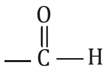
Chapter 11

Aldehydes, Ketones and Carboxylic Acids

INTRODUCTION AND STRUCTURE OF CARBONYL COMPOUND

Carbonyl compound

Organic Compounds having >C = O group are called carbonyl compounds and >C = O group is known as carbonyl or oxo group. It's general formula is $C_n H_{2n}O$ (n = 1, 2, 3......) Carbonyl compounds are grouped into two categories.

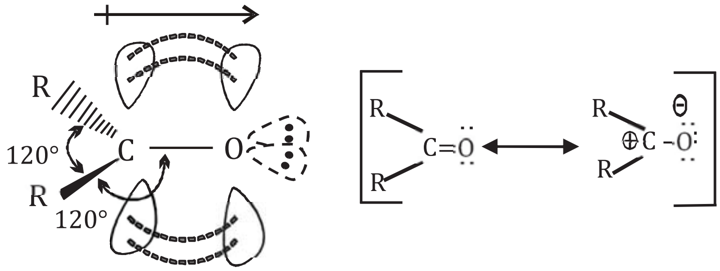
(a) **Aldehydes:** Aldehyde group is  $-\overset{O}{\overset{\|}{C}}-H$ (also known as formyl group).
It is a monovalent group.

(b) **Ketones:** The carbonyl group (>C = O) is a Ketonic group when it's both the valencies are satisfied by alkyl group. It is a bivalent group.

Nomenclature And Structure of Carbonyl Group

Structure And Bonding in Aldehydes and Ketones

The carbonyl carbon atom displays sp^2 hybridization. The unhybridized p-orbital of carbon forms a pi bond through overlap with a p-orbital of oxygen. This results in a double bond between carbon and oxygen, which is characterized by being shorter, stronger, and polar in nature. Orbital diagram for the formation of carbonyl group is as follows



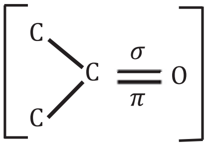
The presence of polarity indicates that nucleophilic addition reactions occur in carbonyl compounds.

The carbonyl group's double bond possesses a significant dipole moment due to the higher electronegativity of oxygen compared to carbon.

Carbonyl carbon act as an electrophile (Lewis's acid)

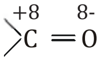
Carbonyl oxygen act as a nucleophile (Lewis's Base)

- Chemical Properties of carboxylic acid



The C—C—O and H—C—O bond angles are of 120°.

Due to electro-negativity difference in C & O atoms, the >C=O group is polar.

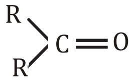


$$>\overset{+8}{C}=\overset{8-}{O}$$

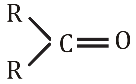
Hence aldehydes and Ketones possess dipole moment.

Ketones are further classified as

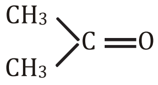
(i) Simple or Symmetrical ketones: Having two similar alkyl groups.



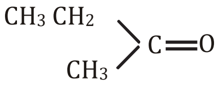
(ii) Mixed or unsymmetrical ketones: Having two different alkyl groups.



Ex: (Ketones) Symmetrical Unsymmetrical



(Acetone or Dimethyl ketone)
2–Propanone



(Ethyl methyl ketone)
2–Butanone

PREPARATION OF ALDEHYDES AND KETONES

General Methods of Preparation

General Method of Only Aldehyde and Ketone

(A) For Both Aldehydes and Ketones

By Oxidation of Alcohols

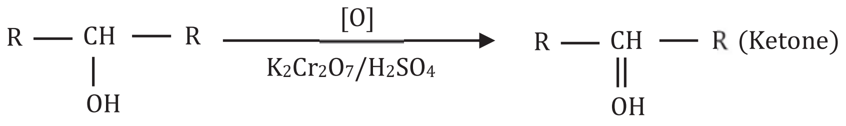
$$\text{Primary alcohols} \xrightarrow{[o]} \text{Aldehydes}$$

$$\text{Secondary alcohols} \xrightarrow{[o]} \text{Ketones}$$

By $K_2Cr_2O_7$ / H_2SO_4

The oxidation of primary alcohols results in the formation of aldehydes, while secondary alcohols, when oxidized, produce ketones. Here, ($K_2Cr_2O_7$ / H_2SO_4) is a strong oxidising agent.

$$RCH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} RCHO \text{ (Aldehyde)}$$



$$R-\underset{\underset{OH}{|}}{CH}-R \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} R-\underset{\underset{OH}{||}}{CH}-R \text{ (Ketone)}$$

Aldehydes are quite susceptible to further oxidation to acids -

$$RCH_2OH \xrightarrow{[o]} R-CHO \xrightarrow{[o]} R-COOH$$

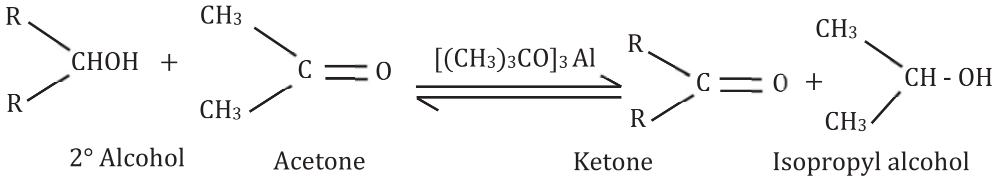
Therefore, the oxidation of primary alcohols is carried out at temperatures significantly higher than the boiling point of aldehydes.

