# **CARBONYL COMPOUNDS**

# 1. Introduction

These have general formula  $C_nH_{2n}O$  and contains > C O group which is present in aldehyde  $\frac{R}{H}C=0$ 

and  $\begin{bmatrix} R \\ R \end{bmatrix} C = O$  ketone. Thus aldehydes and ketones are collectively called as carbonyl compounds

# 5. IUPAC Nomenclature of Aldehydes and Ketones

	Ketones	IUPAC name
1.	O    CH <sub>3</sub> – C – CH <sub>3</sub>	Propanone
2.	O    CH <sub>3</sub> – C – CH <sub>2</sub> – CH <sub>3</sub>	Butanone
3.	$O$ $CH_3 - C - CH_2 - CH_2 - CH_3$	Pentan-2-one
4.	O O II II CH <sub>3</sub> - C - C - CH <sub>3</sub>	Butanedione
5.	CH <sub>3</sub> O CH <sub>3</sub>         CH <sub>3</sub> - CH - C - CH - CH <sub>3</sub>	2, 4-Dimethyl pentan-3-one
6.	$\begin{array}{c} O \\ \parallel \\ C - CH_2 - CH_3 \end{array}$	1-Phenylpropan-1-one
7.	Nurturing potenti	3-Methylcyclopentanone
8.		Cyclohex-2-en-1-one or 2-Cyclohexenone
9.	O OH    CH <sub>3</sub> - C - CH <sub>2</sub> - C - CH <sub>3</sub> CH <sub>3</sub>	4-Hydroxy-4-methyl pentan-2-one

	Ketones	IUPAC name
		201 AC Hame
10.	O      CH₃ – C – H	Ethanol
11.	O     CH <sub>3</sub> - CH <sub>2</sub> - C - H	Propanol
12.	O     CH <sub>3</sub> - CH <sub>2</sub> - CH <sub>2</sub> - C - H <sub>3</sub>	Butanol
13.	OH O	3-Hydroxybutanal
14.	$CH_3 - CH_2 - CH = CH - CHO$	Pent-2-en-1-el
	Br CH₃ O	or Pen-2-enal
15.	Br CH <sub>3</sub> O          CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> - CH - CH - CH <sub>2</sub> - C - H	4-Bromo-3-methyl heptanal
16.	СНО	Cyclohexanecarbaldehyde
17.	ОН	2-Hydroxycyclopentane -1-carbaldehyde
18.	O    	3-Oxopentanal
19.	П СН₃ – С – СН₂ – СООН Ω	3-Oxobutanoic acid
20.	COOH COOH	2-Formylbenzoic acid IIT-JEE AIE
21.	Nurturing pote	ntial through education 2-(3-oxobutyl)-cyclohexanone
22.		2-ethylhex-2-en-1-al
23.		2,5-dimethylheptan-3-one
24.	CH <sub>3</sub> - CH - CH - CH = O	3-chloro-2-methylbutanal
25.	CI CH <sub>3</sub>	3-ethycylobutanone

#### 8. General methods of preparation of Aldehyde and Ketones

#### **(I) Hydration of Alkyne:**

It is addition of water in the presence of heavy metal ion, acetylene on hydration gives aldehyde while any higher alkyne gives ketone.

$$H - C \equiv C - H \xrightarrow{Hg^{++}/H_2SO_4} CH_3 - CH = O$$

$$R - C \equiv C - H \xrightarrow{Hg^{++}/H_2SO_4} R - G - CH_3$$

The preparation of carbonyl compounds from alkyne depends upon R part of (A) and also presence of inductive effect group attached to R.

#### **(II) Hydroboration of alkyne:**

It is used to get aldehyde from alkyne-1. Here reagent is (i) diborane  $(B_2H_6)$  (ii)  $H_2O_2(OH^-)$ 

$$R - C \equiv C - H \xrightarrow{(i) B_2H_6} R - CH_2 - CH = O$$

In this reaction Borane ( $BH_3$ ) is electrophile.

$$3R - C \equiv C - H \xrightarrow{BH_3} (R - CH = CH)_3 B \xrightarrow{H_2O_2} R - CH = CH - OH \rightleftharpoons R - CH_2 - CH = O$$

Higher alkyne except alkyne-1 will give ketone during hydroboration

$$CH_3 - CH_2 - C = C - CH_2 - CH_3 \xrightarrow{(i) BH_3, THF} CH_3 - CH_2 - C - CH_2 - CH_2 - CH_3$$

#### (III) Ozonolysis of alkene:

Ex.

It is used to get carbonyl compounds from alkene. The reaction is

$$R_1 \longrightarrow R_2 \longrightarrow R_2 \longrightarrow R_3 \longrightarrow R_4 \longrightarrow R_2 \longrightarrow R_4 \longrightarrow R_2 \longrightarrow R_4 \longrightarrow R_2 \longrightarrow R_2 \longrightarrow R_4 \longrightarrow R_4$$

$$CH_{3}-CH=C-CH_{3}$$

$$CH_{3}-CH=C-CH_{3}$$

$$CH_{3}-CH=C-CH_{3}$$

$$CH_{3}-CH=CH_{3}$$

$$CH_{3}-CH=CH=CH_{3}$$

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$$CH_{3}-CH=CH_{3}$$

$$CH_{3}-CH=CH_{3}$$

$$CH_{3}-CH=CH_{3}$$

$$CH_{3}-CH=CH_{3}$$

$$CH_{3}$$

$$H_2O \longrightarrow CH_3 - CH = O + CH_3 \longrightarrow CH_3 = O + H_2O_2$$

$$CH_3 - CH_3 = O + H_2O_3$$

### Note:

(I) During the cleavage of ozonide Zn is used to check further oxidation of aldehyde into acid.

