

## Teacher Orientation

Aldehydes, Ketones and Carboxylic Acids contains following topics:

Nomenclature

Preparation

Properties

## Student Orientation

Preparation and Properties Of Aldehydes, Ketones and Carboxylic acids

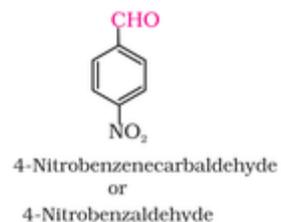
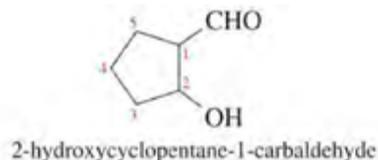
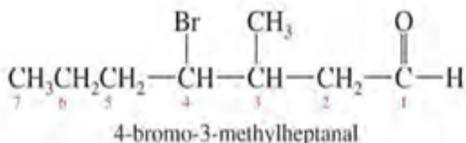
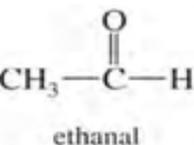
## Concept Detail

# Aldehydes, Ketones and Carboxylic acids

### IUPAC Nomenclature of Aldehydes:

1. Number the longest chain starting from carbon of aldehyde group.
2. Name the compound by changing -e to -al (e.g. ethane to ethanal).

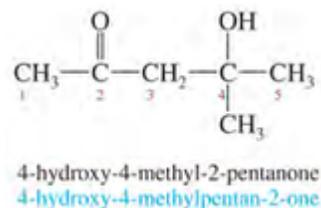
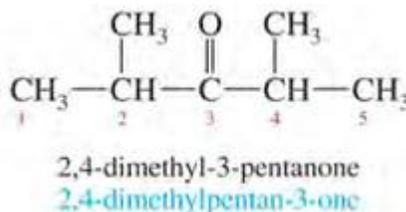
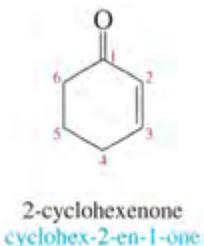
#### Examples:



### IUPAC Nomenclature of ketones:

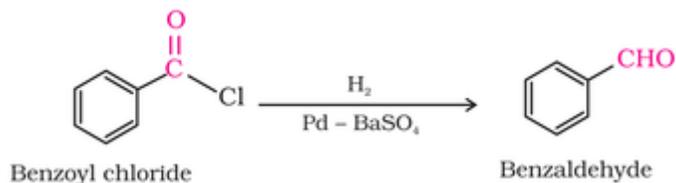
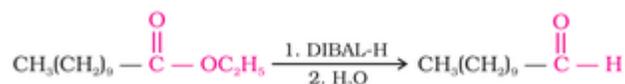
1. Number the longest chain from the end nearest to the carbonyl group.
2. Name the compound by changing -e to -one (e.g. ethane to ethanone).

#### Examples:



### Preparation of Aldehydes:

1. From acyl chloride (Rosenmund reduction) :



## 2. From nitriles:

### (I) Stephen reaction :

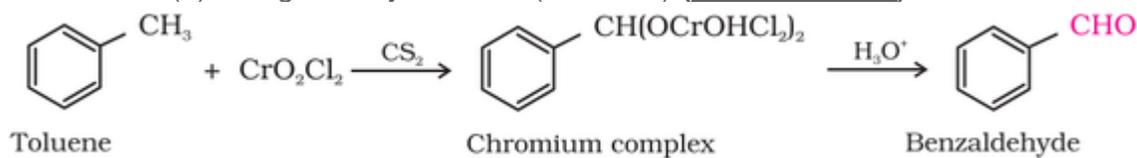


(II) reduction of nitrile by diisobutylaluminium hydride (AlH(i-Bu)<sub>2</sub>) and (DIBAL-H) to imine followed by hydrolysis:

