CHEM 245

Organic Chemistry II

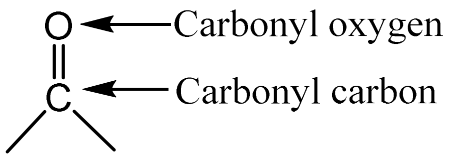
PRE-REQUISITES COURSE; CHEM 240
CREDIT HOURS; 2 (2+0)

ALDEHYDES AND KETONES

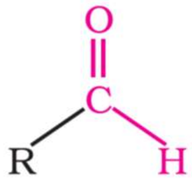
Carbonyl Compounds

- **Organic compounds** containing carbon-oxygen double bond (>C=O) called ***carbonyl group***, which is one of the most important functional groups in organic chemistry.

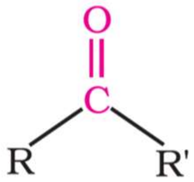
- In **aldehydes**, the carbonyl group is bonded to a carbon and hydrogen.
- In the **ketones**, the carbonyl group is bonded to two carbon atoms.
- In **Carboxylic acids**, the carbonyl group is bonded to oxygen.
- Their **Carboxylic acids derivatives** (e.g. esters, anhydrides, amides and acyl halides).



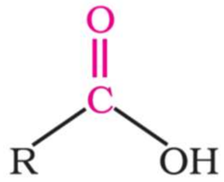
The carbonyl group



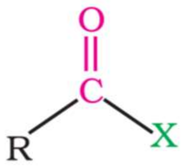
Aldehyde



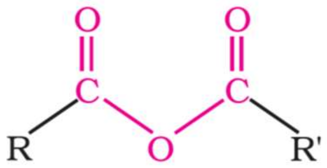
Ketone



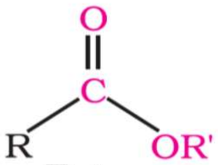
Carboxylic acid



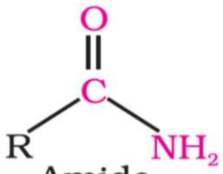
Acyl halide; X = (Halogen)



Acid anhydride



Ester

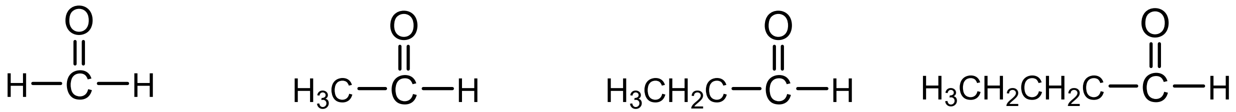


Amide

Nomenclature of Aldehydes

A) Common Names

- The **common names of most aldehydes** are derived from the common names of the corresponding carboxylic acids by *replacing the ending –ic of acid with aldehyde*.

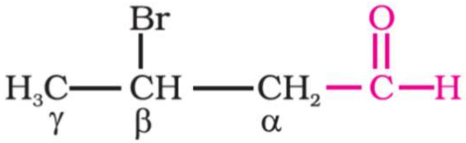


$$H-\overset{\overset{O}{\|}}{C}-H \quad H_3C-\overset{\overset{O}{\|}}{C}-H \quad H_3CH_2C-\overset{\overset{O}{\|}}{C}-H \quad H_3CH_2CH_2C-\overset{\overset{O}{\|}}{C}-H$$

Common name:	Formaldehyde	Acetaldehyde	Propionaldehyde	Butyraldehyde
IUPAC name:	Methanal	Ethanal	Propanal	Butanal

- The location of the substituent in the carbon chain is indicated by Greek letters α, β, γ, δ, etc.

The α-carbon being the one directly linked to the aldehyde group, β-carbon the next, and so on.



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

β-Bromobutyraldehyde

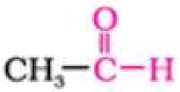
Nomenclature of Aldehydes

B) IUPAC System

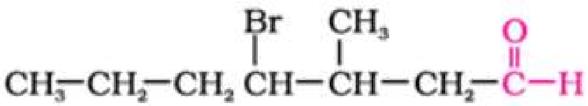
- **Aliphatic aldehydes** are named by **dropping the suffix -*e*** from the name of the hydrocarbon that has the same carbon skeleton as the aldehyde and **replacing it with the suffix *-al***.

