

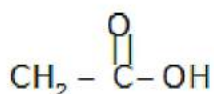
Chapter 11

Aldehydes, Ketones and Carboxylic Acids

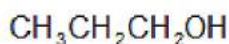
Physical & Chemical Properties of Aldehydes & Ketones

Physical properties of acids and acid derivatives:

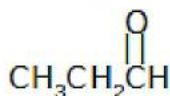
1. Boiling point:



Acetic acid,
bp 118°C

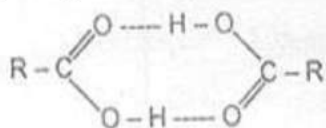


1-propanol
bp 91°C



Propionaldehyde
bp 49°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

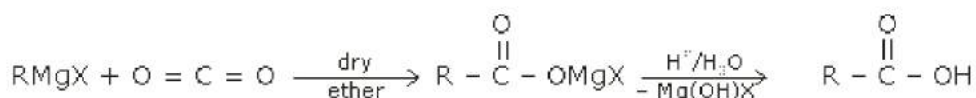
Carboxylic acids form hydrogen bonds with water and the lower molecular weight carboxylic acids (upto 4 carbon atoms) are miscible with water.

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:

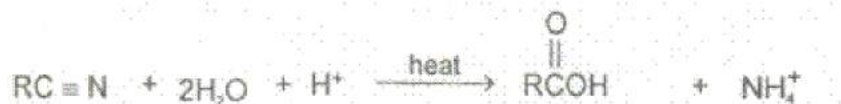


1. Synthesis of carboxylic acids by the carboxylation of Grignard's reagent:



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

Mechanism:



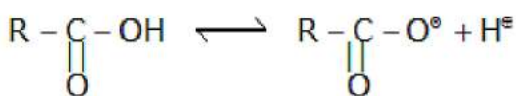
Nitrile

carboxylic acid

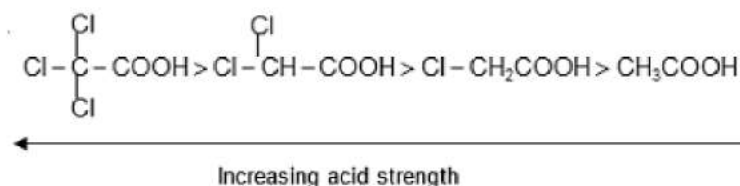
Chemical Reactions

1. Acidic strength %

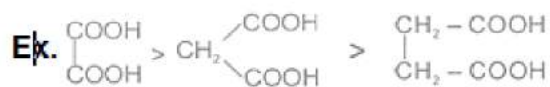
Acidity of carboxylic acids:



Ex.



Ex. $\text{HCOOH} > \text{CH}_3\text{COOH} > \text{CH}_3\text{-CH}_2\text{-COOH}$



Ex. Relative acid strength is:

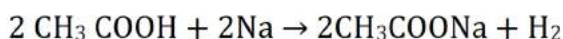
$\text{RCOOH} > \text{HOH} > \text{ROH} > \text{HC}=\text{CH} > \text{NH}_3 > \text{RH}$

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

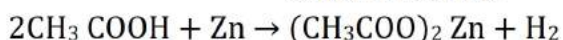
2- Reaction involving removal of proton from -OH group.

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

2. Reaction with metals:

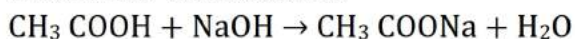


Sodium acetate

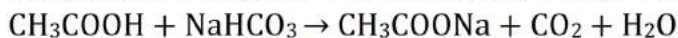
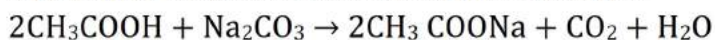


Zinc acetate

3. Reaction with alkalis:



4. Reaction with carbonates and bicarbonates:

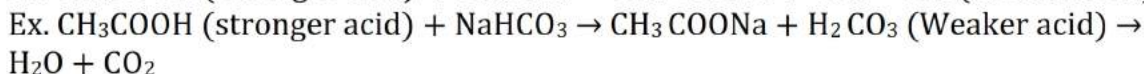
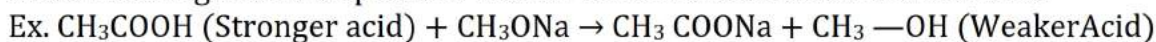


Reaction of carboxylic acid with aqueous sodium carbonate solution produces brisk effervescence. However, most phenols do not produce effervescence. Therefore, the reaction may be used to distinguish between carboxylic acids and phenols.

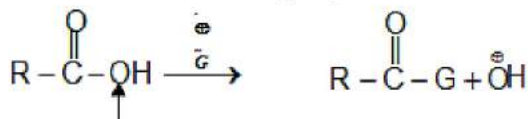
5. Reaction with Grignard's reagent:



Note: A stronger acid displaces a weaker acid from salt of the weaker acid.



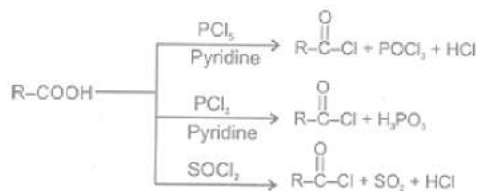
3. Reaction involving replacement of -OH group



Strong bases so not a basicity must be

Good leaving group less than basicity of G⁻

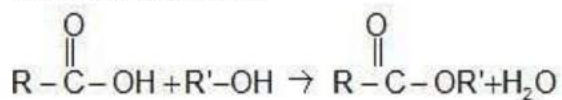
(i) Formation of acid chlorides:



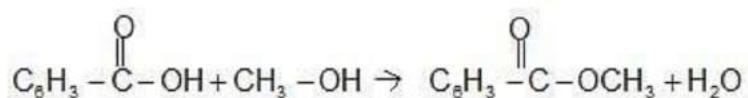
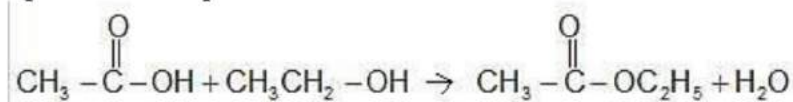
(2) Fisher Esterification:

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

General Reaction:

