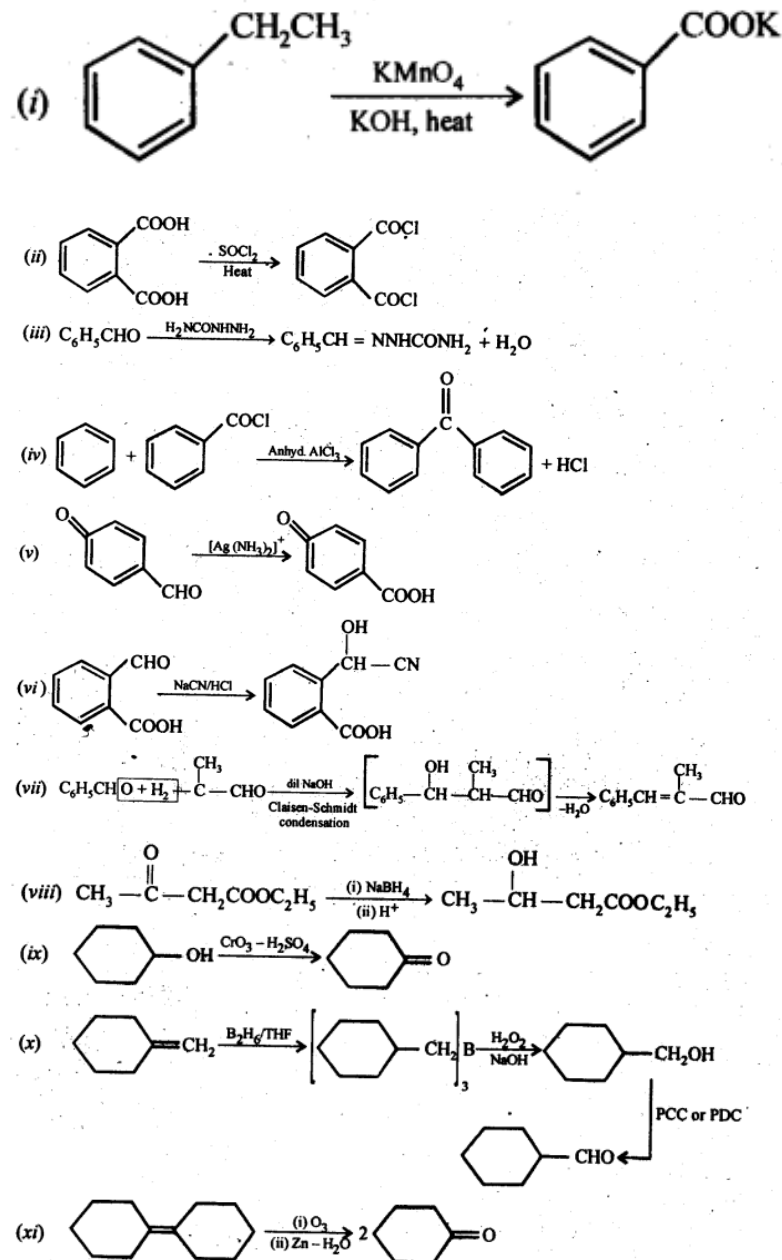




12.17. Complete each synthesis by giving missing starting material, reagent or products.

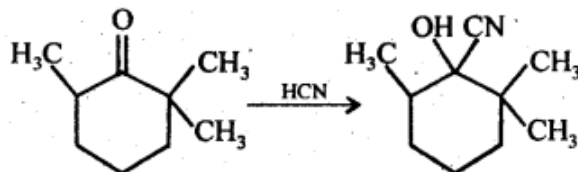
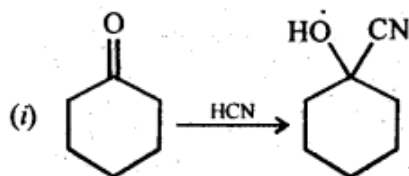
Ans:



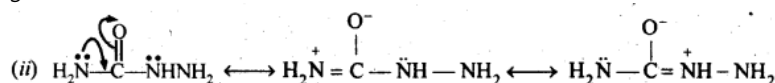
12.18. Give plausible explanation for each of the following:

- Cyclohexanone forms cyanohydrin in good yield but 2,2,6,6-tetramethylcyclohexanone does not
- There are two $-NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.
- During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

Ans:

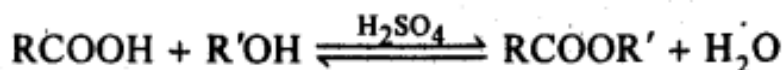


The yield of second reaction is very low because of the presence of three methyl groups at ex-positions with respect to the $C=O$, the nucleophilic attack by the CN^- ion does not occur due to steric hindrance. Since there is no such steric hindrance in cyclohexanone, therefore, nucleophilic attack by the CN^- ion occurs readily and hence cyclohexanone cyanohydrin is obtained in good yield.