Alkane - e + *al* = Alkanal

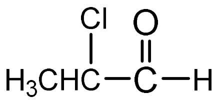
- In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group. **The CHO group is assigned the number 1 position.**


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

Ethanal


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

4-Bromo-3-methylheptanal

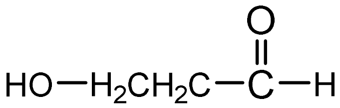

$H_3CH\overset{\overset{Cl}{|}}{C}-\overset{\overset{O}{\|}}{C}-H$

2-Chloropropanal

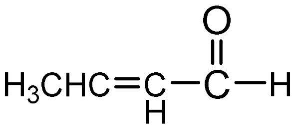
- **The CHO group takes precedence over other functional groups such as -OH, C=C, or C-C triple bond.**


$CH_3-CH_2-CH=CH-\overset{\overset{O}{\|}}{C}-H$

Pent-2-enal


$HO-H_2CH_2C-\overset{\overset{O}{\|}}{C}-H$

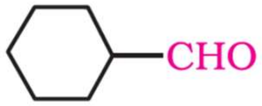
3-Hydroxypropanal


$H_3CHC=\underset{H}{C}-\overset{\overset{O}{\|}}{C}-H$

2-Butenal

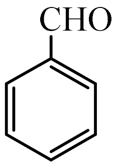
Nomenclature of Aldehydes

- When the **aldehyde group is attached to a ri**ng, the *suffix carbaldehyde is added after the full name of the cycloalkane*.

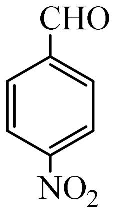


Cyclohexanecarbaldehyde

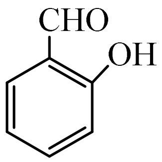
- The name of the simplest **aromatic aldehyde** carrying the aldehyde group on a benzene ring is benzene carbaldehyde.
- However, **the common name benzaldehyde is also accepted by IUPAC**.
- **Other aromatic aldehydes** are hence named as **substituted benzaldehydes**.



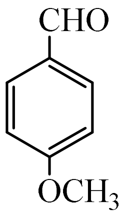
Benzaldehyde
(Benezenecarbaldehyde)



p-Nitrobenzaldehyde
4-Nitrobenzaldehyde
4-Nitrobenzenecarbaldehydealdehyde



o-Hydroxybenzaldehyde
(Salicylaldehyde)



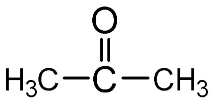
p-Methoxybenzaldehyde
(Anisaldehyde)

Nomenclature of Ketones

A) Common Names

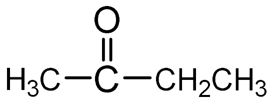
○ The **common names of ketones** are derived by naming two alkyl or aryl groups bonded to the carbonyl group.

Alkyl ketone



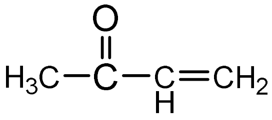
$H_3C-\overset{\overset{O}{\|}}{C}-CH_3$

Acetone
(Dimethyl ketone)



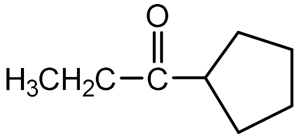
$H_3C-\overset{\overset{O}{\|}}{C}-CH_2CH_3$

Methyl ethyl ketone



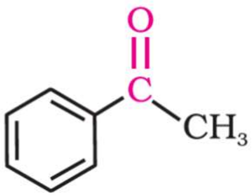
$H_3C-\overset{\overset{O}{\|}}{C}-\underset{H}{C}=CH_2$

Methyl vinyl ketone

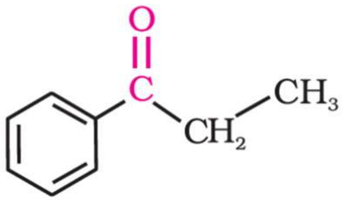


Ethyl cyclopentyl ketone

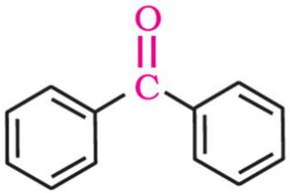
○ Alkyl phenyl ketones are usually named by adding the acyl group as prefix to phenone.



Acetophenone



Propiophenone



Benzophenone

○ The **locations of substituents** are indicated by Greek letters, α, β and so on beginning with the carbon atoms next to the carbonyl group, indicated as α.

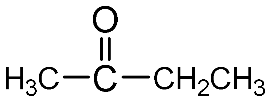
Nomenclature of Ketones

B) IUPAC System

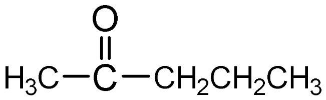
- We find the longest continuous chain carrying the carbonyl group.
- Name the parent structure by **dropping the suffix –e**, and replacing it with the **suffix *-one***.

Alkane - e + *one* = Alkanone

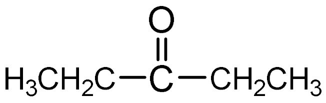
- The **numbering** begins from the end nearer to the carbonyl group.
- The **substituents** are prefixed in alphabetical order along with numerals indicating their positions in the carbon chain.