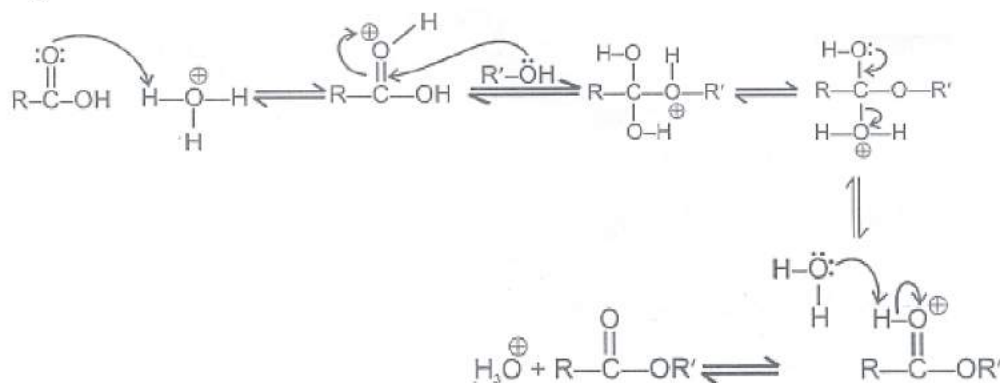


Specific Example:

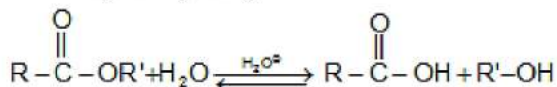


Mechanism:

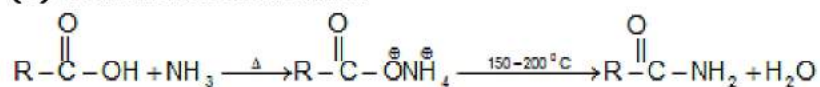
Acid catalysed esterification:



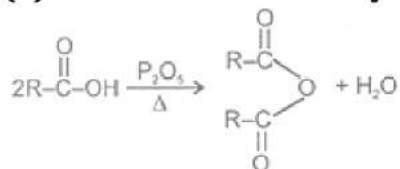
If we follow the forward path in this mechanism, we have the mechanism for the acid catalysed esterification for an acid. If however, we follow the reverse reactions, we have the mechanism for the acid catalysed hydrolysis of an ester. Acid catalysed ester hydrolysis gives:



(3) Formation of amides:



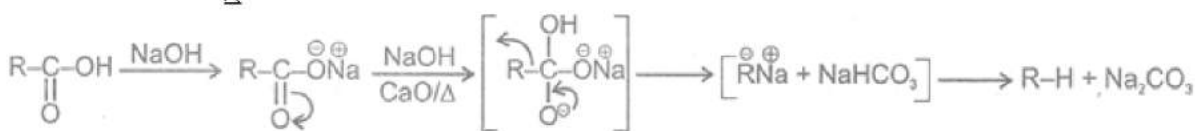
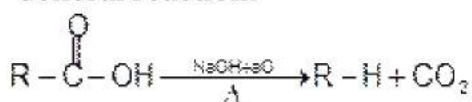
(4) Formation of acid anhydride:



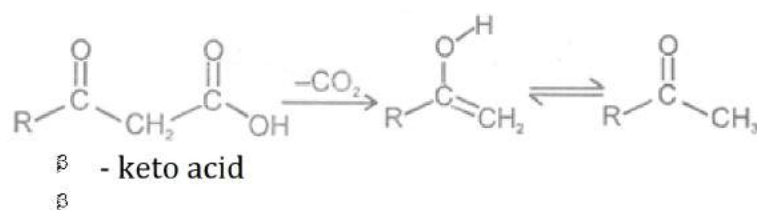
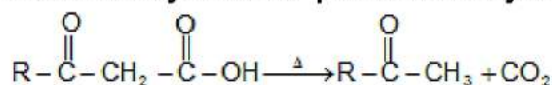
(4) Decarboxylation reactions:

1 Soda-lime decarboxylation:

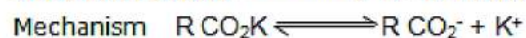
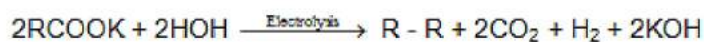
General reaction:



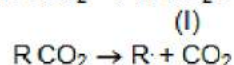
2. Decarboxylation of β keto carboxylic acids :



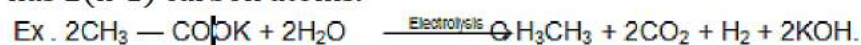
3) Kolbe's electrolysis:



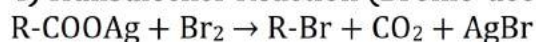
At Anode $\text{R CO}_2^- \rightarrow \text{R CO}_2 + \text{e}^-$ (oxidation)



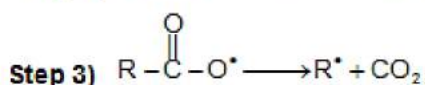
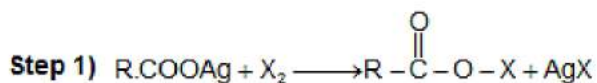
If n is the number of carbon atoms in the salt of carboxylic acid, the alkane formed has $2(n-1)$ carbon atoms.



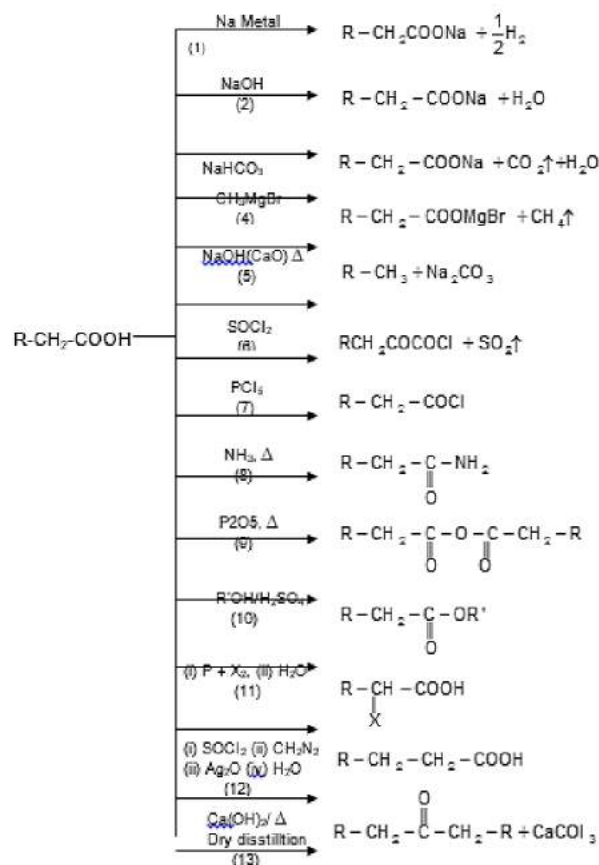
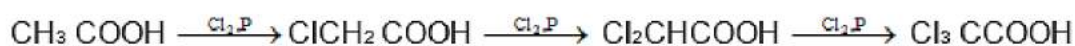
4) Hunsdiecker Reaction (Bromo-decarboxylation):

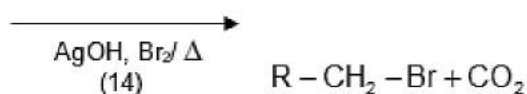


Mechanism:



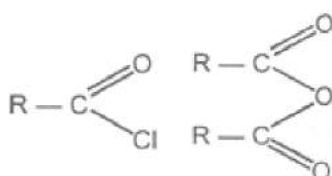
5. HVZ Reaction (Halogenation of aliphatic acids and Substituted acids):



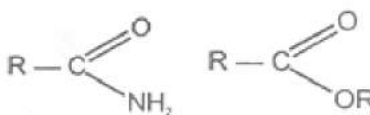


Carboxylic Acid Derivatives

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, -NR₂ or -OR.



