ROADMAP CONVERSION AMINES

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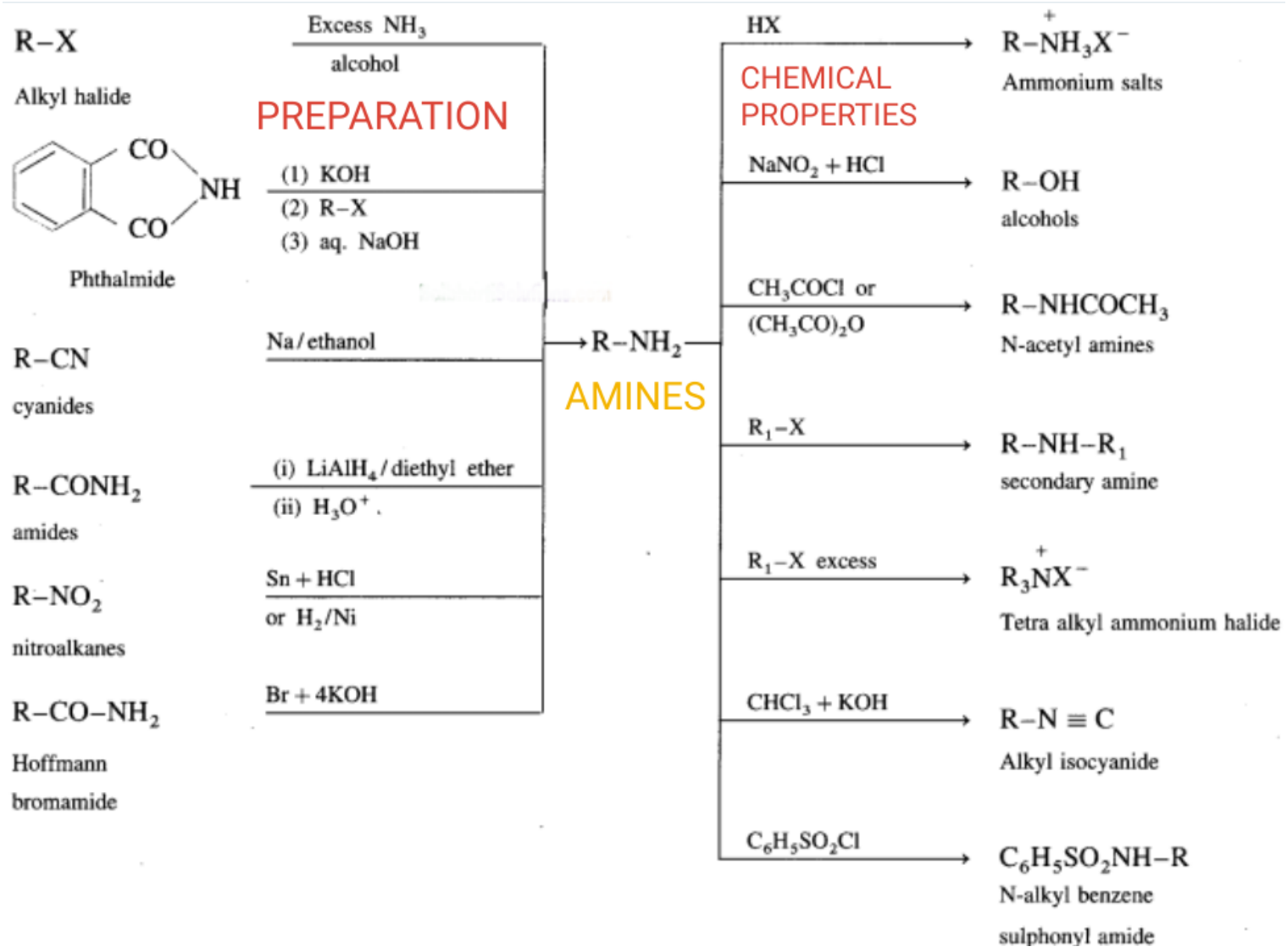
PGT Chemistry
KV No. 2, Gwalior

