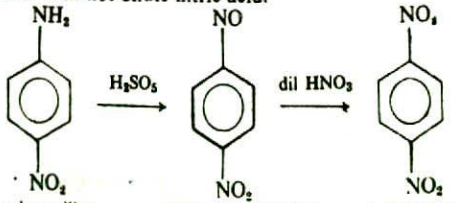
Preparation. Like the other isomer it may be prepared :

(1) By diazotisation of *p*-nitroaniline and treatment with sodium nitrite in the presence of copper powder.



p-nitroaniline — *p*-dinitrobenzene

(2) By oxidation of *p*-nitroaniline with Caro's acid and subsequent treatment of the *p*-nitronitrosobenzene with hot dilute nitric acid.



p-nitroaniline — *p*-nitronitrosobenzene — *p*-dinitrobenzene

Properties. *p*-Dinitrobenzene is a colourless solid, mp 174°C. It resembles closely with the *o*-isomer in chemical behaviour. It can be reduced with Na_2S or $(NH_4)_2S$ in two stages, giving *p*-phenylenediami . One of the two $—NO_2$ groups can be replaced by OH or NH_2 by treatment of *p*-dinitrobenzene with aqueous NaOH or ethanolic ammonia.

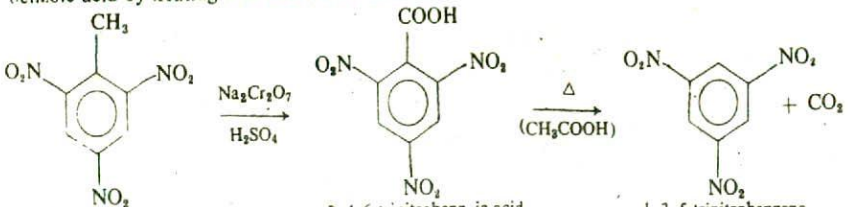
1, 3, 5-TRINITROBENZENE

It is commonly known as TNB.

Preparation. 1, 3, 5-Trinitrobenzene may be obtained :

(1) By heating *m*-dinitrobenzene with a mixture of fuming nitric acid and fuming sulphuric acid for five days.

(2) By oxidation of TNT and then knocking out the CO_2 from the 2, 4, 6-trinitrobenzoic acid by heating it in acetic acid solution.



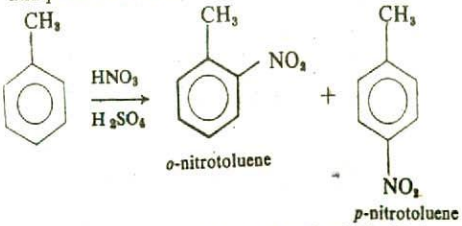
2, 4, 6-trinitrotoluene (TNT) — 2, 4, 6-trinitrobenzoic acid — 1, 3, 5-trinitrobenzene

Properties. 1, 3, 5-Trinitrobenzene crystallises in snow-white leaflets, mp 122°C. It forms well-defined addition compounds with numerous aromatic compounds; hydrocarbons, phenols, etc. One of the three $—NO_2$ groups can be replaced by —OH or $—NH_2$ by the same reagents which attack the *o*- and *p*-dinitrobenzenes.

Trinitrobenzene is a more effective high explosive than TNT. However, it is not actually used because of the difficulty and expense of its manufacture.

NITROTOLUENES

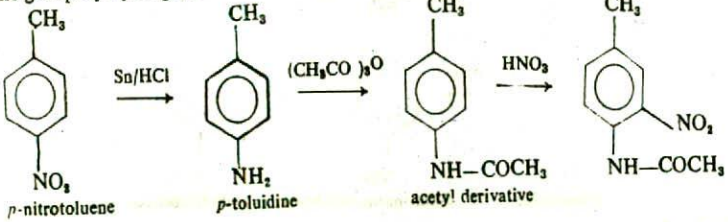
Preparation. Toluene is nitrated more readily than benzene because of the activating effect of the $—CH_3$ group. When treated with a mixture of nitric acid and sulphuric acid, it yields a mixture of *o*- and *p*-nitrotoluenes.



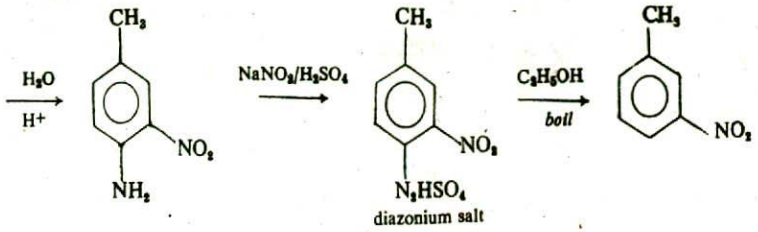
o-nitrotoluene — *p*-nitrotoluene

These isomers may be separated readily by fractional distillation under reduced pressure.

m-Nitrotoluene can be prepared in small amounts (about 4 per cent) by direct nitration of toluene. When needed in large quantities it is obtained indirectly from *p*-nitrotoluene by : (*i*) reduction; (*ii*) acetylation of *p*-toluidine; (*iii*) nitration of acetyl derivative; and (*iv*) replacing the amine group by hydrogen.

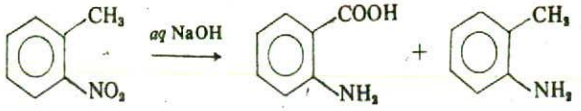


p-nitrotoluene — *p*-toluidine — acetyl derivative



The $-NH_2$ group in toluidine has to be acetylated to protect it from oxidation and to help ortho orientation.

Properties. *o*-Nitrotoluene is a liquid, mp −4°, bp 222°C; *p*-nitrotoluene, mp 54°, bp 238°; *m*-nitrotoluene, mp 16°, bp 227°C. All nitrotoluenes may be reduced in acid solution to give the corresponding toluidines. Upon oxidation with potassium permanganate, they are converted to the respective nitrobenzoic acids the $-CH_3$ group being transformed into $-COOH$ group. *o*-Nitrotoluene when heated with aqueous sodium hydroxide, undergoes an interesting internal oxidation and reduction to form *o*-aminobenzoic acid and *o*-toluidine.

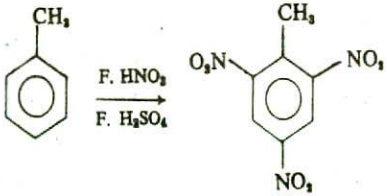


o-nitrotoluene *o*-aminobenzoic acid *o*-toluidine

2, 4, 6-TRINITROTOLUENE

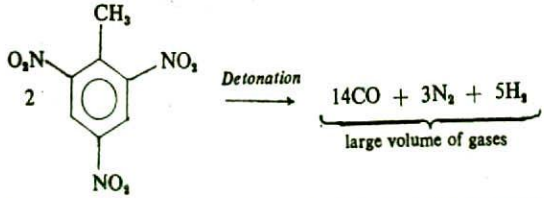
It is extensively used as an explosive and is commorly abbreviated to **TNT**.

Preparation. 2, 4, 6-Trinitrotoluene may be prepared by nitrating toluene with a mixture of fuming nitric acid and fuming sulphuric acid.

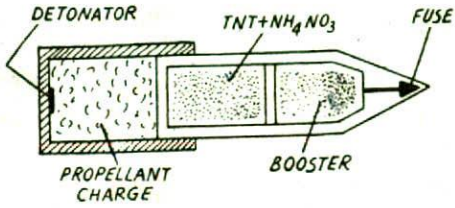


2,4,6-trinitrotoluene

Properties. 2, 4, 6-Trinitrotoluene is a faint yellow crystalline solid, mp 81°C. The molecule loaded with negative nitro groups is under strain, and has enough oxygen for internal combustion. TNT, therefore, explodes violently on detonation On explosion it is believed to explode as follows, leaving no residue.



The sudden liberation of large volume of gases lends intensity to the explosion.



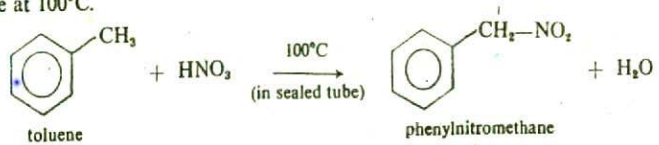
TNT Bomb

TNT is a high explosive and is used for filling bomb shells, hand grenades and torpedoes alone or with other explosives. It is a reasonably safe explosive, requiring strong detonation to set it off. Mixed with ammonium nitrate, it forms the blasting material *amatol* which is used for demolishing old buildings and rocks.

PHENYLNITROMETHANE, $C_6H_5—CH_2—NO_2$

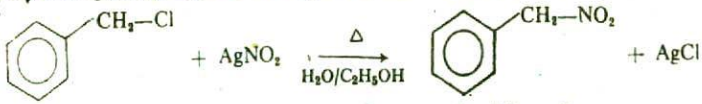
It is isomeric with nitrotoluenes but has the nitro group in the side-chain instead of the ring.

Preparation. It may be prepared : (1) By heating toluene with dilute nitric acid in a sealed tube at 100°C.



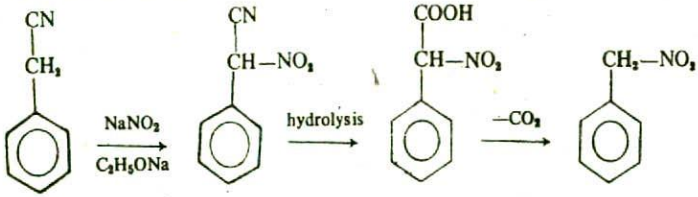
toluene phenylnitromethane

(2) By heating benzyl chloride with aqueous-ethanolic silver nitrite.



benzyl chloride phenylnitromethane

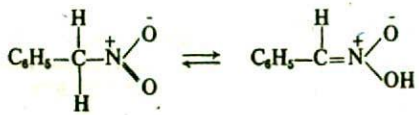
(3) From benzyl cyanide by the following sequence of reactions.



benzyl cyanide phenylnitromethane

This is the best method for the preparation of phenylnitromethane.

Properties. Phenylnitromethane is a yellow oil, bp 226°C. Like the aliphatic primary nitroalkanes, it exhibits tautomerism.



nitro form (*bp* 226°) *aci* form (*mp* 84°)

The equilibrium is much in favour of the *nitro* form. Thus phenylnitromethane dissolves in sodium hydroxide to give sodium salt of the *aci* form, which when treated with a mineral acid liberates the *aci* form. The latter is a solid but on standing it soon changes into the liquid phenylnitromethane, which is mainly the stable *nitro* form. Its tautomerism is the chief reason of interest in this compound.

QUESTIONS

1. What do you understand by the term 'Aromatic nitro compounds' ? Illustrate with examples Give the structure of the function 'nitro group'.

2. Discuss the 'Orbital structure' of nitrobenzene. How resonance of nitrobenzene makes the nitrogen-carbon bond strong ?

3. Give the general methods of introducing $-NO_2$ group in aromatic rings. Why are aromatic nitro compounds more important than aliphatic nitro compounds ?

4. Describe the physical characteristics of aromatic nitro compounds. Why the introduction of a nitro group into the aromatic ring raises the melting and boiling points of these compounds ?

5. Explain why the presence of $-NO_2$ group on benzene ring deactivates it to the attack of electrophiles and why the latter attack at the meta position.

6. List the general chemical reactions of aromatic nitro compounds with special reference to their reduction under different conditions.

7. (*a*) What is nitration ? What is the function of sulphuric acid in this reaction ?

(*b*) What products are obtained by the reduction of nitrobenzene under different reaction conditions.

(Delhi BSc Hons, 1993)

8. How is nitrobenzene prepared ? What are the products obtained when nitrobenzene is reduced in acidic, neutral, and alkaline medium. *(Indore BSc, 1993)*

9. Discuss the mechanism of nitration of benzene. *(Madras BSc, 1994)*

10. Write a note on : Reduction of nitrobenzene under different conditions.

(Karnataka BSc, 1994; Osmania BSc Hons, 1994)

11. Describe the preparation and uses of TNT. *(Anna BSc, 1993; Kerala BSc, 1994)*

12. How will you synthesie 1,3,5-trinitrobenzene from toluene ? *(Madras BSc, 1994)*

Answer. Use the following steps : (i) $3HNO_3/H_2SO_4$, (ii) $Na_2Cr_2O_7/H_2SO_4$, and (iii) heat ($-CO_2$).

13. A compound $C_7H_5O_6N_3$ (A) undergoes oxidation with acidified potassium dichromate to form a mono carboxylic acid (B) $C_7H_3O_8N_3$. When (B) is heated in acetic acid solution, (C) $C_6H_3O_6N_3$ is formed. What are (A), (B), and (C) ?

Answer. (A) *is* 2,4,6-trinitrotoluene ; (B) *is* 2,4,6-trinitrobenzoic acid; and (C) *is* 1,3,5-trinitrobenzene.

14. Compound (A), C_7H_6ONBr, gives the following reactions :

(A) + Sn/HCl → C_7H_8NBr

(B) + $KMnO_4$ → $C_7H_5O_4N$ (B)

(A) + NH_3 → $C_7H_8O_2N_2$

(B) + $NaHCO_3$ → liberates CO_2

Give possible structures for (A).

Answer. (A) is *o*-,*m*-, or *p*-Nitrobenzyl bromide.

Chapter **40**

Aromatic Amines

The amino derivatives of the aromatic hydrocarbons are of two types :

(*a*) *Aryl amines* or *Aromatic amines* in which the $-NH_2$ group (or substituted $-NH_2$ group) is attached directly to a carbon of the benzene ring.

(*b*) *Aryl-alkyl* or *Aralkyl amines* in which the $-NH_2$ group is attached to a carbon of the side-chain.

