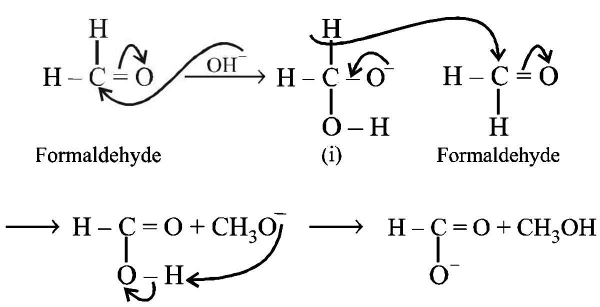
Chapter-26 : Aldehydes, Ketones and Carboxylic Acids

1. **(a)** In this reaction, one molecule is oxidised and other is reduced simultaneously.
2. **(c)** By oxidation of secondary alcohols, ketones are formed.
3. **(c)** In the Cannizzaro reaction, two moles of carbonyl compounds having no α-hydrogen atom when treated with strong alkali undergo, redox or disproportionation reaction.

$$2H-\overset{H}{\overset{|}{C}}=O \xrightarrow{NaOH} H-\overset{O}{\overset{||}{C}}-ONa + CH_3OH$$

Mechanism : First of all base OH^- acts as a nucleophile and attack other one of carbonyl compound to generate a hydroxy alkoxide ion which acts as a hydride ion donor to the other molecule of carbonyl compounds. In the final step there is a exchange of proton from acid to alkoxide ion to get stable product.



4. **(d)** $(HCOO)_2Ca \xrightarrow{\Delta} H-\overset{O}{\overset{||}{C}}-H + CaCO_3$

Calcium formate — formaldehyde

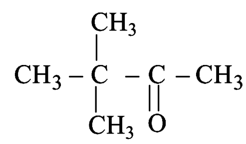
5. **(c)** $CH_3-\overset{O}{\overset{||}{C}}-H + HCN \longrightarrow CH_3-C(OH)(CN)-H \xrightarrow{Hydrolysis} CH_3-CH(OH)-COOH$

2-Hydroxy propanoic acid

6. **(c)** Formalin is an aqueous solution (40%) of formaldehyde.
7. **(b)** Catalyst used in Rosenmund reduction is $Pd/BaSO_4$. Rosenmund Reduction is used for reduction of acid chloride.

$$R-\overset{O}{\overset{||}{C}}-Cl \xrightarrow{Pd/BaSO_4} R-\overset{O}{\overset{||}{C}}-H$$

8. **(b)** Acetaldehyde reacts only with nucleophiles.
Since the mobile *p* electrons of carbon–oxygen double bond are strongly pulled towards oxygen, carbonyl carbon is electron-deficient and carbonyl oxygen is electron-rich. The electron deficient (acidic) carbonyl carbon is most susceptible to attack by electron rich nucleophilic reagents, that is, by base. Hence the typical reaction of aldehydes and ketones is nucleophilic addition.
9. **(a)** Electron attracting groups increase the acidity of carboxylic acid. Since F has highest electron attracting power, therefore CF_3COOH is strongest acid among given choices.
10. **(b)** Pinacolone is 3,3-dimethyl-2 butanone.



11. **(c)** (a) $C_2H_5O-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{CH_3MgBr} CH_3-\overset{O}{\overset{||}{C}}-CH_3$ (Acetone)

(b) $(CH_3)_2C=O \xrightarrow[H_2O]{CH_3MgBr} (CH_3)_3C-OH$ (3° Alcohol)

