

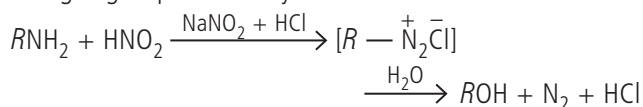
EXAM
 DRILL

Amines

ANSWERS

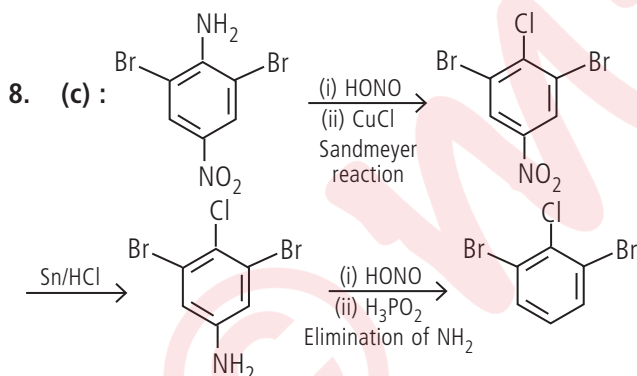
1. Sulphanilic acid
2. *p*-Benzoquinone
3. *N,N*-Dimethylbenzenamine
4. Benzenesulphonyl chloride
5. 3° Amine

6. (a) : Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohols.



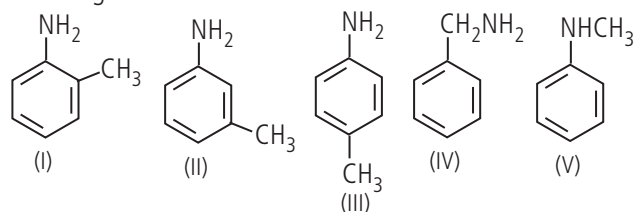
Aromatic amine, secondary and tertiary amines react with nitrous acid in a different manner.

7. (d) : $C_6H_5NH_2 + COCl_2 + KOH \rightarrow C_6H_5NHCOCI + HCl$
 $\xrightarrow{\Delta} C_6H_5NCO + HCl$



9. (b) : Amines are fairly polar, but they boil at temperature lower than those of alcohols of similar chain length and structure. Amines do have higher boiling than alkanes because they possess H-bond donor and acceptors.

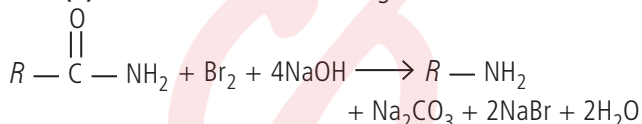
10. (b) : C₇H₉N having one benzene ring may be represented as C₆H₅CH₂N, may be in the form of 1° and 2° amines in the following five isomeric forms.



11. (b)

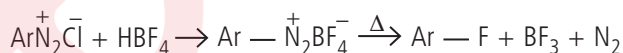
12. (a) : Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

13. (a) : Hoffmann bromamide degradation reaction.



14. (d) : Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules.

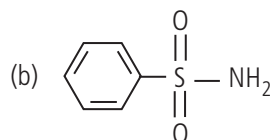
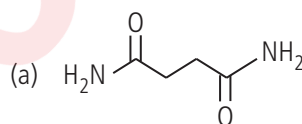
15. (c) : When arene diazonium chloride is treated with fluoroboric acid, arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.



