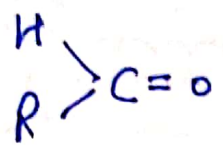
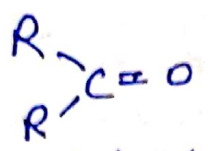


Aldehydes, Ketones And Carboxylic Acid

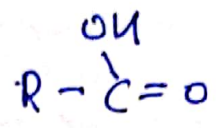
Organic compounds having carbon-oxygen double bond (C=O) are called carbonyl group.



Aldehyde



Ketones



Carboxylic Acid

Nomenclature and Str. of Carbonyl group

F.G of aldehyde : - C=O-H

Suffix used : al

Prefix used : formyl

F.G of Ketones : - C=O-

Suffix used : one

Prefix used : Keto or oxo

Common Name

C₁ → Form

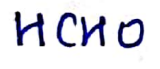
C₄ → Butyl

C₂ → Acet

C₅ → Valer

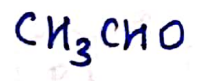
C₃ → Propion

C₆ → Capro



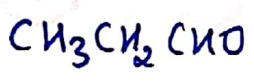
Formaldehyde

Methanal



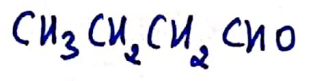
Acetaldehyde

Ethanal



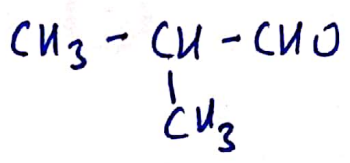
Propionaldehyde

Propanal



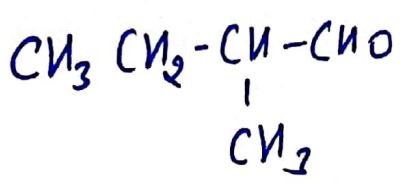
Butyraldehyde

Butanal



Isobutyraldehyde

2-Methyl propanal

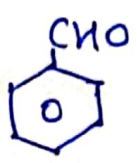


α-Methyl butyraldehyde

2-Methyl butanal

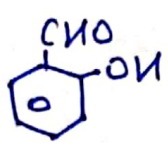
CH_3COCH_3	Dimethyl ketone	Propanone
$\text{CH}_3\text{COCH}_2\text{CH}_3$	Ethylmethyl ketone	Butan-2-one
$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$	Methyl-n-propyl ketone	Pentan-2-one
$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$	Diethyl ketone	Pentan-3-one

Nomenclature of Some Aromatic Aldehydes & Ketones



Benzaldehyde

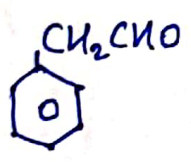
Benzaldehyde
or
Benzene carbaldehyde



Salicylaldehyde

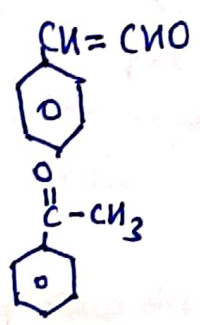
2-Hydroxy
benzaldehyde

or
o-Hydroxybenzaldehyde



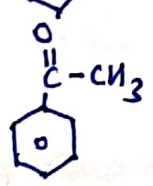
α -Phenylacetaldehyde

2-Phenyl
ethanal



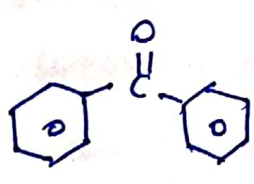
Cinnamaldehyde

3-Phenyl prop-2-enal



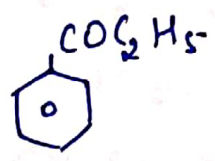
Acetophenone
or Methyl-phenyl ketone

Acetophenone



Diphenyl ketone
or Benzophenone

Benzophenone

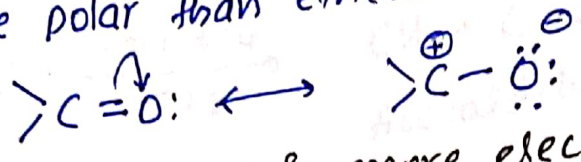


Ethyl-phenyl ketone
or propiophenone

Propiophenone

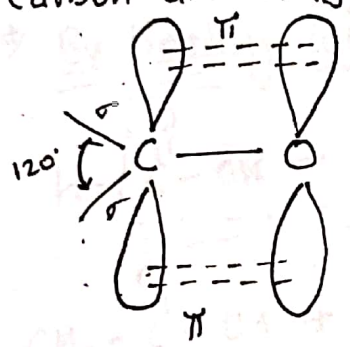
Structure of Carbonyl Group

These are more polar than ethers and have high dipole moment

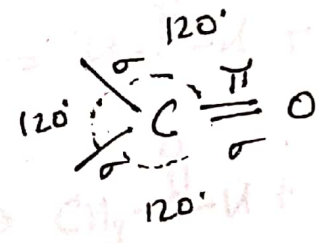
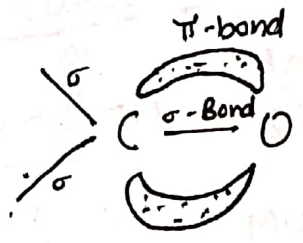


Oxygen of carbonyl group is more electronegative than carbon, so it is polar, carbon carries small +ve charge and oxygen carries small -ve charge

Carbonyl carbon is sp^2 hybridized forming one 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

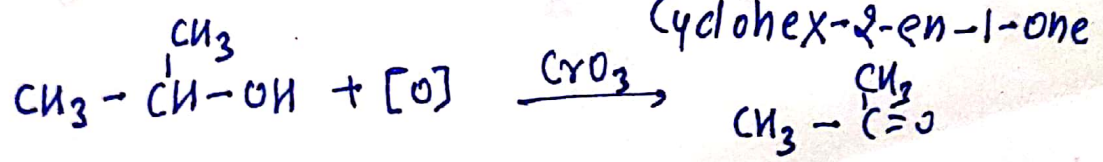
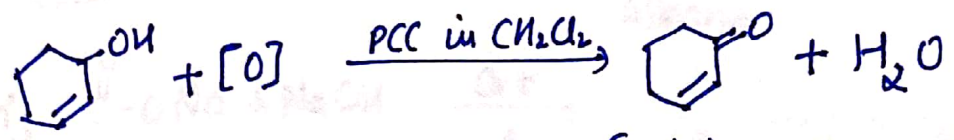
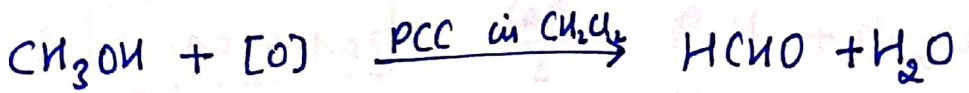
Weak oxidising agents are used

→ Chromium oxide - CrO_3

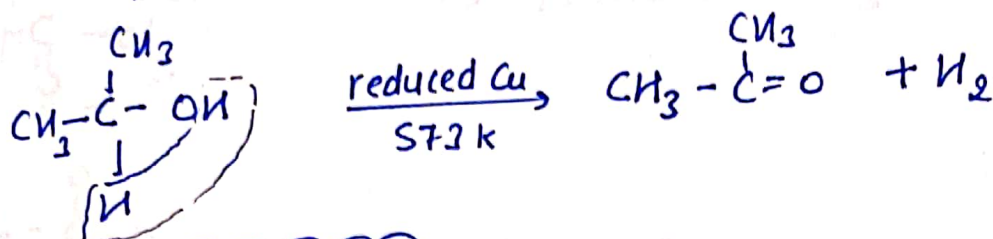
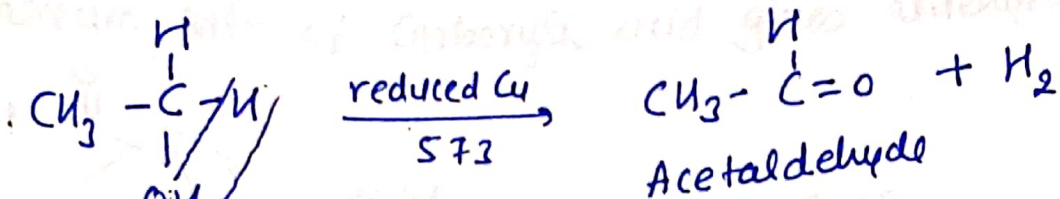
→ PCC (Pyridinium chloro chromate)

1° alcohol → Aldehyde

2° alcohol → Ketone

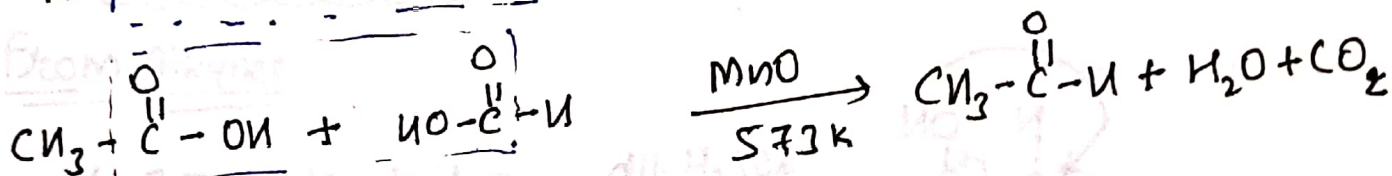
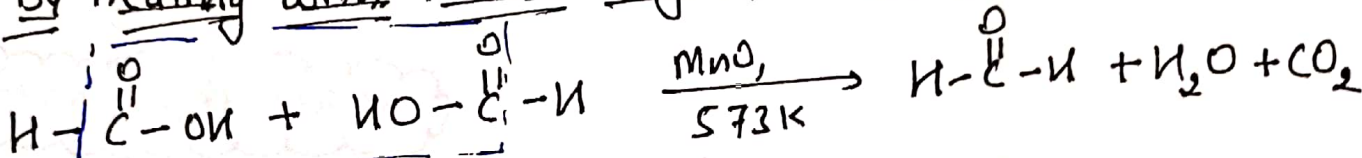


⇒ By dehydrogenation of Alcohols

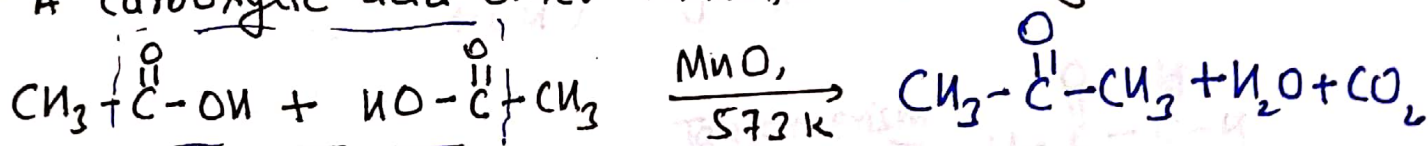


⇒ From Carboxylic Acid

⇒ By heating with MnO (Manganese Oxide)

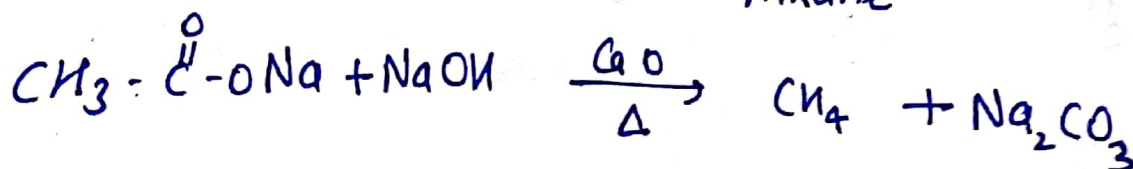
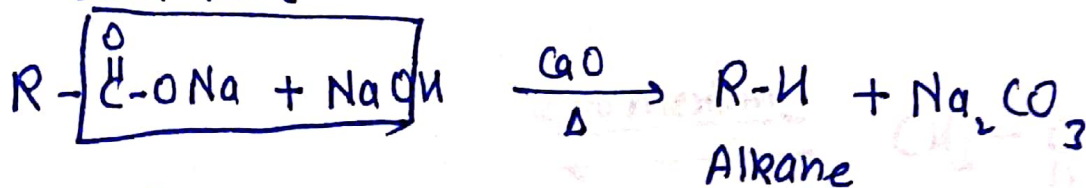


