

PROPERTIES

Physical:- (applicable for ketones also)

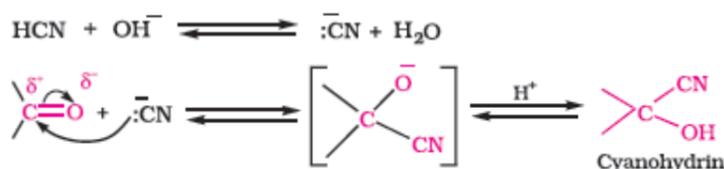
- ✓ **State:** *Liquid* or *solid* at room temperature.
- ✓ **Boiling point:** Boil at higher temperatures than the hydrocarbons and weakly polar compounds such as ethers of comparable molecular masses.
Reason: These are *highly polar molecules*.
- ✓ **Solubility:** The **lower members** are *soluble* in water but the **higher members** are *insoluble*.
Reason: The **lower members** form H-bonds with water. The **higher members** have large sized hydrophobic chain of C-atoms.
- ✓ **Odour:** The lower aldehydes have *pungent* smell and **higher members** have *fruity* smell.

CHEMICAL REACTIONS:-

(i) **Nucleophilic addition reactions** (Mechanism: see text, page 358)

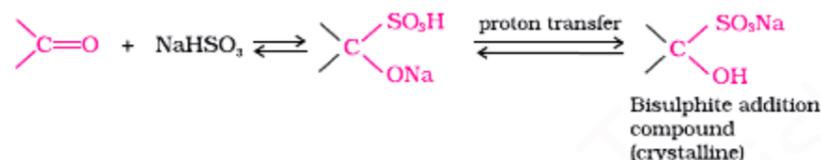
Aldehydes undergo nucleophilic addition reactions onto the **carbonyl group** with a number of nucleophiles such as, HCN, NaHSO₃, alcohols (or diols), ammonia derivatives, and **Grignard reagents**.

a. **Addition of hydrogen cyanide:** Aldehydes react with hydrogen cyanide (HCN) in presence of a base to give cyanohydrins.



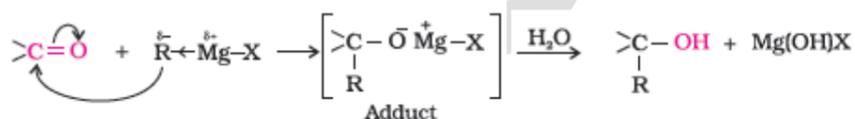
The cyanohydrins are useful synthetic intermediates since it can be converted to *carboxylic acids*, *amines*, *amides* etc.

b. **Addition of sodium hydrogensulphite:** Aldehydes with **sodium hydrogensulphite** gives the addition products (*bisulphite adduct*).

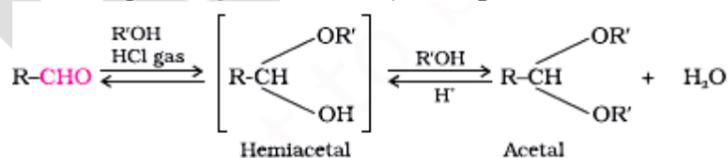


The bisulphate adduct can be converted back to the **original aldehyde** by treating it with **dilute mineral acid or alkali**. Therefore, this reaction is used for the separation and purification of aldehydes.

c. **Addition of Grignard reagents:** Aldehyde with *Grignard reagent* followed by hydrolysis, gives alcohols. **Formaldehyde** gives 1^o alcohols and **other aldehydes** give 2^o alcohols.

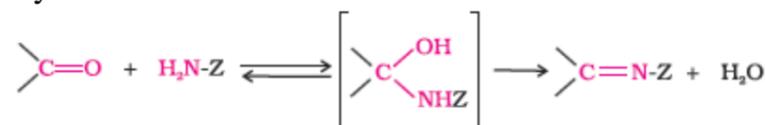


d. **Addition of alcohols:** Aldehydes react with monohydric alcohol in the presence of dry HCl to give *alkoxyalcohol* intermediate (known as hemiacetals), which further react with one molecule of alcohol to give a **gem-dialkoxy** compound known as **acetal**.

