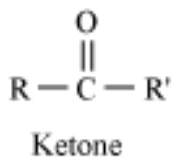
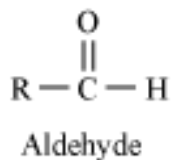


Aldehydes, Ketones and Carboxylic Acids

Nomenclature of aldehydes and ketones –

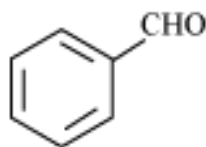


Aldehydes:

Often called by their common names instead of IUPAC names.



Acetaldehyde

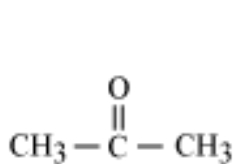


Benzaldehyde

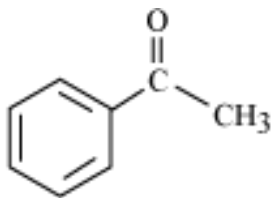
Ketones:

Derived by naming two alkyl or aryl groups bonded to the carbonyl group

Alkyl phenyl ketones are usually named by adding the acyl group as prefix to phenone.



Acetone



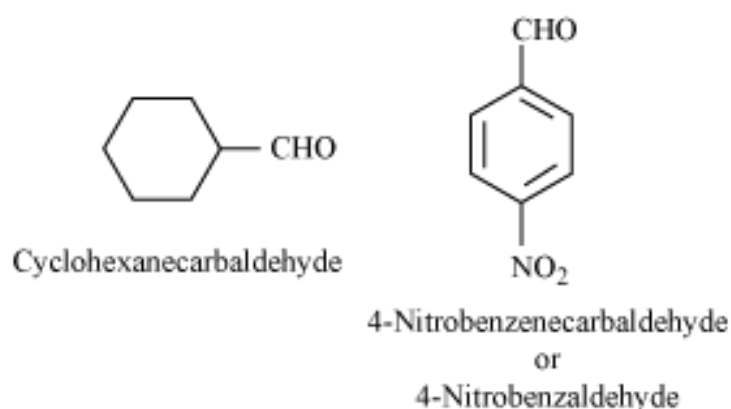
Acetophenone

IUPAC Nomenclature

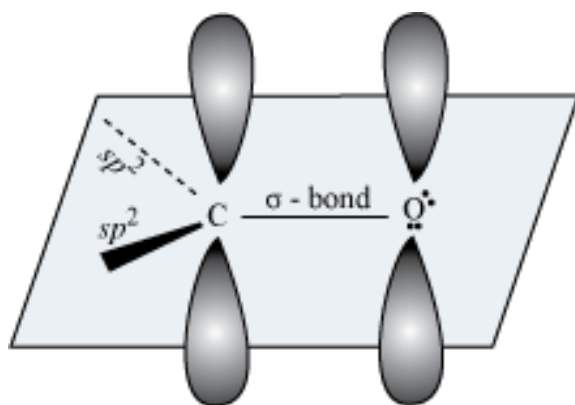
(i) For open-chain aliphatic aldehydes and ketones, IUPAC names are derived from the names of the corresponding alkanes by replacing the ending ‘-e’ with ‘-al’ and ‘-one’ respectively.

- (ii) In the case of aldehydes, the longest chain is numbered starting from the carbon of the aldehydic group.
- (iii) In the case of ketones, the numbering begins from the end nearer to the carbonyl group.
- (iv) Substituents are prefixed in the alphabetical order along with the numerals indicating their positions in the carbon chain.
- (v) Same rule is applicable to cyclic ketones.
- (vi) If the aldehydic group is attached to a ring, then the suffix carbaldehyde is added to the full name of cyclohexane.

Example:



Structure of the carbonyl group –The carbonyl carbon atom is sp^2 hybridised and forms three bonds and one π bond.



C=O double bond is polarised due to higher electronegativity of oxygen relative to carbon.

Carbonyl carbon – an electrophile (Lewis acid)

Carbonyl oxygen – a nucleophile (Lewis base)



Preparation of aldehydes and ketones:

(I) By oxidation of alcohols –

(i) Primary alcohols $\xrightarrow{[O]}$ Aldehydes

(ii) Secondary alcohols $\xrightarrow{[O]}$ Ketones

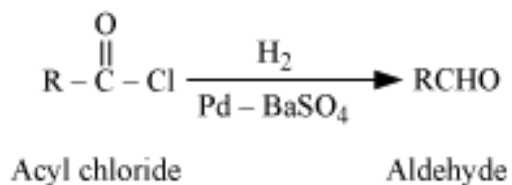
(II) By dehydrogenation of alcohols

(i) Primary alcohols $\xrightarrow{\text{Ag or Cu}}$ Aldehydes

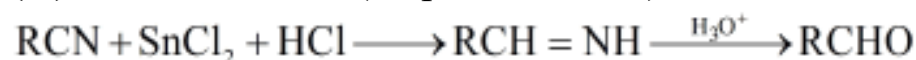
(ii) Secondary alcohols $\xrightarrow{\text{Ag or Cu}}$ Ketones