(II) By this method we can locate double bond in olefin or exact structure of hydrocarbon can be determined by knowing ozonclysis product i.e. by placing double bond at the place oftwo carbonyl oxygen of two carbonyl compounds.

# (V) Dehydrogenation of Alcohol:

Dehydrogenation means removal of hydrogen and reagent used is heated copper.

1º alcohol (RCH<sub>2</sub>OH) 
$$\xrightarrow{\text{Cu/300°C}}$$
 Aldehyde (R-CH = O)

2º alcohol (R<sub>2</sub>CHOH) 
$$\xrightarrow{\text{Cu/300°C}}$$
 Ketone (R<sub>2</sub>C = 0)

3° alcohol 
$$\xrightarrow{\text{Cu/300°C}}$$
 Alkene

# (VI) Dry distillation of Calcium salt of acid:

$$(RCOO)_2Ca$$
  $\xrightarrow{\Delta}$   $R - C - R + CaCO_3$   
Ketone

# (VII) On passing vapours of fatty acids over Magnous oxide at 300°C.

2 RCOOH 
$$\xrightarrow{\text{MnO}/300^{\circ}\text{C}}$$
 R - C - R + CO<sub>2</sub> + H<sub>2</sub>O (Vap) Ketone

On passing mixture of vapours of fatty acid with formic acid we get a mixture of aldehyde, ketone and formaldehyde.

# (VIII) On aqueous alkall hydrolysis of gem-dihalides:

Terminal gemdihalides with give aldehyde while non-terminal will give ketones as follows

$$R - CHCl_2 \xrightarrow{\text{aq. KOH}} R - CH \xrightarrow{\text{OH}} \xrightarrow{-H_2O} R - CH = O$$
Aldehyde

$$R - C - R' \xrightarrow{aq. KOH} R - C - R' \xrightarrow{-H_2O} R - C - R'$$

$$CI \qquad OH \qquad OH \qquad OH \qquad OH$$

$$CI \qquad OH \qquad OH \qquad OH$$

# (IX) Wacker Process:

Alkenes can directly be oxidised to corresponding aldehydes or ketone by treating them with a solution of  $PdCl_2$  containing a catalytic amount of  $CuCl_2$  in presence of air or  $O_2$ . Except ethene any higher alkene will give ketone.

$$CH_2 = CH_2 + H_2O + PdCl_2 \xrightarrow{CuCl_2} CH_3 - CH = O + Pd + 2HCl$$

$$R - CH = CH2 + H2O + PdCl2 \xrightarrow{\text{CuCl}_2} R - C - CH3 + Pd + 2HCl$$

Note: During the reaction PdCl, is reduced to Pd and CuCl, is reduced to Cu(1)

# (X) Preparation of Carbonyl compounds using Grignard's Reagent:

(a) Hydrogen cyanide on treating with Grignard reagent followed by double decomposition with water gives aldehyde via imine.

$$H - C = NH \xrightarrow{R} MgBr \longrightarrow H - C = NMgBr \xrightarrow{H_2O/H^+} H - C = NH \xrightarrow{H_2O/H^+} H - C = O + NH_3$$
 $\downarrow R$ 
 $\downarrow R$ 

Alkylcyanide by using above process gives ketone via ketimine

$$R' - C = NH \xrightarrow{H_2O/H^+} R' - C = NMgBr \xrightarrow{H_2O/H^+} R' - C = NH \xrightarrow{H_2O/H^+} R' - C = O + NH_3$$

$$R = R \xrightarrow{R} R$$
Ketimine Aldehyde

(b) Alkylformate with Grignard reagent gives 2° alcohol via aldehyde while alkyl alkanoate under similar condition gives 3° alcohol via ketone

$$\begin{array}{c} O \\ H - C - OC_2H_5 \\ \text{ethyllmethanoate} \end{array} + R - MgBr \longrightarrow H - C - OC_2H_5 \xrightarrow{H_3O^+} R - CH = O \xrightarrow{(i)} R - MgBr \\ R \\ \end{array} \longrightarrow \begin{array}{c} O \\ H_3O^+ \\ \hline -MgBr(OC_2H_5) \end{array} \rightarrow R - CH = O \xrightarrow{(ii)} R - MgBr \\ \hline (iii) H_2O/H^+ \\ R \\ \end{array} \longrightarrow \begin{array}{c} C - OC_2H_5 \\ R \\ \hline 2 - \text{alcohol} \end{array}$$

$$\begin{array}{c} O\\ I\\ R'-C-OC_2H_5\\ \end{array} + R-MgBr \longrightarrow R'-C-OC_2H_5 \\ \end{array} \begin{array}{c} O\\ H_3O\\ \end{array} \begin{array}{c} O\\ R'-C-OC_2H_5\\ \end{array} \begin{array}{c} H_3O\\ \end{array} \begin{array}{c} R'-C-C=O\\ \end{array} \begin{array}{c} (i) R-MgBr\\ \end{array} \begin{array}{c} R-CH-OH\\ \end{array} \\ R \end{array}$$
 ethyllmethanoate

# (A) Methode used for the preparation of Aldehydes only.

### (i) Rosenmund's reaction:

Here acid chlorides are reduced to aldehyde with  $H_2$  in boiling xylene using palladium as a catalyst supported on barium sulphate.

