

## ALDEHYDES, KETONES & CARBOXYLIC ACIDS- II PUC

### ALDEHYDE AND KETONES

#### Introduction:

Aldehydes and ketones are organic compounds which contain carbonyl group ( $>C=O$ ). Aldehydes are carbonyl compounds which are represented by the general formula  $R-CHO$  where  $R$  is an alkyl or aryl group or hydrogen. Ketones are carbonyl compounds which are represented by the general formula  $R-CO-R'$  where  $R$  and  $R'$  are alkyl or aryl groups.

Aliphatic aldehydes and ketones have the general formula  $C_nH_{2n}O$ .

Aldehydes and ketones are functional isomers.

The IUPAC name of an aldehyde ends with 'al'

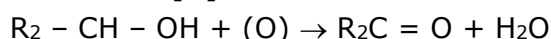
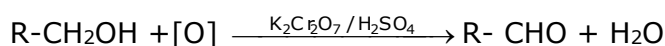
IUPAC name of a ketone ends with '-one'

#### Preparation:

##### (i) By oxidation of alcohols:

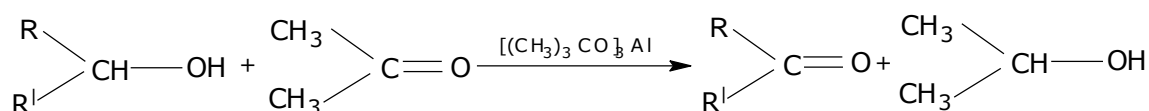
Aldehydes are prepared by oxidation of primary alcohols with acidified potassium dichromate.

Ketones are prepared by the oxidation of secondary alcohols with acidified potassium dichromate



##### (ii) Oppenauer oxidation:

Secondary alcohol is refluxed with excess of acetone in the presence of aluminium tert butoxide to form ketone

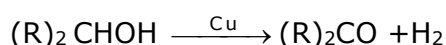
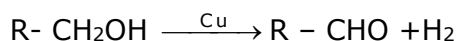


##### (iii) By dehydrogenation:

When vapours of primary alcohols or secondary alcohols are passed over heated copper catalyst at  $300^\circ C$ , aldehydes and ketones are formed.

Even Ag & Pt can be used as catalysts.

Note: Tertiary alcohols do not undergo dehydrogenation



##### (iv) From calcium salts:

Dry distilling calcium salt of fatty acids with calcium formate yields aldehydes.

Ketones are obtained by dry distillation of fatty acids other than calcium formate.

	Calcium salts	Aldehyde/ Ketone
1	Calcium formate	HCHO
2	Calcium formate+calcium acetate	CH <sub>3</sub> CHO

3	Calcium formate + calcium benzoate	C <sub>6</sub> H <sub>5</sub> -CHO
4	Calcium acetate	CH <sub>3</sub> COCH <sub>3</sub>
5	Calcium acetate + Calcium benzoate	Acetophenone (C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> )
6	Calcium benzoate	Benzophenone (C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> )

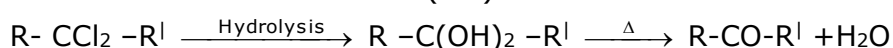
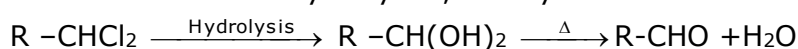
**Note:**

(1) When a mixture of calcium salts is dry distilled, more than one product is formed. For example, when a mixture calcium formate and calcium benzoate is dry distilled, HCHO, C<sub>6</sub>H<sub>5</sub>CHO, C<sub>6</sub>H<sub>5</sub>COC<sub>6</sub>H<sub>5</sub> are obtained.

(2) The carboxylic acids are converted to their calcium salts by treating with milk of lime.

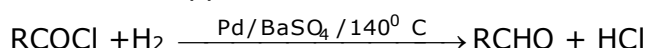
**(V) From geminal dihalides**

When dihalides are hydrolysed, aldehydes & ketones are formed



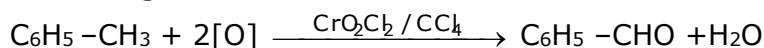
**(vi) Rosenmund's reduction:**

Acid chlorides are reduced to aldehyde by reducing with hydrogen in the presence of Palladium supported over BaSO<sub>4</sub>



**(vii) Etard's reaction:**

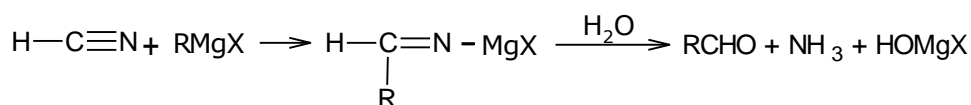
When toluene is oxidized with chromyl chloride in CCl<sub>4</sub>, benzaldehyde is obtained. Even CrO<sub>3</sub> brings about this reaction



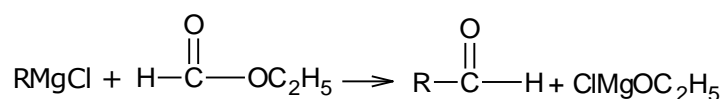
**From Grignard reagent:**

Grignard reagents react with hydrogen cyanide or ethyl formate gives aldehydes, while alkyl cyanides or acid chloride gives ketones.

a)

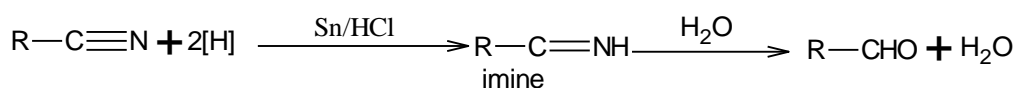


(b)



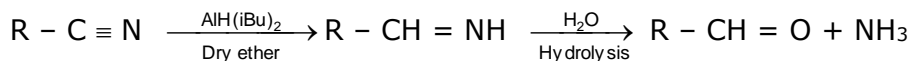
**From nitriles (Stephen reduction):**

Cyanides when reduced by means of stannous chloride and hydrochloric acid is absolute ether followed by hydrolysis yield aldehydes. Ketones cannot be prepared by this method.





alternatively, nitriles can be selectively reduced by diisobutylaluminium hydride,  $[(\text{CH}_3)_2\text{CH}_2\text{CH}_2)_2\text{AlAH}]$ , abbreviated as DIBAL-H to imines which upon hydrolysis gives aldehydes.

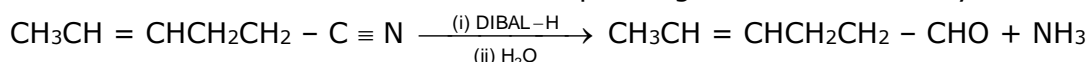


Nitrile

Imine

Aldehyde

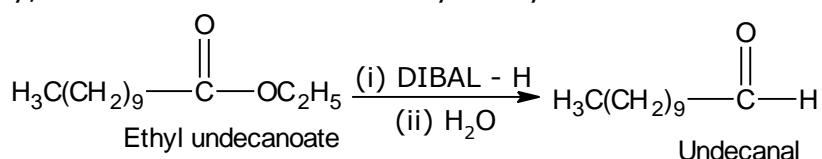
DIBAL-H does not reduce ethylenic double bonds and hence this reagent can be used to reduce unsaturated nitriles to the corresponding unsaturated aldehydes.



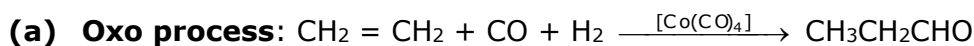
Hex-4-en-1-nitrile

Hex-4-en-1-al

Similarly, esters are reduced to aldehydes by DIBAL-H.

