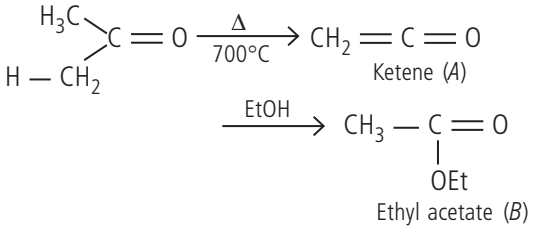
CHAPTER 12

Aldehydes, Ketones and Carboxylic Acids

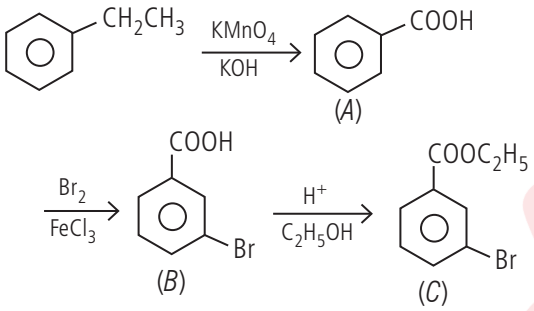
EXAM DRILL

ANSWERS

1. (c) :



2. (b) :

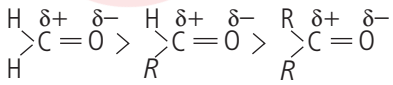


3. (a) : Addition of HCN to carbonyl compounds is nucleophilic addition reaction. The order of reactivity of carbonyl compounds is,

$HCHO > CH_3COCH_3 > PhCOCH_3 > PhCOPh$.

4. (b)

5. (a) : CH_3CHO is most reactive towards nucleophilic addition reactions. Carbonyl compounds are polar with positive charge on carbon atom which is attacked by nucleophiles. Two electron releasing alkyl groups in ketones make carbon less electron deficient than aldehydes. Benzene ring exhibits +*R*-effect which thereby decreases the ease of nucleophilic addition reaction in benzaldehyde and acetophenone. Hence the reactivity order is



6. *p*,*p*-Dihydroxybenzophenone

7. Wolff-Kishner reduction

8. Ethanoic anhydride

9. Acetamide

10. Ethyl benzoate

OR

$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

11. (b)

12. (c) : Carboxyl group being an electron withdrawing group only decreases the electron density at *o*- and *p*-position so, at *m*-position electron density is comparitively higher.

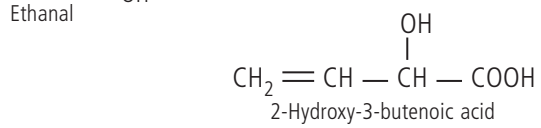
13. (c) : Aromatic carboxylic acids do not undergo Friedel-Crafts reaction, because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.

14. (b)

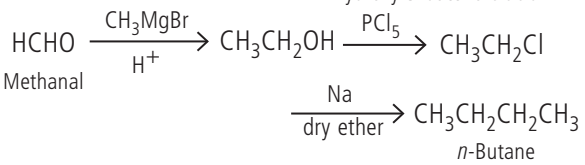
OR

(c) : Aromatic aldehydes and formaldehyde do not contain α-hydrogen and thus undergo cannizzaro reaction. Formaldehyde is more reactive than aromatic aldehydes.

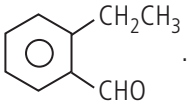
15. (i)



(ii)



16. The compound has two side chains on the benzene ring at adjacent position. As it gives positive Tollens' test, it indicates the presence of –CHO but without α-hydrogen (because it gives +ve Cannizzaro reaction). The structure of the compound is



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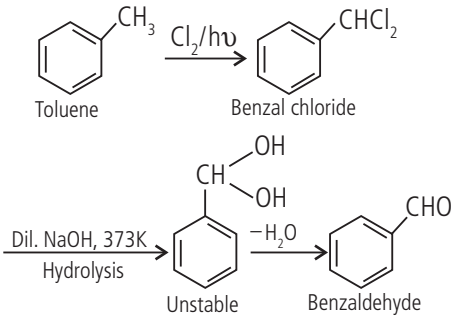
17.