$$R - C - CI + H_2 \xrightarrow{Pd-BaSO_4} R - C \xrightarrow{O} + HCI$$
Boiling Xylene

### (ii) Stephen's reduction:

$$R - C = N \xrightarrow{SnCl_2/HCl} R - CH = NHHCl \xrightarrow{H_2O} R - CH = O + NH_4Cl$$

Aldimine hydrochloride

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# (iii) Oxo-process:

It is also called as carbonylation here alkene reacts with water gas at high temperature and pressure in the presence of cobalt carbonyl catalyst to give aldehyde.

$$R - CH = CH2 \xrightarrow{CO+H2/\Delta, Pressure} R - CH - CH3 + R - CH2 - CH2 - CH = O$$

$$CH = O$$

# (iv) Reimer-Teimann Reaction:

By this method phenolic aldehyde is prepared

# (B) Methods used for the preparation of Ketones only

# (i) Using alkanoyl chloride and Grignard reagent

O II 
$$R - C - CI + R' - Mg - CI \longrightarrow R - C - R' + MgCl_2$$

# (ii) Using alkanoic anhydride and Grignard reagent

$$R - C - O - C - R + R' - MgBr \longrightarrow R - C - R' + Mg \xrightarrow{O} O - C - R$$

# (iii) Using alkanoylchloride and dialkyl cadmium

O II R - C - CI + 
$$R_{2}^{\prime}$$
Cd  $\longrightarrow$  R - C - R' + R' - Cd - CI Alkyl cadmium chloride

$$\begin{array}{c}
O \\
II \\
2R - C - CI + R'_{2}Cd \longrightarrow 2R - C - R' + CdCl_{2} \\
Cadmium \\
Chloride$$
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# (iv) By acylation or benzoylation of aromatic hydrocarbon (Friedel-Carft Reaction)

$$C_6H_6 + CH_3COCI \xrightarrow{Dry} C_6H_5COCH_3 + HCI$$
Acetophenone

$$C_6H_6 + C_6H_6COCI \xrightarrow{Dry} C_6H_5COC_6H_5 + HCI$$

Benzophenone

# (v) By Acid hydrolysis followed by heating of $\beta$ -Ketoester.

$$\begin{array}{c|c} CH_3 - C - CH_2 - C - OC_2H_5 & \xrightarrow{H_2O/H^+} & CH_3 - C - CH_2COOH & \xrightarrow{\Delta} CH_3 - C - CH_3 + CO_2 \\ \beta \quad \alpha & \beta\text{-ketoester} \end{array}$$

# Note : (i) It is $\beta\text{-ketoacid}$ which decarboxylate more readily as it proceeds via six membered cyclic

$$CH_3 - C$$
 $CH_2$ 
 $CH_3 - C$ 
 $CH_2$ 
 $CH_3 - C$ 
 $CH_3 -$ 

Note : (ii)  $\beta$ -ketoester is obtained by claisen ester condensation of two moles of ester using sodium ethoxide as a base.

e.g. 
$$2CH_3COOC_2H_6 \xrightarrow{C_2H_6ONs} CH_3 - C - CH_2 - C - OC_2H_6 + C_2H_5OH$$

**Mechaniam:** 

$$CH_3 - COOC_2H_5 \xrightarrow{B'} CH_2COOC_2H_5 + BH$$

The product  $\beta$  ketoester can be easily obtained by placing anion of one ester at the place of ethoxy part of other ester as –

$$CH_3COOC_2H_5 \xrightarrow{B'} CH_7 - COOC_3H_5$$

$$CH_3 - CH_3 - CH_2 - COOC_2H_5 \longrightarrow CH_3 - C - CH_2COOC_2H_5$$
-ketoester

Note: (iii) If two ester units are same then it is inter molecular claisen ester condensation

Q. Predict the unknown (s) for the following: 
$$2CH_2 - CH_2COOC_2H_5 \xrightarrow{C_2H_5OH_3} A \xrightarrow{H_2O/H^+} B \xrightarrow{\Delta} C + CO_2^{OLYMPIADS}$$

Note: (iv) If two ester units are different then it is crossed Claisen ester condensation

(a) 
$$C_5H_5COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow{C_2H_5ONa} C_5H_5 - \overset{O}{C} - CH_2 - COOC_2H_5$$

$$\beta - \alpha$$

$$\beta - ketoester$$

(b) 
$$CH_3 - CH_2 - COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow{C_2H_5ONa} CH_3 - CH_2 - C - CH_2 - C - OC_2H_5$$

Note: (v) If two ester units are present with in the same molecule then we get cyclic  $\beta$ -ketoester and the reaction is intramolecular Claisen ester condensation.



$$(CH_2)_4$$
 $COOC_2H_5$ 
 $C_2H_5ONa$ 
 $COOC_2H_5$ 
 $COOC_2H_5$ 
 $COOC_2H_5$ 

Note: (vi) Active methylene group hydrogen is too acidic that it can be replaced by alkyl of arylakyl halide in the presence of base like sodium ethoxide.

