CHAPTER 21

Compounds Containing Nitrogen

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. In an acidic medium, ... behaves as the strongest base. (nitrobenzene, aniline, phenol) *(1981 - 1 Mark)*
2. Amongst the three isomers of nitrophenol, the one that is least soluble in water is .... *(1992 - 1 Mark)*
3. The high melting point and insolubility in organic solvents of sulphanilic acid are due to its........structure. *(1994 - 1 Mark)*

C MCQs with One Correct Answer

1. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosamine is *(1981 - 1 Mark)*
   (a) methylamine (b) ethylamine
   (c) diethylamine (d) triethylamine
2. Acetamide is treated separately with the following reagents. Which one of these would give methylamine? *(1983 - 1 Mark)*
   (a) PCl_5 (b) $NaOH + Br_2$
   (c) soda lime (d) hot conc. H_2SO_4
3. Carbylamine test is performed in alcoholic KOH by heating a mixture of: *(1984 - 1 Mark)*
   (a) chloroform and silver powder
   (b) trihalogenatedmethane and a primary amine
   (c) an alkyl halide and a primary amine
   (d) an alkyl cyanide and a primary amine
4. The compound that is most reactive towards electrophilic nitration is : *(1985 - 1 Mark)*
   (a) toluene (b) benzene
   (c) benzoic acid (d) nitrobenzene
5. If two compounds have the same empirical formula but different molecular fomulae they must have
   (a) different percentage composition *(1987 - 1 Mark)*
   (b) different molecular weight
   (c) same viscosity
   (d) same vapour density
6. Amongst the following, the most basic compound is : *(1990 - 1 Mark)*
   (a) Benzylamine (b) Aniline
   (c) Acetanilide (d) *p*-Nitroaniline
7. The formation of cyanohydrin from a ketone is an example of : *(1990 - 1 Mark)*
   (a) Electrophilic addition
   (b) Nucleophilic addition
   (c) Nucleophilic substitution
   (d) Electrophilic substitution
8. Butanonitrile may be prepared by heating :*(1992 - 1 Mark)*
   (a) Propyl alcohol with KCN
   (b) Butyl alcohol with KCN
   (c) Butyl chloride with KCN
   (d) Propyl chloride with KCN
9. In the reaction *p*-chlorotoluene with KNH_2 in liq. NH_3,the major product is: *(1997 - 1 Mark)*
   (a) *o*-toluidine (b) *m*-toluidine
   (c) *p*-toluidine (d) *p*-chloroaniline.
10. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is *(1999 - 2 Marks)*

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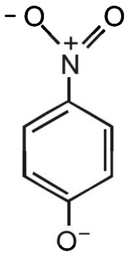

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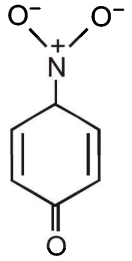

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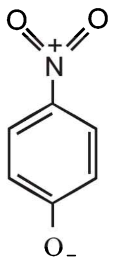

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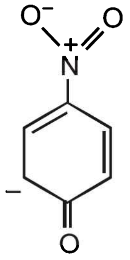
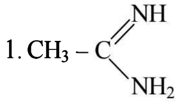


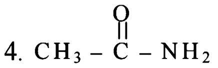
11. Among the following, the strongest base is *(2000S)*
   (a) $C_6H_5NH_2$
   (b) *p*-$NO_2.C_6H_4NH_2$
   (c) *m*-$NO_2.C_6H_4.NH_2$
   (d) $C_6H_5CH_2NH_2$

12. The correct order of basicities of the following compounds is *(2001S)*

1. 
$CH_3-C(=NH)NH_2$

2. $CH_3-CH_2-NH_2$

3. $(CH_3)_2NH$

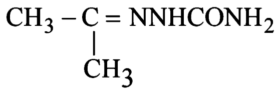
4. 
$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

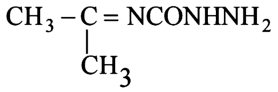
(a) 2 > 1 > 3 > 4 (b) 1 > 3 > 2 > 4

(c) 3 > 1 > 2 > 4 (d) 1 > 2 > 3 > 4

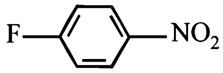
13. Compound 'A' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product 'B' (molecular formula C_3H_6O). 'B' forms a shining silver mirror on warming with ammonical silver nitrate. 'B' when treated with an aqueous solution of $H_2NCONHNH_2.HCl$ and sodium acetate gives a product 'C'. Identify the structure of 'C'.

(a) $CH_3CH_2CH=NNHCONH_2$ *(2002S)*

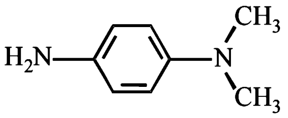
(b) 
$CH_3-\underset{\underset{CH_3}{|}}{C}=NNHCONH_2$

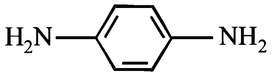
(c) 
$CH_3-\underset{\underset{CH_3}{|}}{C}=NCONHNH_2$

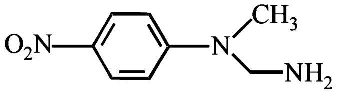
(d) $CH_3CH_2CH=NCONHNH_2$

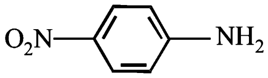
14. 

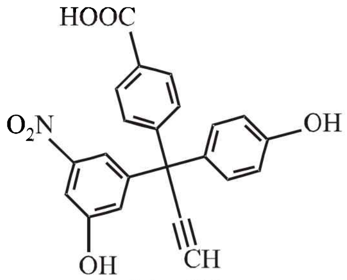
$\xrightarrow[DMF,\ \Delta]{(CH_3)_2NH}$ (A) $\xrightarrow[\substack{0^\circ-5^\circ C\\ ii)\ H_2/Ni}]{i)\ NaNO_2/HCl}$ (B). B is: *(2003S)*

(a) 

(b) 

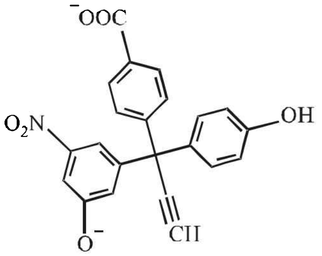
(c) 

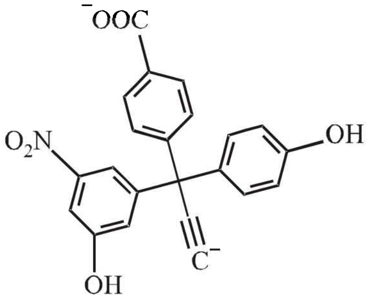
(d) 

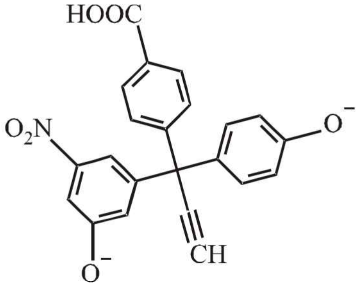
15. 

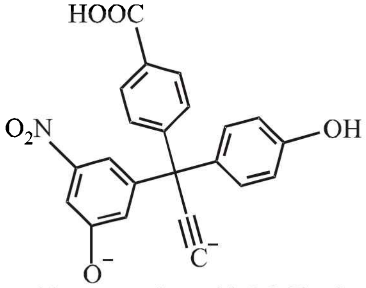
$\xrightarrow{\text{2 moles } NaNH_2}$ **A** ;

The product A will be *(2003S)*

(a) 

(b) 

(c) 

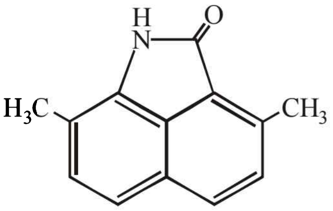
(d) 

16. Benzamide on reaction with $POCl_3$ gives *(2004S)*

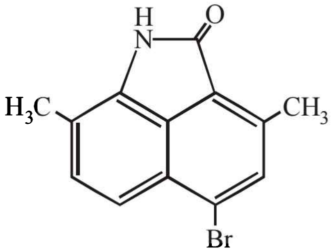
(a) aniline (b) chlorobenzene

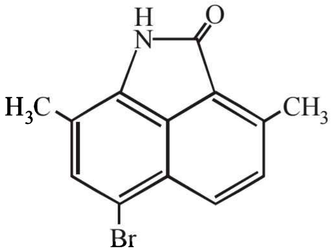
(c) benzylamine (d) benzonitrile

17. The major product obtained when Br_2/Fe is treated with



(2004S)

(a) 

(b) 

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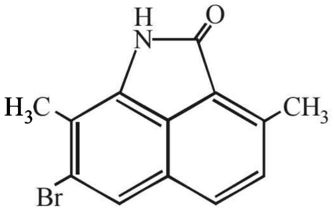

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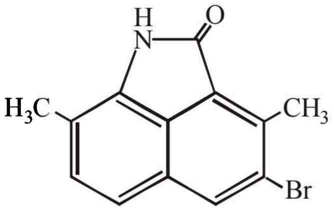
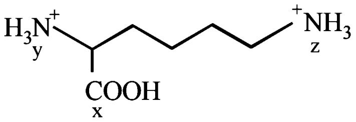


18. In the compound given below the correct order of the acidity of the positions X, Y and Z is *(2004S)*



(a) Z>X>Y (b) X>Y>Z
(c) X>Z>Y (d) Y>X>Z

19. When benzenesulfonic acid and *p*-nitrophenol are treated with $NaHCO_3$, the gases released respectively are *(2006)*

(a) SO_2, NO (b) SO_2, NO_2
(c) CO_2, CO_2 (d) SO_2, CO_2

20. In the following reaction, *(2006)*

$$CH_3NH_2 + CHCl_3 + KOH$$
$$\longrightarrow \text{Nitrogen containing compound} + KCl + H_2O.$$

The nitrogen containing compound is

(a) $CH_3-NH-CH_3$ (b) $CH_3-C\equiv N$

(c) $CH_3-\overset{+}{N}\equiv\overset{-}{C}$ (d) $CH_3-\overset{-}{N}\equiv\overset{+}{C}$

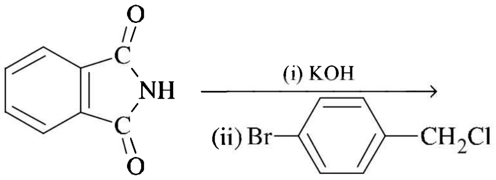
21. The correct stability order of the following resonance structures is *(2009)*

$H_2C=\overset{+}{N}=\overset{-}{N}$ (I) $H_2\overset{+}{C}-N=\overset{-}{N}$ (II)

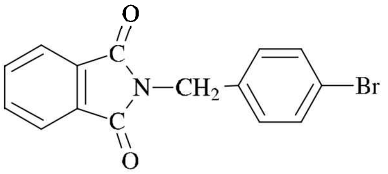
$H_2\overset{-}{C}-\overset{+}{N}\equiv N$ (III) $H_2\overset{-}{C}-N=\overset{+}{N}$ (IV)

(a) (I) > (II) > (IV) > (III)
(b) (I) > (III) > (II) > (IV)
(c) (II) > (I) > (III) > (IV)
(d) (III) > (I) > (IV) > (II)

22. The major product of the following reaction is *(2011 - I)*



(a)



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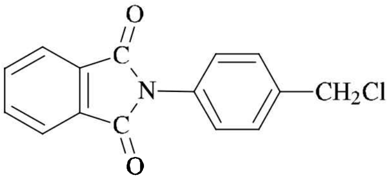

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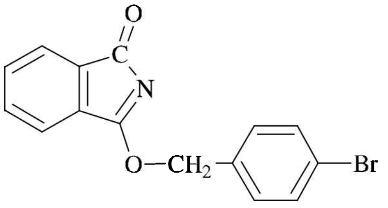

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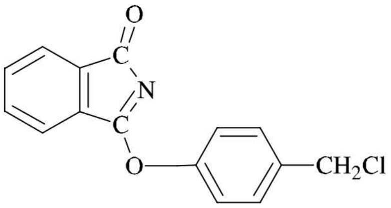
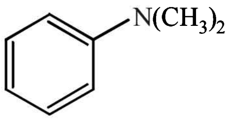


23. Amongst the compounds given, the one that would form a brilliant colored dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is *(2011 - II)*

(a)



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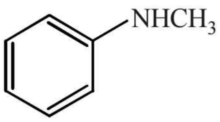

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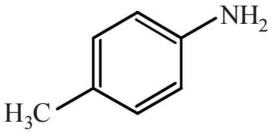

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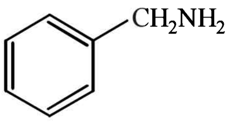


D MCQs with One or More Than One Correct

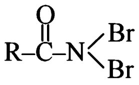
1. The products of reaction of alcoholic silver nitrite with ethyl bromide are *(1991 - 1 Mark)*

(a) ethane (b) ethene
(c) nitroethane (d) ethyl alcohol
(e) ethyl nitrite

2. Reaction of $R-\overset{O}{\overset{||}{C}}-NH_2$ with a mixture of Br_2 and KOH gives R-NH_2 as the main product. The intermediates involved in this reaction are : *(1992 - 1 Mark)*

(a) $R-\overset{O}{\overset{||}{C}}-NHBr$ (b) $R-NHBr$

(c) $R-N=C=O$ (d)



$R-\overset{O}{\overset{||}{C}}-N\begin{smallmatrix}Br\\Br\end{smallmatrix}$

3. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$, the major product formed is *m*-bromonitrobenzene. Statements which are related to obtain the *m*-isomer are *(1992 - 1 Mark)*

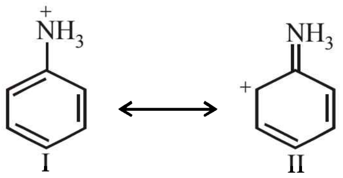
(a) The electron density on meta carbon is more than that on ortho and para positions

(b) The intermediate carbonium ion formed after initial attack of Br^+ at the meta position is least destabilised

(c) Loss of aromaticity when Br^+ attacks at the ortho and para positions and not at meta position

(d) Easier loss of H^+ to regain aromaticity from the meta position than from ortho and para positions.

4. Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below: *(1993 - 1 Mark)*



(a) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions.

(b) II is not an acceptable canonical structure because it is non-aromatic.

(c) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons.

(d) II is an acceptable canonical structure.

5. *p*-Chloroaniline and anilinium hydrochloride can be distinguished by *(1998 - 2 Marks)*

(a) Sandmeyer reaction (b) $NaHCO_3$

(c) $AgNO_3$ (d) Carbylamine test

6. Among the following compounds, which will react with acetone to give a product containing $>C=N$–bond ? *(1998 - 2 Marks)*

(a) $C_6H_5NH_2$ (b) $(CH_3)_3N$

(c) $C_6H_5NHC_6H_5$ (d) $C_6H_5NHNH_2$.

7. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives *(1998 - 2 Marks)*

(a) diphenyl ether (b) *p*-hydroxyazobenzene

(c) chlorobenzene (d) benzene

8. A positive carbylamine test is given by *(1999 - 2 Marks)*

(a) N, N—dimethylaniline

(b) 2, 4–dimethylaniline

(c) N–methyl-*o*-methylaniline

(d) *p*-methylbenzylamine

9. In the reaction $2\mathbf{X}+B_2H_6 \rightarrow [BH_2(\mathbf{X})_2]^+[BH_4]^-$ the amine(s) **X** is (are) *(2009)*

(a) NH_3 (b) CH_3NH_2

(c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

10. Hydrogen bonding plays a central role in the following phenomena *(JEE Adv. 2014)*

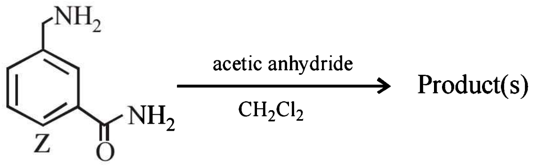
(a) Ice floats in water

(b) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions

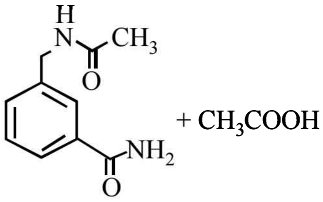
(c) Formic acid is more acidic than acetic acid

(d) Dimerisation of acetic acid in benzene

11. In the reaction shown below, the major product(s) formed is/are *(JEE Adv. 2014)*



(a)



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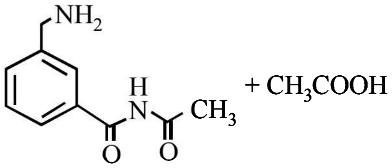

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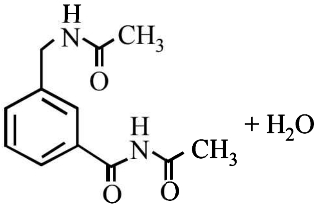

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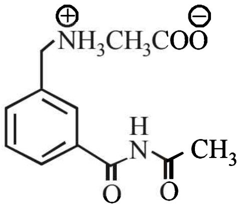
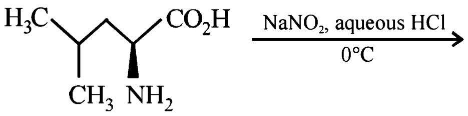


12. The major product of the reaction is *(JEE Adv. 2015)*



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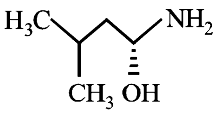

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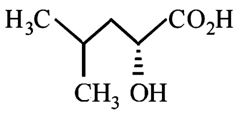

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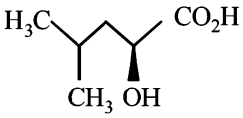

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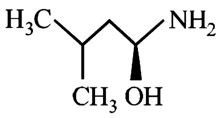
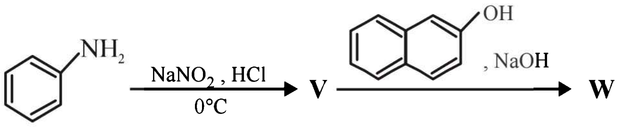
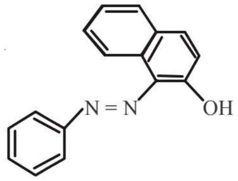


13. In the following reactions, the major product W is



(JEE Adv. 2015)

(a)



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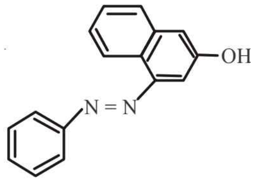
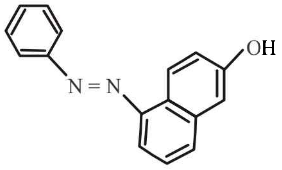


(c)



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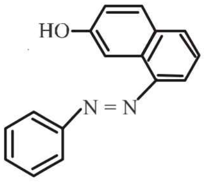
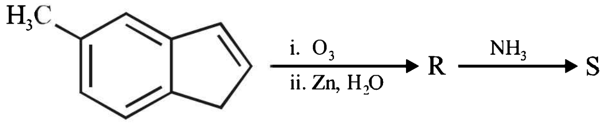
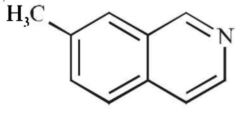


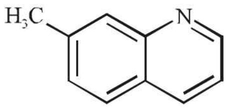
14. In the following reactions, the product S is *(JEE Adv. 2015)*



(a)



(b)



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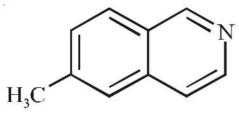

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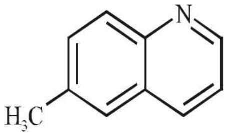
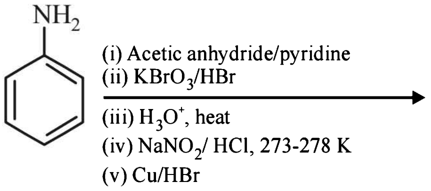
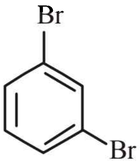


15. The product(s) of the following reaction sequence is(are)

(JEE Adv. 2016)



(a)



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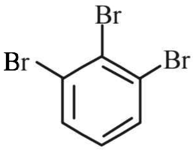
(c)



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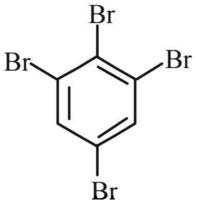


E Subjective Problems

1. Show with equations how the following compounds are prepared (equations need not be balanced) :

(*i*) n-propyl amine from ethyl chloride (in two steps) *(1982 - 1 Mark)*

(*ii*) chlorobenzene from aniline (in two steps). *(1982 - 1 Mark)*

(*iii*) Aniline from benzene *(1983 - 1 Mark)*

(*iv*) Acetoxime from acetaldehyde using the reagents, [$K_2Cr_2O_7/H^+$, $Ca(OH)_2$ and $NH_2OH.HCl$]. *(1984 - 2 Marks)*

(*v*) aniline to chlorobenzene *(1985 - 1 Mark)*

(*vi*) benzaldehyde to cyanobenzene. (in not more than 6 steps) *(1986 - 2 Marks)*

(*vii*) toluene to *m*-nitrobenzoic acid? *(1987 - 1 Mark)*

(*viii*) 4-nitroaniline to 1, 2, 3-tribromobenzene. *(1990 - 2 Marks)*

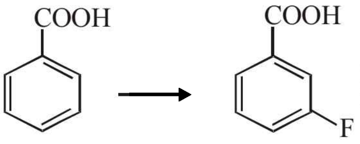
(*ix*) *p*-bromonitrobenzene from benzene in two steps. *(1993 - 2 Marks)*

(*x*) 4-nitrobenzaldehyde from benzene. *(1994 - 2 Marks)*

(*xi*) benzamide from nitrobenzene *(1994 - 2 Marks)*

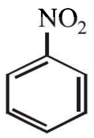
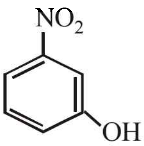
(*xii*) Aniline ⟶ Benzylamine (in 3 steps) *(2000 - 3 Marks)*

(*xiii*)



(in not more than 3 steps)

(2003 - 2 Marks)

(*xiv*) Convert  to  in not more than four steps. *(2004 - 4 Marks)*

2. Give reasons for the following :

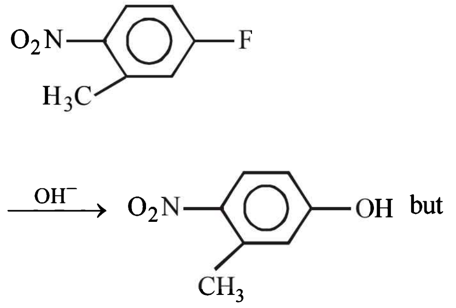
(*i*) Cyclohexylamine is a stronger base than aniline. *(1982 - 1 Mark)*

(*ii*) *o*-Nitrophenol is steam volatile whereas *p*-nitrophenol is not; *(1985 - 1 Mark)*

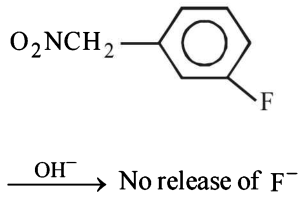
(*iii*) Dimethylamine is a stronger base than trimethylamine. *(1998 - 2 Marks)*

(*iv*) Nitrobenzene does not undergo Friedel-Crafts alkylation *(1998 - 2 Marks)*

(*v*) (a)

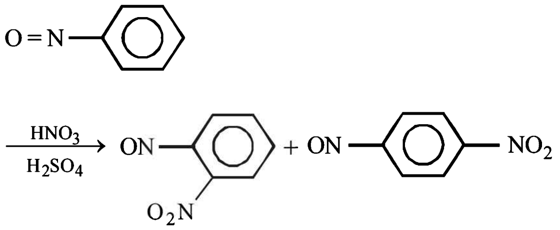


(b)

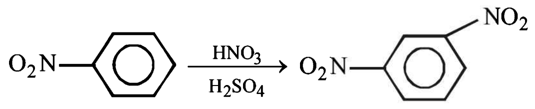


No release of F^- *(2005 - 1 Mark)*

(*vi*)



but



(2005 - 1 Mark)

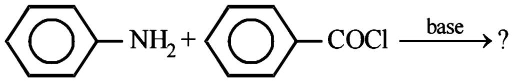
3. Arrange the following :

(*i*) *p*-toluidine, N, N-dimethyl-*p*-toluidine, *p*-nitroaniline, aniline in increasing basicity *(1986 - 1 Mark)*

(*ii*) methylamine, dimethylamine, aniline, N-methylaniline in incerasing order of base strength. *(1988 - 1 Mark)*

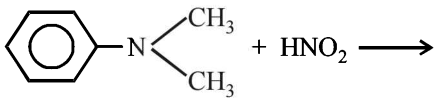
4. Complete the following with appropriate structures :

(*i*)



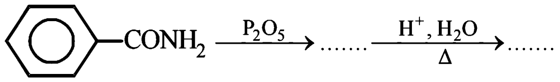
(1986 - 1 Mark)

(*ii*)



(1992 - 1 Mark)

(*iii*)

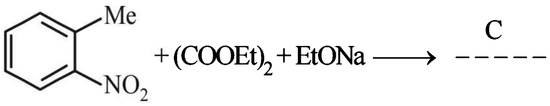


(1992 - 1 Mark)

(*iv*) 2, 4-Dinitroaniline

$\xrightarrow[\text{2. anisole}]{\text{1. NaNO}_2\text{ and HCl at 5°C}}$ C ----- *(1995 - 1 Mark)*

(*v*)



(1997 - 1 Mark)

(*vi*) $CH_3CH_2NH_2 \xrightarrow{(CH_3CO)_2O,\text{ heat}}$ 2 products *(1998 - 2 Marks)*

(*vii*) $CH_3CONHC_6H_5 \xrightarrow{Br_2,\ Fe}$ 2 products *(1998 - 2 Marks)*

5. Write balanced equations for the following reaction : Acetamide is reacted with bromine in the presence of potassium hydroxide. *(1987 - 1 Mark)*

6. Give a chemical test and the reagents used to distinguish between the following pair of compounds : Ethylamine and diethylamine. *(1988 - 1 Mark)*

7. An organic compound A, containing C, H, N and O, on analysis gives 49.32% carbon, 9.59% hydrogen and 19.18% nitrogen. A on boiling with NaOH gives off NH_3 and a salt which on acidification gives a monobasic nitrogen free acid B. The silver salt of B contains 59.67% silver. Deduce the structures of A and B. *(1988 - 3 Marks)*

8. A mixture of two aromatic compounds A and B was separated by dissolving a chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound A, when heated with alcoholic solution of KOH produced a compound C(C_7H_5N) associated with an unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gave a mixture of two isomeric compounds D and E of molecular formula $C_7H_6O_2$. Identify the compounds A, B, C, D, E and write their structures. *(1990 - 4 Marks)*

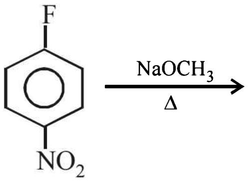
9. A basic, volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic potash. A 0.295 g sample of the substance. dissolved in aq. HCl and treated with $NaNO_2$ solution at 0°C, liberated a colorless, odourless gas whose volume corresponded to 112 ml at STP. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance. Assume that it contains one N atom per molecule. ***(1993 - 4 Marks)***

10. Identify the major product in the following reactions :

(*i*)

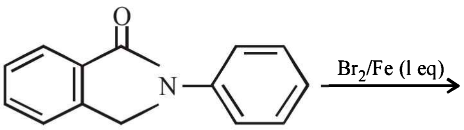
(1993 - 1 Mark)

(*ii*)



(2000 - 1 Mark)

(*iii*)



(2000 - 1 Mark)

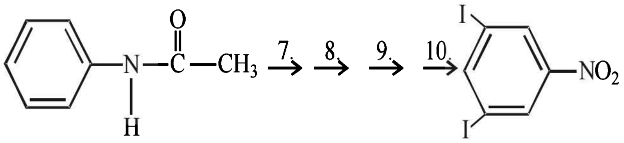
11. Identify, **A** (C_3H_9N) which reacts with benzensulphonyl chloride to give a solid, insoluble in alkali. ***(1993 - 1 Mark)***

12. Write the structure of the foul-smelling compound obtained when aniline is treated with chloroform in the presence of KOH. ***(1996 - 1 Mark)***

13. Acetophenone on reaction with hydroxylamine hydrochloride can produce two isomeric oximes. Write structures of the oximes. ***(1997 - 2 Marks)***

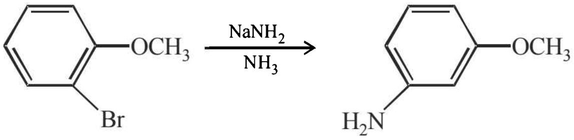
14. Compound A (C_8H_8O) on treatment with NH_2OH. HCl gives B and C. B and C rearrange to give D and E, respectively, on treatment with acid. B, C, D and E are all isomers of molecular formula (C_8H_9NO). When D is boiled with alcoholic KOH an oil F (C_6H_7N) separates out. F reacts rapidly with CH_3COCl to give back D. On the other hand, E on boiling with alkali followed by acidification gives a white solid G ($C_7H_6O_2$). Identify A-G. ***(1999 - 7 Marks)***

15. Complete the following reaction with appropriate reagents :



(1999 - 4 Marks)

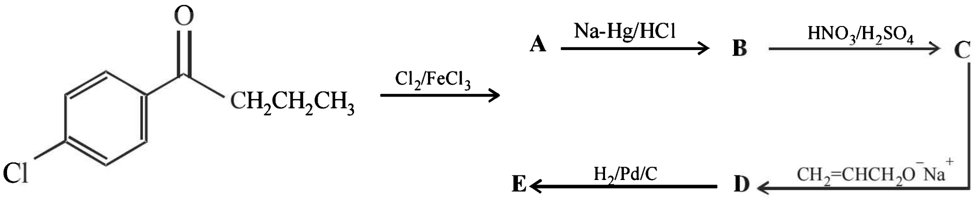
16. Explain briefly the formation of the products giving the structures of the intermediates.



(1999 - 2 Marks)

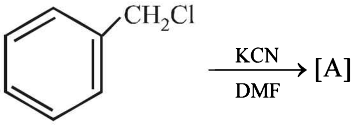
17. How would you synthesise 4–methoxyphenol from bromobenzene in NOT more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme. ***(2001 - 5 Marks)***

18. Write structures of the products **A, B, C, D** and **E** in the following scheme. ***(2002 - 5 Marks)***



19. There is a solution of *p*–hydroxybenzoic acid and *p*-aminobenzoic acid. Discuss one method by which we can separate them and also write down the confirmatory tests of the functional groups present. ***(2003 - 4 Marks)***.

20. Identify (A) to (D) in the following series of reactions. ***(2004 - 4 Marks)***



$$\xrightarrow[C_6H_5CHO,\ heat]{C_2H_5ONa,\ C_2H_5OH} [B]$$

$$\xrightarrow[heat]{H_3O^+} [C] \xrightarrow[(ii)\ CH_3NH_2]{(i)\ SOCl_2} [D]$$

21. $\underset{\substack{\text{(Optical active)}\\ X}}{C_5H_{13}N} \xrightarrow[-N_2]{aq.\ NaNO_2/HCl} \underset{\text{Tertiary alcohol}}{Y} + \text{Some other products}$ *(2005 - 4 Marks)*

(i) Identify (X) and (Y)

(ii) Is (Y) optically active?

(iii) Give structure(s) of intermediate(s), if any, in the formation of (Y) from (X).

