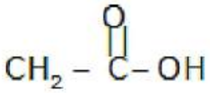
Chapter 11

Aldehydes, Ketones and Carboxylic Acids

Physical & Chemical Properties of Aldehydes & Ketones

Physical properties of acids and acid derivatives:

1. Boiling point:

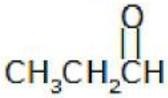


$CH_2 - \overset{O}{\overset{\|}{C}} - OH$

Acetic acid,
bp 118^{0}C

$CH_3CH_2CH_2OH$

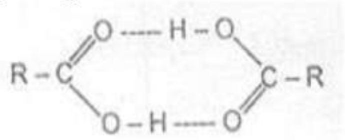
1-propanol
bp91^{0}C



$CH_3CH_2\overset{O}{\overset{\|}{C}}H$

Propionaldehyde
bp49^{0}C

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



Hydrogen bonded acid dimer

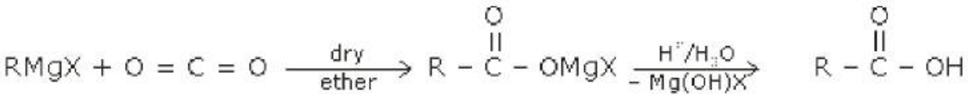
2 Solubility

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, anhydride, nitriles and amides) are soluble in organic solvents such as alcohols, ethers, chlorinated alkanes and aromatic hydrocarbons.

Methods of preparation of carboxylic acids:

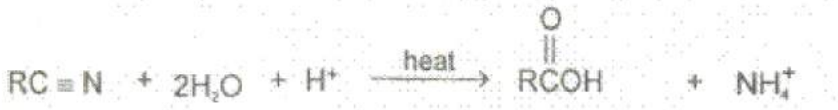
1. Synthesis of carboxylic acids by the carboxylation of Grignard's reagent:



$$RMgX + O=C=O \xrightarrow[\text{ether}]{\text{dry}} R-\overset{O}{\overset{\|}{C}}-OMgX \xrightarrow[-Mg(OH)X]{H^+/H_2O} R-\overset{O}{\overset{\|}{C}}-OH$$

2- Synthesis of Carboxylic acids by the hydrolysis of nitriles:

Mechanism:



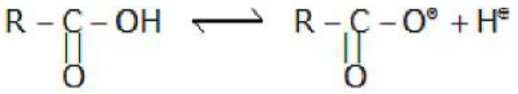
$$RC\equiv N + 2H_2O + H^+ \xrightarrow{\text{heat}} R\overset{O}{\overset{\|}{C}}OH + NH_4^+$$

Nitrile carboxylic acid

Chemical Reactions

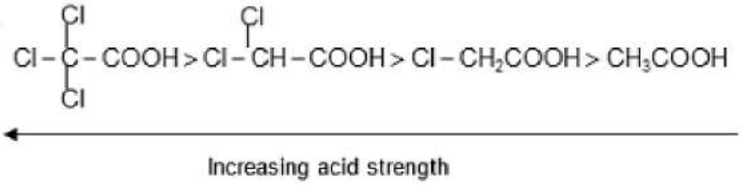
1. Acidic strength %

Acidity of carboxylic acids:



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

Ex.

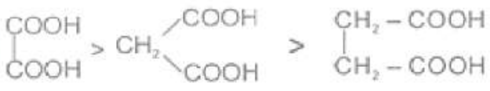


$$Cl-\underset{Cl}{\overset{Cl}{C}}-COOH > Cl-\overset{Cl}{CH}-COOH > Cl-CH_2COOH > CH_3COOH$$

Increasing acid strength

Ex. HCOOH > CH_3COOH > CH_3-CH_2-COOH

Ex.



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} > CH_2\begin{matrix} COOH \\ COOH \end{matrix} > \begin{matrix} CH_2-COOH \\ | \\ CH_2-COOH \end{matrix}$$

Ex. Relative acid strength is:
$RCOOH > HOH > ROH > HC\equiv CH > NH_3 > RH$
Note: Acidity of acids is compared by comparing stability of conjugate base.

2- Reaction involving removal of proton from –OH group.

1.Action with blue litmus: All carboxylic acids turn blue litmus red.
2.Reaction with metals:

$2\ CH_3\ COOH + 2Na \rightarrow 2CH_3COONa + H_2$
Sodium acetate
$2CH_3\ COOH + Zn \rightarrow (CH_3COO)_2\ Zn + H_2$
Zinc acetate

3.Reaction with alkalies:
$CH_3\ COOH + NaOH \rightarrow CH_3\ COONa + H_2O$

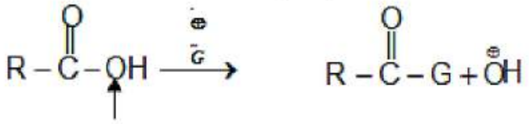
4.Reaction with carbonates and bicarbonates:
$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3\ COONa + CO_2 + H_2O$
$CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + CO_2 + H_2O$

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

5.Reaction with Grignard's reagent:
$R\text{-}CH_2MgBr + R'COOH \xrightarrow{ether} R\text{-}CH_3 + R'COOMgBr$

Note: A stronger acid displaces a weaker acid from salt of the weaker acid.
Ex. CH_3COOH (Stronger acid) + $CH_3ONa \rightarrow CH_3\ COONa + CH_3 —OH$ (WeakerAcid)
Ex. CH_3COOH (stronger acid) + $NaHCO_3 \rightarrow CH_3\ COONa + H_2\ CO_3$ (Weaker acid) → $H_2O + CO_2$

3. Reaction involving replacement of –OH group

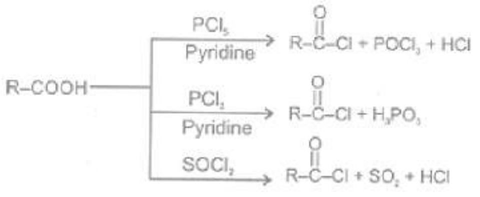


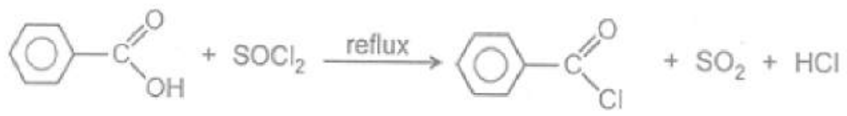
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\overset{\oplus}{G}} R-\overset{O}{\overset{\|}{C}}-G+\overset{\oplus}{O}H$$

Strong bases so not a
Good leaving group

basicity must be
less then basicity of G–

(i) Formation of acid chlorides:

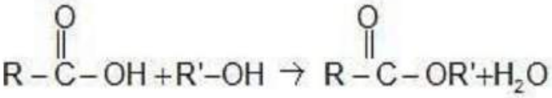




(2) Fisher Esterification:

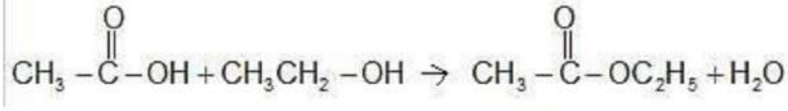
Carboxylic acid react with alcohol to form esters through a condensation reaction known as esterification.