# (C) Pinacol-Pinacolone rearrangement:

Pinacole is obtained when 2 moles of acetone are heated with divalent active metal magnesium followed by treating with water.

$$CH_{3} - C \\ CH_{3} - C \\ CH_{3} \\ CH_{3} + CH_{3} - C - CH_{3} \\ \hline \\ CH_{3} - C \\ CH_{3} \\ CH_{3} - C \\ CH_{3} \\ CH_{$$

Pinacole undergoes rearrangement in acidic media to give pinacolone

$$(CH_3)_2C \xrightarrow{C} C(CH_3)_2 \xrightarrow{H^{\bigoplus} -H_2O} CH_3 - C \xrightarrow{CH_3} C-CH_3$$

$$OH OH CH_3$$
Pinacole Pinacolone

# 9. Chemical Reactions of Carbonyl Compounds:

Carbonyl compounds undergo nucleophilic addition reaction and reactivity order will be:

# (I) Nucleophilic Addition Reaction:

$$C = 0$$
 >  $R$   $C = 0$  >  $R$   $C = 0$  (reactivity order)

# (i) Reaction with alcohol:

Carbonly compounds react with alcohols in the presence of dry HCl gas to give acetal (if aldehyde) and ketal if ketone via formation of unstable hemiacetal and hemlketal respectively.

### Note:

- (i) Acetal is formed to protect aldehyde for a long time.
- (ii) Acetal has functional groups ether.
- (iii) Acetal formed can be decomposed to original aldehyde by dilute acid.
- (iv) On treating with ethyleneglycol we get cyclic acetal or ketal (1, 3-dioxolans)

$$C = O + \begin{vmatrix} CH_2-OH \\ CH_2-OH \end{vmatrix} \xrightarrow{Para toluene \\ sulphonic acid (PTS)} C \begin{vmatrix} O - CH_2 \\ O - CH_2 \end{vmatrix}$$



### **Mechanism:**

(v) Acetal formation is founed to be more favourable than ketal formation. If both the carbonyl groups are present within the molecule.

## (ii) Addition of HCN:

If is base catalysed addition

$$C = O + HCN \xrightarrow{'B'} C - OH$$
 $CN Cyanohydrin$ 

$$H-C=N \xrightarrow{'B'} BH + CN$$

# (iii) Addition of sodiumbisbulphite (NaHSO<sub>2</sub>):

This addition is used to isolate carbonyl compounds from the mixture as we get salt.

$$C = O + NaHSO_3 \longrightarrow C - ONa \longrightarrow C - OH$$
 $SO_3H$ 
 $SO_3Na$ 
(salt)

Salt on acidification gives carbonyl compounds again.

$$\begin{array}{c}
C - OH \xrightarrow{H_2O} \\
C - OH \xrightarrow{-H_2O}
\end{array}$$

$$C = O$$

$$C = OH$$

# (II) Addition elimination reactions:

Certain compounds related to ammonia add to the carbonyl group to form derivatives that are important chiefly for the characterization and identification of aldehydes and , Ketones the product contain a carbon nitrogen double bond resulting from elimination of a molecule of water from the initial addition products.

$$\begin{array}{c} C \\ \parallel \\ O \\ \end{array} + : NH_2OH \xrightarrow{H^+} \begin{bmatrix} -1 \\ -C \\ -NHOH \end{bmatrix} \xrightarrow{C} = NOH + H_2O$$

$$\begin{array}{c} C \\ + : NH_2NHC_6H_5 \xrightarrow{H^+} \begin{bmatrix} -1 \\ -C \\ -NHNHC_6H_6 \end{bmatrix} \xrightarrow{C} = NNHC_6H_6 + H_2O$$

$$\begin{array}{c} C \\ -C \\ -NHNHCONH_2 \xrightarrow{H^+} \end{bmatrix} \xrightarrow{C} = NHNHCONH_2 + H_2O$$

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# (i) Reaction with ammonia derivatives (H<sub>2</sub>N-Z):

This reaction is nucleophilic followed by water elimination:

$$C = O + H_3N-Z \longrightarrow C = N-Z$$

$$\begin{array}{c}
C = O + H2N-Z \longrightarrow C - O \longrightarrow C - OH \longrightarrow C - OH \longrightarrow C - H2O
\end{array}$$

$$\begin{array}{c}
C - OH \longrightarrow C - OH
\end{array}$$

This reaction is carried out in slightly acidic media which will generate a nucleophilic centre for weak base ammonia derivatives.

$$C = 0: + H^{\oplus} \longrightarrow C = 0 - H \longleftrightarrow C - OH$$

On using strong acidic media lone paor of electrons present at N-atom of ammonia derivatives will accept proton forming protonated ammonia derivatives which can not act as nucleophile for carbonyl carbon.

# (III) Beckmann Rearrangement in Oxime:

$$\begin{array}{c}
R' \\
C = N - OH \xrightarrow{H^+ \text{ or}} R - C - NHR' + R - C - NHR \\
R (F + 7)
\end{array}$$
(if R' is bulkier than R)



### **Mechanism:**

### Note:

- (i) Brady's reagent is used to distinguish carbonyl compounds from the mixture.
- (ii) Oxime undergoes Beckmann rearrangement to give its isomer amide.
- (iii) In this reaction the group which is anti to -OH group migrates.

$$C_6H_5$$
  $C = N - OH \xrightarrow{Rearrangement} CH_3 - C - NH - C_6H_5 + C_6H_5 - C - NH - CH_3$ 

$$C_6H_5$$
  $C = N$   $CH_3$   $CH_3$ 

(-CH₃ is anti -OH)

$$C_6H_5$$
 $C = NOH$ 

Rearrangement
 $CH_3 - C - NH - C_6H_5$ 

 $(-C_6H_5$  is anti -OH)

# (IV) Aldol Condensation:

It is condensation between two moles of carbonyl compounds among which at least one must have  $\alpha$ -hydrogen atom in dilute basic media to get  $\alpha,\beta$ -unsaturated aldehyde / ketone via the formation of  $\beta$ -hydroxy aldehyde /ketone.