Both with respect to the methods of preparation and reactions of $-NH_2$ group, aralkyl amines are similar to the aliphatic amines. The aromatic or aryl amines are generally prepared by reduction of the aromatic nitro compounds, which are readily obtained by direct nitration of aromatic hydrocarbons. They differ considerably in a number of respects from aliphatic amines. In this chapter, we will discuss aromatic amines only in detail.

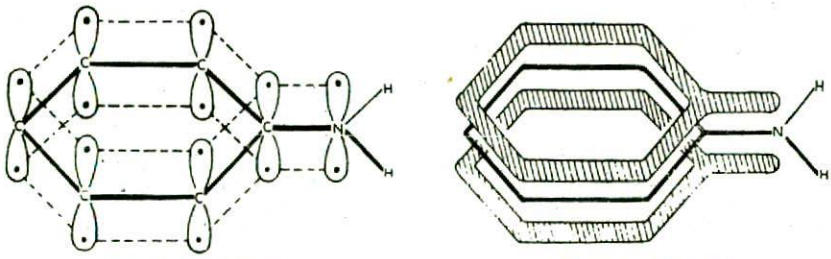
Like the aliphatic amines, the aromatic amines may also be divided into primary, secondary and tertiary amines according as one, two or three hydrocarbon groups are attached to the amino N-atom. Thus :

$Ar-NH_2$	$Ar-\underset{\displaystyle H}{\overset{\displaystyle Ar}{\underset{\vert}{\overset{\vert}{N}}}}$	$Ar-\underset{\displaystyle H}{\overset{\displaystyle R}{\underset{\vert}{\overset{\vert}{N}}}}$	$Ar-\underset{\displaystyle Ar}{\overset{\displaystyle Ar}{\underset{\vert}{\overset{\vert}{N}}}}$	$Ar-\underset{\displaystyle R}{\overset{\displaystyle Ar}{\underset{\vert}{\overset{\vert}{N}}}}$
1° amine	2° amine	2° amine	3° amine	3° amine

The primary amines are further designated as *monoamines*, *diamines* and *triamines* according to the number of NH_2 groups present in the aromatic ring.

STRUCTURE

The molecular structure of aromatic amines will be illustrated by taking example of aniline. This is similar to the structure of monohalogenated benzene compounds. Here the nitrogen atom may be considered as sp^2 hybridised. The three sp^2 orbitals are forming σ bonds with



Atomic Orbital Model Electron Cloud Model

Fig. 40·1. Structure of Aniline

a carbon of the ring and the two H atoms. The pure *p* orbital of the nitrogen containing the unshared electron pair, overlaps with the π orbital system of the benzene ring. The resulting molecular orbital extends over the six carbon atoms of the ring as also the nitrogen atom of NH_2 group.

In the above formulation of the structure of aniline, hybridisation at the nitrogen atom is sp^2, so that the benzene ring, the nitrogen atom as also the H atoms lie in the same plane. But actually the benzene ring and the nitrogen atom lie in the same plane, while the two H atoms lie somewhat out of the plane. Hence it stands to reason that the hybridisation at the N atom could be approximately sp^3 and three of the sp^3 orbitals form σ bonds with carbon of the ring and the two H atoms, the fourth one containing the unshared electron pair interacts with the π system of the ring. Therefore, the nitrogen remains pyramidal.

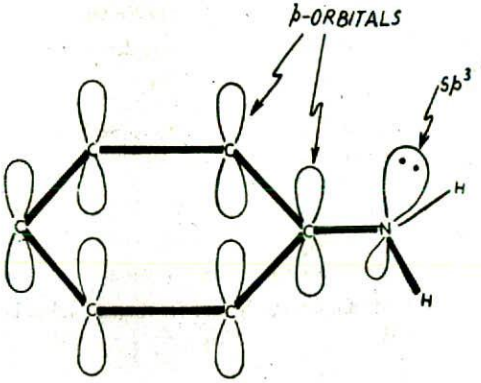
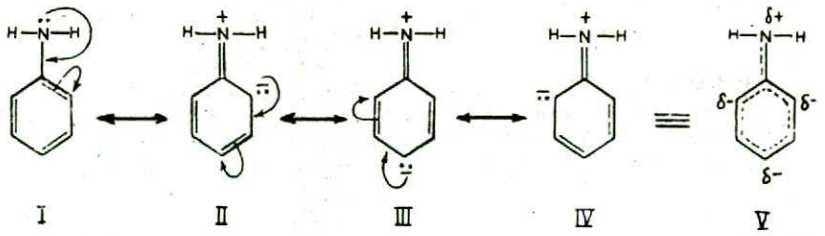


Fig. 40·2. Aniline has pyramidal structure at the nitrogen atom

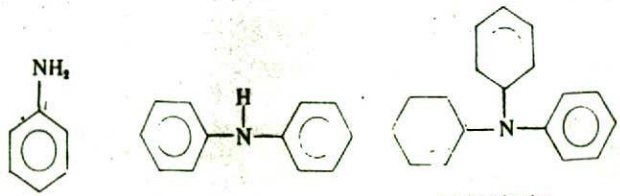
The electronic structure of aniline can be represented as a resonance hybrid of the following four canonical forms.



(2 Kekule forms) resonance hybrid

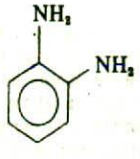
NOMENCLATURE

(1) The aromatic amines may be named by naming the aryl groups bonded to nitrogen, and adding the suffix —amine. If the same group appears more than once, the prefix *di-*, *tri-* etc is used.

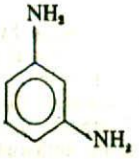


phenylamine diphenylamine triphenylamine

When two or three NH_2 groups are present in the benzene ring, the suffix used is —diamine or —triamine. The positions of NH_2 groups are indicated by prefixing *o*-, *m*- or *p*- ; or by using numbers.



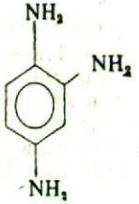
o-phenylenediamine



m-phenylenediamine



p-phenylenediamine



1, 2, 4-benzenetriamine

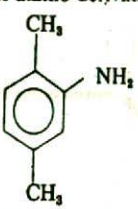
(2) The aromatic amines may be named as amino derivatives of the parent hydrocarbon.



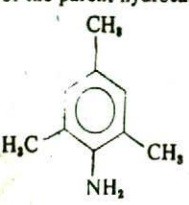
aminobenzene



p-aminotoluene



2-amino-*p*-xylene

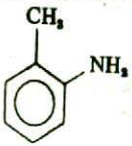


aminomesitylene

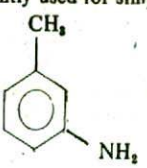
(3) The common names are frequently used for simpler and technical aromatic amines.



aniline



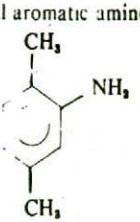
o-toluidine, (2-aminotoluene)



m-toluidine (3-aminotoluene)



p-toluidine (4-aminotoluene)

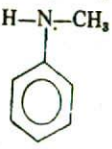


p-xylidene (aminoxylene)

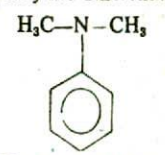
(4) Alkaryl 2° and 3° amines are named as alkyl derivatives of the parent compound ANILINE, the prefix *N* being used to indicate that the alkyl group is specifically located on nitrogen. If more than one nitrogen is present, they are differentiated as *N*, *N'*, *N''*, etc.



p-methylaniline, 4-methylaniline



N-methylaniline



N, *N*-dimethylaniline

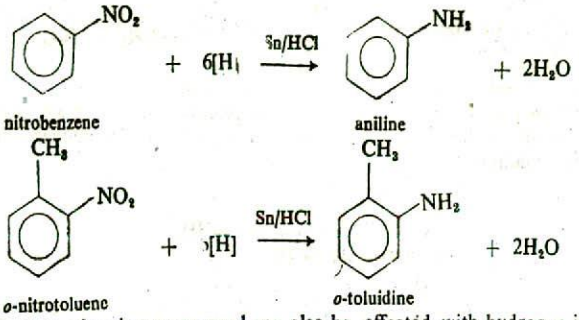


N, *N'*-dimethyl-*p*-diaminobenzene

I. MONOAMINES

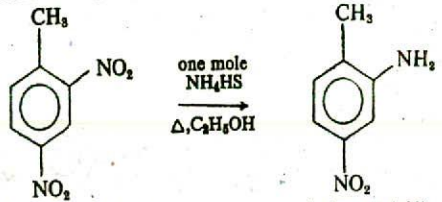
METHODS OF PREPARATION OF MONOAMINES

(1) **Reduction of Nitro Compounds.** Monoamines are nearly always prepared by the reduction of the corresponding nitro compounds. This reduction may be carried with a metal and mineral acid *e.g.* tin, zinc or iron, and HCl or H_2SO_4.



The reduction of a nitro compound can also be effected with hydrogen in the presence of platinum or Raney nickel at room temperature.

When there are two or more nitro groups present in the ring the reduction may be done selectively with ethanolic ammonium hydrogen sulphide, or warm aqueous sodium sulphide, or stannous chloride and hydrochloric acid.

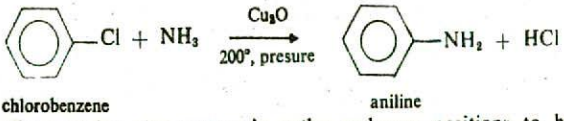


In this way only one $-NO_2$ group is converted to $-NH_2$ group, generally the ortho one is attacked by the reducing agent preferentially.

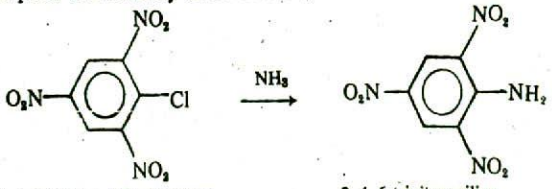
(2) **Ammonolysis of Aryl halides.** Aryl halides react with ammonia in the presence of a catalyst (copper salts) at high temperature and under high pressure to form the corresponding amino compounds.

$$\underset{\text{aryl chloride}}{Ar{-}Cl} + NH_3 \xrightarrow[200^\circ,\ \text{pressure}]{Cu_2O} \underset{1^\circ\ \text{amine}}{Ar{-}NH_2} + HCl$$

For example,

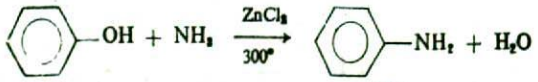


If the ring also contains nitro groups in ortho and para positions to halogen atom ammonolysis takes place conveniently under ordinary conditions.



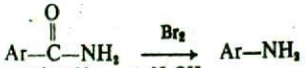
(3) **Ammonolysis of Phenols.** Phenols react with ammonia in the presence of zinc chloride at about 300 C to form the corresponding amines.

$$Ar{-}OH + NH_3 \xrightarrow[300^\circ]{ZnCl_2} Ar{-}NH_2 + H_2O$$

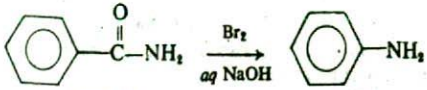
e.g., 

phenol aniline

(4) **Degradation of Amides** (*Hofmann Rearrangement*). Like primary aliphatic amines, primary aromatic amine can be obtained by the degradation of aryl amides with bromine or chlorine in alkaline solution.



aryl amide

e.g., 

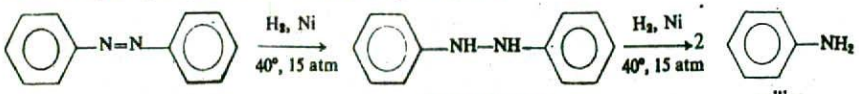
benzamide aniline

(5) **Reduction of Azo Compounds.** The reduction of azo compounds by the way of hydrazo compounds yields primary aromatic amines.



azo compound hydrazo compound 1° amine

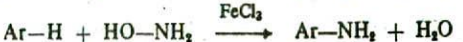
Thus catalytic hydrogenation of azobenzene gives aniline,



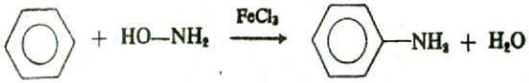
hydrazobenzene (not isolated) aniline

Since azo- and hydrazo-compounds are prepared from nitro compounds, this method is limited to specific cases.

(6) **Action of Hydroxylamine with Hydrocarbons.** Aromatic hydrocarbons react directly with hydroxylamine in the presence of a catalyst ($FeCl_3$, $AlCl_3$) to give monoamines.

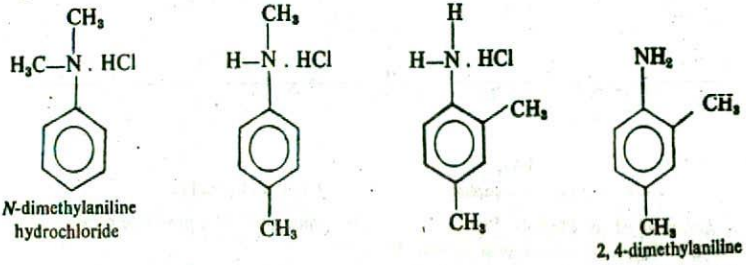


hydroxylamine monoamine

e.g., 

aniline

(7) **Action of Heat on 2° and 3° Alkarylamine hydrochlorides.** (*Hofmann-Martius Rearrangement*). When a secondary or tertiary alkylamine hydrochloride is heated, it rearranges to give homologues of aniline.