16. (a) *N*-methylbenzamide

(b) Dibenzamide

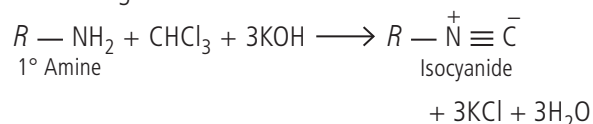
OR



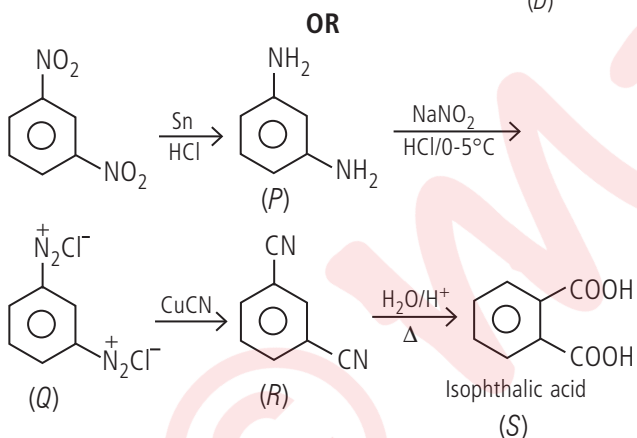
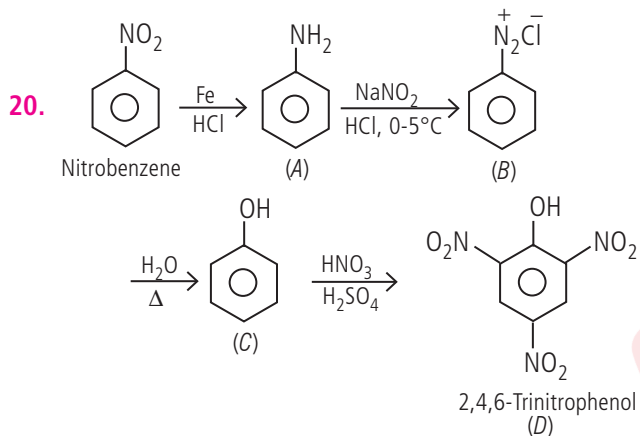
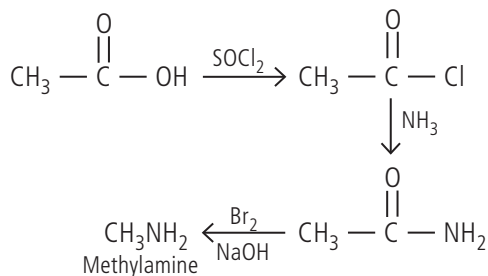
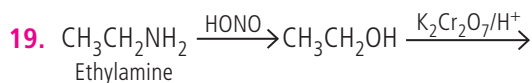
17. (a) This is because amines are polar compounds and form intermolecular hydrogen bond. For example, ethylamine, C₂H₅NH₂, boils at +17°C and propane, C₃H₈ at -42°C.

(b) This is because they are capable of forming hydrogen bonds with water.

18. Carbylamine reaction : Primary amines react with chloroform and a solution of KOH in ethanol to form isocyanides (isonitriles or carbylamine). Secondary and tertiary amines do not give this reaction.



The isocyanides or carbylamines are foul-smelling and can be easily detected. This reaction is used to distinguish primary amines from secondary and tertiary amines.



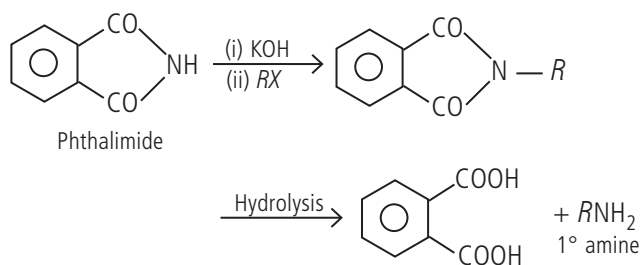
21. Reaction of carboxylic acid with ammonia and heat followed by Hoffmann bromamide reaction.



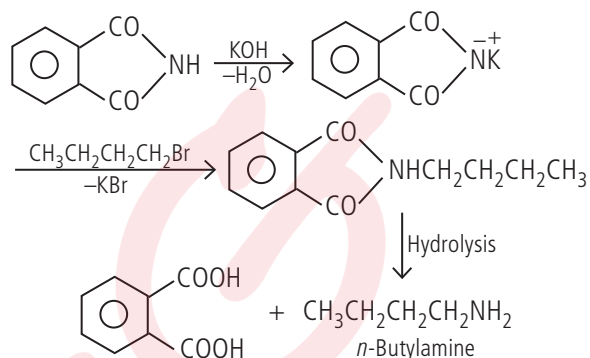
22.

