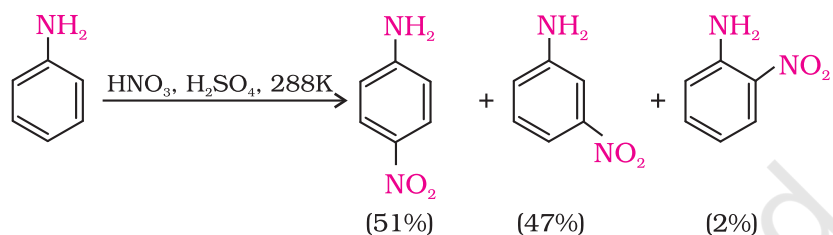
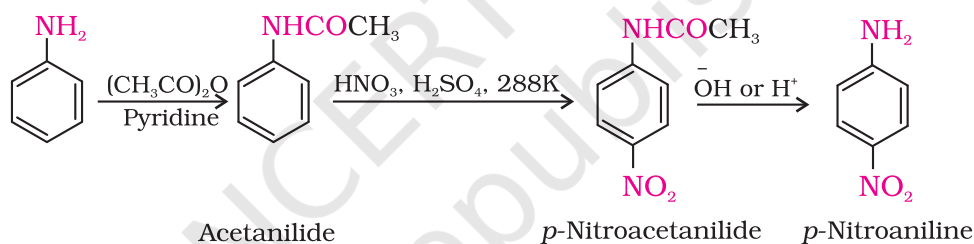


Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance. Therefore, activating effect of  $-\text{NHCOCH}_3$  group is less than that of amino group.

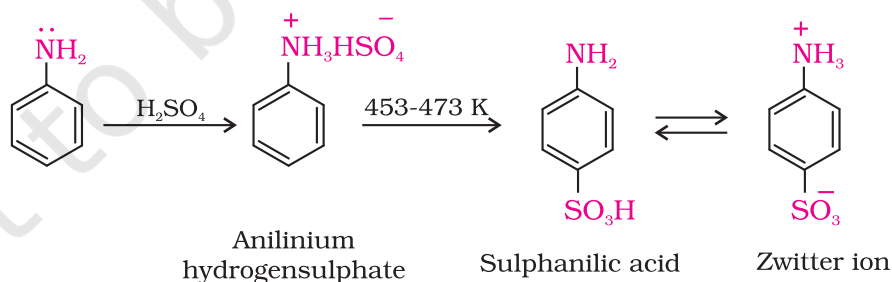
**(b) Nitration:** Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives. Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is *meta* directing. That is why besides the *ortho* and *para* derivatives, significant amount of *meta* derivative is also formed.



However, by protecting the  $-\text{NH}_2$  group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the *p*-nitro derivative can be obtained as the major product.



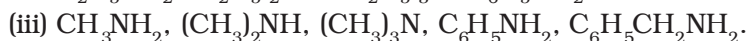
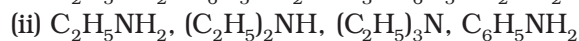
**(c) Sulphonation:** Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate which on heating with sulphuric acid at 453-473K produces *p*-aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product.



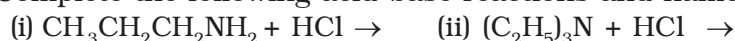
Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

### Intext Questions

13.4 Arrange the following in increasing order of their basic strength:



13.5 Complete the following acid-base reactions and name the products:



13.6 Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

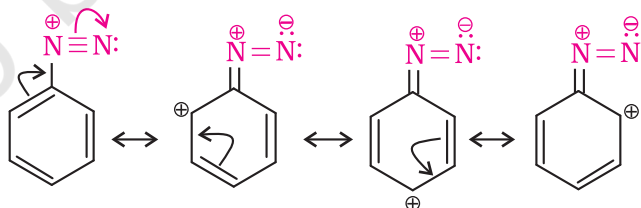
13.7 Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

13.8 Write structures of different isomers corresponding to the molecular formula,  $C_3H_9N$ . Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

## II. DIAZONIUM SALTS

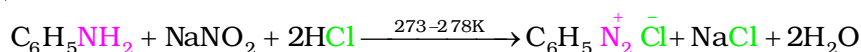
The diazonium salts have the general formula  $RN_2^+ X^-$  where R stands for an aryl group and  $X^-$  ion may be  $Cl^-$ ,  $Br^-$ ,  $HSO_4^-$ ,  $BF_4^-$ , etc. They are named by suffixing diazonium to the name of the parent hydrocarbon from which they are formed, followed by the name of anion such as chloride, hydrogensulphate, etc. The  $N_2^+$  group is called diazonium group. For example,  $C_6H_5N_2^+ Cl^-$  is named as benzenediazonium chloride and  $C_6H_5N_2^+ HSO_4^-$  is known as benzenediazonium hydrogensulphate.