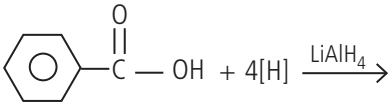


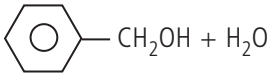
18. (i) $CH_3(CH_2)_4CH = CH_2 \xrightarrow[Zn/H_2O]{O_3}$ Hept-1-ene

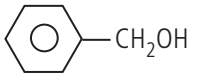
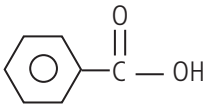
$CH_3(CH_2)_4CHO + HCHO$ Hexanal

(ii) $CH_3(CH_2)_4CH = CH_2 \xrightarrow[H_2O_2/OH^-]{B_2H_6} CH_3(CH_2)_4CH_2CH_2OH$ Hept-1-ene

$\xrightarrow[KMnO_4]{H_2SO_4} CH_3(CH_2)_4CH_2COOH$ Heptanoic acid

19. (i)  Benzoic acid

$\xrightarrow{LiAlH_4}$  Benzyl alcohol

(ii)  Benzyl alcohol $\xrightarrow[H_2SO_4]{Na_2Cr_2O_7}$  Benzoic acid

20. Clemmensen reduction :

$>C=O \xrightarrow[HCl]{Zn\text{-}Hg} >CH_2 + H_2O$

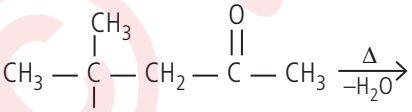
Wolff-Kishner reduction :

$>C=O \xrightarrow[-H_2O]{NH_2NH_2} >C=NNH_2$

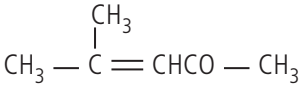
$\xrightarrow[\Delta]{KOH/ethylene\ glycol} >CH_2 + N_2$

OR

$2CH_3 - CO - CH_3 \xrightarrow{Ba(OH)_2}$ Propanone

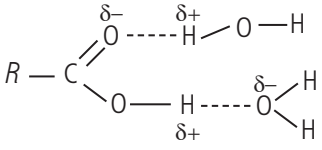
 $\xrightarrow[-H_2O]{\Delta}$ (Ketol)

4-Hydroxy-4-methylpentan-2-one



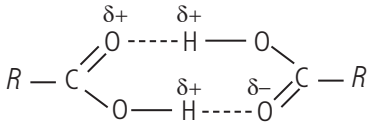
4-Methylpent-3-en-2-one

21. (a) *R*COOH dissolves in water because –COOH of *R*COOH can form H-bonds with water in two ways :

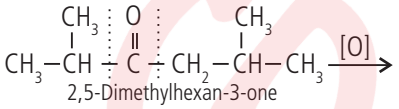


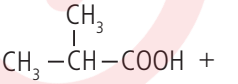
The —*R* group is non-polar and hydrophobic and this effect dominates when *R* posseses more than five carbon atoms. Thereby decreasing its solubility in more polar solvent (as water) but the solubility in less polar solvent such as alcohol increases.

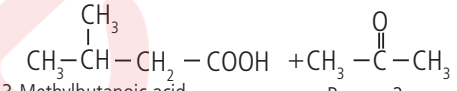
(b) This is due to the presence of H-bonding.



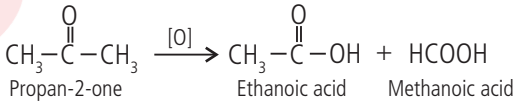
22. 2, 5-Dimethylhexan-3-one is an unsymmetrical ketone, thus oxidation occurs on either side of C = O group.

 2,5-Dimethylhexan-3-one $\xrightarrow{[O]}$

 2-Methylpropanoic acid +

 3-Methylbutanoic acid + Propan-2-one

Propan-2-one on further oxidation yields a mixture of ethanoic acid and methanoic acid.

 Propan-2-one $\xrightarrow{[O]}$ Ethanoic acid + Methanoic acid

Methanoic acid on further oxidation gives CO_2 and H_2O.

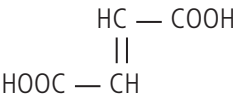
$HCOOH \xrightarrow{[O]} CO_2 + H_2O$

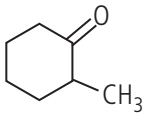
23. (a) 1-Phenylpentane-2,3-dione

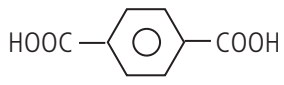
(b) 4-Oxocyclohexane-1-carboxylic acid

(c) Hexane-2,4-dione

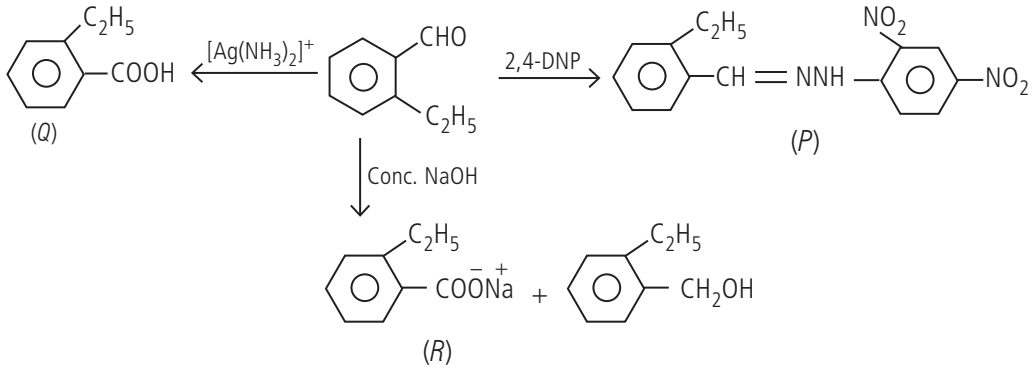
OR

(a) 

(b) 

(c) 

24.