Preparation of aldehydes:

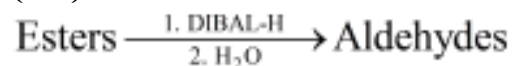
(I) From acyl chloride – (Rosenmund reduction)



(II) From nitriles – (Stephen reaction)

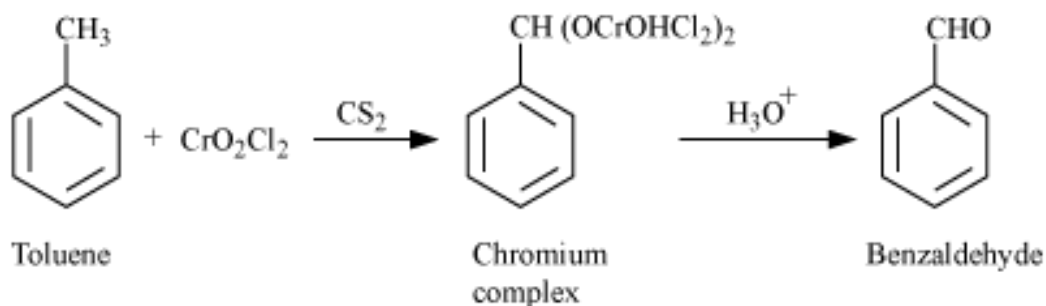


(III) From esters –

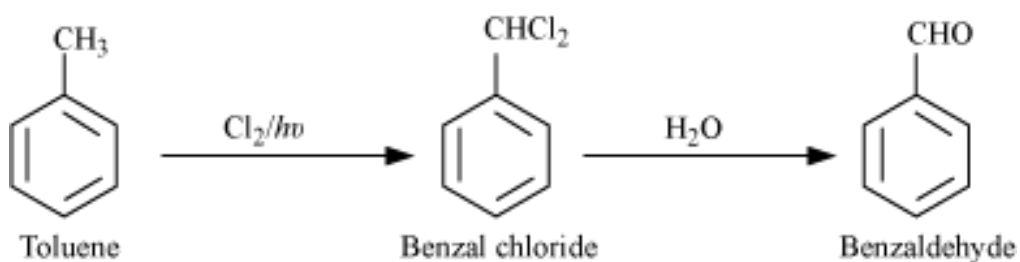


(IV) From hydrocarbons –

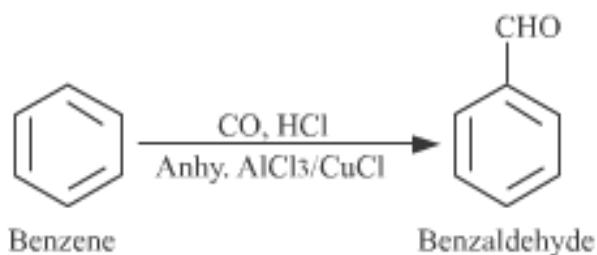
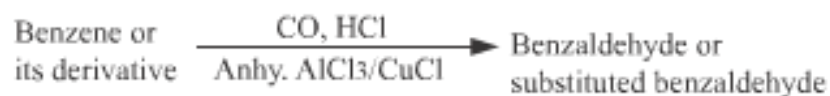
By oxidation of methylbenzene (toluene) (Etard reaction)



By side-chain chlorination, followed by hydrolysis

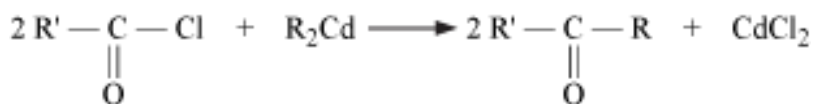


Gatterman–Koch reaction

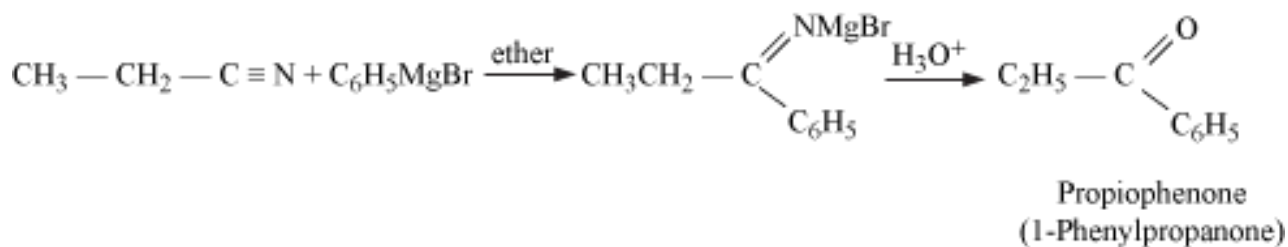


Preparation of ketones:

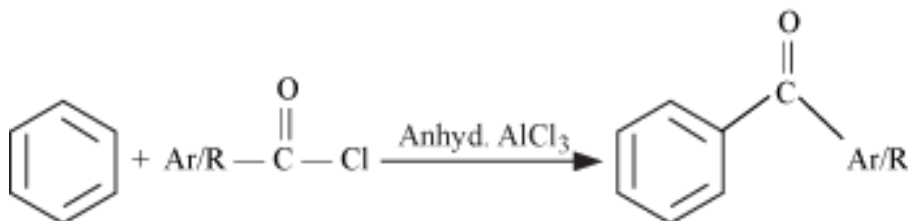
(I) From acyl chlorides –



(II) From nitriles –



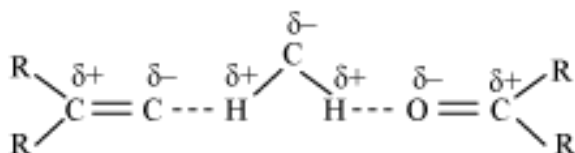
(III) From benzene or substituted benzene – (Friedel–Crafts acylation reaction)



Physical properties of aldehydes and ketones:

Boiling points:

- (i) Due to dipole–dipole interactions in aldehydes and ketones, they have higher boiling points than hydrocarbons and ethers of comparable molecular masses.
- (ii) Due to the presence of intermolecular H-bonding in alcohols, the boiling points of aldehydes and ketones are higher than those of alcohols of comparable molecular masses.



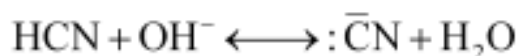
Solubility: The solubility of aldehydes and ketones in water decreases with increase in the length of the alkyl chain.

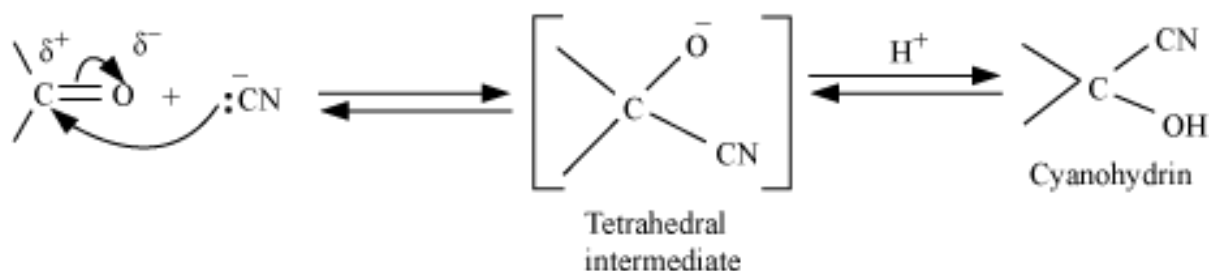
Chemical reactions of aldehydes and ketones:

(A) Nucleophilic addition reactions –

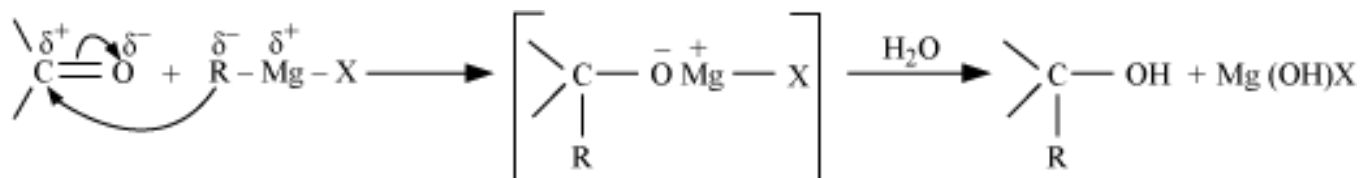
Reactivity: Due to steric and electronic reasons, aldehydes are more reactive than ketones towards nucleophilic addition reactions.

(i) Addition of HCN

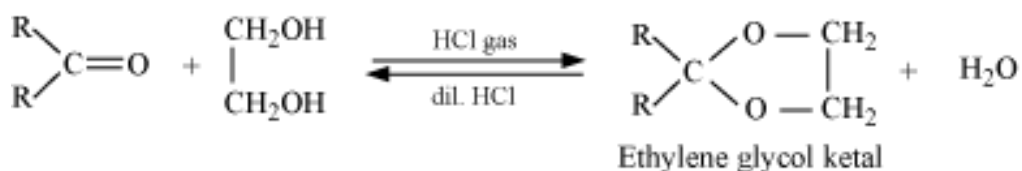
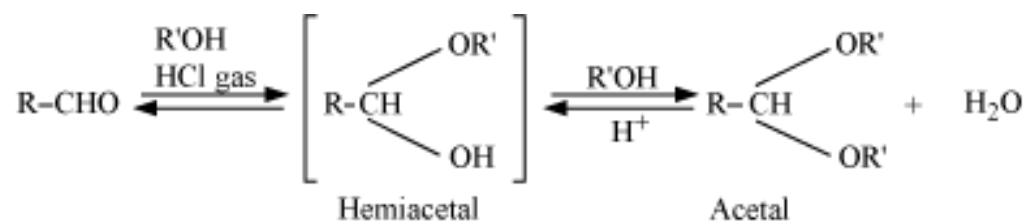




