ALDEHYDES, KETONES AND CARRBOXYLIC ACIDS PREPARATION OF ALDEHYDES AND KETONES

GENERAL METHODS OF PREPARATION

(A) FOR BOTH ALDEHYDES AND KETONES

By Oxidation of Alcohols

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

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

By K₂Cr₂O₇ / H₂SO₄

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.

$$RCH_{2}OH \xrightarrow{[0]}{K_{2}Cr_{2}O_{7}/H_{2}SO_{4}} RCHO (Aldehyde)$$

$$R \xrightarrow{CH} R \xrightarrow{[0]}{K_{2}Cr_{2}O_{7}/H_{2}SO_{4}} R \xrightarrow{CH} R (Ketone)$$

$$H \xrightarrow{OH} OH$$

Aldehydes are quite susceptible to further oxidation to acids -

 $\text{RCH}_2\text{OH} \xrightarrow{[0]} \text{R}\text{--CHO} \xrightarrow{[0]} \text{R}\text{--COOH}$

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, [(CH₃)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^{0} alcohols will get oxidised with CrO₃ / Pyridine, Collin's reagent Ag/O₂ at 250^oC

 $RCH_2OH + [0] \longrightarrow RCHO + H_2O$

By this reaction, good yield of aldehyde is possible.

Dehydrogenation of alcohols



By Hydrolysis of gem dihalides

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



Wacker process

Alkenes can be oxidized to their respective aldehydes or ketones by subjecting them to a solution of PdCl₂, which includes a catalytic quantity of CuCl₂ in the presence of air or O₂.

Except ethene any higher alkene will give ketone.

$$CH_2 = CH_2 + H_2O + \underbrace{CuCl_2}_{\text{Air or }O_2} CH_3 - CH = O + Pd + 2HCl$$

$$CH_2 = CH_2 + H_2O + \underbrace{CuCl_2}_{\text{Air or }O_2} R - C - CH_3 + Pd + 2HCl$$

Note During the reaction PdCl₂ is reduced to Pd and CuCl₂ is reduced to Cu(I)

By Oxidation of diols

When subjected to periodic acid (HIO₄) and lead tetra acetate (CH3COO)₄ Pb, vicinal diols undergo oxidation to produce carbonyl compounds.

$$\begin{array}{c} R - CH - CH - R' + HIO_4 \\ I & I \\ OH & OH \end{array} \xrightarrow{} RCHO + R'CHO + HIO_3 + H_2O \end{array}$$

$$\begin{array}{cccc} R & R \\ I & I \\ R - C - C - R' + HlO_4 & O & O \\ I & I \\ OH & OH & \longrightarrow & R - C - R + R' - C - R + HIO_3 + H_2O \end{array}$$

By Ozonolysis of alkenes

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



Class-12th

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



From Alkyne

Hydration of alkyne: With dill $H_2SO_4 \& 1\% HgSO_4$ at 60-80⁰C.

CHCH + H₂O
$$\longrightarrow$$
 [CH₂CHOH] \rightleftharpoons CH₃ - C - H
(Tautomerization)

Other alkynes give ketone



Hydroboration of alkynes: Reaction with B₂H₆, 2BH₃ or R₂BH give dialkyl borane.

1- alkyne gives other alkyne

Aldehyde



By Thermal decomposition of carboxylic acids

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

2 HCOOH	Mn0 300°C	$\mathrm{HCHO} + \mathrm{H_2O} + \mathrm{CO_2}$
2 CH ₃ COOH	Mn0 300°C	$CH CH_2 C = 0 + CO_2 + H_2 O$
RCOOH + HCOOH	Mn0 300°C	$RCHO + CO_2 + H_2O$
RCOOH + R'COOH	Mn0 300°C	$RCOR' + CO_2 + H_2O$

By Nef's reaction

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



Class-12th

Chemistry

By hydrolysis of carbonyl derivatives

R—CHN—OH	<u>H₂O/H</u>	R—CHO + NH ₂ —OH
(Aldoxime)		(Aldehyde) (Hydroxyl amine)
R > C = N - OH (Ketoxime)	<u>H₂0/H</u> [⊕]	$R > C = O + NH_2 - OH$ (Ketone)
R > C < OR OR OR OR (Acetal)	<u>H₂O/H</u> [●]	R H C = 0 + 2ROH (Aldehyde) (Alcohol)
R > C < OR OR OR OR (Ketal)	H ₂ 0/H [♥]	$R \\ H > C = O + 2ROH (Ketone) (Alcohol)$

By oxidation of alkyl halides

Oxidation takes place by (CH₃)₂SO dimethyl sulphoxide (DMSO).