Test	$\text{CH}_3\text{CH}_2\text{NH}_2$ Ethylamine	$(\text{CH}_3)_2\text{NH}$ Dimethylamine
Carbylamine reaction (with $\text{CHCl}_3 + \text{KOH}$)	It gives a foul smelling compound with $\text{CHCl}_3 + \text{KOH}$	It does not give any foul smell.

23. Gabriel phthalimide synthesis is used for preparing only primary amines. Phthalimide is first treated with KOH and then with alkyl halide to form *N*-alkyl phthalimide. *N*-alkylphthalimide on hydrolysis gives primary amine.



OR



24. 1. Aromatic (and aliphatic amines) owe their basicity due to the lone pair of electrons on nitrogen.

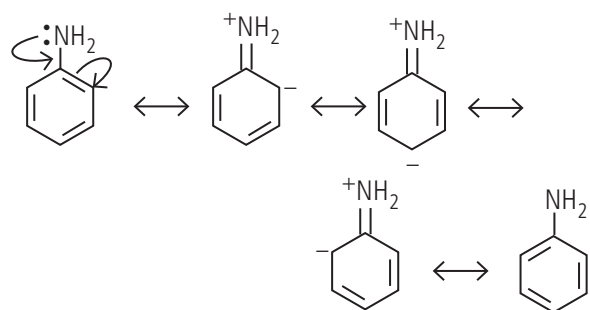
2. In determining the relative basicities, the availability of the nitrogen lone pair electrons for donation of H^+ plays the key role. Anything that withdraws electron density from nitrogen decrease basicity. While anything that releases electron density on nitrogen increases basicity.

3. Electron-releasing groups ($-\text{CH}_3$, $-\text{OCH}_3$, $-\text{NH}_2$) increases the basicity of aromatic amines.

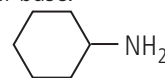
4. Electron-withdrawing groups ($-\text{NO}_2$, $-\text{Br}$, $-\text{COOH}$) decrease the basicity of aromatic amines.

OR

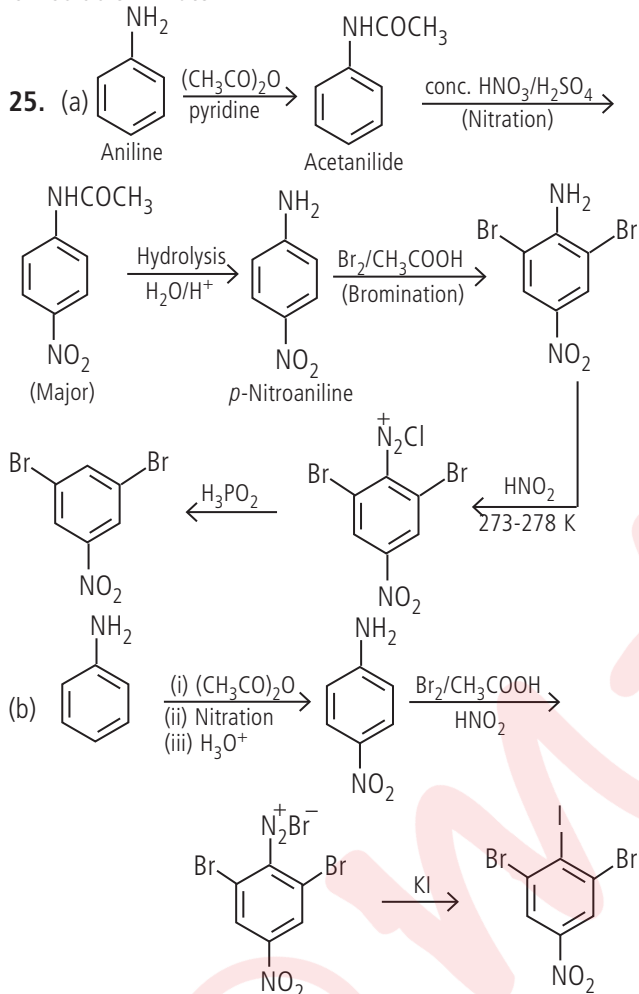
(i) In aniline, the lone pair of N in NH_2 is completely delocalised with the benzene ring. As a result, N acquires a positive charge and electron density on N atom decreases and make it less basic.