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$$\begin{array}{c}
\text{Nurturing potential through education} \\
\beta & \alpha \\
\hline
\text{CH}_{2}\text{-CH} - \text{CH}_{2}\text{-CH} = 0 \\
\hline
\text{OH}
\end{array}$$

$$\begin{array}{c}
\Delta \\
-\text{H}_{2}\text{O}
\end{array}$$

$$\begin{array}{c}
\Delta \\
\text{CH}_{3}\text{-CH} = \text{CH} - \text{CH} = 0 \\
\hline
\alpha, \beta\text{- Unsaturated aldehyde}$$

**Mechanism :** 
$$CH_3 - CH = O \xrightarrow{'B'} CH_2 - CH = O + BH$$

$$CH_3 - CH = O \longrightarrow CH_3 - CH - CH_2 - CH = O \xrightarrow{BH} CH_3 - CH - CH_2 - CH = O$$
Nucleophile
$$O \longrightarrow CH_3 - CH - CH_2 - CH = O \longrightarrow CH_3 - CH - CH_2 - CH = O$$

β-hdroxy aldehyde

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from β-hydroxy aldehyde / ketone, water is eliminated on using either acidic or basic media as –

$$\begin{array}{c} \text{CH}_{3}\text{-CH-CH}_{2}\text{-CH=O} & \xrightarrow{B \text{ (basic media)}} & \text{CH}_{3}\text{-CH-CH-CH=O} \\ & \vdots \text{OH} & & & & & \\ \text{(Acidic } & & & & \\ \text{media)} & & & & & \\ \text{CH}_{3}\text{-CH-CH}_{2}\text{-CH=O} & \xrightarrow{CH} & \text{CH-CH-CH=O} \\ & & & & & \\ \text{CH}_{3}\text{-CH-CH}_{2}\text{-CH=O} & \xrightarrow{CH} & \text{CH-CH-CH=O} \\ & & & & \\ \text{OH} & & & & \\ \end{array}$$

Now try to get carbonyl compounds from  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds as – keep 'H' at  $\alpha$ -position and –OH at  $\beta$ -position of  $\alpha$ , $\beta$  unsaturated carbonyl compounds to get  $\beta$ -hydroxy carbonyl compounds.

 $\alpha,\beta$ -unsaturated carbonyl compound

β-hydroxy carbonyl compound

Now break  $\alpha$  and  $\beta$  carbon as shown below to get carbonyl compound.

$$\begin{array}{c|c}
\beta & \beta & \beta \\
C & C & C & R
\end{array}$$
Base
$$\begin{array}{c|c}
C & C & R
\end{array}$$

$$\begin{array}{c|c}
C & C & R
\end{array}$$

These two carbonyl compounds can be obtained on ozonolysis of hydrocarbon  $C = C + CH_2$  if it is asked.

# Intramolecular aldol condensation:

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Cyclic β-hydroxyketone

By knowing product we can get reactant as in case of intermolecular aldol condensation:

# (V) Cannizzaro reaction:

 $\hat{C}$ arbonyl compounds not having  $\alpha$ -hydrogen atom undergo disproportionation or redox reaction in strong basic media.



(i) 
$$2 \text{ H} - \overset{\text{H}}{\text{C}} = 0 \xrightarrow{\text{HaOH}} \text{H} - \overset{\text{O}}{\text{C}} - \text{ONa} + \text{CH}_3 - \text{OH}$$

i) 
$$2 C_6H_5CH = O HaOH C_6H_5COONa + C_6H_5CH_2OH$$
  
Sodiumbenzoate Benzylalcohol

(iii) 2 
$$CH = O$$
  $NaOH$   $COONa$   $CH_2OH$ 

These reaction are intermolecular cannizzaro reaction:

# **Mechanism:**

$$\begin{array}{c} H - C = O \\ \hline \\ (A) \\ \hline \\ H - C = O \\ \hline \\ (A) \\ \hline \\ H - C = O \\ \hline \\ (A) \\ \hline \\ H - C = O \\ \hline \\ (B) \\ \hline \\ H - C = O \\ \hline \\ (C) \\ \hline \\ (C) \\ ($$

By this mechanism it clear that acid is corresponding to that carbonyl compound over which OH is going easily as nucleophile.

**Note :** It is observed that hydride ion transfer from (I) to Carbonyl compound (B) is rate determining step.

# Crossed Cannizzaro reaction:

On using two types of carbonyl compounds not having  $\alpha$ -hydrogen atom, acid will be corresponding to that aldehyde over which OH will approach without any hindrence.

Ex. (i) 
$$H - C = O + C_6H_5 - CH = O \xrightarrow{O \\ OH} H - C_0 + C_6H_5CH_2OH$$
(A) (B)

(ii) 
$$(CH_2OH)_3C - CH = O + H - C = O \xrightarrow{O} OH \to (CH_2OH)_3C - CH_2OH + H - C \to O$$

in case (i) OH will easily go to (A) and in case (ii) it will go to (B) hence acid will be formate ion in both the cases.

