

Unit: 13

Aldehydes & Ketones

NEB Syllabus

[A] Aliphatic aldehydes and ketones

Introduction, Nomenclature & Isomerism

Preparation of aldehydes and ketones

i) *By dehydrogenation of alcohols*

ii) *By oxidation of alcohols*

iii) *By Ozonolysis of alkenes*

iv) *By catalytic hydration of alkynes*

v) *From Acid Chlorides (Rosenmund's reduction)*

vi) *From Gem dihalides (or dihaloalkanes)*

Physical properties (state, color, odor, boiling point, solubility)

Structure and nature of carbonyl group

Chemical properties

i) *Addition reactions (H_2 , HCN, NaHSO₃, Grignard reagents)*

ii) *Action with ammonia derivatives (NH₂OH, NH₂NH₂, phenyl hydrazine, 2, 4- DNP, semi carbazide)*

iii) *Reducing properties of aldehyde (Reaction with oxidizing agents like Tollen's reagent and Fehling solution)*

iv) *Special reactions: Aldol condensation, Clemmensen's reduction, Wolff's Kishner reduction, Action with PCl₅, Action with LiAlH₄*

v) *Special reactions of Methanal or formaldehyde: Cannizzaro's reaction, action with ammonia, action with phenol (polymerization)*

Formalin & its uses

[B] Aromatic aldehydes and ketones

Preparation of Benzaldehyde from toluene
Preparation of Acetophenone from benzene

Chemical Properties of benzaldehyde

i) *Perkin condensation*

ii) *Benzoin condensation*

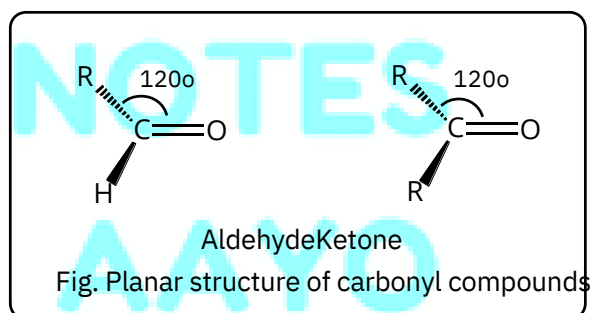
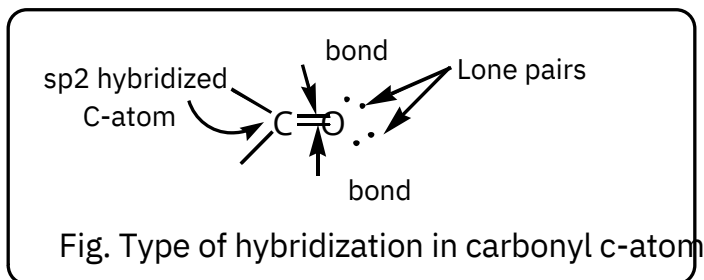
iii) *Cannizzaro's reaction*

iv) *Electrophilic substitution reactions*

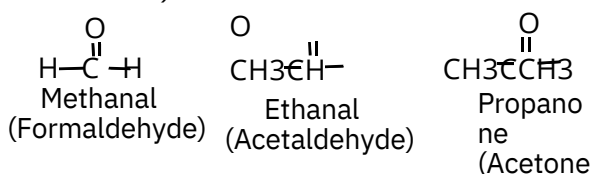
Introduction, Structure of carbonyl group, Nomenclature & Isomerism

Introduction: Organic compounds (aldehydes and ketones) containing carbonyl $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$ are group (collectively called as carbonyl compounds).

- ✓ General formula: $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$ & $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$
- ✓ Structure:



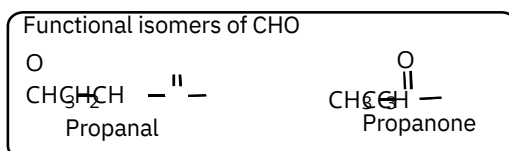
- ✓ Nomenclature: Aldehyde are named as "Alkanal" & ketone are named as "alkanone". (common names are given in brackets)



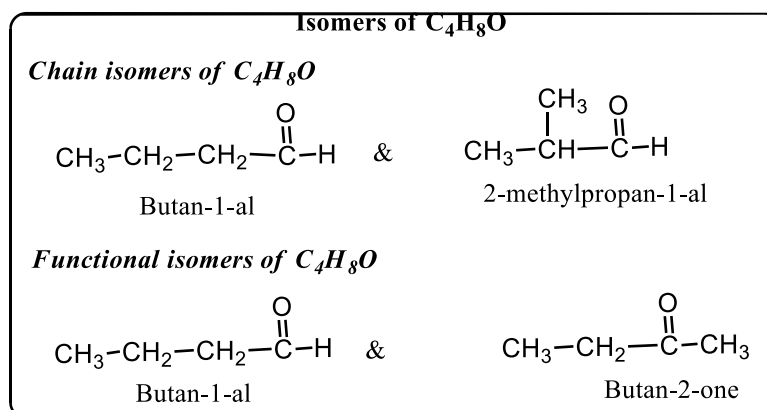
- ✓ Isomerism: Exhibit chain, positional, functional isomerism and sometime also exhibit metamerism (only in ketone) & tautomerism.

Example:

3 6



Note-1: These isomers can be distinguished from each other by iodoform test. Propanone gives positive iodoform test whereas propanal does not.



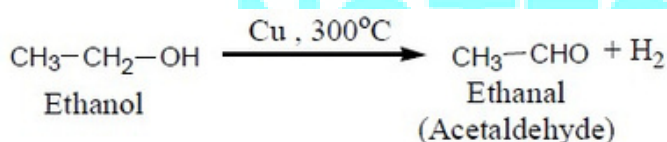
Note-2: The functional isomers of C_4H_8O can be distinguished from each other by iodoform test. Butan-2-one gives positive iodoform test whereas butane-1-al does not.

[A] Aliphatic Aldehydes and Ketones

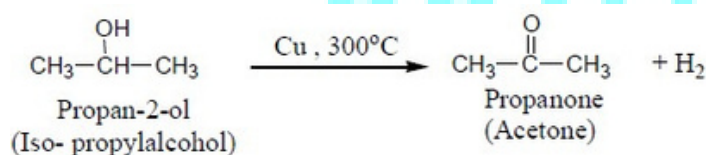
❖ Preparation of aldehyde and ketones

1. By dehydrogenation of alcohols (Removal of hydrogen):

i) Primary alcohols are dehydrogenated into aldehydes



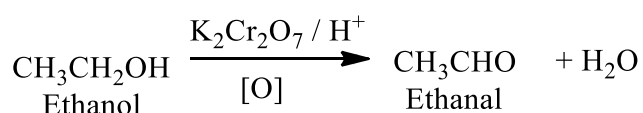
ii) Secondary alcohols are dehydrogenated into ketones



2. By Oxidation of alcohols:

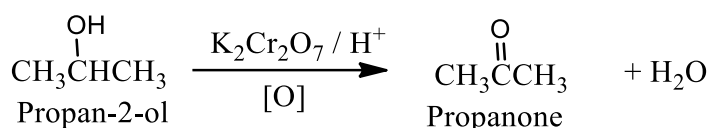
Alcohols are oxidized by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or $\text{Na}_2\text{Cr}_2\text{O}_7$ or acidified / alkaline KMnO_4 solution i.e. (KCrO / H^+ , $\text{NaCrO} / \text{H}^{++}$ or KMnO_4 / H , $\text{KMnO}_4 / \text{OH}$).

i) Primary alcohols are easily oxidized into aldehydes.



NOTE: Strong oxidizing agents may convert the aldehyde produced into carboxylic acids so to prevent the aldehyde produced from further oxidation, it should be distilled off as soon as possible from reaction mixture.

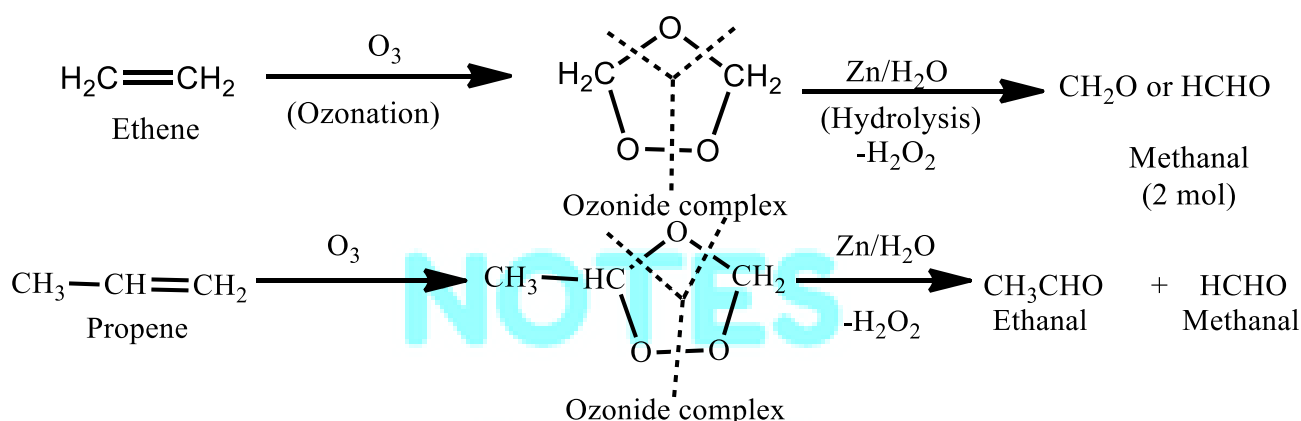
ii) Secondary alcohols are easily oxidized into ketones.



