Carbonyl Compounds (Aldehydes & Ketones)

1. Introduction

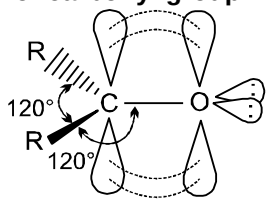
Aldehydes & ketones have general formula $C_nH_{2n}O$ and contains >C=O group. Thus aldehydes (R–CHO) and ketones (R–CO–R) are collectively called as carbonyl compounds.

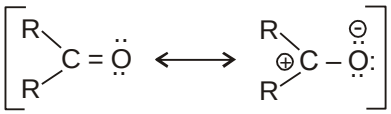
Aldehyde Ketone

2. Strucutre and bonding in aldehydes and ketones

The carbonyl carbon atom is sp^2 hybridized. The unhybridized p-orbital overlaps with a p-orbital of oxygen to form a pi bond. The double bond between carbon and oxygen is shorter, stronger, and polarized.

Orbital diagram of carbonyl group :





major minor

The double bond of the carbonyl group has a large dipole moment because oxygen is more electronegative than carbon.

Section (A) : Preparation of carbonyl compounds

3. Preparation methods of Aldehydes and Ketones

3.1 By oxidation of alcohols :

Primary alcohols $\xrightarrow{[O]}$ Aldehydes

For oxidising primary alcohols to aldehydes PCC (Pyridiniumchloro chromate ($C_6H_5NH^+CrO_3Cl^-$)) may be used.

Secondary alcohols $\xrightarrow{[O]}$ Ketones

For oxidising 2º alcohols to ketones $CrO_3/K_2Cr_2O_7$ may be used.

3.2 By dehydrogenation of (1° & 2°) alcohols :

Dehydrogenation means removal of hydrogen and reagent used is heated copper or silver. The alcohol vapours are passed over heavy metal catalyst to yield the following products.

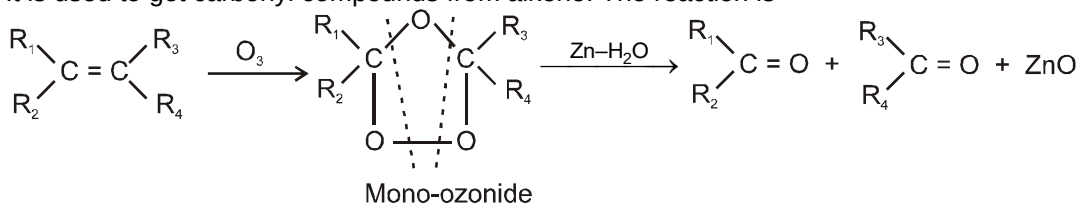
1º alcohol (RCH_2OH) $\xrightarrow[-H_2]{Cu/300^oC}$ Aldehyde (R–CH=O)

2º alcohol (R_2CHOH) $\xrightarrow[-H_2]{Cu/300^oC}$ Ketone ($R_2C=O$)

** 3º alcohol $\xrightarrow[-H_2O]{Cu/300^oC}$ Alkene (Dehydration)

3.3 Ozonolysis of alkene :

It is used to get carbonyl compounds from alkene. The reaction is



Mono-ozonide

Note : (i) During the cleavage of ozonide Zn is used to check further oxidation of aldehyde into acid.
(ii) By this method we can locate double bond in olefin or exact structrue of hydrocarbon can be determined by knowing ozonolysis product i.e. by placing double bond at the place of two carbonyl oxygen atoms of two carbonyl compounds.
(iii) Among the three molecules of carbonyl compounds.
(a) If one molecule contains two carbonyl groups, then hydrocarbon will be alkadiene.
(b) If all the three molecules contain two carbonyl group then hydrocarbon will be cycloalkatriene.
(iv) This method is used for aliphatic carbonyl compounds.

3.4 Wacker process :

Alkenes can directly be oxidised to corresponding aldehydes or ketones by treating them with a solution of $PdCl_2$ containing a catalytic amount of $CuCl_2$ in presence of air or O_2. Except ethene any higher alkene will give ketone.

$$CH_2=CH_2 + H_2O + PdCl_2 \xrightarrow[\text{air or } O_2]{CuCl_2} CH_3–CH=O + Pd + 2HCl$$

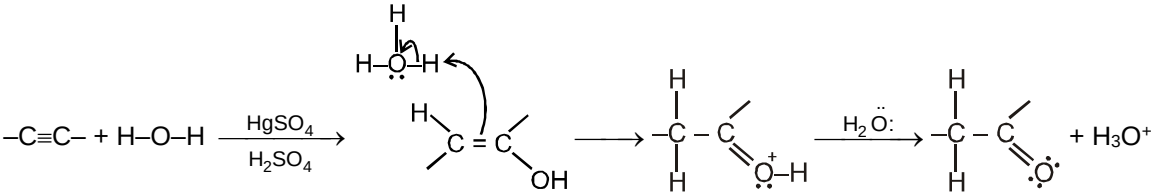
$$R–CH=CH_2 + H_2O + PdCl_2 \xrightarrow[\text{air or } O_2]{CuCl_2} R–\overset{\overset{O}{\|}}{C}–CH_3 + Pd + 2HCl$$

Note : During the reaction $PdCl_2$ is reduced to Pd and $CuCl_2$ is reduced to Cu(I)

3.5 Hydration of alkynes :

$$\underset{\text{Ethyne}}{CH \equiv CH} \xrightarrow[H_2SO_4/HgSO_4]{H_2O} \underset{\text{Ethanal}}{CH_3CHO}$$

Mechanism :



Other alkynes give ketones in this reaction.

$$R–C\equiv C–H \xrightarrow[H_2O]{Hg^{+2}/H_2SO_4} R–\overset{\overset{O}{\|}}{C}–CH_3$$

3.6 Hydroboration of alkyne :

It is used to get aldehyde from terminal alkyne. Here reagent is (i) diborane (B_2H_6) (ii) H_2O_2, OH^-

$$R–C\equiv C–H \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6} R–CH_2–CH=O$$

In this reaction Borane (BH_3) is act as electrophile.

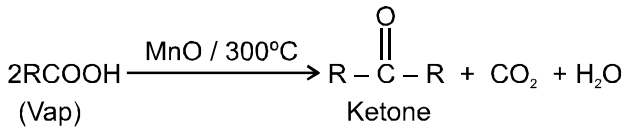
3.7 Dry distillation of calcium salt of acid :

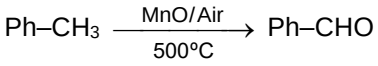
$$(RCOO)2Ca \xrightarrow{\Delta} \underset{\text{Ketone}}{R–\overset{\overset{O}{\|}}{C}–R} + CaCO3$$

Ex. $$(CH3COO)2Ca \xrightarrow{\Delta} CH_3–\overset{\overset{O}{\|}}{C}–CH_3 + CaCO3$$
Calcium acetate

On dry distillation of calcium salt of acetic acid with calcium salt of formic acid we get a mixture of aldehyde, ketone and formaldehyde. Calcium salt of dibasic acid (1, 4 & higher) on distillation) gives cyclic ketones.

3.8 On passing vapours of fatty acids over Mangnous oxide at 300ºC :

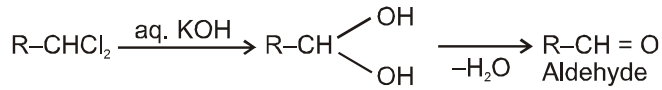


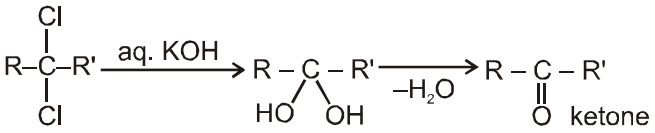


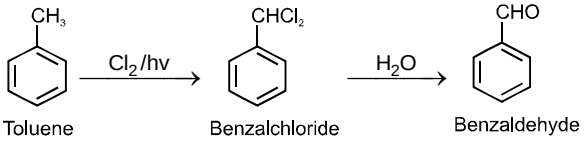
On passing mixture of vapours of fatty acid with formic acid we get a mixture of aldehyde, ketone and formaldehyde.

3.9 On alkaline hydrolysis of gem-dihalides :

Terminal gemdihalides will give aldehyde while non-terminal will give ketone as follows



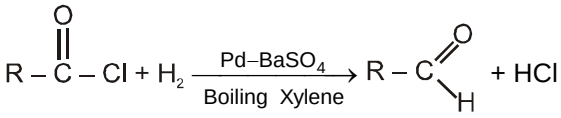




4. Methods used for the preparation of Aldehydes only.

4.1 Rosenmund's reduction :

Here acid chlorides are reduced to aldehyde with H_2 in boiling xylene using palladium as a catalyst supported on barium sulphate.

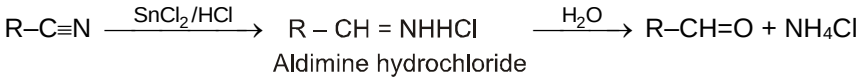


Note : (a) Pd Catalyst is poisoned by $BaSO_4$ (Lindlars catalyst) to check further reduction of aldehyde to alcohol.

(b) Formaldehyde cannot be obtained by this method because HCOCl is unstable at common temperature.

(c) Reaction with acid chloride and dialkyl cadmium or Lithium dialkyl cuprate we can obtain ketone.

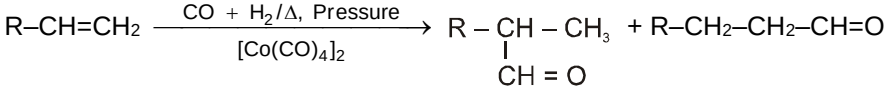
4.2 Stephen's reduction :



4.3 Oxo-process :

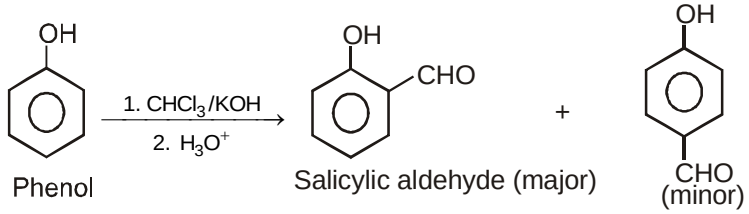
It is also called as carbonylation. Here terminal alkene reacts with water gas at high temperature and pressure in the presence of cobalt carbonyl catalyst to give aldehyde.

Wilkinson catalyst [$RhH(CO)(Ph_3P)_3$] can also be used in promoting the oxo-process.

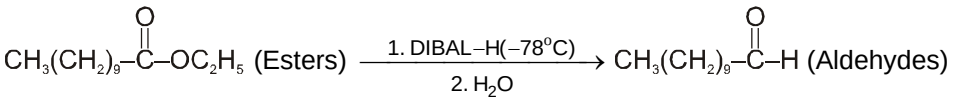


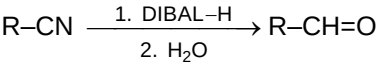
4.4 Reimer-Teimann reaction :

By this method phenolic aldehyde is prepared



4.5 From esters or nitrile :



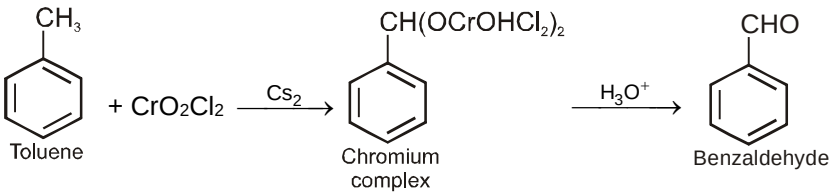


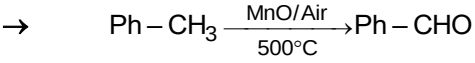
DIBAL-H : Diisobutyl aluminium hydride [$AlH(i\text{-}Bu)_2$] is a reducing agent.

This is less reactive than $LiAlH_4$ and is more sterically hindered and has difficulty in transferring hydride ions.

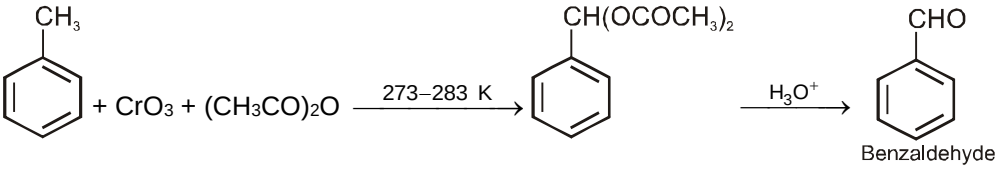
4.6 From hydrocarbons :

By oxidation of methyl benzene and its derivative using chromyl chloride (CrO_2Cl_2). This reaction is called **Etard reaction.**



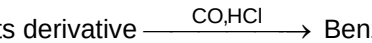


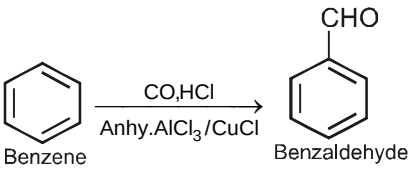
4.7 By oxidation of methyl benzene and its derivative using chromic oxide (CrO_3) in acetic anhydride:



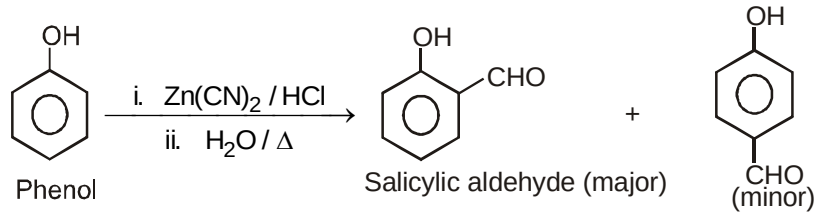
4.8. By Gatterman-Koch reaction:

This reaction is mainly given by aromatic hydrocarbons & Halobenzene



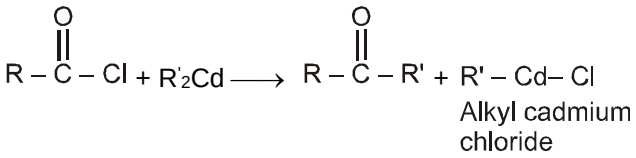


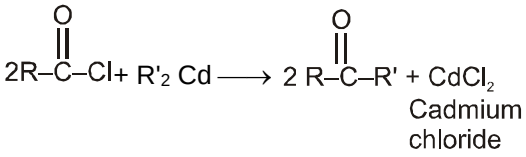
4.9 Gattermann formylation:



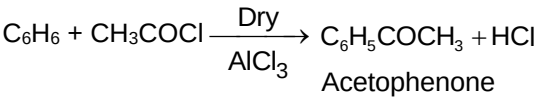
5. Methods used for the preparation of Ketones only

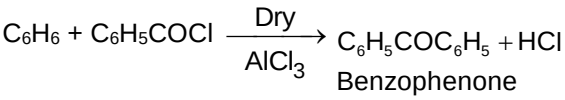
5.1 Using alkanoylchloride and dialkyl cadmium:

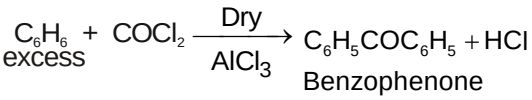




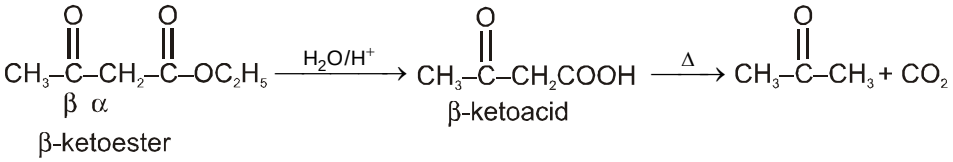
5.2 By acylation or benzoylation of aromatic hydrocarbon (Friedel-Craft Reaction)



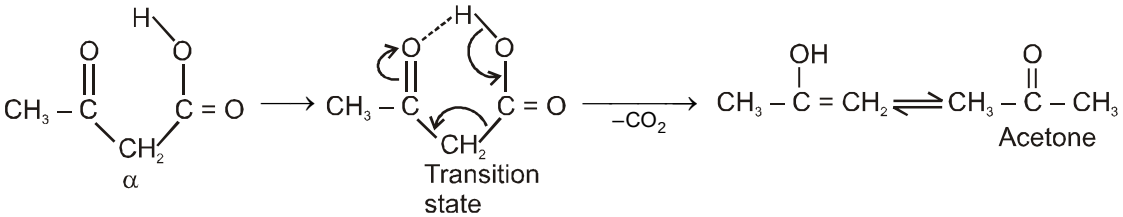




5.3 By acid hydrolysis followed by heating of β-Ketoester:

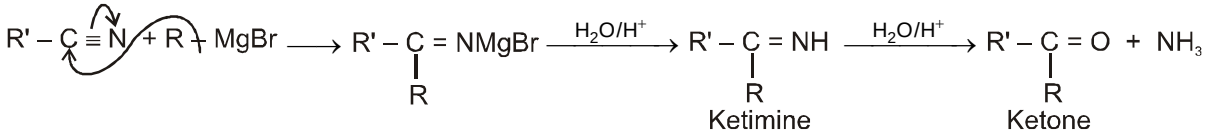


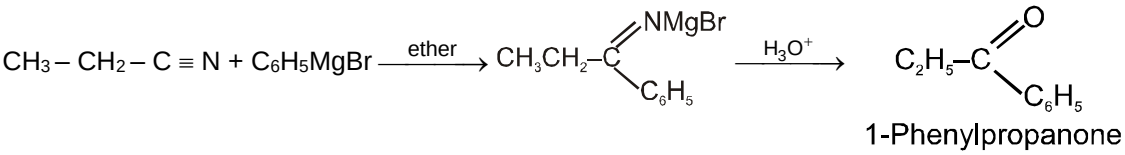
Note : It is β-ketoacid which decarboxylate more readily as it proceeds via six membered cyclic transition-state.



