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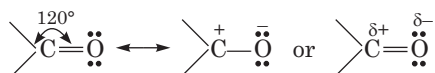
Aldehydes, Ketones and Carboxylic Acids

Aldehydes and Ketones

In aldehydes, the **carbonyl group** ($>\text{C}=\text{O}$) is bonded to carbon and hydrogen, while in the ketones, it is bonded to two carbon atoms.

Nature of Carbonyl Group

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



The electronegativity of oxygen is much higher than that of the carbon, so their electron cloud is shifted towards the oxygen. Therefore, C—O bond is polar in nature.

Nomenclature

- (i) **Nomenclature of aldehydes** In IUPAC system, the suffix 'e' of alkane is replaced by the suffix 'al'. e.g.

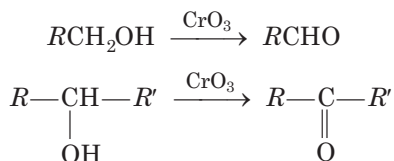
Compound	Common name	IUPAC name
HCHO	Formaldehyde	Methanal
CH ₃ CHO	Acetaldehyde	Ethanal

- (ii) **Nomenclature of ketones** In IUPAC system, the suffix “e” of alkane is replaced by ‘one’. e.g.

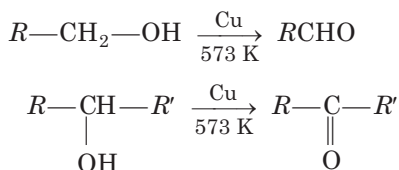
Compound	Common name	IUPAC name
$\text{H}_3\text{C} \cdot \text{COCH}_3$	Dimethyl ketone (acetone)	Propanone
$\text{H}_3\text{C} \cdot \text{COC}_2\text{H}_5$	Ethyl methyl ketone	Butanone

Preparation of Aldehydes and Ketones

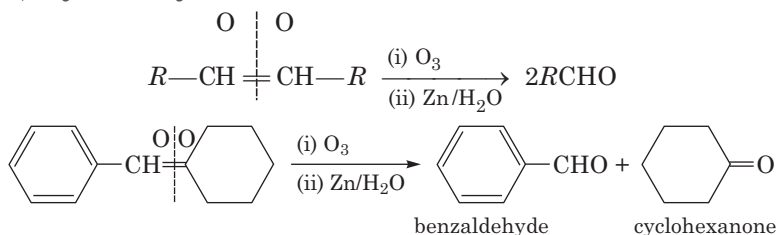
- (i) **By oxidation of alcohols** Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively.



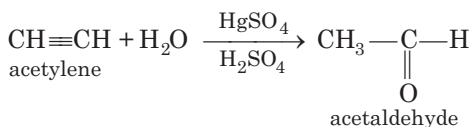
- (ii) **By dehydrogenation of alcohols** In this method, alcohol vapours are passed over heavy metal catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones.

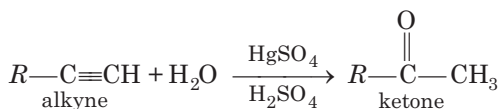
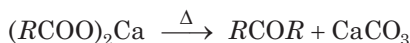


- (iii) **By ozonolysis of alkenes**

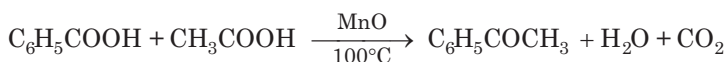
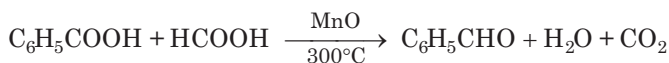
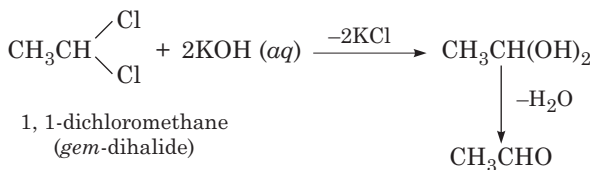
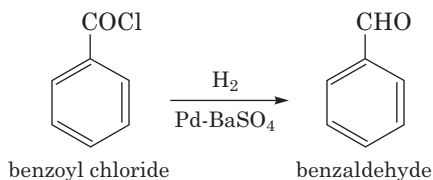


- (iv) **By hydration of alkynes** Acetylene on hydration gives acetaldehyde and other alkynes on hydration give ketones.

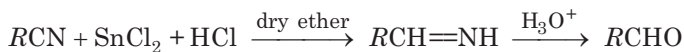


**(v) By heating Ca salt of acid**

To obtain aldehyde, calcium formate and any other Ca salt of acid are heated.

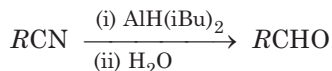
**(vi) By decarboxylation and dehydration of aromatic acids****(vii) From *gem*-dihalides****Preparation of Aldehydes only (Other than Ketones)****(i) Rosenmund reduction**

Formaldehyde cannot be prepared by this method as HCOCl is highly unstable.

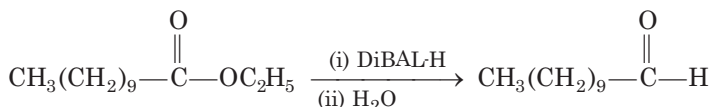
(ii) From nitriles and esters

This reaction is called **Stephen reaction**.

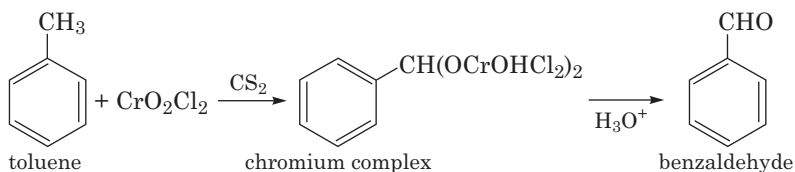
Alternatively, nitriles are selectively reduced by diisobutylaluminium hydride, [DiBAL-H] to imines which on hydrolysis give aldehydes.



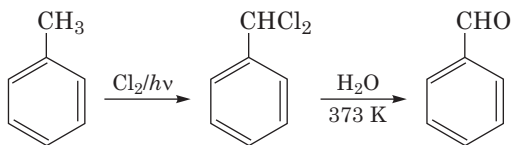
Similarly, esters can also be reduced to aldehydes with DiBAL-H.