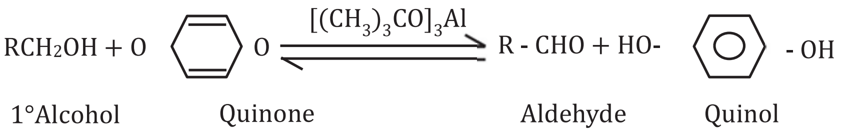
This high temperature causes the aldehydes to vaporize and prevents them from undergoing further oxidation. Aldehydes can be synthesized from primary alcohols, while secondary alcohols can be oxidized to ketones using various reagents such as pyridinium chlorochromate (PCC) in CH_2Cl_2 solvent, pyridinium dichromate (PDC), or Jones reagent (CrO_3+H_2SO_4) in acetone.

Oppenauer Oxidation

The transformation of secondary alcohols into ketones is achieved through the application of a specialized reagent, $[(CH_3)_3CO]_3Al$ (Aluminum-t-butoxide), while being heated in the presence of acetone.

In the case of primary alcohols, they can be oxidized to aldehydes when ketones are substituted with a more effective hydrogen acceptor, such as p-benzoquinone. The balance of this reaction can be managed by adjusting the quantity of acetone, with an excess of acetone promoting the oxidation of the alcohol.





Note: The reaction is the reverse of Meerwein - Ponndorf - verley reduction.

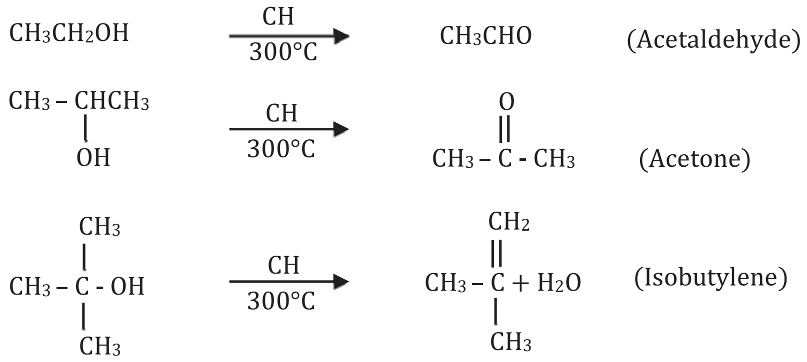
Mild Oxidising Agent

1^o alcohols will get oxidised with CrO_3 / Pyridine, Collin's reagent Ag/O_2 at 250^oC

$$RCH_2OH + [O] \longrightarrow RCHO + H_2O$$

By this reaction, good yield of aldehyde is possible.

Dehydrogenation of alcohols



$$CH_3CH_2OH \xrightarrow[300^\circ C]{CH} CH_3CHO \quad \text{(Acetaldehyde)}$$

$$CH_3-\underset{OH}{\underset{|}{CH}}CH_3 \xrightarrow[300^\circ C]{CH} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \quad \text{(Acetone)}$$

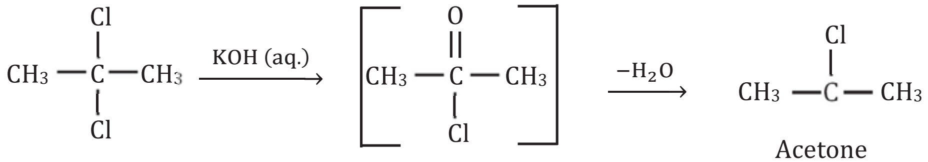
$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH \xrightarrow[300^\circ C]{CH} CH_3-\underset{CH_3}{\underset{|}{\overset{CH_2}{\overset{\|}{C}}}} + H_2O \quad \text{(Isobutylene)}$$

By Hydrolysis of gem dihalides

Terminal gem-dihalides on hydrolysis give aldehydes while the non-terminal dihalides give ketone.

$$CH_3CH{<}\begin{matrix}Cl\\Cl\end{matrix} \xrightarrow{KOH(aq.)} CH_3CH{<}\begin{matrix}Cl\\Cl\end{matrix} \xrightarrow{-H_2O} CH_3CHO$$

Terminal gem-dihalide [unstable] Acetaldehyde



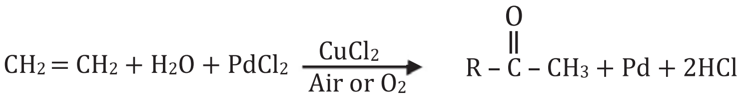
$$CH_3-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-CH_3 \xrightarrow{KOH\ (aq.)} \left[CH_3-\underset{Cl}{\underset{|}{\overset{O}{\overset{\|}{C}}}}-CH_3\right] \xrightarrow{-H_2O} CH_3-\overset{Cl}{\overset{|}{C}}-CH_3$$

Unstable Acetone

Wacker process

Alkenes can be oxidized to their respective aldehydes or ketones by subjecting them to a solution of $PdCl_2$, which includes a catalytic quantity of $CuCl_2$ in the presence of air or O_2.
Except ethene any higher alkene will give ketone.

