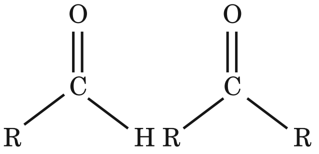
CHAPTER 12

Aldehydes, Ketones & Carboxylic Acids

Aldehydes and ketones

They are the organic compounds containing carbon-oxygen double bond. (> C = O)

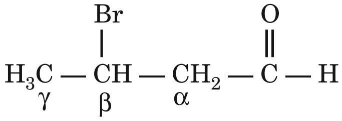
- The carbonyl group is bonded with a carbon and hydrogen in aldehydes and it is bonded to two carbon atoms in ketones.



Aldehyde Ketone

Nomenclature

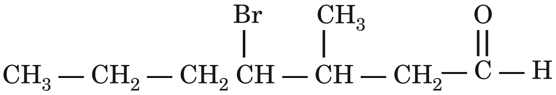
- **Common Names**
  - Instead of IUPAC names, common names are used for aldehydes and ketones.
  - The location of the substituent in the carbon chain is indicated by Greek letters α, β, γ etc, α-carbon being the one directly linked to the aldehyde group, carbon the next, and so on.



$$\underset{\gamma}{H_3C} - \underset{\beta}{\overset{\overset{\displaystyle Br}{|}}{CH}} - \underset{\alpha}{CH_2} - \overset{\overset{\displaystyle O}{\|}}{C} - H$$

β-Bromobutyraldehyde

- **IUPAC Names**
  - They are derived from IUPAC names of corresponding alkanes, by replacing ending e with –al in aldehydes and –one in ketones.
  - Longest carbon chain is numbered starting from the carbon of the aldehyde group while in case of ketones the numbering begins from the end nearer to the carbonyl group.

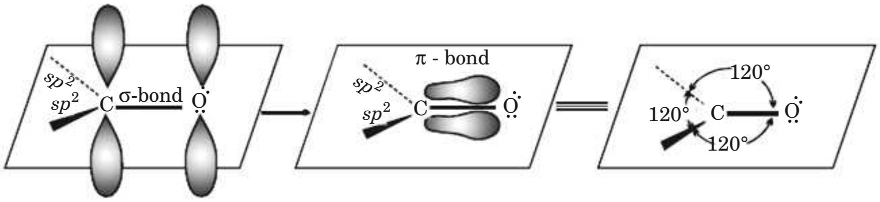


$$CH_3 - CH_2 - CH_2\,\overset{\overset{\displaystyle Br}{|}}{CH} - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - H$$

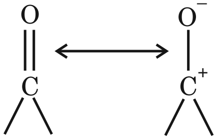
4-Bromo-3-methylheptanal

Structure of the Carbonyl Group

- The carbonyl carbon atom forms three sigma bonds and a π bond with oxygen and is sp^3 hybridized.
- The angles between the bonds is 120° as shown below

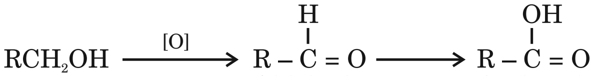


- As oxygen is more electronegative than oxygen, the carbon-oxygen double bond is polarized.



Preparation of Aldehydes and Ketones

- **Oxidation of alcohols**
- By oxidation of primary and secondary alcohols, aldehydes and ketones are prepared.



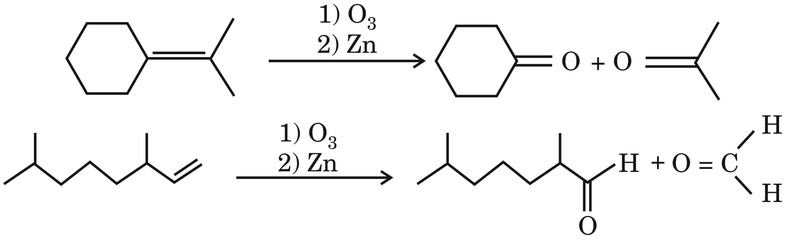
$$RCH_2OH \xrightarrow{[O]} \underset{\text{Aldehyde}}{R-\overset{H}{\overset{|}{C}}=O} \longrightarrow \underset{\text{Carboxylic acid}}{R-\overset{OH}{\overset{|}{C}}=O}$$

Aldehyde Carboxylic acid

- Secondary alcohols are oxidized in presence of CrO_3 to ketones.
- **Dehydrogenation of alcohols**

$$\underset{1^\circ\text{ Alcohol}}{R-CH_2-OH} \xrightarrow[573K]{Cu} \underset{\text{Aldehyde}}{RCHO + H_2}$$

- **Using hydrocarbons**
  - **Using ozonolysis of alkenes**



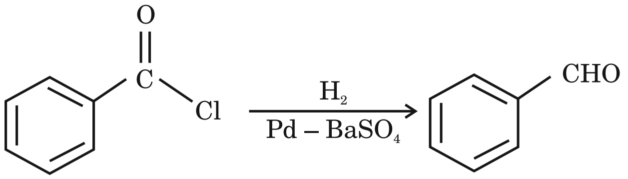
  - **By hydration of alkynes**

    Addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde

Preparation of Alhehydes

- **Rosenmund Reaction:**

  Acid chloride is hydrogenated in presence of a catalyst (Palladium on Barium Sulphate)