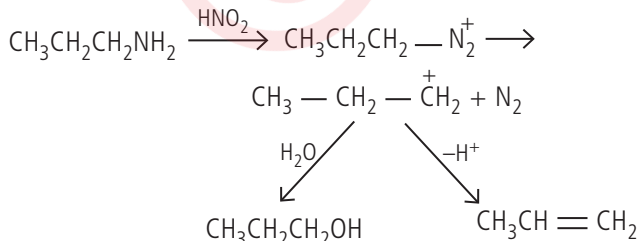
In cyclohexyl amine, cyclohexyl group has +I effect and is electron-releasing. It increases the electron density on N atom and make it a stronger base.



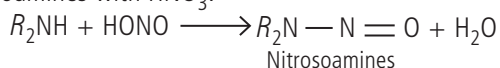
(ii) Ethylamine is soluble in water due to formation of intermolecular hydrogen bonds with water molecules. However, in aniline due to large hydrophobic aryl group the extent of hydrogen bonding decreases considerably and hence aniline is insoluble in water.



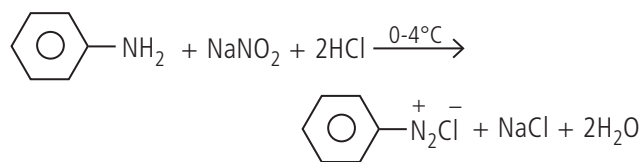
26. Primary aliphatic amines with HNO_2 gives first diazonium salts which are unstable and decompose to liberate N_2 gas and give carbonium ion. The carbonium ion in aqueous medium form an alcohol or lose H^+ form an alkene.



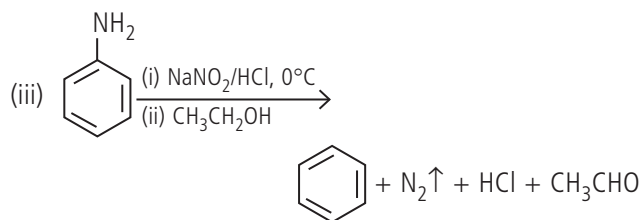
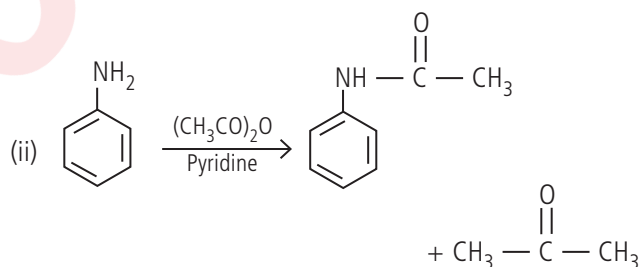
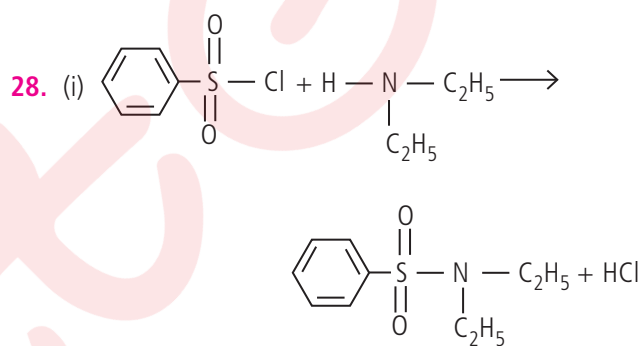
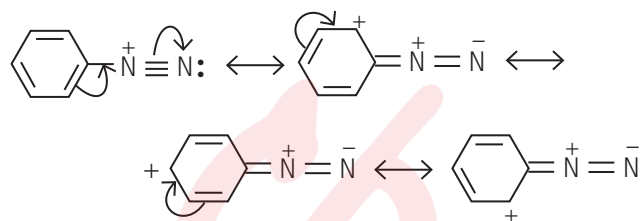
Secondary aliphatic amine gives yellow coloured oily N-nitrosoamines with HNO_3 .