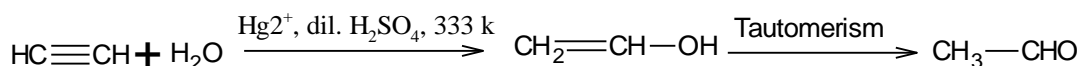


### From alkenes:

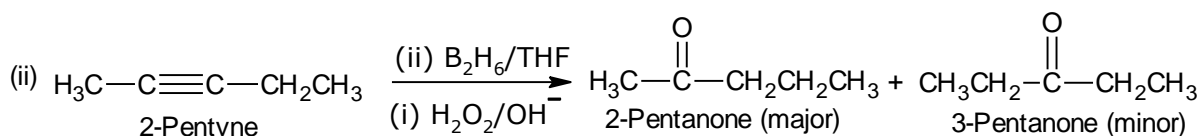
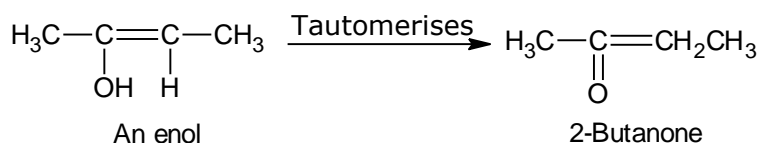
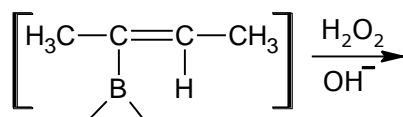
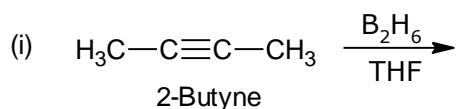
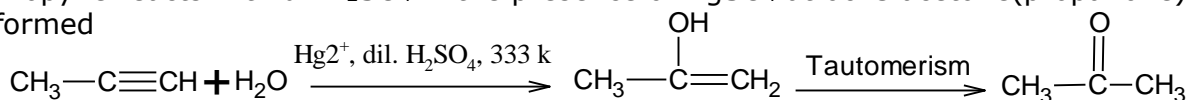


### From alkynes: (Hydration)

a) Acetylene reacts with dilute  $\text{H}_2\text{SO}_4$  in the presence of  $\text{HgSO}_4$  at  $60^\circ\text{C}$ , ethanal is formed



b) Propyne reacts with dil.  $\text{H}_2\text{SO}_4$  in the presence of  $\text{HgSO}_4$  at  $60^\circ\text{C}$  acetone (propanone) is formed





Since C is more electronegative than O, therefore, carbonyl carbon acquires a small positive charge and acts as an electrophile (Lewis acid) while the carbonyl O carries a small negative charge and hence acts as a nucleophile (Lewis base). Thus, the carbonyl group is polar in nature. It may be regarded as a resonance hybrid of structures, I and II (Fig. b). Since resonance structure (II) has a significant contribution towards the resonance hybrid, therefore, aldehydes and ketones have a high dipole moment of 2.3-2.8 D.

## 2. Physical properties.

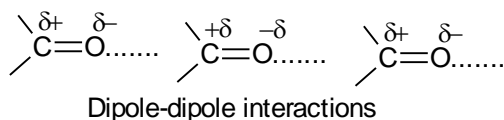
i) **Solubility:** Lower aliphatic aldehydes and ketones (formaldehyde, acetaldehyde, acetone, butanone, etc) are soluble in water due to H-bonding between polar carbonyl group and water

A 40% aqueous solution of formaldehyde is called **formalin**.

The solubility, however, falls off rapidly as the size of the molecule increases.

aromatic aldehydes and ketones on the other hand, are insoluble in water due to large hydrocarbon part. However, they are quite soluble in organic solvents.

ii) **Boiling points:** The boiling points of aldehydes and ketones are somewhat higher than those of the non-polar hydrocarbons and weakly polar ethers of comparable molecular masses due to dipole-dipole interactions.



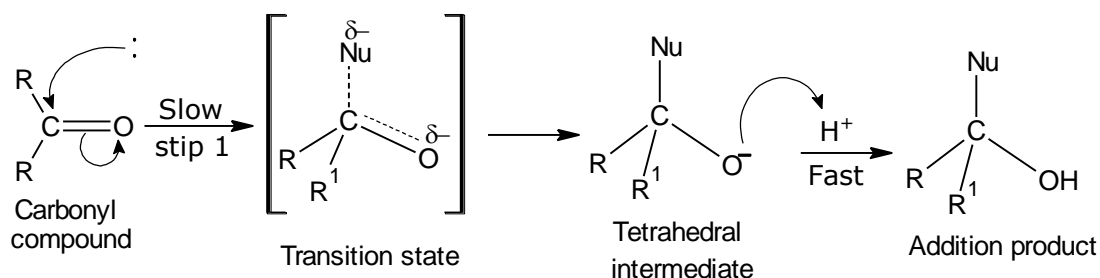
among isomeric aldehydes and ketones, ketones have slightly higher boiling points due to slightly higher dipole moment due to the =I-effect of the two alkyl groups. However, the boiling points of aldehydes and ketones are much lower than those of alcohols and carboxylic acids having comparable masses due to the absence of intermolecular H-bonding.

## Reactivity of aldehydes and ketones towards nucleophilic addition reactions:

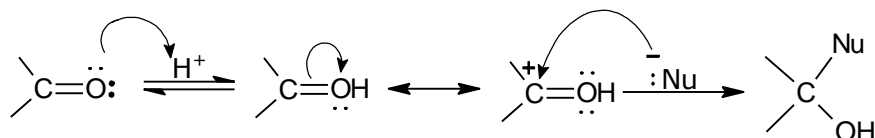
due to greater electronegativity of oxygen than carbon, the carbon atom of the carbonyl group carries a small positive charge and hence behaves as an electrophile. Therefore, a nucleophile readily attacks the electrophilic carbon. Thus, the characteristic reactions of aldehydes and ketones are nucleophilic addition reactions.

### 1. Mechanism of nucleophilic addition reactions.

During the nucleophilic addition reactions, the complete transfer of the  $\pi$ -electrons of the carbon-oxygen double bond occurs, the hybridization of carbon changes from  $sp^2$  to  $sp^3$  and a tetrahedral alkoxide intermediate is formed. This intermediate then picks up a proton either from the solvent (usually  $H_2O$ ) or from the reagent to complete the addition.



- 2. Role of acid catalyst in nucleophilic addition reactions:** If the attacking nucleophile is weak (i.e., alcohols, ammonia and its derivatives), the nucleophilic addition reactions are usually carried out in weakly acidic medium (pH 3-5). The reason being that in presence of acids, carbonyl group gets protonated which, in turn, by resonance increases the positive charge on the carbonyl carbon and thus makes it more electrophilic. As a result, even weak nucleophiles add to the carbonyl group readily

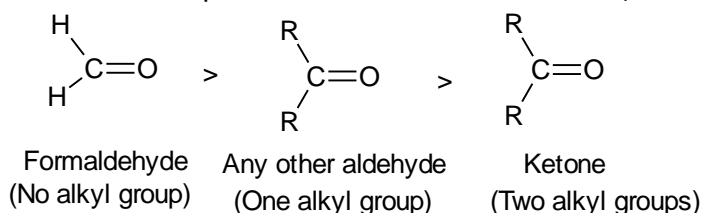


**3. Relative reactivity of aldehydes and ketones:**

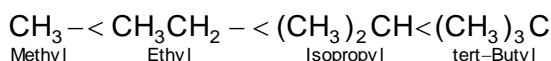
In general, aldehydes (aliphatic or aromatic) are more reactive than ketones because of the following reasons:

- a) Aliphatic aldehydes and ketones:** The relative reactivity of aliphatic aldehydes and ketones depends upon the following two factors:

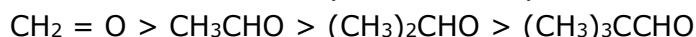
- i) **+I-Effect of alkyl groups:** Alkyl groups have electron-donating inductive effect (+I-effect). Obviously, greater the number of alkyl groups attached to the carbonyl group, higher is the electron density on the carbonyl carbon and hence lower is its reactivity towards nucleophilic addition reactions. Thus, reactivity decreases in the order:



Further as the +I-effect of the alkyl group increases, the reactivity decreases in the same order. Since the +I-effect of the alkyl groups w.r.t. hydrogen increases in the order,



therefore, the reactivity of the aldehydes decreases in the same order:



- ii) **Steric effects:** As the number and size of the alkyl groups attached to the carbonyl carbon increases, the attack of the nucleophile on the carbonyl group becomes more and more difficult due to steric hindrance (crowding) hence the reactivity decreases accordingly. Thus,

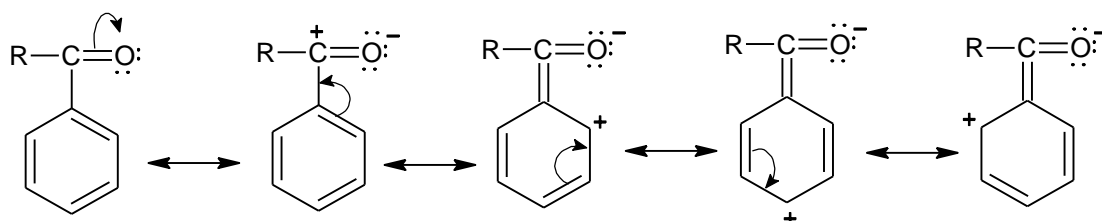
Formaldehyde > Acetaldehyde > Acetone

Butanone > 3-Pentanone

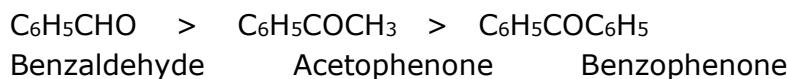
Di-isopropyl ketone > Di-tert-butyl ketone

**b) Aromatic aldehydes and ketones:**

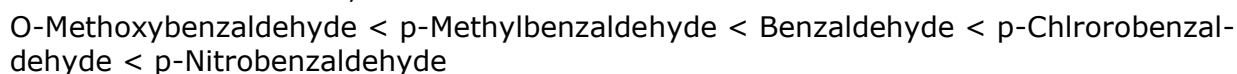
In general, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic analogues. This is due to +R-effect of the benzene ring which reduces the electron-density on the carbonyl carbon as shown below.



However, amongst aromatic aldehydes and ketones, aromatic aldehydes are more reactive than alkyl aryl ketones which, in turns, are more reactive than diaryl ketones. Thus,



further, the presence of electron-donating groups in the benzene ring decreases the electrophilicity of the carbonyl carbon and hence decreases the reactivity of aldehydes and ketones towards nucleophilic addition reaction. Conversely, presence of electron-withdrawing groups in the benzene ring increases the electrophilicity of the carbonyl group and hence increases the reactivity of aldehydes and ketones towards nucleophilic addition reactions. Thus, the rate of addition increases in the order:

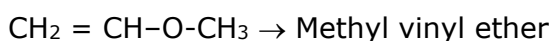
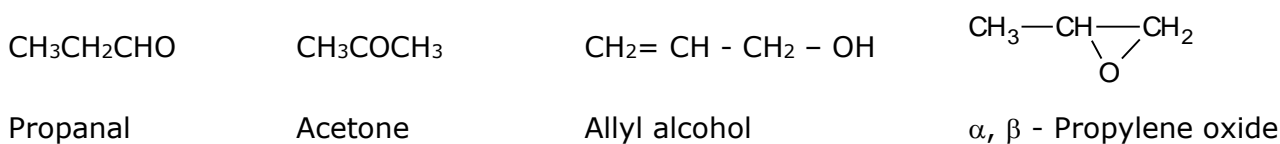


### Isomersim:

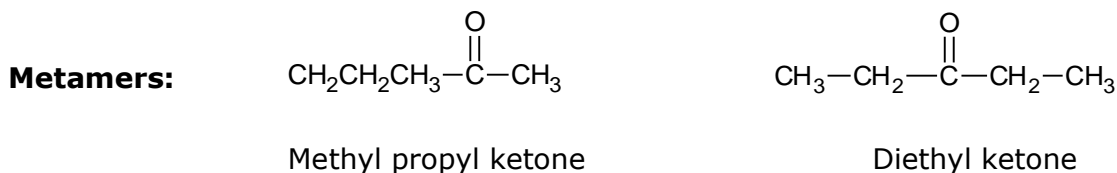
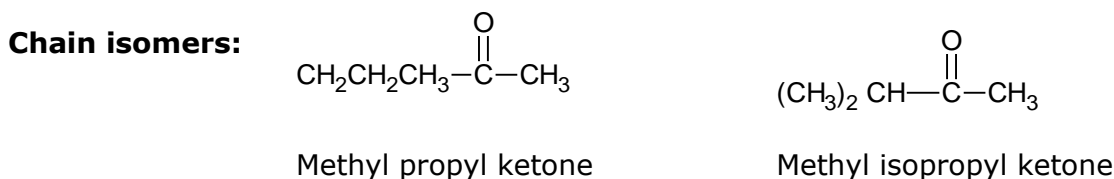
Aldehydes show chain and functional isomerism



### Functional isomers:



### Ketones show chain, functional and metamerism



### Chemical properties:

Aldehydes and ketones are highly reactive compounds

#### 1) Addition reactions:

(a) **with HCN:** Aldehydes and ketones react with HCN to form cyanohydrins.

(b) **with NaHSO<sub>3</sub>**: Aldehydes and ketones with saturated solution of sodium bisulphite to form bisulphite addition compounds. However, acetophenone, diethyl ketone and benzophenone do not give the products due to steric hindrance

## 2) Condensation reactions:

Aldehydes and ketones undergo a number of condensation reactions with the following reagents

- with hydroxyl amine(H<sub>2</sub>N-OH), oximes are formed
- with hydrazine (H<sub>2</sub>N-NH<sub>2</sub>), hydrazones are formed
- with phenyl hydrazine (H<sub>2</sub>N -NHC<sub>6</sub>H<sub>5</sub>), phenyl hydrazones are formed
- with semicarbazide (H<sub>2</sub>N -NHCONH<sub>2</sub>), semicarbazones are formed
- with 2, 4-dinitro phenyl hydrazine (Borsch's reagent), orange yellow crystalline compound is formed.

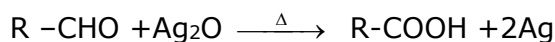
## 3) With Grignard's reagent:

Grignard's reagent reacts with formaldehyde to form an addition compound which on hydrolysis gives primary alcohol. Any other aldehyde reacts with Grignard's reagent to give an addition compound which on hydrolysis gives secondary alcohols. Tertiary alcohols are obtained by the reaction of Grignard reagent with ketones.

## 4) Oxidation of aldehydes:

Aldehydes are easy to oxidize. Mild oxidizing agents like Fehlings solution or Tollen's reagent or Benedict's solution can oxidize aldehydes.

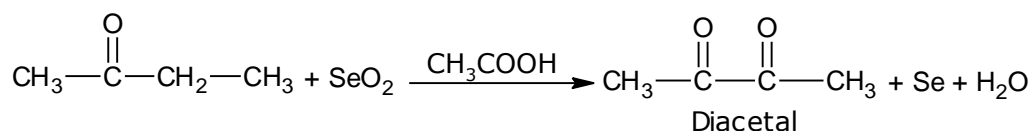
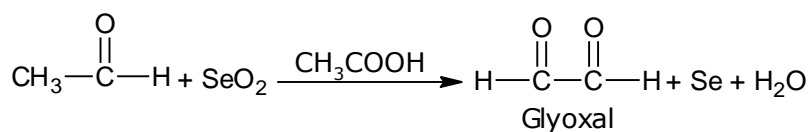
a) **Tollen's reagent**: Tollen's reagent is ammoniacal silver nitrate. It contains [Ag (NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> ions. Aldehydes on heating with Tollen's reagent gives a black precipitate of silver (or shining silver mirror). Aldehydes on oxidation give carboxylic acids with the same number of carbon atoms.



b) **Fehling's solution**: Fehling's solution is alkaline copper sulphate solution containing sodium potassium tartarate (Rochelle salt)

Aldehydes on heating with Fehling's solution give red precipitate cuprous oxide.

**Oxidation with SeO<sub>2</sub>** : The CH<sub>3</sub> group adjacent to C=O is oxidised to -CHO and >CH<sub>2</sub> group is oxidised to >C = O group.





