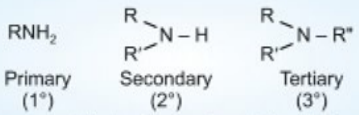
# Amines

13 Chapter

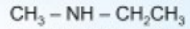
## 1 CLASSIFICATION




- Amines are said to be simple when all the alkyl groups are same and mixed when they are different.

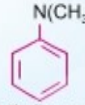
## 2 NOMENCLATURE


Propan-2-amine



N-methylethanamine


Propan-2-en-1-amine



N,N-Dimethylbenzenamine

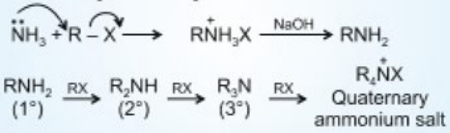
## 3 PREPARATION OF AMINES

**(i) Reduction of nitro compounds**

a. $PhNO_2 \xrightarrow[Ethanol]{H_2/Pd} PhNH_2$

b. $PhNO_2 \xrightarrow[or\ Fe + HCl]{Sn/HCl} PhNH_2$

**(ii) Ammonolysis of Alkyl Halides**




- Ammonolysis has disadvantage of yielding a mixture of primary, secondary, tertiary amines and also quaternary ammonium salt
- Primary amine is obtained as major product by taking large excess of $NH_3$.

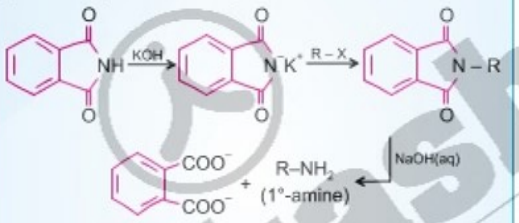
**(iii) Reduction of Nitrites**

$$R{-}CN \xrightarrow[or\ H_2/Ni\ or\ Na(Hg)/C_2H_5OH]{LiAlH_4} R{-}CH_2{-}NH_2$$

**(iv) Reduction of amides**

$$R{-}\overset{O}{\overset{\|}{C}}{-}NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R - CH_2 - NH_2$$

**(v) Gabriel phthalimide Synthesis**




- This method is useful in the preparation of aliphatic primary amine
- Aromatic primary amine  is not prepared by this method because arylhalide donot undergo nucleophilic substitution reaction.

**(vi) Hoffmann bromamide degradation reaction**

$$R{-}\overset{O}{\overset{\|}{C}}{-}NH_2 + Br_2 + 4NaOH \longrightarrow R - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

- Primary amine formed contains one carbon less than that present in the amide.

## 4 PHYSICAL PROPERTIES

- Aniline and other arylamines are usually colourless but get colour on storage due to atmospheric oxidation
- Lower aliphatic amines are soluble in water because they form hydrogen bonds with water molecules.
- Order of boiling points of isomeric amines: Primary > Secondary > Tertiary

## 5 CHEMICAL REACTIONS

**(i) Basic character of amines**

- Order of bascity of amines in gaseous phase:

  tertiary amine > secondary amine > primary amine > $NH_3$
- Basic nature of amines in aqueous medium:

  (a) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

  (b) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
- Aryl amines are less basic than alkylamines because in arylamine the lone pair on nitrogen is involved in resonance.

**(ii) Alkylation**

$$R - \ddot{N}H_2 + CH_3 - Br \longrightarrow RNH - CH_3 + HBr$$

**(iii) Acylation**

$$C_2H_5\ddot{N}H_2 + CH_3 - \overset{O}{\overset{\|}{C}} - Cl \xrightarrow{Base} C_2H_5 - NH - \overset{O}{\overset{\|}{C}} - CH_3 + HCl$$

**(iv) Carbylamine reaction (chemical test)**

$$R - NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R - NC + 3KCl + 3H_2O$$

It is used as a test for primary amines

**(v) Reaction with nitrous acid** (With primary aliphatic amine)

$$R - NH_2 + HNO_2 \xrightarrow[HCl]{NaNO_2} [R - \overset{\oplus}{N_2}Cl^-] \xrightarrow{H_2O} ROH + N_2 + HCl$$