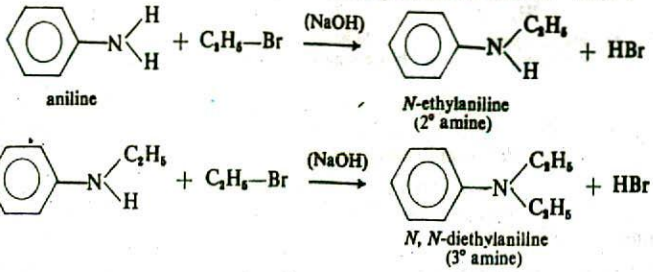


N-dimethylaniline hydrochloride 2, 4-dimethylaniline

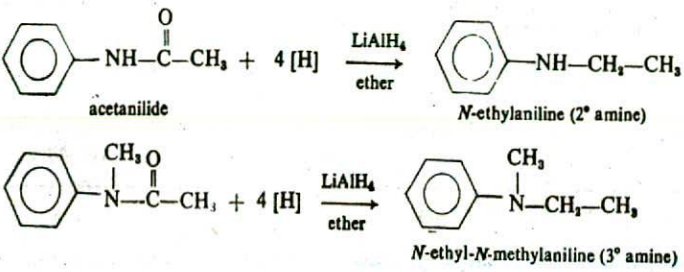
Here the *N*-alkyl group migrates preferentially to the para position, but will migrate to ortho position if para position is blocked.

METHODS OF PREPARATION OF 2° AND 3° AROMATIC AMINES

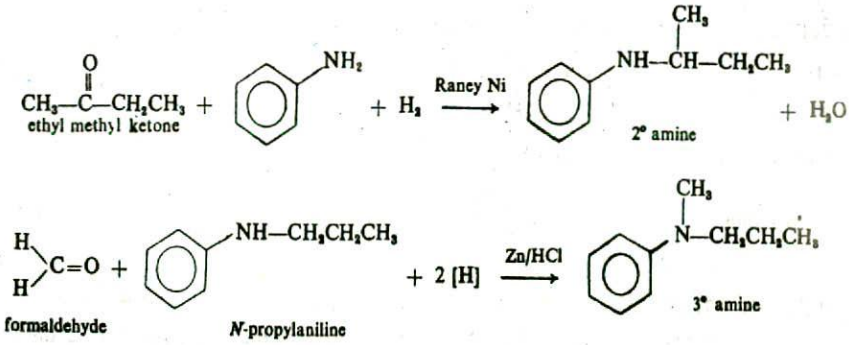
(1) **Alkylation of 1° and 2° Aromatic amines.** Primary and secondary aromatic amines on reaction with alkyl halide, give secondary and tertiary aromatic amines. Thus :



(2) **Reduction of appropriate Anilides.** When anilides are reduced with $LiAlH_4$, secondary and tertiary aromatic amines are formed.



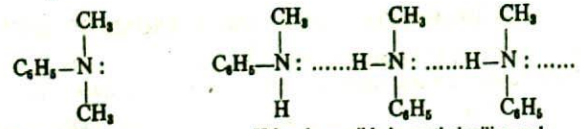
(3) **Reductive amination.** Aldehydes and ketones react with primary or secondary aromatic amines in the presence of a reducing agent to form secondary or tertiary aromatic amines.



PHYSICAL PROPERTIES

(1) Aromatic amines in general are colourless liquids or solids, having characteristic odour which is not unpleasant. They turn brown in air owing to oxidation.

(2) They have relatively high boiling points, on account of their high molecular weights. The aniline (bp 184°) has a higher boiling point than *n*-hexylamine (bp 130°). *N*-methylaniline (bp 196°) boils at a higher temperature than aniline, but *N,N*-dimethylaniline (bp 193°) boils at a lower temperature than methylamine. This is so because hydrogen bonding is not possible with dimethylaniline



No intermolecular H-bonds possible

H-bonds possible in methylaniline and hence higher bp as compared to dimethylaniline

(3) As true for all the disubstituted benzenes, the *para*-substituted anilines, being the most symmetric, have the highest melting points. Thus *p*-toluidine is a solid at room temperature while both the *ortho* and *meta* isomers are liquids.

(4) They are sparingly soluble in water but dissolve in benzene and other organic solvents. However, aniline is considerably more soluble in water (3·6g/100g H_2O) than *n*-hexylamine (0·4 g/100g H_2O).

5) The aromatic amines are highly toxic substances. The liquids are absorbed readily through the skin, and the vapours when inhaled for prolonged periods prove symptoms of toxicity. *N*-phenylanilines are considerably less toxic than *N*-alkyl derivatives. The toxic action of aromatic amines consists of destroying red blood corpuscles, depressant action on heart muscles, and continued exposure leads to mental disturbances.

Table. Physical properties of some Aromatic amines

Name	*Formula*	*mp°C*	*bp °C*	*Solubility (g/100g H_2O)*	K_b
Aniline	$C_6H_5-NH_2$	—6	184	3·6	$4·2\times10^{-10}$
N-Methylaniline	$C_6H_5-NH-CH_3$	—57	196	v. sl. sol.	$7·1\times10^{-10}$
N, *N*-Dimethylaniline	$C_6H_5-N(CH_3)_2$	2·5	193	1·4	11×10^{-10}
o-Toluidine	o-$CH_3-C_6H_4-NH_2$	—24	200	1·5	$2·5\times10^{-9}$
m-Toluidine	m-$CH_3-C_6H_4-NH_2$	—30	203	S. sol.	
p-Toluidine	p-$CH_3-C_6H_4-NH_2$	44	201	S. sol.	2×10^{-9}
Diphenylamine	$C_6H_5-NH-C_6H_5$	53	302		$6·3\times10^{-14}$
Triphenylamine	$C_6H_5-N(C_6H_5)_2$	127	365		$\sim 10^{-20}$

CHEMICAL PROPERTIES

The aromatic amines in general give all the reactions of the amine group (1°, 2° or 3°) of aliphatic amines. However, the reactivity of the amine group is modified owing to the delocalisation of the non-bonded electrons on N-atom into the π-system of the aromatic ring. Thus compared to aliphatic amines, aromatic amines are weak bases and the R—N or N—H bond becomes less susceptible to displacement by nucleophiles. Aryl amines, therefore, form stable diazonium salts, while their aliphatic counterparts are unstable. The interaction of the non-bonded electrons of N atom with the benzene ring system, also activates the benzene ring to attack by electrophiles Thus aromatic amines undergo electrophilic substitution reactions readily in the benzene ring ; while the hydrocarbon group in aliphatic amines is that way quite inert.

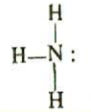
(1) Basicity of Aromatic amines ; Salt formation. While discussing the basic character of aliphatic amines, we had defined basicity as the relative ease with which an amine will accept a proton (H^+) from water. Thus aniline is protonated to give the anilinium ion.

$$C_6H_5\ddot{N}H_2 + \underset{\text{(excess)}}{H-\overset{\curvearrowright}{O}-H} \rightleftharpoons \underset{\text{anilinium}}{C_6H_5-\overset{+}{N}H_3} + \bar{O}H$$

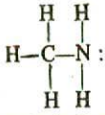
The value of equilibrium constant K_b determines the concentration of $\bar{O}H$ ions or the basicity of aniline.

$$K_b = \frac{[C_6H_5-\overset{+}{N}H_3]\,[\bar{O}H]}{[C_6H_5-\ddot{N}H_2]}$$

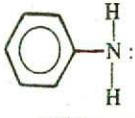
Compared to ammonia (NH_3) or aliphatic amines ($R-\ddot{N}H_2$), the basicity of an aryl amine is significantly reduced



ammonia
($K_b = 1{\cdot}8 \times 10^{-5}$)

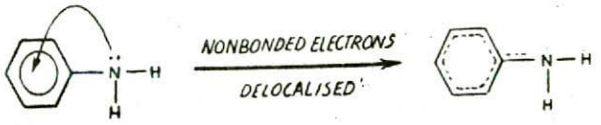


methylamine
($K_b = 7{\cdot}1 \times 10^{-4}$)



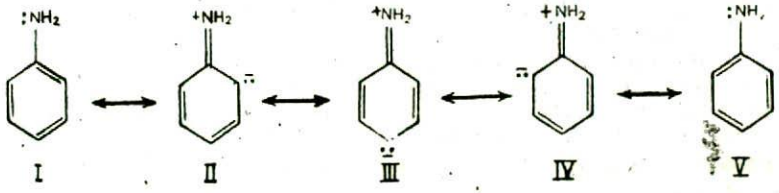
aniline
($K_b = 4{\cdot}2 \times 10^{-10}$)

The explanation of the considerably reduced basicity of aniline is offered by the fact that the non-bonded electrons on the nitrogen atom are delocalised into the π-system of the benzene ring (see orbital model above). Therefore, these electrons which encompass the six carbons of the ring as also the nitrogen atom are less available for interaction with protons from water. Thus the value of K_b for aniline is decreased, making it less basic.

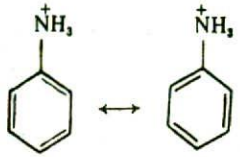


(reduced electron density on N atom makes non-bonded electrons less available)

From another point of view, the aniline structure is capable of existing in the following five resonance forms *i.e.*, two Kekule forms (I and V) and three others (II, III, IV).

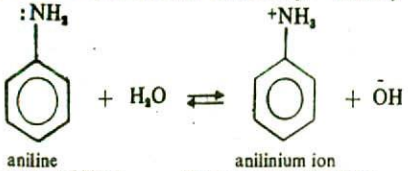


Thus aniline structure is greatly resonance stabilised. On the other hand, the anilinium ion formed by protonation of aniline is less resonance-stabilised as it exists only in two Kekule forms, and no more.



(Resonance forms of anilinium ion)

Hence, the aniline structure which exists in five resonance forms, is more resonance-stabilised than the anilinium ion which can exist in two forms only. That is,



aniline (more resonance-stabilised than anilinium ion)

anilinium ion (less resonance-stabilised than aniline)

Thus protonation of aniline requires energy to overcome the excess resonance energy (ΔH res. $PhNH_3^+ > \Delta H$ res. $PhNH_2$) of aniline. But since the resonance stabilisation of either ammonia or ammonium ion is not possible as for aniline or anilinium ion respectively, the protonation of ammonia requires less energy relative to the protonation of aniline. As a result, the aromatic amines are weaker bases than ammonia and aliphatic amines.

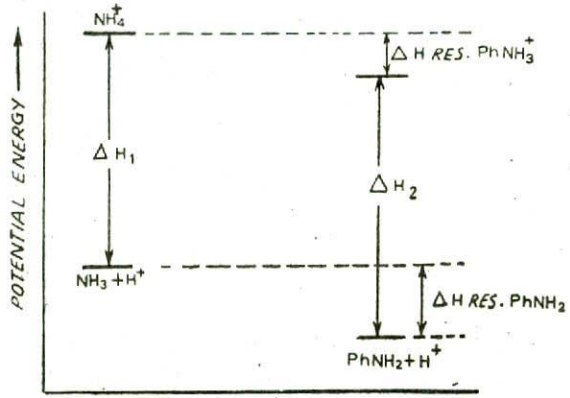


Fig. 40·3. Resonance-stabilised aniline is a weaker base than ammonia.

How is the basicity of aniline affected by substituents on the ring ?

An electronreleasing group ($-NH_2$, $-OCH_3$, $-CH_3$) pushes electrons towards the *N*-atom and makes the nonbonded electron pair more available for protonation. Hence such a substitutent increases the basicity. Thus K_b value for *p*-methoxy aniline is $2{\cdot}0 \times 10^{-9}$ as compared to aniline $4{\cdot}2 \times 10^{-10}$.

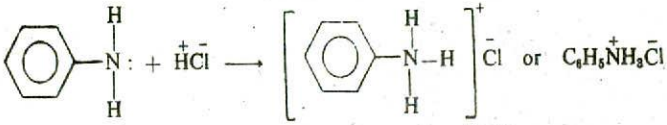
On the other hand an electron-withdrawing group ($-NO_2$, $-SO_3H$, $-COOH$, $-X$) helps pull electrons away from nitrogen and thus makes the nonbonded electron pair less available for protonation. Therefore, such a substituent lowers the basicity. Thus K_b value for *p*-nitroaniline is $1{\cdot}0 \times 10^{-13}$ as compared to aniline, $4{\cdot}2 \times 10^{-10}$.

How is basicity of aniline affected by the presence of substituents on N-atom ?

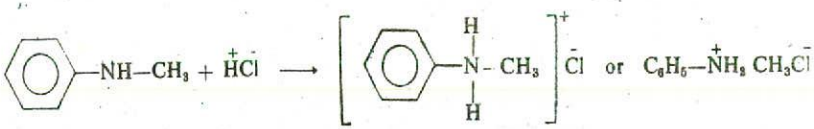
When an alkyl group (electron releasing group) is present on N-atom of aniline, the basicity of aniline is increased. Thus the basicity of *p*-methylaniline is $2{\cdot}0 \times 10^{-9}$ as compared to that of aniline ($4{\cdot}2 \times 10^{-10}$).

When more than one benzene ring are bonded to N-atom, the nonbonded electrons suffer greater delocalisation and are much less available for protonation. The presence of large phenyl groups in the molecule also screens the nonbonded electrons on N-atom and thus reduces the basicity further. As a result, diphenylamine is only a very weak base but triphenyl amine is completely devoid of basic character.