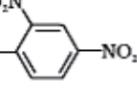
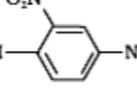


Acetals on *hydrolysis* with **aqueous mineral acids** to give corresponding aldehydes.

e. **Addition of ammonia derivatives:** Nucleophiles like ammonia and its derivatives H₂N-Z are added to the carbonyl group of aldehydes.



Some N-Substituted Derivatives of Aldehydes and Ketones (>C=N-Z)

Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	>C=NH	Imine
-R	Amine	>C=NR	Substituted imine (Schiff's base)
-OH	Hydroxylamine	>C=N-OH	Oxime
-NH ₂	Hydrazine	>C=N-NH_2	Hydrazone
-HN- 	Phenylhydrazine	>C=N-NH- 	Phenylhydrazone
-HN- 	2,4-Dinitrophenylhydrazine	>C=N-NH- 	2,4-Dinitrophenylhydrazone
-NH-C(=O)-NH ₂	Semicarbazide	$\text{>C=N-NH-C(=O)-NH}_2$	Semicarbazone

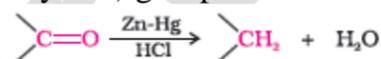
(ii) **Reduction:**

a. **Reduction to alcohols:** When reduced using **sodium borohydride** (NaBH₄) or **lithium aluminium hydride** (LiAlH₄) or H₂ in presence of **Ni, Pd or Pt catalyst** (Catalytic hydrogenation), aldehydes give 1^o alcohols



b. **Reduction to Hydrocarbons:**

Clemmensen reduction: Aldehydes and ketones can be reduced to alkanes on treatment with **zinc amalgam** and **conc. HCl**. During this reaction, the carbonyl group is reduced to CH₂ (methylene) group.

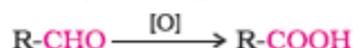


Wolff-Kishner reduction: Carbonyl group can also be reduced to **methylene group**, by treating with **hydrazine** followed by heating with **sodium or potassium hydroxide** in high boiling solvent such as *ethylene glycol*.



(iii) **Oxidation:**

Aldehydes are easily oxidised to **carboxylic acids** on treatment with common oxidising agents like nitric acid, **potassium permanganate**, **potassium dichromate** etc.



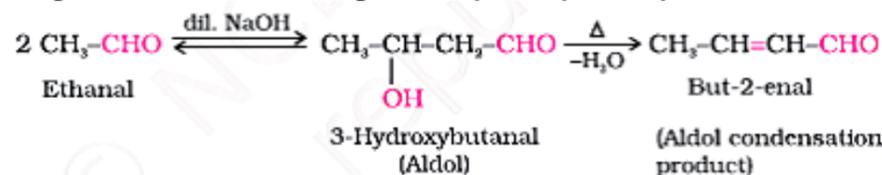
(iv) **Haloform Reaction:**

Aldehydes or ketones having CH₃-CO- group or CH₃-CHOH- group, when treated with **sodium hypohalite** or **halogen** in presence of **NaOH**, yield haloform (CHX₃). During this reaction, the methyl group is converted to haloform.



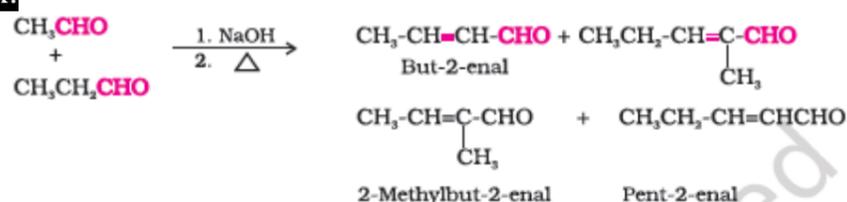
(v) **Aldol condensation Reaction:**

The **α-hydrogens** in aldehydes are acidic. Therefore, aldehydes having at least one **α-hydrogen**, undergo **Aldol condensation** in the presence of a base to give **α-hydroxyaldehydes (aldol)**.