**(vi) Reaction with arylsulphonyl chloride (Hinsberg's reagent)**

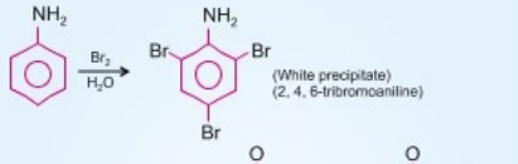
- Reaction with primary amine

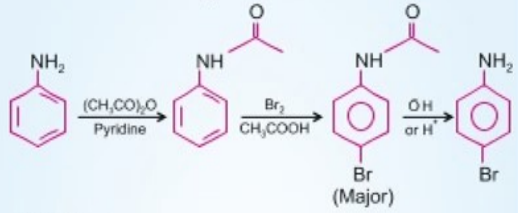
  $PhSO_2Cl + C_2H_5\ddot{N}H_2 \longrightarrow PhSO_2NHC_2H_5$ (Soluble in alkali)
- Reaction with secondary amine

  $PhSO_2Cl + (C_2H_5)_2\ddot{N}H \longrightarrow PhSO_2N(C_2H_5)_2$ (insoluble in alkali)
- Tertiary amines do not react with benzensulphonyl chlorides.

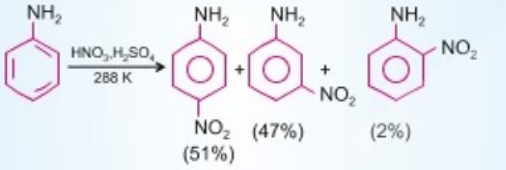
**(vii) Electrophilic substitution reaction:**

**(a) Bromination**

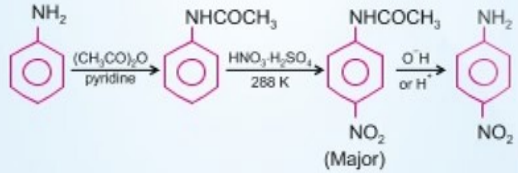



**(b) Nitration**



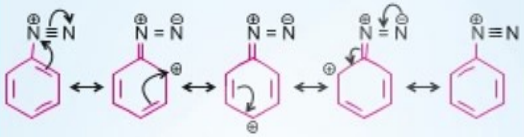

- Controlled nitration reaction




**(c) Sulphonation**


## 6 DIAZONIUM SALTS

- Primary aliphatic amines form highly unstable alkyldiazonium salts.
- Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperature (273-278 K) due to resonance



**(i) Method of preparation of $C_6H_5\overset{\oplus}{N}_2Cl^{\ominus}$**

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278\ K} C_6H_5\overset{\oplus}{N}_2Cl^{\ominus}$$

**(ii) Physical properties**

- Benzenediazonium chloride is colourless crystalline solid and readily soluble in water.
- It is stable in cold but reacts with water when warmed.
- Benzenediazonium Fluoroborate is water insoluble and stable at room temperature.

**(iii) Chemical reactions**

A. Reactions involving displacement of nitrogen

(a) Replacement by halide or cyanide ion

**Sandmeyer reaction**


**Gatterman reaction**


(b) Replacement by iodide ion

$$Ar\overset{\oplus}{N}_2Cl^{\ominus} + KI \rightarrow ArI + KCl + N_2$$

(c) Replacement by fluoride ion

$$Ar\overset{\oplus}{N}_2Cl^{\ominus} + HBF_4 \rightarrow Ar\overset{\oplus}{N}_2BF_4^{\ominus} \xrightarrow{\Delta} Ar - F + BF_3 + N_2$$

(d) Replacement by Hydrogen

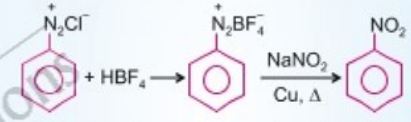
$$Ar\overset{\oplus}{N}_2Cl^{\ominus} + H_3PO_2 + H_2O \rightarrow ArH + N_2 + H_3PO_3 + HCl$$

$$Ar\overset{\oplus}{N}_2Cl^{\ominus} + CH_3CH_2OH \rightarrow ArH + N_2 + CH_3CHO + HCl$$