• A carboxylic acid other than formic acid gives ketones

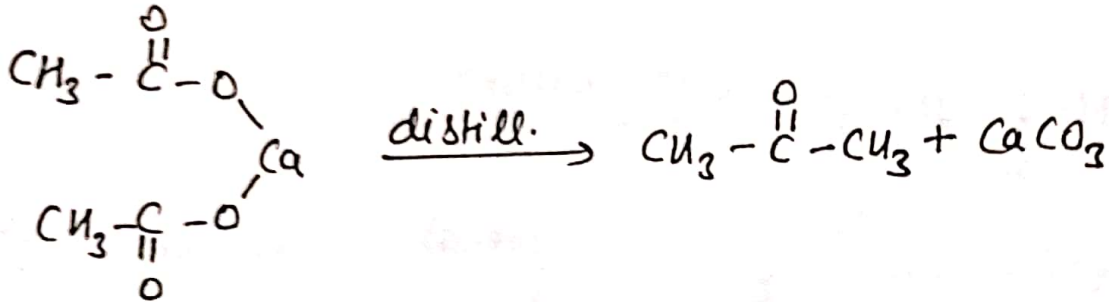
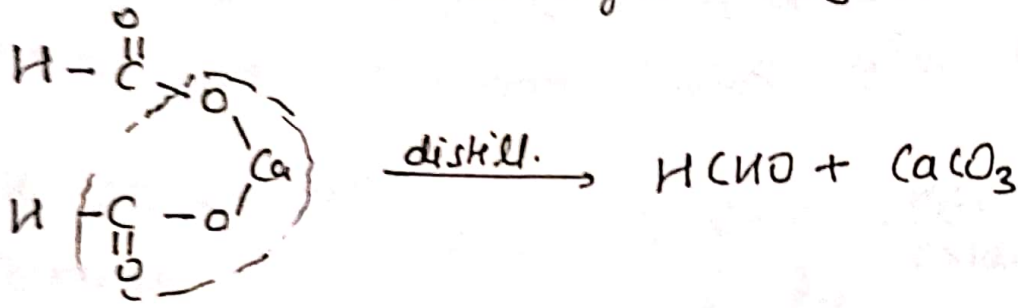


By distillation of calcium salts of Carboxylic Acid

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

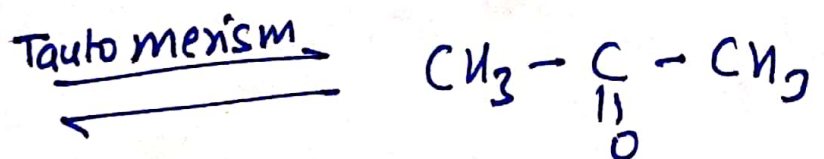
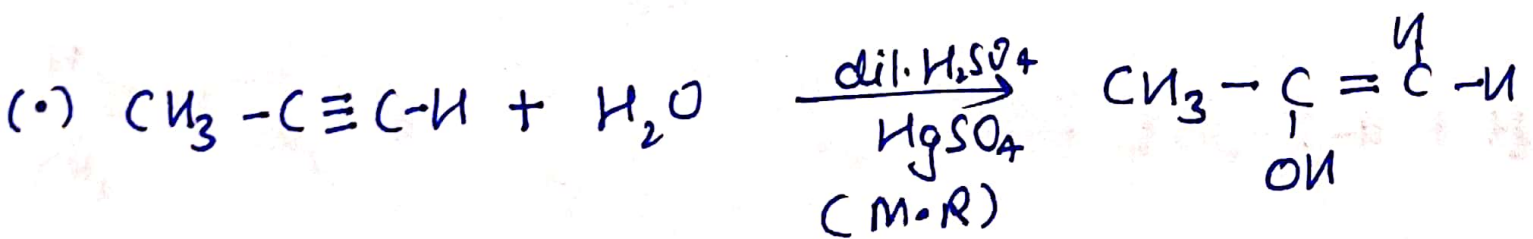
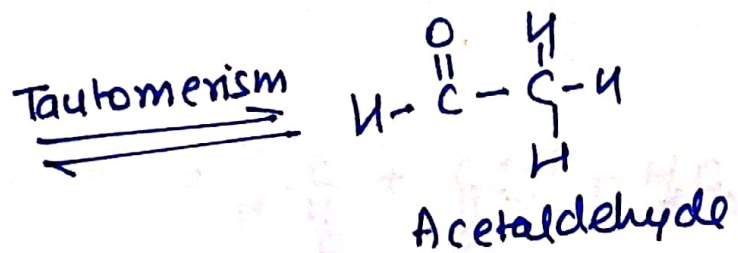
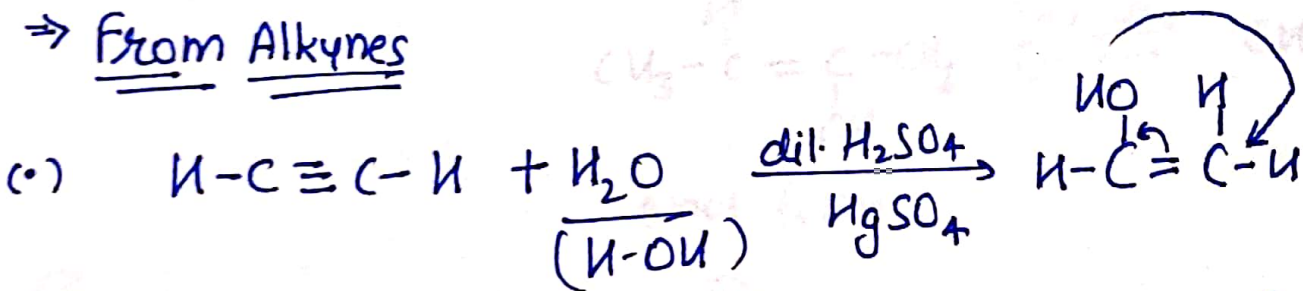


Calcium salt of carboxylic acid gives aldehydes & ketones



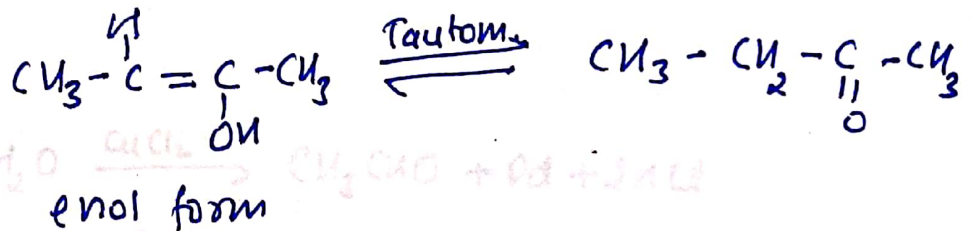
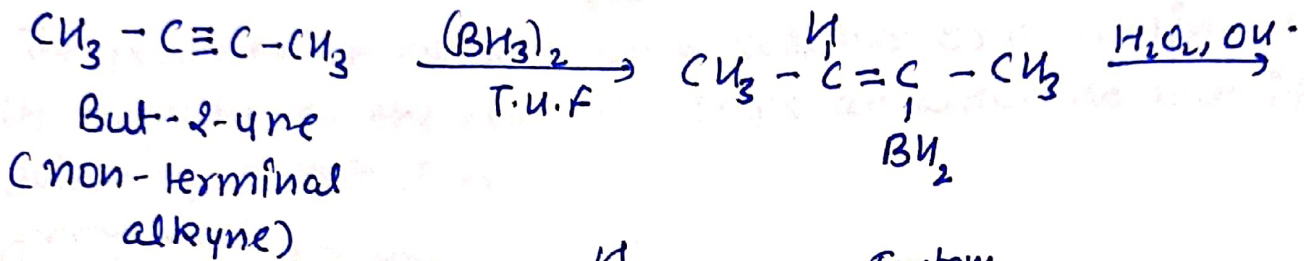
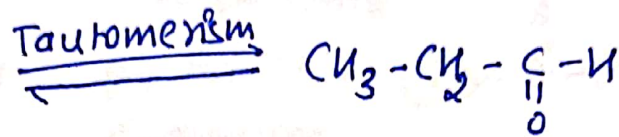
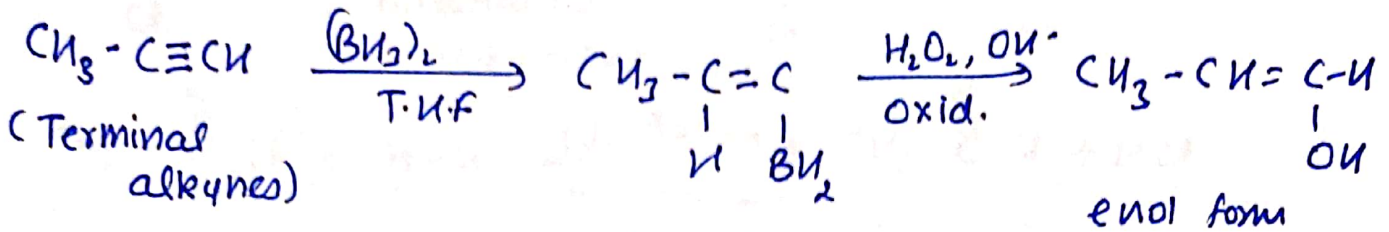
(4.) From Hydrocarbons

⇒ From Alkynes

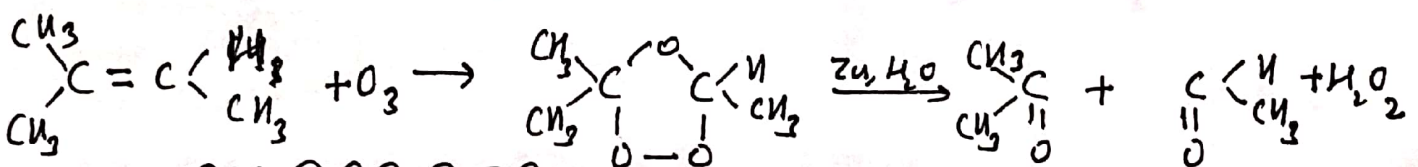
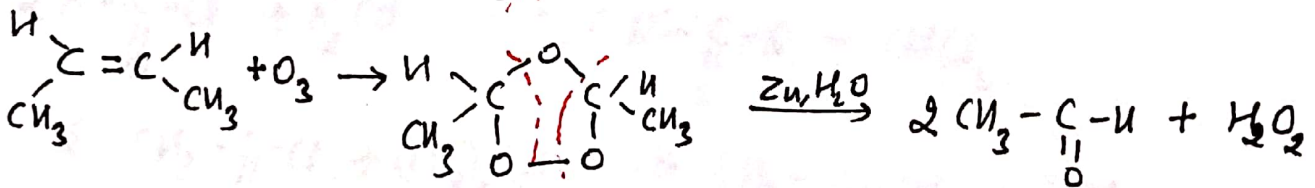
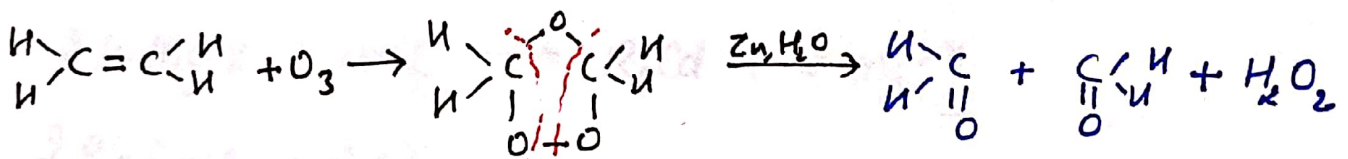