(c) $CH_3OCH_3 \xrightarrow{CH_3MgBr}$ No reaction

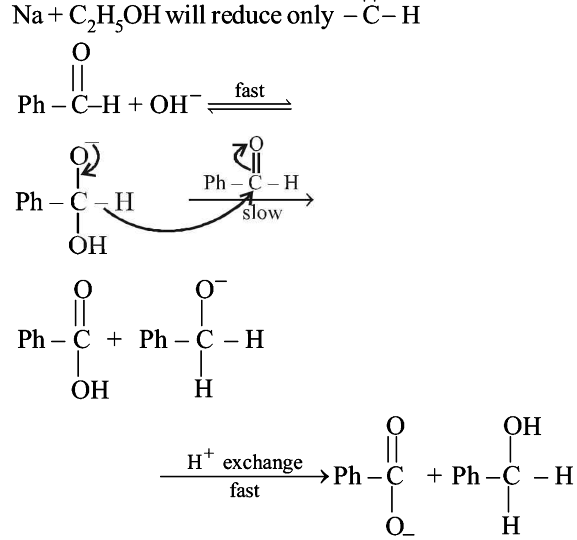
(d) $C_2H_5OH \xrightarrow{CH_3MgBr} CH_4$ (methane)

12. **(d)** $LiAlH_4/H_2O$ will reduce only $-\overset{O}{\overset{||}{C}}-H$

$NaBH_4/H_2O$ will reduce only $-\overset{O}{\overset{||}{C}}-H$

$Na + C_2H_5OH$ will reduce only $-\overset{O}{\overset{||}{C}}-H$

13. **(a)**



14. (c) Aldol condensation is given by carbonyl compounds which have α-hydrogen atoms.
∵ HCHO does not have any α-hydrogen atom, so it does not give aldol condensation.

15. (d) Iodoform test is given by methyl ketones, acetaldehyde and secondary alcohols which contain – CH_3 groups at carbon containing – OH group.

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$$

isobutyl alcohol is a primary alcohol hence doesn't give positive iodoform test.

16. (b) Cannizzaro reaction is given by aldehydes and ketones which do not have α-hydrogen atom. Benzaldehyde (C_6H_5CHO) does not have α-H atom and hence gives Cannizzaro reaction.

17. (a) Ketones on oxidation give carboxylic acids with lesser number of carbon atoms, i.e.,

$$CH_3COCH_3 \xrightarrow{[O]} CH_3COOH + CO_2 + H_2O$$

18. (d) Compounds having – CHO group reduce Tollen's reagent to silver mirror. It is called silver mirror test.

$$\underset{(a)}{H-\overset{\overset{O}{||}}{C}-OH}\ ;\ \underset{(b)}{CH_3-(CHOH)_3-\overset{\overset{O}{||}}{C}-H}$$

Both (a) and (b) have $-\overset{\overset{O}{||}}{C}-H$ group so both of them give positive silver mirror test.

19. (a) The correct order of increasing acid strength
$CF_3COOH > MeOCH_2COOH > CH_3COOH > (Me)_2CH.COOH$
Electron withdrawing groups increase the acid strength and electron donating groups decrease the acid strength.

20. (c) Iodoform test is given by compounds which have CH_3CO group.

$$\underset{\text{2-pentanone}}{CH_3-CH_2-CH_2-\overset{\overset{O}{||}}{C}-CH_3}$$

$$\underset{\text{3-pentanone}}{CH_3-CH_2-\overset{\overset{O}{||}}{C}-CH_2-CH_3}$$

∵ 2-pentanone has CH_3CO group, so it gives iodoform test, while 3-pentanone does not have CH_3CO group, so it does not give iodoform test.
(As it has a chiral C-atom thus it is optically active)

21. (d) At high pH carbonyl group will be less reactive towards ammonia derivatives because in presence of strong acid, ammonia derivative can also undergo protonation to form ion lacking the unshared electrons which thus will no longer be nucleophile.

