

Substitution Reactions

The reaction which involves the direct replacement or substitution of an atom or a group in a molecule by another atom or group without any change in remaining part of molecule is keas substitution.

On the basis of the above substitution reaction.

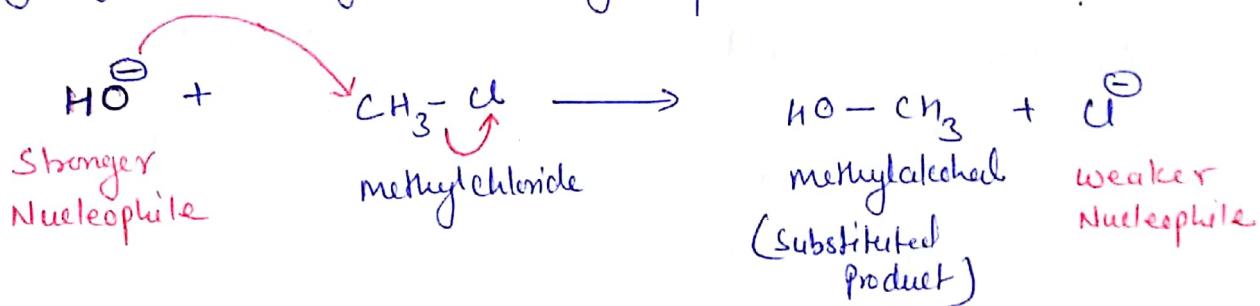
reaction may be of 3 types.

a) Nucleophilic Substitution Reaction (S_N)

When a substitution rxn involves an attack by a nucleophile, the reaction is termed as nucleophilic substitution reaction (S_N).

$S = \text{Substitution}$
 $N = \text{Nucleophilic}$) A strong nucleophile displaces the weaker one.

Eg: Hydrolysis of alkyl halides by aqueous alkali to furnish alcohol

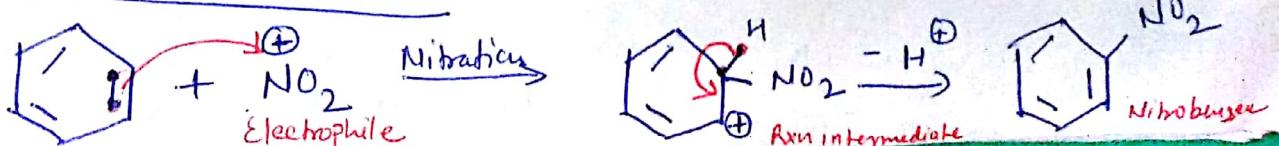


b) Electrophilic Substitution Reaction (S_E)

When the substitution reaction involves an attack by electrophile, the reaction is termed as electrophilic substitution reaction (S_E).

This type of reactions occur mainly in aromatic systems, where the high e-density attracts electrophiles.

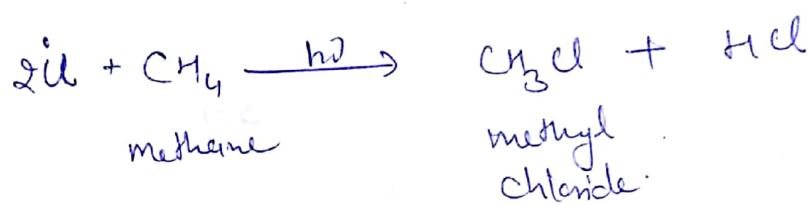
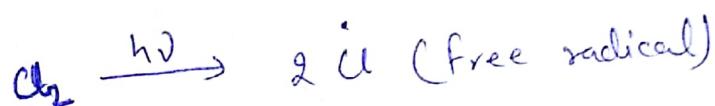
e.g. Nitration of Benzene



C) Free Radical Substitution Reaction

When substitution reaction involves an attack by free radical, reaction is termed as free radical reaction. These reactions are typical reaction of alkanes and other saturated compounds.

e.g. Chlorination of alkane (i.e. methane) in the presence of light



2. Addition Reaction

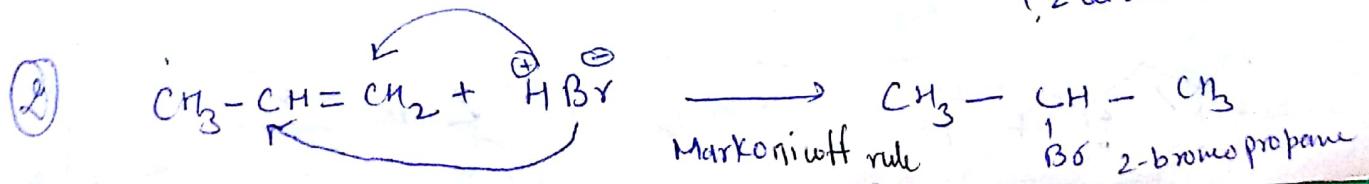
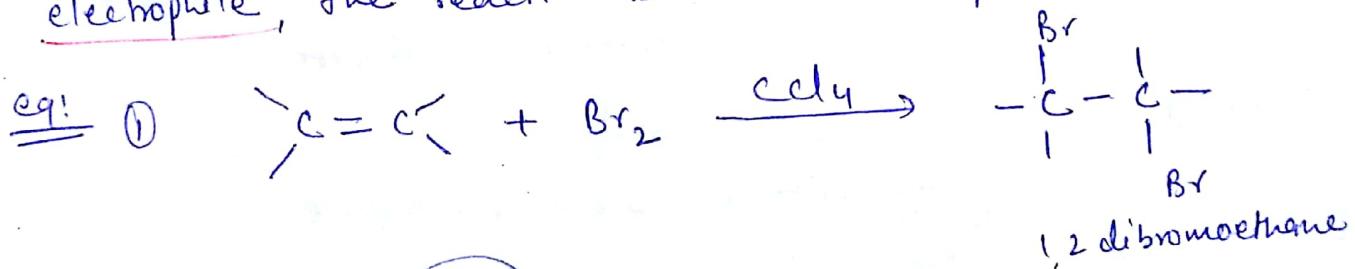
The reaction which involves the addition of two reacting molecules to give a single molecule as a product is called addition reaction.

→ All organic compounds containing double or triple bonds undergo addition reactions.

