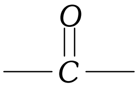
Aldehydes and Ketones Part 1

Introduction.

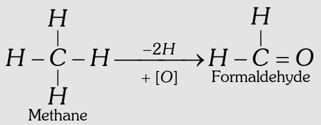
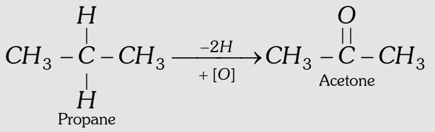
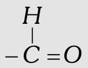
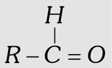
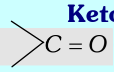
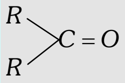
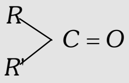
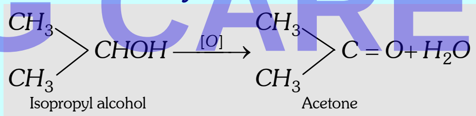
Carbonyl compounds are of two types, aldehydes and ketones. Both have a carbon-oxygen double bond often called as carbonyl group.



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

Carbonyl group

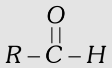
Both aldehyde and ketones possess the same general formula $C_nH_{2n}O$.

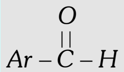
Aldehyde	***Ketone***
Aldehydes may be considered as derivatives of hydrocarbons in which two hydrogen atoms of the end carbon atom have been replaced by a bivalent oxygen atom.	**Ketones may be considered as derivatives of hydrocarbons in which the two hydrogen atoms of a carbon atom present in the middle of carbon chain have been replaced by a bivalent oxygen atom.**
 $\underset{\text{Methane}}{H-\overset{H}{\overset{\vert}{\underset{\underset{H}{\vert}}{C}}}-H} \xrightarrow[+[O]]{-2H} \underset{\text{Formaldehyde}}{H-\overset{H}{\overset{\vert}{C}}=O}$	 $\underset{\text{Propane}}{CH_3-\overset{H}{\overset{\vert}{\underset{\underset{H}{\vert}}{C}}}-CH_3} \xrightarrow[+[O]]{-2H} \underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$
Aldehydes contain the monovalent group  $-\overset{H}{\overset{\vert}{C}}=O$ **(aldehydic group) linked to a hydrogen atom or an alkyl group. Hence, the general formula of the aldehydes is represented as,**  $R-\overset{H}{\overset{\vert}{C}}=O$ **(R may be H or alkyl group).**	**Ketones contain the divalent group**  **(ketonic group) linked to two alkyl groups, same or different. Hence, the general formula of the ketones is represented as,**  **or** 
Aldehydes can also be regarded as the first oxidation products of primary alcohols. $\underset{\text{Primary alcohol}}{RCH_2OH} \xrightarrow{[O]} \underset{\text{Aldehyde}}{RCHO} + H_2O$	**Ketones can also be regarded as the first oxidation products of secondary alcohols.** 

Classification, Structure, Nomenclature and Isomerism.

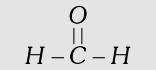
(1) Classification

Aldehydic group is always terminal. Aldehydes can be classified into three categories,

(i) ***Aliphatic aldehydes :***  $R-\overset{O}{\overset{\|}{C}}-H$

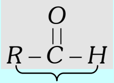
(ii) ***Aromatic aldehydes :***  $Ar-\overset{O}{\overset{\|}{C}}-H$

(iii) ***Unsymmetrical aldehydes :*** All aldehydes except formaldehyde are unsymmetrical.



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

Formaldehyde

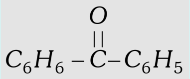
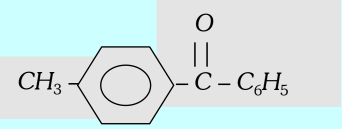


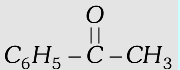
$\underbrace{R-\overset{O}{\overset{\|}{C}}-H}_{\text{Both substituents are different}}$

Ketonic group is never terminal. Ketones can be classified into three categories,

(i) ***Aliphatic ketones :***  $\underset{\text{Symmetrical}}{R-\overset{O}{\overset{\|}{C}}-R}$  $\underset{\text{Unsymmetrical}}{R-\overset{O}{\overset{\|}{C}}-R'}$

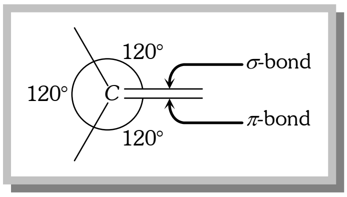
(ii) ***Aromatic ketones :*** In aromatic ketones both substituents are aryl

 $C_6H_6-\overset{O}{\overset{\|}{C}}-C_6H_5$, 

(iii) ***Mixed ketones :*** In mixed ketones one substituent is aryl and other is alkyl.  $\underset{\text{Aryl group}}{C_6H_5}-\overset{O}{\overset{\|}{C}}-\underset{\text{Alkyl group}}{CH_3}$

(2) Structure :

Carbonyl carbon atom is joined to three atoms by sigma bonds. Since these bonds utilise sp^2-orbitals, they lie in the same plane and are 120° apart. The carbon-oxygen double bond is different than carbon-carbon double bond. Since,

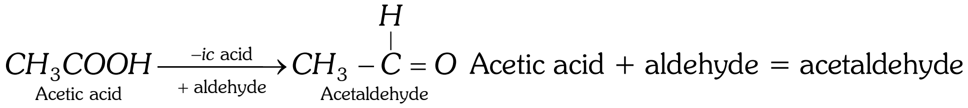


Oxygen is more electronegative, the electrons of the bond are attracted towards oxygen. Consequently, oxygen attains a partial negative charge and carbon a partial positive charge making the bond polar. The high values of dipole moment, $>\overset{\delta+}{C}=\overset{\delta-}{O}$ (2.3 - 2.8D) cannot be explained only on the basis of inductive effect and thus, it is proposed that carbonyl group is a resonance hybrid of the following two structures. $>C=O \longleftrightarrow >\overset{+}{C}-\overset{-}{O}$

(3) **Nomenclature**

(i) ***Aldehyde :*** There are two systems of naming aldehydes,

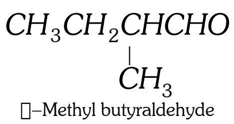
(a) *Common system* : In the common system, aldehydes are named according to the name of the corresponding acid which they form on oxidation. The suffix ***–ic* acid** the name of the acid is replaced by aldehyde. For example, CH_3CHO derived from acetic acid (CH_3COOH) is named as **acetaldehyde**.



$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[+\text{ aldehyde}]{-ic\text{ acid}} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{H}{|}}{C}=O}\ \text{Acetic acid + aldehyde = acetaldehyde}$$

Branching in the aldehyde chain, if any, is indicated by the Greek letters α, β, γ, δ etc. The carbon attached to the $-CHO$ group is α as :

For example, $-\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-CHO$



$$CH_3CH_2\underset{\underset{CH_3}{|}}{CH}CHO$$

□–Methyl butyraldehyde

(b) *IUPAC system* : In the **IUPAC system**, the aldehydes are known as **alkanals**. The name of aldehyde is derived by replacing the terminal **–e** of the name of corresponding alkane by **al**.

For example, $\underset{\text{Methanal}}{HCHO}$ $\underset{\text{Ethanal}}{CH_3CHO}$ $\underset{\text{Propanal}}{C_2H_5CHO}$ Alkane –e + al = Alkanal

(ii) ***Ketone :*** There are two systems of naming ketone,

(a) *Common system* : In the common system, ketones are named by using the names of alkyl group present in the molecule. For example,

$\underset{\text{Dimethyl ketone}}{CH_3COCH_3}$ $\underset{\text{Ethyl methyl ketone}}{CH_3COCH_2CH_3}$ $\underset{\text{Diethyl ketone}}{CH_3CH_2COCH_2CH_3}$

$\underset{\text{Methyl } n\text{–propylketone}}{CH_3COCH_2CH_2CH_3}$ $\underset{\text{Methyl isopropyl ketone}}{CH_3COCH(CH_3)_2}$ $\underset{\text{Benzyl methyl ketone}}{C_6H_5CH_2COCH_3}$

Some of the ketones are known by their old popular names as well. For example, dimethyl ketone, CH_3COCH_3 is still popularly known as acetone.

(b) *IUPAC system* : In this system, longest chain containing the ketonic group is taken as the parent chain. In naming the ketone corresponding to the chain, the following procedure is adopted.

Root word + ane –e + one *i.e.*, Alkanone

The positions of the ketonic group and the substituents are indicated by the locants.

CH_3COCH_3	Propanone
$CH_3COCH_2CH_3$	Butanone-2
$CH_3CH_2COCH_2CH_3$	Pantanone-3
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}COCH_2CH_2CH_3$	2-Methylhexanone-3

(4) **Isomerism :** Aldehydes show **chain** and **functional** isomerism.