22. (d) $CH_3CN \xrightarrow{Na/C_2H_5OH} \underset{[A]}{CH_3CH_2NH_2} \xrightarrow{HNO_2}$

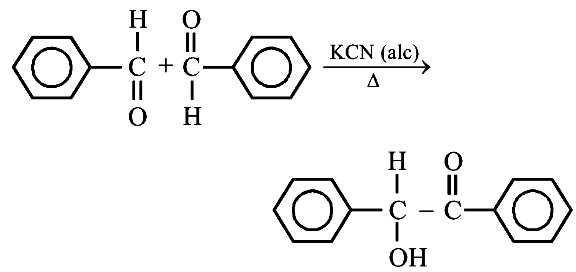
$$\underset{[B]}{CH_3CH_2OH} \xrightarrow{Cu/573K} \underset{[C]}{CH_3CHO}$$

23. (c) From the products formed it is clear that the compound has 5 carbon atoms with a double bond and methyl group on 2[nd] carbon atom.

$$\underset{\underset{(A)}{\text{2-Methyl-2-pentene}}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_3} \xrightarrow{O_3/Zn,H_2O}$$

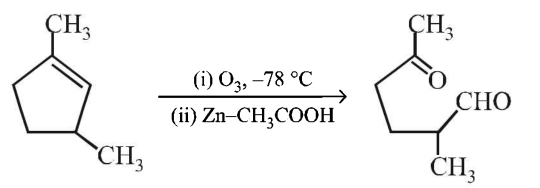
$$\underset{\text{Acetone}}{CH_3-\overset{\overset{CH_3}{|}}{C}=O} + \underset{\text{Propionaldehyde}}{CH_3-CH_2-CHO}$$

24. (b) When benzaldehyde is refluxed with aqueous alcoholic potassium cyanide, two molecules of benzaldehyde condense together to form benzoin



Benzoin

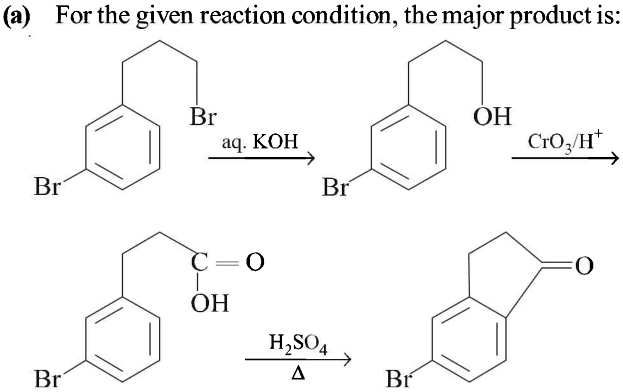
25. (d) When 1, 3-dimethylcyclopentene is heated with ozone and then with zinc and acetic acid, oxidative cleavage leads to keto - aldehyde.



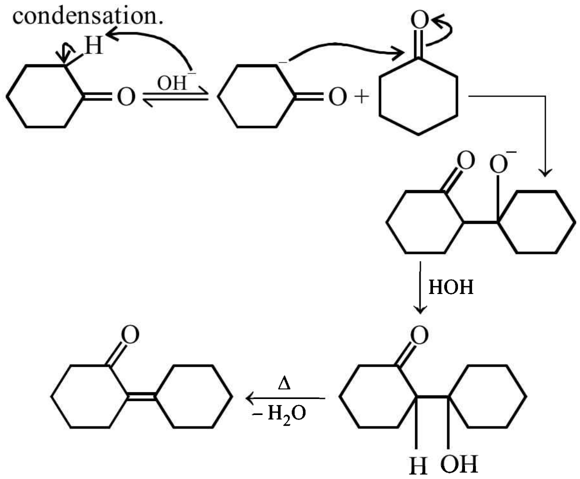
5-keto–2–methylhexanal

26. (d) Dihydrogen sodium phosphate (NaH_2PO_4) does not have a lone pair of electrons on the P atom. As such it can not act as a nucleophile and hence does not react with aldehydes and ketones.

