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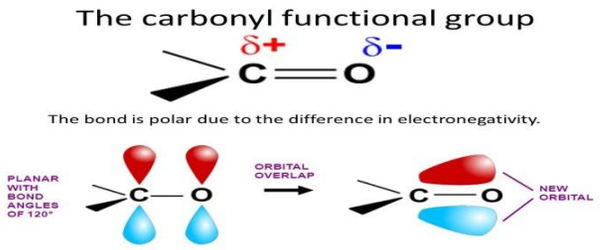
ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

- Aldehydes, ketones, carboxylic acids and their derivatives are commonly called as carbonyl compounds.

Nature of Carbonyl Group

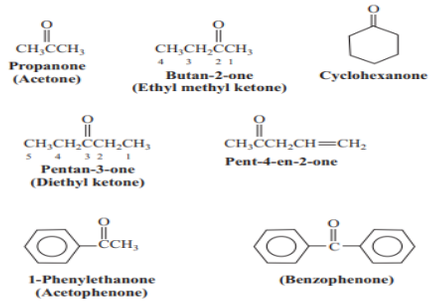
- The carbon and oxygen of the carbonyl group are Sp^2 hybridised and the carbonyl double bond contains one o-bond and one π-bond.



Nomenclature of Aldehydes and Ketones

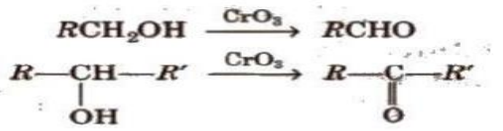
Structure	IUPAC (root names from alkanes)		Common (root names from common names of related carboxylic acids)	
	root	methane	root	formic acid
	aldehyde name	methanal	aldehyde name	formaldehyde
	root	ethane	root	acetic acid
	aldehyde name	ethanal	aldehyde name	acetaldehyde
	root	benzenecarboxylic acid	root	benzoic acid
	aldehyde name	benzenecarbaldehyde	aldehyde name	benzaldehyde

- Ketones are named as alkanones in the IUPAC namenclature. Their names are obtained by replacing final -e in the name of alkane by -one.

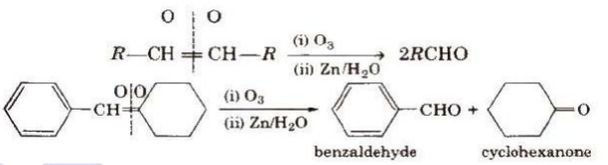


Preparation of Aldehydes and Ketones

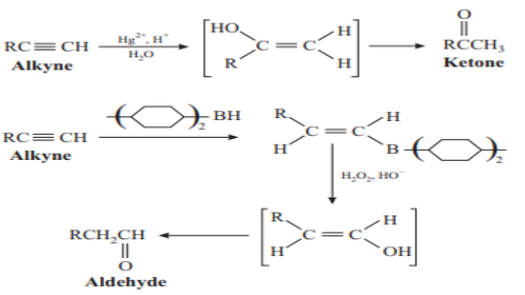
1. Oxidation of Primary and Secondary Alcohols



2. Ozonolysis of Alkenes

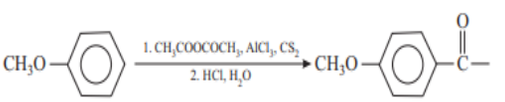


3. Hydration of Alkynes



4. Friedal-Crafts Acylation

- Aromatic ketones can be prepared by Friedel-Crafts acylation (alkanoylation) reaction.



Physical Properties

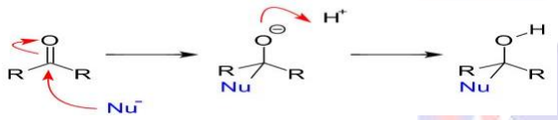
- **Lower members** have unpleasent smell and up to 11 members they are liquids.
- **Solubility:** Aldehydes are more polar in nature.As we know, in ketones two alkyl

groups are present.

- **Boiling points:** Boiling point is always more for polar compounds. ketones have higher boiling points than aldehyde because of more polarity .

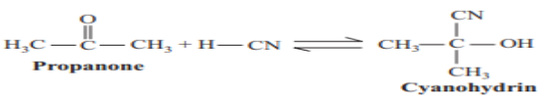
Reactions of Aldehydes and Ketones

- Aldehydes and ketones undergo nucleophilic addition reactions with monohydric alcohols to yield hemiacetals. In this reaction, the carbonyl oxygen is protonated before the nucleophilic attack is carried out by the alcohol. The nucleophilic alcohol is now deprotonated to form the hemiacetal.