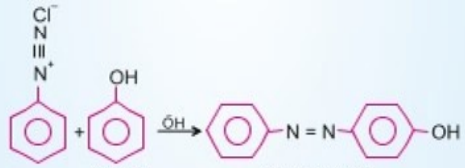
(e) Replacement by hydroxyl group

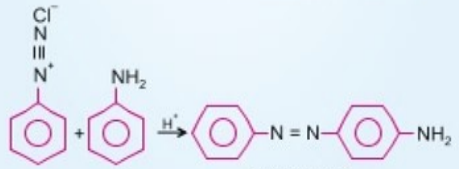
$$Ar\overset{\oplus}{N}_2Cl^{\ominus} + H_2O \xrightarrow{283\ K} ArOH + N_2 + HCl$$

(f) Replacement by $-NO_2$ group




B. Reactions involving retenation of diazo group (Coupling reaction)



## Sharpen Your Understanding

1. Consider the following amines

[NCERT Pg. 396]

$C_2H_5N(CH_3)_2$ (i) $(C_2H_5)_2NH$ (ii) $n-C_4H_9NH_2$ (iii)

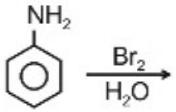
the correct order of their boiling points is

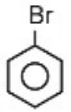
(1) (ii) > (i) > (iii) (2) (iii) > (ii) > (i)

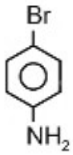
(3) (i) > (ii) > (iii) (4) (ii) > (iii) > (i)

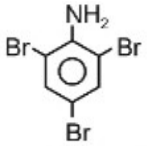
2. Major product of the given reaction is

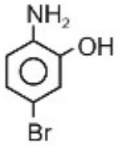
[NCERT Pg. 402]




(1) 

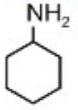

(2) 

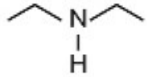

(3) 

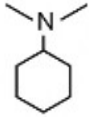

(4) 


3. The amine which will not react with Hinsberg's reagent is [NCERT Pg. 401]

(1) 

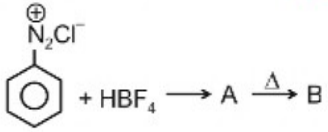

(2) 

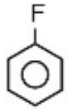

(3) 


(4) 

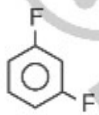

## NCERT Based MCQs

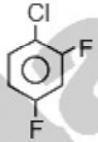
4. In the given reaction sequence major product B is [NCERT Pg. 405]




(1) 


(2) 


(3) 


(4) 


5. Incorrect statement among the following is

[NCERT Pg. 390, 393, 397, 401]

(1) Amines are said to be simple when all alkyl or aryl groups are same

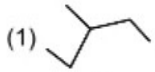
(2) Benzyl amine is more basic than aniline

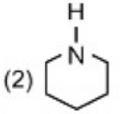
(3) Alkyl nitriles are reduced to primary amine by $LiAlH_4$

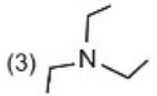
(4) Aliphatic diazonium salts are more stable than aromatic diazonium salts at low temperature

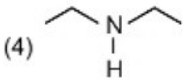
6. Which compound on reaction with chloroform and ethanolic potassium hydroxide form isocyanide?

[NCERT Pg. 401]

(1) 

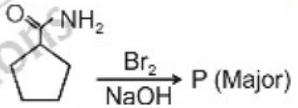

(2) 


(3) 

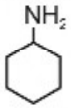

(4) 


7. Consider the following reaction

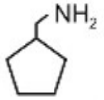
[NCERT Pg. 394]

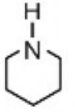



Major product P is

(1) 


(2) 


(3) 


(4) 


8. Correct order of basic strength of given compounds in aqueous medium is

[NCERT Pg. 399]

