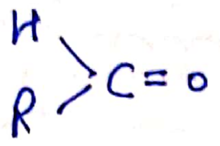
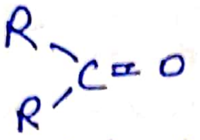
Aldehydes, Ketones And Carboxylic Acid

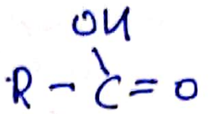
Organic compounds having carbon-oxygen double bond ($>C=O$) are called carbonyl group.



Aldehyde



Ketones



Carboxylic Acid

Nomenclature and Str. of Carbonyl group

F.G of aldehyde :- $\overset{O}{\overset{\|}{C}}-H$

Suffix used : al

Prefix used : formyl

F.G of Ketones : $-\overset{O}{\overset{\|}{C}}-$

Suffix used : one

Prefix used : Keto or oxo

Common Name

C_1 → Form

C_2 → Acet

C_3 → Propion

C_4 → Butyr

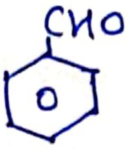
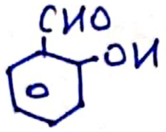
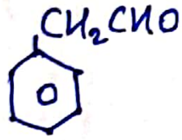
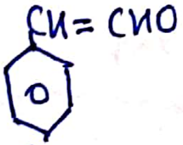
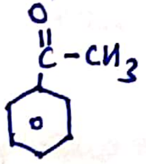
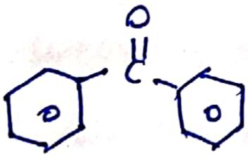
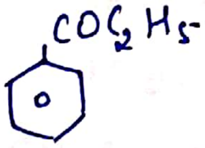
C_5 → Valer

C_6 → Capro

$HCHO$	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
CH_3CH_2CHO	Propionaldehyde	Propanal
$CH_3CH_2CH_2CHO$	Butyraldehyde	Butanal
$CH_3-\underset{CH_3}{\underset{\mid}{CH}}-CHO$	Isobutyraldehyde	2-Methylpropanal
$CH_3CH_2-\underset{CH_3}{\underset{\mid}{CH}}-CHO$	α-Methylbutyraldehyde	2-Methylbutanal

CH_3COCH_3	Dimethyl ketone	Propanone
$CH_3COCH_2CH_3$	Ethylmethyl ketone	Butan-2-one
$CH_3COCH_2CH_2CH_3$	Methyl-n-Propyl ketone	Pentan-2-one
$CH_3CH_2COCH_2CH_3$	Diethyl ketone	Pentan-3-one

Nomenclature of Some Aromatic Aldehydes & Ketones

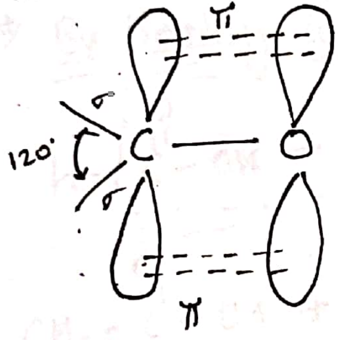
	Benzaldehyde	Benzaldehyde or Benzene carbaldehyde
	Salicylaldehyde or 'o' - Hydroxybenzaldehyde	2- Hydroxy benzaldehyde
	α- Phenylacetaldehyde	2- Phenyl ethanal
	Cinnamaldehyde	3-Phenyl prop-2enal
	Acetophenone or Methyl-phenyl ketone	Acetophenone
	Diphenyl ketone or Benzophenone	Benzophenone
	Ethyl-phenyl ketone or propiophenone	Propiophenone

Structure of Carbonyl Group

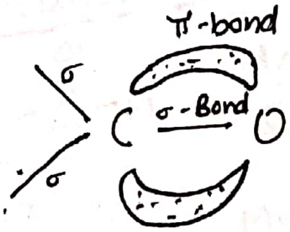
These are more polar than ethers and have high dipole moment $>C\overset{\curvearrowright}{=}\ddot{O}: \longleftrightarrow >\overset{\oplus}{C}-\overset{\ominus}{\ddot{O}}:$

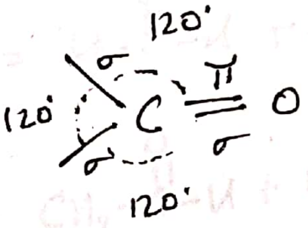
Oxygen of carbonyl group is more electronegative than carbon, So it is polar, Carbon carries small +ve charge and oxygen carries small -ve charge

— Carbonyl carbon is sp^2 hybridized forming one C–O σ bond and one π bond. So there is double bond b/w carbon and oxygen. The geometry is trigonal planar



(a)





Preparation of Aldehydes and Ketones

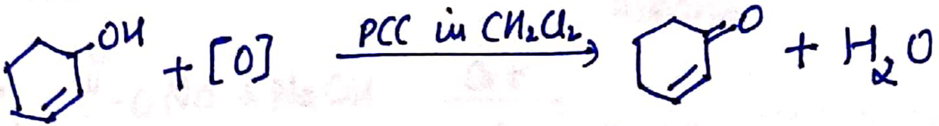
1.) By oxidation of Alcohols

Weak oxidising agents are used

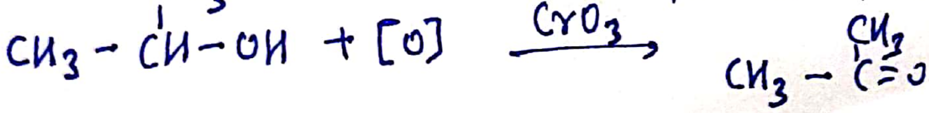
- Chromium oxide - CrO_3
- PCC (Pyridinium chloro chromate)

1° alcohol → Aldehyde   2° alcohol → Ketone

$$CH_3OH + [O] \xrightarrow{PCC\ in\ CH_2Cl_2} HCHO + H_2O$$

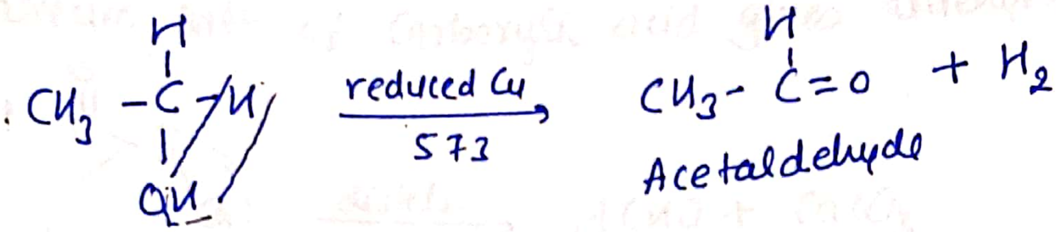


Cyclohex-2-en-1-one



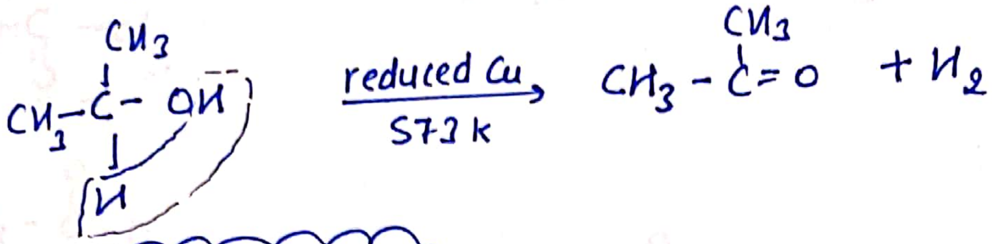
$$CH_3-\overset{CH_3}{\overset{|}{C}H}-OH + [O] \xrightarrow{CrO_3} CH_3-\overset{CH_3}{C}=O$$

⇒ By dehydrogenation of Alcohols



$$CH_3-\overset{H}{\underset{OH}{C}}-H \xrightarrow[573]{\text{reduced Cu}} CH_3-\overset{H}{C}=O + H_2$$

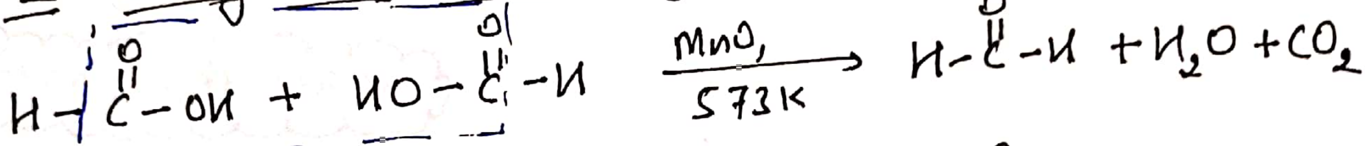
Acetaldehyde



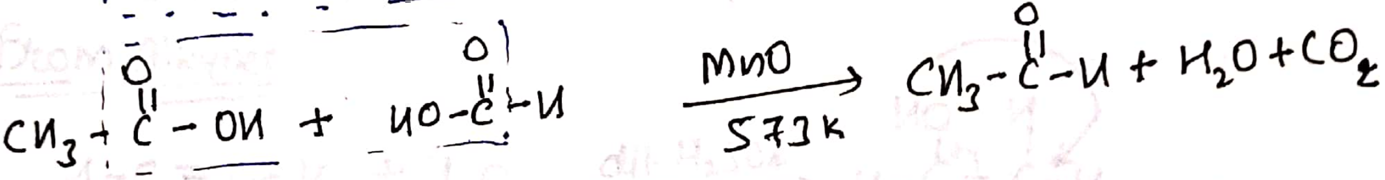
$$CH_3-\overset{CH_3}{\underset{H}{C}}-OH \xrightarrow[573K]{\text{reduced Cu}} CH_3-\overset{CH_3}{C}=O + H_2$$

⇒ From Carboxylic Acid

⇒ By heating with MnO (Manganous Oxide)

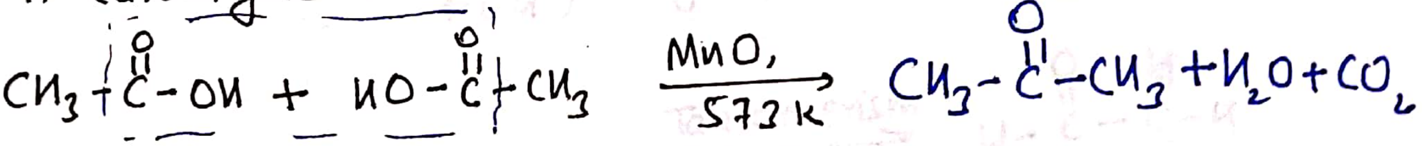


$$H-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-H \xrightarrow[573K]{MnO,} H-\overset{O}{\overset{\|}{C}}-H + H_2O + CO_2$$



$$CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-H \xrightarrow[573K]{MnO} CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O + CO_2$$

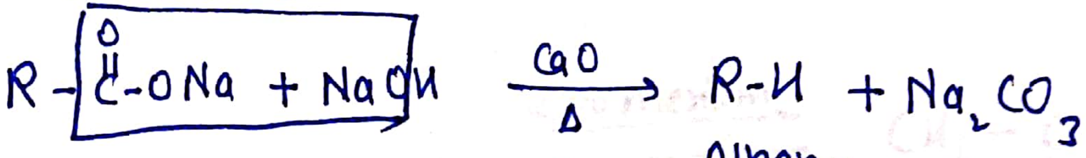
- A carboxylic acid other than formic acid gives ketones



$$CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[573K]{MnO,} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O + CO_2$$

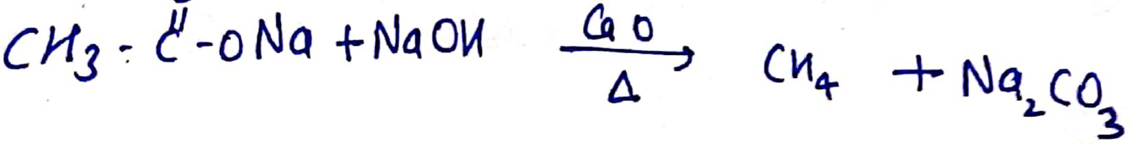
By distillation of Calcium Salts of Carboxylic Acid

- Sodium salt of carboxylic acid is changed into an alkane having one carbon less than acid by heating with soda lime.