Although semicarbazide has two $-NH_2$ groups but one of them (i.e., which is directly attached to $C=O$) is involved in resonance as shown above. As a result, electron density on N of this $-NH_2$ group decreases and hence it does not act as a nucleophile. In contrast, the other $-NH_2$ group (i.e., attached to NH) is not involved in resonance and hence lone pair of electrons present on N atom of this $-NH_2$ group is available for nucleophilic attack on the $C=O$ group of aldehydes and ketones.

(iii) The formation of esters from a carboxylic acid and an alcohol in presence of an acid catalyst is a reversible reaction.



Thus to shift the equilibrium in the forward direction, the water or the ester formed should be removed as fast as it is formed.

12.19. An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tottens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation, it gives ethanoic and propanoic acid. Write the possible structure of the compound.

Ans:

$$C = 69.77\%, H = 11.67\%$$

$$\therefore O = 100 - (69.77 + 11.63)\% = 18.6\%$$

$$\therefore C:H:O = \frac{69.77}{12} : \frac{11.63}{1} : \frac{18.6}{16} = 5.88 : 11.63 : 1.16 :: 5 : 10 : 1$$

$$\text{The empirical formula of the given compound} = C_5H_{10}O$$

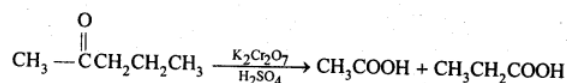
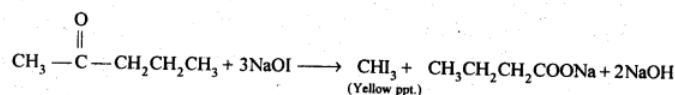
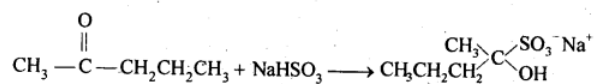
$$\text{Empirical formula mass} = 5 \times 12 + 10 \times 1 + 1 \times 16 = 86$$

$$\text{Molar mass} = 86 \text{ (given)}$$

$$\therefore \text{Molecular formula} = C_5H_{10}O$$

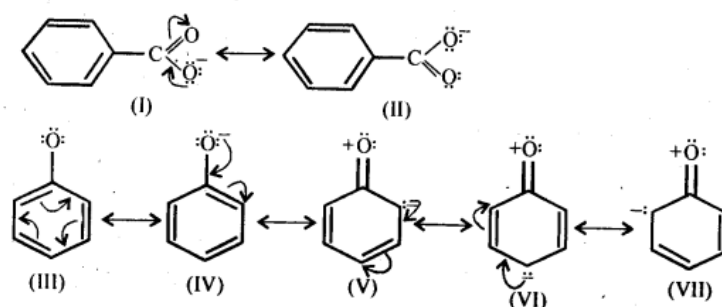
Since the compound form sodium hydrogen sulphite addition product, therefore, it must be either an α -aldehyde or methyl/ cyclic ketone. Since the compound does not reduce Tollens' reagent therefore, it cannot be an aldehyde. Since the compound gives positive iodoform test, therefore, the given compound is a methyl ketone. Since the given compound on vigorous oxidation gives a mixture of ethanoic acid and propanoic acid, therefore, the methyl ketone is pentan-2-one, i.e.,

$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_2\text{CH}_3$. The reactions involved are:



12.20. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

Ans: Consider the resonating structures of carboxylate ion and phenoxide ion.



In case of phenoxide ion, structures (V - VII) carry a negative charge on the less electronegative carbon atom. Therefore, their contribution towards the resonance stabilization of phenoxide ion is very small.

In structures I and II, (carboxylate ion), the negative charge is delocalized over two oxygen atoms while in structures III and IV, the negative charge on the oxygen atom remains localized only the electrons of the benzene ring are delocalized. Since delocalization of benzene electrons contributes little towards the stability of phenoxide ion therefore, carboxylate ion is much more resonance stabilized than phenoxide ion. Thus, the release of a proton from carboxylic acids is much easier than from phenols. In other words, carboxylic acids are stronger acids than phenols.

***** END *****