General Reaction:

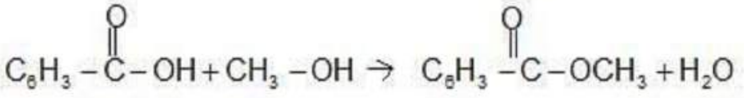


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R'-OH \rightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + H_2O$$

Specific Example:



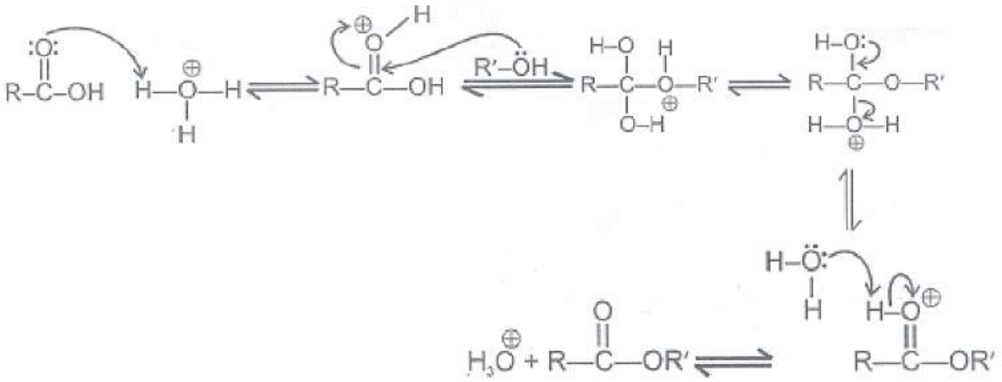
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + CH_3CH_2-OH \rightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 + H_2O$$



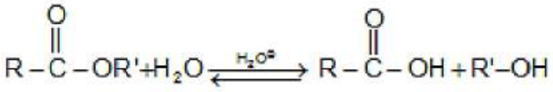
$$C_6H_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + CH_3-OH \rightarrow C_6H_3-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 + H_2O$$

Mechanism:

Acid catalysed esterfication:

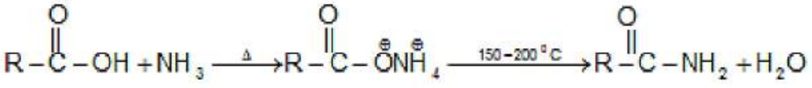


If we follow the forward path in this mechanism, we have the mechanism for the acid catalysed esterification for an acid. If however, we follow the reverse reactions, we have the mechanism for the acid catalysed hydrolysis of an ester. Acid catalysed ester hydrolysis gives:



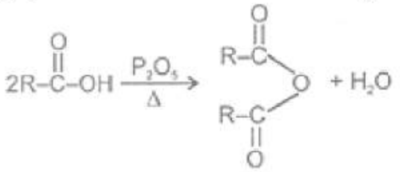
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + H_2O \xrightleftharpoons{H_3O^{\oplus}} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R'-OH$$

(3) Formation of amides:



$$R-\overset{O}{\overset{\|}{C}}-OH+NH_3 \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{N}H_4 \xrightarrow{150-200^{\circ}C} R-\overset{O}{\overset{\|}{C}}-NH_2+H_2O$$

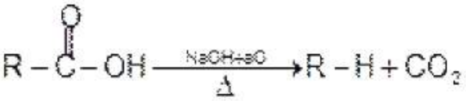
(4) Formation of acid anhydride:



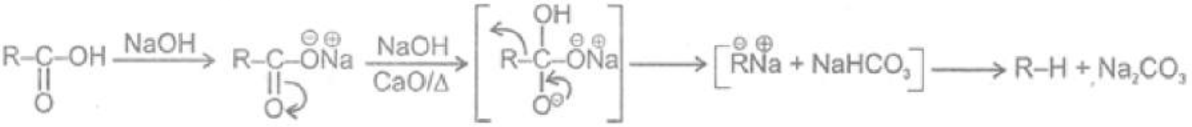
(4) Decarboxylation reactions:

1 Soda-lime decarboxylation:

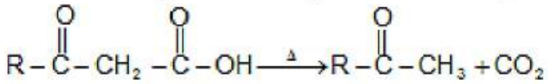
General reaction:



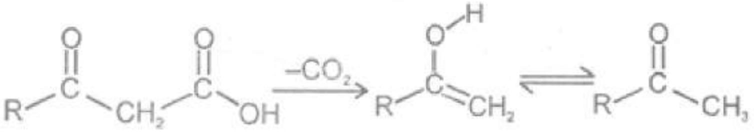
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{NaOH+CaO} R-H+CO_2$$



2. Decarboxylation of β keto carboxylic acids :



$$R-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-CH_3+CO_2$$



β - keto acid

β

3) Kolbe's electrolysis:

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

Mechanism $RCO_2K \rightleftharpoons RCO_2^- + K^+$

At Anode %& $RCO_2^- \rightarrow RCO_2 + e^-$ (oxidation)

(I)

$RCO_2 \rightarrow R\cdot + CO_2$

(II) $R\cdot + R\cdot \rightarrow R-R$

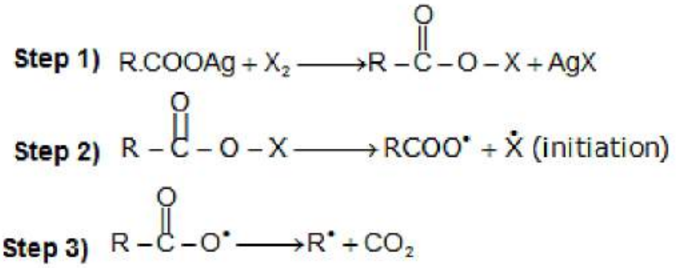
If n is the number of carbon atoms in the salt of carboxylic acid, the alkane formed has 2(n-1) carbon atoms.

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

4) Hunsdiecker Reaction (Brome-decarboxylation):

R-COOAg + $Br_2 \rightarrow$ R-Br + CO_2 + AgBr

Mechanism:



Step 1) $R.COOAg + X_2 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O-X + AgX$

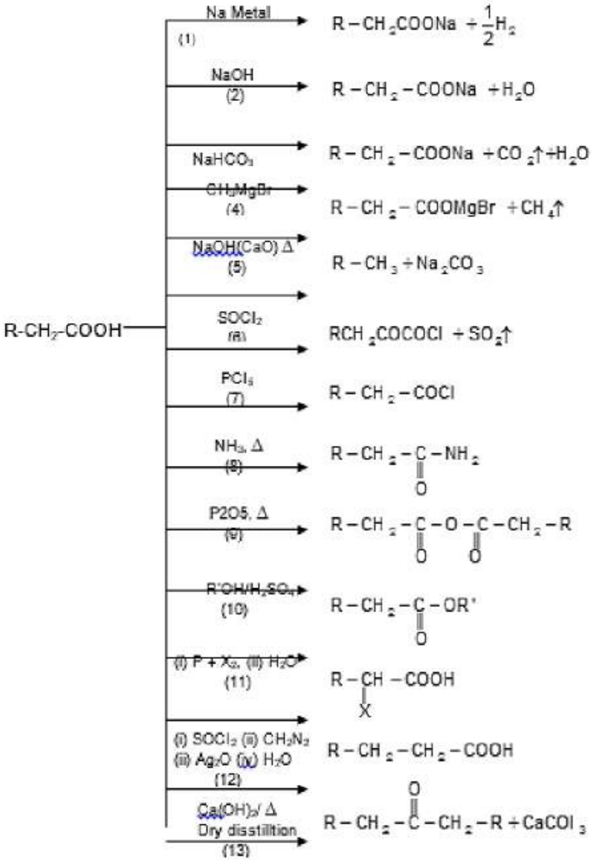
Step 2) $R-\overset{\overset{\displaystyle O}{\|}}{C}-O-X \longrightarrow RCOO^{\bullet} + \dot{X}$ (initiation)

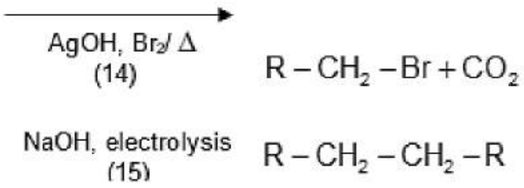
Step 3) $R-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\bullet} \longrightarrow R^{\bullet} + CO_2$

Step 4) $R^{*}\cdot$ + RCOOX □ R—X + RCOO* (Propagation)

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

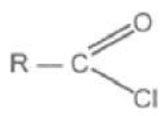
$$CH_3\,COOH \xrightarrow{Cl_2,P} ClCH_2\,COOH \xrightarrow{Cl_2,P} Cl_2CHCOOH \xrightarrow{Cl_2,P} Cl_3\,CCOOH$$



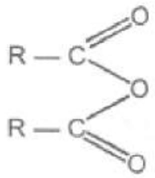


Carboxylic Acid Derivatives

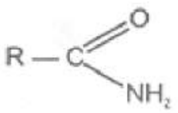
Closely related to the carboxylic acids and to each other are a number of chemical families known as functional derivatives of carboxylic acids: acid chloride, anhydrides, amides, and esters. These derivatives are compounds in which the -OH of a carboxyl group has been replaced by–Cl, -OOCR, -NR_2 or –OR.



