# Aldehydes, Ketones and Carboxylic Acids

CHAPTER 12

## SOCERT FOCUS

1.

## **ANSWERS**

## Topic 1

|       | IUPAC name                | Common name                       |  |  |
|-------|---------------------------|-----------------------------------|--|--|
| (i)   | Heptan-2-one              | Methyl- <i>n</i> -pentylketone    |  |  |
| (ii)  | 4-Bromo-2-methylhexanal   | γ-Bromo-α-methyl<br>caproaldehyde |  |  |
| (iii) | Heptanal                  | Heptanaldehyde                    |  |  |
| (iv)  | 3-Phenylprop-2-enal       | $\beta$ -Phenylacrolein           |  |  |
| (v)   | Cyclopentane carbaldehyde | _                                 |  |  |
| (vi)  | Diphenylmethanone         | Benzophenone                      |  |  |

## Topic 2

**1.** (i) Carbonyl compounds in the presence of an alkali, react with HCN to form an addition product called cyanohydrin.

$$HCN + OH \iff H_2O + CN$$

$$>C = O + HCN \xrightarrow{OH} \left[ \begin{array}{c} > C < O^{-} \\ CN \end{array} \right] \xrightarrow{H^+} C \xrightarrow{CN} OH$$

$$\xrightarrow{Tetrahedral} Cyanohydrin$$

(ii) Acetals are *gem*-dialkoxy compounds formed when aldehydes react with monohydric alcohols in the presence of dry HCl gas.

H<sub>3</sub>C-CHO 
$$\xrightarrow{R'OH, HCI gas}$$
  $\begin{bmatrix} H_3C-CH & OR' \\ OH \end{bmatrix}$   
Hemiacetal  $\xrightarrow{ROH}$  CH<sub>3</sub> - CH  $\xrightarrow{OR'}$  + H<sub>2</sub>O  
Acetal

(iii) Semicarbazone is formed by the reaction between carbonyl compounds and semicarbazide.

$$>C=0+H_2N-NH$$
  $\xrightarrow{O}_{NH_2}$   $\longrightarrow$   $>C=N-NH$   $\xrightarrow{O}_{NH_2}$   $\xrightarrow{NH_2}_{Semicarbazone}$ 

(iv)  $\beta$ -Hydroxy aldehydes are called aldol. Aldehydes and ketones containing at least one  $\alpha$ -H atom undergo a reaction in the presence of dilute alkali to form aldol compounds. *e.g.*,

2CH<sub>3</sub>CHO 
$$\stackrel{\text{dil }\overline{OH}}{\leftarrow}$$
 CH<sub>3</sub>CH  $-$  CH<sub>2</sub>CHO  
Ethanal  $OH$   
3-Hydroxybutanal (aldol)

(v) Hemiacetals are *gem*-alkoxyalcohols which are produced from the addition of one molecule of monohydric alcohol to an aldehyde in the presence of HCl gas.

$$H_3C$$
  $C = 0 + H - OCH_3$   $H_3C$   $CH_3$   $C$ 

(vi) Oximes are formed by reaction between aldehydes or ketones and hydroxylamine. The reaction is carried out in mildly acidic condition.

$$\begin{array}{c} H_{3}C\\H \end{array} > C = 0 + H_{2}N - 0H \xrightarrow{\text{pH 3.5}} H_{3}C\\H \text{ydroxylamine} \xrightarrow{\text{pH 3.5}} H_{3}C > = NOH + H_{2}O\\\text{Oxime} \end{array}$$

(vii) Ketals are obtained when alcohols react with ketone and two OR group get attached to >C = 0 group of ketone.

$$R = 0 + CH_{3}OH \xrightarrow{dryHCl_{(g)}}_{Methanol} R > C \xrightarrow{OCH_{3}}_{Methanol} HCl + H_{2}O$$

(viii) Imines are formed when carbonyl compounds react with ammonia and its derivatives.

$$C = 0 + H_2 N - Z \longrightarrow C = N - Z + H_2 O$$
Carbonyl
Imine

compound

 $\sim$ 

$$Z = H, R, \bigcirc$$
,  $-NH_2, -OH, etc.$ 

(ix) 2, 4-DNP derivatives are formed when

2, 4-dinitrophenylhydrazine reacts with aldehydes or ketones.

$$>= 0 + H_2 NHN \longrightarrow NO_2$$
  
Aldehyde  
or ketone  $O_2 N$ 

2, 4-DNP

$$\xrightarrow{\text{pH 3.5}}$$
 >= N - N - NO<sub>2</sub>  
O<sub>2</sub>N

DNP-derivative

(x) Reaction between aldehydes or ketones with 1° aliphatic or aromatic amines yields a Schiff's base.

$$R - CHO + H_2N - R' \xrightarrow{\text{very dil } H^+} RCH = N - R' + H_2O$$
  
Aldehyde Schiff's base



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Aldol condensation is shown by those aldehydes or ketones 4. which have at least one  $\alpha$ -H atom while Cannizzaro reaction is shown by aldehydes that have no  $\alpha$ -H atom.