5.4 From nitriles :

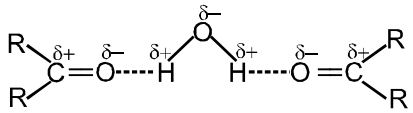
Treatment of nitrile with Grignard reagent followed by hydrolysis gives a ketone.





6. Physical properties of Aldehydes and Ketones :

- Methanal - Gas at room temperature
- Ethanal - Volatile liquid
- Other aldehydes and ketones - Liquid or solid at room temperature
- Boiling points of aldehydes and ketones are higher than those of hydrocarbons and ethers of comparable molecular masses.
  Reason: Weak molecular association in aldehydes and ketones, arising out of the dipole-dipole interactions.
- Boiling points of aldehydes and ketones are lower than those of alcohols of similar molecular masses.
  Reason : Absence of intermolecular hydrogen bonding
- Lower members of aldehydes and ketones are miscible with water in all proportions.
  Reason : They form hydrogen bonds with water.



- Solubility of aldehydes and ketones decreases rapidly on increasing the length of the alkyl chain.
- All aldehydes and ketones are fairly soluble in organic solvents such as ether, methanol, etc.
- Lower aldehydes have sharp pungent odours.
- As the size of aldehydes increases, the odour becomes less pungent and more fragrant.

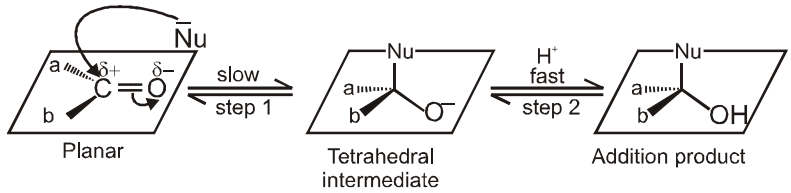
Section (B) : Nucleophilic addition reactions

7. Chemical reactions

7.1 Nucleophilic addition reactions :

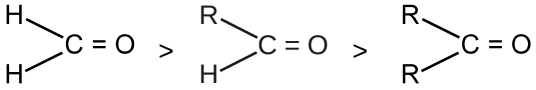
Addition of a nuceophile and a proton across the (C=O) double bond: The reactivity of the carbonyl group arises from the electronegativity of the oxygen atom and the resulting polarization of the carbon-oxygen double bond. The electrophilic carbonyl carbon atom is sp^2 hybridized and flat, leaving it relatively unhindered and open to attack from either face of the double bond.

Mechanism :



Nucleophile (Nu^-) attacks the carbonyl group perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon. In the process, hybridisation of carbon changes from sp^2 to sp^3. A tetrahedral alkoxide is formed as intermediate.

Reactivity : Aldehydes are more reactive than ketones in nucleophilic addition reactions.



There are two factors which influence the reactivity of ketone and aldehyde.

(i) Inductive effect (ii) steric factor

(i) +I effect of alkyl group decrease the amount of charge on C=O group.

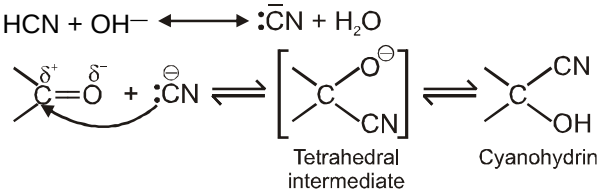
(ii) Steric effect also decreases the reactivity of carbonyl group.

(iii) The Aryl group stabilizes the reactant by resonance and causes a net deactivation effect of the reactant.

Que. Compare reactivity between Benzaldehyde & Propanal.

Ans. Benzaldehyde < Propanal.

(I) Addition of hydrogen cyanide (HCN)



Note : (i) Addition of HCN over aldehyde and ketones gives cyanohydrin.

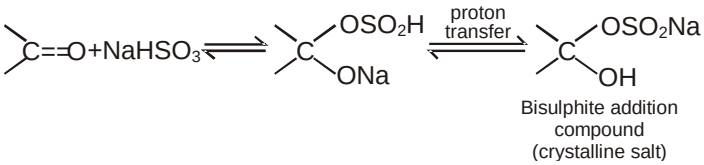
(ii) Cyanohydrin on acid hydrolysis gives α-hydroxy acid.

(iii) Cyanohydrin on treating with $NH_3(l)$ followed by acid hydrolysis gives α-amino acid.

(iv) In case of ketone, cyanohydrin formation is reversible due to bulky group of ketone which hinder the formation.

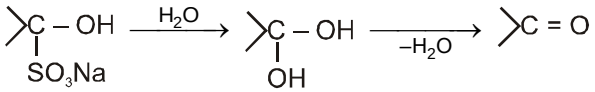
(v) Reaction occurs slowly with pure HCN hence catalysed by a base. CN^- is a stronger nucleophile than OH^- ions and adds readily.

(II) Addition of sodium hydrogen sulphite ($NaHSO_3$)

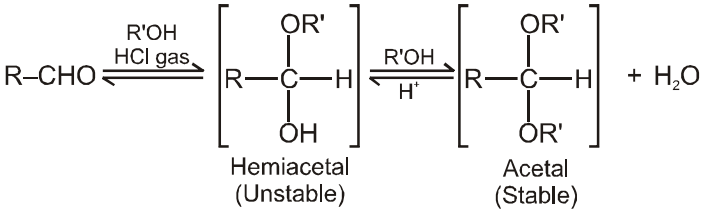


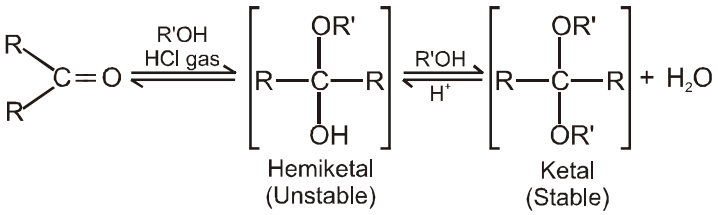
Salt on hydrolysis gives carbonyl compounds again, this reaction is used to separate the aldehydes from mixture.

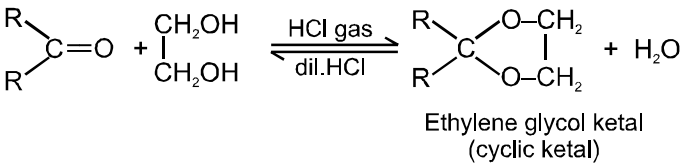
Position of equilibrium lies largely to the right side for most aldehydes and to the left side for most ketones due to steric factors.



(III) Addition of alcohols (ROH) :





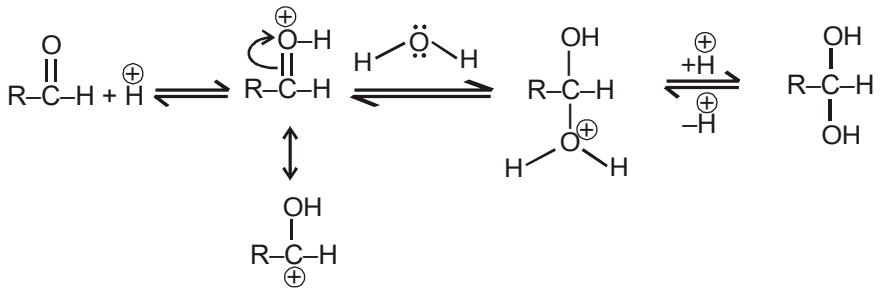


Note : (i) Acetal is formed to protect aldehyde for a long time.
(ii) Acetal has functional groups ether.
(iii) Acetal formed can be decomposed to original aldehyde by dilute acid.
(iv) On treating with ethyleneglycol we get cyclic acetal or ketal.
(v) Acetal formation is found to be more favourable than ketal formation if both the carbonyl groups are present within the molecule.

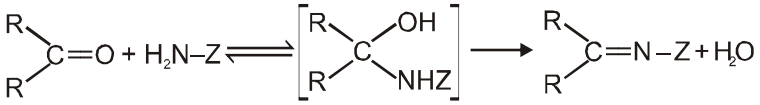
(IV) Addition of water :

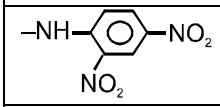
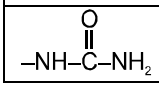
Aldehyde or ketone reacts with water to form gem-diols. Water is a poor nucelophile and therefore adds relatively slowly to the carbonyl group, but the rate of reaction can be increased by an acid catalyst.

Mechanism:

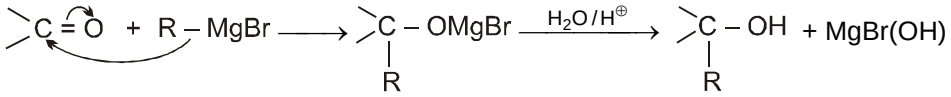


(V) Addition of ammonia and its derivatives (addition elimination reactions) :

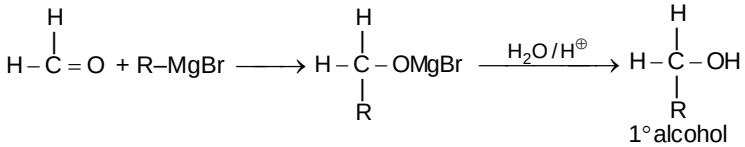


If Z are	Reagents Name	Products
–OH	Hydroxylamine	Oxime
$–NH_2$	Hydrazine	Hydrazone
$–NH–C_6H_5$	Phenylhydrazine	Phenylhydrazone
	2,4-dinitrophenylhydrazine (Brady's reagent) or 2,4-DNP	2,4-dinitrophenylhydrazone (Solid orange precipitate)
	Semicarbazide	Semicarbazone

(VI) Addition of Grignard reagents (Preparation of alcohol) :

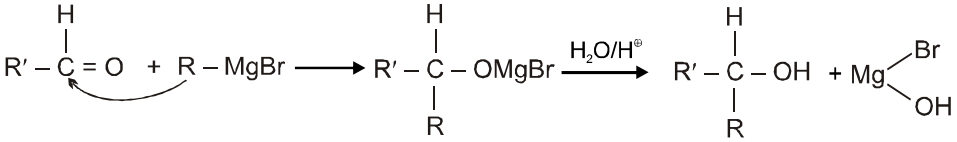


(a) When formaldehyde is treated with Grignard reagent followed by acid hydrolysis primary alcohol is obtained.



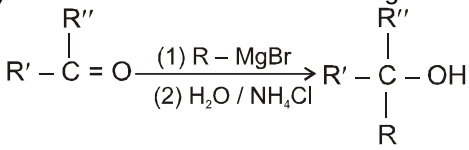
1° alcohol

(b) When aldehyde except formaldehyde is treated with Grignard reagent followed by hydrolysis 2° alcohol is obtained.



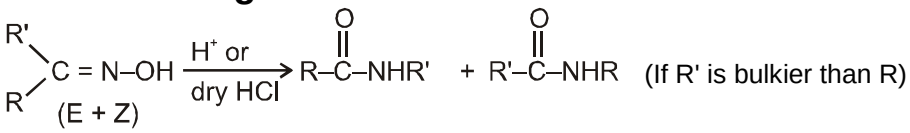
2° alcohol

(c) When ketone is treated with Grignard reagent followed by acid hydrolysis 3° alcohol is obtained.



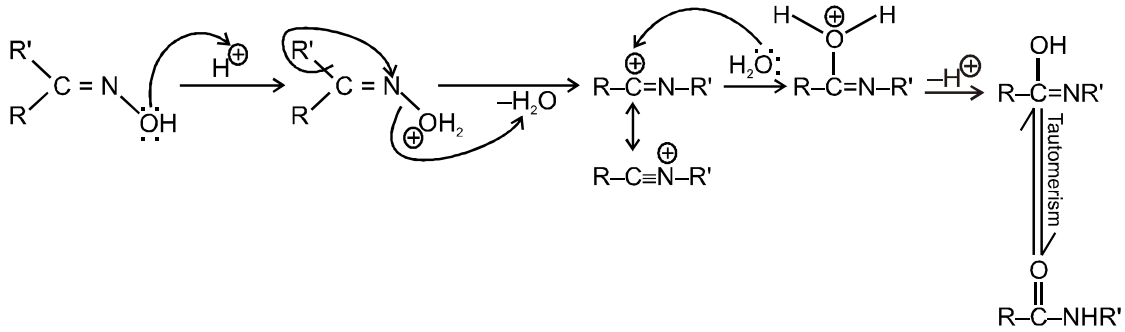
3° alcohol

7.2 Beckmann rearrangement in oximes:



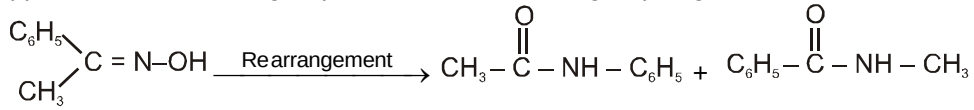
(If R' is bulkier than R)

Mechanism :



Note : (i) Oxime undergoes Beckmann rearrangement to give its isomer amide.
(ii) In this reaction the group which is anti to –OH group migrates.

Ex.



(–CH_3 is anti to –OH)

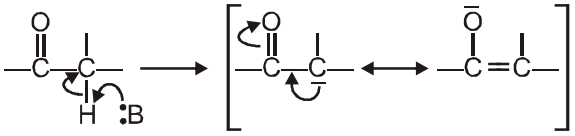
(–C_6H_5 is anti to –OH)

Section (C) : Condensation reactions

7.3 Reactions due to α-hydrogen

α-Hydrogen of aldehydes and ketones are acidic: They undergo a number of reactions due to the acidic nature of α-hydrogen.

Reason for the acidity of α-hydrogen: Strong electron-withdrawing effect of the carbonyl group, and resonance stabilisation of the conjugate base



Resonating structure of conjugate base

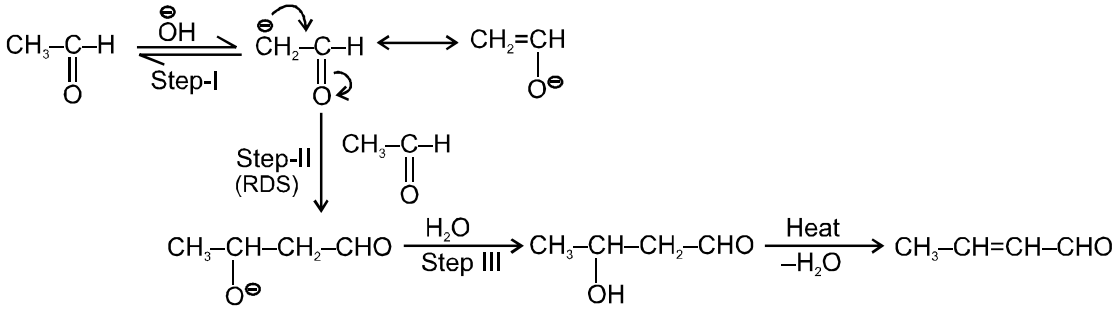
(I) Aldol condensation (or aldol reaction)

Aldehydes and ketones with at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst.