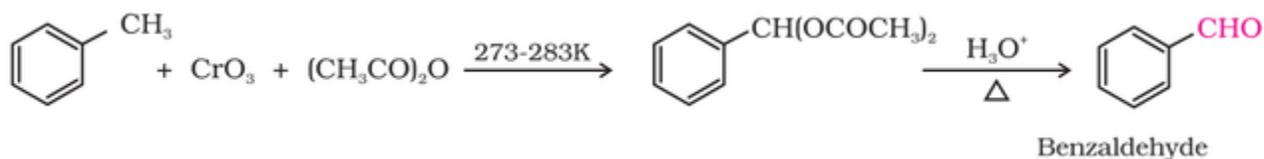
## 3. From aromatic hydrocarbons to aromatic aldehydes:

### (I) By oxidation of methylbenzene:

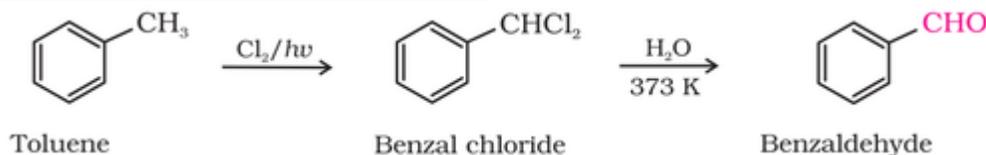
(a) Using chromyl chloride (CrO<sub>2</sub>Cl<sub>2</sub>) (**Etard reaction**):



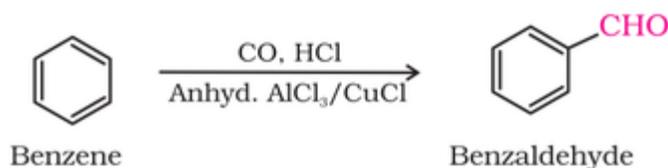
(b) Using chromic oxide (CrO<sub>3</sub>):



### (II) Chlorination followed by hydrolysis:

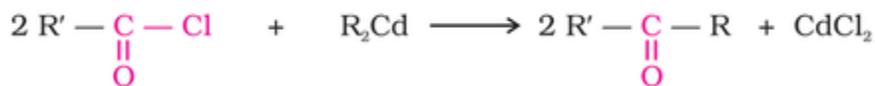


### (III) by Gatterman - Koch reaction:

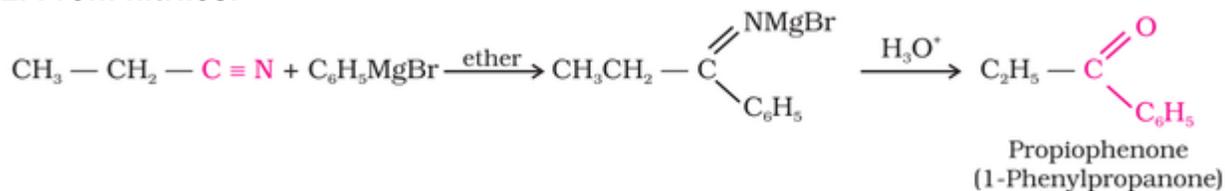


## Preparation of Ketones:

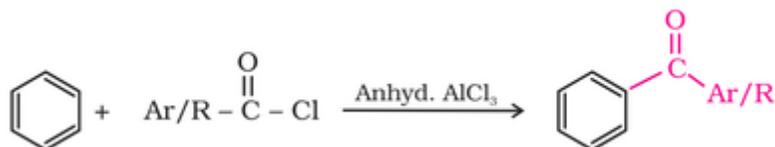
### 1. From acyl chlorides:



## 2. From nitriles:

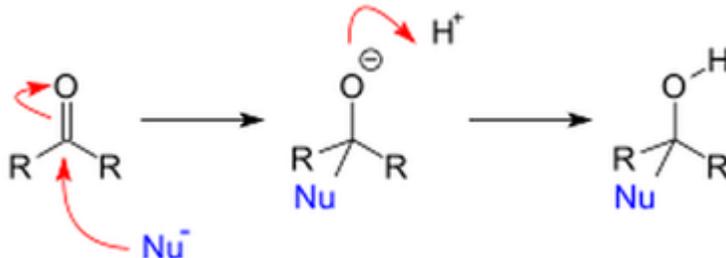


## 3. From Friedel-Crafts acylation reaction:



## Reactions of aldehydes and ketones:

Aldehydes and ketones undergo nucleophilic substitution reaction. In nucleophilic substitution, a species that has extra electron or lone pair of electron attacks the carbonyl carbon of the ketone or the aldehyde leading to an alkoxide intermediate as shown in the middle figure below. This alkoxide intermediate can capture a proton to produce a neutral species as shown below.



## Reactivity of aldehyde vs ketone:

Aldehydes are usually more reactive than Ketones for two reasons: 1. steric and 2 electronic reasons

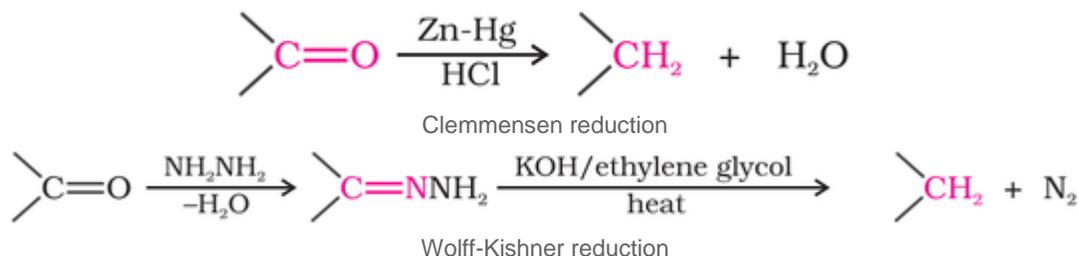
Sterically, the presence of two bulky (large) groups in ketones will hinder the attack of nucleophile to carbonyl carbon in ketone. Aldehydes have only one bulky group around the carbonyl carbon and it is easier for the nucleophile to attack the carbonyl carbon as compared to ketones.

Electronically, aldehyde is also more reactive than ketone because the presence of two alkyl groups in ketones will reduce the electrophilicity (partial positive charge) of the carbonyl carbon due to inductive effect by the alkyl groups. Therefore, attack of nucleophile on carbonyl carbon in ketone is harder than attack of carbonyl carbon in aldehyde making the aldehyde more reactive.

## 2. Reduction:

(i) Reduction of aldehydes and ketones to primary or secondary alcohol using sodium borohydride or lithium aluminum hydride.

(ii) Reduction of aldehydes or ketones to hydrocarbons using **Clemmenson reduction** or **Wolff-Kishner reduction**

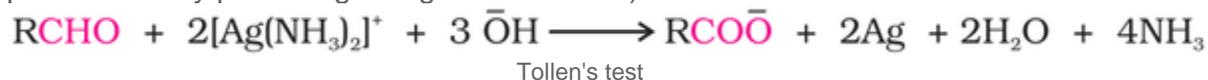


## 3. Oxidation:

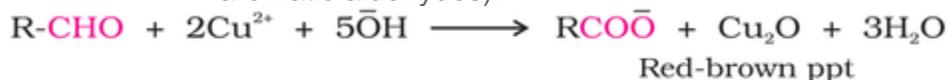
Aldehydes can be easily oxidized to carboxylic acids using nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidizing agents, mainly Tollens' reagent and Fehlings' reagent also oxidize aldehydes.

Oxidation of ketones, however, require more stronger oxidizing agent in more vigorous conditions.