Therefore, the given compounds can be classified as:

| Aldol<br>Condensation | Cannizzaro<br>Condensation | า | Neither      |
|-----------------------|----------------------------|---|--------------|
| 2-Methylpentanal      | Methanal                   |   | Butan-1-ol   |
| Cyclohexanone         | Benzaldehyde               |   | Benzophenone |
| 1-Phenylpropanone     | 2, 2-Dimelthylbutanal      |   |              |
| Phenylacetaldehyde    |                            |   |              |

Aldol condensations :

(ii) 
$$2CH_3 - (CH_2)_2 - CH - CHO \xrightarrow{\text{dil OH}} CH_3$$
  
2-Methylpentanal

$$\begin{array}{c} CH_{3} & CH_{3} \\ I & I \\ CH_{3}(CH_{2})_{2} - C - CH - C - (CH_{2})_{2} - CH_{3} \\ I & I \\ H & OH & CHO \end{array}$$

v) 
$$2 \longrightarrow O \xrightarrow{O} O \longrightarrow{O} O O \longrightarrow{O} O O \longrightarrow{O} O O O O$$

vi) 
$$2 \bigcirc - \text{COCH}_2\text{CH}_3$$

CU

COONa

(vii) 
$$2 \bigcirc$$
 CH<sub>2</sub>CHO  
Phenyl acetaldehyde

Cannizzaro reactions :

- $\xrightarrow{\text{Conc. OH}}$  H<sub>3</sub>COH + HCOONa 2HCHO (i) Methanal
- CHO <u>Conc. OH</u> (iii) 2< CH<sub>2</sub>OH Benzaldehyde



(iii) 
$$2 \text{CH}_3 \text{CHO} \xrightarrow{\text{dd} \cdot \text{Mach}} \text{CH}_3 \text{CH} = \text{CHCHO} - CH_3 \text{CH} = \text{CHCO}_2 \text{H} \xleftarrow{[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^-}_{\text{But-2-enoic acid}} \text{Tollens' reagent}$$

6. The possible products of aldol condensation from propanal and butanal are

(i)  $2CH_3CH_2CHO \xrightarrow{\dim \bar{O}H} CH_3\bar{C}HCHO + CH_3CH_2OH$ Propanal  $H_3C - CH_2 - CH - CH - CHO \leftarrow$ 

3-Hydroxy-2-methylpentanal

(ii) 
$$2CH_3(CH_2)_2CHO \xrightarrow{dil \bar{O}H} CH_3(CH_2)_2CHO + CH_3CH_2\bar{C}HCHO$$
  
Butanal  
 $OH CH_2CH_3$   
 $H_3C - (CH_2)_2 - CH - CH - CHO \leftarrow$ 

2-Ethyl-3-hydroxyhexanal

(iii) When butanal acts as an electrophile and propanal as nucleophile :



(iv) When propanal serves as an electrophile and butanal as nucleophile :

$$CH_{3}CH_{2}CHO + CH_{3}(CH_{2})_{2}CHO \xrightarrow{\text{dil. OH}} OH C_{2}H_{5} \\ \downarrow I \\ H_{3}C - CH_{2} - CH - CH - CHO \xleftarrow{} 2-Ethyl-3-hydroxypentanal}$$

7. (i) It is given that the compound reduces Tollens' reagent. This proves that the compound is an aldehyde. Further, the fact that it undergoes Cannizzaro reaction shows that it lacks an  $\alpha$ -H atom.

(ii) On oxidation it yields 1,2-benzenedicarboxylic acid. This shows that it is an *o*-substituted benzaldehyde.

The only possible structure for the compound with formula  $C_9H_{10}O$  is :



**8.** (a) The given compound does not reduce Tollens' reagent which implies that it is not an aldehyde.

(b) Positive iodoform test proves that it has a  $CH_3$ -C-group.

