ATOMIC ENERGY EDUCATION SOCIETY, Anushaktinagar, Mumbai

class-12 sub.-Chemistry

Lesson:12

Aldehydes, Ketones & Carboxylic Acids

MODULE-1/3

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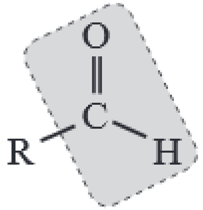
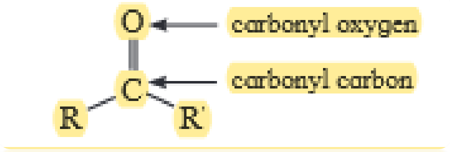
Introduction

- Aldehydes and ketones compounds containing carbonyl group



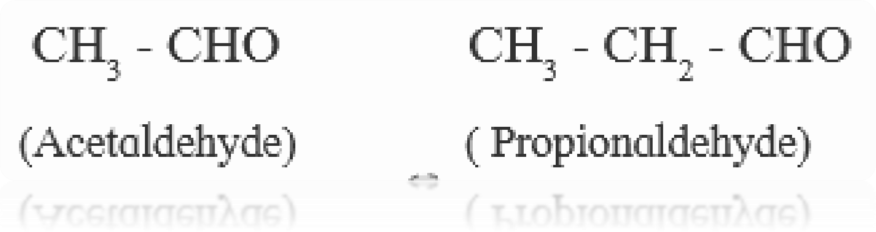
General formula
(R= H or alkyl group)



- Classification of aldehydes, ketones and carboxylic acids: these are classified on the basis of carbon skeleton bonded to carbonyl group.

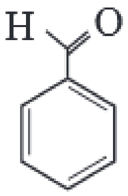
Classification of aldehydes :

- Aldehydes are classified as aliphatic and aromatic aldehydes.
- **Aliphatic aldehydes**: The compounds in which the –CHO group
- (formyl group) is attached directly to sp^3 hybridized c-atom that is saturated c-atom are called aliphatic aldehydes.

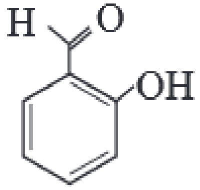


$CH_3 - CHO$	$CH_3 - CH_2 - CHO$
(Acetaldehyde)	(Propionaldehyde)

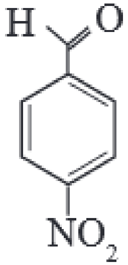
- **b. Aromatic aldehydes:** The compounds in which –CHO group is attached directly to an aromatic ring are called aromatic aldehydes.
- For example



(Benzaldehyde)



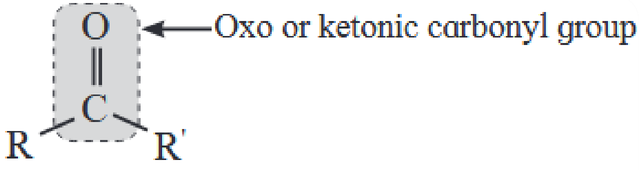
(Salicylaldehyde)



(p-Nitrobenzaldehyde)

Classification of ketones :

- Aliphatic ketones : The compounds in which >C=O group is attached to two alkyl groups are called aliphatic kitones .



General formula
(Where R , R' = alkyl group, identical or different)

- On the basis of types of alkyl groups bonded to carbonyl carbon, aliphatic ketones are further classified as simple and mixed ketones.

Classification of ketones

- i. Simple or symmetrical ketones : The ketones in which both the alkyl groups bonded to carbonyl carbon are identical, are called simple ketones or symmetrical ketones. For example

$H_3C-\overset{O}{\overset{\Vert}{C}}-CH_3$

(Dimethyl ketone) (Acetone)

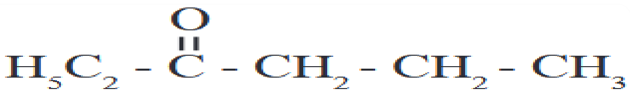
$H_5C_2-\overset{O}{\overset{\Vert}{C}}-C_2H_5$

(Diethyl ketone)