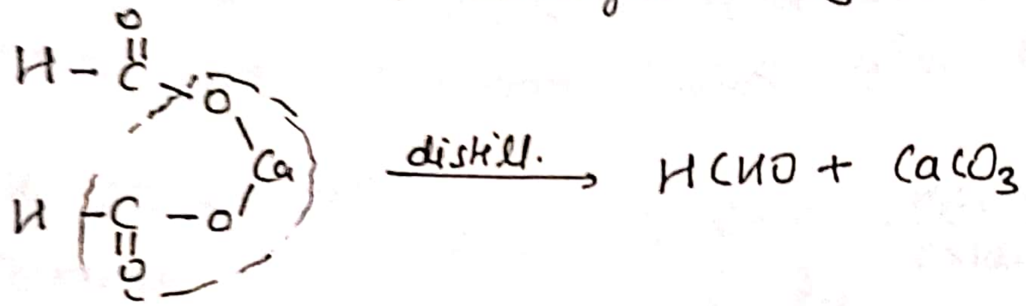
$$R-\boxed{\overset{O}{\overset{\|}{C}}-ONa + NaOH} \xrightarrow[\Delta]{CaO} R-H + Na_2CO_3$$

Alkane

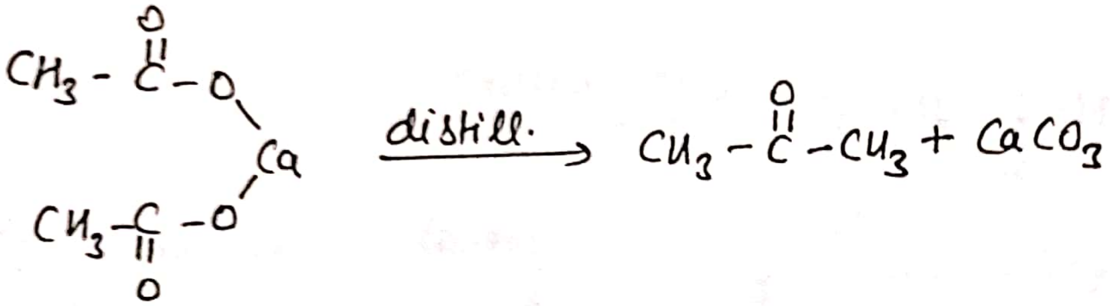


$$CH_3-\overset{O}{\overset{\|}{C}}-ONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

- Calcium salt of Carboxylic acid gives aldehydes & ketones



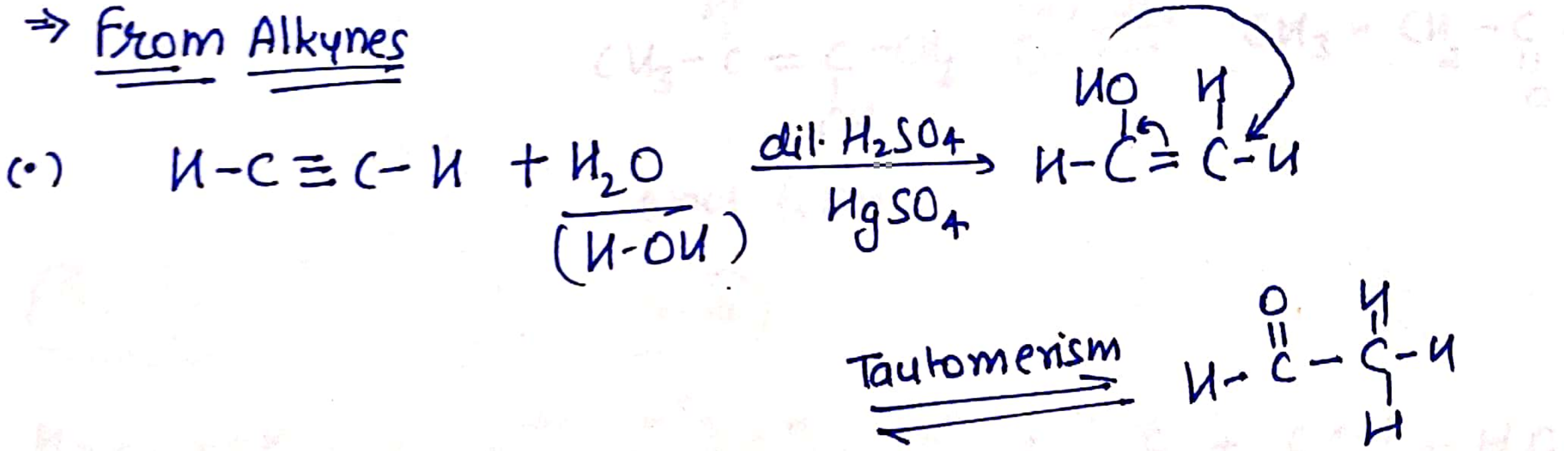
$$(HCOO)_2Ca \xrightarrow{distill.} HCHO + CaCO_3$$



$$(CH_3COO)_2Ca \xrightarrow{distill.} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CaCO_3$$

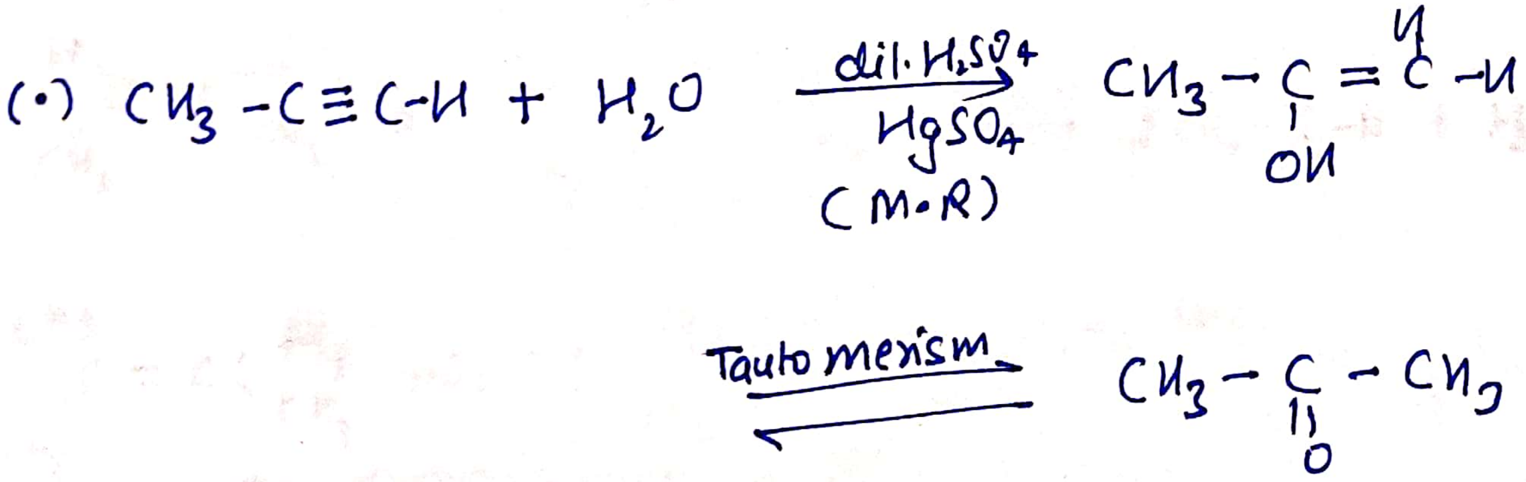
(4.) From Hydrocarbons

⇒ From Alkynes



$$(\cdot)\quad H-C\equiv C-H + \underset{(H-OH)}{H_2O} \xrightarrow[HgSO_4]{dil.\ H_2SO_4} H-\overset{HO}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H \xrightleftharpoons{Tautomerism} H-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H$$

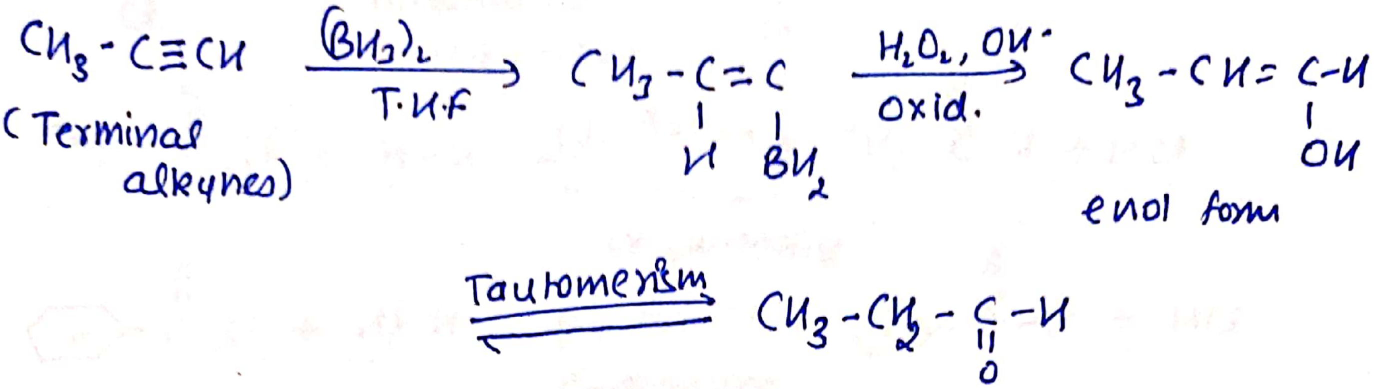
Acetaldehyde



$$(\cdot)\quad CH_3-C\equiv C-H + H_2O \xrightarrow[HgSO_4\ (M\cdot R)]{dil.\ H_2SO_4} CH_3-\underset{OH}{\underset{|}{C}}=\overset{H}{\overset{|}{C}}-H \xrightleftharpoons{Tautomerism} CH_3-\underset{O}{\underset{\|}{C}}-CH_3$$

By Hydroboration - Oxidation of Alkynes

- terminal alkynes ($\equiv CH$) give aldehydes
- non terminal alkynes ($C\equiv CR$) give ketones

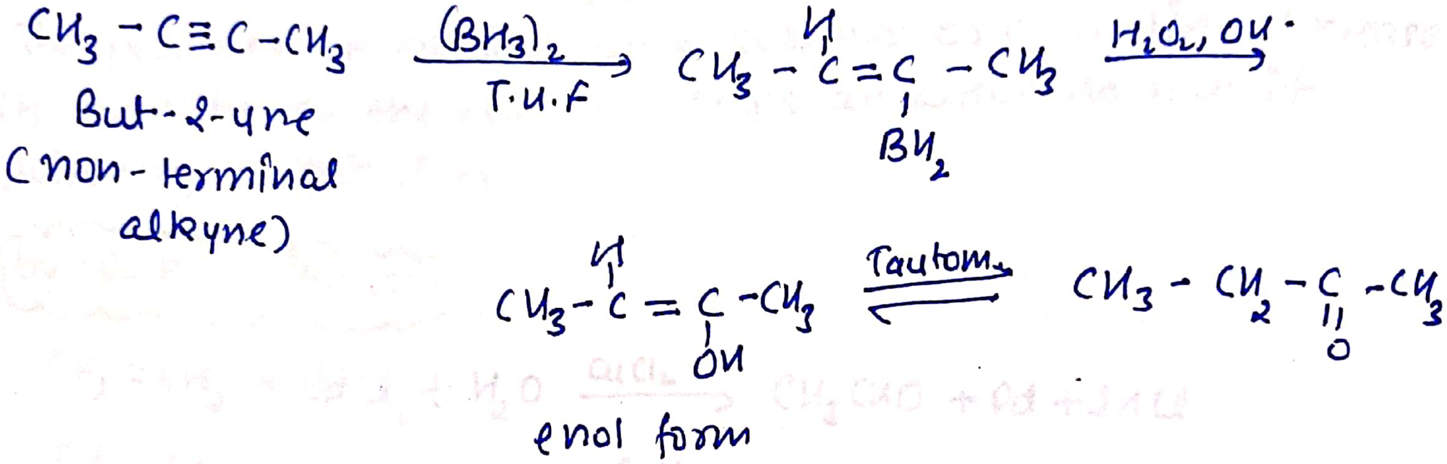


$CH_3-C\equiv CH \xrightarrow[T.H.F]{(BH_3)_2} CH_3-\underset{H}{C}=\underset{BH_2}{C} \xrightarrow[oxid.]{H_2O_2,\ OH^-} CH_3-CH=\underset{OH}{C}-H$