By Hydroboration-oxidation of Alkynes

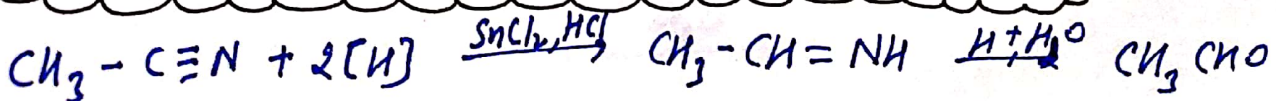
- terminal alkynes ($\text{C}\equiv\text{CH}$) give aldehydes
- non terminal alkynes ($\text{C}\equiv\text{CR}$) give ketones



By Ozonolysis of Alkenes

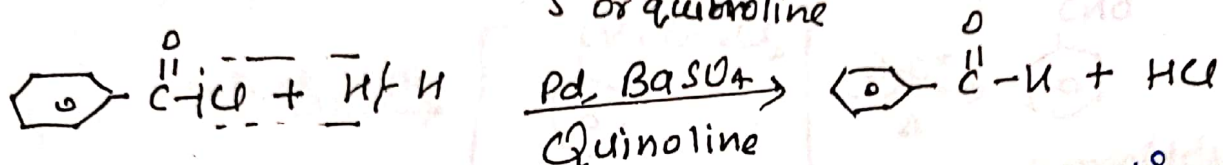
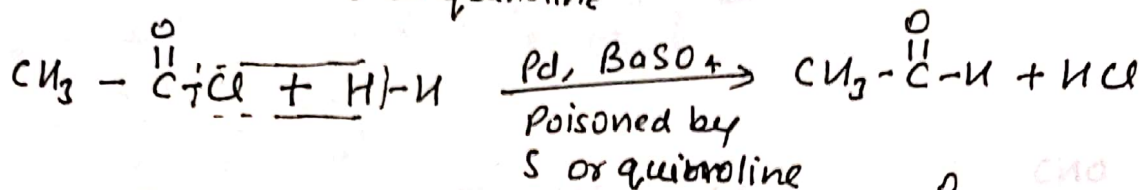
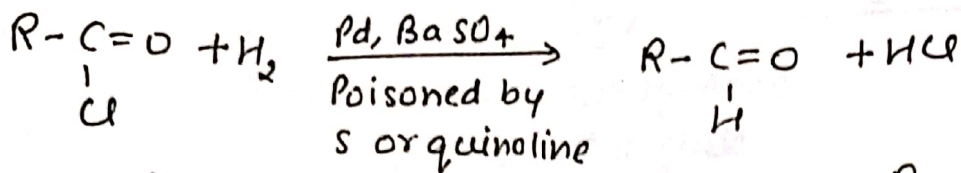


Stephen Reduction or Reduction of Alkyl cyanides



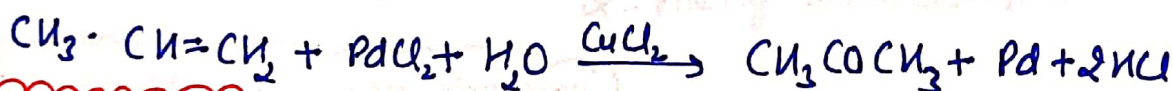
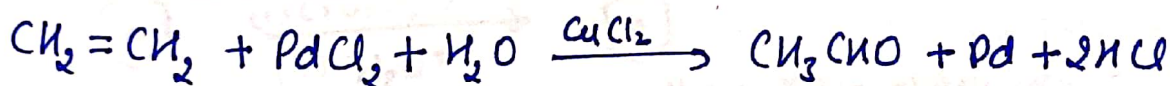
From Acid Chlorides

⇒ Rosenmund Reduction

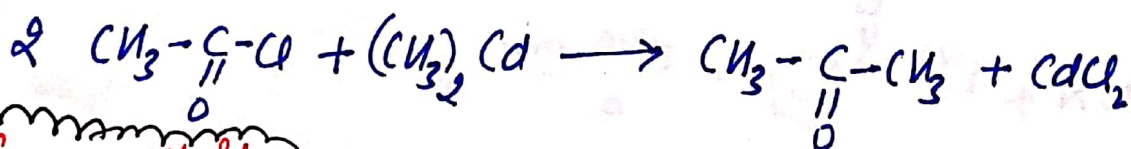
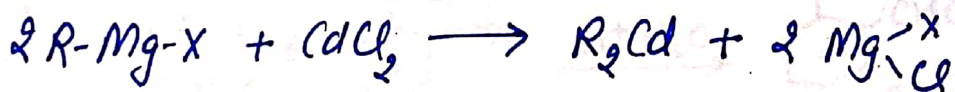


The poisoning of catalyst with sulphur or quinoline decrease its activity. So the reduction stops at aldehyde but if poisoning is not done

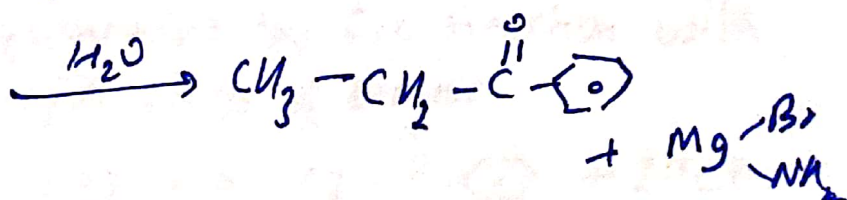
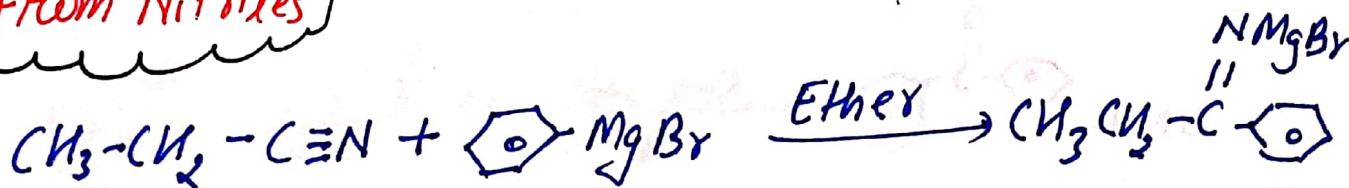
By Wacker's Process



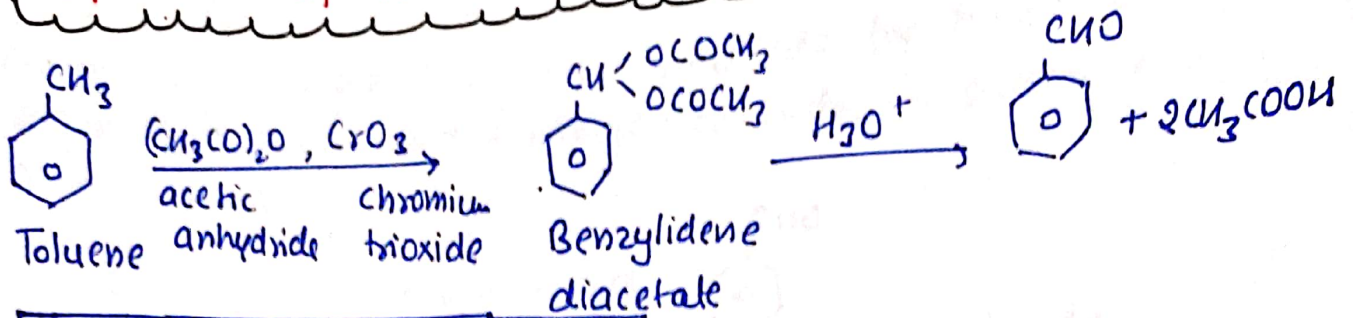
From HCN



From Nitriles

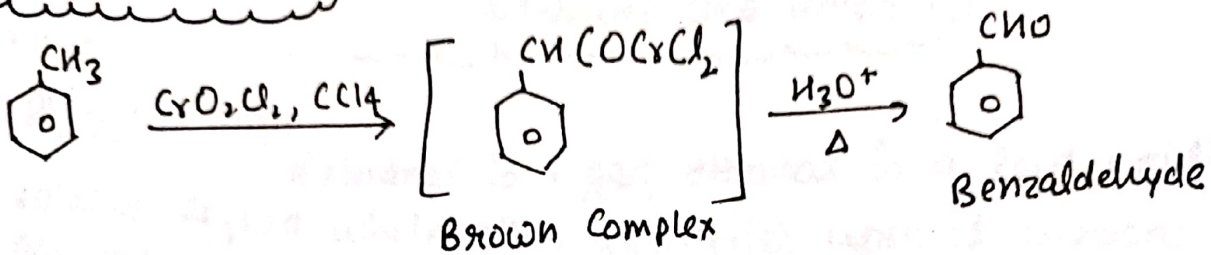


Preparation of Aromatic Aldehydes and Ketones

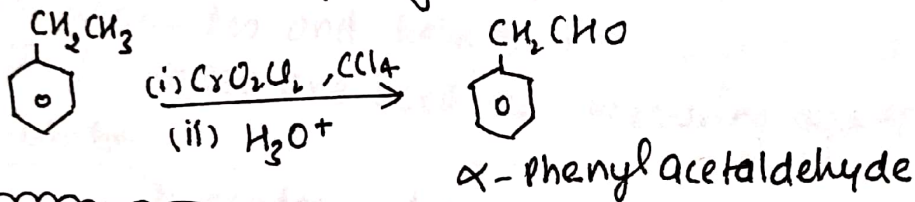


OXIDATION OF ALKYL BENZENE

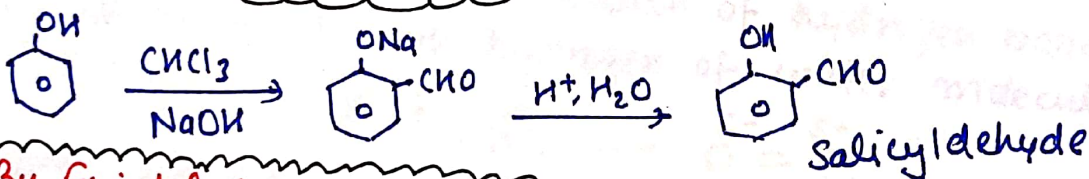
Etard Reaction



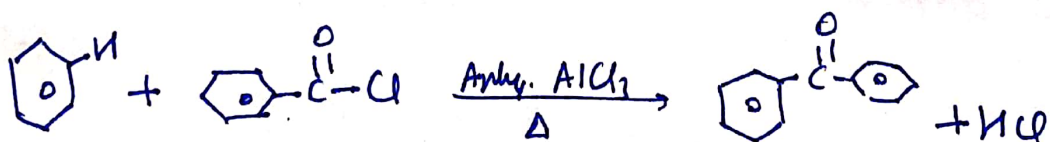
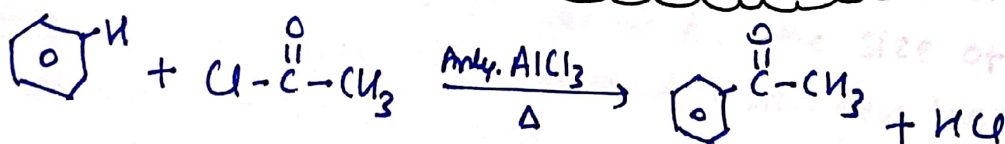
- If bigger side chain is present, then the end carbon is oxidized to aldehyde group.



By Reimer-Tiemann Reaction



By Friedel-Craft acylation and benzoylation

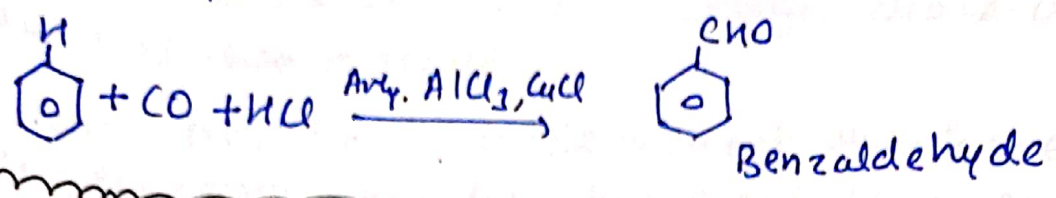


- Preparation of only benzophenone by F.C reaction with carbonyl chloride (Phosgene) with excess of benzene



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

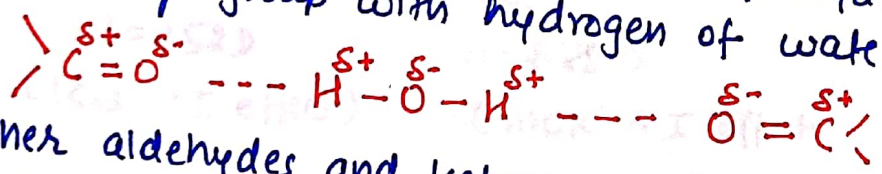
Methanal is a gas, ethanal is a low boiling volatile liquid, while other aldehydes upto 11 carbons are colourless liquids. All ketones are also colourless liquids.