Benzoyl chloride Benzaldehyde

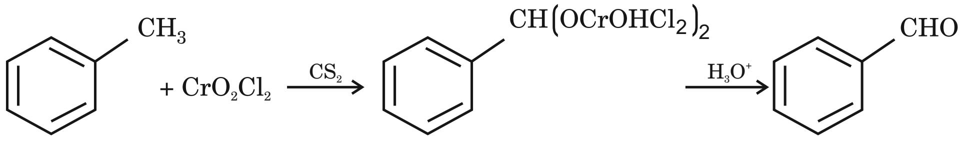
- **Stephen Reaction:**

  Nitrites are reduced to imine which on hydrolysis gives aldehyde.

$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3\overset{+}{O}} RCHO$$

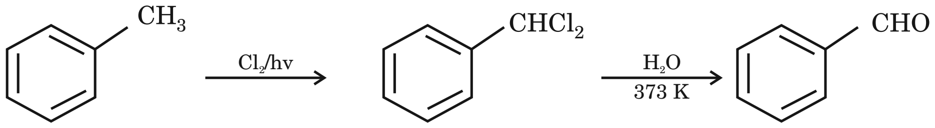
- **From hydrocarbons**
  - **By oxidation of methylbenzene**

    Etard Reaction:



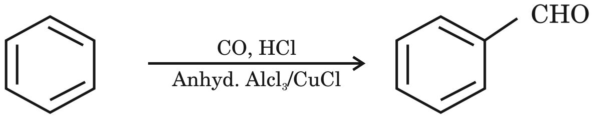
Toluene Chromium complex Benzaldehyde

By side chain chlorination followed by hydrolysis



Toluene Benzal chloride Benzaldehyde

Gatterman-Koch Reaction:

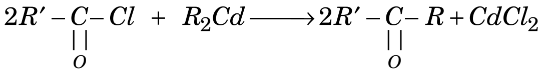


Benzal chloride Benzaldehyde

Preparation of Ketones

- **Using acyl chlorides**

$$2R - Mg - X \ + \ CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$

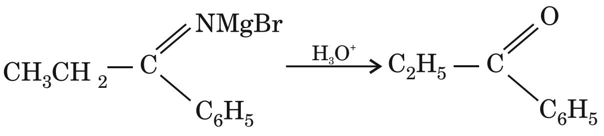


$$2R' - \underset{O}{\underset{||}{C}} - Cl \ + \ R_2Cd \longrightarrow 2R' - \underset{O}{\underset{||}{C}} - R + CdCl_2$$

- **Using nitriles**

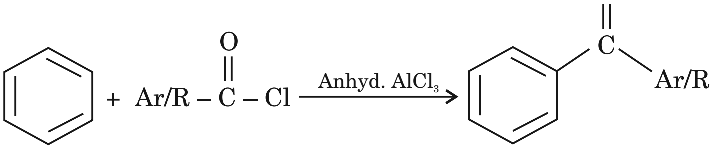
  When nitriles are treated with Grignard reagent followed by hydrolysis, it gives ketones.

$CH_3 — CH_2 — C \equiv N + C_6H_5MgBr \xrightarrow{\text{ether}}$



Propiophenone
(1-Phenylpropanone)

- **Acylation Reaction**

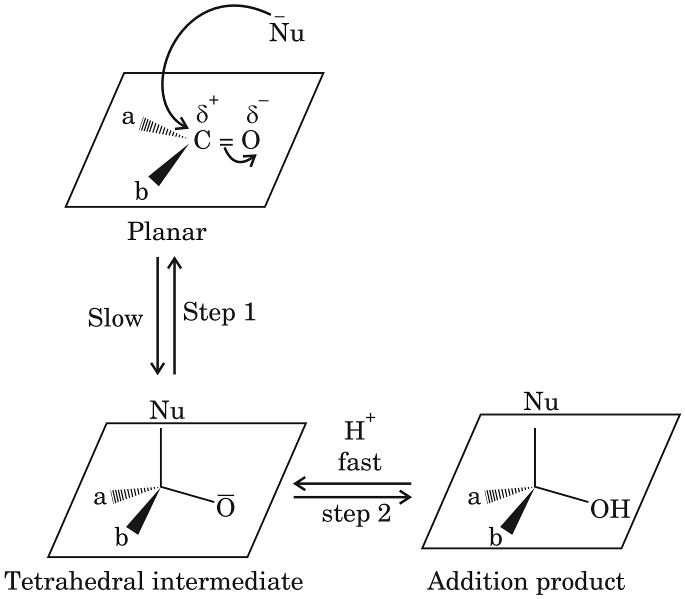


Physical Properties

- A large amount of aldehydes are liquids at room temperature.
- As aldehydes and ketones have hydrogen bonding capacity, they are soluble in water (upto 4 carbon atoms)
- Most of them have high boiling point when compared to hydrocarbons and higher than those of alcohols.