(Terminal alkynes)

enol form

$\underset{}{\xrightleftharpoons{Tautomerism}} CH_3-CH_2-\underset{O}{\underset{\|}{C}}-H$



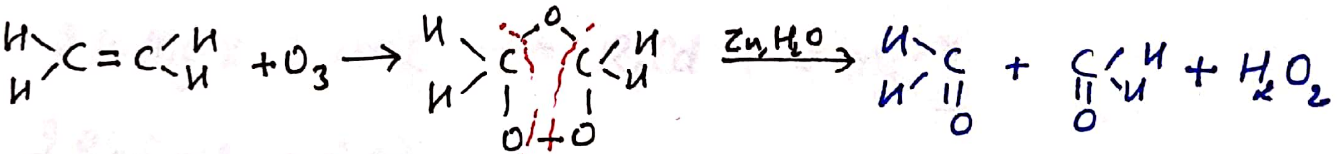
$CH_3-C\equiv C-CH_3 \xrightarrow[T.H.F]{(BH_3)_2} CH_3-\overset{H}{C}=\underset{BH_2}{C}-CH_3 \xrightarrow{H_2O_2,\ OH^-}$

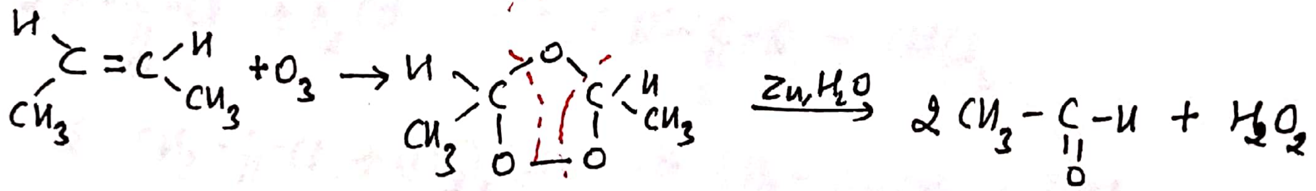
But-2-yne (non-terminal alkyne)

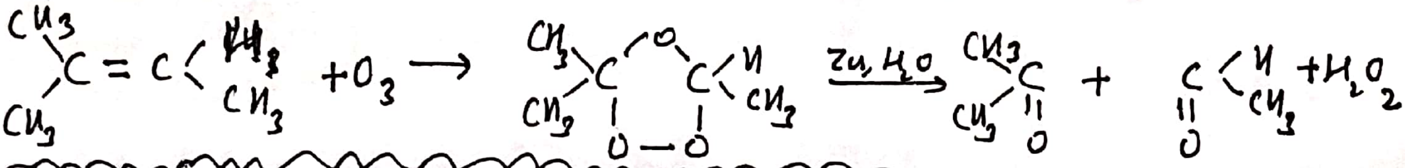
$CH_3-\overset{H}{C}=\underset{OH}{C}-CH_3 \xrightleftharpoons{Tautom.} CH_3-CH_2-\underset{O}{\underset{\|}{C}}-CH_3$

enol form

By Ozonolysis of Alkenes





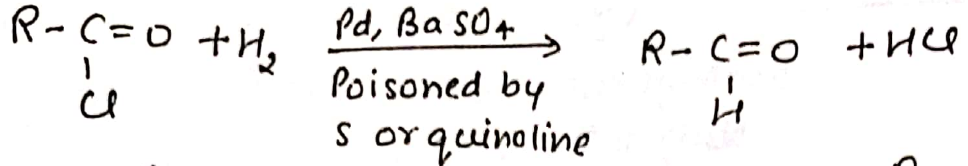


Stephen Reduction or Reduction of Alkyl cyanides

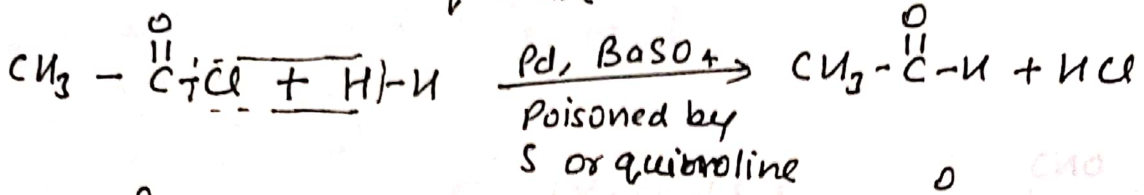
$CH_3-C\equiv N + 2[H] \xrightarrow{SnCl_2, HCl} CH_3-CH=NH \xrightarrow{H^+, H_2O} CH_3CHO$

From Acid Chlorides

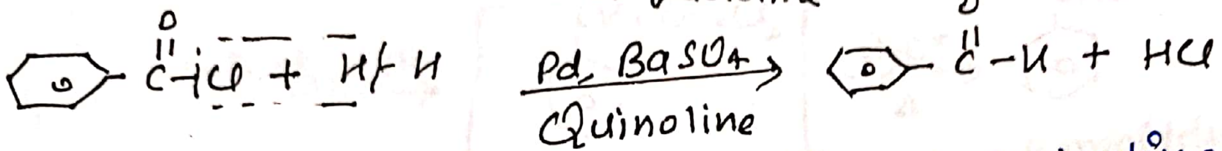
⇒ **Rosenmund Reduction**



$$R-\underset{Cl}{\underset{|}{C}}=O + H_2 \xrightarrow[\text{Poisoned by S or quinoline}]{Pd,\ BaSO_4} R-\underset{H}{\underset{|}{C}}=O + HCl$$



$$CH_3-\overset{O}{\overset{||}{C}}-Cl + H-H \xrightarrow[\text{Poisoned by S or quinoline}]{Pd,\ BaSO_4} CH_3-\overset{O}{\overset{||}{C}}-H + HCl$$



The poisoning of catalyst with sulphur or quinoline decrease its activity. So the reduction stops at aldehyde but if poisoning is not done

By Wacker's Process

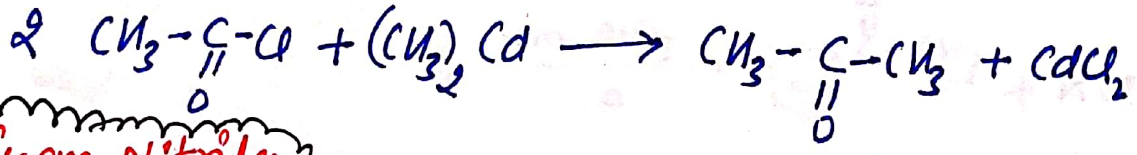
$$CH_2=CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3CHO + Pd + 2HCl$$

$$CH_3\cdot CH=CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3COCH_3 + Pd + 2HCl$$

From HCN

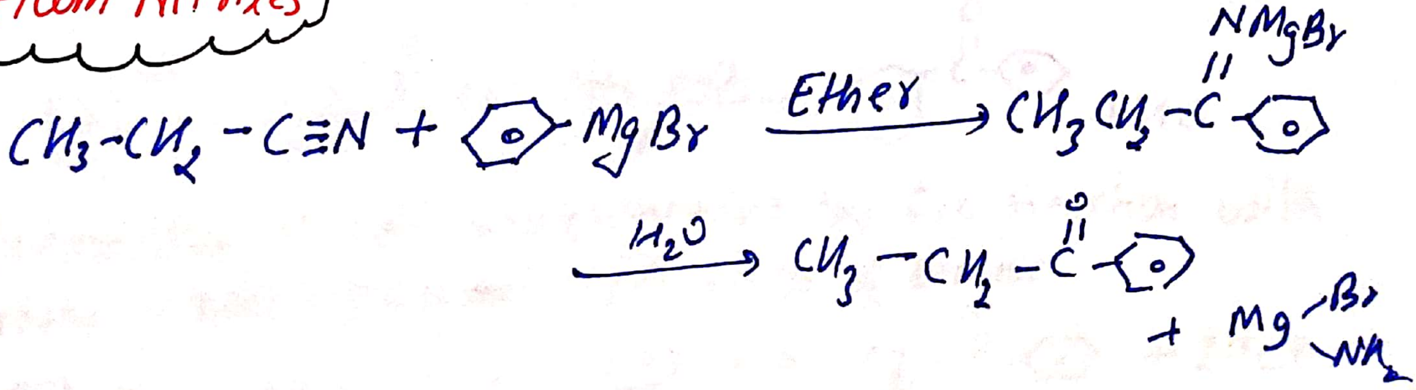
$$2R-Mg-X + CdCl_2 \longrightarrow R_2Cd + 2\,Mg{<}^{X}_{Cl}$$

$$2R'-\underset{O}{\underset{||}{C}}-Cl + R_2Cd \longrightarrow 2R'-\underset{O}{\underset{||}{C}}-R + CdCl_2$$

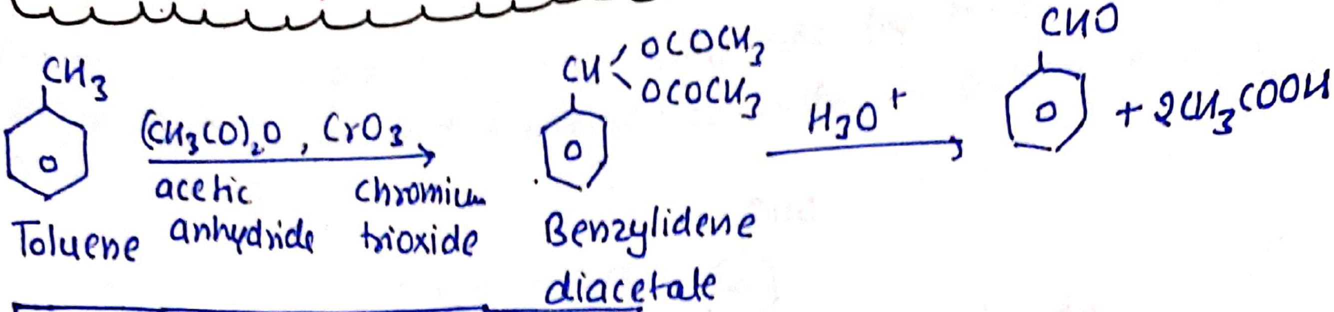


$$2\ CH_3-\underset{O}{\underset{||}{C}}-Cl + (CH_3)_2Cd \longrightarrow CH_3-\underset{O}{\underset{||}{C}}-CH_3 + CdCl_2$$