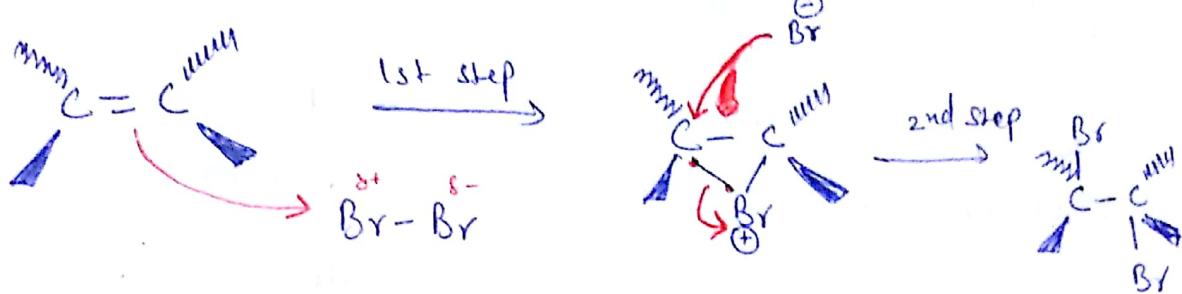
On the basis of type of attacking reagent, addition reactions are divided into following types:

a) Electrophilic Addition Reaction

When the addition reaction involves an attack by an electrophile, the reaction is called electrophilic addition reaction.



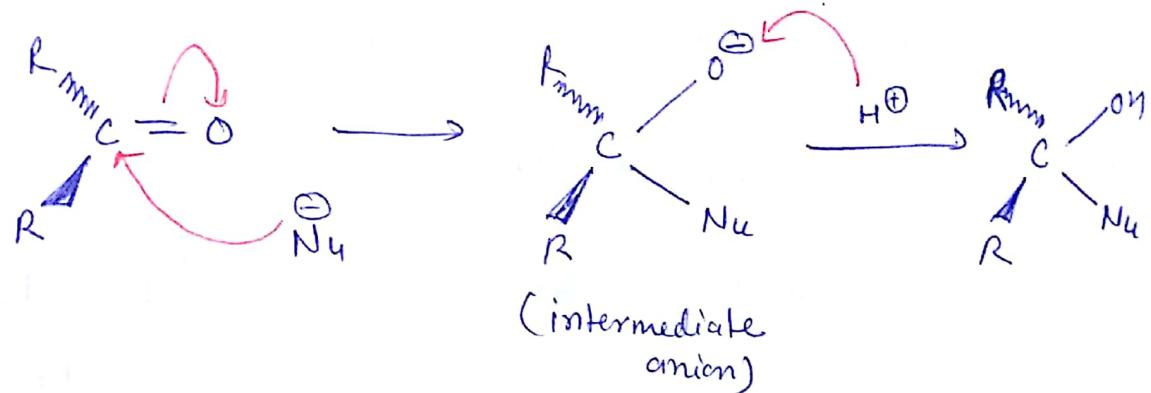
Mechanism



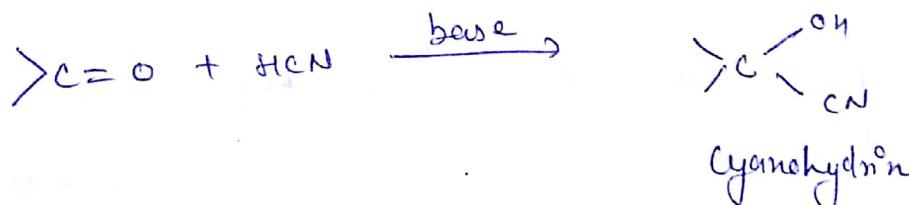
b) Nucleophilic Addition Reaction

When the addition reaction involves an attack by nucleophile the reaction is called nucleophilic addition reaction.

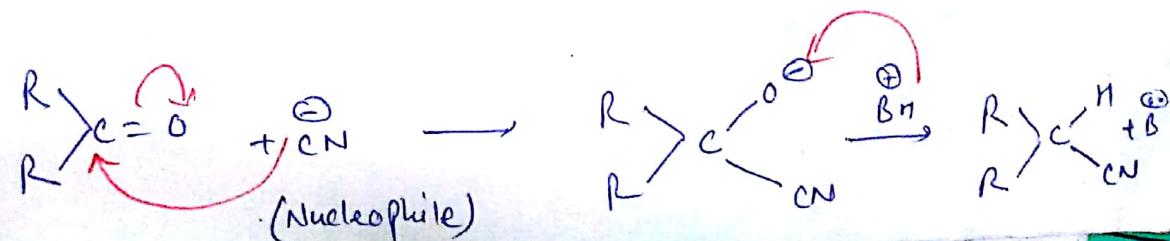
eg: Addition reactions of >C=O compounds are generally nucleophilic addition reactions.



eg: Addition reaction by the base catalysed addition of hydrogen cyanide to ketene.



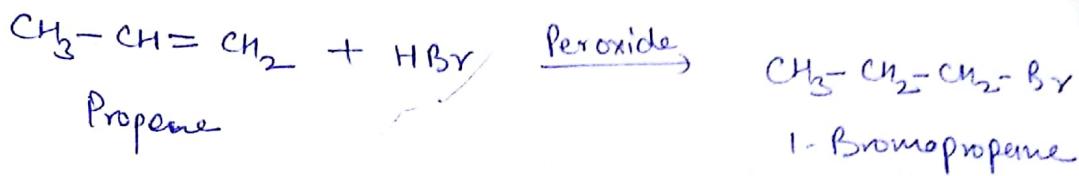
Mechanism



Free-radical Addition

The addition of HBr to alkene, in presence of Peroxide, An elimination group

Proceeds through a free radical mechanism i.e.