Salt Formation. Although aromatic amines are weaker bases than ammonia or aliphatic amines, they form well-defined crystalline salts on reaction with strong mineralacids as HCl or H_2SO_4. For example,

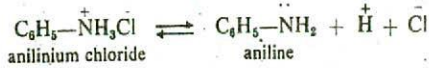


aniline — phenylammonium chloride, anilinium chloride



N-methylamine — *N*-methyl-*N*-phenylammonium chloride, *N*-methylanilinium chloride

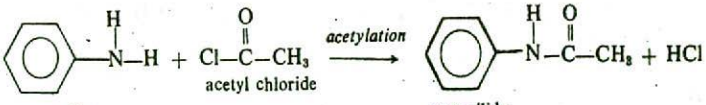
These salts of aromatic amines are soluble in water and undergo hydrolysis to a great extent, giving acidic reaction.



anilinium chloride — aniline

Like salts of aliphatic amines, these salts liberate the original aromatic amine, when treated with an alkali solution.

(2) **Acylation.** The primary and secondary aromatic amines react with aryl chlorides or anhydrides, when the hydrogen atom attached to N-atom is replaced by aryl group (*Acylation*).

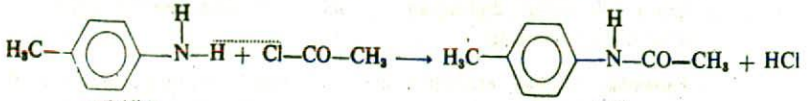


aniline (1° amine) — acetyl chloride — acetanilide, *N*-phenylacetamide



N-methylaniline (2° amine) — *N*-methyl-*N*-phenylbenzamide, *N*-methylacetanilide

The acyl substitution products of aniline thus obtained are amides in which an aryl group has replaced a hydrogen atom of the amide group (—CO—NH_2), and they are termed **Anilides**. Similarly, the acyl substituted toluidines are called **Toluidides**.

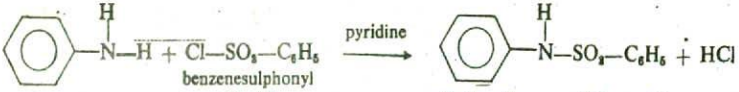


p-toluidine aceto-*p*-toluidine

The acylation reaction is often carried in the presence of a base *e.g.*, sodium hydroxide, or pyridine which helps in the removal of HCl. (*Schotten-Baumann Reaction*)

The anilides or toluidides, *N*-acyl derivatives of other aromatic primary or secondary amines are crystalline solids having sharp melting points. Their preparation and determination of the melting point is used to characterise the parent amino compounds. Acetylation of aromatic amino compounds is also done to protect the —NH_2 group during nitration and other reactions where the reagent employed can attack this group.

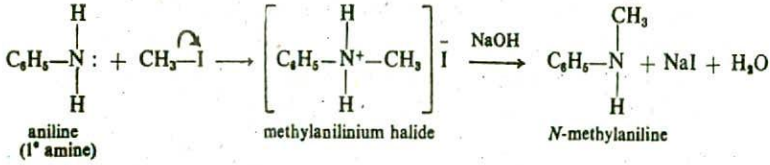
(3) **Sulphonylation.** Here aromatic secondary and tertiary amines are allowed to react with an arylsulphonyl chloride in pyridine. The hydrogen atom attached to N atom is replaced by the sulphonyl group to form *N*-arylsulphonamide. Thus aniline reacts with benzene sulphonyl chloride to form *N*-benzenesulphonamide.



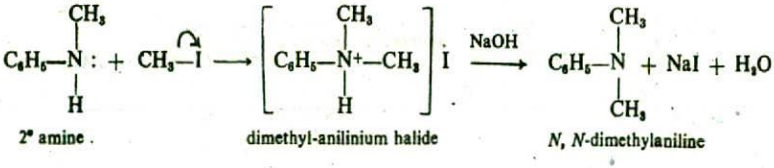
benzenesulphonyl chloride *N*-phenylbenzenesulphonamide

The preparation of *N*-arylsulphonamides may also be used for the identification of aromatic 2° and 3° amines. As described under aliphatic amines, the formation of sulphonamides provides a method (*Hinsberg method*) for the separation of 1°, 2° and 3° amines.

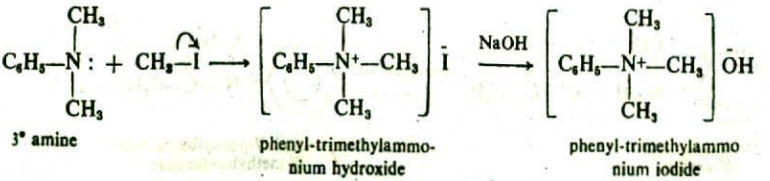
(4) **Alkylation and Arylation.** Like the aliphatic amines, the primary aromatic amines react with alkyl halides to form *mono*-, *di*-, and finally, trialkylammonium salts. These *mono*- and *di*-alkylammonium salts on treatment with sodium hydroxide, are decomposed to yield the free *N*-alkyl and *N*, *N*-dialkyl-arylamines. For example,



aniline (1° amine) methylanilinium halide *N*-methylaniline



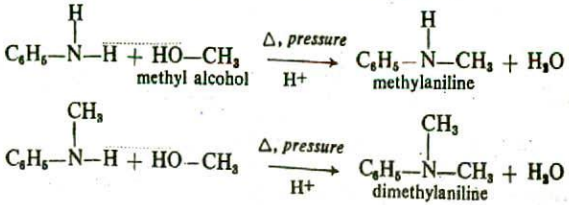
2° amine dimethyl-anilinium halide *N*, *N*-dimethylaniline



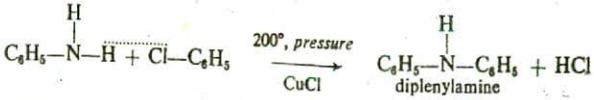
3° amine phenyl-trimethylammonium hydroxide phenyl-trimethylammonium iodide

The quaternary aryl-trialkylammonium salt is converted into the hydroxide which is a strong base. The alkylation of aryl amine to give *N*-alkyl or *N*-dialkyl-arylamines can be carried out directly in one operation in the presence of alkali.

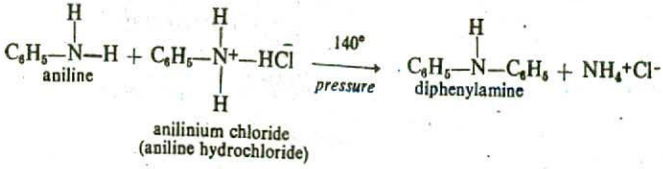
Alkylation of aromatic primary amines may also be done by heating under pressure with an alcohol in the presence of a strong mineral acid (HCl or H_2SO_4).



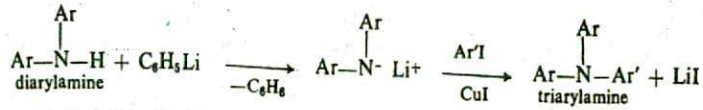
Primary arylamines react with simple aryl halides only with difficulty. Some diphenylamine is produced by heating aniline at 200°C (under pressure) with chlorobenzene in the presence of cuprous chloride.



This *arylation* of aniline can be carried more readily by heating together, under pressure, aniline and anilinium chloride at about 140°C



Reaction of the lithium salt of a diarylamine with an aryl iodide in the presence of traces of cuprous iodide yields the *triarylamine*.

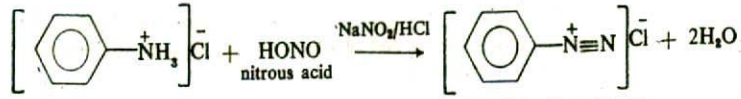


(5) **Reaction with Nitrous acid**. Aromatic amines react with nitrous acid ($NaNO_2$ + HCl), like the aliphatic amines, and the nature of the reaction depends on whether the amine is primary, secondary or tertiary. However, there is close correspondence in the behaviour of aliphatic and aromatic amines in the case of secondary amines only.

(*a*) PRIMARY AMINE. (*i*) *At low temperatures*. At low temperatures (0°—5°C), aromatic primary amines dissolved in strong acids (HCl or H_2SO_4), react with nitrous acid to form water-soluble compounds known as **Diazonium Salts**. Thus, aniline dissolved in hydrochloric acid forms the salt, aniline hydrochloride ($C_6H_5\overset{+}{N}H_3\overset{-}{Cl}$) which reacts with nitrous acid to yield benzenediazonium chloride.



aniline aniline hydrochloride



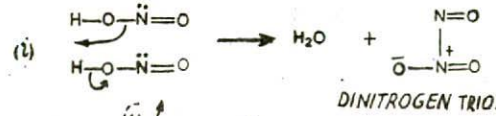
benzenediazonium chloride

(*ii*) ***At higher temperatures.*** At higher temperatures primary aromatic amines form phenols and nitrogen.

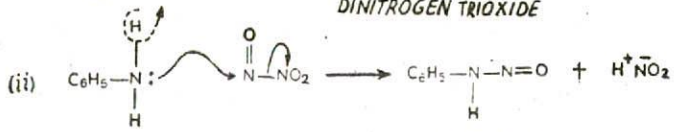


aniline phenol

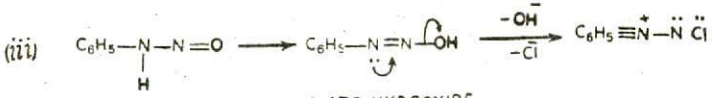
MECHANISM. (*i*) Nitrous acid produces dinitrogen trioxide (N_2O_3) ; (*ii*) Dinitrogen trioxide reacts with primary amine to give the intermediate *N*-nitrosoamine ; (*iii*) *N*-nitrosoamine is transformed into diazonium salt *via* diazo hydroxide ; (*iv*) At higher temperatures the diazonium salt decomposes to yield phenol.



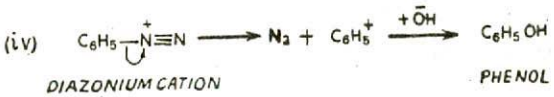
DINITROGEN TRIOXIDE



N-NITROSOAMINE



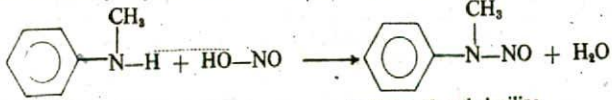
DIAZO HYDROXIDE



DIAZONIUM CATION PHENOL

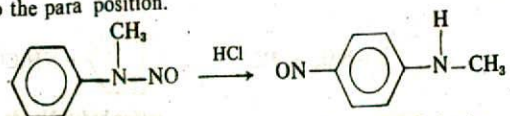
Aliphatic primary amines do not form stable diazonium salts under similar conditions. They react with nitrous acid to yield alcohols and nitrogen. This reaction is, therefore, used as a test for distinguishing between aliphatic and aromatic primary amines.

(*b*) SECONDARY AMINES. The action of nitrous acid on secondary aromatic amines is similar to that on secondary aliphatic amines. The product is nitrosoamine. Thus :



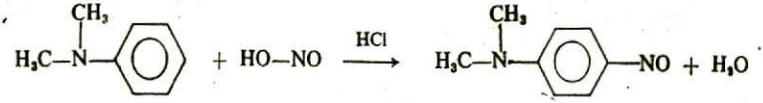
N-methylaniline (2° amine) *N*-nitroso-*N*-methylaniline

The mechanism of the reaction is the same as in step (*ii*) of the mechanism described above. The nitrosoamines obtained are stable substances having yellow colour. They undergo **Fischer-Hepp Rearrangement** when treated with hydrochloric acid in ethanol and ether when —NO group migrates to the para position.



N-nitroso-*N*-methylamine *p*-nitroso-*N*-methylamine

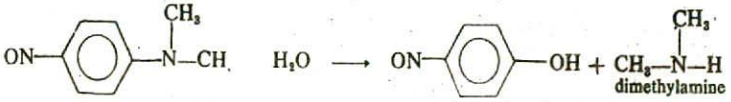
(c) TERTIARY AMINES. Tertiary aromatic amines undergo substitution by a nitroso group (nitrosation) in the para position of the benzene ring, to give the *p*-nitroso derivative of the original amine. For example,



N, N-dimethylaniline — *p*-nitroso-*N, N*-dimethylaniline (*as salt*)

The substitution here takes place under the strong *para* activating effect of the dialkylamino group. If the para position is not free, the nitrosation takes place in the ortho position.

When the *p*-nitroso derivative obtained as above is hydrolysed, with alkali dialkylamino group is detached from the ring, giving *p*-nitrosophenol and dialkylamine.



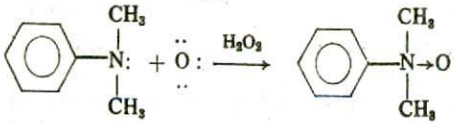
p-nitrosophenol

This is an important source of pure aliphatic secondary amines.

Tertiary *N, N*-dialkyl-aryl amines are not so susceptible to oxidation as are primary and secondary arylamines. When treated with hydrogen peroxide or perbenzoic acid,

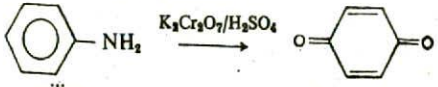
$$C_6H_5–CO–O–OH,$$

they are oxidised to amino oxides. For example,



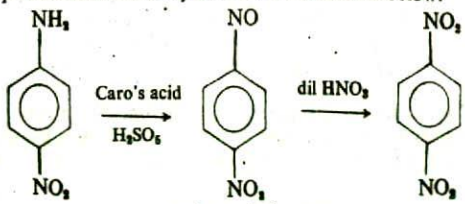
Amine salts are less susceptible to oxidation. Oxidation is an electron-removing process, and the positive charge on the nitrogen atom reduces the ease which an oxidising agent can remove electrons from it. Aromatic amines are, therefore, preferably stored and marked as their salts rather than as free amines.

