MIND MAP

Carbonyl Compound

(a) Aldehydes

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

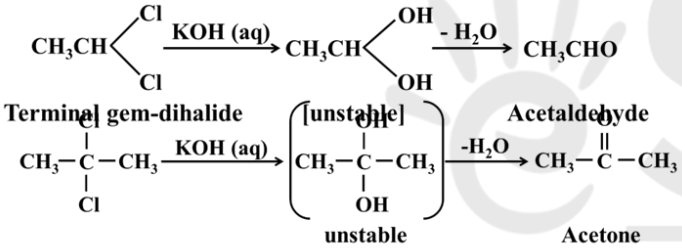
(b) Ketones

The carbonyl group (>C = O) is a Ketonic group when its both the valencies are satisfied by alkyl group. It is a bivalent group.

General Methods of Preparation

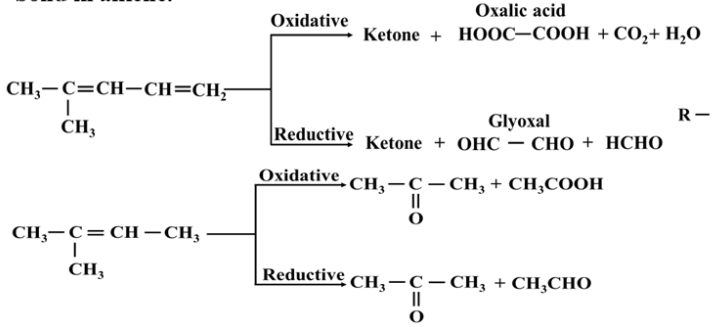
By Hydrolysis of Gem Dihalides

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



By Ozonolysis of Alkenes

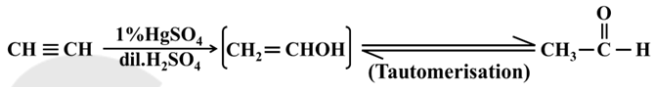
This reaction is used to determine the position of double bond in alkene.



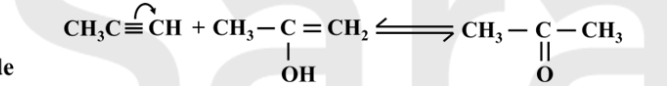
From Alkyne

(a) Hydration (Kucherov reaction)

With dil H_2SO_4 & 1%$HgSO_4$ at 60-80^{0}C.



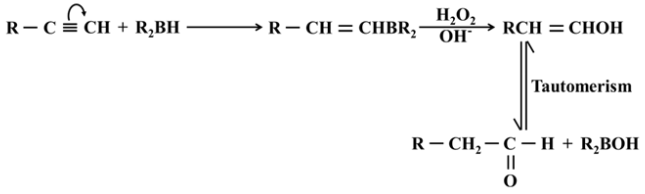
Other Alkynes Give Ketone



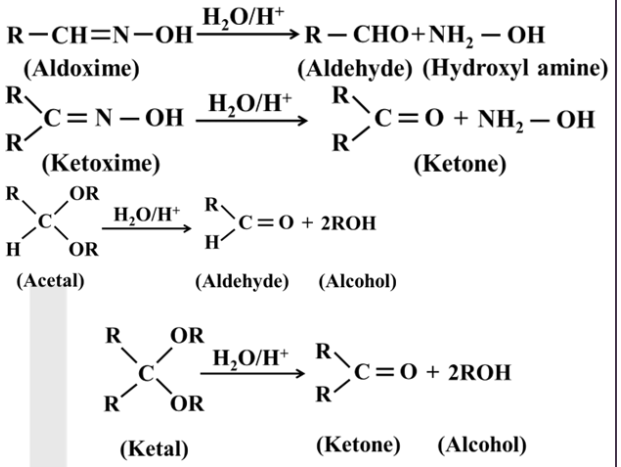
(b) Hydroboration Oxidation

Reaction with B_2H_6, $2BH_3$ or R2BH give dialkyl borane.

