

# **Aldehydes**

**( Aliphatic )**

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# Structure

- When the two valencies of carbonyl group ( $=C=O$ ) is satisfied by alkyl or aryl group and a H-atom, then the compound are known as aldehyde. Its general formula is  $RCHO$  or  $ArCHO$ , where  $R =$  alkyl gr,  $Ar =$  aryl gr and  $-CHO$  is functional group.  
 $R - C = O$
- According to molecular orbital theory, C-O sigma bond is formed by the overlapping of  $sp^2$  hybrid orbital of carbon and  $2p$  atomic orbital of oxygen. The remaining two  $sp^2$  hybrid orbital of carbon forms R-C and C-H sigma bond with the overlapping of  $sp^3$  orbital of R- and  $1s$  orbital of H.
- All the sigma bonds lie in one plane and are inclined an angle of  $120^\circ$  degree from each other. The C-O pi bond is formed by the lateral overlapping of half filled  $2p_z$  orbital of both carbon and oxygen.
- The O-atom is more electro negative hence acquire slight -ve charge and C-atom slight +ve charge. Thus, the carbonyl gr. is polar in nature.

# Nomenclature

1. **Common system** – In this system, the name of aldehyde is obtained by replacing 'ic acid' from the name of the corresponding acid which they give upon oxidation by the suffix 'aldehyde' e.g.

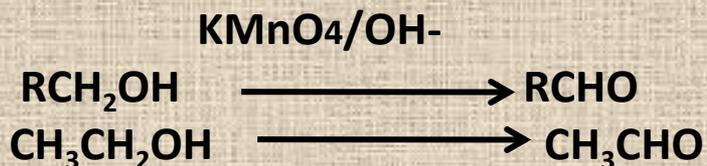
HCHO	Formic acid	Formaldehyde
CH <sub>3</sub> CHO	Acetic acid	Acetaldehyde
CH <sub>3</sub> CH <sub>2</sub> CHO	Propionic acid	Propionaldehyde

2. **IUPAC system** – In this system, aldehydes are named as 'Alkanals' by replacing 'e' of the corresponding alkane by the suffix 'al'.

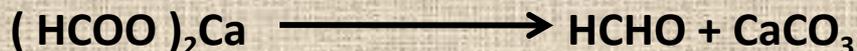
HCHO	Methanal
CH <sub>3</sub> CHO	Ethanal
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	Butanal
CH <sub>2</sub> =CHCH <sub>2</sub> CHO	But- 3-en-1-al
CH <sub>3</sub> CHCHO	2-Methylpropanal
CH <sub>3</sub>	

# Synthesis

1. By the oxidation of alcohols – When primary alcohol is oxidised with alkaline  $\text{KMnO}_4$  or acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ , aldehyde is obtained.



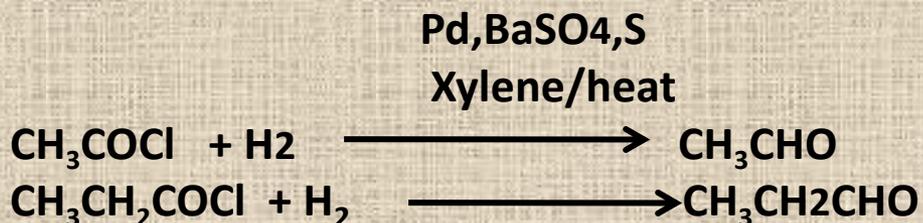
2. By dry distillation of salts of fatty acid :
  - a) Dry distillation of calcium formate gives formaldehyde .



