ORGANIC COMPOUNDS CONTAINING NITROGEN
[JEE ADVANCED PREVIOUS YEAR SOLVED PAPERS]

JEE ADVANCED

Single Correct Answer Type

1. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosoamine is:

a. Methylamine **b.** Ethylamine

c. Diethylamine **d.** Triethylamine

(IIT-JEE 1981)

2. Acetamide is treated separately with the following reagents. Which one of these would give methylamine?

a. PCl_5 **b.** Soda lime

c. $NaOH + Br_2$ **d.** Hot. conc. H_2SO_4

(IIT-JEE 1983)

3. Carbylamine test is performed in alc. KOH by heating a mixture:

a. Chloroform and silver powder

b. Trihalogenated methane and a primary amine

c. An alkyl halide and a primary amine

d. An alkyl cyanide and a primary amine

(IIT-JEE 1984)

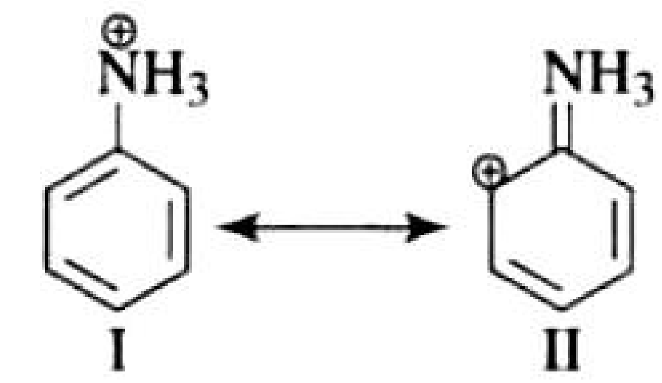
4. Amongst the following the most basic compound is:

a. Benzylamine **b.** Aniline

c. Acetanilide **d.** p-Nitroaniline

(IIT-JEE 1990)

5. Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below:



I II

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 nitrogen has 10 valence electrons.

d. (II) is an acceptable canonical structure.

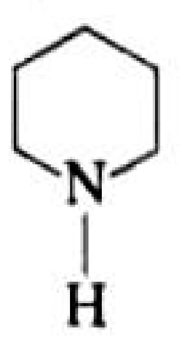
(IIT-JEE 1993)

6. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc H_2SO_4. In the nitrating mixture, HNO_3 acts as a/an

a. base **b.** acid

c. reducing agent **d.** catalyst **(IIT-JEE 1997)**

7. In the following compounds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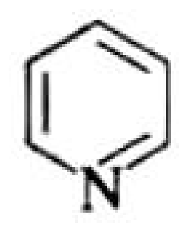
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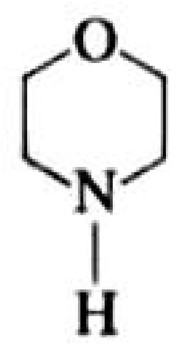
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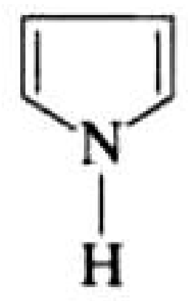
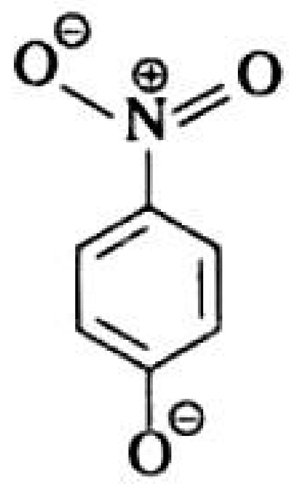

IV

The order of basicity is

a. IV > I > III > II **b.** III > I > IV > II
c. II > I > III > IV **d.** I > III > II > IV

(IIT-JEE 1997)

8. The most unlikely representation of resonance structures of p-nitrophenoxide ion is:

a.


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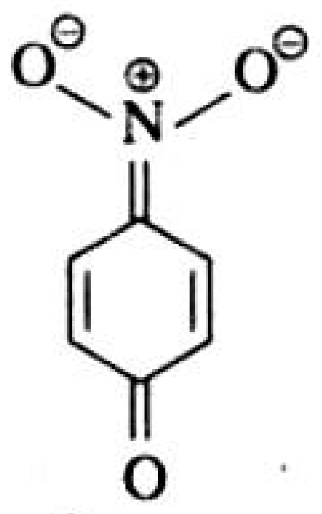
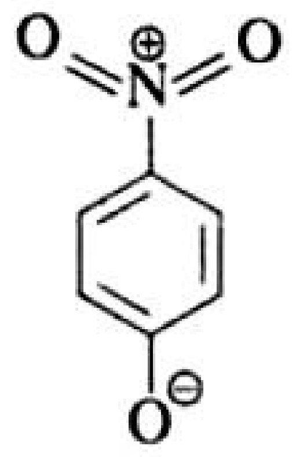
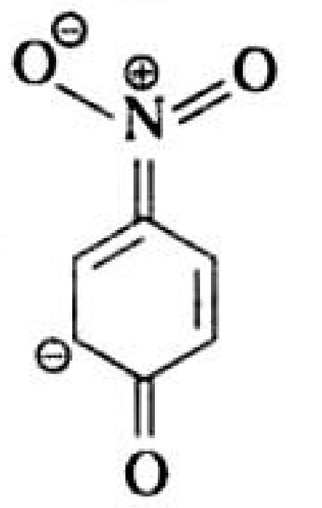


c.


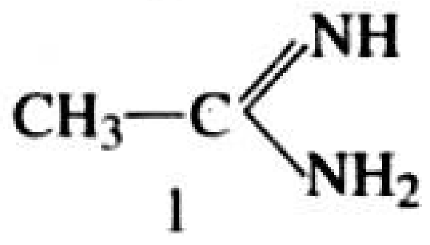
d.


(IIT-JEE 1999)

9. Among the following, the strongest base is:
a. $C_6H_5NH_2$ **b.** $p\text{-}NO_2C_6H_4NH_2$
c. $m\text{-}NO_2.C_6H_4NH_2$ **d.** $C_6H_5CH_2NH_2$

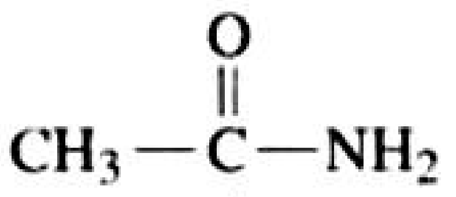
(IIT-JEE 2000)

10. The correct order of basicities of the following compounds is:


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

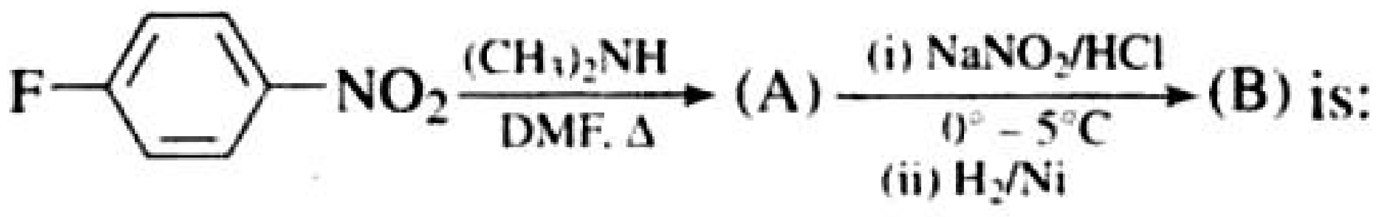
$CH_3-CH_2-NH_2$
2

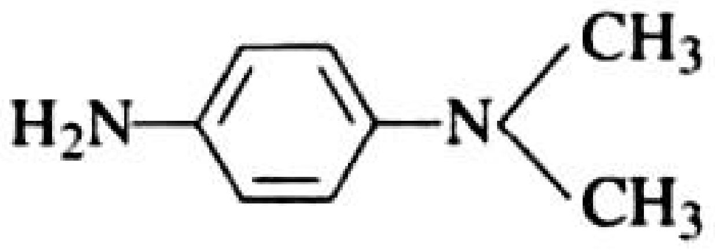
$(CH_3)_2NH$,
3

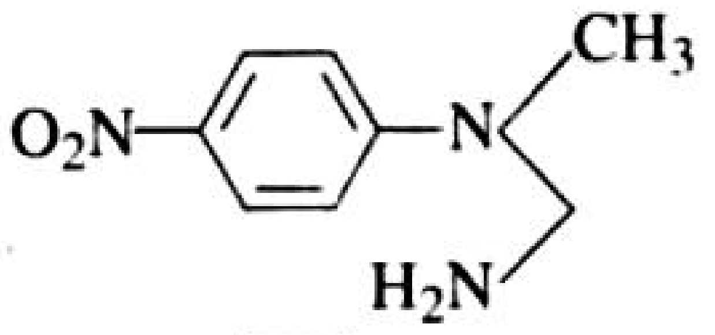

$CH_3-\overset{O}{\overset{||}{C}}-NH_2$
4

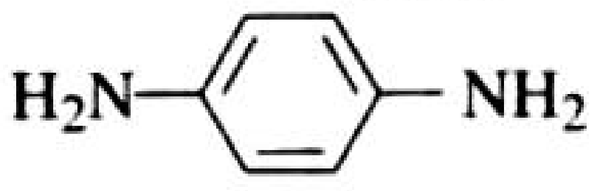
a. (2) > (1) > (3) > (4) **b.** (1) > (3) > (2) > (4)
c. (3) > (1) > (2) > (4) **d.** (1) > (2) > (3) > (4)

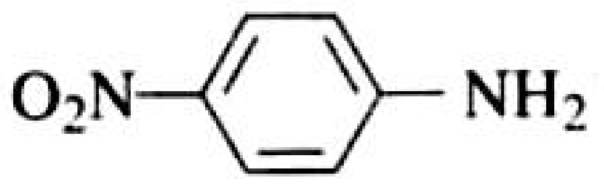
(IIT-JEE 2001)

11.


a.


b.


c.


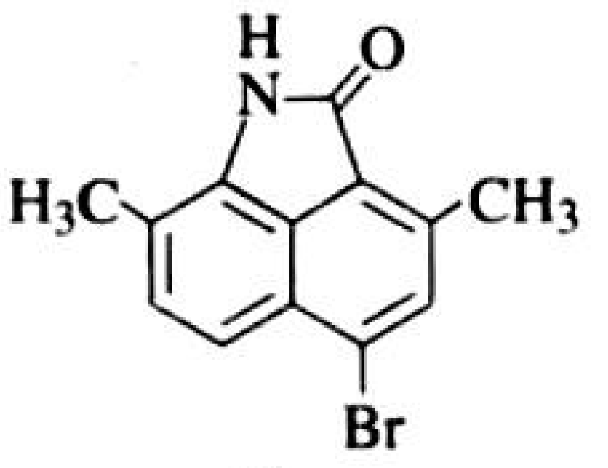
d.


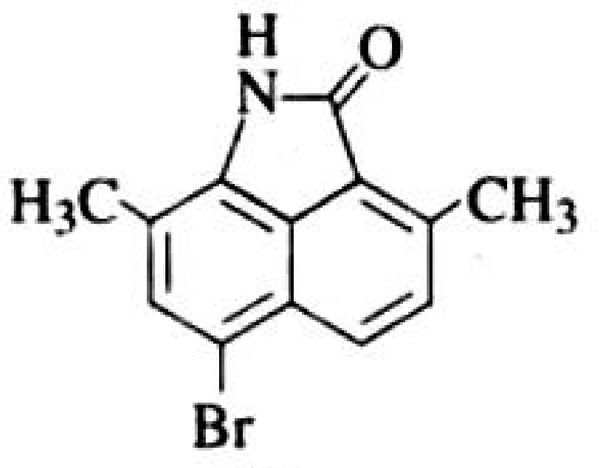
(IIT-JEE 2003)

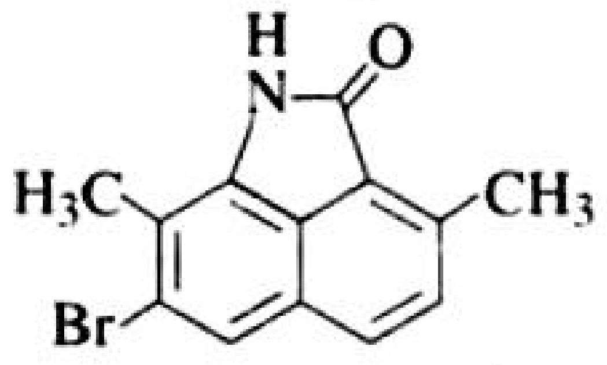
12. Benzamide on reaction with $POCl_3$ gives
a. aniline **b.** chlorobenzene
c. benzylamine **d.** benzonitrile

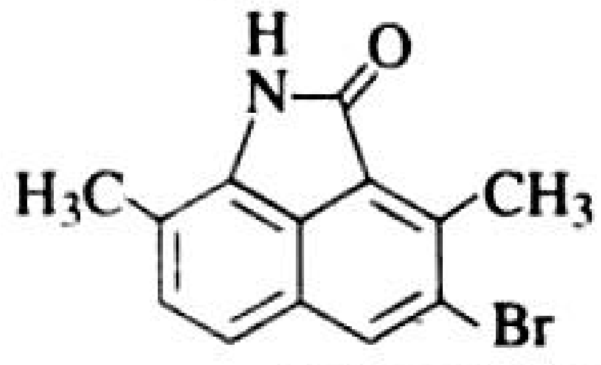
(IIT-JEE 2004)

13. The major product obtained when Be_2/Fe is treated with

a.


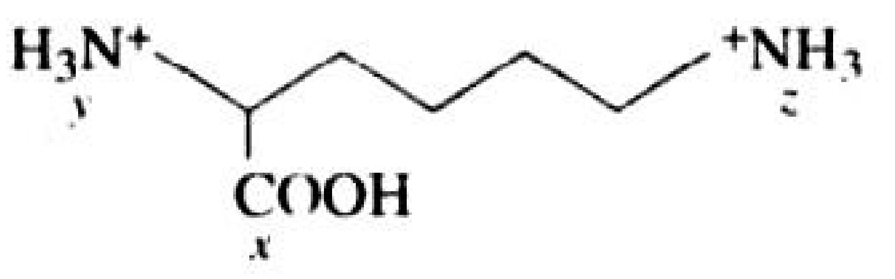
b.


c.


d.


(IIT-JEE 2004)

14. In the compound given below the correct order of the acidity of the positions X, Y and Z is



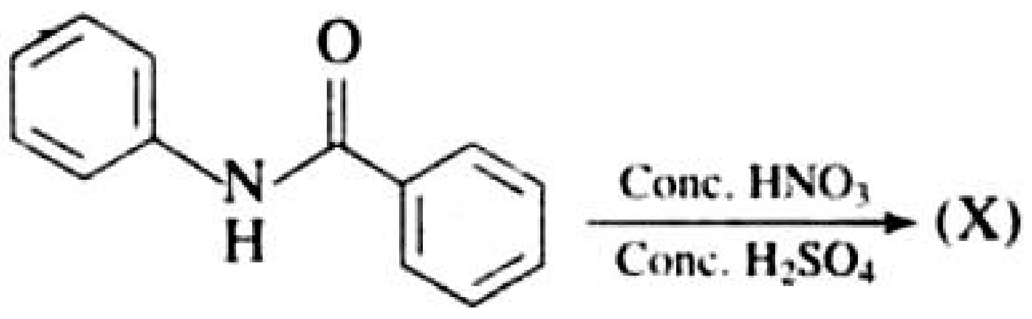
a. Z > X > Y **b.** X > Y > Z
c. X > Z > Y **d.** Y > X > Z

(IIT-JEE 2004)

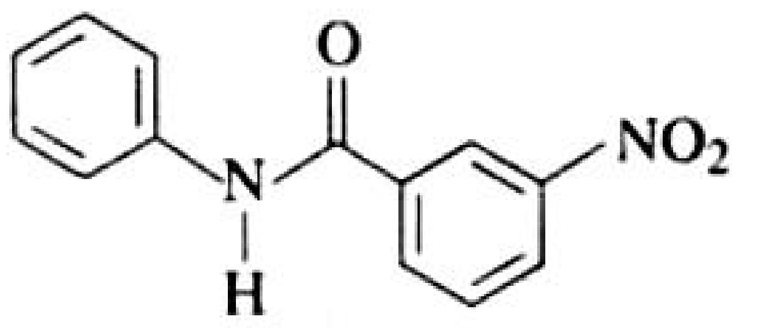
15. In the following reaction,
$CH_3NH_2 + CHCl_3 + KOH \rightarrow$ Nitrogen containing compound + KCl + H_2O. The nitrogen containing compound is
a. $CH_3-NH-CH_3$ **b.** $CH_3-C\neq N$
c. $CH_3\overset{+}{N}\equiv\overset{-}{C}$ **d.** $CH_3-\overset{-}{N}\equiv\overset{+}{C}$

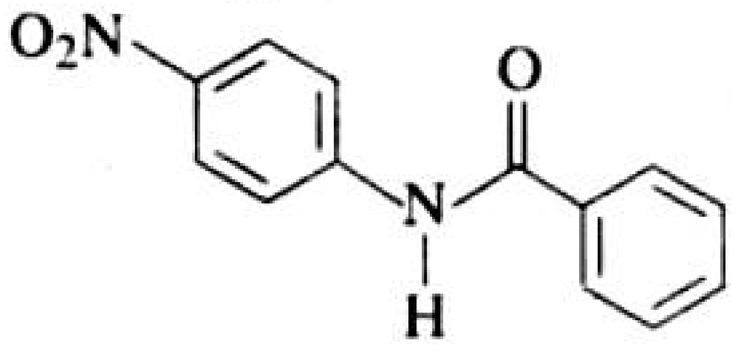
(IIT-JEE 2006)

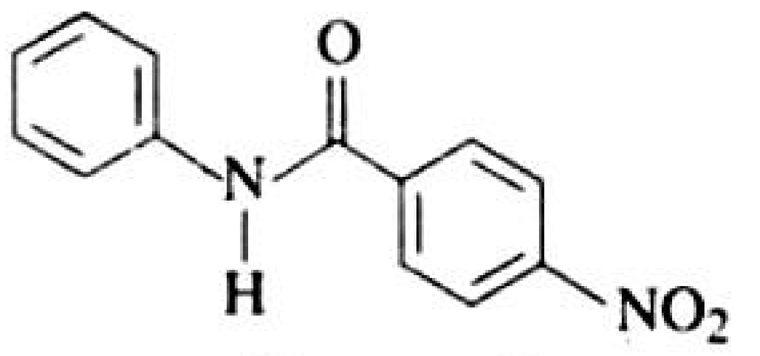
16. In the following reaction,

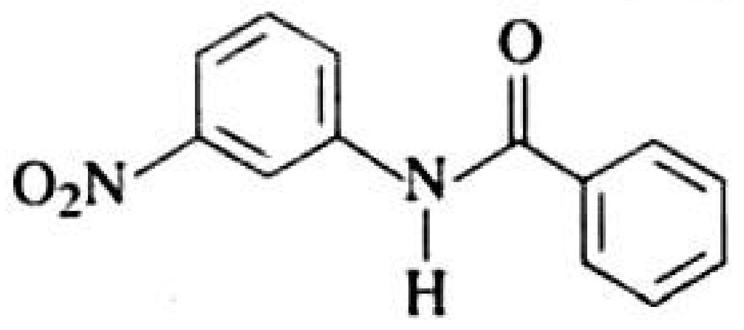


the structure of the major product (X) is:

a.


b.


c.


d.


(IIT-JEE 2007)

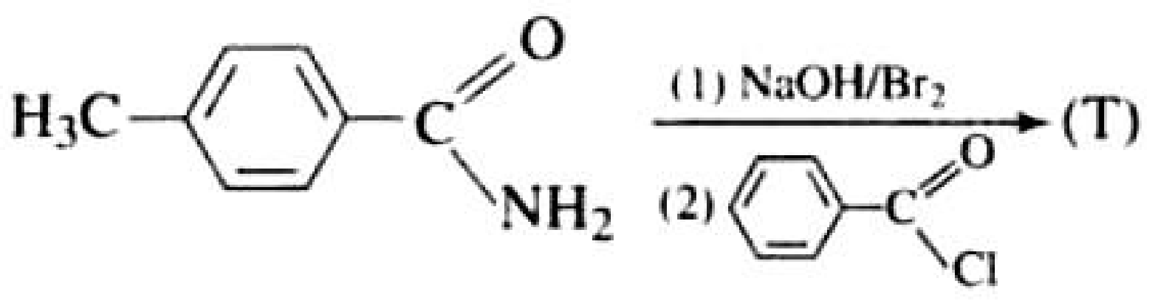
17. The correct stability order of the following resonance structure is

$$\underset{(I)}{H_2C=\overset{+}{N}\equiv\overset{-}{N}}\quad \underset{(II)}{H_2\overset{+}{C}-N\equiv\overset{-}{N}}\quad \underset{(III)}{H_2\overset{-}{C}-\overset{+}{N}\equiv N}\quad \underset{(IV)}{H_2\overset{-}{C}-N\equiv\overset{+}{N}}$$

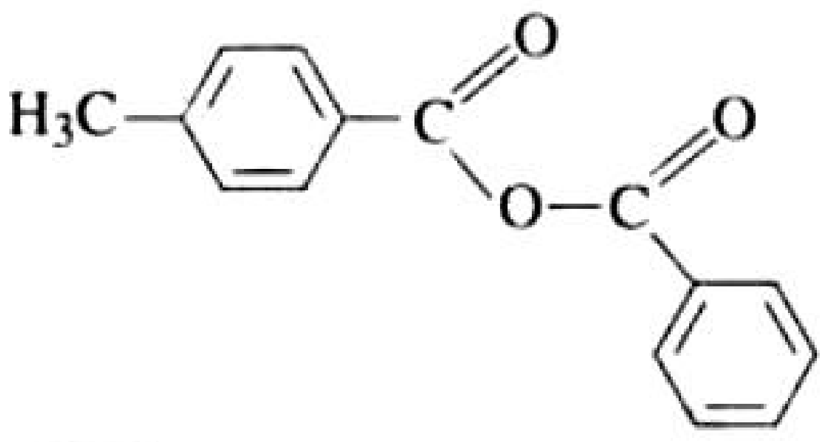
a. (I) > (II) > (IV) > (III) **b.** (I) > (III) > (II) > (IV)
c. (II) > (I) > (III) > (IV) **d.** (III) > (I) > (IV) > (II)

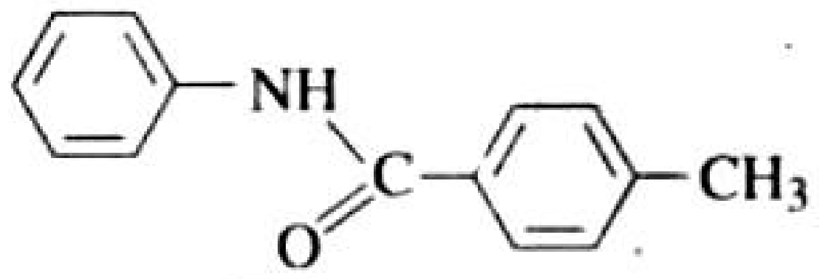
(IIT-JEE 2009)

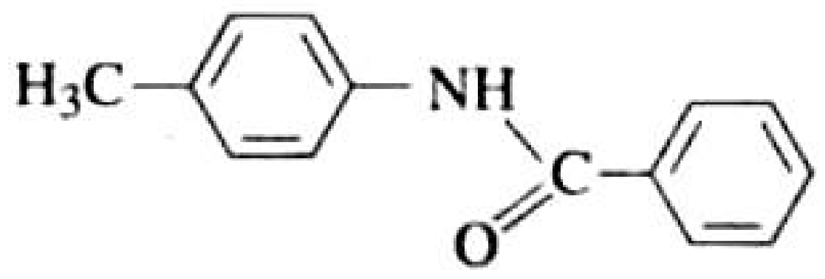
18. In the reaction

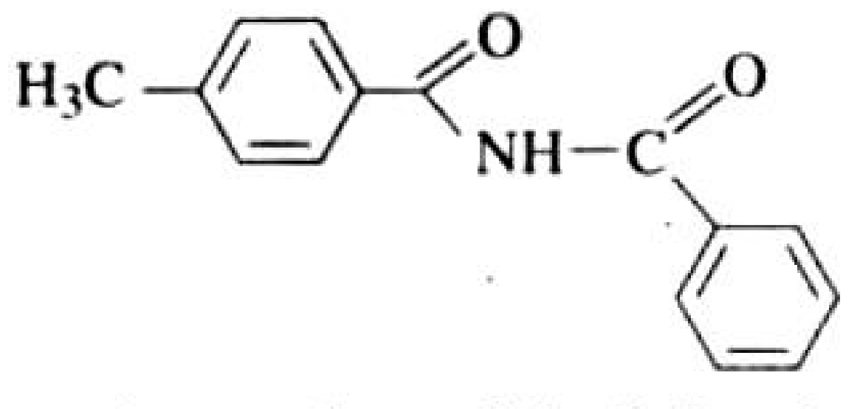


structure of the product (T) is:

a.


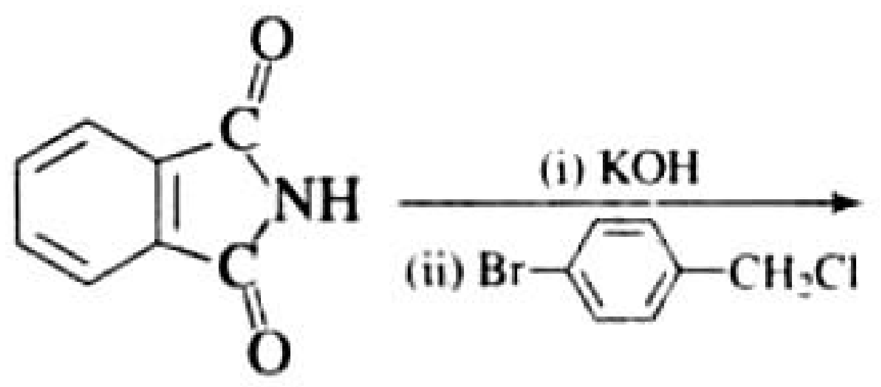
b.


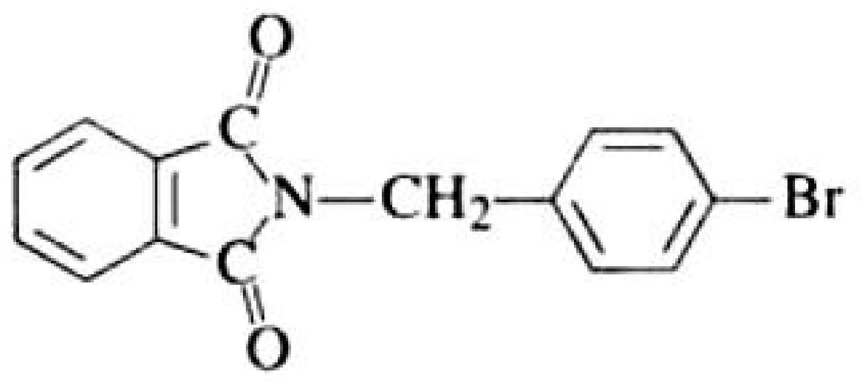
c.


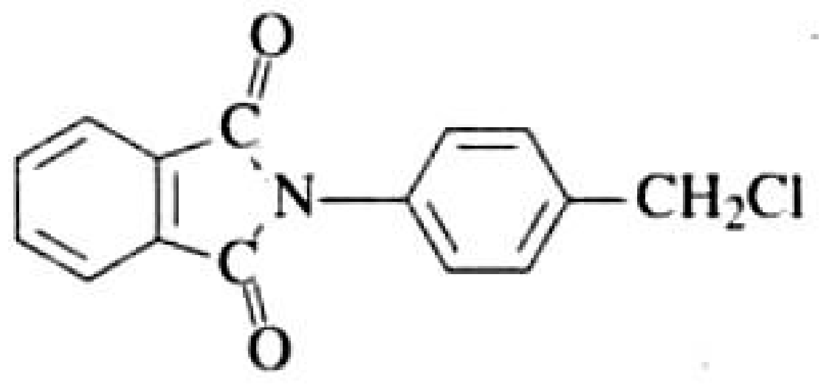
d.


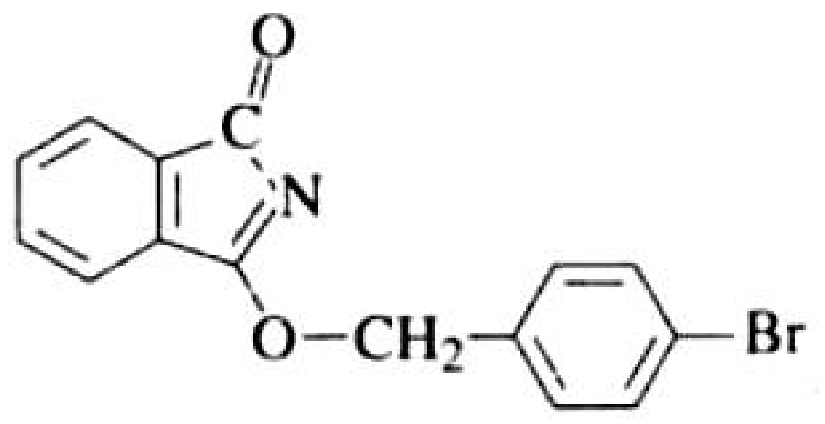
(IIT-JEE 2010)

19. The major product of the following reaction is



a.


b.


c.


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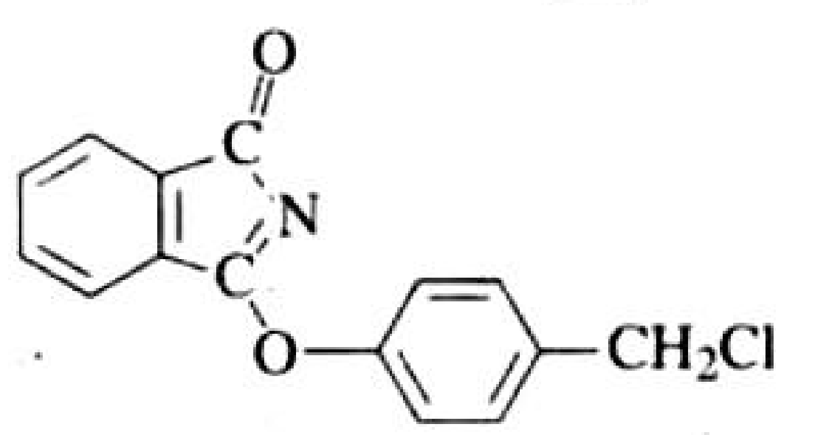
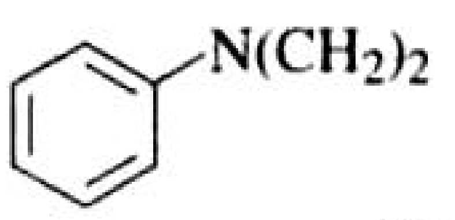
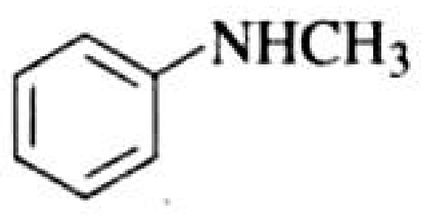


(IIT-JEE 2011)

20. 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

a.


b.