- ii. Mixed or unsymmetrical ketones : The ketones in which two alkyl groups bonded to carbonyl carbon are different, are called mixed ketones or unsymmetrical ketones. For example :

$H_5C_2-\overset{O}{\overset{\Vert}{C}}-CH_3$

(Ethyl methyl ketone)

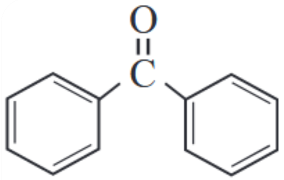


$H_5C_2-\overset{O}{\overset{\Vert}{C}}-CH_2-CH_2-CH_3$

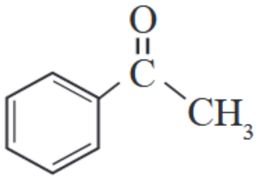
(Ethyl n-propyl ketone)

Classification of ketones

- b. Aromatic ketones : The compounds in which a >C=O group is attached to either two aryl groups or one aryl and one alkyl group are called aromatic ketones.
- For example :



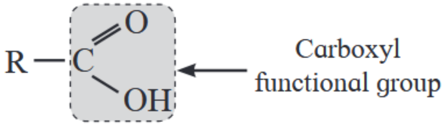
Benzophenone
(Diphenyl ketone)



Acetophenone
(Methyl phenyl ketone)

Classification of carboxylic acids

- Carboxylic acids are classified as aliphatic and aromatic carboxylic acids.



Carboxyl functional group

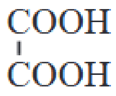
General formula
(R= H or alkyl group)

- a. Aliphatic carboxylic acids : carboxyl (-COOH) group is bonded to an alkyl group are called <u>aliphatic carboxylic acids</u> or <u>fatty acids</u>. (Exception : Formic acid, H-COOH is also classified as aliphatic carboxylic acid though –COOH group is not attached to any carbon).
- For example : $H_3C - COOH$ (Acetic acid) $H_3C - CH_2 - COOH$ (Propionic acid)

- Depending on the number of –COOH groups, mono, di, tri carboxylic acids and so on.
- For example :

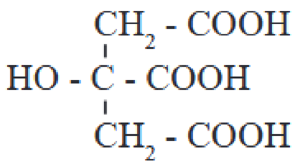
$H_3C - CH_2 - COOH$

Propionic acid
(a monocarboxylic acid)



$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

Oxalic acid
(a dicarboxylic acid)



$$\begin{array}{rl} & CH_2 - COOH \\ & | \\ HO - & C - COOH \\ & | \\ & CH_2 - COOH \end{array}$$

Citric acid
(a tricarboxylic acid)

Nomenclature

- Trivial names of aldehydes :
- Names of aliphatic aldehydes are derived carboxylic acids.
- Ending ‘ic acid’ of carboxylic acid is replaced by the ending ‘aldehyde’.
- In case of carboxylic acids and aldehydes the position of substituent is indicated by labeling the carbon serially as α, β, γ and so on.
- The carbon atom adjacent to carbonyl carbon is labeled as α and next one is β and so on.
-

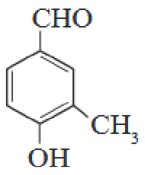
- b. IUPAC names of aldehydes and carboxylic acids :
- The name of an aliphatic aldehyde is by replacing ending ‘e’ of alkane with ‘al ’.
- Aldehyde is named as alkanal.
- The IUPAC name of carboxylic acid is derived from the name of the corresponding alkane by replacing ending ‘e’ of alkane with ‘oic acid ’.
- Alkane ----Alkan<u>al</u>
- Alkane----- Alkan<u>oic</u> <u>acid</u>

- b. IUPAC names of aldehydes ………..:
- The longest chain including –CHO or –COOH group is identified as the parent chain.
- Numbering of the chain is done by giving number 1 to the –CHO or –COOH carbon.
- The name of substituent is included along with its locant.
- Aldehyde (-CHO) grp and carboxyl (-COOH) grp are always terminal.
- When two –CHO grps are present ending ‘e’ of alkane is retained and the suffix ‘dial’ is added parent aldehyde.
- In case of dicarboxylic acids, ‘dioic acid’ is added to the name of the parent alkane.