Aldol is derived from two functional groups aldehyde(s) and alcohol.

Ketones gives ketols (keto + alcohols) groups. The name aldol condensation still applies to their reactions.

Mechanism



Ex. **(a)** $2CH_3–CHO \xrightleftharpoons{\text{dil.NaOH}} CH_3–\underset{\underset{OH}{|}}{CH}–CH_2–CHO \xrightarrow[-H_2O]{\Delta} CH_3–CH=CH–CHO$

Ethanal — 3-Hydroxybutanal (Aldol) — But-2-enal (Aldol condensation product)

(b) $2CH_3–CO–CH_3 \xrightleftharpoons{Ba(OH)_2} CH_3–\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}–CH_2–\overset{\overset{O}{||}}{C}–CH_3 \xrightarrow[-H_2O]{\Delta} CH_3–\overset{\overset{CH_3}{|}}{C}=CH–\overset{\overset{O}{||}}{C}–CH_3$

Propanone — 4-Hydroxy-4-methylpentan-2-one — 4-Methylpent-3-en-one (Aldol condensation product)

(II) Cross-Aldol condensation :

On using two types of carbonyl compounds both having α-hydrogen atoms we get a mixture of four condensed product because two types of carbonyl compounds will give two type of carbanions which will be nucleophile for itself and other molecule.

$CH_3CHO + CH_3CH_2CHO \xrightarrow[(ii)\ \Delta]{(i)\ NaOH}$

$CH_3–CH=CH–CHO$ (Simple or self aldol products)

+

$CH_3–CH_2–CH=\underset{\underset{CH_3}{|}}{C}–CHO$ (Simple or self aldol products)

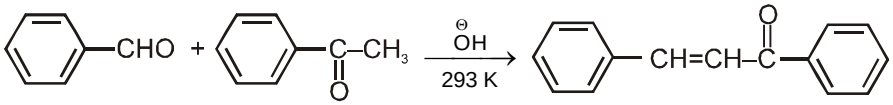
+

$CH_3–CH=\underset{\underset{CH_3}{|}}{C}–CHO$ (Cross aldol products)

+

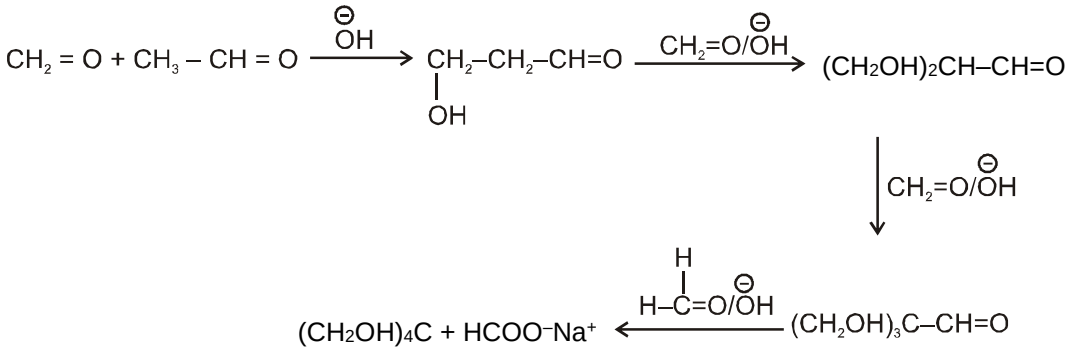
$CH_3–CH_2–CH=CH–CHO$ (Cross aldol products)

Ketones can also be used as one component in cross-aldol reactions.



1,3-Diphenylprop-2-en-1-one
{Benzalacetophenone}
{Major product}

Note : On using formaldehyde and acetaldehyde during crossed aldol all the α-hydrogen atom of acetaldehyde are replaced one by one by hydroxymethyl group because of smaller size of formaldehyde to give trihydroxymethylacetaldehyde which undergoes crossed cannizaro's reaction with formaldehyde to give tetrahydroxymethyl methane and formate ion as a final product.

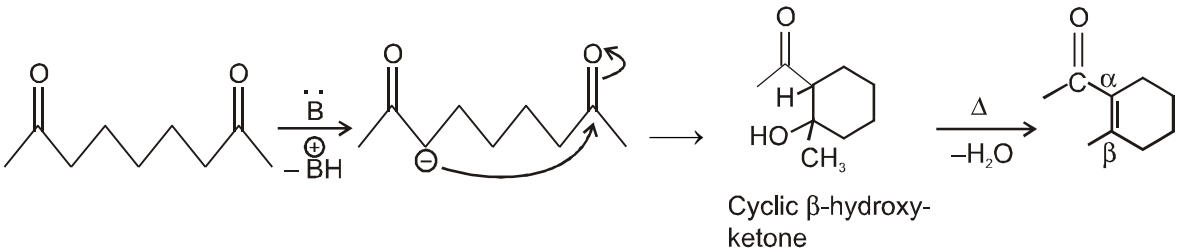


Ex. Show how cinnamaldehyde is prepared by crossed aldol condensation ?

Sol. $C_6H_5CHO + CH_3CHO \xrightarrow[(-H_2O)]{OH^{\ominus}} C_6H_5CH=CH-CHO + H_2O$

(III) Intramolecular aldol condensation :

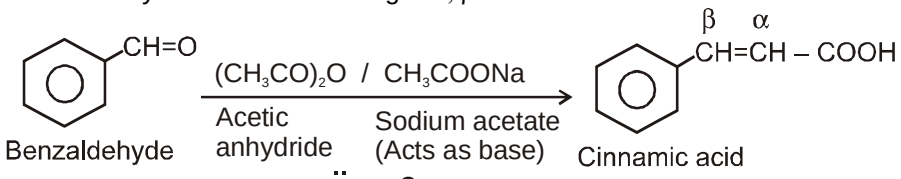
If two carbonyl groups with α-hydrogen atoms are present within the same molecule, then we get cyclic α, β-unsaturated aldehyde / ketones via the formation of cyclic-β-hydroxy aldehyde / ketone in presence of basic medium.

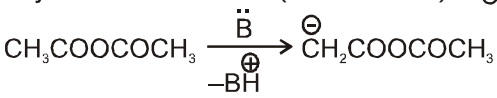


By knowing product we can get reactant as in case of intermolecular aldol condensation :

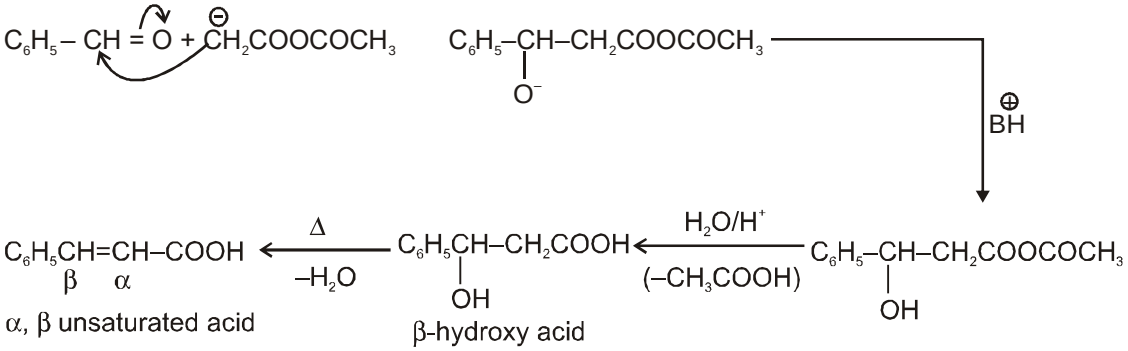
7.4 Perkin reaction :

When aromatic aldehyde like benzaldehyde is treated with anhydride in the presence of sodium salt of acid from which anhydride is derived we get α, β-unsaturated acid.





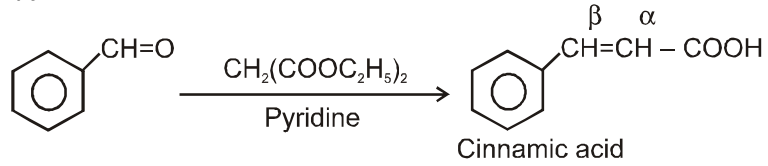
Mechanism :



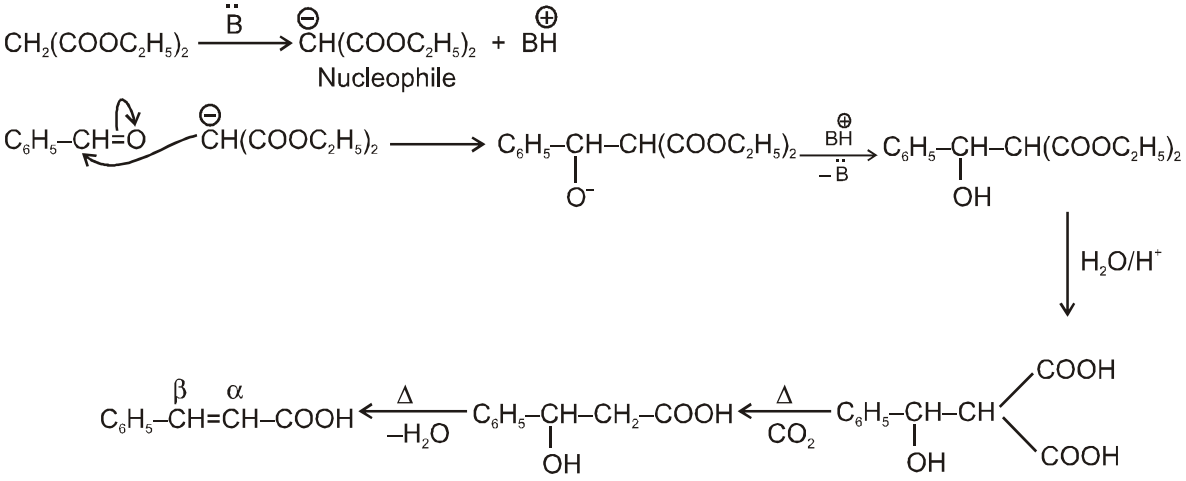
Note : By knowing α, β-unsaturated acid we can get idea about the anhydride used in perkin reaction. This can be done by keeping 'H' at α and –OH at β-carbon atom followed by breaking α, β carbon. By this we can know about acid and it will be anhydride of this acid only.

7.5 Knoevenagel reaction :

It is preparation of α, β-unsaturated acid with carbonyl compound using malonic ester in the presence of pyridine base.



Mechanism :



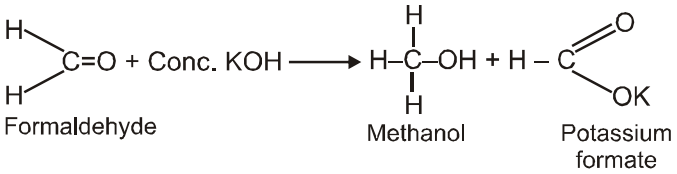
that is we reflux the ester with dilute aqueous HCl or dilute aqueous H_2SO_4.

Section (D) : Cannizzaro's reactions

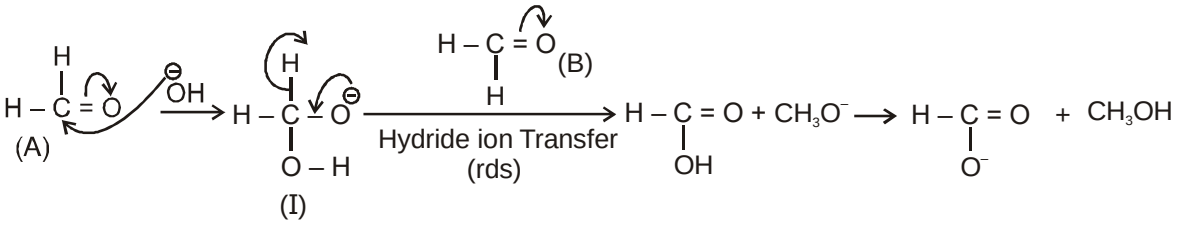
7.6 Cannizzaro reaction :

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

Ex.



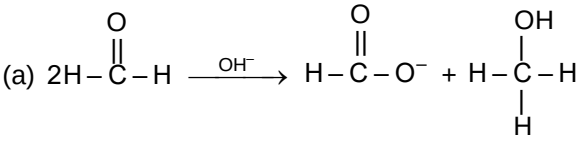
Mechanism :

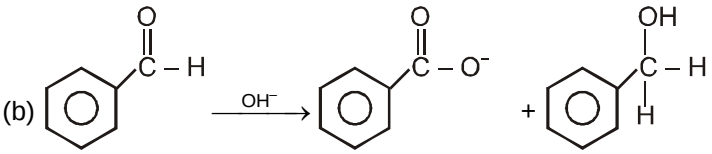


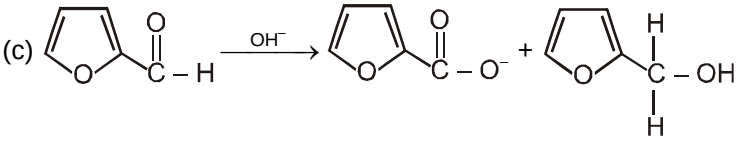
By this mechanism it is clear that acid corresponds to that carbonyl compound over which $\overset{\ominus}{OH}$ can attack easily as nucleophile.

Note : It is observed that hydride ion transfer from (I) to Carbonyl compound (B) is rate determining step.

Ex. Predict the condensation products of these reactions :

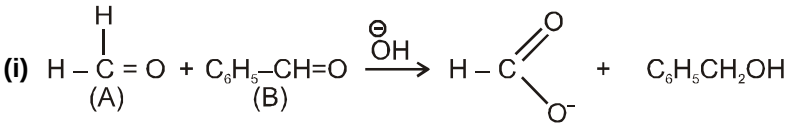
(a) 

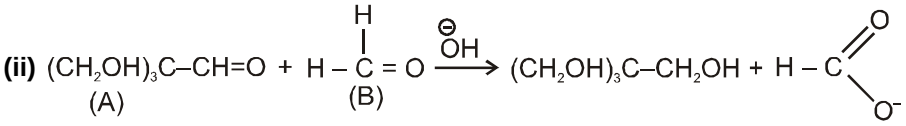
(b) 

(c) 

Crossed Cannizzaro reaction :

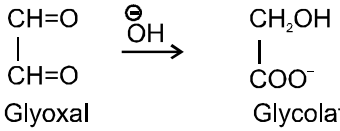
When ever two different aldehyde or ketons without α-hydrogen atom is treated with strong base, the reaction is known as cross cannizzaro reaction. In this reaction one of the reactant (with lesser electron density) get oxidized to carboxylate ion, where as the one with greater electron density is reduced to alcohol.

(i) 

(ii) 

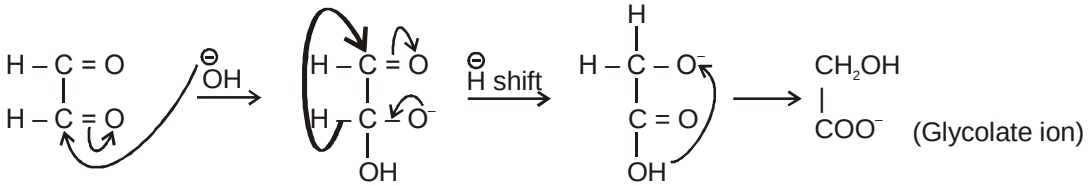
Intramolecular Cannizzaro reacion :

Here two carbonyl groups (without α-hydrogen atom) are present within the same molecule.

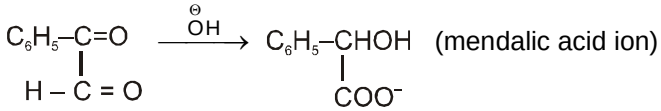


Glyoxal Glycolate ion

Mechanism : $\Rightarrow$ α-keto aldehyde gives internal cannizzaro reaction.



When the reaction is caried out in D_2O, the obtained alcohol contains no α-deuterium.

Ex. 

Note : 1. CH_3CHO does not gives cannizzaro reaction.
2. $(CH_3)_2CH–CH=O$ gives cannizzaro reaction.