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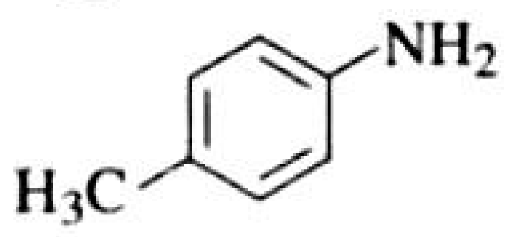
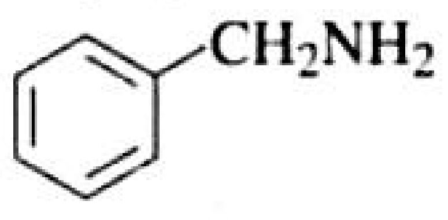
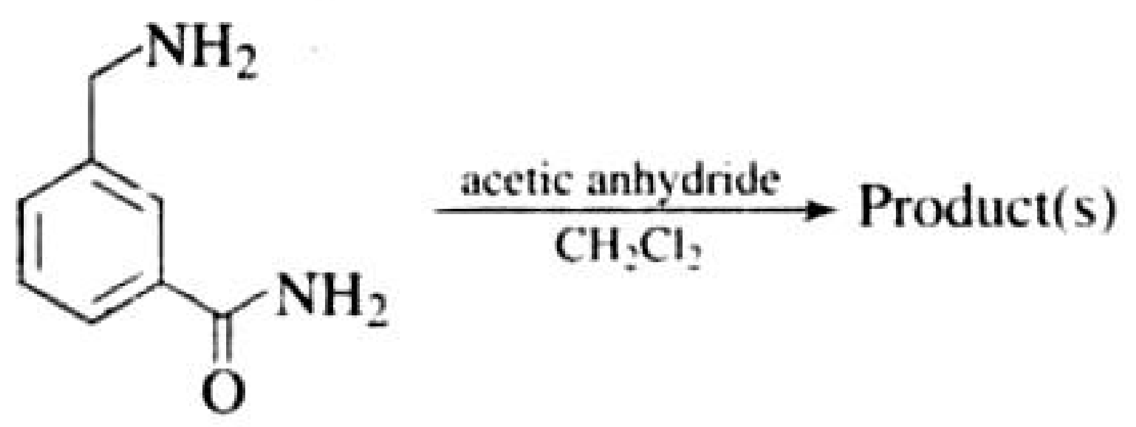
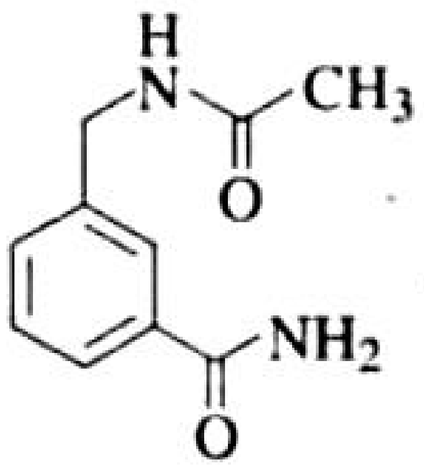


d.


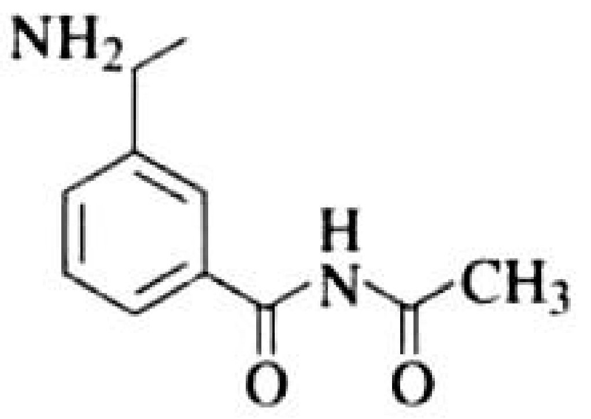
(IIT-JEE 2011)

21. In the reaction shown below, the major product(s) formed is/are

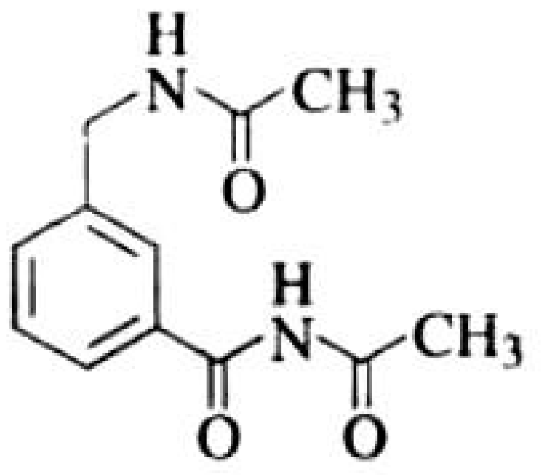


a.


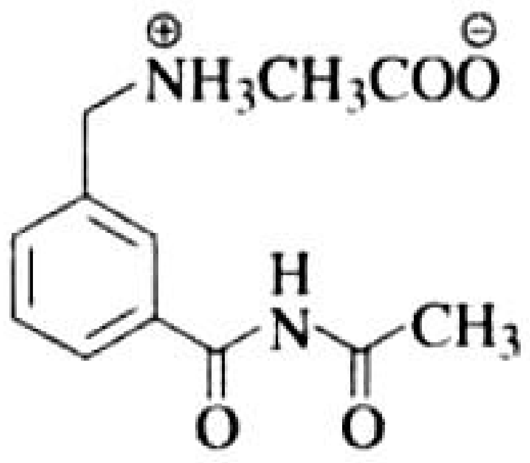
+ CH_3COOH

b.


+ CH_3COOH

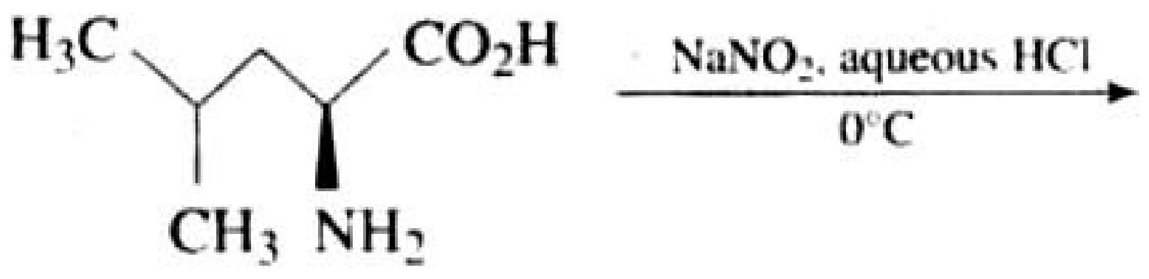
c.


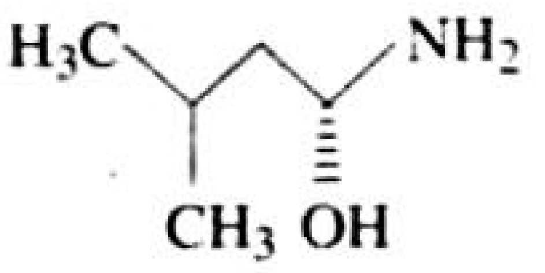
+ H_2O

d.


(JEE Advanced 2014)

22. The major product of the reaction is



a.


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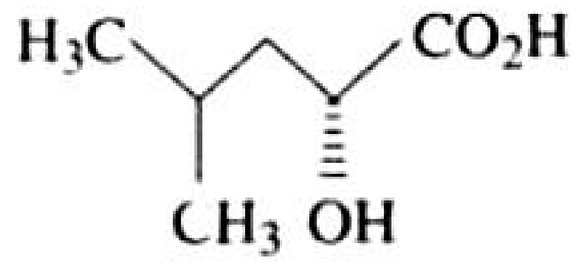

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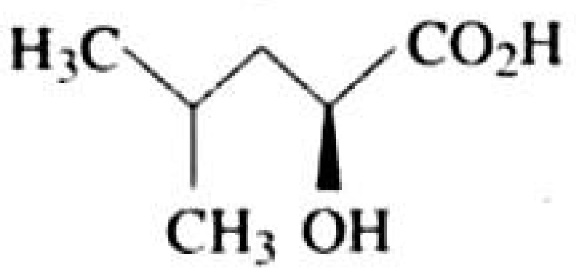
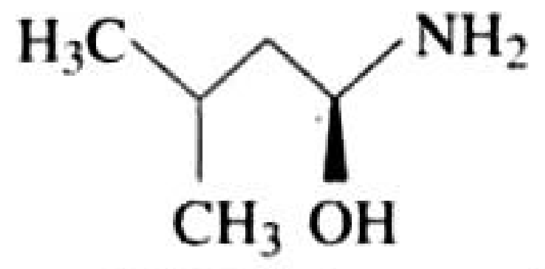
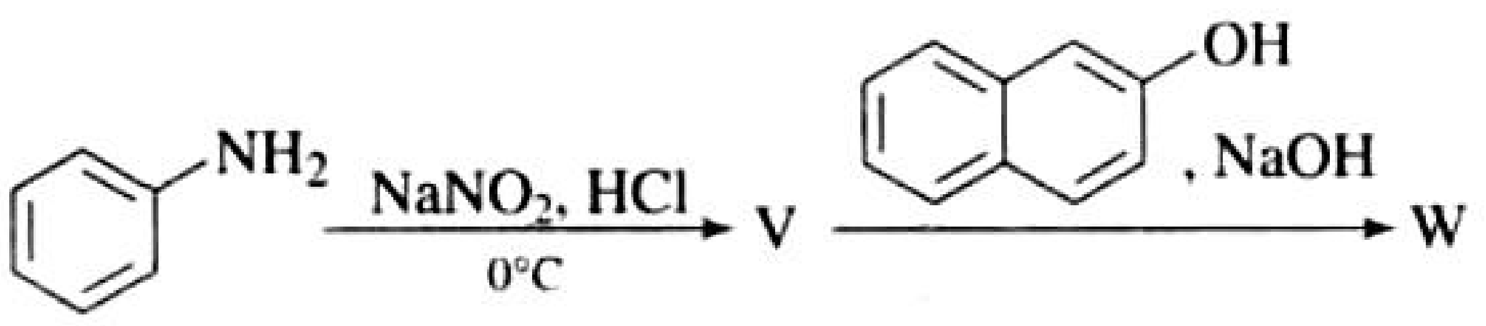
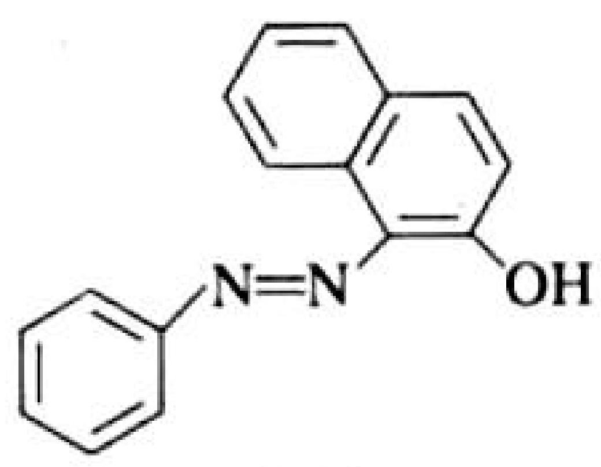


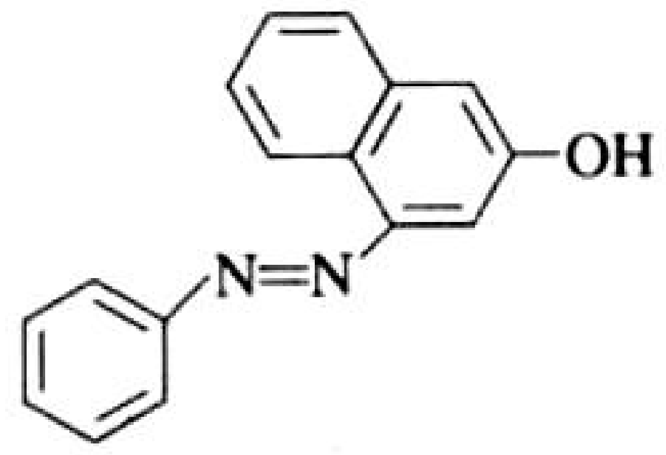
d.


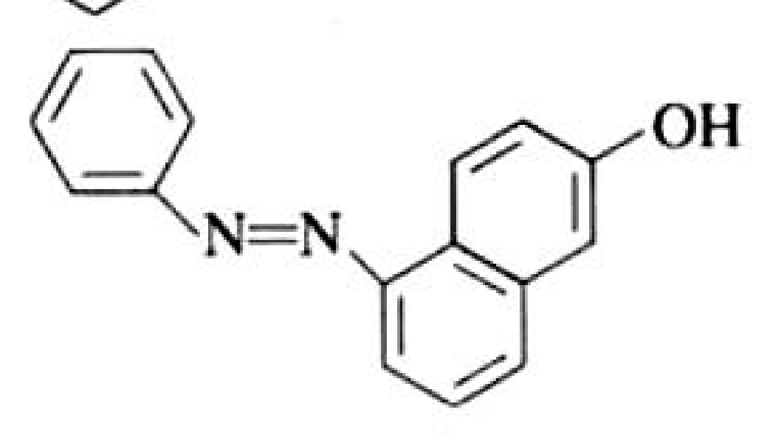
(JEE Advanced 2015)

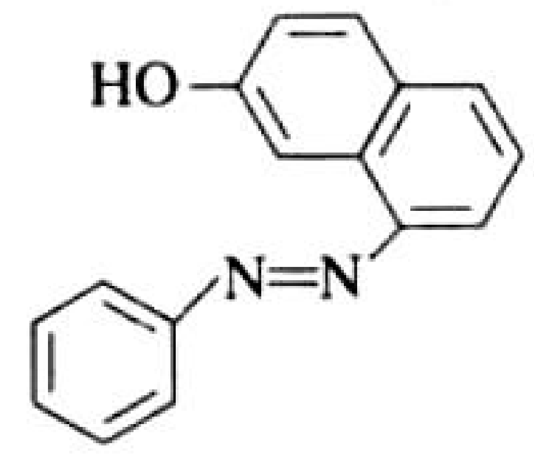
23. In the following reactions, the major product W is



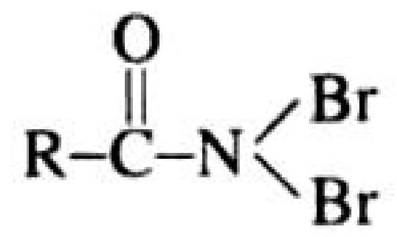
a. 

b. 

c. 

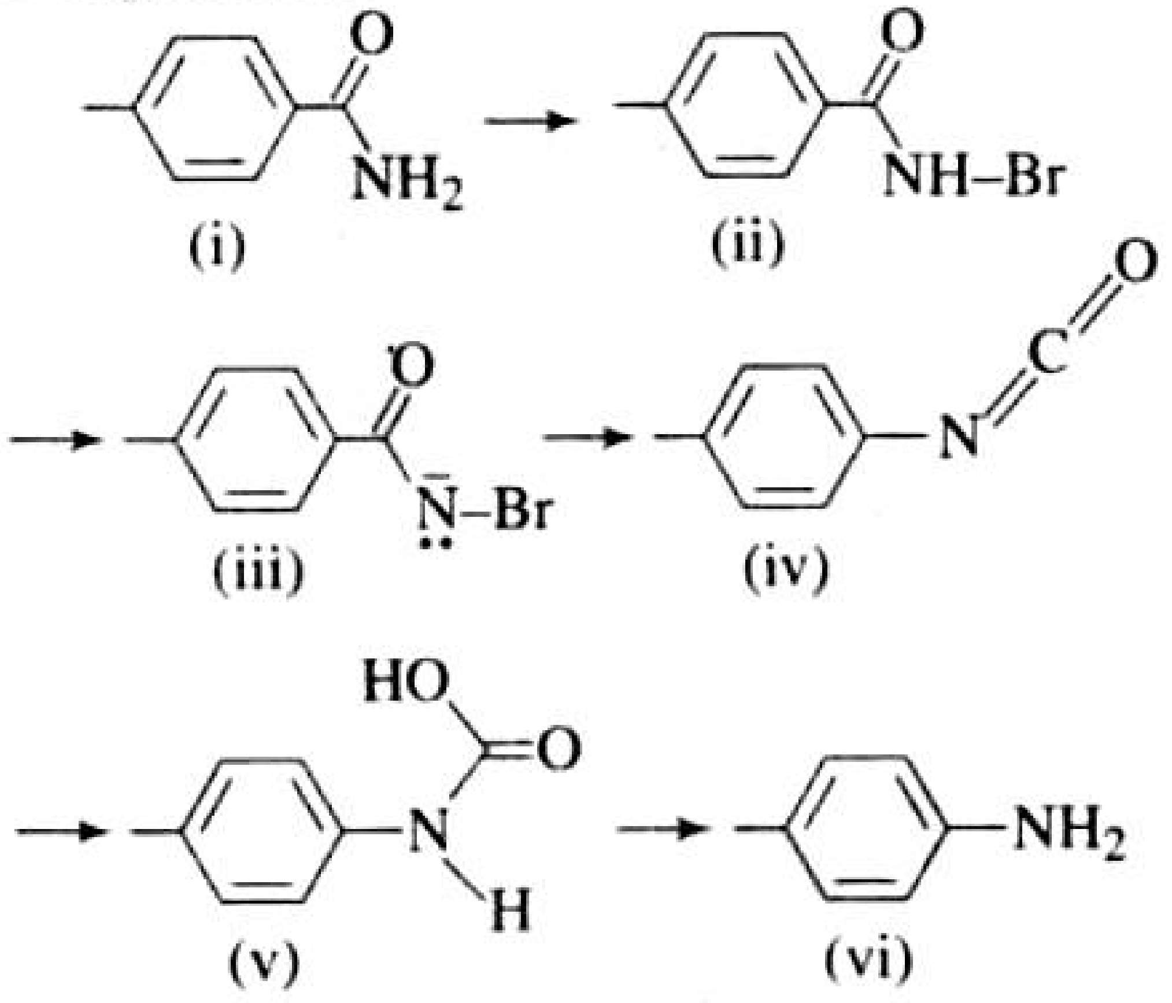
d.  **(JEE Advanced 2015)**

Multiple Correct Answers Type

1. When nitrobenzene is treated with Br_2 in the presence of $FeBr_3$, the major product formed is m-bromonitrobenzene. Statements which are related to obtaining the m-isomer are:
   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 $Br^{\oplus}$ at the meta-position is least destabilized.
   c. Loss of aromaticity when $Br^{\oplus}$ attacks at the ortho- and para-positions and not at meta-position.
   d. Easier loss of $H^{\oplus}$ to regain aromaticity from the meta-position than from the ortho- and para-positions.
   (IIT-JEE 1992)
2. Reaction of $R-\overset{\overset{O}{\|}}{C}-NH_2$ with a mixture of Br_2 and KOH gives $R-NH_2$ as the main product. The intermediates involved in this reaction are:
   a. $R-\overset{\overset{O}{\|}}{C}-NHBr$ **b.** $R-NHBr$
   c. $R-N=C=O$ **d.**  $R-\overset{\overset{O}{\|}}{C}-N\begin{smallmatrix}Br\\Br\end{smallmatrix}$
   (IIT-JEE 1992)
3. p-Chlroaniline and anilinium hydrochloride can be distinguished by:
   a. Sandmeyer reaction **b.** $NaHCO_3$
   c. $AgNO_3$ **d.** Carbylamine test
   (IIT-JEE 1998)
4. Among the following compounds, which will react with acetone to give a product containing $>C=N-$ bond?
   a. $C_6H_5NH_2$ **b.** $(CH_3)_3N$
   c. $C_6H_5NHC_6H_5$ **d.** $C_6H_5NHNH_2$
   (IIT-JEE 1998)
5. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives.
   a. diphenyl ether **b.** p-hydroxyazobenzene
   c. chlorobenzene **d.** benzene **(IIT-JEE 1998)**
6. A positive carbylamine test is given by:
   a. N, N-Dimethyl aniline
   b. 2, 4-Dimethyl aniline
   c. N-Methyl-o-methyl aniline
   d. p-Methyl benzylamine **(IIT-JEE 1999)**

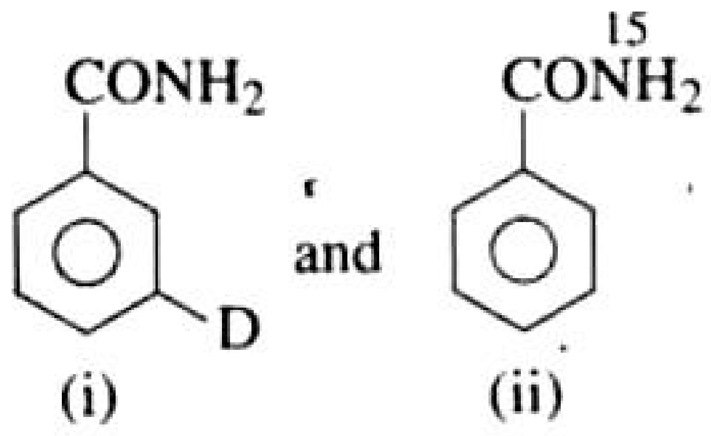
Linked Comprehension Type

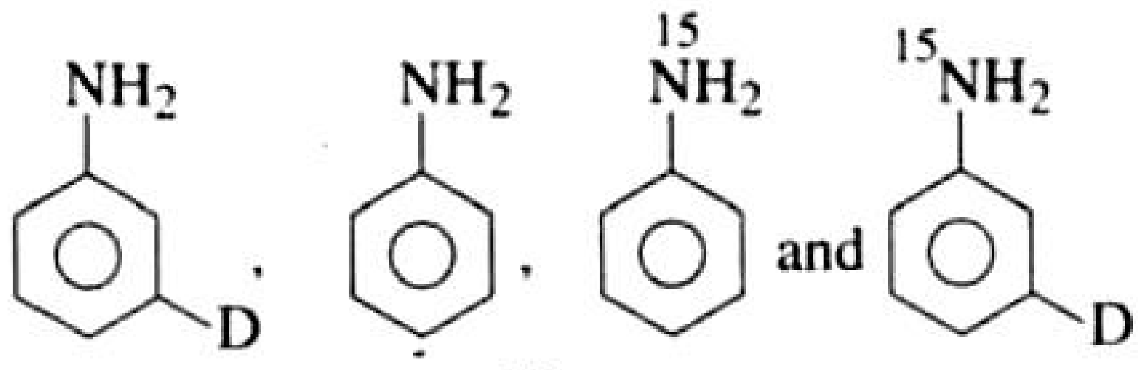
The conversion of an amide to an amine with one carbon atom less by the action of alkaline hydrohalite is known as Hofmann bromamide degradation.

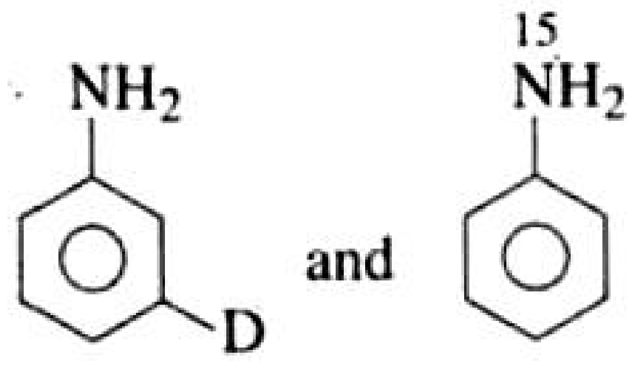


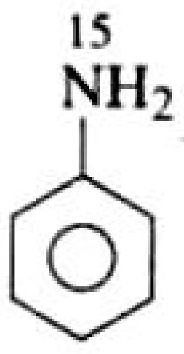
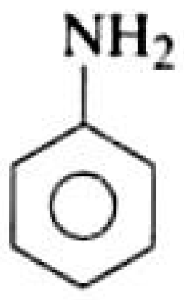
In this reaction, RCONHBr is formed from which the reaction has derived its name. Hofmann reaction is accelerated if the migrating group is more electron-releasing. Hofmann degradation reaction is an intramolecular reaction. **(IIT-JEE 2006)**

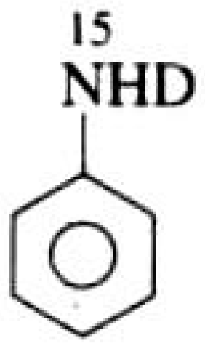
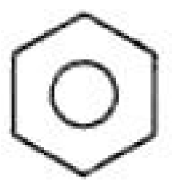
1. How can the conversion of (i) to (ii) be brought about?
   a. KBr **b.** KBr + CH_3OH
   c. KBr + KOH **d.** Br_2 + KOH
2. Which is the determining step in Hofmann bromamide degradation?
   a. Formation of (i) **b.** Formation of (ii)
   c. Formation of (iii) **d.** Formation of (iv)
3. What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation?



a. 

b. 

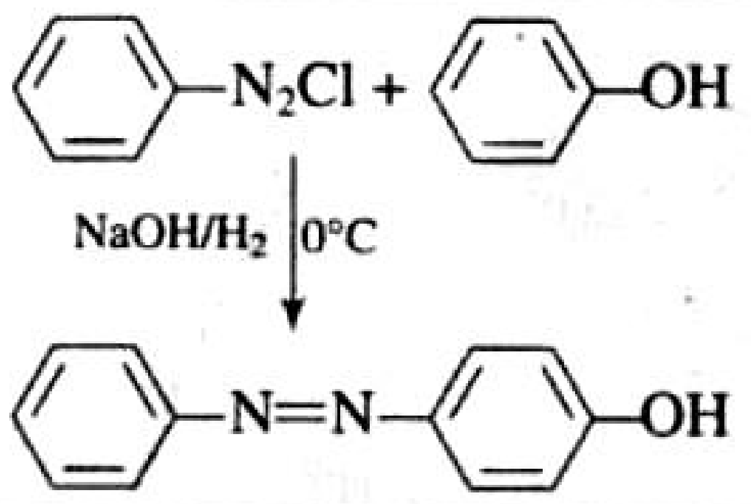
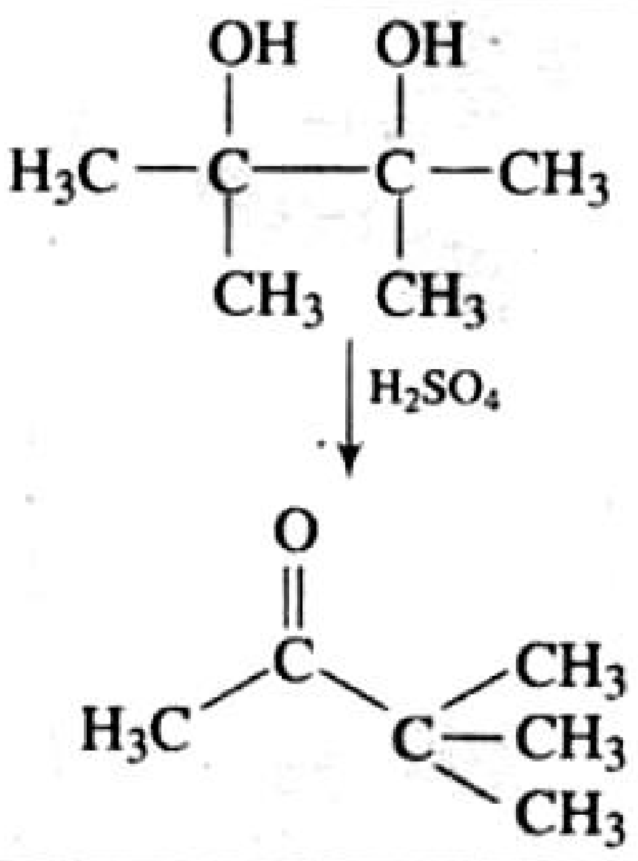
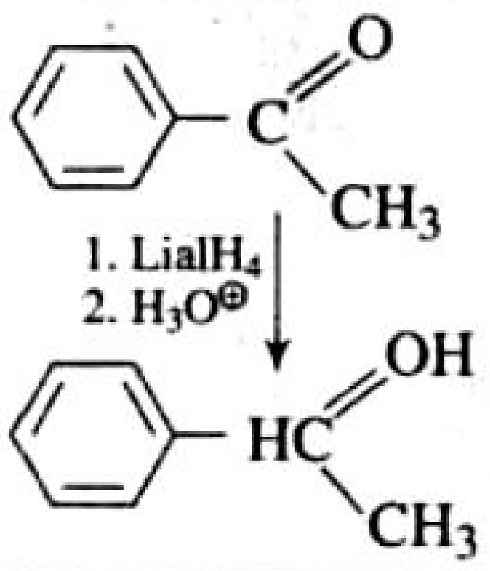
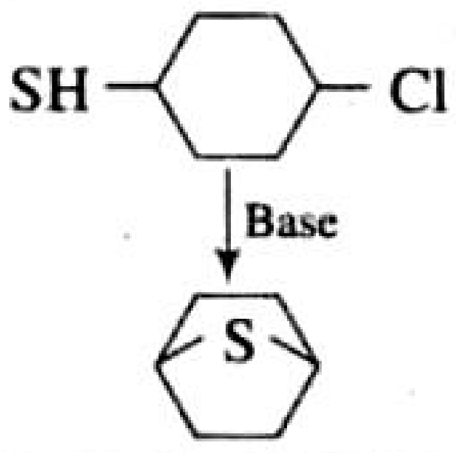
c.  and 

d.  and 

Matching Column Type

Each question has four statements (a, b, c and d) given in Column I and five statements (p, q, r, s, and t) in column II. Any given statement in Column I can have correct matching with one or more statements given in Column II.