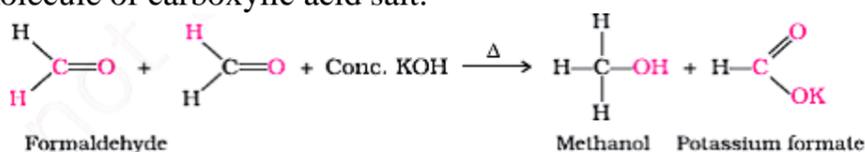
(vi) **Cross aldol condensation:** When aldol condensation is carried out between two different aldehydes or ketones, it gives a mixture of 4 products.

Ex:



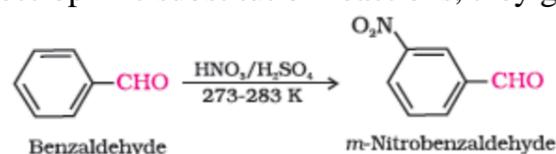
(vii) Cannizzaro reaction

Aldehydes having no α -hydrogen when treated with Conc. alkali (NaOH or KOH) undergo **self oxidation and reduction** (disproportionation) to form one molecule of the alcohol and one molecule of carboxylic acid salt.



(viii) Electrophilic Substitution Reactions:

Aldehydic groups are **meta directing and deactivating**. So on electrophilic substitution reactions, they give meta-derivatives.



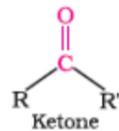
USES

- 1) **40% aqueous solution of Formaldehyde**, known as **formalin** is used to *preserve biological specimens* and to prepare **bakelite**.
- 2) Acetaldehyde is used as a **starting material** in the manufacture of **acetic acid, ethyl acetate, vinyl acetate, polymers and drugs**.
- 3) Benzaldehyde is used in **perfumery** and in **dye** industries.
- 4) Acetone and ethyl methyl ketone are common industrial solvents.
- 5) Many aldehydes and ketones, e.g., *butyraldehyde, vanillin, acetophenone, camphor*, etc. are well known for their odours and flavours.

KETONES

→ **Ketone**: In ketones, the carbonyl group is bonded to two carbon atoms.

General formula

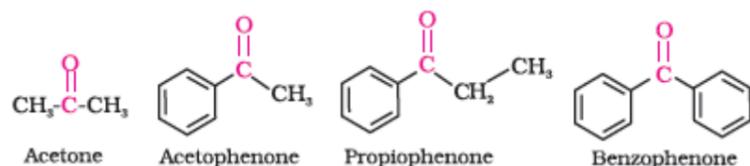


NOMENCLATURE

✚ **Common name**: The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group and by suffixing ketone.

The locations of the substituents are indicated by Greek letters, α , α' , β , β' and so on.

Some ketones have historical common names, **Ex:** acetone (dimethyl ketone).



✚ **IUPAC name**: The IUPAC names of open chain aliphatic ketones are derived from the names of the corresponding alkanes by replacing the ending *-e* with '*-one*'.

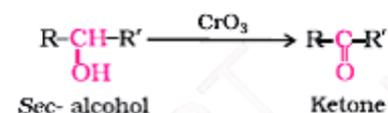
In case of ketones the the longest carbon chain is numbered starting from the carbon of the end nearer to the carbonyl group.