$H_3C-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

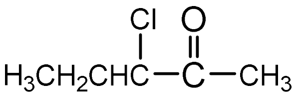
Butanone


$H_3C-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$

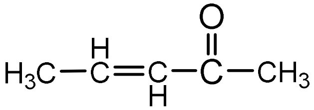
2-Pentanone
(*not* 4-Pentanone)


$H_3CH_2C-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

3-Pentanone

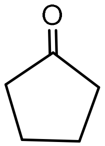

$H_3CH_2CH\overset{Cl}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$

3-Chloro-2-pentanone
(*not* 3-Chloro-4-pentanone)

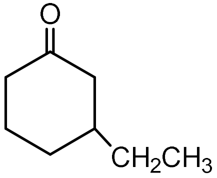

$H_3C-\overset{H}{C}=\underset{H}{C}-\overset{O}{\overset{\|}{C}}-CH_3$

3-Penten-2-one
(*not* 2-Penten-4-one)

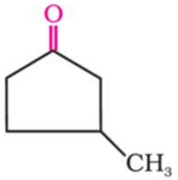
- For **cyclic ketones**, numbering always starts from the C=O group; the carbonyl carbon is numbered one.



Cyclopentanone

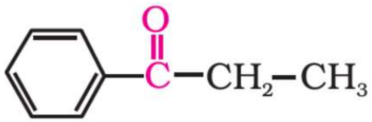


3-Ethlcyclohexanone
(*not* 5-Methylcyclohexanone)

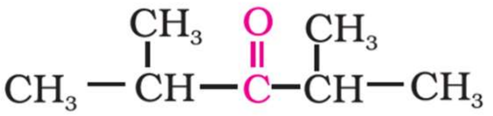


3-Methylcyclopentanone

Nomenclature of Aldehydes and Ketones; Examples

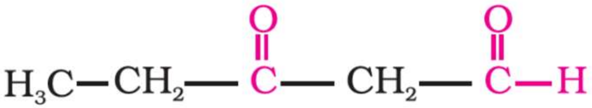


1-Phenylpropan-1-one



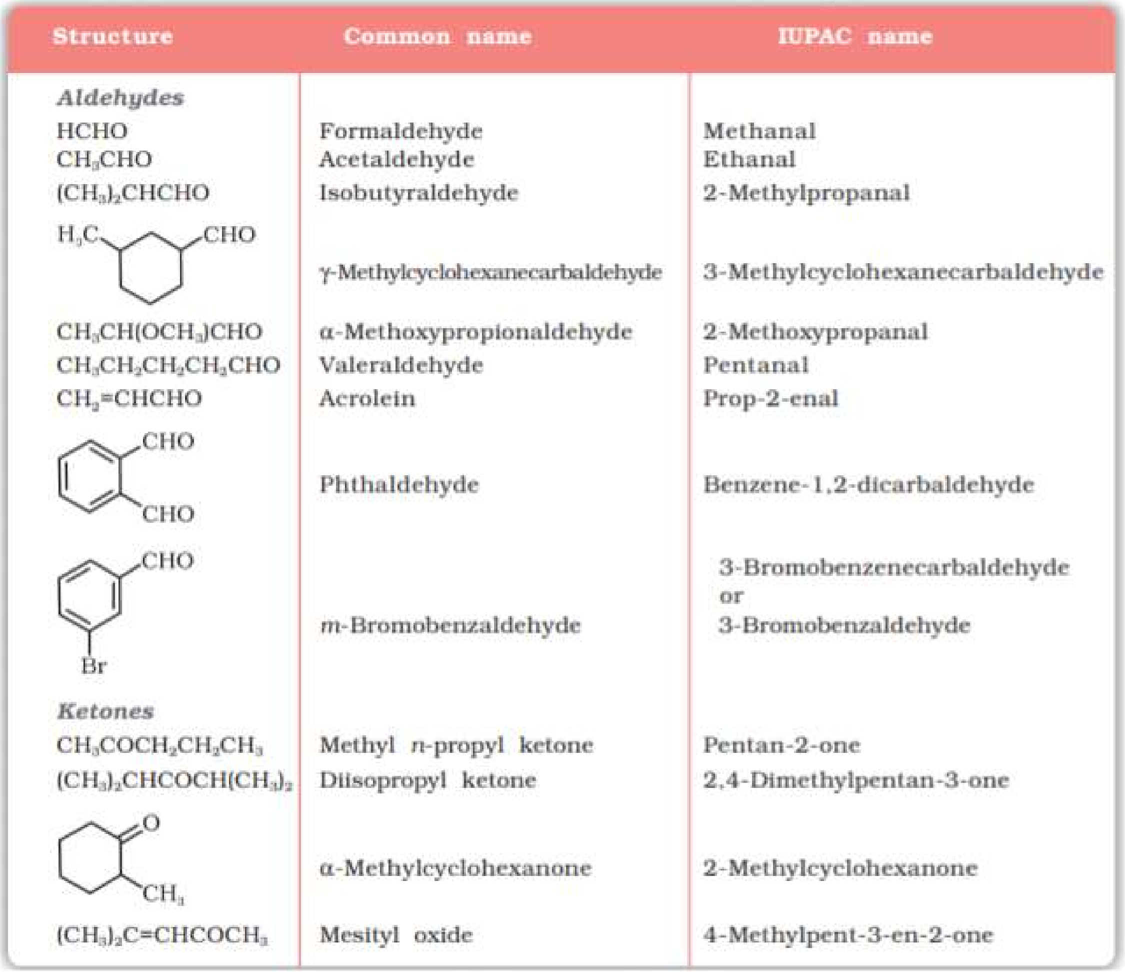
$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