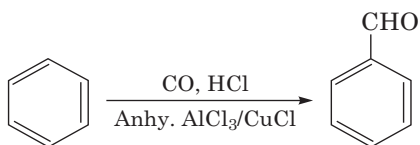
(iii) **Etard reaction**



(iv) **Side chain halogenation followed by hydrolysis of toluene**

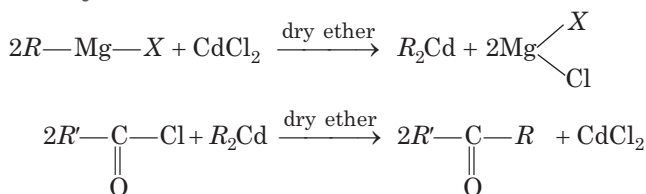


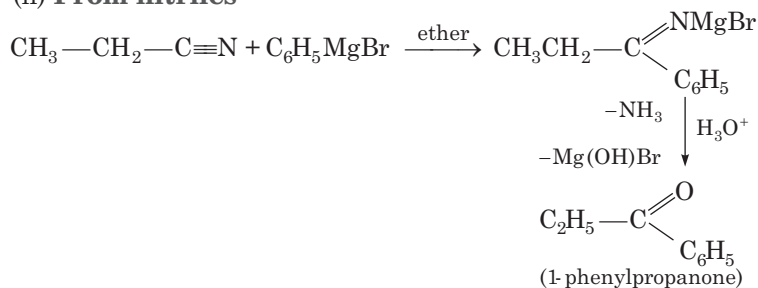
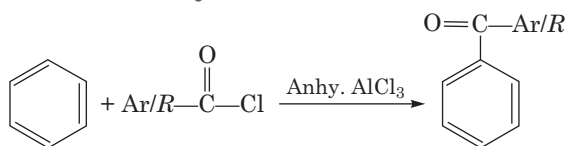
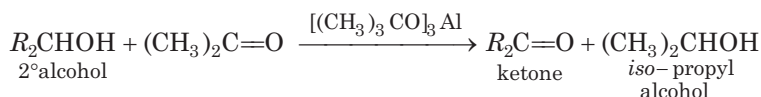
(v) **Gattermann-Koch synthesis**



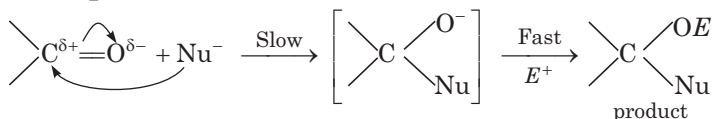
Preparation of Ketones only (Other than Aldehydes)

(i) **From acyl chlorides**

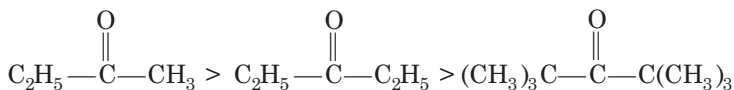
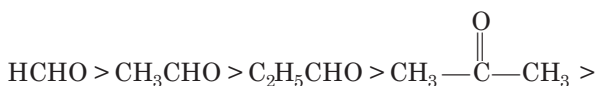


(ii) **From nitriles**(iii) **Friedel-Crafts acylation**(iv) **Oppenauer oxidation****Physical Properties of Aldehydes and Ketones**

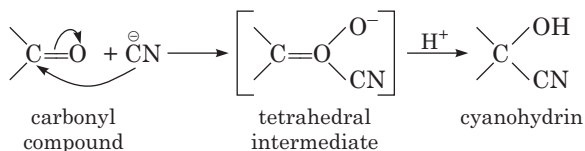
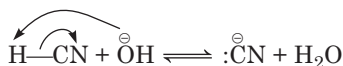
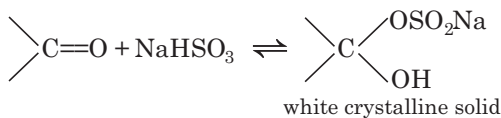
1. Methanal (HCHO) is a gas at room temperature, and its 40% aqueous solution is known as **formalin**. It is a reducing agent, it is used in silvering of mirrors and decolourising vat dyes.
2. Ethanal (CH₃CHO) is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature.
3. The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular mass due to high magnitude of dipole-dipole interactions.
4. Aldehydes and ketones have lower boiling point than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
5. The lower members of aldehydes and ketones are miscible with water due to the formation of hydrogen bond with water. However, the solubility decreases with increase in length of alkyl chain.
6. Acetophenone is a hypnotic (sleep producing drug) so used as a medicine under the name hypnone.

Chemical Reactions of Aldehydes and Ketones**1. Nucleophilic addition reactions**

Reactivity order is

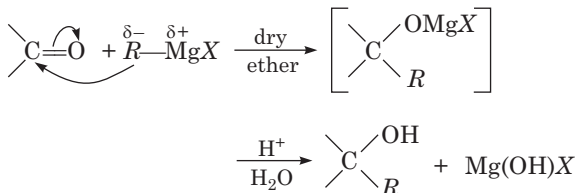


It is due to +I effect of alkyl groups which decreases the positive charge on carbonyl carbon and steric hinderance (The bulky alkyl group hinder the approach of nucleophile).

(i) Addition of hydrogen cyanide (HCN)**(ii) Addition of sodium hydrogen sulphite**

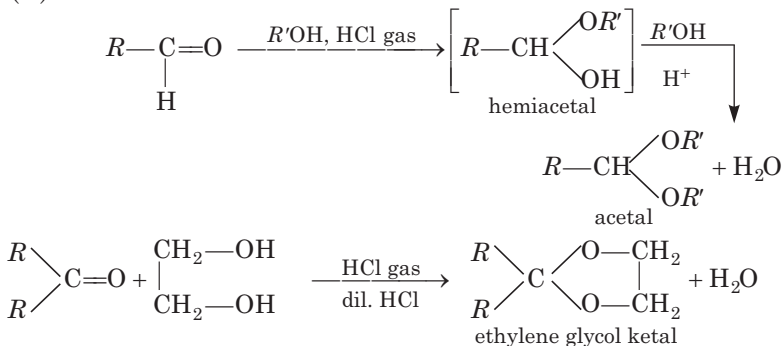
This reaction is used for the separation and purification of aldehydes and ketones. This is because the addition compound formed, is water soluble and can be converted back to the original carbonyl compound by treating with dilute mineral acid or alkali.