1- alkyne gives ⟶ aldehyde
other alkyne ⟶ Ketone

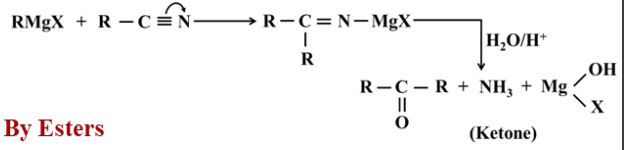


By Hydrolysis of Carbonyl Derivatives



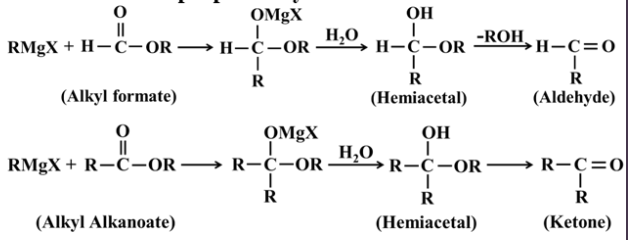
From Grignard Reagents

By Cyanides



By Esters

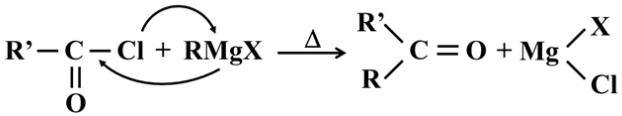
HCHO can't be prepared by this method.



MIND MAP

Carbonyl Compound

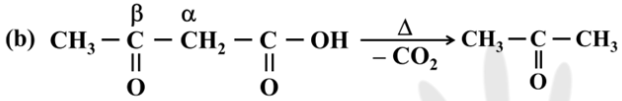
By Acid Chlorides



From β-keto Acids

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

(a) $HCOCH_2COOH \xrightarrow[110^0C]{\Delta} CH_3CHO + CO_2$



From R2CuLi

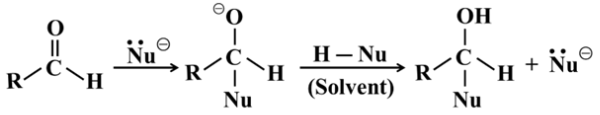
$R_2CuLi + R'COCl \longrightarrow R'COR + RCu + LiCl$

Other methods for Aldehyde and Ketone

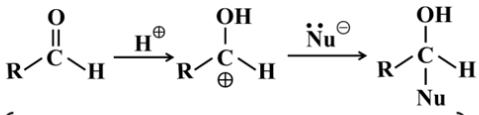
Characteristic Reactions of Aldehydes & Ketones

Nucleophilic Addition Reaction

Base Catalysed



Acid Catalysed



Reactivity of $>C=O$ $\propto$ -M, -I

Or

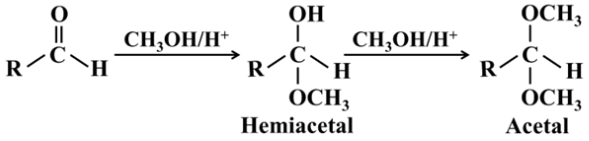
NAR (Nucleophilic Addition Reaction)

Reaction with NaCN & HCN

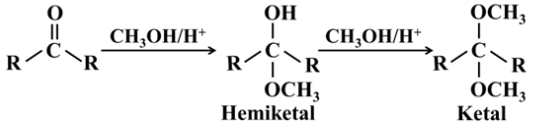
Cyanohydrin

Reaction with Grignard Reagent (RMgX)

Formation of Hemiacetals & Acetals

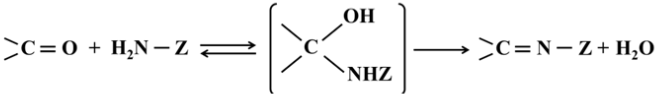


Hemiacetal Acetal



Hemiketal Ketal

Addition with Compounds Containing Nitrogen



Z = Alkyl , aryl , OH, NH_2, C_6H_5NH , $NHCONH_2$ etc.

Some N – Substituted Derivatives of Aldehydes and Ketones (> C = N – Z)

Z	Regent Name	Carbonyl derivative	Product Name
$-H$	Ammonia	$>C=NH$	Imine
$-R$	Amine	$>C=NR$	Substituted imine (Schiff's base)
$-OH$	Hydroxylamine	$>C=N-OH$	Oxime
$-NH_2$	Hydrazine	$>C=N-NH_2$	Hydrazone
$-HN-C_6H_5$	Phenylhydrazine	$>C=N-NH-C_6H_5$	Phenylhydrazone
$-HN-C_6H_3(NO_2)_2$ (2,4)	2,4 Dinitrophenyl-hydrazine	$>C=N-NH-C_6H_3(NO_2)_2$ (2,4)	2,4 Dinitrophenyl-hydrazone
$-NH-C(=O)-NH_2$	Semicarbazide	$>C=N-NH-C(=O)-NH_2$	Semicarbazone

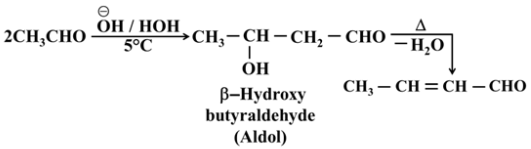
Note

2,4 – DNP – derivatives are yellow, orange or red solids, useful for characterisation of Aldehydes and Ketones.