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# (VI) Perkin reaction:

When aromatic aldehyde like benzaldehyde is treated with anhydride in the presence of sodium salt of acid from which anhydride is derived we get  $\alpha,\beta$ -unsaturated acid.

e.g. 
$$CH = O$$

$$CH = O$$

$$CH_3CO)_2 / CH_3COONa$$

$$Acetic Sodium acetate anhydride (Acts as base)$$

$$Cinnamic acid$$

Mechanism: 
$$CH_3COOCOCH_3 \xrightarrow{\ddot{B}} CH_2COOCOCH_3$$

$$C_{6}H_{5}-CH=O+CH_{2}COOCOCH_{3}\longrightarrow C_{6}H_{5}-CH-CH_{2}COOCOCH_{3}$$

$$C_{6}H_{5}CH=CH-COOH\xrightarrow{\Delta} C_{6}H_{5}CH-CH_{2}COOH\xrightarrow{(-CH_{3}COOH)} C_{6}H_{5}-CH-CH_{2}COOCOCH_{3}$$

$$\alpha,\beta \text{ unsaturated acid}$$

$$\beta-\text{hydroxy acid}$$

# (VII) Reformatsky reaction:

When carbonyl compound and  $\alpha$ -halogenated ester are heated with zinc followed by treating with water we get  $\beta$ -hydroxyester.

This reaction can be represented as -

$$Br - CH - COOC_2H_5$$
  $Zn/\Delta \rightarrow Br - Zn$   $CH - COOC_2H_5$   $Br$   $R$ 

$$C = O + Br - Zn - CH - COOC2H5$$

$$C - CH - COOC2H5$$

$$OZnBr$$

$$C - CH - COOC2H5$$

$$OH R$$

$$\beta$$
-hydroxyester

# (VIII) Witting reaction:

It is used to get alkene from carbonyl compound using phosphorus ylide via the formation of cyclic structure betaine.



$$CH = O \qquad C - P(Ph)_3 \longrightarrow C - O \longrightarrow C = C + O = P(Ph)_3$$

$$C - P(Ph)_3 \longrightarrow C = C + O = P(Ph)_3$$
Betaine

**Note:** Phosphorus ylides are prepared from alkylhalide and triphenylphosphine in the presence of base like sodium ethoxide as –

$$R-CH_{2}-Br \xrightarrow{(C_{6}H_{5})_{3}P} \xrightarrow{\bigcirc} R-CH_{2}-P(C_{6}H_{5})_{3} \xrightarrow{Base} R-CH-P(Ph)_{3} \text{ or } R-CH=P(Ph)_{3} \\ -Br & Phosphorus ylide}$$

Q. Predict the product for the following:

(i) 
$$CH_2 = P(Ph)_3 \longrightarrow$$

(ii) 
$$P(Ph)_3 \longrightarrow P(Ph)_3$$

(iii) 
$$CH_3$$
  $C = O + CH_3 - CH - P(Ph)_3$   $\longrightarrow$ 

Ex. 
$$Ph_3P = CH_2 \longrightarrow CH_2$$
 [JEE-96]

Ex. 
$$CH_3CH_2$$
 0 (i)  $KCN/H_2SO_4$  (ii)  $LiAlH_4$  [JEE-96]

# (IX) Baeyer-Villiger oxidation:

It is preparaton of ester from ketone using peracid.

$$R' = O \xrightarrow{R"COOOH} R-C-OR' + R"COOH$$

### Mechanism:

$$R = 0: \xrightarrow{H^{\oplus}} R - C = OH \iff R - C - OH \xrightarrow{R'' - C - O - O} R''$$

Q. Predict product for the following

$$C_6H_5$$
 $C = O \xrightarrow{C_6H_5 - C - O - O - H} Product$ 

#### (X) **Haloform reaction:**

Acetaldehyde and methylalkyl ketones react rapidly with halogen (Cl<sub>2</sub>, Br<sub>2</sub> or I<sub>2</sub>) in the presence of alkali to give haloform and acid salt.

O O 
$$\parallel$$
 R - C - CH<sub>3</sub>  $\xrightarrow{Br_2/NaOH}$  R - C - ONa + CHBr<sub>3</sub> (Bromoform)

In this reaction -CH<sub>2</sub> of CH<sub>2</sub> -C- group is converted into haloform as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone give acid salt having carbon atom corresponding to alkyl ketone.

# (a) Halogenation

### (b) Alkalihydrolysis

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$$\begin{array}{ccc}
0 & 0 \\
\parallel & & \parallel \\
R - C - CH_3 & \xrightarrow{Br_3} R - C - CBr_3
\end{array}$$
 (Halogenation)

O O 
$$\parallel$$
 R - C - CBr<sub>3</sub>  $\stackrel{\text{NaOH}}{\longrightarrow}$  CHBr<sub>3</sub> + R - C - ONa (Alkalihydrolysis)

**Note :** This reaction is used to distinguish the presence of  $CH_3$  –C– group.

Which of the following is correct order of rate of halogenation of acetone? Q.21

(a) 
$$Cl_2 > Br_2 > I_2$$

(a) 
$$Cl_2 > Br_2 > I_2$$
 (b)  $Br_2 > I_2 > Cl_2$  (c)  $I_2 > Cl_2 > Br_2$  (d)  $Cl_2 = Br_2 = I_2$ 

(c) 
$$I_2 > Cl_2 > Br_2$$

(d) 
$$Cl_2 = Br_2 = I_2$$



## (XI) Clemmensen reduction:

Used to get alkane from carbonyl compounds.