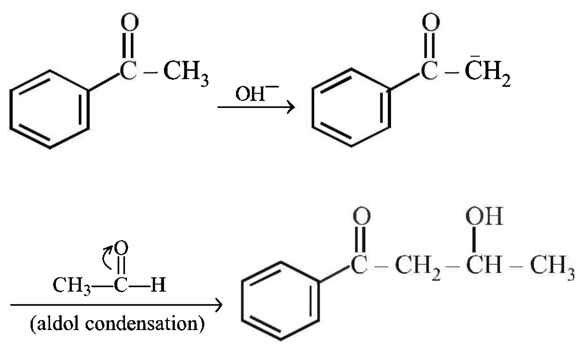
27. (a) For the given reaction condition, the major product is:



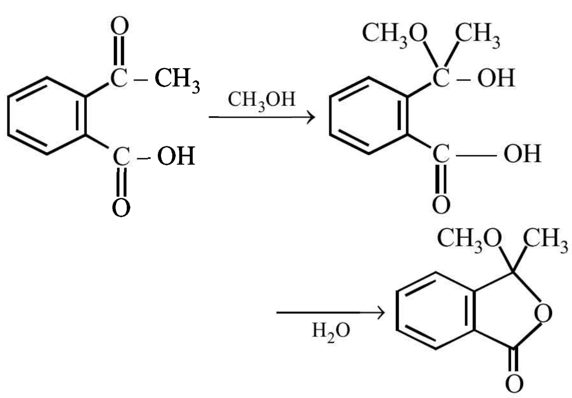
28. **(c)** In the presence of base, cyclohexanone show aldol condensation.



29. **(c)** Reaction mechanism involved:



30. **(d)**



31. **(a)** $C_6H_5COOC_2H_5 \xrightarrow{CH_3MgBr} C_6H_5-\underset{CH_3}{\overset{OMgBr}{C}}-OC_2H_5$

$\xrightarrow{-Mg(OC_2H_5)Br} C_6H_5-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow[CH_3MgBr]{Excess}$

$C_6H_5-\underset{CH_3}{\overset{OMgBr}{C}}-CH_3 \xrightarrow{H_2O} C_6H_5-\underset{OH}{\overset{CH_3}{C}}-CH_3$

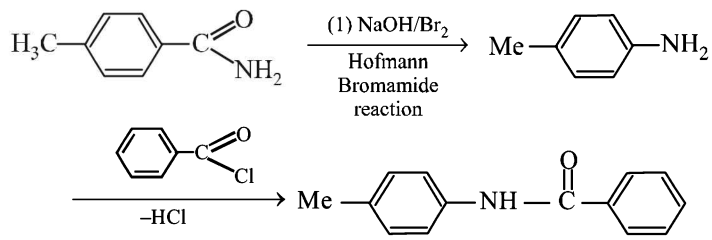
$\xrightarrow[\Delta]{Conc.\ H_2SO_4} \underset{(B)}{C_6H_5-\overset{CH_3}{C}=CH_2} \xrightarrow{Ozonolysis}$

$C_6H_5COCH_3 + HCHO$

$C_6H_5COCH_3 \xrightarrow{3I_2+4NaOH} CHI_3$

32. **(a)** Aldol condensation involves an aldehyde or ketone having an α–hydrogen atom. This type of condensation occurs in presence of dilute base (i.e., dil NaOH).
Only CH_3COCH_3 will give aldol condensation (Both HCHO and C_6H_5CHO lack α-hydrogen).

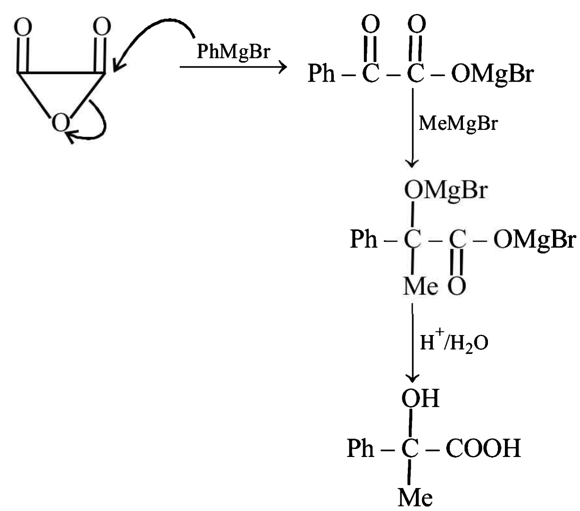
33. **(c)**



34. **(a)** $LiAlH_4$ can reduce COOH group and not the double bond.