S. No.	Reagent	Group Out	Group In	Remark
1	Br_2 / NaOH or NaOBr	$-CONH_2$	$-NH_2$	Step Down (Hoffmann Bromamide)
2	HNO_2 or $NaNO_2$/HCl	$-NH_2$	-OH	HONO
3	$CHCl_3$ / alc KOH	$-NH_2$	-NC	Carbyl amine
4	$LiAlH_4$	-CN	$-CH_2NH_2$	Reduction
5	Sn / HCl or Fe/HCl	$-NO_2$	$-NH_2$	Reduction
6	$NaNO_2$ / dil HCl / 273-278 K	$-NH_2$	$-N_2^+Cl^-$	Diazo reaction
7	CuCl / HCl or Cu/HCl	$-N_2^+Cl^-$	-Cl	Sandmeyer or Gattermann
8	CuBr / HBr or Cu/HBr	$-N_2^+Cl^-$	-Br	Sandmeyer or Gattermann
9	CuCN / KCN	$-N_2^+Cl^-$	-CN	Sandmeyer
10	KI	$-N_2^+Cl^-$	-I	
11	HBF_4 / Δ	$-N_2^+Cl^-$	-F	
12	H_3PO_2 or CH_3CH_2OH	$-N_2^+Cl^-$	-H	
13	H_2O / 283 K	$-N_2^+Cl^-$	-OH	
14	HBF_4/ $NaNO_2$, Cu / Δ	$-N_2^+Cl^-$	$-NO_2$	
15	C_6H_5-OH	$-N_2^+Cl^-$	$-N=N-C_6H_5$-OH	Coupling (p-hydroxy)
16	$C_6H_5-NH_2$	$-N_2^+Cl^-$	$-N=N-C_6H_5-NH_2$	Coupling (p-amino)


R–X
Alkyl halide
CO
NH
CO
Phthalmide
R–CN
cyanides
R–CONH2
amides
R–NO2
nitroalkanes
R–CO–NH2
Hoffmann
bromamide
Excess NH3
alcohol
PREPARATION
(1) KOH
(2) R–X
(3) aq. NaOH
Na / ethanol
(i) LiAlH4 / diethyl ether
(ii) H3O+ .
Sn + HCl
or H2/Ni
Br + 4KOH
R–NH2
AMINES
HX
CHEMICAL
PROPERTIES
NaNO2 + HCl
CH3COCl or
(CH3CO)2O
R1–X
R1–X excess
CHCl3 + KOH
C6H5SO2Cl
R–NH3X+
Ammonium salts
R–OH
alcohols
R–NHCOCH3
N-acetyl amines
R–NH–R1
secondary amine
R3NX+
Tetra alkyl ammonium halide
R–N ≡ C
Alkyl isocyanide
C6H5SO2NH–R
N-alkyl benzene
sulphonyl amide

Q1. Write chemical equations for the following conversions: **[NCERT EXAMPLES]**

(i) $CH_3–CH_2–Cl$ into $CH_3–CH_2–CH_2–NH_2$
(ii) $C_6H_5–CH_2–Cl$ into $C_6H_5–CH_2–CH_2–NH_2$

(i) $CH_3–CH_2–Cl \xrightarrow{\text{Ethanolic NaCN}} CH_3–CH_2–C\equiv N \xrightarrow{\text{reduction}} CH_3–CH_2–CH_2–NH_2$