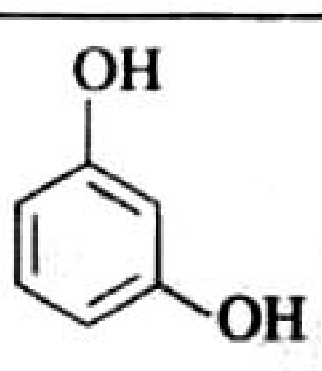
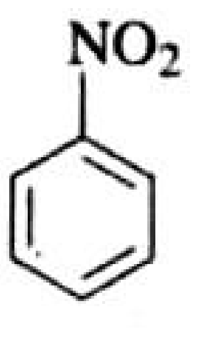
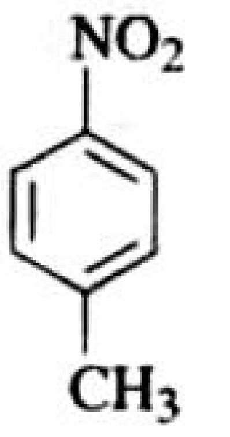
1. Match the reactions in Column I with appropriate options in Column II. **(IIT-JEE 2000)**

Column I	Column II
a. 	**p.** Racemic mixture
b. 	**q.** Addition reaction
c. 	**r.** Substitution reaction
d. 	**s.** Coupling reaction
	t. Carbocation intermediate

2. Match each of the compounds in Column I with its characteristic reaction(s) in Column II. **(IIT-JEE 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

3. Match the four starting material (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. **(JEE Advanced 2014)**

List I	List II
P. $H-\equiv-H$	1. Scheme I (i) $KMnO_4$, $HO^{\ominus}$, heat (ii) $H^{\oplus}$, H_2O (iii) $SOCl_2$ (iv) NH_3 $? \xrightarrow{\qquad} C_7H_6H_2O_5$
Q. 	2. Scheme II (i) Sn/HCl (ii) CH_3COCl (iii) conc. H_2SO_4 (iv) HNO_3 (v) dil. H_2SO_4, heat (vi) $HO^{\ominus}$ $? \xrightarrow{\qquad} C_6H_6H_2O_3$
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 $? \xrightarrow{\qquad} C_6H_5NO_3$
S. 	4. Scheme III (i) conc. H_2SO_4, 60°C (ii) conc. HNO_3, conc. H_2SO_4 (iii) dil. H_2SO_4, heat $? \xrightarrow{\qquad} C_6H_5NO_4$

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

Assertion-Reasoning Type

Read the following questions and answer as per the directions given below:

a. Statement 1 is true, Statement 2 is true; Statement 2 is the correct explanation for Statement 1.

b. Statement 1 is true, Statement 2 is true; Statement 2 is NOT the 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:** 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 nitrogen is no longer available for resonance.

(IIT-JEE 2001)

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

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 extended conjugation.

(IIT-JEE 2008)

Fill in the Blanks Type

1. In an acidic medium, ______ behaves as the strongest base (nitrobenzene, aniline, phenol). **(IIT-JEE 1981)**

2. Amongst the three isomers of nitrophenol, the one that is least soluble in water is ______ **(IIT-JEE 1992)**

3. The high melting point and insolubility of sulphanilic acid in organic solvents are due to its ______ structure. **(IIT-JEE 1994)**

Subjective Type

1. State the equations for the preparation of the following compounds. (Equations need not to be balanced).

i. Chlorobenzene from aniline (in two steps).

ii. *n*-Propyl amine from ethyl chloride (in two steps). **(IIT-JEE 1982)**

2. Why cyclohexylamine is a stronger base than aniline. **(IIT-JEE 1982)**

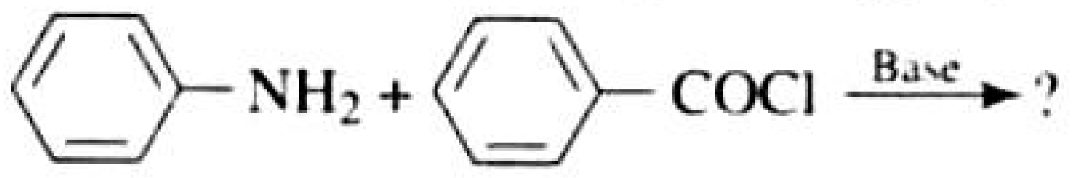
3. State the conditions under which the following preparation is carried out. Give the necessary equations which need not to be balanced: 'Aniline from benzene'. **(IIT-JEE 1983)**

4. How would you convert?
'Aniline to chlorobenzene'. **(IIT-JEE 1985)**

5. Why *o*-nitrophenol is steam volatile whereas *p*-nitrophenol is not. **(IIT-JEE 1985)**

6. For nitromethane molecule, write structure(s) (i) showing significant resonance (ii) indicating tautomerism **(IIT-JEE 1986)**

7. Complete the following with appropriate structures:



(IIT-JEE 1986)

8. Arrange p-toluidine, N, N-dimethyl-p-toluidine, p-nitroaniline, aniline in increasing basicity **(IIT-JEE 1986)**

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

i. benzaldehyde to cyanobenzene (in not more than 6 steps)

ii. toluene to m-nitrobenzoic acid? **(IIT-JEE 1987)**

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

11. Give a chemical test and the reagents used to distinguish between the following: 'Ethylamine and diethylamine'. **(IIT-JEE 1988)**

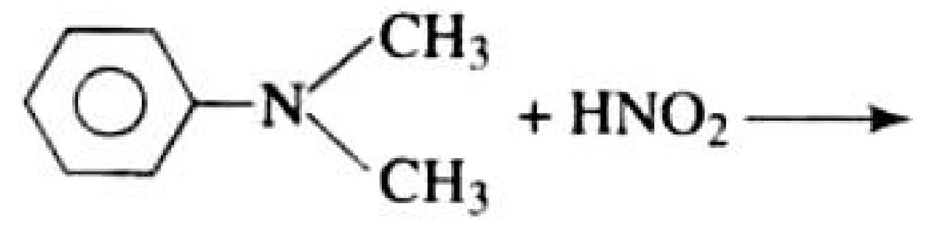
12. Arrange the following in increasing order of base strength: methylamine, dimethylamine, aniline, N-methylaniline. **(IIT-JEE 1988)**

13. An organic compound (A) containing C, H, N and O on analysis gives 49.32% C, 9.59% H, and 19.18% N. (A) on boiling with NaOH gives NH_3 and a salt which on acidification gives a monobasic nitrogen-free acid (B). The silver salt of (B) contains 59.6% silver. Deduce the structures of (A) and (B). **(IIT-JEE 1988)**

14. How will you bring about the following conversion? '4-nitroaniline to 1, 2, 3-tribromobenzene'. **(IIT-JEE 1990)**

15. A mixture of two aromatic compounds (A) and (B) was separated by dissolving it in 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), and (E) and write their structures. **(IIT-JEE 1990)**

16. Write the structure of the major organic product expected from the following reaction.



(IIT-JEE 1992)

17. Compound (X) containing chlorine on treatment with strong ammonia gives a solid Y which is free from chlorine. (Y) analysed as: (C) = 49.31%, H = 9.59% and N = 19.18% and reacts with Br_2 and caustic soda to give a basic compound (Z). (Z) reacts with HNO_2 to give ethanol. Suggest structures for (X), (Y), and (Z).

(IIT-JEE 1992)

18. A basic volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic potash. A 0.295 gm sample of the substance dissolved in aqueous HCl and treated with $NaNO_2$ solution at 0°C liberated a colourless, 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, assuming that it contains one N atom per molecule. **(IIT-JEE 1993)**

19. Outline a synthesis of p-bromonitrobenzene from benzene in two steps. **(IIT-JEE 1993)**

20. Give the structure of A (explanations are not required). 'A (C_3H_9N) reacts with benzenesulphonyl chloride to give a solid insoluble in alkali.' **(IIT-JEE 1993)**

21. Complete the following with appropriate structure:

i. $\text{2, 3-Dinitroaniline} \xrightarrow[\text{(ii) Anisole}]{\text{(i) NaNO}_2\text{ and HCl at 5°C}} (A)$

ii. $\text{2, 4-Dinitroaniline} \xrightarrow[\text{2. anisole}]{\text{1. NaNO}_2\text{ and HCl at 5°C}} C$

(IIT-JEE 1995)

22. Write the structure of the foul-smelling compound obtained when aniline is treated with chloroform in the presence of KOH. **(IIT-JEE 1996)**

23. Following reaction gives two products. Write the structures of the products.

i. $CH_3CH_2NH_2 \xrightarrow{(CH_3CO)_2O,\ \text{heat}} (A)$

ii. $CH_3CONHC_6H_5 \xrightarrow{Br_2,\ Fe} (A)$ **(IIT-JEE 1998)**

24. **i.** Why dimethylamine is a stronger base than trimethylamine.

ii. Why nitrobenzene does not undergo Friedel-Crafts alkylation **(IIT-JEE 1998)**

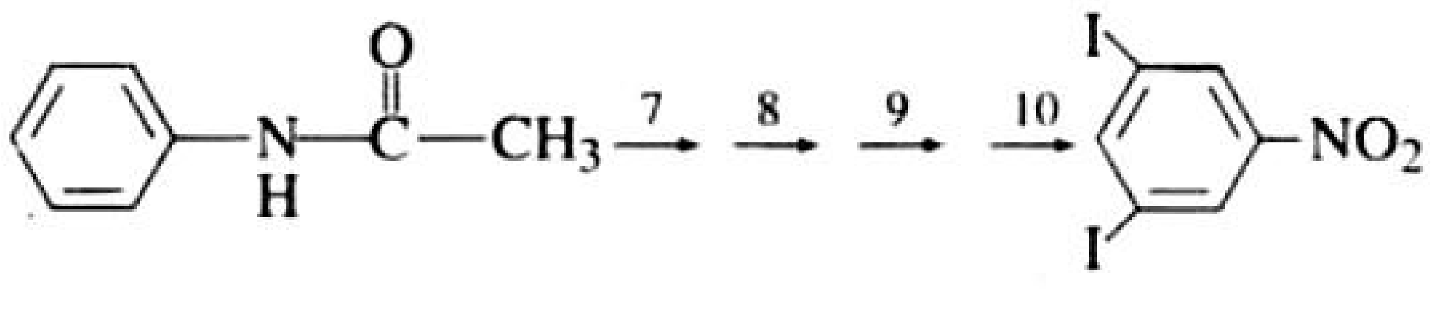
25. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon 42.86%, hydrogen 2.40%, nitrogen 16.67%, and oxygen 38.07%. **(IIT-JEE 1999)**

i. Calculate the empirical formula of the minor product.

ii. When 5.5 gm of the minor product is dissolved in 45 gm of benzene, the boiling point of the solution is 1.84°C higher than that of pure benzene. Calculte the molar mass of the minor product and determine its molecular and structural formulae.

(Molal elevation constant of benzene = 2.53 K kg mol^{-1})

26. Complete the following reaction with appropriate reagents:



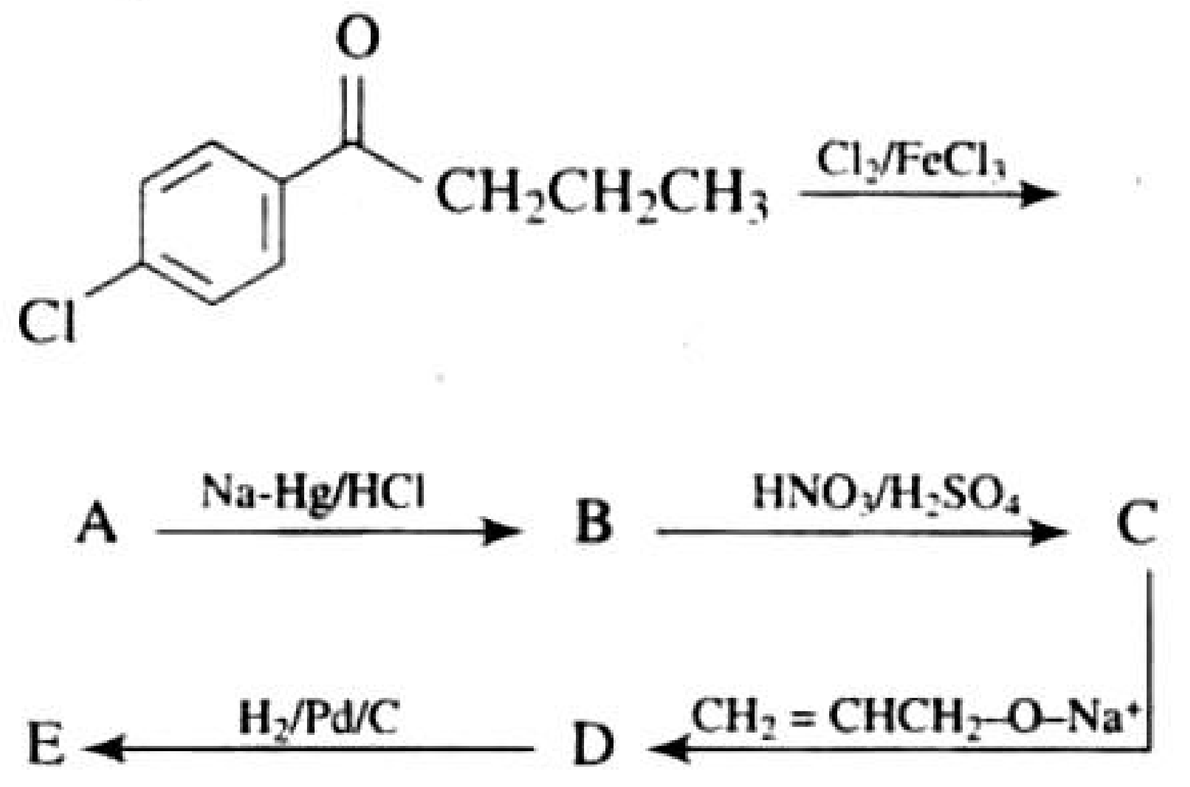
(IIT-JEE 1999)

27. 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. **(IIT-JEE 1999)**

28. How would you bring about the following conversion (in three steps)?

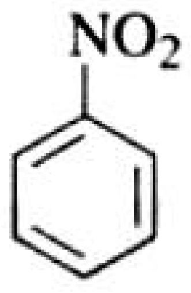
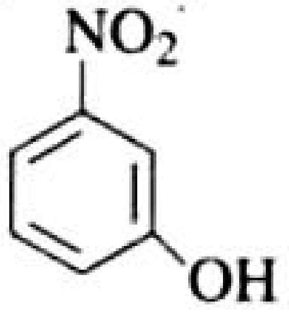
Aniline → Benzylamine **(IIT-JEE 2000)**

29. Write structures of the products A, B, C, D and E in the following scheme.



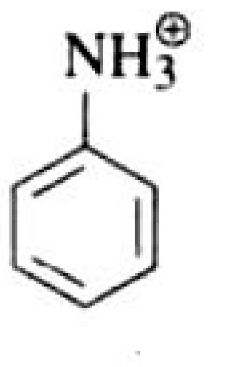
(IIT-JEE 2002)

30. There is a solution of p-hydroxybenzoic acid and p-amino benzoic acid. Discuss one method by which we can separate them and also write down the confirmatory test of the functional groups present. **(IIT-JEE 2003)**

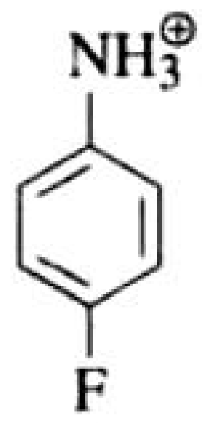
31. Convert  to  in not more than four steps.

(IIT-JEE 2003)

32. Which of the following is more acidic and why? **(IIT-JEE 2004)**



(I)



(II)

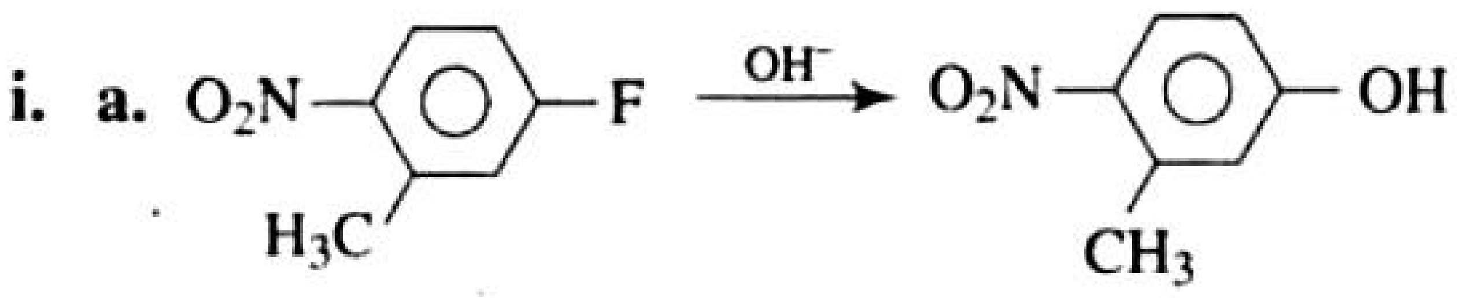
(IIT-JEE 2004)

33. $\underset{\substack{\text{Optically acitve}\\ (X)}}{C_5H_{13}N} \xrightarrow[-N_2]{NaNO_2/HCl} (Y)$ (Tertiary alcohol) + Other product.

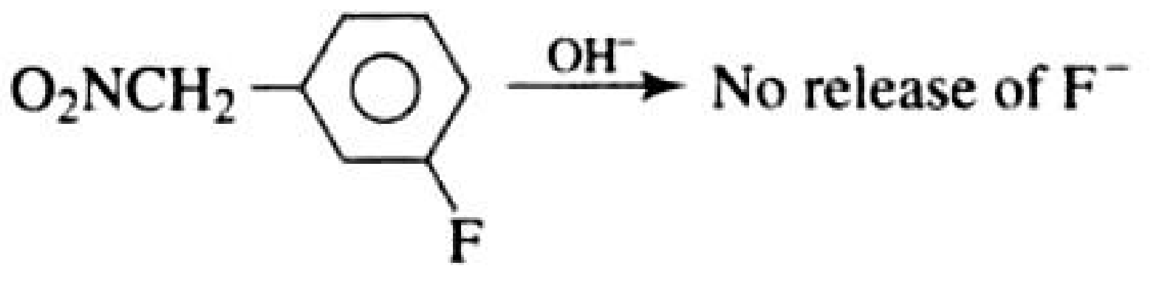
Find (X) and (Y). Is (Y) optically active? Write the intermediate steps. **(IIT-JEE 2005)**

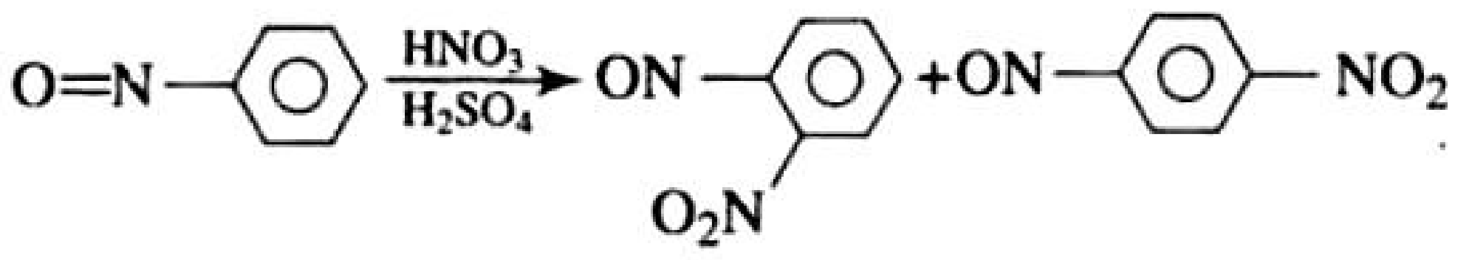
34. Give reasons for the following:

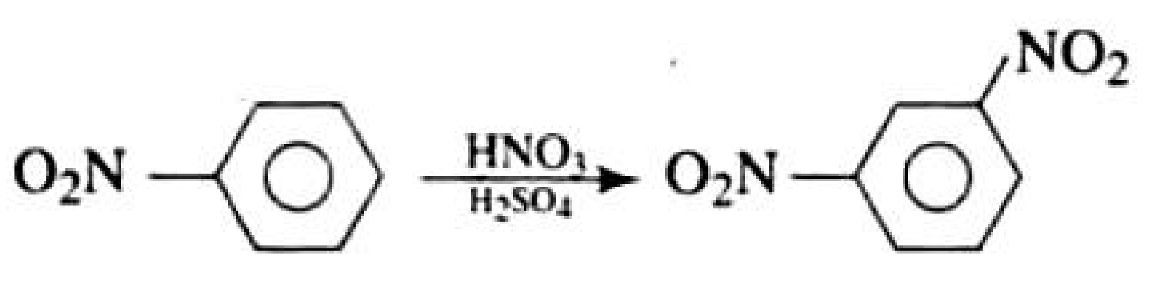
i. **a.**



b.



ii. 

but 

(IIT-JEE 2005)

Answer Key

JEE Advanced

Single Correct Answer Type

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

Multiple Correct Answers Type

1. a., d. **2.** a., c. **3.** a., b., c.
4. a., d. **5.** b. **6.** b., d.

Linked Comprehension Type

1. d. **2.** d. **3.** b.

Matching Column Type

1. (a) → (r), (s), (t); (b) → (t); (c) → (p), (q); (d) → (r)
2. (a) → (p), (q), (s), (t); (b) → (s), (t); (c) → (p); (d) → (r
3. (c)

Assertion–Reasoning Type

1. d. **2.** d.

Fill in the Blanks Type

1. Aniline **2.** o-Nitrophenol **3.** Zwitter ion

Subjective Type

3. Aniline from benzene:
4. Aniline from chlorobenzene

Hints and Solutions

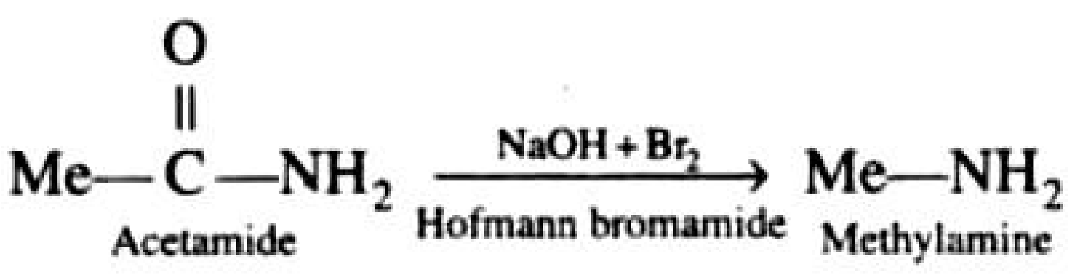
JEE ADVANCED

Single Correct Answer Type

1. c. 2° amines react with HNO_2 at low temperature to give oily nitrosamine.

$$Et_2NH + HNO_2 \rightarrow \underset{\text{N-Nitroso-N-ethyl ethanamine}}{Et_2N-N=O+H_2O}$$

2. c.

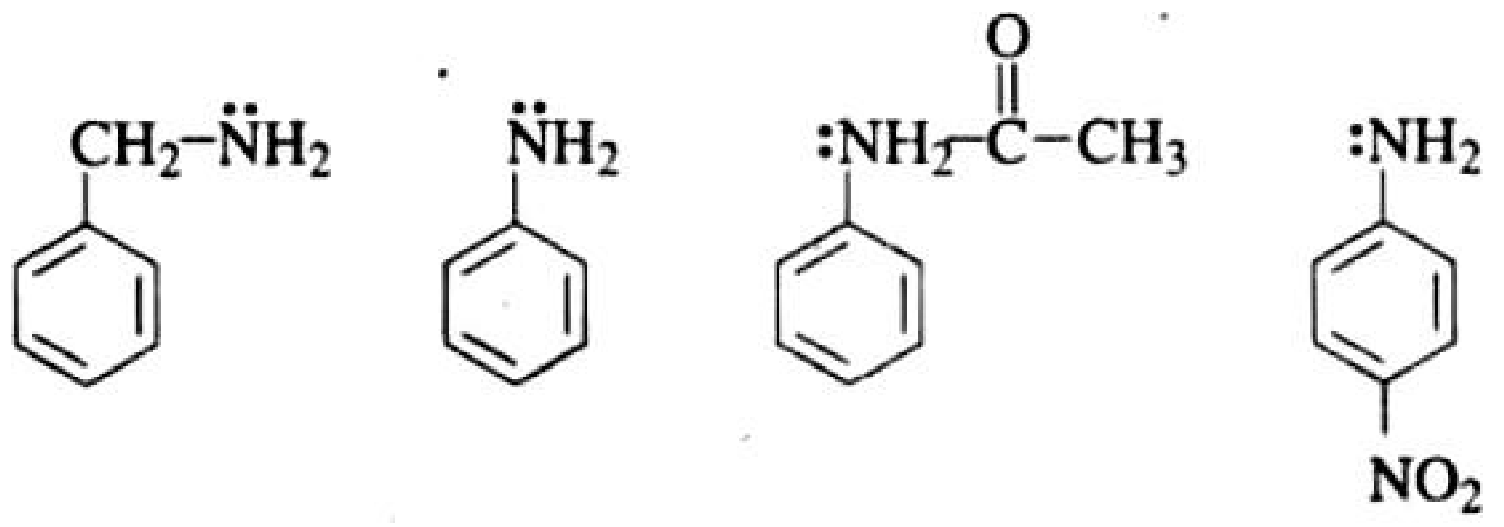


$$\underset{\text{Acetamide}}{Me-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow[\text{Hofmann bromamide}]{NaOH+Br_2} \underset{\text{Methylamine}}{Me-NH_2}$$

3. b. $\underset{1^\circ\text{ amine}}{R-NH_2} + CHCl_3 + 3KOH\ (\text{alc.})$

$$\xrightarrow[\text{test}]{\text{Carblyamine}} \underset{\text{Alkyl isocyanide}}{R-N \equiv C} + 3KCl + 3H_2O$$

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



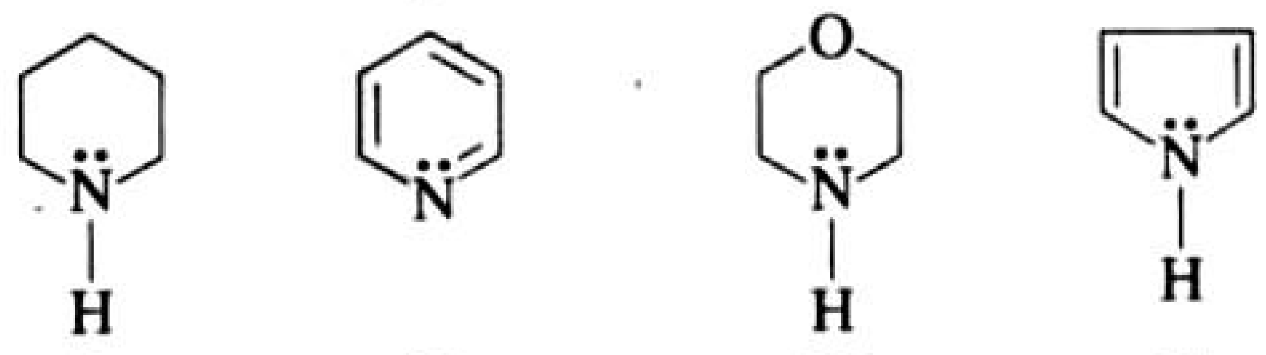
5. c. (II) is not acceptable canonical structure because N has 10 valence $\bar{e}$'s.

6. a. H_2SO_4 is a stronger acid than HNO_3.

$$HNO_3 + H_2SO_4 \rightarrow H_2{}^+NO_3 + HSO_4^-$$
$$H_2{}^+NO_3 \longrightarrow H_2O + NO_2^+$$

Thus, here HNO_3 act as a base.

7. d.



I lp belongs to sp^3 orbital aromatic

II lp is in sp^2 orbital, hence not a part of some extent sextet

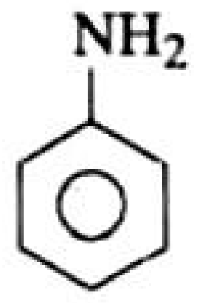
III lp belongs to sp^3 but dispersed to p-orbital towards O

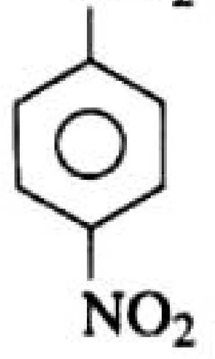
IV Although N is sp^2 hybridised, lp on N is in hence forms a part of aromatic, i.e., sextet (disbersed)

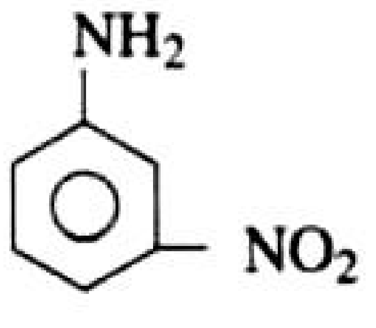
Thus, protonation is most difficult in IV followed by II, III and I. The overall order of basicity is: I > III > II > IV.

8. c. Option (c) is an unlikely structure because N atoms form five bonds and contain positive charge.

9. d. Option (d) is an aliphatic amine; so it is stronger base than aromatic amine. Moreover, EWG [$(-NO_2)$ at o, m, or p] decreases the basic character.

a. 

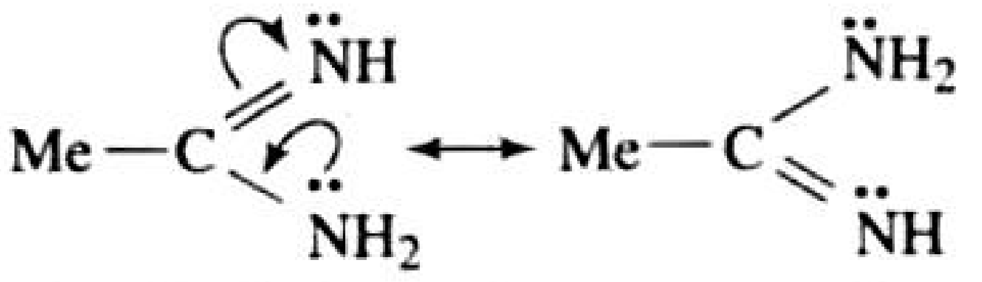
b. 

c. 

In aromatic amines lp on N is involved in resonance.

(d) > (a) > (c) > (b).

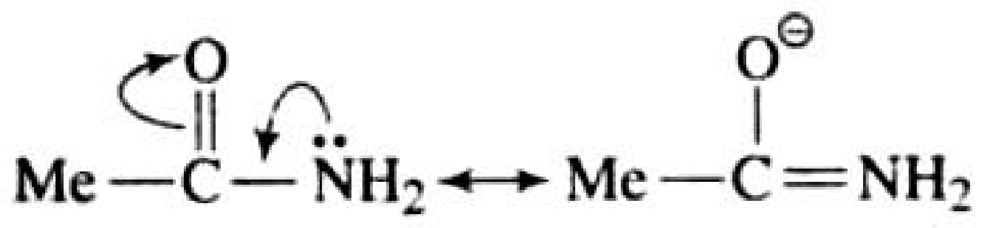
10. b. (1) > (3) > (2) > (4).

(1) 

More basic due to the presence of two LP $\bar{e}$'s on each N.

