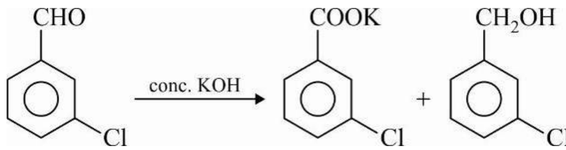
Daily Tutorial Sheet 3	JEE Advanced (Archive)

31.(D) m-Chlorobenzaldehyde does not contains α -H atom. It is an example of Cannizzaro reaction.



32. Iodoform reaction is an oxidation reaction in which hypoiodite, OI^- acts as oxidizing agent :

$$R-\overset{\overset{\displaystyle O}{||}}{C}-CH_3 + 3OI^- \longrightarrow RCOO^- + CHI_3 + 2HO^-$$

Iodide(I^-) is a reducing agent, does not give iodoform reaction.

33. $CH_3CHO < CH_3COCH_3 < CH_3COCH_2CHO < CH_3COCH_2COCH_3$

Observe that β-diketones have quite a stable enol due to intramolecular H-bonding, conjugation and hyperconjugation.

$$CH_3-\overset{\overset{\displaystyle OH\cdots\cdots\cdots}{|}}{C}=CH-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$$

34.(B) $C_6H_5COCl + H_2 \xrightarrow{Pd-BaSO_4} C_6H_5CHO + HCl$

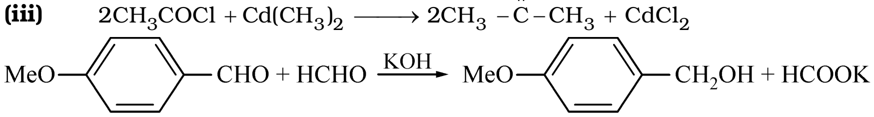
(Rosenmund reduction)

35. $C_6H_5CH_2-\overset{\overset{\displaystyle O}{||}}{C}-CH_3 \xrightarrow[\text{(ii) } H^+]{\text{(i) } CH_3MgBr} C_6H_5-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3$

36. **(i)** $PCl_5 + SO_2 \longrightarrow \underset{B}{POCl_3} + \underset{A}{SOCl_2}$ **(ii)** $SOCl_2 + CH_3COOH \longrightarrow CH_3COCl + SO_2 + HCl$

(iii) $2CH_3COCl + Cd(CH_3)_2 \longrightarrow 2CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3 + CdCl_2$

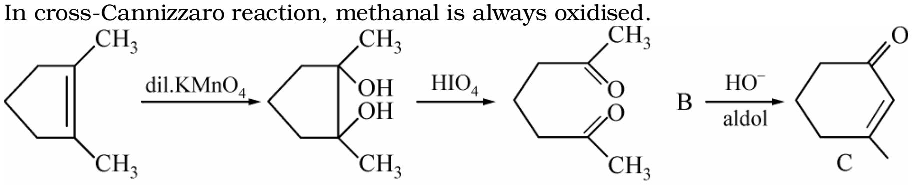
37.



(Cannizzaro reaction)

In cross-Cannizzaro reaction, methanal is always oxidised.

38.



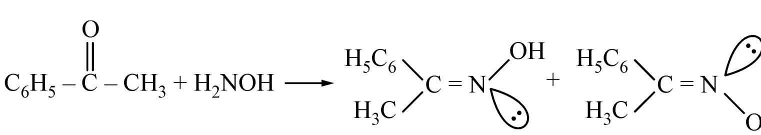
B

39. $KCN + H_2SO_4 \longrightarrow KHSO_4 + HCN$

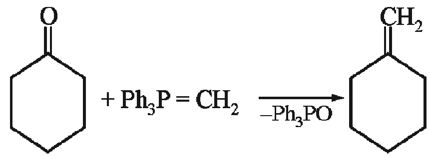
$$CH_3CH_2-\overset{\overset{\displaystyle O}{||}}{C}-H + HCN \longrightarrow CH_3CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CN \xrightarrow{LiAlH_4} CH_3CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_2NH_2$$

Observe that the products formed are racemised.

40.