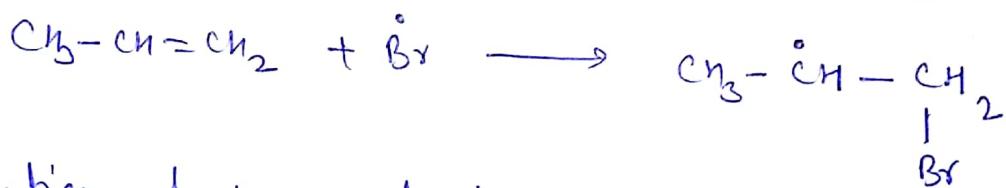


Mechanism

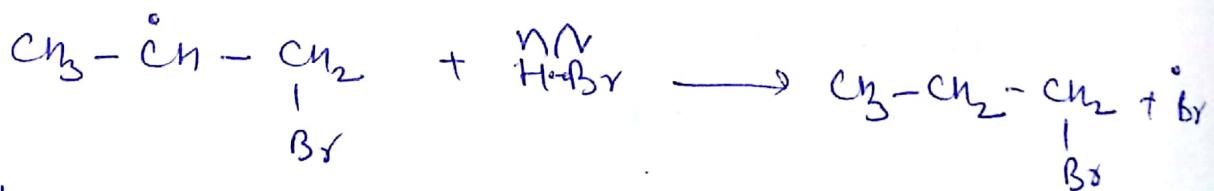
i) Formation of Br (free radical)



ii) Addition of Br to alkene



iii) Formation of the product



When Br attacks the alkene (Step II) the more stable free radical is formed. The stability of free radicals like that of carbocation is in the order $\boxed{3^\circ > 2^\circ > 1^\circ}$

S_N_1

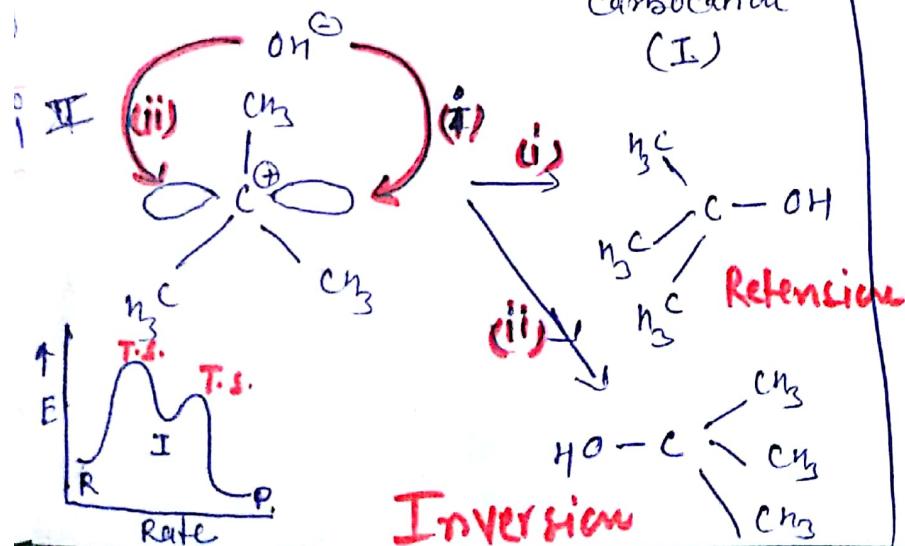
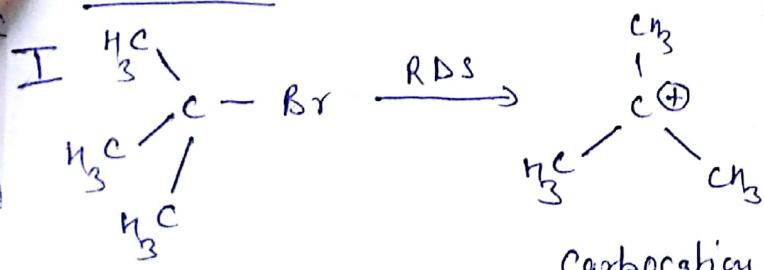
- Unimolecular Nucleophilic Substitution Reaction
- Rate of reaction $\propto [RX]$
- Two step method.
- 1st step is rate determining step
- Order of reactivity :- $3^\circ > 2^\circ > 1^\circ$ alkyl halide

Formation of Intermediate (Carbocation, R^+)

Stereochemistry :- 1) Inversion of configuration

2) Retention of configuration

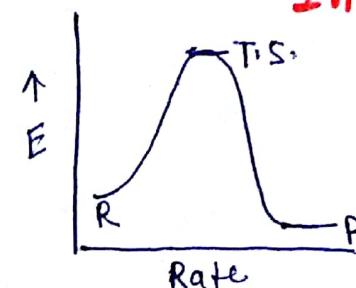
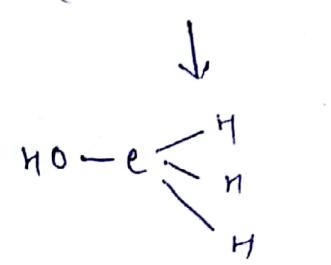
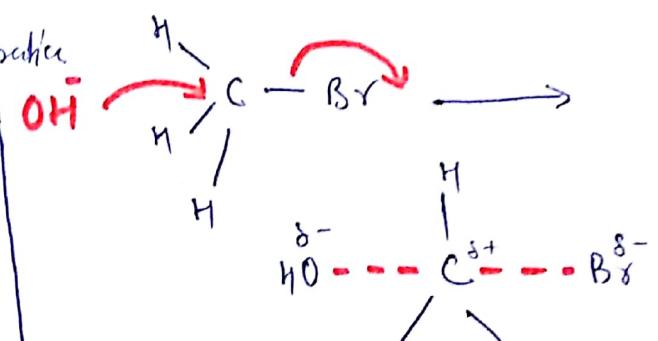
Reaction:



S_N_2

- Bimolecular Nucleophilic substitution Reaction
- Rate of reaction $\propto [RT][OH^-]$
- One step method
- Order of reactivity - $1^\circ > 2^\circ > 3^\circ$ alkyl halide
- Formation of Transition state
- Stereochemistry : - Inversion of configuration

Reaction:-



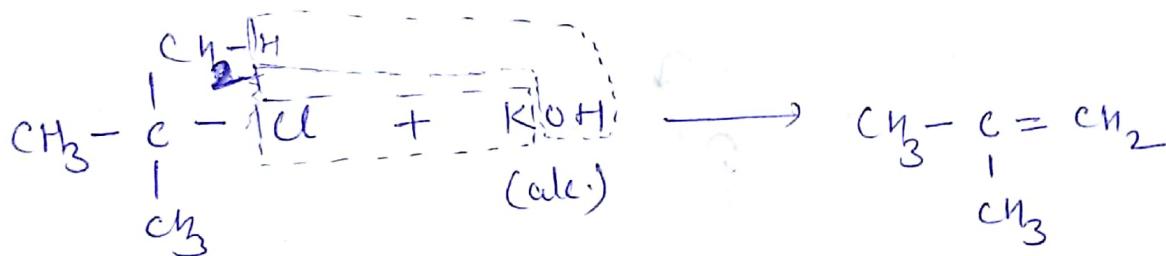
Peroxides Elimination Reaction

An elimination reaction involves the loss of two atoms or group from the same or adjacent atoms of substance to form a multiple (double or triple) bond.

