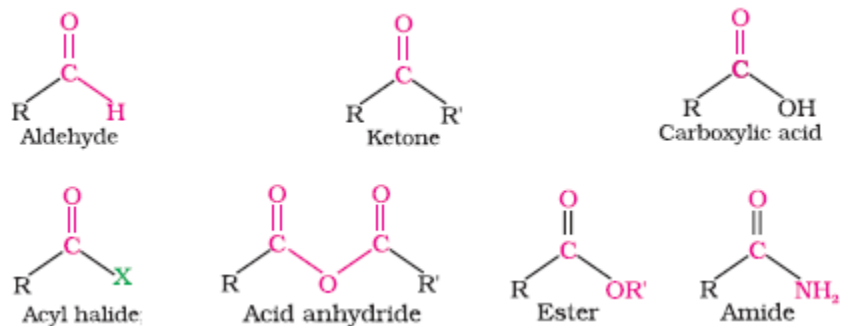


Chapter- 12: Aldehydes, Ketones and Carboxylic Acid

1. Carbonyl Group: The functional group $>C=O$ is called carbonyl group. Organic compounds containing carbonyl group are may be Aldehydes, ketones or carboxylic acids and their derivatives like as

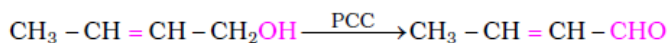
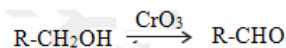
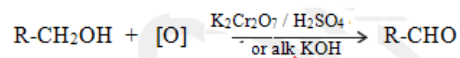


2. Common and IUPAC name of some Aldehydes and Ketones:

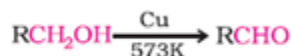
Structure	Common name	IUPAC name
Aldehydes		
HCHO	Formaldehyde	Methanal
CH ₃ CHO	Acetaldehyde	Ethanal
(CH ₃) ₂ CHCHO	Isobutyraldehyde	2-Methylpropanal
	γ -Methylcyclohexane	3-Methylcyclohexanecarbaldehyde
CH ₃ CH(OCH ₃)CHO	α -Methoxypropionaldehyde	2-Methoxypropanal
CH ₃ CH ₂ CH ₂ CH ₂ CHO	Valeraldehyde	Pentanal
CH ₂ =CHCHO	Acrolein	Prop-2-enal
	Phthalaldehyde	Benzene-1,2-dicarbaldehyde
	<i>m</i> -Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
Ketones		
CH ₃ COCH ₂ CH ₂ CH ₃	Methyl <i>n</i> -propyl ketone	Pentan-2-one
(CH ₃) ₂ CHCOCH(CH ₃) ₂	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α -Methylcyclohexanone	2-Methylcyclohexanone
(CH ₃) ₂ C=CHCOCH ₃	Mesityl oxide	4-Methylpent-3-en-2-one

3. Preparation of Aldehydes

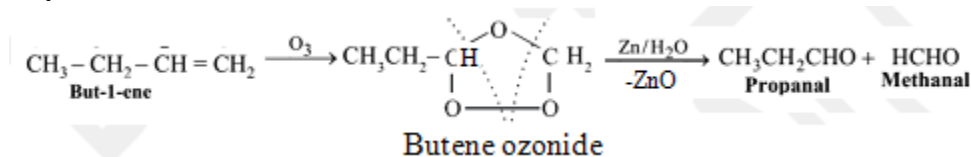
1) By Oxidation of Primary Alcohols:



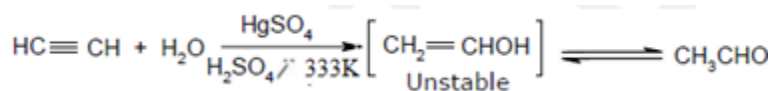
2) By Dehydrogenation of Primary Alcohols:



3) By Ozonolysis of Alkenes:

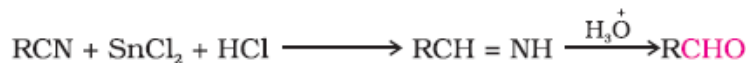


4) By Hydration of Alkynes:

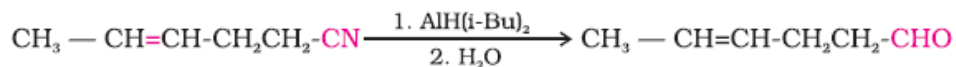
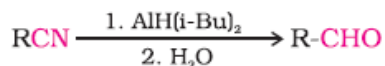


5) By Reduction of Nitriles:

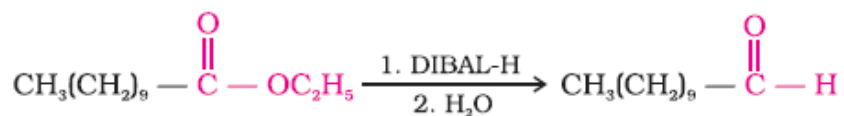
i) **Stephen Reaction:** By reduction of nitrile, it gives imine, which on hydrolysis gives corresponding aldehyde.