2,4-Dimethylpentan-3-one



$$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

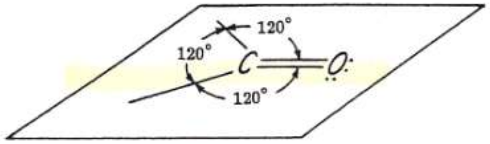
3-Oxopentanal

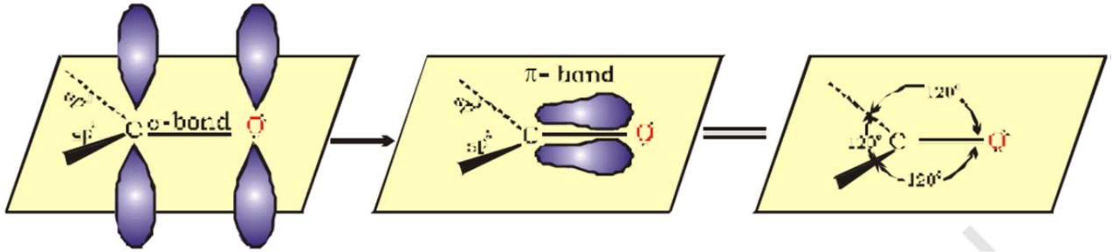


Structure	Common name	IUPAC name
Aldehydes		
$HCHO$	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$(CH_3)_2CHCHO$	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexanecarbaldehyde	3-Methylcyclohexanecarbaldehyde
$CH_3CH(OCH_3)CHO$	α-Methoxypropionaldehyde	2-Methoxypropanal
$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
$CH_2{=}CHCHO$	Acrolein	Prop-2-enal
	Phthaldehyde	Benzene-1,2-dicarbaldehyde
	m-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
Ketones		
$CH_3COCH_2CH_2CH_3$	Methyl *n*-propyl ketone	Pentan-2-one
$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
$(CH_3)_2C{=}CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one

Structure of the Carbonyl Group

- The carbonyl carbon atom is ***sp^2-hybridised*** and forms ***three sigma (σ) bonds and one π-bond***.
- In addition, *the oxygen atom also has two non bonding electron pairs*.
- The **bond angles are approximately 120°** as expected of a trigonal coplanar structure





Orbital diagram for the formation of carbonyl group

- The carbon-oxygen double bond ***is polarized*** due to higher electronegativity of oxygen relative to carbon.
- Hence, ***the carbonyl carbon is an electrophilic*** (Lewis acid), and ***carbonyl oxygen, a nucleophilic*** (Lewis base).
- The high polarity of the carbonyl group is explained on the basis of **resonance**.

Questions

Write the structures of the following compounds:

1) α-Methoxy propionaldehyde
2) 3-Hydroxybutanal
3) 2-Hydroxycyclopentane carbaldehyde
4) 4-Oxopentanal
5) 4-Fluoroacetophenone

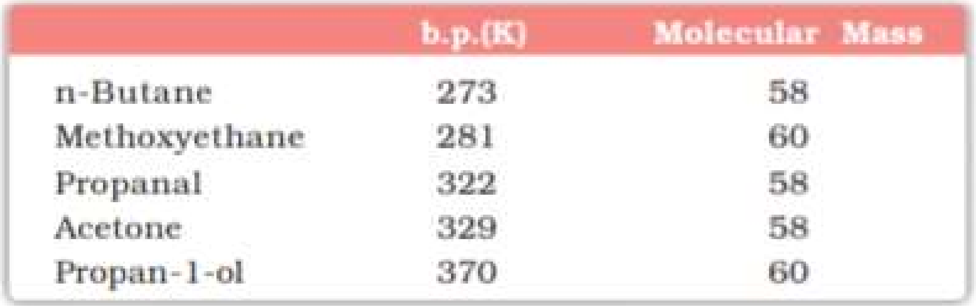
Physical Properties of Aldehydes and Ketones

○ Physical State

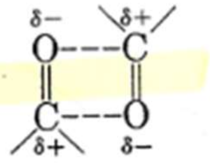
- **Methanal** is a gas at room temperature.
- **Ethanal** is a volatile liquid.
- **Other aldehydes and ketones** are liquid or solid at room temperature.