## 5) Oxidation of ketones:

Ketones are difficult to oxidize. Hence, mild oxidizing agents like Fehling's solution and Tollen's reagent cannot oxidise ketones. However, strong oxidizing agents like acidified  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$  can oxidise ketones to carboxylic acids. The acid formed contains lesser number of carbon atoms than the parent ketone. In the case of unsymmetrical ketone, the products are governed by Popoff's rule.

**Popoff's rule:** During oxidation of ketones, the keto group stays with the smaller alkyl group

For example, in 2-Pentanone, the products formed are propanoic acid and acetic acid.

## 6. Reduction of aldehydes and ketones :

(i) Aldehydes on reduction with Zn and dil HCl,  $\text{LiAlH}_4$  give primary alcohols. Ketones on similar reduction give secondary alcohols. For example, acetaldehyde on reduction gives ethanol while acetone on reduction gives isopropyl alcohol.

(ii) **Clemmensen's reduction:** When aldehyde or a ketone is reduced with Zn - Hg/Conc HCl, hydrocarbons are formed.

$>\text{C} = \text{O}$  group is reduced to  $>\text{CH}_2$  group. For example, acetone gives propane. Acetophenone on reduction gives ethyl benzene.

(iii) **Reduction to alkanes :** Carbonyl compounds on reduction with HI and red P give alkane.

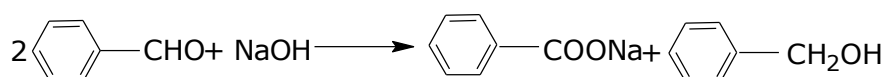


iv) Aldehydes or ketone reacts with hydrazine and KOH & potassium tert-butoxide at high boiling solvent such as ethylene glycol gives alkane. (**Wolf Kishner Reduction**)

## 7. Special reactions:

(i) **Cannizzaro's reaction :** Aldehydes which do not contain  $\alpha$  - hydrogen when heated with a concentrated solution of alkali, undergo oxidation and reduction to give alcohol and a salt of carboxylic acid. (Disproportionation reaction)

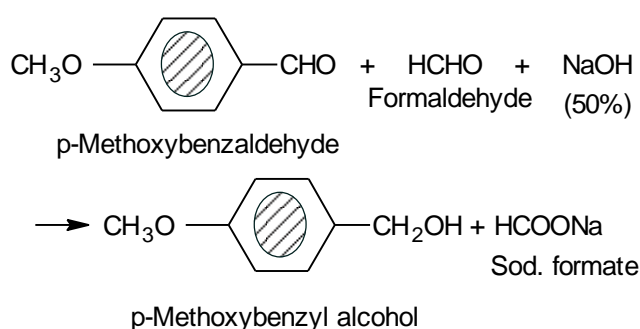
For example,



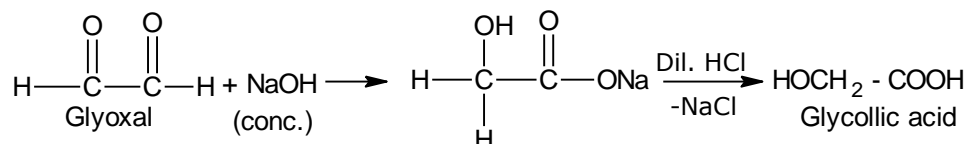
Note: When benzaldehyde reacts with formaldehyde, in the presence of NaOH, benzyl alcohol and sodium formate are obtained. (Crossed Cannizzaro's reaction)

### Crossed Cannizzaro reaction:

Like crossed aldol condensation, crossed Cannizzaro reaction can take place between two different aldehydes to give all the four possible products. Therefore, such a reaction is of little synthetic utility. However, if one of the aldehydes is formaldehyde, the crossed cannizzaro reaction is of great synthetic importance. The reason being that during the reaction, HCHO being the most reactive aldehyde, is exclusively oxidized to sodium formate while the other aldehyde is always reduced to alcohol. For example,



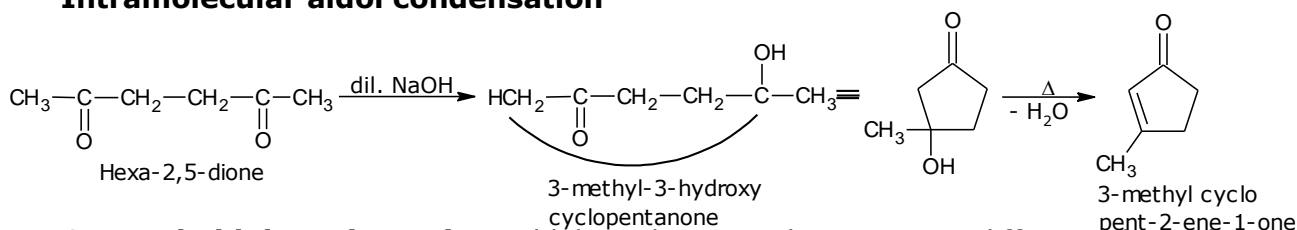
**Intramolecular Cannizzaro reaction.** Dialdehydes which do not contain  $\alpha$ -hydrogens undergo intramolecular Cannizzaro reaction in presence of strong alkali. For example,



(ii) **Aldol condensation:** Aldehydes and ketones having  $\alpha$ -hydrogen atom undergo self condensation in the presence of dilute alkali forming  $\beta$ -hydroxy aldehydes and  $\beta$ -hydroxy ketones. For example, acetaldehyde gives acetaldol, acetone gives diacetone alcohol.

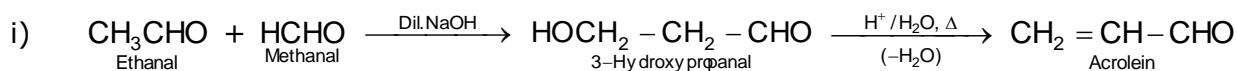
Note: Acetaldol on heating loses water to give crotonaldehyde. ( $\text{CH}_3\text{-CH=CH-CHO}$ )

**Intramolecular aldol condensation**

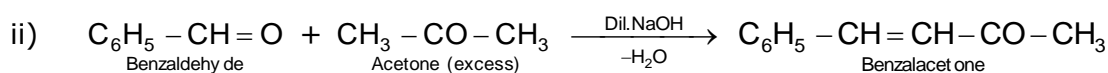
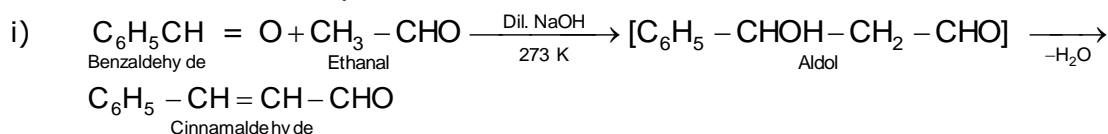


- Crossed aldol condensation:** Aldol condensation between two different aldehydes or ketones or between one aldehyde and one ketone is called **crossed aldol condensation**. Such condensations usually give a mixture of four products depending upon which aldehyde acts as the electrophile and which acts as the nucleophile. These products are usually difficult to separate. However, if one of the aldehydes does not possess  $\alpha$ -hydrogen atoms. (e.g., formaldehyde, benzaldehyde, etc.) then crossed aldol condensations are of great synthetic utility.

For example,



with benzaldehyde, the initially formed aldols in situ undergo dehydration to give  $\alpha, \beta$  unsaturated aldehydes or ketones.



Such a base-catalysed crossed aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or ketone is called Claisen Schmidt condensation.

(iii) **Perkin's reaction:** Benzaldehyde on heating with acetic anhydride in the presence of fused sodium acetate at 180°C gives cinnamic acid. (C<sub>6</sub>H<sub>5</sub>-CH=CH-COOH)

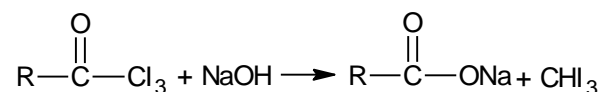
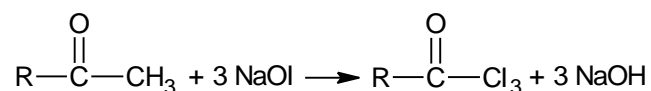
(iv) **Claisen condensation:** Benzaldehyde reacts with acetaldehyde in the presence of dil NaOH to form cinnamaldehyde. (C<sub>6</sub>H<sub>5</sub>-CH=CH-CHO)

(v) **Benzoin condensation:** Benzaldehyde reacts with alcoholic KCN to form benzoin (C<sub>6</sub>H<sub>5</sub>CH(OH)COC<sub>6</sub>H<sub>5</sub>).