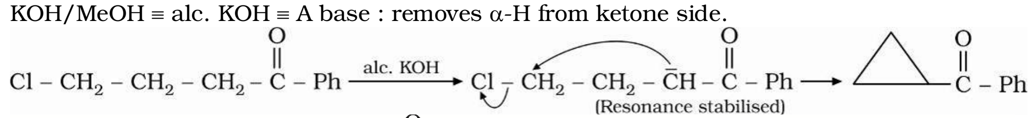
41. **(i)**



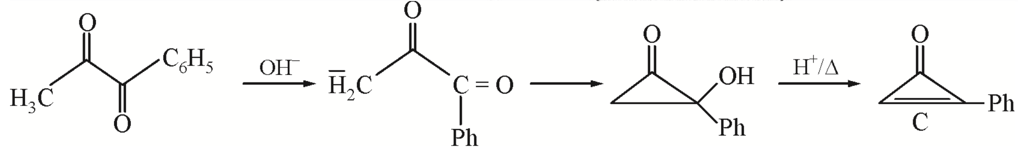
(Wittig reaction)

A

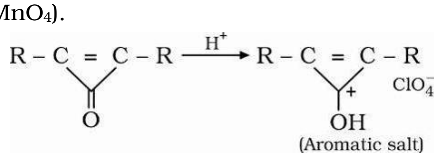
(ii) KOH/MeOH ≡ alc. KOH ≡ A base : removes α-H from ketone side.

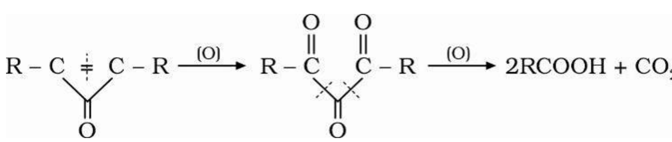


(iii)



(iv) $HClO_4$ is a strong acid and a fairly good oxidising agent. There are two possibilities. In the first, $HClO_4$ will protonate carbonyl group to give an aromatic (highly stable) salt. In another, $HClO_4$ as oxidising agent will do cleavage of carbon-carbon double bond and α-Dicarbonyl compounds (like $KMnO_4$).





42. Let summarise the whole problem in the form of reactions.

$$H_3C.\underset{}{\overset{CH_3}{\overset{|}{C}}}H.CH_2CH_3 \xleftarrow{H_2} \underset{(C_5H_{10})}{A} \xrightarrow[\text{Markov. addition}]{HBr} \underset{(\text{having Br})}{B} \xrightarrow{AgOH} \underset{(C_5H_{12}O,\ \text{alcohol})}{C} \xrightarrow{(O)} \underset{(\text{ketone})}{D}$$

Let us draw some conclusions from the above set of reactions.

(i) The molecular formula $C_5H_{10}(C_nH_{2n})$ for A indicates that it is an alkene having one double bond.

(ii) Since the alcohol C on oxidation gives a ketone D, C, must be a secondary alcohol and hence B must be a secondary bromide.

(iii) The structure of 2-methylbutane, the hydrogenated product of A, indicates that the secondary bromide must have following structure.

$$CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{Br}{\overset{|}{C}}H-CH_3$$
(B)

(iv) Thus the corresponding olefin A must have structure A which on Markovnikov's addition of HBr gives the bromide B. The other possible alkene A' will not give B when HBr is added on it according to Markovnikov's rule. Rather it will give 2-Bromo-2-methyl butane.

$$\underset{(A)}{CH_3-\overset{CH_3}{\overset{|}{C}}H.CH=CH_2} \qquad \underset{(A')}{CH_3\overset{CH_3}{\overset{|}{C}}=CH.CH_3}$$

Thus the reaction involved can be represented as below :

$$\underset{\text{3-Methylbut-1-ene, A}}{CH_3-\overset{CH_3}{\overset{|}{C}}H\cdot CH=CH_2} \xrightarrow{HBr} \underset{\text{2-Bromo-3-methylbutane, B}}{CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{Br}{\overset{|}{C}}H-CH_3} \xrightarrow{AgOH} \underset{\text{2-Methylbutane-2,-01}}{CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{OH}{\overset{|}{C}}H-CH_3} \xrightarrow{(O)} \underset{\text{2-Methylbutanone-2, D}}{CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{O}{\overset{||}{C}}-CH_3}$$

43. $C_6H_5-CO-CO-C_6H_5 \xrightarrow{LiAlH_4} C_6H_5-\overset{*}{C}HOH-\overset{*}{C}HOH-C_6H_5$

The molecule after reduction possesses two asymmetric carbon (*) with a plane of symmetry in molecule.

Hence, the number of stereoisomers $(d, l \text{ and } m) = 3$

44.(C) $MeO-$ is an electron releasing group when bounded to phenyl ring, via +M effect.

Presence of electron releasing group facilitates the release of hydride ion.