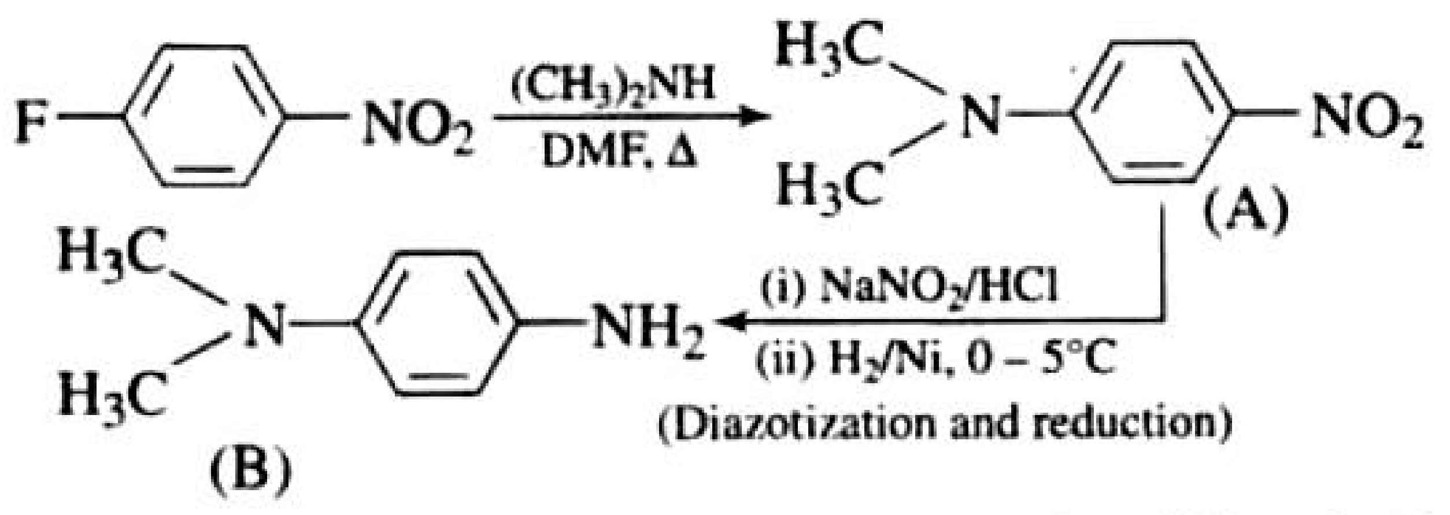
(2) $EtNH_2$. Due to +I effect of (Et) group, but +I effect of two Me groups is greater than +I effect of (Et) group. Hence, (3) is more basic than (2).

(3) $(CH_3)_2NH$. Due to (+I) effect of two Me groups.

(4) 

(Amides are resonance stabilised; so they are the weakest bases. Amides behave as amphoteric.)

11. a.



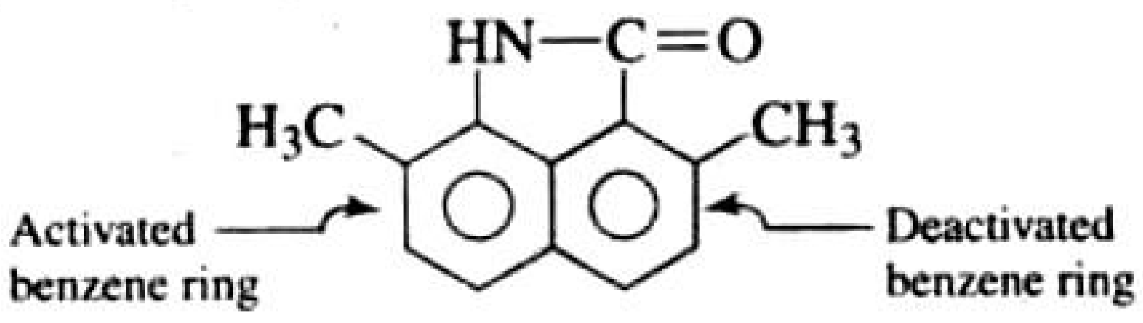
Also NO_2 makes aryl halides undergo nucleophilic substitution. R_2NH is very strong nucleophile.

12. d. $POCl_3$ is a dehydrating agent. Hence

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

13. b. —NH is an activating group whereas as >C = O is a deactivating group.

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



14. b.

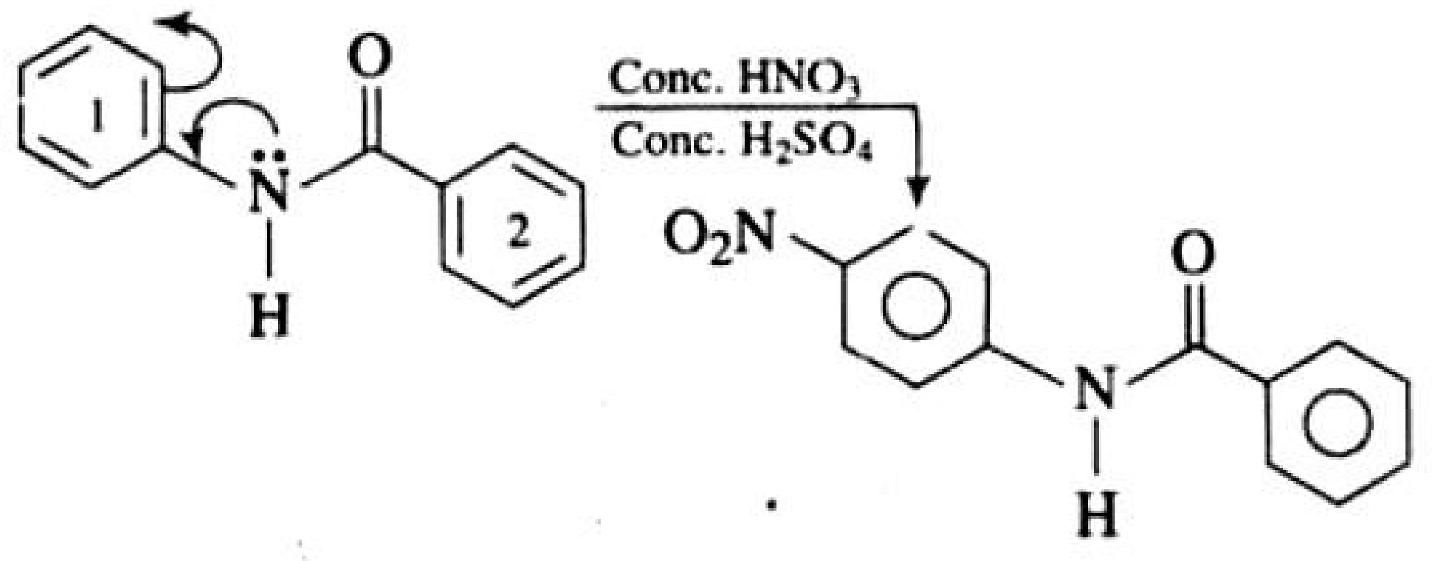
i. Position (X) is most acidic due to –COOH group.

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

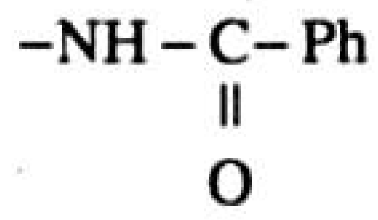
15. c. This is an example of carbylamine reaction

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

16. b.



Ring 1 is more active, electrophilic substitution takes place over ring 1. (as lone pair of N is involved in resonance)



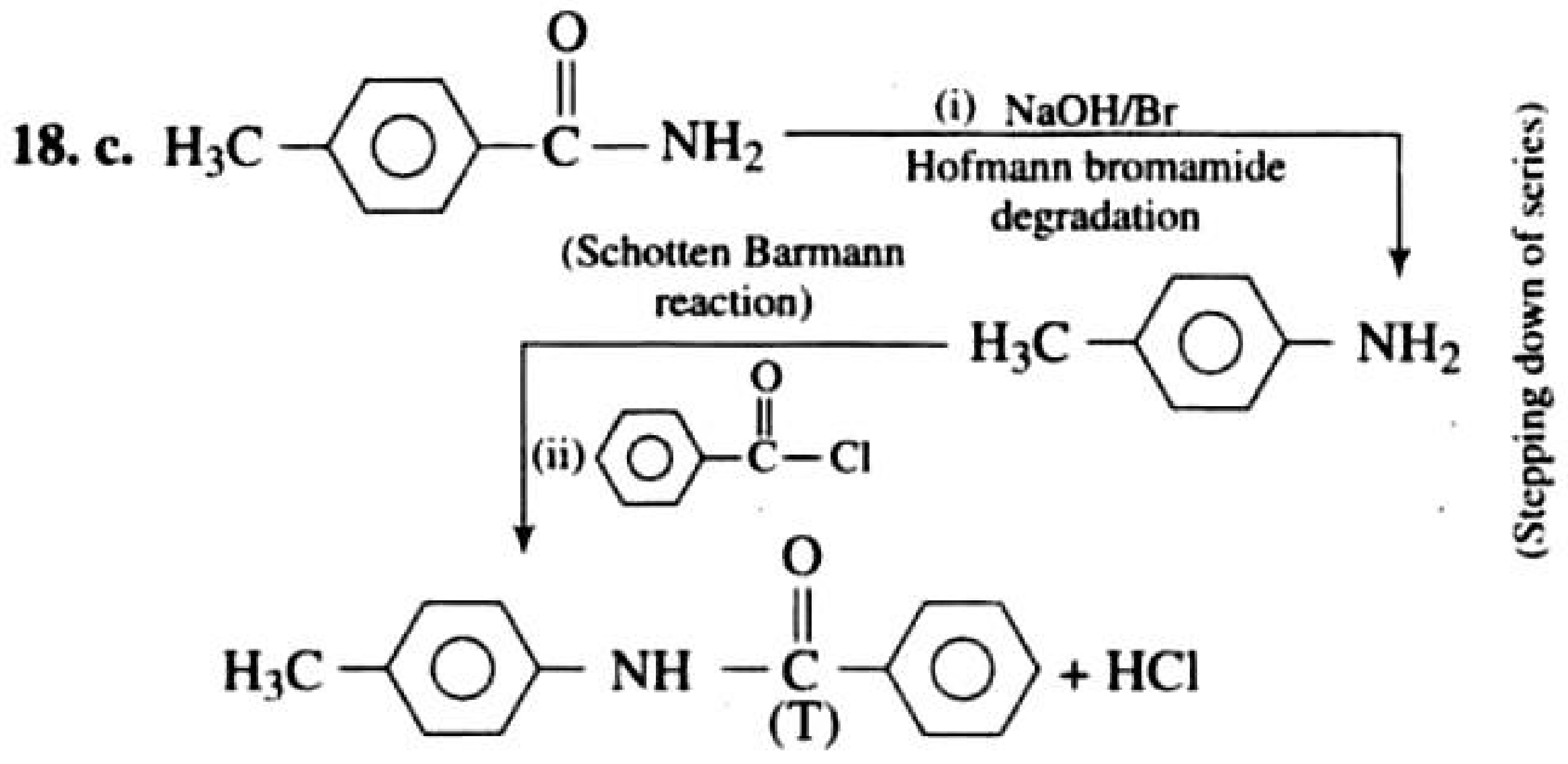
$-NH-\underset{\underset{O}{\|}}{C}-Ph$ is ortho-para directing, para-product is predominating.

17. b.

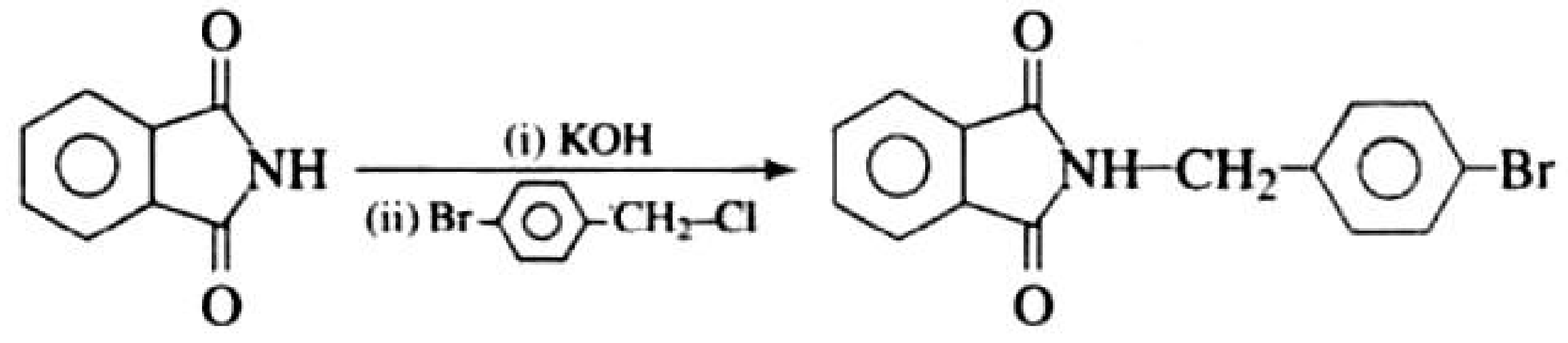
$$H_2C=N^+\equiv N^- > H_2C^- - \overset{+}{N}\equiv N > H_2C^+ - N\equiv N^- > H_2C^- - N\equiv \overset{+}{N}$$

I	III	II	IV
Octet complete, 6 covalent bond, –ve charge on N	Octet complete, 6 covalent bond, –ve charge on C	Octet complete, 5 covalent bond, –ve charge on N	Octet complete, 5 covalent bond, –ve charge on C

18. c.

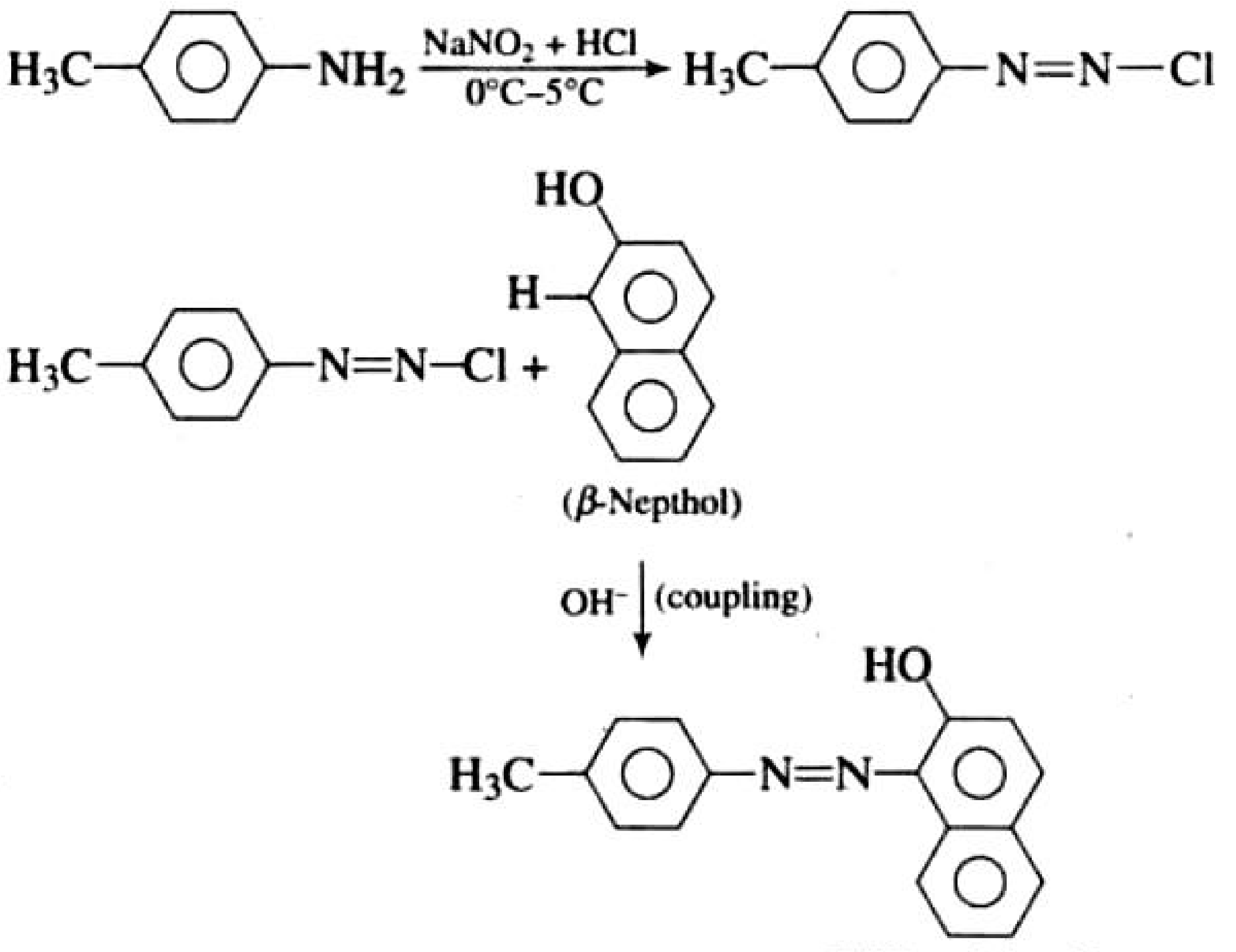


19. a.



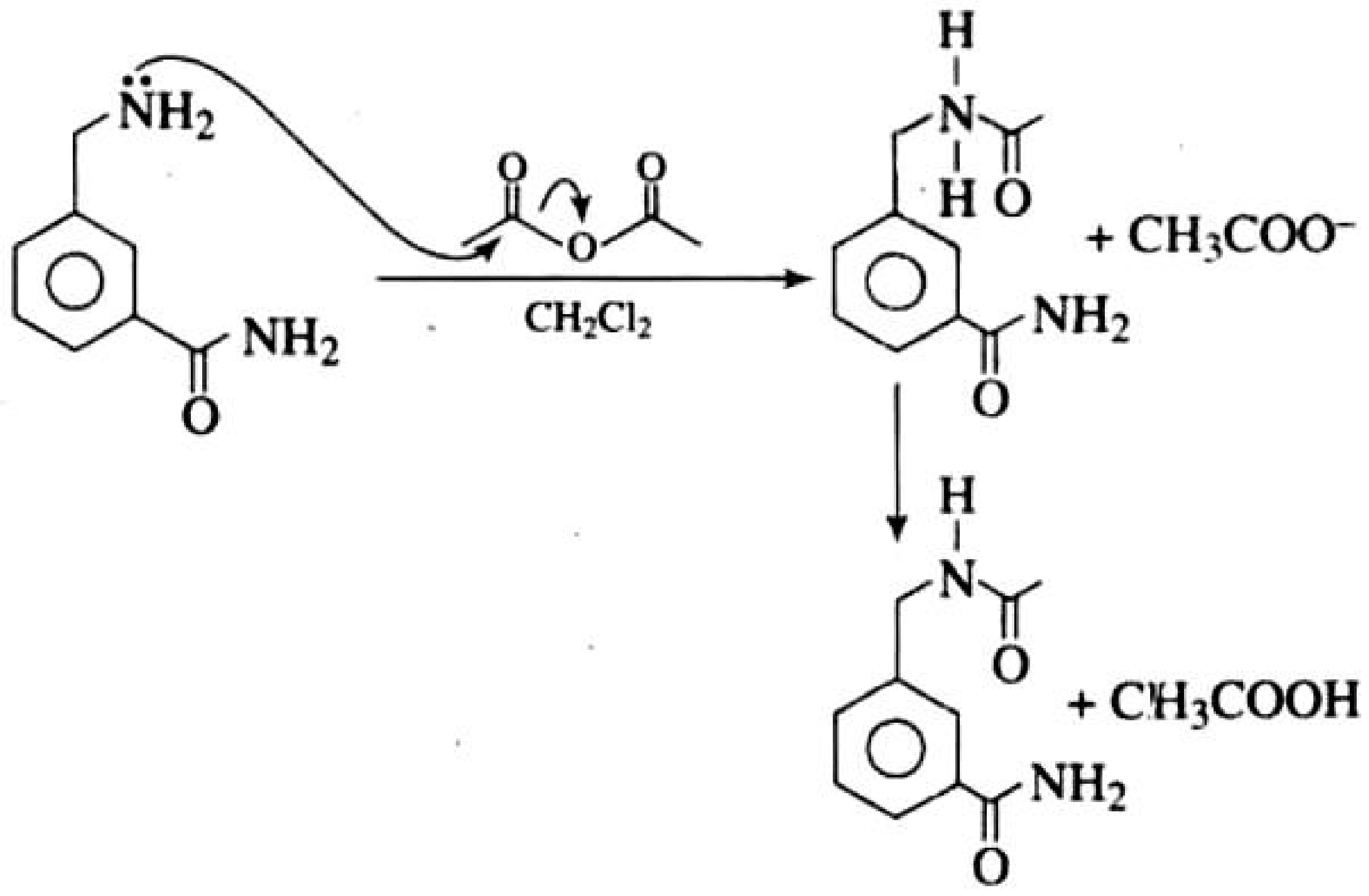
[**Reason:** Due to partial double bond character along C̄—Br bond prevents the attack of nucleophile at phenylic position]

20. c.



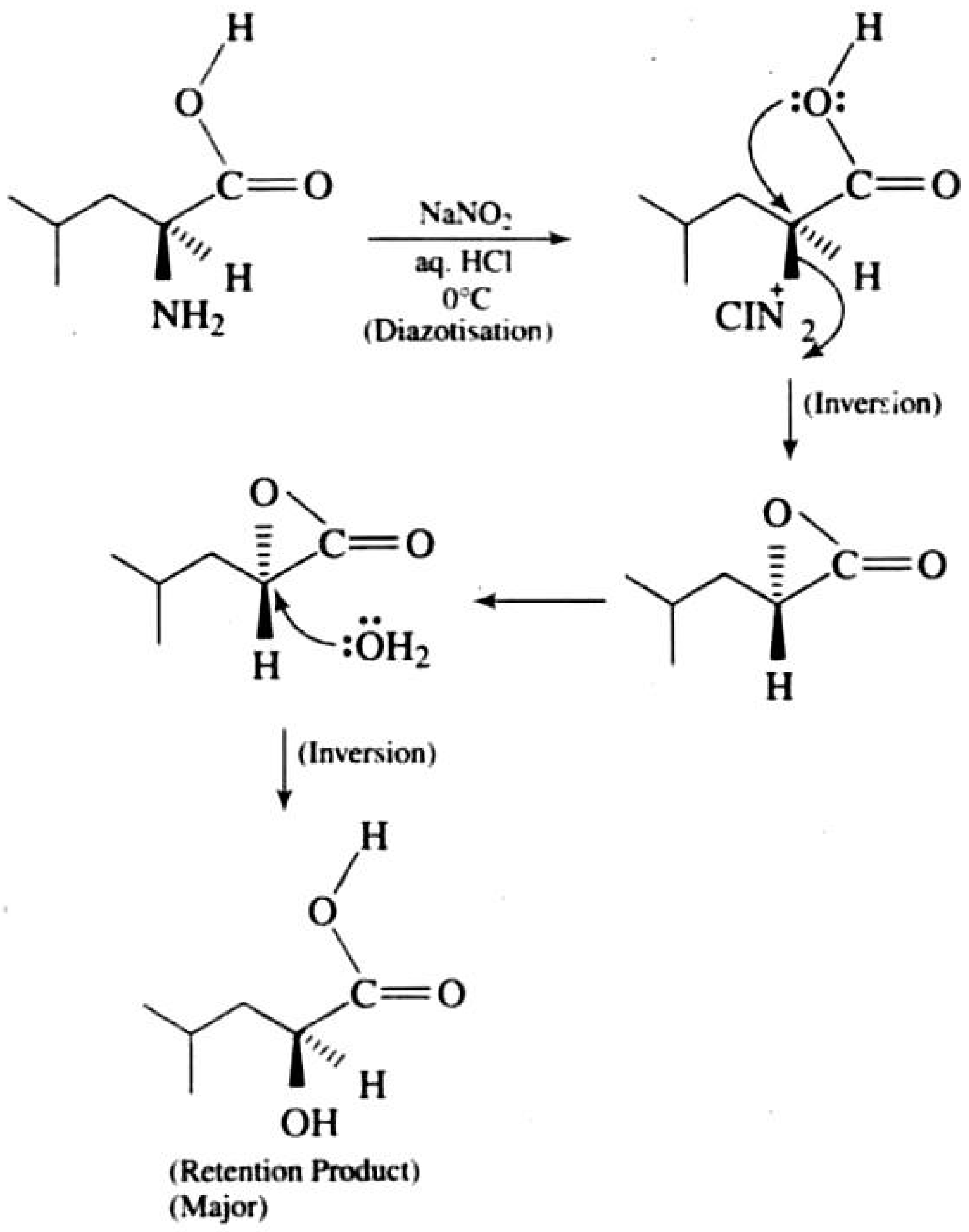
Brilliant Colour Dye

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



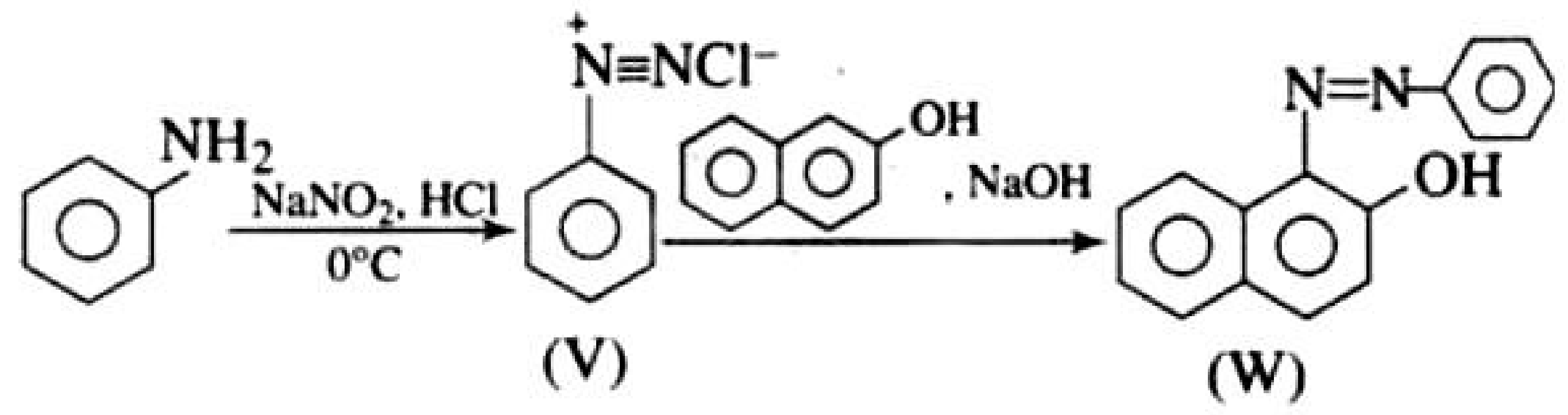
(JEE Advanced 2015)

22. c.



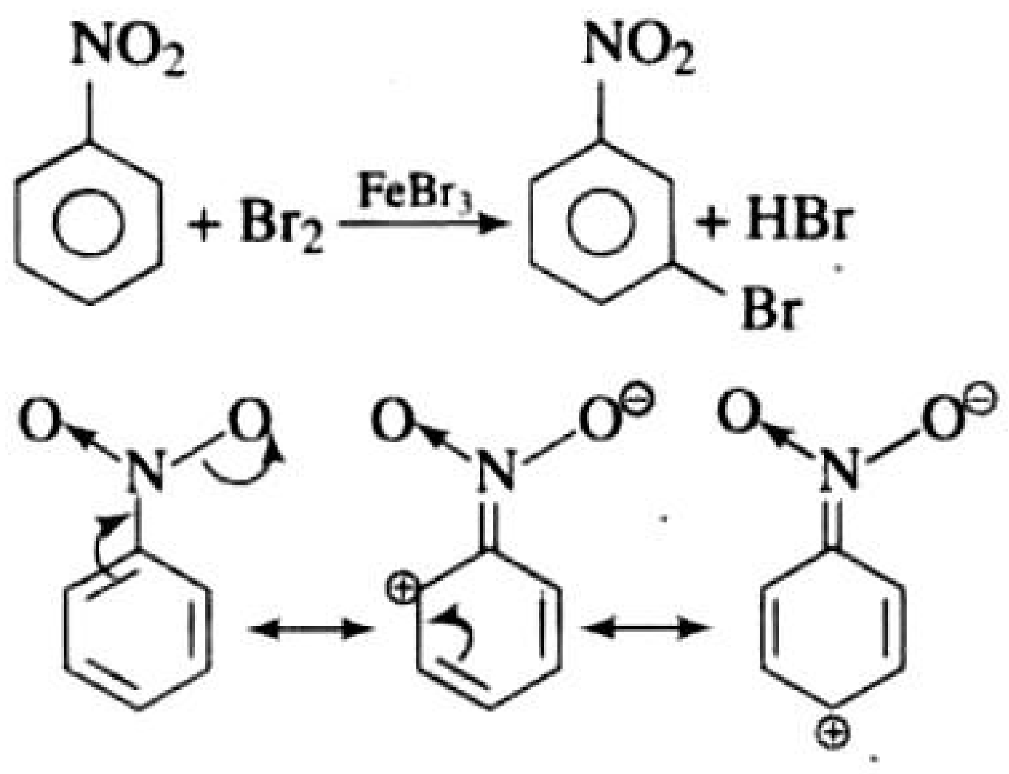
(Retention Product)
(Major)

23. a.



Multiple Correct Answers Type

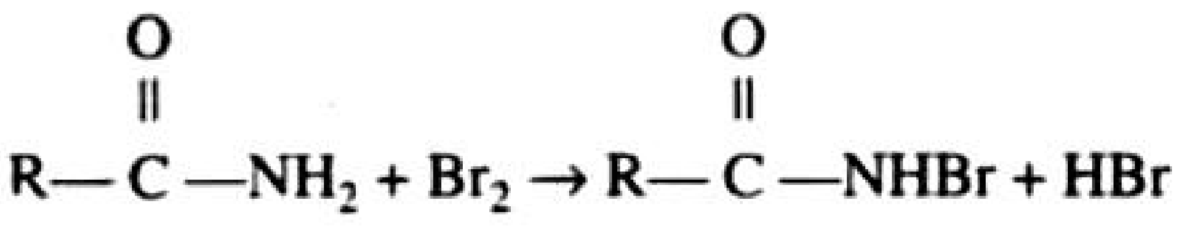
1. **a., d.**



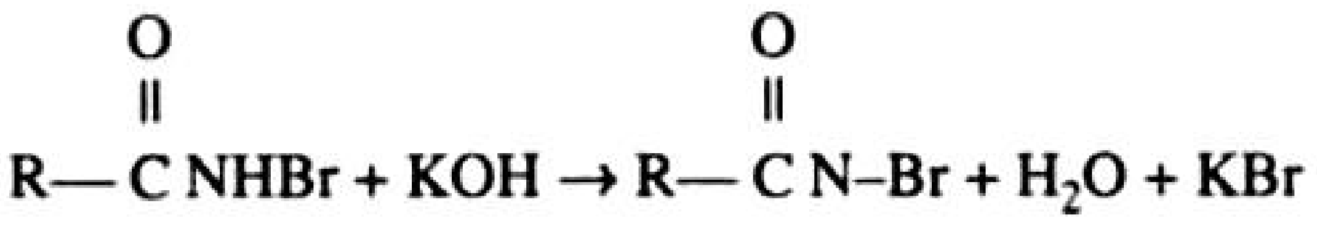
Positive charge is developed at ortho and para positions du to $-NO_2$ group.