$$C = O \xrightarrow{Zn - Hg/HCI} CH_{2}$$

$$Sp^{2}$$

$$C = O \xrightarrow{H^{\oplus}} C = O \xrightarrow{H^{\oplus}} C - OH \xrightarrow{Zn \to Zn^{2+} + 2e^{\ominus}} C - OH \xrightarrow{2H^{\oplus}} CH \xrightarrow{En \to Zn^{2+} + 2e^{\ominus}} CH$$

Ex. Fill in the blanks with appropriate structures of reaction products in the following transformations

$$0 - HOOC - C_6H_5 - CH_2 - C_6H_5 \xrightarrow{SOCl_2} G$$

$$G \xrightarrow{anhydrous} H \qquad H \xrightarrow{Zn - Hg} I$$
[JEE-95]

Sol. 0 - HOOC - 
$$C_6H_4$$
 -  $CH_2$  -  $C_6H_5$   $\xrightarrow{SOCl_2}$   $CH_2$   $COCI$   $+ SO_2 + HCI$   $COCI$   $(Z)$   $(H)$ 

# (XII) Wolf-Kishner reduction:

(Used to get alkane from carbonyl compounds

$$C = 0$$

$$\frac{NH_2 - NH_2/KOH}{Using high boiling 19} CH_2 all through education solvent (ethylene glycol) sp3$$

$$C = N - NH_{2} \xrightarrow{B} C = N - NH_{2} \xrightarrow{B} C = N - NH_{2} \xrightarrow{B} C = N \xrightarrow{B} C = N - NH_{2} \xrightarrow{B} C = N - NH_{2$$

Page # 20 CARBONYL COMPOUNDS

# (XIII) Addition of Grignard reagent over Carbonyl compound:

It gives alcohol

$$C - OMgBr \xrightarrow{H_2O/H^{\oplus}} C - OH + MgBr - OH$$

# (XIV) Reduction of Carbonyl Compounds:

# (i) Reduction to alcohols

e.g. 
$$R = 0 \xrightarrow{H_2/NI \text{ or Pt or Pd}} R \xrightarrow{OH} CH$$

$$R = 0 \xrightarrow{H_2/NI \text{ or Pt or Pd}} R \xrightarrow{OH} CH$$

$$R = 0 \xrightarrow{H_2/NI \text{ or Pt or Pd}} R \xrightarrow{OH} CH$$

$$R = 0 \xrightarrow{H_2/NI \text{ or Pt or Pd}} R \xrightarrow{OH} CH$$

$$R = 0 \xrightarrow{H_2/NI \text{ or Pt or Pd}} R \xrightarrow{OH} CH$$

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$$R = 0 \xrightarrow{H_2/NI \text{ or Pt or Pd}} R \xrightarrow{OH} CH$$

$$R = 0 \xrightarrow{H_2/NI \text{ or Pt or Pd}} R \xrightarrow{OH} R \xrightarrow{OH} R$$

$$R = 0 \xrightarrow{H_2/NI \text{ or Pt or Pd}} R \xrightarrow{OH} R \xrightarrow{OH} R$$

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$$R = 0 \xrightarrow{H_2/NI \text{ or Pt or Pd}} R$$

$$R = 0 \xrightarrow{H_2/NI \text{ or Pt or Pd}} R$$

$$R = 0 \xrightarrow{H_2/NI \text{ or Pt$$

$$CH_{3}CH_{2}CCH_{3} \xrightarrow{(1) \text{ NaBH}_{4}} CH_{3}CH_{2}CH_{2}CHCH_{3}$$

$$CH_{3}CH_{2}CH_{2}CH_{2}CHCH_{3}$$

## (ii) Reduction to pinacols

$$\begin{array}{c|c} CH_3 & CH_3 \\ \hline \\ CH_3 - C + C - CH_3 \\ \hline \\ O & O \end{array} \begin{array}{c} (i) \ Mg \\ \hline \\ (ii) \ H_2O \end{array} \begin{array}{c} CH_3 \\ \hline \\ CH_3 - C - CH_3 \\ \hline \\ OH \end{array} \begin{array}{c} CH_3 \\ \hline \\ C - CH_3 \\ \hline \\ OH \end{array} \begin{array}{c} IIT-JEE | AIEEE | CH_3 - CH_3 \\ \hline \\ CH_3 - C - CH_3 \\ \hline \\ CH_3 - C - CH_3 - CH_3 \\ \hline \\ CH_3 - C - CH_3 - CH_3 - CH_3 \\ \hline \\ CH_3 - C - CH_3 - CH_3 - CH_3 - CH_3 \\ \hline \\ CH_3 - C - CH_3 - CH_3 - CH_3 - CH_3 - CH_3 \\ \hline \\ CH_3 - C - CH_3 \\ \hline \\ CH_3 - CH_3 \\ \hline \\ CH_3 - CH_3 \\ \hline \\ CH_3 - CH_3 \\ \hline \\ CH_3 - CH_3 \\ \hline \\ CH_3 - CH_3 \\ \hline \\ CH_3 - CH_3 \\ \hline \\ CH_3 - CH$$