$CH_2=CH-COOH \xrightarrow{LiAlH_4} CH_2=CH-CH_2OH$

35. **(c)**



36. **(a)** Salicylic acid, because it stabilizes the corresponding salicylate ion by intramolecular H-bonding.

37. **(b)** $CH_3-\underset{OH}{\overset{H}{C}}-COOH + HO-CH_2-CH=CH_2$

$\downarrow$

$CH_3-\underset{OH}{\overset{H}{C}}-CO-O-CH_2-CH=CH_2$

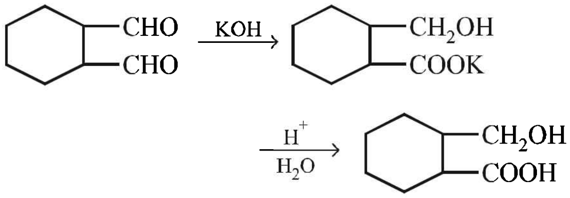
38. **(a)** $CH_3COOH \xrightarrow{PCl_5} CH_3COCl + HCl$

$\therefore$ A is PCl_5. It can also be $SOCl_2$.

39. (b) $CH_3-\underset{|}{\overset{OH}{C}}H-CH_2-\overset{O}{\overset{||}{C}}-CH_3 \; + \; CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-CHO$

Two products are formed.

40. (a) It is an example of intramolecular cannizaro reaction.



41. (a) Of all the acid derivatives, acid chlorides, i.e. CH_3COCl is most reactive.
The order of reactivity of acid derivatives decreases in the following order,
$RCOCl > (RCO)_2O > RCOOR > RCONH_2$.

42. (b) Generally benzene ring is very resistant to oxidation thus side chain is always oxidised to – COOH group. But if the side chain is tert-alkyl group, oxidation is difficult, but on vigrous oxidation benzene ring is oxidised.

$$C_6H_5-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow[\Delta]{KMnO_4} HOOC-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$$

43. (b) $C_6H_5MgBr \xrightarrow[(ii)\ H_3^+O]{(i)\ CO_2} \underset{(P)}{C_6H_5COOH}$

44. (d) More the positive charge on carbonyl carbon, more be the reactivity of that compound. Electron withdrawing groups increases the positive charge on carbonyl carbon.

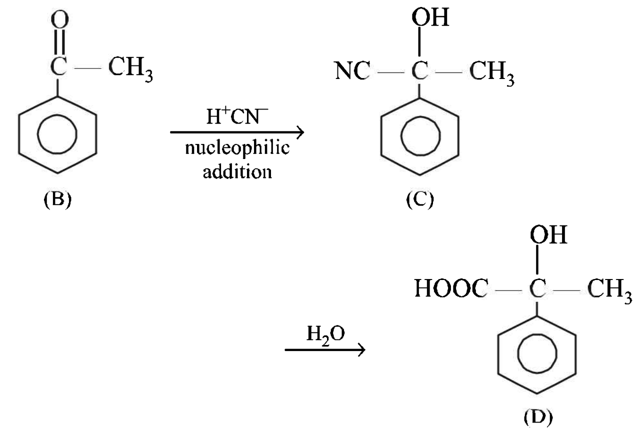
45. (a) Addition of HCN to carbonyl compounds is nucleophilic addition reaction. The order of reactivity of carbonyl compounds is
Aldehydes (smaller to higher) Ketones (smaller to higher), Then

$HCHO > CH_3COCH_3 > Ph.COCH_3 > PhCOPh$

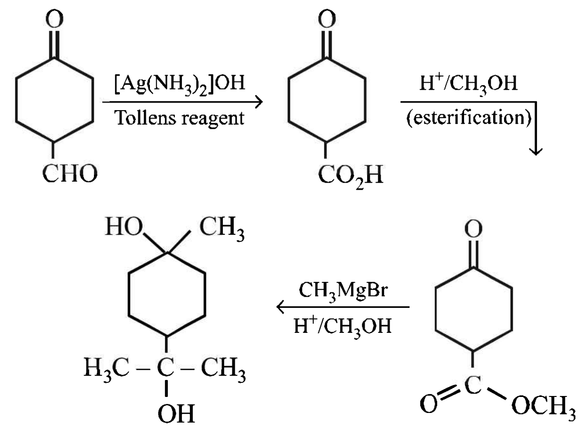
The lower reactivity of Ketones is due to presence of two alkyl group which shows +I effect. The reactivity of Ketones decreases as the size of alkyl group increases.