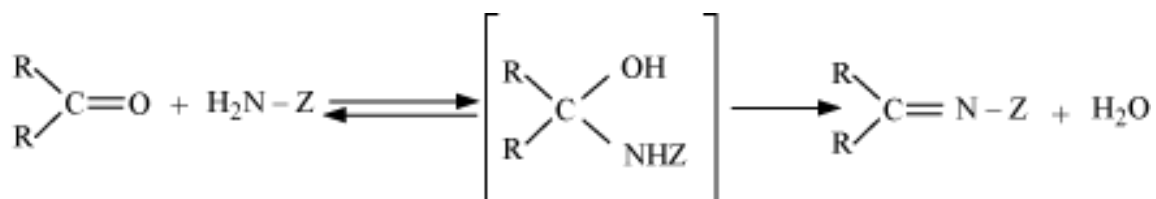
(ii) Addition of Grignard reagents



(iii) Addition of alcohols



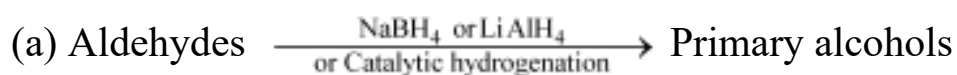
(iv) Addition of ammonia and its derivatives



Z = alkyl, aryl, OH, NH₃, C₆H₅NH, NHCONH₂, etc

(B) Reduction –

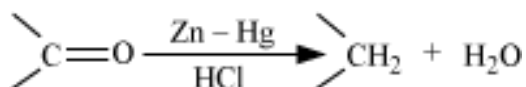
(i) Reduction to alcohols



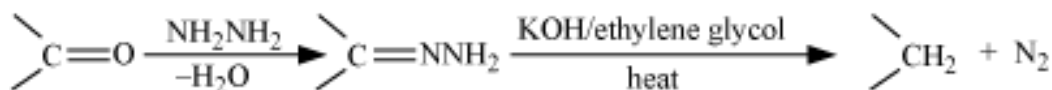
(b) Ketones $\xrightarrow[\text{or Catalytic hydrogenation}]{\text{NaBH}_4 \text{ or LiAlH}_4}$ Secondary alcohols

(ii) Reduction to hydrocarbons

(a) Clemmenson reduction

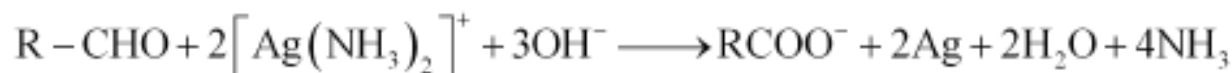


(b) Wolf-Kishner reduction

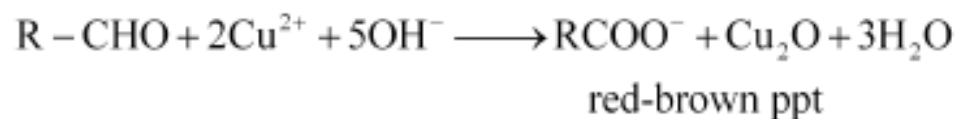


(C) **Oxidation:** Tests to distinguish between aldehydes and ketones –

(i) **Tollen's test:** Tollen's reagent is Ammoniac silver nitrate solution. Ketones do not respond to this test.

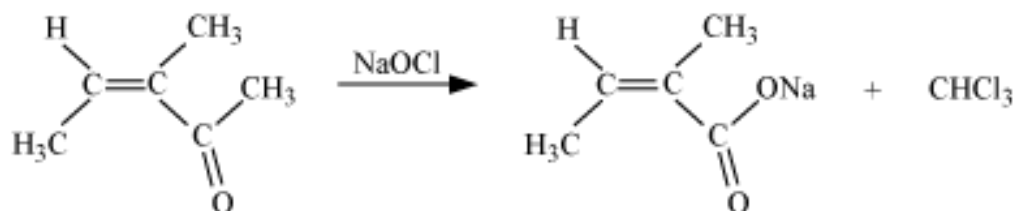
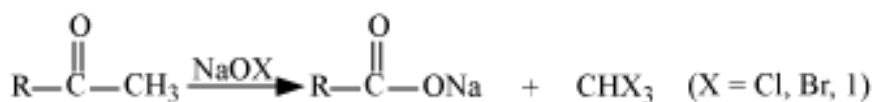


(ii) **Fehling's test:** Ketones as well as aromatic aldehydes do not respond to this test.