Primary aliphatic amines form highly unstable alkyldiazonium salts (refer to Section 13.6). Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (273-278 K). The stability of arenediazonium ion is explained on the basis of resonance.



### 13.7 Method of Preparation of Diazonium Salts

Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid at 273-278K. Nitrous acid is produced in the reaction mixture by the reaction of sodium nitrite with hydrochloric acid. The conversion of primary aromatic amines into diazonium salts is known as **diazotisation**. Due to its instability, the diazonium salt is not generally stored and is used immediately after its preparation.



## 13.8 Physical Properties

Benzenediazonium chloride is a colourless crystalline solid. It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state. Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

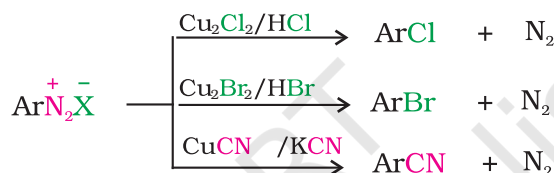
## 13.9 Chemical Reactions

The reactions of diazonium salts can be broadly divided into two categories, namely (A) reactions involving displacement of nitrogen and (B) reactions involving retention of diazo group.

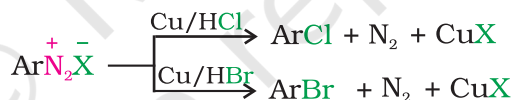
### A. Reactions involving displacement of nitrogen

Diazonium group being a very good leaving group, is substituted by other groups such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$  and  $\text{OH}^-$  which displace nitrogen from the aromatic ring. The nitrogen formed escapes from the reaction mixture as a gas.

1. *Replacement by halide or cyanide ion:* The  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{CN}^-$  nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion. This reaction is called **Sandmeyer reaction**.

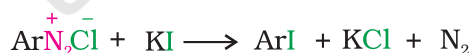


Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as **Gatterman reaction**.



The yield in Sandmeyer reaction is found to be better than Gattermann reaction.

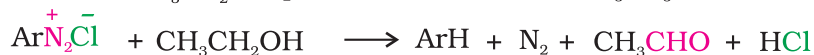
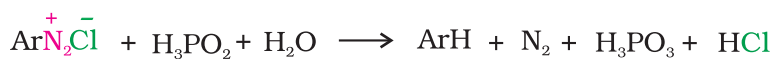
2. *Replacement by iodide ion:* Iodine is not easily introduced into the benzene ring directly, but, when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.



3. *Replacement by fluoride ion:* When arenediazonium chloride is treated with fluoroboric acid, arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.



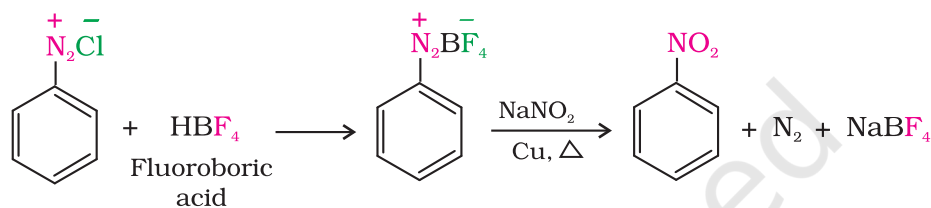
4. *Replacement by H:* Certain mild reducing agents like hypophosphorous acid (phosphinic acid) or ethanol reduce diazonium salts to arenes and themselves get oxidised to phosphorous acid and ethanal, respectively.



5. *Replacement by hydroxyl group*: If the temperature of the diazonium salt solution is allowed to rise upto 283 K, the salt gets hydrolysed to phenol.

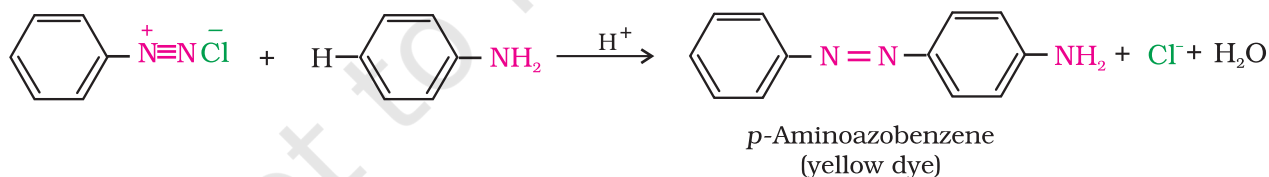
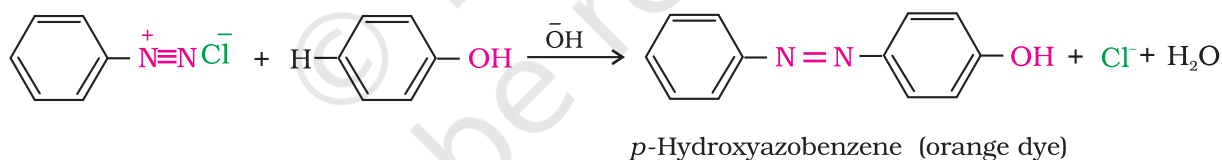


6. *Replacement by -NO<sub>2</sub> group*: When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by -NO<sub>2</sub> group.