On the basis of rate determining step, elimination reactions are divided into two types.

i) Unimolecular (E_1): In this elimination reaction, rate determining step depends on one molecule only.

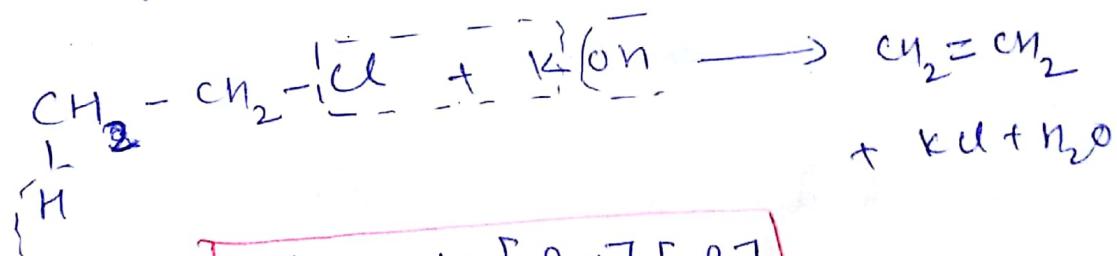
e.g.: Dehydrohalogenation of tertiary alkyl halides



$$\boxed{\text{Rate} = k[\text{RX}]}$$

ii) Bimolecular (E_2): In this elimination reaction, rate determining step involves two molecule.

e.g.: dehydrohalogenation of primary alkyl halide



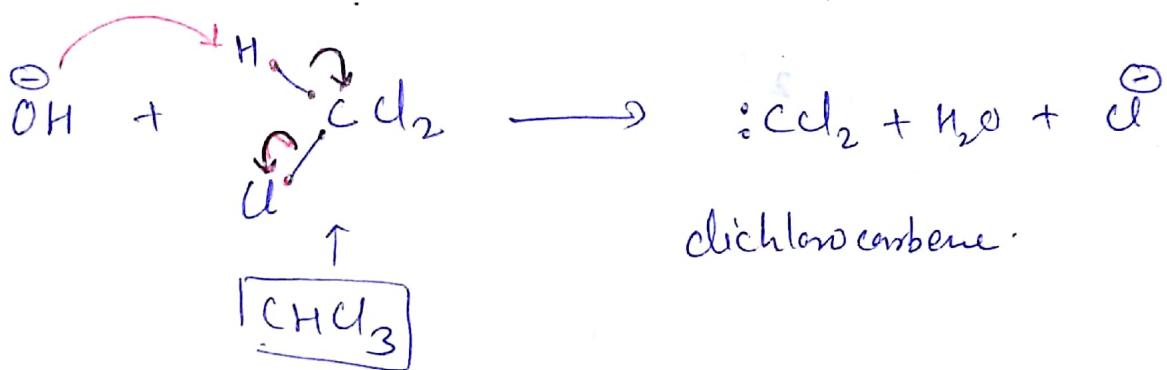
$$\boxed{\text{Rate} = k[\text{RX}][\text{B}]}$$

Depending upon the relative positions of the atoms or groups eliminated, these reactions are classified as α , β , γ elimination reactions.

a) α -Elimination Reaction

In these reactions, the loss of two atoms or groups takes place from the same atom of the substrates Substrate molecule.

e.g.: base-catalysed dehydrohalogenation of chloroform to form dichlorocarbene.

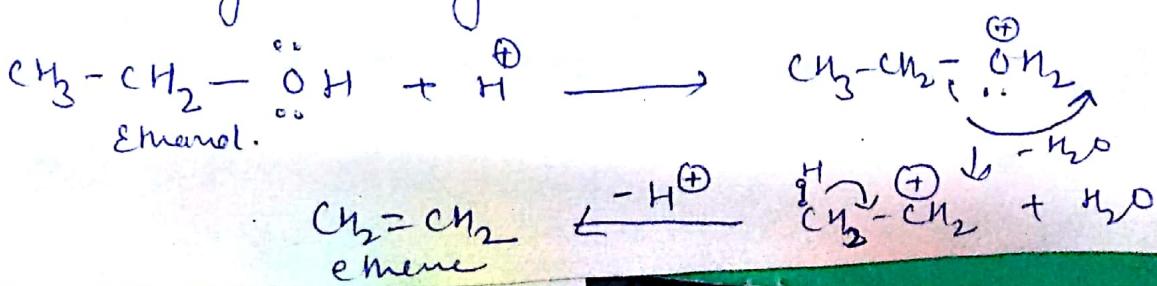


b) β - Elimination Reaction

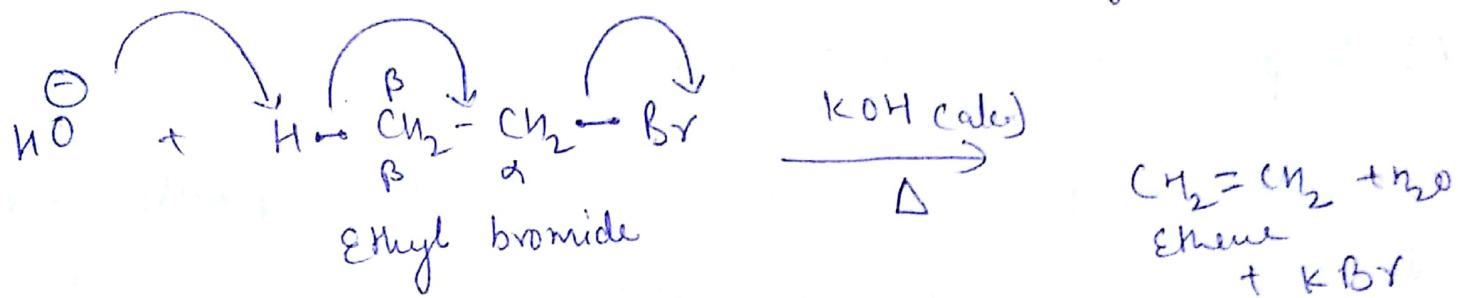
In these reactions, the loss of two atoms or groups takes place from the adjacent atoms of the ~~substrate~~ substrate molecule.