○ Boiling Points

- The boiling points of aldehydes and ketones are **higher than hydrocarbons and ethers** of comparable molecular masses.
- Also, their boiling points are **lower than those of alcohols** of similar molecular masses *due to absence of intermolecular hydrogen bonding*.



	b.p.(K)	Molecular Mass
n-Butane	273	58
Methoxyethane	281	60
Propanal	322	58
Acetone	329	58
Propan-1-ol	370	60



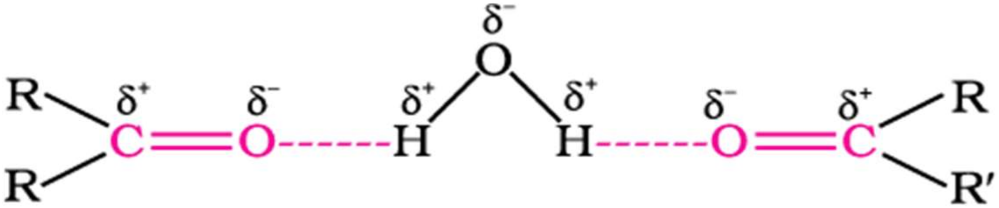
Dipole-dipole attractions among carbonyl compounds

Dipole-dipole attractions, although important, are not as strong as interactions due to hydrogen bonding.

Physical Properties of Aldehydes and Ketones

○ Solubility in Water

- The ***lower members of aldehydes and ketones*** such as methanal, ethanal and propanone are ***miscible with water*** in all proportions, because *they form hydrogen bond with water*.



- However, *the solubility of aldehydes and ketones decreases* rapidly *on increasing the length of alkyl chain*.
- All aldehydes and ketones are *fairly soluble in organic solvents* like benzene, ether, methanol, chloroform, etc.
- The lower aldehydes have sharp pungent odors.
- As the size of the molecule increases, the odor becomes less pungent and more fragrant.
- In fact, many naturally occurring aldehydes and ketones are used in the blending of perfumes and flavoring agents.

Questions

Arrange the following compounds in the increasing order of their boiling points:

$CH3CH2CH2CHO$, $CH3CH2CH2CH2OH$, $H5C2\text{-}O\text{-}C2H5$, $CH3CH2CH2CH3$

Solution

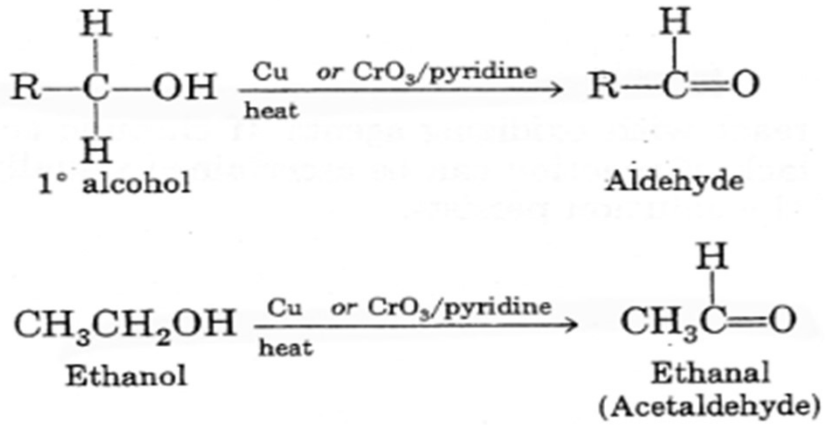
The molecular masses of these compounds are in the range of 72 to 74. Since only butan-1-ol molecules are associated due to extensive intermolecular hydrogen bonding, therefore, the boiling point of butan-1-ol would be the highest. Butanal is more polar than ethoxyethane. Therefore, the intermolecular dipole-dipole attraction is stronger in the former. n-Pentane molecules have only weak van der Waals forces. Hence increasing order of boiling points of the given compounds is as follows:

$CH3CH2CH2CH3 < H5C2\text{-}O\text{-}C2H5 < CH3CH2CH2CHO < CH3CH2CH2CH2OH$

Preparation of Aldehydes and Ketones

1. By oxidation of Alcohols

Aldehydes and ketones are generally prepared by **oxidation of primary and secondary alcohols***, respectively.*



$$R-\overset{H}{\underset{H}{C}}-OH \xrightarrow[\text{heat}]{\text{Cu} \quad or\ CrO_3/\text{pyridine}} R-\overset{H}{C}=O$$