Structure	Common name	IUPAC name
Ketones		
$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ketone	Pentan-2-one
$(\text{CH}_3)_2\text{CHCOCH}(\text{CH}_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α -Methylcyclohexanone	2-Methylcyclohexanone
$(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$	Mesityl oxide	4-Methylpent-3-en-2-one

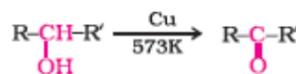
METHODS OF PREPARATION

Ketones are prepared by -

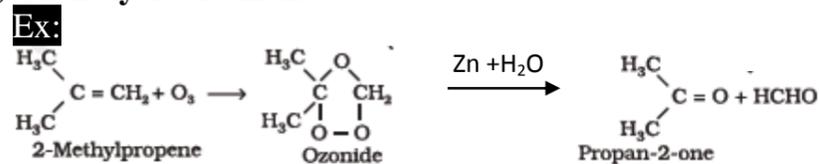
(1) Oxidation of 2° alcohols



(2) Dehydrogenation of 2° alcohols

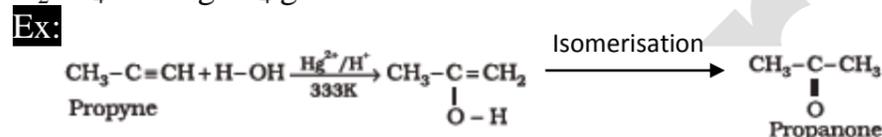


(3) Ozonolysis of alkenes



(4) Hydration of alkynes

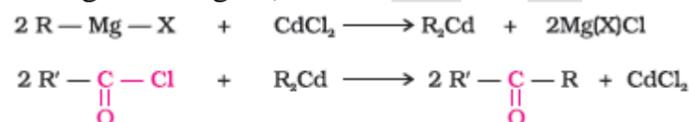
Addition of water to alkynes (except ethyne) in the presence of H_2SO_4 and HgSO_4 give ketones.



(5) Reaction of acyl chloride with dialkylcadmium

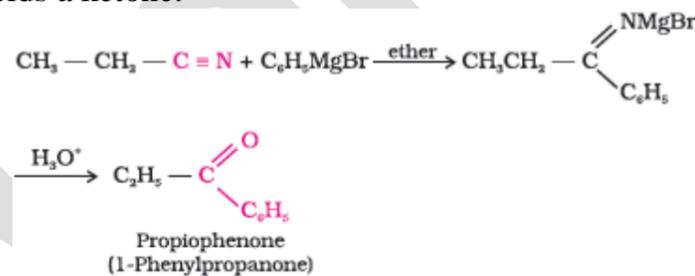
Acid chlorides react with **dialkylcadmium**, give ketones.

(**Dialkyl cadmium** is prepared by the reaction of cadmium chloride with Grignard reagent).



(6) From nitriles:

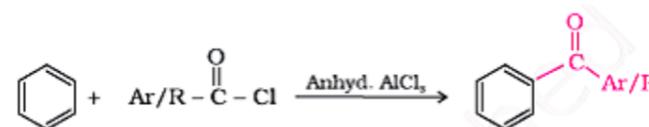
Treating a **nitrile** with **Grignard reagent** followed by hydrolysis yields a ketone.



Aromatic ketones may be prepared by-

(7) Friedel-Crafts acylation of aromatic hydrocarbons

When **benzene** or **substituted benzene** is treated with **acid chloride** in the presence of **anhydrous aluminium chloride**, gives aromatic ketone.



PROPERTIES

Chemical:-

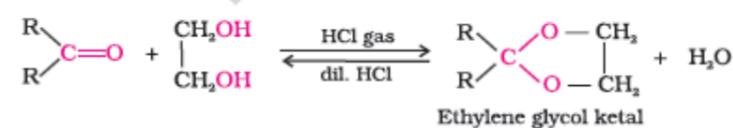
Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons.

- **Sterically**, the presence of two bulky alkyl groups in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes.
- **Electronically**, ketones are less reactive because of the electron releasing nature of the two alkyl groups reduces the electrophilicity of the carbonyl carbon.