NOTE : Ketone resist the further oxidation under normal condition.

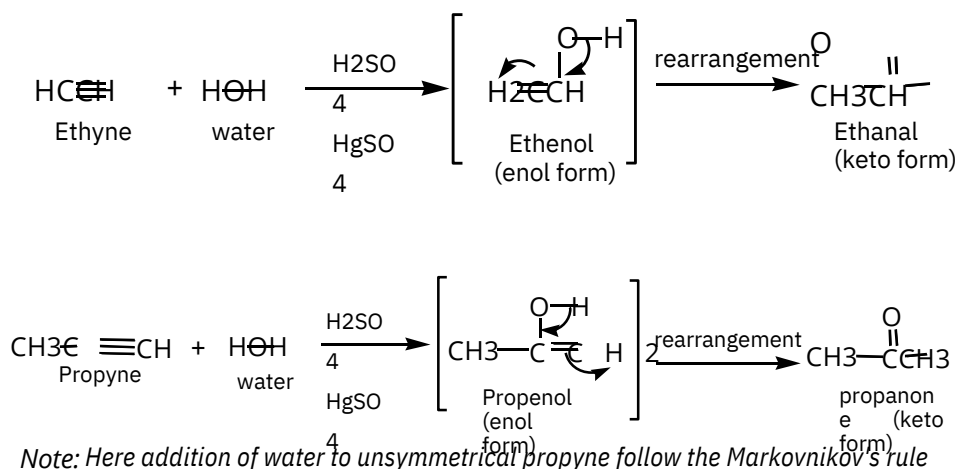
3. By Ozonolysis of alkenes:

Alkenes reacts with ozone to form ozonide, which on heated with zinc dust and water gives aldehydes and ketones.

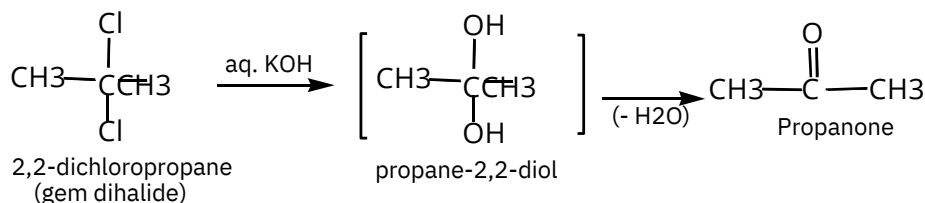
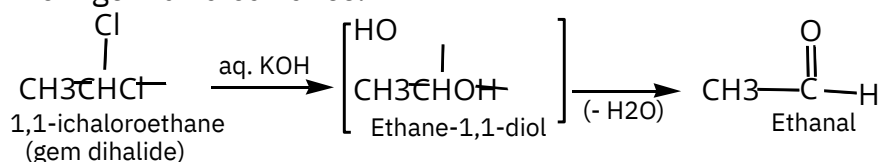


NOTE: Here Zn is used in hydrolysis in order to prevent the oxidation of product by hydrogen peroxide produced after hydrolysis. Zn gets first oxidized into zinc oxide before product.

4. From catalytic hydration of alkynes:



5. From gem dihaloalkanes:

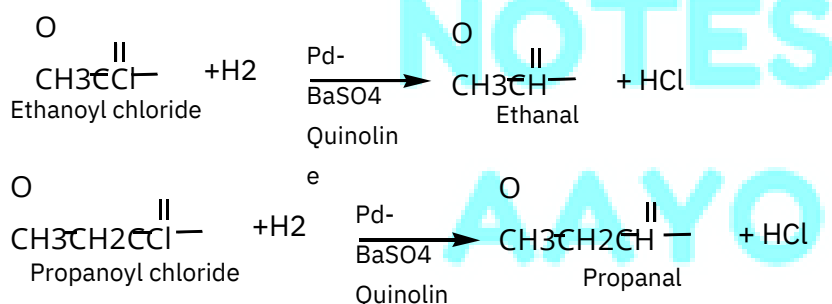


NOTE: Geminal (from Latin Gemini = twins), abbreviated as gem & Vicinal (from Latin vicinus = neighbor), abbreviated as vic.

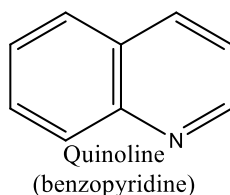
From Acid chlorides:

6 When acid chloride reacts with hydrogen in presence of palladium placed over barium sulphate, partially poisoned by quinoline (Rosenmund's catalyst) gives aldehyde.

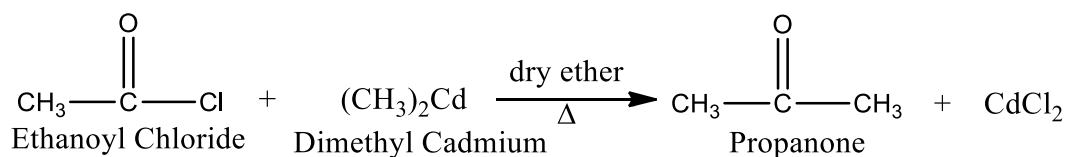
This reaction is called Rosenmund's reduction.



NOTE: Here quinoline is used as organic base to remove acidic byproducts. Barium sulphate (BaSO₄) is used as catalytic poison to decrease the catalytic rate of Palladium based reduction reaction otherwise the aldehyde obtained may reduce into alcohol.



But, ketones can be prepared from acid chlorides by reacting with dialkyl cadmium in presence of dry ether.



NEB Past Questions (Related to preparation of aldehyde and ketone)

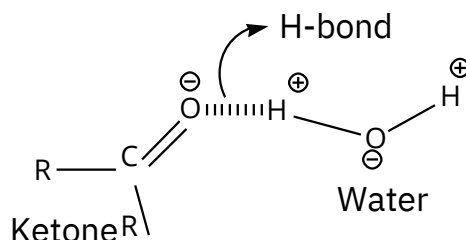
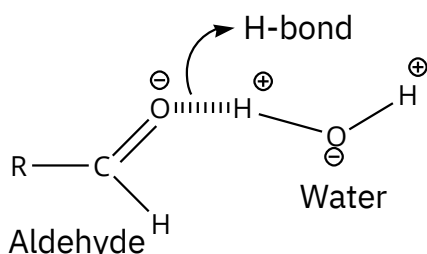
1. NEB 2073 set C the preparation of propanone Give suitable chemical reaction for from i) 2, 2-dibromopropane ii) Propan-2-ol.
2. NEB 2073 set D the preparation of ethanal Give suitable chemical reaction for from i) 1,1-dibromoethane , ii) ethyne iii) ethanoyl chloride
3. NEB 2070 Set C & B supp. preparation of ethanal
4. NEB 2067 propanone prepared How is from i) Isopropyl alcohol ii) 2,2- dichloropropane (3)
5. NEB 2072 supp. propanone prepared How is from i) 2,2- dichloropropane ii) Isopropyl alcohol ii) propyne (3)
6. NEB 2069 supp. set B the preparation of ethanal Give suitable chemical reaction for from i) ethyne , ii) ethanoyl chloride iii) 1,1- dichloroethane (3)
7. NEB 2055 general method of preparation of aldehydes. (5)
8. NEB 2072 set C of Rosenmund's reduction (1)

NOTES
AAYO

Physical properties of aldehyde and ketones

1. Solubility:

Lower members (Methanal, ethanal and propanone) are slightly soluble in water due to their ability to form intermolecular H-bond with water molecule. The solubility in water is decreases with the increase in the hydrocarbon portion (alkyl part) which is hydrophobic in nature.



2. Boiling point:

Aldehydes and ketones have higher boiling point than corresponding hydrocarbons, ethers but lower than that of alcohol and carboxylic acid of comparable molecular mass. This is because of the polar nature of carbonyl group and the molecules are associated with each other by dipole-dipole force of attraction.