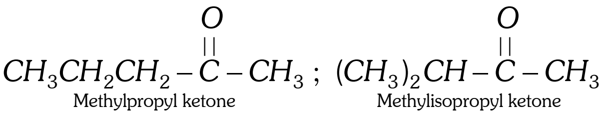
Chain isomers : $\underset{n\text{–Butanal}}{CH_3CH_2CH_2CHO}$ $\underset{\text{2-Methylpropanal } (iso\text{–Butanal})}{(CH_3)_2CHCHO}$

(i) ***Functional isomers*:**

$\underset{\text{Propanal}}{CH_3CH_2CHO}\,;\underset{\text{Acetone}}{CH_3COCH_3}\,;\underset{\text{Allyl alcohol}}{CH_2=CHCH_2OH}\,;\underset{\alpha,\beta-\text{Propylene oxide}}{\underset{O}{CH_3\,CH-CH_2}}\,;\underset{\text{Methyl vinyl ether}}{CH_2=CH.O.CH_3}$

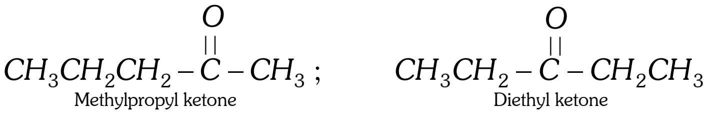
Ketones show **chain, functional and metamerism.** Examples of functional isomerism is given above in aldehydes.

(ii) ***Chain isomers* :**



$\underset{\text{Methylpropyl ketone}}{CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{||}}{C}-CH_3}\;;\;\underset{\text{Methylisopropyl ketone}}{(CH_3)_2CH-\overset{\overset{\displaystyle O}{||}}{C}-CH_3}$

(iii) ***Metamers* :**



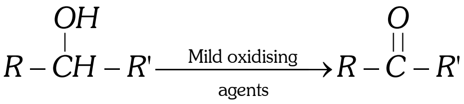
$\underset{\text{Methylpropyl ketone}}{CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{||}}{C}-CH_3}\;;\qquad\underset{\text{Diethyl ketone}}{CH_3CH_2-\overset{\overset{\displaystyle O}{||}}{C}-CH_2CH_3}$

Preparation of carbonyl compounds.

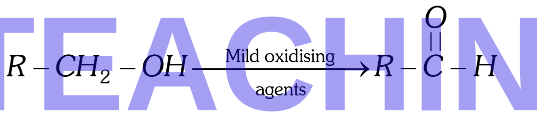
Preparation of only aliphatic or aliphatic as well as aromatic carbonyl compounds.

(1) From alcohols

(i) Primary and secondary alcohols on oxidation give aldehydes and ketones respectively.



$$R-\overset{\overset{\displaystyle OH}{|}}{C}H-R'\xrightarrow[\text{agents}]{\text{Mild oxidising}}R-\overset{\overset{\displaystyle O}{||}}{C}-R'$$



$$R-CH_2-OH\xrightarrow[\text{agents}]{\text{Mild oxidising}}R-\overset{\overset{\displaystyle O}{||}}{C}-H$$

Mild oxidising agents are :

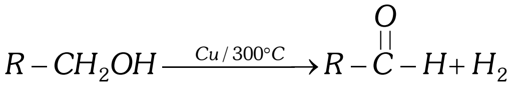
(a) X_2 (b) Fenton reagent (c) $K_2Cr_2O_7/\overset{\oplus}{H}$ (d) Jones reagent

(e) Sarret reagent (f) MnO_2 (g) Aluminium tertiary butoxide

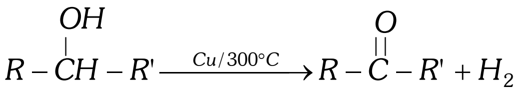
Note:

- *When the secondary alcohols can be oxidised to ketones by aluminium tert-butoxide,* $[(CH_3)_3CO]_3Al$ *the reaction is known as oppenauer oxidation. Unsaturated secondary alcohols can also be oxidised to unsaturated ketones (without affecting double bond) by this reagent.*
- *The yield of aldehydes is usually low by this methods. The alcohols can be converted to aldehydes stage by treating with oxidising agent pyridinium chloro-chromate* $(C_5H_5NH^+CrO_3Cl^-)$*. It is abbreviated as PCC and is called* ***Collin's reagent****. This reagent is used in non-aqueous solvents like* CH_2Cl_2 *(dichloro methane). It is prepared by mixing pyridine,* CrO_3 *and* HCl *in dichloromethane. This is a very good reagent because it checks the further oxidation of aldehydes to carboxylic acids.*

(ii) **Dehydrogenation of 1° and 2° alcohols by *Cu*/300° or *Ag*/300°C**.



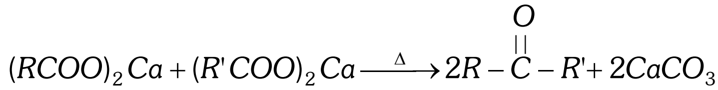
$$R-CH_2OH\xrightarrow{Cu/300°C}R-\overset{\overset{\displaystyle O}{||}}{C}-H+H_2$$



$$R-\overset{\overset{\displaystyle OH}{|}}{C}H-R'\xrightarrow{Cu/300°C}R-\overset{\overset{\displaystyle O}{||}}{C}-R'+H_2$$

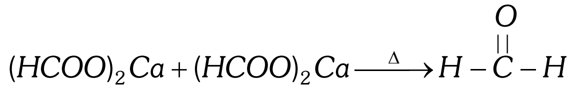
(2) From carboxylic acids

(i) ***Distillation of Ca, Ba, Sr or Th salts of monobasic acids*:** Salt of monobasic acids on distillation give carbonyl compounds. Reaction takes place as follows,

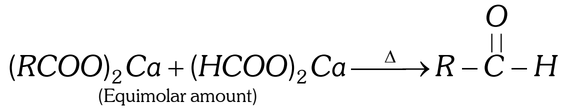


$$(RCOO)_2Ca + (R'COO)_2Ca \xrightarrow{\Delta} 2R-\overset{\overset{O}{||}}{C}-R' + 2CaCO_3$$

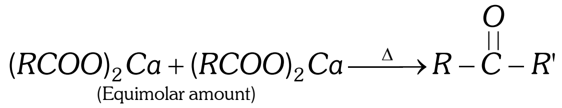
Thus in the product, one alkyl group comes from one carboxylic acid and other alkyl group from other carboxylic acid.



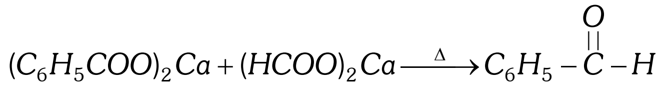
$$(HCOO)_2Ca + (HCOO)_2Ca \xrightarrow{\Delta} H-\overset{\overset{O}{||}}{C}-H$$



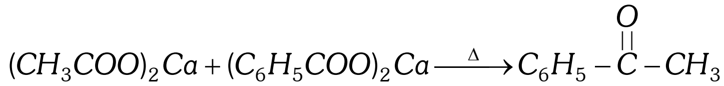
$$\underset{\text{(Equimolar amount)}}{(RCOO)_2Ca + (HCOO)_2Ca} \xrightarrow{\Delta} R-\overset{\overset{O}{||}}{C}-H$$



$$\underset{\text{(Equimolar amount)}}{(RCOO)_2Ca + (RCOO)_2Ca} \xrightarrow{\Delta} R-\overset{\overset{O}{||}}{C}-R'$$

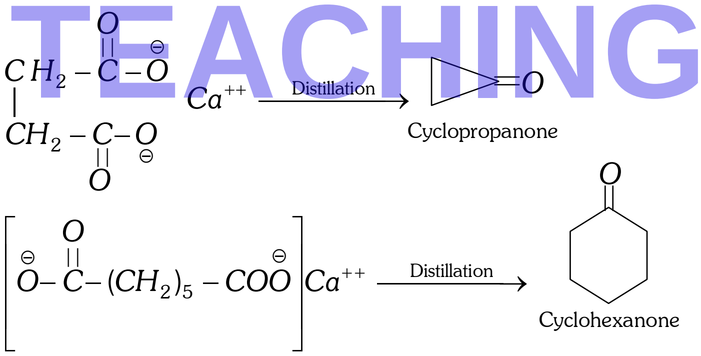


$$(C_6H_5COO)_2Ca + (HCOO)_2Ca \xrightarrow{\Delta} C_6H_5-\overset{\overset{O}{||}}{C}-H$$



$$(CH_3COO)_2Ca + (C_6H_5COO)_2Ca \xrightarrow{\Delta} C_6H_5-\overset{\overset{O}{||}}{C}-CH_3$$

Calcium salts of dibasic acid (1, 4 and higher) on distillation give cyclic ketones.

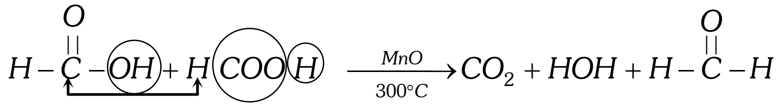


(ii) *Catalytic decomposition of carboxylic acids or Decarboxylation and Dehydration of acids by MnO/ 300°C.*

(a) This reaction takes place between two molecules of carboxylic acids. Both may be the same or different.