2. **a., c.**

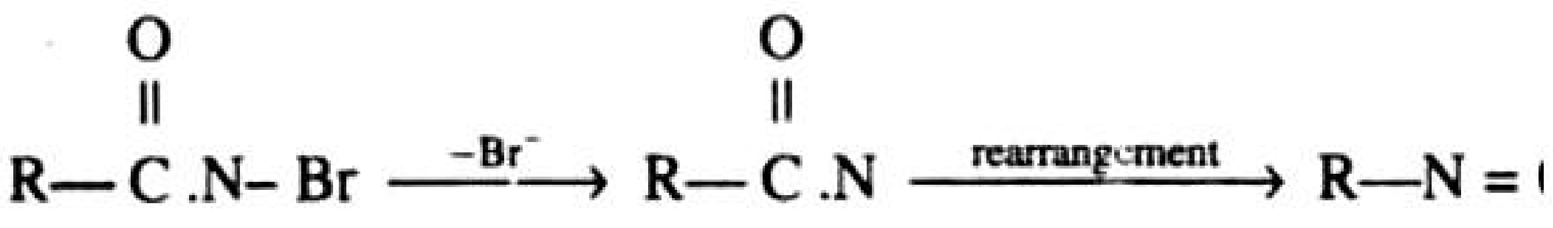
This is an example of Hoffmann degradation of amides.



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



$$R-\overset{O}{\overset{\|}{C}}\,NHBr + KOH \rightarrow R-\overset{O}{\overset{\|}{C}}\,N\text{-}Br + H_2O + KBr$$



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

$$=O \xrightarrow{H_2O} R-NH_2$$

3. a., b. c.

Sandmeyer reaction on p-chloroaniline gives p-dichloro-benzene, which is a solid (m.p. 325 K) while that on anilinium chloride gives chlorobenzene which is a liquid (b.p. 405 K). Further, anilinium hydrochloride is an acid salt and hence liberates CO_2 from $NaHCO_3$ and gives white ppt. of AgCl with $AgNO_3$ solution.

$$C_6H_5\overset{+}{N}H_3Cl^- + NaHCO_3 \rightarrow CO_2 + H_2O + NaCl + C_6H_5NH_2$$

$$C_6H_5\overset{+}{N}H_3Cl^- + AgNO_3 \rightarrow AgCl + C_6H_5\overset{+}{N}H_3NO_3^-$$

p-chloroaniline is neither acidic (actually it is basic) nor contains an ionic chlorine and hence does not give the above reactions.

Thus options (a), (b) and (c) are correct.

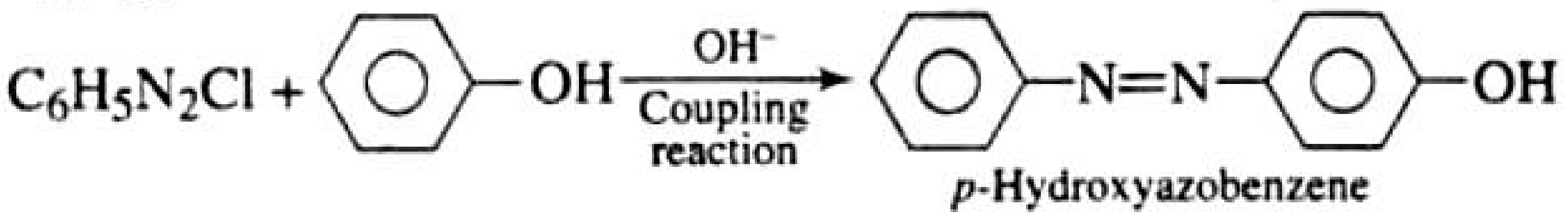
However, both p-chloroaniline and anilinium hydrochloride, being 1° amines, give carbylamine test.

4. a., d.

$$C_6H_5NH_2 + O = C(CH_3)_2 \xrightarrow[-H_2O]{} C_6H_5N = C(CH_3)_2$$

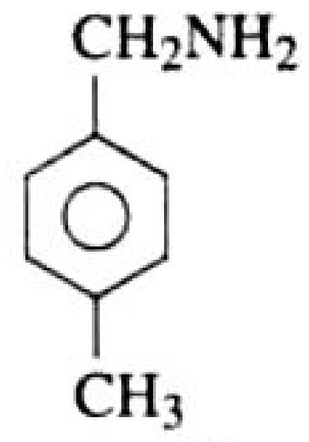
$$C_6H_5NHNH_2 + O = C(CH_3)_2 \xrightarrow[-H_2O]{} C_6H_5NHN = C(CH_3)_2$$

5. b.

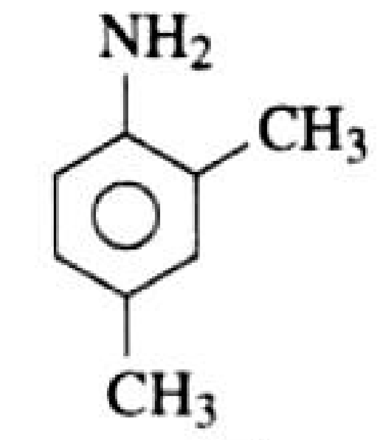


6. b., d.

Carbylamine test is given by primary amines. Therefore, 2, 4-dimethyl aniline and p-methyl benzylamine will give positive carbylamine test.



(d)



(b)

a. is 3° amine

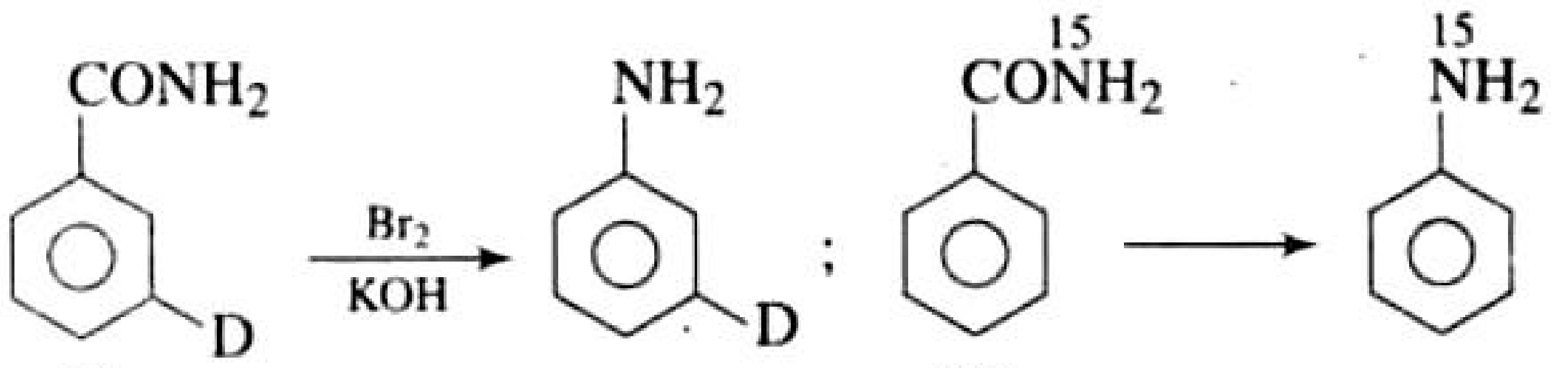
c is 2° amine

Linked Comprehension Type

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)

Matching Column Type

1. (a) → (r), (s), (t); (b) → (t); (c) → (p), (q); (d) → (r)

a. (r), (s), (t)

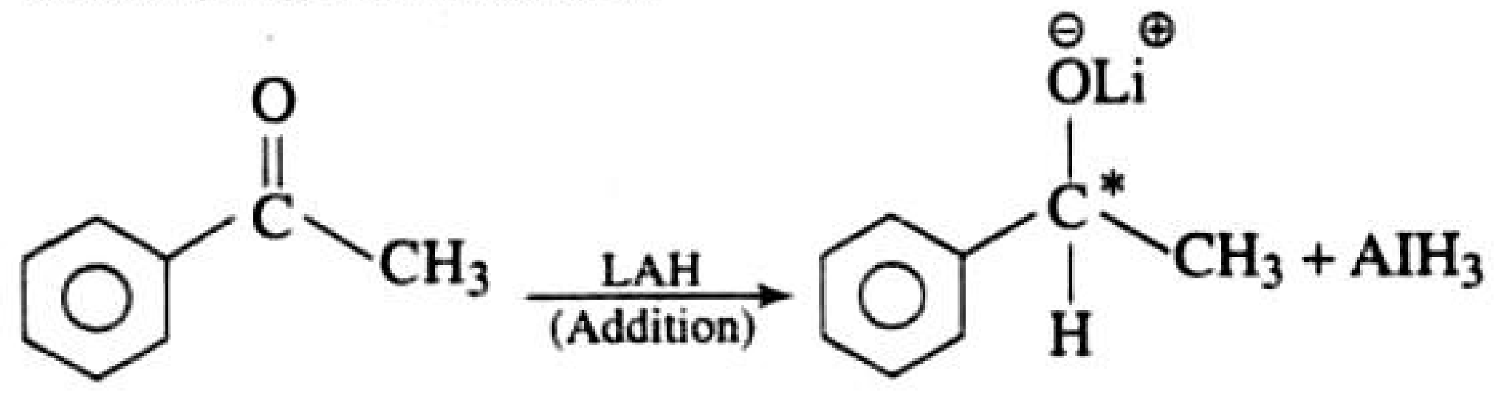
It is example of electrophilic substitution reaction which results in a coupled product; hence it is coupling reaction also. It also involves carbocation intermediate.

b. (t)

Pinacole–pinacolone rearrangement. In this reaction, the intermediate is carbocation.

c. (p), (q)

It is an example of addition reaction by carbonyl compounds and both enantiomers will be formed. Hence, racemic mixture will be obtained.



d. (r)

It is an example of nucleophilic substitution. (Intramolecular)

2. (a) → (p), (q), (s), (t); (b) → (s), (t); (c) → (p); (d) → (r)

a. $CH_3CH_2CH_2CN \xrightarrow[SnCl_2/HCl]{Pd-C/H_2\ or} CH_3CH_2CH_2CH_2NH_2$

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

b. $CH_3CH_2OCOCH_3 \xrightarrow{DIABL-H} CH_3CH_2OH$

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

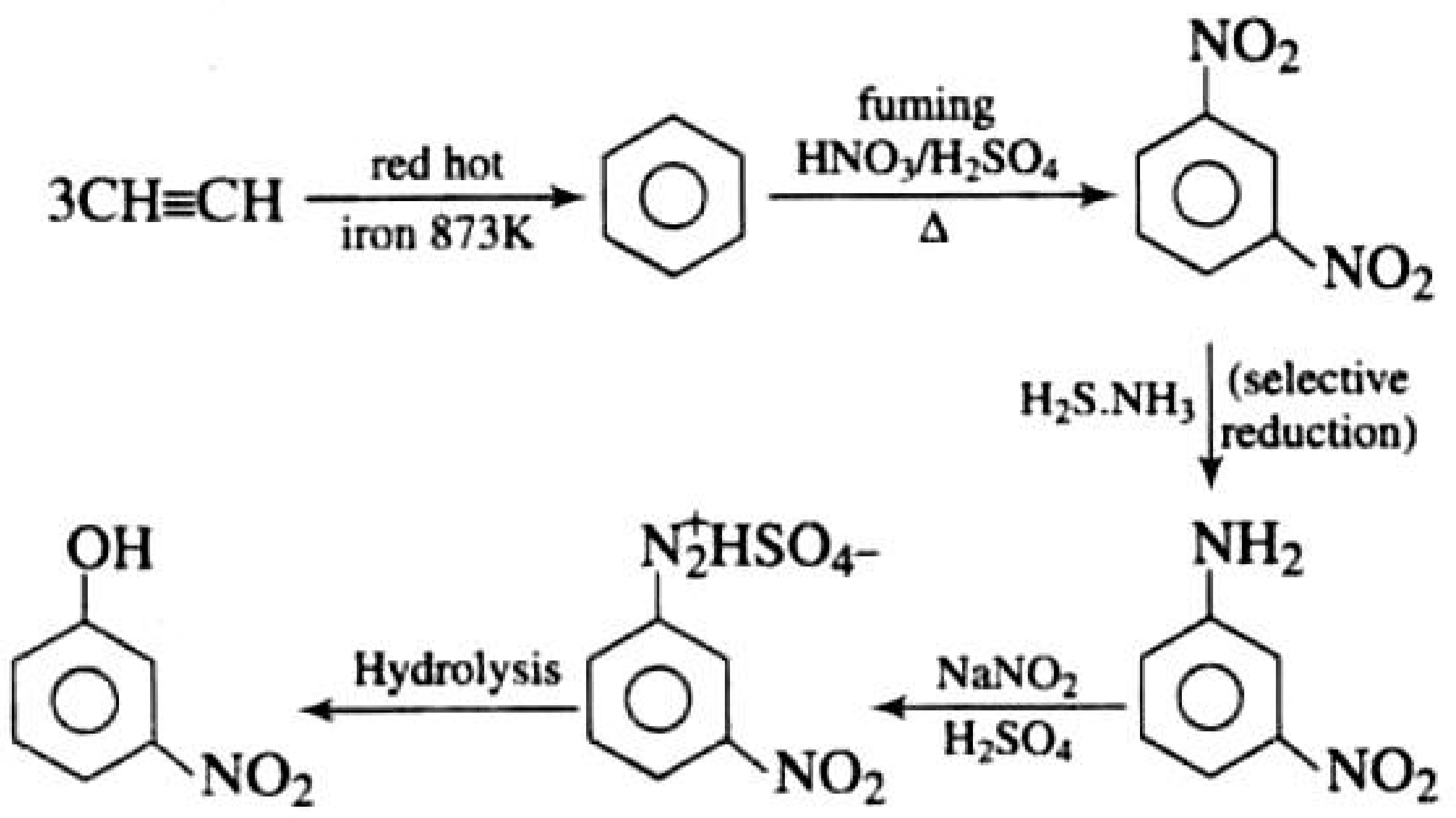
c. $CH_3CH{=}CHCH_2OH \xrightarrow{Pd-C/H_2} CH_3CH_2CH_2CH_2OH$

d. $CH_3CH_2CH_2CH_2NH_2 \xrightarrow[KOH]{CHCl_3} CH_3CH_2CH_2CH_2NC$

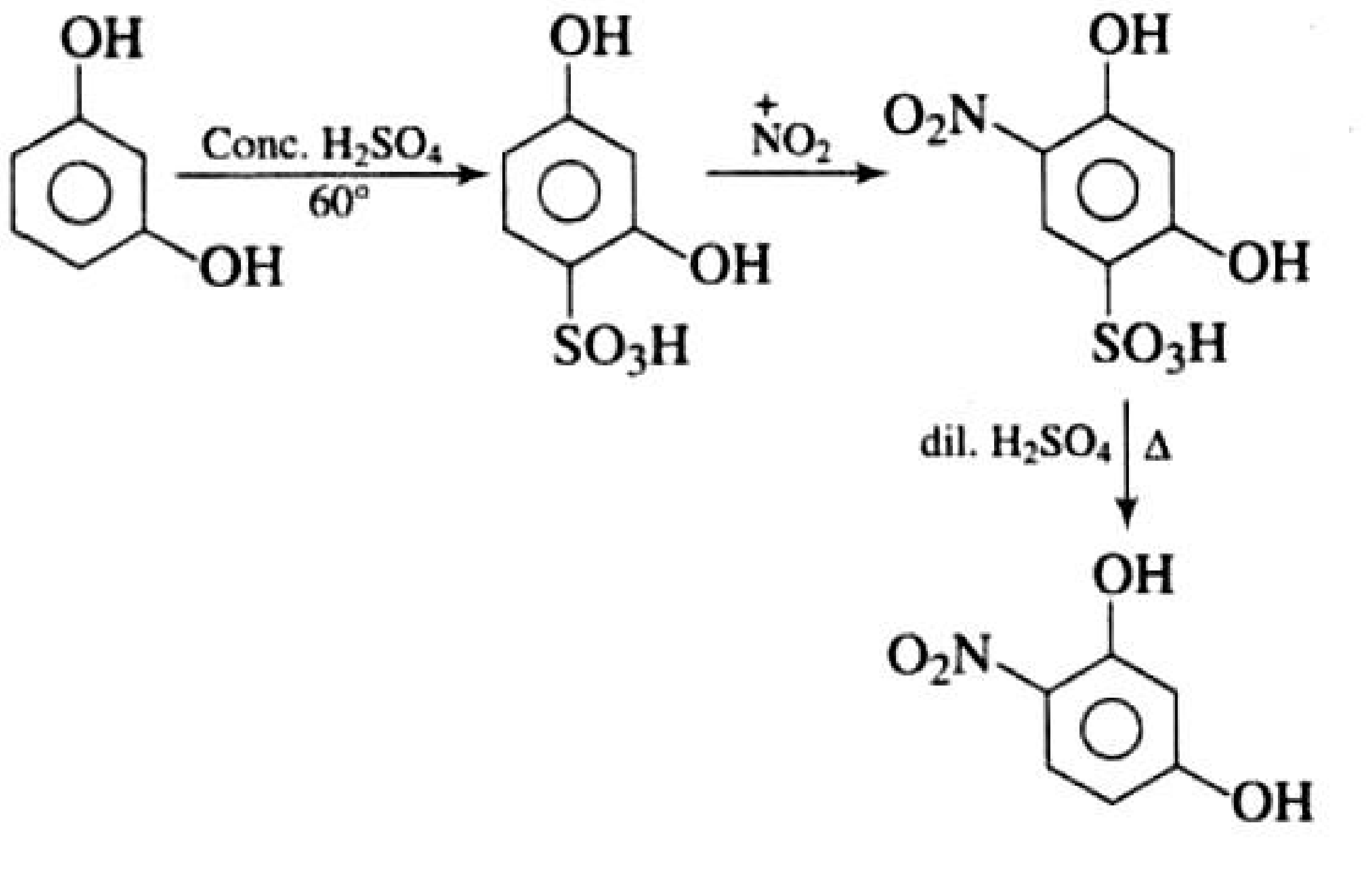
Isonitrile (foul smelling)

3. c.

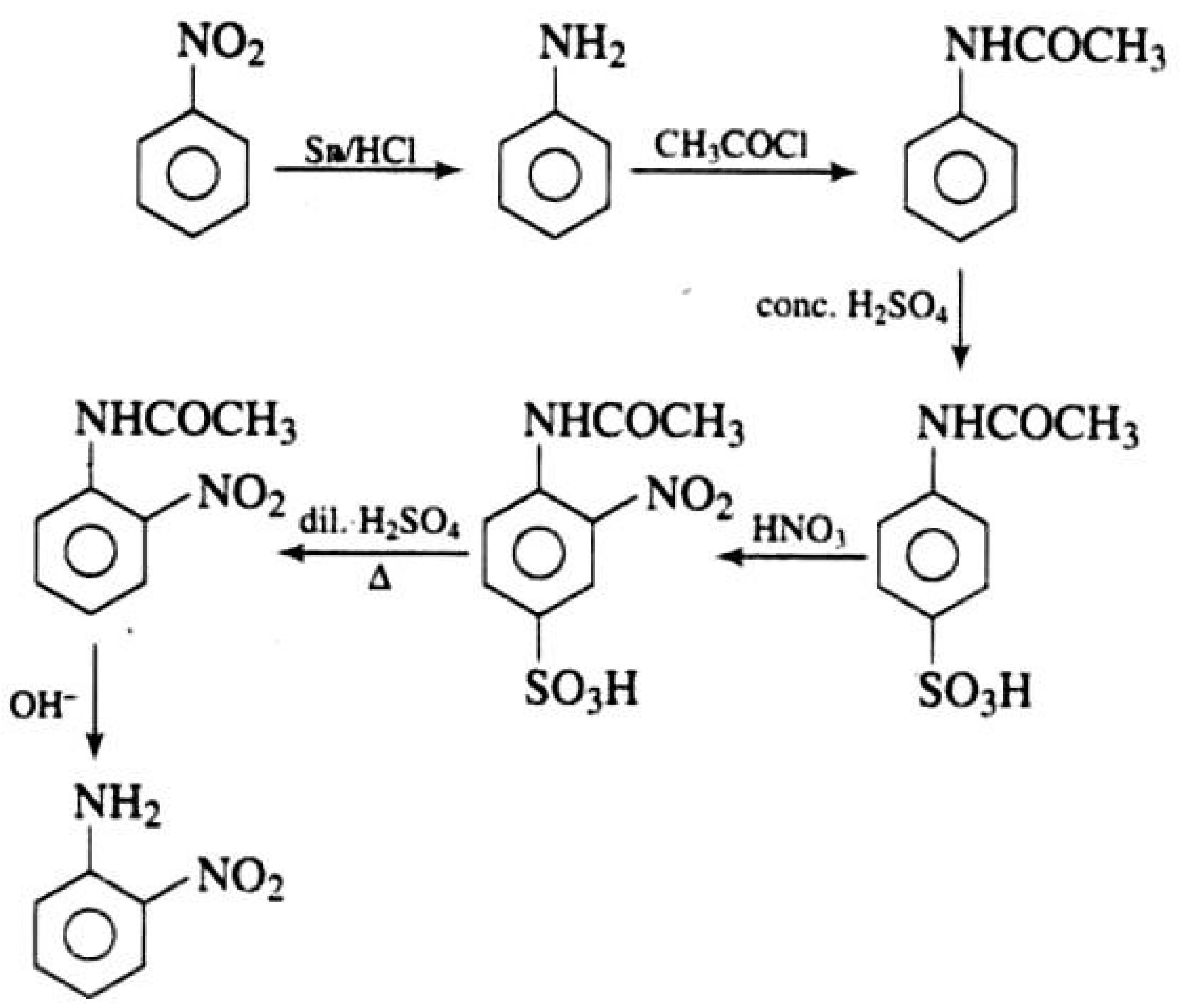
(P)



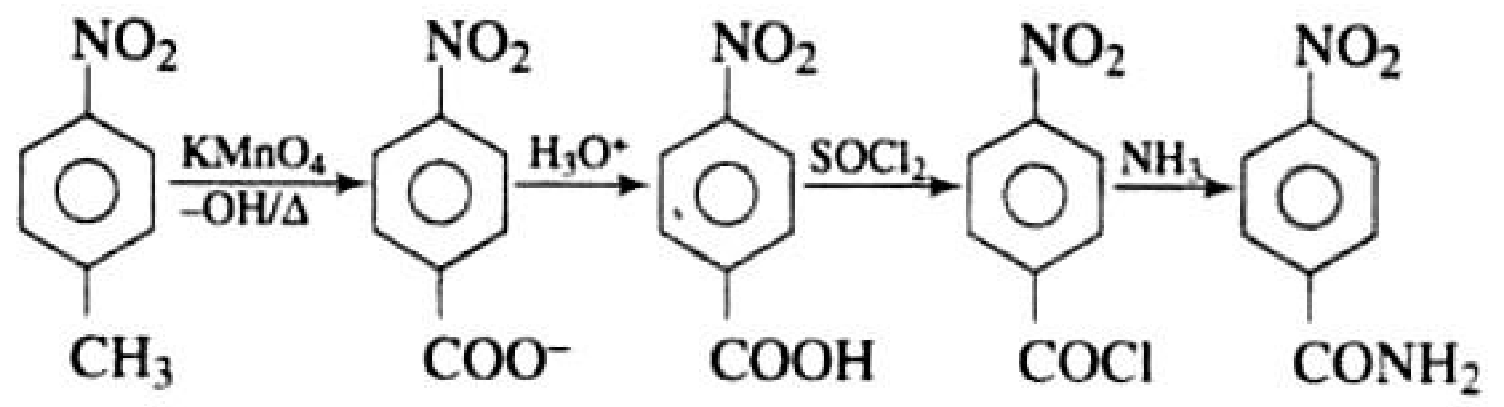
(Q)



(R)



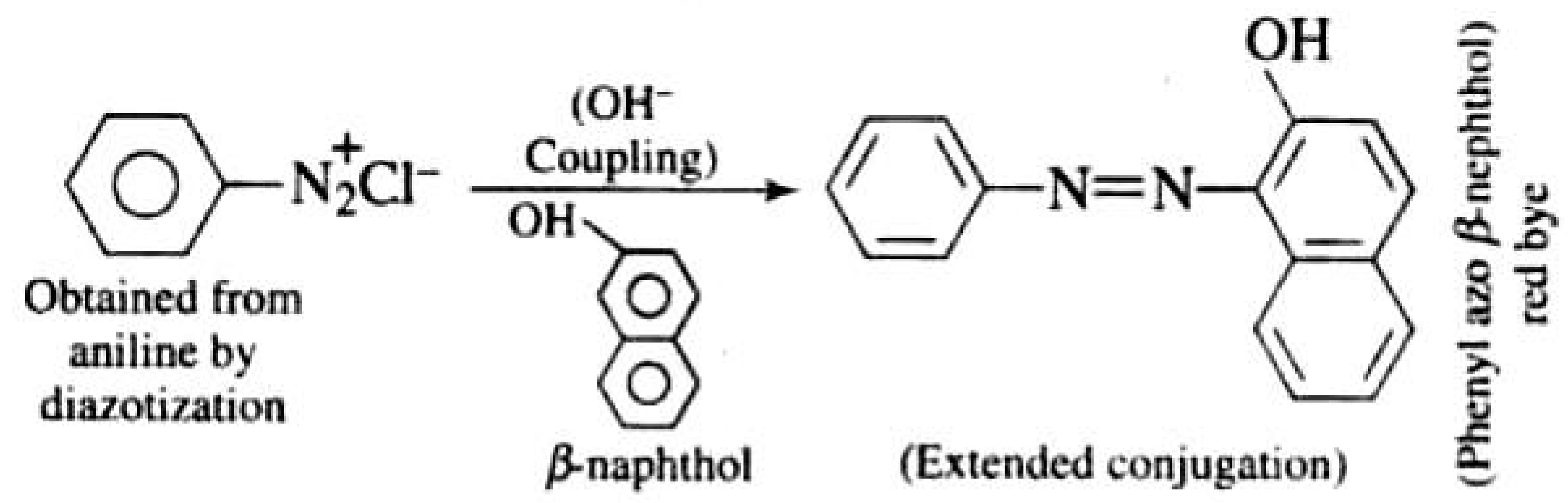
(S)



Assertion-Reasoning Type

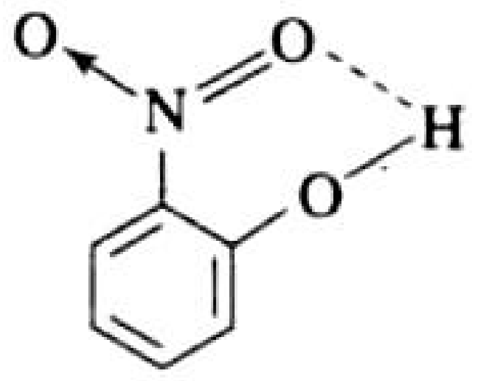
1. d. In strongly acidic medium, aniline is protonated, so LP $\overline{e}$'s are not available to produce mesomeric or electromeric effect; thus, aniline becomes less reactive towards SE reactions.
Statement I is incorrect, but statement II is correct.

2. d. Gives orange-red coloured precipitate.
Statement I is incorrect.
Colour of a compound is due to (besides other factor) extended conjugation. Hence, Statement II is correct.

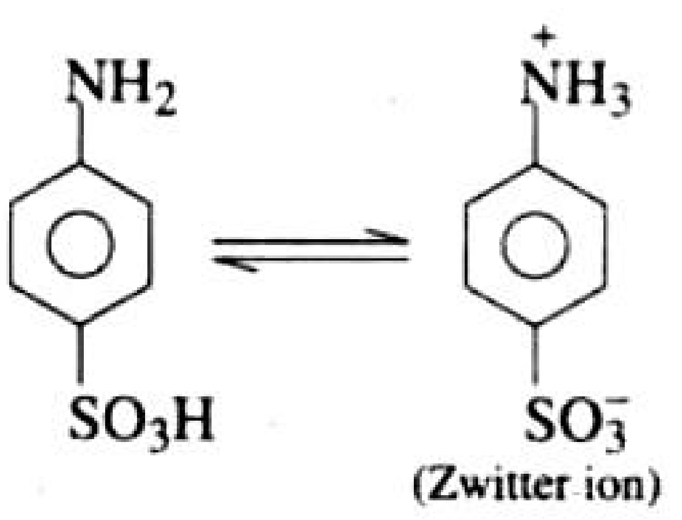


Fill in the Blanks Type

1. **Aniline** because of lone pair of electrons, secondly N is less electronegative than 'O' of OH.
2. **o-Nitrophenol** due to chelation i.e. intramolecular hydrogen bonding.