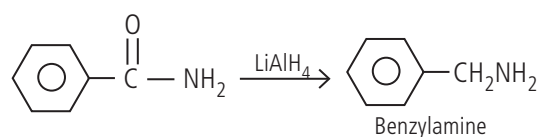
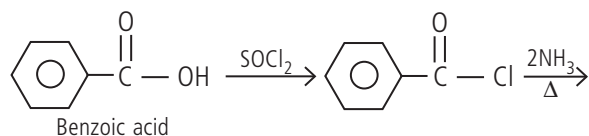
27. (i) Benzene diazonium chloride is obtained by treating aniline with NaNO_2 and HCl in ice cold solution. The reaction is called diazotisation.

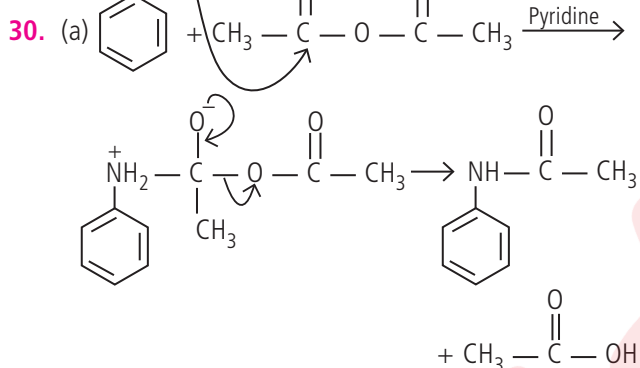
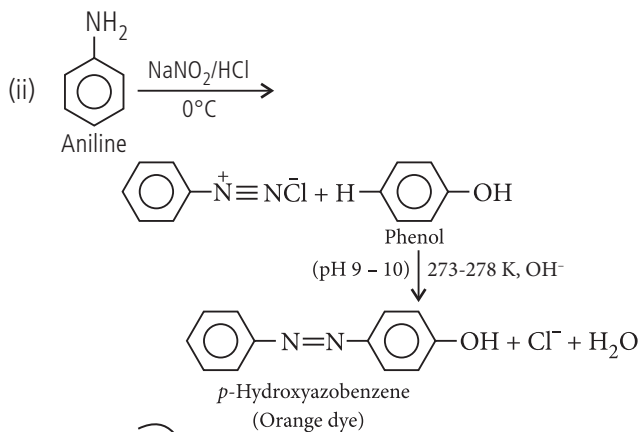


(ii) Aryl diazonium ions $\text{C}_6\text{H}_5\text{N}_2^+$ is more stable than $\text{R}-\text{N}_2^+$ due to resonance.



29. (i) Following steps are involved:

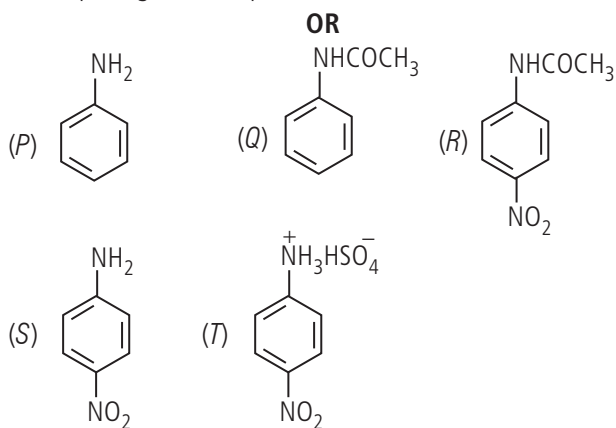




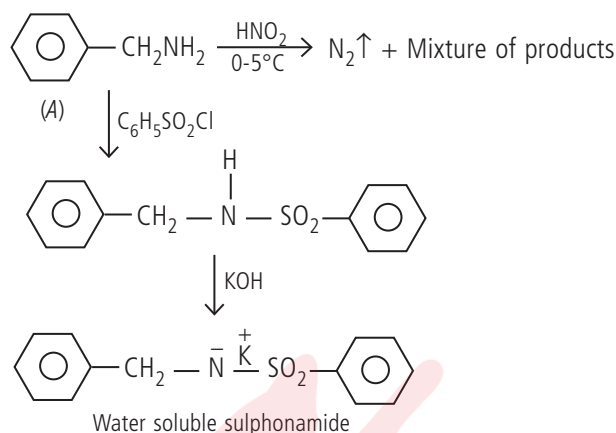
Reactivity of aromatic amines is very high so when acetylation of aniline occurs with acid anhydride it gets converted into acetanilide in which l.p. on nitrogen is in conjugate ion with oxygen atom due to resonance hence the reactivity reduce.