MIND MAP

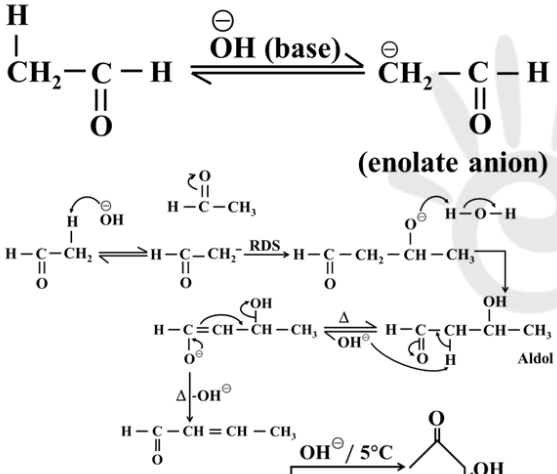
Aldol, Cannizzaro & Haloform

Aldol Condensation

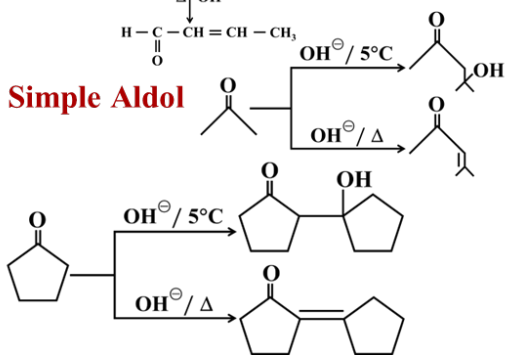


In aqueous base, two acetaldehyde molecules react to form β-hydroxy aldehyde called Aldol.
The reaction is called Aldol Reaction.

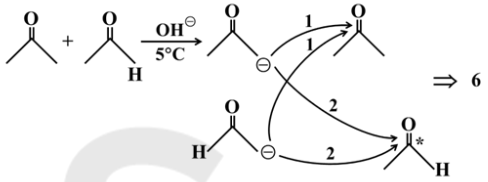
Mechanism

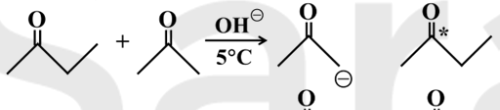


Simple Aldol

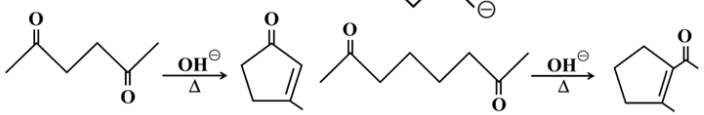


Cross Aldol



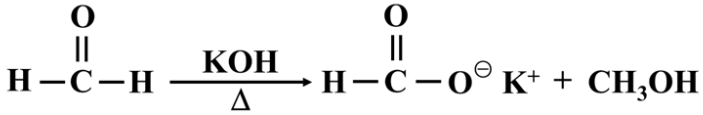


Intramolecular Aldol

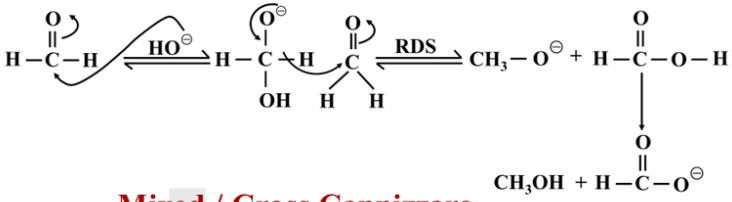


Cannizzaro Reaction

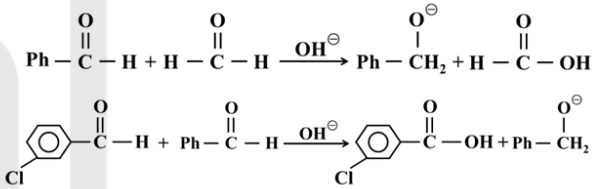
This reaction is given by aldehyde having no α- hydrogen in the presence of conc. NaOH/Δ or KOH/Δ.