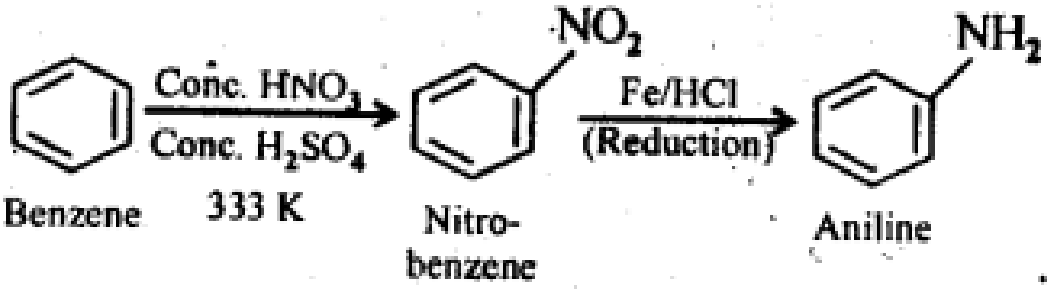
Chloroethane — Propanenitrile — Propan-1-amine

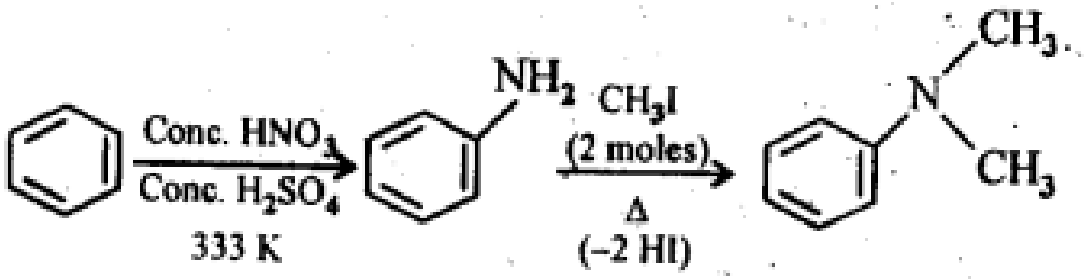
(ii) $C_6H_5–CH_2–Cl \xrightarrow{\text{Ethanolic NaCN}} C_6H_5–CH_2–C\equiv N \xrightarrow{H_2/Ni} C_6H_5–CH_2–CH_2–NH_2$

Chlorophenylmethane (Benzyl chloride) — Phenylethanenitrile (Benzyl cyanide) — 2-Phenylethanamine

Q2. How will you convert **[NCERT INTEX]**

(i) Benzene into aniline
(ii) Benzene into N, N-dimethylaniline
(iii) $Cl–(CH_2)_4–Cl$ into hexan-1,6-diamine

(i) 

(ii) 