eq:

(i) Acid-catalysed dehydration of alcohol



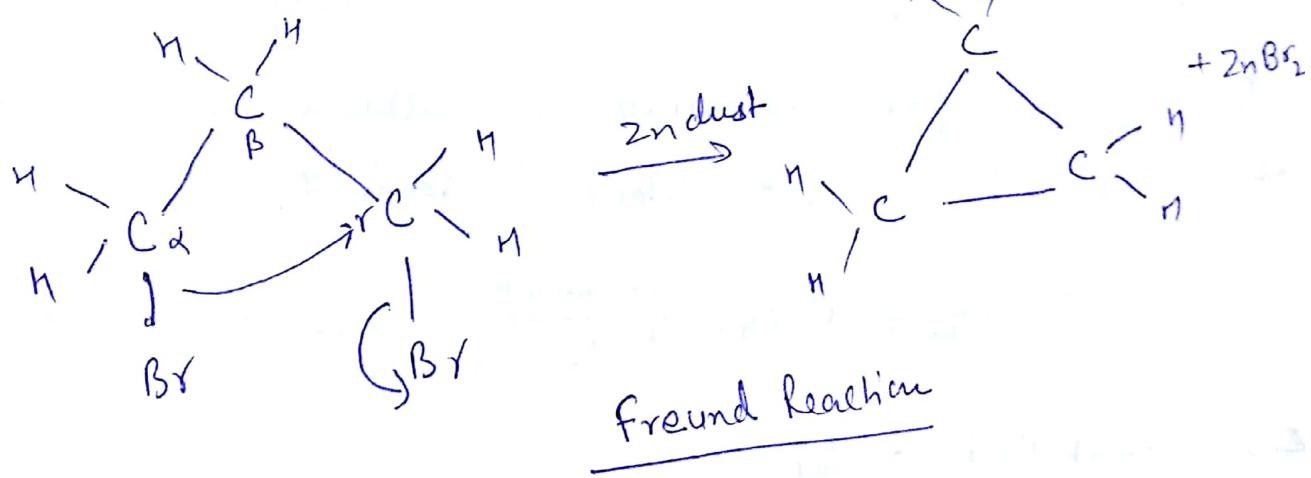
Base catalysed dehydrohalogenation of alkyl halides:



β -Elimination Reaction

In these reactions, loss of two atoms or groups takes place from α & β positions of the substrate molecule leading to the formation of three membered rings.

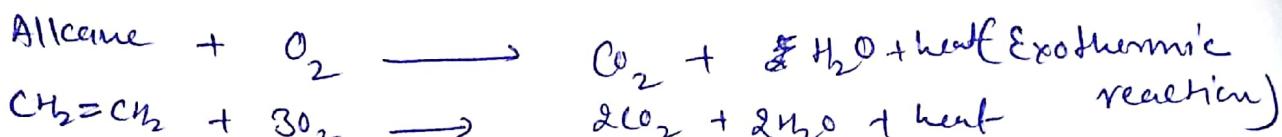
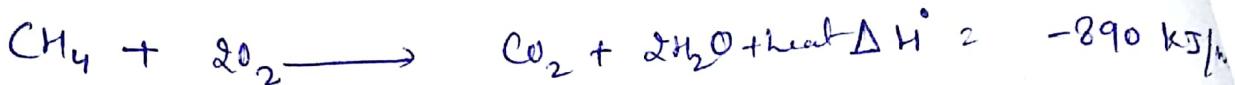
e.g.:



Oxidation (Addition of O₂)

A) Complete Oxidation (Combustion)

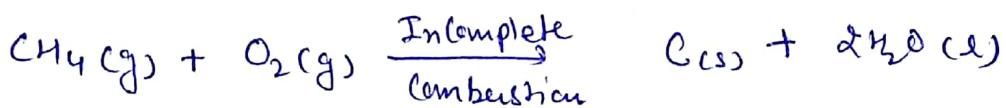
Alkenes on burning in air or O₂ get completely oxidised to CO₂ + H₂O with the evolution of large amount of heat.



B) Incomplete oxidation of combustion :-

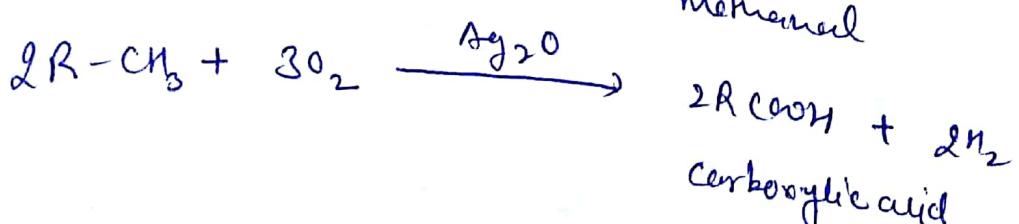
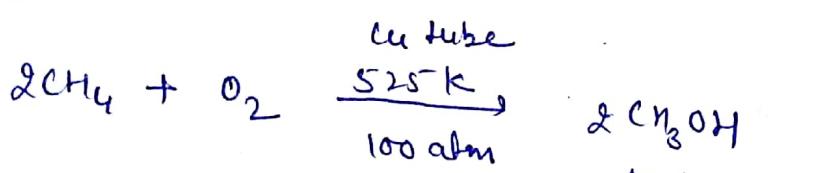


During incomplete combustion of alkane with insufficient amount of air or O₂, carbon black is formed.