(iii) **Addition of Grignard reagent**



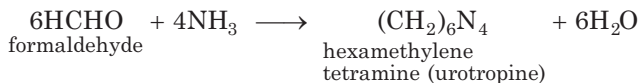
The type of alcohol formed depends upon the aldehyde or ketone used (formaldehyde \rightarrow 1° alcohols, other aldehydes \rightarrow 2° alcohols and ketones \rightarrow 3° alcohols).

(iv) **Addition of lower alcohols**

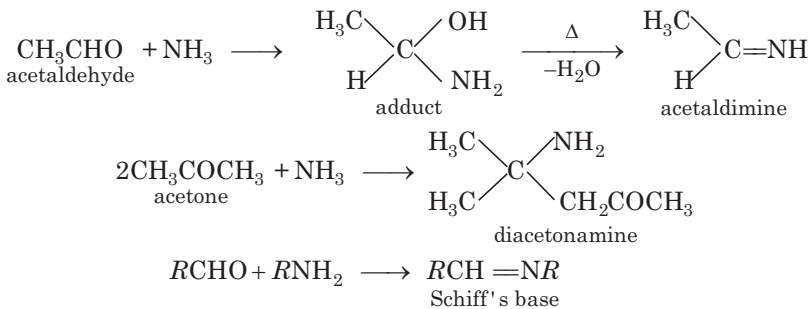


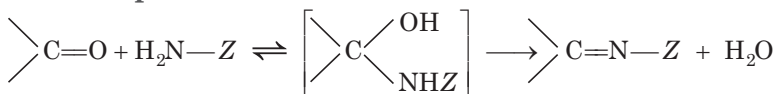
(v) **Addition of ammonia and its derivatives**

Reaction with ammonia





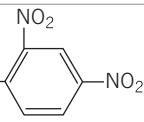
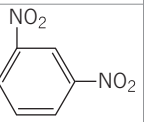


Urotropine on controlled nitration gives the well known explosive RDX (Research and development explosive).



2. Nucleophilic Addition Elimination Reactions

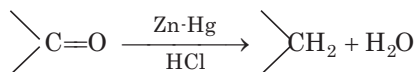
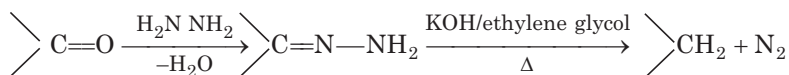
where, Z = alkyl, aryl, —OH, —NH₂, —C₆H₅NH, —NHCONH₂ etc.

Some N-substituted Derivatives of Aldehydes and Ketones

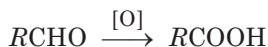
Z	Reagent name	Carbonyl derivative	Product name
—R	Amine	>C=N-R	Substituted imine (Schiff's base)
—OH	Hydroxyl amine	>C=N-OH	Oxime
—NH ₂	Hydrazine	>C=N-NH_2	Hydrazone
—NH— 	Phenyl-hydrazine	>C=N-NH- 	Phenylhydrazone
—NH— 	2,4-dinitro-phenyl hydrazine	>C=N-NH- 	2,4-dinitro-phenyl hydrazone
—NH— 	Semi-carbamide	>C=N-NH- 	Semi-carbazone

3. Reduction

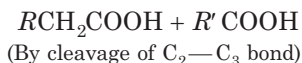
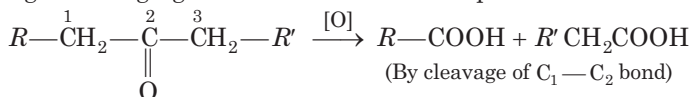
Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride (NaBH₄) or lithium aluminium hydride [LiAlH₄].

Clemmensen reduction**Wolff-Kishner reduction****4. Oxidation**

Aldehydes get easily oxidised to carboxylic acids by HNO₃, KMnO₄, K₂Cr₂O₇, etc., or even by mild oxidising agent.

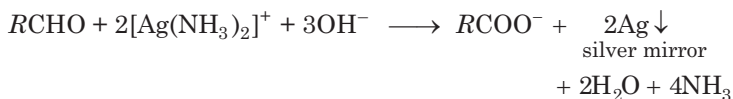


Ketones are generally oxidised under vigorous conditions, i.e. by strong oxidising agents and at elevated temperature.

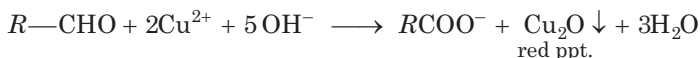


During oxidation of unsymmetrical ketones the point of cleavage is such that keto group stays preferentially with the smaller alkyl group (**Popoff's rule**).

- (i) **Tollen's test** Aldehydes give bright silver mirror with Tollen's reagent (ammoniacal silver nitrate).



- (ii) **Fehling's test** Fehling solution gives a reddish brown precipitate with aldehydes. (except benzaldehyde)

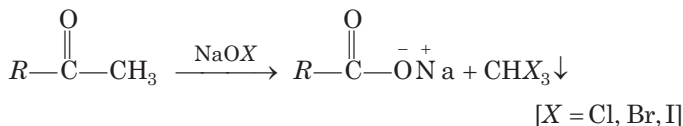


[Fehling solution is a mixture of Fehling solution A and Fehling solution B in 1 : 1 ratio. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate which is also called, Rochelle salt.]

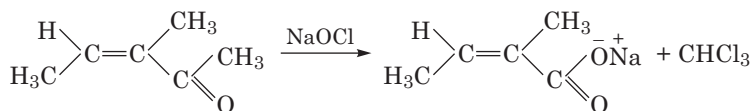
- (iii) **Benedict solution** With it, aldehydes (except benzaldehyde) also give red ppt. of Cu₂O.

- (iv) **Schiff's reagent** It is an aqueous solution of magenta or pink coloured rosaniline hydrochloride which has been decolourised by passing SO₂. Aldehydes give pink colour with this reagent but ketones do not.

5. Haloform reaction Aldehydes and ketones having at least one methyl group [3-α hydrogen] linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to haloform.