(iii) $Cl-(CH_2)_4-Cl \xrightarrow[\Delta]{2\ KCN\ (alc.)} NC-(CH_2)_4-CN$

1, 4-Dichlorobutane — Hexane-1, 6-dinitrile

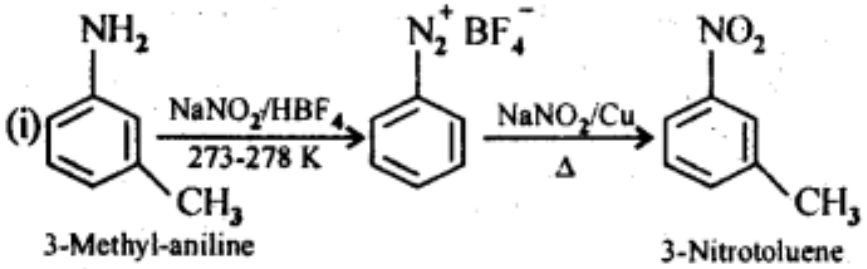
1. LAH 2. H_3O^+

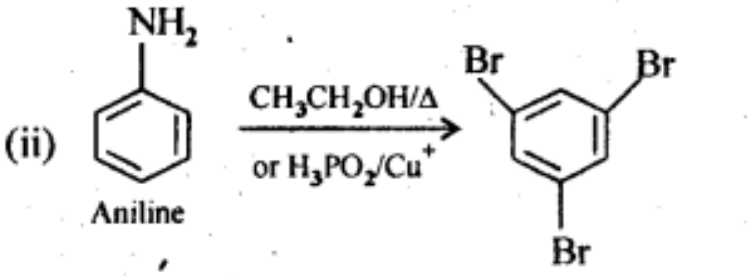
$H_2N-(CH_2)_6-NH_2$

Hexane-1, 6-diamine

Q3. Convert **[NCERT INTEX]**

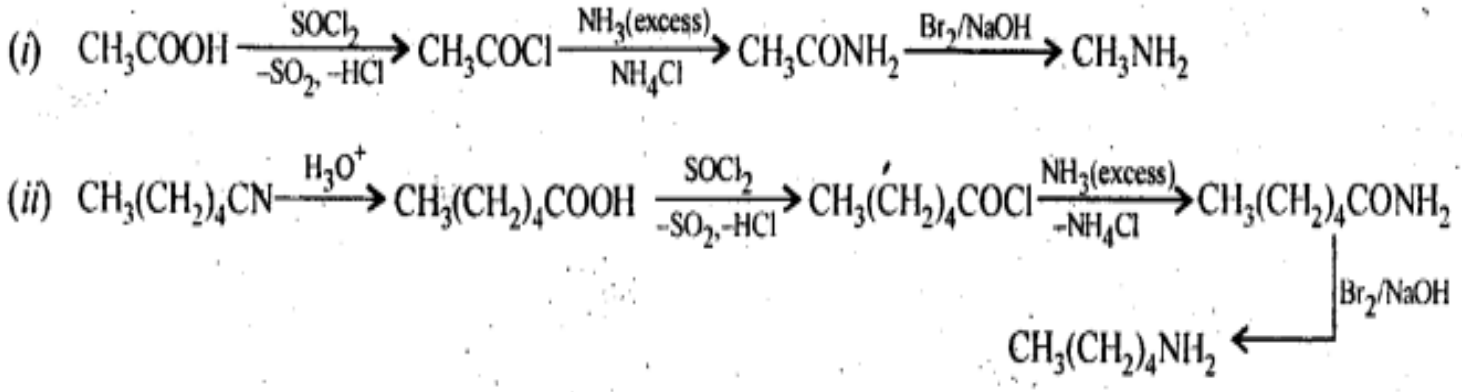
(i) 3-Methylaniline into 3-nitrotoluene
(ii) Aniline into 1,3,5 - tribromobenzene.





Q4. How will you convert: **[NCERT EXERCISE]**

(i) Ethanoic acid into methanamine
(ii) Hexanenitrile into 1-aminopentane
(iii) Methanol to ethanoic acid
(iv) Ethanamine into methanamine
(v) Ethanoic acid into propanoic acid
(vi) Methanamine into ethanamine
(vii) Nitromethane into dimethylamine
(viii) Propanoic acid into ethanoic acid?



(iii) $CH_3OH \xrightarrow[-POCl_3]{PCl_5} CH_3Cl \xrightarrow{KCN(alc)} CH_3CN \xrightarrow{H_3O^+} CH_3COOH$

(iv) $CH_3CH_2NH_2 \xrightarrow[-N_2,\ -H_2O]{HONO} CH_3CH_2OH \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3CHO \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3COOH \xrightarrow{NH_3} CH_3COONH_4 \xrightarrow[-H_2O]{} CH_3CONH_2 \xrightarrow{Br_2/NaOH} CH_3NH_2$

(v) $CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow[or\ PI_3]{P + I_2} CH_3CH_2I \xrightarrow[-KI]{KCN} CH_3CH_2CN \xrightarrow{H^+/H_2O} CH_3CH_2COOH$

(vi) $CH_3NH_2 \xrightarrow[-N_2,\ -H_2O]{HONO} CH_3OH \xrightarrow[or\ PI_3]{P + I_2} CH_3I \xrightarrow[-KI]{KCN} CH_3CN \xrightarrow{Na/C_2H_5OH} CH_3CH_2NH_2$