7.7 Reduction reactions

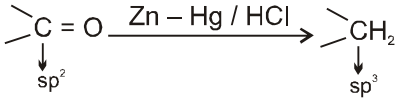
(I) Reduction to alcohols :

Aldehydes $\xrightarrow[\text{or Catalytic hydrogenation}]{NaBH_4 \text{ or } LiAlH_4}$ Primary alcohols

Ketones $\xrightarrow[\text{or Catalytic hydrogenation}]{NaBH_4 \text{ or } LiAlH_4}$ Secondary alcohols

(II) Clemmensen reduction :

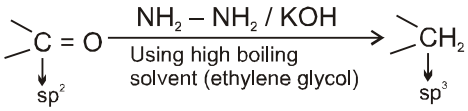
Used to get alkane from carbonyl compounds.



Note : Generally this reaction is avoided if **acid sensitive** groups are present in the carbonyl compounds.

(III) Wolf-Kishner reduction :

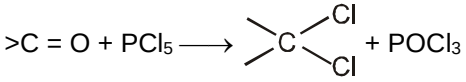
Used to get alkane from carbonyl compounds.

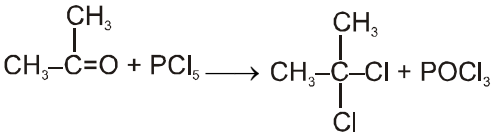


Note : Generally this reaction is avoided if **base sensitive** groups are present in the carbonyl compounds

(IV) Reaction with PCl_5 :

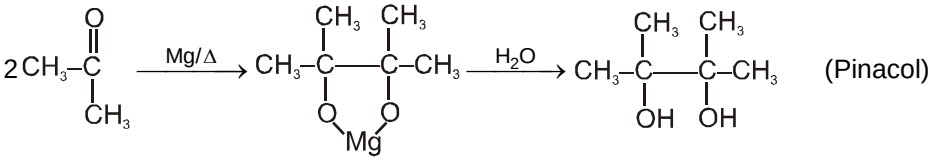
Carbonyl compounds give gemdihalides



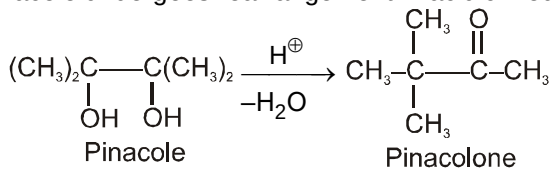
(i) $CH_3CH{=}O + PCl_5 \longrightarrow CH_3{-}CHCl_2 + POCl_3$ **(ii)** 

(V) Preparation of Pinacol:

Pinacole is obtained when 2 moles of acetone are heated with magnesium metal followed by treating with water.



Pinacole undergoes rearrangement in acidic medium to give pinacolone



Section (E) : Redox reactions

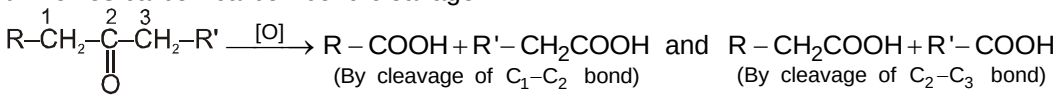
7.8 Oxidation of Aldehydes :

- Aldehydes are oxidised to carboxylic acids by common oxidising agents such as $KMnO_4$, HNO_3, $K_2Cr_2O_7$, etc.

  $R{-}CHO \xrightarrow{[O]} RCOOH$

- Aldehydes are also oxidised by mild oxidising agents such as Tollen's reagent and Fehling's reagent. On the other hand, ketones are not oxidised by mild oxidising agents.

- Ketones are oxidised under vigorous conditions, i.e., by strong oxidising agents and at elevated temperatures.
  It involves carbon-carbon bond cleavage.



(a) Tollen's reagent :

It is ammonical silver nitrate solution, prepared by adding ammonium hydroxide to $AgNO_3$ solution. During reaction, first Ag_2O is formed which is dissolved in ammoniumhydroxide to give Tollen's reagent.

$$2AgNO_3 + 2NH_4OH \longrightarrow Ag_2O + NH_4NO_3 + H_2O$$

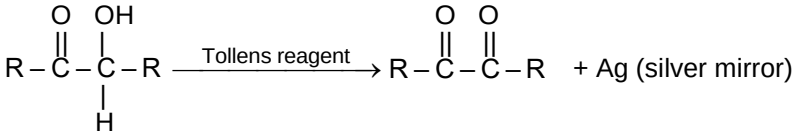
$$Ag_2O + 4NH_4OH \longrightarrow \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]OH} + 3H_2O$$

Tollen's reagent is weak oxidising agent. It gives Ag mirror test with aldehyde.

$$R - CH = O + 2Ag(NH_3)_2^{\oplus} + 3OH^{\ominus} \longrightarrow RCOO^{\ominus} + 2Ag + 2NH_3 + 2H_2O$$

$$R - CH = O + Ag_2O \longrightarrow R - COOH + 2Ag \text{ (Silver mirror)}$$

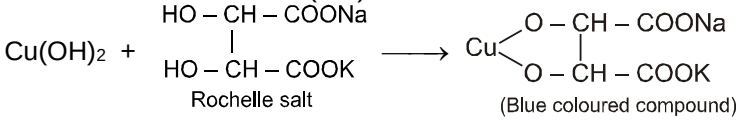
Note : α-hydroxy ketones also gives tollens test :



(b) Fehling's solution :

It is an alkaline solution of cupric ion complexed with sodium potassium tartarate.
There are two solutions in Fehling solution
Solution (A) : $CuSO_4$ solution and
Solution (B) : Alkaline solution of sodium potassiumtartarate.
When these two solutions are mixed, we get deep blue coloured solution.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$



Equal volume of both the solutions are heated with aldehyde to give red brown precipitate of cuprous oxide (Cu_2O) which confirms the presence of aldehyde.

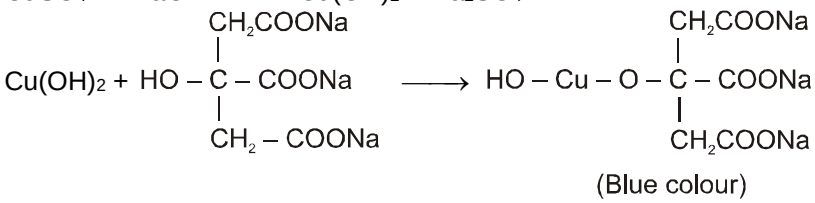
$$R - CHO + \underset{\text{Blue}}{2CuO} \longrightarrow RCOOH + Cu_2O \text{ (Red ppt)}$$

$$RCHO + 2Cu^{2+} + 3OH^{\ominus} \longrightarrow RCOO^{\ominus} + \underset{\text{(Red ppt)}}{2Cu^{\oplus}} + 2H_2O$$

(c) Benedict solution :

It also consists of two solutions.
Solution (A) : $CuSO_4$ solution and
Solution (B) : Alkaline solution of sodium Citrate.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$



Aldehyde gives positive test with Benedict solution.

$$RCH{=}O + \underset{\text{(blue)}}{2Cu^{2+}} + 3OH^{\ominus} \longrightarrow RCOO^{\ominus} + \underset{\text{(Red ppt.)}}{2Cu^{\oplus}} + 2H_2O$$

(d) Schiff's reagent :

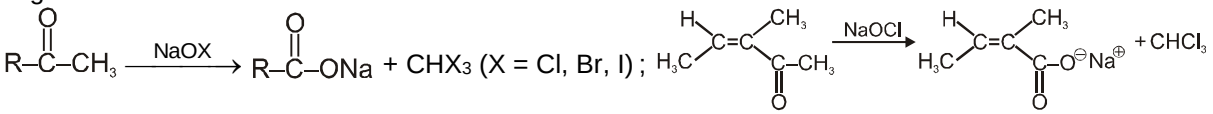
It is dilute solution of rosaniline hydrochloride whose pink colour has been discharged by passing SO_2. Aldehyde restores pink colour when treated with schiff's reagent (Magenta solution in H_2SO_3).
Benzaldehyde does not gives Fehling, Bendict & Schiff's test

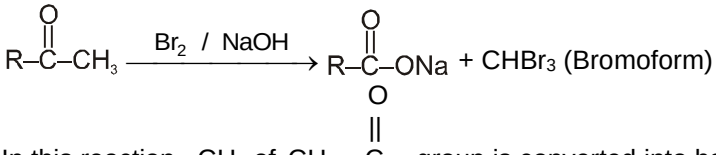
Section (F) : α-Halogenation, haloform, α-deuteration reactions

7.9 Oxidation reactions

(I) Haloform reaction :

Acetaldehyde and methylalkyl ketones react rapidly with halogen (Cl_2, Br_2 or I_2) in the presence of alkali to give haloform and acid salt.





In this reaction $-CH_3$ of CH_3-C- group is converted into haloform as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone give acid salt having carbon atom corresponding to alkyl ketone.
Preparation of haloform from methylketone involves two steps.

(a) Halogenation : $R-C(=O)-CH_3 \xrightarrow{Br_2} R-C(=O)-CBr_3$ (Halogenation)

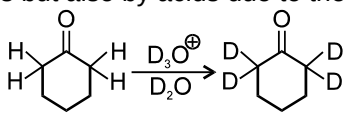
(b) Alkaline-hydrolysis : $R-C(=O)-CBr_3 \xrightarrow{NaOH} CHBr_3 + R-C(=O)-ONa$ (Alkaline-hydrolysis)

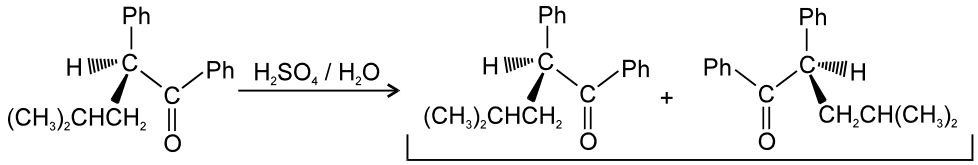
Note : This reaction is used to distinguish the presence of CH_3-C- group.

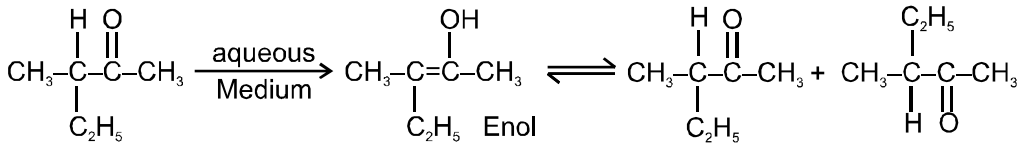
Acetoacetic ester does not give this reaction because it contains active methylene group.

(II) Racemisation and D-exchange :

Exchange of α-hydrogen from deuterium as well as racemization at the α-carbon are catalyzed not only by bases but also by acids due to the phenomenon of tautomerisation.

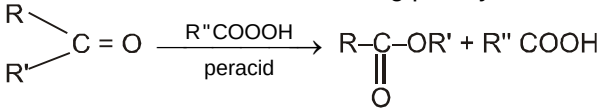
1. 

2. 

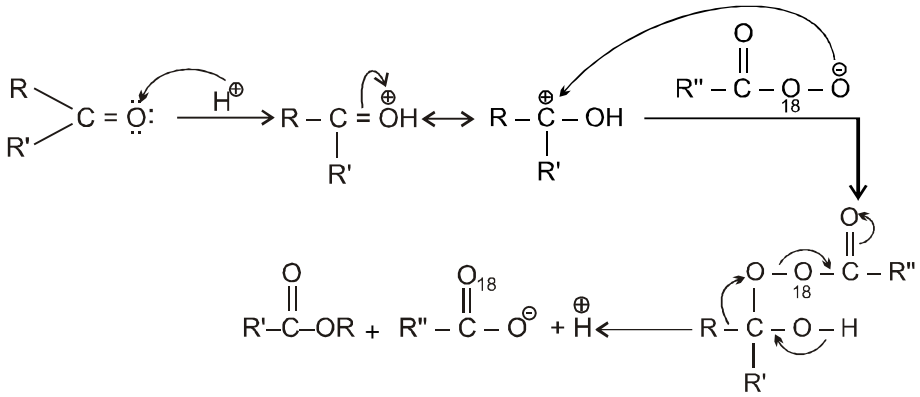
3. 

(III) Baeyer-Villiger oxidation :

It is preparation of ester from ketone using peroxyacid.



Mechanism :



Note : In unsymmetrical ketones, preference of insertion of oxygen atom in decreasing order is :
H > 3ºR > 2ºR > Ph > 1ºR > CH_3

7.10 Other miscellaneous reactions :

(I) $CH_2 = O$ (Formaldehyde)

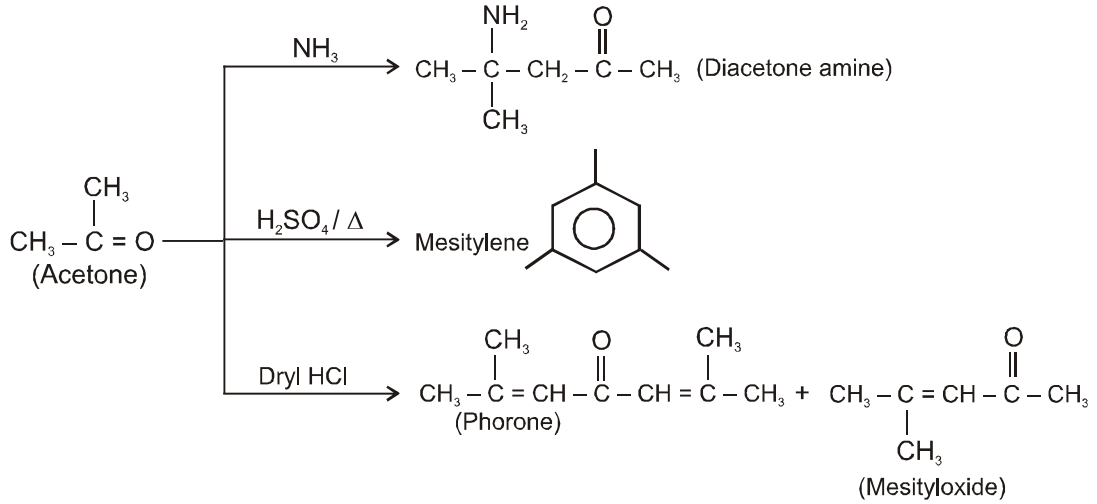
- NH_3 → Hexamethylene tetramine (urotropine)
- Evaporated to drynes → $(CH_2OCH_2OCH_2O)_n$, n = 6 to 50 Paraformaldehyde
- Kept at room tempt for a longtime → Trioxane (metaformaldehyde)

(II) $CH_3 - CH = O$ (Acetaldehyde)

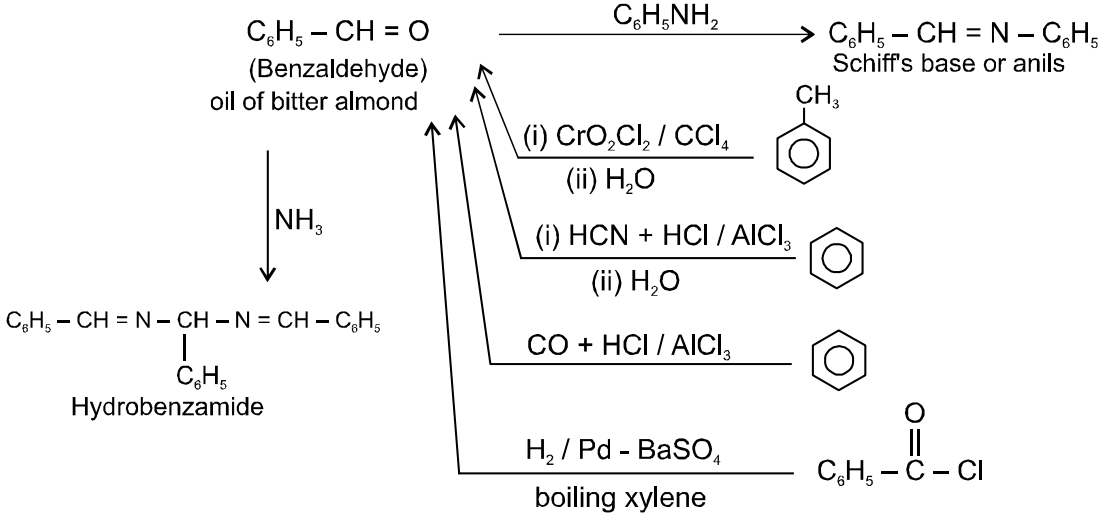
- NH_3 → $CH_3 - CH(NH_2) - OH$ (Acetaldehyde ammonia) → $.3H_2O$ (cyclic trimer)
- conc. H_2SO_4 (few drops) → Cyclic trimer (paraldehyde) — used as hypnotic
- Dry HCl → Cyclic tetramer (Metaldehyde) $(CH_3CHO)_4$

2,4,6-Trimethyl 1,3,5-trioxane

(III)



(IV)



8. Uses of Aldehydes and Ketones

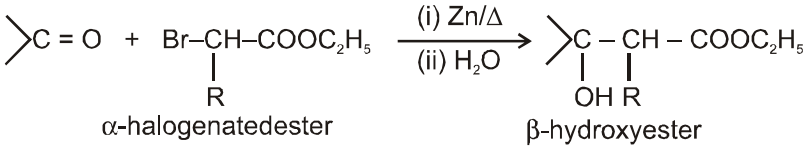
- Act as solvents.
- Act as starting materials and reagents for the synthesis of other products.
- Formalin (40% solution of formaldehyde)- Used for preserving biological specimens, bakelite, urea , formaldehyde glues and other polymers products.
- Acetaldehyde used in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.
- Benzaldehyde used in perfumery and in dye industries.
- Butyraldehyde, vanillin, camphor, etc., are well known for their odours and flavours.
- Acetone and ethyl methyl ketone are common industrial solvents.