F Match the Following

DIRECTIONS (Q. No.1): *Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example :*

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

	p	q	r	s	t
A	●	○	○	●	●
B	○	●	●	○	○
C	●	●	○	○	○
D	○	○	○	●	○

1. Match each of the compounds in **Column I** with its characteristic reaction(s) in **Column II**. *(2009)*

Column I	**Column II**
(A) $CH_3CH_2CH_2CN$	(p) Reduction with Pd–C/H_2
(B) $CH_3CH_2OCOCH_3$	(q) Reduction with $SnCl_2$/HCl
(C) CH_3–CH=CH–CH_2OH	(r) Development of foul smell on treatment with chloroform and alcoholic KOH
(D) $CH_3CH_2CH_2CH_2NH_2$	(s) Reduction with diisobutylaluminium hydride(DIBAL-H)
	(t) Alkaline hydrolysis

DIRECTIONS (Q. No. 2) : Match the four starting materials **(P, Q, R, S)** given in **List-I** with the corresponding reaction schemes **(I, II, III, IV)** provided in **List-II** and select the correct answer using the code given below the lists.

2. **List - I** **List - II** *(JEE Adv. 2014)*

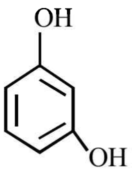
P. $H-C\equiv C-H$

1. Scheme I

(i) $KMnO_4$, $HO^{\ominus}$, heat (ii) $H^{\oplus}$, H_2O

(iii) $SOCl_2$ (iv) NH_3 ? $\longrightarrow C_7H_6N_2O_3$

Q.

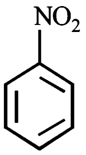


2. Scheme II

(ii) Sn/HCl (ii) CH_3COCl (iii) conc. H_2SO_4 (iv) HNO_3 (v) dil. H_2SO_4,

heat (vi) $HO^{\ominus}$? $\longrightarrow C_6H_6N_2O_2$

R.



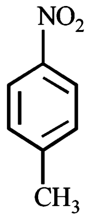
3. Scheme III

(i) red hot iron, 873 K (ii) fuming HNO_3, H_2SO_4, heat

(iii) $H_2S.NH_3$ (iv) $NaNO_2$, H_2SO_4 (v) hydrolysis

? $\longrightarrow C_6H_5NO_3$

S.



4. **Scheme IV**

(i) conc. H_2SO_4, 60°C
(ii) conc. HNO_3, conc. H_2SO_4
(iii) dil. H_2SO_4, heat ? $\longrightarrow$ $C_6H_5NO_4$

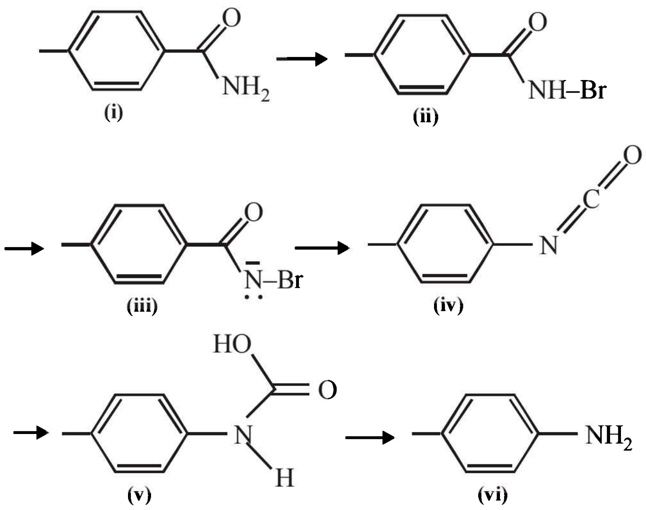
Code:

	P	Q	R	S
(a)	1	4	2	3
(b)	3	1	4	2
(c)	3	4	2	1
(d)	4	1	3	2

G Comprehension Based Questions

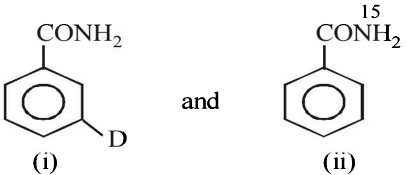
PASSAGE - 1

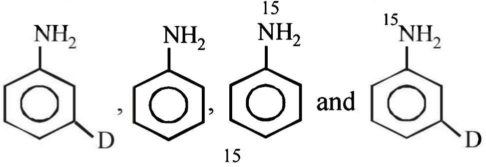
The conversion of an amide to an amine with one carbon atom less by the action of alkaline hydrohalite is known as Hofmann bromamide degradation.



In this reaction, RCONHBr is formed from which the reaction has derived its name. Hofmann reaction is accelerated if the migrating group is more electron-releasing. Hofmann degradation reaction is an intramolecular reaction.

1. How can the conversion of (i) to (ii) be brought about? *(2006 - 5M, –2)*
   (a) KBr (b) KBr + CH_3ONa
   (c) KBr + KOH (d) Br_2 + KOH
2. Which is the rate determining step in Hofmann bromamide degradation? *(2006 - 5M, –2)*
   (a) Formation of (i) (b) Formation of (ii)
   (c) Formation of (iii) (d) Formation of (iv)
3. What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation? *(2006 - 5M, –2)*



(a)


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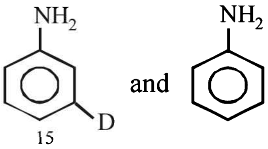

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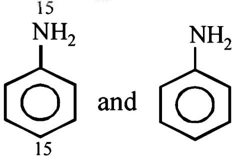
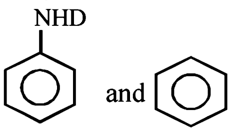
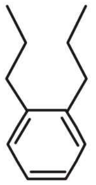


(d)


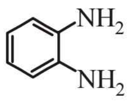
PASSAGE - 2

Treatment of compound O with $KMnO_4/H^+$ gave P, which on heating with ammonia gave Q. The compound Q on treatment with Br_2/NaOH produced R. On strong heating, Q gave S, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound T. *(JEE Adv. 2016)*

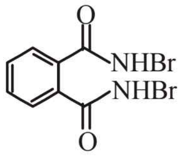


(O)

4. The compound R is

(a)


(b)


(c)


(d)


5. The compound T is

(a) glycine (b) alanine
(c) valine (d) serine

H Assertion & Reason Type Questions

Read the following Statement-1(Asseration) and Statement -2 (Reason) and answer as per the options given below :

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(c) Statement-1 is True, Statement-2 is False
(d) Statement-1 is False, Statement-2 is True

1. **Statement - 1:** *p*-Nitrophenol is a stronger acid than *o*-nitrophenol.

Statement - 2 : Intramolecular hydrogen bonding makes the *o*-isomer weaker than the *p*-isomer. *(1989 - 2 Marks)*

2. **Statement - 1:** Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.

Statement - 2 : Cyanide (CN^-) is a strong nucleophile. *(1998 - 2 Marks)*

3. **Statement - 1 :** In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

Statement-2 : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance. *(2001S)*

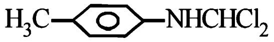
4. **Statement - 1 :** Aniline on reaction with $NaNO_2$ / HCl at 0°C followed by coupling with β-naphthol gives a dark blue precipitate.

and

Statement - 2 : The colour of the compound formed in the reaction of aniline with $NaNO_2$/HCl at 0°C followed by coupling with β-naphthol is due to the extended conjugation. *(2008)*

Section-B JEE Main / AIEEE

1. When primary amine reacts with chloroform in ethanolic KOH then the product is **[2002]**
   (a) an isocyanide
   (b) an aldehyde
   (c) a cyanide
   (d) an alcohol.

2. The reaction of chloroform with alcoholic KOH and p-toluidine forms **[2003]**
   (a) 
   $H_3C-C_6H_4-N_2Cl$
   (b) 
   $H_3C-C_6H_4-NHCHCl_2$
   (c) 
   $H_3C-C_6H_4-NC$
   (d) 
   $H_3C-C_6H_4-CN$

3. The correct order of increasing basic nature for the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is **[2003]**
   (a) $(CH_3)_2NH < NH_3 < CH_3NH_2$
   (b) $NH_3 < CH_3NH_2 < (CH_3)_2NH$
   (c) $CH_3NH_2 < (CH_3)_2NH < NH_3$
   (d) $CH_3NH_2 < NH_3 < (CH_3)_2NH$

4. Ethyl isocyanide on hydrolysis in acidic medium generates
   (a) propanoic acid and ammonium salt **[2003]**
   (b) ethanoic acid and ammonium salt
   (c) methylamine salt and ethanoic acid
   (d) ethylamine salt and methanoic acid

5. Which one of the following methods is neither meant for the synthesis nor for separation of amines? **[2005]**
   (a) Curtius reaction
   (b) Wurtz reaction
   (c) Hofmann method
   (d) Hinsberg method

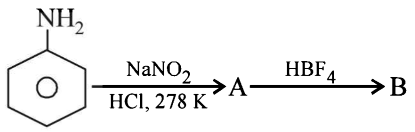
6. Amongst the following the most basic compound is **[2005]**
   (a) p-nitroaniline (b) acetanilide
   (c) aniline (d) benzylamine

7. An organic compound having molecular mass 60 is found to contain $C = 20\%$, $H = 6.67\%$ and $N = 46.67\%$ while rest is oxygen. On heating it gives NH_3 alongwith a solid residue. The solid residue give violet colour with alkaline copper sulphate solution. The compound is **[2005]**
   (a) $CH_3CH_2CONH_2$ (b) $(NH_2)_2CO$
   (c) CH_3CONH_2 (d) CH_3NCO

8. Which one of the following is the strongest base in aqueous solution ? **[2007]**
   (a) Methylamine (b) Trimethylamine
   (c) Aniline (d) Dimethylamine.

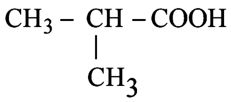
9. In the chemical reaction,
   $CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow (A) + (B) + 3H_2O$, the compounds (A) and (B) are respectively **[2007]**
   (a) C_2H_5NC and 3KCl
   (b) C_2H_5CN and 3KCl
   (c) $CH_3CH_2CONH_2$ and 3KCl
   (d) C_2H_5NC and K_2CO_3.

10. In the chemical reactions,



   the compounds 'A' and 'B' respectively are **[2010]**
   (a) nitrobenzene and fluorobenzene
   (b) phenol and benzene
   (c) benzene diazonium chloride and fluorobenzene
   (d) nitrobenzene and chlorobenzene

11. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is : **[JEE M 2013]**
   (a) 2 (b) 5
   (c) 4 (d) 6

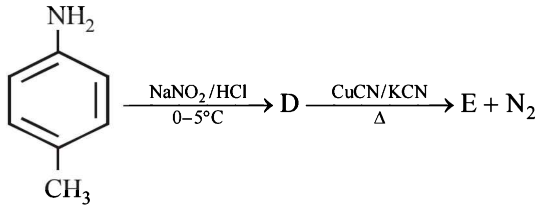
12. An organic compound A upon reacting with NH_3 gives B. On heating B gives C. C in presence of KOH reacts with Br_2 to given $CH_3CH_2NH_2$. A is : **[JEE M 2013]**
   (a) CH_3COOH (b) $CH_3CH_2CH_2COOH$
   (c) 
   $CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH$
   (d) CH_3CH_2COOH

13. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was : **[JEE M 2013]**
   (a) Methyl isocyanate (b) Methylamine
   (c) Ammonia (d) Phosgene

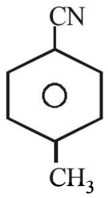
14. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is: **[JEE M 2014]**
   (a) an alkanol (b) an alkanediol
   (c) an alkyl cyanide (d) an alkyl isocyanide

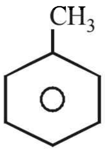
15. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? **[JEE M 2014]**
   (a) $(CH_3)_2NH$ (b) CH_3NH_2
   (c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

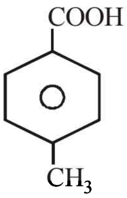
16. In the reaction **[JEE M 2015]**

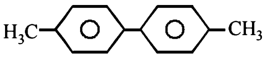


the product E is :

(a)


(b)


(c)


(d)


17. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are : **[JEE M 2016]**

(a) Two moles of NaOH and two moles of Br_2.
(b) Four moles of NaOH and one mole of Br_2.
(c) One mole of NaOH and one mole of Br_2.
(d) Four moles of NaOH and two moles of Br_2.

21 Compounds Containing Nitrogen

Section-A : JEE Advanced/ IIT-JEE

A **1.** aniline **2.** *o*-nitrophenol **3.** dipolar ion

C **1.** (c) **2.** (b) **3.** (b) **4.** (a) **5.** (b) **6.** (a) **7.** (b)
8. (d) **9.** (b) **10.** (c) **11.** (d) **12.** (b) **13.** (a) **14.** (a)
15. (a) **16.** (d) **17.** (b) **18.** (b) **19.** (NA) **20.** (c) **21.** (b)
22. (a) **23.** (c)

D **1.** (c, e) **2.** (a, c) **3.** (a, d) **4.** (c) **5.** (c) **6.** (a, d) **7.** (b)
8. (b, d) **9.** (a,b,c) **10.** (a, b, d) **11.** (a) **12.** (c) **13.** (a) **14.** (a) **15.** (b)

E **3.** (i) N, N-dimethyl-p-toluidine, < *p*-nitroaniline < aniline < *p*-toluidine.
(ii) aniline-N-methylamine < methylaniline < dimethylaniline

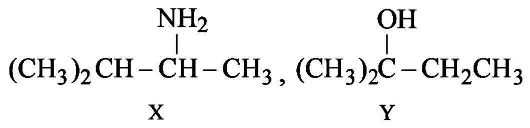
7. $CH_3CH_2CONH_2, CH_3CH_2COOH$

8. $\underset{A}{\text{aniline}}, \underset{B}{\text{phenol}}, \underset{C}{\text{phenyl isocyanide}}, \underset{D}{\text{salicylaldehyde}}, \underset{E}{p\text{-hydroxybenzaldehyde}}$

9. isopropylamine **11.** ethylmethylamine **12.** PhNC

14. $\underset{A}{C_6H_5COCH_3}, \underset{B}{\textit{syn}\text{-}C_6H_5C(=NOH)CH_3}, \underset{C}{\textit{anti}\text{-}C_6H_5C(=NOH)CH_3},$
$\underset{D}{CH_3CO.NHC_6H_5}, \underset{E}{CH_3NHCOC_6H_5}, \underset{F}{C_6H_5NH_2}, \underset{G}{C_6H_5COOH}$

21.



$$\underset{X}{(CH_3)_2CH-\overset{\overset{NH_2}{|}}{C}H-CH_3}, \quad \underset{Y}{(CH_3)_2\overset{\overset{OH}{|}}{C}-CH_2CH_3}$$

F **1.** **(A)– p, q, s, t; (B) – s, t; (C) – p; (D) – r** **2.** (c)

G **1.** (d) **2.** (d) **3.** (b) **4.** (a) **5.** (b)

H **1.** (a) **2.** (d) **3.** (d) **4.** (d)

Section-B : JEE Main/ AIEEE

1. (a) **2.** (c) **3.** (b) **4.** (d) **5.** (b) **6.** (d) **7.** (b)
8. (d) **9.** (a) **10.** (c) **11.** (b) **12.** (d) **13.** (a) **14.** (d)
15. (a) **16.** (a) **17.** (b)

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. **aniline.**

2. ***o*-Nitrophenol;** this isomer involves intramolecular hydrogen bonding whereas the other two isomers have intermolecular hydrogen bonding. Because of this, the former is less polar and hence least soluble in polar solvent water.

3. **Dipolar ion.** (Salt like)

C. MCQs with ONE Correct Answer

1. **(c)** NOTE : *Secondary amines* (aliphatic as well as aromatic) *react with nitrous acid to form* **N-nitrosoamines**.

$$(C_2H_5)_2NH + HONO \rightarrow \underset{\text{N-Nitrosodiethylamine}}{(C_2H_5)_2N-N=O} + H_2O$$

2. **(b)** $\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{NaOH + Br_2} \underset{\text{Methylamine}}{CH_3NH_2}$

3. (b) **NOTE :** Only primary aliphatic and aromatic amines give this test.