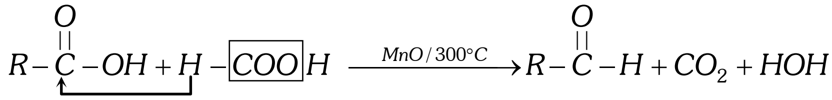
(b) If one of the carboxylic acids is $HCOOH$ then this acid undergoes decarboxylation because this acid is the only monobasic acid which undergoes decarboxylation even in the absence of catalyst.

Case I : When both are $HCOOH$



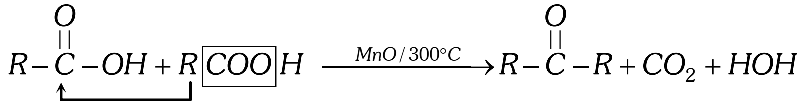
$$H-\overset{\overset{O}{||}}{C}-\enclose{circle}{OH}+\enclose{circle}{H}\enclose{circle}{COO}\enclose{circle}{H} \xrightarrow[300°C]{MnO} CO_2 + HOH + H-\overset{\overset{O}{||}}{C}-H$$

Case II : When only one is formic acid.



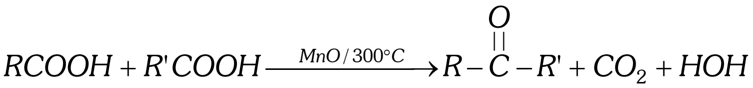
$$R-\overset{\overset{O}{||}}{C}-OH + H-\boxed{COO}H \xrightarrow{MnO/300°C} R-\overset{\overset{O}{||}}{C}-H + CO_2 + HOH$$

Case III : When none is formic acid.



$$R-\overset{\overset{O}{||}}{C}-OH + R\boxed{COO}H \xrightarrow{MnO/300°C} R-\overset{\overset{O}{||}}{C}-R + CO_2 + HOH$$

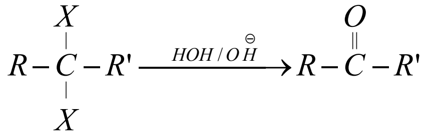
Or



$$RCOOH + R'COOH \xrightarrow{MnO/300°C} R-\overset{O}{\overset{||}{C}}-R' + CO_2 + HOH$$

(3) From gem dihalides : Gem dihalides on hydrolysis give carbonyl compounds

(i) $R-CHX_2 \xrightarrow{HOH/\overset{\ominus}{O}H} R-CHO$

(ii) 

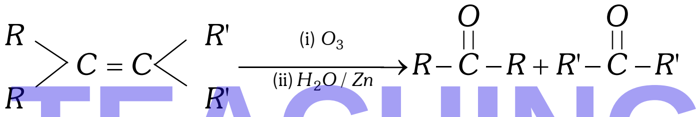
$$R-\underset{X}{\overset{X}{C}}-R' \xrightarrow{HOH/\overset{\ominus}{O}H} R-\overset{O}{\overset{||}{C}}-R'$$

Note : ✹ *This method is not used much since aldehydes are affected by alkali and dihalides are usually prepared from the carbonyl compounds.*

(4) From alkenes

(i) ***Ozonolysis*** **:** Alkenes on reductive ozonolysis give carbonyl compounds

$$R-CH=CH-R \xrightarrow[\text{(ii)}\,H_2O/Zn]{\text{(i)}\,O_3} R-CHO + RCHO$$



$$R_2C=CR'_2 \xrightarrow[\text{(ii)}\,H_2O/Zn]{\text{(i)}\,O_3} R-\overset{O}{\overset{||}{C}}-R + R'-\overset{O}{\overset{||}{C}}-R'$$

Note : ✹ *This method is used only for aliphatic carbonyl compounds.*

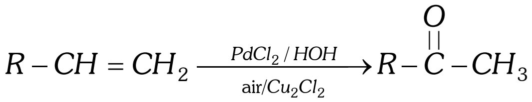
(ii) ***Oxo process*** **:** This method converts terminal alkenes into aldehydes.

$$R-CH=CH_2 + CO + H_2 \xrightarrow[150°C,\ 300\ atm]{CO_2(CO)_8} R-CH_2-CH_2-CHO$$

Note : ✹ *Oxo process is used only for the preparation of aldehydes.*

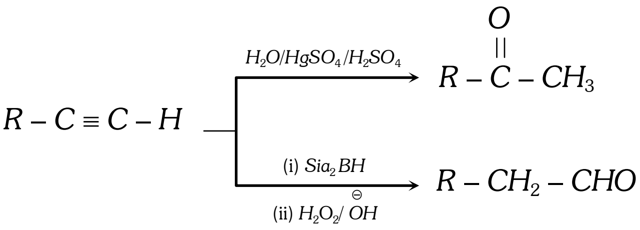
(iii) ***Wacker process*** **:** This reaction converts alkenes in carbonyl compounds.

(a) $CH_2=CH_2 \xrightarrow[\text{air}/Cu_2Cl_2]{PdCl_2/HOH} CH_3-CHO$

(b) 

$$R-CH=CH_2 \xrightarrow[\text{air}/Cu_2Cl_2]{PdCl_2/HOH} R-\overset{O}{\overset{||}{C}}-CH_3$$

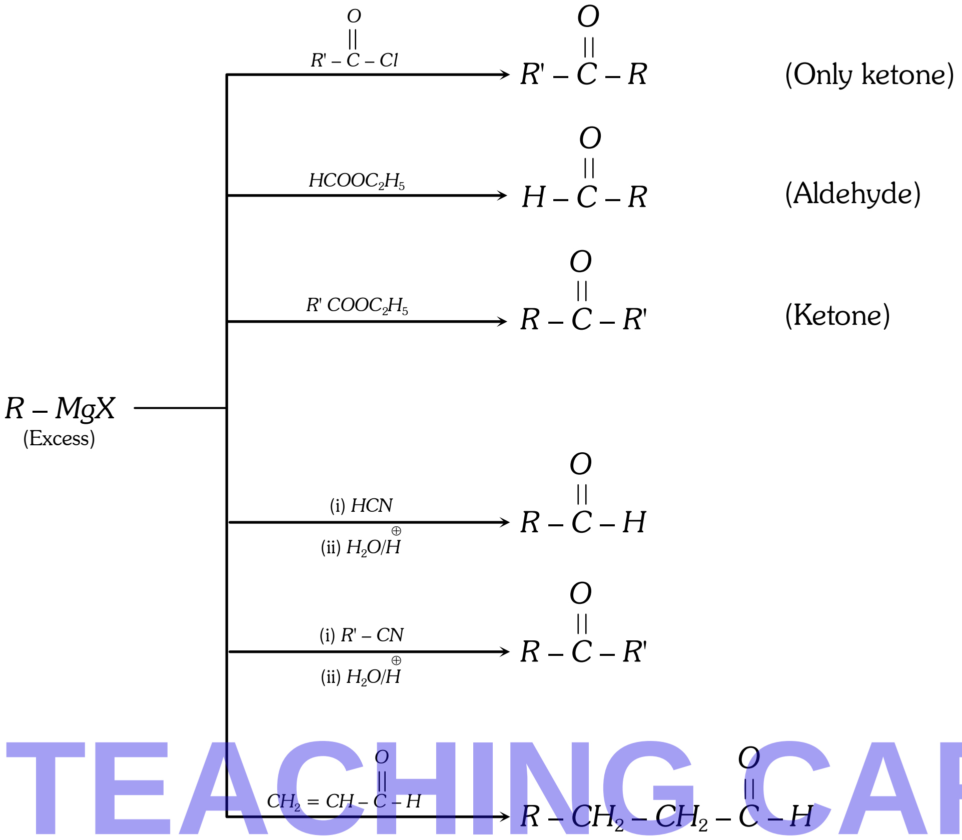
(5) From alkynes : Alkynes on hydration and on boration – oxidation give carbonyl compounds.



$$R-C\equiv C-H \xrightarrow{H_2O/HgSO_4/H_2SO_4} R-\overset{O}{\overset{||}{C}}-CH_3$$

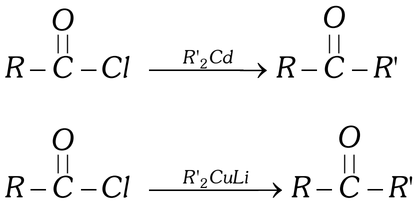
$$R-C\equiv C-H \xrightarrow[\text{(ii)}\,H_2O_2/\overset{\ominus}{O}H]{\text{(i)}\,Sia_2BH} R-CH_2-CHO$$

(6) From Grignard reagents : Carbonyl compounds can be prepared from Grignard reagents by following reactions:



(7) **From acid chloride**

(i) Acid chlorides give nucleophilic substitution reaction with dialkyl cadmium and dialkyl lithium cuprate to give ketones. This is one of the most important method for the preparation of ketones from acid chlorides.