(i) **Tollen's test** (used to distinguish aldehydes from ketones, aldehydes give positive test by producing a bright silver mirror):



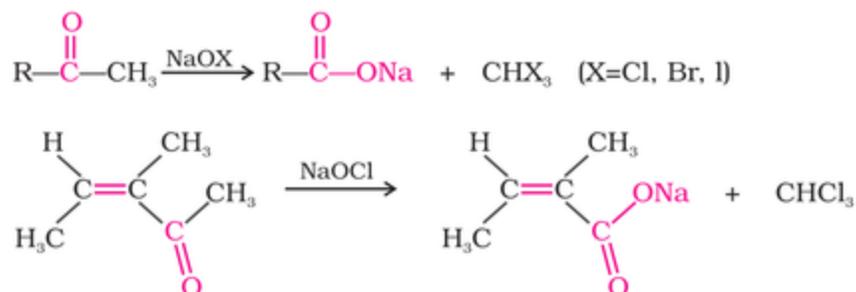
(ii) **Fehling's test** (used to distinguish aldehydes from ketones, aldehydes give positive test by producing a red-brown ppt. except aromatic aldehydes):



Fehling's test

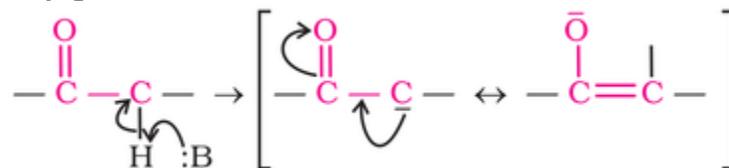
(iii) **Oxidation of methyl ketones using haloform reaction:** both aldehydes and ketones having at least one methyl group

attached to the carbonyl carbon will react to give a product having one less carbon atom as shown in the reaction below:



#### 4. Reaction due to $\alpha$ -hydrogen:

Aldehydes and ketones also undergo reaction due to acidic nature of alpha hydrogen atom. The acidic nature of alpha hydrogen of aldehydes and ketones is due to strong electron withdrawing nature of carbonyl group and resonance stabilization of conjugate base as shown below:

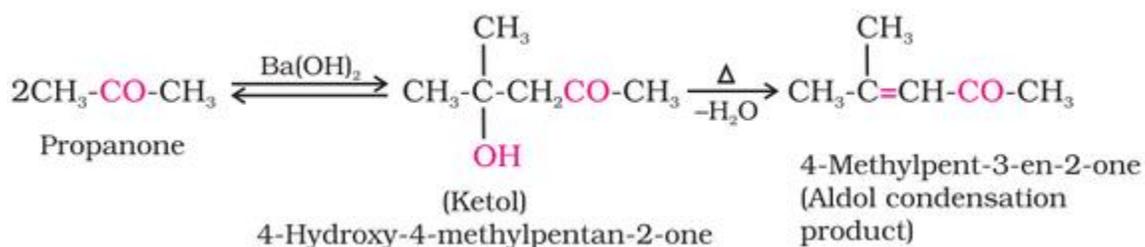
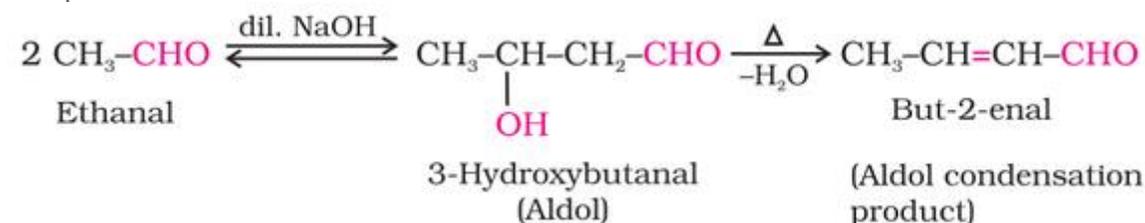


negative charge on alpha carbon is stabilized by the carbonyl group.