25. (a) Cannizzaro reaction is given by aldehydes without α-hydrogen. Aldehydes which do not have α-hydrogen in the presence of conc. alkali undergo self redox reaction. One aldehyde gets oxidised to form salt of a carboxylic acid and other aldehyde gets reduced to form 1° alcohol.

Example : $2HCHO \xrightarrow{\text{Conc. NaOH}} CH_3OH + HCOO^-Na^+$

This reaction is also called a disproportionation reaction.

(b) $CH_3CH_2CH{=}CH{-}CHO \xrightarrow[HCl]{Zn/Hg} CH_3CH_2CH{=}CH{-}CH_3$

26. Propanal and 2-methylpropanal both have α-hydrogen atom, thus, these undergo cross-aldol condensation in which each one of them can act either as an electrophile or a nucleophile. Thus,

(i) CH_3CH_2CHO (Propanal, Electrophile) + $CH_3CH(CH_3)CHO$ (2-Methylpropanal, Nucleophile) $\xrightarrow{\text{dil NaOH}}$ $CH_3CH_2CH(OH)C(CH_3)_2CHO$ (3-Hydroxy-2 2-dimethylpentanal)

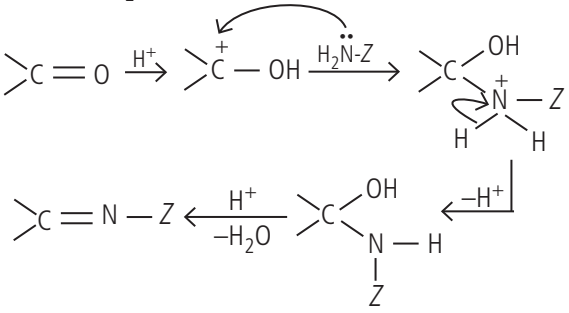
(ii) $CH_3CH(CH_3)CHO$ (Electrophile) + CH_3CH_2CHO (Nucleophile) $\xrightarrow[NaOH]{Dil.}$ $CH_3CH(CH_3)CH(OH)CH(CH_3)CHO$ (3-Hydroxy-2, 4-dimethylpentanal)

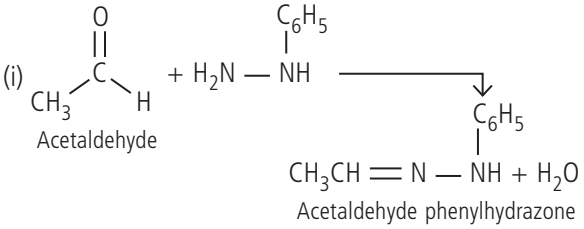
Also, self aldol-condensation also takes place.

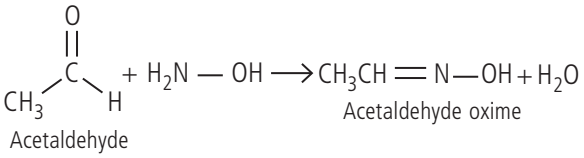
(iii) $2CH_3CH_2CHO \xrightarrow[NaOH]{Dil.}$ $CH_3CH_2CH(OH)CH(CH_3)CHO$ (3-Hydroxy-2-methylpentanal)

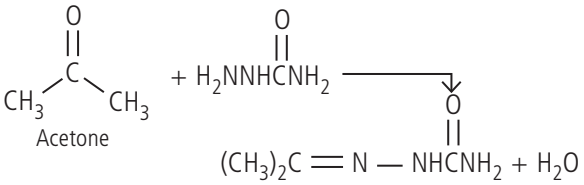
(iv) $2CH_3CH(CH_3)CHO \xrightarrow[NaOH]{Dil.}$ $CH_3CH(CH_3)CH(OH)C(CH_3)_2CHO$ (3-Hydroxy-2,2,4 trimethylpentanal)

27. (a) The reaction of carbonyl group with H_2N-*Z* is an acid catalysed reaction.