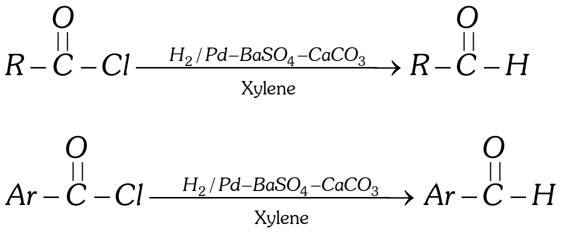
$$R-\overset{\overset{O}{||}}{C}-Cl\xrightarrow{R'_2Cd}R-\overset{\overset{O}{||}}{C}-R'$$

$$R-\overset{\overset{O}{||}}{C}-Cl\xrightarrow{R'_2CuLi}R-\overset{\overset{O}{||}}{C}-R'$$

(Only used for the preparation of ketones)

In this method product is always ketone because $R \neq H$ and also $R' \neq H$.

(ii) ***Rosenmunds reduction*** **:** Acid chlorides on partial reduction give aldehydes. This reduction takes place in the presence of Lindlars catalyst.



$$R-\overset{\overset{O}{||}}{C}-Cl\xrightarrow[\text{Xylene}]{H_2/Pd-BaSO_4-CaCO_3}R-\overset{\overset{O}{||}}{C}-H$$

$$Ar-\overset{\overset{O}{||}}{C}-Cl\xrightarrow[\text{Xylene}]{H_2/Pd-BaSO_4-CaCO_3}Ar-\overset{\overset{O}{||}}{C}-H$$

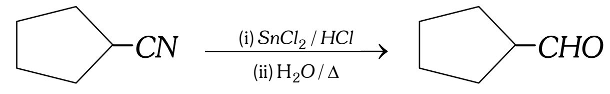
(Only used for aldehydes)

(8) **From cyanides**

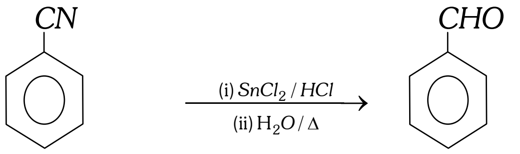
(i) ***Stephen aldehyde synthesis*** : Conversion of cyanides into aldehydes by partial reduction with $SnCl_2 / HCl$, followed by hydrolysis, is known as Stephens aldehyde synthesis.

$$R-C\equiv N \xrightarrow[\text{(ii) } H_2O/\Delta \text{ or steam distillation}]{\text{(i) } SnCl_2/HCl/\text{ether}} R-CHO$$ (Only used for aldehydes)

Example :

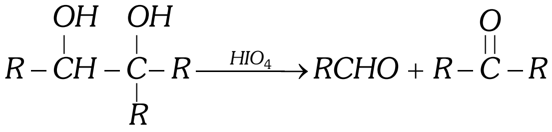


Cyclopentane nitrile → Cyclopentanaldehyde



Benzenenitrile → Benzaldehyde

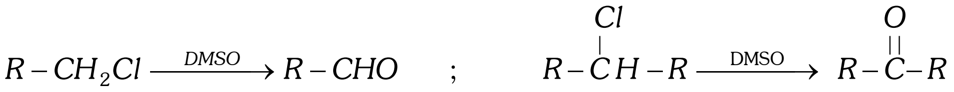
(9) **From vic diols :** Vic diols on periodate oxidation give carbonyl compounds.



$$R-\overset{OH}{\overset{|}{C}H}-\underset{\underset{R}{|}}{\overset{OH}{\overset{|}{C}}}-R \xrightarrow{HIO_4} RCHO + R-\overset{O}{\overset{||}{C}}-R$$

Note : ✸ $Pb(OCOCH_3)_4$ *also gives similar oxidation products.*

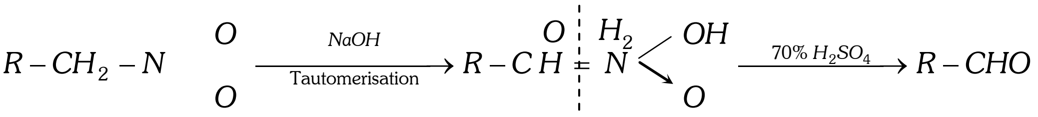
(10) **From Alkyl halides and benzyl halides :** These compounds on oxidation give carbonyl compounds.

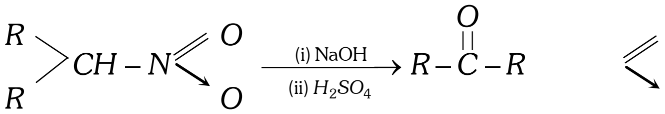


$$R-CH_2Cl \xrightarrow{DMSO} R-CHO \quad ; \quad R-\overset{Cl}{\overset{|}{C}}H-R \xrightarrow{\text{DMSO}} R-\overset{O}{\overset{||}{C}}-R$$

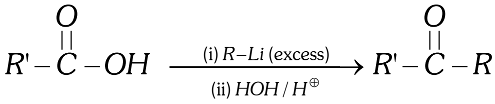
$$C_6H_5-CH_2Cl \xrightarrow[\text{(ii) } H_2O/H^{\oplus} \text{ or } Cu(NO_3)_2 \text{ or } Pb(NO_3)_2]{\text{DMSO or (i) } (CH_2)_6N_4} C_6H_5-CHO$$

(11) **From nitro alkanes :** Nitro alkanes having at least one α-hydrogen atom give carbonyl compounds on treatment with conc $NaOH$ followed by 70% H_2SO_4. The reaction is known as **Nef** carbonyl synthesis.





(12) **Reaction with excess alkyl lithium :** Carboxylic acids react with excess of organo lithium to give lithium salt of gem diols which on hydrolysis give ketones.



$$R'-\overset{O}{\overset{||}{C}}-OH \xrightarrow[\text{(ii) } HOH/H^{\oplus}]{\text{(i) } R{-}Li \text{ (excess)}} R'-\overset{O}{\overset{||}{C}}-R$$

Preparation of only aromatic carbonyl compounds

(1) **From methyl arenes :** Methyl arenes can be converted into aldehydes by the following reagents

$$C_6H_5-CH_3 \xrightarrow[\text{(ii) } HOH]{\text{(i) } CrO_2Cl_2} C_6H_5CHO$$

$$C_6H_5-CH_3 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CrO_3/(CH_3CO)_2O/CH_3COOH} C_6H_5CHO$$

$$C_6H_5-CH_3 \xrightarrow[500°C]{\text{Air}/MnO} C_6H_5CHO$$

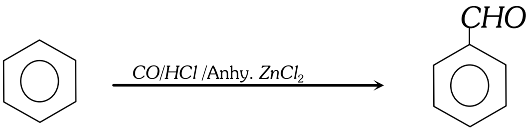
(2) **From chloro methyl arenes :** Chloromethyl arenes on oxidation give aromatic aldehydes.

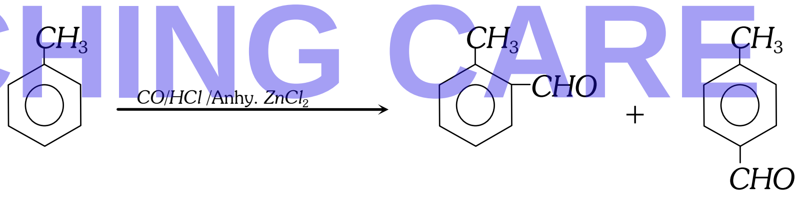
$$C_6H_5-CH_2Cl \xrightarrow{Cu(NO_3)_2/\Delta} C_6H_5CHO$$

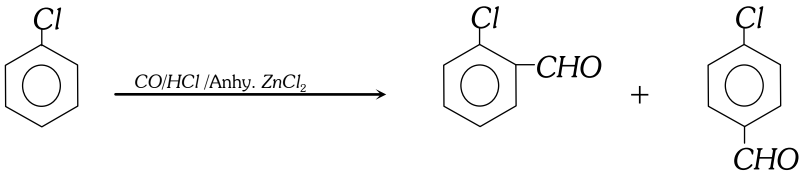
$$C_6H_5-CH_2Cl \xrightarrow{Pb(NO_3)_2/\Delta} C_6H_5-CHO$$

$$C_6H_5-CH_2Cl \xrightarrow[\text{(ii) } H_2O]{\text{(i) } (CH_2)_6N_4/\Delta} C_6H_5-CHO$$

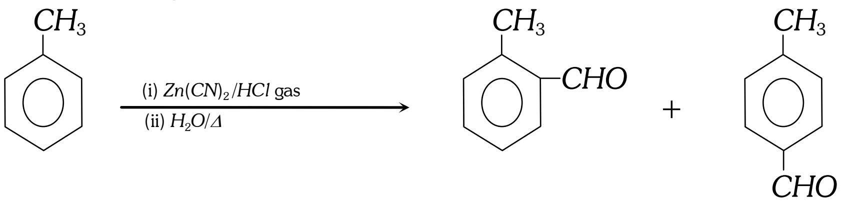
(3) **Gattermann – Koch formylation :** This reaction is mainly given by aromatic hydrocarbons and halobenzenes.