(Note: cannot form intermolecular H- bond with each other)

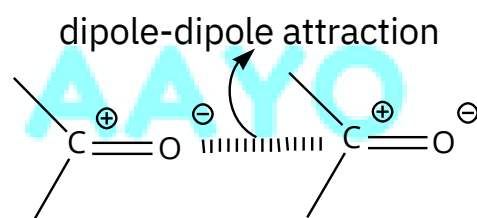
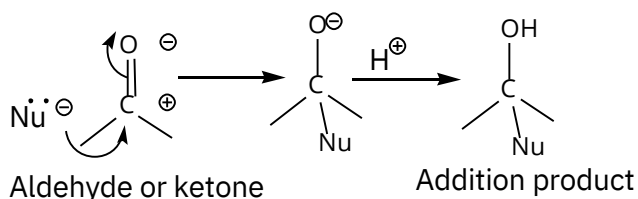


Fig. Dipole- Dipole interactions in aldehyde or ketone

Chemical properties of aldehyde and ketones

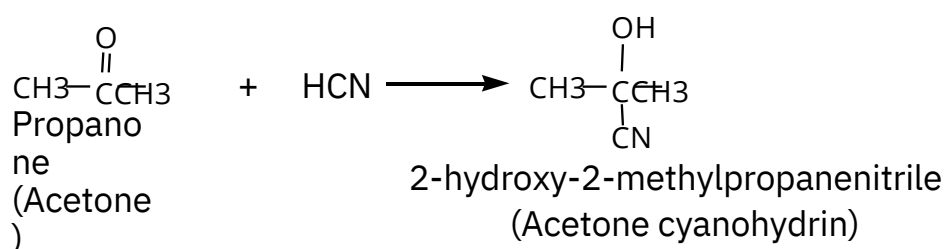
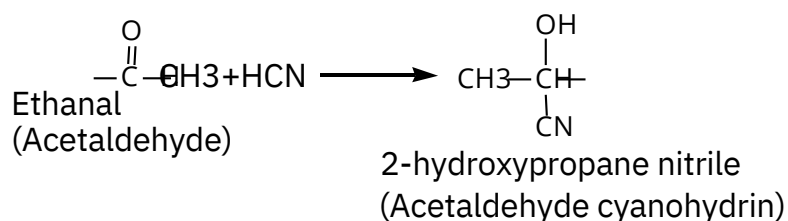
1. Addition Reactions:

Due to electronegativity difference between C-atom and O-atom in carbonyl group, the C-atom acquires partial positive charge and O- atom acquires partial negative charge. Therefore the C-atom of carbonyl carbon can be easily attacked by nucleophiles (cyanide ion, C-atom of Grignard reagent, N-atom with lone pair electrons in ammonia and its derivatives etc.) followed by addition of proton to give final addition product.

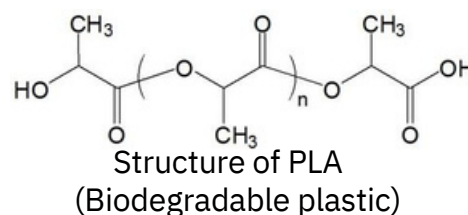
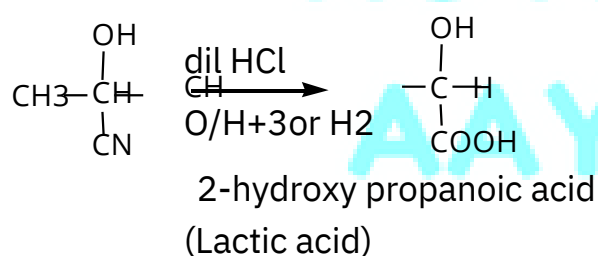


Examples

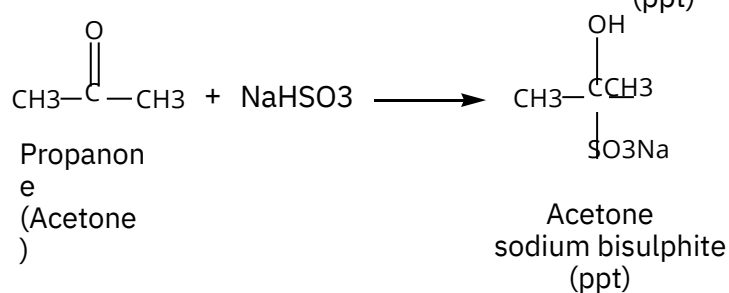
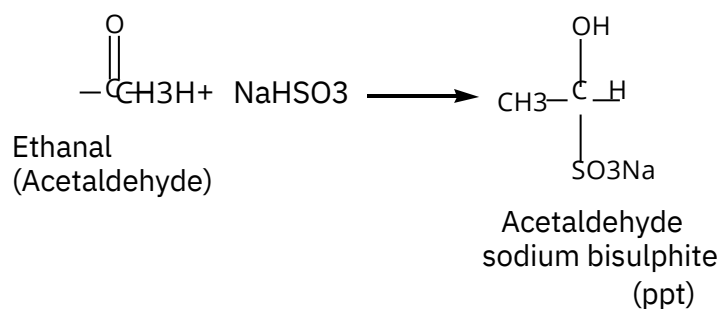
a) Addition of HCN



Note: Cyanohydrins are important in organic synthesis to produce hydroxy acids such as 2-hydroxy propanoic acid (Lactic acid) and this lactic acid can be used to produce a biodegradable polymer (biodegradable plastic) like polylactic acid (PLA)

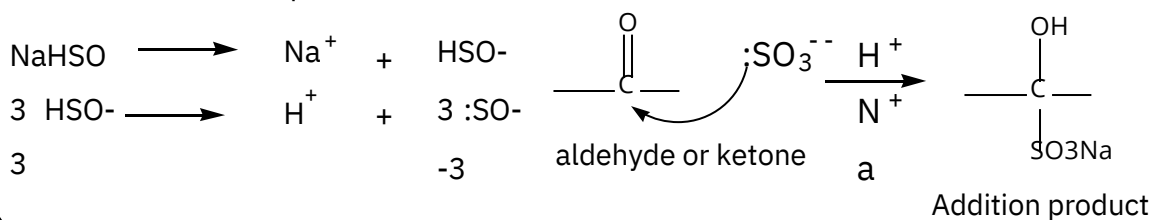


b) Addition of NaHSO₃



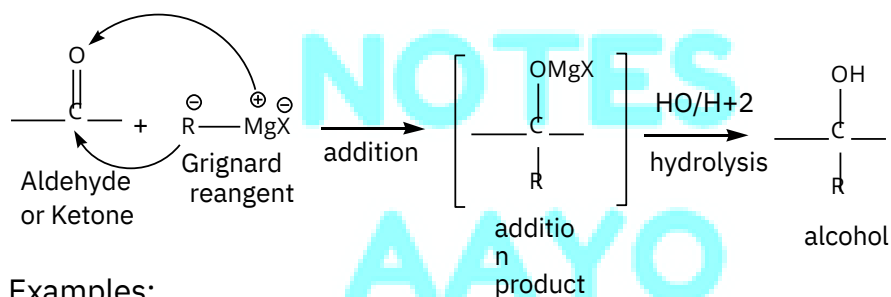
Note:

Mechanism of bisulphite addition

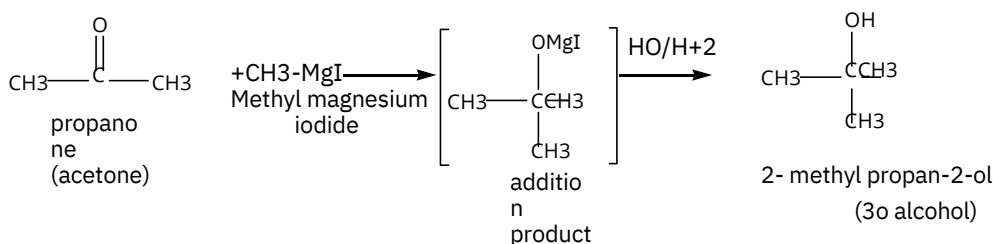
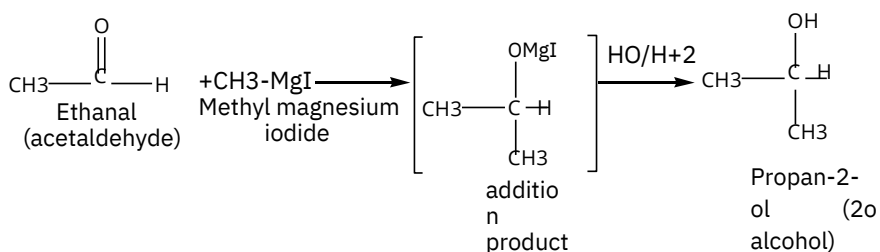
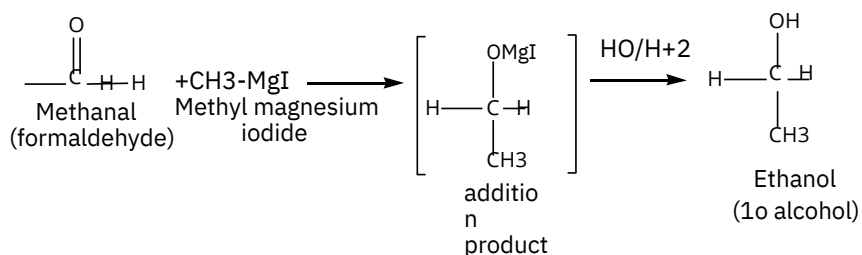


This reaction is very important in the purification and the separation of aldehyde and ketones. When this bisulphite addition product is hydrolyzed using dil HCl then aldehyde and ketone can be recovered.