(b) $\text{CH}_3\text{-NH}_2$ is more basic than $\text{C}_6\text{H}_5\text{-NH}_2$ because in case of aniline the lone pair of -NH_2 (amino group) is in conjugation with benzene ring due to which e^- density is less available on N-atom hence higher the electron density on N-atom, more will be the basicity.

(c) Nitration is carried out with conc. HNO_3 in the presence of conc. H_2SO_4 . In the presence of these acids, the -NH_2 group of aniline gets protonated and is converted into -NH_3^+ group. This positively charged group acts as a strong electron withdrawing and *meta*-directing group. Hence, the incoming electrophile goes to *m*-position.



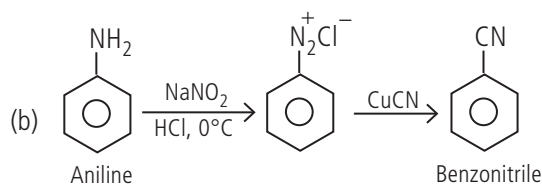
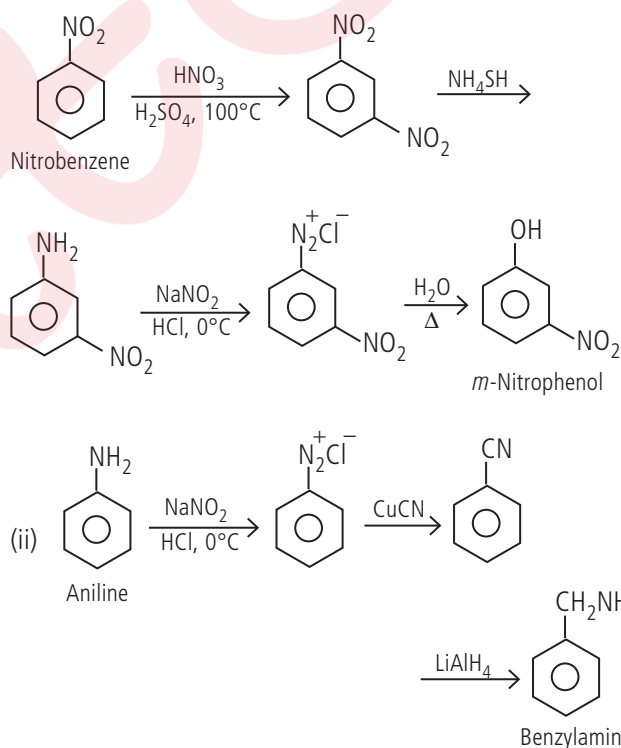
31. (a) : The compound (A) is benzylamine.



(b) (i) *N*-phenylpropan-2-amine
(ii) 4-methylbenzenamine

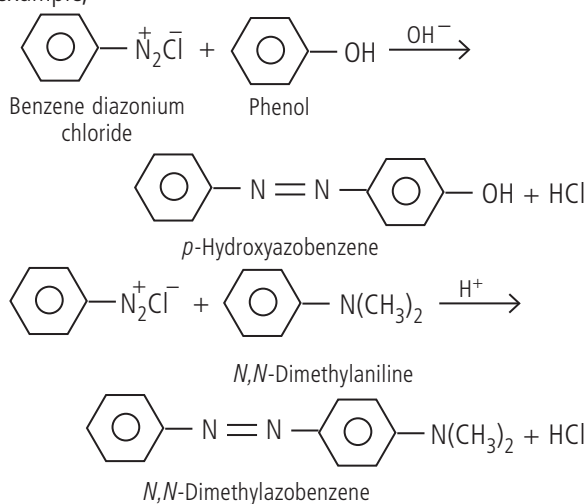
OR

(a) (i) Following steps are involved.



32. Diazo coupling reactions : Diazonium salts react readily with phenols and dialkylamines ($\text{C}_6\text{H}_5\text{NR}_2$) to form highly coloured derivatives known as azo compounds, Ar-N=N-Ar .