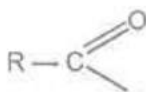
Acid chloride Anhydride



Amide

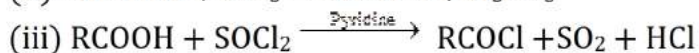
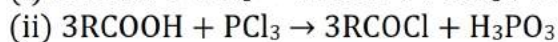
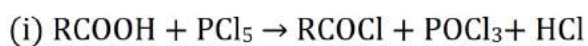
Ester

They all contain the acyl group

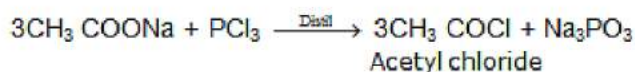


(A) Acid halides:

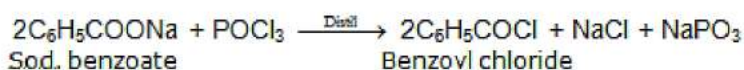
Methods of preparation of Acyl halides:



Ex.

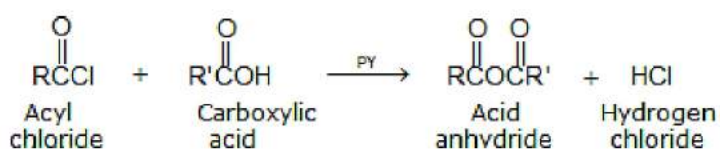


Ex.



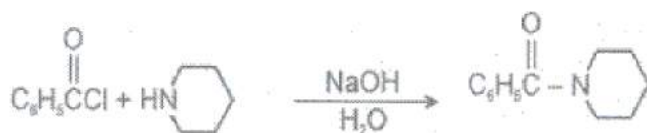
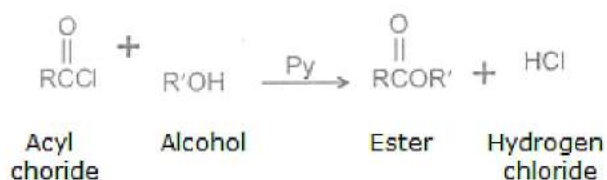
Chemical Reactions:

1. Reaction with carboxylic acids:



2. Reaction with alcohols:

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

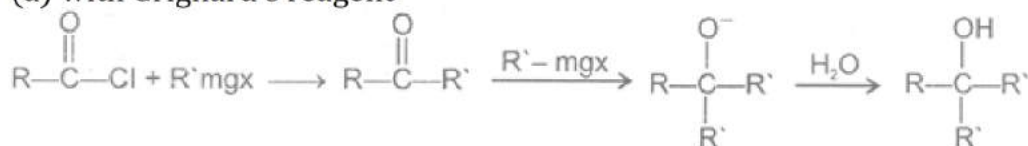


3) Hydrolysis:

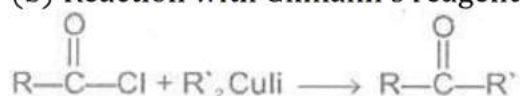


4) Reaction of acid halide with organometallic compounds:

(a) with Grignard's reagent-

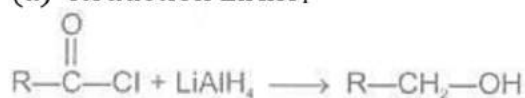


(b) Reaction with Gilman's reagent-

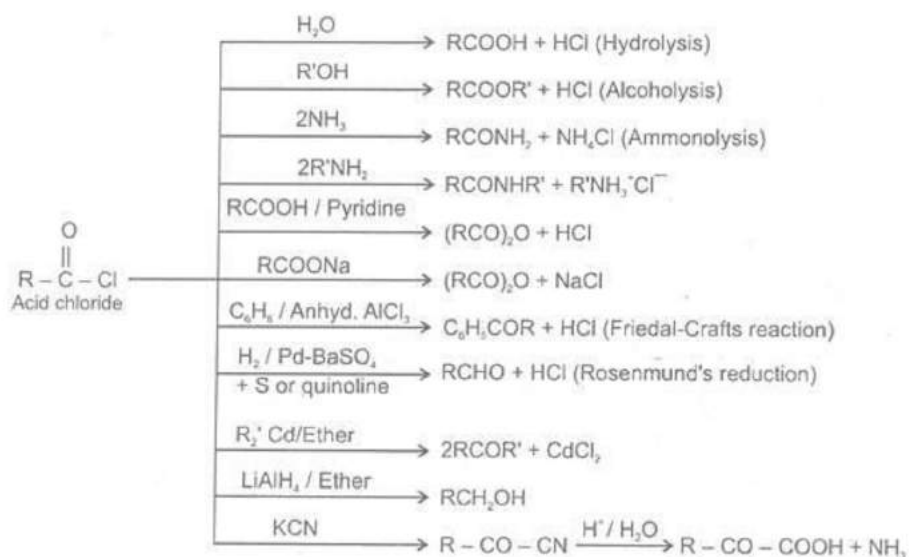
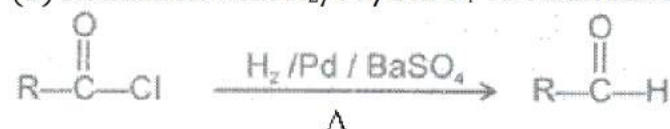


5) Reduction of acid halide:

(a) Reduction LiAlH_4



(b) Reduction with $\text{H}_2/\text{Pd}/\text{BaSO}_4$ Rosenmund reduction-



(B) Acid amides

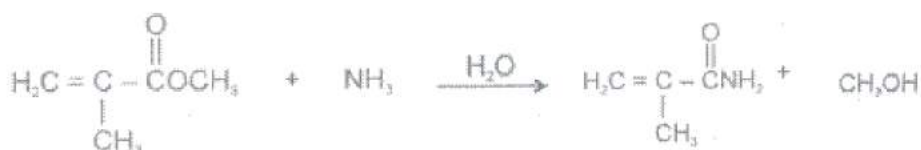
Methods of preparation of acids amides:

1. By reaction of esters with ammonia and amines.



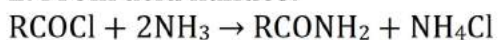


Ammonia is more nucleophilic than water, making it possible to carry out this reaction using aqueous ammonia.