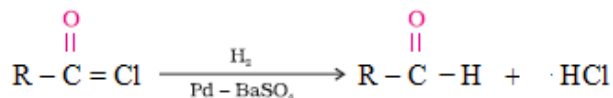
ii) Nitriles are selectively reduced by DIBAL-H (Di isobutyl aluminum hydride) to aldehyde.



6) By Reduction of Esters:

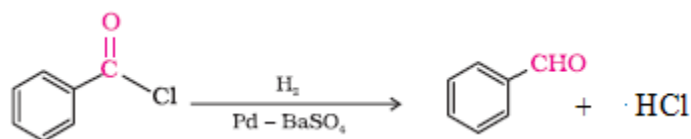


7) **Rozenmund Reduction:** Hydrogenation of Acyl Chloride in presence of Pd deposited over BaSO₄.



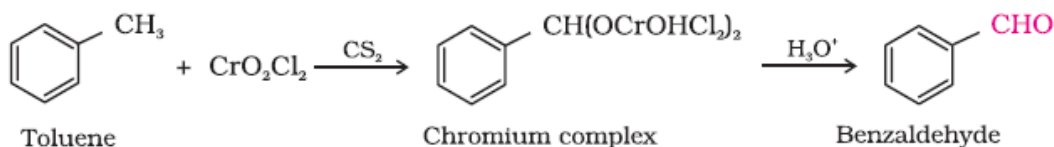
4. Preparation of Benzaldehyde

1) **Rozenmund Reduction:** Hydrogenation of Benzoyl Chloride in presence of Pd deposited over BaSO₄.

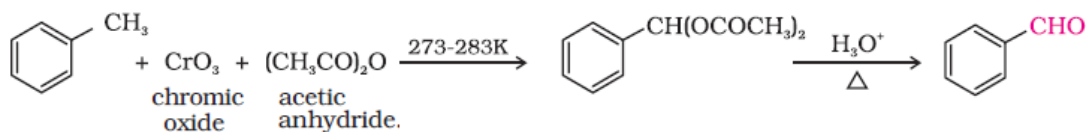


2) **By Oxidation of Toluene (Hydrocarbon):**

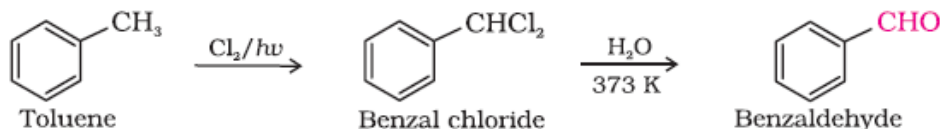
i) **Etard Reaction:** Chromyl chloride oxidizes methyl group to a chromium complex which on hydrolysis gives corresponding aldehyde.



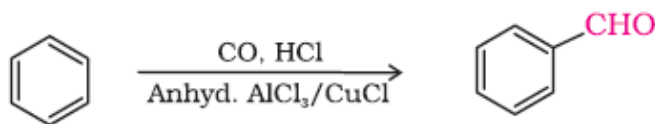
ii) **Oxidation by Chromic Oxide:**



3) **By side chain chlorination of Toluene followed by hydrolysis:**



4) **By Gatterman-koch reaction:**



5. Preparation of Ketones

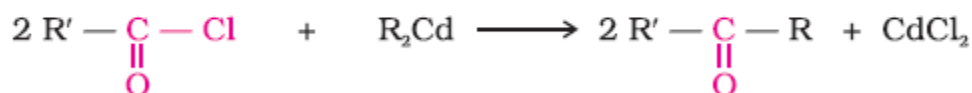
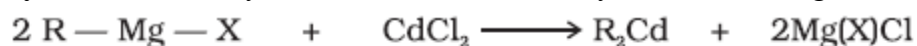
1) **By Oxidation of Secondary Alcohol:**

2) **By Dehydrogenation of Secondary Alcohol:**

3) **By Ozonolysis of Alkene:**

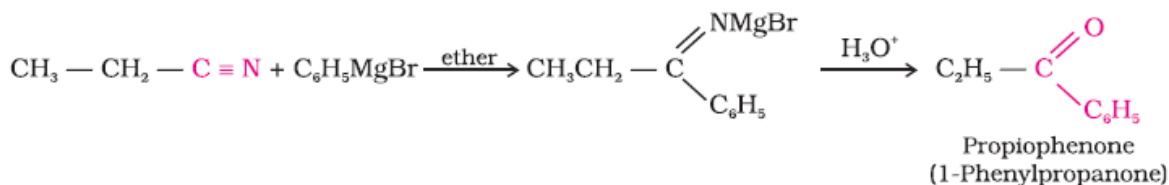
4) **By Hydration of Alkynes:**

5) **From Acyl Chlorides:** Acyl chloride reacts with dialkyl cadmium and gives ketone.