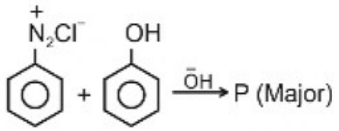
$(C_2H_5)_3N$ (a) $NH_3$ (b) $(C_2H_5)_2NH$ (c) $C_2H_5NH_2$ (d)

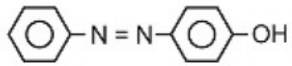
(1) (a)>(c)>(d)>(b) (2) (c)>(b)>(a)>(d)

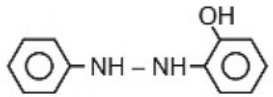
(3) (c)>(a)>(d)>(b) (4) (c)>(d)>(a)>(b)

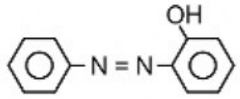
9. In the given reaction major product P is

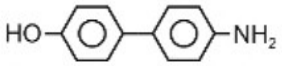
[NCERT Pg. 406]



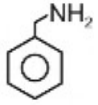
(1) 

(2) 

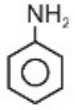
(3) 

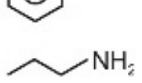
(4) 

10. Which among the following compounds cannot be prepared by Gabriel phthalimide synthesis? [NCERT Pg. 394]

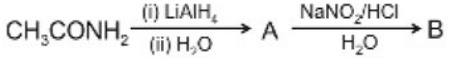
(1) 

(2) 

(3) 

(4) 

11. Consider the given set of reactions



Major product B is [NCERT Pg. 393, 401]

(1) $CH_3COOH$

(2) $CH_3CH_2OH$

(3) $CH_3CH_2Cl$

(4) $CH_3CH_2NO_2$

12. When benzene diazonium chloride is treated with ethanol then the product obtained is [NCERT Pg. 405]

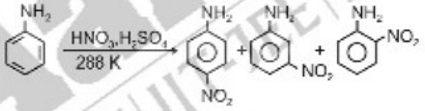
(1) Aniline

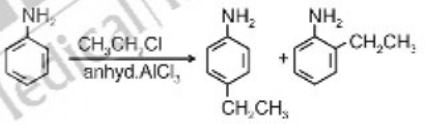
(2) Phenetole

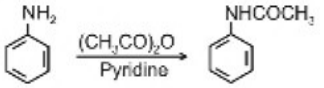
(3) Benzene

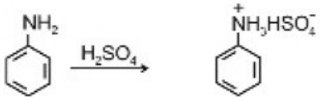
(4) p-chlorophenol

13. Which of the following reaction does not occur? [NCERT Pg. 403]

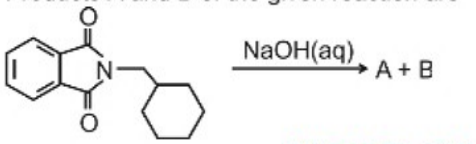
(1) 

(2) 

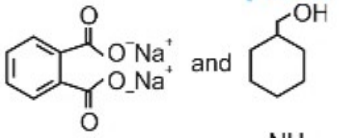
(3) 

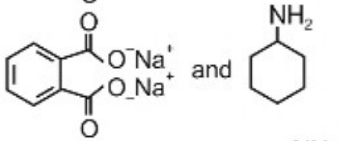
(4) 

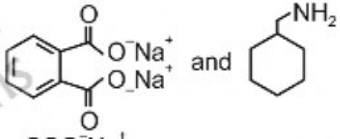
14. Products A and B of the given reaction are

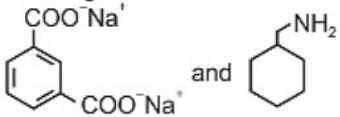


[NCERT Pg. 394]

(1) 

(2) 

(3) 

(4) 

15. Consider the following statements

(a) Hoffman bromamide degradation reaction is used for the preparation of secondary amines.

(b) Benzenediazonium fluoroborate is readily soluble in water.

(c) In Gattermann reaction, diazonium salt solution is treated with corresponding halogen acid in presence of copper powder.