$$CH_2=CH_2 + H_2O + PdCl_2 \xrightarrow[\text{Air or } O_2]{CuCl_2} CH_3-CH=O + Pd + 2HCl$$



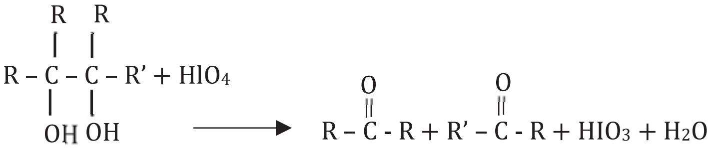
$$CH_2=CH_2 + H_2O + PdCl_2 \xrightarrow[\text{Air or } O_2]{CuCl_2} R-\overset{O}{\overset{\|}{C}}-CH_3 + Pd + 2HCl$$

Note During the reaction $PdCl_2$ is reduced to Pd and $CuCl_2$ is reduced to Cu(I)

By Oxidation of diols

When subjected to periodic acid (HIO_4) and lead tetra acetate $(CH3COO)_4$ Pb, vicinal diols undergo oxidation to produce carbonyl compounds.

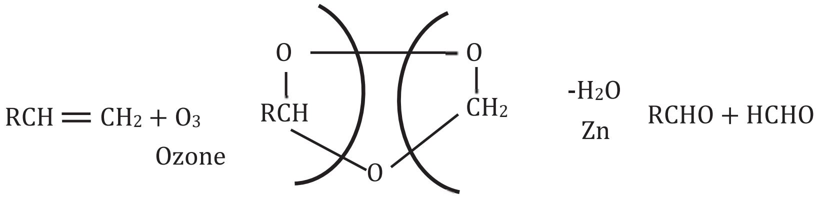
$$R-\underset{OH}{CH}-\underset{OH}{CH}-R' + HIO_4 \longrightarrow RCHO + R'CHO + HIO_3 + H_2O$$



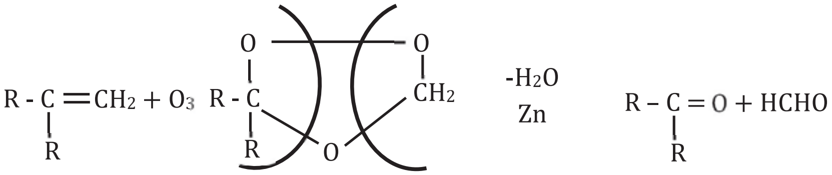
$$R-\overset{R}{\underset{OH}{C}}-\overset{R}{\underset{OH}{C}}-R' + HIO_4 \longrightarrow R-\overset{O}{\overset{\|}{C}}-R + R'-\overset{O}{\overset{\|}{C}}-R + HIO_3 + H_2O$$

By Ozonolysis of alkenes

This reaction is used to determine the position of double bond in alkene.



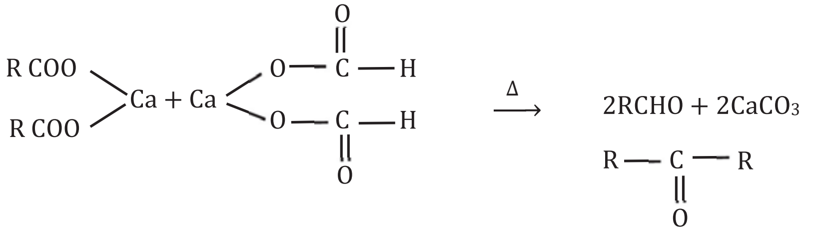
Ozonide



Unbranched alkene → Aldehyde

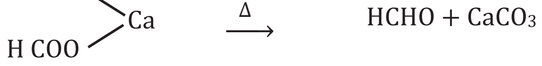
Branched alkene → Ketone

By Dry Distillation of Ca-Salts of Carboxylic Acid



Calcium format

(Also and HCHO formed)



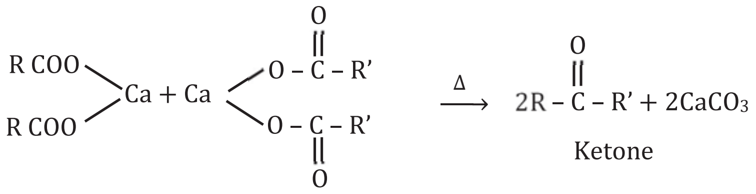
$$(HCOO)_2Ca \xrightarrow{\Delta} HCHO + CaCO_3$$

$$(RCOO)_2Ca \xrightarrow{\Delta} R_2C{=}O + CaCO_3$$

Calcium-alkenoate

Ketone

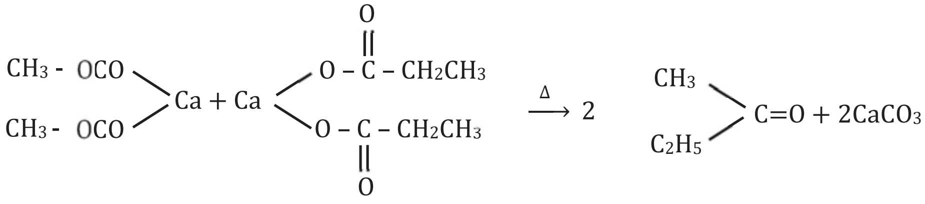
Calcium salts of acids other then formic acid on heating together gives ketone



$$\begin{matrix}R\,COO\\ R\,COO\end{matrix}\!\!>\!Ca + Ca\!<\!\!\begin{matrix}O-\overset{O}{\overset{\|}{C}}-R'\\ O-\underset{O}{\underset{\|}{C}}-R'\end{matrix} \xrightarrow{\Delta} 2R-\overset{O}{\overset{\|}{C}}-R' + 2CaCO_3$$