9. Other miscellaneous named reactions :

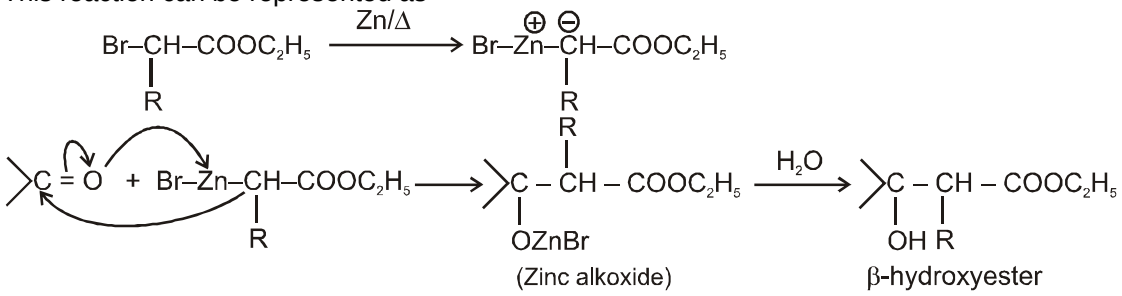
9.1 Reformatsky reaction :

When carbonyl compound and α-halogenated ester are heated with zinc followed by treating with water we get β-hydroxyester.

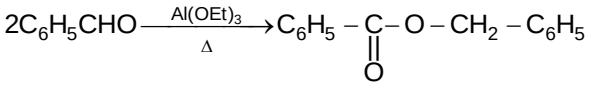
The organozinc reagent generated is less reactive than a Grignard reagent, it does not add to the ester group.



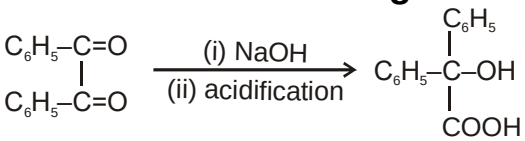
This reaction can be represented as –



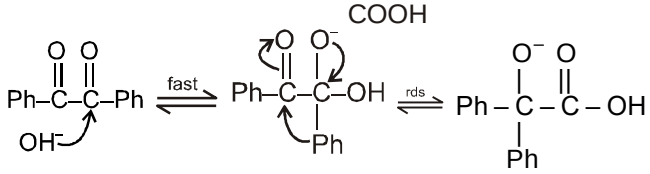
9.2 Tischenko reaction:



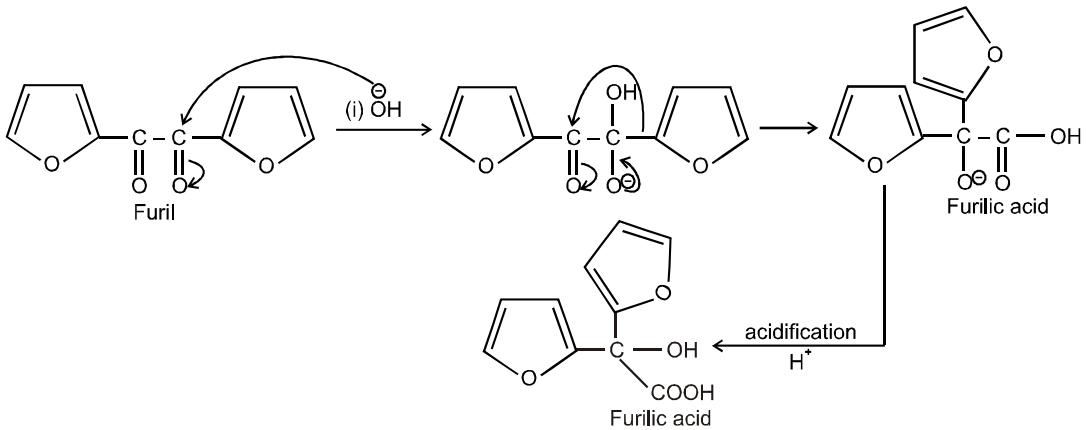
9.3 Benzil-benzilic acid rearrangement :



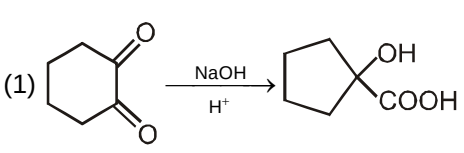
Mechanism :

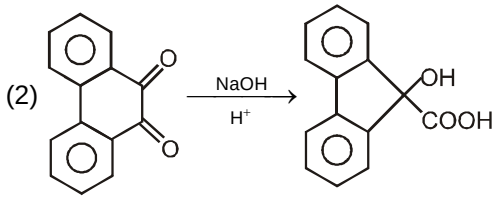


Conversion of furil to furilic acid with mechanism :



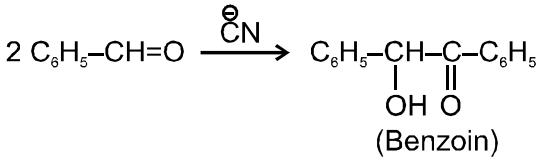
Predict the products of the following reactions :



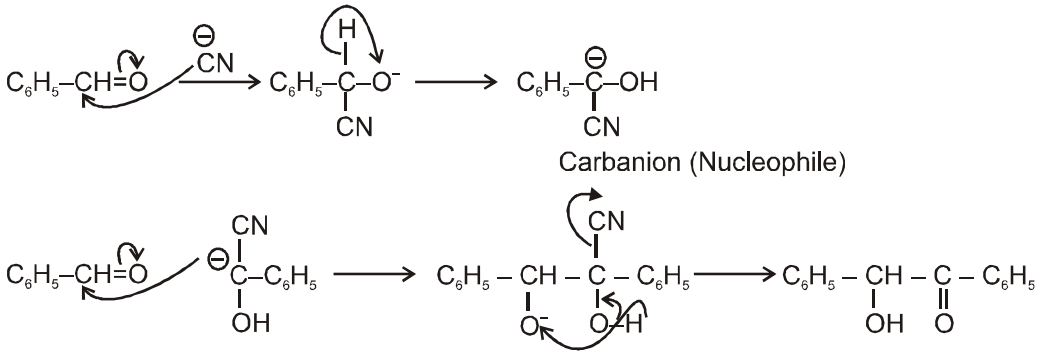


9.4 Benzoin Condensation :

During this reaction benzoin is obtained when an ethanolic solution of benzaldehyde is heated with strong alkali potassium cyanide or sodium cyanide.



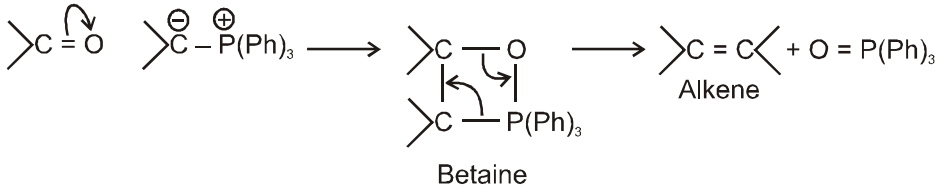
Mechanism :



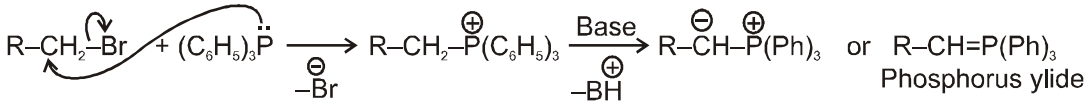
9.5 Wittig reaction :

It is used to get alkene from carbonyl compound using phosphorus ylide via the formation of cyclic structure betaine.

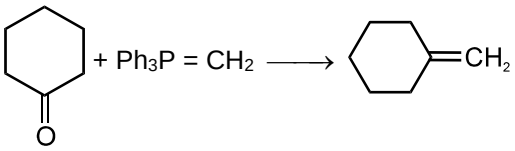
Mechanism :



Note : Phosphorus ylides are prepared from alkylhalide and triphenylphosphine in the presence of base like sodium ethoxide as –



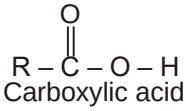
Ex.



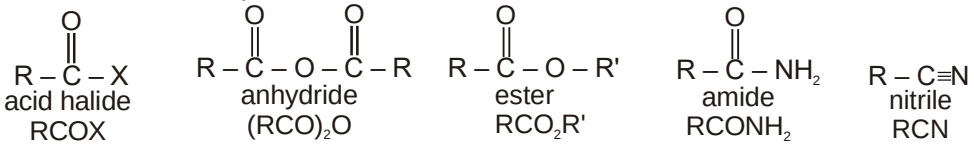
Carboxylic Acids & Acid Derivatives

Introduction :

Compounds containing the carboxyl group are distinctly acidic and are called **carboxylic acids**.There general formula is $C_nH_{2n}O_2$.



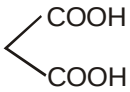
Carboxylic acid derivatives are compounds with functional groups that can be converted to carboxylic acids by a simple acidic or basic hydrolysis. The most important acid derivatives are esters, amides, nitriles, acid halides and anhydrides.



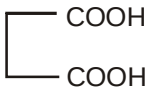
Dicarboxylic acids :

If the compound containing two carboxyl groups, these are known as dicarboxylic acid.
For example :

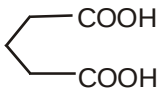
Oxalic acid
Ethanedioic acid



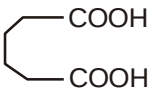
Malonic acid
Propanedioic acid



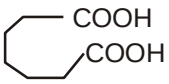
Succinic acid
Butanedioic acid



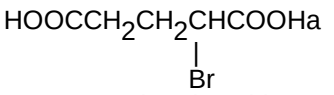
Glutaric acid
Pentanedioic acid



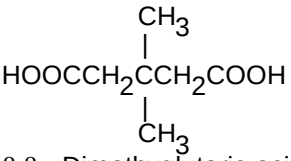
Adipic acid
Hexanedioic acid



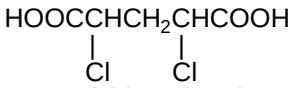
Pimelic acid
Heptanedioic acid



α – Bromoglutaric acid
2 – Bromopentanedioic acid



β,β – Dimethyglutaric acid
3,3 – Dimethylpentanedioic acid

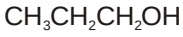


α,α – Dichloroglutaric acid
2,4 – Dichloropentanedioic acid

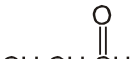
Physical properties of acids and acid derivatives :

(1) Boiling point : The boiling point of carboxylic acids are higher than that of alcohols, ketones or aldehydes of similar molecular weight.

acetic acid,
bp 118ºC

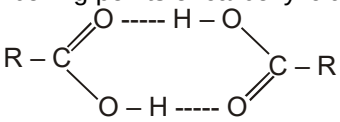


1-propanol
bp 97ºC



Propionaldehyde
bp 49ºC

The high boiling points of carboxylic acids is the result of formation of a stable hydrogen-bonded dimer.



hydrogen bonded acid dimer

(2) Melting points :

Melting point of carboxylic acids : There is no regular pattern in melting point of carboxylic acid (up to 10 carbon atoms) having even number of C atoms are higher than neighbouring members having odd number of C atoms because carboxylic acid and methyl group in even members lie in opposite side of zig-zag carbon chain hence they fit better into crystal lattice resulting in higher melting points.Vice-versa is observed in case of carboxylic acid having odd no. of carbon atoms.

Higher melting point

Lower melting point

Amides have surprisingly high boiling points and melting points compared with other compounds of similar molecular weight. Primary and secondary amides participate in strong hydrogen bonding.

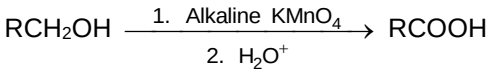
(3) Solubility:

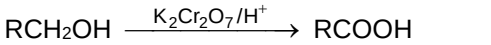
Carboxylic acids form hydrogen bonds with water and the lower molecular - weight carboxylic acids (upto 4 carbon atoms) are miscible with water.
Acid derivatives (esters, acid chlorides, anhydrides, nitriles and amides) are soluble in common organic solvents such as alcohols, ethers, chlorinated alkanes and aromatic hydrocarbons. Acid chlorides and anhydrides cannot be used in nucleophilic solvents such as H_2O and alcohols, because they react with these solvents.

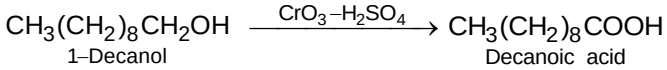
(4) Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature, higher acids are wax like solids due to their low volatility.

Section (G) : Carboxylic acid (Preparation Methods)

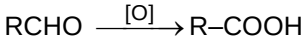
1. From primary alcohols







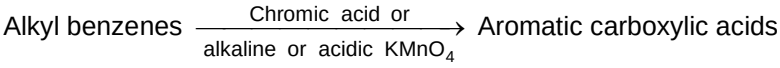
2. From aldehydes



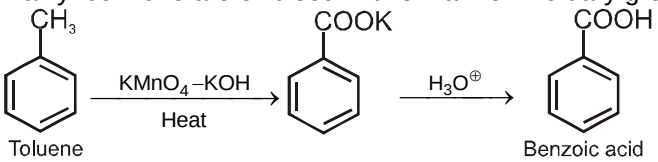
Oxidising agents - HNO_3, $KMnO_4$, $K_2Cr_2O_7$

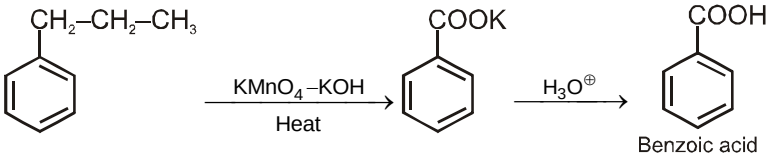
Mild oxidising agents - Tollen's reagent and Fehling's reagent

3. From alkyl benzenes

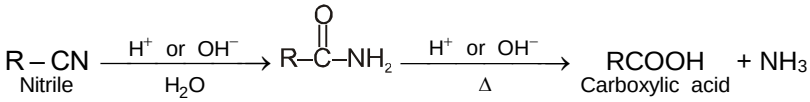


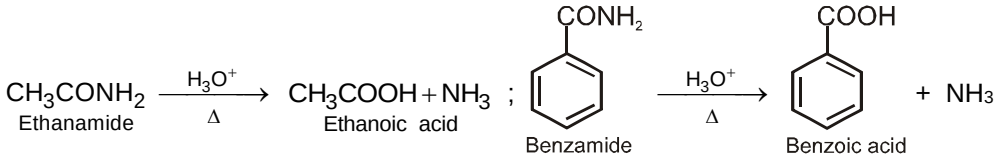
1° and 2° alkyl benzene are oxidised in this manner. Tertiary group is not affected.