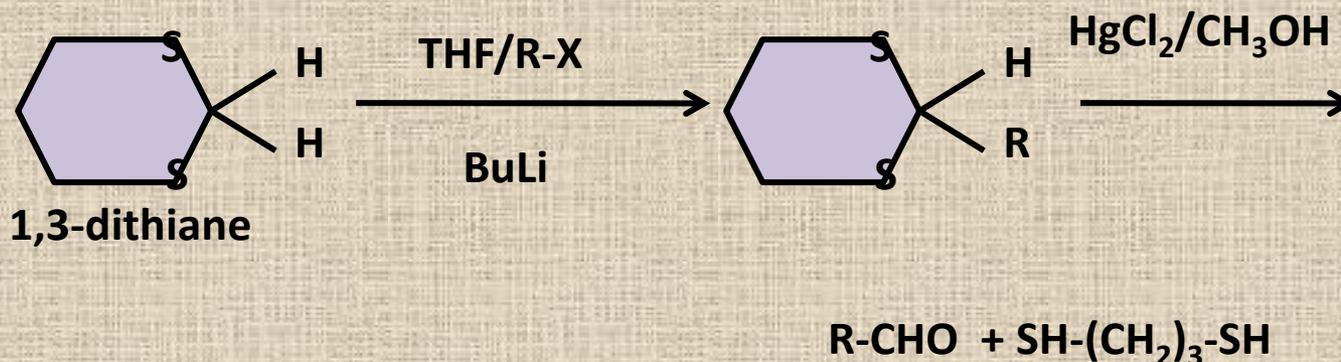
- b) Dry distillation of mixture of calcium formate and calcium acetate gives acetaldehyde.



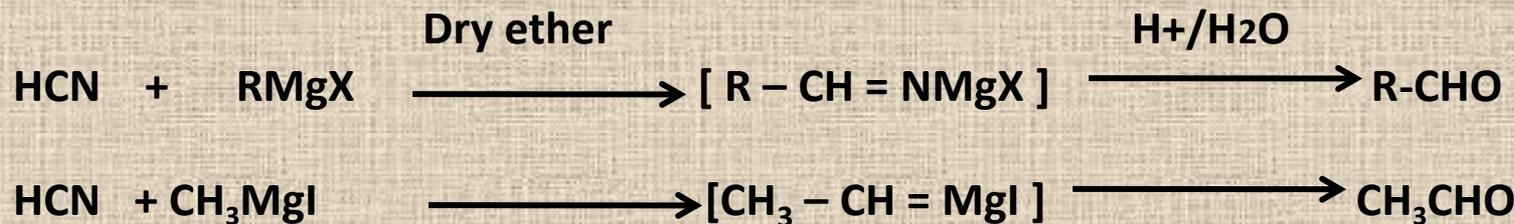
3. From acid chloride ( Rosenmund reduction ) - Aldehyde can be easily prepared by the reduction of acid chloride.



4. From 1,3 – Dithiane – Alkyl derivative of 1,3 – dithiane on hydrolysis with HgCl<sub>2</sub> in methanol gives corresponding aldehydes.



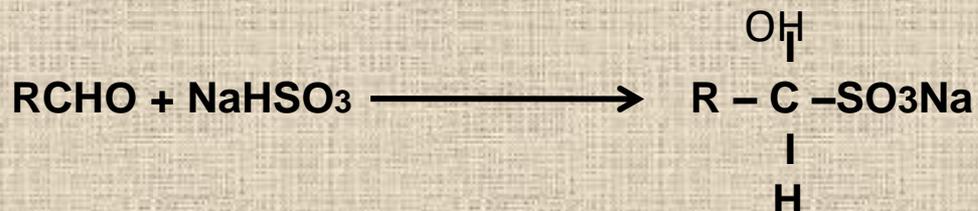
5. From nitriles – HCN on treatment with Grignard reagent in dry ether, aldehyde is produced.



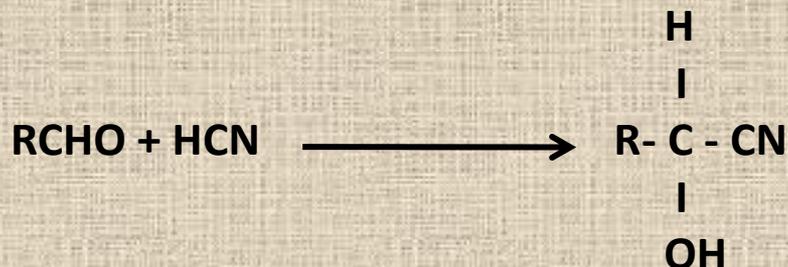
# Chemical Reactions

## Addition reactions :

a) Reaction with sodium bisulphite – Aldehydes react with saturated solution of NaHSO<sub>3</sub> to give a addition product.



b) Reaction with HCN – Aldehyde reacts with HCN to produce cyanohydrin.