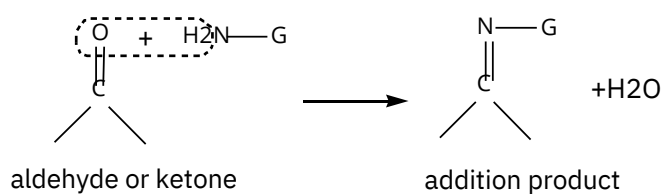
c) Addition of Grignard reagent: (synthesis of 1o, 2o & 3o alcohols)



Examples:



2. Action with Ammonia derivatives (addition followed by elimination of water):

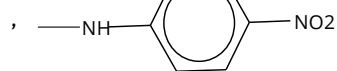
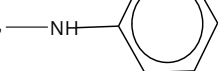


Where,

G = -OH,

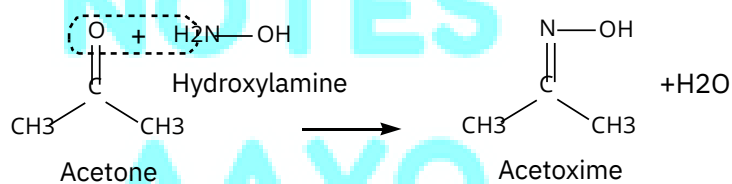
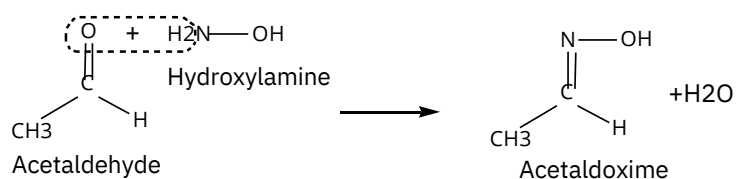
-NH₂,

-NHCONH₂,

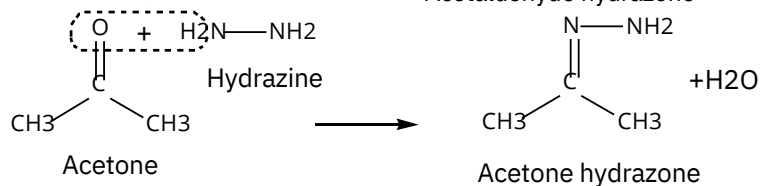
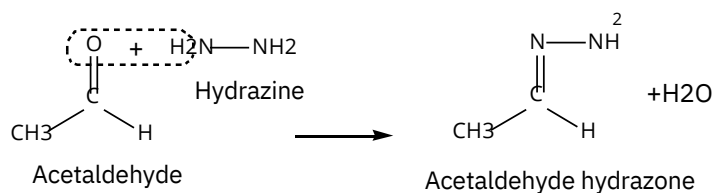


Examples

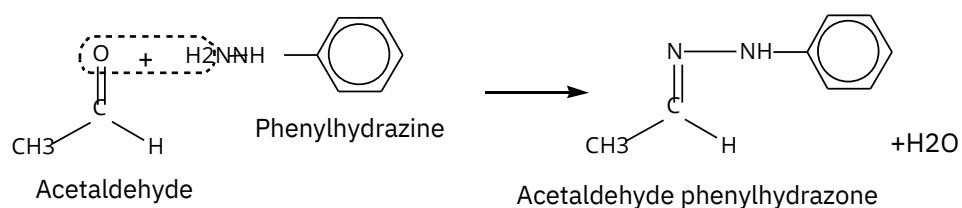
a. Reaction with hydroxyl amine:

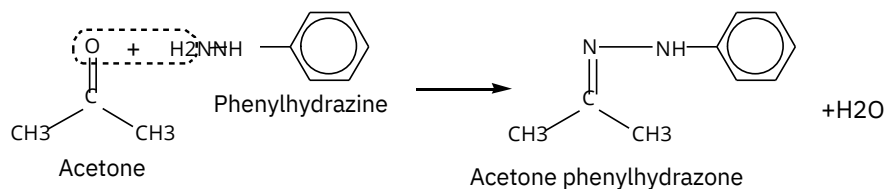


b. Reaction with hydrazine:

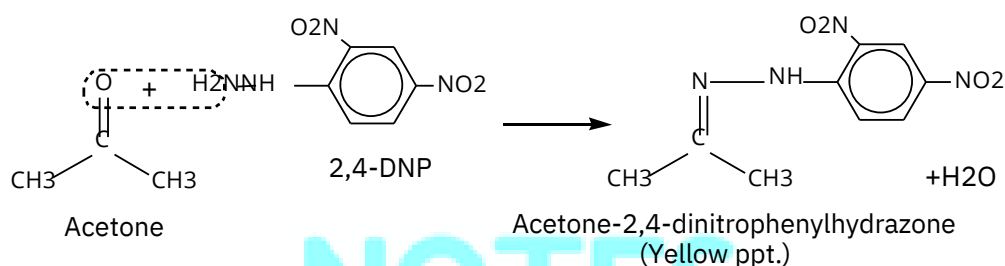
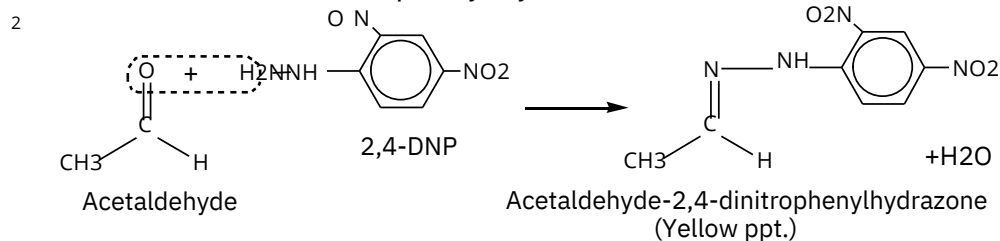


c. Reaction with phenyl hydrazine:



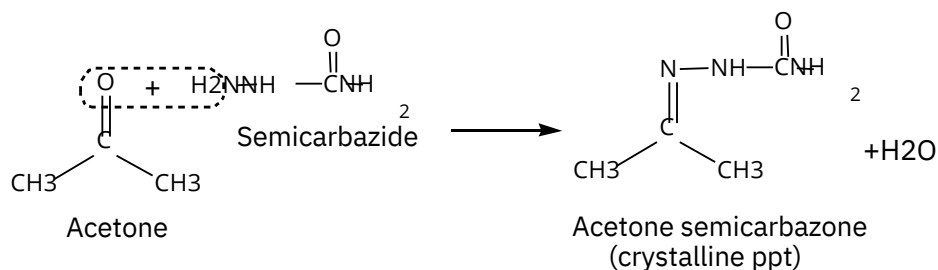
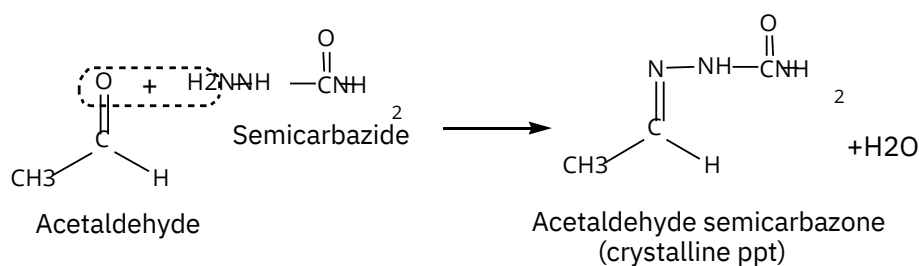


d. Reaction with 2,4-dinitrophenyl hydrazine (2,4-DNP):



Note: reaction is used to distinguish carbonyl compounds (aldehydes & ketones) from other class of organic compounds. This reaction *can be used as laboratory test reaction for carbonyl compounds* & also known as 2, 4-DNP test or simply DNP or DNPH test.

e. Reaction with Semi carbazide:

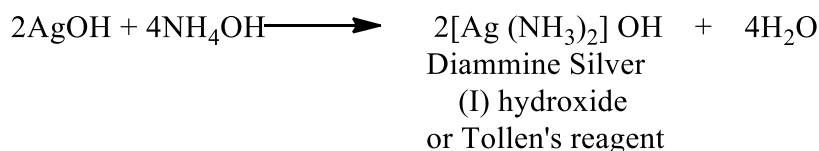
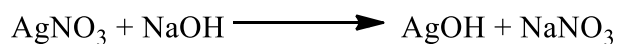


3.Reducing properties of aldehyde (or Oxidation of aldehyde)

Aldehydes are easily oxidized by mild oxidizing agent (Tollen's reagent, Fehling solution) and strong oxidizing agents (acidified KMnO₄ or K₂Cr₂O₇ solution) but ketones are not easily oxidized under normal condition.

Tollen's reagent

Ammoniacal silver nitrate solution [Diammine silver (I) hydroxide] is called *Tollen's Reagent* & is prepared by following process:



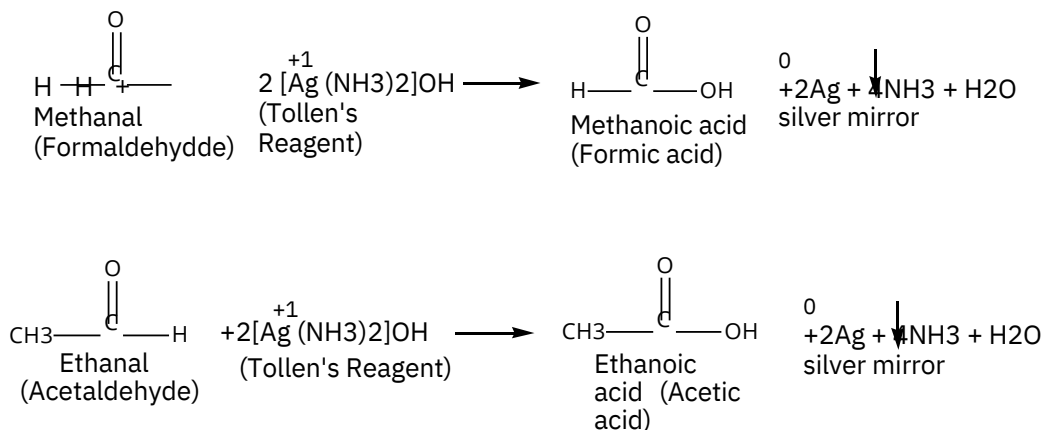
Bernhard Tollens
(1841- 1918)

Tollen's Test or Silver mirror Test

The test reaction in which aldehyde reduces the Tollen's reagent into free metallic silver which is deposited around the inner wall of test tube and aldehyde itself gets oxidized into carboxylic acid is called Tollen's test or Silver mirror test.