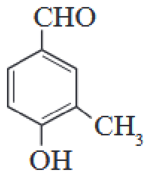
- b. IUPAC names of aldehydes and carboxylic acids:
- In IUPAC nomenclature an alicyclic compound in which –CHO group is attached directly to the ring is named as a carb-aldehyde.
- The suffix ‘carb-aldehyde’ is added after the full name of parent cycloalkane structure.
- Similarly an alicyclic compound having a carboxyl group directly attached to alicyclic ring is named as cycloalkane carboxylic acid

Substituted aromatic aldehydes and carboxylic acids

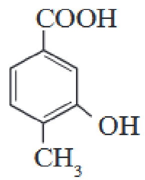
- When two or more different functional groups are attached to a ring, the higher priority grp is given lower number.
- ***NOTE:- The principal functional group is decided on the basis of the following order of priority.-COOH > $-SO_3H$ > -COOR > -COCl > $-CONH_2$ > -CN> -CHO>C = O > -OH > $-NH_2$ > C = C > -C ≡ C-***
- When –CHO group, appears as substituent prefix 'formyl' is used in the IUPAC name



(4-Hydroxy-3-methylbenzaldehyde)



(4-Hydroxy-3-methylbenzaldehyde)



(3-Hydroxy-4-methylbenzoic acid)

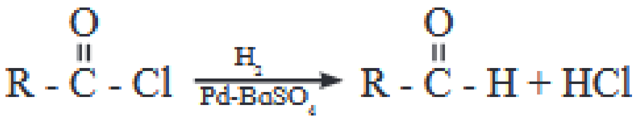
- a. Trivial names of ketones:
- The trivial names of aliphatic ketones are based on the names of alkyl groups or aryl groups attached to carbonyl carbon.
- Names of alkyl or aryl groups are written in alphabetical order followed by the word ketone.
- In substituted aliphatic ketones the position of sub. is indicated by labeling the carbon serially as α, b, γ and so on.
- Names of aromatic ketones are based on a phenone.

- b. The IUPAC names of aliphatic ketones:
- Name of the alkanes by replacing ending ‘e’ of alkane with ‘one’.
- They are named as alkan-one. The longest chain of carbon atoms containing the ketonic carbonyl group is numbered from the end closer to the carbonyl carbon.
- Alkane_____Alkanone
- When two >C=O groups are present, then ending ‘e’ of alkane is retained and the suffix ‘dione’ is added to the name of parent ketone indicating the locants of ketonic carbonyl groups.
- In case of polyfunctional ketones, higher priority group is given lower number.
- When ketonic carbonyl is a lower priority group it is named as 'oxo', preceded by the locant.

Compound	**Trivial name**	**IUPAC name**
CH_3-CO-CH_3	Dimethyl ketone (Acetone)	Propanone
CH_3-CO-CH_2-CH_3	Ethyl methyl ketone	Butanone
CH_3-CO-CH_2-CH_2-CH_3	Methyl n-propyl ketone	Pentan-2-one
CH_3-CH_2-CO-CH_2-CH_3	Diethyl ketone	Pentan-3-one
CH_3-CH(Br)-CO-CH_2-CH_2-CH_3	α-Bromoethyl-n-propyl ketone	2-Bromohexan-3-one

Preparation of aldehydes and ketones

- From acyl chlorides (Acid chlorides) :
- Aldehydes and ketones both can be obtained from acyl chloride, but the reactions involved are different.



$$\mathrm{R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[Pd\text{-}BaSO_4]{H_2} R-\overset{O}{\overset{\|}{C}}-H + HCl}$$

(Acyl chloride) (Aldehyde)

- Preparation of aldehyde from acyl chloride:
- Acyl chloride is reduced to corresponding aldehyde by hydrogen using a palladium catalyst poisoned with barium sulfate. This reaction is known as Rosenmund reduction.

- b. Preparation of ketone (aliphatic and aromatic) from acyl chloride:
- Preparation of aliphatic ketones from acyl chloride:
- ketones are obtained from acyl chloride by reaction with dialkyl cadmium which is prepared by the treatment of cadmium chloride with Grignard reagent.