Ex.

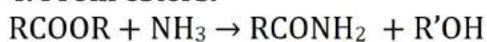
2. From acid halides:



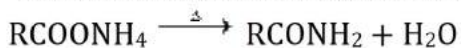
3. From anhydride:



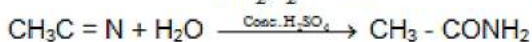
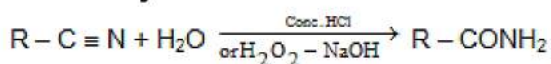
4. From esters:



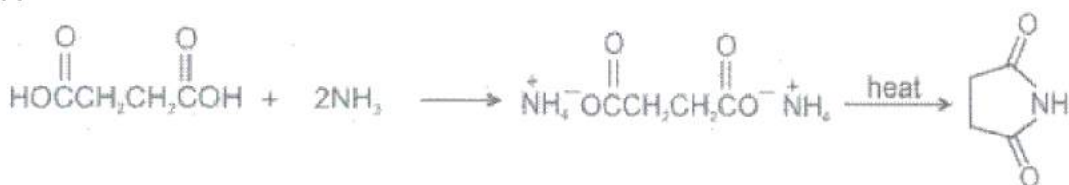
5. From ammonium salt of carboxylic acid:



6. From cyanides:



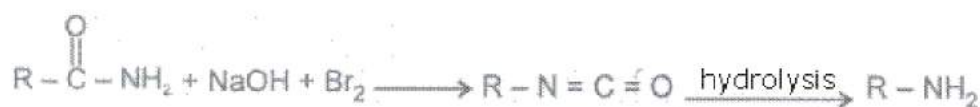
7.



Chemical Reactions:

(1) Hoffmann rearrangement:

General reaction-



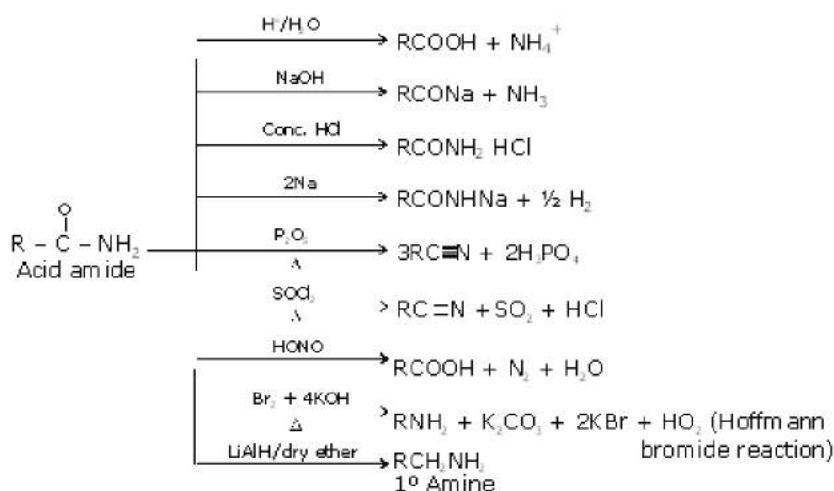
(2) Hydrolysis of amides-



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

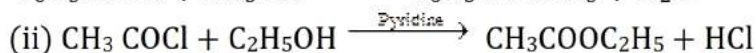
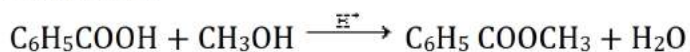
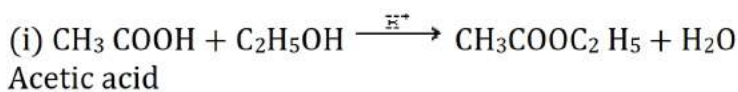


Summary of Reaction of Amide:



(C) Esters

Methods of Preparation:

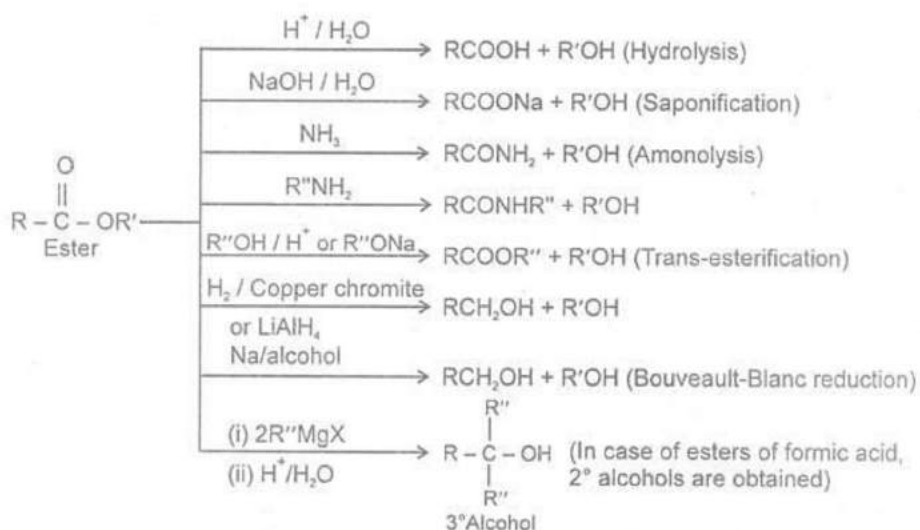


Alcohols react with acyl chlorides by nucleophilic acyl substitution to yield esters. These reactions are typically performed in the presence of a weak base such as pyridine.





Summary of reaction of esters:



(D) Acid anhydrides

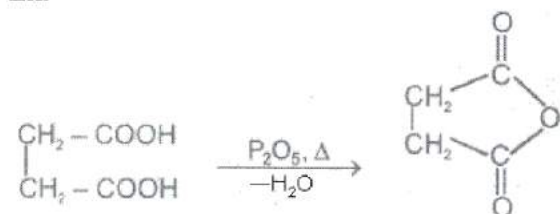
Methods of Preparation of acid anhydrides:

1- From carboxylic acids

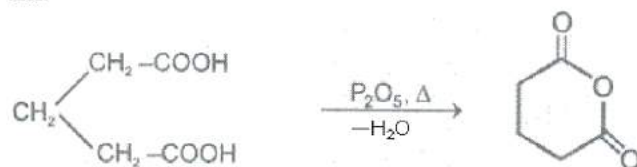
Ex.