**(i) Aldol condensation:** Aldehydes and ketones having at least one hydrogen  $\alpha$ -hydrogen undergoes reaction in weakly

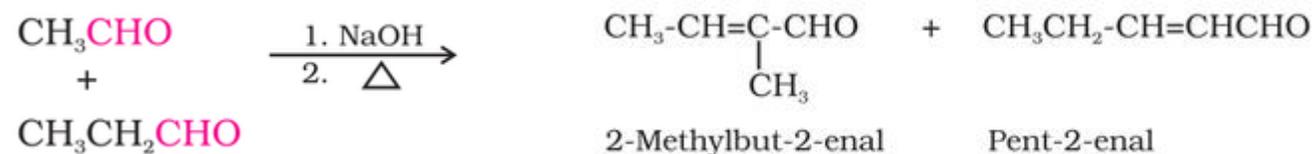
basic condition to form  $\beta$ -hydroxy aldehydes (aldol) or  $\beta$ -hydroxy ketones (ketol), respectively.  $\beta$ -hydroxy aldehydes (aldol) or  $\beta$

hydroxy ketones (ketol) readily loses water to give  $\alpha,\beta$ -unsaturated carbonyl compounds.



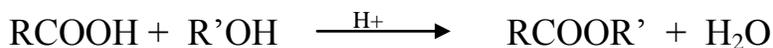
**2. Cross aldol condensation:** When aldol condensation is carried out between two different aldehydes or ketones or an aldehyde

and a ketone having alpha-hydrogen, the reaction is called cross aldol condensation.



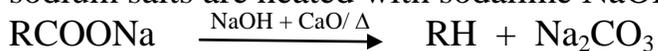
from one molecule of ethanal and one molecule of propanal





### **3. DECARBOXYLATION:**

Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime NaOH and CaO in the ratio 3: 1 .



### **Activity**

1. Perform an activity to detect which out of two test tubes-A and B contain aldehyde.
2. Perform an activity to detect the presence of functional groups in the given organic compounds.

### **Instant Diagnosis Questions**

1. Which reagent is used to convert primary alcohols to aldehydes?
2. Aldehydes and ketones are soluble in water. Why?
3. Which types of compounds undergo Cannizzaro reaction?
4. Which is more reactive towards nucleophilic substitution reactions –Aldehydes or ketones?

### **Formative Assignments**

1. Toluene with CrO<sub>3</sub> and Acetic anhydride forms benzaldehyde. Explain.
2. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.
3. Carbonyl carbon of carboxylic acid is less electronegative than aldehydes and ketones give reason.
4. Carboxylic acids are having higher boiling points than aldehydes, ketones and even alcohols of comparable molecular masses. Explain.
5. Carboxylic acids are stronger acids than phenol though both possess resonance stabilization of respective anions.

## Levelwise Assignment

### Level 1

Q1. Explain the following reactions:

- 1) Rosenmund reaction
- 2) Wolf-Kishner reaction
- 3) Cannizaro reaction

Q2. Which acid of each pair shown here would you expect to be stronger -  $\text{CH}_3\text{COOH}$  or  $\text{FCH}_2\text{COOH}$ ?

### Level 2

Distinguish between the following:-

- (a) Phenol and alcohol
- (b) Benzaldehyde and Propanal
- (c) Acetic acid and formic acid
- (d) Benzophenone and acetophenone
- (e) Ethanal and propanal

### Level 3

1.

**Which acid of each pair shown here would you expect to be stronger?**

(i)  $\text{CH}_3\text{CO}_2\text{H}$  or  $\text{CH}_2\text{FCO}_2\text{H}$       (ii)  $\text{CH}_2\text{FCO}_2\text{H}$  or  $\text{CH}_2\text{ClCO}_2\text{H}$

(iii)  $\text{CH}_2\text{FCH}_2\text{CH}_2\text{CO}_2\text{H}$  or  $\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$

(iv)  $\text{F}_3\text{C}-\text{C}_6\text{H}_4-\text{COOH}$  or  $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{COOH}$

2. Give explanation for each of the following:

- i) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-Trimethylcyclohexanone does not.

- ii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

## **Project**

- 1) Prepare a road map for
  - i) preparation of aldehydes and ketones
  - ii) chemical properties of aldehydes and ketones
- 2) Construct a table that compares and contrasts the key properties of aldehydes and ketones.