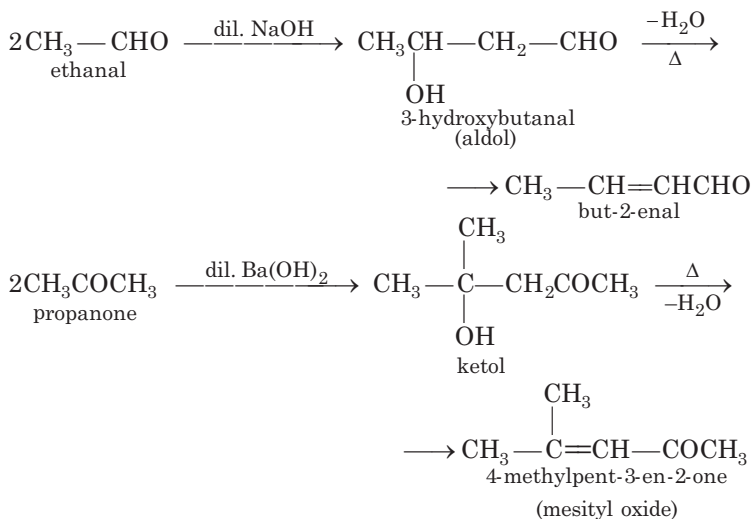
This oxidation does not affect a carbon-carbon double bond, if present in the molecule.



Iodoform reaction with sodium hypoiodite is also used for the detection of CH_3CO —group or $\text{CH}_3\text{CH}(\text{OH})$ —group by producing yellow solid CHI_3 .

6. Reactions due to α -Hydrogen

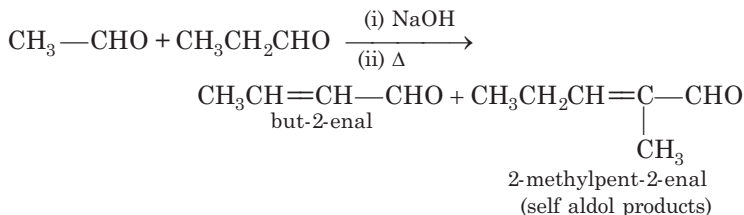
(i) Aldol condensation

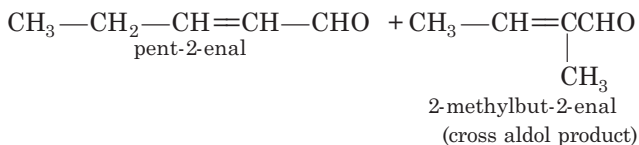


Its further condensation gives phorone.

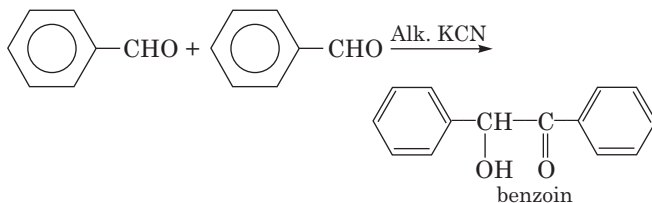
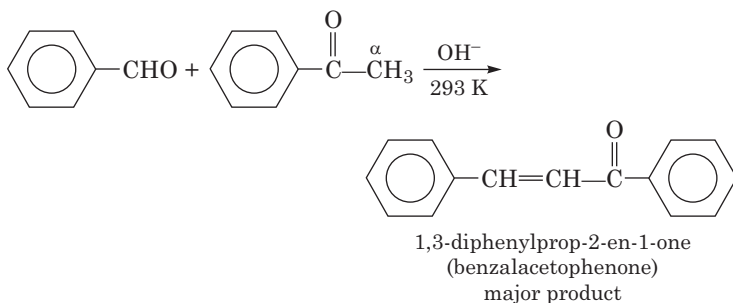
This reaction is exhibited by those aldehydes and ketones which have at least one α -hydrogen.

(ii) **Cross aldol condensation** It is carried out between the two different aldehydes or ketones. It gives a mixture of four products.





Base catalysed crossed aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or ketone is called **Claisen-Schmidt condensation** or **Claisen reaction**

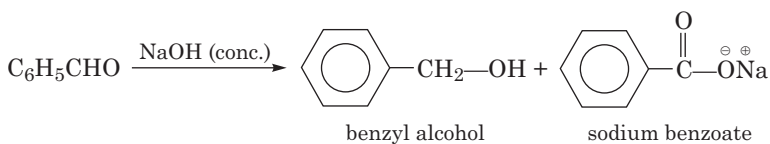
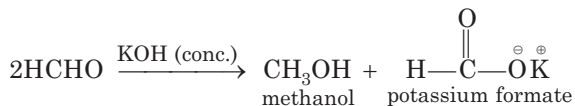


The above reaction is called **Benzoin condensation**, not the cross aldol condensation.

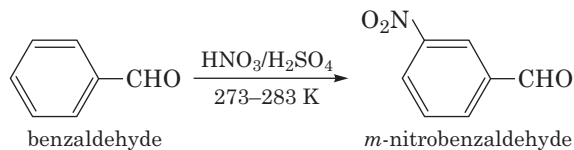
7. Other Important Reactions

(i) **Cannizzaro reaction**

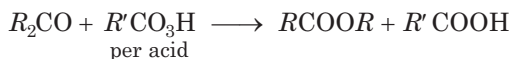
Aldehydes which do not have any α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali.



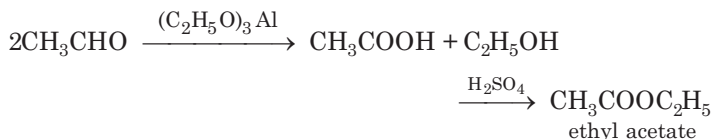
- (ii) **Electrophilic substitution reaction** Aromatic aldehydes and ketones undergo electrophilic substitution. Carbonyl group shows + *R* effect, therefore acts as a deactivating and *meta* directing group.



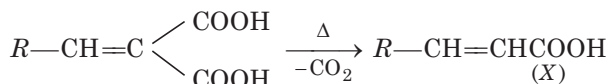
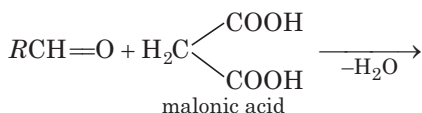
- (iii) **Baeyer-Villiger oxidation** With Caro's acid (H_2SO_5) or per benzoic acid ($\text{C}_6\text{H}_5\text{CO}_3\text{H}$) or peracetic acid ($\text{CH}_3\text{CO}_3\text{H}$), aliphatic ketones give ester.