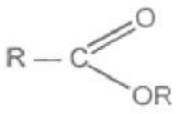
Acid chloride



Anhydride

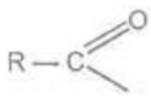


Amide



Ester

They all contain the acyl group



(A) Acid halides:

Methods of preparation of Acyl halides:

(i) $RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$
(ii) $3RCOOH + PCl_3 \rightarrow 3RCOCl + H_3PO_3$
(iii) $RCOOH + SOCl_2 \xrightarrow{\text{Pyridine}} RCOCl + SO_2 + HCl$

Ex.

$$3CH_3\,COONa + PCl_3 \xrightarrow{Distil} 3CH_3\,COCl + Na_3PO_3$$

Acetyl chloride

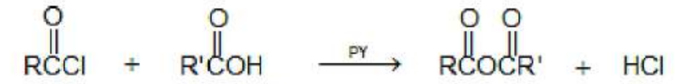
Ex.

$$2C_6H_5COONa + POCl_3 \xrightarrow{Distil} 2C_6H_5COCl + NaCl + NaPO_3$$

Sod. benzoate — Benzoyl chloride

Chemical Reactions:

1. Reaction with carboxylic acids:

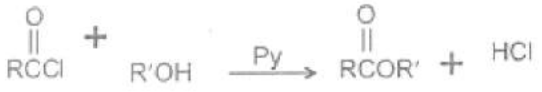


$$R\overset{O}{\overset{\|}{C}}Cl + R'\overset{O}{\overset{\|}{C}}OH \xrightarrow{PY} R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R' + HCl$$

Acyl chloride — Carboxylic acid — Acid anhydride — Hydrogen chloride

2. Reaction with alcohols:

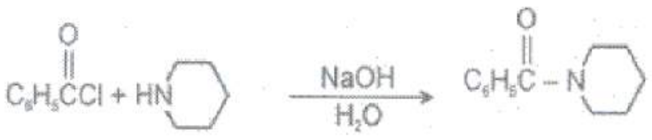
Acyl chlorides react with alcohols to form esters. The reaction is typically carried out in the presence of pyridine.



$$R\overset{O}{\overset{\|}{C}}Cl + R'OH \xrightarrow{Py} R\overset{O}{\overset{\|}{C}}OR' + HCl$$

Acyl choride — Alcohol — Ester — Hydrogen chloride

$$R\overset{O}{\overset{\|}{C}}Cl + R_2'NH + HO^- \longrightarrow R\overset{O}{\overset{\|}{C}}NR_2' + H_2O + Cl^-$$



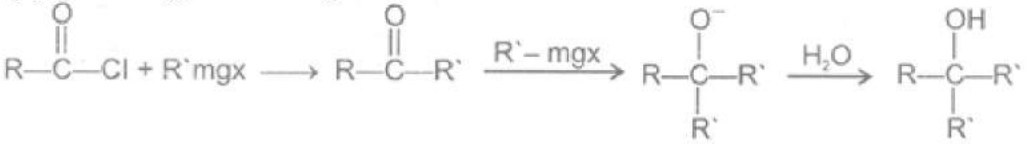
3) Hydrolysis:

$$R\overset{O}{\overset{\|}{C}}Cl + H_2O \longrightarrow R\overset{O}{\overset{\|}{C}}OH + HCl$$

$$C_6H_5CH_2\overset{O}{\overset{\|}{C}}Cl + H_2O \longrightarrow C_6H_5CH_2\overset{O}{\overset{\|}{C}}OH + HCl$$

4) Reaction of acid halide with organometallic compounds:

(a) with Grignard's reagent-



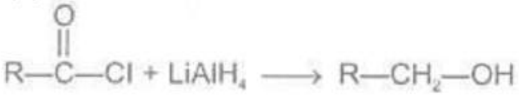
$$R-\overset{O}{\overset{\|}{C}}-Cl + R^{`}mgx \longrightarrow R-\overset{O}{\overset{\|}{C}}-R^{`} \xrightarrow{R^{`}-mgx} R-\underset{R^{`}}{\underset{|}{\overset{O^{-}}{\overset{|}{C}}}}-R^{`} \xrightarrow{H_2O} R-\underset{R^{`}}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R^{`}$$

(b) Reaction with Gilmann's reagent-

$$R-\overset{O}{\overset{\|}{C}}-Cl + R^{`}_2Culi \longrightarrow R-\overset{O}{\overset{\|}{C}}-R^{`}$$

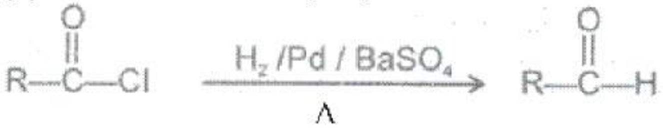
5) Reduction of acid halide:

(a) Reduction $LiAlH_4$

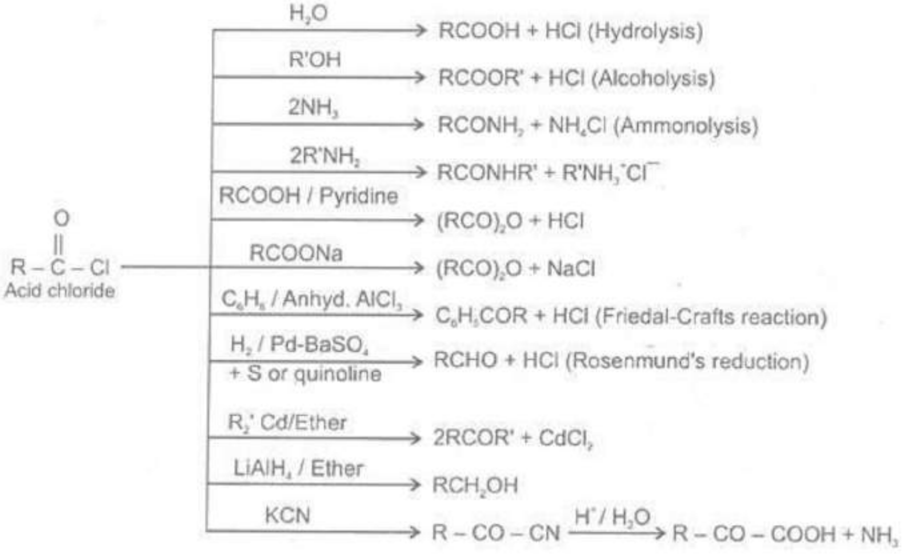


$$R-\overset{O}{\overset{\|}{C}}-Cl + LiAlH_4 \longrightarrow R-CH_2-OH$$

(b) Reduction with $H_2/Pd/BaSO_4$ Rosenmund reduction-



$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\Lambda]{H_2/Pd/BaSO_4} R-\overset{O}{\overset{\|}{C}}-H$$