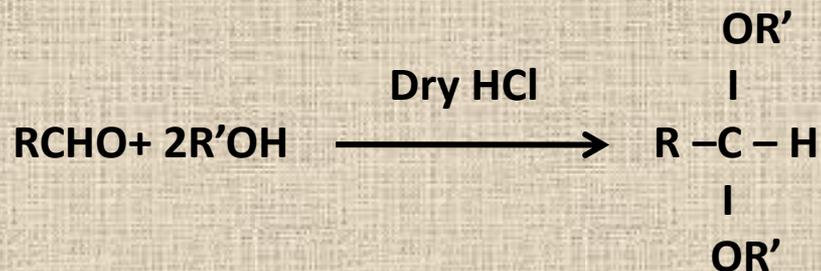


c) Reaction with Grignard reagent – Aldehyde reacts with Grignard reagent to gives addition product which on further hydrolysis give alcohols.  
Formaldehyde gives primary and rest of the aldehyde gives secondary alcohol.

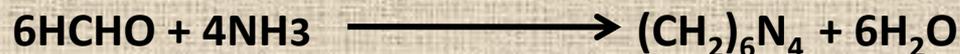


## Chemical reaction continued ....

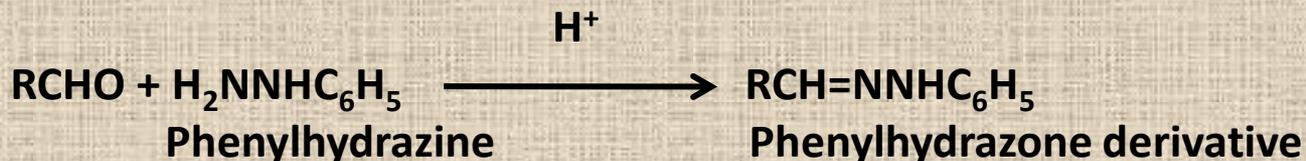
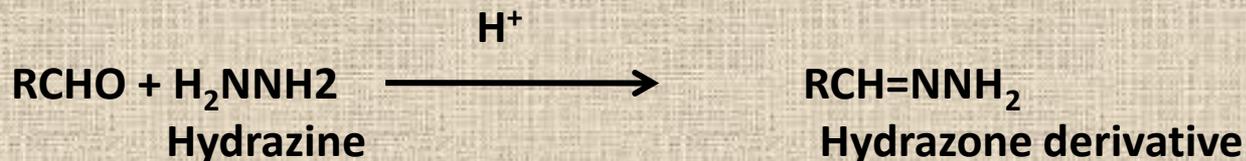
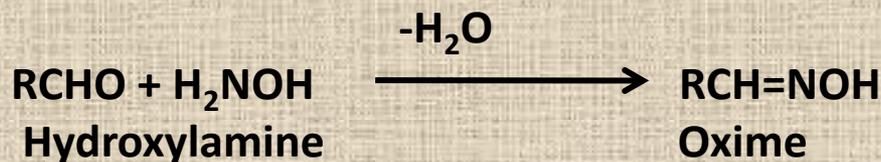
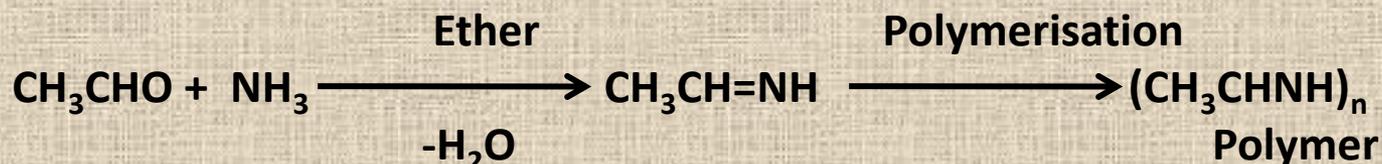
d) Reaction with alcohols – Aldehyde reacts with alcohols in presence of dry HCl gas to produce acetals.