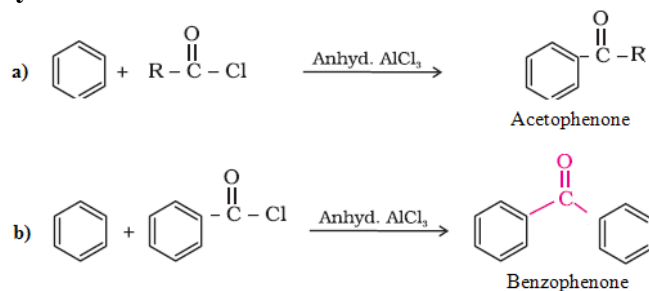


6. Preparation of Aromatic Ketones

1) From Nitriles:



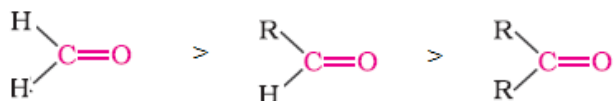
2) By Friedel Crafts acylation reaction:



7. Relative Reactivity of Aldehyde and Ketones: Aldehydes are more reactive than ketones in nucleophilic addition reactions due to steric and electronic effect (Inductive effect).

Electronic Effect: Greater positive charge on carbon of carbonyl group means greater reactivity. Electron releasing alkyl group (-R) is more on ketone than aldehyde so positive charge is reduced in ketones as compared to aldehyde. Thus ketones are less reactive than aldehydes.

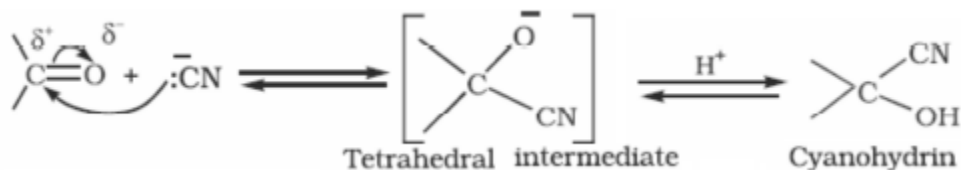
Steric Effect: As the number and size of alkyl group increases, the hindrance to the attack of nucleophile also increases and reactivity decreases. Thus ketones are less reactive than aldehydes due to comparatively more availability of alkyl group.



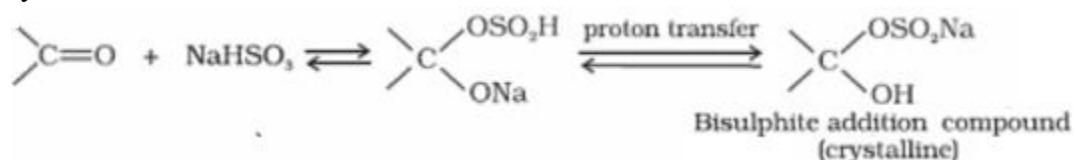
8. Chemical Properties of aldehydes and ketones:

1) Nucleophilic Addition Reactions:

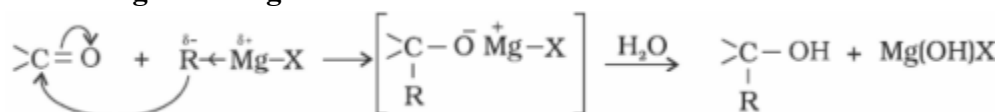
i) Addition of HCN:



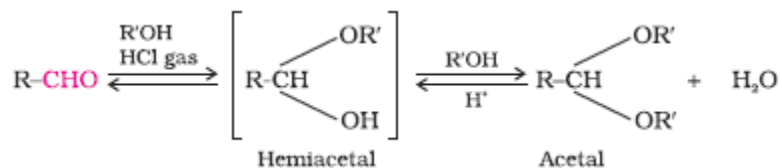
ii) **Addition of Sodium hydrogensulphite:** This reaction is useful for separation and purification of aldehydes and ketones.