(6) **Oxidation**. Aromatic amines are readily oxidised. In fact they are so sensitive in this respect that they undergo slow aerial oxidation on storage and become dark in colour. Thus freshly distilled aniline is colourless but soon turns yellow and then dark red on exposure to the air. The product of oxidation of an aromatic amine depends on the conditions of oxidation and the reagent used. Vigorous oxidation of primary aromatic amines with pot. dichromate and sulphuric acid results in the formation of quinones.



aniline — *p*-benzoquinone

Caro's acid (permonosulphuric acid) oxidises the primary $-NH_2$ group to the nitroso group. Pertrifluoroacetic acid (CF_3COOH) oxidises the primary amino group to the nitro group. These reactions are used for preparing aromatic nitro compounds which are not formed by direct nitration. Thus *p*-dinitrobenzene may be made as indicated below.



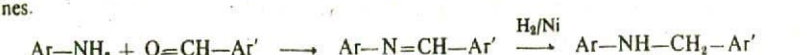
p-nitrosonitrobenzene

(7) **Reaction with Aldehydes.** Primary aromatic amines react with aldehydes in a manner similar to that of the primary aliphatic amines, giving condensation products. Thus when aniline reacts with an aldehyde on warming to give **Anils** or **Schiff's bases**. These products are most stabl when the aldehyde is an aromatic one e.g., benzaldehyde.



aniline benzaldehyde bezyledeneaniline (Schiff's base)

The Schiff's bases are readily hydrolysed by aqueous acids to give back the original amine and aldehyde. Therefore, the formation of Schiff's bases offers a means of protecting the NH_2 group. They are also easily reduced and may be used for the preparation of secondary amines.



arylamine aryl aldehyde Schiff's base a 2° amine

The Schiff's base obtained from aromatic amines and aromatic aldehydes are crystalline solids, often useful for the identification of either the amine or the aldehyde.

(8) **Carbylamine Reaction.** Like primary aliphatic amines, primary aromatic amines react with chloroform and ethanolic potash, to form *Carbylamines* (isocyanides or isonitriles). These have very disagreeable odour The reaction is, therefore, used as a test for the detection of amides, and for chloroform.



aniline phenyl carbylamine

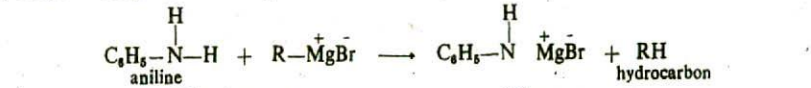
(9) **Reaction with Carbon Disulphide.** Unlike the aliphatic primary amines, aniline does not react with carbon disulphide at room temperature. When aniline and carbon disulphide are heated together, thiocarbanilide (*s*-diphenylthiourea) and H_2S are obtained.



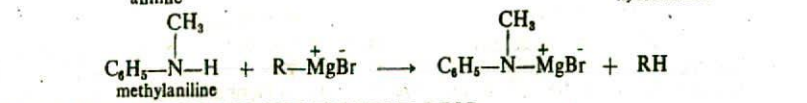
thiocarbanilide, diphenylthiourea

When thiocarbanilide is boiled with strong hydrochloric acid *phenyl isothiocyanate* (phenyl mustard oil), having a very pungent odour is the product. This may be used as a test for primary amines.

(10) **Reaction with Grignard Reagents.** Primary and secondary aromatic amines react with Grignard reagents to form hydrocarbons. Thus,



aniline hydrocarbon



methylaniline

B. REACTIONS INVOLVING THE BENZENE RING

As discussed before under the structure of aromatic amines, the nonbonding electron pair on nitrogen atom of $-NH_2$ group is delocalised into the benzene ring. As a result, the overall negative character of benzene ring is increased and it becomes negative relative to NH_2. Hence the benzene ring is greatly activated to the attack of electrophiles (E^+), and there would be less possibility of attack by a nucleophile (Nu^-). Again, the resonance effect in aniline molecule stated earlier, places a negative charge on the ortho and para positions to the $-NH_2$ group. An electrophile will, therefore, attack the carbon atoms of the ring at these positions preferentially.

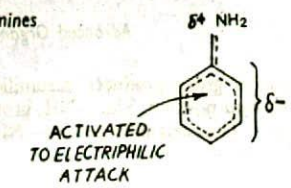


Fig. 40·4. Delocalisation of nonbonding electron pair of N into benzene ring makes it negative and activates it to electrophilic attack.

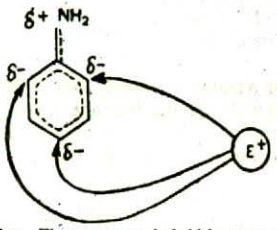
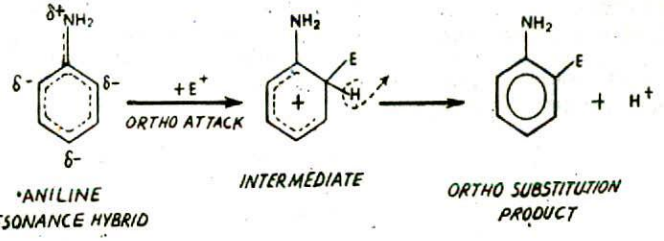
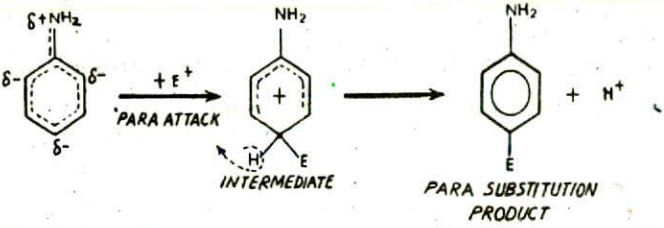


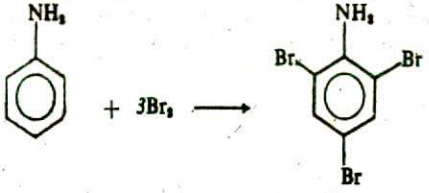
Fig. 40·5. The resonance hybrid bears negative charge on the ortho and para positions which are the points of attack by electrophile E+.

Thus arylamines undergo electrophilic substitution in the benzene ring readily and the $-NH_2$ group directs the new entrant to the ortho and para positions. Thus,



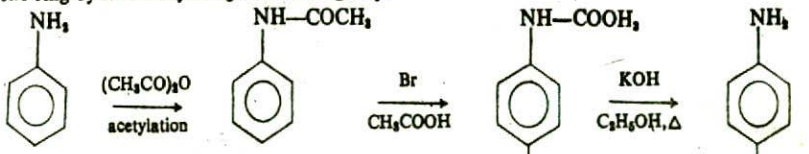


(1) **Bromination.** When an aromatic amine is treated with chlorine- or bromine-water, halogenation occurs readily. Thus the benzene ring in aniline is so greatly activated by $-NH_2$ group that treatment with aqueous bromine at once forms 2, 4, 6-tribromoaniline.



2,4,6-tribromoaniline

In order to get mono-substitution in the ring, it becomes necessary to deactivate the benzene ring by first acetylating the amino group.



acetanilide

p-bromoacetanilide

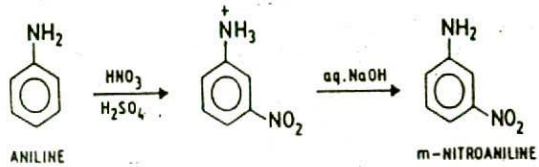
p-bromoanilide

The reaction of acetic anhydride with the amino group produces acetanilide. This is brominated with aqueous bromine in acetic acid in the *para* position. The $-NH_2$ group is finally regenerated by the alkaline hydrolysis of the anilide. The acetamide group ($-NH-COCH_3$) is more resonance stabilised in comparison to $-NH_2$ group. Thus :

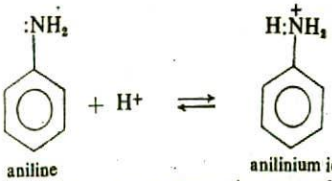


This implies that the unshared electron pair on the N atom of the acetamido group is not as available for donation to the ring by a resonance mechanism as is the pair of electrons on the amino group. Hence the ring of acetanilide is less active than the ring of aniline toward electrophilic reagents.

(2) **Nitration.** Direct nitration of an aromatic ring which contains unprotected primary or secondary amino group ($-NH_2$ or $-NHR$) is unsatisfactory because of the susceptibility of amines toward oxidation. However, such nitration of aniline, for example, by use of $HNO_3+H_2SO_4$ mixture yields *m*-nitroaniline.

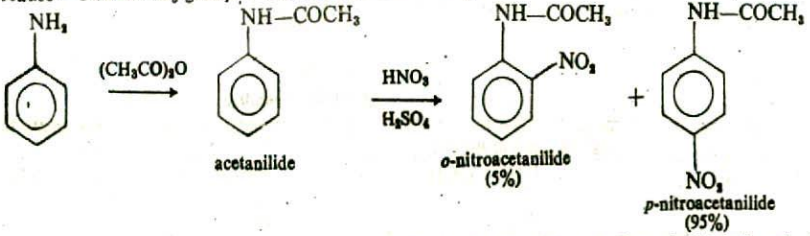


This is explained by the fact that in strong acids, aniline exists mainly as anilinium ion.



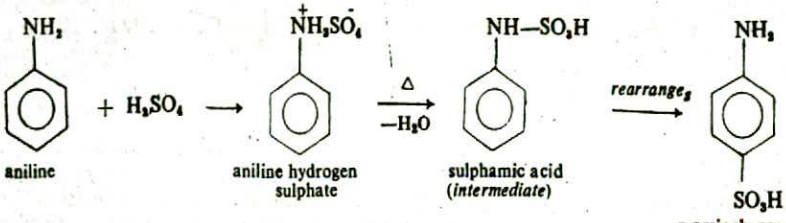
The N atom of the anilinium ion no longer has an unshared electron pair (to cause *ortho-para* direction) but has a positive charge. This directs the entering $-NO_2$ group to the meta position. However, some aniline is destroyed by oxidation of $-NH_2$ caused by nitric acid.

If it is desired to prepare *o*- or *p*-nitroaniline by nitration, it can be done by first protecting the $-NH_2$ group of aniline by acetylation. The products are *o*- and *p*-nitroacetanilide, because $-NHCOCH_3$ group is *ortho* and *para* directing.

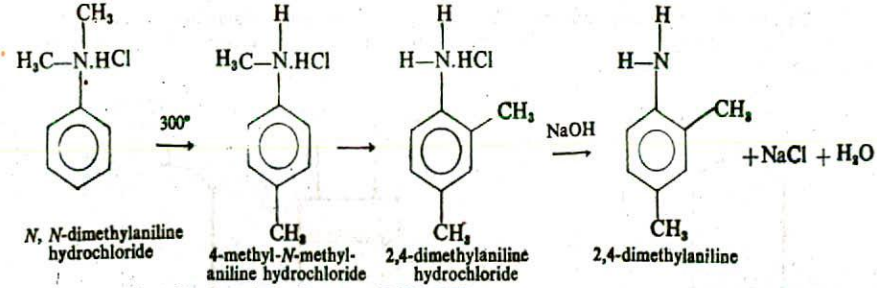


The corresponding nitroaniline is obtained by the alkaline hydrolysis of the acetanilide.

(3) **Sulphonation.** Primary aromatic amines can be sulphonated without prior protection of $-NH_2$ group, presumably because sulphuric acid is a weaker oxidising agent than nitric acid. Thus aniline can be sulphonated to give *p*-aminobenzenesulphonic acid or sulphanilic acid. Aniline reacts with sulphuric acid to form aniline hydrogen sulphate. It is assumed that heating at 180–200°C forms phenylsulphamic acid. This undergo rearrangement to yield *p*-aminobenzenesulphonic acid.



(4) **Hofmann-Martius Rearrangement.** When *N*-alkyl- or *N*, *N*-dialkylanilines are heated in strong acid media at 300°C, intermolecular migration of alkyl groups occurs. Thus when *N*,*N*-dimethylaniline hydrochloride is strongly heated, one methyl group migrates preferentially to the *para* position of the ring. The *N*-methylaniline hydrochloride so produced then undergoes migration of the remaining methyl group to the *ortho* position, since the *para* position has been blocked. This reaction is known as *Hofmann-Martius Rearrangement* and may be used for the preparation of homologues of aniline.



ANILINE, *Phenylamine*, *Aminobenzene*, $C_6H_5—NH_2$

The compound was discovered by Unverdorben in 1826 as one of the products of the destructive distillation of the naturally occurring dyestuff *indigo*. Runge (1834) demonstrated its presence in coal-tar. In 1840 Fritzsche obtained aniline by the distillation of indigo with concentrated alkali, found its formula to be C_6H_7N, and gave it the name aniline (Sanskrit, *nila*=*indigo*).

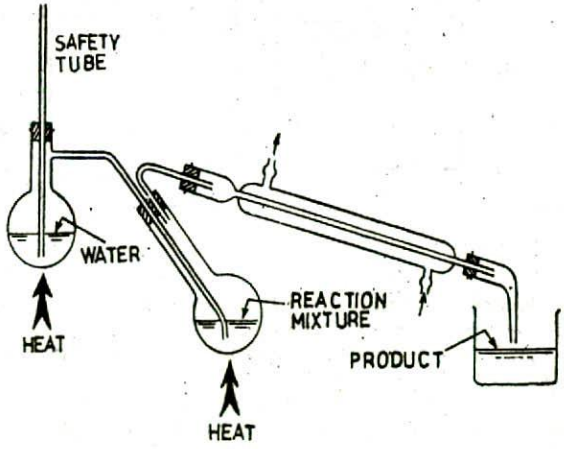


Fig. 40·6. Steam distillation to recover aniline from the reaction mixture.