Ketone

To prepare ethyl methyl ketone Calcium acetate and Calcium propionate are used

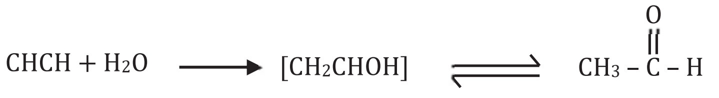


$$\begin{matrix}CH_3-OCO\\ CH_3-OCO\end{matrix}\!\!>\!Ca + Ca\!<\!\!\begin{matrix}O-\overset{O}{\overset{\|}{C}}-CH_2CH_3\\ O-\underset{O}{\underset{\|}{C}}-CH_2CH_3\end{matrix} \xrightarrow{\Delta} 2\ \begin{matrix}CH_3\\ C_2H_5\end{matrix}\!\!>\!C=O + 2CaCO_3$$

Calcium Acetate Calcium propionate Ethyl methyl ketone

From Alkyne

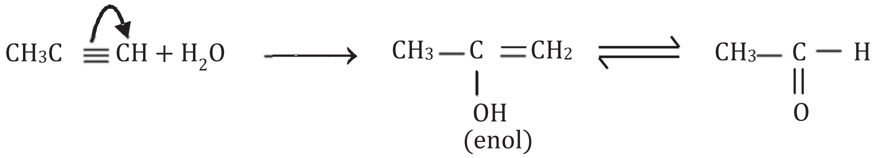
Hydration of Alkyne: With dill H_2SO_4 & 1% $HgSO_4$ at 60-80^{0}C.



$$CHCH + H_2O \longrightarrow [CH_2CHOH] \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-H$$

(Tautomerization)

Other Alkynes give ketone

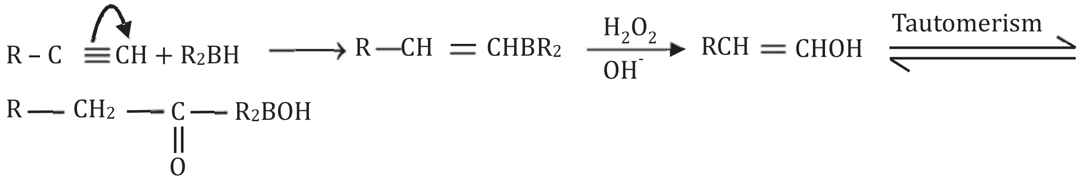


$$CH_3C\equiv CH + H_2O \longrightarrow CH_3-\underset{OH}{\underset{|}{C}}=CH_2 \rightleftharpoons CH_3-\underset{O}{\underset{\|}{C}}-H$$

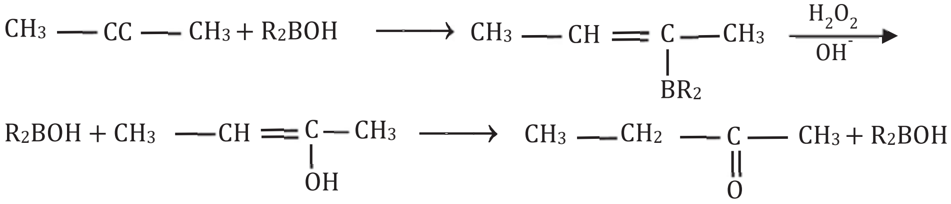
(enol)

Hydroboration of Alkynes: Reaction with B_2H_6, $2BH_3$ or R_2BH give dialkyl borane.

1 – alkyne gives → Aldehyde
other alkyne → Ketone



$$R-C\equiv CH + R_2BH \longrightarrow R-CH=CHBR_2 \xrightarrow[OH^-]{H_2O_2} RCH=CHOH \xrightleftharpoons{\text{Tautomerism}} R-CH_2-\underset{O}{\underset{\|}{C}}-R_2BOH$$



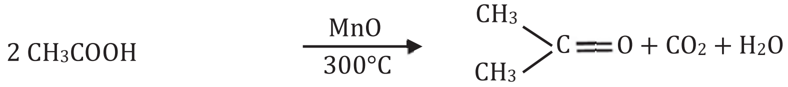
$$CH_3-CC-CH_3 + R_2BOH \longrightarrow CH_3-CH=\underset{BR_2}{\underset{|}{C}}-CH_3 \xrightarrow[OH^-]{H_2O_2}$$

$$R_2BOH + CH_3-CH=\underset{OH}{\underset{|}{C}}-CH_3 \longrightarrow CH_3-CH_2-\underset{O}{\underset{\|}{C}}-CH_3 + R_2BOH$$