$CHX_3 + RNH_2 + 3KOH \rightarrow RNC + 3KX + 3H_2O$

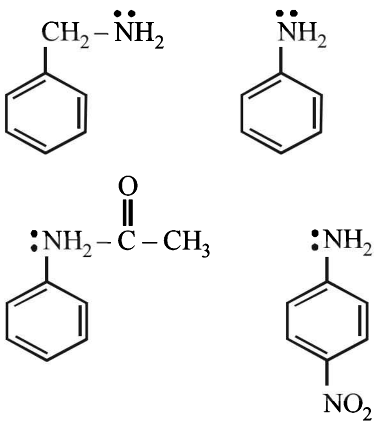
4. (a) **TIPS/Formulae :** Toluene has electron-donating methyl group. Hence reacts fastest while others have either electron withdrawing groups (*i.e.* $-COOH$ or $-NO_2$ etc.) or no substituent.

5. (b) **TIPS/Formulae :**

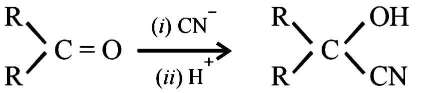
Empirical Formula = n × Molecular formula

Solution : Since the molecular formula is n times the empirical formula, therefore, different compounds having the same empirical formula must have different molecular weights.

6. (a) In benzylamine, electron pair on nitrogen is not delocalised due to lack of conjugation; while in all other compounds it is delocalised and hence lesser available for protonation.



7. (b) **TIPS/Formulae :** The addition is initiated by the attack of CN^- group which is a nucleophile.

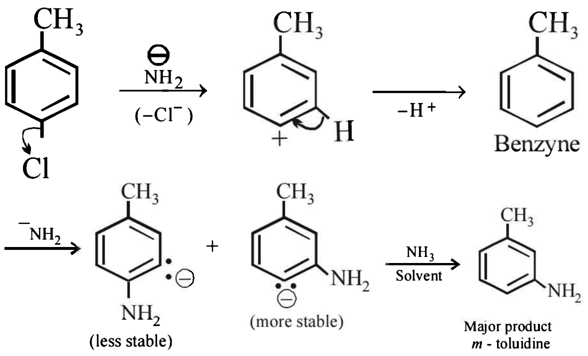


Ketone cyanohydrin

8. (d) **TIPS/Formulae :** In the formation of cyanohydrin number of carbon atoms in parent chain increases by one.

$$CH_3CH_2CH_2Cl + alc.\ KCN \xrightarrow{100°C} CH_3CH_2CH_2CN + KCl$$

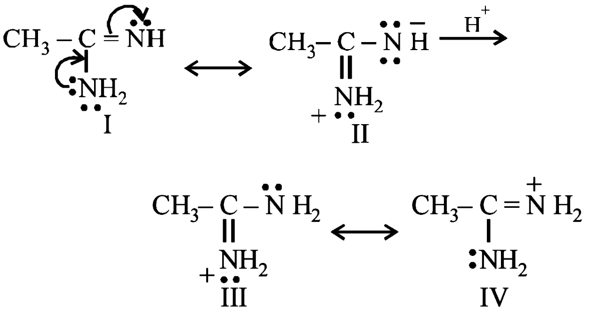
9. (b)



10. (c) N can't have more than 8 electrons in its valence shell as it does not have any *d* orbital. In (c), N has 10 electrons.

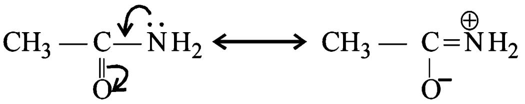
11. (d) Aliphatic amines are more basic than aromatic amines because in aliphatic amines electron pair on nitrogen is not involved in resonance.

12. (b)



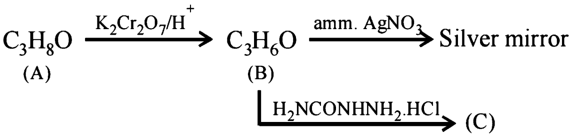
The protonated form of II would be III which is more stable because here the contributing structures (III) and (IV) are equivalent.

In $CH_3-\ddot{N}H-CH_3$, the availability of electron pair increases due to the +I effect of two CH_3 groups while in $CH_3CH_2NH_2$, +I effect of only one ethyl group is operative. In $CH_3-\underset{\underset{O}{\|}}{C}-NH_2$, the electron availability on nitrogen decreases due to resonance as shown below



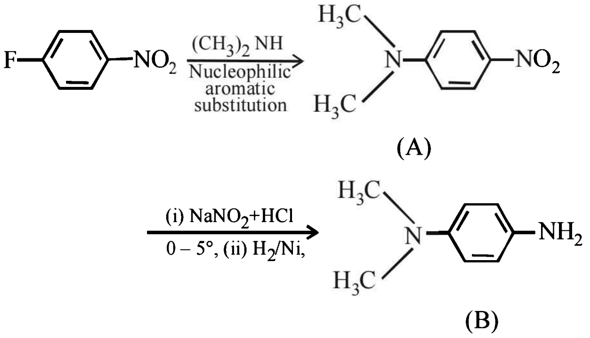
Therefore, the order of basic strength would be $1 > 3 > 2 > 4$.

13. (a)



NOTE : Reaction of (B) indicates that it is an aldehyde which thus should be C_2H_5CHO or CH_3CH_2CHO, hence C should be $CH_3CH_2CH{=}NNHCONH_2$

14. (a)



15. (a) Two moles of NH_2 ions will abstract two moles of most acidic hydrogen out of the four moles of hydrogen present per mole of the acidic compound. The acidic strength is in the order:

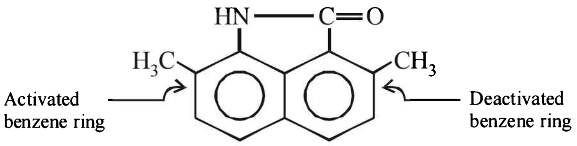
–COOH > –OH (phenolic having NO_2 group) > –OH (phenolic) > alkynic H.

16. **(d)** **NOTE :** $POCl_3$ is a dehydrating agent. Hence

$$C_6H_5CONH_2 \xrightarrow{POCl_3} C_6H_5CN + H_2O$$

17. **(b)** **TIPS/Formulae :**–NH is an activating group whereas as $>C=O$ group is a deactivating group.

Hence electrophilic substitution will be governed by the ring having $>NH$ group.



18. **(b)** (i) Position (X) is most acidic due to – COOH group.

(ii) $-NH_3^+$ group at position Y is more acidic than at Z because of presence of electron withdrawing – COOH group in close proximity. Hence $-NH_3^+$ group at position Z is least acidic.

19. **(NA)** None of the given options is correct. Benzene sulphonic acid, being stronger acid than carbonic acid, would liberate CO_2 when treated with sodium bicarbonate, but *p*-nitrophenol, being less acidic than carbonic acid, will not liberate CO_2.

20. **(c)** This is an example of carbylamine reaction

$$CHCl_3 + RNH_2 + KOH \longrightarrow R-N^+ \equiv C^- + 3KCl + 3H_2O$$

21. **(b)** $H_2C=N^+=N^- > H_2C^- - N^+ \equiv N$

I: Octet complete, 6 covalent bond, –ve charge on N

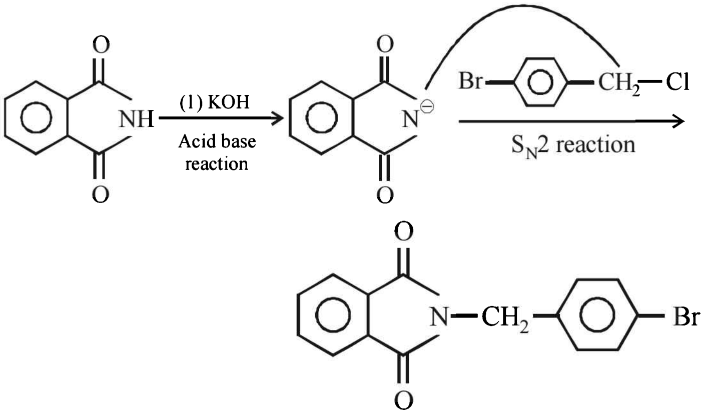
III: Octet complete, 6 covalent bond, –ve charge on C

$> H_2C^+ - N = N^- > H_2C^- - N = N^+$

II: Octet incomplete, 5 covalent bond, –ve charge on N

IV: Octet incomplete, 5 covalent bond, –ve charge on C

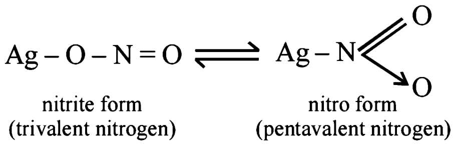
22. **(a)**

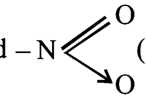


23. **(c)** Only primary aromatic amines undergo diazotisation followed by coupling.

D. MCQs with ONE or More Than One Correct

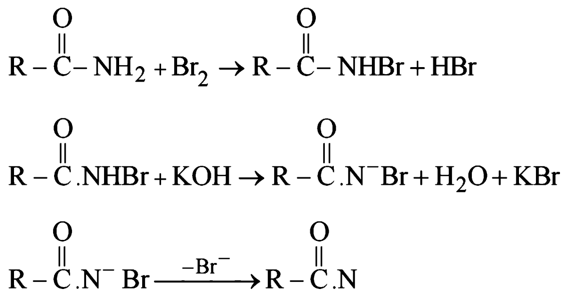
1. **(c, e)** **TIPS/Formulae :** Silver nitrite, being a salt of nitrous acid, occurs in two tautomeric forms.



NO_2^- ion from $AgNO_2$ may exist in two tautomeric forms, –O – N = O (nitrite ion) forming **alkyl nitrites**, and  (nitro group) forming **nitroalkanes**.

$$2\,C_2H_5Br + 2AgNO_2 \rightarrow C_2H_5NO_2 + C_2H_5ONO + 2\,AgBr$$

2. **(a, c)** This is an example of Hoffmann degradation of amides.



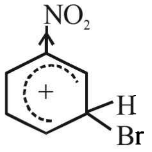
$$R-\overset{\overset{\displaystyle O}{||}}{C}-NH_2 + Br_2 \rightarrow R-\overset{\overset{\displaystyle O}{||}}{C}-NHBr + HBr$$

$$R-\overset{\overset{\displaystyle O}{||}}{C}.NHBr + KOH \rightarrow R-\overset{\overset{\displaystyle O}{||}}{C}.N^-Br + H_2O + KBr$$

$$R-\overset{\overset{\displaystyle O}{||}}{C}.N^-\,Br \xrightarrow{-Br^-} R-\overset{\overset{\displaystyle O}{||}}{C}.N$$

$$\xrightarrow{\text{rearrangement}} R-N=C=O \xrightarrow{H_2O} R-NH_2$$

3. **(a, d)** **TIPS/Formulae :** Nitro group decreases the electron density at the *meta*-position in comparison to ortho and para position due to –I and –M effects.



The above intermediate is a resonance hybrid of three structures, hence is more stable than the corresponding intermediate from *ortho* and *para*-attack.

4. **(c)** In Ist structure N has complete octet, whereas in IInd structure N has 10e in its valence shell.

Because of 1 double and 3 single bonds of N.

5. **(c)** **TIPS/Formulae :** Anilinium hydrochloride has ionisable chlorine whereas chlorobenze has non ionizable chlorine. Thus anilium hydrochloride gives white precipitate of AgCl with $AgNO_3$.

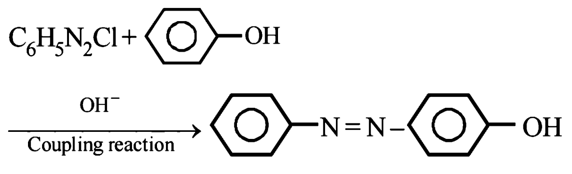
$$C_6H_5NH_3^+Cl^- + AgNO_3 \rightarrow C_6H_5NH_3^+NO_3^- + AgCl\downarrow$$

In chloroaniline, –Cl is directly attached to benzene ring, hence it is non-reactive.

6. **(a, d)** $C_6H_5NH_2 + O=C(CH_3)_2 \xrightarrow[-H_2O]{} C_6H_5N=C(CH_3)_2$

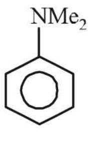
$C_6H_5NHNH_2 + O=C(CH_3)_2 \xrightarrow[-H_2O]{} C_6H_5NHN=C(CH_3)_2$

7. **(b)**

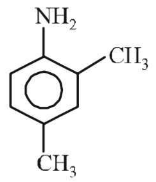


p-Hydroxyazobenzene

8. **(b, d)** **NOTE :** Only primary amines give carbylamine test. Hence 2,4-dimethylanilinc and p-methyl–benzylamine both give this test.



(a)



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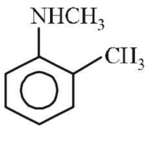
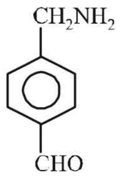


(c)



(d)

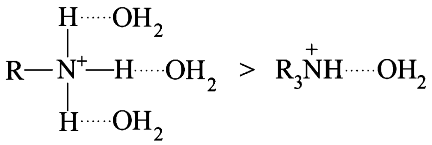
9. **(a,b,c)** Lower amines like NH_3, CH_3NH_2 and $(CH_3)_2NH$ break diborane molecule unsymmetrically, while larger amines like $(CH_3)_3N$, C_5H_5N break diborane in symmetrical manner.

$$B_2H_6 + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+[BH_4]^-$$

$$B_2H_6 + 2NH_3 \longrightarrow 2H_3B \longleftarrow N(CH_3)_3$$

10. **(a, b, d)** In ice, water molecules are excessively H-bonded giving a cage-like structure which is lighter than water. Primary amines are more basic than tertiary amine, because the protonated 1° amines are extensively H-bonded and hence more stable than the corresponding protonated 3° amines.

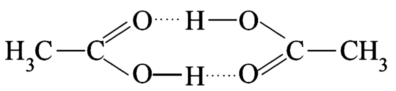
$$R-\ddot{N}H_2 \xrightarrow{H^+} R-\overset{+}{N}H_3;\ R_3\ddot{N} \xrightarrow{H^+} R_3\overset{+}{N}H$$



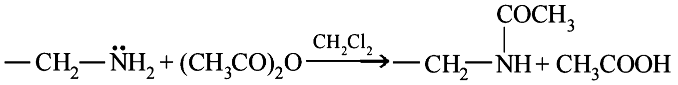
$$R-\overset{\overset{H\cdots OH_2}{|}}{\underset{\underset{H\cdots OH_2}{|}}{N^+}}-H\cdots OH_2 \;>\; R_3\overset{+}{N}H\cdots OH_2$$

More stable Less stable

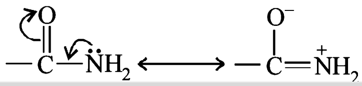
Acetic acid undergoes dimerisation in benzene.



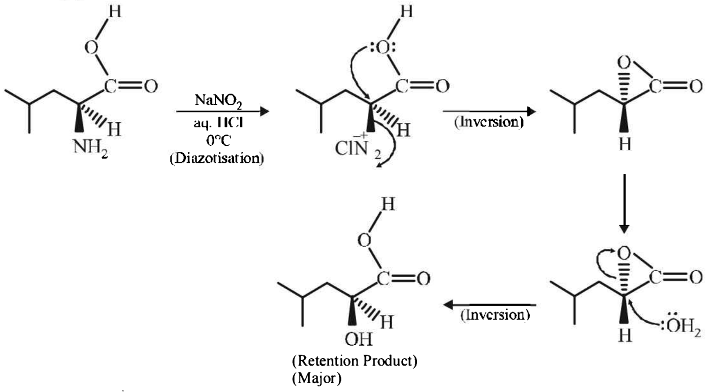
11. **(a)** $-\ddot{N}H_2$ group is acetylated by acetic anhydride in methylene chloride (solvent). Note that $-CONH_2$ group does not undergo acetylation because here lone pair of electrons is delocalised.