 $R-CH_{2}-X + (CH_{3})_{2}SO \longrightarrow RCHO + (CH_{3})_{2}S + HX$ Alkyl halide
(Aldehyde) (Dimethyl thio ether) $X \qquad (CH_{3})_{2}S=0 \qquad R - C - R$

Ketone

From Grignard reagents

By Cyanides using RMgX

$$RMgX + R - C \stackrel{\frown}{=} N \longrightarrow R - C = N - MgX \xrightarrow{H_2O/H^{\oplus}} R - C - R + NH_3 + Mg \begin{pmatrix} OH \\ X \\ 0 \\ (Ketone) \end{pmatrix}$$

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



Class-12th



By acid chlorides using RMgX



From β -keto acids

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

(a)
$$H - C - CH_2 - C - OH$$
 Δ $H_3CHO + CO_2$

(B) FOR ALDEHYDES ONLY

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Reduction of acyl halides, esters and nitriles

Alkenes can be oxidized to their respective aldehydes or ketones by subjecting them to a solution of PdCl₂, which includes a catalytic quantity of CuCl₂ in the presence of air or O₂. 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.

Class-12th



Rosenmund's reduction

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

 $RCOCI + \frac{Pd/BaSO_4}{Quinoline or sulphur} RCHO + HCl$ $RCOCI + \frac{P}{Quinoline or Sulphur} RCH \longrightarrow RCH_2OH$

Formaldehyde cannot be prepared by this method.

Ex. $C_2H_5COCl + H_2$ $Pd/BaSO_4$ $C_2H_5CHO + HCl$ Propionyl ChloridePropenal

Reimer-Tiemann Reaction

By this method phenolic aldehyde is prepared



Stephen's reduction

Alkyl cyanides are reduced by SnCl₂ and HCl.

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

From hydrocarbons

By oxidation of methyl benzene and its derivative using chromyl chloride (CrO₂Cl₂)



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 $\frac{CO_3HCl}{Anhy.AlCl_3/CuCl}$ 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.

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

R
Aldimine Aldehyde

Oxo reaction or hydro formylation

In this reaction symmetrical alkene gives 1⁰ aldehydes while unsymmetrical alkene gives isomeric aldehyde (Chain isomers).

$$CH_{2}CH_{2} \xrightarrow{CO + H_{2}} \xrightarrow{CO} CH_{3}CH_{2}CHO$$

$$CH_{3} - CHCH_{2} + CO + H_{2} \xrightarrow{CO} CH_{3}CH_{2}CHO + CH_{3} - CH - CH_{3}$$

$$\downarrow CHO$$

For Ketones only From Grignard's reagent



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

$$\begin{array}{ccc} C_{6}H_{6}+CH_{3}COCl & \frac{Dry}{AlCl_{3}} \rightarrow & C_{6}H_{5}COCH_{3}+HCL \\ & & & & & & & & \\ C_{6}H_{6}+C_{6}H_{5}COCl & \frac{Dry}{AlCl_{3}} \rightarrow & C_{6}H_{5}COC_{6}H_{5}+HCL \\ & & & & & & & & \\ & & & & & & & \\ C_{6}H_{6}+COCl_{2} & \frac{Dry}{AlC_{3}} \rightarrow & C_{6}H_{5}COC_{6}H_{5}+HCL \\ & & & & & & & \\ excess & & & & & & \\ \end{array}$$

Ex.:

Chemistry

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.

 $CH_{3}COCI + \frac{C_{2}H_{5}}{C_{2}H_{5}} Cd \longrightarrow \frac{CH_{3}}{C_{2}H_{5}} C = O + \frac{C_{2}H_{5}}{Cl} Cd$

From R₂CuLi: R_2 CuLi + R'COCl \longrightarrow R'COR + RCu + LiCl

By hydrolysis of Aceto Acetic Ester (AAE)

$$\begin{array}{c} CH_3 - C - CH_2 - C - OC_2H_5 \xrightarrow{H_3O} CH_3 - C_2H_5OH \end{array} \xrightarrow{\beta} CH_3 - C_2H_2 - C_2H_5OH \xrightarrow{\beta} CH_3 - C_2H_3 - C_2H_3$$

$$(\beta - \text{keto acid})$$
 (Acetone)