(c) The oxidation products are indicative of the presence of 5 carbon atoms.

To find the exact molecular formula

%C = 69.77%, %H = 11.63%

$$C: H: O = \frac{69.77}{12} : \frac{11.63}{1} : \frac{18.6}{16}$$

The structure based on inferences a, b and c is

$$H_3C - C - CH_2CH_2CH_3$$

Reactions involved are :



Propionic acid

### **Topic 3**

- 1. (i) 4-Methylpentanal
- 6-Chloro-4-ethylhexan-3-one (ii)
- But-2-en-1-al (iii)
- (iv) Pentane-2, 4-dione
- (v) 3, 3, 5-Trimethylhexan-2-one
- (vi) 3, 3-Dimethylbutanoic acid
- (vii) Benzene-1, 4-dicarbaldehyde

2. (i) 
$${}^{4}_{CH_{3}} - {}^{3}_{CH} - {}^{2}_{CH_{2}} - {}^{1}_{CHO}$$

(ii) 
$$O_2N - O - COCH_2CH_3$$

(iii) CH

(iv) 
$${}^{1}_{CH_{3}} - {}^{2}_{C} - {}^{3}_{CH} = {}^{4}_{C} - {}^{5}_{CH_{3}}$$
  
O CH<sub>3</sub>

(v) 
$${}^{1}_{CH_{3}} - {}^{2}_{C} - {}^{3}_{CH_{2}} - {}^{4}_{CH_{3}} - {}^{5}_{CH_{3}}$$
  
 ${}^{1}_{O}$   ${}^{1}_{Cl}$ 

(vi) 
$${}^{5}_{CH_{3}} - {}^{4}_{CH} - {}^{3}_{CH} - {}^{2}_{CH_{2}} - {}^{1}_{COOH}$$
  
 ${}^{|}_{C_{6}H_{5}} {}^{|}_{Br}$ 



(viii) 
$${}^{6}_{CH_{3}} - {}^{5}_{C} \equiv {}^{4}_{C} - {}^{3}_{CH} = {}^{2}_{CH} - {}^{1}_{COOH}$$

- $B + C \xrightarrow{\operatorname{CrO}_3/\operatorname{H}^+} B$ Carboxylic Alcohol
  acid dilute 🔪  $(C_8H_{16}O_2)$   $H_3O^+$ -H<sub>2</sub>O  $CH_3 - CH_2 - CH = CH_2$ But-1-ene
- Compound (A) upon hydrolysis produces one molecule each (i) of a carboxylic acid and alcohol. This indicates that (A) is an ester. (ii) (C) upon oxidation produces (B) proving that (C) and (B) have same no. of carbon atoms.

(iii) (C) on dehydration produces but-1-ene. This, coupled with the fact that it gives a carboxylic acid (B) on oxidation shows that (C) is a primary alcohol.

$$\therefore (C) \text{ is } CH_3 - CH_2 - CH_2 - CH_2OH$$
  
Butan-1-ol

(B) is H<sub>3</sub>C--(CH<sub>2</sub>)<sub>2</sub>-COOH Butanoic acid

and hence, (A) is

C

$$H_3C-(CH_2)_2-C-O-(CH_2)_3-CH_3$$
  
Butyl butanaote

0

The reactions involved may be summarized as :

$$CH_{3}(CH_{2})_{2} \xrightarrow{-C}_{(A)} \xrightarrow{O} -(CH_{2})_{3}CH_{3} \xrightarrow{dil H^{+}} CH_{3}(CH_{2})_{2}CH_{2}OH + CH_{3}(CH_{2})_{2}-COOH$$

$$(C) \qquad (B)$$

$$H_{3}CH_{2}CH_{2}CH_{2}OH \xrightarrow{CrO_{3}/H^{+}} CH_{3}CH_{2}CH_{2}COOH$$

$$(C) \qquad \downarrow H^{+}/\Delta \qquad (B)$$

$$CH_{2}CH_{2}CH=CH_{2}$$

## **Topic 4**

1. (i) The reaction between carbonyl compounds and HCN proceeds via the nucleophilic attack of CN<sup>-</sup> on carbonyl carbon. Such an attack takes place faster if the carbonyl carbon is not attached to large alkyl groups. Less is the steric hindrance, more reactive is the compound.