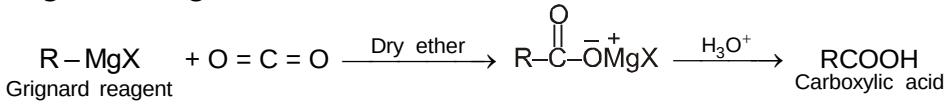


4. From nitriles and amides

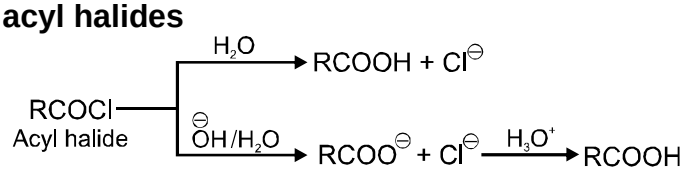




5. From Grignard reagents



6. From acyl halides



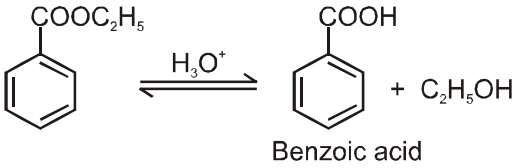
7. From acyl anhydrides

$$\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{2C_6H_5COOH}$$

$$\underset{\text{Benzoic ethanoic anhydride}}{C_6H_5COOCOCH_3} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Ethanoic acid}}{CH_3COOH}$$

8. From esters

$$\text{Ester} \xrightarrow{\text{Acidic hydrolysis}} \text{Carboxylic acid}$$

Ex. 

Benzoic acid

$$\text{Ester} \xrightarrow{\text{Basic hydrolysis}} \text{Carboxylate} \xrightarrow{H_3O^+} \text{Carboxylic acid}$$

Ex. $\underset{\text{Ethyl butanoate}}{CH_3CH_2CH_2COOC_2H_5} \xrightleftharpoons{NaOH} CH_3CH_2CH_2COONa + C_2H_5OH$

$CH_3CH_2CH_2COONa \xrightarrow{H_3O^+} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$

Section (H) : Carboxylic acid (Chemical Properties)

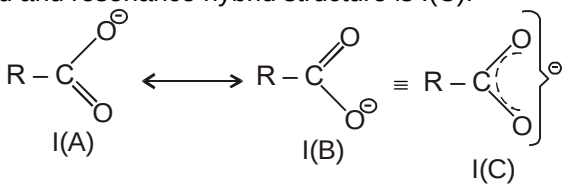
Chemical Reactions of carboxylic acid :

(1) Acidic Nature : Acidity of carboxylic acids :

$$R-\underset{\underset{O}{\|}}{C}-OH \rightleftharpoons R-\underset{\underset{O}{\|}}{C}-O^{\ominus} + H^{\oplus}$$

(I)

(i) $R-\underset{\underset{O}{\|}}{C}-O^{\ominus}$ (I) exists as two equivalent canonical structures I(A) and I(B). This ion is resonance stablised and resonance hybrid structure is I(C).



(ii) $R-\underset{\underset{O}{\|}}{C}-O^{\ominus}$ ion is more stable due to resonance, hence carboxylic acids are acidic in nature.

(iii) Electron withdrawing group (–I effect) stablises the anion and hence, increases acidic nature.

Ex. $F-CH_2-COOH > Cl-CH_2COOH > Br-CH_2COOH > I-CH_2COOH$

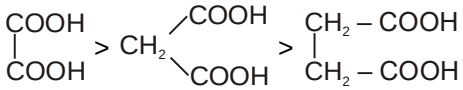
Increasing acid strength

Ex. $Cl_3C-COOH > Cl-CH(Cl)-COOH > Cl-CH_2COOH > CH_3COOH$

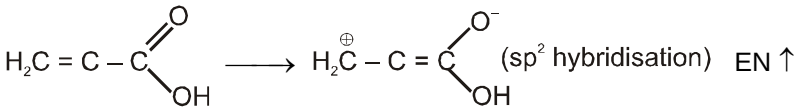
Increasing acid strength

(iv) Electron releasing group (+I effect) destablises the anion and hence decreases acidic nature.

Ex. $HCOOH > CH_3COOH > CH_3-CH_2-COOH$

Ex. 

Direct attachement of groups such as phenyl or vinyl to the carboxylic acid increases its acidity.



Ex. Relative acid strength is: RCOOH > HOH > ROH > HC ≡ CH > NH_3 > RH

Note : Acidity of acids is compared by compairing stability of conjugate base.

(2) Reaction involving removal of proton from –OH group :

(i) Action with blue litmus : All carboxylic acids turn blue litmus into red.

(ii) Reaction with metals :

$$2\,CH_3COOH + 2Na \longrightarrow \underset{\text{Sodium acetate}}{2CH_3COONa} + H_2; \qquad 2CH_3COOH + Zn \longrightarrow \underset{\text{Zinc acetate}}{(CH_3COO)_2Zn} + H_2$$

(iii) Reaction with alkalies :

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

(iv) Reaction with carbonates and bicarbonates :

$$2CH_3COOH + Na_2CO_3 \longrightarrow 2CH_3COONa + CO_2 + H_2O$$

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$$

Reaction of carboxylic acid with aqueous sodium bicarbonate solution produces brisk effervescence. However most phenols do not produce effervescence. Therefore, the reaction may be used to distinguish between carboxylic acids and phenols.

(v) Reaction with grignard reagent :

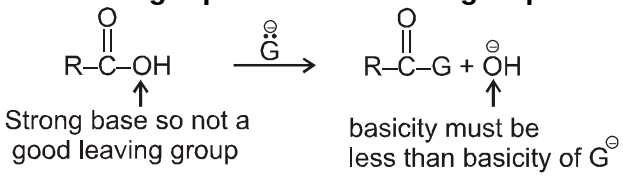
$$R–CH_2MgBr + R'COOH \xrightarrow{\text{ether}} R–CH_3 + R'COOMgBr$$

Feasible reaction : ***A stronger acid displaces a weaker acid from the salt of the weaker acid.***

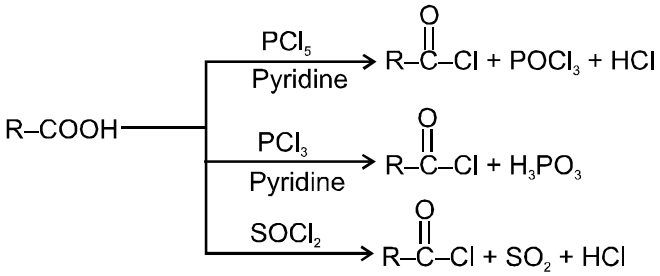
Ex. CH_3COOH (Stronger acid) + $CH_3ONa \longrightarrow CH_3COONa + CH_3–OH$ (Weaker Acid)

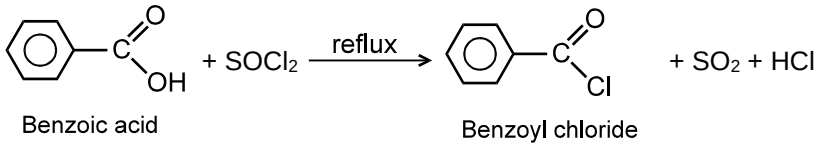
Ex. CH_3COOH (stronger acid) + $NaHCO_3 \longrightarrow CH_3COONa + H_2CO_3$ (Weaker acid) $\longrightarrow H_2O + CO_2\uparrow$
(It is lab test of carboxylic acid)

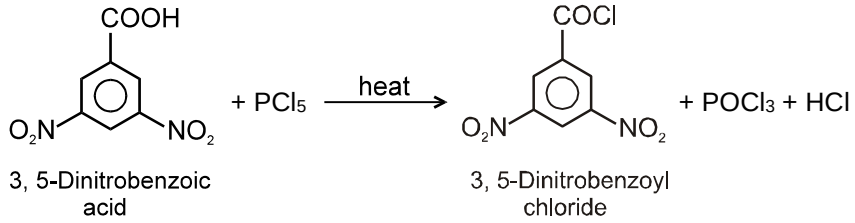
(3) Reaction involving replacement of –OH group :



(i) Formation of acid chlorides :



Ex. 

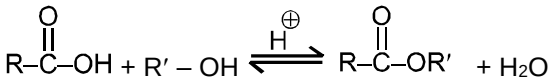
Ex. 

3, 5-Dinitrobenzoic acid — 3, 5-Dinitrobenzoyl chloride

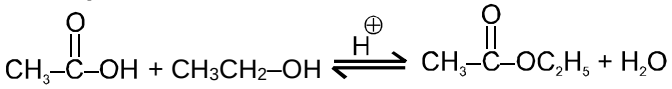
(ii) Fisher Esterification :

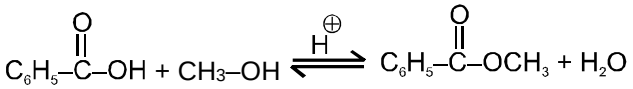
Carboxylic acid react with alcohol to form esters through a condensation reaction known as esterification.

General Reaction :

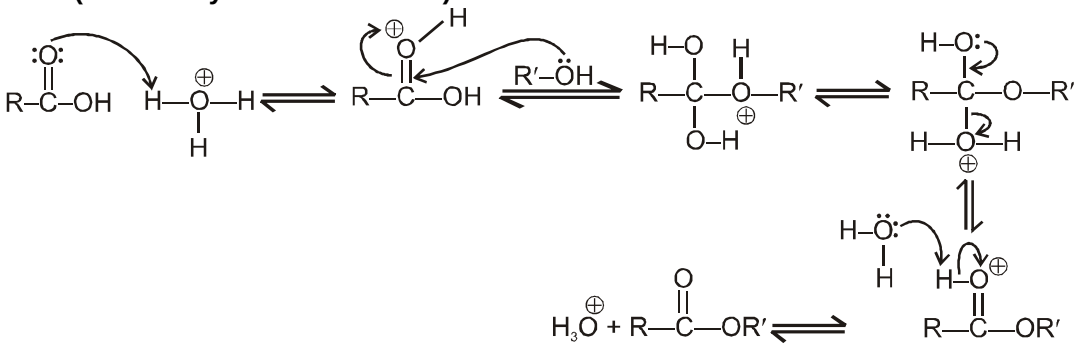


Specific Examples:



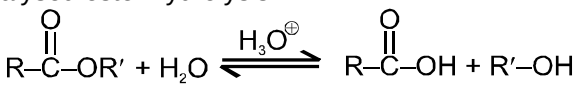


Mechanism : (Acid catalysed esterification)



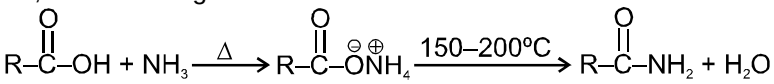
If we follow the forward reactions in this mechanism, we have the mechanism for the acid catalysed esterification of an acid. If however, we follow the reverse reactions, we have the mechanism for the acid catalysed hydrolysis of an ester.

Acid catalysed ester hydrolysis.

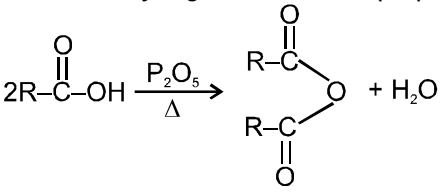


which depends upon condition we choose. If we want to esterify an acid, use an excess amount of the alcohol and, if possible remove the water as it is formed.

If we want to hydrolyse an ester, we use a large amount of water i.e. dil HCl or dil H_2SO_4.

(iii) Formation of amides : 

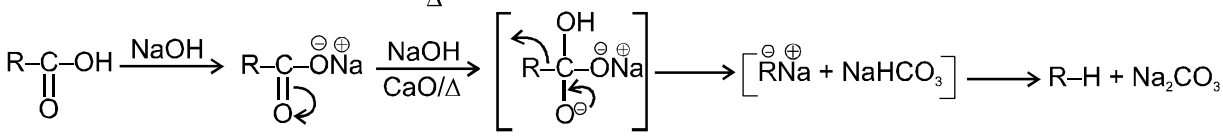
In fact amides can not be prepared from carboxylic acids and amines unless the ammonium salt is heated strongly to dehydrate it. This is not usually a good method of preparing amides.

(iv) Formation of acid anhydride : 

(4) Decarboxylation reactions :

(i) Soda-lime decarboxylation :

General reaction : $R-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[\Delta]{NaOH + CaO} R-H + CO_2$

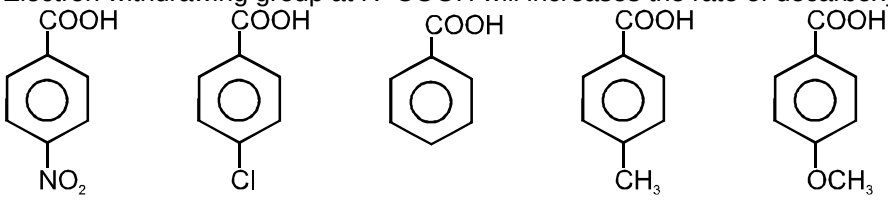


In this reaction carbanion intermediate is formed.

Rate of reaction depends upon the stability of carbanion intermediate.

Electron withdrawing group at R–COOH will increases the rate of decarboxylation.

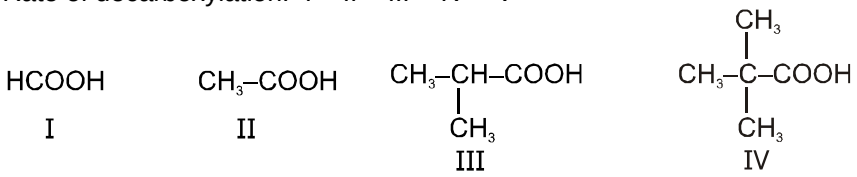
Ex.



I II III IV IV

Rate of decarboxylation. I > II > III > IV > V

Ex.

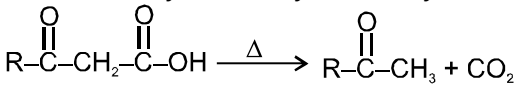


I II III IV

Rate of decarboxylation. I > II > III > IV

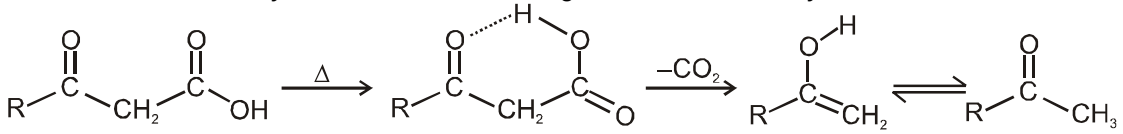
(ii) Decarboxylation of β-keto carboxylic acids:

β-keto acids decarboxylate readily when they are heated to 100–150ºC.



There are two reasons for ease of decarboxylation.

When the acid itself decarboxylates, it can do so through a six membered cyclic transition state :

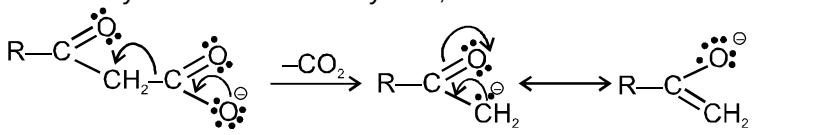


β-keto acid

6 member cyclic transition state

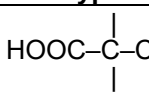
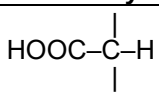
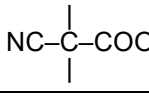
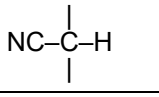
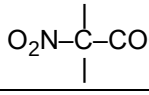
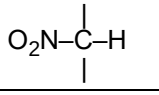
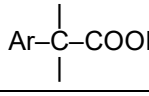
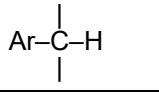
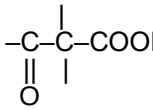
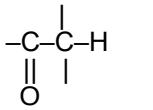
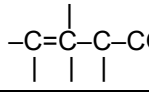
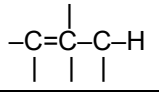
This reaction produces an enol directly and avoids an anionic intermediate. The enol then tautomerises to a methyl ketone.

When the carboxylate anion decarboxylates, it forms a resonance stabilized enolate anion.



Resonance stabilized anion

Alphatic acids that do undergo successful decarboxylation have certain functional groups or double or triple bonds in the α or β positions.

		Acid type	Decarboxylation product
(1)	Malonic		
(2)	α-Cyano		
(3)	α-Nitro		
(4)	α-Aryl		
(5)	β-Keto		
(6)	β,γ-Unsaturated		

(iii) Kolbe's electrolysis

$2RCOOK + 2HOH \xrightarrow{\text{Electrolysis}} R - R + 2CO_2 + H_2 + 2KOH$

If n is the number of carbon atoms in the salt of carboxylic acid, the alkane formed has 2(n–1) carbon atoms.