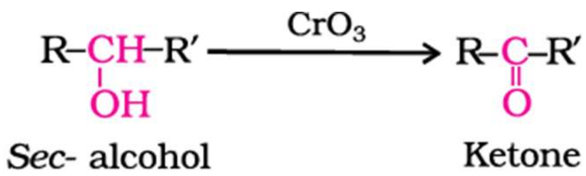
1° alcohol

Aldehyde

$$CH_3CH_2OH \xrightarrow[\text{heat}]{\text{Cu} \quad or\ CrO_3/\text{pyridine}} CH_3\overset{H}{C}=O$$

Ethanol

Ethanal
(Acetaldehyde)



$$R-\underset{OH}{CH}-R' \xrightarrow{CrO_3} R-\underset{O}{\overset{}{C}}-R'$$

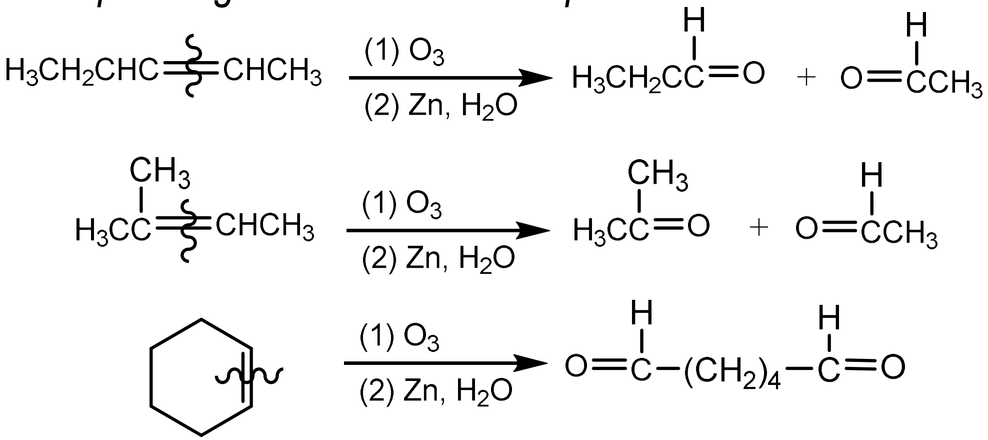
Sec- alcohol

Ketone

Preparation of Aldehydes and Ketones

2. From Hydrocarbons

(i) Ozonolysis of Alkenes: *Ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes, ketones or a mixture of both depending on the substitution pattern of the alkene.*

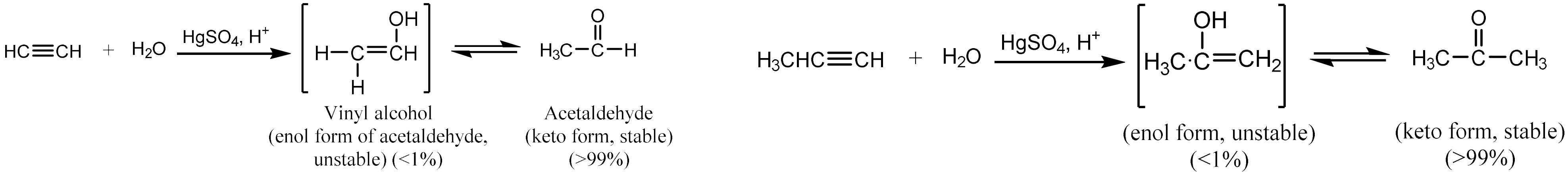


$$H_3CH_2CHC{=}CHCH_3 \xrightarrow[(2)\ Zn,\ H_2O]{(1)\ O_3} H_3CH_2C\overset{H}{C}{=}O + O{=}\overset{H}{C}CH_3$$

$$H_3C\overset{CH_3}{C}{=}CHCH_3 \xrightarrow[(2)\ Zn,\ H_2O]{(1)\ O_3} H_3C\overset{CH_3}{C}{=}O + O{=}\overset{H}{C}CH_3$$

$$\xrightarrow[(2)\ Zn,\ H_2O]{(1)\ O_3} O{=}\overset{H}{C}{-}(CH_2)_4{-}\overset{H}{C}{=}O$$

(ii) Hydration of Alkynes: *Addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde. All other alkynes give ketones in this reaction*



$$HC{\equiv}CH + H_2O \xrightarrow{HgSO_4,\ H^+} \left[H{-}\underset{H}{C}{=}\overset{OH}{C}H\right] \rightleftharpoons H_3C{-}\overset{O}{\overset{\|}{C}}{-}H$$

Vinyl alcohol
(enol form of acetaldehyde, unstable) (<1%)

Acetaldehyde
(keto form, stable)
(>99%)

$$H_3CC{\equiv}CH + H_2O \xrightarrow{HgSO_4,\ H^+} \left[H_3C{\cdot}\overset{OH}{C}{=}CH_2\right] \rightleftharpoons H_3C{-}\overset{O}{\overset{\|}{C}}{-}CH_3$$