(ii) The presence of any electron withdrawing group or electronegative atom in carboxylic acid molecule increases the acidic strength of the acid. Moreover, the acidity decreases if the atom/group is bonded further off the  $\alpha$ -carbon.

3. Given :



COOH group polar and H is lost as  $H^+$ .

4-Nitrobenzoic acid 3, 4-Dinitrobenzoic acid

2. The given set of compounds may be distinguished by the following reaction.

| Compound   | Compound   | Compound   |
|--|--|--|
| Reagent $\downarrow \rightarrow$   | I  | П  |
| <ul> <li>(i) Ammoniacal silver<br/>nitrate</li> <li>2[Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup></li> <li>(Tollens' reagent)</li> </ul> | $\begin{array}{c} CH_3 - CH_2 - CHO \\ Propanal \\ CH_3 CH_2 COO^- + 2Ag \\ Silver mirror \\ \end{array} + 2H_2 O + 4NH_3$   | $H_{3C} \xrightarrow{O} H_{3} \xrightarrow{O} No reaction$ $H_{3C} \xrightarrow{O} H_{3} \xrightarrow{O} H_{3$ |
| (ii) NaOl  | $\begin{array}{c} O \\ C - CH_3 \\ \hline O \\ Acetophenone \end{array} \xrightarrow{Iodoform test} O + CHI_3 \downarrow \\ Yellow ppt. \end{array}$                     | $\rightarrow$ No reaction<br>Benzophenone  |
| (iii) NaHCO <sub>3</sub>   | $ \begin{array}{c} \text{OH} \\ \hline \text{OH} \\ \hline \text{Phenol} \\ \end{array} \rightarrow \text{No reaction} $   | $\begin{array}{c} \begin{array}{c} \text{COOH} \\ \hline \\ \hline \\ \\ \end{array} \end{array}  \begin{array}{c} & - \\ \\ \hline \\ \\ \end{array} \end{array}  \begin{array}{c} & - \\ \\ \end{array} + H_2O \\ H_2O \\ \end{array} + CO_2 \uparrow \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $  |
| (iv) NaHCO <sub>3</sub>  | $\begin{array}{c} \text{COOH} \\ \bigcirc \\ \text{Benzoic acid} \end{array} \xrightarrow{-+} \\ \bigcirc \\ + H_2O + CO_2 \uparrow \\ \text{Effervescence} \end{array}$ | $\underbrace{\bigcirc}_{\text{Ethyl benzoate}}^{\text{COOC}_2\text{H}_5} \text{No reaction}$   |
| (v) NaOl   | $CH_3-CH_2-C-CH_2-CH_3$<br>Pentan-3-one No reaction  | $\begin{array}{c} O \\ II \\ CH_3 - C - (CH_2)_2 CH_3 \\ Pentan-2-one \\ CHI_3 \downarrow + CH_3 (CH_2)_2 - C \\ Iodoform \\ (yellow ppt.) \end{array}$  |
| (vi) NaOl  | $\overset{\text{CHO}}{\bigcup} \longrightarrow \text{No reaction}$ Benzaldehyde  | $\begin{array}{c} O \\ C - CH_3 \\ O \\ O \\ Acetophenone \end{array} + \begin{array}{c} COONa \\ + CHI_3 \\ Yellow ppt. \end{array}$  |
| (vii) NaOl   | $\begin{array}{ccc} CH_{3}CHO \longrightarrow & 2CHI_{3}\downarrow + HCOON^{+}a\\ Ethanal & Yellow ppt. \end{array}$   | CH <sub>3</sub> CH <sub>2</sub> CHO → No reaction<br>Propanal  |



(iv) Benzene to *m*-Nitroacetophenone :



(ix) Benzoic acid to *m*-Nitrobenzyl alcohol :



5. (i) Acetylation : Acetylation is the process of

introducing  $R - \dot{C} - group$  in compounds that contain a replaceable hydrogen atom. The best example of acetylation is Friedel-Crafts acylation reaction where *R*CO group is introduced on the benzene ring.

Reagents employed for the purpose of acylation are acyl chloride, acid anhydride etc. *e.g.*, Friedel-Crafts acylation:



(ii) **Cannizzaro reaction :** Cannizzaro reaction is given by aldehydes or ketones that lack,  $\alpha$ -hydrogen atom. Such carbonyl compounds in the presence of conc. NaOH and heat undergo disproportionation reaction to produce the corresponding carboxylate ion and alcohol.