Ex. $2CH_3 - COOK + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3CH_3 + 2CO_2 + H_2 + 2KOH.$

(iv) Hunsdiecker Reaction (Bromo-decarboxylation) :

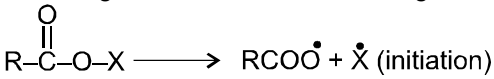
$R–COOAg + Br_2 \longrightarrow R–Br + CO_2 + AgBr$

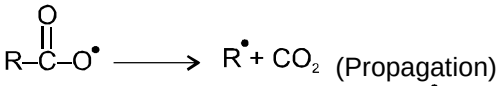
Heavy metal salt of acid is heated with Br_2 it results in decarboxylations.

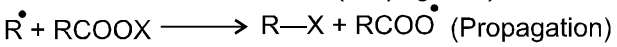
Metal can be silver ion, mercuric ion, or lead (IV) ion.

Mechanism :

Step 1 :

Step 2 : 

Step 3 : 

Step 4 : 

Although bromine is the most often used halogen, chlorine and iodine have also been used.

When iodine is the reagent, the ratio between the reactant is very important and determines the product.

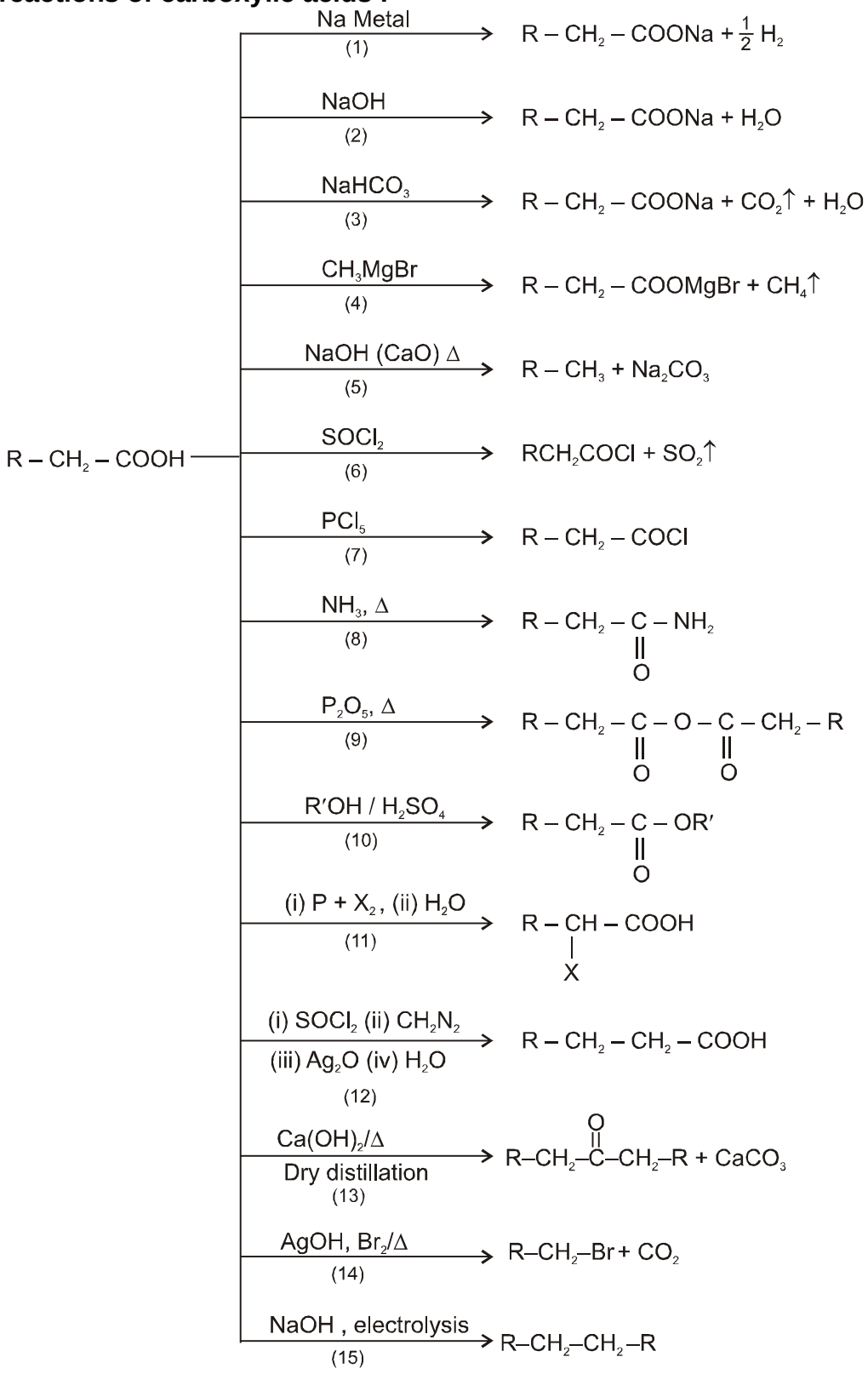
A 1 : 1 ratio of salt to iodine gives alkyl halide, as above. A 2 : 1 ratio, however gives the ester RCOOR. This is called Simonini reaction and sometimes used to prepare carboxylic ester. The yield of alkyl halide follows the order Primary > Secondary > Tertiary

(5) HVZ Reaction (Halogenation of aliphatic acids and Substituted acids) :

In the presence of a small amount of phosphorus, aliphatic carboxylic acids react smoothly with chlorine or bromine to yield a compound in which α-hydrogen has been replaced by halogen.

$CH_3COOH \xrightarrow{Cl_2,\text{Red P}} ClCH_2COOH \xrightarrow{Cl_2,\text{Red P}} Cl_2CHCOOH \xrightarrow{Cl_2,\text{Red P}} Cl_3CCOOH$

Summary of reactions of carboxylic acids :



Uses of Carboxylic Acids

* Methanoic acid - In rubber, textile, dyeing, leather and electroplating industries.
* Ethanolic acid - As a solvent and as a vinegar in food industry.
* Hexanoic acid - In the manufacture of nylon-6, 6.
* Higher fatty acids - For the manufacture of soaps and detergents.

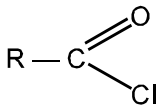
Esters of benzoic acid - In perfumery.

Sodium benzoate - As a food preservative.

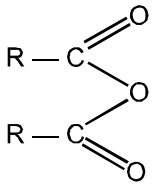
Section (I) : Acid Derivatives (Acid Halide, Ester, Anhydride & Amide)

Carboxylic Acid Derivatives :

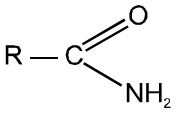
Closely related to the carboxylic acids and to each other are a number of chemical families known as **functional derivatives of carboxylic acids:** acid chlorides, anhydrides, amides, and esters, These derivatives are compounds in which the –OH of a carboxyl group has been replaced by –Cl, –OOCR, $–NH_2$, or –OR`.



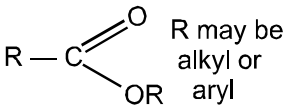
Acid chloride



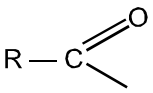
Anhydride



Amide



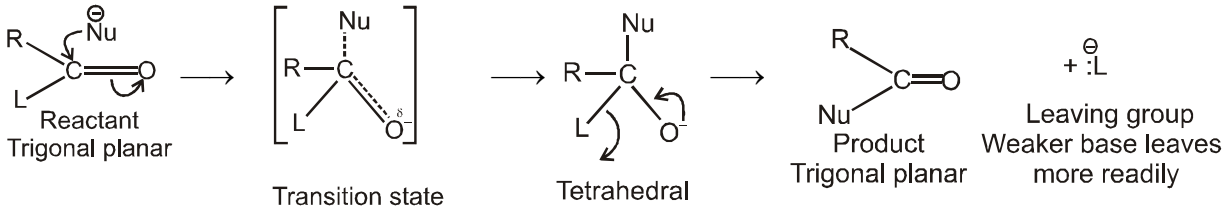
Ester

They all contain the **acyl group,** 

Like the acid to which it is related, an acid derivative may be aliphatic or aromatic, substituted or unsubstituted; whatever the structure of the rest of the molecule, the properties of the functional group remain essentialy the same.

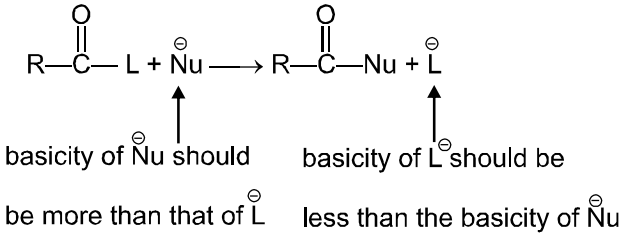
Characteristic reaction of acid derivatives (Nucleophilic acyl substitution) :

Nucleophilic acyl substitution usually takes place by an **addition-elimination** mechanism.The incoming nucleophile adds to the carbonyl to form a tetrasubstituted intermediate with a tetrahedral carbon.



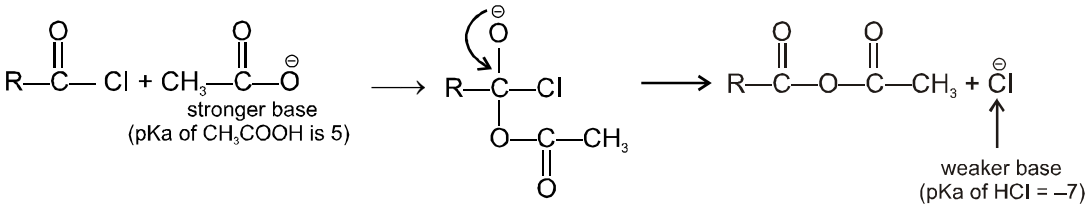
The tetrahedral intermediate formed when a nucleophile attacks the carbonyl carbon of a carboxylic acid derivative is not stable and cannot be isolated.

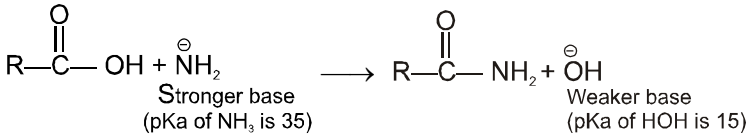
A pair of nonbonding electrons on the oxygen reforms the π bond, and either $L^{\ominus}$ or $Nu^{\ominus}$ is eliminated with its bonding electrons. Whether $L^{\ominus}$ or $Nu^{\ominus}$ is eliminated depends on their relative basicities. The weaker base is preferentially eliminated because the weaker the base, the better it is a leaving group.

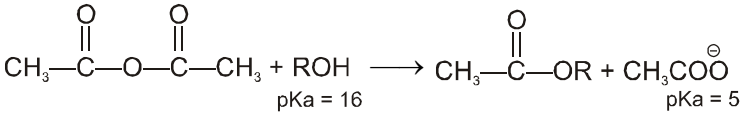


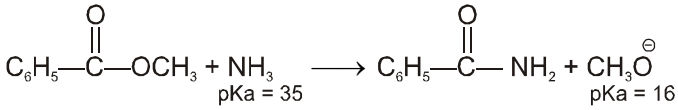
Thus carboxylic acid derivative will undergo a nucleophilic acyl substitution reaction provided that the incoming nucleophile is a stronger base than the group that is to be replaced. If the incoming nucleophile and the group attached to acyl group in the starting material have similar basicities, the

tetrahedral intermediate can expect either group with similar ease. A mixture of starting material and substitution product will result.

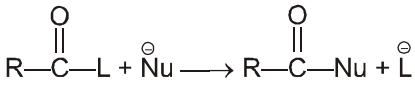
(i) 

(ii) 

(iii) 

(iv) 

Condition for acyl nucleophilic substitution reaction :



(i) L must be better leaving group than $Nu^{\ominus}$, i.e., basicity of Nu should be more than that of $L^{\ominus}$

(ii) $Nu^{\ominus}$ must be a strong enough nucleophilic to attack RCOL.

(iii) Carbonyl carbon must be enough electrophilic to react with $Nu^{\ominus}$.

Reactivity order : $R-\overset{O}{\overset{\|}{C}}-Cl > R-\overset{O}{\overset{\|}{C}}-OR > R-\overset{O}{\overset{\|}{C}}-OH > R-\overset{O}{\overset{\|}{C}}-NH_2$

(A) Acid halides :

Methods of preparation of Acyl halides :

(i) $RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

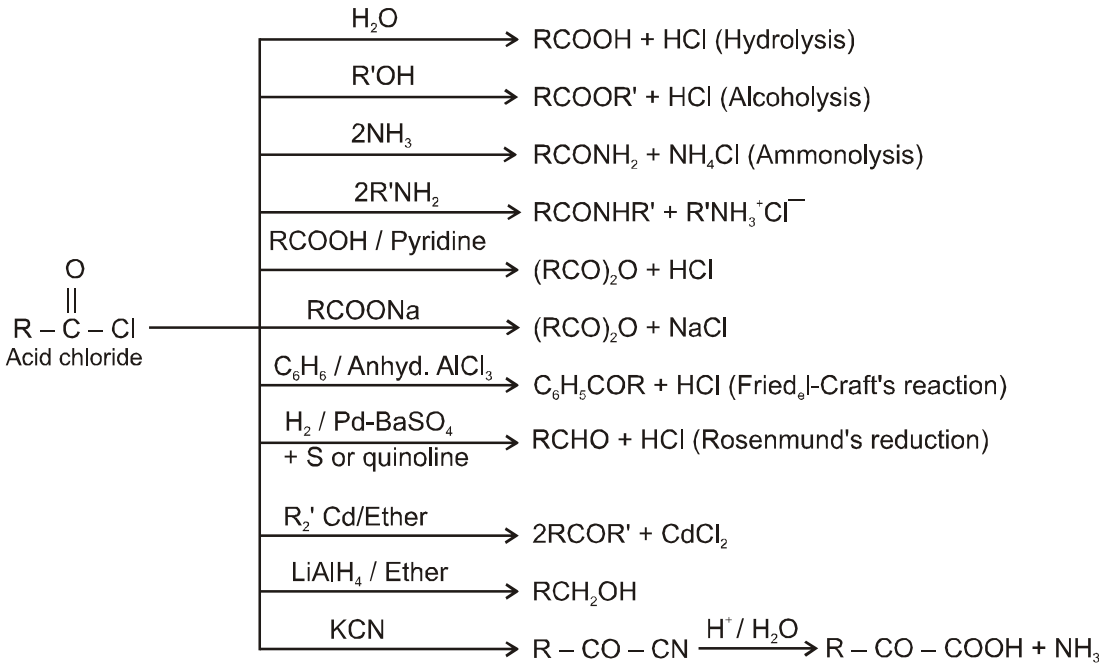
(ii) $3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$

(iii) $RCOOH + SOCl_2 \xrightarrow{\text{Pyridine}} RCOCl + SO_2 + HCl$

Ex. $3CH_3COONa + PCl_3 \xrightarrow{\text{Distil}} \underset{\text{Acetyl chloride}}{3CH_3COCl} + Na_3PO_3$

Ex. $\underset{\text{Sod. benzoate}}{2C_6H_5COONa} + POCl_3 \xrightarrow{\text{Distil}} \underset{\text{Benzoyl chloride}}{2C_6H_5COCl} + NaCl + NaPO_3$

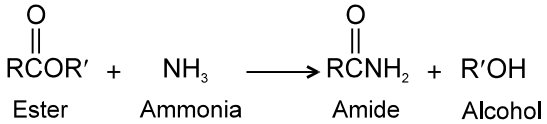
Chemical Reactions :



(B) Acid amides :

Methods of preparation of acids amides :

(1) By reaction of esters with ammonia and amines :



Ammonia is more nucleophilic than water, making it possible to carry out this reaction using aqueous ammonia.