The correct statement(s) is/are [NCERT Pg. 394, 405]

(1) (a) and (b) only (2) (b) and (c) only

(3) (c) only (4) (b) only

16. Aniline and N-methylaniline can be chemically distinguished by [NCERT Pg. 401]

(1) $CHCl_3|KOH|\Delta$

(2) Aqueous $H_2SO_4$

(3) Aqueous NaOH

(4) $CH_3COCl$/pyridine

17. Hinsberg's reagent is [NCERT Pg. 401]

(1) $SOCl_2$ (2) $C_6H_5SO_2Cl$

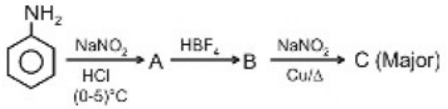
(3) $C_6H_5COCl$ (4) $NaNO_2/HCl$

18. The amine which is most basic in gas phase is [NCERT Pg. 398]

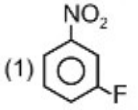
(1) $CH_3NH_2$ (2) $NH_3$

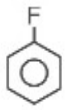
(3) $(CH_3)_2NH$ (4) $(CH_3)_3N$

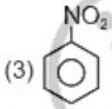
19. Consider the following reaction sequence

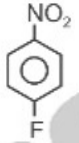



Product C is [NCERT Pg. 404, 406]

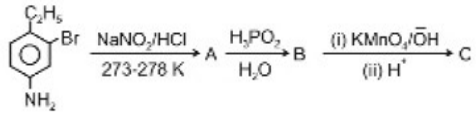
(1) 


(2) 

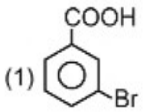

(3) 

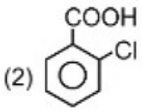

(4) 

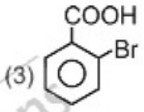

20. Product C of the given reaction sequence is

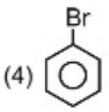



[NCERT Pg. 407]

(1) 

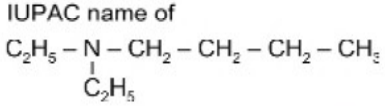

(2) 


(3) 


(4) 


## Thinking in Context

1. IUPAC name of




_____. [NCERT Pg. 391]

2. Nitrobenzene is reduced to _____ in presence of Sn/HCl. [NCERT Pg. 392]

3. Number of resonating structures in aniline is _____. [NCERT Pg. 399]

4. _____ reacts with acetyl chloride in presence of base giving N, N-diethylethanamide. [NCERT Pg. 400]

5. Carbylamine reaction is a chemical test of _____ amines. [NCERT Pg. 401]

6. Aliphatic diazonium salts in aqueous medium liberate _____ gas quantitatively and _____. [NCERT Pg. 401]

7. _____ reacts with primary and secondary amines to form sulphonamide. [NCERT Pg. 401]

8. _____ amines do not react with benzene sulphonyl chloride [NCERT Pg. 402]

9. Activating effect of-$NHCOCH_3$ group is _____ than that of $-NH_2$ group [NCERT Pg. 403]

10. Structure of sulphanilic acid is _____. [NCERT Pg. 403]

11. Aniline does not undergo Friedel-Crafts reaction due to salt formation with _____. [NCERT Pg. 403]

12. Benzenediazonium chloride is _____ in water. [NCERT Pg. 405]

13. The conversion of primary aromatic amines into diazonium salts is known as _____. [NCERT Pg. 404]

14. When diazonium salt solution is treated with _____, iodobenzene is formed. [NCERT Pg. 405]

15. Ethanol reduces diazonium salts to arenes and itself get oxidised to _____. [NCERT Pg. 405]

16. If the temperature of diazonium salt solution is allowed to rise upto 283 K, the salt gets hydrolysed to _____. [NCERT Pg. 406]

17. p-aminoazobenzene is _____ colour dye [NCERT Pg. 406]

18. Coupling reaction of diazonium salt with aniline yields p-aminoazobenzene is an example of _____ reaction. [NCERT Pg. 406]

19. In strongly acidic medium, aniline is protonated to form anilinium ion which is _____ directing towards electrophilic substitution reaction. [NCERT Pg. 403]

20. Basic nature of aniline is _____ than that of ammonia. [NCERT Pg. 399]

❑ ❑ ❑