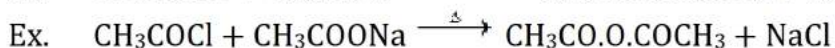
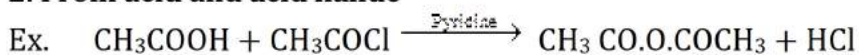
Ex.



Ex.

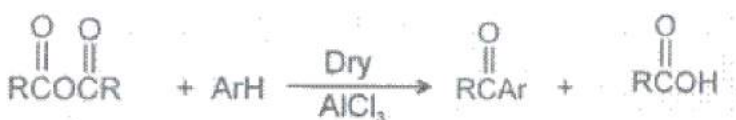


2. From acid and acid halide



Chemical Reactions

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



2. Reaction with alcohols-

Ex.

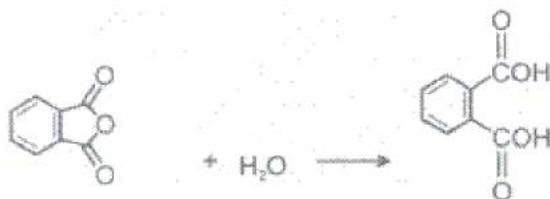


3. Reaction with ammonia and amines-



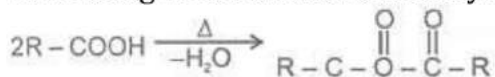
4. Hydrolysis-

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



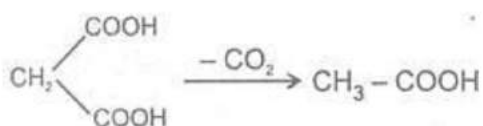
5. Heating Effects:

a. Heating effect on monocarboxylic acid

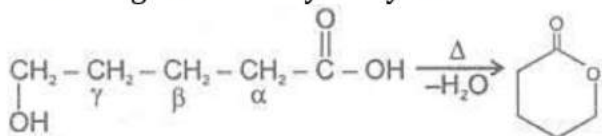


b. Heating effect on dicarboxylic acid

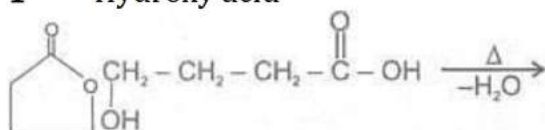




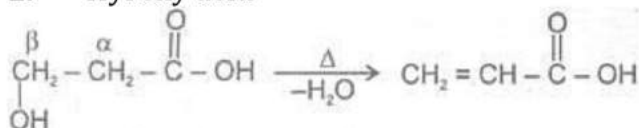
c. Heating effect on Hydroxy acids



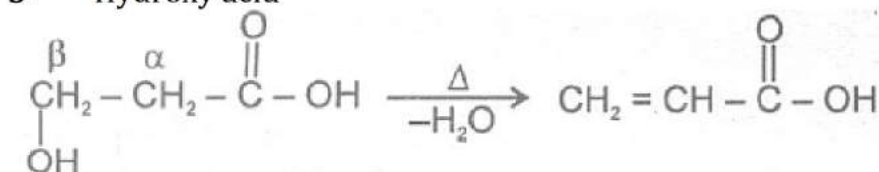
1- δ - Hydroxy acid



2. γ - Hydroxy acid

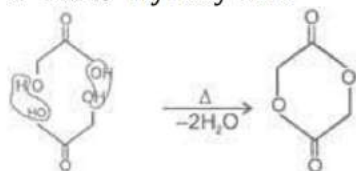


3- β - Hydroxy acid

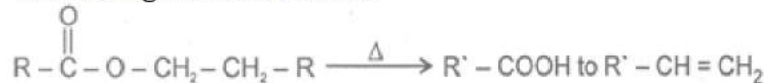


Since 4 or 8 membered rings are less stable therefore β -Hydroxy acids on heating produce α,β unsaturated carboxylic acid.

4- An α -Hydroxy acid



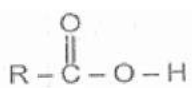
5. Heating effect on esters



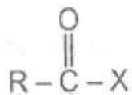
This reaction follows syn elimination & Hoffman product is formed.

Doc: Nomenclature of Carboxylic Acids

Introduction:



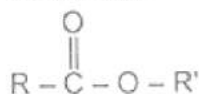
Carboxylic acid



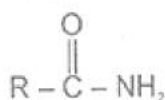
Acid halide



anhydride



Ester

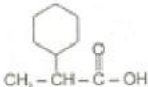


Amide

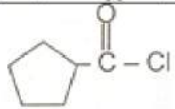
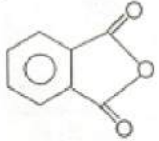


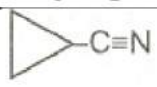
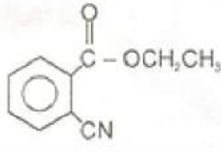
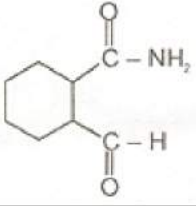
Nitrile

Table - 1: IUPAC Nomenclature of Acid derivatives:

S.No.	Compound	IUPAC Name
1	$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	Methanoic acid
2	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	Ethanoic acid
3		2- Cyclohexylpropanoic acid
4	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}(\text{CH}_2\text{CH}_2\text{CH}_3)-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	3- Oxo-2- propylbutanoic acid
5	$\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	4- Aminobutanoic acid
6	$\text{CH}_3\text{CH}_2\overset{\text{PH}}{\underset{ }{\text{CH}}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	3- Phenylpentanoic acid
7	$\text{CH}_3-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	3- Methylbutanoic acid
8	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{F}$	Ethanoylchloride



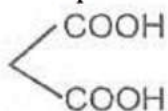
9	$\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{Cl}$	Propanoylchloride
10	$\text{CH}_3 - \overset{\text{Br}}{\underset{ }{\text{CH}}} - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{Br}$	3-Bromobutanoylbromide
11		Cyclopentanecarbonyl chloride
12	$\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3$	Ethanoid anyhydride
13	$\text{CF}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{CF}_3$	Trifluoroethanoic anhydride
14		1,2- Benzenedicarboxylic anhydride