46. (a)

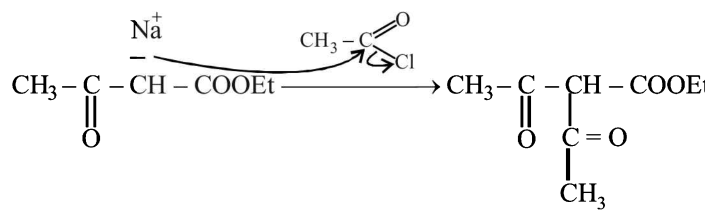
$$CH_3COOH \xrightarrow[\text{Thionyl chloride}]{SOCl_2} CH_3-\overset{O}{\overset{||}{C}}-Cl \xrightarrow[\text{anhy } AlCl_3 \text{ Friedel craft acylation}]{\text{Benzene}}$$



47. (a)

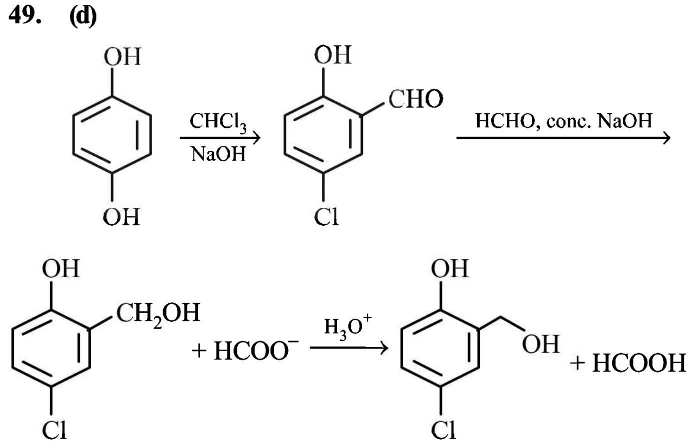


48. (a) $CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-OEt \xrightarrow{\text{Na (1 mole)}}$

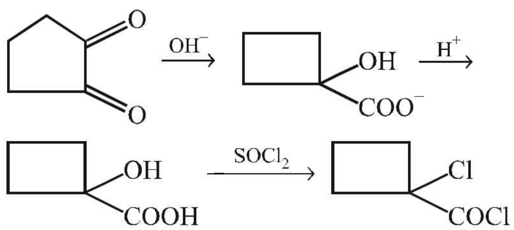


$$\xrightarrow{\text{Ketonic hydrolysis}} CH_3-\underset{O}{\underset{||}{C}}-CH_2-\underset{O}{\underset{||}{C}}-CH_3$$

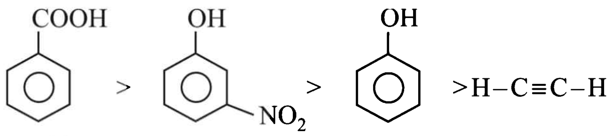
49. (d)



50. (c) 1^{st} reaction is benzylic acid rearrangement.

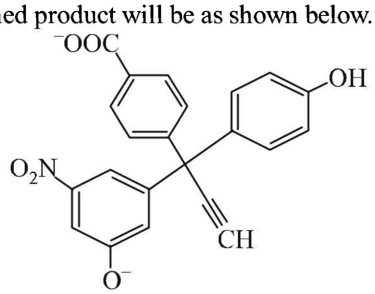


51. (a) The acidic strength of the attached groups is in the following order:

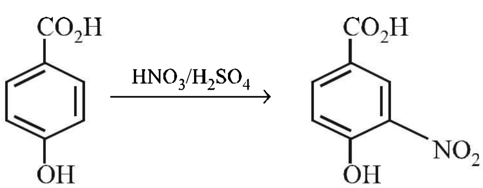


(Due to attachment of electron attractive group acidic strength increases and carboxylic acids are more acidic than phenols).