## 8. With Grignard reagent:

Grignard reagent reacts with formaldehyde to form an addition compound which hydrolysis gives **primary alcohols**. Any other aldehydes reacts with Grignard's reagent to give an addition compound which on hydrolysis gives **secondary alcohols**. **Tertiary alcohols** are obtained by the reaction of Grignard reagent with ketones.

**9. Haloform reaction :** Oxidation of acetaldehyde or methyl ketones with Sodium Hypohalite (NaOH) or (X<sub>2</sub> + NaOH) gives haloform CHX<sub>3</sub>. The reaction is practical value to identify these compounds by forming CHI<sub>3</sub>.



## Iodoform reaction:

Aldehydes and ketones having CH<sub>3</sub>CO- group react with I<sub>2</sub> and NaOH to form yellow crystals of iodoform. For example, acetaldehyde and acetone give iodoform.

**10. Bayer-Villiger oxidation :** Oxidation of aliphatic Ketones by organic per acids, e.g. perbenzoic acid, peracetic acid or monoperothalic acid to form esters or their hydrolysed products :

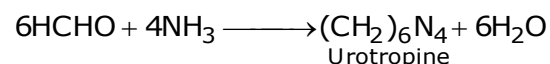


**11. Schiff's reagent** is an aqueous solution of rosaniline hydrochloride decolourised with sulphur dioxide.

Only aldehydes give immediate pink colour with Schiff's reagent.

## 12. Reaction with Ammonia:

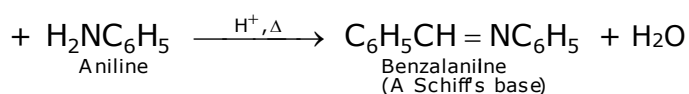
Acetaldehyde gives an addition compound : acetaldehyde – ammonia.



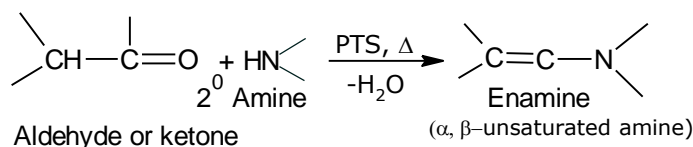
Urotropine on nitration gives RDX with composition:  $[(\text{CH}_2)_3\text{N}_3(\text{NO}_2)_3]$   
 Acetaldehyde gives an addition compound : acetaldehyde – ammonia.  
 Benzaldehyde gives a condensation compound hydrobenzamide.  
 Acetone gives a condensation product diacetone ammonia.  
 Acetophenone gives an addition compound acetophenone – ammonia.

13. Acetophenone reacts with chlorine to give phenacyl chloride used in tear gas.

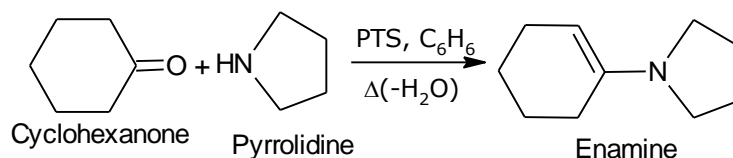
**14. Reaction with primary amines.** Aldehydes and ketones react with  $1^\circ$  amines in presence of catalytic amount of an acid to form aldimines, Schiff's bases or azomethines. Among these, the most stable Schiff's bases are those which are derived from aromatic aldehydes and aromatic  $1^\circ$  amines. For example,



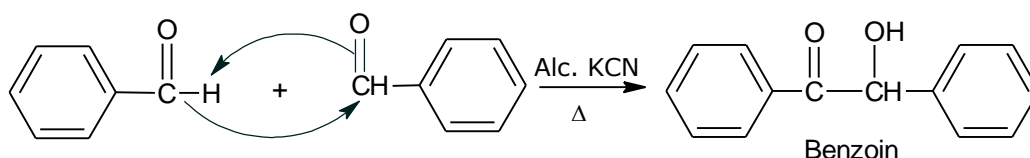
**Reaction with secondary amines.** Aldehydes and ketones which contain at least one  $\alpha$ -hydrogen react with secondary amines in presence of p-toluenesulphonic acid (PTS) to form  $\alpha, \beta$ -unsaturated amines called **enamines**.



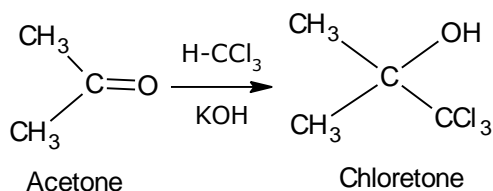
Among these the most stable enamines are those which are derived from cyclic ketones and cyclic secondary amines such as pyrrolidine, morpholine, piperidine, etc. For example,



**15. Reaction with alcoholic potassium cyanide.** On heating with an ethanolic solution of KCN, two molecules of an aromatic aldehyde undergo condensation to form benzoin. This reaction is called **benzoin condensation**. For example,

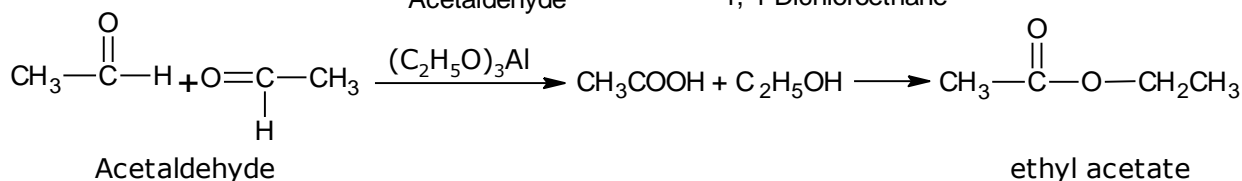
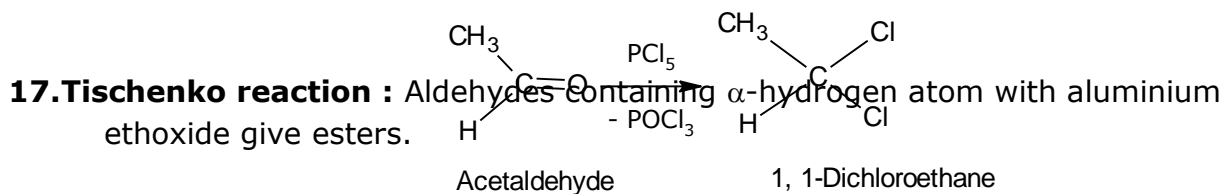


**16. Reaction with chloroform.** Ketones condense with chloroform in presence of alkali to form addition products. For example, acetone gives chloretone which is used as an hypnotic.

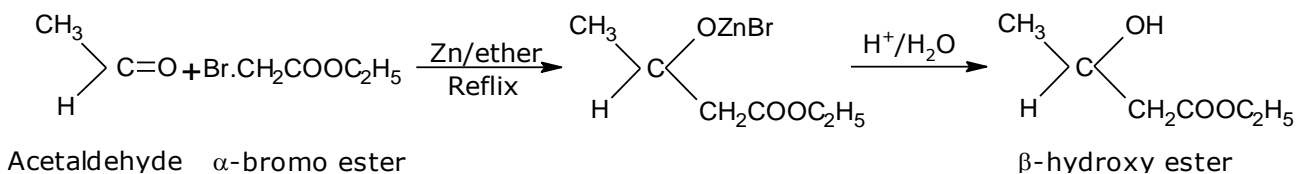


Aldehydes do not give this reaction.