By Thermal Decomposition of Carboxylic Acids

Vapour of carboxylic acids when passed over MnO/300^{0}C give carbonyl compounds

$$2\,HCOOH \xrightarrow[300°C]{MnO} HCHO + H_2O + CO_2$$



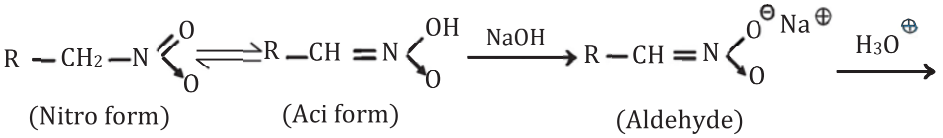
$$2\,CH_3COOH \xrightarrow[300°C]{MnO} (CH_3)_2C{=}O + CO_2 + H_2O$$

$$RCOOH + HCOOH \xrightarrow[300°C]{MnO} RCHO + CO_2 + H_2O$$

$$RCOOH + R'COOH \xrightarrow[300°C]{MnO} RCOR' + CO_2 + H_2O$$

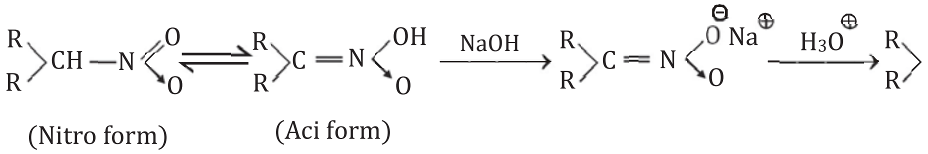
By Nef's Reaction

Nitro alkanes are used in this reaction. The α–H of nitro alkane shows acidic nature.



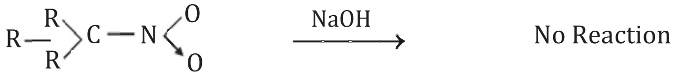
R – CHO + N_2O + H_2O+NaOH

1° nitro alkane



C =O + N_2O + H_2O + NaOH

(Ketone) 2° nitro alkane

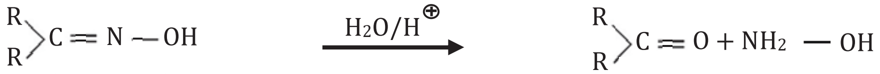


(3° nitro alkane)

By Hydrolysis of Carbonyl Derivatives

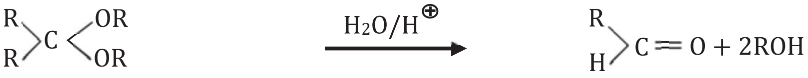
$$R{-}CHN{-}OH \xrightarrow{H_2O/H^{\oplus}} R{-}CHO + NH_2{-}OH$$

(Aldoxime) (Aldehyde) (Hydroxyl amine)



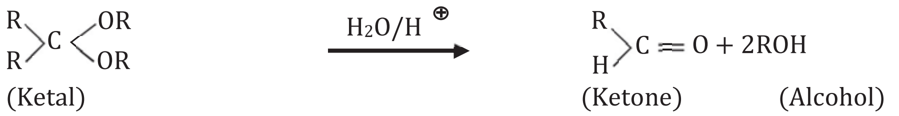
$$R_2C{=}N{-}OH \xrightarrow{H_2O/H^{\oplus}} R_2C{=}O + NH_2{-}OH$$

(Ketoxime) (Ketone)



$$R_2C(OR)_2 \xrightarrow{H_2O/H^{\oplus}} RHC{=}O + 2ROH$$

(Acetal) (Aldehyde) (Alcohol)

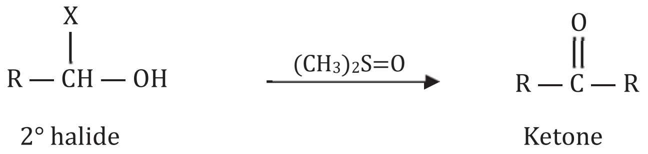


By Oxidation of Alkyl Halides

Oxidation takes place by $(CH_3)_2SO$ dimethyl sulphoxide (DMSO).

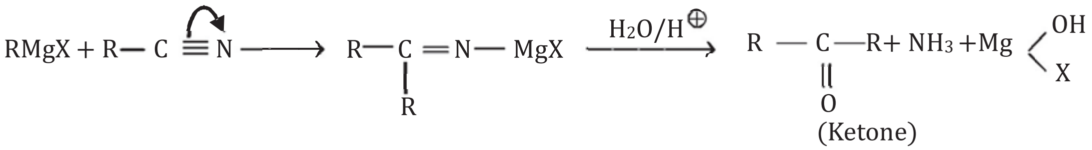
$$R—CH_2—X + (CH_3)_2SO \longrightarrow RCHO + (CH_3)_2S + HX$$

Alkyl halide (Aldehyde) (Dimethyl thio ether)