Chemical Properties

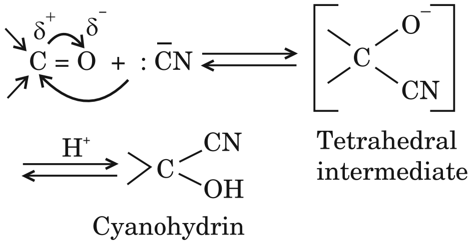
Nucleophilic Addition Reactions



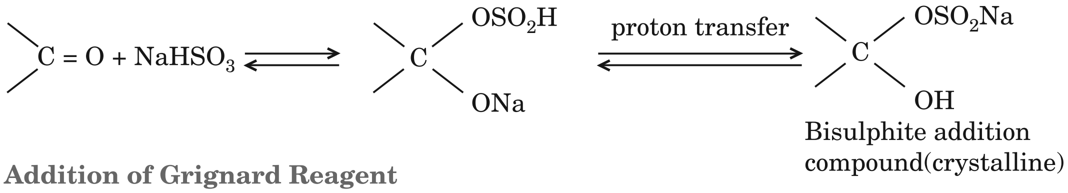
- **Addition of hydrogen cyanide:**

  Cyanohydrins are obtained when aldehydes and ketones are treated with

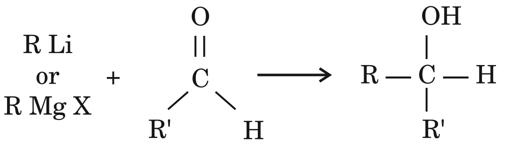
  $$\mathrm{HCN} + \mathrm{OH}^- \rightleftharpoons :\bar{\mathrm{C}}\mathrm{N} + \mathrm{H_2O}$$



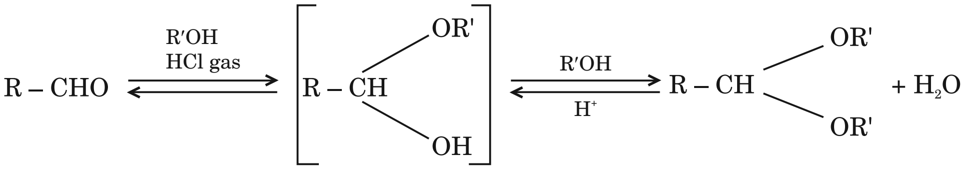
- **Addition of sodium hydrogensulphite**



- **Addition of Grignard Reagent**

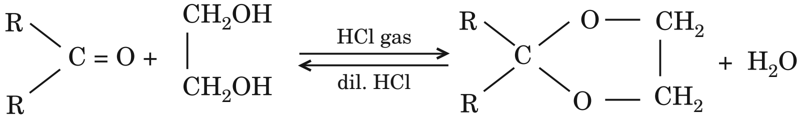


- **Addition of alcohols**



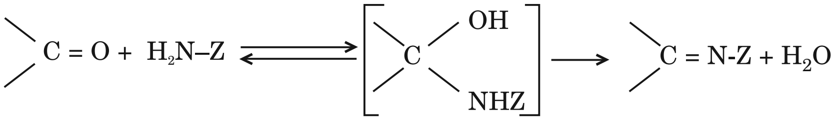
Hemiacetal Acetal

Ketones don't react with monohydric alcohols but react with dihydric alcohols to give ketals.



Ethylene glycol ketal

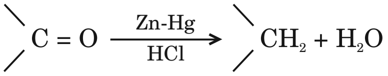
- **Addition of ammonia**



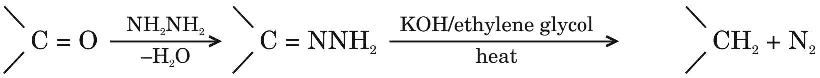
Reduction Reactions

- **Clemmensen Reduction or Wolf Kishner Reduction:**

  The carbonyl group is reduced to CH_2 group as shown below



(Clemmensen reduction)



(wolff-Kishner reduction)

- **Reduction to alcohols**

  In presence of $NaBH_4$, a primary alcohol is obtained while in presence of $LiAlH_4$, a secondary alcohol is obtained.

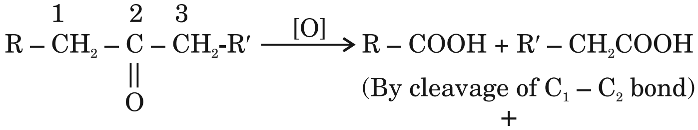
$$R-CHO+2[H]\xrightarrow{LiAlH_4}R-CH_2-OH$$

Oxidation

- On oxidation, aldehydes result in carboxylic acids on treatment with nitric acid, and mild oxidizing agents like Tollen's reagent and Fehling's reagent.

$$R-CHO\xrightarrow{[O]}R-COOH$$

- Ketones are oxidized by strong oxidizing agents at high temperatures which involves the cleavage of carbon-carbon bond.



$$\overset{1}{R-CH_2}-\underset{\underset{O}{||}}{\overset{2}{C}}-\overset{3}{CH_2}\text{-}R'\xrightarrow{[O]}R-COOH+R'-CH_2COOH$$

(By cleavage of $C_1 - C_2$ bond)