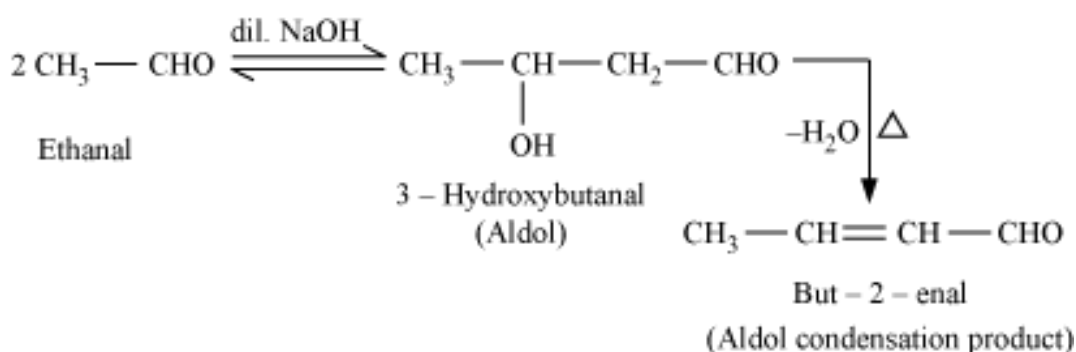
(iii) Oxidation by haloform reaction –

Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom undergo this reaction.

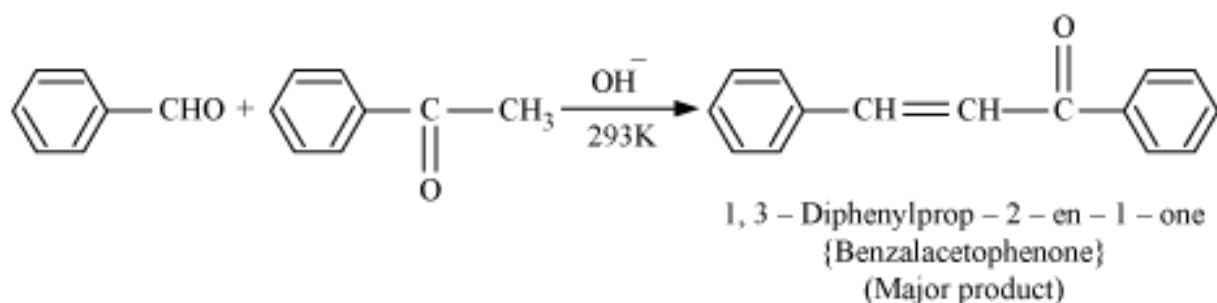


Reactions due to α -hydrogen –

Aldol condensation (aldol reaction): Aldehydes and ketones having at least one α -hydrogen undergo this reaction.



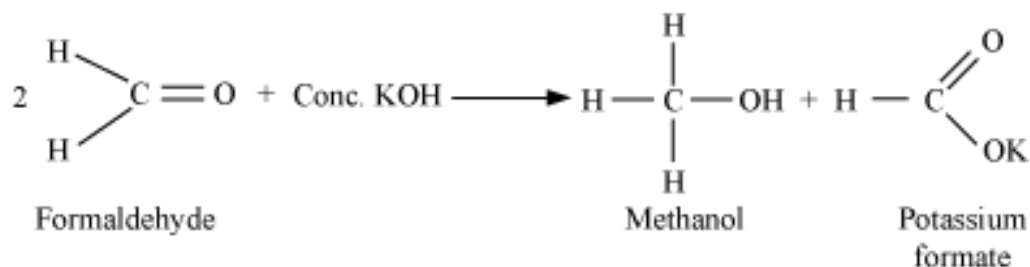
Cross aldol condensation: Aldol condensation between two different aldehydes and/or ketones



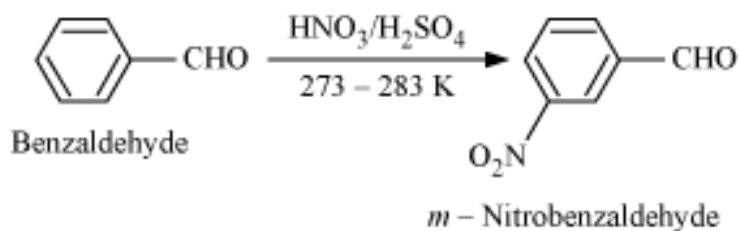
If both of them contain α -hydrogen, then they give a mixture of four products.

Other reactions –

Cannizzaro reaction: Aldehydes that do not have an α -hydrogen atom undergo this reaction.



Electrophilic substitution reaction:



Uses of Aldehydes and Ketones

- (i) As solvents.
- (ii) As starting materials and reagents for the synthesis of other products.
- (iii) Acetaldehyde – In the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.
- (iv) Benzaldehyde – In perfumery and in dye industries.
- (v) Butyraldehyde, vanillin, camphor, etc., are well known for their odours and flavours.
- (vi) Acetone and ethyl methyl ketone – Common industrial solvents.