(enol form, unstable)
(<1%)

(keto form, stable)
(>99%)

Preparation of Aldehydes and Ketones

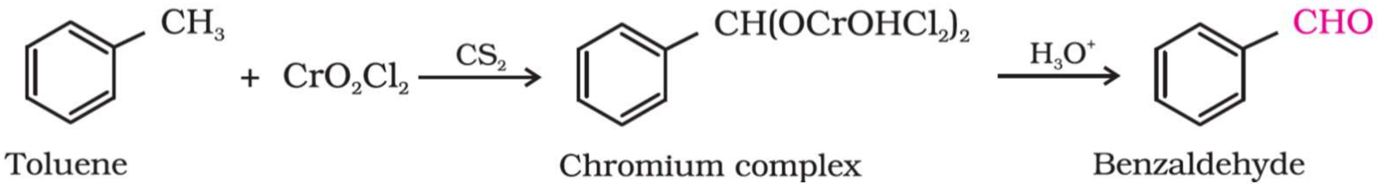
2. From Hydrocarbons

(iii) By oxidation of methylbenzene

Strong oxidizing agents oxidize toluene and its derivatives to benzoic acids.
However, it is possible to stop the oxidation at the aldehyde stage with suitable reagents.

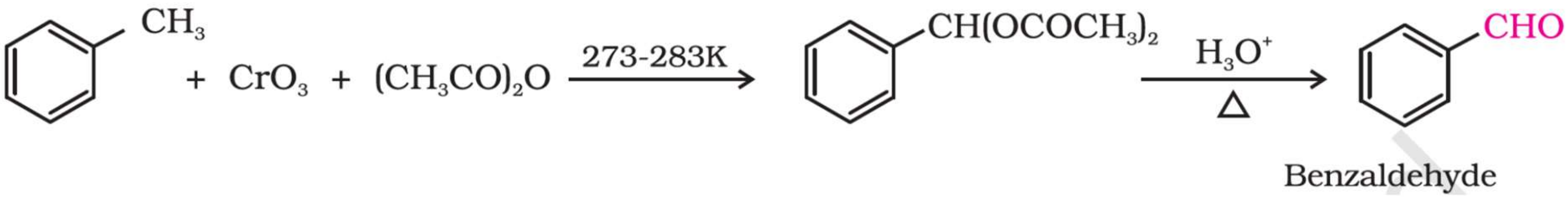
(a) Use of chromyl chloride (CrO_2Cl_2) (Etard reaction):

Chromyl chloride oxidizes methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.



(b) Use of chromic oxide (CrO_3):

Toluene or substituted toluene is converted to benzylidene diacetate on treating with chromic oxide in acetic anhydride.
The benzylidene diacetate can be hydrolysed to corresponding benzaldehyde with aqueous acid.



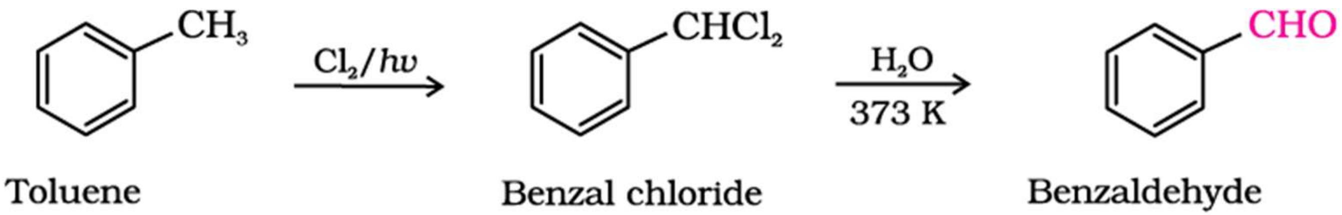
Preparation of Aldehydes and Ketones

2. From Hydrocarbons

(iv) By side chain chlorination followed by hydrolysis

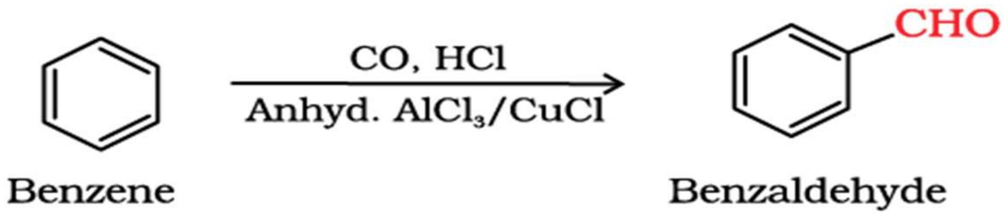
Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde.

This is a commercial method of manufacture of benzaldehyde.