From Nitriles

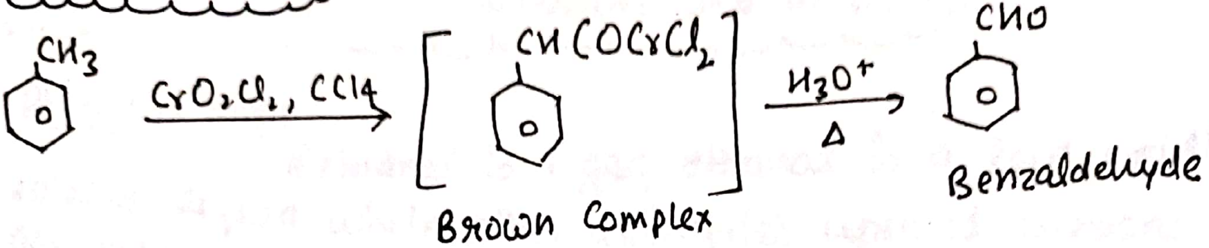


Preparation of Aromatic Aldehydes and Ketones

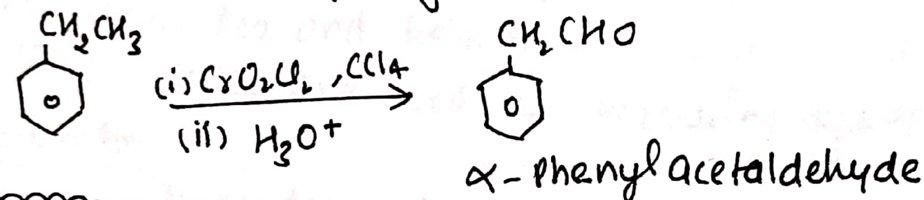


OXIDATION OF ALKYL BENZENE

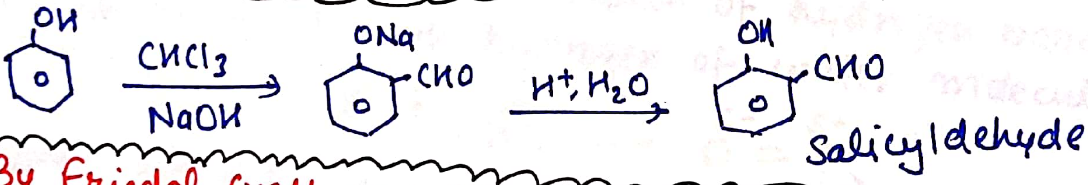
⇒ Etard Reaction



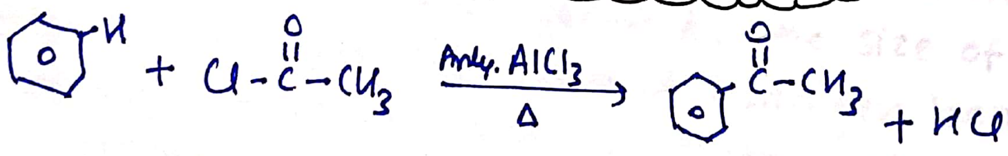
- If bigger side chain is present, then the end carbon is oxidized to aldehyde group.

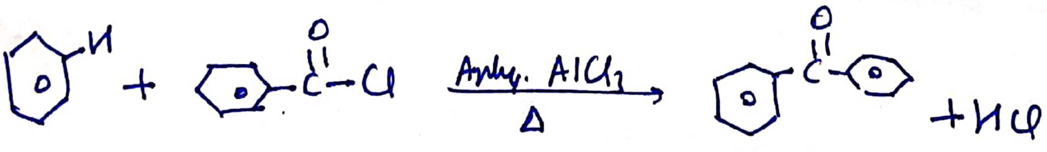


By Reimer-Tiemann Reaction



By Friedal craft acylation and benzoylation

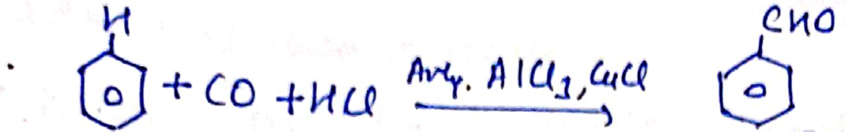




- Preparation of only benzophenone by F.C reaction with carbonyl chloride (Phosgene) with excess of benzene

By Gattermann Koch Reaction

Benzene is changed into benzaldehyde by reaction with carbon mono oxide and hydrogen chloride, in presence of $AlCl_3$ catalyst.



Physical Properties of Aldehydes and Ketones

→ **Physical State**

Methanal is a gas, ethanal is a low boiling volatile liquid, while other aldehydes upto 11 carbons are colourless liquids. All ketones are also colourless liquids.

→ **Smell**

Methanal and ethanal have unpleasant smell while higher aldehydes and ketones have pleasant and fruity smell. So these are used as flavouring agents in perfumes etc.

→ **Solubility**

Aldehydes and ketones upto 4 carbons are soluble in water, because of formation of hydrogen bonding of carbonyl group with hydrogen of water molecules.

$$>\overset{\delta+}{C}=\overset{\delta-}{O}\;---\;\overset{\delta+}{H}-\overset{\delta-}{O}-\overset{\delta+}{H}\;---\;\overset{\delta-}{O}=\overset{\delta+}{C}<$$

Higher aldehydes and ketones are insoluble in water because of larger hydrophobic alkyl group. As the size of alkyl group increases, the possibility of hydrogen bonding decrease.

- Although these are soluble in organic solvents like benzene, ether, $CHCl_3$ etc.

→ **Boiling Point**

They have higher b.pt than hydrocarbons of comparable molecular masses, because carbonyl group is polar group. So these have dipole-dipole interaction.

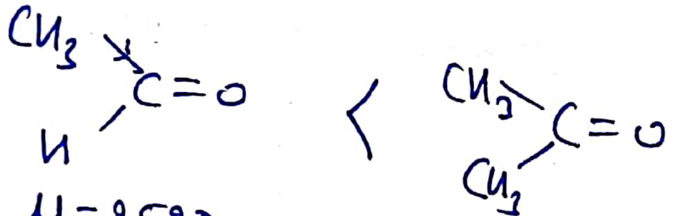
- They have less b.pt than alcohols because of absence of intermolecular hydrogen bonding.
- Among aldehydes and ketones, ketones have higher b.pt than aldehydes, because ketones are more polar, have higher dipole moment and more stronger dipole-dipole attractions than aldehydes
- Ketones have higher dipole moment than isomeric aldehydes because they have two alkyl groups, so more +I effect.

Increasing order of boiling point:

•) $CH_3(CH_2)_3CH_3$ < $CH_3CH_2CH_2CHO$ < $CH_3COCH_2CH_3$ < $CH_3(CH_2)_2CH_2OH$

n-pentane, Butanal, Butanone, Butan-1-ol

•)



$\mu = 2.52D$ (less +I effect)

$\mu = 2.88D$ (more +I effect

Chemical Reaction of Aldehydes and Ketones

→ Difference b/w ethylenic double bond ($>C=C<$) and carbonyl double bond ($>C=O$):

- Alkenes give electrophilic addition reaction while carbonyl compounds give nucleophilic addition reaction
- Alkenes give addition reaction with halogens, halogen acids (HX) and sulphuric acid etc while carbonyl compound do not give addition reactions with these reagents
- Alkenes have no resonance while carbonyl group have two resonating str.
- Alkenes are non polar while carbonyl group is polar.

Reaction of Aldehydes and Ketones

→ Nucleophilic addition reaction

→ Nucleophilic addition reaction followed by removal of H_2O

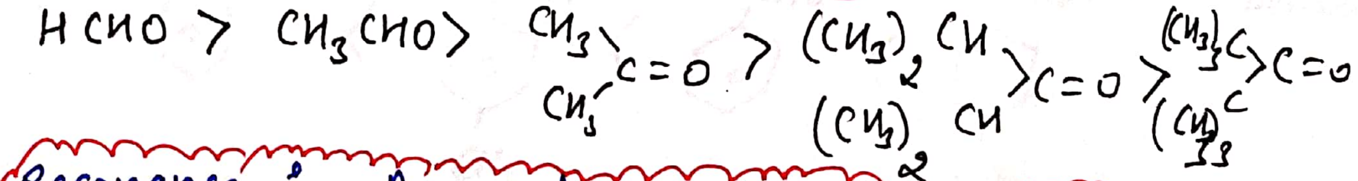
→ Oxidation Reaction

→ Reduction Reaction

→ Miscellaneous Reaction

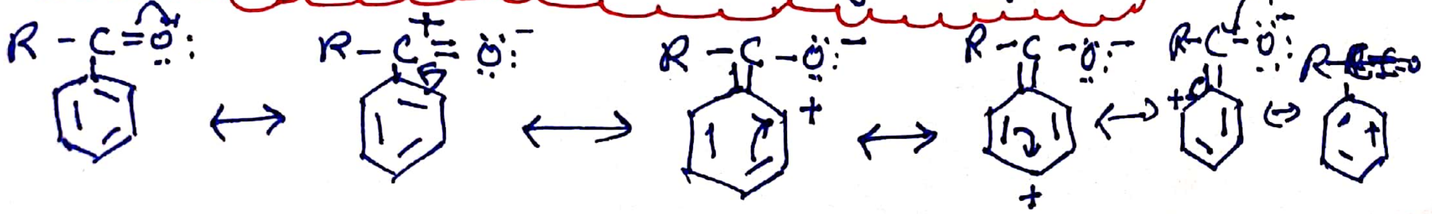
→ Electrophilic Sub. Rxn due to Benzene Ring.

Decreasing order of reactivity of carbonyl compound is



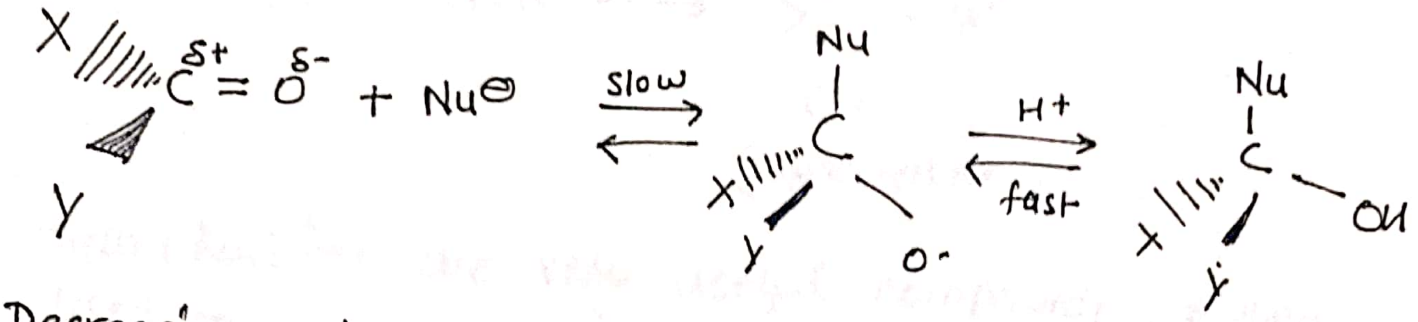
$$HCHO > CH_3CHO > \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>C=O > \begin{matrix} (CH_3)_2CH \\ (CH_3)_2CH \end{matrix}\!>C=O > \begin{matrix} (CH_3)_3C \\ (CH_3)_3C \end{matrix}\!>C=O$$

Resonance in Aromatic Carbonyl Compounds

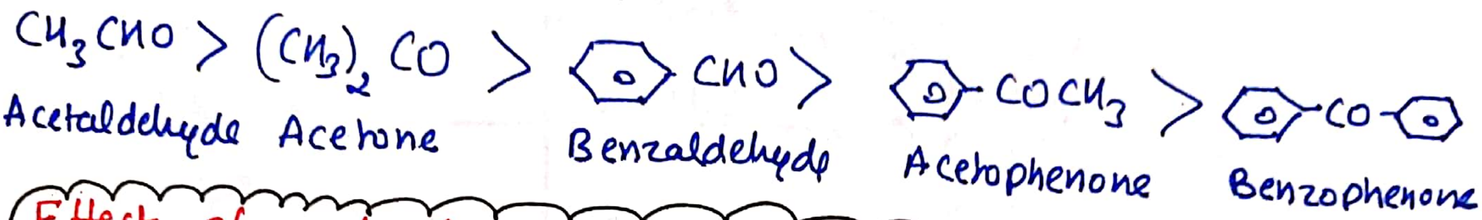


(A.) Nucleophilic Addition Rxn

Mechanism



Decreasing order of reactivity



⇒ Effect of substituent on Reactivity of Aromatic Aldehydes and Ketones

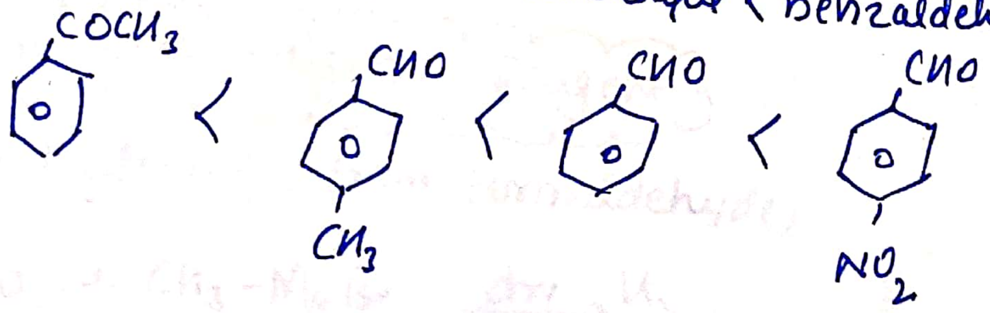
⇒ Effect of electron releasing group:-

These groups increases the electron density on carbonyl carbon and so decreases the +ve charge and decrease the reactivity.