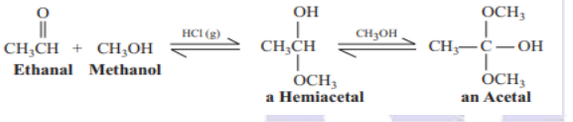


1. Formation of Cyanohydrins

Carbonyl compounds react with hydrogen cyanide to yield ***cyanohydrins***.

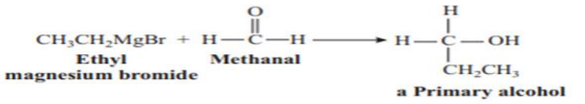


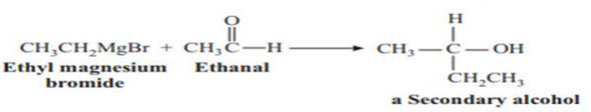
2. Formation of Hemiacetals

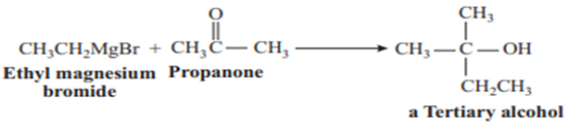


3. Formation of Alcohols

Grignard reagents (RMgX) react with aldehydes and ketones to give alcohols.

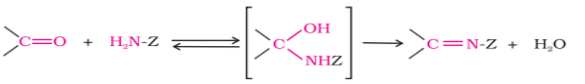






B. Addition-Elimination or Condensation Reactions

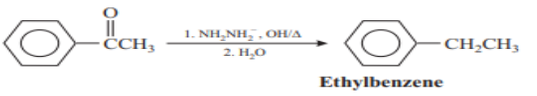
1. Reaction with Ammonia and its Derivatives



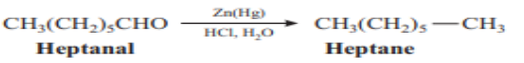
Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$, etc.

C. De-oxygenation Reactions

1. Wolff-Kishner Reduction



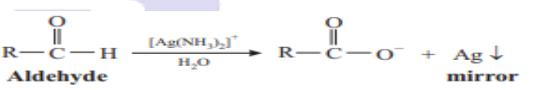
2. Clemmensen Reduction



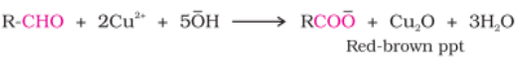
D. Oxidation of Aldehydes

- Unlike ketones, aldehydes can be easily oxidised to carboxylic acids using a variety of oxidising agents.

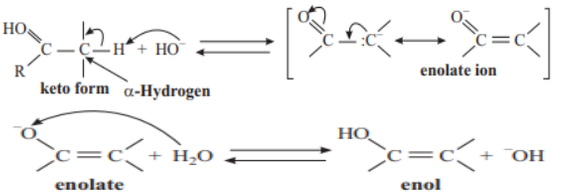
1. Tollens' test



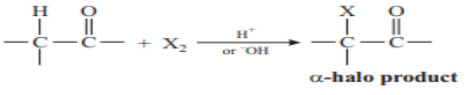
2. Fehling's test



E. Reactions at α-Hydrogen



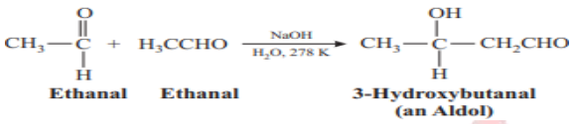
1. Halogenation



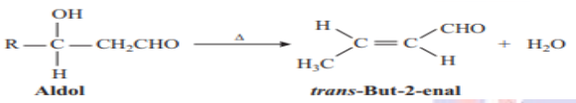
$(X_2 = Cl_2, Br_2 \text{ or } I_2)$

2. Aldol Condensation

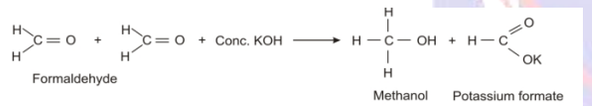
- Aldehydes having α − hydrogen atom on reaction with dil. NaOH give aldols.

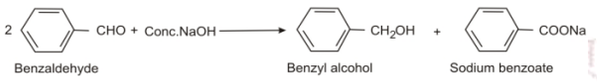


- The aldol addition product on heating undergoes dehydration to give an α, β–unsaturated aldehyde which is a condensation product.