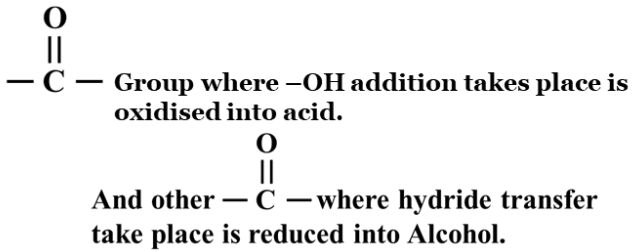
Mechanism



Mixed / Cross Cannizzaro



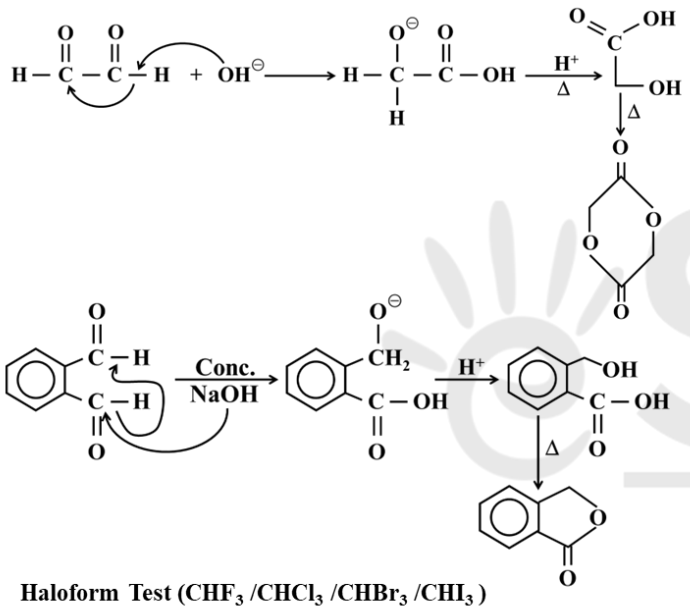
Trick



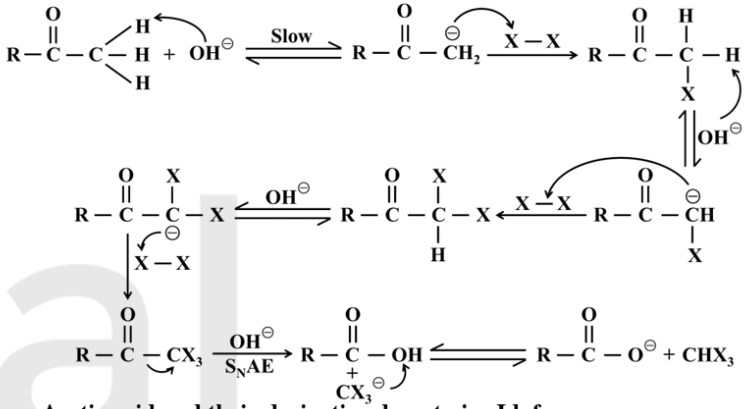
MIND MAP

Aldol, Cannizzaro & Haloform

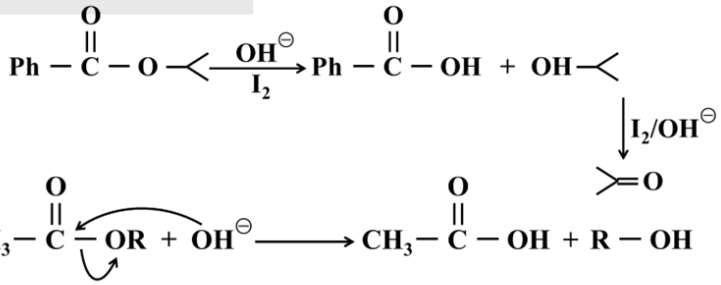
Intramolecular Cannizzaro



Mechanism

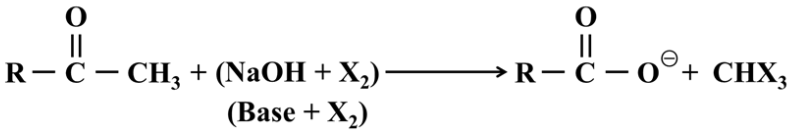


Acetic acid and their derivative do not give Idoform except ester.