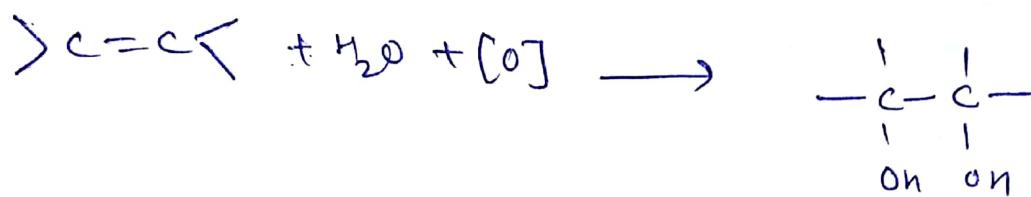
C) Controlled oxidation

Alkenes get converted into alcohol, aldehydes or acids in presence of metal catalysts and in limited supply of oxygen at high pressure.



Controlled Oxidation with KMnO_4

i) Use of cold, dilute, neutral or alkaline KMnO_4

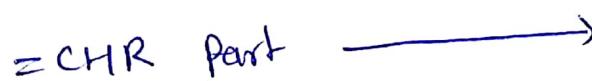
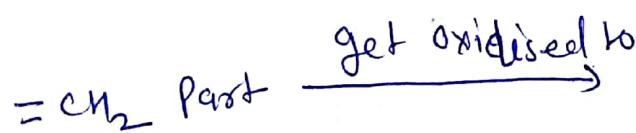


Vicinal diol (glycol)

ii) Oxidation with KMnO_4 under drastic condition:

- high temp
- high concentration of KMnO_4
- acidic medium
- The carbon-carbon ~~and~~ multiple bond is completely cleaved and the final products formed are $-\text{COOH}$ if C=C and CO_2 depending upon the nature of multiple bond.

In case of alkene



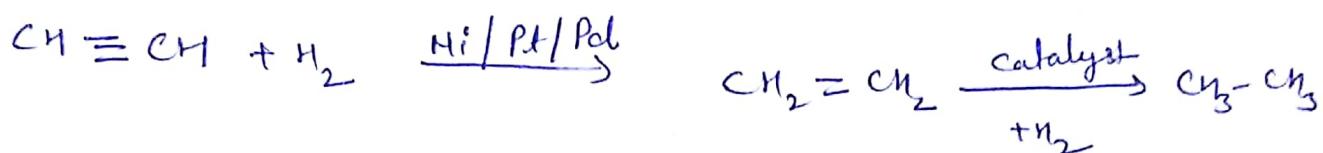
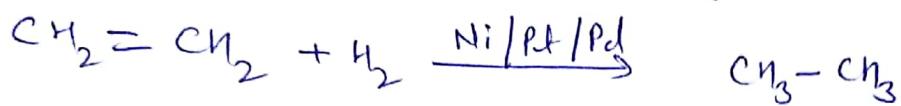
RCOOH (carboxylic acid)



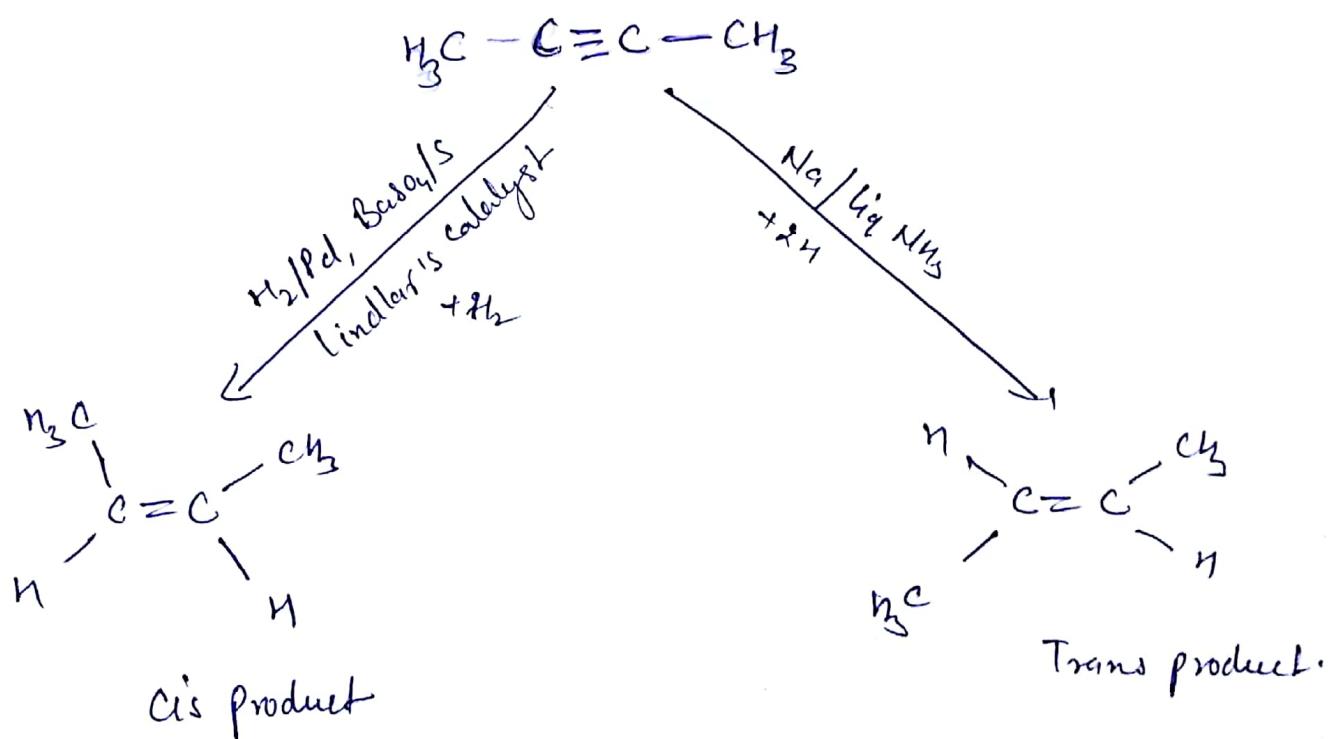
$\text{R}'\overset{\text{||}}{\underset{\text{C}}{\text{C}}}\text{R}'$ (ketone)

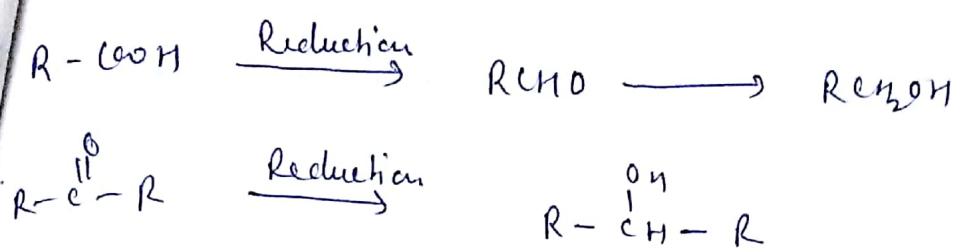
Reduction. (Addition of dihydrogen)

Alkenes react readily with dihydrogen in the presence of finely-divided Ni, Pt, Pd as catalyst.