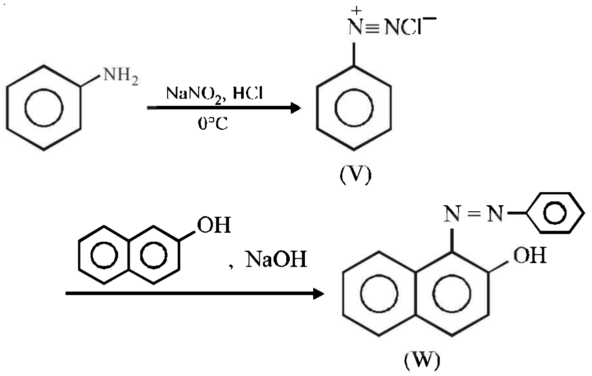
$$-CH_2-\ddot{N}H_2 + (CH_3CO)_2O \xrightarrow{CH_2Cl_2} -CH_2-\overset{\overset{COCH_3}{|}}{N}H + CH_3COOH$$



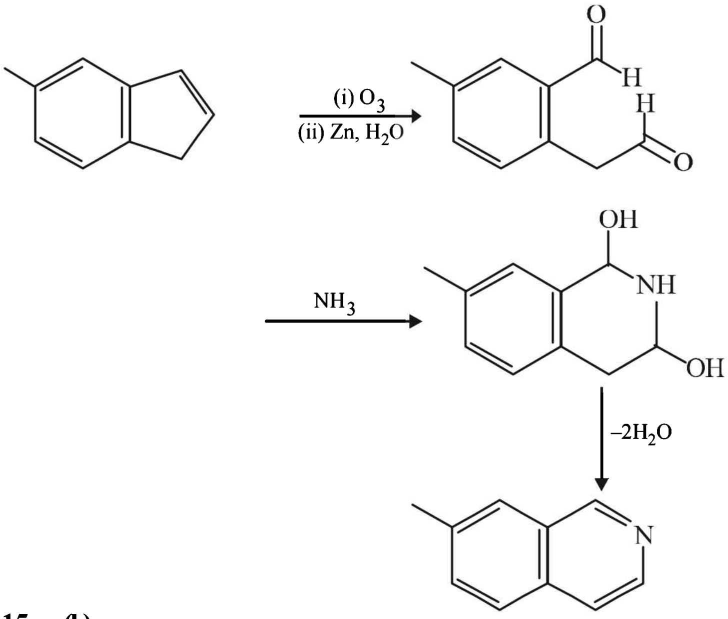
12. **(c)**



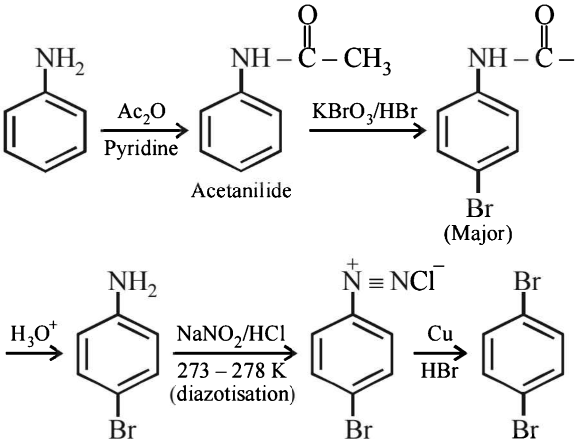
13. **(a)**



14. **(a)**



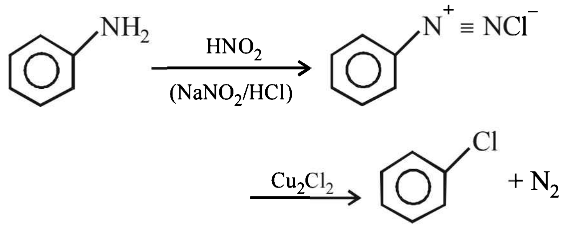
15. **(b)**



E. Subjective Problems

1. (*i*) $CH_3CH_2.Cl + alc.\ KCN \rightarrow CH_3.CH_2.CN \xrightarrow[\text{reduction}]{H_2|Ni} CH_3.CH_2.CH_2.NH_2$

(*ii*)



(*iii*) $C_6H_6 \xrightarrow[HNO_3\text{ (conc.)}]{H_2SO_4\text{(conc.)}} C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5NH_2$

(*iv*) $CH_3CHO \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH \xrightarrow[\text{distill}]{Ca(OH)_2}$

$CH_3COCH_3 \xrightarrow{NH_2OH.HCl} \underset{\text{Acetoxime}}{(CH_3)_2C{=}NOH}$

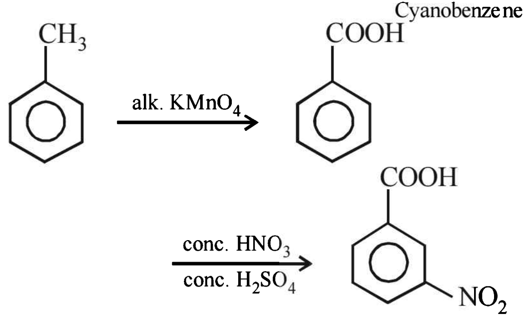
(*v*) Consult (ii)

(*vi*) $C_6H_5CHO \xrightarrow{\text{Oxi.}} C_6H_5COOH$

$\xrightarrow[\text{(ii) }\Delta]{\text{(i) }NH_3} C_6H_5CONH_2 \xrightarrow[KOH]{Br_2} C_6H_5NH_2$

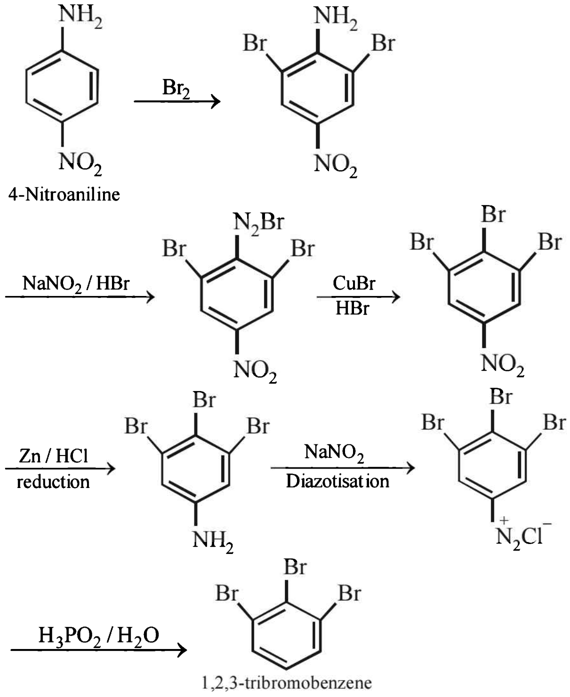
$\xrightarrow[0°C]{HONO} C_6H_5N_2Cl \xrightarrow{CuCN} \underset{\text{Cyanobenzene}}{C_6H_5CN}$

(*vii*)

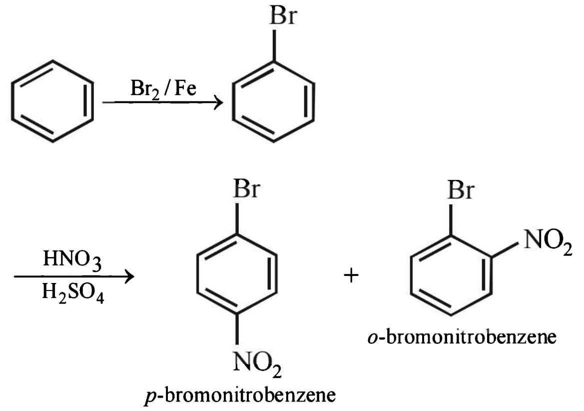


m-nitrobenzoic acid

(*viii*)

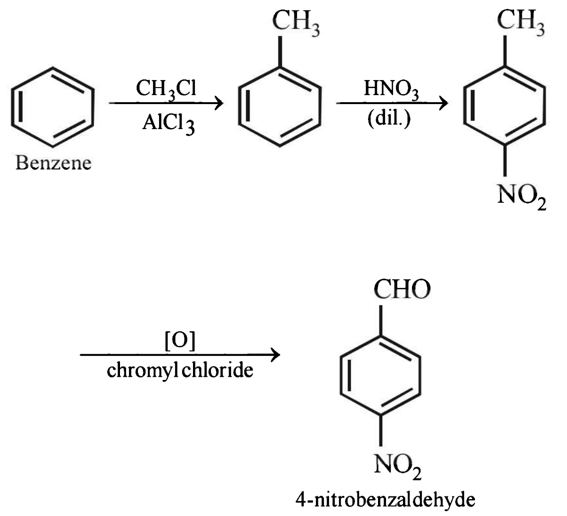


(*ix*)

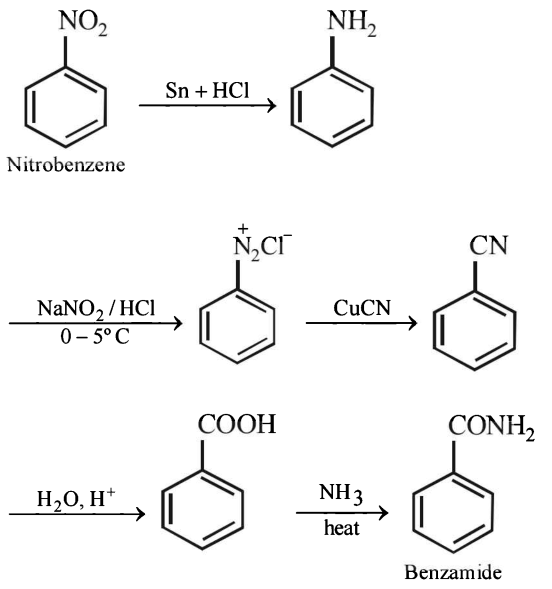


On fractional crystallization para isomer crystallizes first.

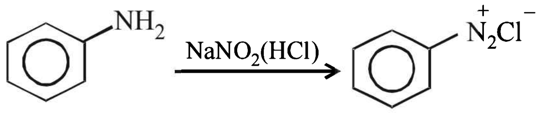
(*x*)

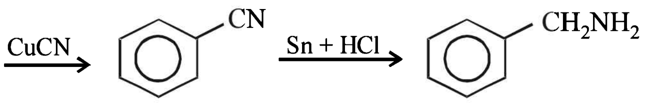


(*xi*)

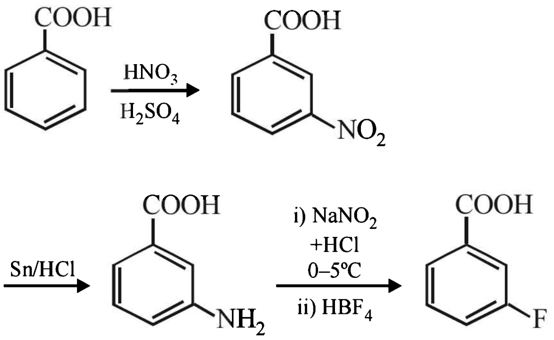


(*xii*)

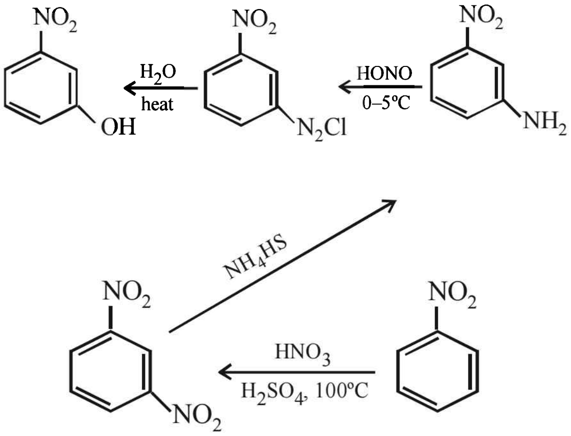




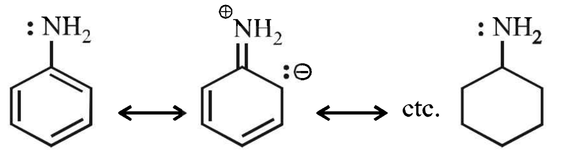
(*xiii*)



(*xiv*) Going backward, we can easily solve the problem.



2. (*i*) Aniline is weak base than cyclohexylamine because of resonance while there is no resonance in cyclohexylamine.



Resonating Structures of aniline

Cyclohexylamine (No resonance)

(*ii*) *o*-nitrophenol shows intramolecular H-bonding and *p*-nitrophenol shows intermolecular H- bonding and thus its several molecules associate with each other. The *ortho* isomer goes with the steam due to its low boiling point.

(*iii*) **TIPS/Formulae :** Two factors operate in deciding the basicity of alkyl amines.

(a) Inductive effect (b) Solvation effect

(a) **Inductive effect.** The alkyl group being electron releasing increases the charge density on nitrogen. This in turn increases the basicity of amines. The expected order of basicity is

$R_3N > R_2NH > RNH_2 > NH_3$

(b) **Solvation effect.** Because of the positive charge carried by the conjugate acid of an amine, it is stabilised by the hydrogen bonding with the solvent water. The larger the number of hydrogens attached to the nitrogen in the conjugate acid, the larger is its stability and thus larger is the basicity of the corresponding base. The expected order of basicity of the alkylamines will be

$NH_3 > RNH_2 > R_2NH > R_3N$

The inductive and solvent effects predict the opposite trend in the basicity of alkyl amines. In going from R_2NH to R_3N the solvation effect plays a more dominating role as compared to the inductive effect making R_2NH more basic than R_3N.

A simple explanation is that the steric factor in R_3N makes the availability of a lone pair of electrons on nitrogen poor than in the dialkylamine, predicting R_2NH a stronger base than R_3N.

(*iv*) The nitro group in nitrobenzene strongly deactivates the benzene ring due to – I and – M effects. This decreases the reactivity of benzene ring towards Friedel - Crafts alkylation.

(*v*) **TIPS/Formulae :** $–NO_2$ group is electron withdrawing, hence *m*-directing whereas $–CH_2NO_2$ is not.

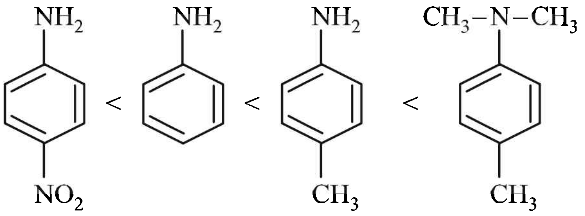
(a) Given compound is an aryl fluoride having electron-withdrawing $–NO_2$ group at *para* position of fluoride atom which activates the fluoride due to – M and – E effects for nucleophilic substitution (S_NAr), hence reaction with NaOH will liberate F^- as NaF.

(b) The given compound is an aryl fluoride having $–CH_2NO_2$ group in the *meta* position which is not capable of activating aryl fluoride (absence of –M and –E effects because NO_2 group is present in *m*-position and also not conjugated to benzene ring) for nucleophilic substitution, hence aq. NaOH will not displace fluorine here, i.e. no F^- will be formed.

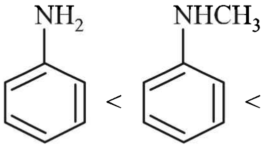
(*vi*) (a) $-\ddot{N}=O$ group is electron releasing, hence *o*-, *p*-directing

(b) $–NO_2$ group is electron withdrawing, hence *m*-directing

3. (*i*) **TIPS/Formulae :** Presence of +I group increases the basicity whereas presence of –I group decreases the basicity.