This test is given by aliphatic aldehydes (like formaldehyde, acetaldehyde etc.) and aromatic aldehyde (like Benzaldehyde) whereas ketones fail to give this test.

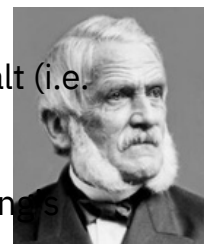
Examples:



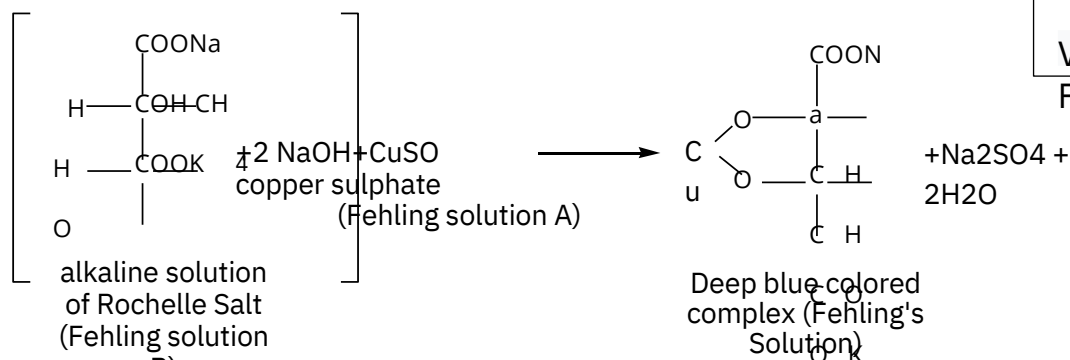
Fehling's solution or Fehling

The alkaline aqueous solution of CuSO_4 containing some Rochelle salt (i.e. sodium potassium tartrate) is called Fehling's solution.

The solution is prepared by mixing equal parts of alkaline solution of Rochelle salt (Fehling's solution A) to aqueous CuSO_4 solution (Fehling's solution B).



Herman
Von
Fehling

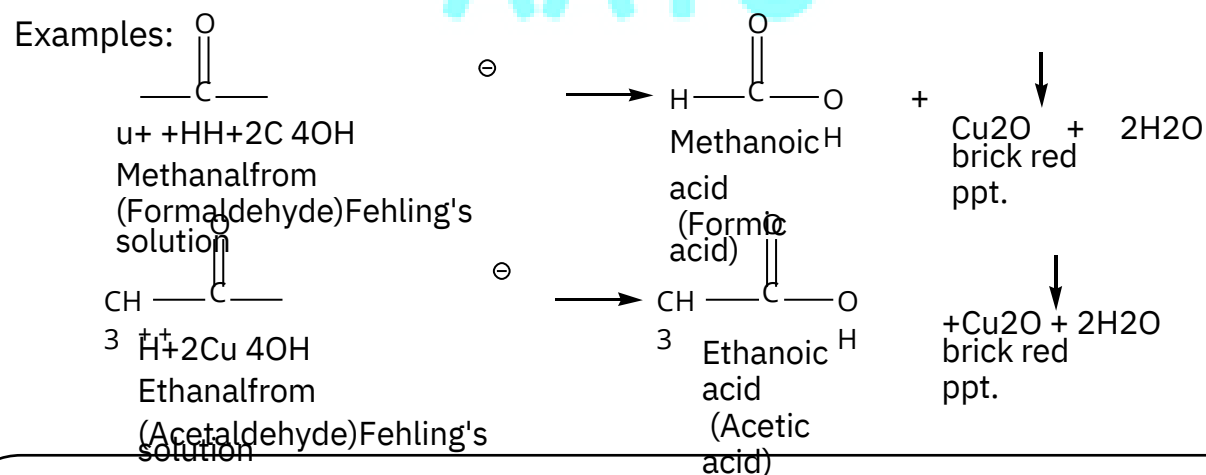


Simply Fehling Solution is $2\text{C} + 4\text{OH}$

written as Fehling's solution

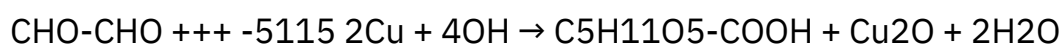
The test reaction in which aldehyde reduces the cupric [Cu^{++} (aq.)] ions of Fehling solution into cuprous oxide (Cu_2O) which is obtained as and respective aldehyde itself gets Oxidized to carboxylic acid is called brick red ppt Fehling's solution test.

This test is only given by aliphatic aldehyde (like formaldehyde, acetaldehyde etc.) but aromatic aldehyde like benzaldehyde & ketones fail to give this test.



Note: Diagnosis of Diabetes (Clinical chemistry)

If Person suffering from diabetes, their urine contains significant amount of glucose and glucose also contains aldehyde functional group ($-\text{CHO}$) which reduces cupric (Cu^{++}) ions of Fehling's or Benedict's solution to cuprous (Cu^+ ion) & itself gets oxidized into Gluconic acid. The formation brick red ppt of cuprous oxide (Cu_2O) is the indication of glucose in urine of diabetic patient.



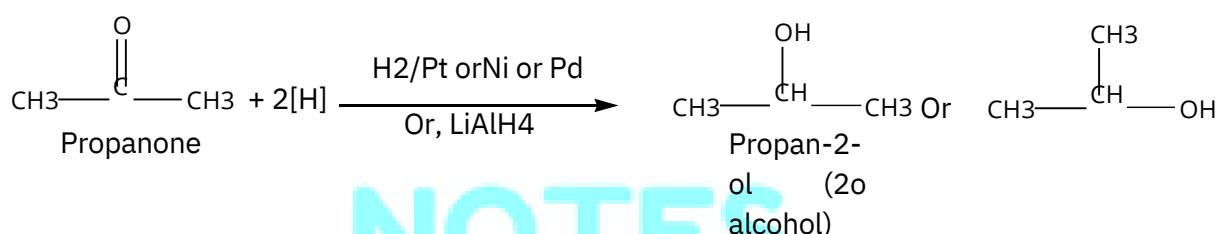
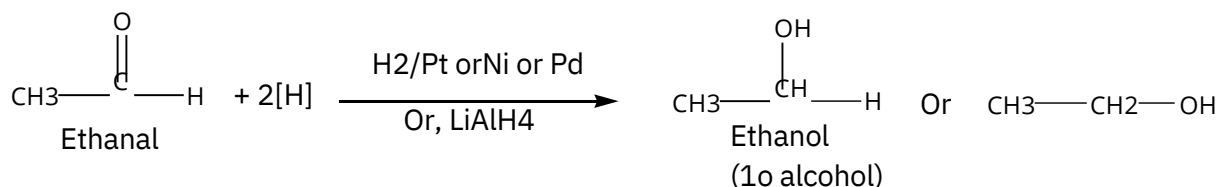
Glucose Benedict's soln. Gluconic acid
(From urine) (or Fehling's solution)

4.Reduction of aldehyde and ketones :

a.Reduction by using H_2/Pt or H/Ni or H_2/Pd or $LiAlH_4$

Aldehyde gives *primary alcohol* and ketone gives *secondary alcohol* on reduction with above reagents.

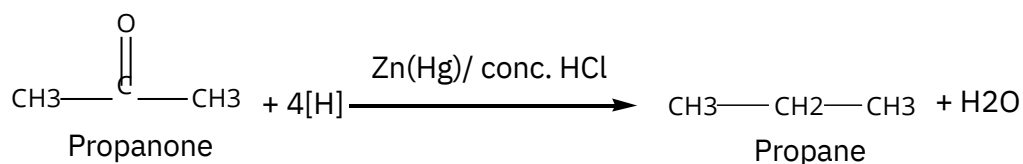
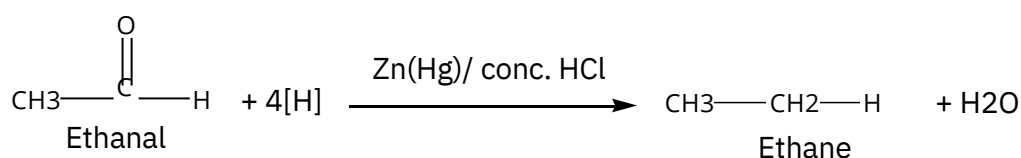
Examples:



b. Reduction by using Zinc amalgam ($Zn-Hg$) in conc. HCl (Clemmensen reduction)

Aldehyde and ketone are reduced into respective alkanes by amalgamated zinc in presence of conc. HCl is known as Clemmensen reduction.