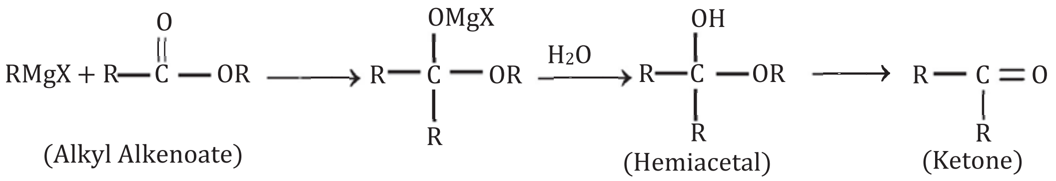


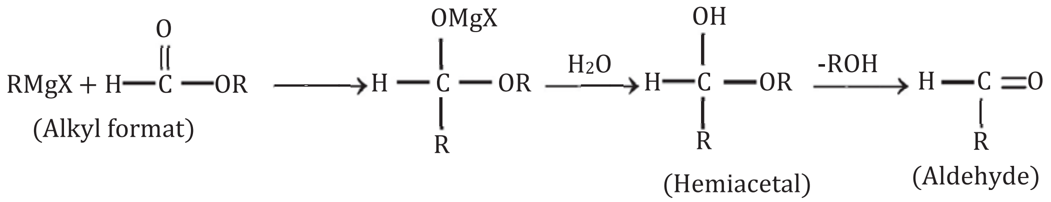
From Grignard Reagents

By Cyanides using RMgX

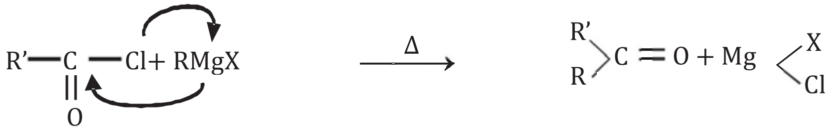


By Esters using RMgX: HCHO can't be prepared by this method.





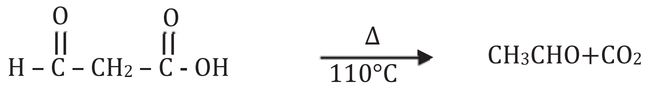
By acid chlorides using RMgX



From β-keto acids

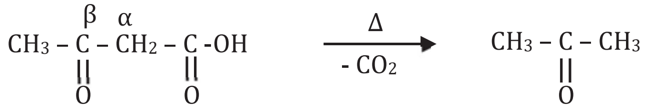
The decarboxylation reaction takes place via formation of six membered ring transition state.

(a)



$$H-\overset{\overset{O}{\parallel}}{C}-CH_2-\overset{\overset{O}{\parallel}}{C}-OH \xrightarrow[110°C]{\Delta} CH_3CHO+CO_2$$

(b)

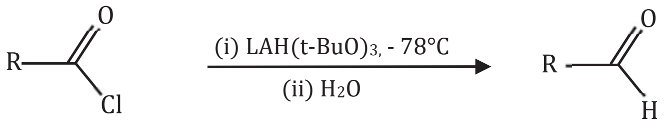


$$CH_3-\underset{\underset{O}{\parallel}}{\overset{\beta}{C}}-\overset{\alpha}{CH_2}-\underset{\underset{O}{\parallel}}{C}-OH \xrightarrow[-CO_2]{\Delta} CH_3-\underset{\underset{O}{\parallel}}{C}-CH_3$$

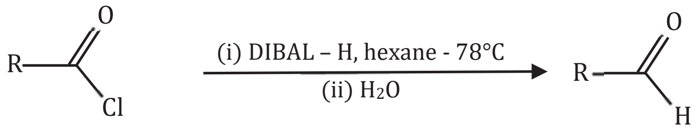
(B) For Aldehydes Only

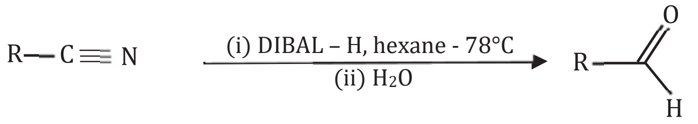
Reduction of acyl halides, esters and nitriles

Alkenes can be oxidized to their respective aldehydes or ketones by subjecting them to a solution of $PdCl_2$, which includes a catalytic quantity of $CuCl_2$ in the presence of air or O_2. $LiAIH[OC(CH_3)_3]$, at –78°C.



DIBAL-H can be used to reduce both esters and nitriles to yield aldehydes. This reduction process should be conducted under low-temperature conditions. Subsequent hydrolysis of the intermediates produces the aldehyde.





Rosenmund's reduction

Quinoline or sulfur serves as a catalyst inhibitor, regulating the subsequent conversion of aldehydes into alcohols.

$$RCOCl + H_2 \xrightarrow[\text{Quinoline or sulphur}]{Pd/BaSO_4} RCHO + HCl$$

$$RCOCl + H_2 \xrightarrow{Pd} RCHO \longrightarrow RCH_2OH$$

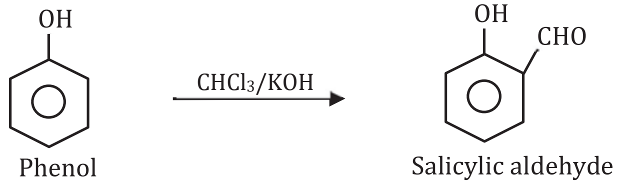
Formaldehyde cannot be prepared by this method.