3. Cannizzaro Reaction

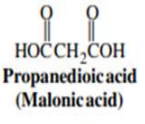


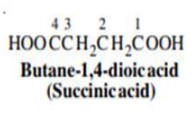


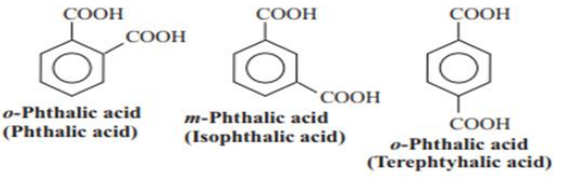
CARBOXYLIC ACIDS

- Carbon compounds containing a carboxyl functional group, –COOH are called ***carboxylic acids***. The carboxyl group consists of a carbonyl group attached to a hydroxyl group, hence its name carboxyl. Carboxylic acids may be aliphatic (RCOOH) or aromatic (ArCOOH) depending on the group, alkyl or aryl, attached to carboxylic carbon.

Nomenclature



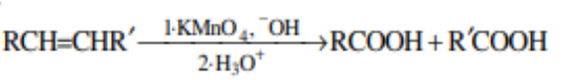




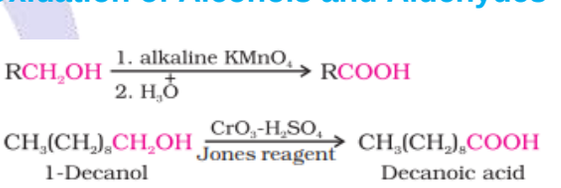
- Their IUPAC names have been derived from the corresponding alkanes by replacing the letter 'li of the alkane with 'oic' and adding suffix 'acid' at the end, thus, monocarboxylic acids are called alkanoic acids.

Preparation of Carboxylic Acids

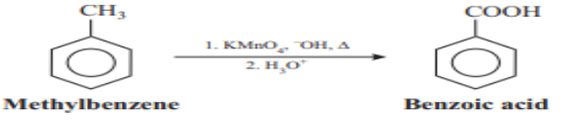
1. Oxidation of Alkenes



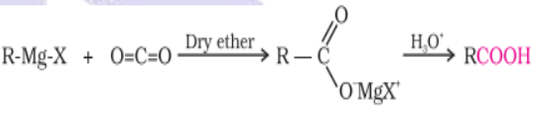
2. Oxidation of Alcohols and Aldehydes



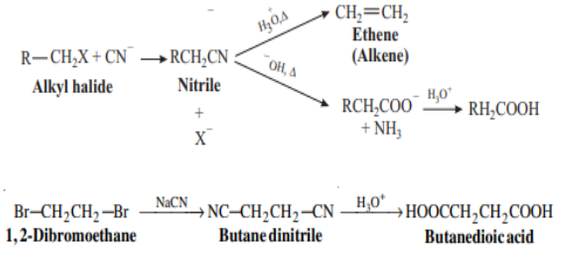
3. Oxidation of Alkylbenzenes



4. Carbonation of Grignard Reagents



5. Hydrolysis of Nitriles and Cyanohydrins



Structure and Physical Properties

- Similar to the aldehydes and ketones, the carboxyl carbon atom is sp^2 hybridised.

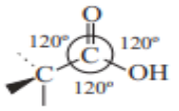
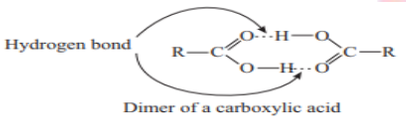


Fig. 27.3: Structure of the carboxyl group

1. Solubility: As the size of the alkyl group increases, the solubility of the acid decreases and polarity is reduced.

2. Boiling points: Due to intramolecular hydrogen bonding dimerization of acid takes place and boiling point of carboxylic acid is higher than expected.



Dimer of a carboxylic acid

3. The melting points of aliphatic carboxylic acids do not show a regular pattern. The first ten members show an alteration effect, i.e. the melting point of an acid containing even number of carbon atoms is higher than the next lower and next higher homologues containing odd number of carbon atoms.

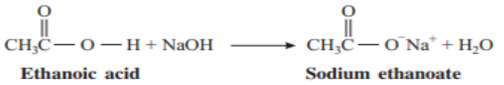
Acidity of Carboxylic Acids

- Carboxylic acids are acidic in nature. They dissociate in water according to following equilibrium to give a proton and the carboxylate ion.