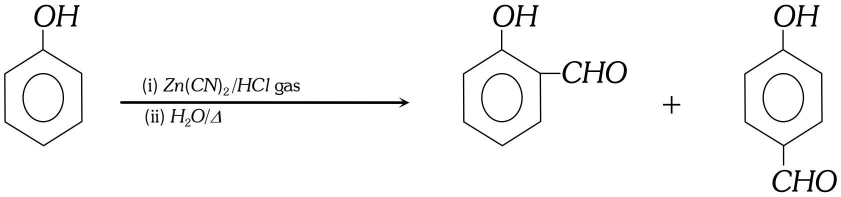


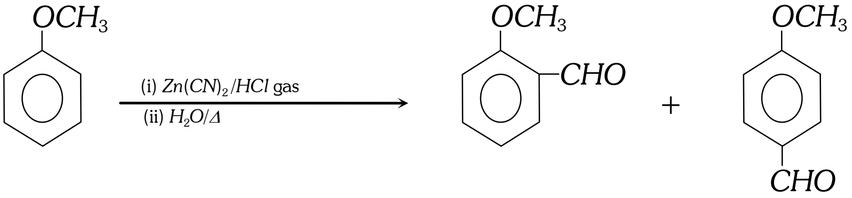




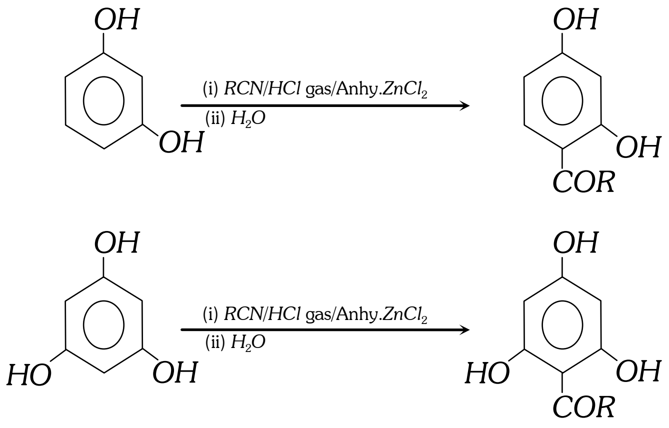
(4) **Gattermann formylation :** This reaction is mainly given by alkyl benzenes, phenols and phenolic ethers.



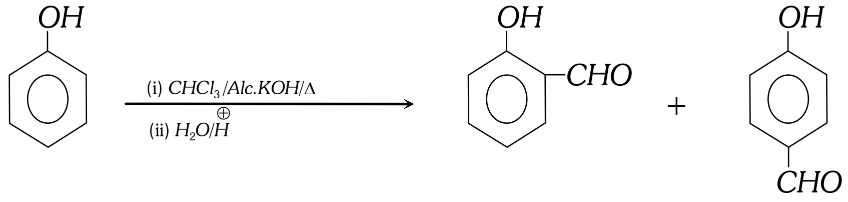




(5) Houben – Hoesch reaction : This reaction is given by *di* and polyhydric benzenes.



(6) Reimer – Tiemann reaction : Phenol gives *0*- and *p*- hydroxy benzaldehyde in this reaction.



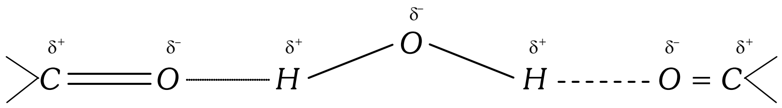
Physical properties of carbonyl compounds.

The important physical properties of aldehydes and ketones are given below,

(1) Physical state : Methanal is a pungent smell gas. Ethanal is a volatile liquid, b.p. 294 K. Other aldehydes and ketones containing up to eleven carbon atoms are *colourless liquids* while still higher members are solids.

(2) Smell : With the exception of lower aldehydes which have unpleasant odours, aldehydes and ketones have generally pleasant smell. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones have been used in blending of perfumes and flavouring agents.

(3) Solubility : Aldehydes and ketones upto four carbon atoms are miscible with water. This is due to the presence of hydrogen bonding between the polar carbonyl group and water molecules as shown below :



With the increase in the size of alkyl group, the solubility decreases and the compounds with more than four carbon atom are practically insoluble in water. All aldehydes and ketones are, however, soluble in organic solvents such as ether, alcohol, etc. The ketones are good solvents themselves.

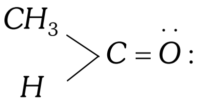
(4) Boiling points : The boiling points of aldehydes and ketones are higher than those of non polar compounds (hydrocarbons) or weakly polar compounds (such as ethers) of comparable molecular masses. However, their boiling points are lower than those of corresponding alcohols or carboxylic acids. This is because aldehydes and ketones are polar compounds having sufficient intermolecular dipole-dipole interactions between the opposite ends of $C = O$ dipoles.

$$>\overset{\delta^+}{C} = \overset{\delta^-}{O} \cdots\cdots\cdots >\overset{\delta^+}{C} = \overset{\delta^-}{O} \cdots\cdots\cdots >\overset{\delta^+}{C} = \overset{\delta^-}{O} \cdots\cdots\cdots$$

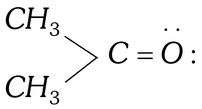
However, these dipole-dipole interactions are weaker than the intermolecular hydrogen bonding in alcohols and carboxylic acids. Therefore, boiling points of aldehydes and ketones are relatively lower than the alcohols and carboxylic acids of comparable molecular masses.

Compounds	$CH_3CH_2CH_2CH_2CH_3$ **Pentane**	$CH_3CH_2OCH_2CH_3$ **Ethoxyethane**	$CH_3CH_2CH_2CH_2OH$ **Butan - 1-ol**	$CH_3CH_2CH_2CHO$ **Butanal**	$CH_3COCH_2CH_3$ **Butan-2-one**
Molecular mass	**72**	**74**	**74**	**72**	**72**
Boiling point (K)	**309**	**308**	**391**	**349**	**353**

Among the carbonyl compounds, ketones have slightly higher boiling points than the isomeric aldehydes. This is due t0.o the presence of two electrons releasing groups around the carbonyl carbon, which makes them more polar.



Acetaldehyde
μ=2.52 D
b.pt.=322 K



Acetone
μ=2.88 D
b.pt.=329 K

(5) **Density :** Density of aldehydes and ketones is less than that of water.

Chemical properties of carbonyl compounds.

Carbonyl compounds give chemical reactions due to carbonyl compounds group and α-hydrogens.

Chemical reactions of carbonyl compounds can be classified into following categories.

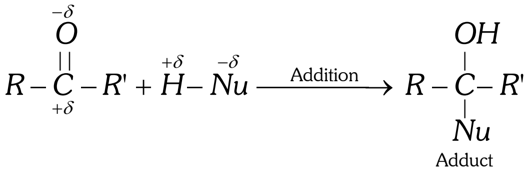
(1) Nucleophilic addition reactions
(2) Addition followed by elimination reactions
(3) Oxidation
(4) Reduction
(5) Reactions due to α-hydrogen
(6) Condensation reactions and
(7) Miscellaneous reactions

(1) Nucleophilic addition reactions

(i) Carbonyl compounds give nucleophilic addition reaction with those reagents which on dissociation give electrophile as well as nucleophile.

(ii) If nucleophile is weak then addition reaction is carried out in the presence of acid as catalyst.

(iii) Product of addition reactions can be written as follows,

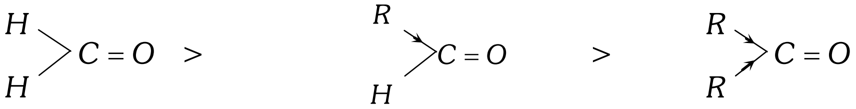


$$R-\underset{+\delta}{\overset{\overset{-\delta}{O}}{\overset{||}{C}}}-R' + \overset{+\delta}{H}-\overset{-\delta}{Nu} \xrightarrow{\text{Addition}} \underset{\text{Adduct}}{R-\underset{Nu}{\overset{OH}{C}}-R'}$$

In addition reactions nucleophile adds on carbonyl carbon and electrophile on carbonyl oxygen to give adduct.