CHEMICAL REACTIONS:-

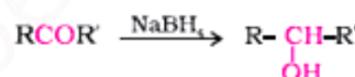
(i) Nucleophilic addition reactions

- a. **Addition of hydrogen cyanide (HCN)** gives cyanohydrins.
- b. **Addition of sodium hydrogensulphite** gives *bisulphite adduct*.
- c. **Addition of Grignard reagents** give 3° alcohols.
- d. **Addition of alcohols** form ketals



(ii) Reduction

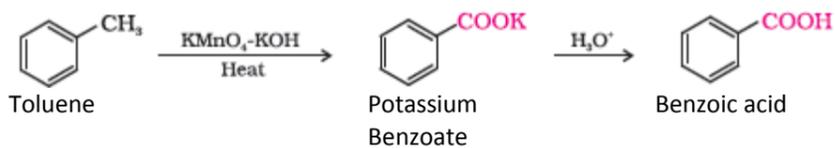
a. **Reduction to alcohols**: Ketones give secondary alcohols.



Aromatic carboxylic acids may be prepared by-

(6) Side-chain oxidation of alkylbenzenes

Oxidation of alkyl benzenes with **chromic acid** or acidic or alkaline **potassium permanganate** gives aromatic carboxylic acids. 1° and 2° alkyl groups are oxidised in this manner while 3° group is not affected.



PROPERTIES

Physical:-

- ✓ **Physical state:** Aliphatic carboxylic acids upto 9 C-atoms are **colourless liquids** with **unpleasant smell**.

The higher acids are **waxy solids** and are **odourless**.

- ✓ **Boiling point:** Carboxylic acids are **higher boiling liquids** than aldehydes, ketones and alcohols of comparable molecular masses.

Reason:- Presence of intermolecular H-bonding.

- ✓ **Solubility:** The **first 4 acids are soluble in water** and the **solubility decreases** with increasing number of C- atoms.

Reason:- Simple acids have the ability to **form H-bonds with water** while **higher acids** are insoluble in water due to the increased **hydrophobic interaction** of hydrocarbon part.

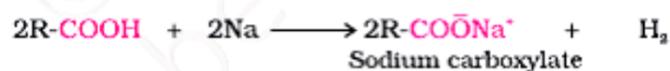
Carboxylic acids are also **soluble in less polar organic solvents** like benzene, ether, alcohol, chloroform, etc.

Chemical:-

- **Acidity:** Carboxylic acids are **more acidic** than alcohols and most of simple phenols. (For details, see text, page 372)

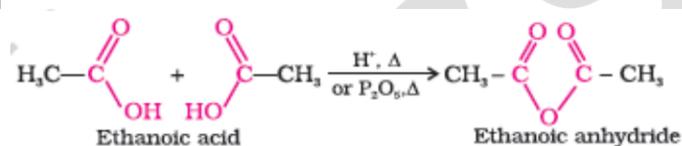
CHEMICAL REACTIONS:-

- (i) **Reactions with metals and alkalis:** Like alcohols and phenols, carboxylic acids react with electropositive metals and liberate H- gas.

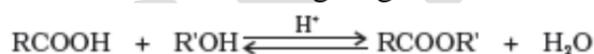


- (ii) **Reactions with mineral acids:** Carboxylic acids on heating with mineral acids like H_2SO_4 or with P_2O_5 undergo dehydration to give **acid anhydrides**.

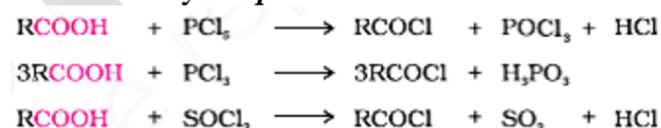
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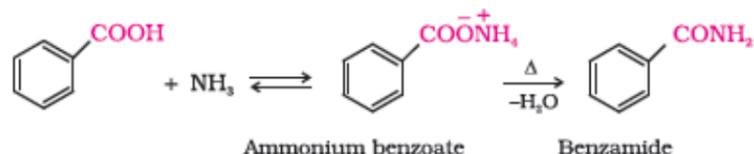
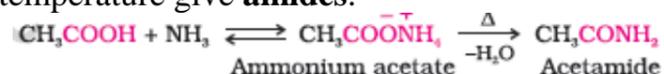
- (iii) **Reaction with alcohol (Esterification):** Carboxylic acids when heated with alcohols or phenols in the presence of a mineral acid like conc. H_2SO_4 or HCl gas, gives esters.