### B. Reactions involving retention of diazo group coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the -N=N- bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form *p*-hydroxyazobenzene. This type of reaction is known as coupling reaction. Similarly the reaction of diazonium salt with aniline yields *p*-aminoazobenzene. This is an example of electrophilic substitution reaction.



### 13.10 Importance of Diazonium Salts in Synthesis of Aromatic Compounds

From the above reactions, it is clear that the diazonium salts are very good intermediates for the introduction of -F, -Cl, -Br, -I, -CN, -OH, -NO<sub>2</sub> groups into the aromatic ring.

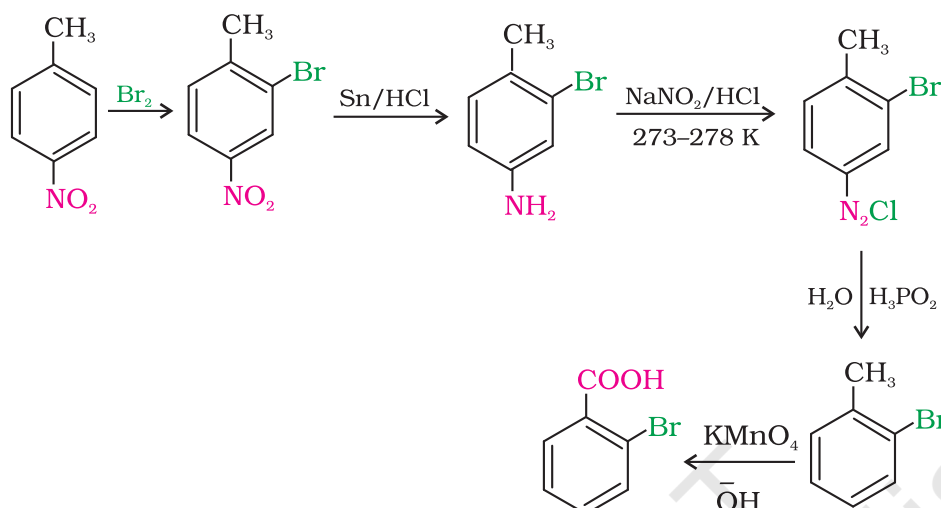
Aryl fluorides and iodides cannot be prepared by direct halogenation. The cyano group cannot be introduced by nucleophilic substitution of chlorine in chlorobenzene but cyanobenzene can be easily obtained from diazonium salt.

Thus, the replacement of diazo group by other groups is helpful in

preparing those substituted aromatic compounds which cannot be prepared by direct substitution in benzene or substituted benzene.

How will you convert 4-nitrotoluene to 2-bromobenzoic acid ?

*Example 13.5*



*Solution*

*Intext Question*

**13.9** Convert

- 3-Methylaniline into 3-nitrotoluene.
- Aniline into 1,3,5-tribromobenzene.

*Summary*

**Amines** can be considered as derivatives of ammonia obtained by replacement of hydrogen atoms with alkyl or aryl groups. Replacement of one hydrogen atom of ammonia gives rise to structure of the type  $\text{R-NH}_2$ , known as **primary amine**. **Secondary amines** are characterised by the structure  $\text{R}_2\text{NH}$  or  $\text{R-NHR}'$  and **tertiary amines** by  $\text{R}_3\text{N}$ ,  $\text{RNR}'\text{R}''$  or  $\text{R}_2\text{NR}'$ . Secondary and tertiary amines are known as simple amines if the alkyl or aryl groups are the same and mixed amines if the groups are different. Like ammonia, all the three types of amines have one unshared electron pair on nitrogen atom due to which they behave as **Lewis bases**.

Amines are usually formed from nitro compounds, halides, amides, imides, etc. They exhibit hydrogen bonding which influence their physical properties. In **alkylamines**, a combination of electron releasing, steric and H-bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. Alkyl amines are found to be stronger bases than ammonia. In **aromatic amines**, electron releasing and withdrawing groups, respectively increase and decrease their basic character. **Aniline** is a weaker base