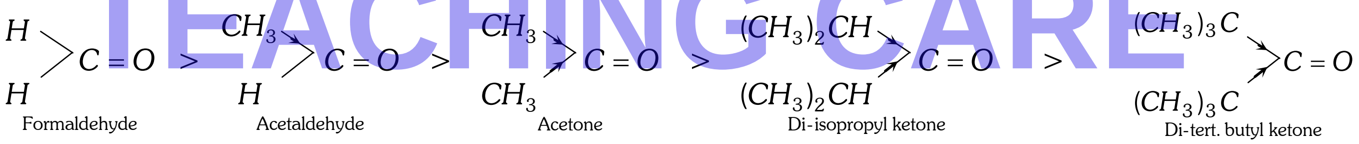
(iv) ***Relative reactivity of aldehydes and ketones :*** Aldehydes and ketones readily undergo nucleophilic addition reactions. However, *ketones are less reactive than aldehydes.* This is due to electronic and stearic effects as explained below:

(a) *Inductive effect* : The relative reactivities of aldehydes and ketones in nucleophilic addition reactions may be attributed to the amount of positive charge on the carbon. *A greater positive charge means a higher reactivity.* If the positive charge is dispersed throughout the molecule, the carbonyl compound becomes more stable and its reactivity decreases. Now, alkyl group is an electron releasing group (+I inductive effect). Therefore, electron releasing power of two alkyl groups in ketones is more than that of one in aldehyde. As a result, the electron deficiency of carbon atom in the carbonyl group is satisfied more in ketones than in aldehydes. Therefore, the reduced positive charge on carbon in case of ketones discourages the attack of nucleophiles. *Hence ketones are less reactive than aldehydes. Formaldehyde with no alkyl groups is the most reactive of the aldehydes and ketones.* Thus, the order of reactivity is:



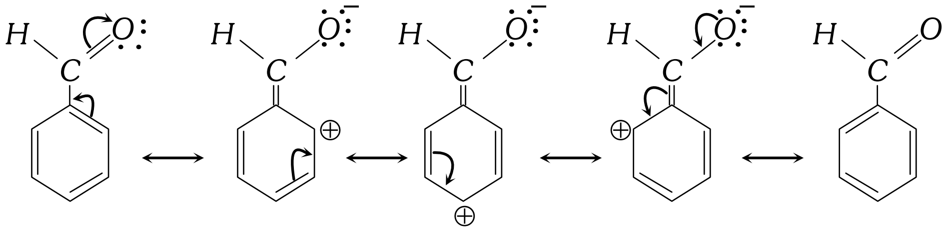
Formaldehyde > Aldehyde > Ketone

(b) *Stearic effect* : The size of the alkyl group is more than that of hydrogen. In aldehydes, there is one alkyl group but in ketones, there are two alkyl groups attached to the carbonyl group. The alkyl groups are larger than a hydrogen atom and these cause hindrance to the attacking group. This is called **stearic hindrance**. *As the number and size of the alkyl groups increase, the hindrance to the attack of nucleophile also increases and reactivity decreases. The lack of hindrance in nucleophilic attack is another reason for the greater reactivity of formaldehyde.* Thus, the reactivity follows the order:



Formaldehyde > Acetaldehyde > Acetone > Di-isopropyl ketone > Di-tert. butyl ketone

In general, **aromatic aldehydes and ketones are less reactive than the corresponding aliphatic analogues.** For example, *benzaldehyde is less reactive than aliphatic aldehydes.* This can be easily understood from the resonating structures of benzaldehyde as shown below:



I II III IV V

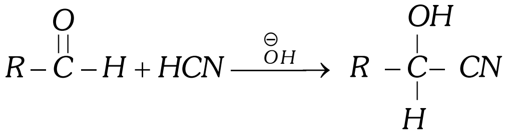
It is clear from the resonating structures that due to electron releasing (+I effect) of the benzene ring, the magnitude of the positive charge on the carbonyl group decreases and consequently it becomes less susceptible to the nucleophilic attack. Thus, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehyde and ketones. The order of reactivity of aromatic aldehydes and ketones is,

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} > \underset{\text{Acetophenone}}{C_6H_5COCH_3} > \underset{\text{Benzophenone}}{C_6H_5COC_6H_5}$$

Some important examples of nucleophilic addition reactions

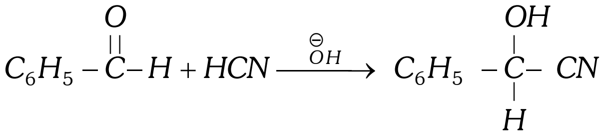
Some important nucleophilic addition reactions of aldehydes and ketones are given below,

Addition of *HCN* : Carbonyl compounds react with *HCN* to form cyanohydrins. This reaction is catalysed by base.



$$R-\overset{\overset{O}{||}}{C}-H + HCN \xrightarrow{\overset{\ominus}{OH}} R-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CN$$

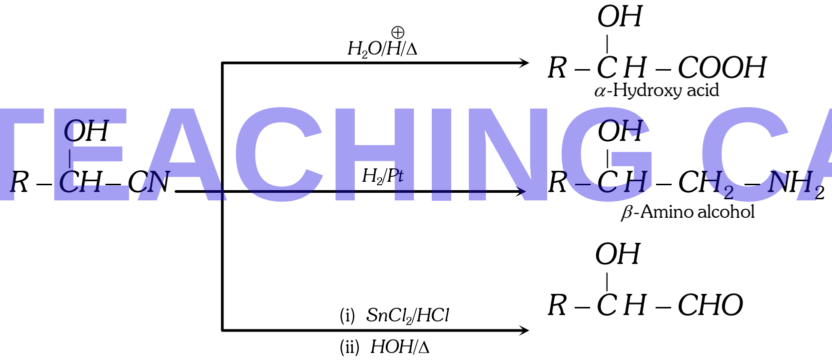
Cyanohydrin



$$C_6H_5-\overset{\overset{O}{||}}{C}-H + HCN \xrightarrow{\overset{\ominus}{OH}} C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CN$$

Note : ✸ *Because HCN is a toxic gas, the best way to carry out this reaction, to generate hydrogen cyanide during the reaction by adding HCl to a mixture of the carbonyl compound and excess of NaCN.*

- ✸ *Benzophenone does not react with HCN.*
- ✸ *Except formaldehyde, all other aldehydes gives optically active cyanohydrin (racemic mixture).*
- ✸ *This reaction is synthetically useful reaction for the preparation of α-hydroxy acids, β-amino alcohols and α-hydroxy aldehydes.*

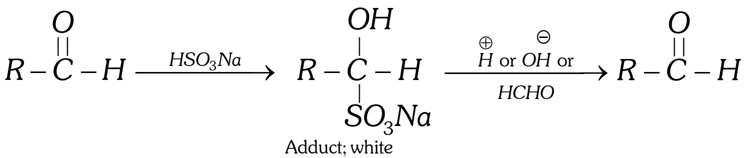


(If *R* is CH_3 then product is lactic acid).

Addition of sodium bisulphite : Sodium bisulphite dissociates as follows:

$$NaHSO_3 \longrightarrow \underset{\text{Electrophile}}{H^{\oplus}} + \underset{\text{Nucleophile}}{S^{\ominus}O_3Na}$$

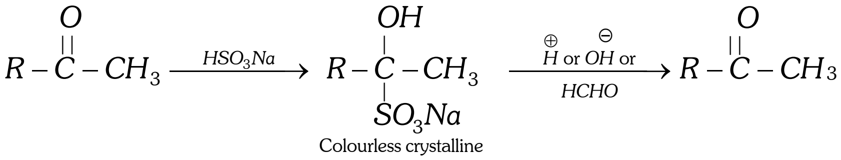
(i) All types of aldehydes give addition reaction with this reagent. The adduct of aldehyde is white crystalline compound which again converts into aldehyde on treatment with acid, base or *HCHO*.



$$R-\overset{\overset{O}{||}}{C}-H \xrightarrow{HSO_3Na} R-\underset{\underset{SO_3Na}{|}}{\overset{\overset{OH}{|}}{C}}-H \xrightarrow[HCHO]{\overset{\oplus}{H} \text{ or } \overset{\ominus}{OH} \text{ or}} R-\overset{\overset{O}{||}}{C}-H$$

Adduct; white crystalline in nature

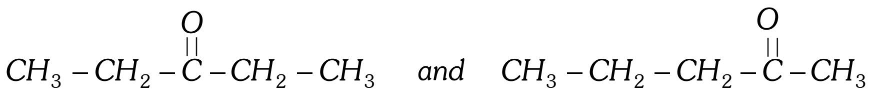
(ii) Only aliphatic methyl ketones give addition reaction with sodium bisulphite.



$$R-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow{HSO_3Na} R-\underset{\underset{SO_3Na}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \xrightarrow[HCHO]{\overset{\oplus}{H} \text{ or } \overset{\ominus}{OH} \text{ or}} R-\overset{\overset{O}{||}}{C}-CH_3$$

Colourless crystalline product

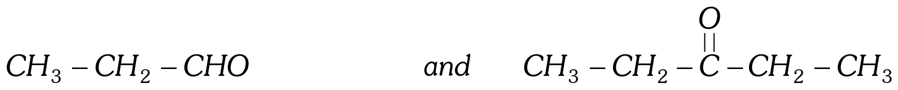
Note : ✸ *This reagent can be used for differentiation between ketones and aliphatic methyl ketones, e.g.*



$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 \quad \text{and} \quad CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

$$C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3 \quad \text{and} \quad CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

✸ *This reagent can be used for the separation of aldehydes and aliphatic methyl ketones from the mixture, e.g.*

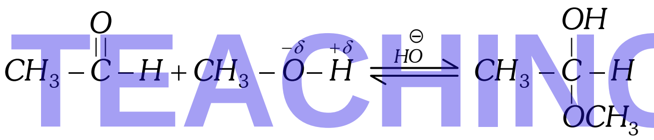


$$CH_3-CH_2-CHO \quad \text{and} \quad CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

These two compounds can be separated from their mixture by the use of $NaHSO_3$*. Higher aliphatic ketones and aromatic ketones do not react with* $NaHSO_3$*.*

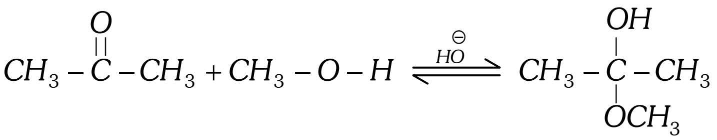
Addition of alcohols : Carbonyl compounds give addition reaction with alcohols. This reaction is catalysed by acid and base. Nature of product depends on the catalyst.