→ 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.



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.

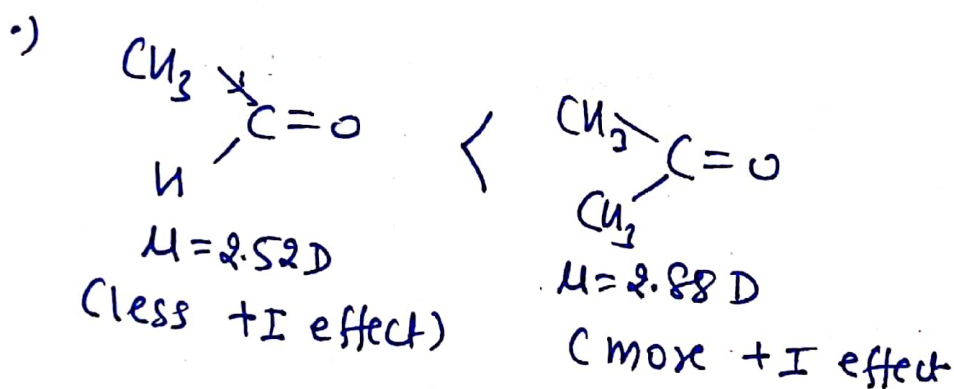
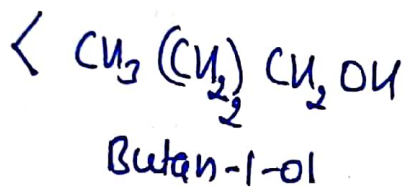
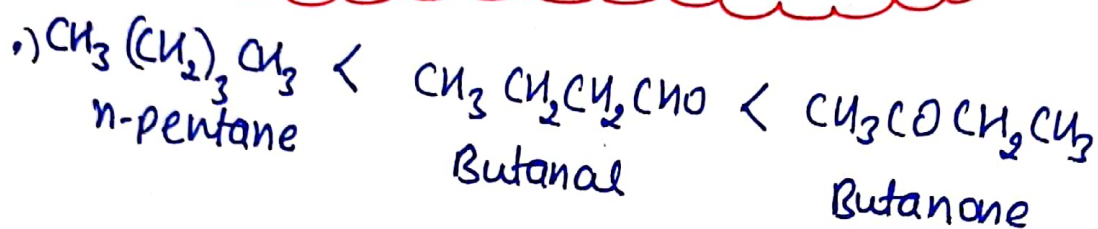
- Although these are soluble in organic solvents like benzene, ether, CCl_4 etc.

→ 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:



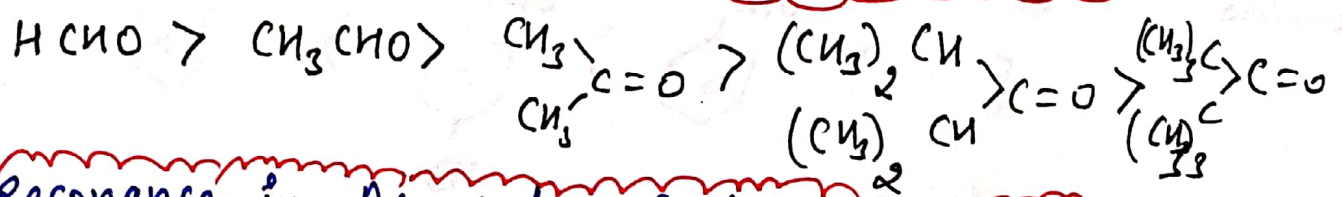
Chemical Reaction of Aldehydes and Ketones

- ⇒ 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 groups have two resonating str.
 - Alkenes are non polar while carbonyl groups is polar.

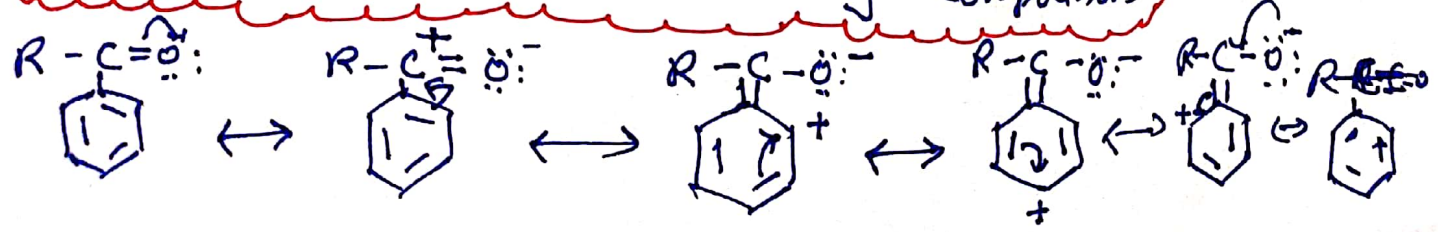
Reaction of Aldehydes and Ketones

- 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

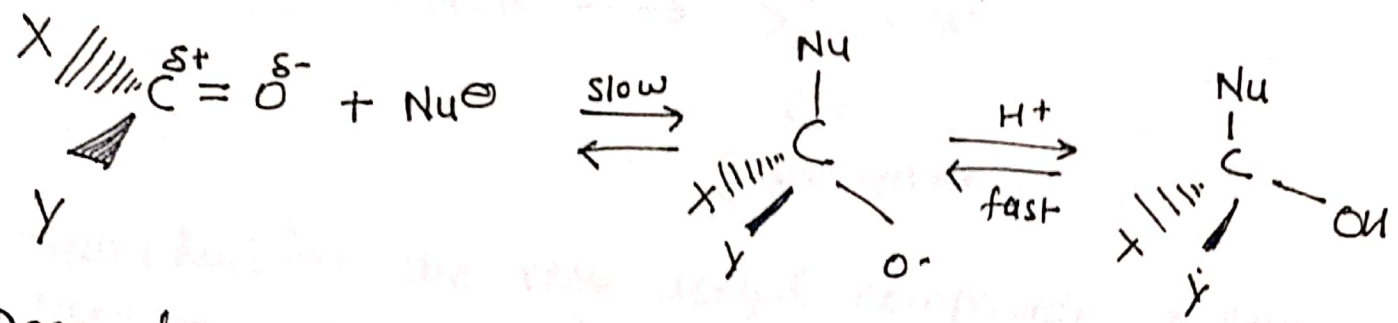


Resonance in Aromatic Carbonyl Compounds

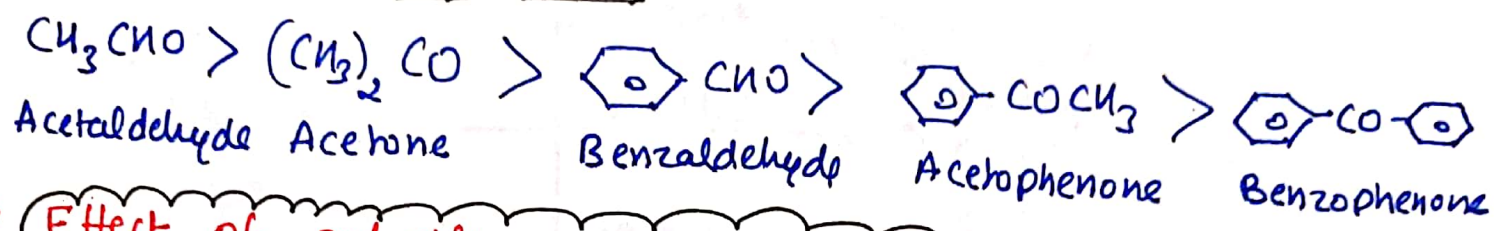


(A) Nucleophilic Addition Rxn

Mechanism



Decreasing order of reactivity



Effect of substituent on Reactivity of Aromatic Aldehydes and Ketones

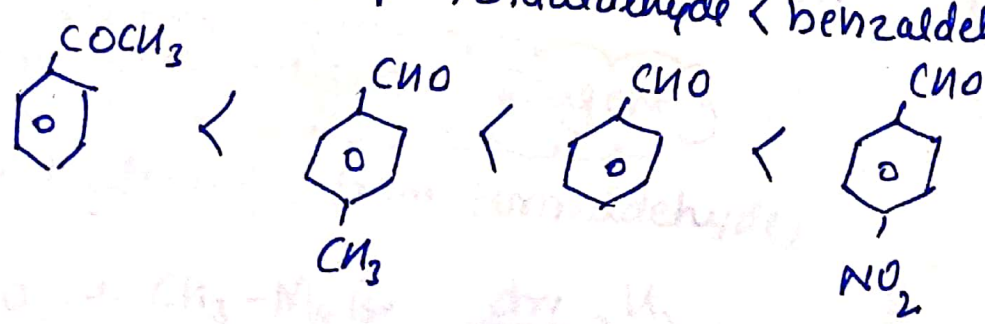
⇒ Effect of electron releasing group:-

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

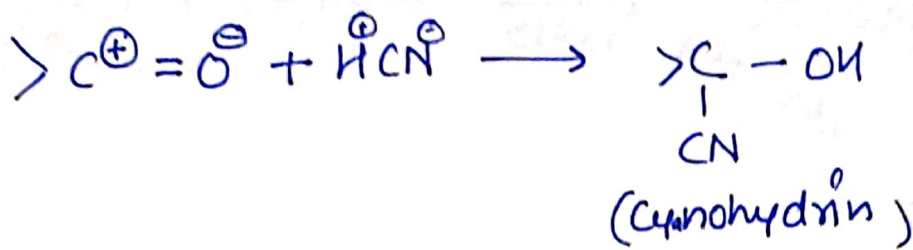
⇒ Effect of electron withdrawing group:-

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.