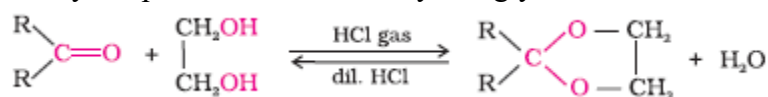
iii) Addition of Grignard reagent:



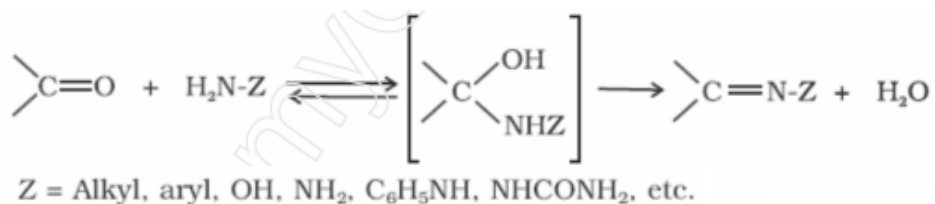
iv) Addition of Alcohols:



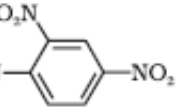
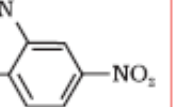


Ketones don't react with monohydric alcohol, it react with ethylene glycol under similar conditions and to form cyclic product known as ethylene glycol ketal.



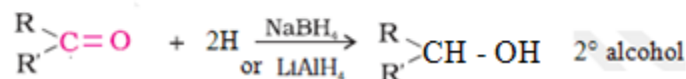
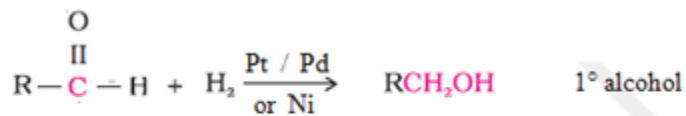
v) Addition of Ammonia and its derivatives:



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

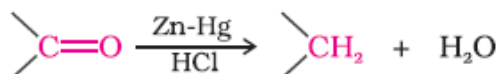
2) Reduction of aldehydes and ketones:

i) Reduction to alcohols:



ii) Reduction to hydrocarbon:

a) Clemmensen reduction:

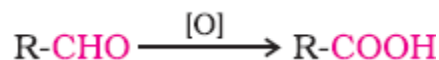


b) Wolff-Kishner reduction:



3) Oxidation of aldehydes and ketones:

i) **Oxidation of aldehydes:** Aldehydes are easily oxidised to carboxylic acid with common oxidising agent ($\text{K}_2\text{Cr}_2\text{O}_4 / \text{H}_2\text{SO}_4$ or $\text{KMnO}_4 / \text{H}_2\text{SO}_4$) or mild oxidising agent like Tollen's reagent or Fehling's solution.

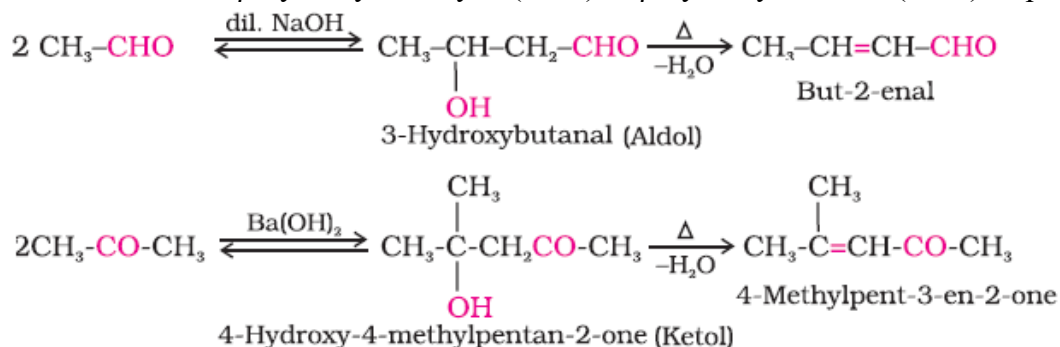


ii) **Oxidation of ketones:** Ketones undergo oxidation under vigorous conditions with cleavage of carbon-carbon bond.

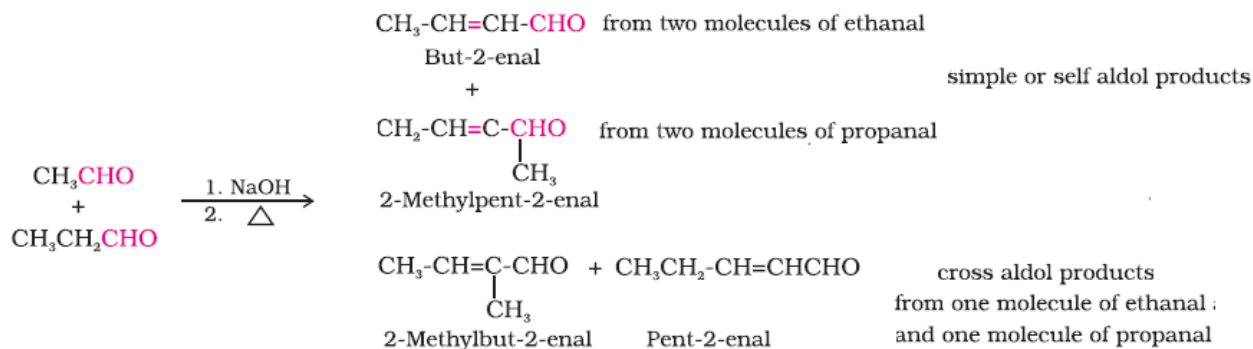


4) Reaction of aldehydes and ketones due to α -hydrogen:

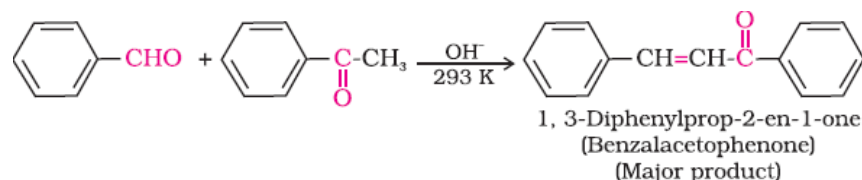
i) **Aldol condensation:** Aldehyde and ketone having at least one α -hydrogen atom on treatment with dilute alkali to form β -hydroxyl aldehyde (aldol) or β -hydroxyl ketones (ketol) respectively.



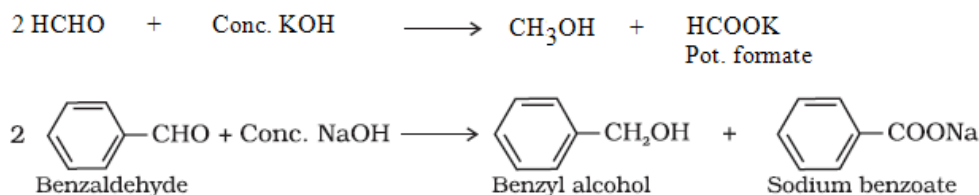
ii) Cross aldol condensation: When aldol condensation is carried out b/w two different aldehyde or two different ketones or b/w aldehyde and ketone is called cross aldol condensation. If both of them contain α -hydrogen atoms, it gives a mixture of four products.



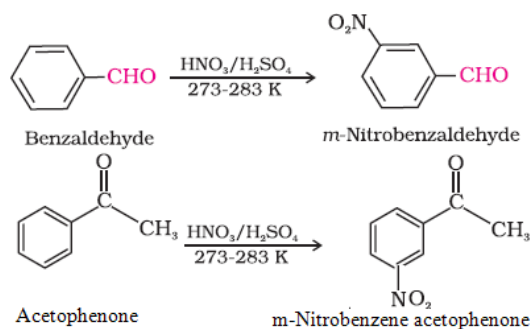
Aldehyde and ketone can also be used in cross aldol condensation like as



5) Cannizzaro reaction: Aldehyde which do not have α -hydrogen atom undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali to form alcohol and salt of acid.



6) Electrophilic substitution reaction of aldehyde and ketone: Carbonyl group is electron withdrawing and therefore they are deactivating and m-directing.



9. Test to distinguish aldehydes and ketones: As ketones are not oxidised by mild oxidising agent like Tollen's reagent and Fehling's solution so these reagent are used to distinguish aldehyde from ketones.

1) Tollen's test: When aldehydes are treated with Tollen's reagent (ammonical silver nitrate solution), they form silver mirror on the inner side of the test tube. Ketones do not form silver mirror image and so do not give this test.



2) Fehling test: Fehling solution is a mixture of two solution, Fehling solution A (aq. Solution of CuSO_4) and Fehling solution B (alkaline solution of sodium potassium tartarate). When aldehyde is heated with Fehling reagent it forms redish brown ppt of cuprous oxide but ketones do not give this test.

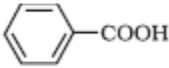
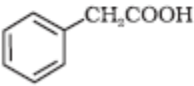
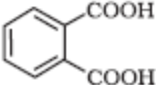


10. Uses of Aldehyde and ketones:

- 1) A 40% solution of formaldehyde is known as formalin is used to preserve biological specimens and to prepare Bakelite.
- 2) Benzaldehyde is used in perfumery and in dye industries.
- 3) Acetone and ethyl methyl ketone are common industrial solvent.