Ex.

$$\underset{\text{Propionyl Chloride}}{C_2H_5COCl + H_2} \xrightarrow[\text{Quinoline or sulphur}]{Pd/BaSO_4} \underset{\text{Propenal}}{C_2H_5CHO + HCl}$$

Reimer-Tiemann Reaction

By this method phenolic aldehyde is prepared



Stephen's reduction

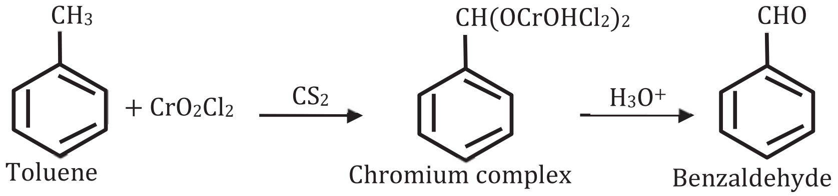
Alkyl cyanides are reduced by $SnCl_2$ and HCl.

$$R - C \equiv N \xrightarrow{SnCl_2/HCl} R - CHNH \xrightarrow{H_3O^+} RCHO + NH_3$$

$$R - C \equiv N \xrightarrow{SnCl_2/HCl} R - CHNH \xrightarrow{H_3O^+} RCHO + NH_3$$

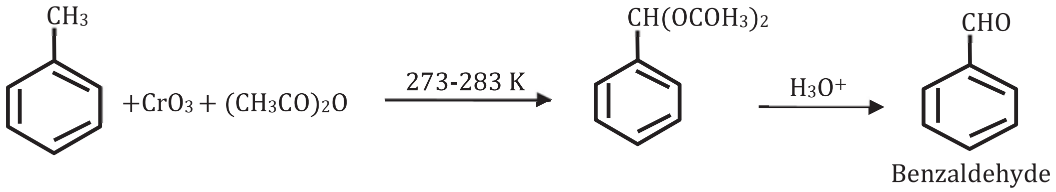
From hydrocarbons

By oxidation of methyl benzene and its derivative using chromyl chloride (CrO_2Cl_2)



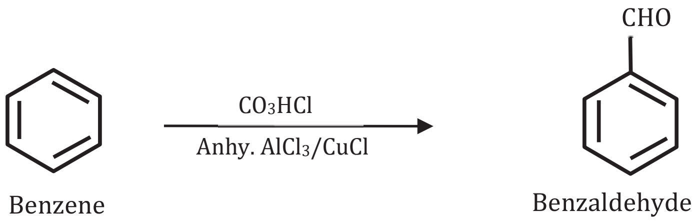
This reaction is called Etard reaction.

By oxidation of methyl benzene and its derivative using chromic oxide (CrO_3) in acetic anhydride



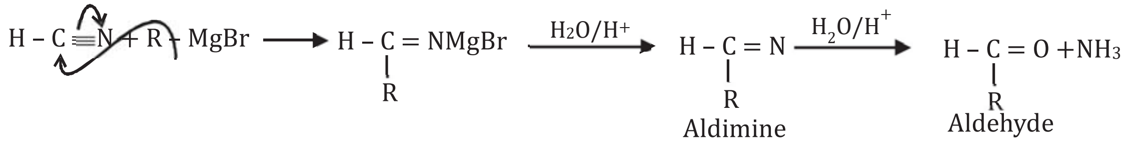
By Gattermann-Koch reaction:

Benzene or its derivative $\xrightarrow[\text{Anhy.AlCl}_3/\text{CuC}]{\text{CO}_3\text{HCl}}$ Benzaldehyde or substituted benzaldehyde



By hydrogen cyanide:

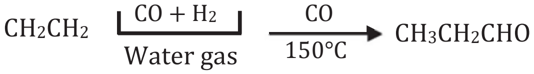
When hydrogen cyanide reacts with a Grignard reagent and then undergoes double decomposition with water, it leads to the formation of an aldehyde through an aldimine intermediate.



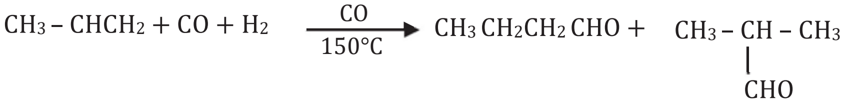
$$H-C\equiv N + R-MgBr \longrightarrow \underset{\substack{|\\R}}{H-C}=NMgBr \xrightarrow{H_2O/H^+} \underset{\substack{|\\R\\\text{Aldimine}}}{H-C}=N \xrightarrow{H_2O/H^+} \underset{\substack{|\\R\\\text{Aldehyde}}}{H-C}=O + NH_3$$

Oxo reaction or hydro formylation

In this reaction symmetrical alkene gives 1^0 aldehydes while unsymmetrical alkene gives isomeric aldehyde (Chain isomers).



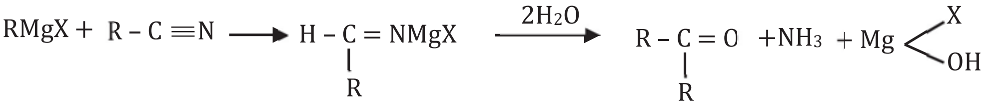
$$CH_2CH_2 \underbrace{CO + H_2}_{\text{Water gas}} \xrightarrow[150^\circ C]{CO} CH_3CH_2CHO$$



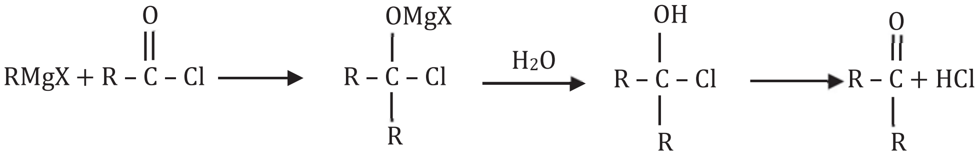
$$CH_3-CHCH_2 + CO + H_2 \xrightarrow[150^\circ C]{CO} CH_3CH_2CH_2CHO + CH_3-\underset{\substack{|\\CHO}}{CH}-CH_3$$