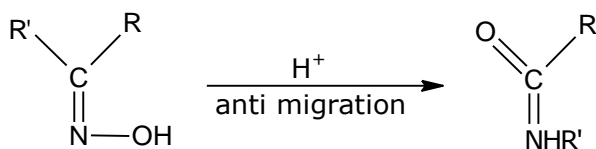
**Reaction with phosphorus pentachloride.** Aldehydes and ketones react with phosphorus pentachloride to form gem-dihalides. For example,



**18. Reformatsky reaction :** It is the reaction between an  $\alpha$ -bromo acid ester and a carbonyl compound (aldehyde or ketone) in the presence of zinc to form a  $\beta$ -hydroxy ester.

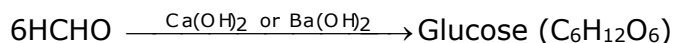
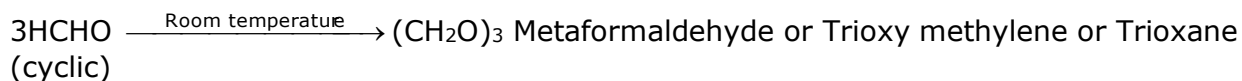


**19. Beckmann's rearrangement :** It is rearrangement of keto oxime to N-substituted acid amide in presence of Conc.  $\text{H}_2\text{SO}_4$ , PPA,  $\text{SOCl}_2$ ,  $\text{PCl}_5$  etc.

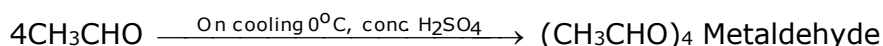
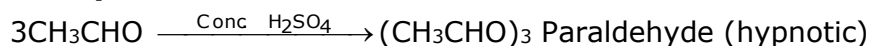


## 20. Polymerization

### Formaldehyde:

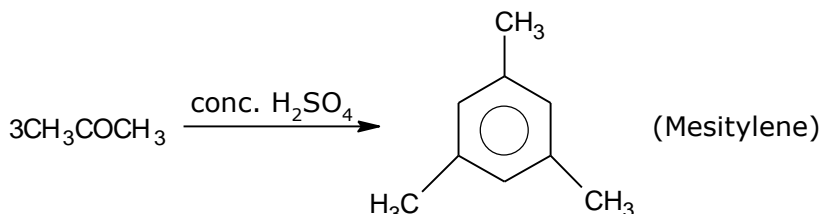
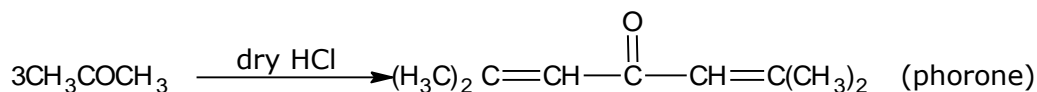
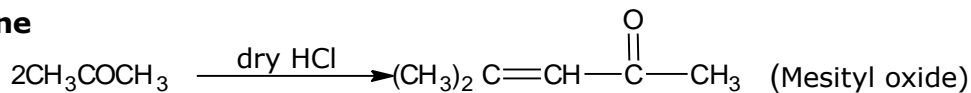


### Acetaldehyde

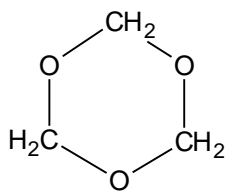
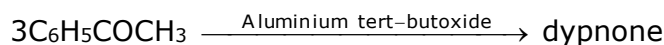


## Auto condensation

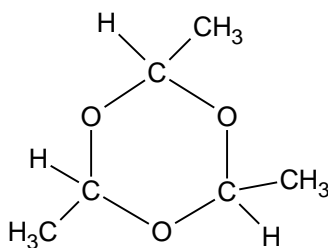
### Acetone



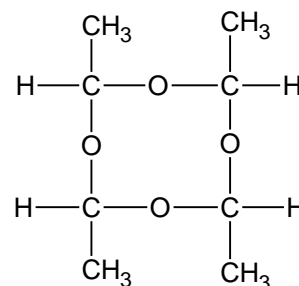
### Acetophenone



Trioxane



Paraldehyde



Metaldehyde

## 21. Uses of aldehydes and ketones.

### a) Formaldehyde:

(i) A 40 % aqueous solution of HCHO is called formalin which is used to preserve biological specimens.

(ii) It is condensed with Phenol to give bakelite.

### b) Benzaldehyde:

(i) Used in the preparation of benzoyl chloride, cinnamic acid, benzoin etc.

(ii) used in perfume industry.

### c) Acetophenone:

(i) used as a hypnotic under the trade name hyponone.

(ii) used in the preparation of phenacyl chloride ( $\text{C}_6\text{H}_5\text{COCH}_2\text{Cl}$ ) which is used in tear gas.

## Monocarboxylic acids

- Functional group – COOH. General formula: RCOOH.
- General formula of fatty acid, that is, of a saturated monocarboxylic acid:  
 $\text{C}_n\text{H}_{2n+1}\text{COOH}$  or  $\text{C}_n\text{H}_{2n}\text{O}_2$

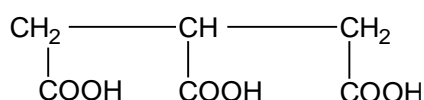
### IUPAC names:

- HCOOH ( formic acid) – Methanoic acid
- CH<sub>3</sub>COOH (acetic acid) – Ethanoic acid
- C<sub>6</sub>H<sub>5</sub>COOH (benzoic acid) – Benzoic acid
- C<sub>6</sub>H<sub>4</sub>(OH)COOH Salicylic acid - (2 – hydroxy benzoic acid)

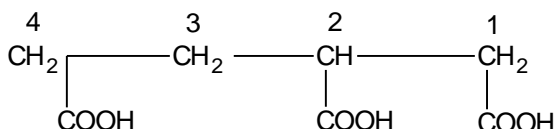
The dicarboxylic acids are generally called by their common names. According to IUPAC system, the suffix dioic acid is added to the name of the parent alkane is Alkanedioic acids.

Formula	Common Name	IUPAC Name
HOOC – COOH	Oxalic acid	Ethane-1,2-dioic acid
HOOCCH <sub>2</sub> COOH	Malonic acid	Propane-1,3-dioic acid
HOOCCH <sub>2</sub> CH <sub>2</sub> COOH	Succinic acid	Butane-1,4-dioic acid
HOOC (CH <sub>2</sub> ) <sub>3</sub> COOH	Glutaric acid	Pentane-1,5-dioic acid
HOOC (CH <sub>2</sub> ) <sub>4</sub> COOH	Adipic acid	Hexane-1,6-dioic acid

While naming tricarboxylic acids, the acid is named as a derivative of parent alkane which does not include the carbon atoms of the carboxylic groups. These are named by use of suffix tricarboxylic acid.



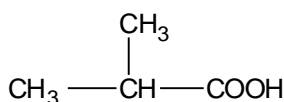
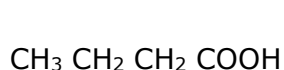
Propane – 1, 2, 3 – tricarboxylic acid



Butane – 1, 2, 4 – tricarboxylic acid

**Isomerism:** Monocarboxylic acids show chain and functional isomerism.

### 1. Chain isomerism



Butanoic acid

2 – methyl propanoic acid

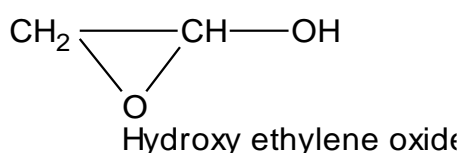
### 2. Functional isomerism:

With the esters of the acids, hydroxyl carbonyl compounds and hydroxyl oxiranes molecular formula – C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>

CH<sub>3</sub>COOH  
Acetic acid

HCOOCH<sub>3</sub>  
methyl formate

OHC-CH<sub>2</sub>-OH  
Glycol aldehyde



### Methods of Preparation

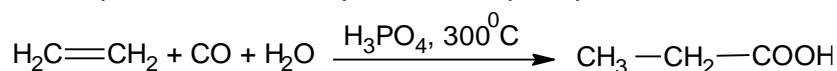
- By acid hydrolysis of cyanides or trihalogen derivatives : Heating with dil. HCl  
 $R - CN + HCl + 2H_2O \rightarrow RCOOH + NH_4Cl$
- By oxidation of alcohols, aldehydes or ketones – common oxidising agents like acidified  $K_2Cr_2O_7$ , alkaline  $KMnO_4$  are used.  
 $R - CHO + (O) \rightarrow RCOOH$
- By passing a mixture of alcohol vapours and air over platinum black catalyst  
 $RCH_2OH + O_2 \rightarrow RCOOH + H_2O$
- From Grignard reagent – using  $CO_2$  and hydrolysing the addition product.
- By the hydrolysis of esters – using acid or a base (by saponification).