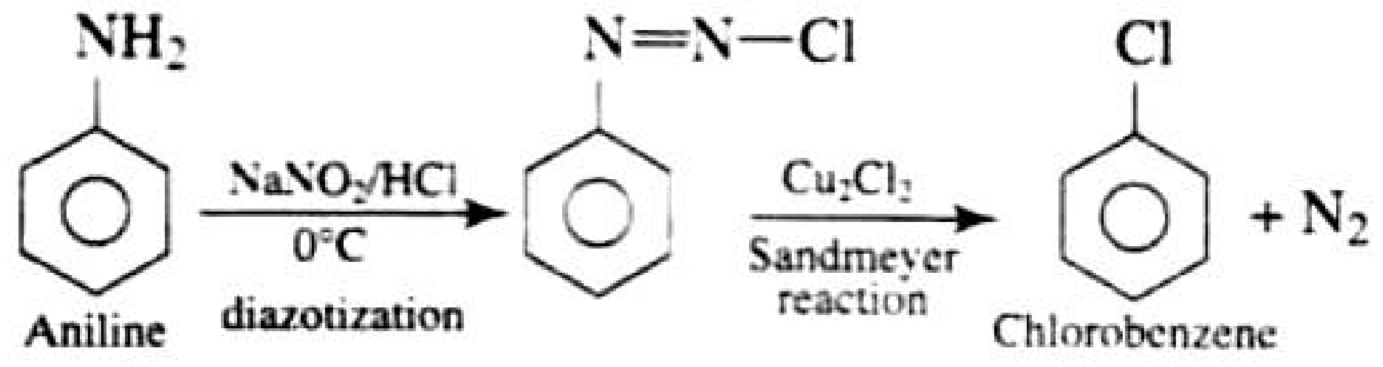


3. **Zwitter ion**



Subjective Type

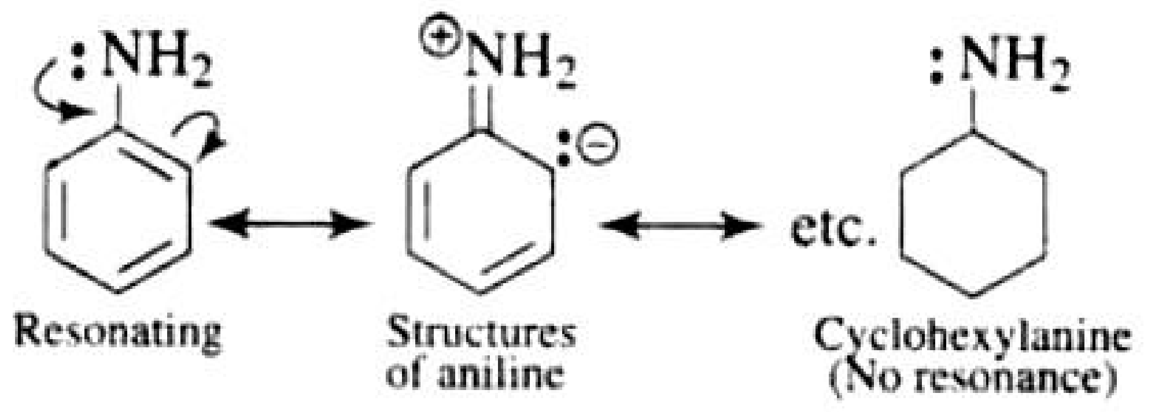
1. i.



ii. $\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + \text{Alc. KCN} \longrightarrow CH_3CH_2CN$ (Stepping up of series)

$$\xrightarrow[\text{(Reduction)}]{H_2/Ni} CH_2—CH_2—CH_2NH_2$$

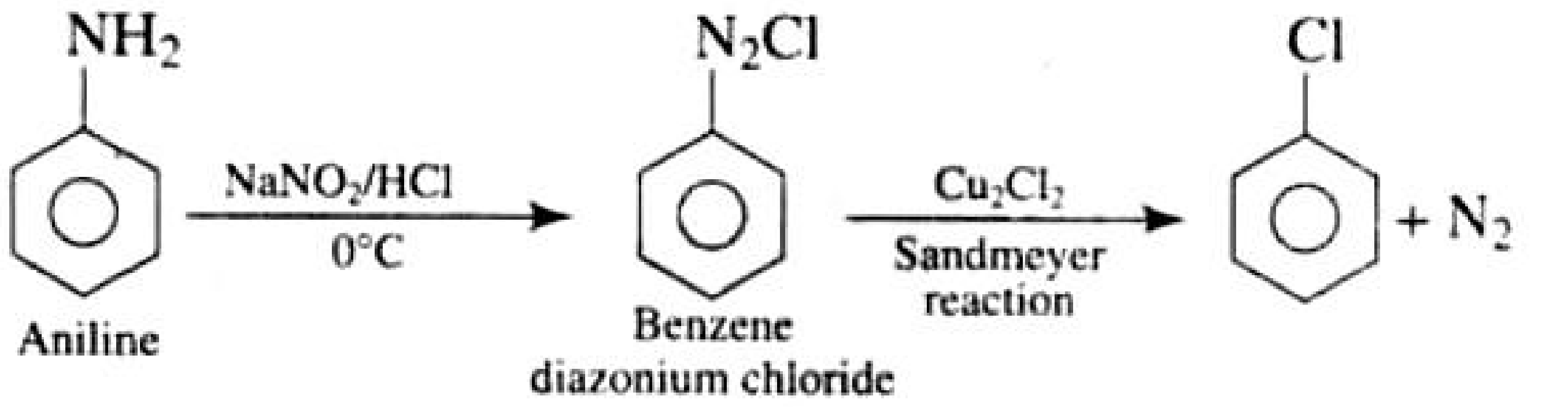
2. Aniline is weak base than cyclohexylamine because of resonance while there is no resonance in cyclohexylamine.



3. **Aniline from benzene:**

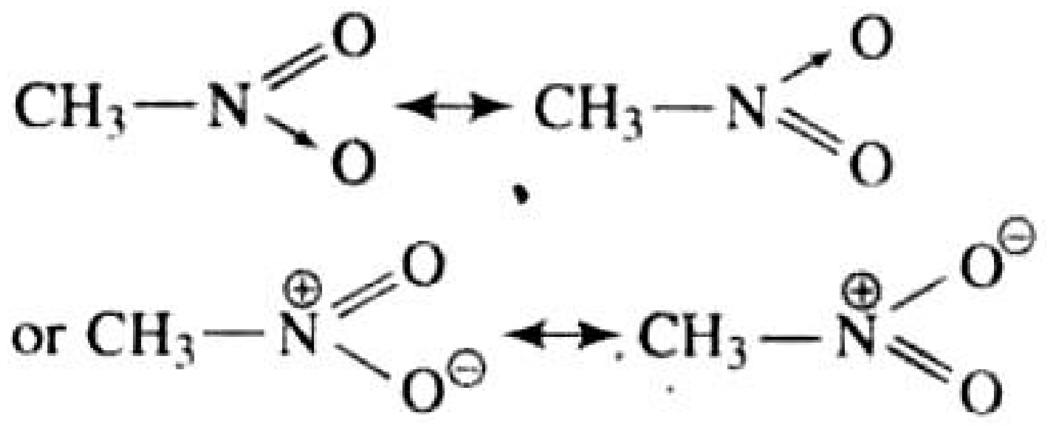
$$\underset{\text{Benzene}}{C_6H_6} \xrightarrow[\text{Conc. } H_2SO_4 \text{ (Nitration)}]{\text{Conc. } HNO_3} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow[\text{(Reduction)}]{Sn/HCl} \underset{\text{Aniline}}{C_6H_5—NH_2}$$

4. **Aniline to chlorobenzene:**



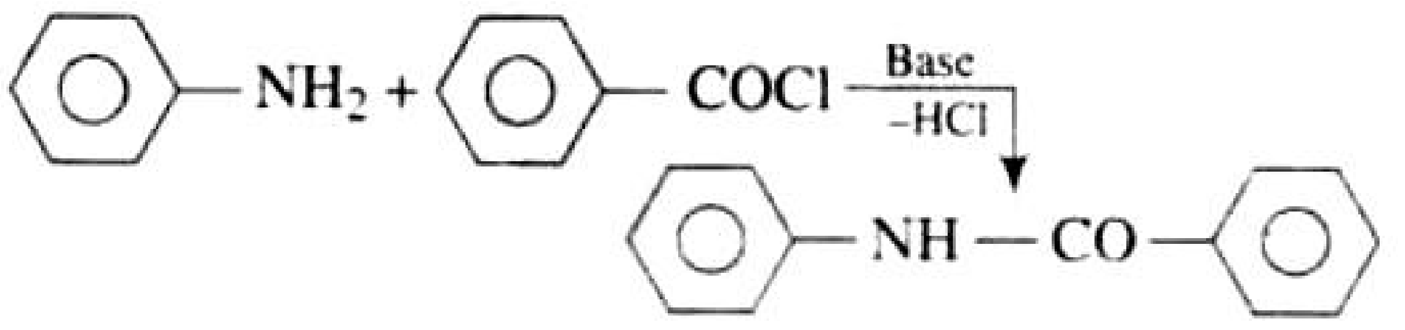
5. *o*-Nitrophenol shows intramolecular H-bonding and *p*-nitrophenol shows intermolecular H-bonding and thus its several molecules associate with each other. The ortho isomer goes with the steam due to its low boiling point.

6. i.

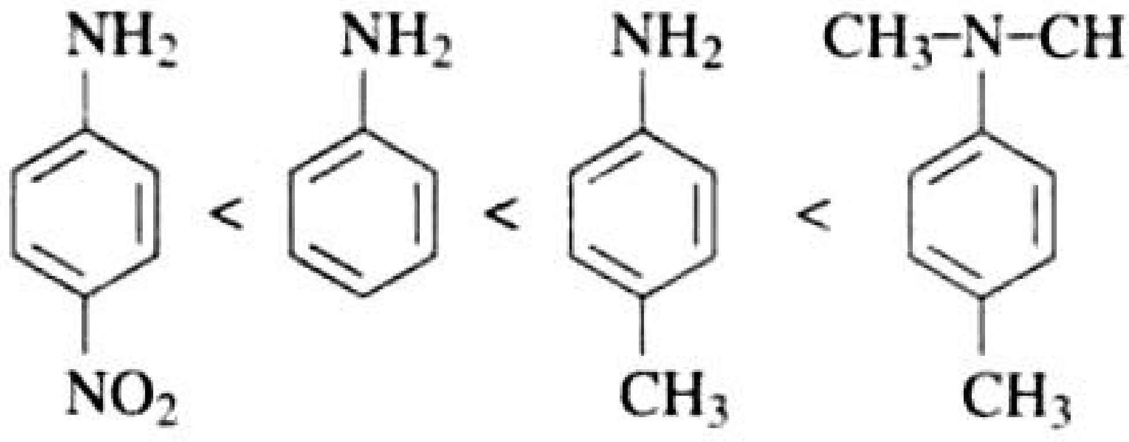


ii.

7.



8. Presence of +I group increases the basicity, whereas the presence of –I group decreases the basicity.

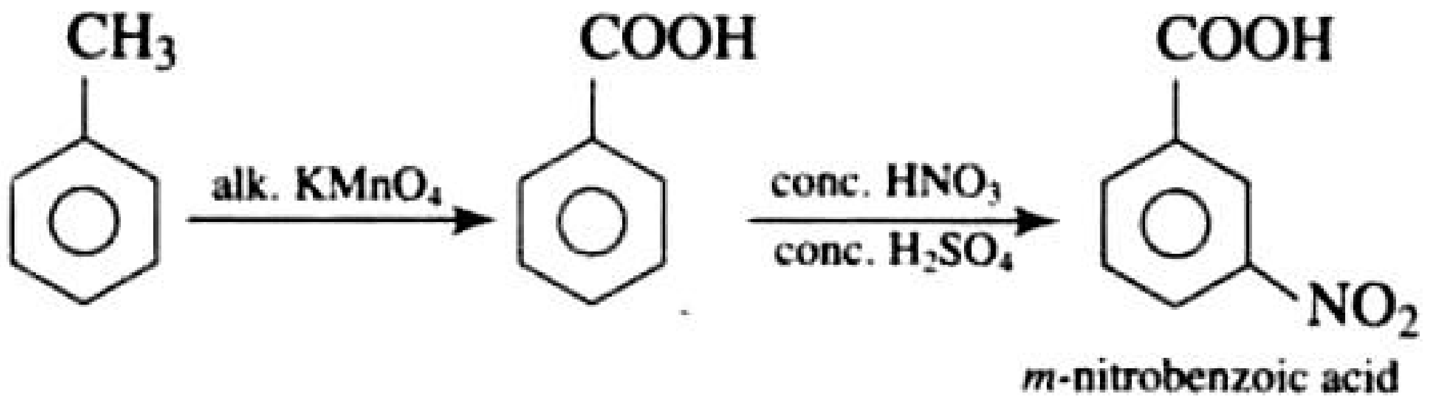


9. i. $C_6H_5CHO \xrightarrow{\text{Oxi.}} C_6H_5COOH$

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

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

ii.

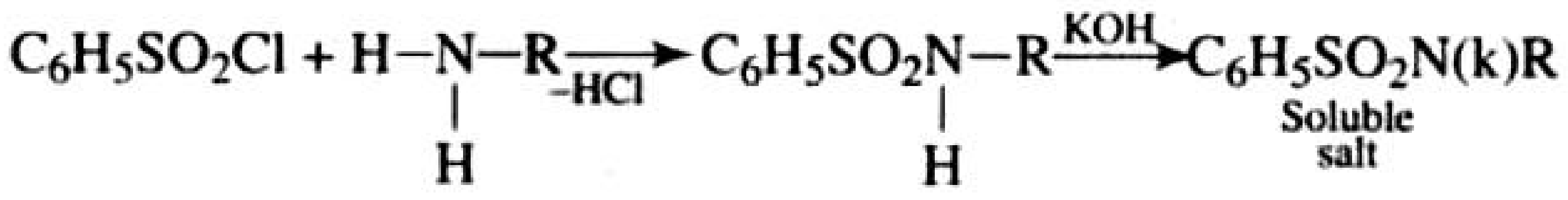


10. Hoffmann degradation reaction.

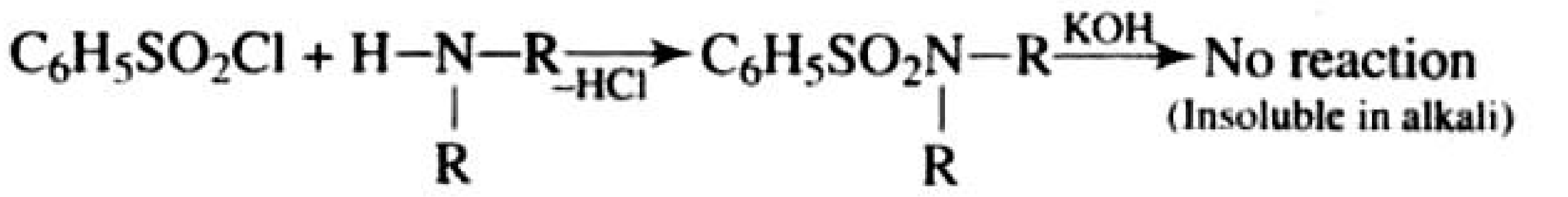
$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \longrightarrow$$

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

11. Test with benzene sulphonyl chloride ($C_6H_5SO_2Cl$)
Ethylamine (primary amine) forms N-ethyl benzene sulphonamide which dissolves in KOH because of the presence of an acidic hydrogen on the N atom.
On the other hand, diethyl amine (secondary amine) forms N, N-diethyl benzene sulphonamide, which does not dissolve in KOH due to the absence of acidic hydrogen on N atom.



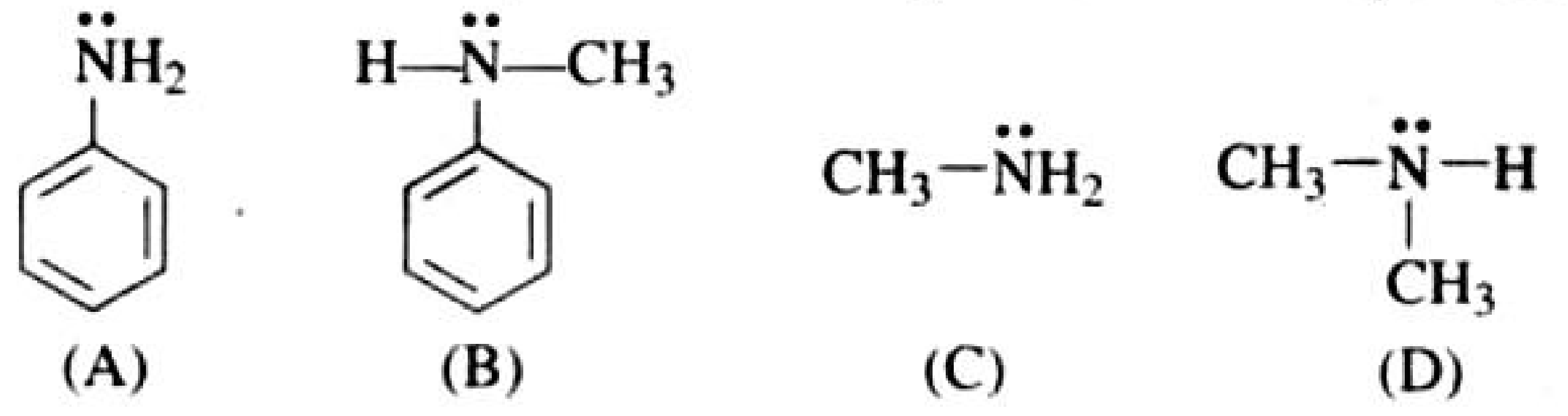
$$C_6H_5SO_2Cl + H-\underset{\substack{|\\H}}{N}-R \xrightarrow[-HCl]{} C_6H_5SO_2\underset{\substack{|\\H}}{N}-R \xrightarrow{KOH} \underset{\text{Soluble salt}}{C_6H_5SO_2N(k)R}$$



$$C_6H_5SO_2Cl + H-\underset{\substack{|\\R}}{N}-R \xrightarrow[-HCl]{} C_6H_5SO_2\underset{\substack{|\\R}}{N}-R \xrightarrow{KOH} \underset{\text{(Insoluble in alkali)}}{\text{No reaction}}$$

12. The increasing order of basic strength:

Aniline < N-Methylaniline < Methylamine < Dimethylamine



In (D) the presence of two R groups due to +I effect is maximum basic.
In (C) only one R group.
In (A) and (B) lone pair on N is involved is resonance. In (B) +I group of CH_3 makes it more basic than (A).

13. i. For empirical formula of A:

Element	Percentage	Relative no. of atoms $= \frac{\text{percentage}}{\text{atomic mass}}$	Simplest ratio
C	49.32	$\frac{49.32}{12} = 4.11$	3
H	9.59	$\frac{9.59}{1} = 9.59$	7
N	19.18	$\frac{19.18}{14} = 1.37$	1
O	21.91	$\frac{21.91}{16} = 1.37$	1

∴ Empirical formula of (A) = C_3H_7NO
Empirical formula weight of (A) = 73

ii. Molecular weight of acid (B) can be derived as:

$$\frac{\text{Wt. of Ag}}{\text{Ew of Ag}} = \frac{\text{Wt. of salt}}{\text{Ew of Ag salt}}$$

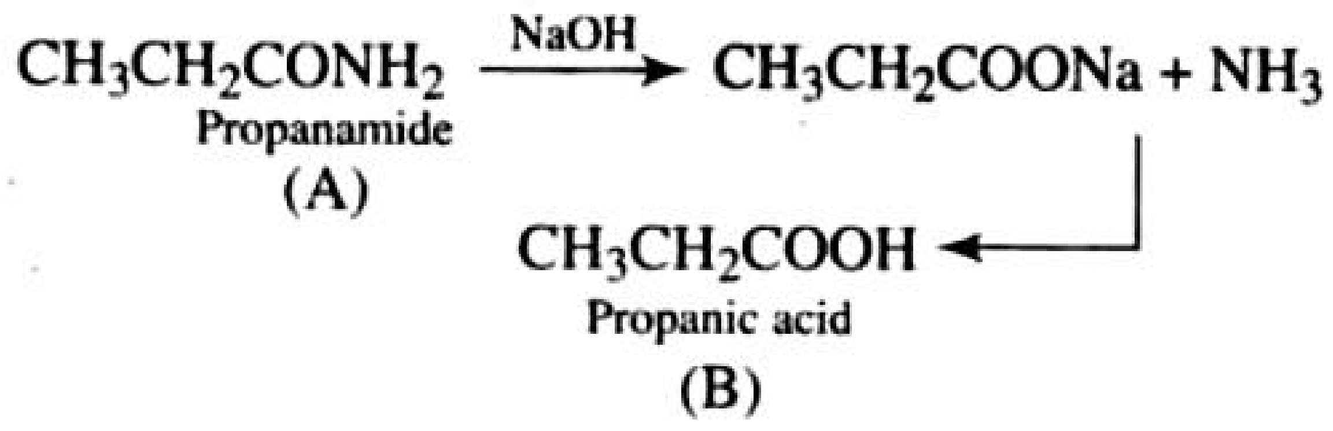
$$\frac{59.67}{108} = \frac{100}{E + (108 - 1)}$$

$$\therefore \quad = 74$$

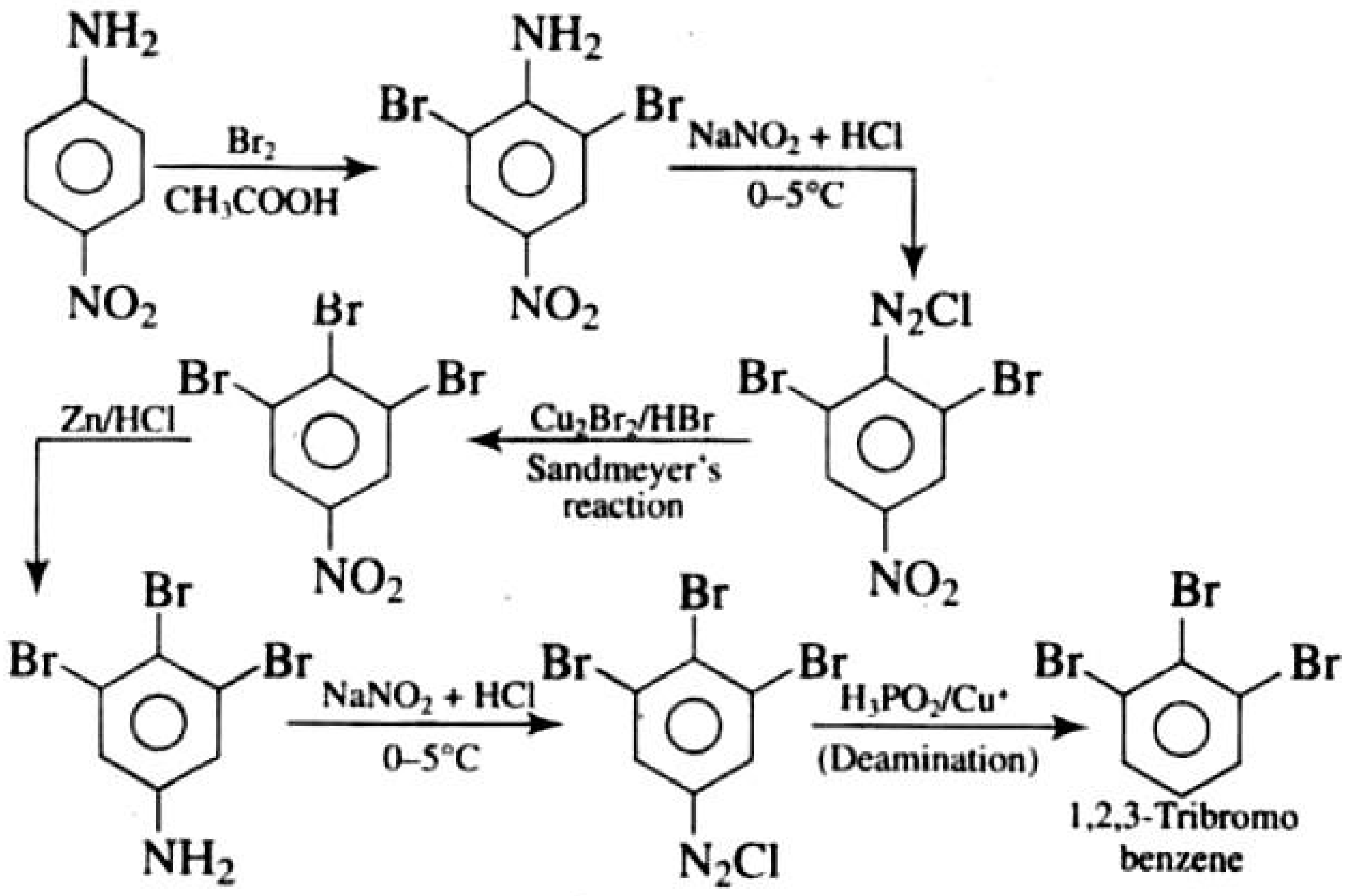
∴ Equivalent weight of acid = 74
∴ Molecular weight of acid = 74 × 1 = 74
(∵ Basicity = 1)

iii. Acid (B) is monobasic and, thus, (B) is $C_nH_{2n+1}COOH$
∴ $12n + 2n + 1 + 12 + 32 + 1 = 74$
∴ $n = 2$
So, acid (B) is CH_3CH_2COOH

iv. Since (B) is obtained by the action of (A) with NaOH followed by hydrolysis, so (A) is $CH_3CH_2CONH_2$



14. 4-Nitroaniline to 1, 2, 3-tribromobenzene:



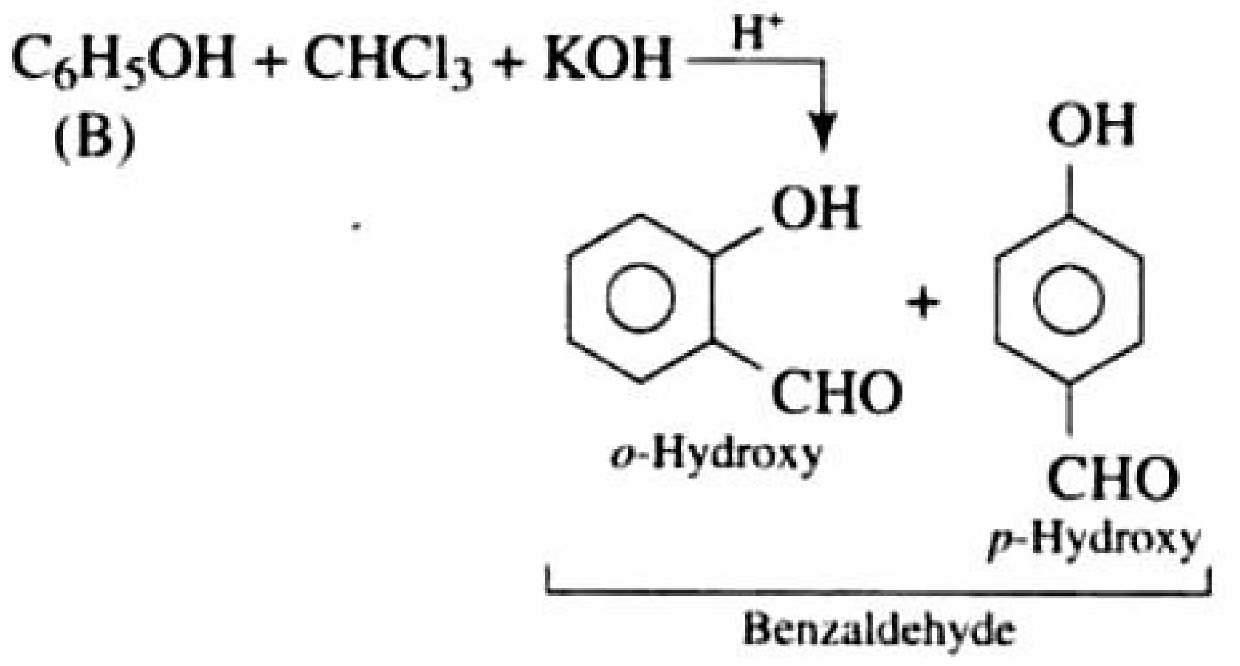
15. i. Given,
Mixture of (A) and (B)

$$\xrightarrow[+KOH(Aq.)]{CHCl_3} \underset{(A)}{\text{Organic layer}} + \underset{(B)}{\text{Alkaline aqueous layer}}$$

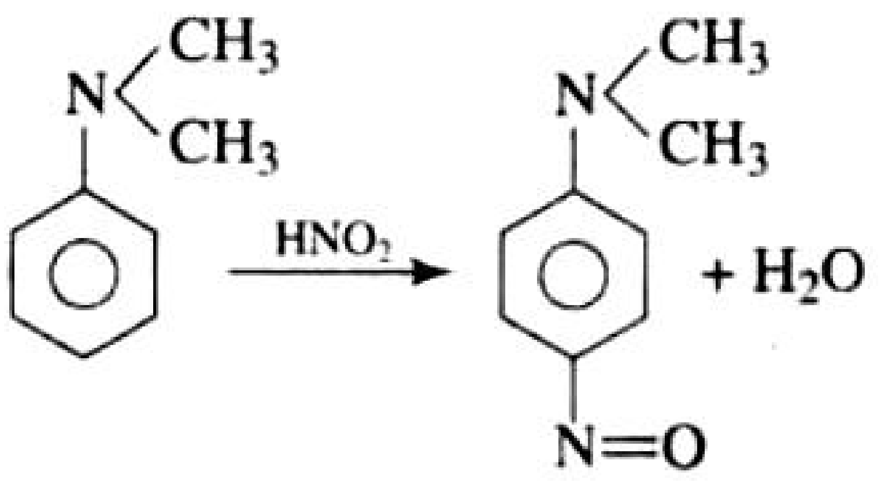
ii. Organic layer on treating with KOH (alc.) produces (C) of unpleasant odour (C_7H_5N) and, thus, (C) is C_6H_5NC. This is carbylamine reaction. Therefore, (A) is $C_6H_5NH_2$.

$$\underset{(A)}{C_6H_5NH_2} + CHCl + 3KOH(aq). \longrightarrow \underset{(C)}{C_6H_5NC} + 3KCl + 3H_2O$$

iii. Alkaline layer on treating with $CHCl_3$ followed with acidification gives two isomers (D) and (E) ($C_7H_6O_2$). This is Riemer–Teimann's reaction and, thus, (B) is C_6H_5OH.



16.



17. **Concept** from question

$$\underset{\substack{\text{Acid}\\\text{chloride}}}{X} \xrightarrow{NH_3} \underset{\text{Amide}}{Y} \xrightarrow[\substack{NaOH\\\text{Hoffmen's}\\\text{bromamide}}]{Bx_2} Z \xrightarrow{HONO} \text{Alcohol}$$

⇒ Z is 1° amine.

In compound (Y) the percentage of C = 49.31

The percentage of H = 9.59

The percentage of N = 19.18

The percentage of O = 100 – %C – %H – %N

∴ = 100 – 78.08 = 21.92%

Empirical formula of compound (Y):

Element	Percentage	At. wt.	Relative number	Ratio
C	49.31	12	49.31/12 = 4.10	4.10/1.37 = 3.
H	9.59	1	9.59/1 = 9.59	9.59/1.37 = 7
N	19.18	14	19.18/14 = 1.37	1.37/1.37 = 1
O	21.92	16	21.92/16 = 1.37	1.37/1.37 = 1

Hence, empirical formula of compound Y is C_3H—NO. On the basis of the empirical formula, its molecular formula may be equal to its empirical formula.

Hence, compound Y is $CH_3CH_2CONH_2$ because it gives Hofmann's bromamide reaction with Br_2 and caustic soda and gives a basic compound Z. Z reacts with HNO_2 to give ethanol.

$$\underset{(Y)}{CH_3CH_2CONH_2} + Br_2 + 4KOH \longrightarrow \underset{(Z)}{CH_3CH_2NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

$$\underset{(Z)}{CH_3CH_2NH_2} + HNO_2 \longrightarrow \underset{\text{Ethanol}}{CH_3CH_2OH} + N_2 + H_2O$$

Compound (Y) is obtained with compound (X) (which has chlorine) on treatment with strong ammonia. So, compound (X) is CH_3CH_2COCl.

$$\underset{\substack{\text{Propionyl chloride}\\\text{Compound (X)}}}{CH_3CH_2COCl} + NH_3 \longrightarrow \underset{\text{Compound (Y)}}{CH_3CH_2CONH_2}$$

Hence, compounds are:

$$(X) = CH_3\text{—}CH_2\text{—}\underset{\underset{O}{\|}}{C}\text{—}Cl,$$

$$(Y) = CH_3\text{—}CH_2\text{—}\underset{\underset{O}{\|}}{C}\text{—}NH_2, \text{ and}$$

$$(Z) = CH_3\text{—}CH_2\text{—}NH_2.$$

18. A basic, volatile nitrogen compound is primary amine.

$$RNH_2 + CHCl_3 + 3KOH\ (\text{Alcoholic}) \longrightarrow \underset{\left(\substack{\text{Foul}\\\text{smelling gas}}\right)}{RNC} + 3KCl + 3H_2O$$

$$NaNO_2 + HCl \xrightarrow{0°C} NaCl + HNO_2$$

$$\underset{\text{(it contains one N atom)}}{RNH_2 + HNO_2} \xrightarrow{0°C} R-OH + \underset{\text{(Colourless gas)}}{N_2} + H_2O$$

At STP 112 ml of colourless gas is evolved with 0.295 gm sample of substance after treatment with aqueous HCl and $NaNO_2$ at 0°C.

So, at STP 22400 ml colourless gas will be evolved with $\frac{0.295 \times 22400}{112}$ = 59 gm of sample of such substance after above treatment.

Hence, the molecular weight of RNH_2 is 59.