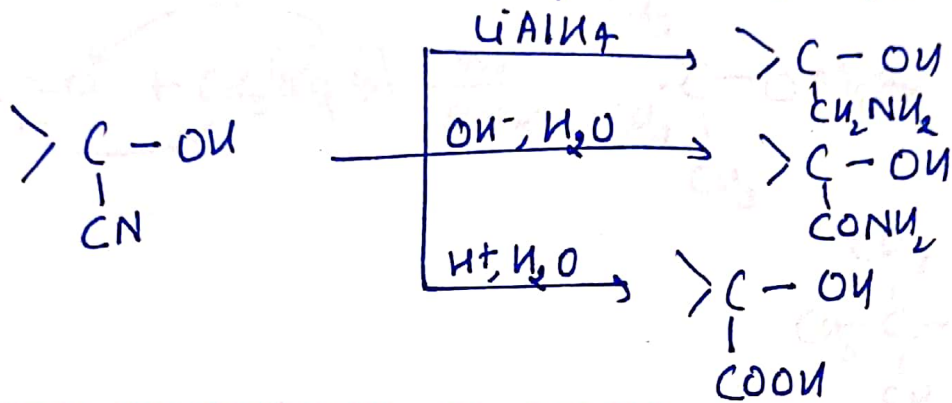
Acetophenone < p-tolualdehyde < benzaldehyde < p-nitro benzaldehyde



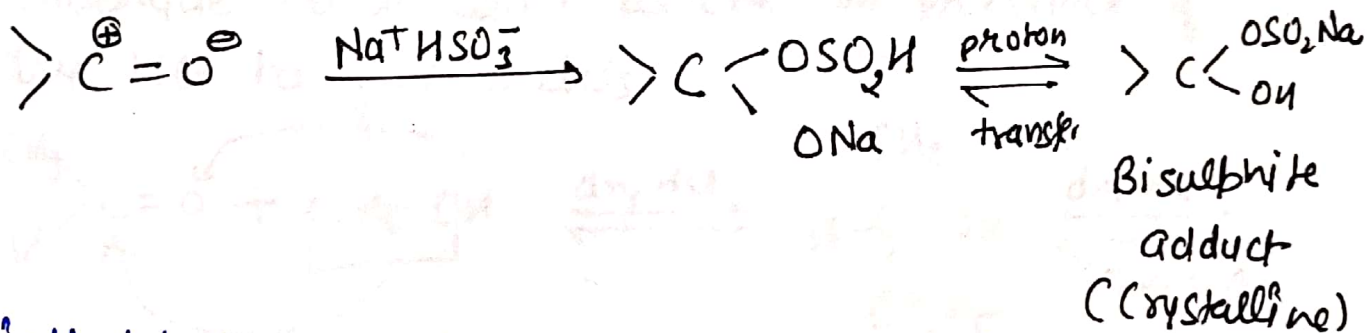
Reaction with HCN



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



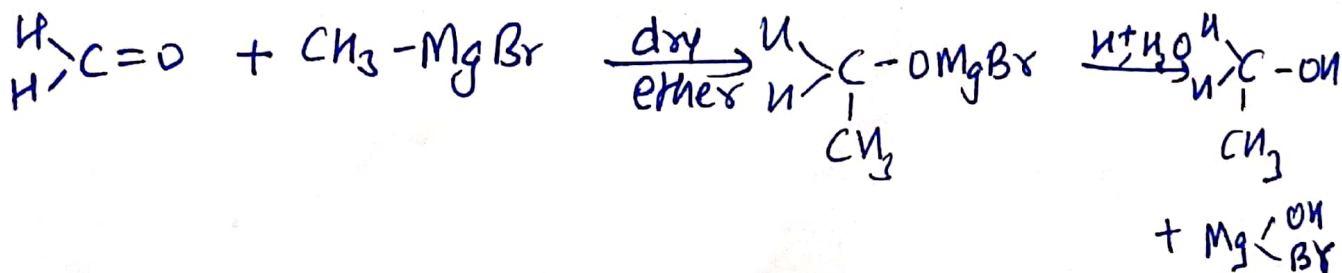
Reaction with sodium bisulphite (NaHSO₃)



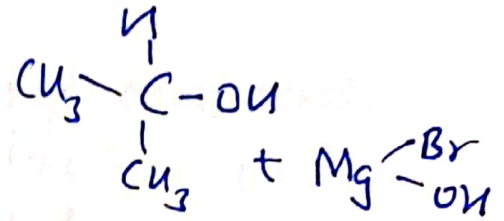
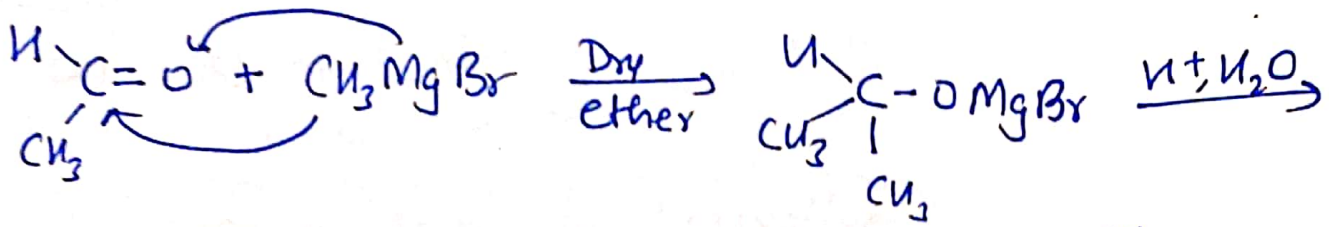
• Diethyl ketone, acetophenone and benzophenone do not give this reaction due to more steric hinderance

Reaction with Grignard Reagent

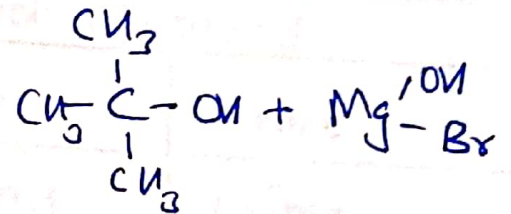
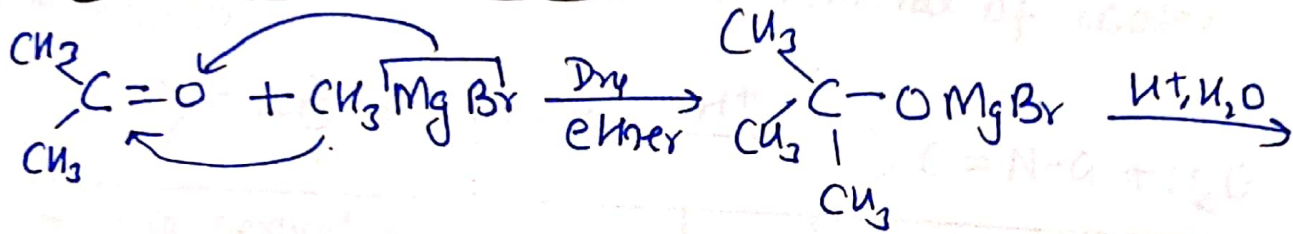
with 1° alcohol (from formaldehyde)



All other aldehydes give 2° Alcohol

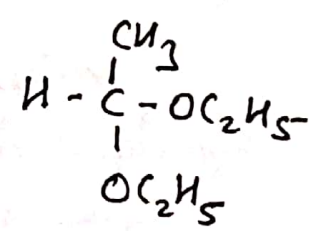
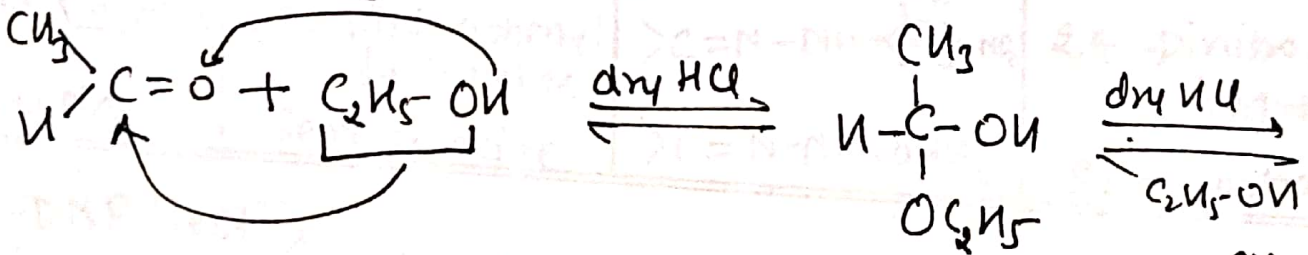


⇒ Ketones give 3° Alcohols

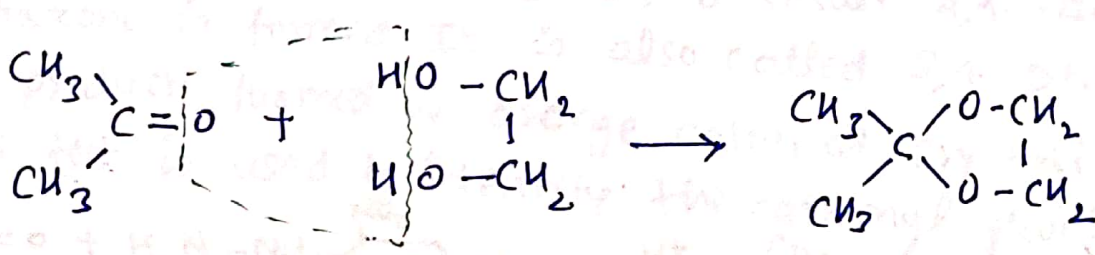


Addition of Alcohols

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



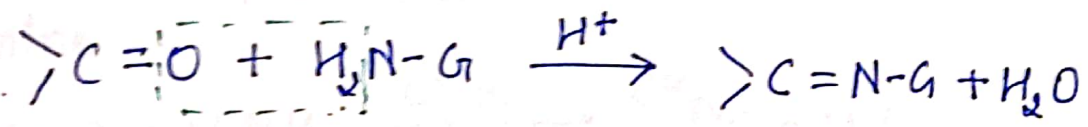
⇒ Ketones



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 containing nitrogen double bond with the removal of water molecules

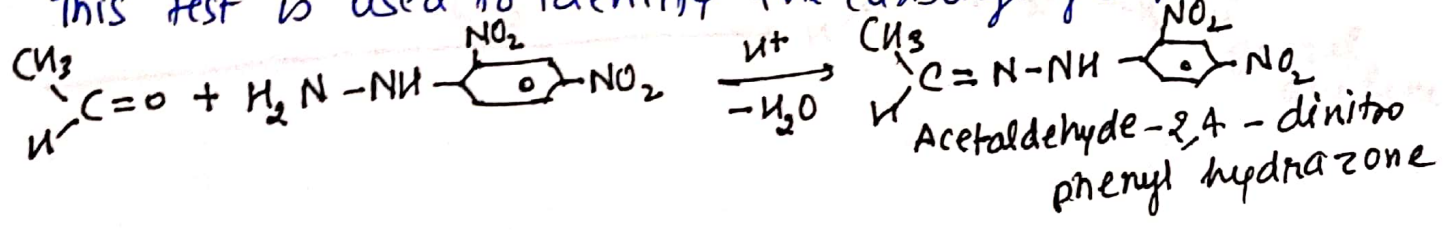


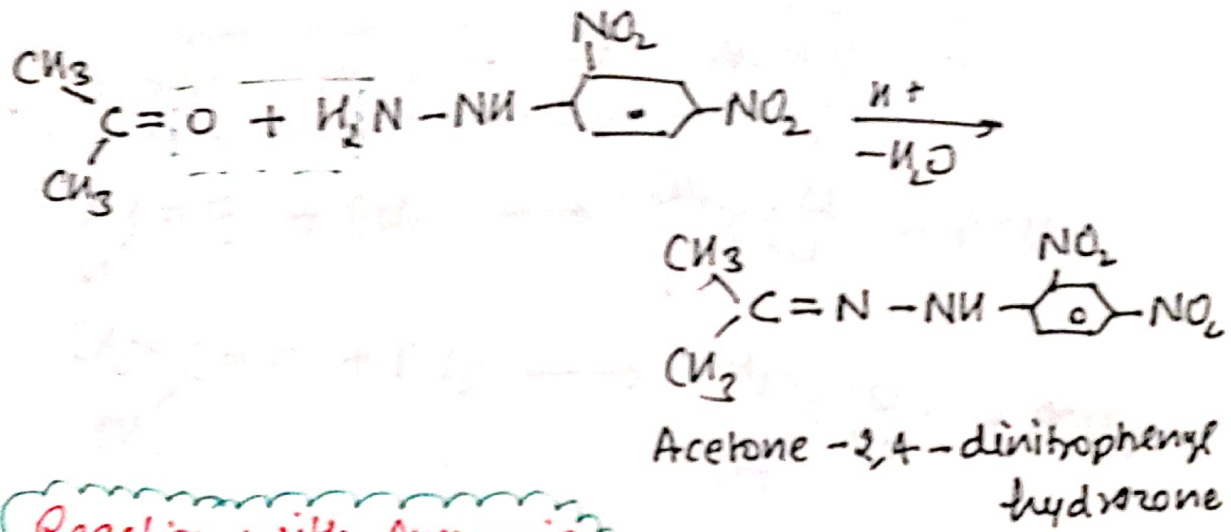
Ammonia Derivative Used		Product Obtained	
NH ₂ -G Structure	Name	Structure	Name
NH ₂ OH	Hydroxylamine	>C=N-OH	Oxime
H ₂ N-NH ₂	Hydrazine	>C=N-NH ₂	Hydrazone
H ₂ N-NH-C ₆ H ₅	Phenyl hydrazine	>C=N-NH-C ₆ H ₅	Phenyl hydrazone
H ₂ N-NH-C ₆ H ₃ (NO ₂) ₂	2,4-Dinitrophenyl hydrazine	>C=N-NH-C ₆ H ₃ (NO ₂) ₂	2,4-Dinitrophenyl hydrazone
NH ₂ CO NH ₂	Semicarbazide	>C=N-NHCONH ₂	Semicarbazone

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.