+

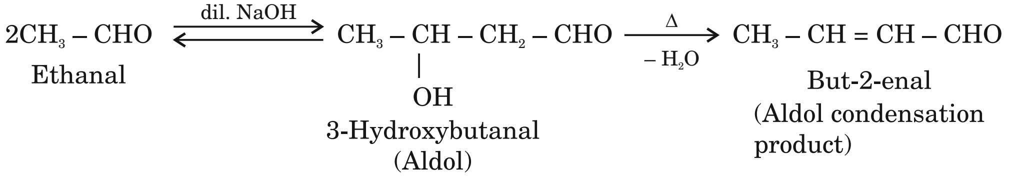
$R — CH_2COOH + R' — COOH$

(By cleavage of C_2 - C_3 bond)

Reactions due to α hydrogen.

- **Aldol Condensation**

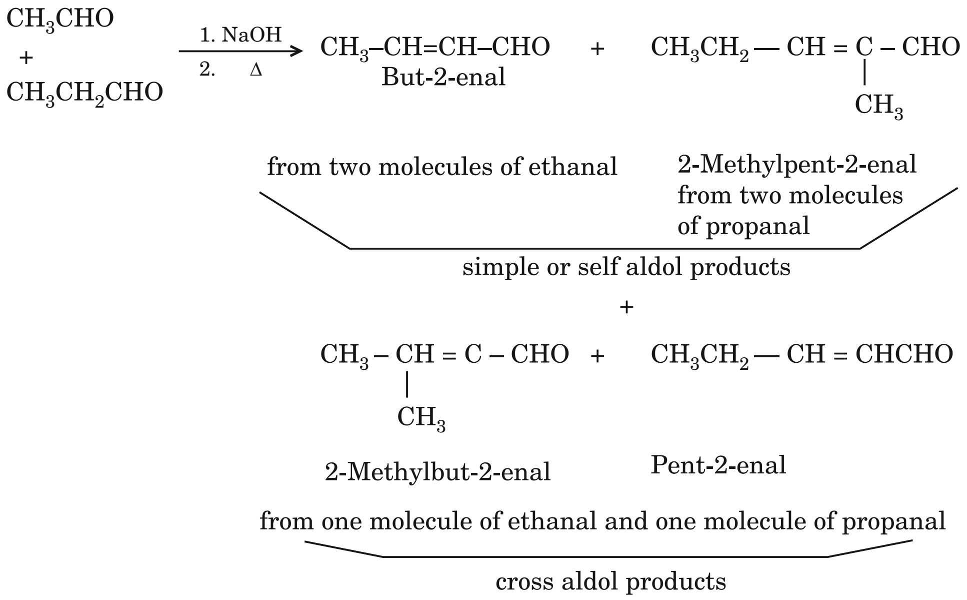
  β hydroxyl aldehydes or β hydroxyl ketones are obtained when Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst.



$$\underset{\text{Ethanal}}{2CH_3-CHO} \overset{\text{dil. NaOH}}{\rightleftharpoons} \underset{\text{3-Hydroxybutanal (Aldol)}}{CH_3-\underset{\substack{|\\ OH}}{CH}-CH_2-CHO} \xrightarrow[-H_2O]{\Delta} \underset{\text{But-2-enal (Aldol condensation product)}}{CH_3-CH=CH-CHO}$$

- **Cross Aldol Condensation**

  When two different aldehydes or/and ketones undergo aldol condensation, it is known as cross aldol condensation.



$$\begin{matrix} CH_3CHO \\ + \\ CH_3CH_2CHO \end{matrix} \xrightarrow[2.\ \Delta]{1.\ NaOH} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO} + CH_3CH_2-CH=\underset{\substack{|\\ CH_3}}{C}-CHO$$

$$\underbrace{\text{from two molecules of ethanal} \qquad \text{2-Methylpent-2-enal from two molecules of propanal}}_{\text{simple or self aldol products}}$$

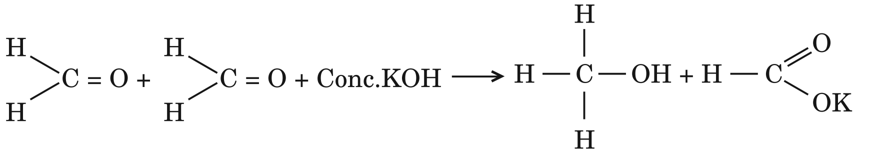
$$+$$

$$\underbrace{\underset{\text{2-Methylbut-2-enal}}{CH_3-\underset{\substack{|\\ CH_3}}{CH}=C-CHO} + \underset{\text{Pent-2-enal}}{CH_3CH_2-CH=CHCHO}}_{\substack{\text{from one molecule of ethanal and one molecule of propanal} \\ \text{cross aldol products}}}$$

Other Reactions

- **Cannizzaro Reaction:**

  In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

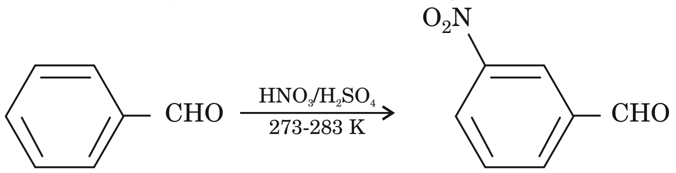


$$\begin{matrix}H\\ \diagdown\\ \diagup\\ H\end{matrix}C=O + \begin{matrix}H\\ \diagdown\\ \diagup\\ H\end{matrix}C=O + \text{Conc.KOH} \longrightarrow \underset{\text{Methanol}}{H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH} + \underset{\text{Potassium formate}}{H-C\begin{matrix}\nearrow O\\ \searrow OK\end{matrix}}$$

Methanol Potassium formate

- **Electrophilic Substitution**

  Aromatic aldehydes and ketones undergo this reaction.