**Acid catalysed hydrolysis :**  $R COOR_1 + H_2O \rightarrow RCOOH + R_1OH$

**Base catalysed hydrolysis:**  $R COOR_1 + NaOH \rightarrow RCOONa + R_1OH$

### Carbonylation of alkenes (Koch reaction)

When a mixture of alkene, carbon monoxide and steam is heated under pressure at  $300^\circ C$  in presence of catalyst such as phosphoric acid, monocarboxylic acid is formed.



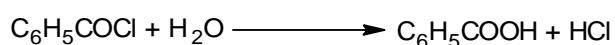
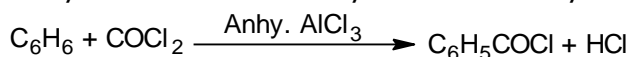
### Heating sodium alkoxide with carbon monoxide:

Carbon monoxide on heating with sodium alkoxide at 423 K under pressure, sodium salt of the fatty acid is obtained which on treatment with acids yields fatty acids



### From benzene by Friedel crafts reaction

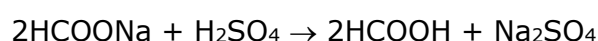
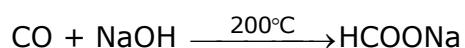
Benzene is converted into benzoyl chloride by action of carbonyl chloride in presence of anhydrous  $AlCl_3$ . Benzoyl chloride on hydrolysis gives benzoic acid



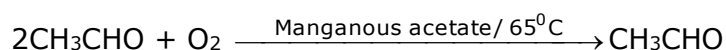
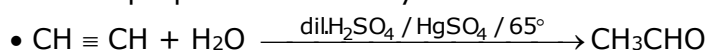
### Special methods

Formic acid:

- Formic acid is obtained by heating oxalic acid crystals with glycerol at  $110^\circ C$
- Formic acid is manufactured as follows



Acetic acid is prepared from acetylene as follows





- Acetic acid is manufactured using ethanol and air by quick vinegar process in the presence of bacterium aceti. Product obtained as called vinegar
- It is also obtained by oxidation of butane by air using cobalt acetate catalyst.

Benzoic acid:

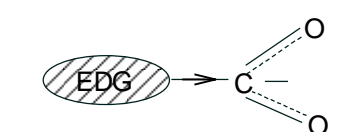
1. By oxidizing an aromatic compound with a side chain.
2. by heating toluene with air to 300°C – V<sub>2</sub>O<sub>5</sub> catalyst.
3. by hydrolysis of benzoyl chloride  $\text{RCOCl} + \text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{HCl}$

### General information

- First four members of fatty acids are liquids miscible with water
- A few of the next higher numbers (C<sub>5</sub> to C<sub>10</sub>) are liquids.
- Still higher members are solids.
- Due to hydrogen bonding carboxylic acids have higher M.P and B.P than expected. Due to hydrogen bonding they dimerise.
- Solubility of lower member in water is due to hydrogen bonding.
- The acid character of fatty acids decreases with the increase in molecular weight.

### Effect of substituents on the Relative Acidity of Aliphatic Monocarboxylic Acids.

Electron-donating groups decrease and electron-withdrawing groups increase the acidity of carboxylic acids as explained below:

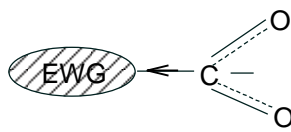


Electron-donating group (EDG)

destabilizes the carboxylate ion

by intensifying the negative

charge and hence decreases the acidity of the carboxylic acid



Electron-withdrawing group (EWG)

stabilizes the carboxylate ion

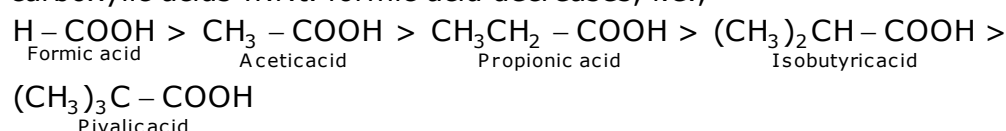
by dispersing the -ve charge and hence increases the acidity of the carboxylic acid

The effect of some important electron withdrawing substituents in increasing the acidity of carboxylic acids follows the order:



### Effect of Electron-donating Substituents:

As the +I-effect of the alkyl group increases, the relative acidity of alkyl substituted carboxylic acids w.r.t. formic acid decreases, i.e.,



- Electron withdrawing groups attached to the carbon chain increase the acidic nature of the acid by -I effect and electron donating group decreases the acid strength by +I effect. Hence Salicylic acid > formic acid > benzoic acid > acetic acid > Propionic More the number of electron withdrawing groups attached to the carbon chain higher is the acidic strength.

Thus:  $\text{CH}_3\text{COOH} < \text{CH}_2\text{ClCOOH} < \text{CHCl}_2\text{COOH} < \text{CCl}_3\text{COOH}$

- Carboxylic acids do not give general reactions of carbonyl group  $> \text{C} = \text{O}$  since  $\text{RCOO}^-$  (carboxylate ion) is resonance stabilized and free  $> \text{C} = \text{O}$  is not present.

### Properties:

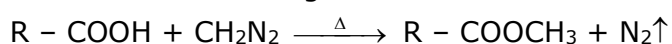
- All acids form salts with NaOH.  
 $\text{R} - \text{COOH} + \text{NaOH} \rightarrow \text{RCOONa} + \text{H}_2\text{O}$
- All acids liberate  $\text{CO}_2$  from  $\text{NaHCO}_3$ .  
 Phenolic group is weaker than the  $-\text{COOH}$  group. Hence the phenolic group of salicylic acid does not react with  $\text{NaHCO}_3$ .  
 $\text{R} - \text{COOH} + \text{NaHCO}_3 \rightarrow \text{RCOONa} + \text{CO}_2\uparrow + \text{H}_2\text{O}$  (effervescence)
- Acids form esters with alcohols in the presence of Conc.  $\text{H}_2\text{SO}_4$  as a dehydrating agent.  
 $\text{R} - \text{COOH} + \text{R}_1 - \text{OH} \xrightarrow{\text{H}_2\text{SO}_4 / \Delta} \underset{\text{esters}}{\text{RCOOR}_1} + \text{H}_2\text{O}$   
 Salicylic acid with methanol gives the ester methyl salicylate having the smell of wintergreen which is similar to that of iodex.
- On heating with sodalime, decarboxylation takes place.  
 $\text{RCOONa} + \text{NaOH} \rightarrow \text{RH} + \text{Na}_2\text{CO}_3$
- On heating with ammonia, acid amides are formed.  
 $\text{RCOOH} + \text{NH}_3 \rightarrow \text{RCOONH}_4 \xrightarrow{\text{Heat}} \underset{\text{Amide}}{\text{RCONH}_2} + \text{H}_2\text{O}$

### Reduction:

It depends on the nature of the reducing agent. With  $\text{LiAlH}_4$  (lithium aluminium hydride) in ether solution or with hydrogen in the presence of copper chromite ( $\text{CuCr}_2\text{O}_4$ ) catalyst or  $\text{BH}_3 / \text{THF}$  (or diborane,  $\text{B}_2\text{H}_6$ ) or  $\text{H}_2/\text{Ru}$ , etc., reduce monocarboxylic acids easily into primary alcohols.

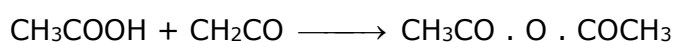
### Reaction with $\text{CH}_2\text{N}_2$ :

Diazomethane undergoes condensation with carboxylic acid to give an ester.