- (iv) **Tischenko's reaction** It is a modified form of Cannizzaro reaction.

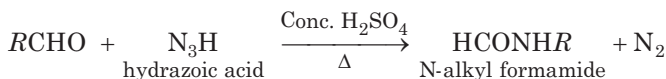


- (v) **Knoevenagel's reaction** It involves condensation between active methylene group and carbonyl groups in the presence of base.



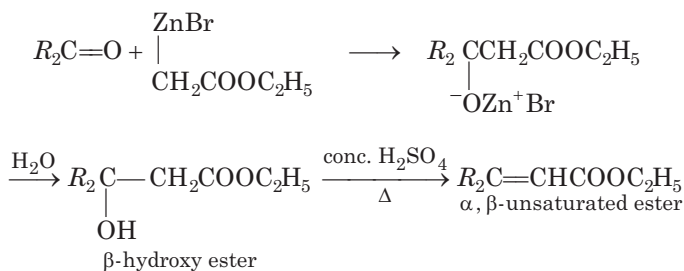
If $R = \text{CH}_3$, X is crotonic acid and if $R = \text{C}_6\text{H}_5$, X is cinnamic acid.

- (vi) **Schmidt reaction**

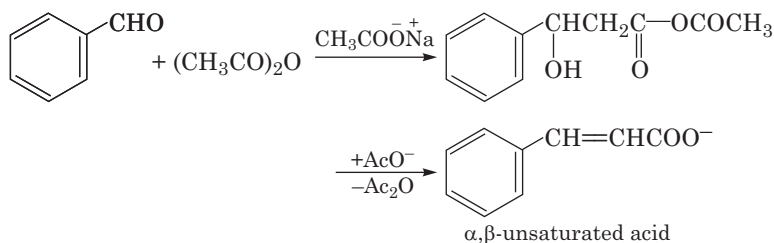


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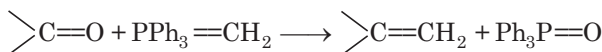
(vii) Reformatsky reaction



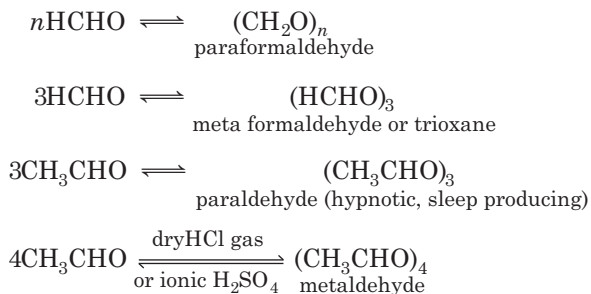
(viii) Perkin's reaction



(ix) Wittig reaction



(x) Polymerisation



Carboxylic Acids

These are the compounds which have $\text{—}\overset{\overset{\text{O}}{||}}{\text{C}}\text{—OH}$ group [carboxyl group]. The word carboxyl is a combination of two words carbonyl ($>\text{C}=\text{O}$) and hydroxyl (—OH).

Classification

Depending upon the number of —COOH groups, they are classified as

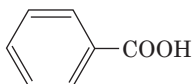
- (i) monocarboxylic acids ; containing one —COOH group
- (ii) dicarboxylic acids : containing two —COOH groups.

Sources of carboxylic acids

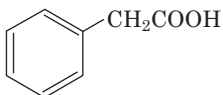
Formula	Common name	Source
HCOOH	Formic acid	Red ant (formica)
CH_3COOH	Acetic acid	Vineger (acetum)
$\text{C}_3\text{H}_7\text{COOH}$	Butyric acid	Butter (butyrum)

Nomenclature

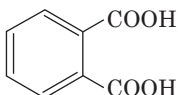
Their IUPAC names have been derived from the corresponding alkanes by replacing the letter 'e' of the alkane with 'oic' and adding suffix 'acid' at the end. Thus, monocarboxylic acids are called **alkanoic acids**.



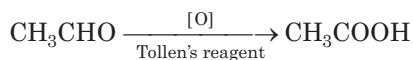
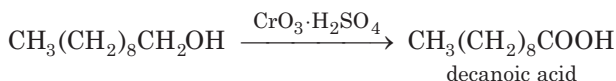
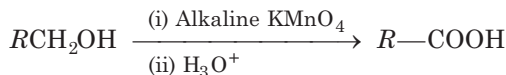
Benzoic acid
(Benzoic acid)



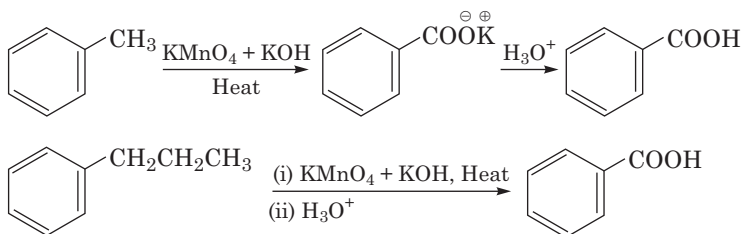
2-phenylethanoic acid



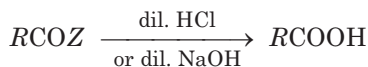
Benzoic acid-1, 2-dicarboxylic acid (phthalic acid)

Methods of Preparation of Monocarboxylic Acids**(i) From primary alcohols and aldehydes**

- (ii) **From alkyl benzenes** Alkyl benzene when treated with strong oxidising agent like H_2CrO_4 (chromic acid), acidic or alkaline KMnO_4 gives benzoic acid.