Laboratory Preparation. In the laboratory aniline is prepared by the reduction of nitrobenzene with tin and hydrochloric acid. Actually the aniline is produced as a complex salt, phenylammonium chlorostannate, from which it is liberated with sodium hydroxide.

$$2\,C_6H_5{-}NO_2 + Sn + 6HCl \longrightarrow \underset{\text{phenylammonium chlorostannate}}{(C_6H_5{-}\overset{+}{N}H_3)_2SnCl_6^{2-}} + 2H_2O$$

$$(C_6H_5\overset{+}{N}H_3)_2SnCl_6^{2-} + 8NaOH \longrightarrow \underset{\text{aniline}}{2\,C_6H_5NH_2} + Na_2SnO_3 + 5H_2O + 6NaCl$$

Hydrochloric acid is gradually added to a mixture of tin and nitrobenzene, care being taken to keep the temperature below 60°C. The mixture obtained is refluxed at 100°C, until the smell of nitrobenzene has disappeared. It is then cooled and treated with aqueous NaOH solution. The complex compound, phenylammonium chlorostannate, is thus broken and aniline is liberated. The aniline is separated from the reaction mixture by steam-distillation.

Manufacture. Aniline is produced industrially by three methods.

(1) *By Vapour-Phase Reduction of Nitrobenzene.* Aniline is now prepared by the reduction of nitrobenzene with hydrogen and a copper catalyst (copper supported on silica) in the gas phase.

$$\underset{\text{nitrobenzene}}{C_6H_5{-}NO_2} + 3H_2 \xrightarrow[\Delta]{cat.} \underset{\text{aniline}}{C_6H_5{-}NH_2} + 2H_2O$$

This reaction is carried out at 270°C and 20 psi pressure, using excess of hydrogen. This process of making aniline is a continuous one and has largely superseded the traditional process described below.

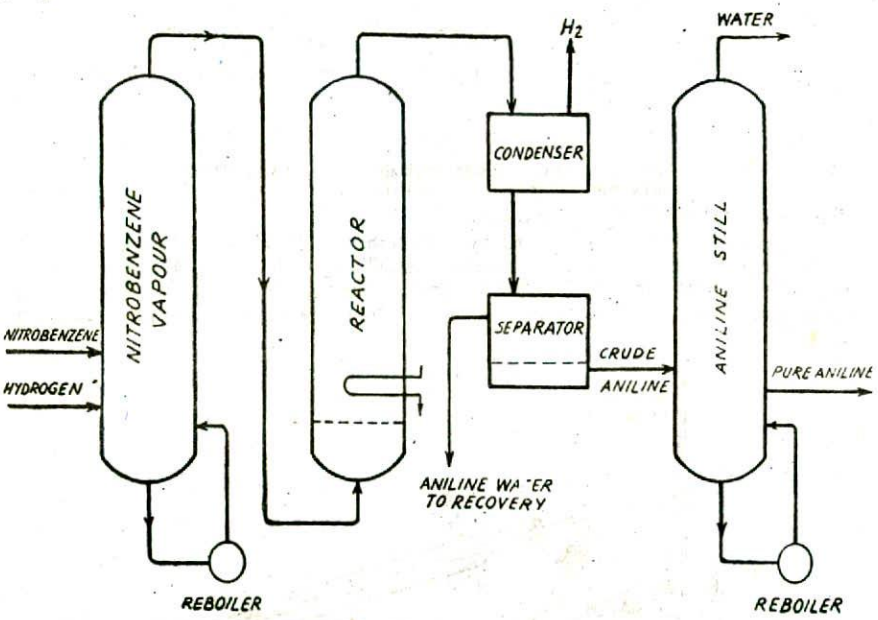


Fig. 40·7. Flowsheet of Aniline manufacture by vapour-phase reduction of nitrobenzene.

(2) *Reduction of Nitrobenzene by Fe and HCl.* This method has been used since long for the large scale production of aniline. Iron filings and hydrochloric acid is used for the reduction of nitrobenzene. This reaction, in simplified form, is as follows.

$$4\,C_6H_5{-}NO_2 + 9Fe + 4H_2O \longrightarrow 4\,C_6H_5{-}NH_2 + 3\,Fe_3O_4$$

This method has now limited application and the method (1) given above has almost replaced it.

(3) *By Ammonolysis of Chlorobenzene.* Aniline has also been manufactured by ammonolysis of chlorobenzene, using a copper catalyst (Cu_2O or $CuCl_2$) at 150—250°C.

$$C_6H_5{-}Cl + \underset{(excess)}{2NH_3} \xrightarrow[150-250^\circ]{cat.} C_6H_5{-}NH_2 + NH_4Cl$$

This process is uneconomical unless chlorobenzene is available as a byproduct fro chlorobenzene/phenol plant.

Properties. (*Physical*). Aniline is a colourless liquid, bp 184°C, mp —6°C, sp gr 1·02 at 20°C. It has a faint characteristic odour. It is sparingly soluble in water but dissolves readi in ethanol, ether and chloroform. It is steam-volatile, and hence can be steam-distilled fro a mixture containing inorganic substances. It is poisonous by penetration through skin.

(*Chemical*). Aniline molecule is made of one NH_2 group bonded to a carbon atom the benzene ring. Therefore, it undergoes two series of reactions : (*a*) those of the NH_2 group and (*b*) those of the benzene ring. At the NH_2 group, aniline behaves like the aliphatic pr mary amines, but it is only a weak base. In the benzene ring, it undergoes the usual electr philic substitution reactions in the *ortho* and *para* positions to the NH_2 group. The ami group activates the benzene ring with the result that these substitution reactions are easier carry out than in the benzene itself.

The reactions of aniline have already been discussed in detail under the general reactio of monoamines. However a resume of those reactions is given below by way of recapitulatio

REACTIONS OF —NH_2 GROUP :

(1) $+ HCl \longrightarrow \underset{\text{anilinium chloride}}{C_6H_5{-}\overset{+}{N}H_3\bar{Cl}}$

(2) $+ CH_3I \xrightarrow[(NaOH)]{} \underset{\text{N-methylaniline}}{C_6H_5{-}NH{-}CH_3} \xrightarrow[2.\ NaOH]{1.\ CH_3I} \underset{\text{N,N-dimethylaniline}}{C_6H_5{-}N(CH_3)_2} \xrightarrow{CH_3I} \underset{4^\circ \text{ salt}}{C_6H_5\overset{+}{N}(CH_3)_3}$

(3) $+ C_6H_5{-}\overset{+}{N}H_3\bar{Cl} \xrightarrow[pressure]{140^\circ} \underset{\text{diphenylamine}}{C_6H_5{-}NH{-}C_6H_5} + NH_4Cl$

(4) $+ CH_3{-}CO{-}Cl \xrightarrow[\text{or } pyridine]{NaOH} \underset{\text{acetanilide}}{C_6H_5{-}NH{-}CO{-}CH_3} + NaCl + H_2O$



aniline

(5) $+ C_6H_5{-}SO_2{-}Cl \xrightarrow{base} \underset{\substack{N\text{-phenylbenzenesulphon-}\\ \text{amide}}}{C_6H_5{-}NH{-}SO_2{-}C_6H_5} + HCl$

(6) $+ HCl \longrightarrow C_6H_5{-}\overset{+}{N}H_3\,\bar{Cl} \xrightarrow[0-5^\circ]{HNO_2} \underset{\substack{\text{benzenediazonium}\\ \text{chloride}}}{C_6H_5{-}\overset{+}{N}{\equiv}N\bar{Cl}}$

(7) $+ HO{-}NO \longrightarrow \underset{\text{phenol}}{C_6H_5{-}OH} + N_2 + H_2O$

(8) $+ C_6H_5{-}CHO \longrightarrow \underset{\text{benzylideneaniline}}{C_6H_5{-}N{=}CH{-}C_6H_5} + H_2O$

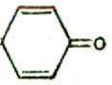
(9) $+ CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{phenyl isocyanide}}{C_6H_5{-}\overset{+}{N}{\equiv}\bar{C}} + 3KCl + 3H_2O$

(10) $+ C_6H_5{-}NH_2 + CS_2 \xrightarrow{\Delta} \underset{\text{thiocarbanilide}}{C_6H_5{-}NH{-}CS{-}NH{-}C_6H_5} + H_2O$

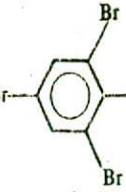
(11) $+ R{-}MgBr \longrightarrow C_6H_5{-}NH{-}\overset{+}{M}gBr\bar{} + \underset{\text{hydrocarbon}}{RH}$

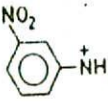
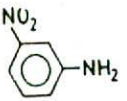
(12) + $COCl_2$ ⟶ $C_6H_5-N=C=O$ + 2 HCl
phenyl isocyanate

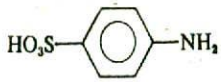
(13) + $C_6H_5-\overset{+}{N}_2\overset{-}{Cl}$ $\xrightarrow[0°C]{NaOH}$ $C_6H_5-N=N-NH-C_6H_5$ + HCl
diazoaminobenzene

(14) [O] $\xrightarrow{K_2Cr_2O_7/H_2SO_4}$ 
p-benzoquinone

SUBSTITUTION REACTIONS OF THE BENZENE RING :

(1) 
aniline
+ $3Br_2$ $\xrightarrow{H_2O}$  + 3HBr
2, 4, 6-tribromoaniline

(2)
aniline
HNO_3 $\xrightarrow{H_2SO_4}$  $\xrightarrow{aq\ NaOH}$ 
m-NITROANILINE

(3) + H_2SO_4 $\xrightarrow{\Delta}$ 
p-aminobenzenesulphonic acid

Uses. About 40,000 tons of aniline are now produced annually : (1) It was of great industrial importance in the nineteenth century as an intermediate for synthetic dyes. At present about one-sixth of the total aniline produced is used for this purpose.

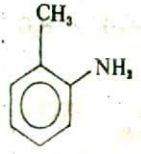
(2) About half of the aniline goes into the manufacture of rubber chemicals (antioxidants and vulcanization accelerators).

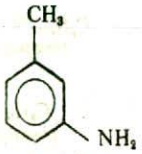
(3) The consumption of aniline for making isocyanates required for polyurethane plastics used for insulation, is ever on the increase.

(4) Other uses of aniline are for preparing : (*i*) medicines and drugs, sulpha drugs ; (*ii*) photographic chemicals (hydroquinone) ; (*iii*) several derivatives such as acetanilide, sulphanilic acid, nitroanilines, etc.

TOLUIDINES, *Aminotoluenes*, $CH_3-C_6H_4-NH_2$

The three aminotoluenes are known as toluidines

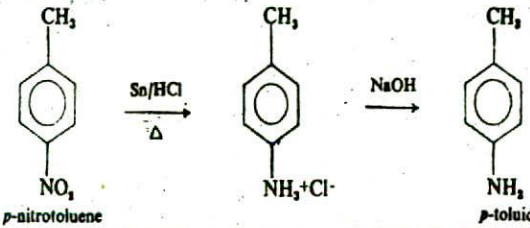

o-toluidine
(2-aminotoluene)


m-toluidine
(3-aminotoluene)


p-toluidine
(4-aminotoluene)

They are isomeric with benzylamine, $C_6H_5-CH_2-NH_2$.

Preparation. Toluidines are obtained by reducing the corresponding nitrotoluenes with a metal and acid. Thus,

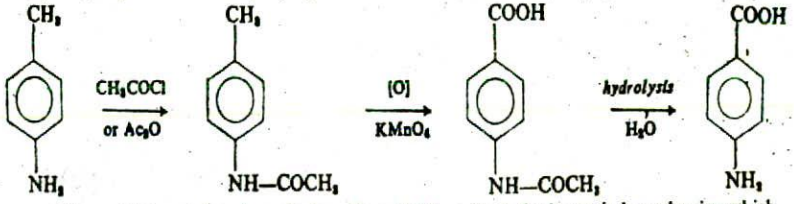


p-nitrotoluene *p*-toluidine

Properties. *o*- and *m*-Toluidines are colourless oily liquids, bp 200° and 203° C respectively. *p*-Toluidine is a white crystalline solid, mp 201° C. All toluidines are insoluble in water and soluble in most organic solvents. They are toxic.

The properties of the $-NH_2$ group are not greatly changed by the methyl group in the ring. Therefore, toluidines give all the reactions of aniline. They form salts and can be diazotised.

The oxidation of toluidines after protecting the $-NH_2$ group by acetylation and subsequent hydrolysis yields the corresponding aminobenzoic acids. For example,



This could be employed to distinguish toluidines from the isomeric benzylamine which on oxidation forms benzoic acid. *o*- and *p*-Toluidines are important dye intermediates.

SECONDARY AMINES

They may be purely aromatic or mixed aliphatic-aromatic according as both the hydrocarbon groups attached to the N atom are aryl, or one alkyl and the other aryl.