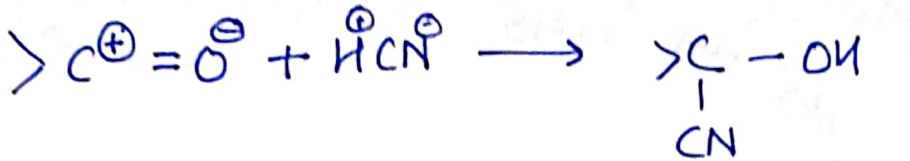
⇒ Effect of electron withdrawing group:-

These group decreases the electron density on carbonyl carbon and increases the +ve charge, So, a nucleophile can attack this carbon more easily. And reactivity increases.

Acetophenone < p-tolualdehyde < benzaldehyde < p-nitro benzaldehyde



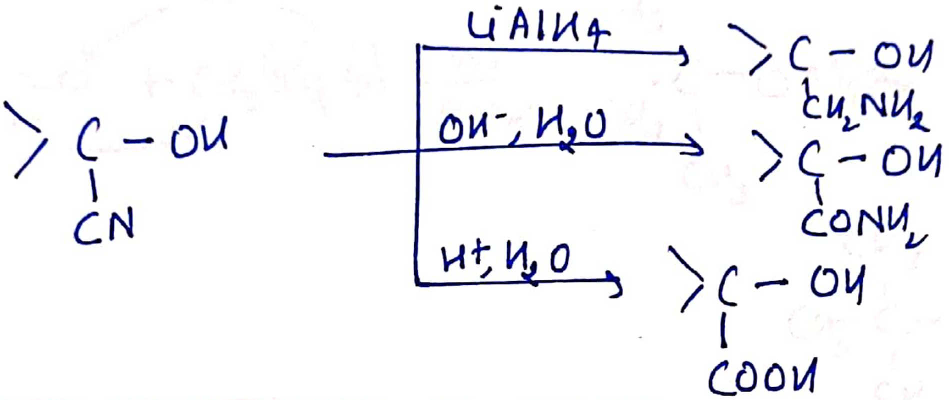
Reaction with HCN



$$>\overset{\oplus}{C}=\overset{\ominus}{O} + \overset{\oplus}{H}\overset{\ominus}{CN} \longrightarrow >\underset{CN}{\underset{|}{C}}-OH$$

(Cyanohydrin)

Cyanohydrins are very useful compounds, as they are used to synthesise many other compounds.

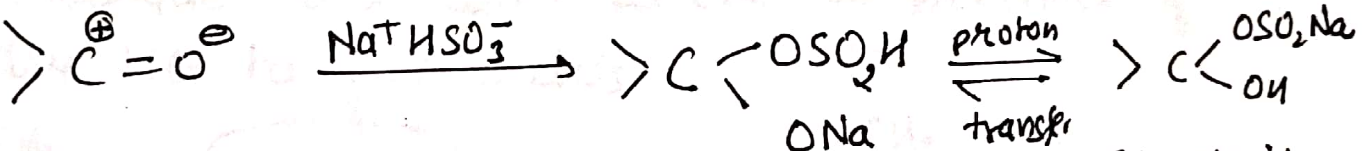


$$>\underset{CN}{\underset{|}{C}}-OH \xrightarrow{LiAlH_4} >\underset{CH_2NH_2}{\underset{|}{C}}-OH$$

$$>\underset{CN}{\underset{|}{C}}-OH \xrightarrow{OH^-,\ H_2O} >\underset{CONH_2}{\underset{|}{C}}-OH$$

$$>\underset{CN}{\underset{|}{C}}-OH \xrightarrow{H^+,\ H_2O} >\underset{COOH}{\underset{|}{C}}-OH$$

Reaction with sodium bisulphite ($NaHSO_3$)



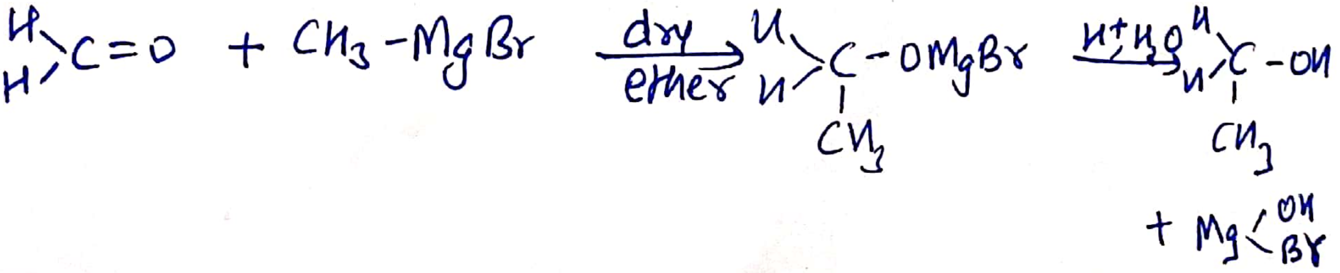
$$>\overset{\oplus}{C}=\overset{\ominus}{O} \xrightarrow{Na^+HSO_3^-} >C\begin{smallmatrix}OSO_2H\\ ONa\end{smallmatrix} \underset{transfer}{\overset{proton}{\rightleftharpoons}} >C\begin{smallmatrix}OSO_2Na\\ OH\end{smallmatrix}$$

Bisulphite adduct (Crystalline)

- Diethyl ketone, acetophenone and benzophenone do not give this reaction due to more steric hinderance

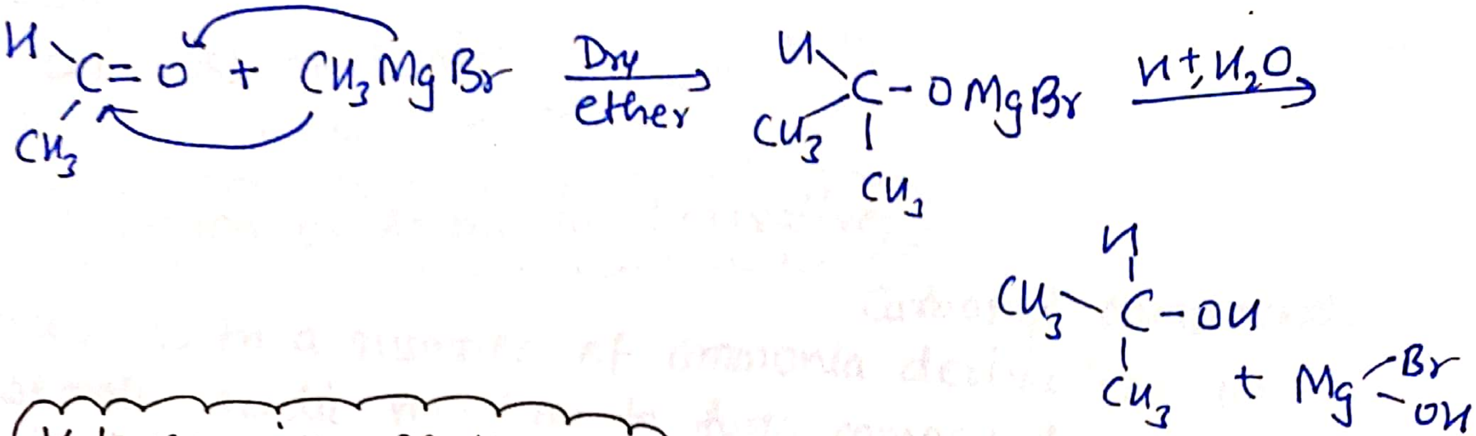
Reaction with Grignard Reagent

~~with~~ 1° alcohol (from formaldehyde)

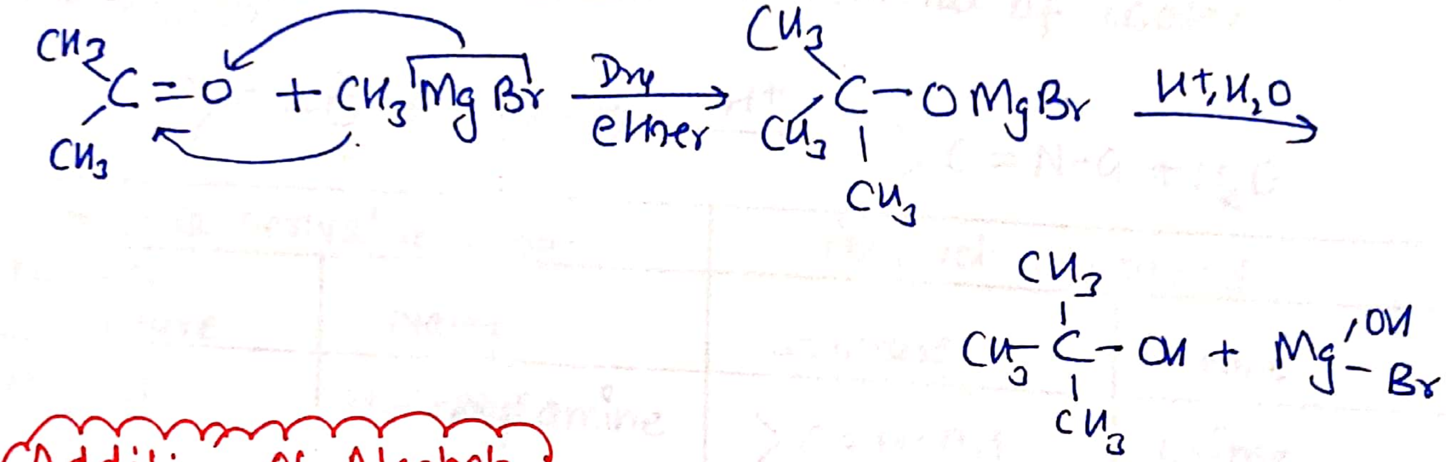


$$\begin{smallmatrix}H\\ H\end{smallmatrix}>C=O + CH_3-MgBr \xrightarrow[ether]{dry} \begin{smallmatrix}H\\ H\end{smallmatrix}>\underset{CH_3}{\underset{|}{C}}-OMgBr \xrightarrow{H^+,\ H_2O} \begin{smallmatrix}H\\ H\end{smallmatrix}>\underset{CH_3}{\underset{|}{C}}-OH + Mg\begin{smallmatrix}OH\\ Br\end{smallmatrix}$$