15	$\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{H}$	Ethanoic methanoic anhydride
16	$\text{CH}_3\text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{CF}_3$	Trifluoroethanoic propanoic anhydride
17		Cyclopropane carbonitrile
18	$\text{CH}_3 - \text{CH}_2 - \overset{\text{CN}}{\underset{ }{\text{CH}}} - \text{CH}_2 - \text{COOH}$	3- Cyanopentanoic acid
19		Ethyl-o-cyanobenzoate
20		2- Formylcyclohexane carboxamide
21	$\text{CH}_3 - \text{CH}_2 - \overset{\text{OH}}{\underset{ }{\text{CH}}} - \text{C} \equiv \text{N}$	2- Hydroxyutane nitrile

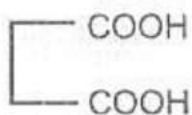


Dicarboxylic Acids

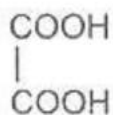
If the substituent is a second carboxyl group, we have a dicarboxylic acid. For example:



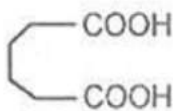
Oxalic acid or Ethanedioic acid



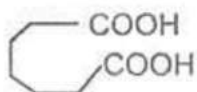
Malonic acid -1, 3- dioic acid



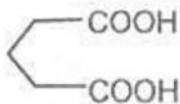
Succinic acid -1, 4- dioic acid



Glutaric acid
Pentane-1, 5-dioic acid



Adipic acid
Hexane-1, 6-dioic acid



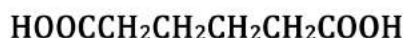
Pimelic acid
Heptane-1, 7- dioc acid



Malonic acid
Propanedioic acid



Succinic acid
Butanedioic acid



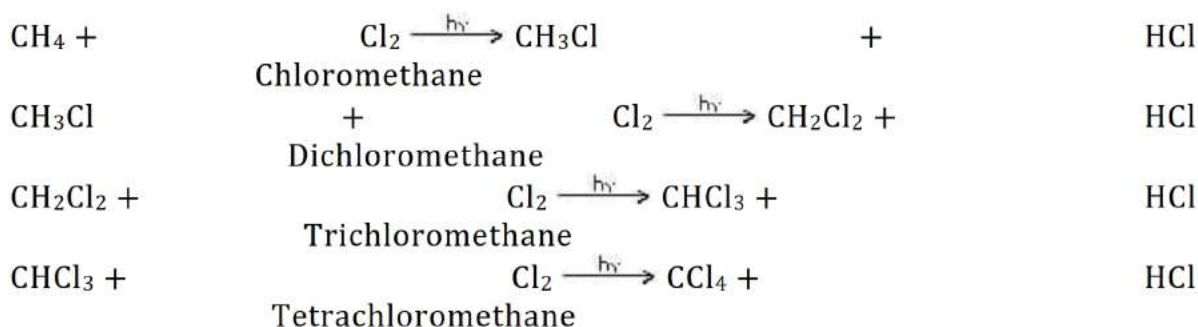
Adipic acid
Hexanedioic acid

Polyhalogen Compounds

Polyhalogen derivatives:

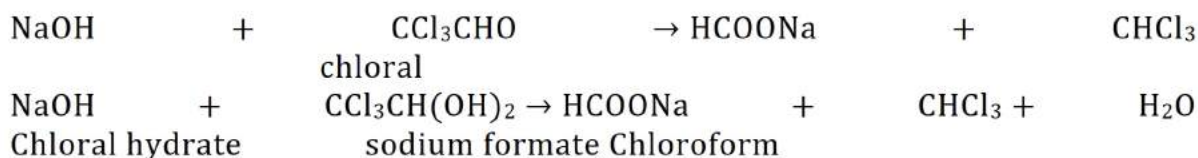
Trichloromethane (Chloroform), CHCl_3

Preparation:



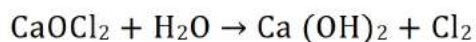
The mixture of CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 can be separated by fractional distillation.

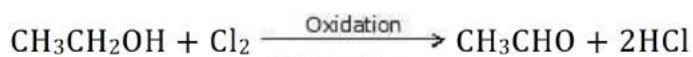
2. From chloral hydrate, Pure chloroform can prepare.



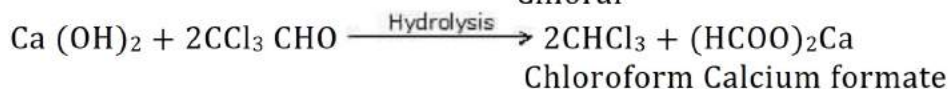
3. **Laboratory Method:** From ethanol or acetone, by reaction with a paste of bleaching powder and water.

In case of ethanol, the reaction occurs as follows:





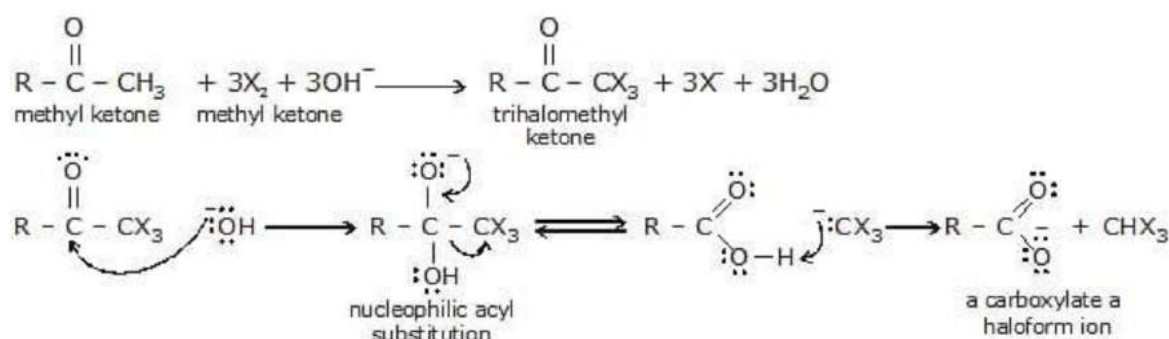
Chloral



4. From carbon tetrachloride:



5. Haloform reaction:



Haloform)