(B) Acid amides

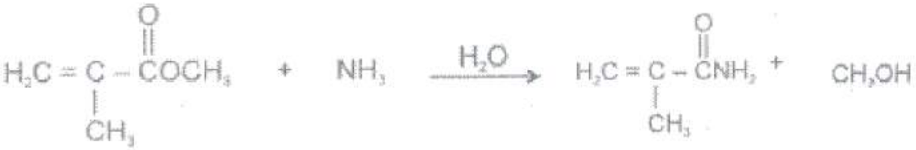
Methods of preparation of acids amides:

1. By reaction of esters with ammonia and amines.

$$R\overset{O}{\overset{\|}{C}}OR' + NH_3 \longrightarrow R\overset{O}{\overset{\|}{C}}NH_2 + R'OH$$

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

Ex.



$$H_2C=\underset{CH_3}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}OCH_3 + NH_3 \xrightarrow{H_2O} H_2C=\underset{CH_3}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}NH_2 + CH_3OH$$

2. From acid halides:
$RCOCl + 2NH_3 \rightarrow RCONH_2 + NH_4Cl$

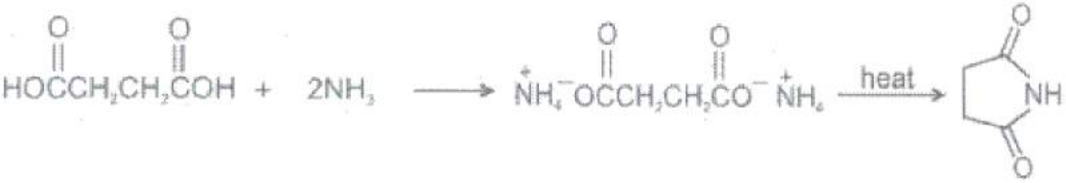
3. From anhydride:
$(RCO)_2O + 2NH_3 \rightarrow RCONH_2 + RCOO\,NH_4$

4. From esters:
$RCOOR + NH_3 \rightarrow RCONH_2 + R'OH$

5. From ammonium salt of carboxylic acid:
$RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$
$CH_3\,COONH_4 \xrightarrow{\Delta} CH_3CONH_2$

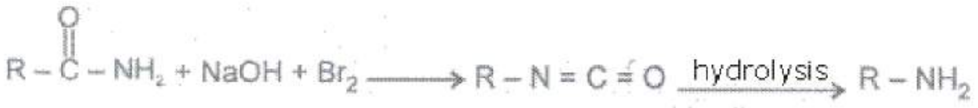
6. From cyanides:
$R-C\equiv N + H_2O \xrightarrow[\text{or}\,H_2O_2-NaOH]{\text{Conc. HCl}} R-CONH_2$
$CH_3C=N + H_2O \xrightarrow{\text{Conc. }H_2SO_4} CH_3-CONH_2$

7.



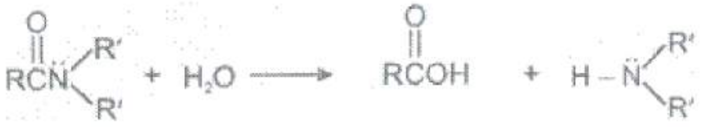
Chemical Reactions:

(1) Hoffmann rearrangement:
General reaction-



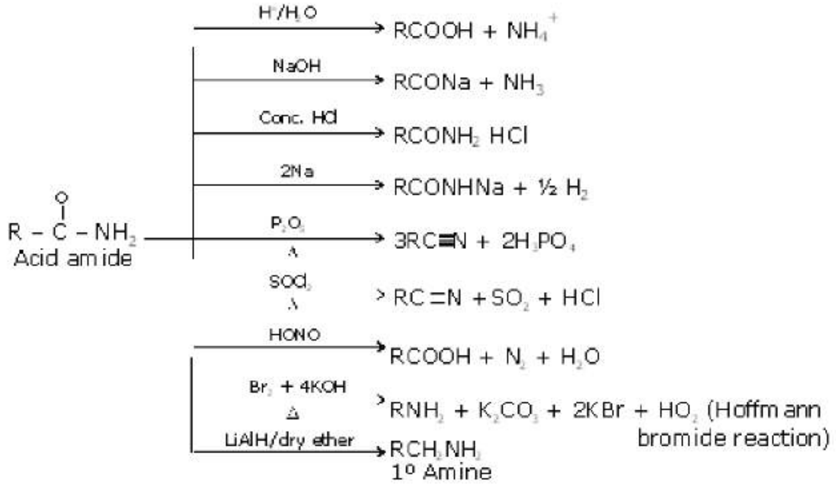
$$R-\overset{O}{\overset{\|}{C}}-NH_2 + NaOH + Br_2 \longrightarrow R-N=C=O \xrightarrow{\text{hydrolysis}} R-NH_2$$

(2) Hydrolysis of amides-



In acid, however, the amine is protonated, giving an ammonium ion, $R_2'\overset{+}{N}H_2$

Summary of Reaction of Amide:



(C) Esters

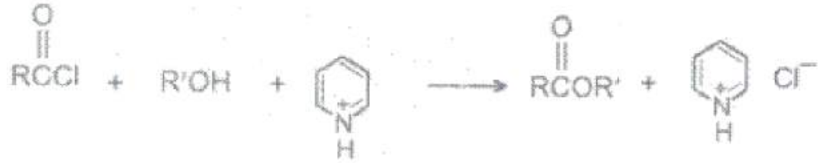
Methods of Preparation:

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

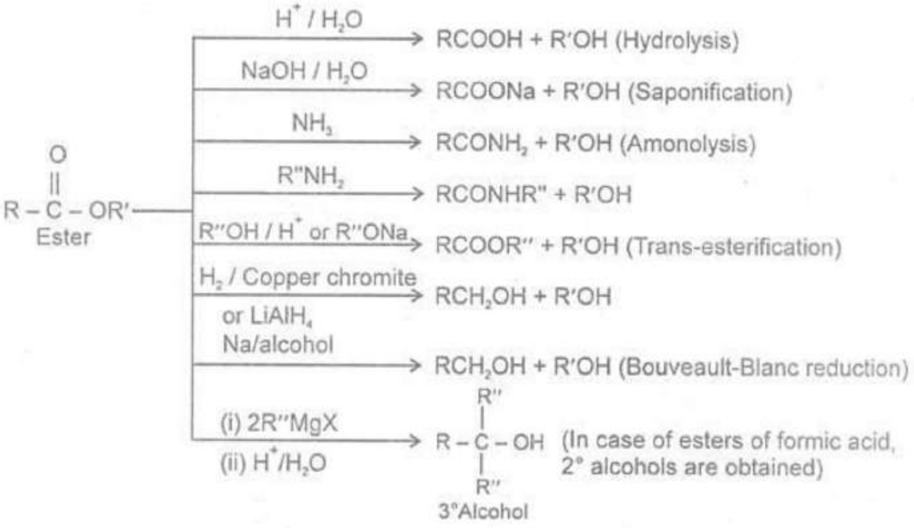
$C_6H_5COOH + CH_3OH \xrightarrow{H^+} C_6H_5COOCH_3 + H_2O$

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

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.



Summary of reaction of esters:



(D) Acid anhydrides

Methods of Preparation of acid anhydrides:

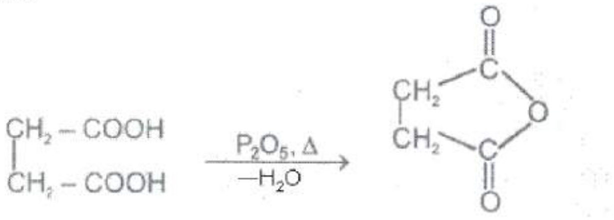
1- From carboxylic acids

Ex.