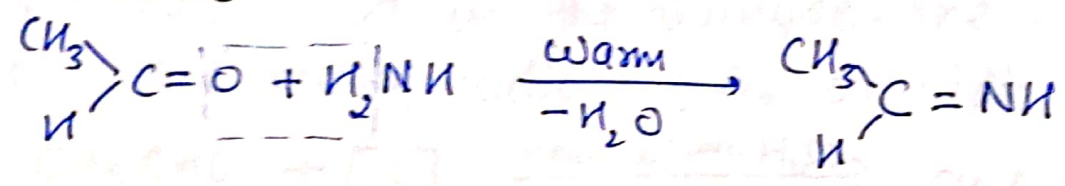
This test is used to identify the carbonyl group



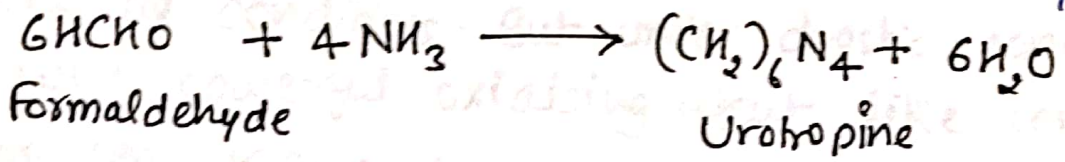


Reaction with Ammonia

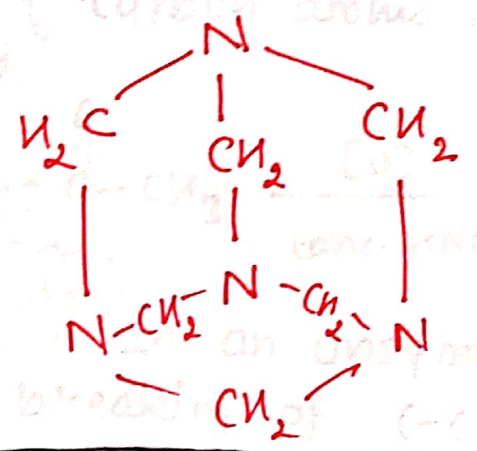
Except formaldehyde, other aliphatic aldehydes react with ammonia and form an imine



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

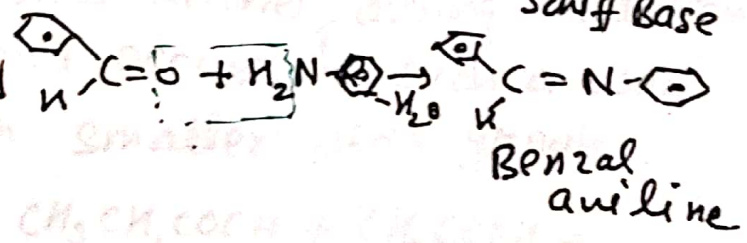
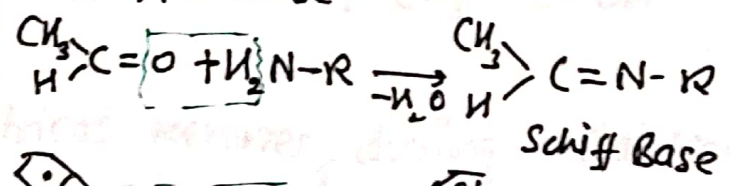


Str. of Urotropine:



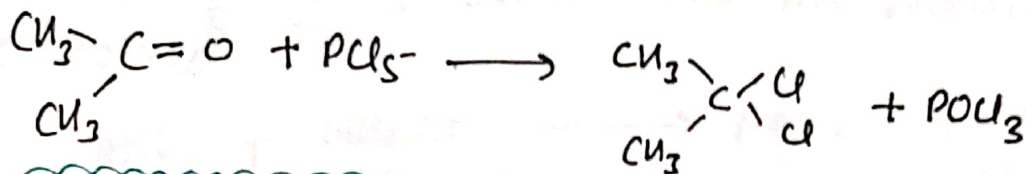
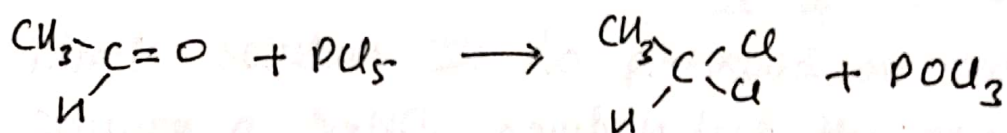
Reaction with Primary Amines

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



Reaction with Phosphorous Pentachlorides

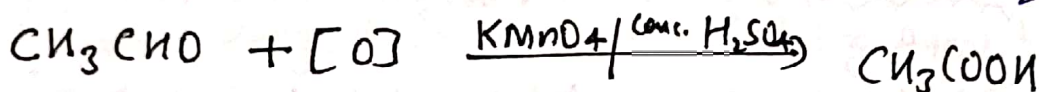
(17)



Oxidation Reaction

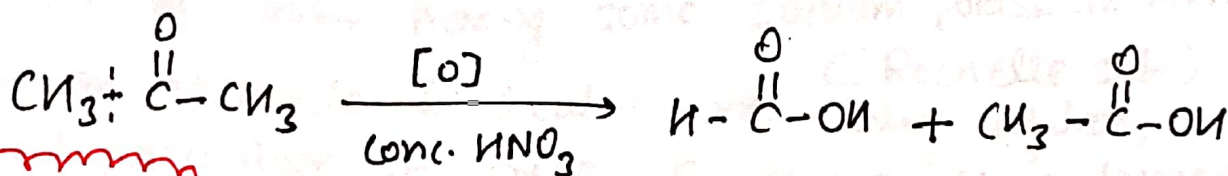
(i) Oxidation of Aldehydes

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 $\text{K}_2\text{Cr}_2\text{O}_7$.



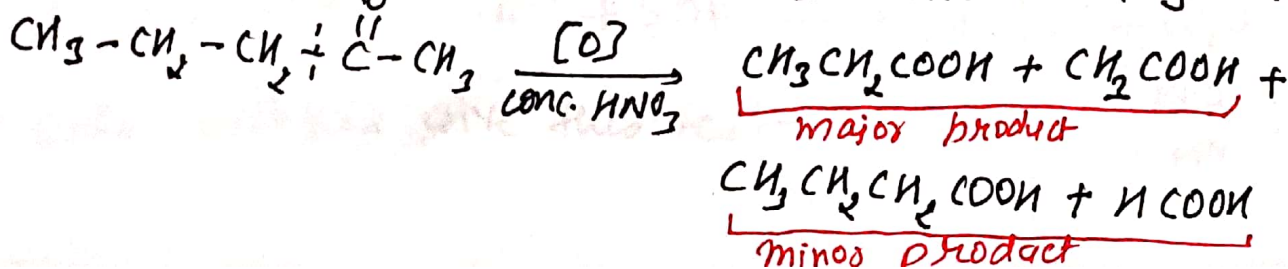
Oxidation of Ketones

Ketones are not easily oxidised under ordinary conditions. But under drastic conditions and with powerful oxidising agent like conc HNO_3 , KMnO_4 or conc. $\text{K}_2\text{Cr}_2\text{O}_7$ / 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.



Popoff's Rule

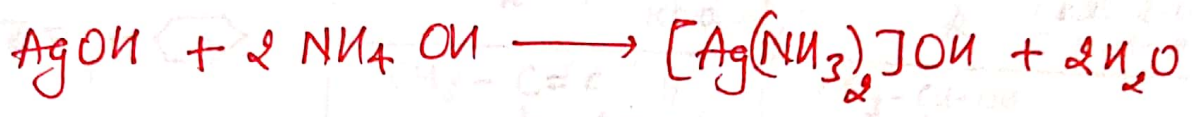
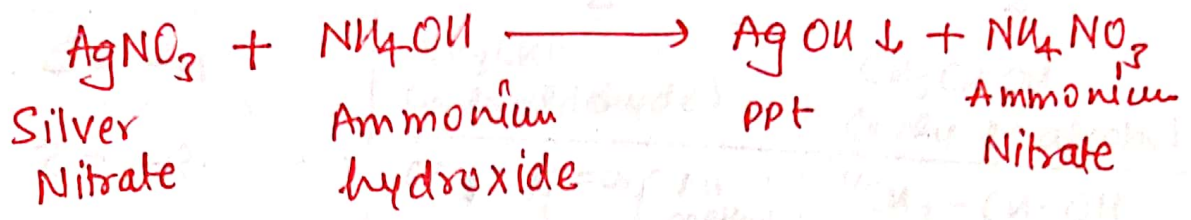
In an unsymmetrical ketones, during oxidation the breaking of C-C bond occurs in such a way that keto group goes with smaller alkyl group.



Scanned by CamScanner

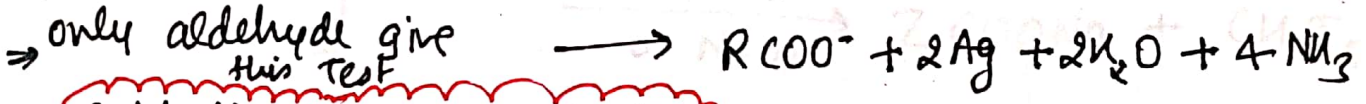
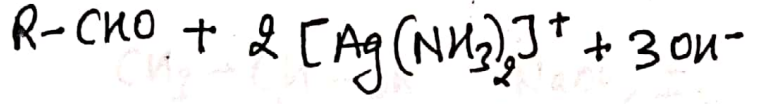
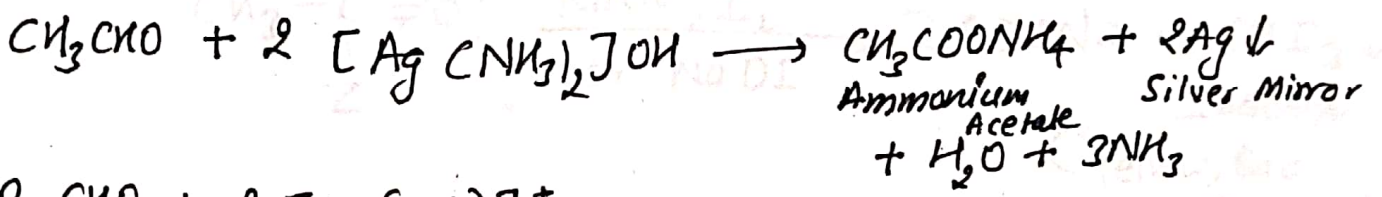
Oxidation by Tollen's Reagent

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



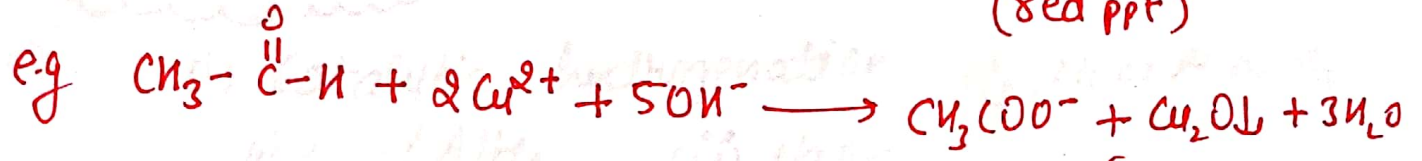
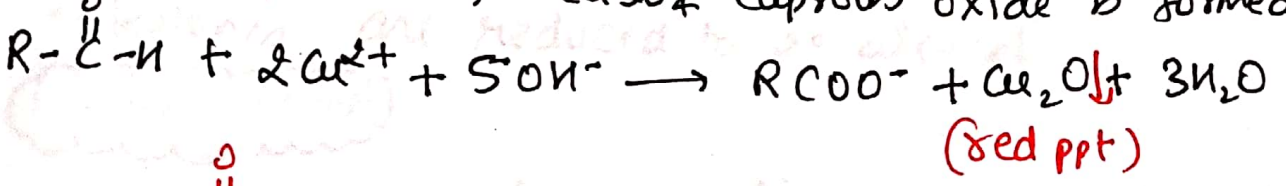
Tollen's Reagent