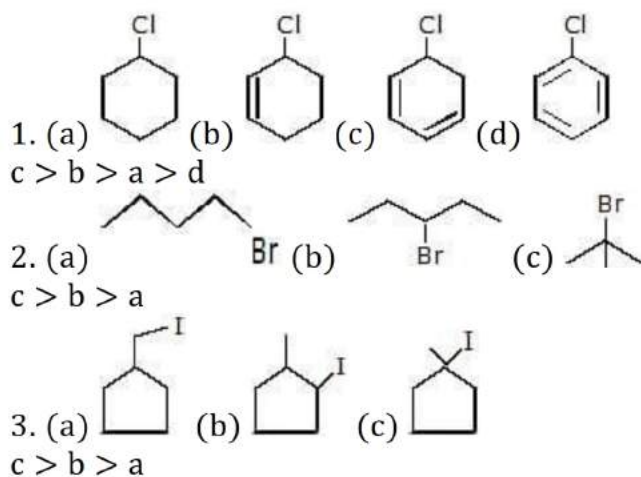
Step 1: Attack of the

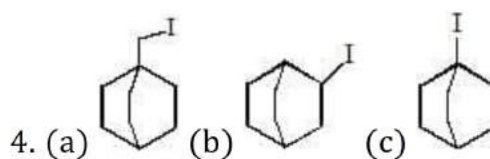
Step 2: Elimination

Step 3: Proton transfer

nucleophile of the leaving group

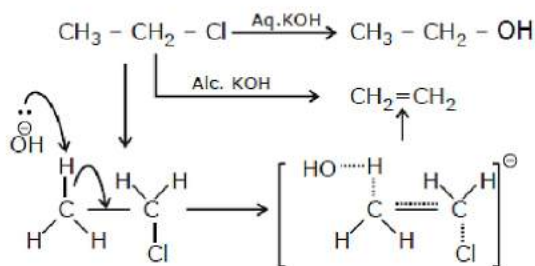
Prob. Compare rate of elimination (Dehydro halogenation in presence of alcoholic KOH) i.e., E2:





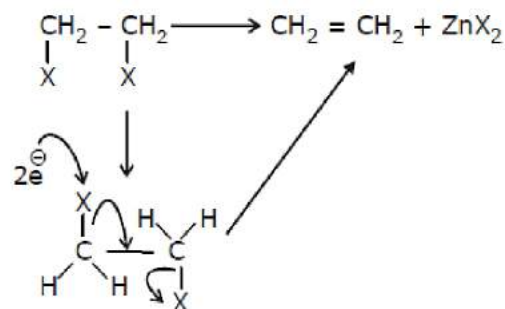
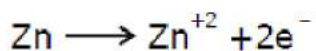
$b > a > c$

Dehalogenation: - ($-X_2$) E2



Anti elimination

Dehalogenation: - ($-X_2$) E2



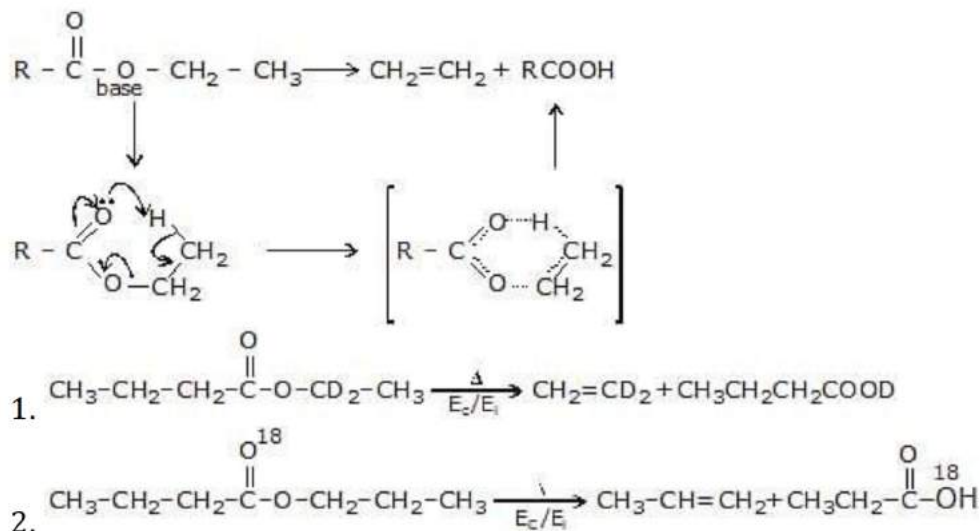
Anti elimination

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:



1.8.2 Physical properties of chloroform

Chloroform is a colourless, heavy liquid which has sweetish, sickly odour and taste. It boils at 334° 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.

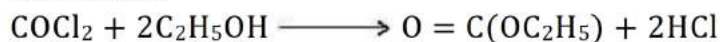
1.8.3 Chemical properties of chloroform:

1. Action of sun light and air-



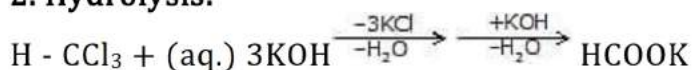
Phosgene

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.



diethyl carbonate

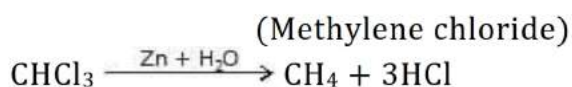
2. Hydrolysis:



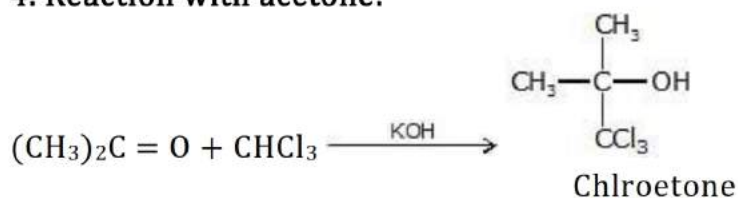
3. Reduction:



HCl
Dichloromethane

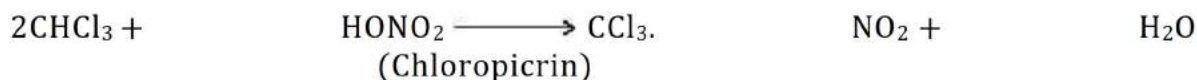


4. Reaction with acetone:



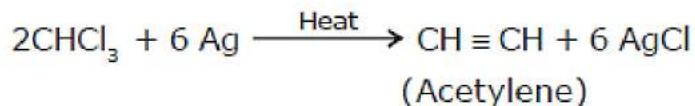
Use: Chloretone is used as hypnotic (a sleep inducing) drug.

5. Reaction with nitric acid:

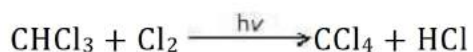


Use: Chloropicrin is used as an insecticide and war gas.