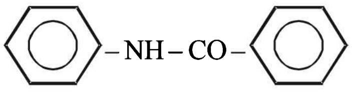
(*ii*)



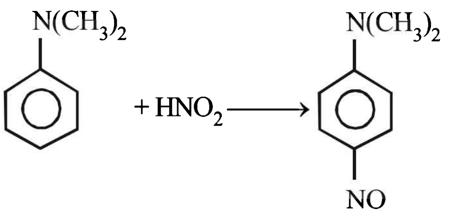
$< CH_3NH_2 < (CH_3)_2NH$

The ease with which the lone pair of electron (unshared) on the N-atom co-ordinates with a proton determines the relative basic strength of amines.

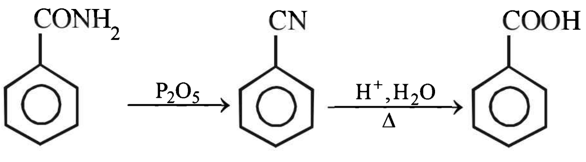
4. (*i*)



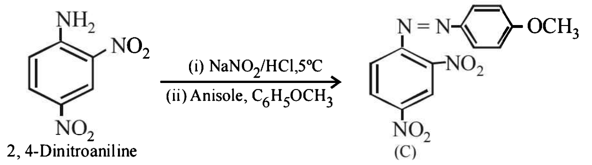
(*ii*)



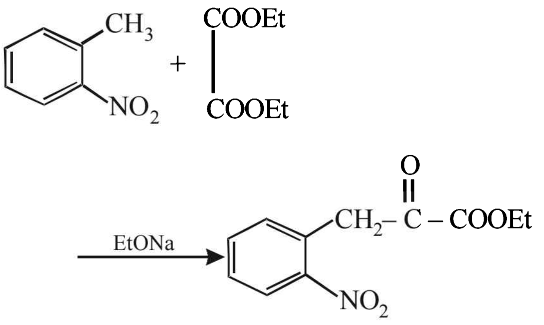
(*iii*)



(*iv*)



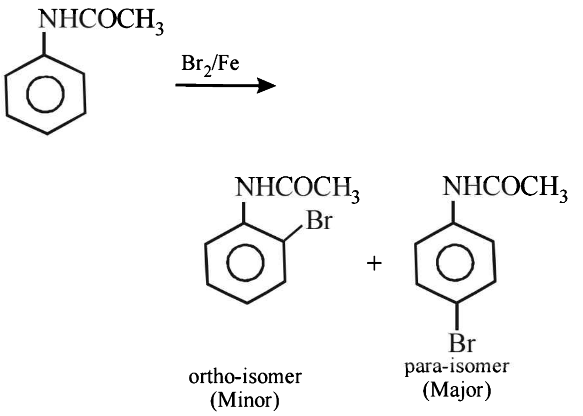
(*v*)



(*vi*) $CH_3-CH_2-NH_2 \xrightarrow{(CH_3CO)_2O}$

$CH_3-CH_2-NH-COCH_3+CH_3COOH$

(*vii*)



5. Hoffmann degradation reaction.

$$\underset{\text{Acetamide}}{CH_3CONH_2}+Br_2+4KOH\rightarrow$$

$$\underset{\text{Methylamine}}{CH_3NH_2}+K_2CO_3+2KBr+2H_2O$$

6. **NOTE :** Carbylamine reaction is a distinction test for primary amines. All primary amines (alphatic or aromatic) on heating with alcoholic KOH and $CHCl_3$ give unpleasant or foul smell of isocyanide which is easily detected.

$$C_2H_5NH_2+CHCl_3+3KOH_{(alc.)}$$

$$\longrightarrow \underset{\substack{\text{bad smell}\\ \text{ethyl isocyanide}}}{C_2H_5NC}+3KCl+3H_2O$$

Diethylamine , a 2° amine, does not respond this test.

7. *Determination of empirical formula :*

	C	**H**	**N**	**O**
% age	49.32	9.59	19.18	21.91
mole	$\frac{49.32}{12}$	$\frac{9.59}{1}$	$\frac{19.18}{14}$	$\frac{21.91}{16}$
	=4.11	=9.59	=1.37	=1.37
(Dividing by 1.37)				
Simplest ratio	3	7	1	1

$\therefore$ Empirical formula of A will be C_3H_7NO and empirical formula wt = 73

Calculation of molecular wt. of (B)

We know, meq. of Ag = meq. of Ag salt

$$\text{or}\quad \frac{\text{Wt. of Ag}}{\text{Eq. wt. of Ag}}=\frac{\text{Wt. of salt}}{\text{Eq. wt. of salt}}$$

$$\text{or}\quad \frac{59.67}{108}=\frac{100}{E_{salt}}\quad \textit{or}\ E_{salt}=181$$

$E_{salt}=E_{Ag}+E_{Anion}\Rightarrow E_{anion}=181-108=73$

For monobasic acid (B), adding one H,

Mol. wt. = Eq. wt. + 1 = 73 + 1 = 74

B being monobasic can be represented as $C_nH_{2n+1}COOH$

$\Rightarrow 74=12n+(2n+1).1+12+16+16+1 \Rightarrow n=2$

$\therefore B=C_2H_5COOH$

Nature of A : Since B is obtained by the action of A with NaOH followed by hydrolysis, so A is an amide, $CH_3CH_2CONH_2$.

Reaction :

$$\underset{\substack{(A)\\ \text{(Propanamide)}}}{CH_3CH_2CONH_2}\xrightarrow{NaOH}CH_3CH_2COONa$$

$$\xrightarrow{HOH}\underset{\substack{(B)\\ \text{(Ethanoic acid)}}}{CH_3CH_2COOH}$$

8. **TIPS/Formulae :**

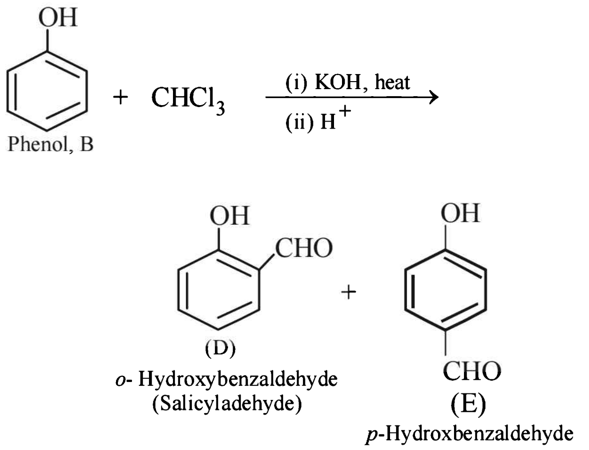
(i) Carbylamine reaction involves reaction of a primary amine with alc. KOH and $CHCl_3$ which results a product containing isocyanide group with unpleasant smell.

(ii) Riemer-Tiemann reaction of phenol produces *o* and *p* isomers.

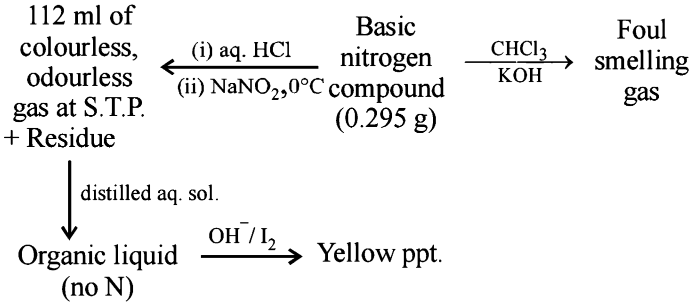
Solution of compound A in chloroform when treated with alcoholic KOH yields compound C (C_7H_5N) having an unpleasant odour which may be due to isocyanide. Hence the above reaction may be an example of carbylamine reaction. Therefore, compound A must be aniline ($C_6H_5NH_2$) and C must be phenylisocyanide (C_6H_5NC).

$$\underset{\text{Aniline, A}}{C_6H_5NH_2} + CHCl_3 + 3KOH \rightarrow \underset{\text{Phenyl isocyanide, C}}{C_6H_5NC} + 3KCl + 3H_2O$$

Alkaline aqueous layer of B when heated with chloroform gives D and E which are isomeric with each other and have molecular formula $C_7H_6O_2$. This indicates the possibility that Reimer-Tiemann reaction would have taken place. Hence compound B must be phenol and compounds D and E are *o*- and *p*-hydroxybenzaldehydes. This can be represented in the following way.



9. Let us summarise the given facts.



Reaction of the original compound with alcoholic potash and chloroform to give foul smelling gas indicates that it contains a primary $-NH_2$ group.

$$\underset{\text{(Basic compound)}}{R-NH_2} + CHCl_3 + KOH \longrightarrow \underset{\text{Carbylamine (foul smelling)}}{R-NC\uparrow}$$

Determination of mol. weight of the amine :

112 ml. of gas is evolved at S.T.P. by 0.295 g of amine

22400 ml. of gas is evolved by $= \dfrac{0.295}{112} \times 22400 = 59$

Hence the mol. wt. of the amine = 59

$\therefore$ Mol. wt. of the alkyl group = 59 – 16 = 43

Nature of alkyl gp. of mol. wt. 43 = C_3H_7-

Thus the amine may be either

$$CH_3CH_2CH_2NH_2 \text{ or } \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHNH_2$$

The reaction of amine with $NaNO_2$ at 0°C and all other reactions may thus be written as below.

$$\underset{n\text{-Propylamine}}{CH_3CH_2CH_2NH_2} \xrightarrow[\text{(ii) } NaNO_2/0°C]{\text{(i) HCl}} CH_3CH_2CH_2OH + N_2\uparrow$$

$$\downarrow \text{aq.sol.distill}$$

$$CH_3CH_2CH_2OH$$

$$\downarrow OH^-,\ I_2$$

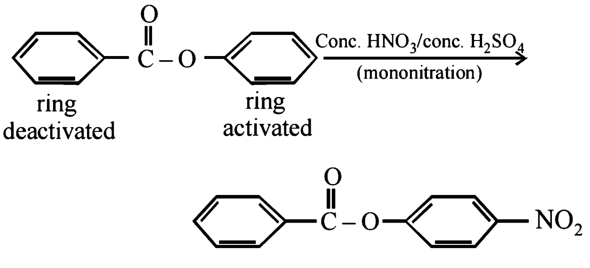
No yellow ppt.

$$\underset{\text{Isopropylamine}}{(CH_3)_2CHNH_2} \longrightarrow (CH_3)_2CHOH + N_2\uparrow$$

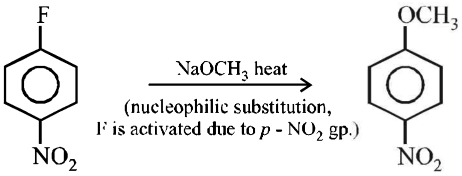
$$\longrightarrow (CH_3)_2CHOH \xrightarrow[\text{(Haloform reaction)}]{OH^-, I_2} \underset{\text{(yellow)}}{CHI_3\downarrow}$$

NOTE : Since the given reactions correspond to isopropylamine, the original compound may be propylamine or **isopropylamine**, $(CH_3)_2CHNH_2$.

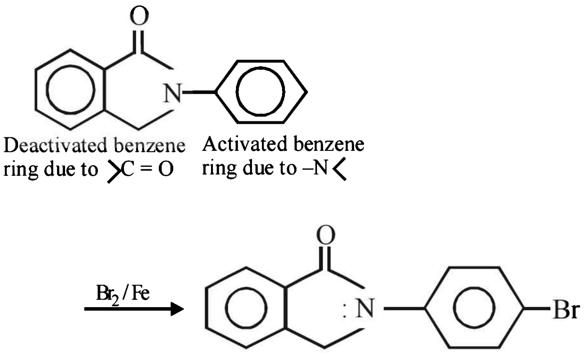
10. (*i*)



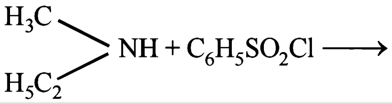
(*ii*)



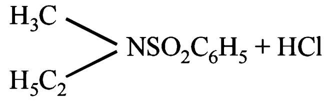
(*iii*)



11. A (C_3H_9N) is a 2° amine $CH_3-NH-C_2H_5$ (ethymethylamine) because the benzene sulphonyl chloride is solid and insoluble in alkali.



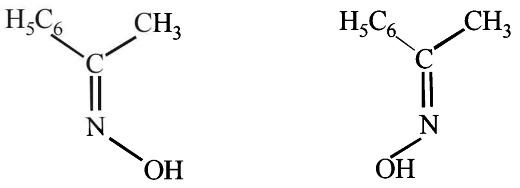
$$\begin{matrix} H_3C \\ H_5C_2 \end{matrix}\!\!>\!NH + C_6H_5SO_2Cl \longrightarrow$$



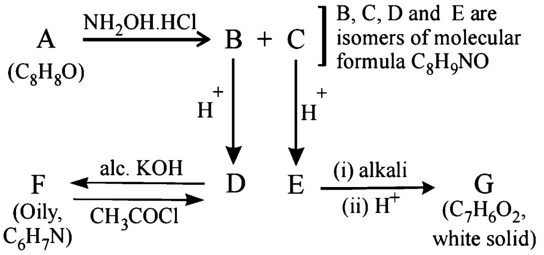
N, N-ethylmethylbenzene sulphonamide
(Insoluble in alkali)

12. $C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{Phenyl isonitrile (foul smelling)}}{C_6H_5N \equiv C} + 3\,KCl + 3H_2O$

13.



14. Summarise the given facts.



From the above set, following conclusions can be drawn.

(i) Since the oily compound F (C_6H_7N) reacts with acetyl chloride, it must have - NH_2 or > NH group. Thus (F) can be written as $C_6H_5NH_2$ or C_6H_5-NH-H, i.e., it is $C_6H_5NH_2$ and hence D is $C_6H_5NHCOCH_3$.

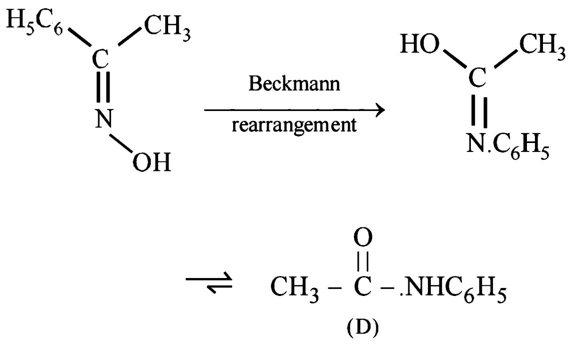
$$\underset{(F)}{C_6H_5NH_2} \underset{\text{alc. KOH}}{\overset{CH_3COCl}{\rightleftarrows}} \underset{(D)}{C_6H_5NHCOCH_3}$$

(ii) Compound E on treatment with alkali followed by acidification gives a white solid compound (G), $C_7H_6O_2$. Thus (G) seems to be an acid, hence it is C_6H_5COOH.

(iii) Since (D) and (E) are isomers of the formula C_8H_9NO, and give $C_6H_5NH_2$ and C_6H_5COOH respectively, both should be amides having different alkyl or aryl group. Thus (D) should be $C_6H_5NHCOCH_3$, and (E) must be $CH_3NHCOC_6H_5$.

(iv) Since compounds (D) and (E) are formed by the rearrangement of compounds (B) and (C) respectively. Compounds (B) and (C) should be oximes > C = NOH (recall that oximes rearrange to amides - **Beckmann rearrangement**). Further oximes having different alkyl (aryl) groups show geometrical isomerism (*syn* and *anti*), compounds (B) and (C) must have following structures.