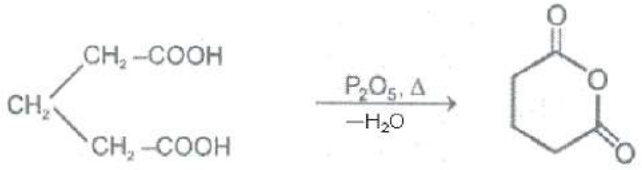
$CH_3COOH + HOOCCH_3 \xrightarrow{P_2O_5,\Delta} CH_3CO.O.COCH_3 + H_2O$

Acetic acid Acetic anhydride

Ex.



Ex.



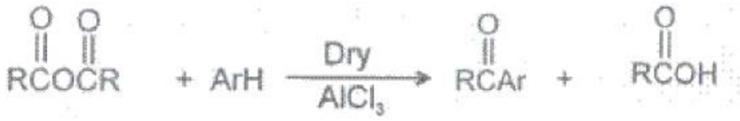
2. From acid and acid halide

Ex. $CH_3COOH + CH_3COCl \xrightarrow{\text{Pyridine}} CH_3\,CO.O.COCH_3 + HCl$

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

Chemical Reactions

1. Reaction with aromatic compounds (Friedel crafts acylation)-



$$R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R + ArH \xrightarrow[AlCl_3]{Dry} R\overset{O}{\overset{\|}{C}}Ar + R\overset{O}{\overset{\|}{C}}OH$$

2. Reaction with alcohols-
Ex.

$$R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R + R'OH \longrightarrow R\overset{O}{\overset{\|}{C}}OR' + R\overset{O}{\overset{\|}{C}}OH$$

3. Reaction with ammonia and amines-

$$R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R + 2R_2'NH \longrightarrow R\overset{O}{\overset{\|}{C}}NR_2' + R\overset{O}{\overset{\|}{C}}O^{-}\;H_2\overset{+}{N}R_2'$$

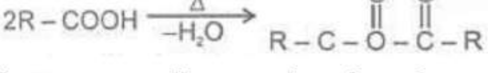
4. Hydrolysis-

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

$$R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R' + H_2O \longrightarrow R\overset{O}{\overset{\|}{C}}OH + R'-\overset{O}{\overset{\|}{C}}-O-H$$

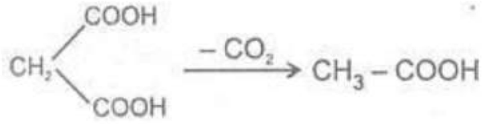
5. Heating Effects:

a. Heating effect on monocarboxylic acid

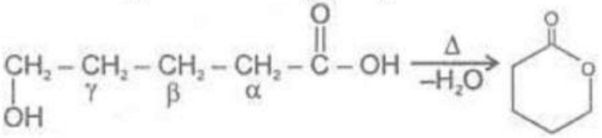


$$2R-COOH \xrightarrow[-H_2O]{\Delta} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$$

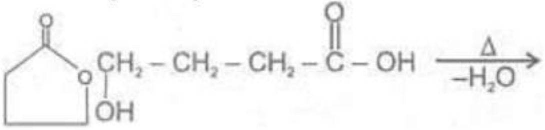
b. Heating effect on dicarboxylic acid



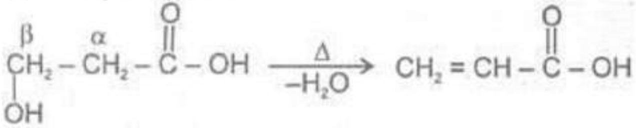
c. Heating effect on Hydroxy acids



1- $\delta-$ Hydroxy acid

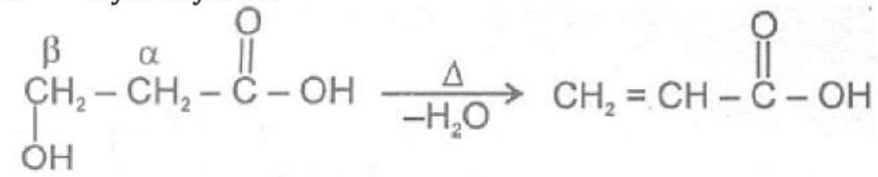


2. $\gamma-$ Hyroxy acid



$$\underset{OH}{\overset{\beta}{CH_2}} - \overset{\alpha}{CH_2} - \overset{O}{\overset{||}{C}} - OH \xrightarrow[-H_2O]{\Delta} CH_2 = CH - \overset{O}{\overset{||}{C}} - OH$$

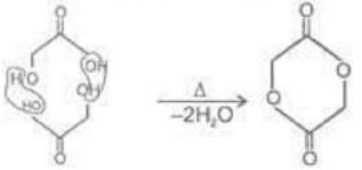
3- $\beta-$ Hydroxy acid



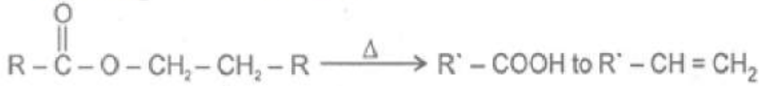
$$\underset{OH}{\overset{\beta}{CH_2}} - \overset{\alpha}{CH_2} - \overset{O}{\overset{||}{C}} - OH \xrightarrow[-H_2O]{\Delta} CH_2 = CH - \overset{O}{\overset{||}{C}} - OH$$

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

4- An α -Hyroxy acid



5. Heating effect on esters

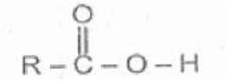


$$R - \overset{O}{\overset{||}{C}} - O - CH_2 - CH_2 - R \xrightarrow{\Delta} R' - COOH \text{ to } R' - CH = CH_2$$

This reaction follows syn elimination & Hoffman product is formed.

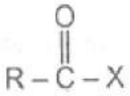
Doc: Nomenclature of Carboxylic Acids

Introduction:

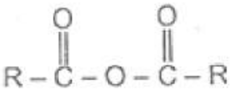


$R-\overset{O}{\overset{\|}{C}}-O-H$

Carboxylic acid



$R-\overset{O}{\overset{\|}{C}}-X$

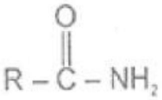


$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$

Acid halide anhydride

$R-\overset{O}{\overset{\|}{C}}-O-R'$

Ester



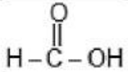
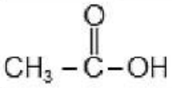
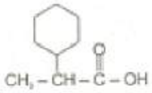
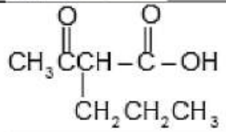
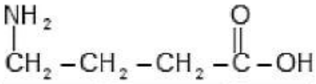
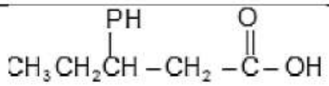
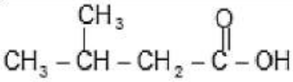
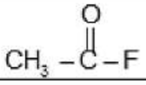
$R-\overset{O}{\overset{\|}{C}}-NH_2$

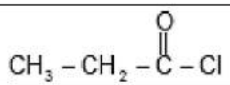
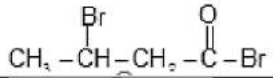
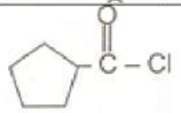
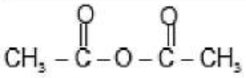
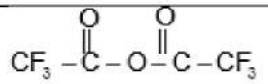
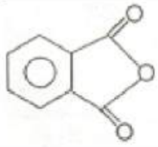
Amide