For Ketones only

From Grignard's reagent



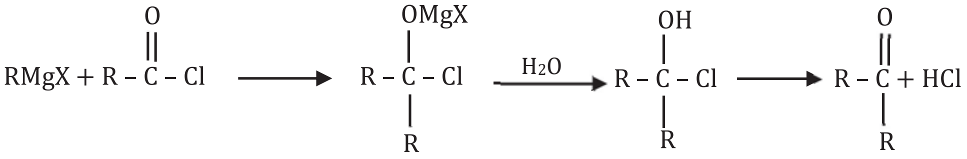
$$RMgX + R-C\equiv N \longrightarrow H-\underset{\substack{|\\R}}{C}=NMgX \xrightarrow{2H_2O} R-\underset{\substack{|\\R}}{C}=O + NH_3 + Mg\begin{smallmatrix}X\\OH\end{smallmatrix}$$



$$RMgX + R-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow R-\overset{\overset{OMgX}{|}}{\underset{\underset{R}{|}}{C}}-Cl \xrightarrow{H_2O} R-\overset{\overset{OH}{|}}{\underset{\underset{R}{|}}{C}}-Cl \longrightarrow R-\overset{\overset{O}{\|}}{\underset{\underset{R}{|}}{C}}+HCl$$

$$RMgX + R-\overset{\overset{O}{\|}}{C}-NH_2 \longrightarrow RH + (RCONH)Mg(X)$$

; Ketone does not form.



$$RMgX + R-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow R-\overset{\overset{OMgX}{|}}{\underset{\underset{R}{|}}{C}}-Cl \xrightarrow{H_2O} R-\overset{\overset{OH}{|}}{\underset{\underset{R}{|}}{C}}-Cl \longrightarrow R-\overset{\overset{O}{\|}}{\underset{\underset{R}{|}}{C}}+HCl$$

By acylation or benzoylation of aromatic hydrocarbon (Friedel-Crafts Reaction)

$$C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{Dry} C_6H_5COCH_3 + HCL$$

Acetophenone

$$C_6H_6 + C_6H_5COCl \xrightarrow[AlCl_3]{Dry} C_6H_5COC_6H_5 + HCL$$

Benzophenone

$$\underset{\text{excess}}{C_6H_6} + COCl_2 \xrightarrow[AlCl_3]{Dry} C_6H_5COC_6H_5 + HCL$$

Benzophenone

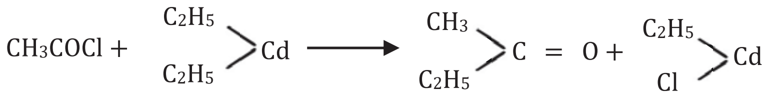
From diallyl Cadmium

RCdR' (diallyl Cadmium) is an organometallic compound.

$$RCOCl + RCdR' \longrightarrow RCOR' + RCdCl$$

This process is more advantageous compared to the Grignard Reaction because the ketones produced can subsequently react with Grignard reagents to yield tertiary alcohols.

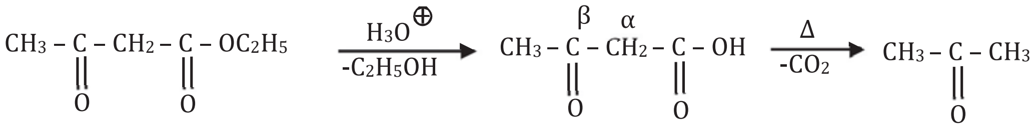
Ex.:



$$CH_3COCl + \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>Cd \longrightarrow \begin{matrix}CH_3\\C_2H_5\end{matrix}\!>C = O + \begin{matrix}C_2H_5\\Cl\end{matrix}\!>Cd$$

From R_2CuLi: $R_2CuLi + R'COCl \longrightarrow R'COR + RCu + LiCl$

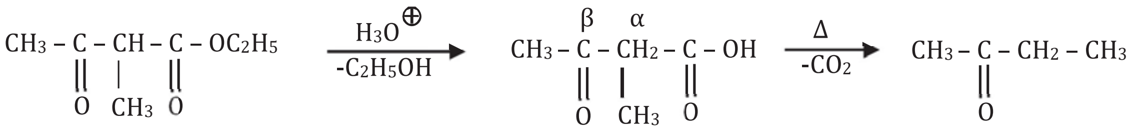
By hydrolysis of Aceto Acetic Ester (AAE):



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow[-C_2H_5OH]{H_3O^{\oplus}} CH_3-\overset{\beta}{\underset{\underset{O}{\|}}{C}}-\overset{\alpha}{CH_2}-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[-CO_2]{\Delta} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

(β - keto acid) (Acetone)

Ex:



$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow[-C_2H_5OH]{H_3O^{\oplus}} CH_3-\overset{\beta}{\underset{\underset{O}{\|}}{C}}-\overset{\alpha}{\underset{\underset{CH_3}{|}}{CH_2}}-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[-CO_2]{\Delta} CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$$