(2) From acid halides :

$RCOCl + 2NH_3 \longrightarrow RCONH_2 + NH_4Cl$

(3) From anhydride :

$(RCO)_2O + 2NH_3 \longrightarrow RCONH_2 + RCOONH_4$

(4) From ammonium salt of carboxylic acid :

$RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$

$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2$

Amm. acetate — Acetamide

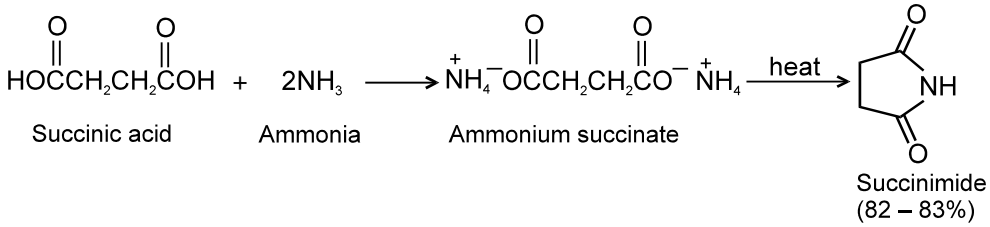
(5) From cyanides :

$R - C \equiv N + H_2O \xrightarrow[\text{or } H_2O_2 - NaOH]{\text{conc. HCl}} R - CONH_2$

$CH_3C \equiv N + H_2O \xrightarrow{\text{conc. } H_2SO_4} CH_3 - CONH_2$

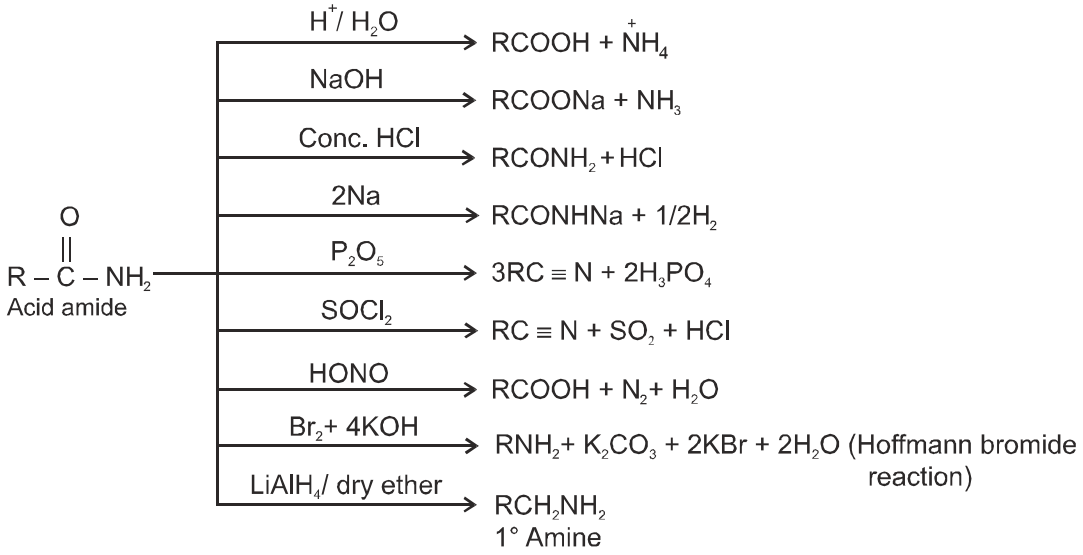
Acetonitrile — Acetamide

(6)



Succinimide
(82 – 83%)

Chemical Reactions :



Ex. (A) $\xrightarrow{NaOH/\Delta}$ Salt (B) + gas (C) [It is alkaline and change the colour of litmus paper]
(having C,H,N,O)
↓ acidification
Acid (D) [Ag–Salt of D contains 59.6% Ag]

Ans. $CH_3–CH_2–CONH_2$

(C) Esters :

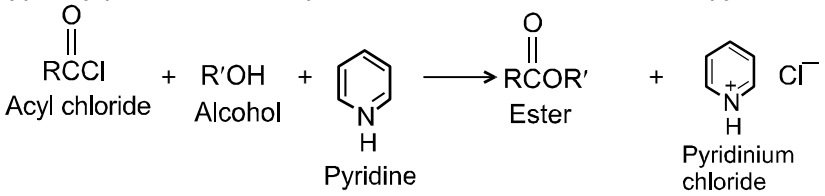
Methods of Preparation :

(i) $CH_3COOH + C_2H_5OH \xrightarrow{H^+} CH_3COOC_2H_5 + H_2O$
Acetic acid

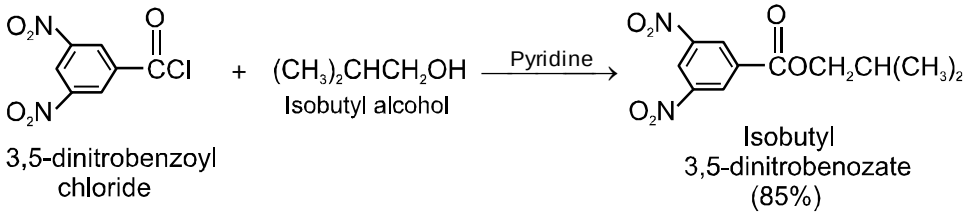
$C_6H_5COOH + CH_3OH \xrightarrow{H^+} C_6H_5COOCH_3 + H_2O$

(ii) $CH_3COCl + C_2H_5OH \xrightarrow{Pyridine} CH_3COOC_2H_5 + HCl$

Alcohols react with acyl chlorides by nucleophilic acyl substitution to yield esters. These reactions are typically performed in the presence of a weak base such as pyridine.

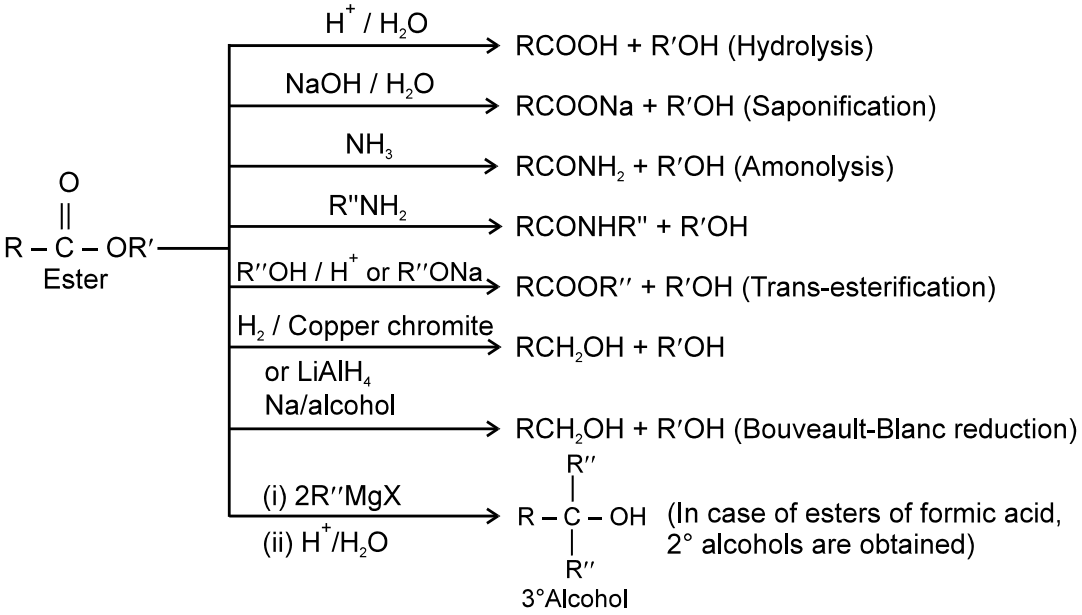


Ex.



Ex. $C_6H_5COCl + CH_3CH_2OH \xrightarrow{NaOH} C_6H_5COOCH_2CH_3 + HCl$

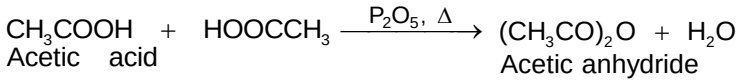
Chemical Reactions :



(D) Acid anhydrides :

Methods of Preparation of acid anhydrides :

(1) From carboxylic acids :



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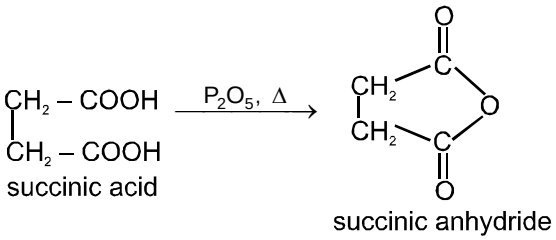

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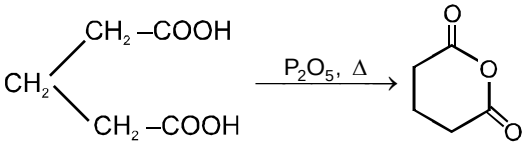

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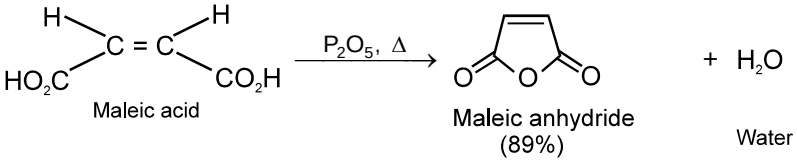

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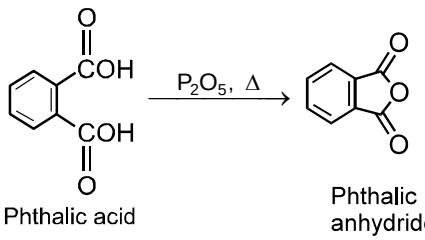


Five or six membered cyclic anhydride are stable

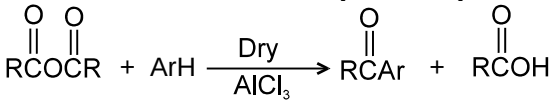
(2) From acid and acid halide :

Ex. $CH_3COOH + CH_3COCl \xrightarrow{Pyridine} CH_3CO.O.COCH_3 + HCl$

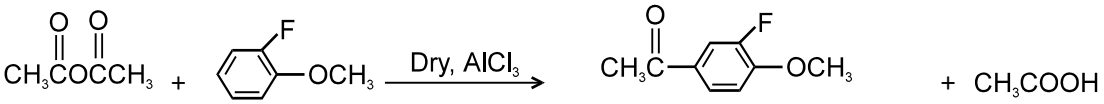
Ex. $CH_3COCl + CH_3COONa \xrightarrow{\Delta} CH_3CO.O.COCH_3 + NaCl$

Chemical Reactions

(1) Reaction with aromatic compounds (Friedel crafts acylation) :



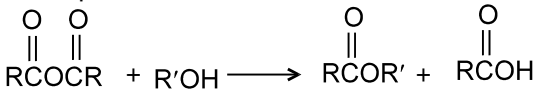
Ex.



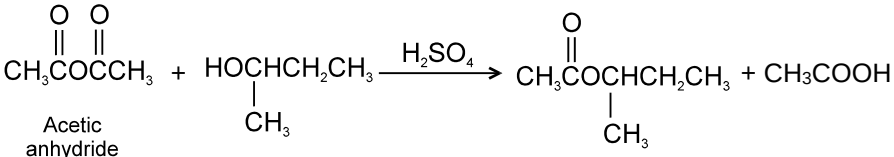
Acetic anhydride — o-Fluoroanisole — 3-Fluoro-4-methoxyacetophenone (70 – 80%) — Acetic acid

(2) Reaction with alcohols :

Acid anhydrides react with alcohols to form esters. The reaction may be carried out in the presence of pyridine or it may be catalysed by acids. In the example shown, only one acyl group of acetic anhydride becomes incorporated into the ester; the other becomes the acyl group of an acetic acid molecule.



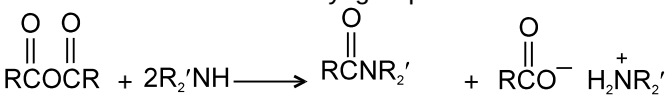
Ex.

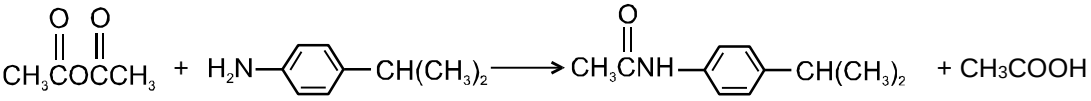


Acetic anhydride — sec-Butyl alcohol — sec-Butyl acetate (60%)

(3) Reaction with ammonia and amines :

Acid anhydrides react with ammonia and amines to form amides. Two molar equivalents of amine are required. In the example shown, only one acyl group of acetic anhydride becomes incorporated into the amide and the other becomes the acyl group of the amine salt of acetic acid.

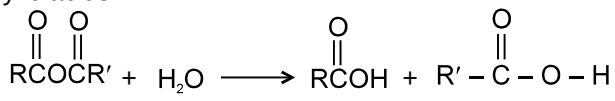


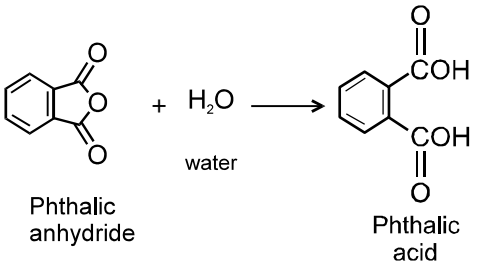


Acetic anhydride — p-isopropylaniline — p-isopropylacetanilide (98%)

(4) Hydrolysis :

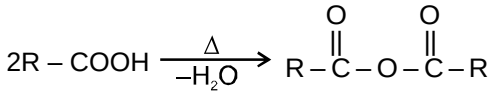
Acid anhydrides react with water to yield two carboxylic acid functions. Cyclic anhydrides yield dicarboxylic acids.



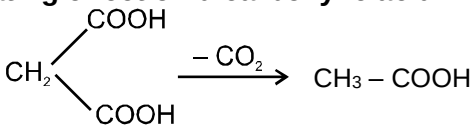


Heating Effects :

(a) Heating effect on monocarboxylic acid :

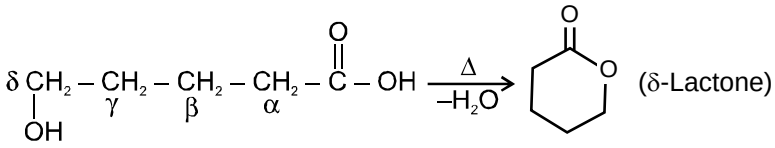


(b) Heating effect on dicarboxylic acid :

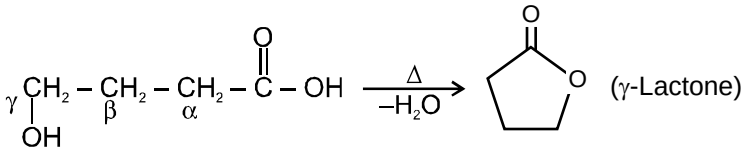


(c) Heating effects on Hydroxy acids :

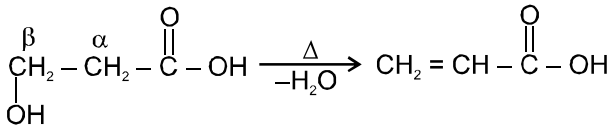
(1) δ–Hydroxy acid



(2) γ–Hydroxy acid

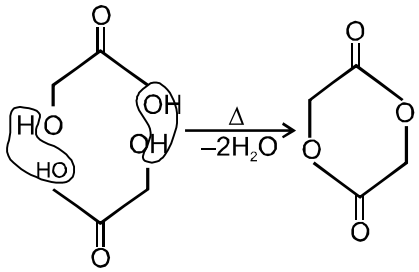


(3) β–Hydroxy acid

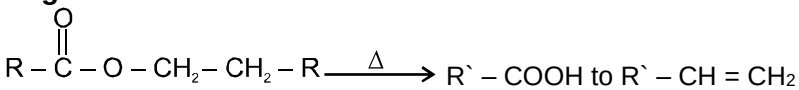


Since 4 or 8 membered rings are less stable the refore β-Hydroxy acids on heating produce α, β unsaturated carboxylic acid.

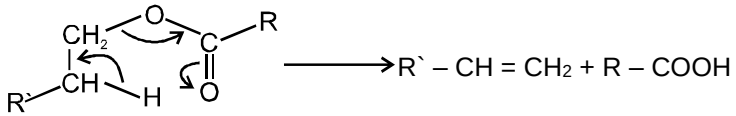
(4) α–Hydroxy acid



(d) Heating effects on esters :



Mech :



This reaction follows syn elimination & hoffman product is formed.