(v) By Gatterman – Koch reaction

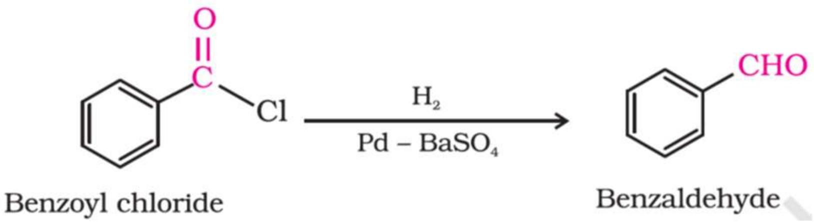
When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminum chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.



Preparation of Aldehydes and Ketones

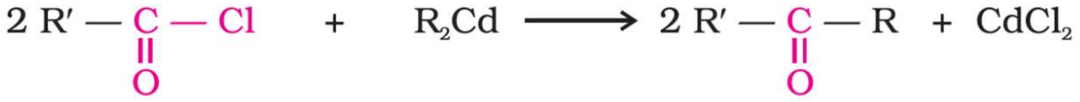
3. From Acyl Chloride (Acid Chloride) (*Rosenmund Reduction*)

- *Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate, **gives aldehyde**.*



- *Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, **gives ketones**.*

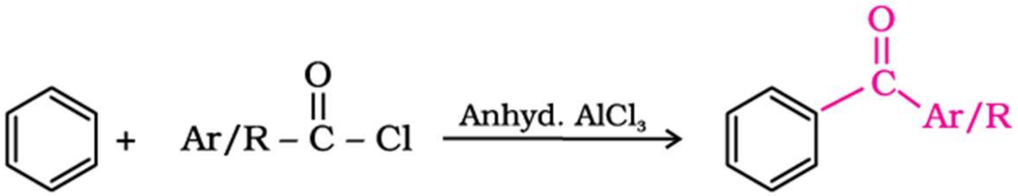
$$2\,R-Mg-X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$



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

4. From Benzene or Substituted Benzenes (Friedel-Crafts acylation reaction)

*When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminum chloride, it affords the corresponding **ketone**.*



Preparation of Aldehydes and Ketones

5. From Nitriles and Esters (*Stephen Reaction*)

- ***Nitriles are reduced*** *to corresponding imine with stannous chloride in the presence of hydrochloric acid,* ***which on hydrolysis*** *give corresponding* ***aldehyde****.*

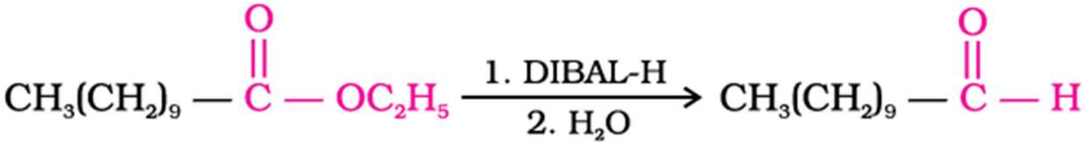
$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3\overset{+}{O}} RCHO$$

- ***Nitriles*** *are selectively reduced by diisobutylaluminium hydride, (DIBAL-H) to imines followed by hydrolysis to* ***aldehydes****:*

$$RCN \xrightarrow[\text{2. } H_2O]{\text{1. } AlH(i\text{-}Bu)_2} R\text{-}CHO$$

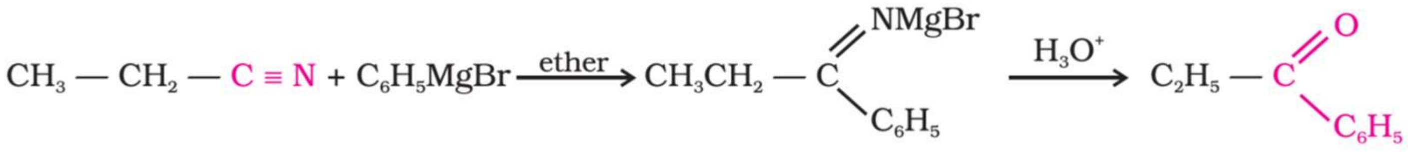
$$CH_3 - CH{=}CH\text{-}CH_2CH_2\text{-}CN \xrightarrow[\text{2. } H_2O]{\text{1. } AlH(i\text{-}Bu)_2} CH_3 - CH{=}CH\text{-}CH_2CH_2\text{-}CHO$$

- ***Esters are also reduced*** *to* ***aldehydes*** *with DIBAL-H.*



$$CH_3(CH_2)_9 - \overset{O}{\overset{\|}{C}} - OC_2H_5 \xrightarrow[\text{2. } H_2O]{\text{1. DIBAL-H}} CH_3(CH_2)_9 - \overset{O}{\overset{\|}{C}} - H$$

- ***Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone****.*



Propiophenone
(1-Phenylpropanone)