Nomenclature

In the IUPAC system, aliphatic carboxylic acids are named as follows:

- (i) By replacing the ending ‘– e’ in the name of the corresponding alkane with ‘– oic acid’
- (ii) Carboxylic carbon is numbered one.

(iii) If more than one carboxyl groups are present, then the ending ‘-e’ of the alkane is retained.

(iv) The number of carboxyl groups is indicated by adding prefix, *d*, tri, etc. to the term ‘*oic*’.

For example:

(a) CH_3COOH :

Common name: Acetic acid

IUPAC name: Ethanoic acid

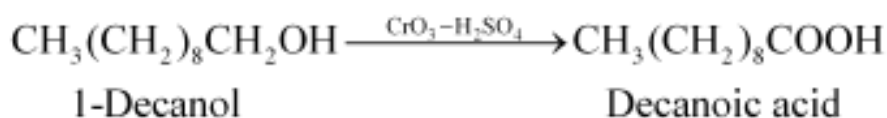
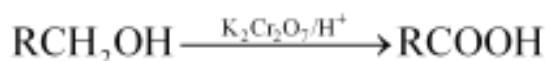
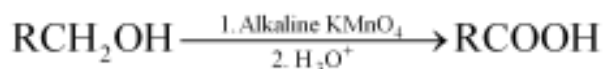
(b) $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$:

Common name: Adipic acid

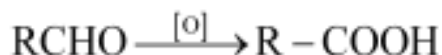
IUPAC name: Hexanedioic acid

Methods of Preparation of Carboxylic Acid

(i) From primary alcohols



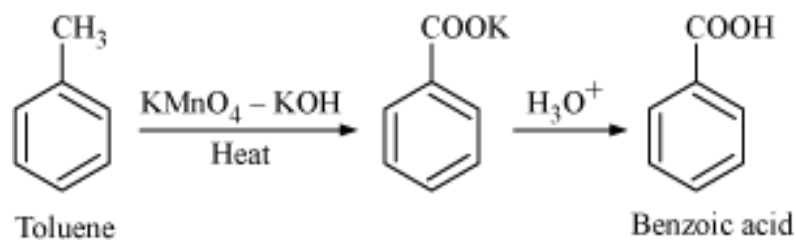
(ii) From primary aldehydes



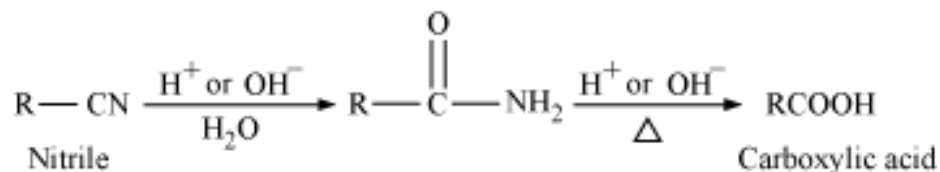
Oxidising agents – HNO_3 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$