Benzaldehyde m-Nitrobenzaldehyde

Uses of Aldehydes and Ketones

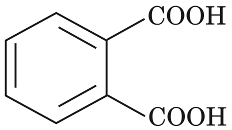
- Formalin solution (Formaldehyde) is used in preserving biological specimens and to prepare polymer products.
- Many aldehydes and ketones have a pleasant smell and flavor.
- Acetaldehyde is used as a starting material to manufacture acetic acid, polymers and drugs.

Carboxylic Acids

- These are the carbon compounds containing –*COOH* functional group.
- Carboxylic acids may be aliphatic (*RCOOH*)or aromatic (*ArCOOH*) depending on the group, alkyl or aryl, attached to carboxylic carbon.

Nomenclature

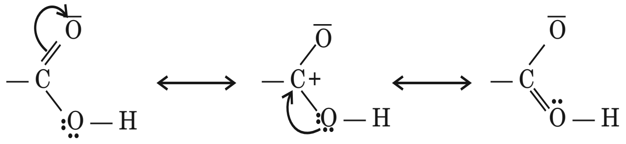
- Many of the carboxylic acids are known by their common names. Example: Ethanoic Acid is called as Acetic acid.
- In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending –e in the name of the corresponding alkane with – oic acid.
- In numbering the carbon chain, the carboxylic carbon is numbered one. Example: The IUPAC name of is



is Benzene-1, 2-dicarboxylic acid.

Structure of Carboxyl Group

- The bonds are in one plane and the angle between the bonds is 120°.
- Due to difference in electrophilic nature, resonance is present as shown below:



Preparation of Carboxylic Acids

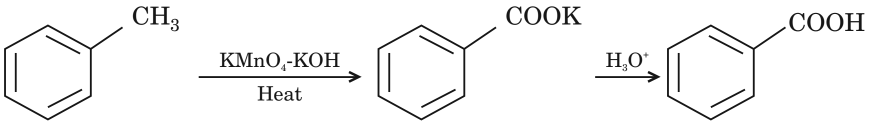
- **From primary alcohols and aldehydes**

  In the presence of oxidizing agents like potassium permanganate and potassium dichromate, primary alcohols are oxidized to carboxylic acids.

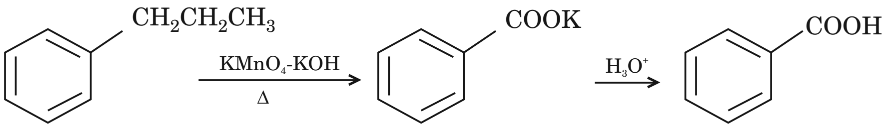
$$RCH_2OH \xrightarrow[2.\ H_3O^{\oplus}]{1.\ \text{alkaline } KMnO_4} RCOOH$$

$$\underset{\text{1−Decanol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow{CrO_3-H_2SO_4} \underset{\text{Decanoic acid}}{CH_2(CH_2)_8COOH}$$

- **From alkylbenzenes:**



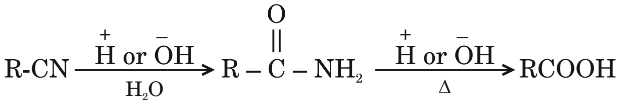
Benzoic acid



Benzoic acid

- **Using nitriles and amides**

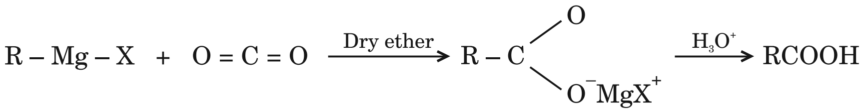
  To stop the reaction at the amide stage, mild reaction conditions are used.



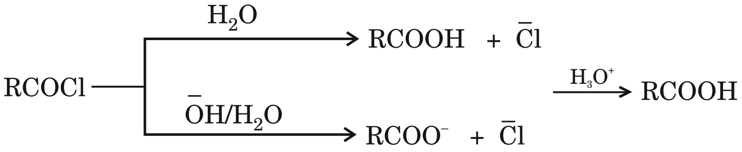
$$R\text{-}CN \xrightarrow[H_2O]{\overset{+}{H}\text{ or }\overset{-}{O}H} R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[\Delta]{\overset{+}{H}\text{ or }\overset{-}{O}H} RCOOH$$

- Using Grignard Reagent

  Salts of carboxylic acids are formed when Grignard's reagent react with carbon dioxide(dry ice) which on acidification with mineral acid give carboxylic acids.