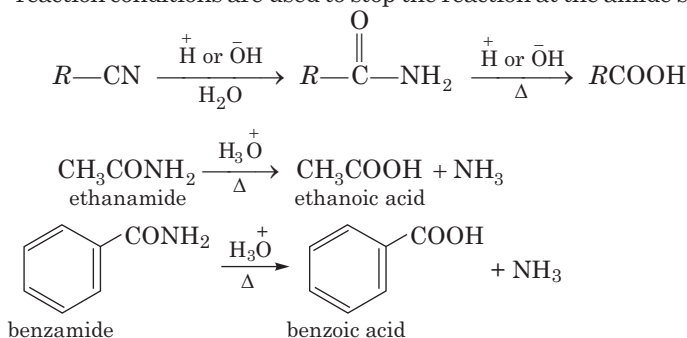
- (iii) **From acid derivatives** All acid derivatives like amides (RCONH_2), acid halides (RCOCl), esters (RCOOR'), acid anhydrides (RCO—O—COR) on hydrolysis give carboxylic acids. All acid derivatives break from RCO^+ .



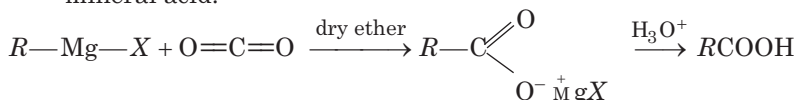
$\text{Z} = \text{—NH}_2, \text{—X} (\text{X} = \text{Cl, Br, I}), \text{OR}', \text{RCOO—}$ etc.

Ease of hydrolysis : $\text{RCOCl} > (\text{RCO})_2\text{O} > \text{RCOOR}' > \text{RCONH}_2$

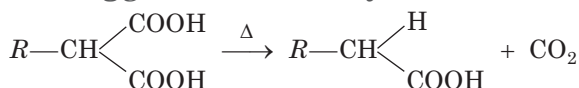
- (iv) **From nitriles and amides** Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or OH^- as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.



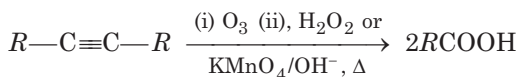
- (v) **From Grignard's reagent** Grignard's reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid.



(vi) **By heating geminal dicarboxylic acids**

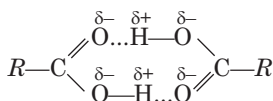


(vii) **From alkynes**

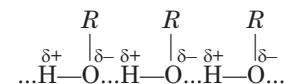


Physical Properties of Carboxylic Acids

1. Aliphatic carboxylic acids up to nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids.
2. The lower carboxylic acids are freely miscible with water due to the presence of intermolecular hydrogen bonding with H_2O molecules. However, the solubility in water decreases gradually due to increase in the size of alkyl group.
3. Monocarboxylic acids have higher boiling points as compared to the alcohols of comparable molecular masses due to the presence of stronger intermolecular hydrogen bonding as shown below.



hydrogen bonding in
carboxylic acids



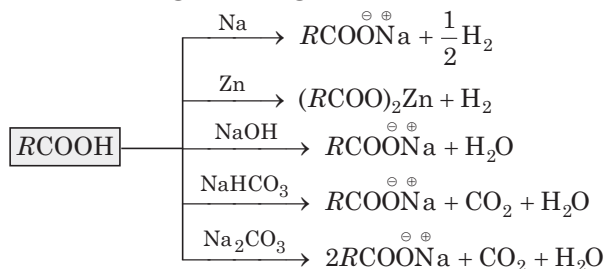
hydrogen bonding in alcohols

4. Melting points of aliphatic monocarboxylic acids shows alternation or oscillation effect, i.e. the m.p. of an acid with even number of carbon atoms is higher than the next lower and next higher homologue containing odd number of carbon atoms. This is because, in case of acids with even number of carbon atoms, the terminal $-\text{CH}_3$ and $-\text{COOH}$ groups lie on the opposite sides of the *zig-zag* chain. As a result, they get closely packed in the crystal lattice.
5. Glacial acetic acid is completely pure acetic acid and represents the solid state of acetic acid. Below 16.6°C temperature pure acetic acid is converted into ice like solid hence, it is called glacial acetic acid.

Chemical Properties of Carboxylic Acids

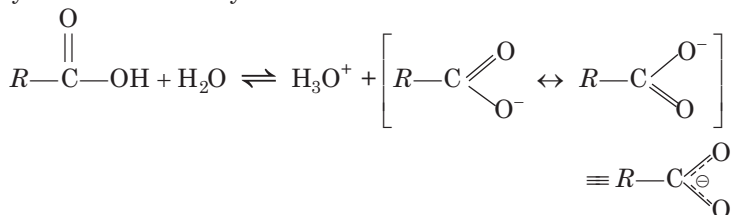
Carboxylic acids do not give reactions of carbonyl groups as it enters into resonance with lone pair of O of —OH group.

Some important chemical reactions shown by carboxylic acids are as follows :

1. Reaction Involving Cleavage of O—H Bond

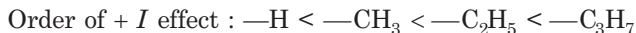
Above reactions are used to detect the presence of carboxyl group in an organic compound.

Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.

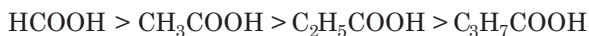


The strength of the acid is expressed in terms of the dissociation constant (K_a), also called acidity constant. A stronger acid has higher K_a but lesser $\text{p}K_a$ value ($\text{p}K_a = -\log K_a$).

The electron releasing substituents (+I effect) decrease the acidic strength of the carboxylic acids by destabilising the carboxylate ion.

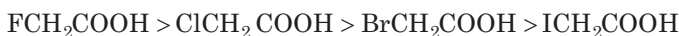
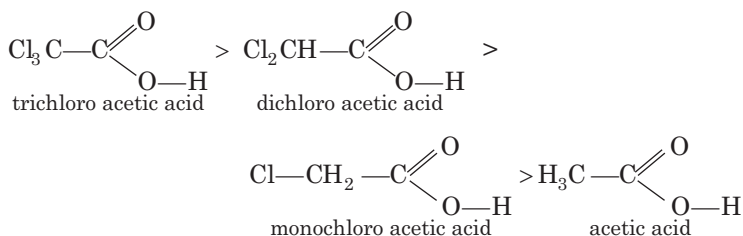


Therefore, the order of acidic strength is

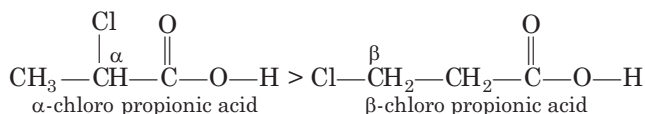


The electron withdrawing substituents (–I effect) such as halogen atoms (X), nitro (–NO₂) group increase the acidic strength by decreasing the magnitude of the negative charge on the carboxylate anion and thus stabilising it. The release of H⁺ ion becomes easy.