Mild oxidising agents – Tollen’s reagent and Fehling’s reagent

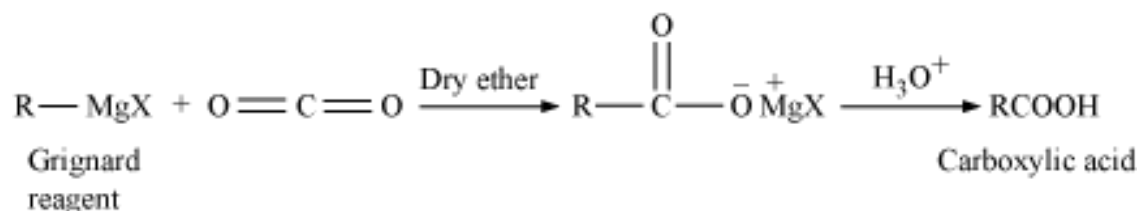
(iii) From alkyl benzenes



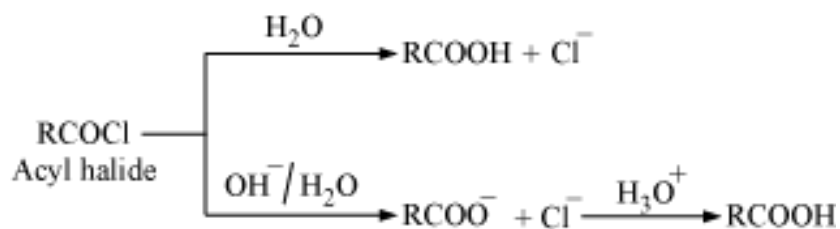
(iv) From nitriles and amides



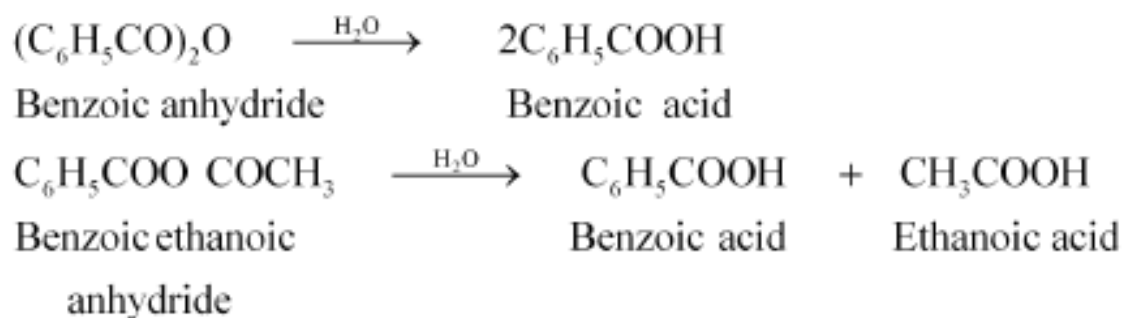
(v) From Grignard reagents



(vi) From acyl halides

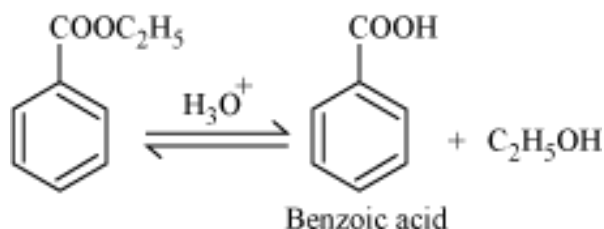


(vii) From acyl anhydrides

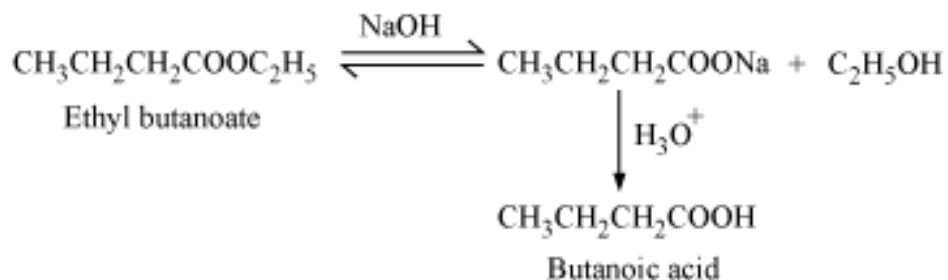


(viii) From esters:

Acidic hydrolysis:



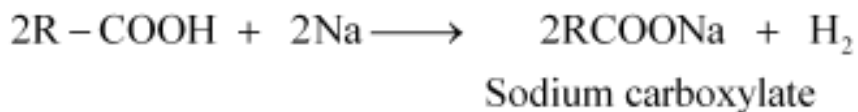
Basic hydrolysis:



Chemical reactions:

(I) Reactions that involve cleavage of O–H bond: Acidity

(a) Reactions with metals and alkalies

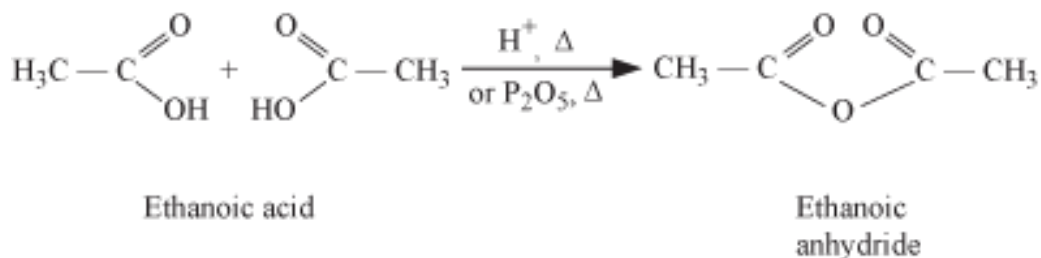


(b) Carboxylic acids are more acidic than phenols because the carboxylate ion is more stable than phenoxide ion.

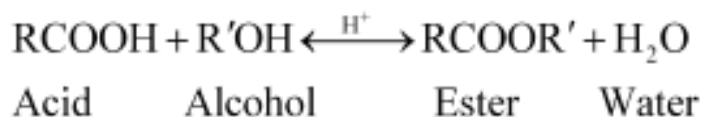
(c) Electron-withdrawing groups increase the acidity of carboxylic acid while electron-donating groups decrease the acidity.