⇒ All other aldehydes give 2° Alcohol

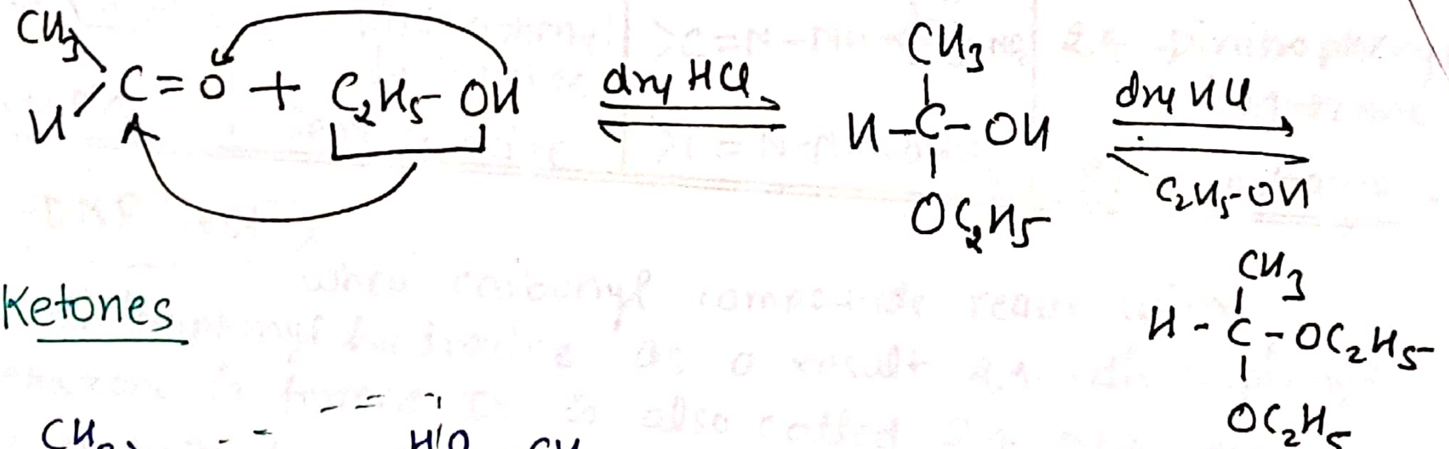


⇒ Ketones give 3° Alcohols

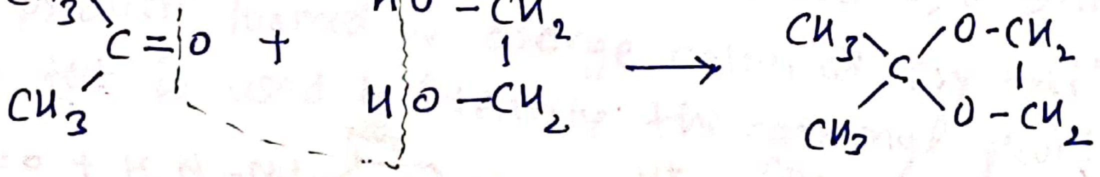


Addition of Alcohols

(•) Aldehyde react with alcohol in presence of dry HCl to give acetals



⇒ Ketones

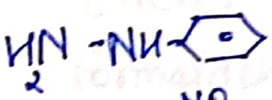
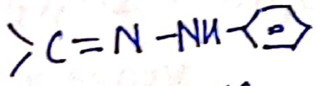
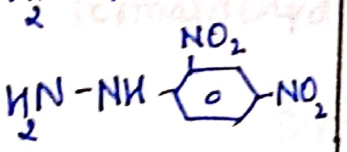
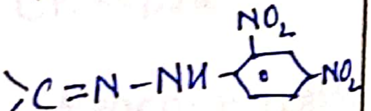


Nucleophilic Addition Rxn followed by loss of water:

⇒ Addition of Ammonia Derivatives

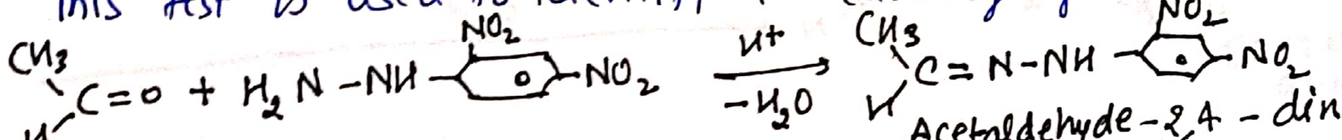
Carbonyl compounds react with a number of ammonia derivatives in weakly acidic medium to form compounds containg nitrogen double bond with the removal of water molecules

$$>C=O + H_2N-G \xrightarrow{H^+} >C=N-G + H_2O$$

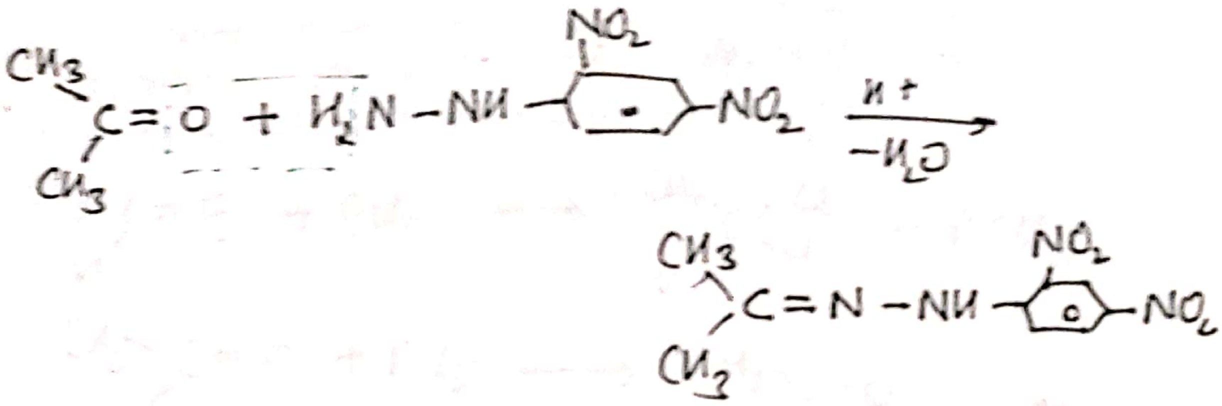
Ammonia Derivative Used		Product Obtained	
NH_2-G Structure	Name	Structure	Name
NH_2OH	Hydroxylamine	$>C=N-OH$	Oxime
H_2N-NH_2	Hydrazine	$>C=N-NH_2$	Hydrazone
	Phenyl hydrazine		Phenyl hydrazone
	2,4-Dinitrophenyl hydrazine		2,4-Dinitrophenyl hydrazone
NH_2CONH_2	Semicarbazide	$>C=N-NHCONH_2$	Semi Carbazone

2,4-DNP Test

When carbonyl compounds reacts with 2,4-dinitrophenyl hydrazine as a result 2,4-dinitrophenyl hydrazone is formed. It is also called 2,4-DNP test. The product formed is orange coloured crystalline solid. This test is used to identify the carbonyl group.



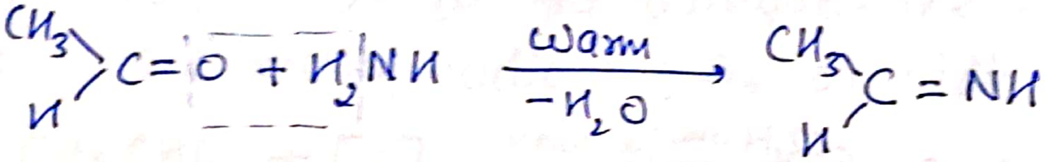
Acetaldehyde-2,4-dinitro phenyl hydrazone



Acetone-2,4-dinitrophenyl hydrazone

Reaction with Ammonia

Except formaldehyde, other aliphatic aldehydes react with ammonia and form an imine



$$\overset{CH_3}{\underset{H}{>}}C=O + H_2NH \xrightarrow[-H_2O]{\text{warm}} \overset{CH_3}{\underset{H}{>}}C=NH$$

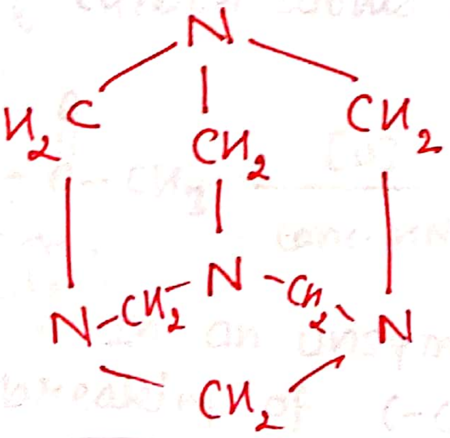
⇒ Formaldehyde reacts with four molecules of ammonia and form hexamethylenetetraamine also called urotropine. It is used as a medicine to treat urinary infections

$$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$$

Formaldehyde

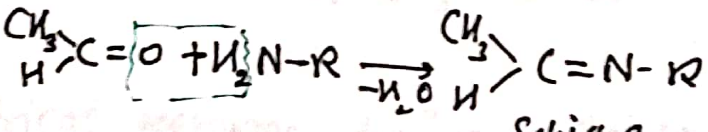
Urotropine

Str. of Urotropine



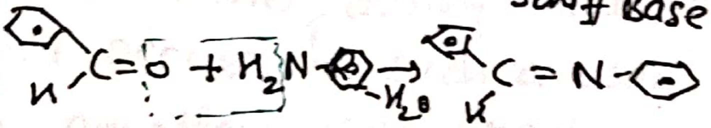
Reaction with Primary Amines

Aldehyde and ~~ketones~~ react with primary amines and form azomethines, also called Schiff's base



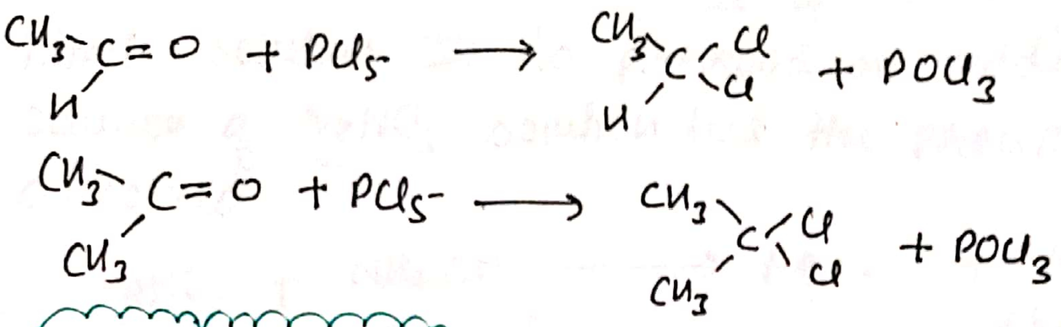
$$\overset{CH_3}{\underset{H}{>}}C=O + H_2N-R \xrightarrow[-H_2O]{} \overset{CH_3}{\underset{H}{>}}C=N-R$$

Schiff Base



Benzal aniline

Reaction with Phosphorous Pentachlorides



$$CH_3-\underset{H}{C}=O + PCl_5 \longrightarrow CH_3-\underset{H}{C}\begin{smallmatrix}Cl\\Cl\end{smallmatrix} + POCl_3$$

$$CH_3-\underset{CH_3}{C}=O + PCl_5 \longrightarrow CH_3-\underset{CH_3}{C}\begin{smallmatrix}Cl\\Cl\end{smallmatrix} + POCl_3$$