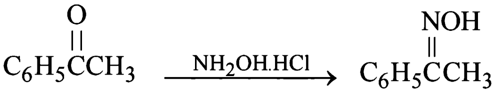
Recall that Beckmann rearrangement involves migration of *anti* -alkyl or aryl group, i.e.,



Since (D) is formed from (B), and (E) from (C), (B) and (C) should have following structures.

(B) (C)

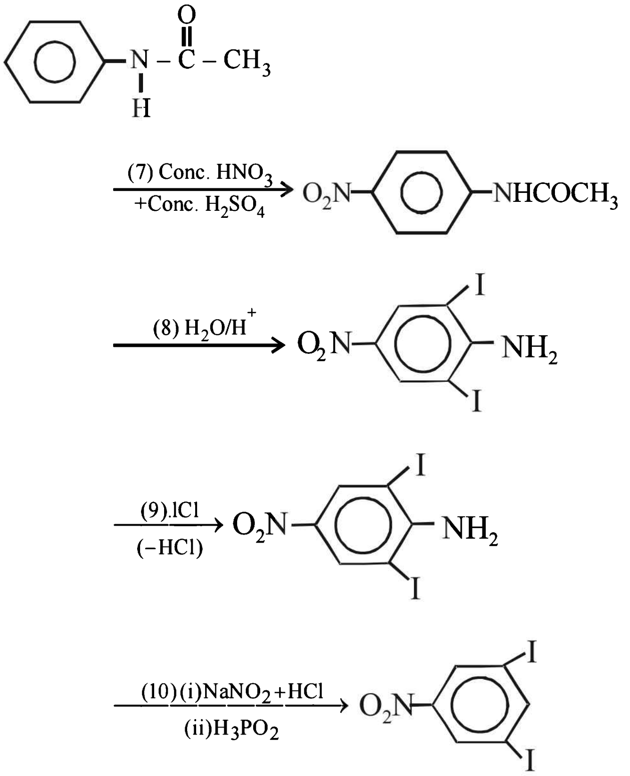
(v) Lastly, oximes (B) and (C) are formed from (A), the latter should be a ketone of the formula $C_6H_5COCH_3$,



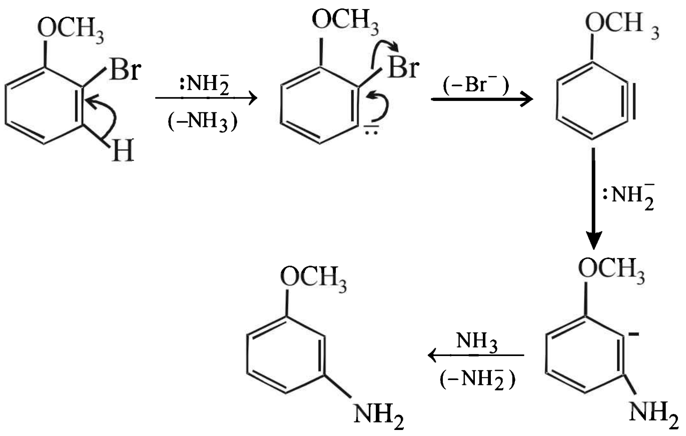
$$\underset{(A)}{C_6H_5\overset{\overset{O}{||}}{C}CH_3} \xrightarrow{NH_2OH.HCl} \underset{(B)\,\&\,(C)}{C_6H_5\overset{\overset{NOH}{||}}{C}CH_3}$$

(A) (B) & (C)

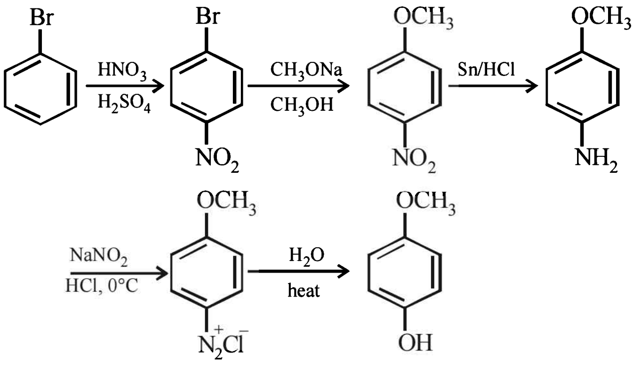
15.



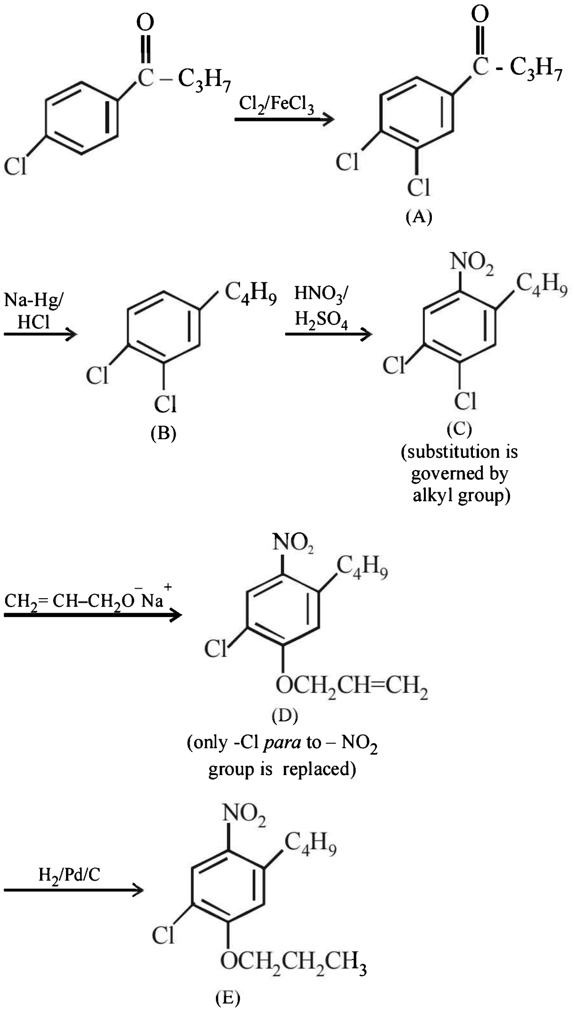
16. The reaction proceeds via benzyne formation



17.



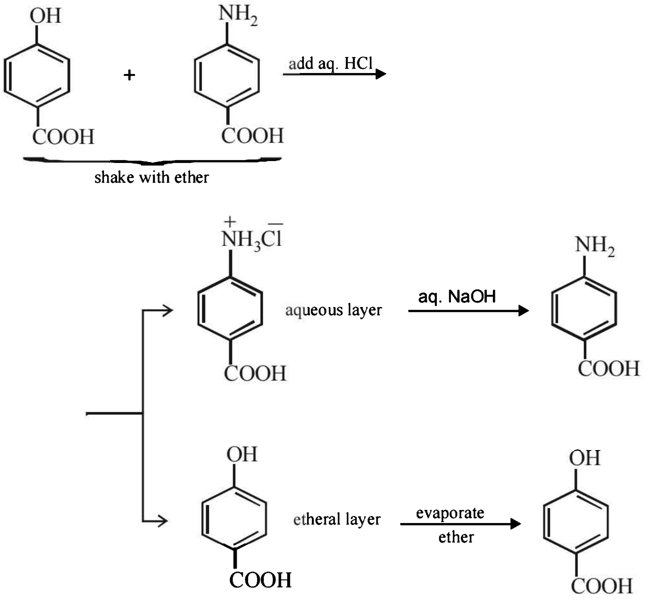
18.



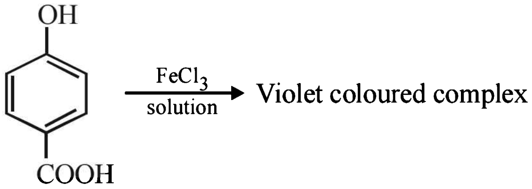
(C) (substitution is governed by alkyl group)

(D) (only -Cl *para* to – NO_2 group is replaced)

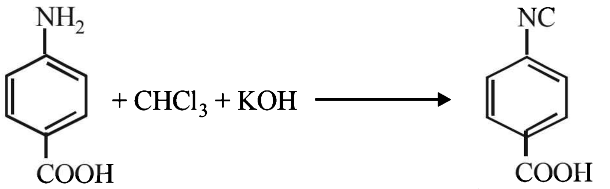
19.



Test of phenolic group :



Test of 1° amino group :

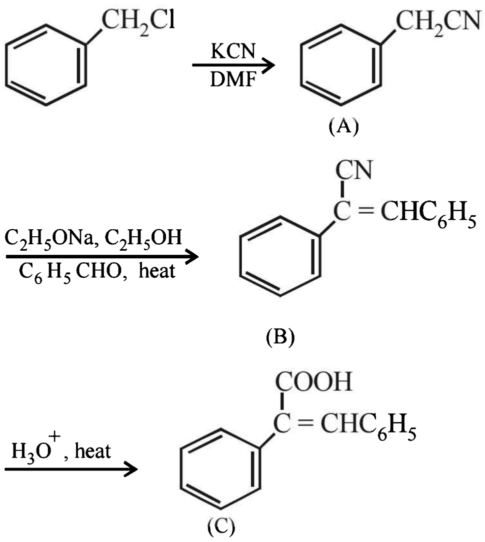


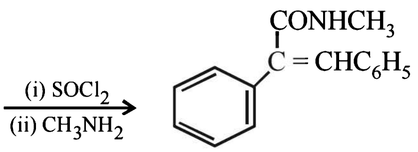
(characteristic foul smell of isocyanide)

Test of – COOH group :

$$-COOH \xrightarrow{NaHCO_3} \underset{\text{With effervescences}}{CO_2\uparrow} \xrightarrow[\text{water}]{\text{lime}} \text{Milky solution}$$

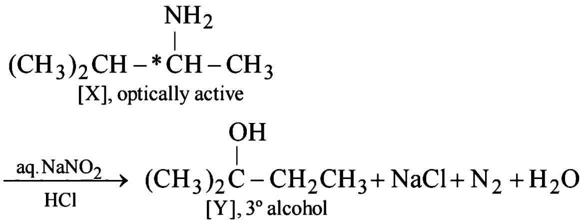
20.





(D)

21. (i)

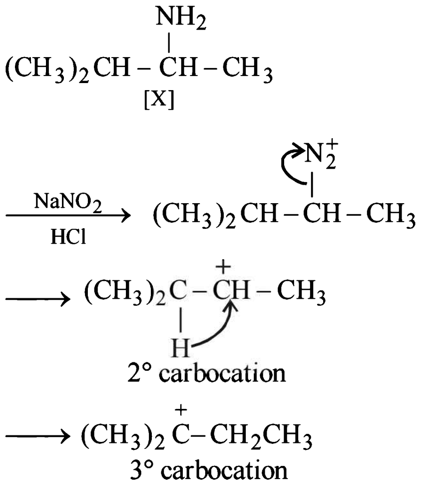


$(CH_3)_2CH-{}^{*}\overset{NH_2}{C}H-CH_3$ [X], optically active

$\xrightarrow[HCl]{aq.NaNO_2} (CH_3)_2\overset{OH}{C}-CH_2CH_3 + NaCl + N_2 + H_2O$ [Y], 3° alcohol

(ii) [Y], a 3° alcohol is optically inactive.

(iii) Formation of [Y] from [X].

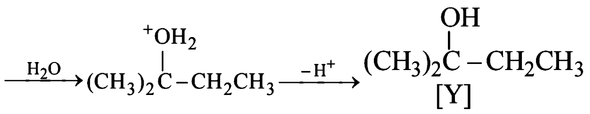


$(CH_3)_2CH-\overset{NH_2}{C}H-CH_3$ [X]

$\xrightarrow[HCl]{NaNO_2} (CH_3)_2CH-\overset{N_2^+}{C}H-CH_3$

$\longrightarrow (CH_3)_2\underset{H}{C}-\overset{+}{C}H-CH_3$ 2° carbocation

$\longrightarrow (CH_3)_2\overset{+}{C}-CH_2CH_3$ 3° carbocation



$\xrightarrow{H_2O} (CH_3)_2\overset{^+OH_2}{C}-CH_2CH_3 \xrightarrow{-H^+} (CH_3)_2\overset{OH}{C}-CH_2CH_3$ [Y]

F. Match the Following

1. (A)– p, q, s, t; (B) – s, t; (C) – p; (D) – r

(A) $CH_3CH_2CH_2CN \xrightarrow[DIBAL-H]{Pd-C/H_2 \text{ or}} CH_3CH_2CH_2CH_2NH_2$

$CH_3CH_2CH_2CN \xrightarrow[\text{(Stephen reduction)}]{SnCl_2/HCl} CH_3CH_2CH_2CHO$

$CH_3CH_2CH_2CN \xrightarrow[H_2O]{OH^-} CH_3CH_2CH_2COO^-$

(B) $CH_3CH_2OCOCH_3 \xrightarrow{DIBAL-H} CH_3CH_2OH$

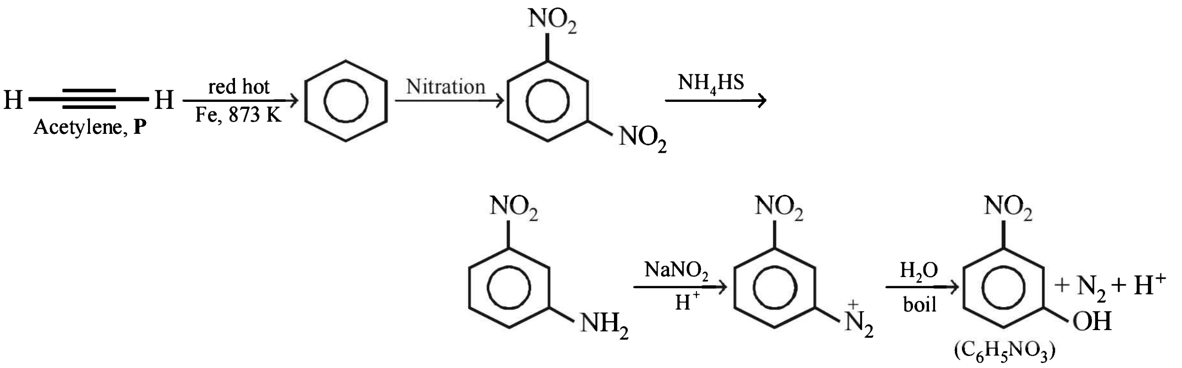
$CH_3CH_2OCOCH_3 \xrightarrow[H_2O]{OH^-} CH_3CH_2OH + CH_3COO^-$

(C) $CH_3CH=CHCH_2OH \xrightarrow{Pd-C/H_2} CH_3CH_2CH_2CH_2OH$

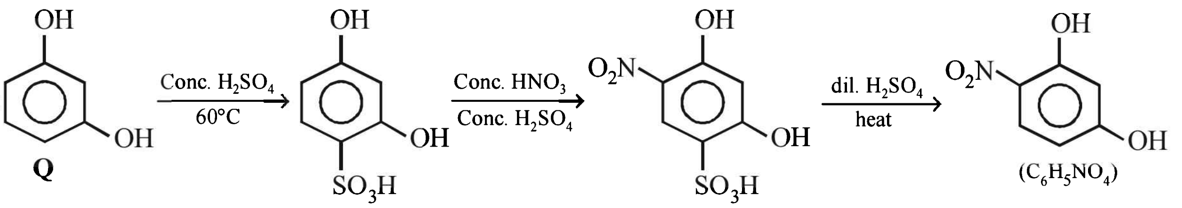
(D) $CH_3CH_2CH_2CH_2NH_2 \xrightarrow[KOH]{CHCl_3} CH_3CH_2CH_2CH_2NC$

Isonitrile (foul smelling)