Carboxylic Acid

1. Common and IUPAC names of some Carboxylic Acids:

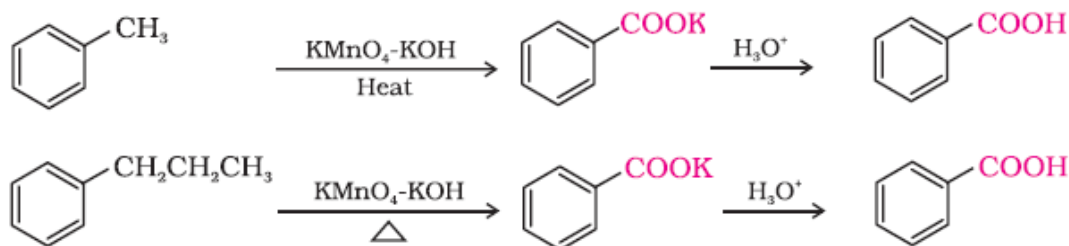
Structure	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH ₃ COOH	Acetic acid	Ethanoic acid
CH ₃ CH ₂ COOH	Propionic acid	Propanoic acid
CH ₃ CH ₂ CH ₂ COOH	Butyric acid	Butanoic acid
(CH ₃) ₂ CHCOOH	Isobutyric acid	2-Methylpropanoic acid
HOOC-COOH	Oxalic acid	Ethanedioic acid
HOOC-CH ₂ -COOH	Malonic acid	Propanedioic acid
HOOC-(CH ₂) ₂ -COOH	Succinic acid	Butanedioic acid
HOOC-(CH ₂) ₃ -COOH	Glutaric acid	Pentanedioic acid
HOOC-(CH ₂) ₄ -COOH	Adipic acid	Hexanedioic acid
HOOC-CH ₂ -CH(COOH)-CH ₂ -COOH	-	Propane-1, 2, 3-tricarboxylic acid
	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
	Phenylacetic acid	2-Phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

2. Methods of Preparation of Carboxylic Acids:

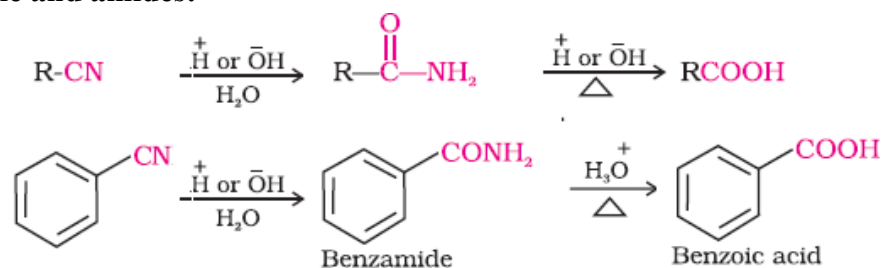
1) By oxidation of primary alcohols

2) By oxidation of aldehydes

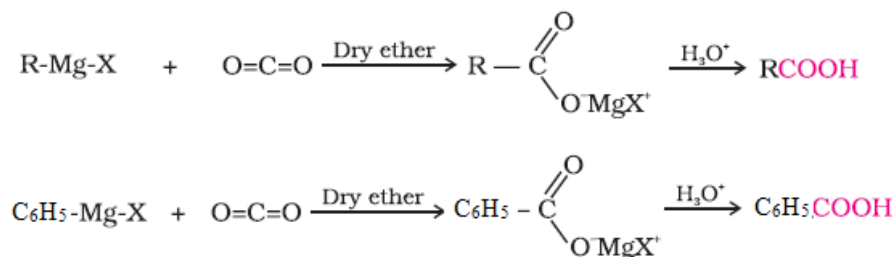
3) **By oxidation of Alkyl Benzene:** Aromatic carboxylic acid can be prepared by oxidation of alkyl benzene. Only primary and secondary alkyl groups are oxidised by this manner.



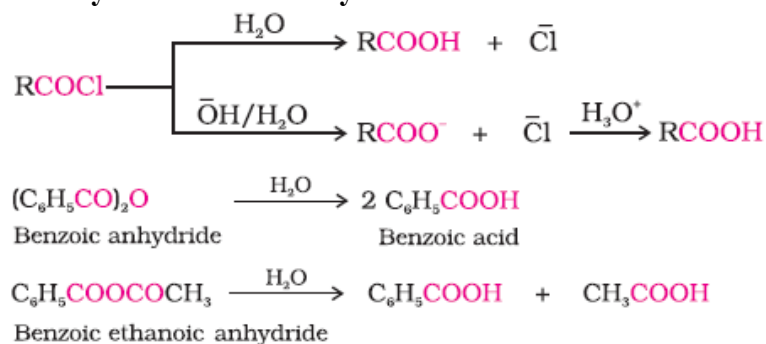
4) From nitrile and amides:



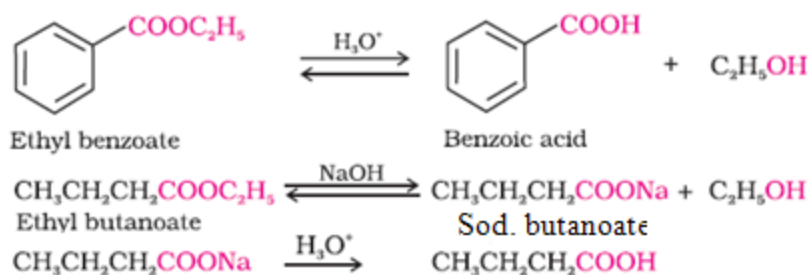
5) By Grignard reagent:



6) From hydrolysis of acyl halides and anhydrides:



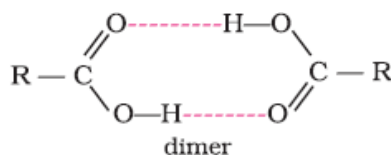
7) **From hydrolysis of esters:** Acidic hydrolysis of esters directly gives carboxylic acid while basic hydrolysis first gives carboxylates then after acidification give carboxylic acids.



3. Physical properties of carboxylic acids:

1) **Solubility:** As the size of alkyl group increases, solubility of carboxylic acid in water decreases b/c non-polar part of acid increases.

2) **Boiling point:** Carboxylic acid having higher boiling point than aldehydes, ketones even alcohols of comparable molecular masses b/c the intermolecular hydrogen bonds formed in carboxylic acids are stronger than those in alcohol.

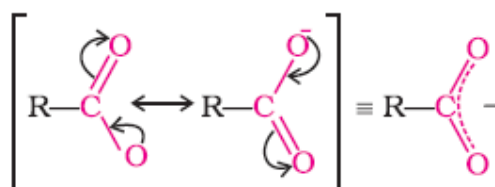


Intermolecular hydrogen bonds in carboxylic acids

4. **Acidity of carboxylic acids:** Carboxylic acids are more acidic than alcohols and phenol. They ionize to give H^+ ions and hence as acids. The strength of acid depends on stability of anion formed.



The Carboxylate ion formed is stabilized through resonance by effective delocalization of the negative charge.

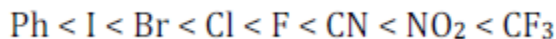


Carboxylate ion stabilized by two equivalent resonance structures in which the negative charge is effectively delocalized between two more electronegative oxygen atoms. On the other hand in case of phenols, negative charge is less effectively delocalized over one oxygen atom and less electronegative carbon atoms in phenoxide ion. Therefore, the carboxylate ion exhibits higher stability in comparison to phenoxide ion. Hence, the carboxylic acids are more acidic than phenols.

The acidity of carboxylic acids further depends on the nature of substituent attached to the carboxyl group.

i) **Effect of electron donating group on the acidity of carboxylic acid:** Electron donating groups decreases the stability of the Carboxylate ions by increasing the negative charge and hence, decreases acidity of carboxylic acids.

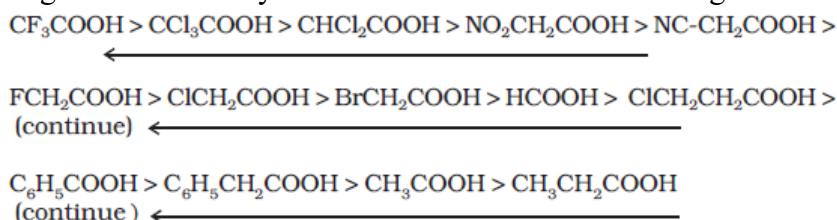
ii) **Effect of electron withdrawing group on the acidity of carboxylic acid:** An electron withdrawing group increases the stability of the Carboxylate ions by delocalizing the negative charge and hence, increases acidity of carboxylic acids. The effect of the following groups in increasing order of acidity is as



iii) **Effect of number of electron withdrawing group:** As the number of electron withdrawing groups increases, -I effect increases hence increasing the acid strength.

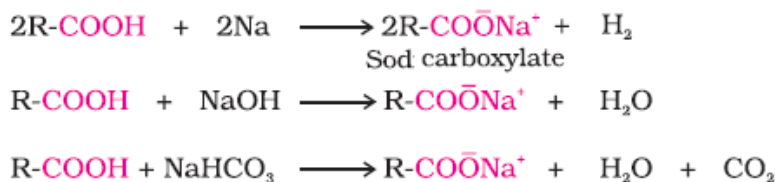
iv) **Effect of position of electron withdrawing group:** As the distance b/w electron withdrawing group and Carboxylic group increases, electron withdrawing influence decreases.