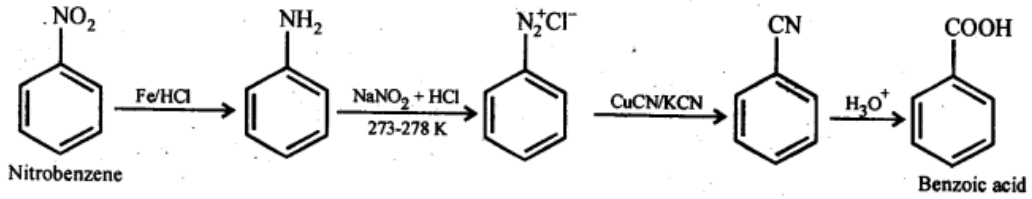
(vii) $CH_3NO_2 \xrightarrow{Sn/HCl} CH_3NH_2 \xrightarrow{CHCl_3,\ KOH,\ \Delta} CH_3NC \xrightarrow{LiAlH_4} CH_3NHCH_3$

(viii) $CH_3CH_2COOH \xrightarrow[\Delta]{NH_3} CH_3CH_2CONH_2 \xrightarrow{Br_2/NaOH} CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow{Alk.\ KMnO_4} CH_3COOH$

Q5. Accomplish the following conversions: **[NCERT EXERCISE]**

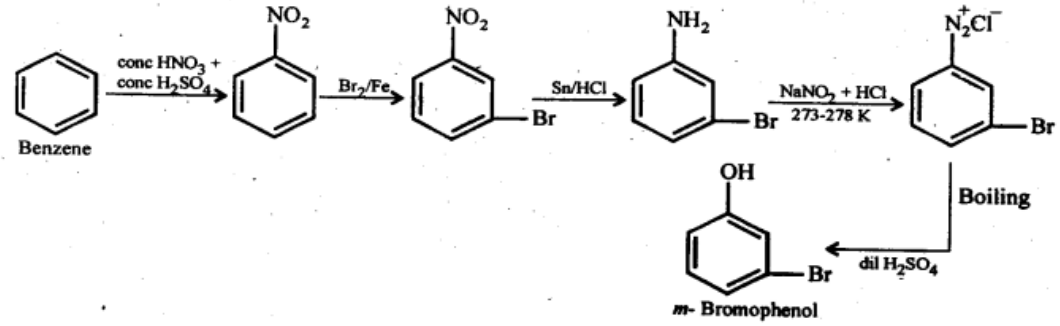
(i) Nitrobenzene to benzoic acid
(ii) Benzene to *m*-bromophenol
(iii) Benzoic acid to aniline
(iv) Aniline to 2,4,6-tribromofluorobenzene
(v) Benzyl chloride to 2-phenylethanamine
(vi) Chlorobenzene to *p*-chloroaniline
(vii) Aniline to *p*-bromoaniline
(viii) Benzamide to toluene
(ix) Aniline to benzyl alcohol.

(i)



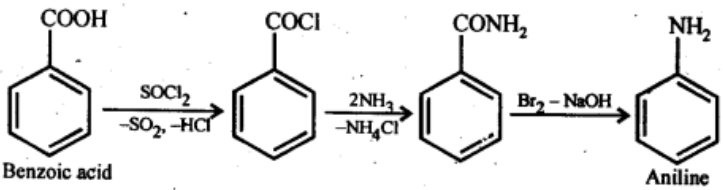
Nitrobenzene — Benzoic acid

(ii)



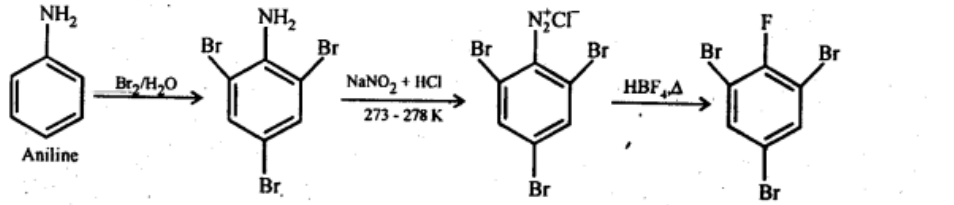
Benzene — *m*- Bromophenol

(iii)