Tollen's Reagent is a weak oxidizing Agent



Oxidation by Fehling Solution

Fehling solution is an alkaline solution of CuSO_4 having some sodium potassium tartrate when an aldehyde is treated with Fehling solution, a red precipitate of Cu_2O Cuprous oxide is formed



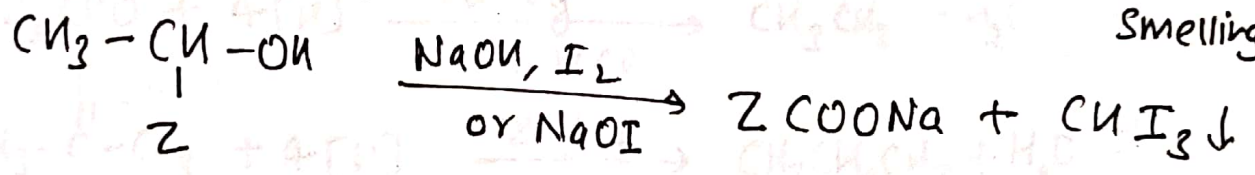
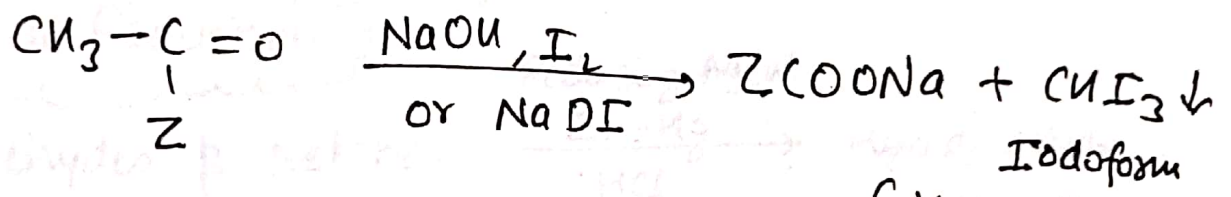
⇒ only Aldehyde give this test (Red ppt)

Iodoform Test

Following compounds give iodoform test
→ among aldehyde, only ethanal give this test

	$\text{CH}_3 - \underset{\text{Z}}{\text{C}} = \text{O}$	$\text{CH}_3 - \underset{\text{Z}}{\text{CH}} = \text{O}$
(i) $\text{Z} = -\text{H}$	CH_3CHO (only aldehyde)	$\text{CH}_3\text{CH}_2\text{OH}$ (only 1° alcohol)
(ii) $\text{Z} = -\text{R}$	$\text{CH}_3 - \underset{\text{R}}{\text{C}} = \text{O}$ (All methyl ketones)	$\text{CH}_3 - \underset{\text{R}}{\text{CH}} - \text{OH}$ (all 2°-ol but not 1°)
(iii) $\text{Z} = -\text{C}_6\text{H}_5$	$\text{CH}_3 - \underset{\text{C}_6\text{H}_5}{\text{C}} = \text{O}$ Acetophenone	$\text{CH}_3 - \underset{\text{C}_6\text{H}_5}{\text{CH}} - \text{OH}$ 1-phenyl ethanol

Reaction



Reduction to Alcohol

Aldehydes and ketones on reduction with reducing agents give alcohols.

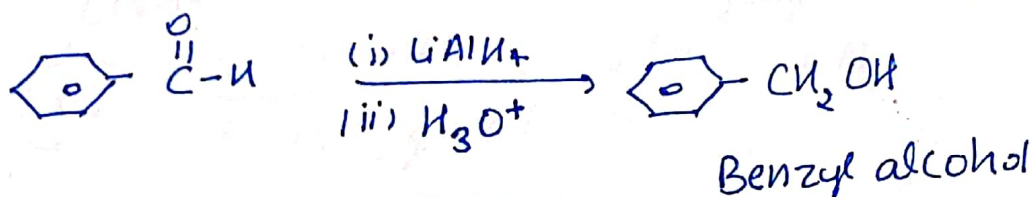
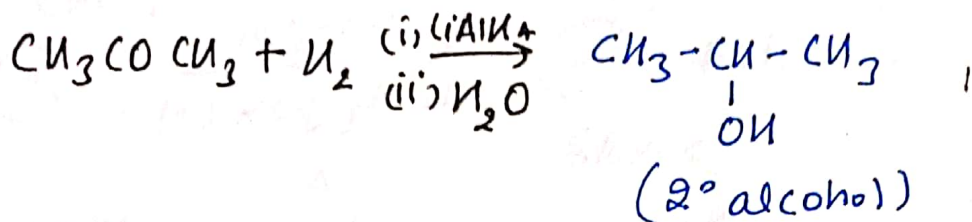
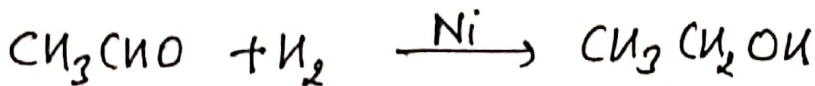
- Aldehydes are reduced to 1° alcohol
- Ketones are reduced to 2° alcohol

Reducing Agent

- (i) Catalytic hydrogenation: H_2, Ni or Pt or Pd
- (ii) LiAlH_4 (ii) NaBH_4

• LiAlH₄ is stronger reducing agent.

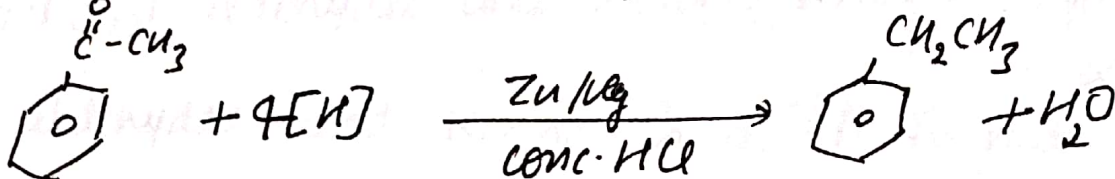
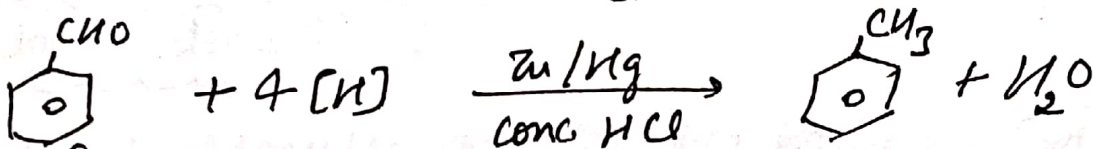
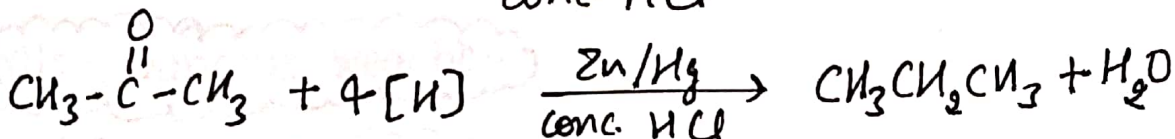
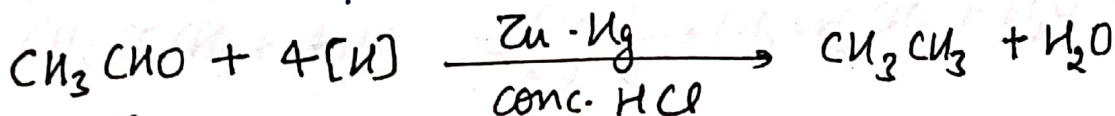
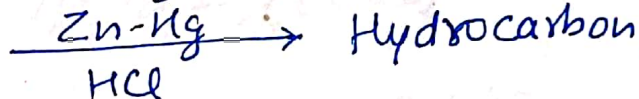
• LiAlH₄ and NaBH₄ do not reduce carbon-carbon double bonds (C=C) and double bond of benzene ring



Clemmensen Reduction

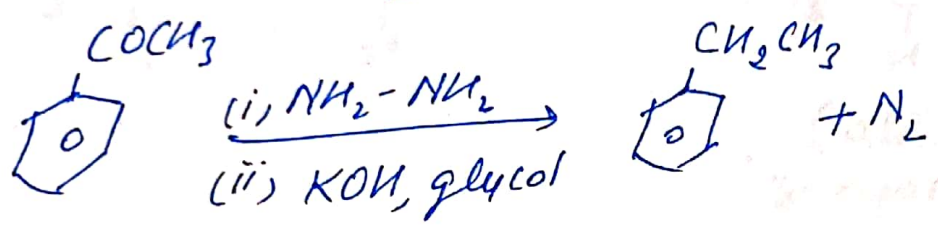
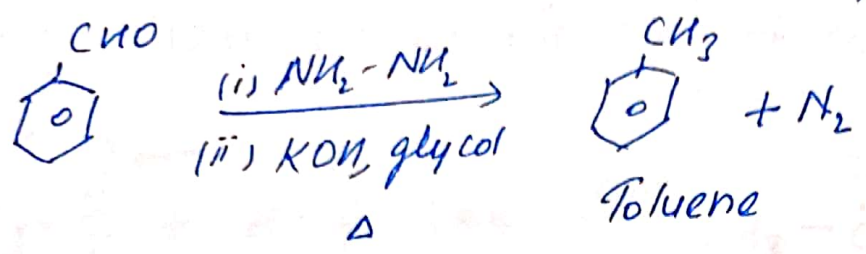
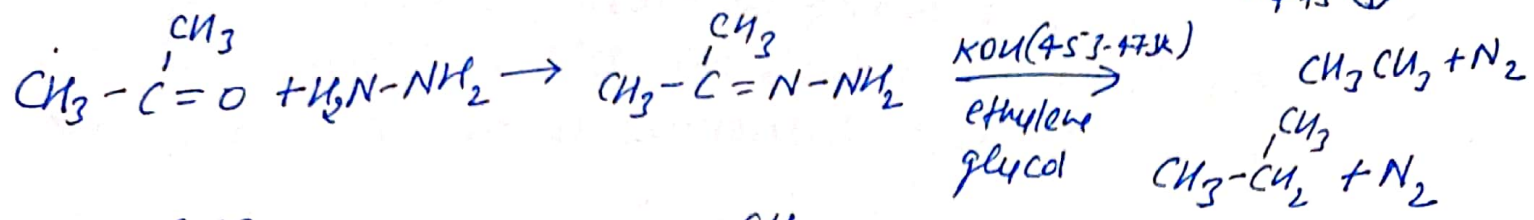
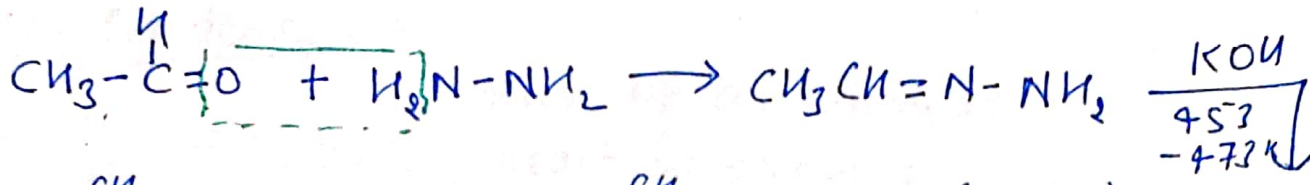
Aldehydes & Ketones

Reducing Agent

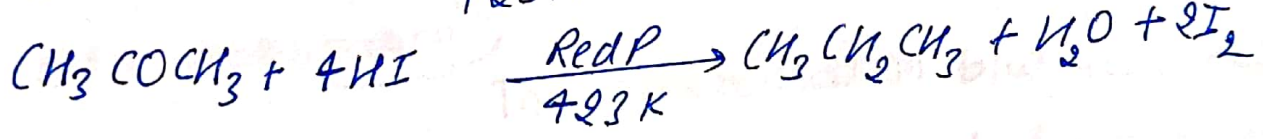
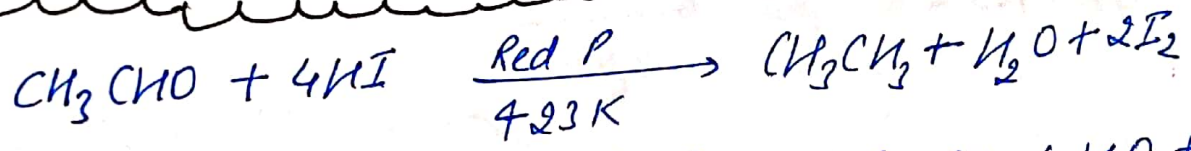


Wolf-Kishner Reduction

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.