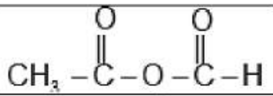
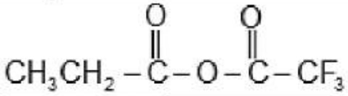
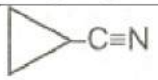
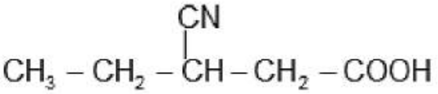
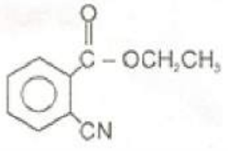
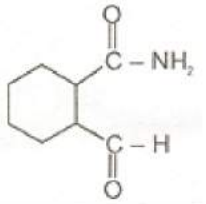
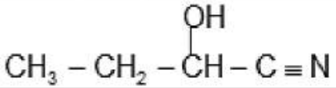
$R-C\equiv N$

Nitrile

Table – 1: IUPAC Nomenclature of Acid derivatives:

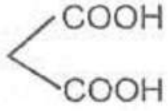
S.No.	**Compound**	**IUPAC Name**
1	 $H-\overset{O}{\overset{\|}{C}}-OH$	Methanoic acid
2	 $CH_3-\overset{O}{\overset{\|}{C}}-OH$	Ethanoic acid
3		2- Cyclohexylpropanoic acid
4	 $CH_3\overset{O}{\overset{\|}{C}}\underset{CH_2CH_2CH_3}{CH}-\overset{O}{\overset{\|}{C}}-OH$	3- Oxo-2- propylbutanoic acid
5	 $\overset{NH_2}{CH_2}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$	4- Aminobutanoic acid
6	 $CH_3CH_2\overset{PH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-OH$	3- Phenylpentanoic acid
7	 $CH_3-\overset{CH_3}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-OH$	3- Methylbutanoic adic
8	 $CH_3-\overset{O}{\overset{\|}{C}}-F$	Ethanoylchloride

9	 $CH_3-CH_2-\overset{\overset{O}{\Vert}}{C}-Cl$	Propanoylchloride
10	 $CH_3-\overset{\overset{Br}{\vert}}{CH}-CH_2-\overset{\overset{O}{\Vert}}{C}-Br$	3-Bromobutanoylbromide
11		Cyclopentancarbonyl chloride
12	 $CH_3-\overset{\overset{O}{\Vert}}{C}-O-\overset{\overset{O}{\Vert}}{C}-CH_3$	Ethanoid anyhydride
13	 $CF_3-\overset{\overset{O}{\Vert}}{C}-O-\overset{\overset{O}{\Vert}}{C}-CF_3$	Trifluoroethanoic anhydride
14		1,2- Benzenedicarboxylic anhydride

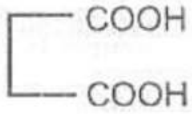
15	 $CH_3-\overset{\overset{O}{\Vert}}{C}-O-\overset{\overset{O}{\Vert}}{C}-H$	Ethanoic methanoic anhydride
16	 $CH_3CH_2-\overset{\overset{O}{\Vert}}{C}-O-\overset{\overset{O}{\Vert}}{C}-CF_3$	Trifluoroethanoic propanoic anhydride
17		Cyclopropane carbonitrile
18	 $CH_3-CH_2-\overset{\overset{CN}{\vert}}{CH}-CH_2-COOH$	3- Cyanopentanoic acid
19		Ethyl-o-cyanobenzoate
20		2- Formylcyclohexane carboxamide
21	 $CH_3-CH_2-\overset{\overset{OH}{\vert}}{CH}-C\equiv N$	2- Hydroxyutane nitrile

Dicarboxylic Acids

If the subsituent is a second carboxyl group, we have a dicarboxylic acid. For example:

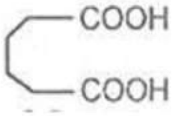


Oxalic acid or Ethanedioic acid

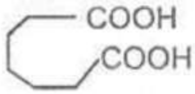


Malonic acid -1, 3- dioic acid

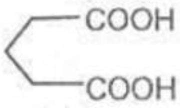
Succinic acid -1, 4- dioic acid



Glutaric acid
Pentane-1, 5-dioic acid



Adipic acid
Hexane-1, 6-dioic acid



Pimelic acid
Heptane-1, 7- dioc acid

$HOOCCH_2COOH$

Malonic acid
Propanedioic acid

$HOOCCH_2CH_2COOH$

Succinic acid
Butanedioic acid

$HOOCCH_2CH_2CH_2CH_2COOH$

Adipic acid
Hexanedioic acid

Polyhalogen Compounds

Polyhalogen derivatives:

Trichloromethane (Chloroform), $CHCl_3$

Preparation:

$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$
Chloromethane

$CH_3Cl + Cl_2 \xrightarrow{h\nu} CH_2Cl_2 + HCl$
Dichloromethane

$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} CHCl_3 + HCl$
Trichloromethane

$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$
Tetrachloromethane

The mixture of CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 can be separated by fractional distillation.

2. From chloral hydrate, Pure chloroform can prepare.

$NaOH + CCl_3CHO \rightarrow HCOONa + CHCl_3$
chloral

$NaOH + CCl_3CH(OH)_2 \rightarrow HCOONa + CHCl_3 + H_2O$
Chloral hydrate sodium formate Chloroform

3. Laboratory Method: From ethanol or acetone, by reaction with a paste of bleaching powder and water.

In case of ethanol, the reaction occurs as follows:

$CaOCl_2 + H_2O \rightarrow Ca\ (OH)_2 + Cl_2$

$CH_3CH_2OH + Cl_2 \xrightarrow{\text{Oxidation}} CH_3CHO + 2HCl$

$CH_3CHO + 3Cl_2 \xrightarrow{\text{Chlorination}} CCl_3CHO + 3HCl$

Chloral

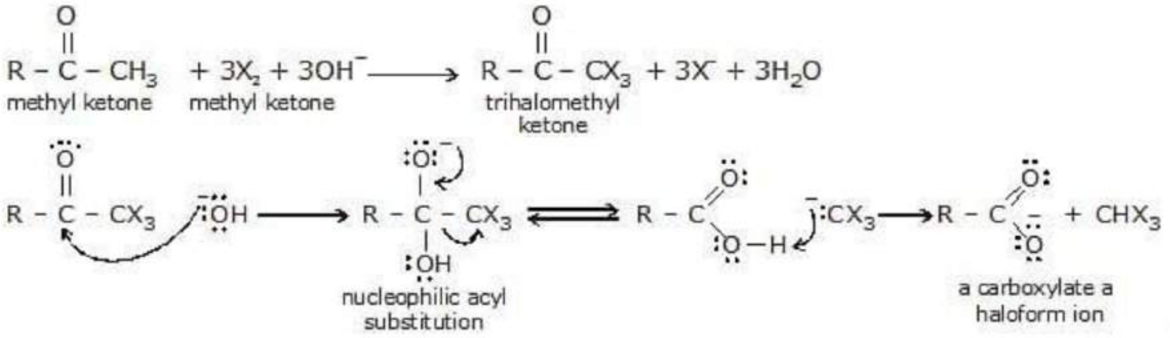
$Ca(OH)_2 + 2CCl_3CHO \xrightarrow{\text{Hydrolysis}} 2CHCl_3 + (HCOO)_2Ca$

Chloroform Calcium formate

4. From carbon tetrachloride:

$CCl_4 + 2[H] \xrightarrow[\text{Heat}]{Fe/H_2O} CHCl_3 + HCl$ (partial reduction)

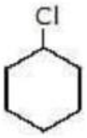
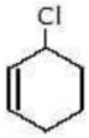
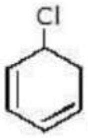
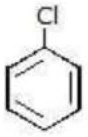
5. Haloform reaction:



(

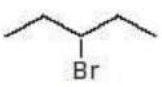
Haloform)
Step 1: Attack of the
Step 2: Elimination
Step 3: Proton transfer
nucleophile of the leaving group

Prob.Compare rate of elimination (Dehydro halogenation in presence of alcoholic KOH) i.e., E2:

1. (a)

(b)

(c)

(d)


c > b > a > d

2. (a)

(b)

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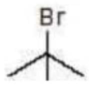
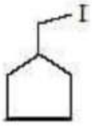


c > b > a

3. (a)

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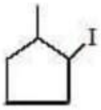
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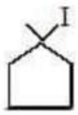
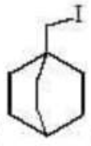
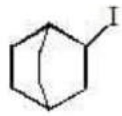


c > b > a

4. (a)



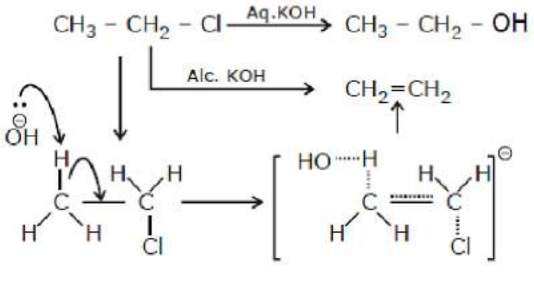
(b)



(c)

b > a > c

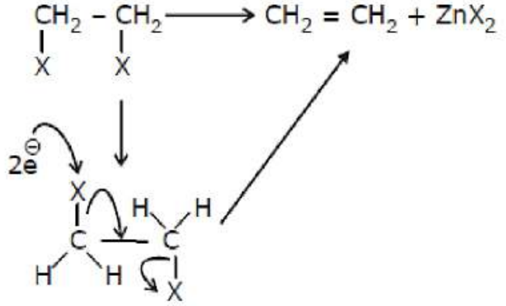
Dehalogenation: - (-X_2) E2



Anti elimination

Dehalogenation: - (-X_2) E2

$Zn \longrightarrow Zn^{+2} + 2e^-$



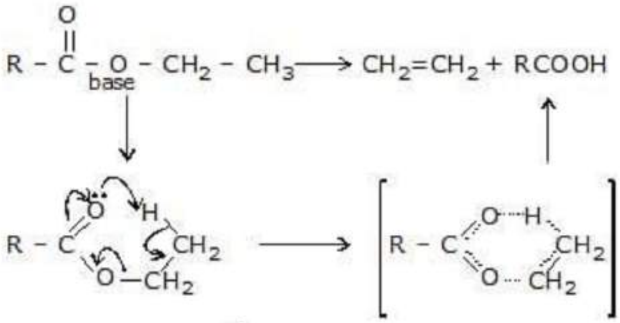
Anti elimination

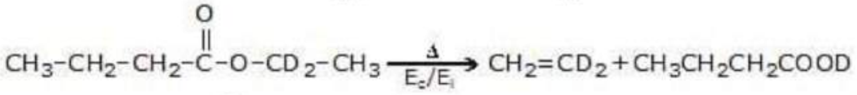
E_c or E_i (Intramolecular or cyclic elimination mechanism):

(1) Lg and Base present in same molecule.
(2) It proceeds by cyclic transition state.
(3) Overall it is syn elimination.
(4) Hoffmann is major product as it is obtained by least hindered site of cyclic transition state.
(5) No rearrangement.

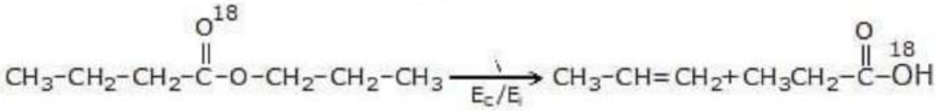
Example of E_c/E_i:

Pyrolysis of Ester:



1. 

$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CD_2-CH_3 \xrightarrow[E_c/E_i]{\Delta} CH_2=CD_2+CH_3CH_2CH_2COOD$

2. 

$CH_3-CH_2-CH_2-\overset{\overset{O^{18}}{\|}}{C}-O-CH_2-CH_2-CH_3 \xrightarrow[E_c/E_i]{} CH_3-CH=CH_2+CH_3CH_2-\overset{\overset{O}{\|}}{C}-\overset{18}{O}H$

1.8.2 Physical properties of chloroform

Chloroform is a colourless, heavy liquid which has sweetish, sickly odour and taste. It boils at 334º K and is slightly soluble in water. It is heavier than water. As inhaling of the vapours of chloroform induces unconsciousness therefore it can be used as an anaesthetic agent for surgery.

1.8.3 Chemical properties of chloroform:

1. Action of sun light and air-

$2\ CHCl_3 + O_2 \xrightarrow{\text{Sun light}} 2COCl_2 + 2HCl$

Phosgene

As chloroform is used for anaesthetic purposes, therefore in order to maintain a high purity of chloroform, this reaction can be avoided by storing it in dark bottles, completely filled upto the brim. The use of dark bottles (brown or blue) cuts off active light radiations and filling upto brim keeps out air. Apart from this a small amount of ethanol (1%) is usually added to bottles of chloroform. Addition of a little ethanol fixes the toxic $COCl_2$ as non-poisonous diethyl carbonate.

$COCl_2 + 2C_2H_5OH \longrightarrow O = C(OC_2H_5) + 2HCl$

diethyl carbonate

2. Hydrolysis:

$$H - CCl_3 + (aq.)\ 3KOH \xrightarrow[-H_2O]{-3KCl} \xrightarrow[-H_2O]{+KOH} HCOOK$$

3. Reduction:

$$Zn + 2HCl \longrightarrow ZnCl_2 + 2[H]$$

$$CHCl_3 + 2[H] \longrightarrow CH_2Cl_2 + HCl$$

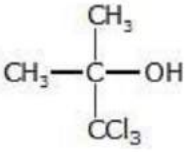
Dichloromethane

(Methylene chloride)

$$CHCl_3 \xrightarrow{Zn + H_2O} CH_4 + 3HCl$$

4. Reaction with acetone:

$$(CH_3)_2C = O + CHCl_3 \xrightarrow{KOH}$$



$$(CH_3)_2C(OH)CCl_3$$

Chlroetone

Use: Chloretone is used as hypnotic (a sleep inducing) drug.

5. Reaction with nitric acid:

$$2CHCl_3 + HONO_2 \longrightarrow CCl_3.NO_2 + H_2O$$

(Chloropicrin)

Use: Chloropicrin is used as an insecticide and war gas.

6. Reaction with silver powder:

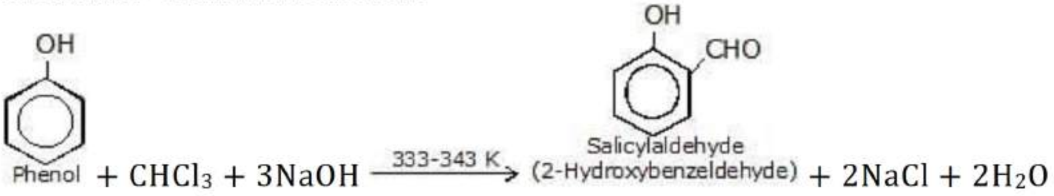
$$2CHCl_3 + 6\ Ag \xrightarrow{Heat} CH \equiv CH + 6\ AgCl$$

(Acetylene)

7. Chlorination:

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$$

8. Reimer-Tiemann reaction:



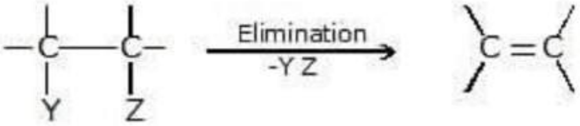
1.8.4 Uses of chloroform

1. As solvent in oils and varnishes.
2. As preservative for anatomical specimens.
3. As laboratory reagent.
4. As an anesthetic.