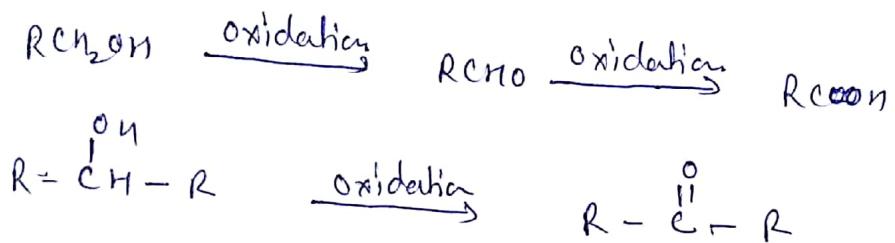


Reduction of alkyne to alkene can stage can be carried out with the use of Lindlar's catalyst (Pd/C or CaCO_3 and partially deactivated with poison such as sulphur or quinoline). It can also be carried out with Na in liq NH_3 (Birch Reduction)





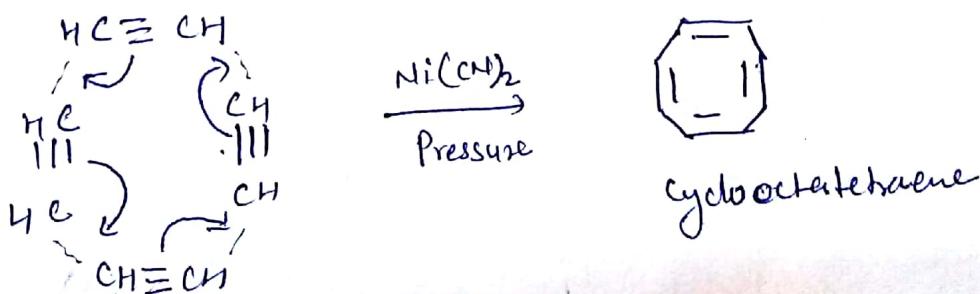
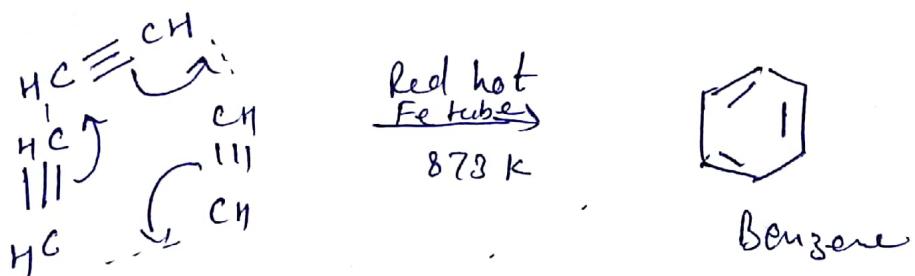
Oxidation



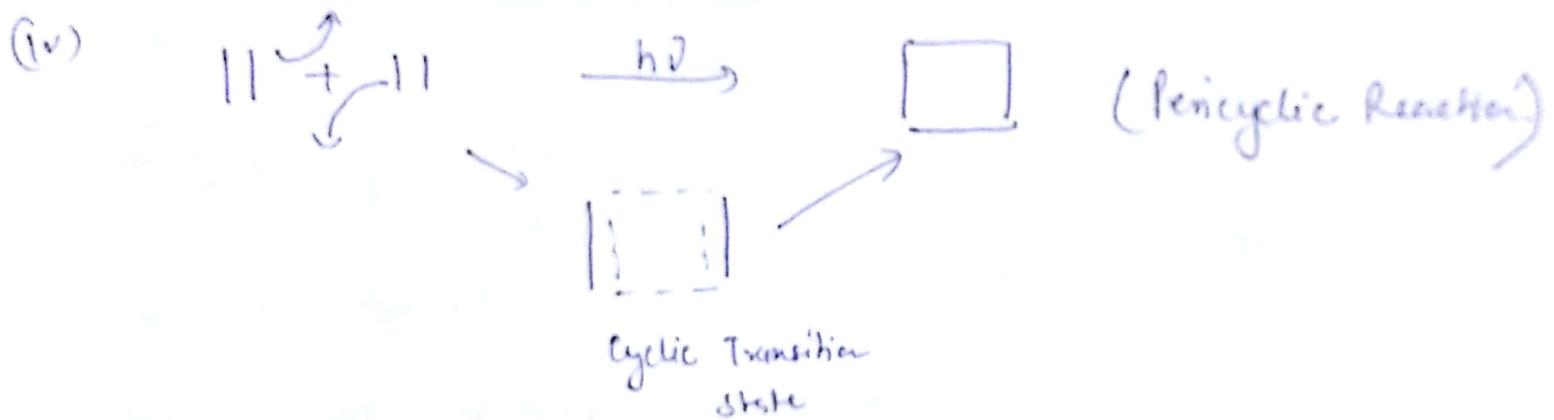
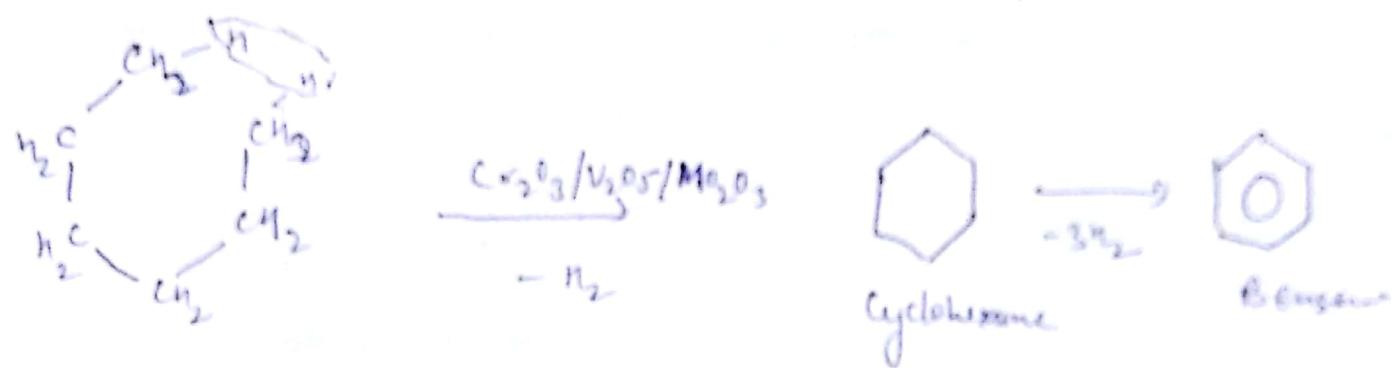
Cyclisation :-