Case I : Addition catalysed by base : In the presence of base one equivalent of an alcohol reacts with only one equivalent of the carbonyl compound. The product is called hemiacetal (in case of aldehyde) and hemiketal (in case of ketone). The reaction is reversible. There is always equilibrium between reactants and product.



$$CH_3-\overset{\overset{O}{\|}}{C}-H+CH_3-\overset{-\delta}{O}-\overset{+\delta}{H} \xrightleftharpoons{\overset{\ominus}{HO}} CH_3-\underset{OCH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-H$$

Hemiacetal

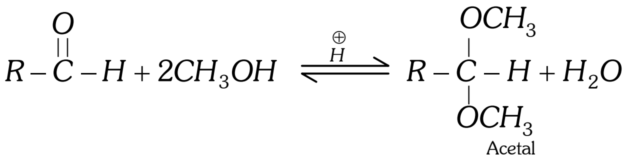


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3+CH_3-O-H \xrightleftharpoons{\overset{\ominus}{HO}} CH_3-\underset{OCH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_3$$

Hemiketal

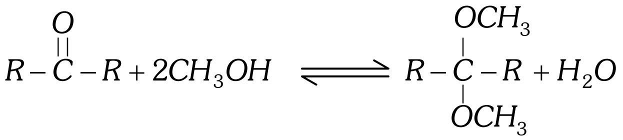
Hemiacetals and hemiketals are **α-alkoxy alcohols**.

Case II : Addition catalysed by acid : In the presence of acid one equivalent of carbonyl compound reacts with two equivalents of alcohol. Product of the reaction is acetal (in case of aldehyde) or ketal (in case of ketone).



$$R-\overset{\overset{O}{\|}}{C}-H+2CH_3OH \xrightleftharpoons{\overset{\oplus}{H}} R-\underset{OCH_3}{\overset{OCH_3}{\underset{|}{\overset{|}{C}}}}-H+H_2O$$

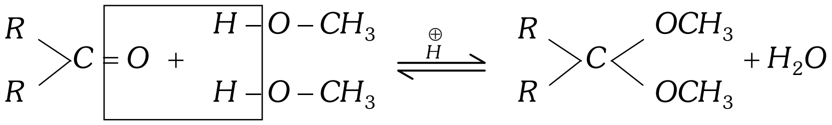
Acetal



$$R-\overset{\overset{O}{\|}}{C}-R+2CH_3OH \rightleftharpoons R-\underset{OCH_3}{\overset{OCH_3}{\underset{|}{\overset{|}{C}}}}-R+H_2O$$

Ketal

(i) Formation of acetals and ketals can be shown as follows:

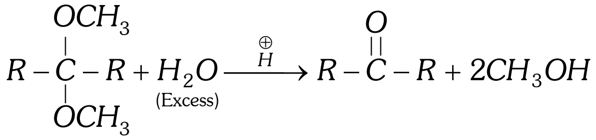


$$\begin{matrix}R\\R\end{matrix}\!>\!C=\boxed{O + \begin{matrix}H-\\H-\end{matrix}}\begin{matrix}O-CH_3\\O-CH_3\end{matrix} \xrightleftharpoons{\overset{\oplus}{H}} \begin{matrix}R\\R\end{matrix}\!>\!C\!<\!\begin{matrix}OCH_3\\OCH_3\end{matrix} + H_2O$$

(ii) Acetals and ketals are gem dialkoxy compounds.

(iii) High yield of acetals or ketals are obtained if the water eliminated from the reaction is removed as it formed because the reaction is reversible.

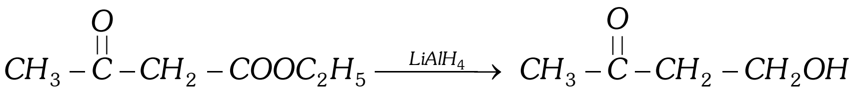
(iv) Acetals and ketals can be transformed back to corresponding aldehyde or ketone in the presence of excess of water.



$$R-\underset{OCH_3}{\overset{OCH_3}{C}}-R + \underset{\text{(Excess)}}{H_2O} \xrightarrow{\overset{\oplus}{H}} R-\overset{O}{\overset{\|}{C}}-R + 2CH_3OH$$

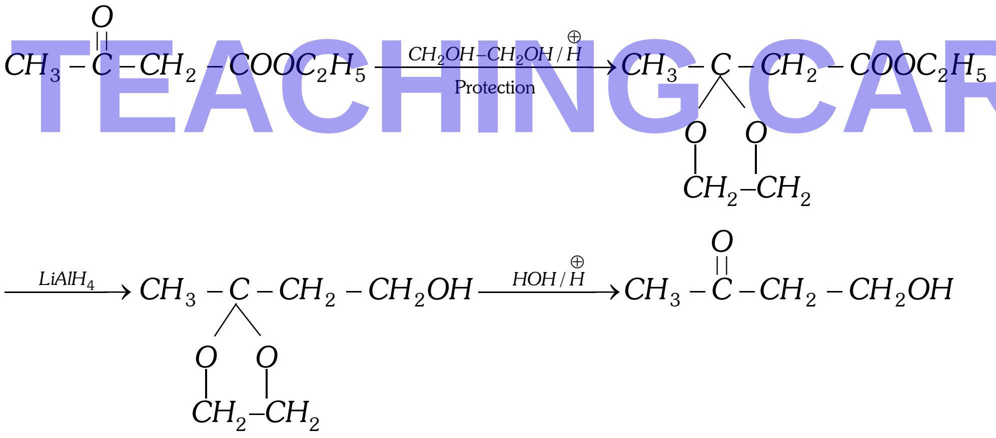
Ketal

This reaction is very useful reaction for the protection of carbonyl group which can be deprotected by hydrolysis. Glycol is used for this purpose. Suppose we want to carry out the given conversion by $LiAlH_4$.



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOC_2H_5 \xrightarrow{LiAlH_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2OH$$

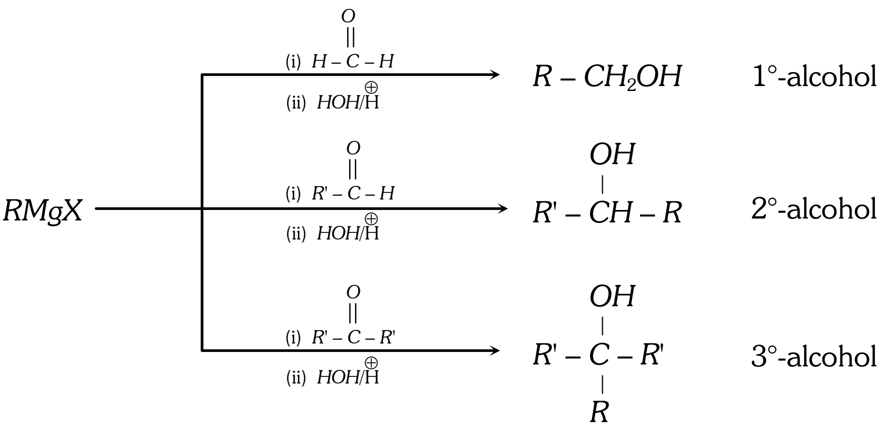
This can be achieved by protection of $>C=O$ group and then by deprotection



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOC_2H_5 \xrightarrow[\text{Protection}]{CH_2OH-CH_2OH/\overset{\oplus}{H}} CH_3-\underset{\underset{CH_2-CH_2}{O\quad O}}{C}-CH_2-COOC_2H_5$$

$$\xrightarrow{LiAlH_4} CH_3-\underset{\underset{CH_2-CH_2}{O\quad O}}{C}-CH_2-CH_2OH \xrightarrow{HOH/\overset{\oplus}{H}} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2OH$$

Addition of Grignard reagents : Grignard reagents react with carbonyl compounds to give alcohols. Nature of alcohol depends on the nature of carbonyl compound.