Acidic strength order



This is because $-I$ effect decreases in the order : $\text{F} > \text{Cl} > \text{Br} > \text{I}$.

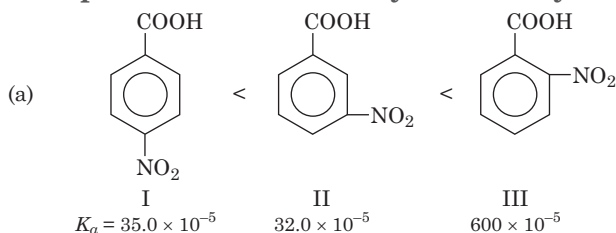


This is because $-I$ effect decreases with distance.

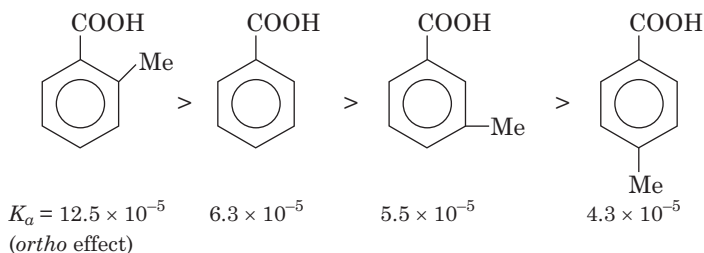
Per acetic acid (CH_3COOOH) is a weaker acid than acetic acid as acetate ion is stabilised by resonance.

Acidic strength of aromatic acids The parent member of the family is benzoic acid which is a weaker acid ($K_a = 6.3 \times 10^{-5}$) than formic acid ($K_a = 17.7 \times 10^{-5}$) but stronger than acetic acid.

Some important order of acidity of carboxylic acids are



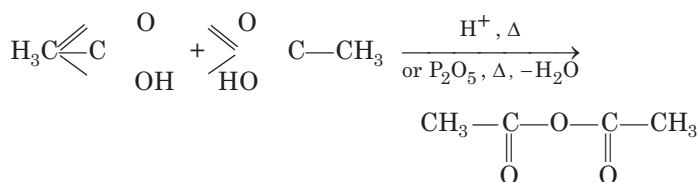
(b) Similarly, K_a values of methyl substituted (toluic acids) at 298 K are as follows :



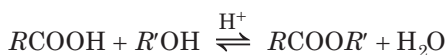
From the K_a values, it is evident that with the exception of *o*-isomer, both *p* and *m*-toluic acids are weaker acids than benzoic acid whereas the three isomeric nitro benzoic acids are stronger acids than benzoic acid.

2. Reactions involving cleavage of C—OH bond

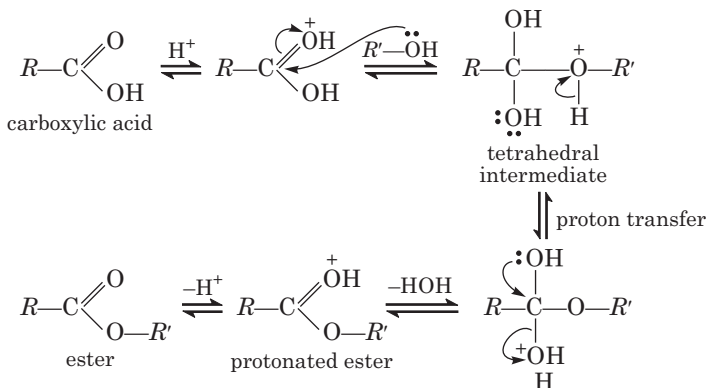
(i) Formation of anhydride



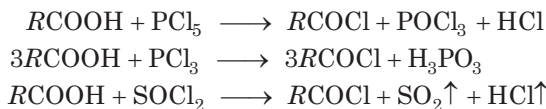
(ii) Esterification



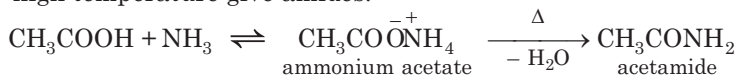
Mechanism

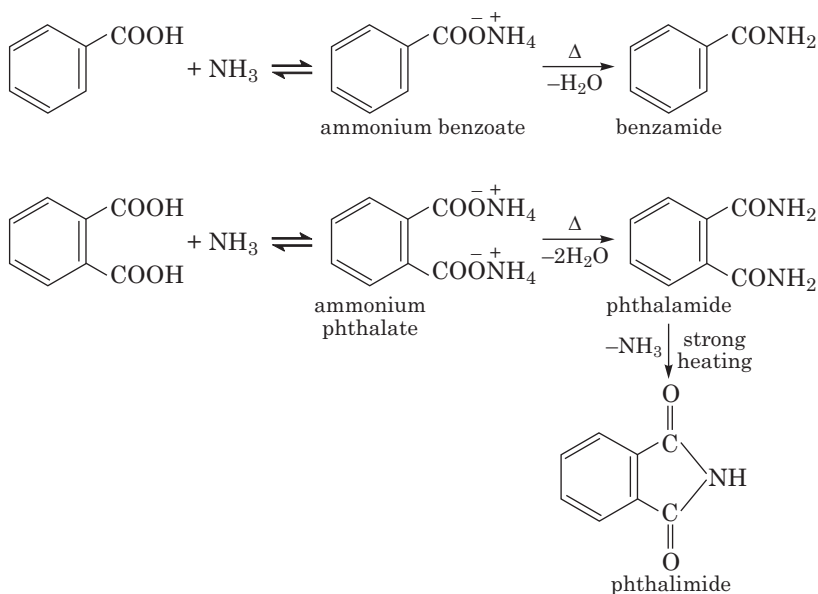


(iii) Reactions with PCl_5 , PCl_3 and SOCl_2



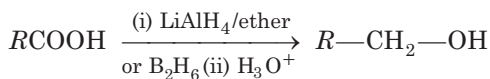
(iv) **Reaction with ammonia** Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature give amides.