Elimination Reactions & Reaction with Metals

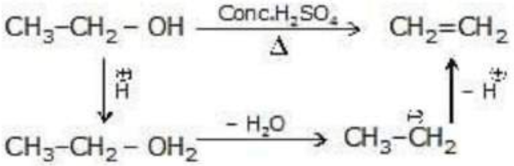
1.7.2 Elimination reactions:

In an elimination reaction two atoms or groups (YZ) are removed from the substrate with formation of pi bond.



depending on the reagents and conditions involved, an elimination may be a first order (E_1) or second order (E_2).

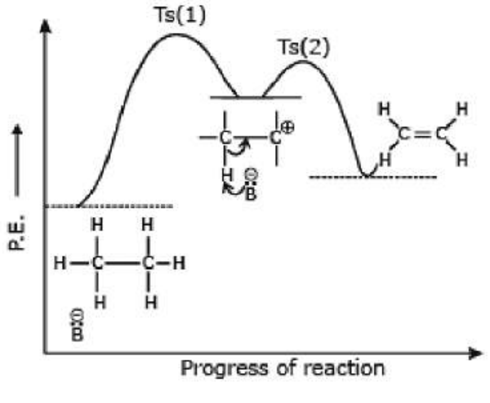
Dehydration of Alohol (E1):



Characteristics of E_1 reaction:

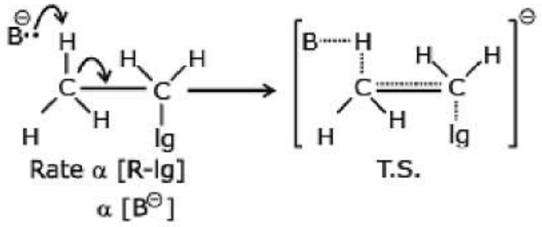
(i) It is unimolecular, two step process.
(ii) It is first order reaction.
(iii) Reaction intermediate is carbocation, so rearrangement is possible.
(iv) In the second step, a base abstracts a proton from the carbon atom adjacent to the carbocation, and forms alkene.

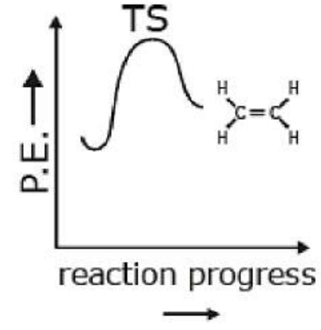
(v) Kinetics → Rate $\propto$ [Substrate]
Rate $=$ k[Substrate]



E₂- **elimination:**

$$\overset{\ominus}{B} \qquad H-CH_2-CH_2-lg \longrightarrow CH_2=CH_2 + lg^{\ominus}$$





Bi-molecular reaction, second order kinetic.

1. Leaving group leads when base is taking proton from adjacent carbon.
2. It is a single step reaction.
3. Rate a single step reaction.

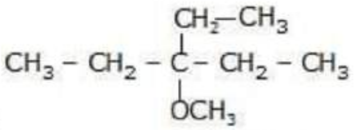
Rate a Leaving group tendency-

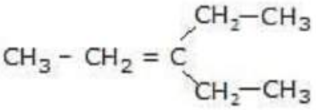
4. It shows elemental as well as kinetic isotopic effect with leaving group (lg) as well as at β-position.
5. Normally, Saytzeff product is major.
6. Transition state mechanism therefore rearrangement is not possible.
7. The orientation of proton & leaving group should be anti-planar for E2.
8. **Positional orientation of elimination:** Mostly, E_1 and E_2 eliminations give two or more possible elimination products, the product with the most highly substituted double bond will predominate. This rule is called the Saytzeff or Zaitsev rule (i.e., most stable alkene will be the major product).
9. E_2-elimination is favour by:
(1) Moderate leaving group (lg)
(2) Strong base (RO^-, Alc. KOH)
(3) Polar aprotic solvent.
(4) High conc. of base.
(5) High temperature.

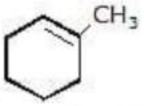
Reactivity towards E_2: R - I > R - Br > R - Cl > R – F

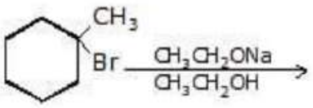
Ex. Predict the elimination products of the following reactions.
(a) Sec. butyl bromide + $\overset{+}{N}a\overset{-}{OEt} \xrightarrow{\Delta}$
(b) 3-Bromo-3-ethylpentane + $CH_3OH \longrightarrow$
(c) 2-Bromo-3-ethylpentane + MeONa $\xrightarrow{\Delta}$
(d) 1-Bromo-2-methylcyclohexane + EtONa $\xrightarrow{\Delta}$

Sol. (a) $CH_3 - CH = CH - CH_3$

(b)

$$CH_3 - CH_2 - \underset{OCH_3}{\overset{CH_2-CH_3}{C}} - CH_2 - CH_3$$

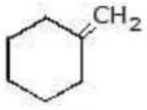
(c)

$$CH_3 - CH_2 = C\begin{matrix} \diagup CH_2-CH_3 \\ \diagdown CH_2-CH_3 \end{matrix}$$

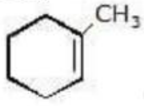
(d)


Ex.11


major + minor

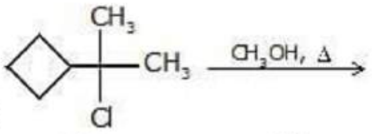
Write the structure of major and minor product.

Sol.  (minor)

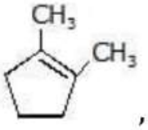
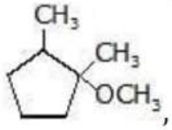
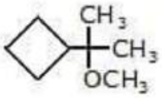
 (major)

Comparison of E_1 and E_2 elimination:

Promoting factors	**E_1**	**E_2**
(i) Base	Weak base	Strong base required
(ii) Solvent	Good ionizing solvent	Wide variety of solvent
(iii) Substrate	3° > 2° > 1°	3° > 2° > 1°
(iv) Leaving group	Better one required	Better one required
Characteristics		
(i) Kinetics	K [R- X], I order	K [R - X] [Base], IIst order
(ii) Orientation	Saytzeff alkene	Saytzeff alkene
(iii) Stereochemistry	No special geometry is required.	transition state must be co-planar.

Ex.12 

P + Q + R

Sol. P is , Q is , R 

Q.6 Arrange the compounds of each set in order of reactivity towards dehydrohalogenation by strong base

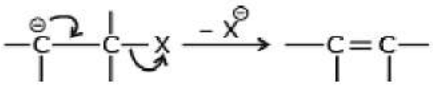
(a) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
(b) 1-Bromo-3-methylbutane, 2-bromo-2-methylbutane-2-Bromo-3-methylbutane
(c) 1-Bromobutane,1-Bromo-2,2-dimethylpropane, 1-bromo-2-methylbutane, 1-Bromo-3-methylbutane

(C) mechanism of E_1 CB reaction (Unimolecular conjugate base reaction):
The E_1 CB or carbanion mechanism: In the E_1 CB, H leaves first and then the X. This is a two step process, the intermediate is a carbanion.

Mechanism:

Step-1: Consists of the removal of a proton, H^+ by a base generating a carbanion.

Step-2: Carbanion loses a leaving group to form alkene.



Condition: For the E_1 CB, substrate must be containing acidic hydrogen and poor leaving groups (i.e., bad lg).