(iii) **Cross-aldol condensation** : Aldol condensation is the reaction that takes place, when aldehydes or ketones with at least one  $\alpha$ -H atom react in the presence of dilute alkali to produce  $\beta$ -hydroxy aldehydes or ketones. When two different aldehydes or ketones are taken, it gives a mixture of products. Such a reaction is called cross-aldol condensation.

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Ketones can also be used as one component in the cross aldol reactions





(iv) **Decarboxylation**: Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is called decarboxylation.

$$R - COONa \xrightarrow{\text{NaOH} + CaO}_{\text{Heat}} R - \text{H} + \text{Na}_2\text{CO}_3$$
6. (i) 
$$CH_2\text{CH}_3 \xrightarrow{\text{KMnO}_4}_{\text{KOH, }\Delta} \xrightarrow{\text{COOK}}_{O} \xrightarrow{\text{COOK}}_{O}$$
(ii) 
$$COOH \xrightarrow{\text{SOCI}_2/\Delta}_{O} \xrightarrow{\text{CO}}_{O} \xrightarrow{\text{COOK}}_{O}$$
(iii) 
$$COOH \xrightarrow{\text{SOCI}_2/\Delta}_{O} \xrightarrow{\text{CO}}_{O} \xrightarrow{\text{COOK}}_{O}$$
(iii) 
$$O - CHO \xrightarrow{\text{H}_2\text{N} \xrightarrow{\text{NHNH}_2}}_{O} \xrightarrow{\text{N} - \text{NH} \xrightarrow{\text{NH}_2}}_{O}$$
(iv) 
$$O \xrightarrow{\text{CO}}_{+ \text{Anhyd. AlCl}_3} \xrightarrow{\text{O}}_{O} \xrightarrow{\text{H}_2\text{CO}}_{O} \xrightarrow{\text{H}_2\text{CO}}_{O} \xrightarrow{\text{H}_2\text{NHNH}_2}_{O}$$
(iv) 
$$O \xrightarrow{\text{H}_2\text{N} \xrightarrow{\text{H}_2\text{N}}}_{+ \text{Anhyd. AlCl}_3} \xrightarrow{\text{H}_2\text{N}}_{+ \text{HCl}}$$





Reaction (a) is an example of cyanohydrin formation by the nucleophilic attack of cyanide ion on the carbonyl carbon. In cyclohexanone, this attack takes place easily and cyanohydrin is formed. But in II, attack of the Nu<sup>-</sup> is sterically hindered due

to the presence of the three methyl groups. As a result, the reaction does not occur.

(ii) Semicarbazide has the following resonance structures arising due to the electron withdrawing nature of the O atom.



From the given structures we find that the lone pair of electrons on N atoms on either side of  $\supset C=O$  group are delocalised, involved in resonance. Therefore, they are not available for carrying out the nucleophilic attack on the aldehyde or ketone. But, the  $-NH_2$  (terminal one) is intact, *i.e.* it is not involved in resonance and thus its, lone pair is available for attack on carbonyl compound.

This is why the semicarbazone is formed through this N atom only.

(iii) 
$$RCOOH + R'OH \xrightarrow{H^{T}} RCOOR' + H_2O$$
  
acid alcohol ester

The esterification reaction is a reversible reaction. If water and the ester are allowed to remain in the reaction mixture the hydrolysis of the ester would take place. Hence, water or ester should be removed as soon as it is formed. 8. (i) Phenoxide ion has the following resonating structures :



Carboxylate ion has the following resonance structures.

$$R - \zeta \overset{O}{\underset{A}{\bigcirc}} \longleftrightarrow R - \zeta \overset{O}{\underset{B}{\bigcirc}} \equiv \begin{bmatrix} R - \zeta \overset{O}{\underset{B}{\bigcirc}} \end{bmatrix}$$

(ii) Phenoxide ion is a resonance hybrid of structures I to V, where each structure has a contribution of 20% in the resonance hybrid. On the other hand, each of the two contributing structures of carboxylate ion contribute 50% towards the resonance hybrid. Therefore, the carboxylate ion tends to be more stable than the phenoxide ion and hence has higher acidity.

(iii) The negative charge that rests on the electronegative O atom in carboxylate ion. We know that the presence of negative charge on an electronegative atom makes the ion more stable. For the same reason  $RCOO^-$  is more stable than the phenoxide ion where the oxygen has no negative charge on it. For the above two reasons carboxylate ion is more stable and has higher acidity than phenol.

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