Oxidation Reaction

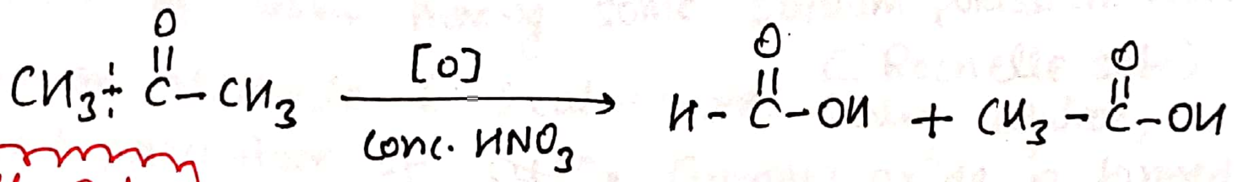
(i) Oxidation Of Aldehydes

Aldehydes are easily oxidised to corresponding carboxylic acids having same number of carbons as in the aldehyde. The oxidising agent used are mostly acidic $KMnO_4$ or acidic $K_2Cr_2O_7$.

$$CH_3CHO + [O] \xrightarrow{KMnO_4/\text{conc. } H_2SO_4} CH_3COOH$$

Oxidation Of Ketones

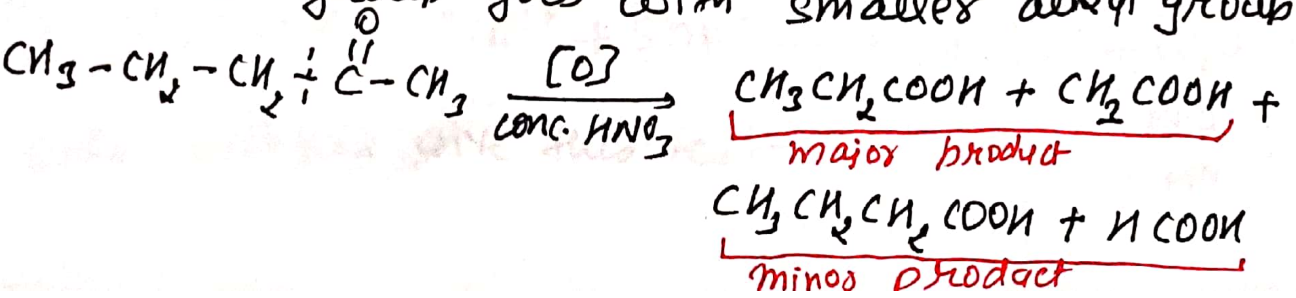
Ketones are not easily oxidised under ordinary conditions. But under drastic conditions and with powerful oxidising agent like conc HNO_3, $KMnO_4/H_2SO_4$ or conc. $K_2Cr_2O_7$/conc. H_2SO_4. Cleavage of C-C bond takes place and a mixture of carboxylic acids having less no. of carbon atoms than the original ketones are formed.



$$CH_3 \vdots \overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{Conc. } HNO_3]{[O]} H-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Popoff's Rule

In an unsymmetrical ketones, during oxidation the breaking of C-C bond occurs in such a way that keto group goes with smaller alkyl group.



$$CH_3-CH_2-CH_2 \vdots \overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{conc. } HNO_3]{[O]} \underbrace{CH_3CH_2COOH + CH_3COOH}_{\text{major product}} + \underbrace{CH_3CH_2CH_2COOH + HCOOH}_{\text{minor product}}$$

Oxidation by Tollen's Reagent

It is an ammonical silver nitrate solution. It is prepared by adding NH_4OH solution of $AgNO_3$ solution till the precipitates get dissolved.

$$\underset{\text{Silver Nitrate}}{AgNO_3} + \underset{\text{Ammonium hydroxide}}{NH_4OH} \longrightarrow \underset{\text{ppt}}{AgOH\downarrow} + \underset{\text{Ammonium Nitrate}}{NH_4NO_3}$$

$$AgOH + 2NH_4OH \longrightarrow \underset{\text{Tollen's Reagent}}{[Ag(NH_3)_2]OH} + 2H_2O$$

Tollen's Reagent is a weak Oxidizing Agent

$$CH_3CHO + 2[Ag(NH_3)_2]OH \longrightarrow \underset{\text{Ammonium Acetate}}{CH_3COONH_4} + \underset{\text{Silver Mirror}}{2Ag\downarrow} + H_2O + 3NH_3$$

$$R-CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$$

⇒ only aldehyde give this Test

Oxidation by Fehling Solution

Fehling solution is an alkaline solution of $CuSO_4$ having some sodium potassium tartrate (Rochelle salt) when an aldehyde is heated with Fehling solution, a red precipitate of ~~$CuSO_4$~~ Cuprous oxide is formed

$$R-\overset{\overset{O}{\|}}{C}-H + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + \underset{\text{(red ppt)}}{Cu_2O\downarrow} + 3H_2O$$

e.g. $CH_3-\overset{\overset{O}{\|}}{C}-H + 2Cu^{2+} + 5OH^- \longrightarrow CH_3COO^- + \underset{\text{(Red ppt)}}{Cu_2O\downarrow} + 3H_2O$

⇒ Only Aldehyde give this test

Iodoform Test

Following compounds give iodoform Test

→ among aldehyde, only ethanal give this Test

	$CH_3-\underset{Z}{C}=O$	$CH_3-\underset{Z}{CH}=O$
(i) $Z = -H$	CH_3CHO (only aldehyde)	CH_3CH_2OH (only 1° alcohol)
(ii) $Z = -R$	$CH_3-\underset{R}{C}=O$ (All methyl ketones)	$CH_3-\underset{R}{CH}-OH$ (all 2-ol but 2°)
(iii) $Z = -$ 	$CH_3-C=O$  Acetophenone	$CH_3-CH-OH$  1-phenyl ethanol

Reaction

$$CH_3-\underset{Z}{C}=O \xrightarrow[\text{or } NaOI]{NaOH,\ I_2} ZCOONa + CHI_3\downarrow$$

Iodoform
(Yellow, Bad Smelling)

$$CH_3-\underset{Z}{CH}-OH \xrightarrow[\text{or } NaOI]{NaOH,\ I_2} ZCOONa + CHI_3\downarrow$$

Reduction to Alcohol

Aldehydes and ketones on reduction with reducing agents give alcohols.

- Aldehydes are reduced to 1° alcohol
- ketones are reduced to 2° alcohol

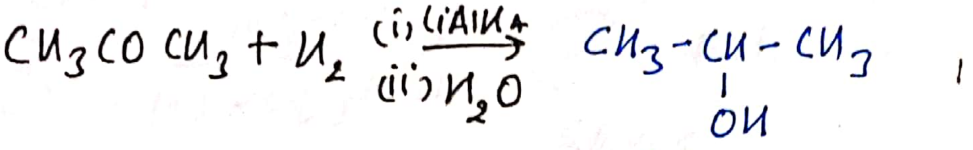
Reducing Agent

(i) Catalytic hydrogenation : H_2, Ni or Pt or Pd

(ii) $LiAlH_4$ (iii) $NaBH_4$

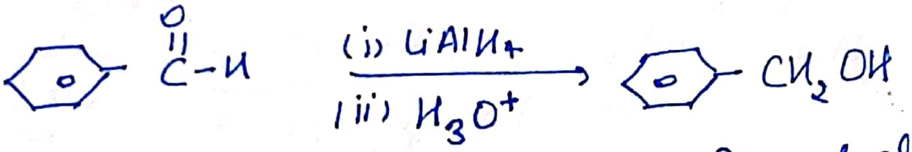
- $LiAlH_4$ is stronger reducing agent.
- $LiAlH_4$ and $NaBH_4$ do not reduce carbon-carbon double bonds ($C=C$) and double bond of benzene ring

$$CH_3CHO + H_2 \xrightarrow{Ni} CH_3CH_2OH$$



$$CH_3COCH_3 + H_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$$

(2° alcohol)



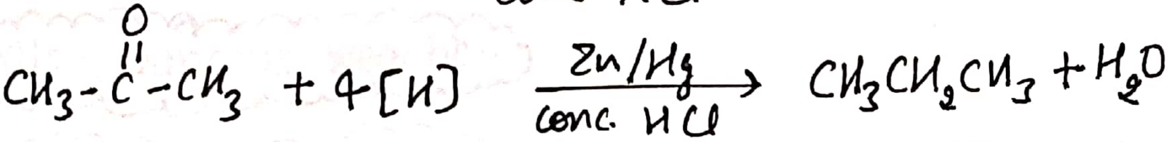
Benzyl alcohol

Clemmensen Reduction

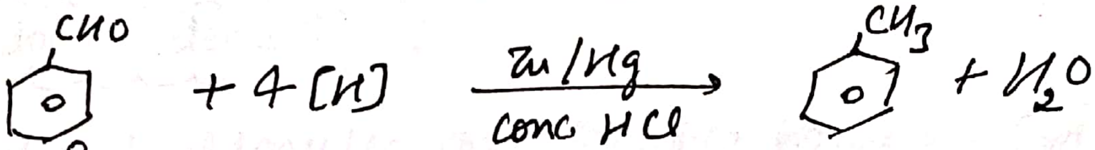
Aldehydes & Ketones $\xrightarrow[HCl]{Zn-Hg}$ Hydrocarbon

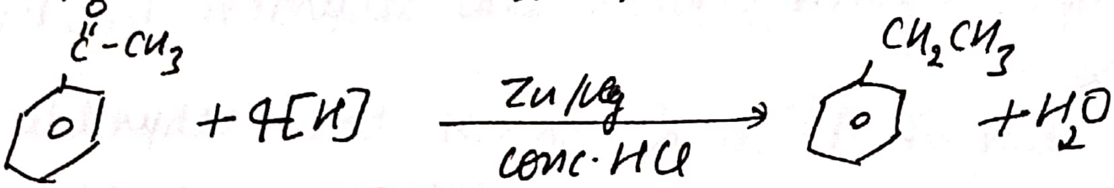
Reducing Agent

$$CH_3CHO + 4[H] \xrightarrow[conc.\ HCl]{Zn-Hg} CH_3CH_3 + H_2O$$



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 4[H] \xrightarrow[conc.\ HCl]{Zn/Hg} CH_3CH_2CH_3 + H_2O$$





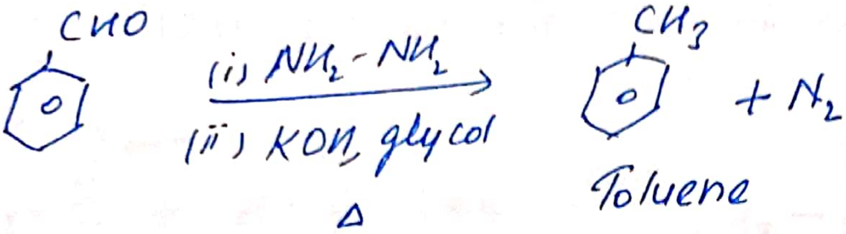
Wolf - Kishner Reduction

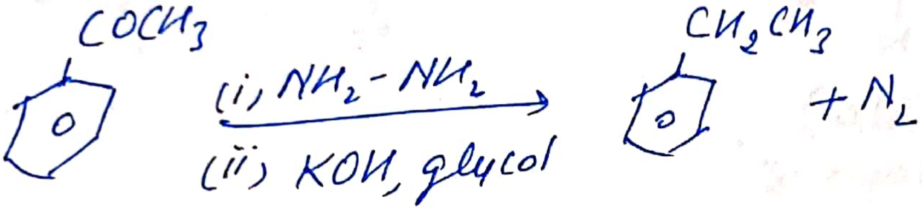
In this method firstly aldehyde or ketone is allowed to react with hydrazine. The hydrazone formed, then react with strong base like KOH or potassium tert butoxide and heated at 453 - 473 K.