Ar—NH—Ar	Ar—NH—R
2° aromatic amine	2° aliphatic-aromatic amine

DIPHENYLAMINE, $C_6H_5-NH-C_6H_5$

Preparation. It may be prepared : (1) By heating phenol with aniline in the presence of zinc chloride at 260° C.

$$\underset{\text{phenol}}{C_6H_5-OH} + \underset{\text{aniline}}{C_6H_5-NH_2} \xrightarrow[260°]{ZnCl_2} \underset{\text{diphenylamine}}{C_6H_5-NH-C_6H_5} + H_2O$$

(2) By heating acetanilide with bromobenzene and potassium carbonate in the presence of copper powder (*Ullmann Reaction*).

$$\underset{\text{acetanilide}}{C_6H_5-NH-COCH_3} + C_6H_5Br + K_2CO_3 \xrightarrow[Reflux]{Cu} C_6H_5-NH-C_6H_5 + CH_3COOK + KBr$$

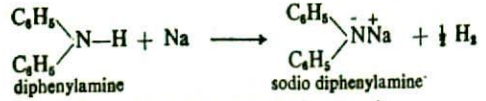
(3) By heating aniline and its hydrochloride at 140°C under pressure. (*Commercial*)

$$\underset{\text{aniline hydrochloride}}{C_6H_5-\overset{+}{N}H_3\overset{-}{Cl}} + \underset{\text{aniline}}{C_6H_5-NH_2} \xrightarrow{140°} C_6H_5-NH-C_6H_5 + NH_4Cl$$

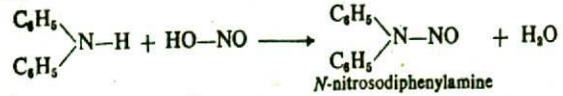
Properties. Diphenylamine is a white, pleasant-smelling crystalline solid, mp 54°C. It is practically insoluble in water but dissolves readily in ethanol and ether. In addition to the other usual reactions of aliphatic secondary amines, it shows the following reactions.

(1) Diphenylamine ($K_b = 6{\cdot}3 \times 10^{-14}$) is a weaker base than aniline ($K_b = 4{\cdot}2 \times 10^{-10}$), since it contains two phenyl groups against one in the latter. It forms salts which are completely hydrolysed in aqueous solutions.

(2) When heated with sodium or sodamide, it forms sodio derivatives more readily than does aniline.



(3) It reacts with nitrous acid to form the *N*-nitrosoamine.



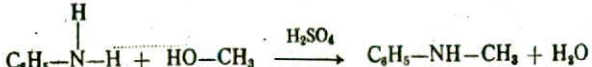
(4) Its solutions in concentrated sulphuric acid give an intense blue colour with a trace of nitrous or nitric acid or their salts. (*Test*)

Uses. Diphenylamine is used : (1) as a reagent for testing nitrites or nitrates ; (2) as internal indicator in oxidation titrations ; (3) in high-boiling baths ; (4) stabiliser for smokeless powders ; and (5) in the manufacture of phenothiazine, an intestinal disinfectant.

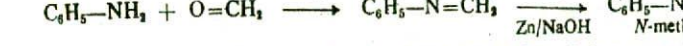
N-METHYLANILINE, *Phenylmethylaniline*, C_6H_5—NH—CH_3

It is a mixed aliphatic-aromatic secondary amine. It may be obtained by the methylation of aniline with a calculated amount of methyl iodide or dimethyl sulphate. Industrially *N*-methylaniline is prepared by the following methods.

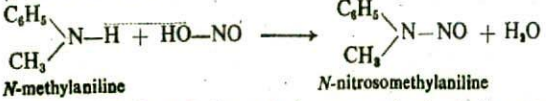
(1) By heating aniline and methyl alcohol together with some sulphuric acid under pressure.



(2) By condensing aniline with formaldehyde (CH_2=O) and reducing the product with zinc and NaOH.



Properties. *N*-methylaniline is a colourless liquid, bp 194°C. It is a somewhat stronger base ($K_b = 7{\cdot}1 \times 10^{-10}$) than aniline ($K_b = 4{\cdot}2 \times 10^{-10}$) owing to partial aliphatic character. Its reactions are those typical of aliphatic secondary amines except the substitution reaction in *o*- and *p*- positions of the benzene ring. It reacts with nitrous acid to form a pale-yellow nitrosoamine which gives Liebermann Nitroso reaction.



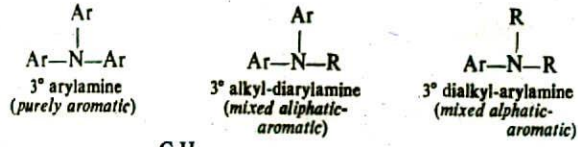
When its hydrochloride is heated, the methyl group migrates to the *para* position of the ring, forming *p*-toluidine hydrochloride.



N-Methylaniline is used for making certain dyes.

TERTIARY AMINES

They may be purely aromatic or mixed aromatic-aliphatic according as all the hydrocarbon groups attached to the N atom are aryl, or some are aryl while the remaining are alkyl.



TRIPHENYLAMINE, $(C_6H_5)_3N$

It is a typical purely aromatic tertiary amine. It may be prepared : (1) By heating diphenylamine with iodobenzene together with potassium carbonate in the presence of copper. (*Ullmann reaction*)

$$(C_6H_5)_2NH + I{-}C_6H_5 \xrightarrow[(K_2CO_3)]{Cu} (C_6H_5)_3N + HI$$

diphenylamine → triphenylamine

(2) By heating sodiodiphenylamine and bromobenzene at 300°.

$$(C_6H_5)_2NNa^+ + Br{-}C_6H_5 \xrightarrow{300^\circ} (C_6H_5)_3N + NaBr$$

sodiodiphenylamine

Properties. Triphenylamine is a colourless, crystalline solid, mp 127°C. Since the three negative phenyl groups almost completely neutralise the basic character of the trivalent N atom, it is extremely weak base ($\sim 10^{-20}$). However, its salts with HF, HBF_4, and $HClO_4$ have been prepared under special conditions. Thus,

$$(C_6H_5)_3N + HBF_4 \xrightarrow[benzene)]{(moist} (C_6H_5)_3NH^+BF_4^-$$

triphenylamine → triphenylammonium borofluorate

It dissolves in warm concentrated sulphuric acid producing an intense blue colour.

***N,N*-DIMETHYLANILINE**, $C_6H_5N(CH_3)_2$

It is a mixed aromatic-aliphatic tertiary amine and is by far the most important of the alkylanilines. It is often referred to as simply dimethylaniline.

Proparation. Dimethylaniline may be obtained : (1) By the direct methylation of aniline (1 mole) and methyl chloride (2 moles) or with dimethyl sulphate.

$$C_6H_5NH_2 + 2CH_3{-}Cl \longrightarrow C_6H_5N(CH_3)_2 + 2HCl$$

aniline → *N,N*-dimethylaniline

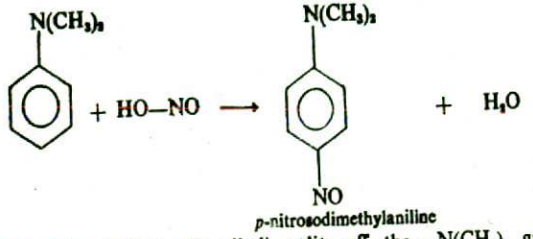
(2) By heating aniline with excess of methyl alcohol in presence of sulphuric acid

$$C_6H_5NH_2 + 2CH_3OH \xrightarrow[(excess)]{H_2SO_4} C_6H_5N(CH_3)_2 + 2H_2O$$

The excess of methyl alcohol suppresses the formation of monomethylaniline.

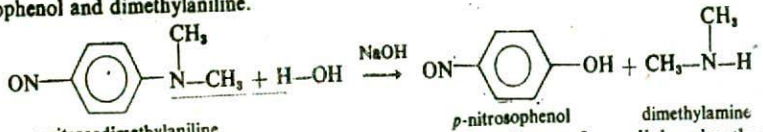
Properties. Dimethylaniline is an oily liquid, bp 193°C. As a base ($K_a = 11 \times 10^{-10}$) it is weaker than aniline ($K_b = 4{\cdot}2 \times 10^{-10}$). It combines with acids to form salts and with alkyl halides to give quaternary ammonium salts. The hydrogen atom in the para position of the ring is very reactive and can be replaced by various atoms or groups.

(1) Dimethylaniline reacts with nitrous acid to form *p*-nitrosodimethylaniline (green flakes).



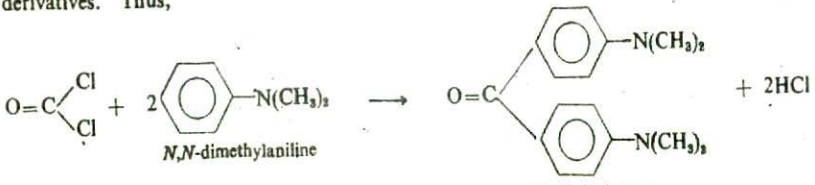
p-nitrosodimethylaniline

p-Nitrosodimethylaniline when boiled with alkali, splits off the $-N(CH_3)_2$ group, forming *p*-nitrosophenol and dimethylaniline.



p-nitrosodimethylaniline — *p*-nitrosophenol — dimethylamine

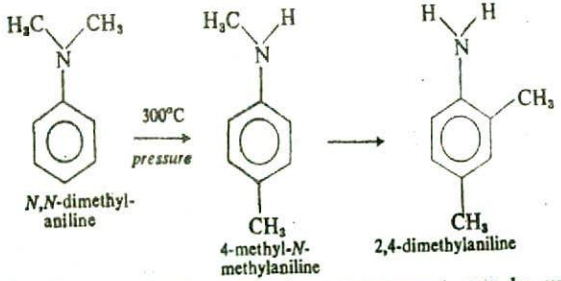
(2) It condenses with formaldehyde and carbonyl chloride to form diphenylmethane derivatives. Thus,



N,N-dimethylaniline — Michler's ketone

Michler's ketone is an intermediate in the production of dyes of the triphenylmethane class.

(3) When its hydrochloride is heated to 300°C under pressure, one or both methyl groups migrate from the N atom preferentially to the *para* position, and if it is already blocked, to the *ortho* position.



N,N-dimethyl-aniline — 4-methyl-*N*-methylaniline — 2,4-dimethylaniline

This reaction known as Hofmann-Martius rearrangement may be used to prepare nomologues of benzene by knocking out NH_2 group from the ring.

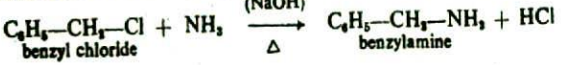
Uses. Dimethylaniline is used : (1) for preparing Michler's ketone; ; (2) for the synthesis of homologues of benzene ; and (3) in the manufacture of Methylene Blue.

ARALKYL AMINES

BENZYLAMINE, *α-Aminotoluene*, $C_6H_5-CH_2-NH_2$

It is the simplest member of the class. It is isomeric with toluidines.

Preparation. Benzylamines may be prepared : (1) By heating benzyl chloride with ammonia under pressure.



benzyl chloride — benzylamine

(2) By the reduction of phenyl cyanide or benzaldoxime with sodium and ethanol.

$$\underset{\text{phenyl cyanide}}{C_6H_5-C\equiv N} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{benzylamine}}{C_6H_5-CH_2-NH_2}$$

$$\underset{\text{benzaldoxime}}{C_6H_5-CH=N-OH} + 4[H] \xrightarrow{Na/C_2H_5OH} C_6H_5-CH_2-NH_2 + H_2O$$

(3) By Hofmann reaction from phenylacetamide.

$$\underset{\text{phenylacetamide}}{C_6H_5-CH_2-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow{Br_2/KOH} C_6H_5-CH_2-NH_2$$

Properties. Benzylamine is a colourless liquid, bp 185°C, having ammonical odour. I is freely soluble in water. It is a stronger base than aniline, being only slightly weaker tha aliphatic amines.

Benzylamine resembles the aliphatic primary amines in so far as the reactions of —NH group are concerned. In fact, it would be regarded as phenyl-substituted methylamine

(1) Since the amino group is attached to a carbon atom adjacent to the ring, the carbon nitrogen bond may be readily broken by catalytic hydrogenation

$$\underset{\text{benzylamine}}{C_6H_5-CH_2-NH_2} + H_2 \xrightarrow{\text{Raney Ni}} \underset{\text{toluene}}{C_6H_5-CH_3} + NH_3$$

(2) When heated with an acid and sodium nitrite, benzylamine gives benzyl alcoho and nitrogen gas, like aliphatic amines.

$$C_6H_5-CH_2-NH_2 + HNO_2 \longrightarrow \underset{\text{benzyl alcohol}}{C_6H_5-CH_2-OH} + N_2 + H_2O$$

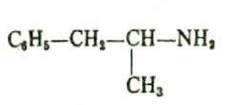
Unlike aryl amines, it does not form diazonium salts.

(3) On oxidation with potassium permanganate, it is converted to benzoic acid.

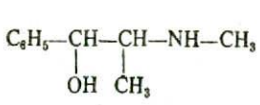
$$C_6H_5-CH_2-NH_2 \xrightarrow{[O]} \underset{\text{benzoic acid}}{C_6H_5-COOH}$$

β-PHENYLETHYLAMINE, $C_6H_5-CH_2-CH_2-NH_2$

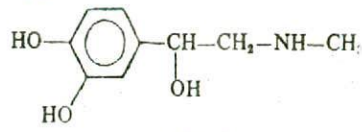
It can be obtained by the standard methods used for the preparation of aliphatic amines Its chemical reactions are also similar to them. It is particularly of interest because of its activ physical action in stimulating the sympathetic nervous system. It is the parent of a number o drugs in which the specific physiological action is markedly pro nounced.