### Reaction with ketene:

Forms acid anhydride.

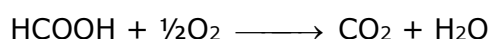


Acetic acid      Ketene      Acetic anhydride

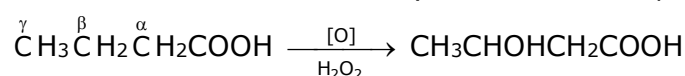
Reduction: On heating with conc. HI and red P at  $200^\circ\text{C}$  or by catalytic reduction, the  $-\text{COOH}$  converts into  $-\text{CH}_3$  to form an alkane.

### Reactions due to Alkyl Group:

- (ii) Oxidation: Monocarboxylic acids except formic acid are extremely resistant to oxidation. Formic acid on oxidation gives carbon dioxide and water.

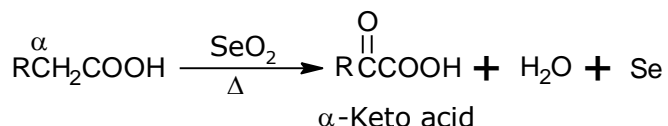


However, prolonged heating with powerful oxidizing agents oxidizes acids into carbon dioxide and water. With 3%  $\text{H}_2\text{O}_2$ , they are oxidised to  $\beta$ -hydroxy acids.

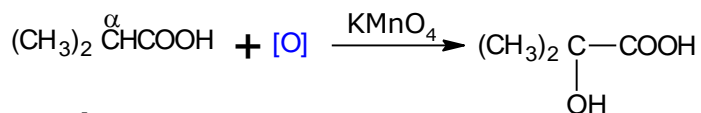


Butyric acid       $\beta$ -Hydroxy butyric acid

Oxidation of  $\alpha$ -methylene group takes place by  $\text{SeO}_2$  to give  $\alpha$ -keto acid.



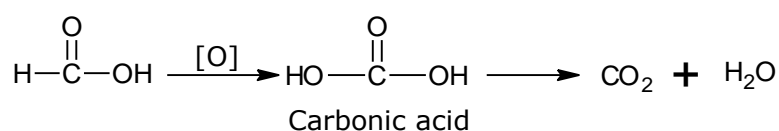
When oxidised with  $\text{KMnO}_4$ , the  $\alpha$ -H atom is oxidised to  $-\text{OH}$  group.



### Special properties

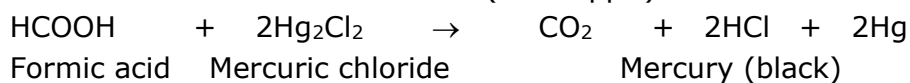
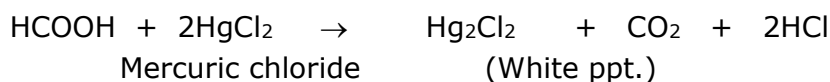
#### Reducing property

Like aldehydes, formic acid behaves as a reducing agent. It is oxidised to an unstable acid, carbonic acid, which decomposes into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

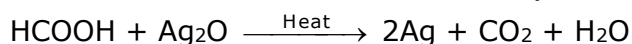


(a) It decolorizes acidified potassium permanganate solution and turns  $\text{K}_2\text{Cr}_2\text{O}_7$  solution green.

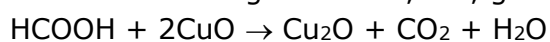
(b) It reduces mercuric chloride to mercurous chloride which change to mercury black.



(c) It reduces ammoniacal silver nitrate (Tollens' reagent).

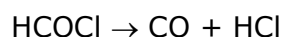


(d) It reduces Fehling's solution, i.e., gives red precipitate of cuprous oxide



Red ppt.

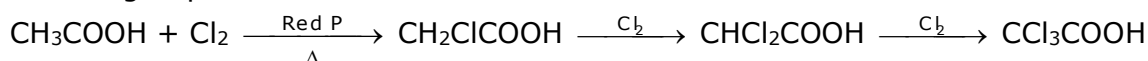
- Among all acids, formic acid
- gets dehydrated to CO by conc.  $\text{H}_2\text{SO}_4$
- $\text{PCl}_3$ ,  $\text{PCl}_5$  etc., react with formic acid giving unstable formyl chloride which decomposes to CO



- It liberates (as an acid)  $\text{CO}_2$  from  $\text{NaHCO}_3$  with effervescence.

#### ➤ Acetic acid

Halogenation: The  $\alpha$ -H atoms are highly reactive due to the presence of electronegative  $-\text{COOH}$  group.



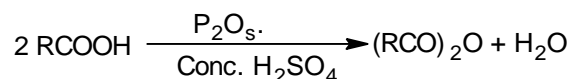
Chloroacetic acid    dichloroacetic acid    Trichloroacetic acid

When a carboxylic acid that contains  $\alpha$ -hydrogen atoms is treated with  $\text{Cl}_2$  or  $\text{Br}_2$  in presence of a catalyst (P, I, Fe, etc.), the  $\alpha$ -hydrogen atoms are replaced by chlorine or bromine atoms. The reaction occurs in presence of sunlight or on boiling. This reaction is known as Hell-Volhard-Zelinsky (HVZ) reaction.

- Kolbe's reaction: Electrolysis of sodium acetate yields ethane.

### Formation of acid anhydrides (Dehydration)

Mono carboxylic acids, when heated in presence of a strong dehydrating agent such as phosphorus pentoxide or conc.  $\text{H}_2\text{SO}_4$  form anhydrides by elimination of a water molecule from molecules of the monocarboxylic acid.

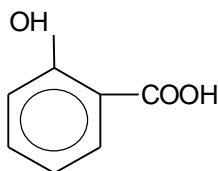


### Formic acid does not form an anhydride

#### ➤ Benzoic acids

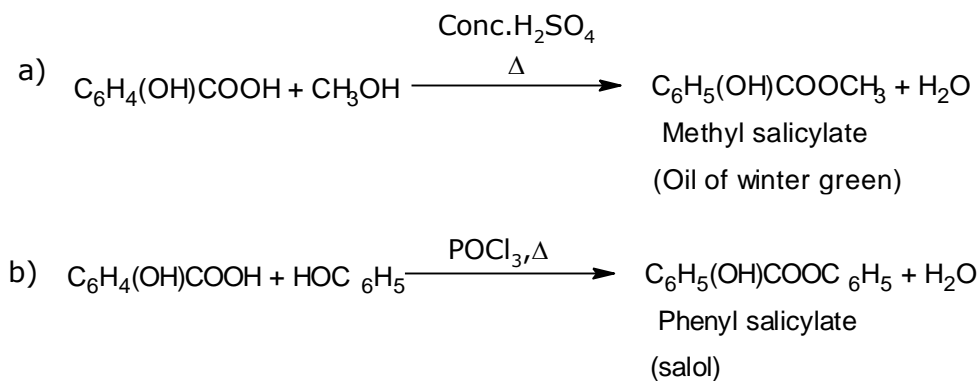
- Electron withdrawing –  $\text{COOH}$  group attached to the ring deactivates the ring. Hence it is m – directing group.
- Benzoic acid undergoes electrophilic substitution reactions like nitration, sulphonation and halogenation to give m – substituted acid derivatives.

### Salicylic acid (O – Hydroxy benzoic acid)

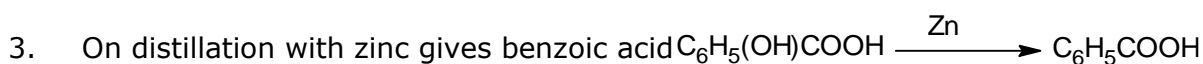


is an example for bifunctional compound contains carboxyl and phenolic group.

#### 1. Esterification:



2. Gives violet colour with neutral ferric chloride



4. Reacts with acetylchloride to give acetyl salicylic acid (aspirin)

5. On treating with excess of bromine water gives white precipitate of 2, 4, 6 tribromo phenol

6. On heating with conc.  $\text{HNO}_3$  & Conc.  $\text{H}_2\text{SO}_4$  gives picric acid.