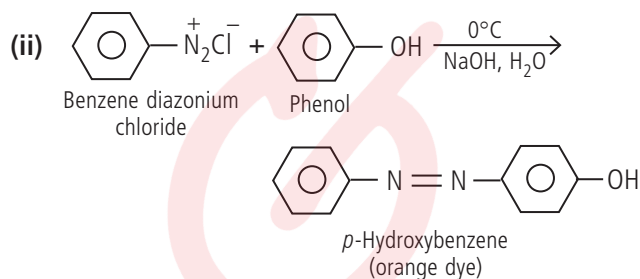
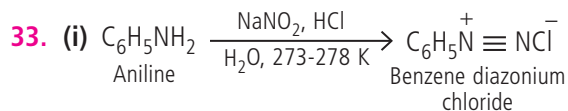
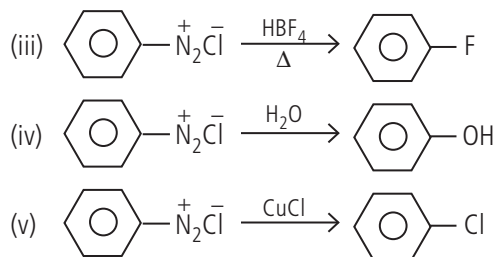
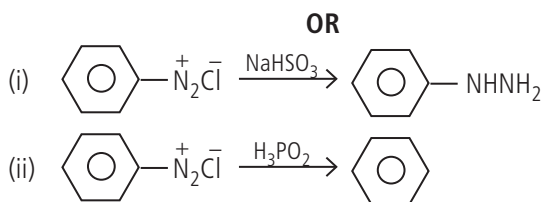
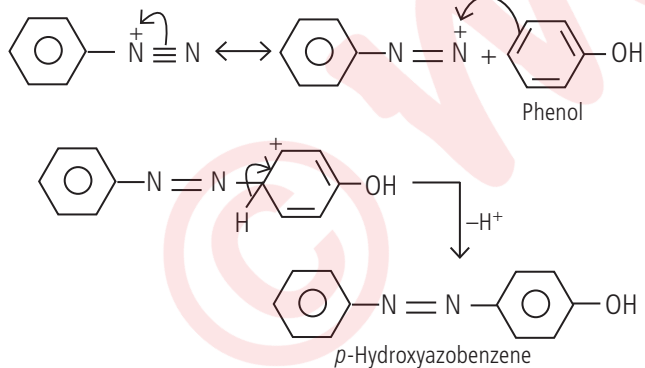
For example,



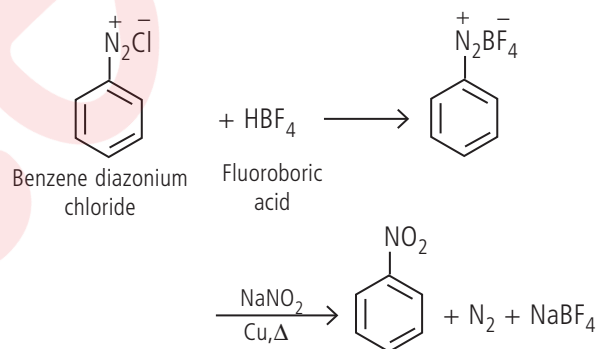
Such reactions in which the diazonium ion is joined or 'coupled' to the ring of a phenol or an aromatic amine are called diazo coupling reactions. While the coupling with phenols is carried in slightly alkaline solution, the coupling with aromatic amines is carried in slightly acidic solutions.

Mechanism:

Diazo coupling reactions take place by a typical electrophilic aromatic substitution mechanism. The benzene diazonium ion acts as an electrophile and attacks the *para* position of phenols and aromatic amines. Phenols and aromatic amines are activated compounds. The $-\text{OH}$ and $-\text{NH}_2$ groups increase the electron density of the ring at the *ortho* and *para* positions.



(iii) The major product obtained is nitrobenzene.



(iv) Aryl chloride and bromide can also be prepared by Gattermann reactions which involves the treatment of diazonium salt with Cu/HCl or Cu/HBr respectively.