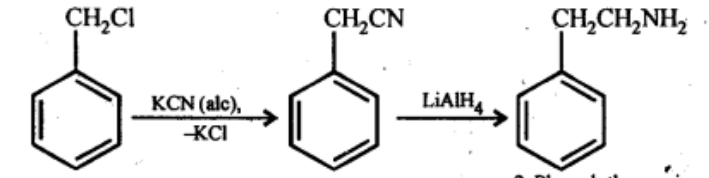
Benzoic acid — Aniline

(iv)



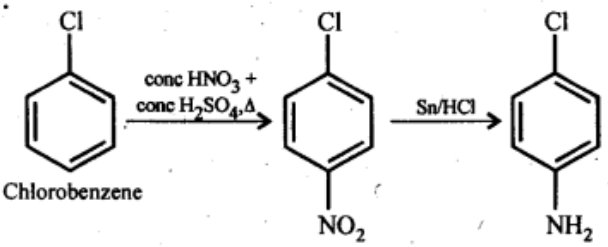
Aniline — 2, 4, 6– Tribromofluorobenzene

(v)



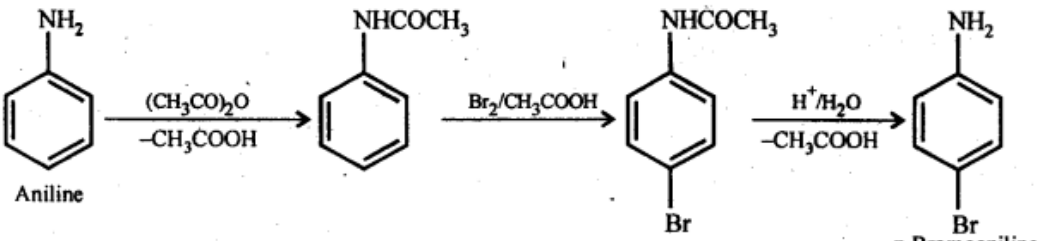
Benzyl chloride — 2-Phenylethanamine

(vi)



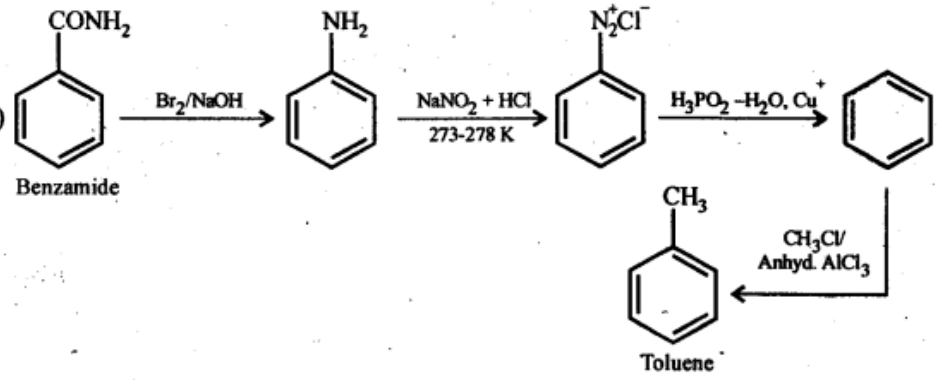
Chlorobenzene — *p*-Chloroaniline

(vii)



Aniline — *p*-Bromoaniline

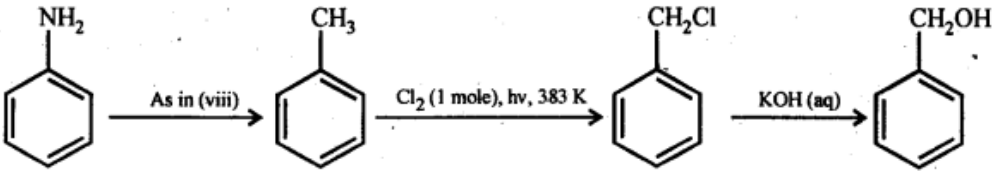
(*viii*)



Benzamide

Toluene

(*ix*)



Analine

Benzyl alcohol