The two moles of NH_2^- ions will abstract two moles of more acidic hydrogen out of the four moles of hydrogen present per mole of the given acidic compounds. Hence after abstraction of two moles of hydrogen the obtained product will be as shown below.

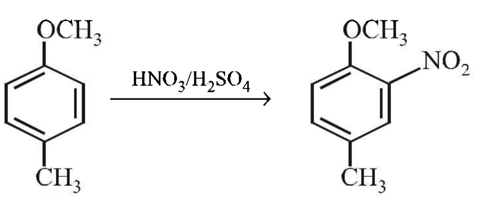


52. (c)



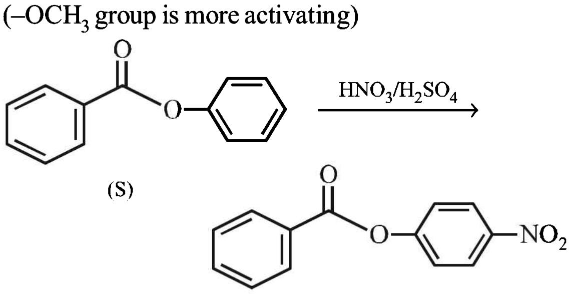
(P)

(OH group is activing)



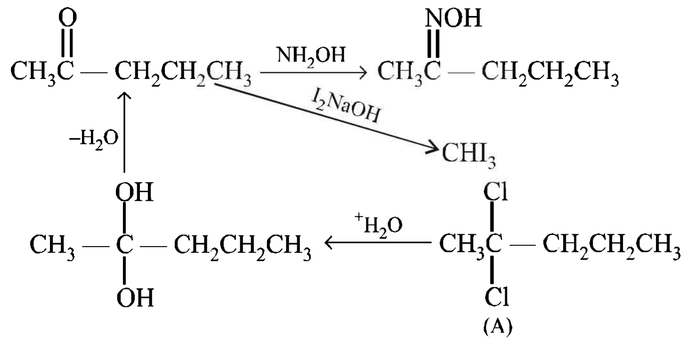
(Q)

($-OCH_3$ group is more activating)

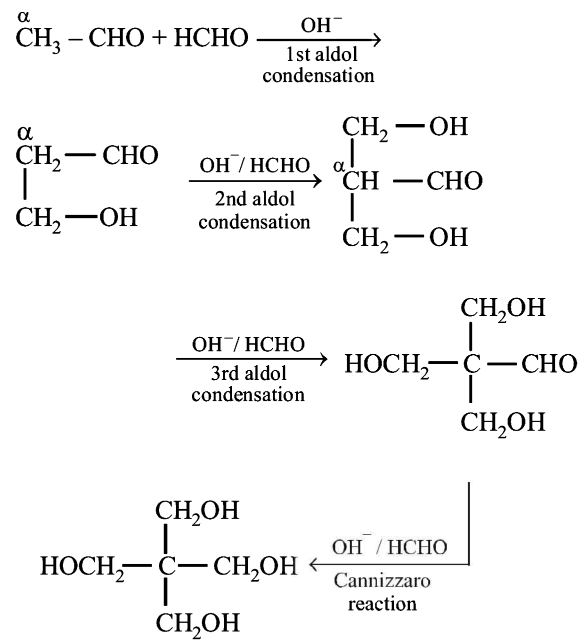


(Benzene ring having –O– is activated)

53. (a) As A reacts with hydroxylamine it means A may be aldehyde or ketone, but it does not react with Fehling solution hence A must be a ketone. Secondly it forms iodoform which is a characteristic reaction of methyl ketone.



54. (c)



55. (b)