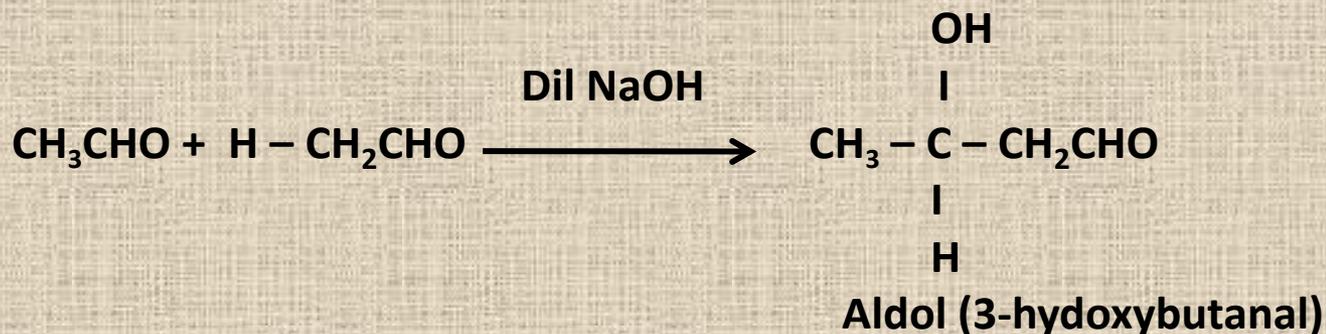
2. Reaction with ammonia and ammonia derivatives –



Hexamethylenetetramine or urotropine



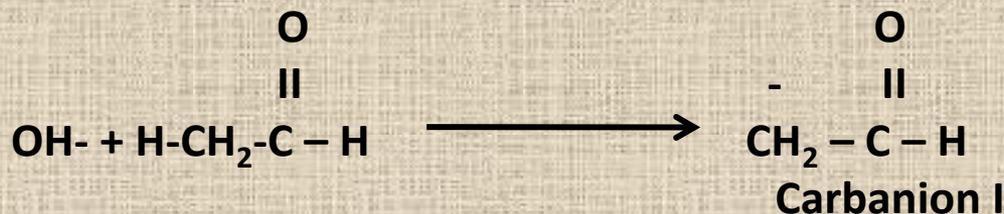
**3. Aldol Condensation** - When two molecules of aldehydes having alpha H-atom react in presence of dilute alkali to form alpha hydroxyaldehyde is called aldol condensation.e.g.



**Mechanism – i) Ionisation of NaOH :**



**ii) Attack of OH<sup>-</sup> to first molecule of aldehyde :**



**iii) Attack of carbanion 1 to second molecule of aldehyde**



## Chemical reaction continued .....

Formation of aldol by abstracting H<sup>+</sup> from water :



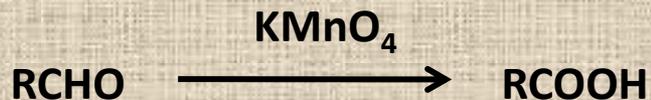
4. Knoevenagel condensation – It involves the condensation of aliphatic aldehyde with active methylene compound in presence of base to form alpha, beta – unsaturated compound.



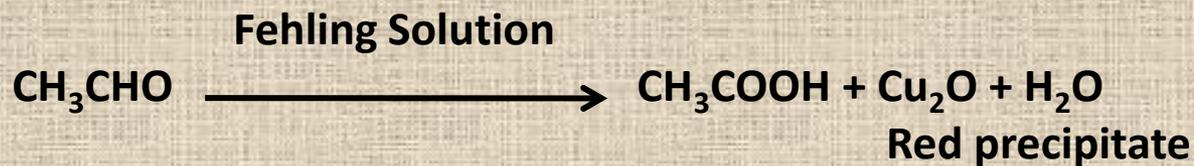
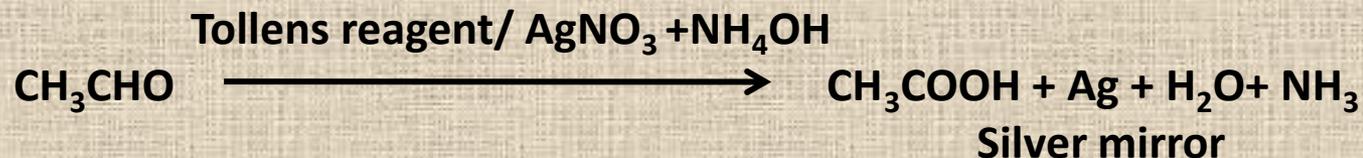
5. Wittig reaction - Wittig reaction involves the reaction between aldehyde with methylenetriphenylphosphorane to prepare alkene.



6. Oxidation reaction –



*Chemical reaction continued .....*



( Fehling solution I & II are the solution of copper sulphate and sodium potassium tartrate respectively)

**THANK YOU**