∴ Weight of $R + 14 + 2 = 59$

Weight of $R = 43$

So, R is C_3H_7 — (∵ weight of C_3H_7 — = 43).

Thus, the given substance is

(i) $CH_3CH_2CH_2 - NH_2$ (ii) $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH-NH_2$

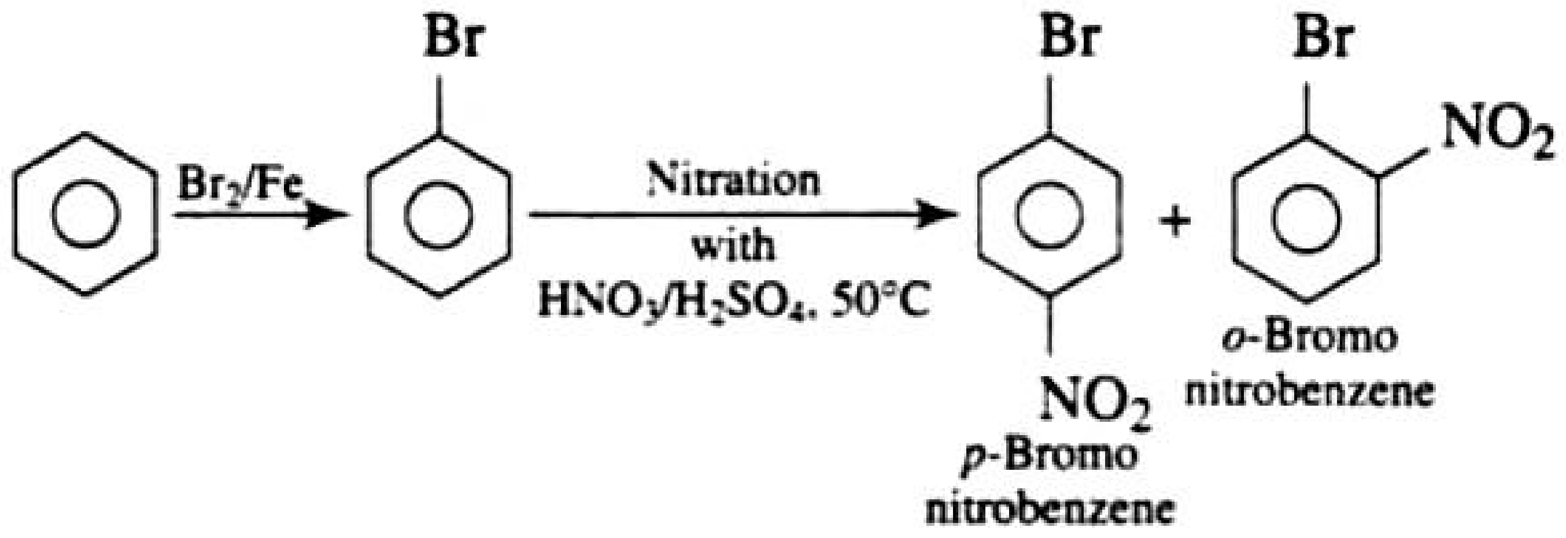
Substance (i) gives $CH_3CH_2CH_2 - OH$ with dil. HCl and $NaNO_2$ at 0°C which does not give yellow precipitate (Iodoform test) with I_2 and alkali, while substance (ii)

gives $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>OH$ on treatment with dil HCl and $NaNO_2$ at 0°C which gives yellow precipitate with I_2 and alkali.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\!-NH_2 + NaNO_2 + HCl \xrightarrow{0°C} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\!-OH + NaCl + H_2O$$

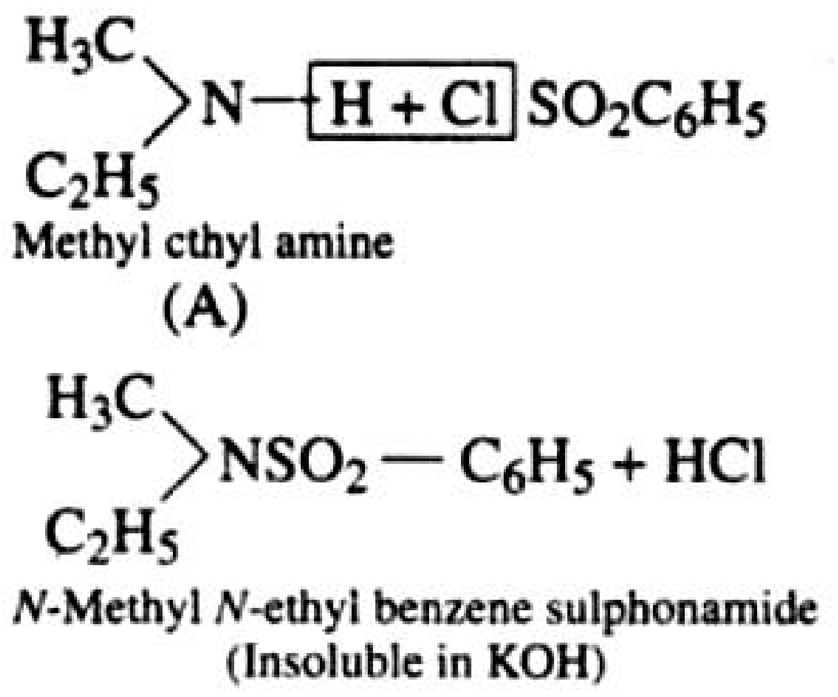
$$\begin{matrix} Me \\ Me \end{matrix}\!\!>\!\!-OH + 4I_2 + 6NaOH \rightarrow \underset{\substack{\text{Yellow ppt.}\\\text{(Iodoform)}}}{CHI_3\downarrow} + CH_3COONa + 5NaI + 5H_2O$$

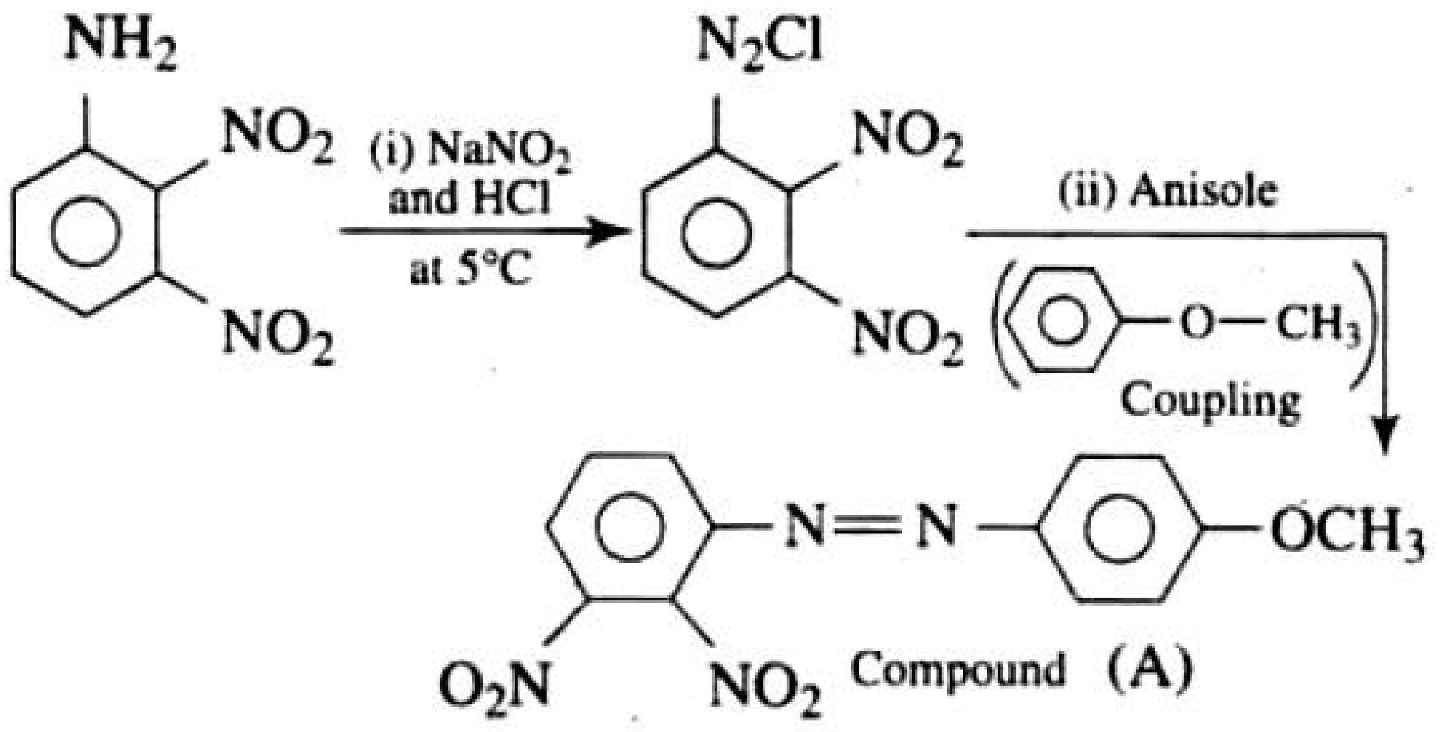
Hence, the basic substance is $\begin{matrix} Me \\ Me \end{matrix}\!\!>\!\!- NH_2$

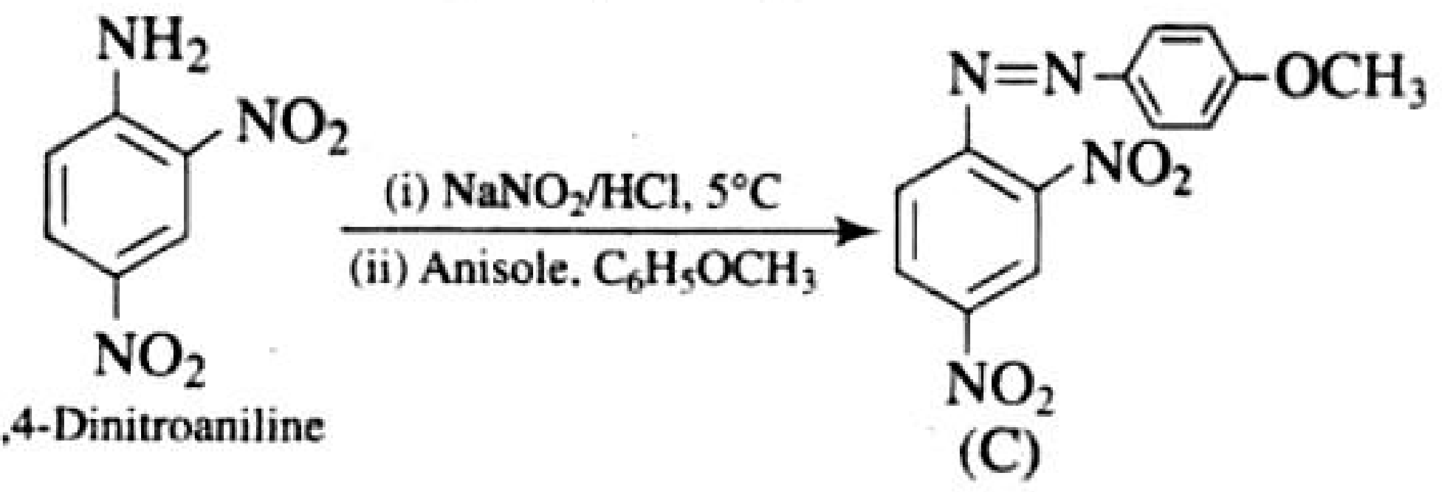
19. 

Hence, these are separated by fractional crystallization.

20. Solid insoluble in alkali itself indicates 2° amine.



21. i. 

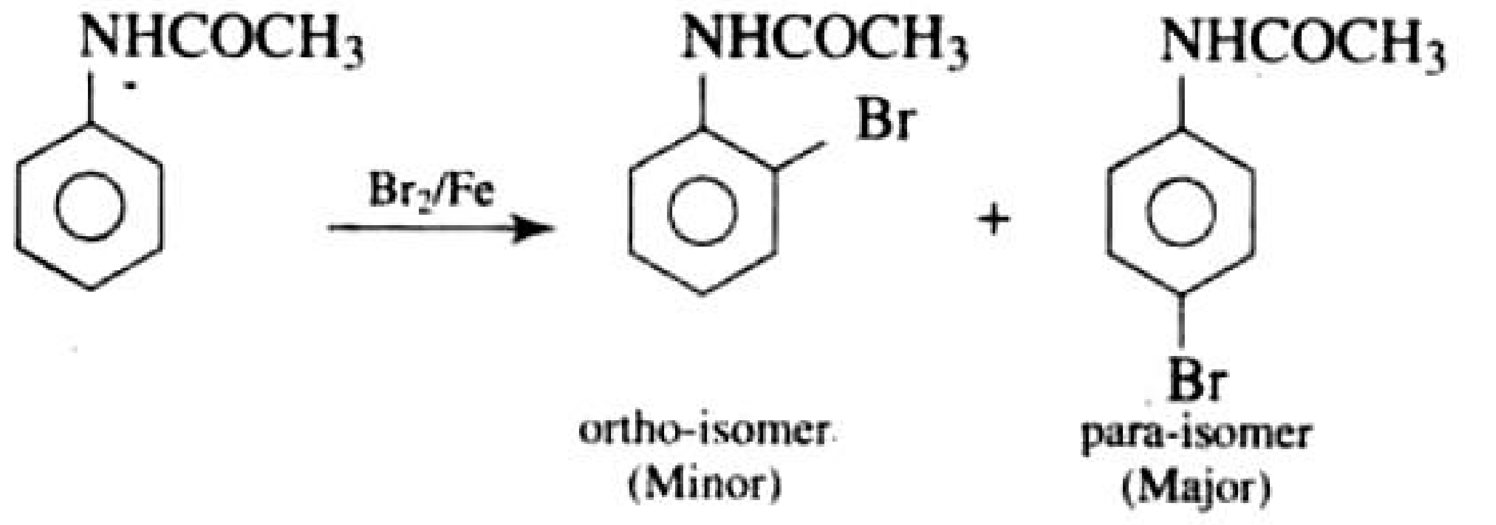
ii. 

22. $C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O$

Aniline Chloroform (Alcoholic) (Foul smelling compound, i.e., phenyl isocyanide)

23. i. $CH_3-CH_2-NH_2 \xrightarrow{(CH_3CO)_2O}$

$CH_3-CH_2-NH-COCH_3 + CH_3COOH$

ii. 

24. i. 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. **Solvent 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.

Thus, 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.

ii. 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.

25. i. Empirical formula of minor product of nitration of nitrobenzene:

Element	**Percentage**	**At. wt.**	**Relative number of moles**	**Whole no. ratio**
C	42.86	12	$\frac{42.86}{12} = 3.57$	$\frac{3.57}{1.19} = 3.00$
H	2.40	1	$\frac{2.40}{1} = 2.40$	$\frac{2.40}{1.19} = 2.00$
N	16.67	14	$\frac{16.67}{14} = 1.19$	$\frac{1.19}{1.19} = 1.00$
O	38.07	16	$\frac{38.07}{16} = 2.37$	$\frac{2.37}{1.19} = 1.99 \simeq 2.0$

Hence, the empirical formula of minor product = $C_3H_2NO_2$

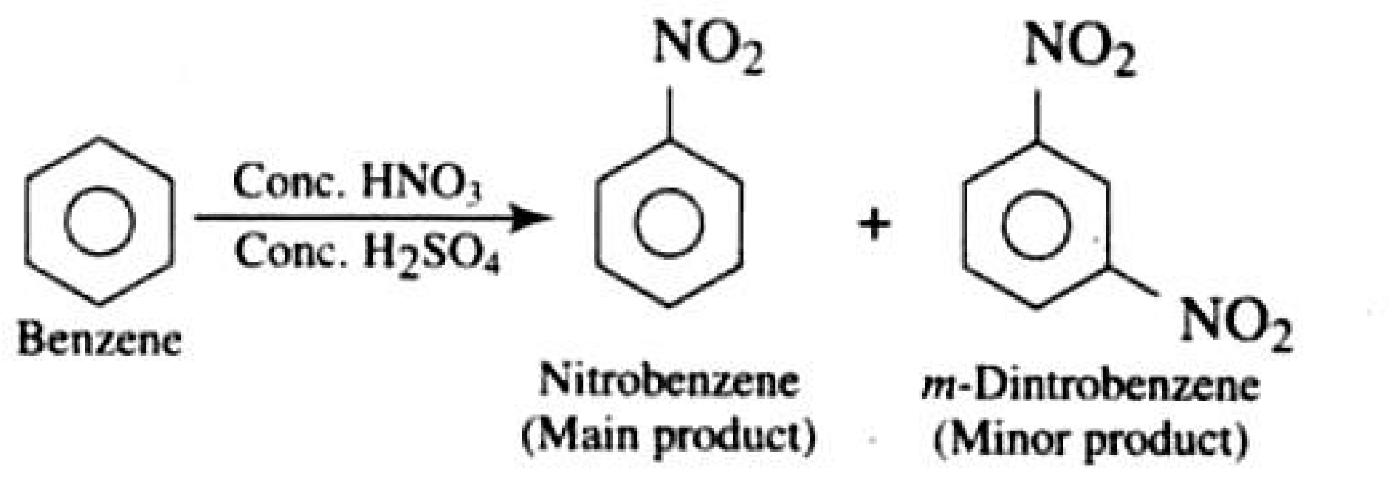
ii. MW of minor product $(m) = \frac{1000 \times K_b}{\Delta T_b} \times \frac{w}{W}$

$$= \frac{1000 \times 2.53}{1.84} \times \frac{5.5}{45} = 168$$

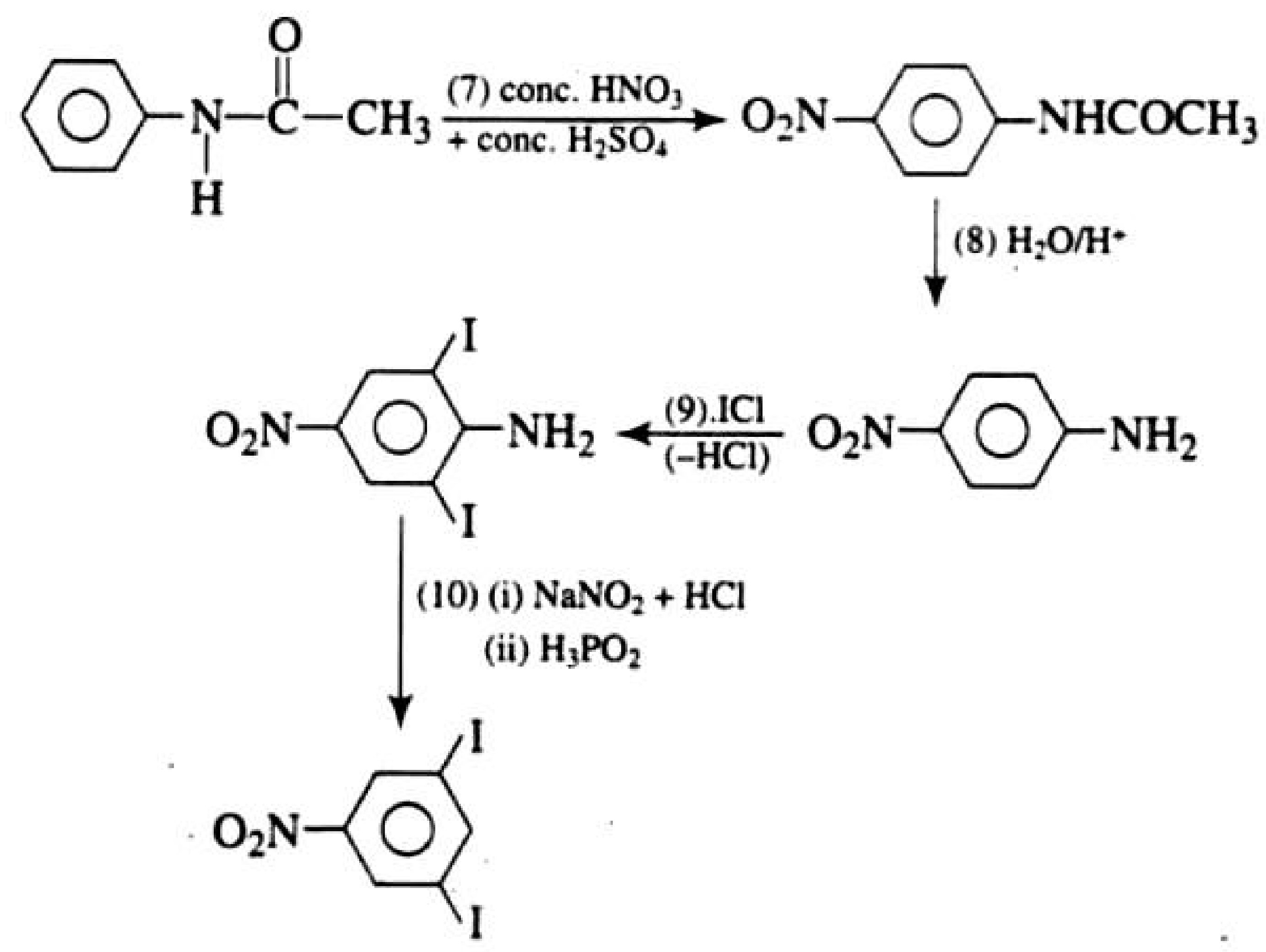
$$\therefore \quad n = \frac{\text{MW}}{\text{Wt. of empirical formula}} = \frac{168}{36 + 2 + 14 + 32} = 2$$

Hence, the molecular formula of the minor product is = 2 × $C_3H_2NO_2 = C_6H_4N_2O_4$

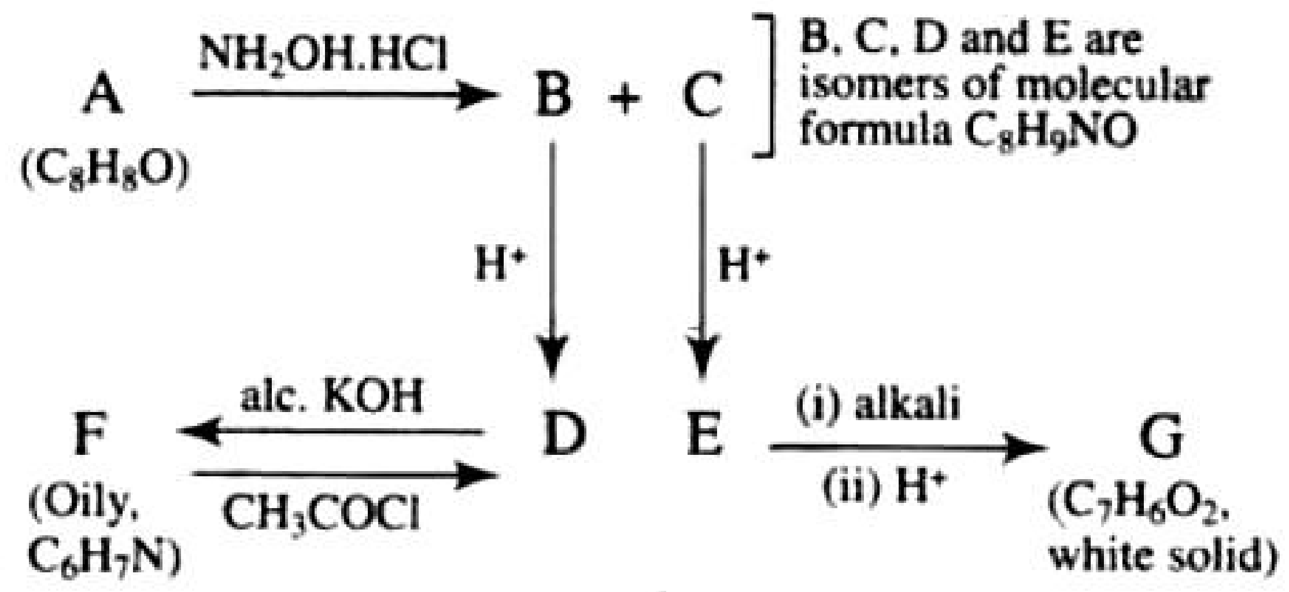
Hence,



26.



27. Given



Conclusions

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 $C_6H_5NHCOCH_3$.

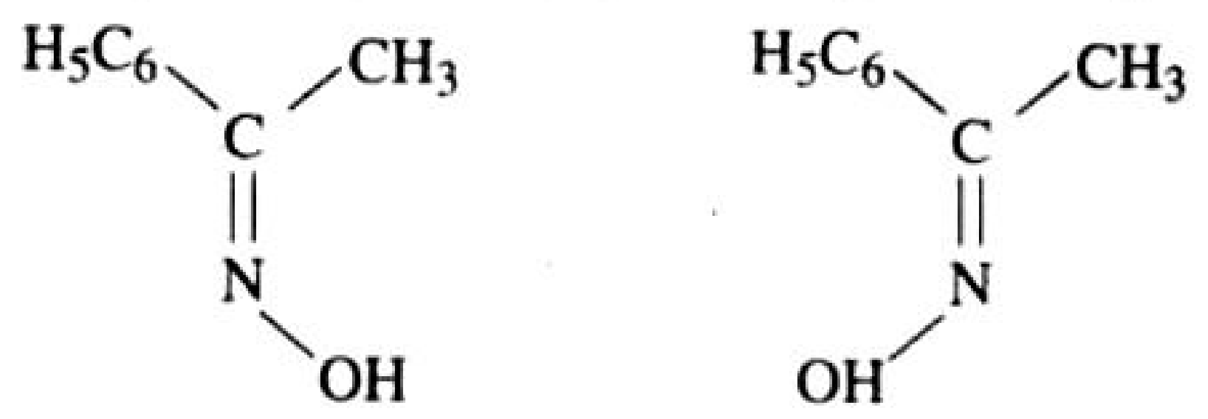
$$C_6H_5NH_2 \underset{\text{alc. KOH}}{\overset{CH_3COCl}{\rightleftharpoons}} C_6H_5NHCOCH_3$$

(F) (D)

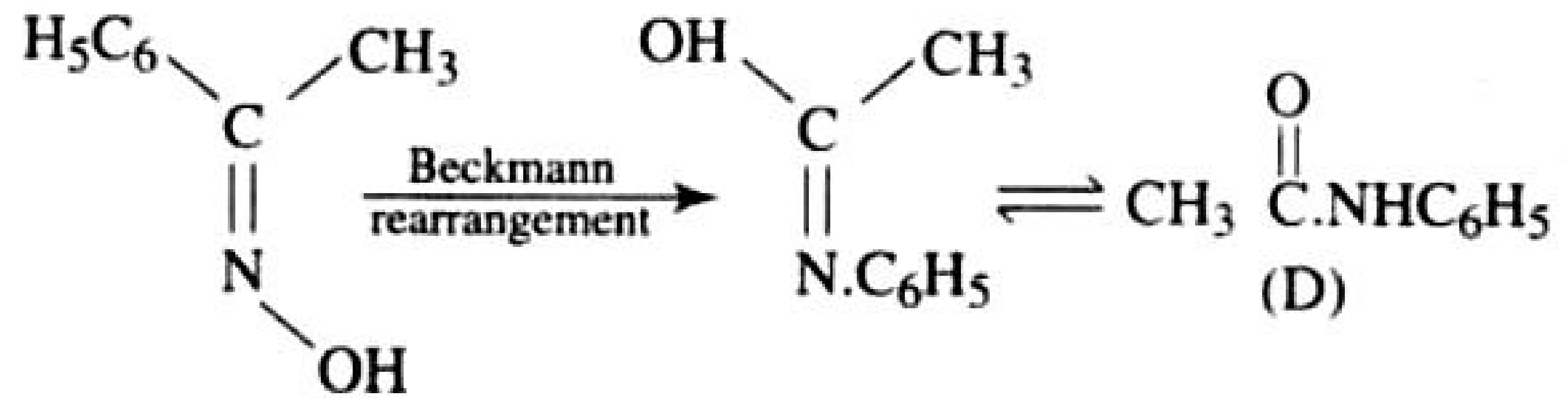
ii. Compound E on treatment with alkali followed by acidification gives a white solid compound (G), $C_7H_6O_2$. Thus (G) seems to be an acid, hence it is C_6H_5COOH.

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 $CH_3NHCOC_6H_5$.

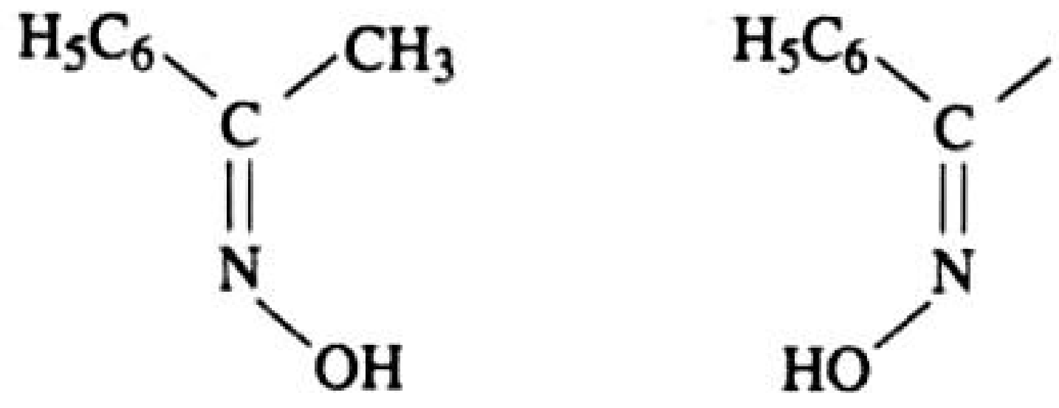
iv. Since compounds (D) and (E) are formed by the rearrangement of compounds (B) and (C) respectively. Compounds (B) and (C) should be oximes $> C = NOH$ (recall that oximes rearrange to amides—**Beckmann rearrangement**). Further oximes having different alkyl (aryl) groups show geometrical isomerism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

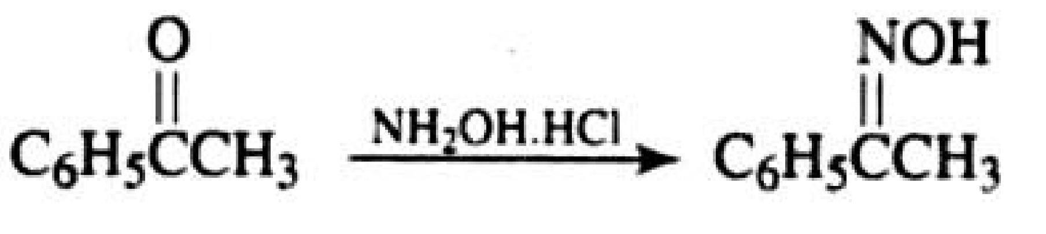


Since (D) is formed from (B), and (E) from (C), (B) and (C) should have following structures.