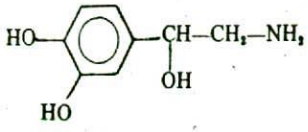
benzedrine
(produces temporary increase in alertness; lessened fatigue)



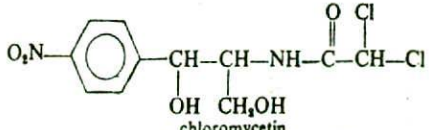
ephedrine
(used for treatment of bronchial asthma)



adrenalin
(dilates arteries, increases blood pressure ; used for treatment of bronchial asthma)



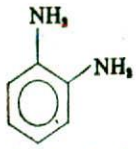
norepinephrine
(powerful bronchidilator ; used for treatment of bronchial asthma)



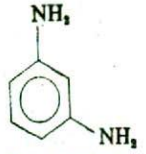
chloromycetin
(used for treatment of typhoid fever ; highly toxic)

DIAMINES

The diaminobenzenes are generally known as ***phenylenediamines***.



o- phenylenediamine
(1, 2-diaminobenzene)



m-phenylenediamine
(1, 3-diaminobenzene)

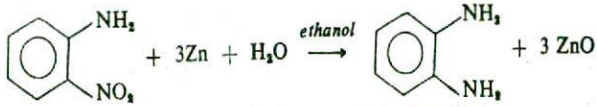


p-phenylenediamine
(1, 4-diaminobenzene)

Their methods of preparation and chemical behaviour are analogous to those of mono-nines. They give certain specific reactions due to the presence of two $-NH_2$ groups in the ıme benzene ring.

PHENYLENEDIAMINE, 1,2-*Diaminobenzene, Benzene*-1,2-*diamine*

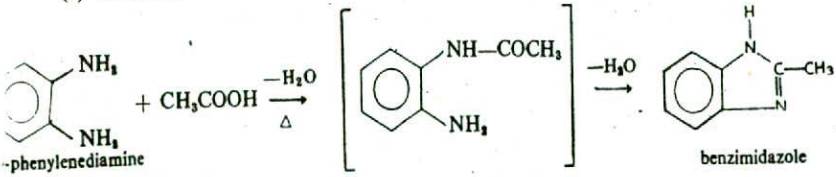
Preparation. It is best prepared by reduction of *o*-nitroaniline with zinc dust and queous ethanolic sodium hydroxide.



o-nitroaniline *o*-phenylenediamine

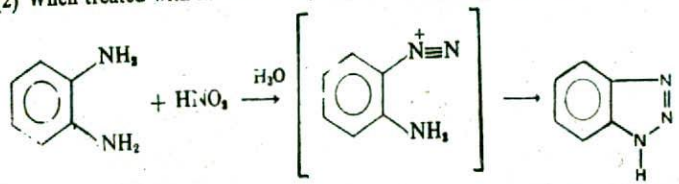
Properties. *o*-Phenylenediamine is a colourless, crystalline solids. It quickly turns rown in air due to oxidation. It gives the reactions of nuclear NH_2 group in duplicate and ehaves as a diacid base. Owing to the close proximity of the two amino groups, its most ıportant characteristic property is the ability to form condensed ring heterocyclic compounds ith suitable reagents.

(1) When heated with acetic acid, it forms *Benzimidazoles*.



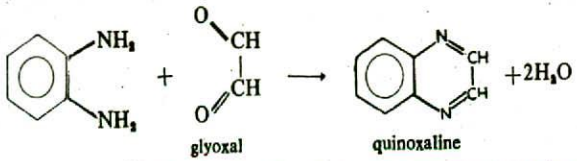
-phenylenediamine benzimidazole

(2) When treated with nitrous acid ($NaNO_2$+*aq* acetic acid) *Benztriazole* is formed.



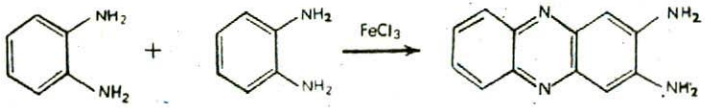
diazonium salt with CH_3COO^- (not isolated) benztriazole

(3) It condenses with glyoxal to form *Quinoxaline.*



glyoxal quinoxaline

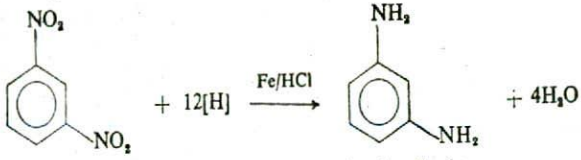
(4) When it is treated with ferric chloride solution, 2,3-diaminophenozine (*dark red*), is produced.



2,3-DIAMINOPHENOZINE
(DARK RED)

m-**PHENYLENEDIAMINE**, 1,3-*Diaminobenzene*, *Benzene*-1,3-*diamine*

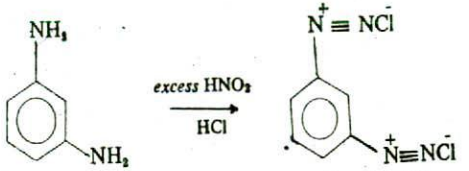
Preparation It is best obtained by the reduction of *m*-dinitrobenzene with iron and hydrochloric acid.



m-dinitrobenzene *m*-phenylenediamine

Properties. *m*-Phenylenediamine is a white crystalline solid, mp 63°C, turning brown in air. It is a diacid base and gives the usual reaction of aromatic $-NH_2$ group twice over.

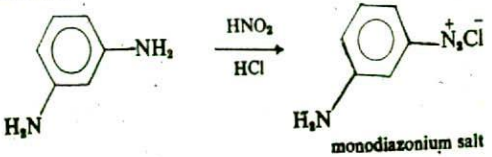
(1) When treated with excess of sodium nitrite in concentrated hydrochloric acid, *m*-phenylenediamine undergoes diazotisation at both the amino groups to form a *bis*-diazonium salt.



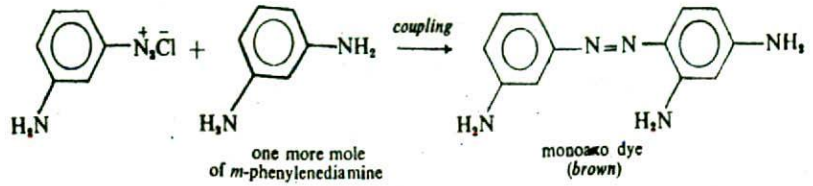
m-phenylenediamine *bis*-diazonium salt

(2) *Formation of Bismark Brown.* With limited quantities of nitrite on its aqueous solutions, the *mono*- or *bis*-diazonium salt produced reacts with more of *m*-phenylenediamine to form the brown dye **Bismark Brown.** This dye is, in fact, a mixture of two brown dyes.

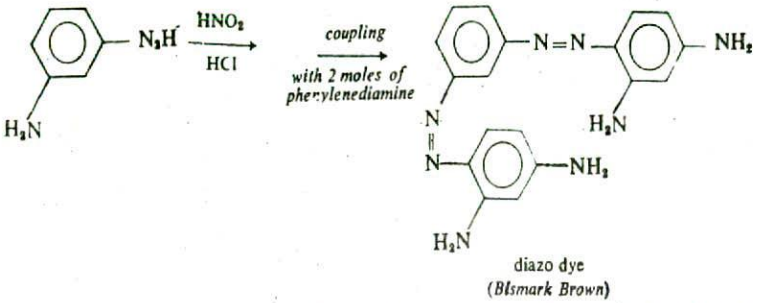
(*a*) *Monoazo dye* :



monodiazonium salt



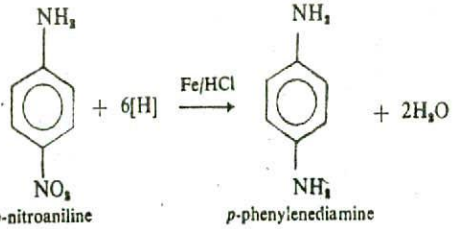
(*b*) *Diazo dye.* When both the $-NH_2$ groups in *m*-phenylenediamine are diazotised, they couple with two more molecules of *m*-phenylenediamine, giving a brown diazo dye.



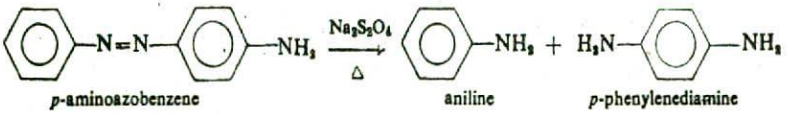
This reaction occurs even in very dilute solutions and is used in a colorimetric method for the detection and estimation of nitrites in drinking water. It is also a delicate test for nitrites in the laboratory when a yellow colour is produced even when only traces are present. Bismark Brown is a dye of considerable merit and is used for making boot polishes.

p-**PHENYLENEDIAMINE**, *1,4-Diaminobenzene, Benzene -1,4-diamine*

Preparation. (1) Like the *o*-isomer it is prepared by the reduction of *p*-nitroaniline with iron and hydrochloric acid.



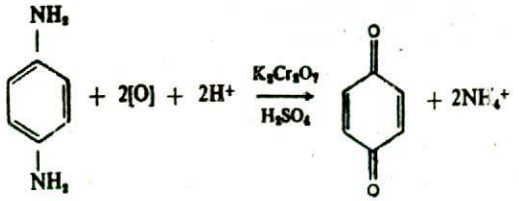
(2) It may also be obtained conveniently by the reduction of *p*-aminoazobenzene with $Na_2S_2O_4$.



Properties. *p*-Phenylenediamine is a white crystalline solid, mp 147°C.

(1) It reacts with nitrous acid in the ordinary way to form *bis*-diazonium salt which is used in the preparation of azo dyes.

(2) On vigorous oxidation with potassium dichromate and sulphuric acid, it gives *p*-benzoquinone.

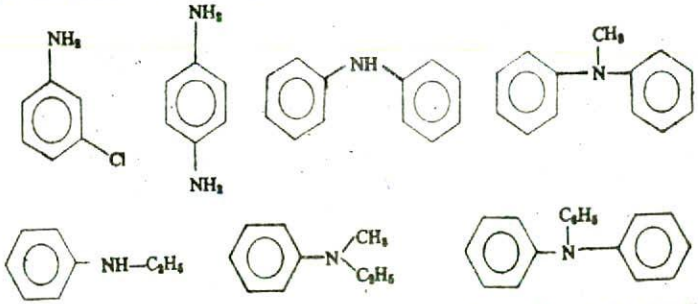


p-phenylenediamine *p*-benzoquinone

Uses. *m*-Phenylenediamine is an excellent photographic developer. It is also used as a hair dye since it is readily oxidised to a brown-black dye in alkali solution.

QUESTIONS

1. How are aromatic amines defined ? Illustrate with examples.
2. Discuss the molecular orbital structure of aromatic amines taking example of aniline. How will you represent the electronic structure of aniline ?
3. Assign names to the following amines and their derivatives.



4. Describe the methods of preparation of aromatic monoamines, taking example of aniline. How will you proceed to prepare 5-nitro-*o*-toluidine ?
5. Give outline of the following methods of preparation of aromatic amines :
   (*a*) Reductive amination ;
   (*b*) Hofmann-Martius Rearrangement ;
   (*c*) Degradation of amides;
   (*d*) Ammonolysis of aryl halides ;
   (*e*) Ammonolysis of phenols;
   (*f*) Reduction of Nitro compounds.
6. Give briefly the physical properties of aromatic amines. Why their boiling points are higher than the aliphatic amines of comparable molecular weights ?
7. Discuss the relative basic character of ammonia, methylamine and aniline. Explain the weak basic character of aniline in particular.
8. How is basicity of aniline affected by substituents on the benzene ring or on the nitrogen atom ?
9. Give the general chemical reactions of aryl amines ?
10. Write notes on : (*a*) Action of nitrous acid on aromatic 1°, 2° and 3° amines; (*b*) Reaction of aromatic amines with aldehydes; (*c*) Fischer-Hopp Rearrangement; (*d*) Acylation of aryl amines.
11. How do you explain the activation of benzene ring to electrophilic attack as also the *ortho* and *para* directive influence of $-NH_2$ group ?
12. How is aniline prepared on a laboratory scale and on a commercial scale ? Summarise its chemical reactions.
13. Give the preparation, properties and uses of toluidines, diphenylamine, *N*-methylaniline, and triphenylamine.

14. Give one method of synthesis of β-phenylmethylamine. Name the important drugs derived from it.

15. Write a note on phenylenediamines. How is Bismark Brown prepared ?

16. Explain : Aromatic amines are weaker bases than ammonia. (*Panjab BSc, 1994*)

17. How is *N,N*-dimethylaniline prepared ? Describe any one method of preparation of phenylhydrazine. How is benzylamine prepared ? (*Bombay BSc, 1993*)

18. (*a*) How is aniline obtained from nitrobenzene ? (*b*) How does aniline react with the following reagents :

(*i*) Acetic anhydride, (*ii*) Benzoyl chloride, (*iii*) $CHCl_3$/alc. KOH, and (*iv*) Sodium nitrite/HCl (*Annamalai BSc, 1993*)

19. What happens when aniline is heated with ethyl acetate at 110°C in the presence of concentrated H_2SO_4 ? (*Baroda BSc, 1993*)

20. How will you synthesise benzylamine from benzene ? (*Saugar BSc, 1994*)

21. How will you synthesise aniline from benzoic acid ?

Hint. Use the following steps : (*i*) $SOCl_2$, (*ii*) NH_3, and (*iii*) Br_2/NaOH. (*Patna BSc, 1993*)

22. How will you distinguish between :

(*a*) Aniline and benzylamine ; and (*b*) Benzy lamine and benzamide. (*Magadh BSc Hons, 1994*)

Hint. (*a*) Aniline reacts with nitrous acid ($NaNO_2$/HCl/0-5°C) to form a diazonium salt which gives red azo dye with 2-naphthol in NaOH solution; and (*b*) Benzylamine dissolves in dilute HCl at room temperature.

23. How will you distinguish between aniline and *N, N*-dimethylaniline ? (*Banaras BSc, 1994*)

Hint. Use Hinsberg test. Aniline (1°amine) reacts with benzenesulphonyl chloride to give a solid sulphonamide derivative which is soluble in NaOH solution. *N,N*-Dimethylaniline (3° amine) does not react with benzenesulphonyl chloride.

24. Explain : Ethylamine is a stronger base than aniline. (*Poona BSc, 1993*)