$$CH_3-\overset{H}{\overset{|}{C}}=O + H_2N-NH_2 \longrightarrow CH_3CH=N-NH_2 \xrightarrow[453-473K]{KOH}$$

$$CH_3-\overset{CH_3}{\overset{|}{C}}=O + H_2N-NH_2 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}=N-NH_2 \xrightarrow[\text{ethylene glycol}]{KOH(453-473K)} CH_3CH_3 + N_2$$

$$CH_3-\overset{CH_3}{\overset{|}{CH_2}} + N_2$$





Reduction with HI / Red P

$$CH_3CHO + 4HI \xrightarrow[423K]{Red\ P} CH_3CH_3 + H_2O + 2I_2$$

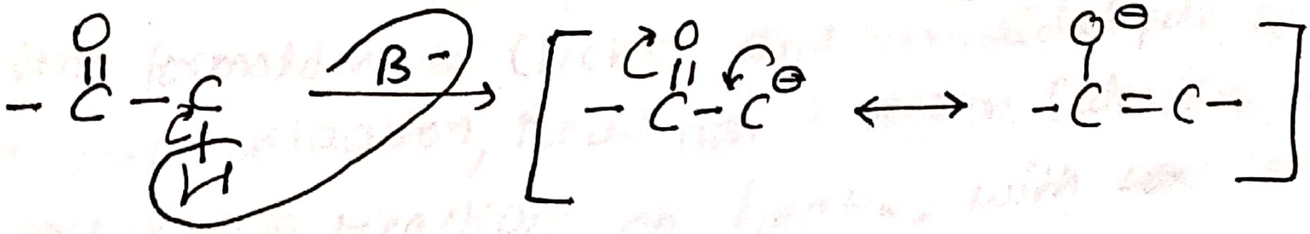
$$CH_3COCH_3 + 4HI \xrightarrow[423K]{Red\ P} CH_3CH_2CH_3 + H_2O + 2I_2$$

⇒ Miscellaneous Reaction

⇒ Aldol Condensation

Reaction of aldehydes and ketones having α - hydrogen.

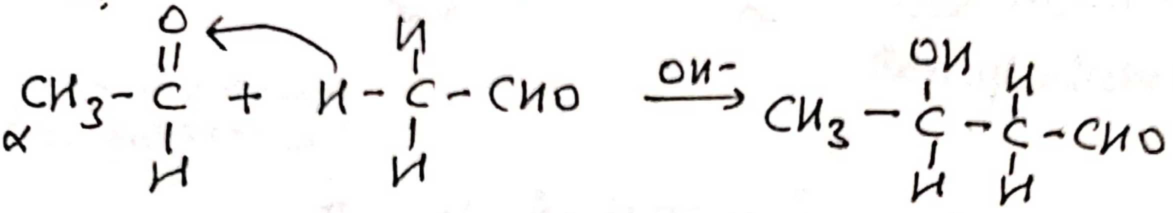
α-hydrogen of aldehydes and ketones is acidic in nature due to resonance stabilisation of conjugate base.



Aldol Condensation

2 moles of an aldehyde or ketone having α-hydrogen, react in presence of dil. alkali to produce aldol, which on further heating, gets dehydrated to an unsaturated aldehyde or ketone

[Aldol = Ald+ol i.e combination of carbonyl group + alcohol group]



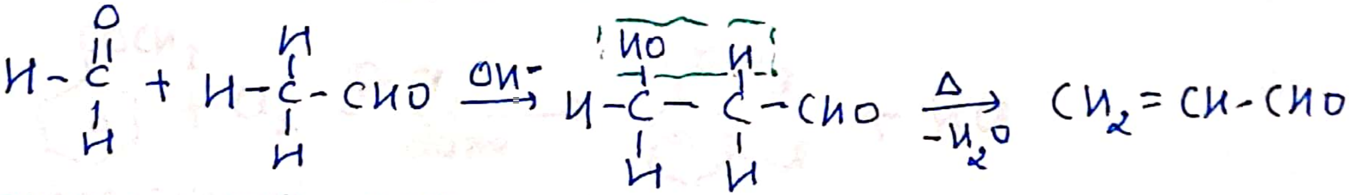
$$\underset{\alpha}{CH_3}-\underset{H}{\overset{O}{\overset{\|}{C}}} + H-\underset{H}{\overset{H}{C}}-CHO \xrightarrow{OH^-} CH_3-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{H}{C}}-CHO$$

(aldol)
3-Hydroxybutanal

$$\xrightarrow[-H_2O]{\Delta} CH_3\,CH=CH\,CHO$$

Cross Aldol Condensation

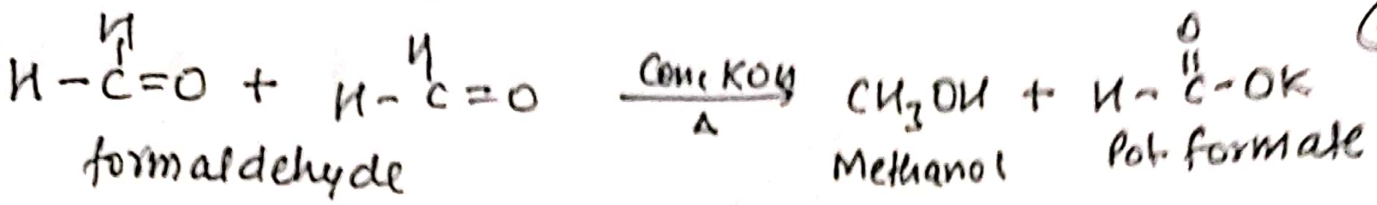
The condensation b/w two different carbonyl compounds (one of which must have α-hydrogen) in the presence of a base NaOH or $Ba(OH)_2$ is called cross aldol condensation.



$$H-\underset{H}{\overset{O}{\overset{\|}{C}}} + H-\underset{H}{\overset{H}{C}}-CHO \xrightarrow{OH^-} H-\underset{H}{\overset{HO}{C}}-\underset{H}{\overset{H}{C}}-CHO \xrightarrow[-H_2O]{\Delta} CH_2=CH-CHO$$

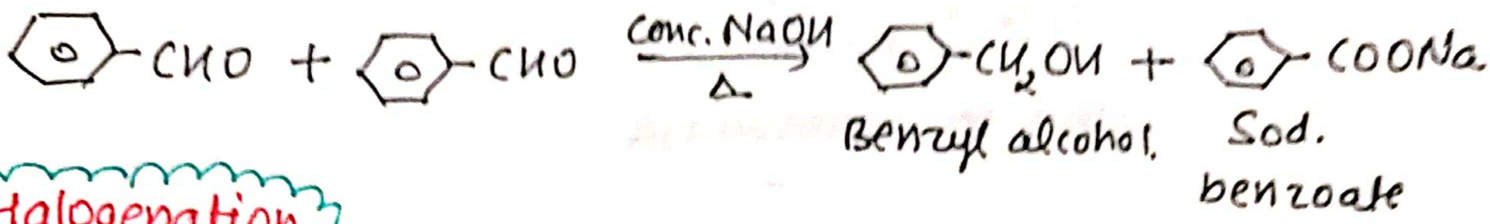
Cannizzaro's Reaction

Aldehydes which do not have 'α' hydrogen atom like formaldehyde (HCHO) and benzaldehyde ($\bigodot$-CHO) undergo self oxidation, reduction reaction (also called disproportionation reaction) on heating with conc. alkali



$$H-\overset{H}{\overset{|}{C}}=O + H-\overset{H}{\overset{|}{C}}=O \xrightarrow[\Delta]{\text{Conc. KOH}} CH_3OH + H-\overset{O}{\overset{\|}{C}}-OK$$

Here one molecule of formaldehyde is reduced to methyl alcohol and other is oxidized to salt of carboxylic acid. Similarly.



Halogenation

The α-hydrogen in aldehydes and ketones is acidic and can be displaced with halogen under suitable conditions

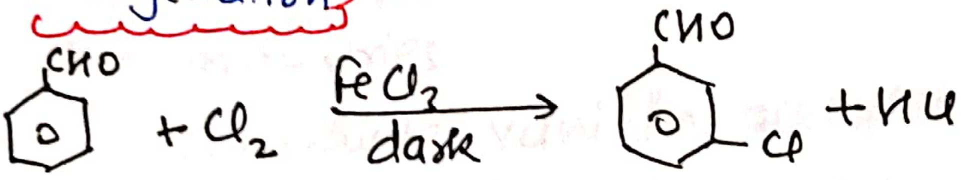
$$CH_3CHO + 3Cl_2 \longrightarrow CCl_3CHO + 3HCl$$

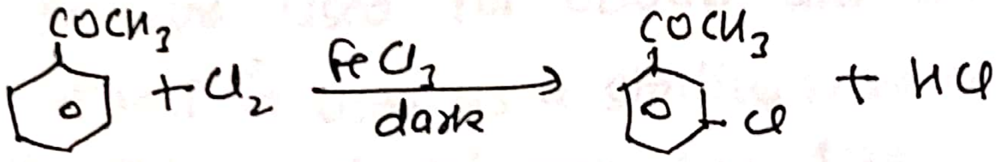
Chloral

Electrophilic Substitution Reaction

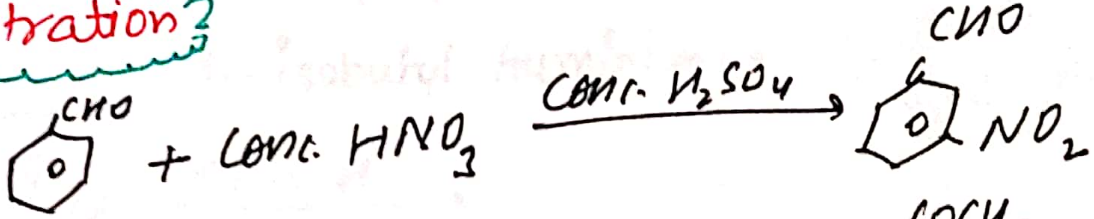
Aldehydes and Ketones are meta directing deactivating group.

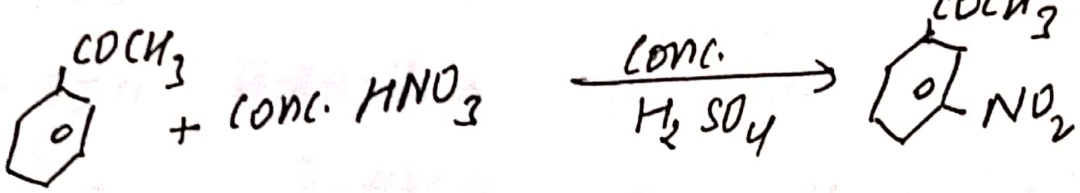
⇒ Halogenation





⇒ Nitration





Sulphonation

Benzaldehyde-m-sulphonic acid

Acetophenone-m-sulphonic acid

Uses of Aldehydes and Ketones

- These are used as solvent in industries
- 40% aqueous solution of formaldehyde is called formalin solution. It is used to preserve biological specimens.
- Formaldehyde is used to prepare bakelite, urea-formaldehyde resin etc.
- Benzaldehyde is used in perfumery and in dye industries
- Butyraldehyde, vanilin, acetophenone and camphor etc. are used for odours and flavours etc.
- ethanal is used as a starting material for the formation of acetic acid, polymer and drugs

DiBAL-H di-isobutyl Auminium Hydride $(CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2)_2Al-H$

$$CH_3-\overset{O}{\overset{||}{C}}-Cl \xrightarrow{Di-BAL-H} CH_3-\overset{O}{\overset{||}{C}}-H$$

$$CH_3-C\equiv N \xrightarrow{Di-BAL-H} CH_3-\overset{O}{\overset{||}{C}}-H$$

$$CH_3-\overset{O}{\overset{||}{C}}-OC_2H_5 \xrightarrow{Di-BAL-H} CH_3-\overset{O}{\overset{||}{C}}-H + C_2H_5OH.$$