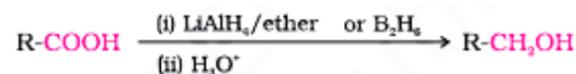
- (iv) **Reactions with PCl_3 , PCl_5 and SOCl_2 :** Carboxylic acids on treating with PCl_3 , PCl_5 or SOCl_2 , gives **acid chlorides**. Reaction with **thionyl chloride** (SOCl_2) is preferred because the byproducts are gases and are easily escaped from the reaction mixture so that yield **pure acid chloride**.



- (v) **Reaction with ammonia:** Carboxylic acids react with ammonia to give **ammonium salts** which on further heating at high temperature give **amides**.

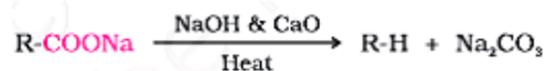


- (vi) **Reduction:** Carboxylic acids when reduced with **lithium aluminium hydride** or with **diborane** in ether solution, 1° alcohols are formed.

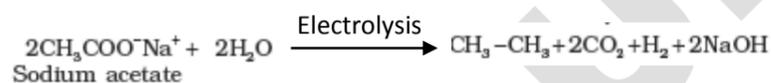


- (vii) **Decarboxylation:**

- a. When **sodium salts** of carboxylic acid are heated with **sodalime** (a mixture of NaOH and CaO), they undergo decarboxylation to form alkanes.

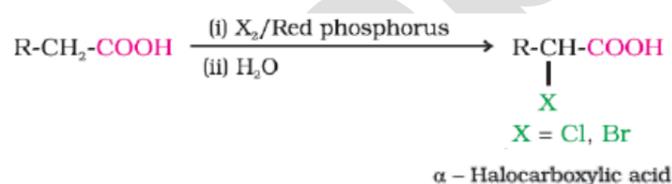


- b. **Kolbe's electrolysis:** When an aqueous solution of **sodium** or **potassium salt** of carboxylic acid is electrolysed, it produce alkanes having twice the number of C-atoms that present in the alkyl group of the acid.



- (viii) **Halogenation [Hell-Volhard Zelinsky reaction]**

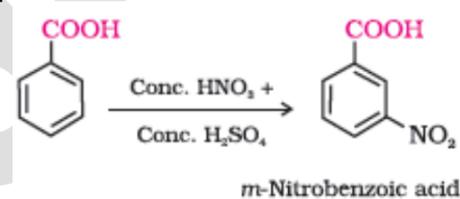
Carboxylic acids undergo **α -halogenation** with Cl_2 and Br_2 in the presence of **red phosphorus**, gives **α -halocarboxylic acids**.



- (ix) **Electrophilic substitution reactions:**

The $-\text{COOH}$ group is a deactivating group and meta-directing. So on electrophilic substitution reactions, they yield meta derivatives.

Ex:



USES

- 1) **Methanoic acid** (formic acid) is used in rubber, textile, dyeing, leather and electroplating industries.
- 2) **Ethanoic acid** (acetic acid) is used as solvent and as vinegar in food industry.
- 3) **Hexanedioic acid** (adipic acid) is used in the manufacture of nylon-6, 6.
- 4) Esters of **benzoic acid** are used in perfumery.
- 5) **Sodium benzoate** is used as a food preservative.
- 6) **Higher fatty acids** are used for the manufacture of soaps and detergents.