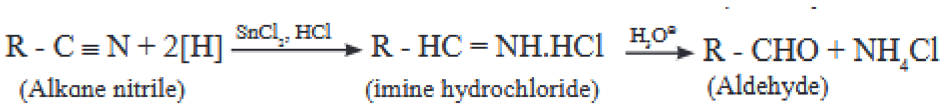
$$2R-MgX + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$

$$\underset{\text{(Acyl chloride)}}{2R'-COCl} + R_2Cd \longrightarrow \underset{\text{(Ketone)}}{2\,R'-CO-R} + CdCl_2$$

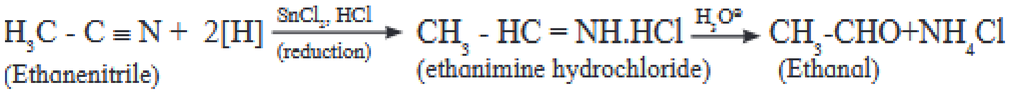
$$\underset{\text{(Ethanoyl chloride)}}{2CH_3-COCl} + \underset{\text{(Dimethyl cadmium)}}{(CH_3)_2Cd} \longrightarrow \underset{\text{Propanone (Acetone)}}{2CH_3\text{-}CO\text{-}CH_3} + CdCl_2$$

$$\underset{\text{(Benzoyl chloride)}}{2C_6H_5-COCl} + \underset{\text{(Dimethyl cadmium)}}{(CH_3)_2Cd} \longrightarrow \underset{\text{(Acetophenone)}}{C_6H_5-CO-CH_3} + CdCl_2$$

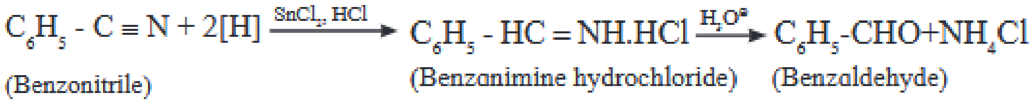
- c. From nitriles : Aldehydes and ketones both can be obtained from nitriles but by different reaction.
- Preparation of aldehydes from nitriles: Nitriles are reduced to imine hydrochloride by stannous chloride in presence of HCl which on acid hydrolysis give corresponding aldehydes. This reaction is called Stephen reaction.



$$\underset{\text{(Alkane nitrile)}}{R-C\equiv N+2[H]}\xrightarrow{SnCl_2,\ HCl}\underset{\text{(imine hydrochloride)}}{R-HC=NH.HCl}\xrightarrow{H_3O^{\oplus}}\underset{\text{(Aldehyde)}}{R-CHO}+NH_4Cl$$



$$\underset{\text{(Ethanenitrile)}}{H_3C-C\equiv N+\ 2[H]}\xrightarrow[\text{(reduction)}]{SnCl_2,\ HCl}\underset{\text{(ethanimine hydrochloride)}}{CH_3-HC=NH.HCl}\xrightarrow{H_3O^{\oplus}}\underset{\text{(Ethanal)}}{CH_3\text{-}CHO}+NH_4Cl$$

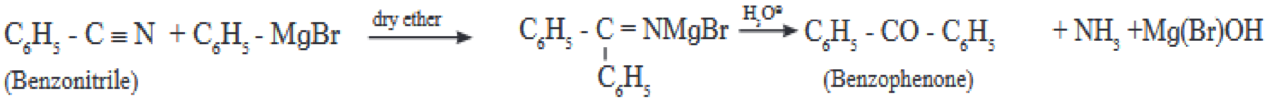


$$\underset{\text{(Benzonitrile)}}{C_6H_5-C\equiv N+2[H]}\xrightarrow{SnCl_2,\ HCl}\underset{\text{(Benzanimine hydrochloride)}}{C_6H_5-HC=NH.HCl}\xrightarrow{H_3O^{\oplus}}\underset{\text{(Benzaldehyde)}}{C_6H_5\text{-}CHO}+NH_4Cl$$