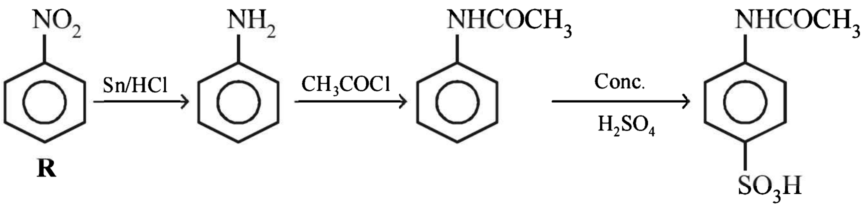
2. **(c)** **Scheme (III) :**

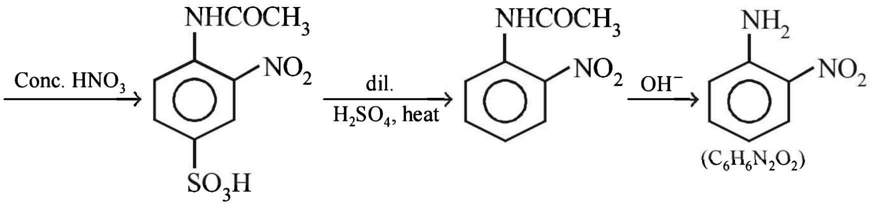


Scheme (IV) :

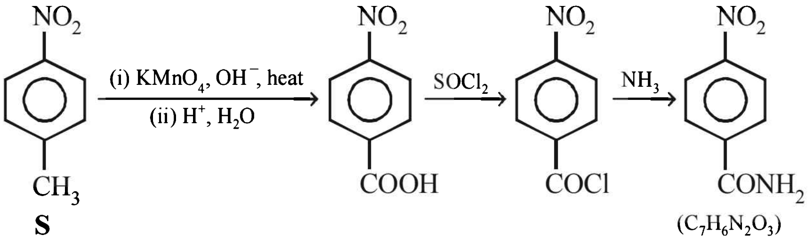


Scheme (II) :



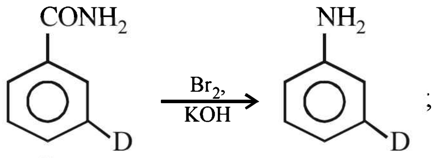


Scheme (I) :

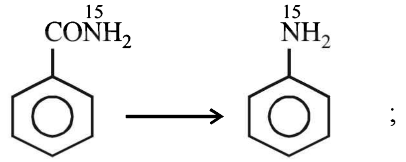


G. Comprehension Based Questions

1. **(d)** The reagent used in Hofmann bromamide reaction is alkaline halogen (NaOH or KOH + X_2).
2. **(d)** Conversion of (iii) to (iv) involving rearrangement is the slowest step. Species (iii) is electron deficient (N has only 6 electrons), hence it has a tendency to get its octet completed by migration of alkyl group.
3. **(b)** Since the reaction is intramolecular, no cross product will be formed.

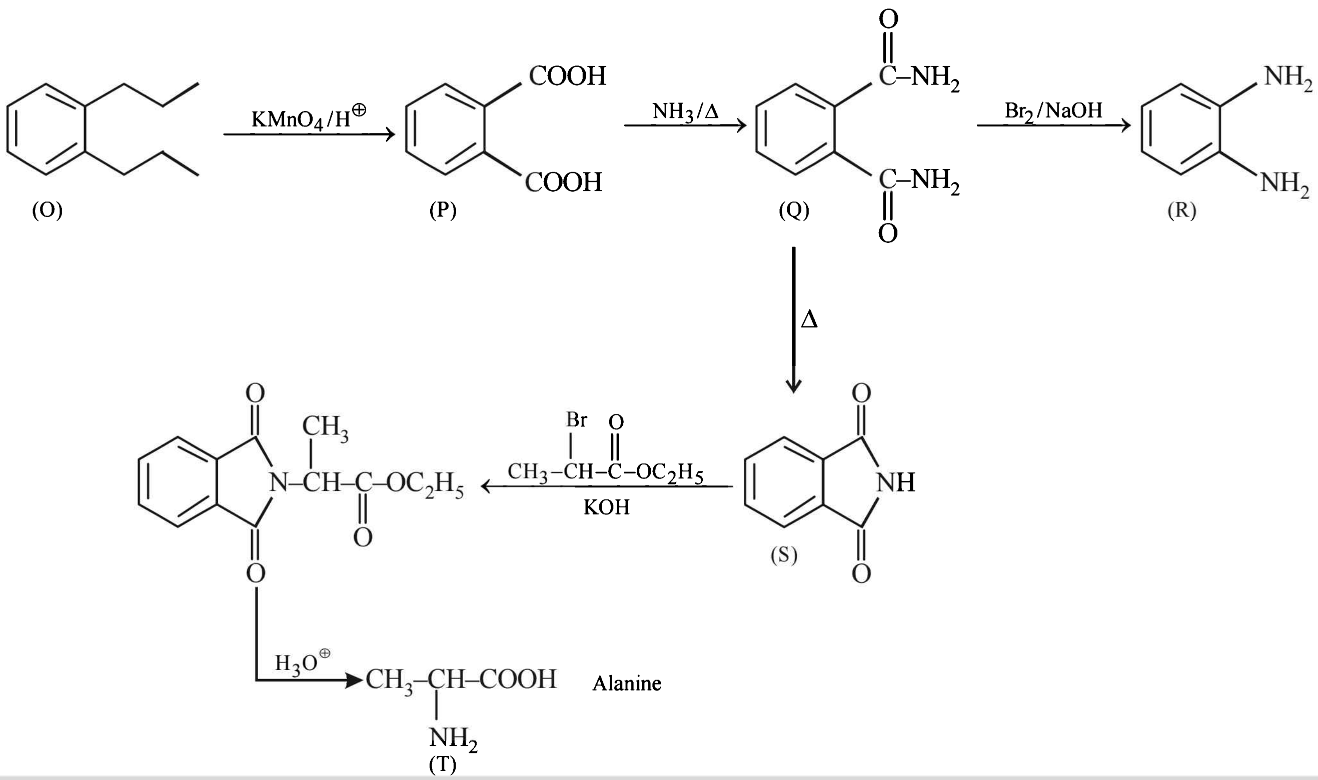


(i)



(ii)

4. **(a)**
5. **(b)**

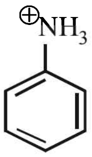


H. Assertion & Reason Type Questions

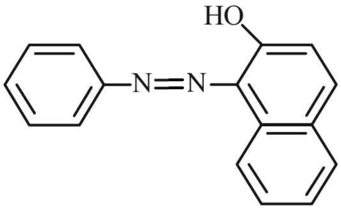
1. **(a)** In *o*-nitrophenol intramolecular H-bonding is possible because OH and NO_2 groups are close to each other. This makes the *ortho* isomer less acidic as its capacity to donate a proton (H-atom) decreases. There is no such intramolecular H–bonding in the *p*-isomer.

2. **(d)** Chlorobenzene is resonance stabilized.
Thus aryl halides (chlorobenzene) do not undergo nucleophilic substitution. Reason is correct.

3. **(d)** **TIPS/FORMULAE :** Electron donating tendency to a double bond is called +M effect and the transfer of electrons take place towards the attacking reagent due to +E effect.
In strongly acidic conditions, aniline becomes protonated with the result lone pair of electrons is not available to produce +E and +M effects. Thus here aniline becomes less reactive towards electrophilic substitution. On the other hand, the $-\overset{\oplus}{N}H_3$ group exerts strong –I effect causing deactivation of the ring.



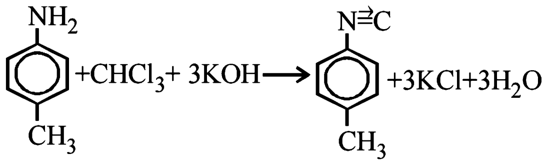
4. **(d)** The colour of the azo dye formed will be orange red but not blue. However, the colour of dye can said to be due to extended conjugation due to presence of azo group.



Section-B JEE Main/ AIEEE

1. **(a)** $C_2H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_2H_5N \equiv C + 3KCl + 3HCl$
(Ethyl isocyanide)

2. **(c)**



3. **(b)** The alkyl groups are electron releasing group (+ I), thus increases the electron density around the nitrogen thereby increasing the availability of the lone pair of electrons to proton or lewis acid and making the amine more basic. Hence more the no. of alkyl group more basic is the amine. Therefore the correct order is
$NH_3 < CH_3NH_2 < (CH_3)_2N$

4. **(d)** Ethyl isocyanide on hydrolysis form primary amines.

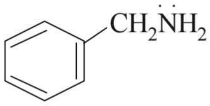
$$CH_3CH_2N \equiv C + H_2O \xrightarrow{H^+}$$

$$CH_3CH_2NH_2 + HCOOH$$

Therefore it gives only one mono chloroalkane.

5. **(b)** Wurtz reaction is for the preparation of hydrocarbons from alkyl halide

$$RX + 2Na + XR \longrightarrow R - R + 2NaX$$

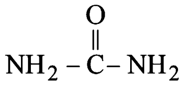
6. **(d)** Benzylamine  is most basic. In others the basic character is suppressed due to Resonance (see applications of resonance).

7. **(b)**

Element	*%*	*Relative number of atoms*	*Simple Ratio*
C	20%	$20/12 = 1.66$	$1.66/1.66 = 1$
H	6.67%	$6.67/1 = 6.67$	$6.67/1.66 = 4.16$
N	46.67%	$46.67/14 = 3.33$	$3.33/1.66 = 2.02$
O	26.64%	$26.64/16 = 1.66$	$1.66/1.66 = 1.0$

The compound is CH_4N_2O

Empirical weight = 60; Mol. wt. = 60; $\therefore n = \dfrac{60}{60} = 1$

Molecular formula = CH_4N_2O; 
$NH_2 - \overset{\overset{O}{\|}}{C} - NH_2$

On heating urea loses ammonia to give Biuret

$$2NH_2CONH_2 \longrightarrow H_2NCO.NH.CONH_2 + NH_3$$

Biuret with alkaline $CuSO_4$ gives violet colour. Test for –CONH– group.

8. **(d)** **NOTE :** Aromatic amines are less basic than aliphatic amines. Among aliphatic amines the order of basicity is 2° > 1° > 3°. The electron density is decreased in 3° amine due to crowding of alkyl group over N atom which makes the approach and bonding by a proton relatively difficult. Therefore the basicity decreases. Further Phenyl group show – I effect, thus decreases the electron density on nitrogen atom and hence the basicity.
∴ dimethylamine (2° aliphatic amine) is strongest base among given choices.
∴ The correct order of basic strength is
Dimethylamine > Methyl amine > Trimethyl amine > Aniline.

9. (a) This is carbylamine reaction.

$$CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5NC + 3KCl + 3H_2O$$

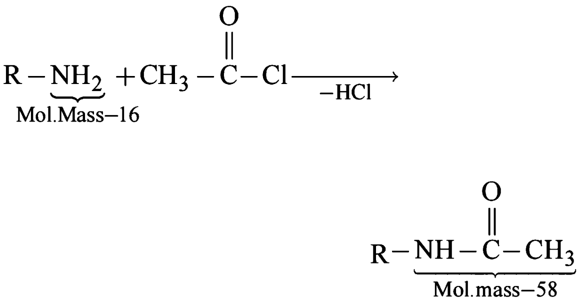
10. (c) Primary aromatic amines react with nitrous acid to yield arene diazonium salts.

$$\underset{\text{1° Aromatic amine}}{ArNH_2} + NaNO_2 + 2HX \xrightarrow{\text{cold}} \underset{\text{Arenediazonium salt}}{Ar—N=N^+X^-} + NaX + 2H_2O$$

The diazonium group can be replaced by fluorine by treating the diazonium salt with fluoroboric acid (HBF_4). The precipitated diazonium fluoroborate is isolated, dried and heated until decomposition occurs to yield the aryl fluoride. This reaction is known as **Balz-Schiemann reaction.**

$$Ar—N_2^+X^- \xrightarrow{HBF_4} Ar—N_2^+BF_4^-\downarrow \xrightarrow{\text{heat}} Ar—F + BF_3 + N_2$$

11. (b)



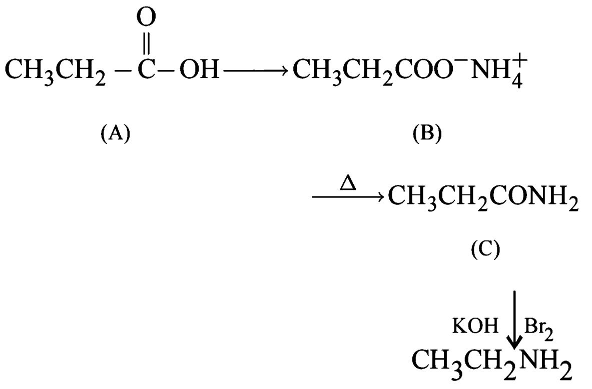
$$R-\underbrace{NH_2}_{\text{Mol.Mass–16}} + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow[-HCl]{} R-\underbrace{NH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}_{\text{Mol.mass–58}}$$

Now since the molecular mass increases by 42 unit as a result of the reaction of one mole of CH_3COCl with one-NH_2 group and the given increase in mass is 210. hence the number of $–NH_2$ group is = 210/42 = 5

12. (d)

$$\underset{\text{(I)}}{A \xrightarrow{NH_3} B} \underset{\text{(II)}}{\xrightarrow{\Delta} C} \underset{\text{(III)}}{\xrightarrow[KOH]{Br_2}} CH_3CH_2NH_2$$

Reaction (III) is a Hofmann bromamide reaction formation of $CH_3CH_2NH_2$ is possible only from a compound $CH_3CH_2CONH_2$ which can be obtained from the compound $CH_3CH_2COO^-NH_4^+$ (B) in (II) reaction further propanic acid (CH_3CH_2COOH) on reaction with NH_3 produce $CH_3CH_2COO^-NH_4^-$ (reaction I) hence the reaction will be



$$\underset{\text{(A)}}{CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \longrightarrow \underset{\text{(B)}}{CH_3CH_2COO^-NH_4^+} \xrightarrow{\Delta} \underset{\text{(C)}}{CH_3CH_2CONH_2} \xrightarrow[\text{KOH}]{Br_2} CH_3CH_2NH_2$$

13. (a) Methyl isocyanate $CH_3-N=C=O$

14. (d) $R-CH_2-NH_2 + CHCl_3 + 3KOH\,(alc) \longrightarrow$

Carbylamine reaction

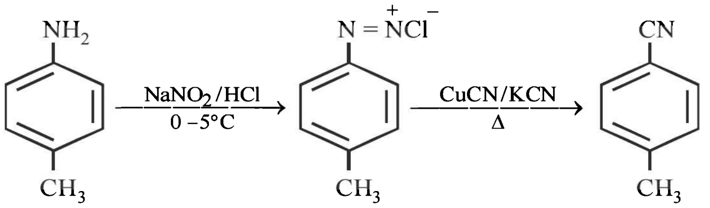
$$\underset{\text{Alkyl isocynide}}{R-CH_2-NC} + 3KCl + 3H_2O$$

15. (a) Arylamines are less basic than alkyl amines and even ammonia. This is due to resonance. In aryl amines the lone pair of electrons on N is partly shared with the ring and is thus less available for sharing with a proton.

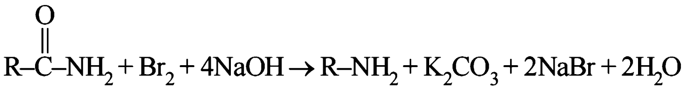
In alkylamines, the electron releasing alkyl group increases the electron density on nitrogen atom and thus also increases the ability of amine for protonation. Hence more the no. of alkyl groups higher should be the basicity of amine. But a slight discrepancy occurs in case of trimethyl amines due to steric effect. Hence the correct order is

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$$

16. (a)



17. (b) 4 moles of NaOH and one mole of Br_2 is required during production of one mole of amine during Hoffmann's bromamide degradation reaction.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \rightarrow R-NH_2 + K_2CO_3 + 2NaBr + 2H_2O$$