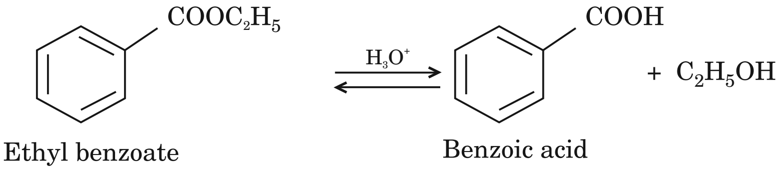
- **Using acyl halides and anhydrides**



$$\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow{H_3O} \underset{\text{Benzoic acid}}{2C_6H_5COOH}$$

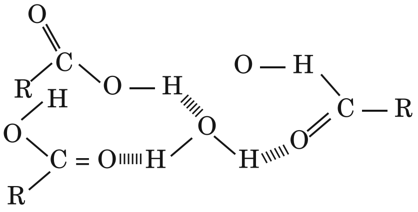
- **Using esters**

  Esters when subjected to acidic hydrolysis give carboxylic acids.



Physical Properties

- Lower members are colorless liquid having pungent smell and the higher members are odourless waxy solid.
- The ability to form intermolecular hydrogen bonds causes carboxylic acids to have higher boiling point.



Hydrogen bonding of
RCOOH with H_2O

Chemical Reactions

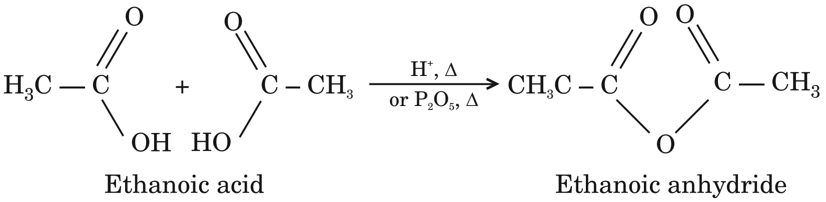
- **Reactions with metals and alkalies**

  On reacting with metals, the carboxylic acids evolve hydrogen.

$$2R-COOH + 2Na \longrightarrow \underset{\text{Sodium carboxylate}}{2R-C\bar{O}ONa^+} + H_2$$

$$R-COOH + NaOH \longrightarrow R-CO\bar{O}Na^+ + H_2O$$

- **Formation of anhydride**



- **Esterification:**

  $RCOOH + PCl_5 \longrightarrow RCOCl + PCl_3 + HCl$

  $3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$

  $RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$

- **Reactions with** $PCl_5, PCl_3, SOCl_2$

  The hydroxyl group gets replaced by chlorine atom.

  $RCOOH + R'OH \xrightleftharpoons{H^+,\ \Delta} RCOOR' + H_2O$

- **Reaction with ammonia**

  Reaction of carboxylic acids with ammonia gives ammonium salts which when heated further gives amides.

$$CH_3COOH + NH_3 \rightleftharpoons \underset{\text{Ammonium acetate}}{CH_3CO\bar{O}\overset{+}{N}H_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$

Reactions involving –COOH group

- **Reduction**

  Carboxylic acids, when reduced by diborane give primary alcohols.

  $R-COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4 \text{ / ether or } B_2H_6} R-CH_2OH$

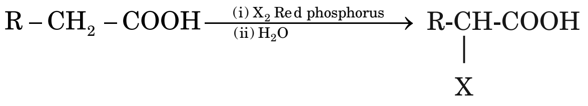
- Decarboxylation: The loss of carbon dioxide from carboxylic acids to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio 3 :1) is called decarboxylation.

  $R-COONa \xrightarrow[\text{Heat}]{\text{NaOH \& CaO}} R-H + Na_2CO_3$

Substitution Reactions

- **Halogenation (Hell Volhard-Zelinsky Reaction)**

  Carboxylic acids which have an -hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus which results in α halocarboxylic acids.



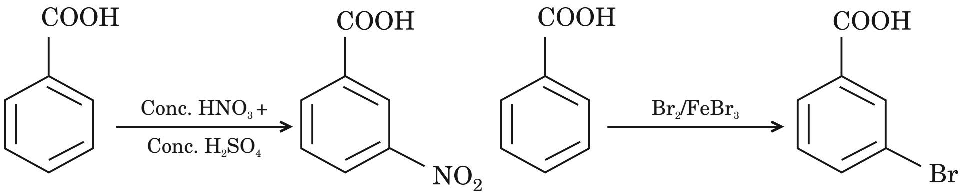
$$R-CH_2-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2 \text{ Red phosphorus}} R\text{-}\underset{\underset{X}{|}}{CH}\text{-}COOH$$

X = Cl, Br

α - Halocarboxvlic acid

- **Ring Substitution**

  In aromatic carboxylic acids, carboxyl group acts as a deactivating and meta-directing group.



m-Nitrobenzoic acid

m-Bromobenzoic acid

Applications of Carboxylic Acids

- Ethanoic acid is used as vinegar and as solvent.
- Methanoic acid is used in rubber, dyeing, leather,textile, and electroplating industries.
- Esters of benzoic acid are often used in perfume industry.
- For the manufacturing of soaps and detergents, higher fatty acids are used.