Carboxylic acid — Carboxylate ion

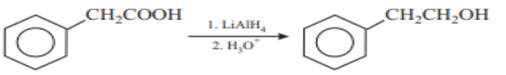
Reactions of Carboxylic Acids

1. Formation of Salts



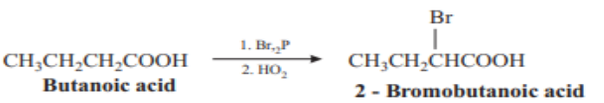
Ethanoic acid — Sodium ethanoate

2. Reduction of Carboxylic Acids



Phenylethanoic acid — 2-Phenylethanol

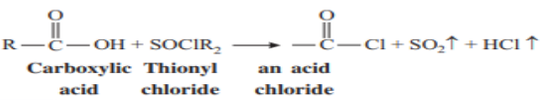
3. Hell-Volhard-Zelinski Reaction



Butanoic acid — 2 - Bromobutanoic acid

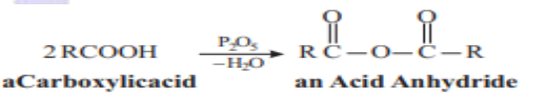
4. Synthesis of Acid Derivatives

(i) Formation of Acid Chlorides



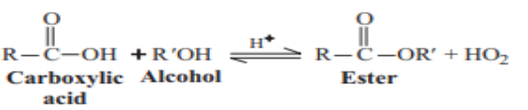
Carboxylic acid — Thionyl chloride — an acid chloride

(ii) Formation of Acid Anhydrides



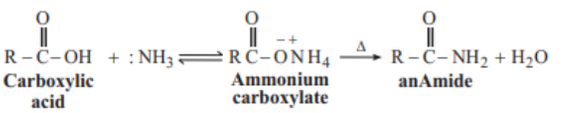
aCarboxylicacid — an Acid Anhydride

(iii) Formation of Esters



Carboxylic acid — Alcohol — Ester

(iv) Formation of Amides

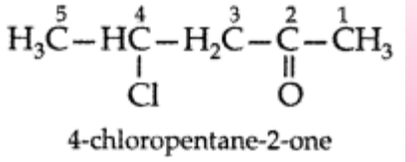


Carboxylic acid — Ammonium carboxylate — anAmide

Test Yourself

Question: Draw the structure of 4-chloropentan-2-one.

Answer:



4-chloropentane-2-one

Check Yourself

1. The oxidation of toluene to benzal-dehyde by chromyl, chloride is called

(A) Etard reaction

(B) Riemer-Tiemann reaction

(C) Wurtz reaction

(D) Cannizzaro's reaction

2. Which of the following will not give aldol condensation?

(A) Phenyl acetaldehyde

(B) 2-Methylpentanal

(C) Benzaldehyde

(D) 1-Phenylpropanone

3. Which of the following compounds does not react with $NaHSO_3$?

(A) HCHO (B) $C_6H_5COCH_3$

(C) CH_3COCH_3 (D) CH_3CHO

4. The product of hydrolysis of ozonide of 1-butene are

(A) ethanol only

(B) ethanal and methanal

(C) propanal and methanal

(D) methanal only

5. Benzoyl Chloride on reduction with H_2/Pd-$BaSO_4$ produces

(A) benzoic acid

(B) benzyl alochol

(C) benzoyl sulphate

(D) benzaldehyde

Stretch Yourself

1. Give a chemical test to distinguish between Benzoic acid and Phenol.
2. Formaldehyde does not take part in Aldol condensation. Why?
3. Aldehydes and Ketones have lower boiling points than corresponding alcohols. Why ?
4. Give the structure and IUPAC name of the product formed when propanone is reacted with methylmagnesium bromide followed by hydrolysis.
5. Rearrange the following compounds in the increasing order of their boiling points:

$CH_3 - CHO$, $CH_3 - CH_2 - OH$, $CH_3 - CH_2 -$

Answers

Check Yourself

Answer: 1(A); 2(C); 3(B); 4(C); 5(D)

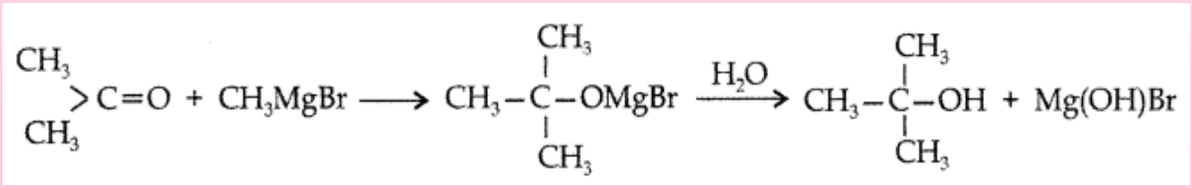
Stretch Yourself

1. Benzoic acid forms a brisk effervescence with NaHCO3 solution but phenol does not respond to this test.

2. Formaldehyde does not contain a-hydrogen atom. Therefore it does not take part in aldol condensation.

3. It is due to weak molecular association in aldehydes and ketones arising out of the dipole- dipole interactions.

4.



IUPAC name: 2-methylpropan-2-ol.

5.