(B) (C)

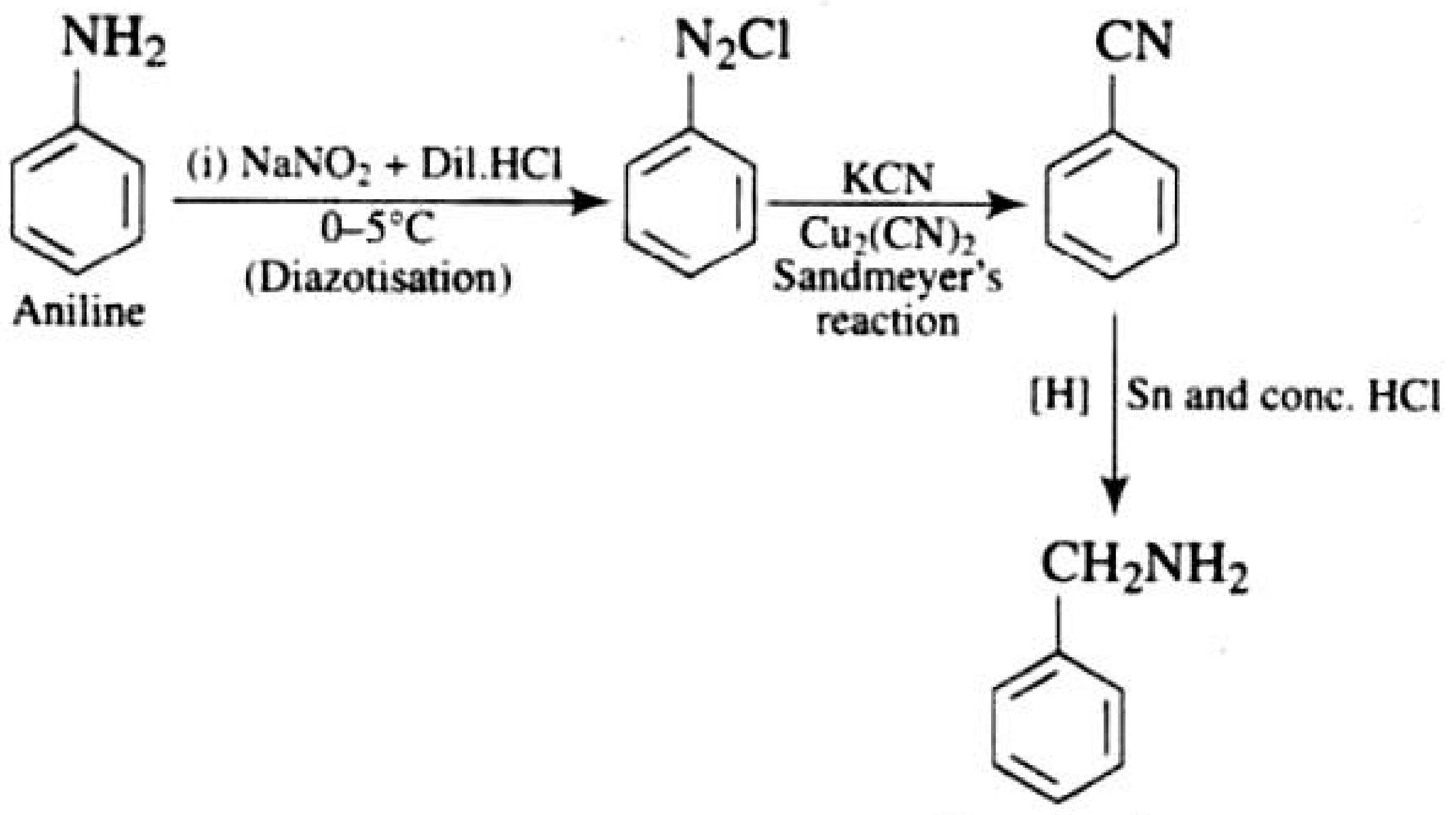
v. Lastly, oximes (B) and (C) are formed from (A), the latter should be a ketone of the formula $C_6H_5COCH_3$.



$$C_6H_5\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{NH_2OH.HCl} C_6H_5\overset{NOH}{\overset{\|}{C}}CH_3$$

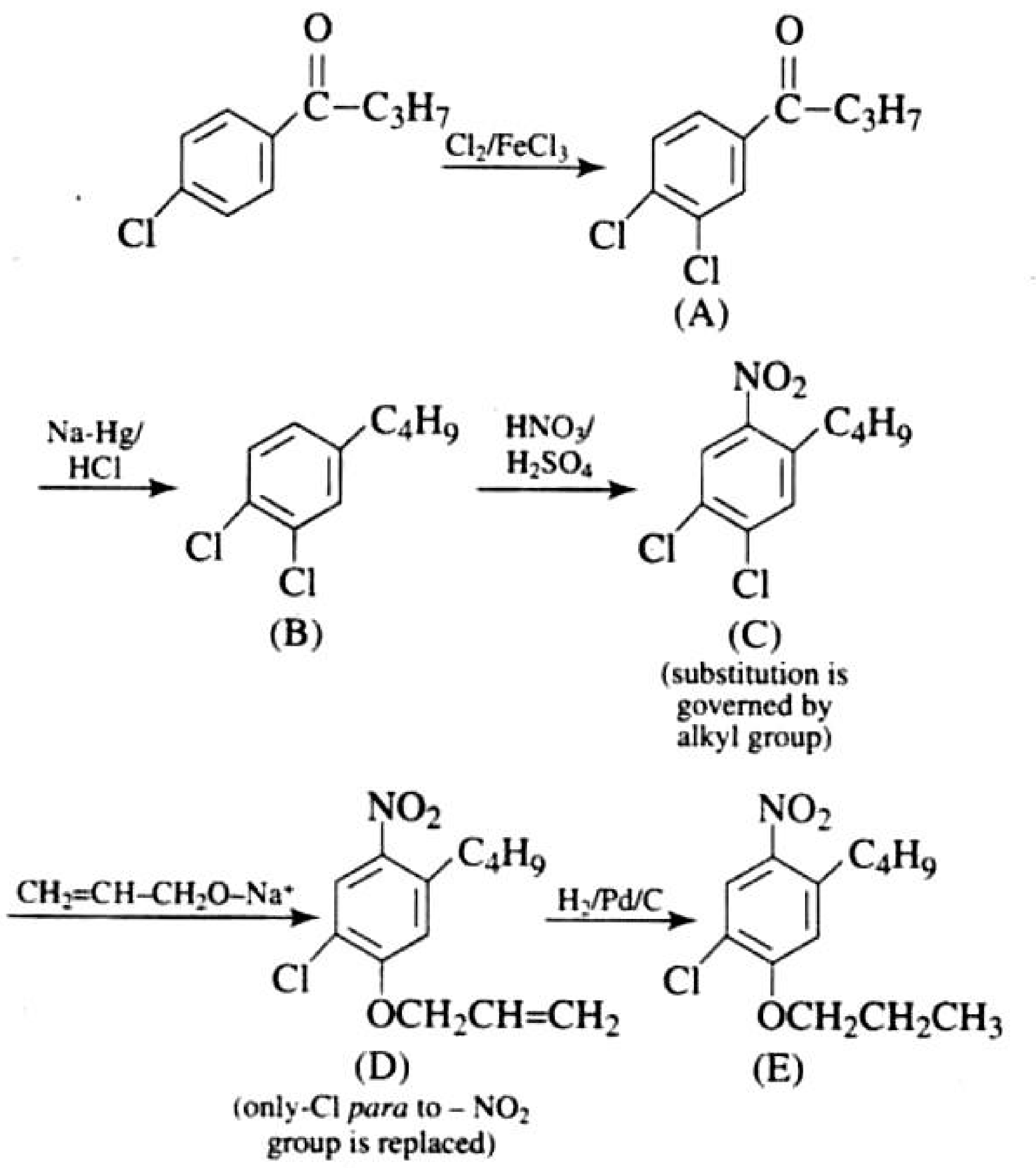
(A) (B) and (C)

28. Aniline → Benzylamine

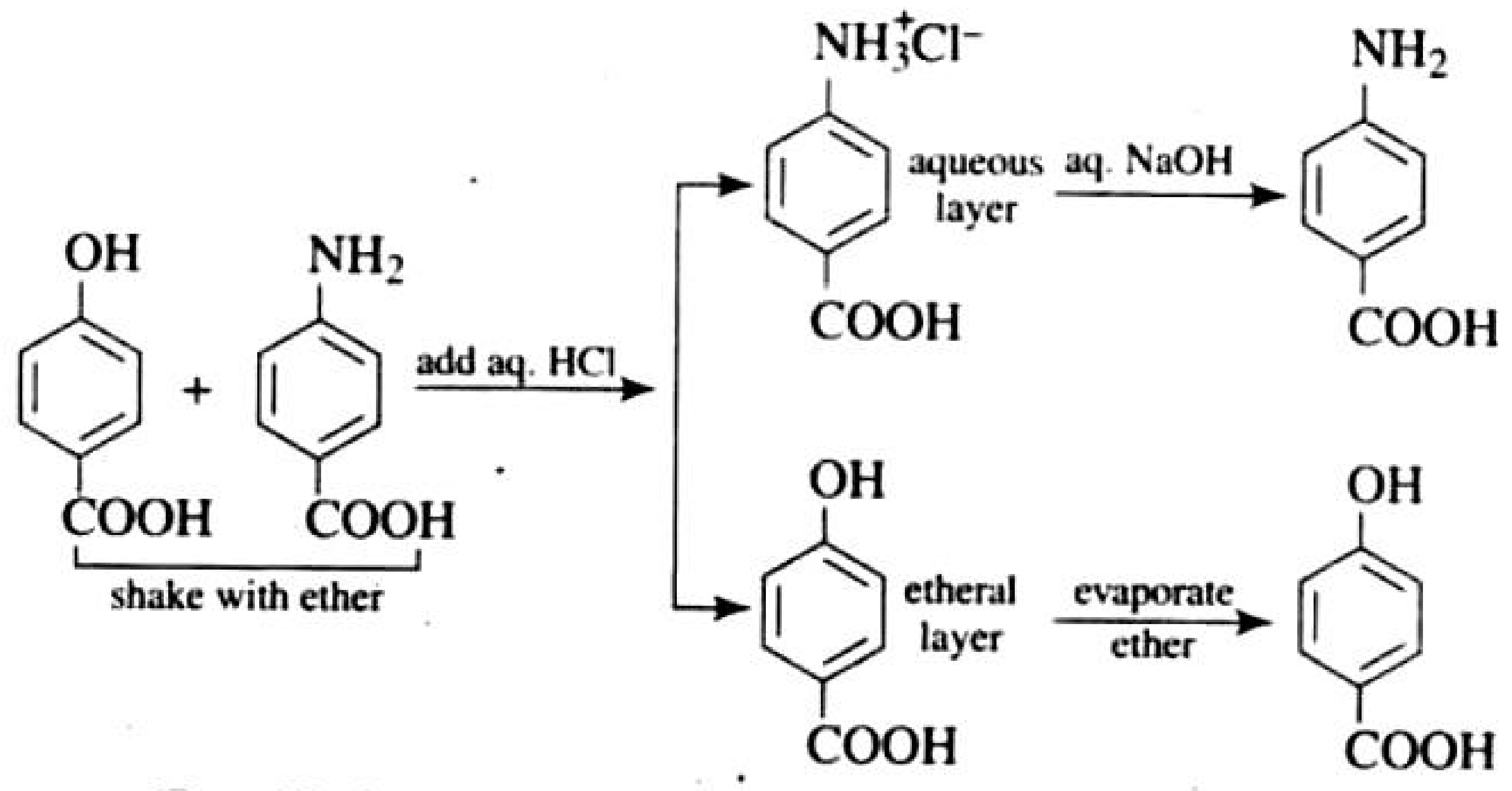


Benzyl amine

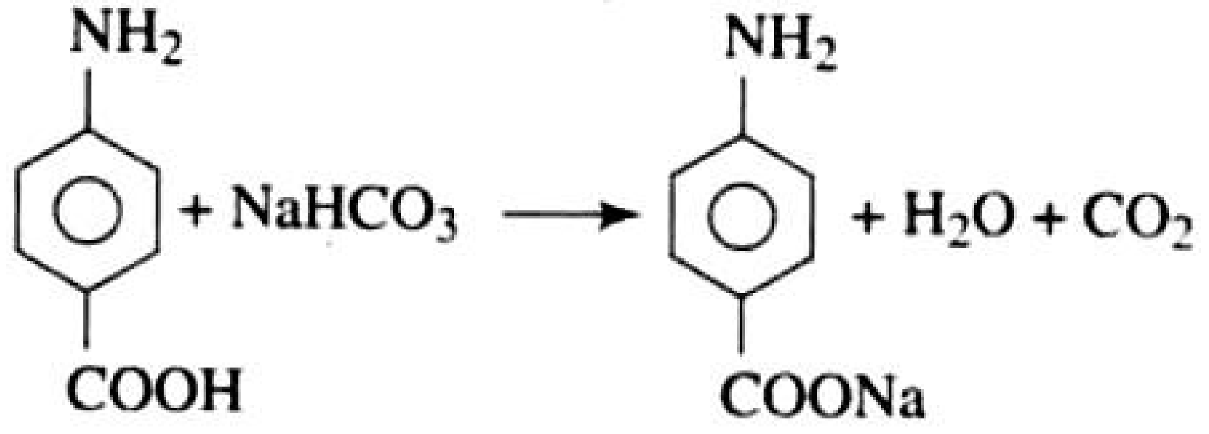
29.

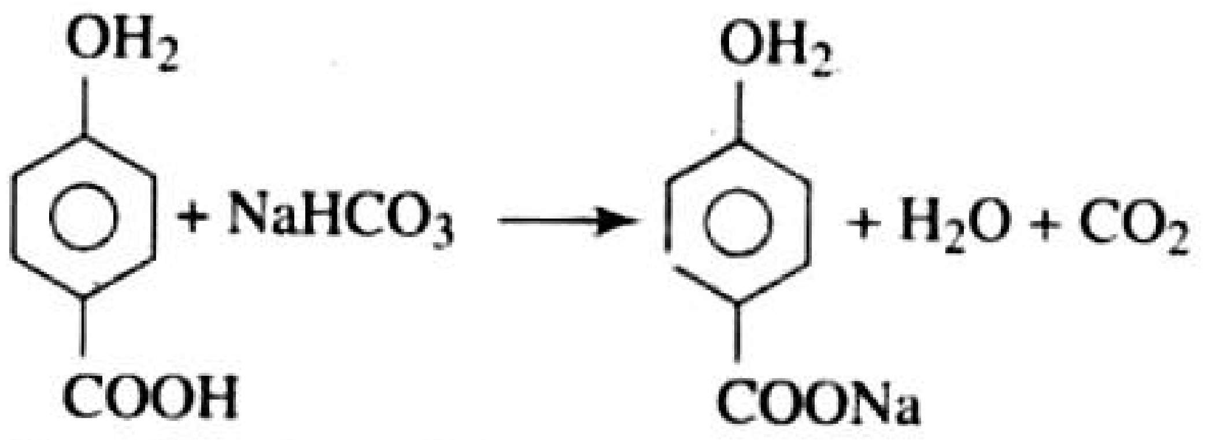


30. For the separation of p-hydroxy benzoic acid and p-aminobenzoic acid, the solution is treated with HCl. Therefore, p-aminobenzoic acid remains in solution as form of ammonium salt, while p-hydroxybenzoic acid is not soluble (so it separated easily).

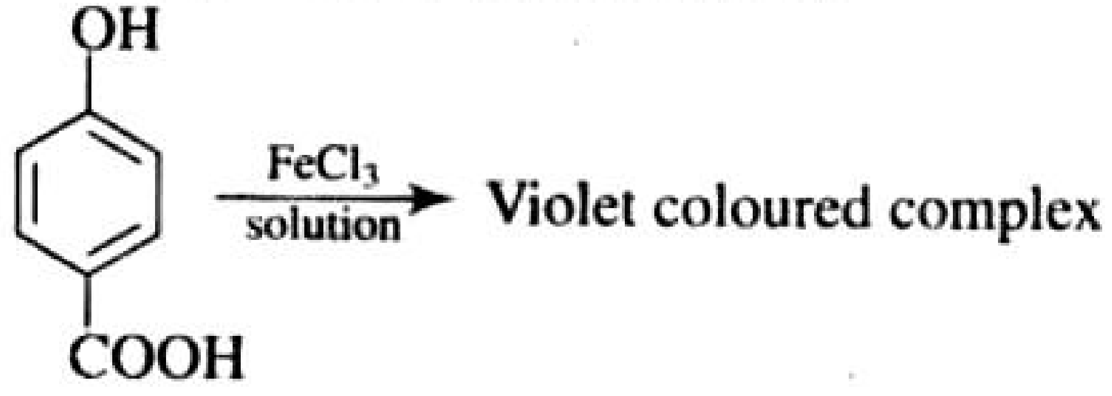


Test (1): With $NaHCO_3$ both evolve effervescenes of CO_2.

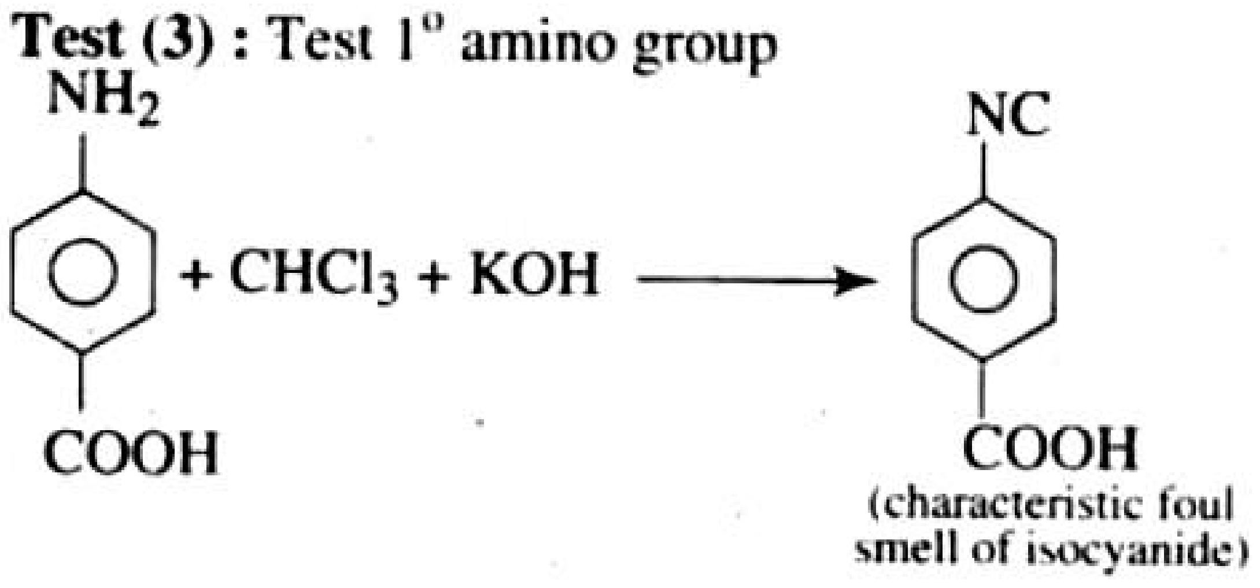




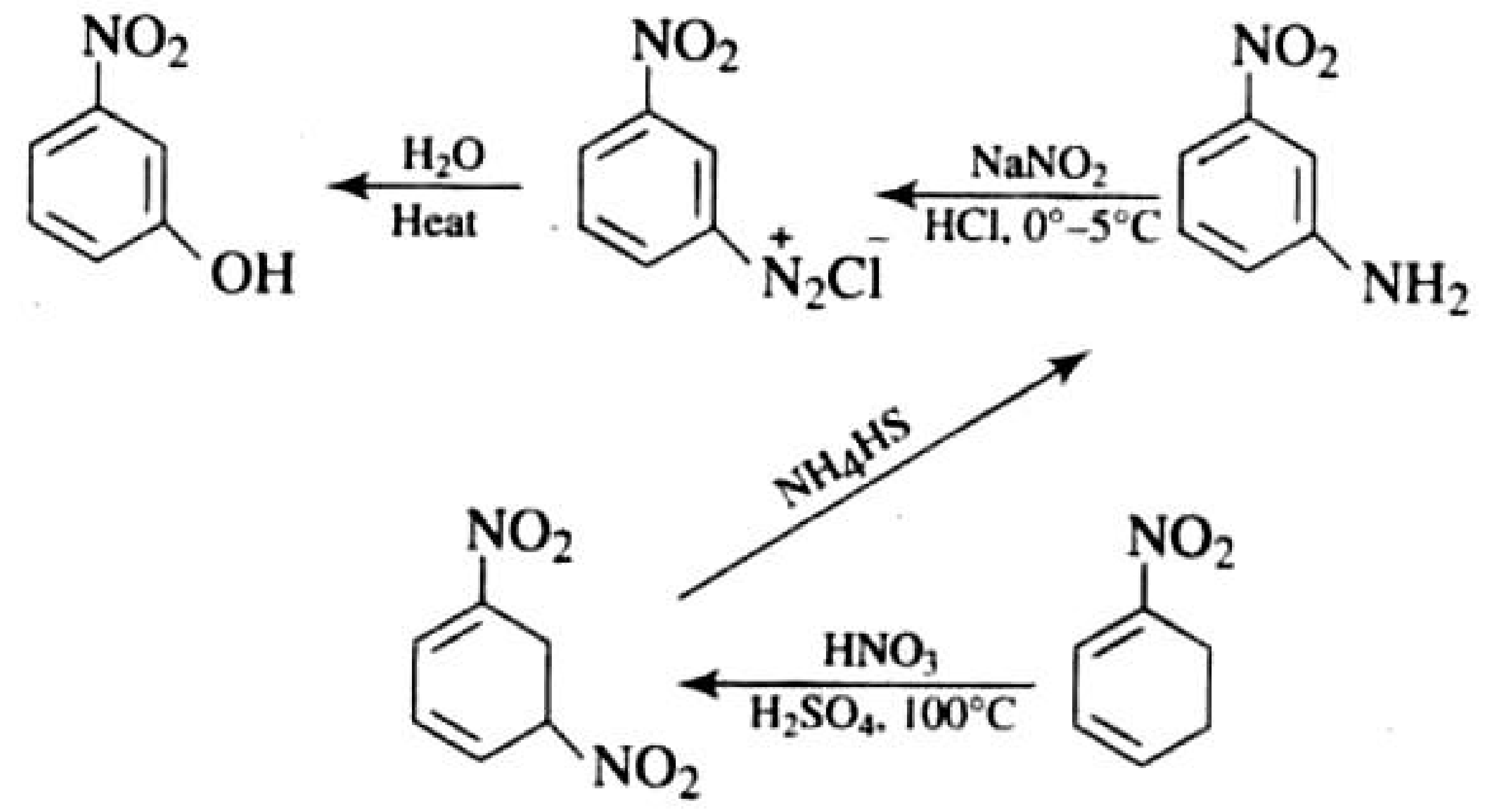
Test (2) : Test of phenolic group



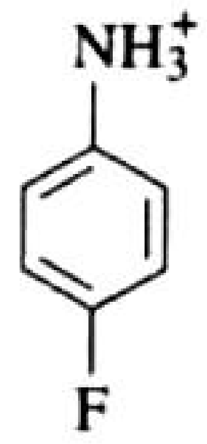
Test (3) : Test 1° amino group



31.

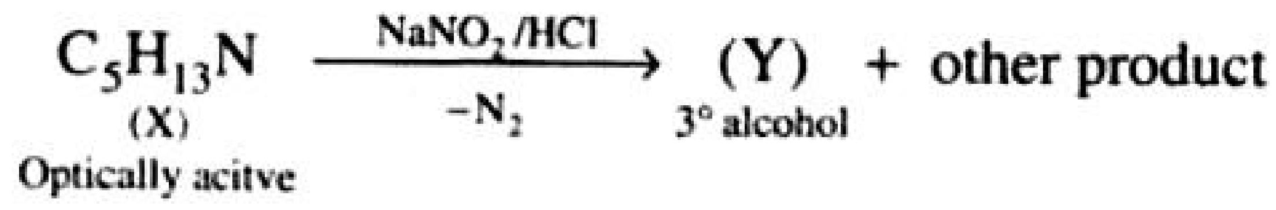


32.



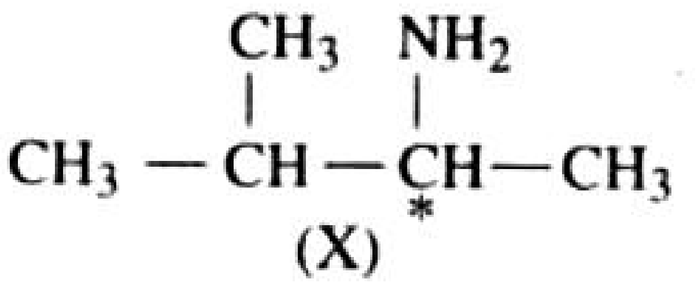
is more acidic due to the (–I) effect of the fluorine atom present.

33.



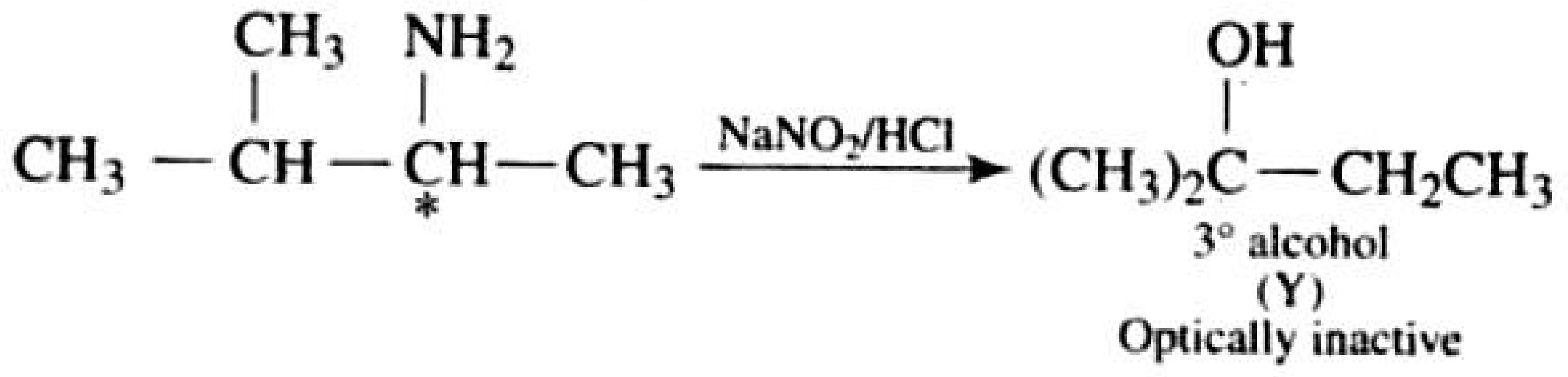
$$\underset{\substack{(X)\\ \text{Optically acitve}}}{C_5H_{13}N} \xrightarrow[-N_2]{NaNO_2/HCl} \underset{3^\circ\ \text{alcohol}}{(Y)} + \text{other product}$$

$C_5H_{13}N$ shows the following structure which is optically active.

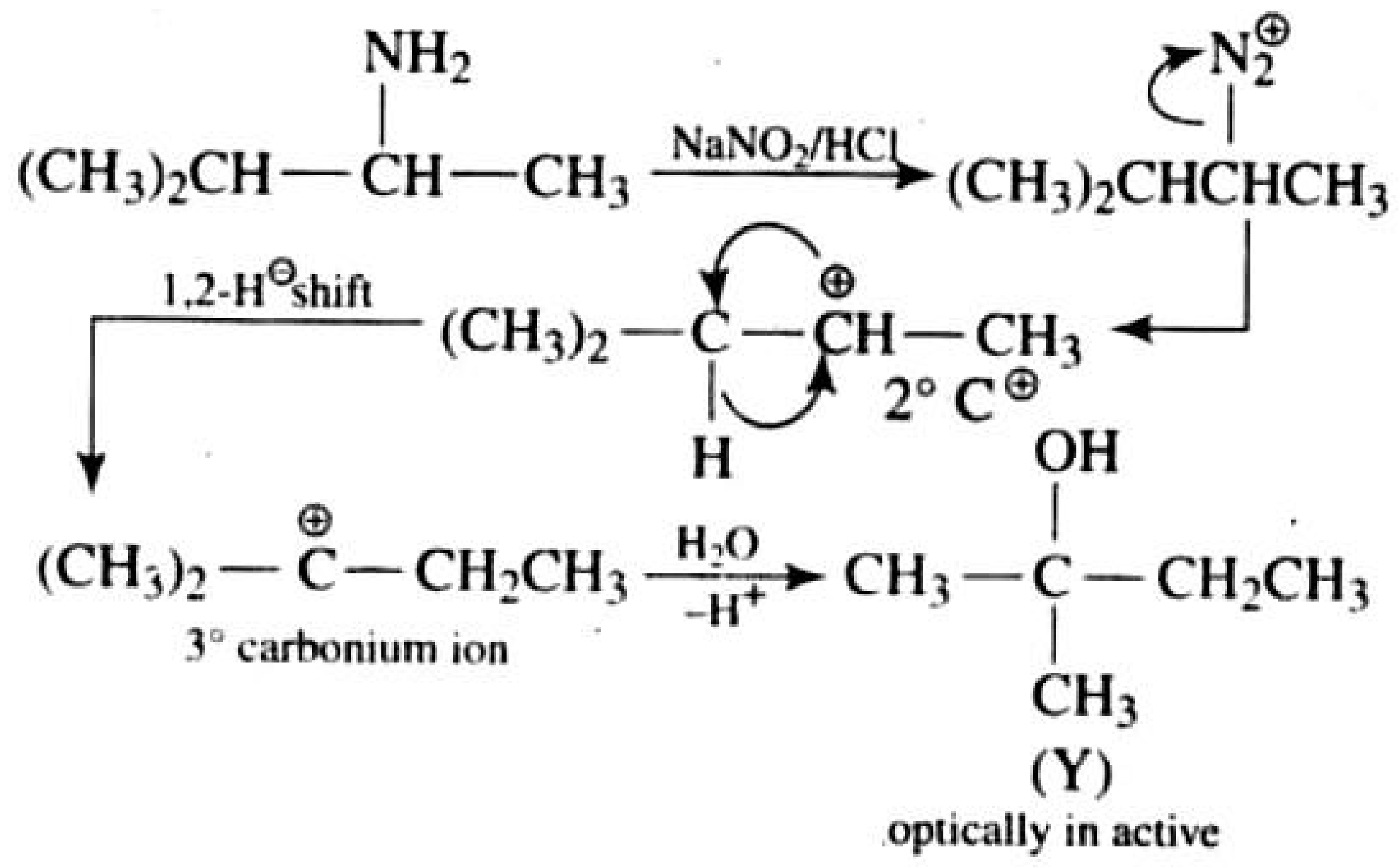


$$\underset{(X)}{CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{NH_2}{|}}{C}H^*-CH_3}$$

on treatment with $NaNO_2/HCl$.



Intermediate steps are as follows:



34. **i.** 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 effect 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 conjugate to benzene ring) for nucleophilic substitution, hence aq. NaOH will not displace fluorine here, i.e. no F^- will be formed.

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

b. $-NO_2$ group is electron withdrawing, hence m-directing