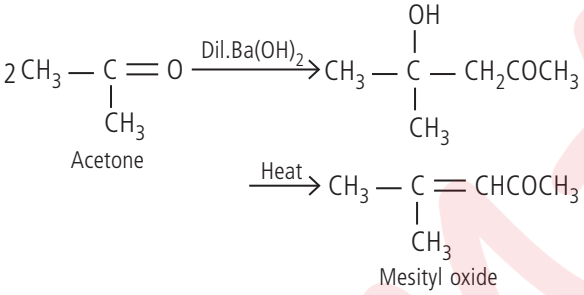


(b) (i) 

(ii) 

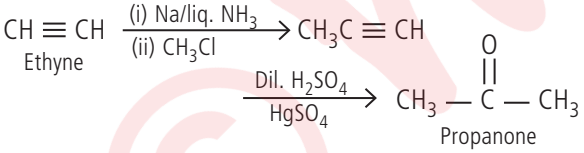
(iii) 

28. (a) We remove aldehydes as soon as it is formed thus preventing its further oxidation to carboxylic acid.

(b) 

(c) (i) 2-Chloro-4-oxohexanal

(ii) 4-Hydroxy-2-oxohexane-1,6-dial

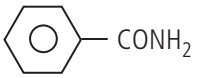
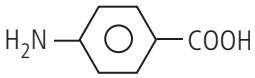
(d) 

29. (a) (i) $(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH <$ CH_3CHCH_2COOH (Br) $< CH_3CH_2CHCOOH$ (Br)

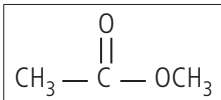
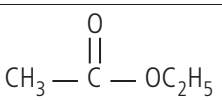
(ii) 4-Methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid < 3,4-dinitrobenzoic acid

(iii) Benzoic acid < 2-methylbenzoic acid < 3-nitrobenzoic acid < 2,4-dinitrobenzoic acid

(b) (i) Test - $NaHCO_3$

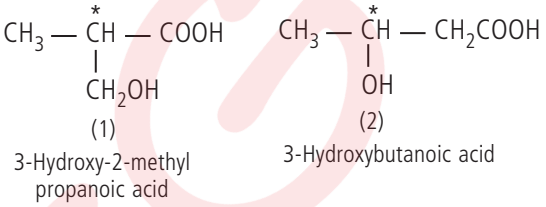
 Benzamide	 *p*-Aminobenzoic acid
No brisk effervescence	It gives brisk effervescence

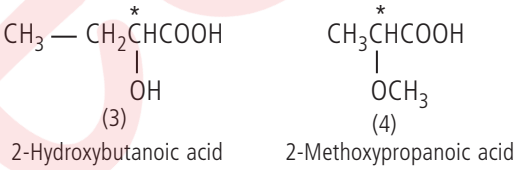
(ii) Test - Hydrolysis in acid followed by I_2/NaOH

 Methyl acetate	 Ethyl acetate
No yellow ppt. Methylacetate on hydrolysis gives methanol which does not undergo iodoform test.	On hydrolysis gives ethanol which gives yellow ppt. of iodoform.

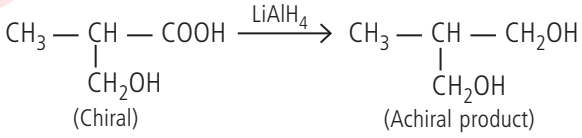
OR

(a) All four isomers contain –COOH group as they evolve CO_2 on reaction with aqueous $NaHCO_3$.



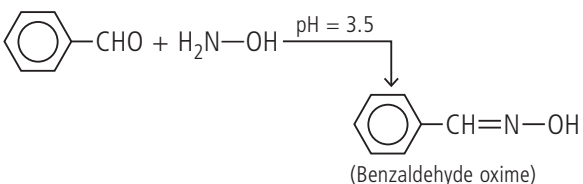


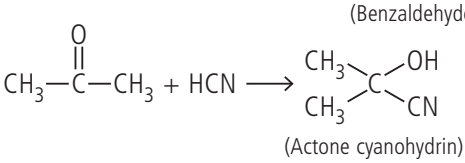
(b) $LiAlH_4$ converts –COOH to $-CH_2OH$. Only (1) is reduced to an achiral product.



(c) The ether (4) differs from (2) and (3), in that it is inert to oxidation by $KMnO_4$, hence does not decolourise $KMnO_4$. (2) gives a positive iodoform test and iodoform test can be used to distinguish (2) from (3).

30. (i) 120°

(ii) 

(iii) 

(iv) $CH_3CH{=}O + H_2N{-}NH{-}\underset{\underset{O}{\|}}{C}{-}NH_2 \longrightarrow CH_3{-}CH{=}NNH{-}\underset{\underset{O}{\|}}{C}{-}NH_2$

Ethanal semicarbazone

(v) $CH_3{-}\underset{\underset{O}{\|}}{C}{-}H + HOCH_3 \overset{H^+}{\rightleftharpoons} CH_3{-}CH(OH)(OCH_3) \overset{H^+,\ CH_3OH}{\rightleftharpoons} CH_3{-}CH(OCH_3)_2$

(Acetal)

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