# (XV) Reaction with PCI<sub>5</sub>:

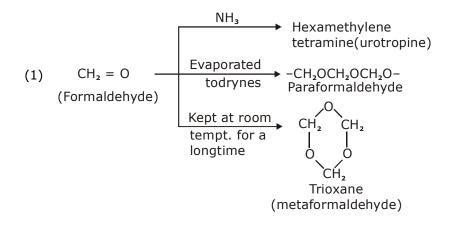
Carbonyl compounds give gemdihalides

$$>C = O + PCl_5 \longrightarrow C Cl + POCl_3$$

(i) 
$$CH_3CH = O + PCI_5 \longrightarrow CH_3 - CHCI_2 + POCI_3$$

(ii) 
$$CH_3 - C = O + PCI_5 \longrightarrow CH_3 - C - CI + POCI_3$$

### Other reaction:



$$CH_{3} - CH = O$$

$$(2) \quad (Acetaldehyde) \qquad CH_{3} - CH = O$$

$$(Acetaldehyde) \qquad Cyclic trimer (paraldehyde)$$

$$Cyclic tetramer (Metaldehyde)$$

(3) 
$$CH_3 - CH = O$$

$$(Acetone)$$

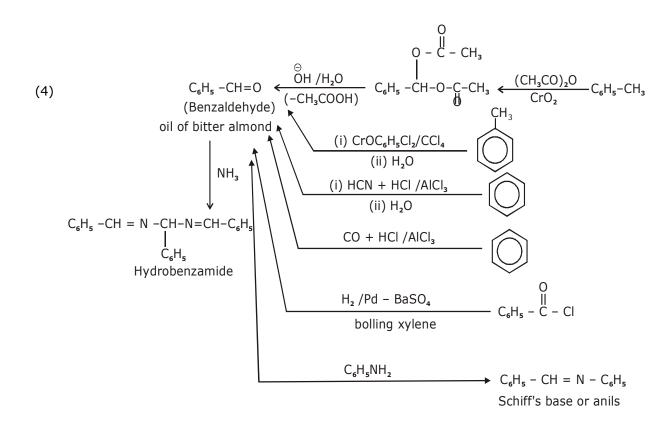
$$CH_3 - CH = O$$

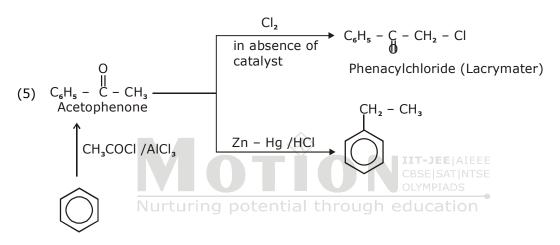
$$(Acetone)$$

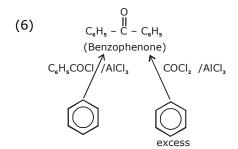
$$CH_3 - CH_2 - C - CH_2$$

$$CH_3 - CH_3 - CH_3$$

$$CH_3 -$$







# Some important reagents used for identification of aldehyde.

# (i) Tollen's reagent:

It is ammonical silver nitrate solution, prepared by adding ammonium hydroxide to AgNO<sub>3</sub> solution. During reaction, first Ag<sub>3</sub>O is formed which is dissolved in ammoniumhydroxide to give Tollen's reagent.

$$2AgNO_3 + 2NH_4OH \xrightarrow{2} Ag_2O + NH_4NO_3 + H_2O$$
  
 $Ag_2O + 4NH_4OH \xrightarrow{2} 2[Ag(NH_3)_2]OH + 3H_2O$   
Tollen's reagent

Tollen's reagent is weak oxidising agent, it gives Ag mirror test with aldehyde.

$$R - CH = O + 2Ag(NH_3)^{\oplus}_2 + 3OH \xrightarrow{\bigcirc} RCOO + 2Ag + 2NH_3 + 2H_2O$$

$$R - CH = O + Ag_2O \longrightarrow R-COO + 2Ag$$
 (Silver mirror)

# (ii) Fehling's solution:

It is an alkaline solution of cupric ion complexed with sodium potassium tartarate. Two solutions are kept by naming Fehling solution (I) ( $CuSO_4$  solution) and Fehling solution (II) (Alkaline solution of sodium potassium tartarate). When these two solutions are mixed we get deep blue coloured solution.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

Equal volume of both the solution are heated with aldehyde to give red brown precipitate of cuprous oxide ( $Cu_2O$ ) which confirms the presence of aldehyde.

$$R - CHO + 2CuO \longrightarrow RCOOH + Cu_2O (Red ppt)$$

RCHO – 2Cu<sup>2+</sup> + 3OH
$$^{\ominus}$$
 → RCOO $^{\ominus}$  + 2Cu $^{\oplus}$  + 2H<sub>2</sub>O (Red ppt)

### (iii) Banadict solution:

It is solution of  $CuSO_4$ , sodium citrate and sodium carbonate. It also consists of two solution. Solution (I) is alkaline solution of sodium citrate and solution (II) is  $CuSO_4$  solution.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

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$$CH_2COONa$$
  $CH_2COONa$   $CH_2COONa$   $CH_2COONa$   $CU(OH)_2 + HO - C - COONa  $CH_2COONa$   $CH_2COONa$   $CH_2COONa$  (Blue colour)$ 

Aldehyde gives positive test with Benedict solution.

$$RCH = O + 2Cu^{2+} + 3OH \xrightarrow{\bigcirc} RCOO^{\bigcirc} + 2Cu^{\oplus} + 2H_2O$$
(Red ppt)

# (iv) Schiff's reagent:

It is dilute solution of rossniline hydrochloride whose rad colour has been discharged by passing  $SO_2$ . Aldehyde reatores red colour when treated with schiff's reagent (Magenta solution in  $H_2SO_4$ ).

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