EXERCISE

1. Which of the aldehyde is most reactive?

(*a*) C_6H_5-CHO (*b*) CH_3 CHO

(*c*) HCHO (*d*) All equally reactive

2. Which of the following is general formula of aldehyde and ketone

(*a*) $C_nH_{2n+2}O$ (*b*) $C_nH_{2n}O_2$

(*c*) $C_nH_{2n}O$ (*d*) $C_nH_{2n+1}O$

3. The end product in the following sequence of reaction is

$$HC \equiv CH \xrightarrow[20\%,\ H_2SO_4]{1\%\ Hg\ SO_4} A \xrightarrow{CH_3MgX} B \xrightarrow{[O]}$$

(*a*) Acetic acid (*b*) Isopropyl alcohol

(*c*) Acetone (*d*) Ethanol

4. Which one of the following compounds is prepared in the laboratory from benzene by a substitution reaction

(*a*) Glyoxal

(*b*) Cyclohexane

(*c*) Acetophenone

(*d*) Hexabromo Cyclohexane

5. From which of the following tertiary butyl alcohol is obtained by the action of methyl magnesium iodide.

(*a*) HCHO (*b*) CH_3 CHO

(*c*) CH_3COCH_3 (*d*) CO_2

6. Dry heating of calcium acetate gives

(*a*) Acetaldehyde (*b*) Ethane

(*c*) Acetic acid (*d*) Acetone

7. Identify the product C in the series.

$$CH_3CN \xrightarrow{Na/C_2H_5OH} A \xrightarrow{HNO_2} B \xrightarrow{Cu/573K} C$$

(*a*) CH_3COOH (*b*) CH_3CH_2NHOH

(*c*) CH_3CONH_2 (*d*) CH_3CHO

8. Which of the following organic compounds exhibits positive Fehling test as well as iodoform test

(*a*) Methanal (*b*) Ethanol

(*c*) Propanone (*d*) Ethanal

9. C_2H_5CHO and $(CH_3)_2CO$ can be distinguished by testing with

(*a*) Phenyl hydrazine (*b*) Hydroxylamine

(*c*) Fehling solution (*d*) Sodium bisulphite

10. Which of the following will not give iodoform test

(*a*) Ethanal (*b*) Ethanol

(*c*) 2-Propanone (*d*) 3-Pentanone

11. Formaldehyde when treated with KOH gives methanol and Potassium formate. The reaction is known as

(*a*) Parkin reaction

(*b*) Claisen reaction

(*c*) Cannizzaro reaction

(*d*) Knoevenagel reaction

12. The addition of HCN to carbonyl compounds is an example of

(*a*) Nucleophilic substitution

(*b*) Electrophilic addition

(*c*) Nuclophilic additon

(*d*) Electrophilic substitution

13. Palmitic acid is

(*a*) $C_{16}H_{31}$ COOH (*b*) CO_{17} H_{35} COOH

(*c*) C_{15} H_{31} COOH (*d*) C_{17} H_{31} COOH

14. $(RCO)_2$ NH is

(*a*) Primary amine (*b*) Secondary amine

(*c*) Secondary amide (*d*) Tertiary amide

15. Wax are long chain compounds belonging to the class.

(*a*) Acids (*b*) Alcohols

(*c*) Esters (*d*) Ethers

16. Urea

(*a*) is an amide of carbonic acid

(*b*) It is diamide of carbonic acid

(*c*) Gives carbonic acid on hydrolysis

(*d*) Resembles Carbonic acid.

17. Glycerol on oxidation with bismuth nitrate produce

(*a*) Glyceric acid (*b*) Glyoxalic acid

(*c*) Oxalic acid (*d*) Meso oxalic acid

18. Acetic acid is manufactured by the fermentation of

(*a*) Ethanol (*b*) Methanol

(*c*) Ethanal (*d*) Methanal

19. Which of the following acids has the smallest dissociation constant.

(*a*) $CH_3CHFCOOH$ (*b*) FCH_2 CH_2 COOH

(*c*) Br CH_2 CH_2 COOH (*d*) CH_3 CH Br COOH

20. The reaction of acetamide with water is an example of

(*a*) Alcoholysis (*b*) Hydrolysis

(*c*) Ammonolysis (*d*) Saponification

21. The acid which reduces Fehling solution is

(*a*) Methanoic acid (*b*) Ethanoic acid

(*c*) Butanoic acid (*d*) Propanoic acid

22. In CH_3COOH and HCOOH will be

(*a*) Less acidic (*b*) Equally acidic

(*c*) More acidic (*d*) None

Answer Keys

1. (*c*) **2.** (*c*) **3.** (*c*) **4.** (*c*) **5.** (*c*) **6.** (*d*) **7.** (*d*) **8.** (*d*) **9.** (*c*) **10.** (*d*)
11. (*c*) **12.** (*c*) **13.** (*c*) **14.** (*c*) **15.** (*c*) **16.** (*b*) **17.** (*d*) **18.** (*a*) **19.** (*c*) **20.** (*b*)
21. (*a*) **22.** (*c*)