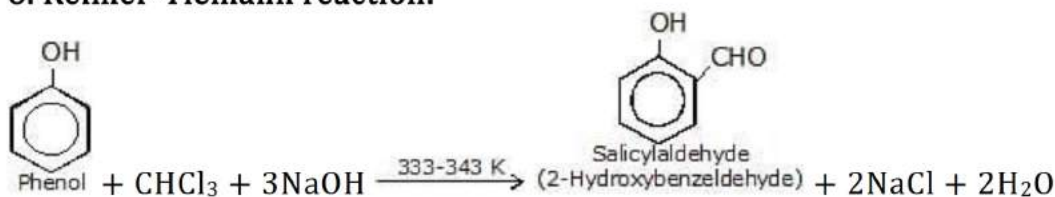
6. Reaction with silver powder:



7. Chlorination:



8. Reimer-Tiemann reaction:



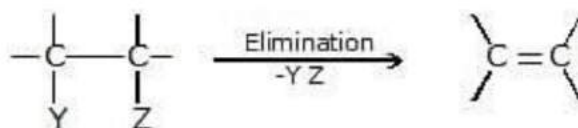
1.8.4 Uses of chloroform

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

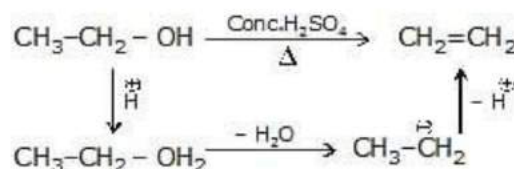
1.7.2 Elimination reactions:

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 Alcohol (E_1):

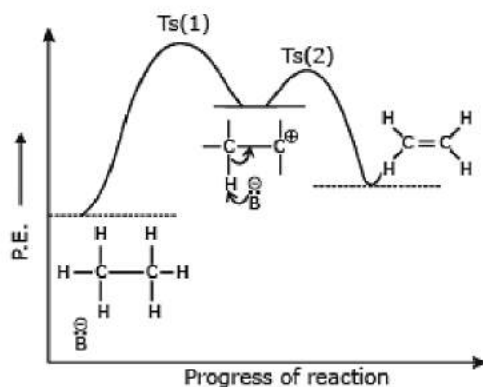


Characteristics of E_1 reaction:

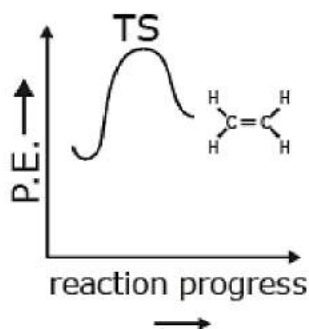
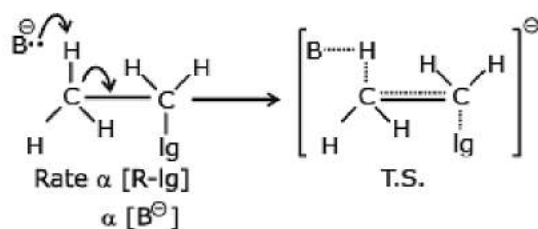
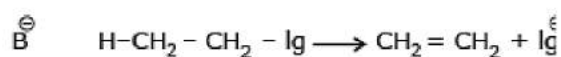
- (i) It is unimolecular, two step process.
- (ii) It is first order reaction.
- (iii) Reaction intermediate is carbocation, so rearrangement is possible.
- (iv) In the second step, a base abstracts a proton from the carbon atom adjacent to the carbocation, and forms alkene.



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



E₂- elimination:



Bi-molecular reaction, second order kinetic.

1. Leaving group leaves 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, E₁ and E₂ 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. E₂-elimination is favour by:

(1) Moderate leaving group (lg)

(2) Strong base (RO⁻, Alc. KOH)

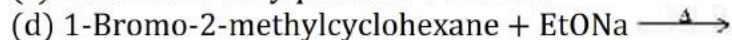
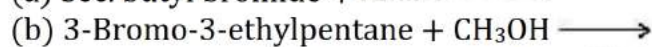
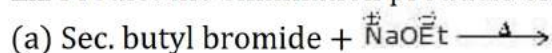
(3) Polar aprotic solvent.

(4) High conc. of base.

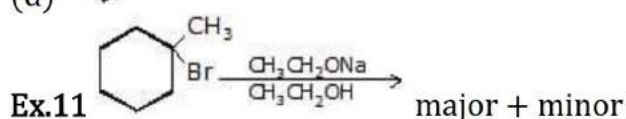
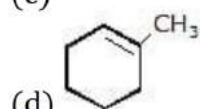
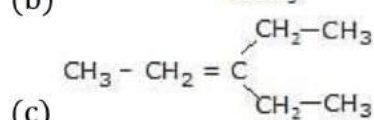
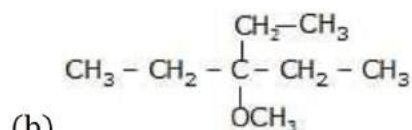
(5) High temperature.

Reactivity towards E₂: R - I > R - Br > R - Cl > R - F

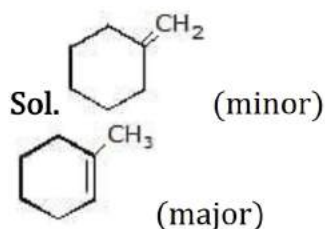
Ex. Predict the elimination products of the following reactions.



Sol. (a) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$

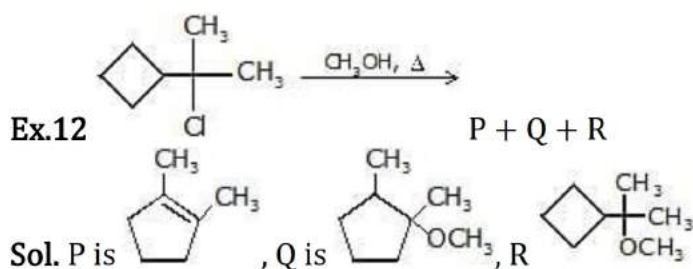


Write the structure of major and minor product.



Comparison of E₁ and E₂ 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], II st order
(ii) Orientation	Saytzeff alkene	Saytzeff alkene
(iii) Stereochemistry	No special geometry is required.	transition state must be co-planar.



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

- 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
- 1-Bromo-3-methylbutane, 2-bromo-2-methylbutane-2-Bromo-3-methylbutane
- 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-bromo-2-methylbutane, 1-Bromo-3-methylbutane

(C) mechanism of E₁ CB reaction (Unimolecular conjugate base reaction):

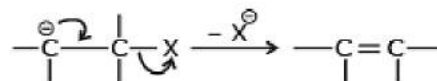
The E₁ CB or carbanion mechanism: In the E₁ CB, H leaves first and then the X. This is a two step process, the intermediate is a carbanion.

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 E₁ CB, substrate must be containing acidic hydrogen and poor leaving groups (i.e., bad lg).