(II) Reactions that involve cleavage of C–OH bond

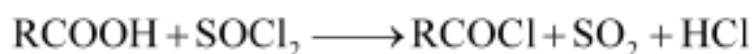
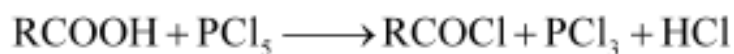
(a) Formation of anhydride



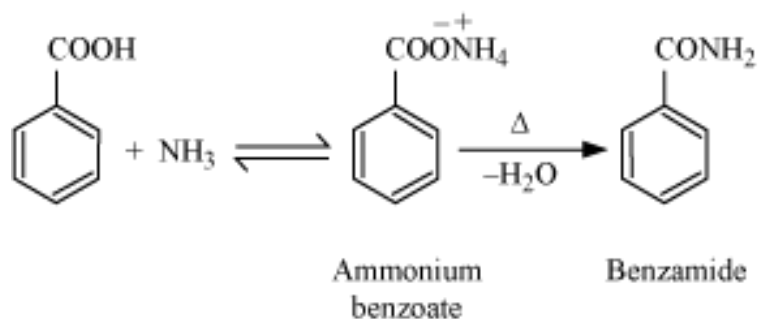
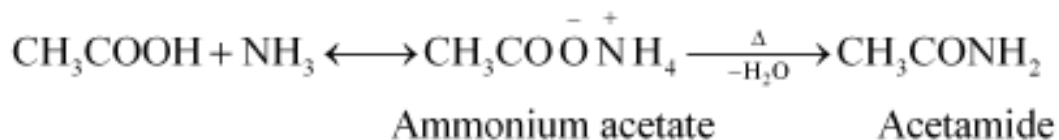
(b) Esterification: Catalyst Conc. H_2SO_4 or HCl gas



(c) Reactions with PCl_5 , PCl_3 , and SOCl_2

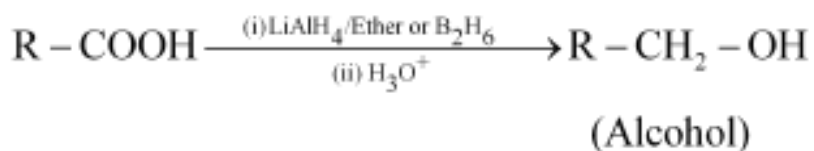


(d) Reaction with ammonia

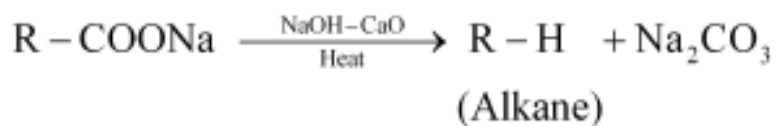


(iii) Reactions that involve $-\text{COOH}$ group

(a) Reduction



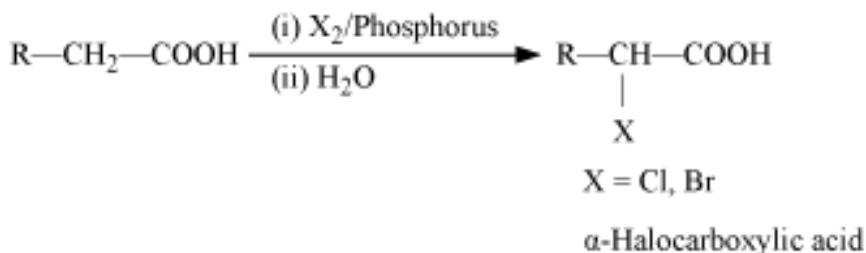
(b) De-carboxylation



(c) Substitution reactions in the hydrocarbon part

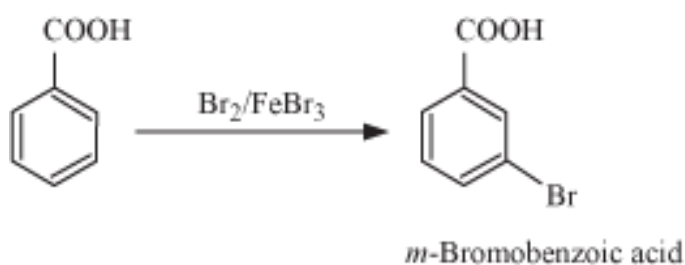
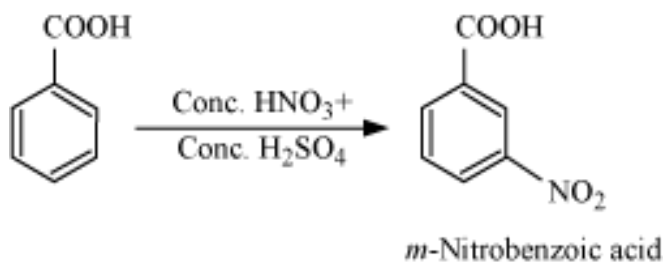
(d) Halogenations

(i) Hell-Volhard-Zelinsky reaction



Carboxylic acids having an α -hydrogen undergo this reaction.

(ii) Ring substitution



Uses of Carboxylic Acids

(i) Methanoic acid – In rubber, textile, dyeing, leather and electroplating industries

(ii) Ethanoic acid – As a solvent and as a vinegar in food industry

(iii) Hexanoic acid – In the manufacture of nylon-6, 6

(iv) Higher fatty acids – For the manufacture of soaps and detergents

(v) Esters of benzoic acid – In perfumery

(vi) Sodium benzoate – As a food preservative