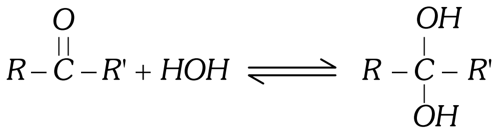


$$RMgX \xrightarrow[\text{(ii) } HOH/\overset{\oplus}{H}]{\text{(i) } H-\overset{O}{\overset{\|}{C}}-H} R-CH_2OH \qquad 1°\text{-alcohol}$$

$$RMgX \xrightarrow[\text{(ii) } HOH/\overset{\oplus}{H}]{\text{(i) } R'-\overset{O}{\overset{\|}{C}}-H} R'-\overset{OH}{\overset{|}{C}H}-R \qquad 2°\text{-alcohol}$$

$$RMgX \xrightarrow[\text{(ii) } HOH/\overset{\oplus}{H}]{\text{(i) } R'-\overset{O}{\overset{\|}{C}}-R'} R'-\underset{\underset{R}{|}}{\overset{OH}{\overset{|}{C}}}-R' \qquad 3°\text{-alcohol}$$

Addition of water : Carbonyl compounds react with water to give gem diols. This reaction is catalysed by acid. The reaction is reversible reaction.

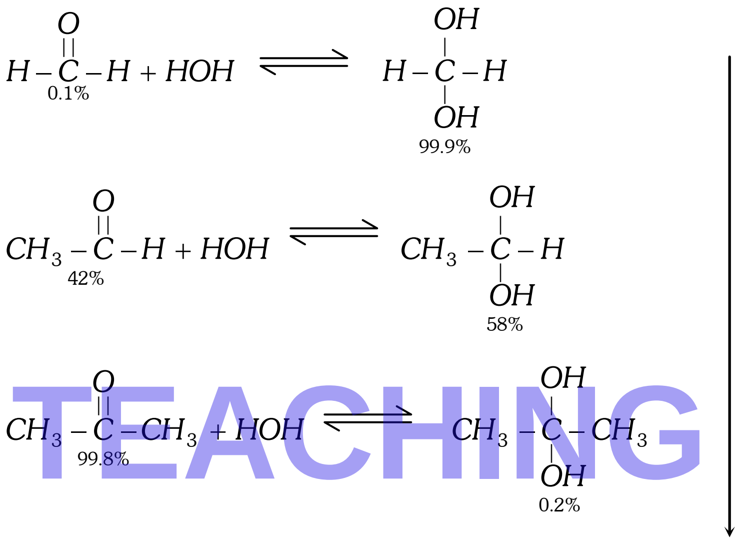


$$R-\overset{O}{\overset{||}{C}}-R' + HOH \rightleftharpoons R-\overset{OH}{\underset{OH}{C}}-R'$$

Gem diols are highly unstable compounds hence equilibrium favours the backward direction. The extent to which an aldehyde or ketone is hydrated depends on the stability of gem diol.

Stability of gem diols depend on the following factors:

(i) Steric hindrance by +I group around α-carbon decreases the stability of gem diols. +I group decreases stability of gem diol and hence decreases extent of hydration.



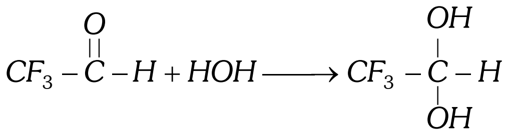
$$\underset{0.1\%}{H-\overset{O}{\overset{||}{C}}-H} + HOH \rightleftharpoons \underset{99.9\%}{H-\overset{OH}{\underset{OH}{C}}-H}$$

$$\underset{42\%}{CH_3-\overset{O}{\overset{||}{C}}-H} + HOH \rightleftharpoons \underset{58\%}{CH_3-\overset{OH}{\underset{OH}{C}}-H}$$

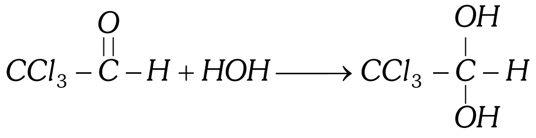
$$\underset{99.8\%}{CH_3-\overset{O}{\overset{||}{C}}-CH_3} + HOH \rightleftharpoons \underset{0.2\%}{CH_3-\overset{OH}{\underset{OH}{C}}-CH_3}$$

(i) +I power of +I group is in increasing order
(ii) Stability in decreasing order

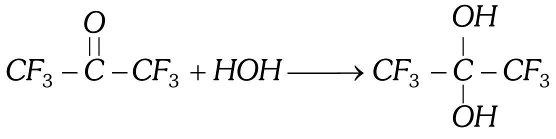
(ii) Stability of gem diols mainly depends on the presence of –I group on α-carbon. More is the –I power of the group more will be stability of gem diols.



$$CF_3-\overset{O}{\overset{||}{C}}-H + HOH \longrightarrow CF_3-\overset{OH}{\underset{OH}{C}}-H$$



$$CCl_3-\overset{O}{\overset{||}{C}}-H + HOH \longrightarrow CCl_3-\overset{OH}{\underset{OH}{C}}-H$$



$$CF_3-\overset{O}{\overset{||}{C}}-CF_3 + HOH \longrightarrow CF_3-\overset{OH}{\underset{OH}{C}}-CF_3$$

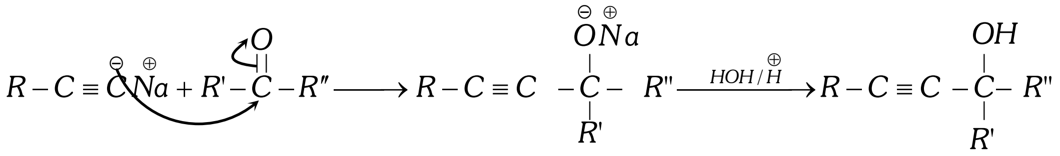
These gem diols are highly stable due to the presence of –I group on α-carbon.

(iii) Intramolecular hydrogen bonding increases stability of gem diols. –I groups present on carbon having gem diol group increases strength of hydrogen bond.

Strength of hydrogen bond $\propto -I$ power of the group.

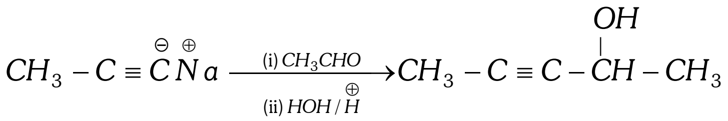
More is the strength of hydrogen bond more will be the stability of gem diol.

Addition of terminal alkynes : Sodium salt of terminal alkynes react with carbonyl compounds to give alkynol. This reaction is known as **ethinylation**.

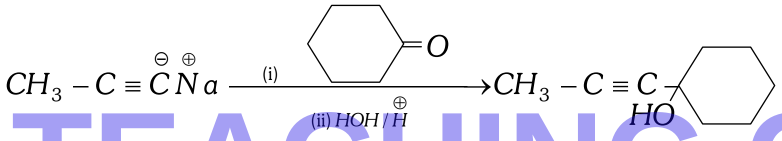


Some examples are,

$$CH_3-C\equiv\overset{\ominus}{C}\overset{\oplus}{N}a\xrightarrow[\text{(ii) } HOH/\overset{\oplus}{H}]{\text{(i) } HCHO}CH_3-C\equiv C-CH_2OH$$



$$CH_3-C\equiv\overset{\ominus}{C}\overset{\oplus}{N}a\xrightarrow[\text{(ii) } HOH/\overset{\oplus}{H}]{\text{(i) } CH_3CHO}CH_3-C\equiv C-\overset{OH}{\overset{|}{C}H}-CH_3$$



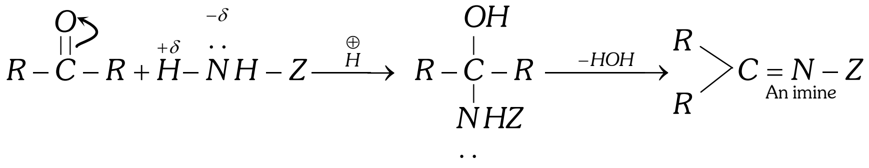
(2) **Addition followed by elimination reactions :** This reaction is given by ammonia derivatives (NH_2-Z).

(i) In nucleophilic addition reactions poor nucleophile such as ammonia and ammonia derivatives requires acid as catalyst.

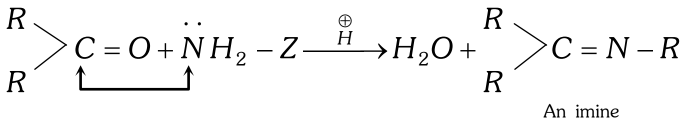
(ii) If the attacking atom of the nucleophile has a lone pair of electrons in the addition product, water will be eliminated from the addition product. This is called a nucleophilic addition elimination.

Primary amines and derivatives of ammonia react with carbonyl compounds to give adduct.

In adduct nucleophilic group has lone pair of electrons. It undergoes elimination to give product known as imine. An imine is a compound with a carbon-nitrogen double bond.



The overall reaction can be shown as follows:



$$\begin{matrix}R\\R\end{matrix}\!\!>C=O+\ddot{N}H_2-Z\xrightarrow{\overset{\oplus}{H}}H_2O+\begin{matrix}R\\R\end{matrix}\!\!>C=N-R$$