Thus, the increasing orders of acidity for different acids are as following



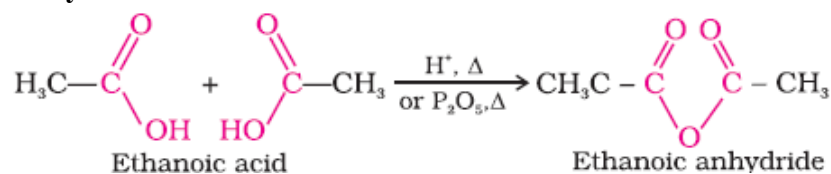
5. Chemical properties of carboxylic acids:

1) Reaction involving cleavage of O-H bond:

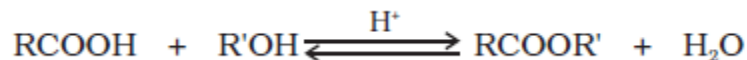


2) Reaction involving cleavage of C- OH bond:

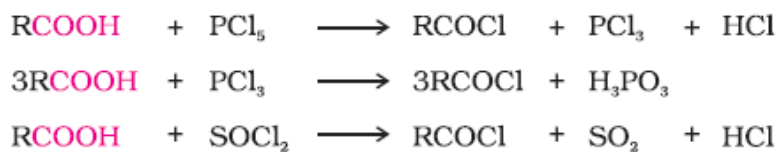
i) Formation of anhydride:



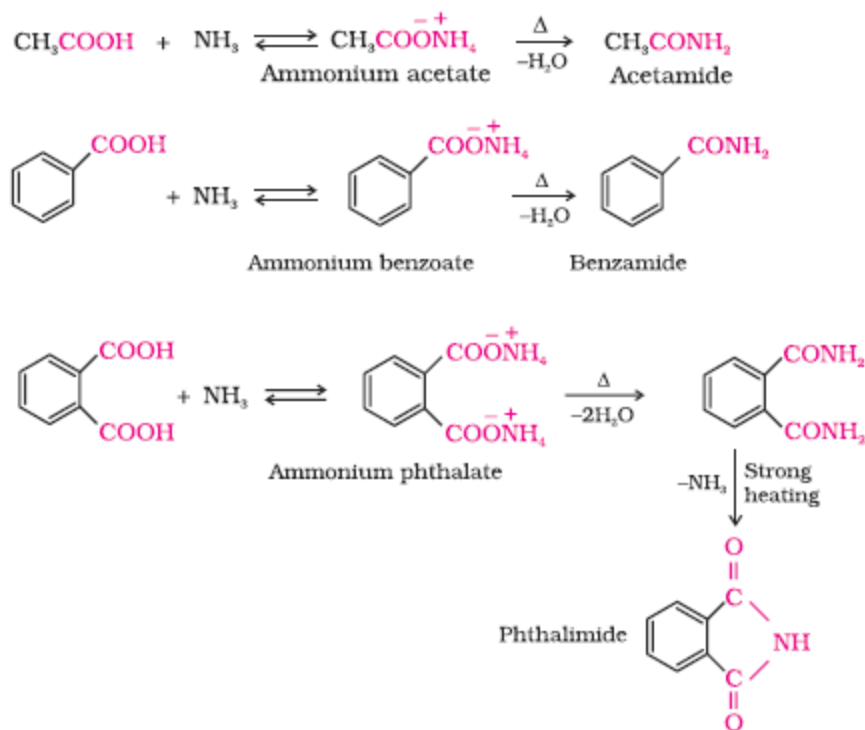
ii) Esterification:



iii) Reaction with PCl₅, PCl₃ and SOCl₂:

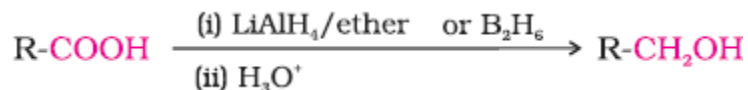


iv) Reaction with Ammonia:

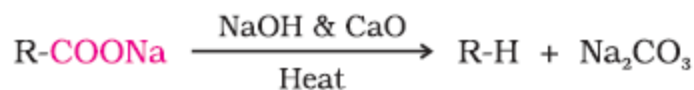


3) Reaction involving cleavage of -COOH group:

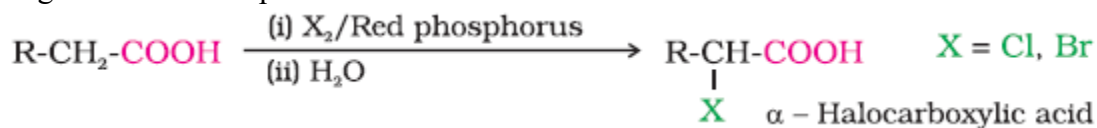
i) Reduction:



ii) Decarboxylation:



iii) **Hell- Volhard Zelinsky reaction (Halogenation):** Carboxylic acid having an α - hydrogen are, halogenated at the α - position on treatment with chlorine or bromine.



4) **Ring substitution reaction in aromatic carboxylic acid:** Its undergo electrophilic substitution reaction in which -COOH group act as deactivating and meta directing group.