Examples:



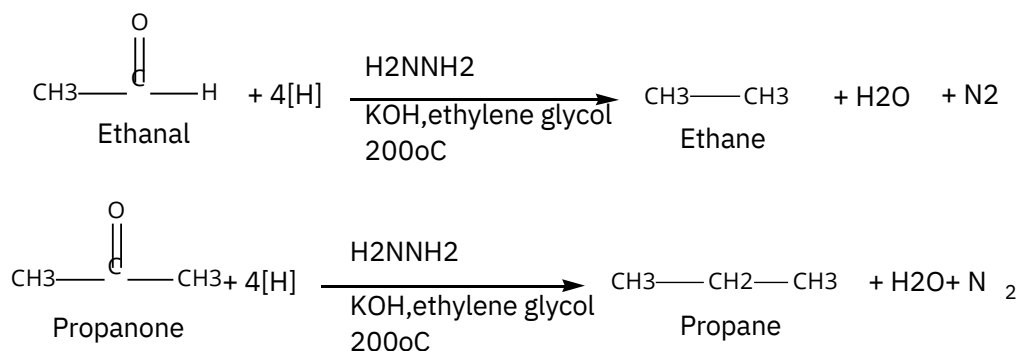
a. Reduction by using Hydrazine (NH_2NH_2) in presence of KOH & glycol (Wolff-Kishner reduction)

Aldehyde and ketone reduced to alkane

are respective with mixture of hydrazine (NH_2NH_2)

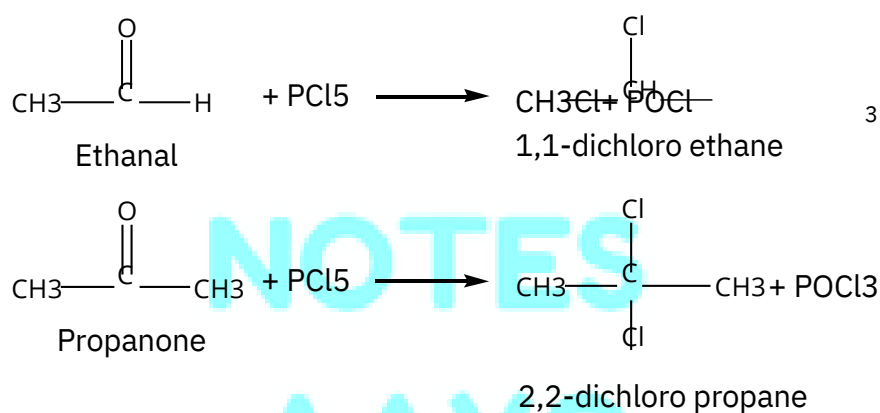
and alkali like KOH in ethylene glycol is known as Wolff-Kishner reduction.

Examples:



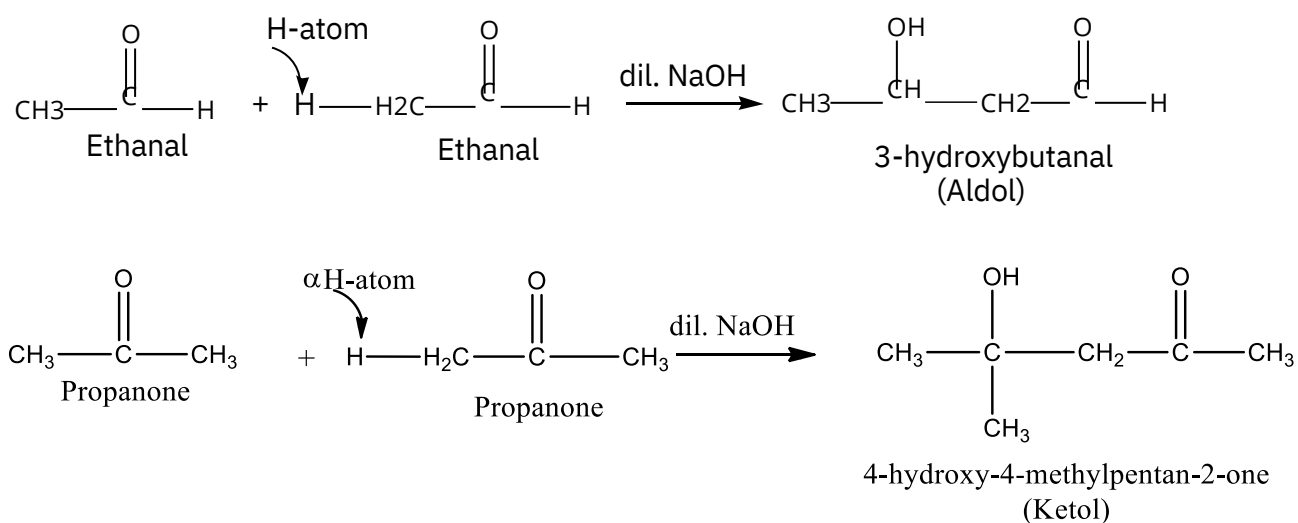
5. Reactions with PCl

Oxygen of carbonyl group of aldehyde & ketone is replaced by two Cl-atoms.



6. Aldol Condensation:

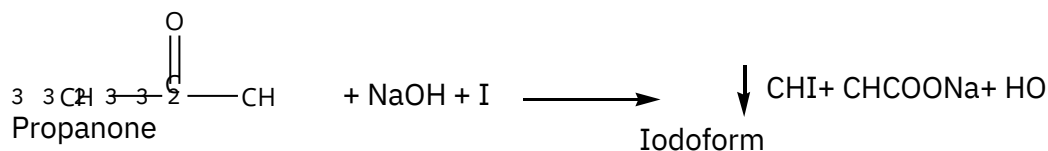
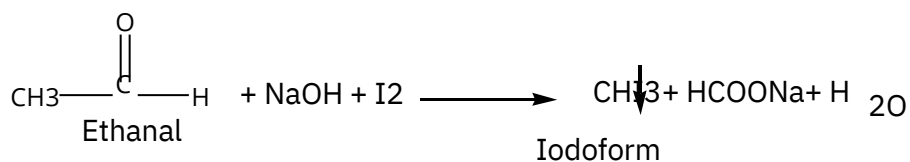
Aldehyde & ketones containing α -hydrogen undergoes condensation in presence of dil NaOH or dil KOH to give α -hydroxy aldehyde (aldol) or α -hydroxyketone (ketol) is commonly known as aldol condensation reaction.



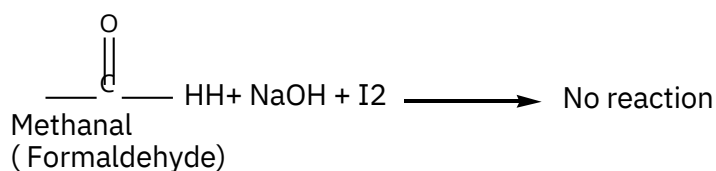
NOTE: An aldol condensation between two different aldehydes or ketones is called mixed or cross aldol condensation.

7. Iodoform reaction or Iodoform test:

Aldehyde or ketone containing methyl keto group i.e. $\text{CH}_3\text{CO}-$ group on reaction with excess iodine in presence of NaOH to give yellow precipitate of iodoform with characteristics hospital smell is called iodoform reaction.



Formaldehyde or Methanal does not give this test. So we can distinguish Ethanal or acetaldehyde from formaldehyde by iodoform test in laboratory.

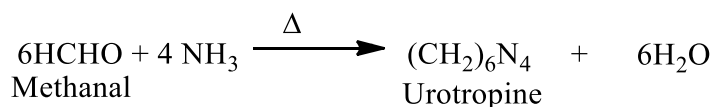


Similarly, Butan-2-one gives positive iodoform test whereas butane-1-al does not give iodoform test therefore they can be distinguished by this test also.

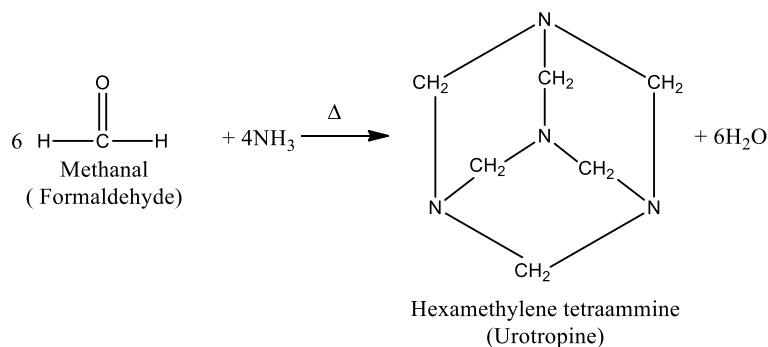
8.Special reactions of Methanal:

a.Reaction of formaldehyde or methanal with ammonia:

When formaldehyde reacts with ammonia then Hexamethylene tetraamine (Urotropine) is formed, which is used as urinary antiseptic.