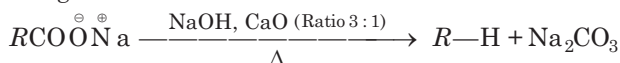
3. Chemical reactions involving —COOH group

(i) Reduction

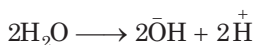
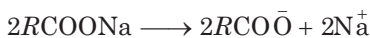


(ii) Decarboxylation

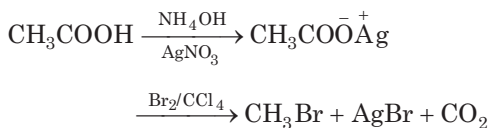
- Using sodalime



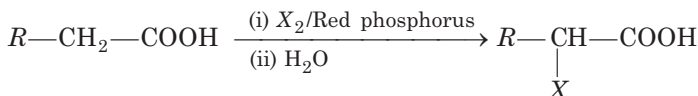
- Electrolytic decarboxylation (Kolbe electrolysis)



(iii) Hunsdiecker reaction

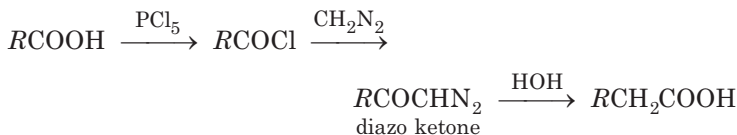


4. **Substitution reactions in the hydrocarbon part** α -hydrogen atoms in carboxylic acids are acidic in nature and can be easily replaced by halogen atoms in HVZ reaction



The reaction is known as Hell-Volhard-Zelinsky reaction.

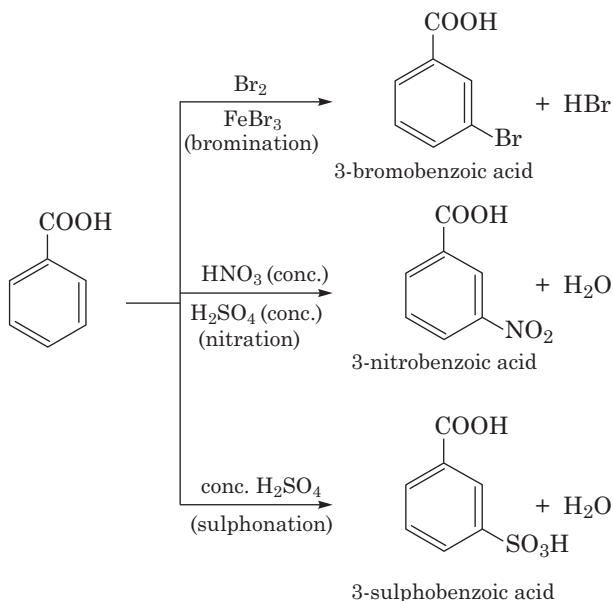
5. **Arndt-Eistert reaction** It is method of converting lower carboxylic acids to their higher homologues.



5. **Reducing property** Among carboxylic acids, formic acid is the only acid that acts as reducing agent. It reduces, acidified KMnO_4 to MnSO_4 , HgCl_2 to Hg , Tollen's reagent to silver mirror and Fehling's solution to red ppt. and itself gets oxidised to CO_2 and H_2O .



7. **Electrophilic substitution reactions of aromatic acids** $-\text{COOH}$ group shows $-R$ effect, therefore, acts as a deactivating and *meta*-directing group. Carboxylic acids do not undergo Friedel-Craft's reaction because the carboxylic group is deactivating and the catalyst AlCl_3 (anhy.) gets bonded to the carboxyl group.

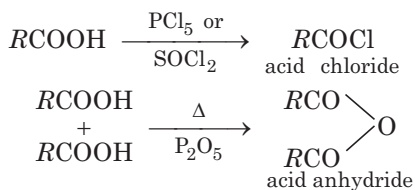


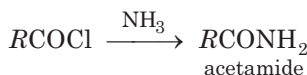
Uses

1. Formic acid is used in leather tanning, textile dyeing and finishing.
2. Acetic acid is used in the manufacture of rayon and in plastics, in rubber and silk industries, in cooking and in vinegar (a 8-10% solution of acetic acid).
3. Benzoic acid and its salts are used as urinary antiseptics.
4. Formic acid can act as a reducing agent.

Derivatives of Carboxylic Acids

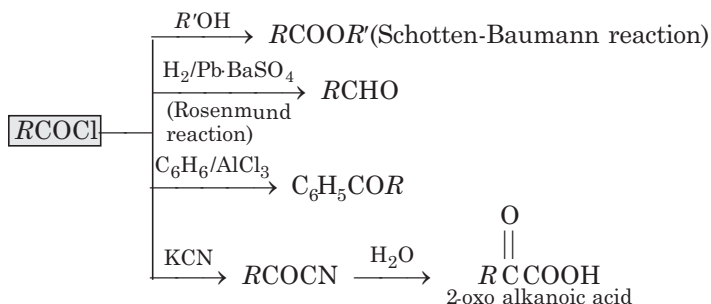
These are obtained when —OH group of carboxylic acids is replaced by Cl, NH₂, OR' and OCOR and are called respectively acid chloride, acid amide, ester and acid anhydride.



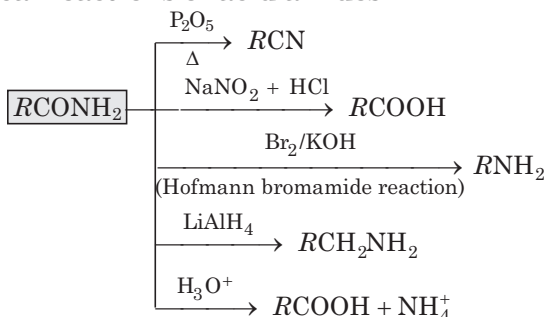


Properties of Acid Derivatives

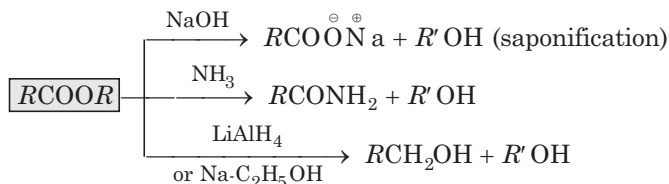
1. Chemical reactions of acid halides



2. Chemical reactions of acid amides



3. Chemical reactions of ester



4. Chemical reactions of anhydrides