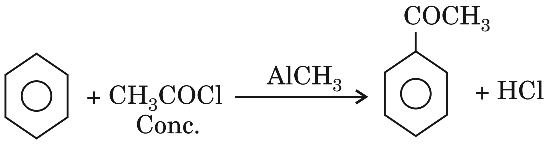
Solutions

1. Among Carbonyl Compounds, reactivity decrease with increase with alkyl groups and alkyl groups (+I effect) decrease positive character on C-atom. Thus the correct order of reactivity is, HCHO > $CH_3CHO > C_6H_5CHO$

2. Both aldehydes and ketones have the same general formula $CnH_{2n}O$.

3. $$HC \equiv CH \xrightarrow[20\%\ H_2SO_4]{1\%Hg\ SO_4} \underset{(A)}{CH_3CHO} \xrightarrow[H_2O]{CH_3MgX}$$

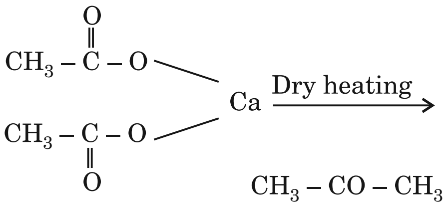
$$\underset{[B]}{CH_3CHOHCH_3} \xrightarrow{[O]} \underset{Acetone}{CH_3COCH_3}$$

4. 

Acetophenone

It is Friedel – crafts reaction.

5. $$\underset{Acetone}{CH_3CO\ CH_3} \xrightarrow{CH_3MgI} \underset{tert-Butyl\ alcohol}{(CH_3)_3\ COH}$$

6. 

$$\begin{matrix} CH_3-\overset{O}{\overset{\|}{C}}-O \\ CH_3-\underset{O}{\underset{\|}{C}}-O \end{matrix} Ca \xrightarrow{Dry\ heating}$$

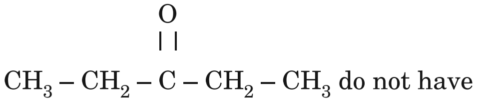
$$\underset{Acetone}{CH_3-CO-CH_3} + CaCO_3$$

7. $$CH_3CN \xrightarrow{Na/C_2H_5OH} CH_3CH_2NH_2$$

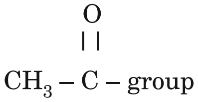
$$\xrightarrow{HNO_2} CH_3CH_3OH \xrightarrow{Cu/573\ K} \underset{[C]}{CH_3CHO}$$

8. Ethanal among the given compounds gives positive iodoform test.

9. $C_2H_5CHO + 2Cu^{2+} + 5OH^- \longrightarrow Cu_2O + 3H_2O +$
$C_2\,H_5\,COO^-\ CH_3COCH_3 + 2Cu^{+2} + 5OH^- \longrightarrow$
No reaction

10. 

$CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH_2-CH_3$ do not have



$CH_3-\overset{O}{\overset{||}{C}}-$ group

11. In cannizzaro's reaction the substance is oxidized and other is reduced.

$$HCHO + HCHO \xrightarrow{KOH} CH_3OH + HCOOK$$

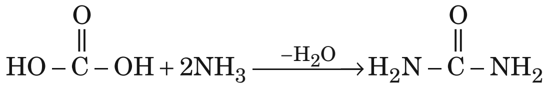
12. Addition of HCN to carbonyl compounds is an example of nucleophilic addition.

13. Fromula of Palmitic acid is $C_{15}H_{31}$ COOH

14. $R-CONH_2$ and $(RCO)_2$ NH
Primary amide Secondary amide

15. Wax are long chain ester

16. Urea is diamide of carbonic acid.

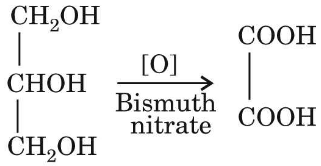


$$\mathrm{HO-\overset{\overset{\displaystyle O}{\|}}{C}-OH+2NH_3\xrightarrow{-H_2O}H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2}$$

Carbonic acid Urea

So, two mole of NH_3 are required that is why it is called the diamide of carbonic acid.

17.



$$\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{CH_2OH}\end{array}\xrightarrow[\text{Bismuth nitrate}]{[O]}\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array}$$

Glycerol Meso oxalic acid

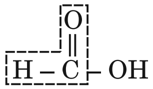
Thus, glycerol produce meso-oxalic acid.

18. $C_2H_5OH \xrightarrow{\text{Acetobacter}} CH_3COOH$

19. Br CH_2 CH_2 COOH is least acidic or has less k_a i.e., dissociation constant. It is (a) due to lesser – 1 effect of Br than F and (b) Br atom further away form – COOH group.

20. The reaction of acetamide with water is an example of hydrolysis

21. Methanoic acid resemble with aldehyde due to its structure. So it reduces Fehlings reagent.



$$\mathrm{H-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$

Aldehydic group

22. Presence of methyl group decrease the acidic character of acetic acid due to positive inductive effect (+I).