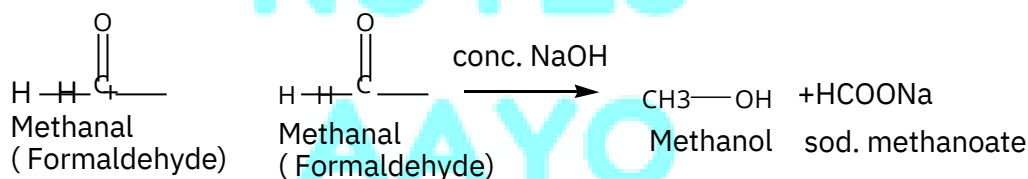


Or,



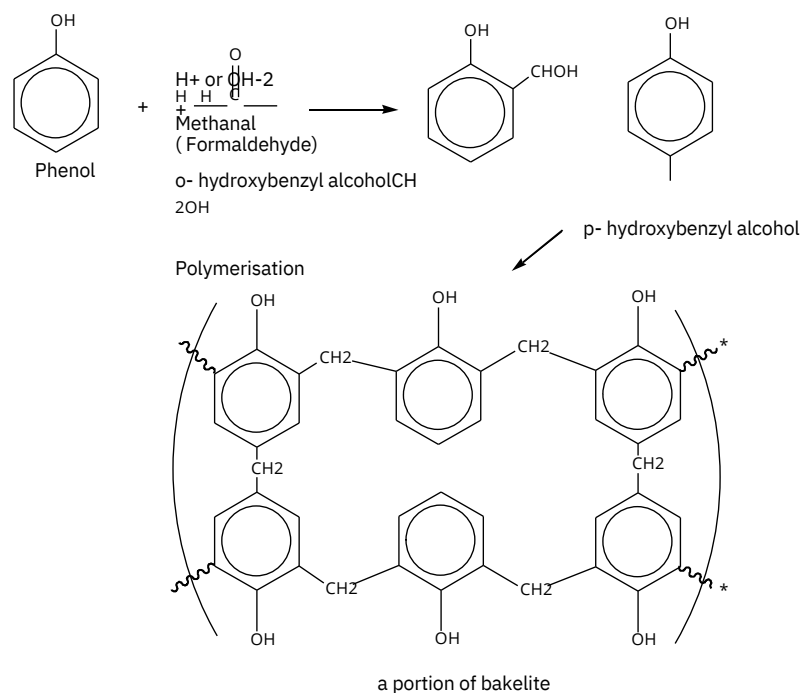
b.Cannizzaro reaction:

Aldehydes with no α -hydrogen atom undergoes reaction in presence of conc. NaOH to form alcohol and sodium salt of carboxylic acid is called Cannizzaro's reaction.



c. Reaction with phenol (Polymerization reaction)

➤ Thermosetting plastic Bakelite is formed.



❖ Formalin and its uses

Forty percent aqueous solution of formaldehyde solution (40% aq. HCHO) is called formalin. It has pungent smell.

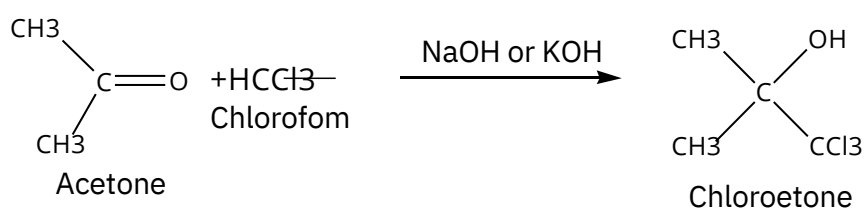
It can be used as

- i) Preservative agent for biological specimens
- ii) Disinfectant

Special reaction of Propanone or acetone

Reaction with Chloroform:

➤ Chloroetone (sleep inducing drug) is formed.

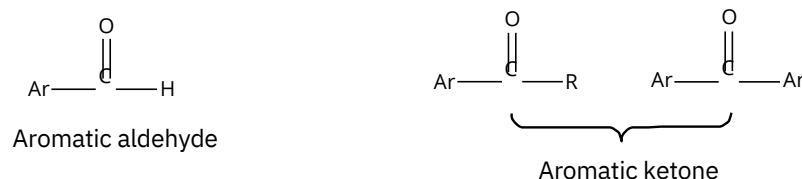


NOTES
AAYO

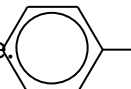
[B] Aromatic Aldehydes and Ketones

Introduction: Carbonyl group ($>C=O$) attached to aryl group are called aromatic aldehyde and ketones.

General formula:

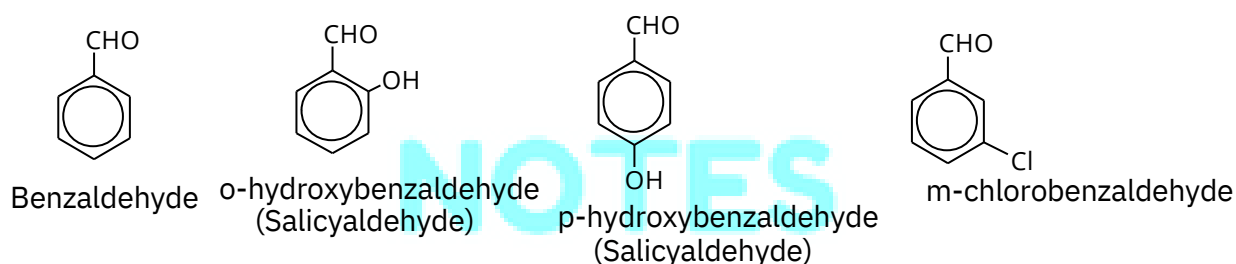


Where,

Ar = usually Phenyl group i.e. 

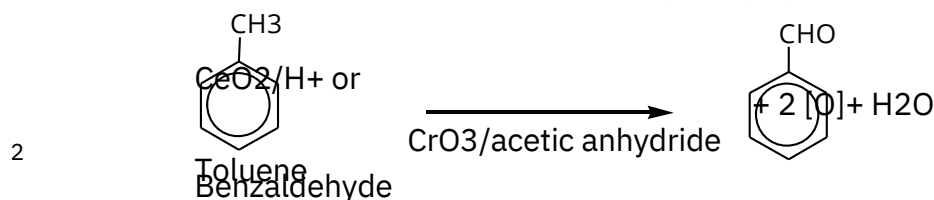
R = CH_3 - or C_2H_5 - etc..

Nomenclature:



Preparation of Benzaldehyde

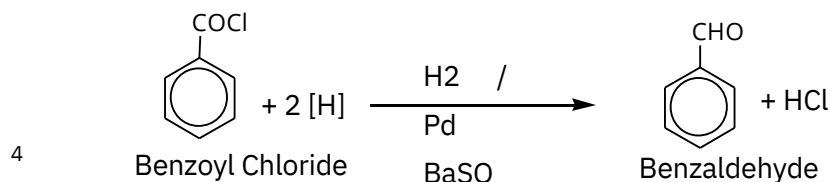
1. Oxidation of Toluene:



NOTE: Ce = Cerium (Lanthanide, d-block) element with atomic number 58, mass number 140.11

Cr = Chromium (transition, d-block) element with atomic number 24, mass number 51.99

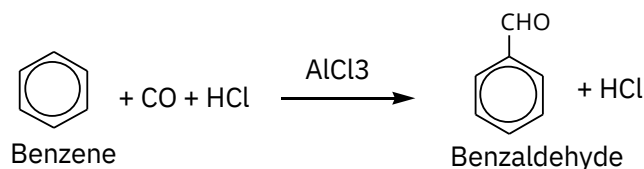
2. Rosenmund's reduction:



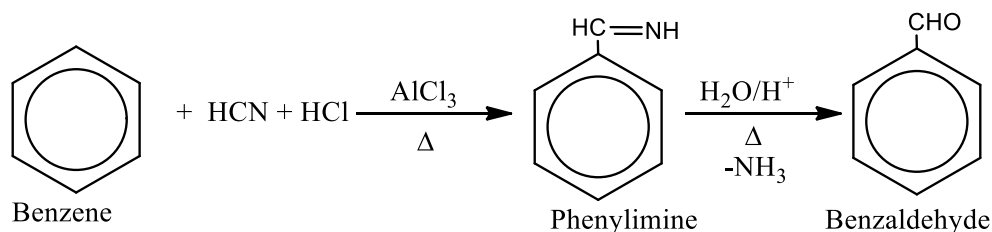
Pd = Palladium (transition, d-block) element with atomic number 46, mass number

106.42)

3. From Benzene (Gattermann-Koch Aldehyde synthesis)

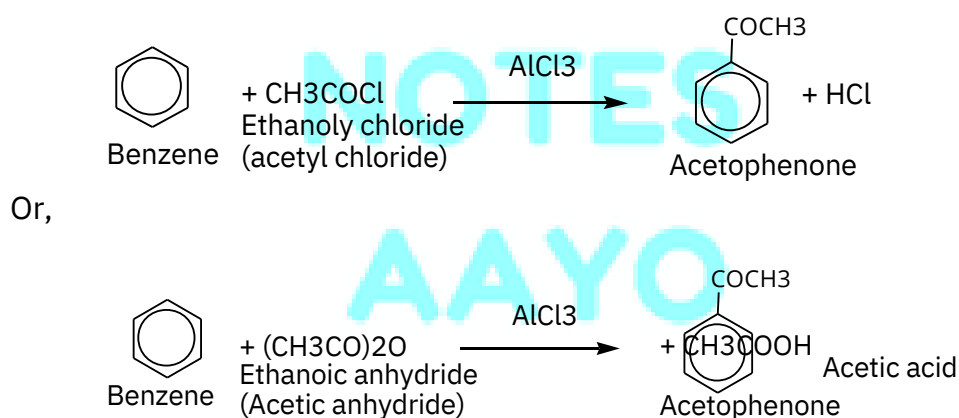


NOTE: Gattermann's aldehyde synthesis



Preparation of Acetophenone

1. Friedel Craft's acylation:



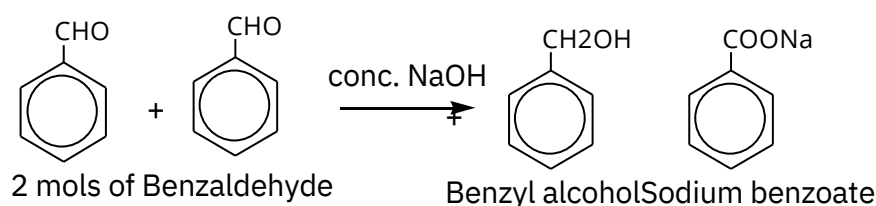
Physical Properties of Benzaldehyde:

- Benzaldehyde is colorless oily liquid with bitter almond odor, it readily dissolves in alcohol and ether. It boils at 179°C.