Haloform Test (CHF_3 /$CHCl_3$ /$CHBr_3$ /CHI_3)

Yellow Crystalline



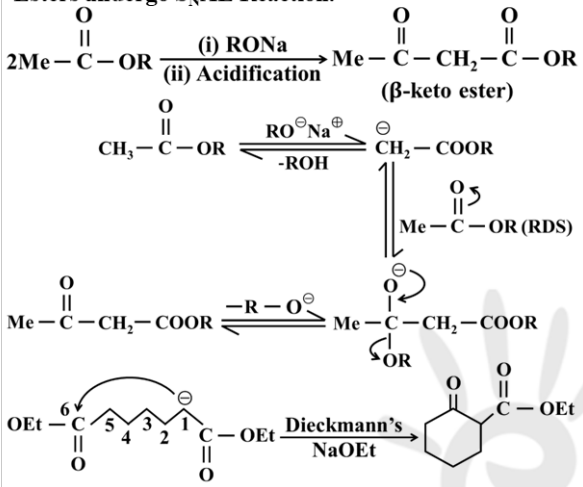
(Base + X_2)

MIND MAP

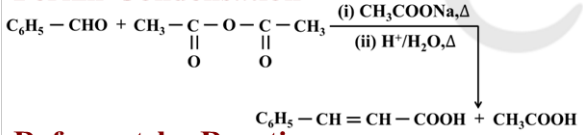
Name Reaction

Claisen Condensation

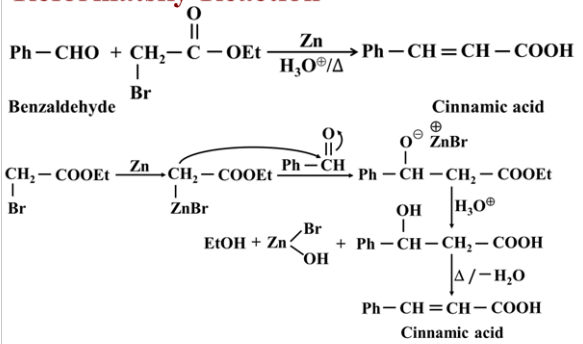
Esters undergo S_NAE Reaction.



Perkin Condensation

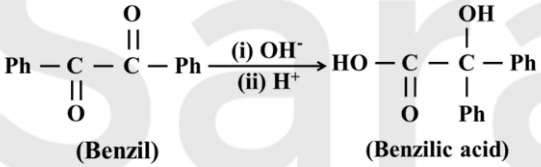


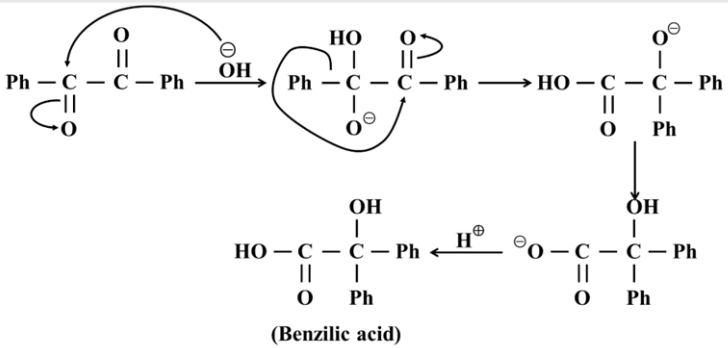
Reformatsky Reaction



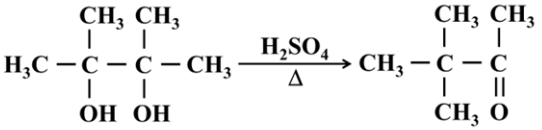
Benzil-Benzilic Rearrangement or Benzilic Acid Rearrangement

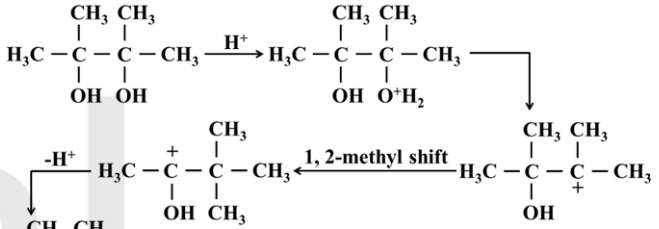
The base catalysed reaction of 1,2-diketones to a salt of –2–hydroxy carboxylic acid is known as Benzilic acid rearrangement, this reaction is mainly applicable when aryl group is present on both carbonyl carbons.





Pinacol Pinacolone Rearrangement





Migratory order

H>Ph>3°>2°>1°

This order is strictly followed in Pinacole Pinacolone Rearrangement