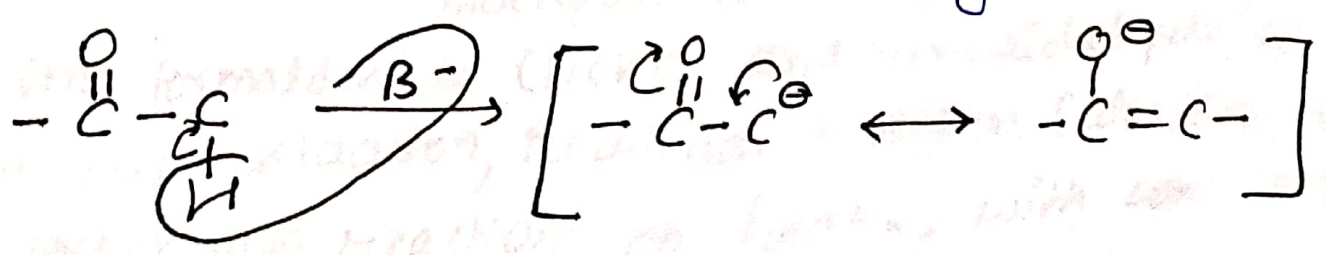
Reduction with HI/Red P



Miscellaneous Reaction

Aldol Condensation

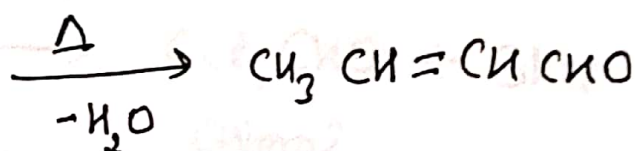
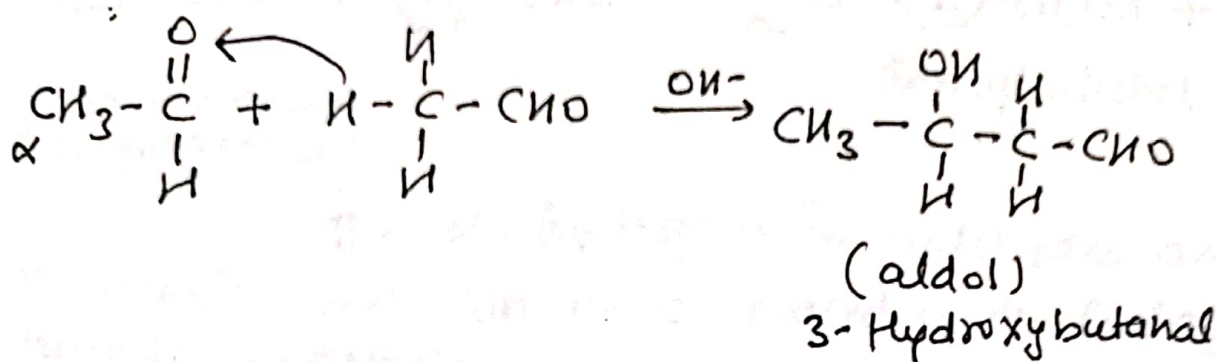
Reaction of aldehydes and ketones having α -hydrogen:
 α -hydrogen of aldehydes and ketones is acidic in nature due to resonance stabilisation of conjugate base.



Aldol Condensation

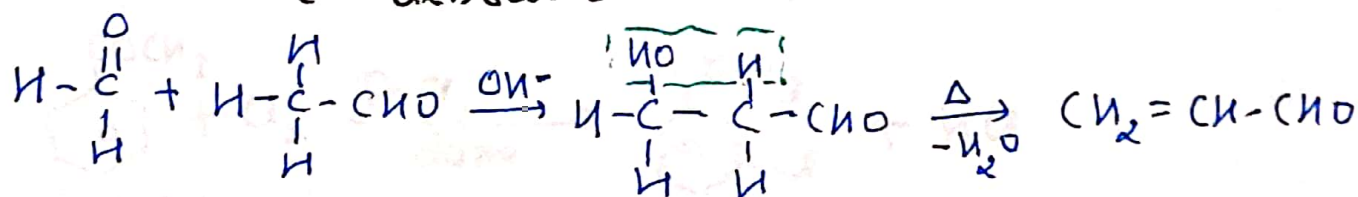
2 moles of an aldehyde or ketone having α -hydrogen, react in presence of dil. alkali to produce aldol, which on further heating, gets dehydrated to an unsaturated aldehyde or ketone

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



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 $\text{Ba}(\text{OH})_2$ is called cross aldol condensation.



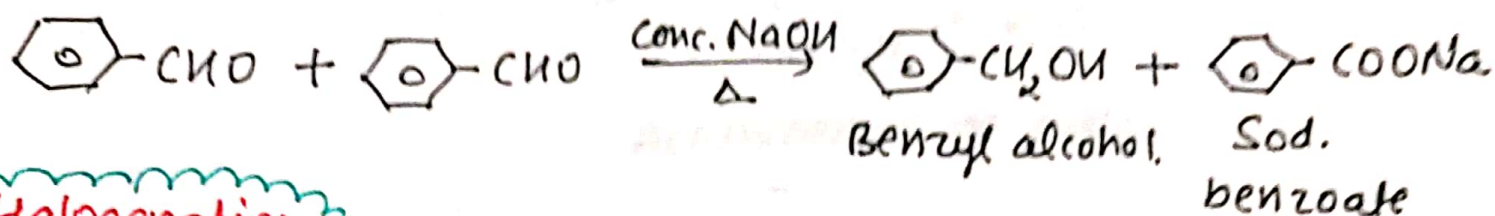
Cannizzaro's Reaction

Aldehydes which do not have ' α ' hydrogen atom like formaldehyde (HCHO) and benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) undergo self oxidation, reduction reaction (also called disproportionation reaction) on heating with conc. alkali



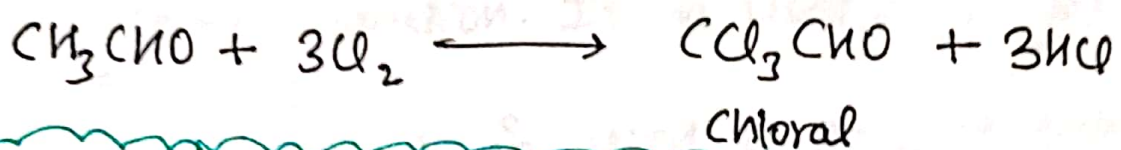


Here one molecule of formaldehyde is reduced to methyl alcohol and other is oxidized to salt of carboxylic acid. Similarly.



Halogenation

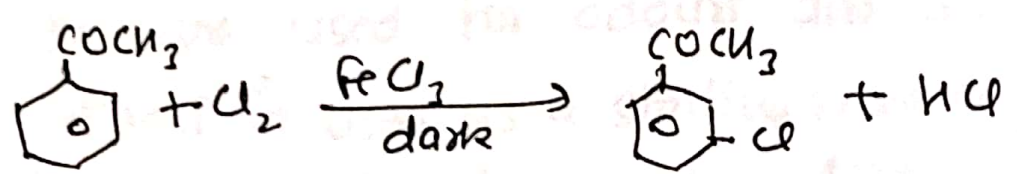
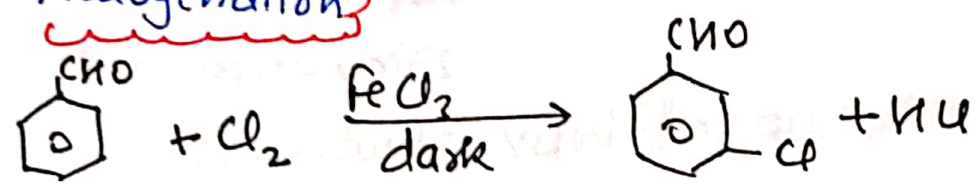
The α -hydrogen in aldehydes and ketones is acidic and can be displaced with halogen under suitable conditions



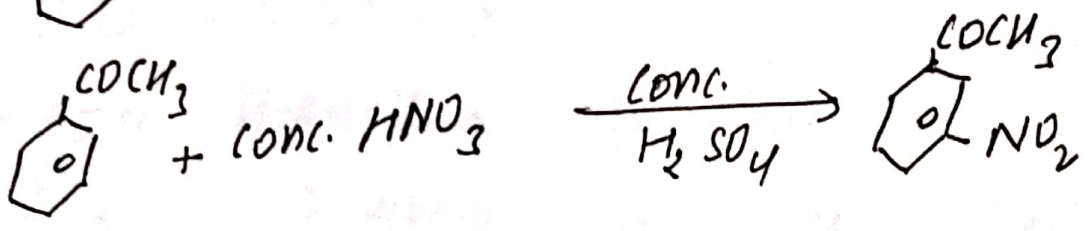
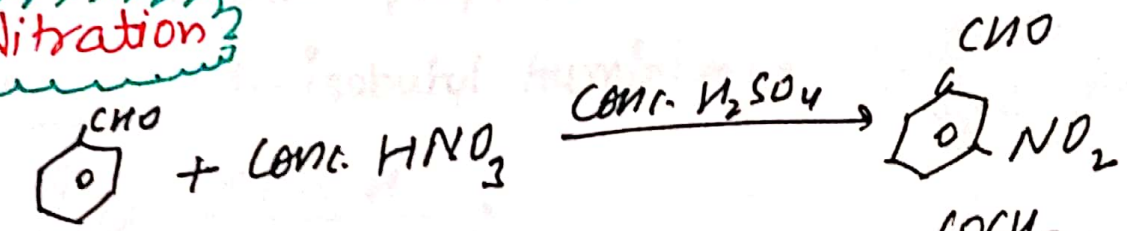
Electrophilic Substitution Reaction

Aldehydes and ketones are meta directing deactivating group.

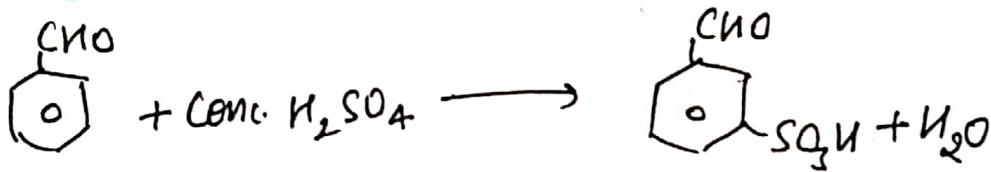
⇒ Halogenation



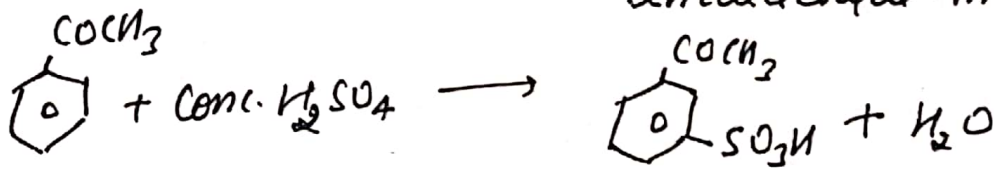
⇒ Nitration



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, vanillin, 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 Aluminium Hydride $\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Al-H}$