- Alternatively, nitriles are also reduced by diisobutylaluminium hydride (DIBAl-H) or $AlH(i\text{-}Bu)_2$ to imines followed by acid hydrolysis to aldehydes. An advantage of this method is that double or triple bond present in the same molecule is not reduced..

$$\underset{\text{(Pent-3-enenitrile)}}{H_3C-CH=CH-CH_2-C\equiv N} \xrightarrow[H_3O^{\oplus}]{AlH(i\text{-}Bu)_2} \underset{\text{(Pent-3-enal)}}{H_3C-CH=CH-CH_2-CHO}$$

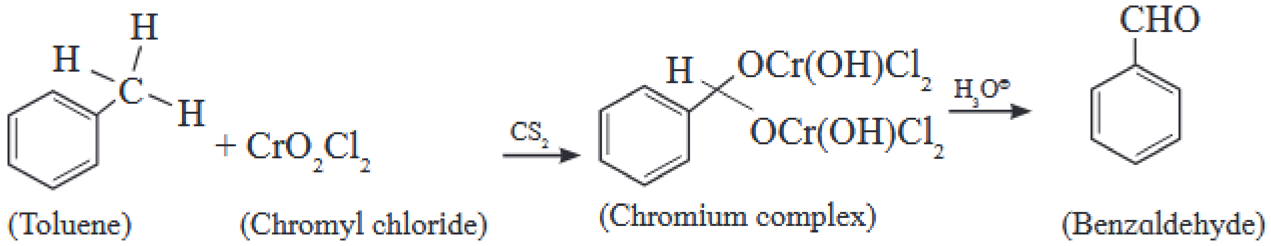
- Preparation of ketones from nitriles: Ketones are prepared by reacting nitriles with Grignard reagent in dry ether as solvent followed by acid hydrolysis.



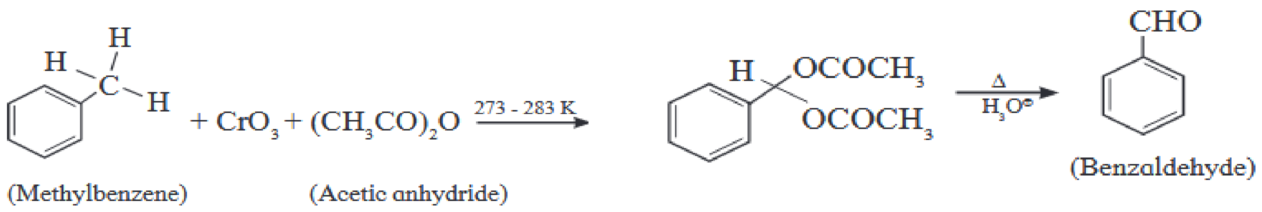
$$\underset{\text{(Benzonitrile)}}{C_6H_5-C\equiv N} + C_6H_5-MgBr \xrightarrow{\text{dry ether}} \underset{\displaystyle C_6H_5}{C_6H_5-\overset{}{C}=NMgBr} \xrightarrow{H_3O^{\oplus}} \underset{\text{(Benzophenone)}}{C_6H_5-CO-C_6H_5} + NH_3 + Mg(Br)OH$$

- d. From aromatic hydrocarbons : Aromatic aldehydes and ketones are both prepared from aromatic hydrocarbons but by different methods.
- Preparation of aromatic aldehydes from hydrocarbon Strong oxidizing agents transform -CH3 group bonded to aromatic ring into carboxyl group (-COOH). For obtaining aromatic aldehyde from methyl arene the following special methods are used.

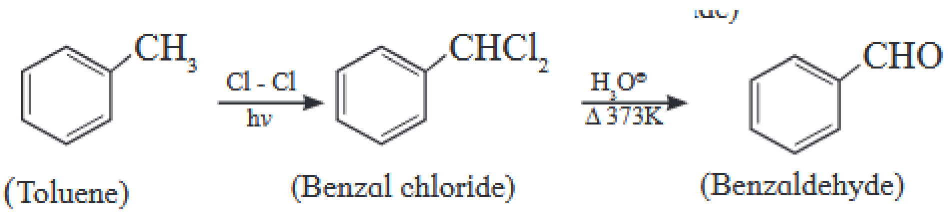
- i. Etard reaction : Methyl group in methyl benzene (or methyl arene) is oxidized by chromyl chloride in carbon disulfide as solvent, to form a chromium complex, from which benzaldehyde is obtained on acid hydrolysis. This reaction is known as Etard reaction.