Chemical properties of Benzaldehyde:

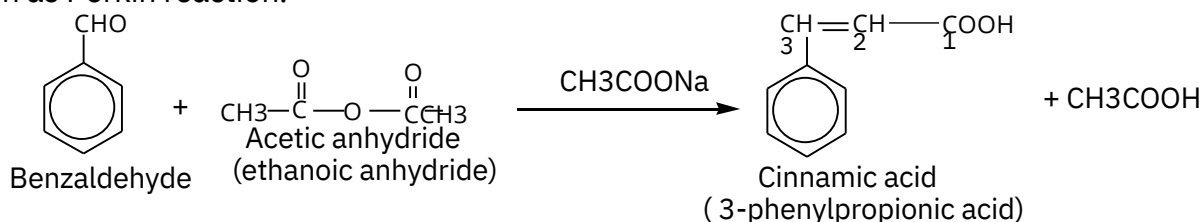
1. Cannizzaro's reaction:

Two moles of Benzaldehyde with no α -hydrogen atom undergoes disproportion (self-oxidation reduction) reaction in presence of conc. NaOH to form alcohol and sodium salt of carboxylic acid is called Cannizzaro's reaction.



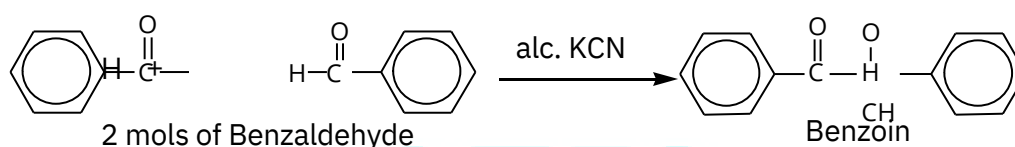
2. Perkin reaction:

Aromatic aldehyde like benzaldehyde when heated with acetic anhydride in presence of sodium acetate as base then cinnamic acid (, - unsaturated acid) is formed. This reaction is commonly known as Perkin reaction.



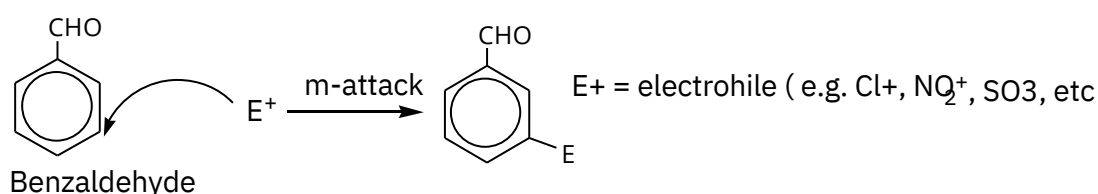
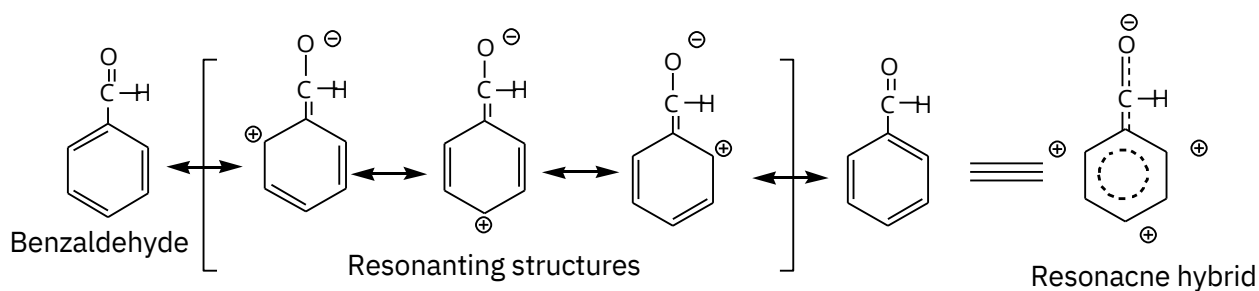
3. Benzoin condensation:

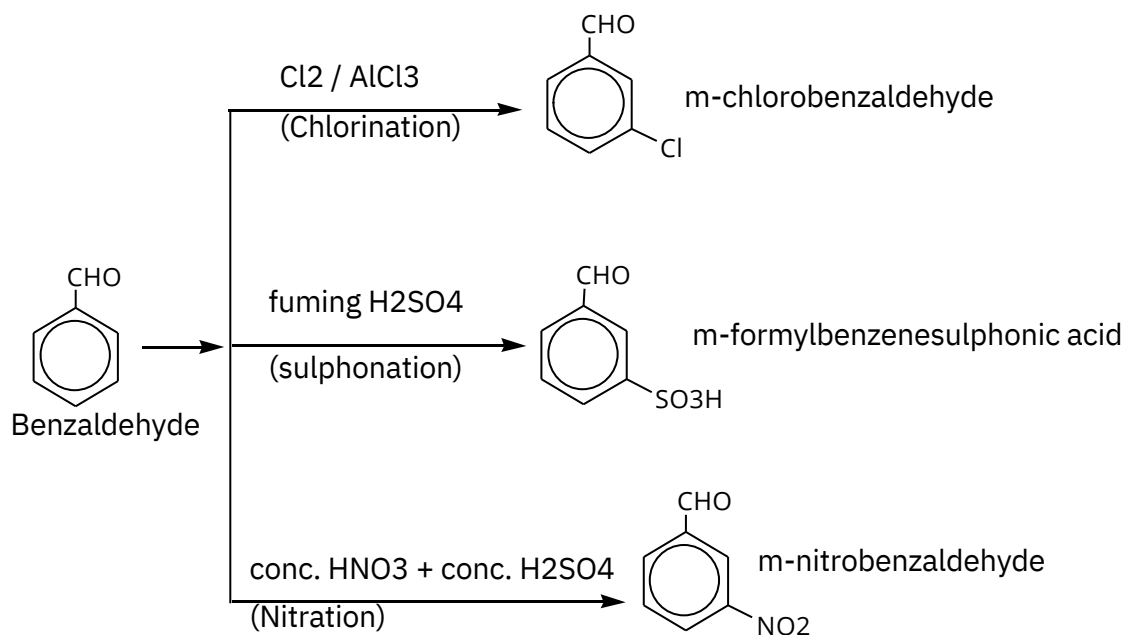
When benzaldehyde is heated with alcoholic solution of KCN, two moles of benzaldehyde condense with each other to give benzoin. This reaction is commonly known as Benzoin condensation.



4. Electrophilic substitution reactions:

-CHO group in Benzaldehyde is meta directing. Due to resonance in benzaldehyde the electron density at ortho and para position decreases in comparison to meta position. Therefore, the incoming electrophile will prefer to attack at meta position.





NOTES
AAYO

What happens when benzaldehyde is treated with i) Conc NaOH solution ii) hydrazine

How does benzaldehyde reacts with i) Conc NaOH solution ii) acetic anhydride (1+1)

How does benzaldehyde reacts with i) Conc NaOH solution ii) acetic anhydride (1+1)

What happens when benzaldehyde is treated with i) Conc NaOH solution

(1)What happens when benzaldehyde is heated with i) LiAlH₄ (ii) acetic anhydride in presence of sodium acetate

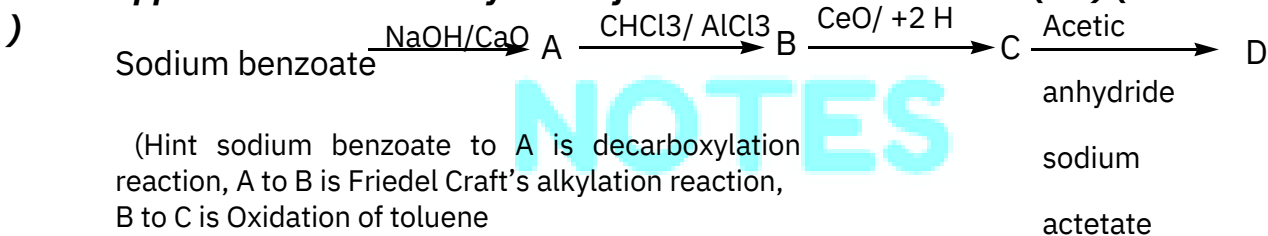
Write an example of Perkin condensation. (1)

Give an example of each of following reactions i) Benzoin condensation (1)

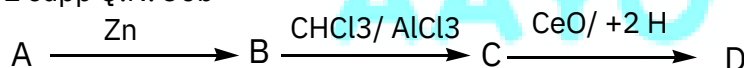
Give an example (with formula) each from aliphatic and aromatic aldehydes which gives Cannizzaro's reaction.

what action takes place when benzaldehyde is heated with ethanoic anhydride in presence of sodium ethanoate? (2.5) (Hint: Perkin's reaction)

what happens when benzaldehyde is refluxed with alcoholic KCN? (2.5) (Hint:



NEB 2072 supp Q.N. 30b



Compound D gives methyl benzene when heated with alc. KOH and hydrazine