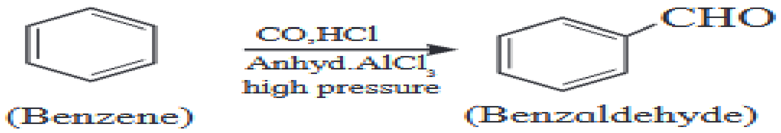
- By oxidation of methyl arene using CrO3:
- Methylarene is converted into a benzylidene diacetate on treatment with chromium oxide in acetic anhydride at 273-278 K. The diacetate derivative on acid hydrolysis gives corresponding aldehyde



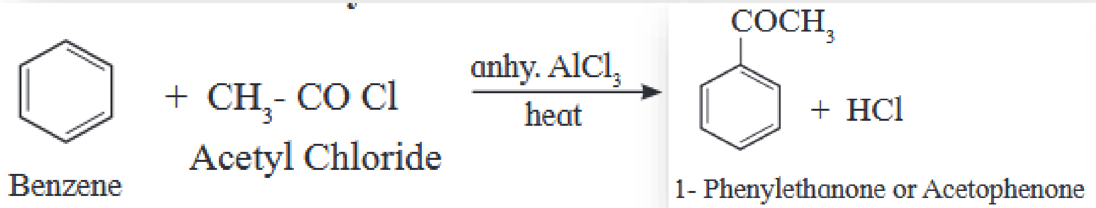
- iii. By side chain chlorination of toluene:
- Side chain chlorination of toluene gives benzal-chloride which on acid hydrolysis at 373K gives benzaldehyde. Benzaldehyde, is manufactured commercially by this method.

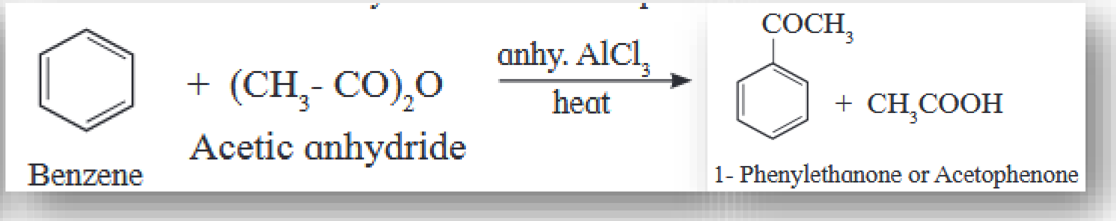


- Benzene or substituted benzene is treated under high pressure with carbon monoxide and hydrogen chloride in presence of anhydrous aluminium chloride or cuprous chloride to give benzaldehyde or substituted benzaldehyde. This reaction is known as Gatterman- Koch reaction

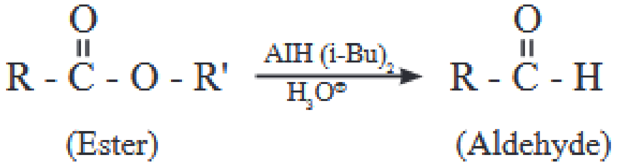


- Preparation of Aromatic ketones from hydrocarbons :
- By Friedel-crafts acylation of arene :





- Preparation of aldehydes only from esters :
- Aliphatic or aromatic esters are reduced to aldehydes by using diisobutylaluminium hydride DIBAL-H or $AlH(i\text{-}Bu)_2$. The reaction is usually carried out at 195K to prevent further reduction of the aldehyde produced.



$$\underset{\text{(Ester)}}{R-\overset{\overset{O}{\|}}{C}-O-R'} \xrightarrow[H_3O^{\oplus}]{AlH\,(i\text{-}Bu)_2} \underset{\text{(Aldehyde)}}{R-\overset{\overset{O}{\|}}{C}-H}$$

THANK YOU