Cyclic Polymerization

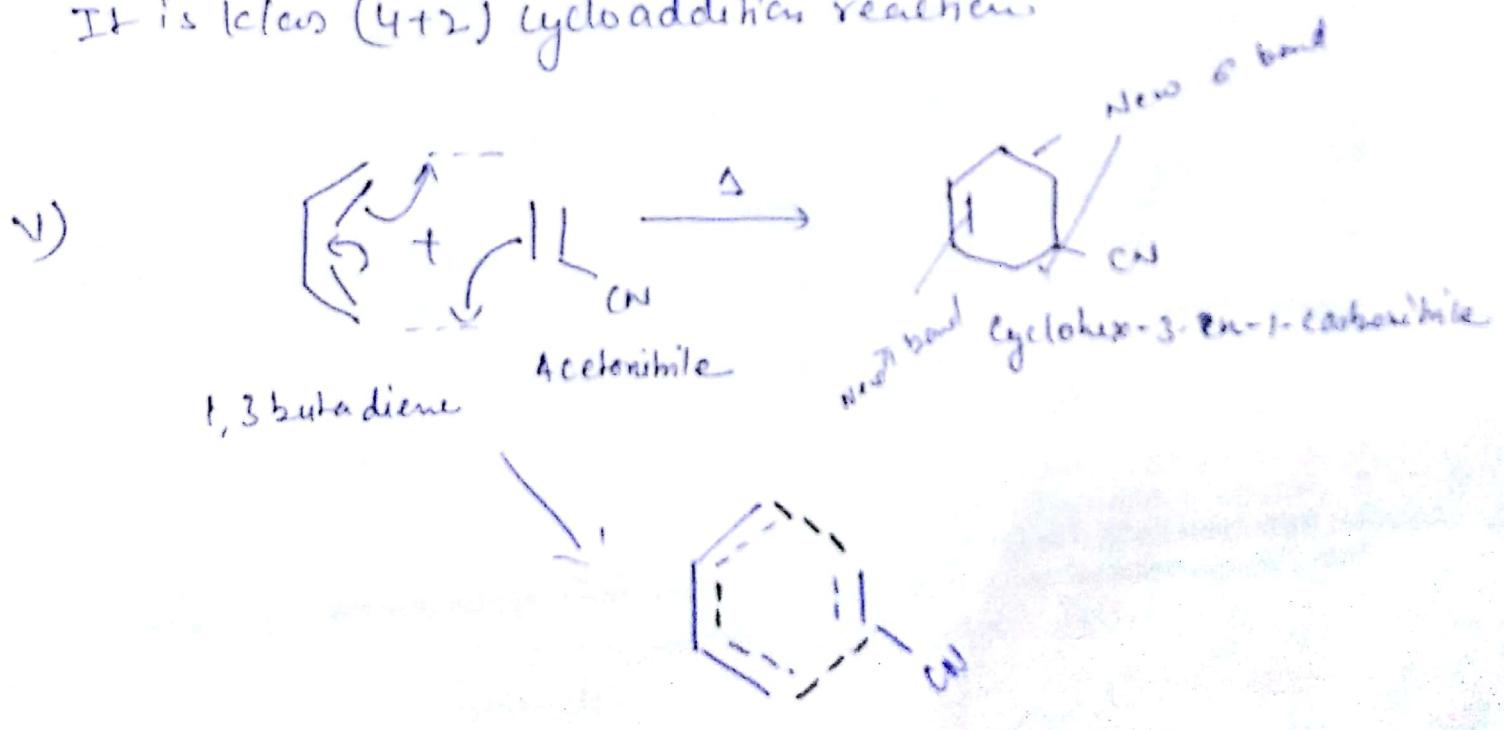
When acetylene is passed through red hot tube of iron or ~ quartz it trimerises to form benzene



ii) When vapour of hexane are passed over heated catalyst consisting of Cr_2O_3 , Mo_2O_3 + V_2O_5 at 773 K under 10-20 atm press. cyclization + aromatization occurs simultaneously to yield benzene.



Another example of pericyclic reaction is Diels-Alder's reaction.
It is [4+2] cycloaddition reaction.



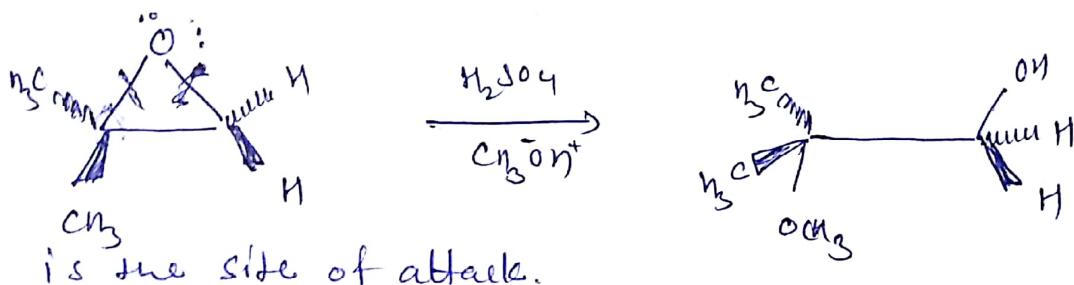
Ring Opening Reactions

Basic Ring Opening → When an asymmetric epoxide undergoes solvolysis in basic methanol, ring opening occurs by S_N^2 mech.



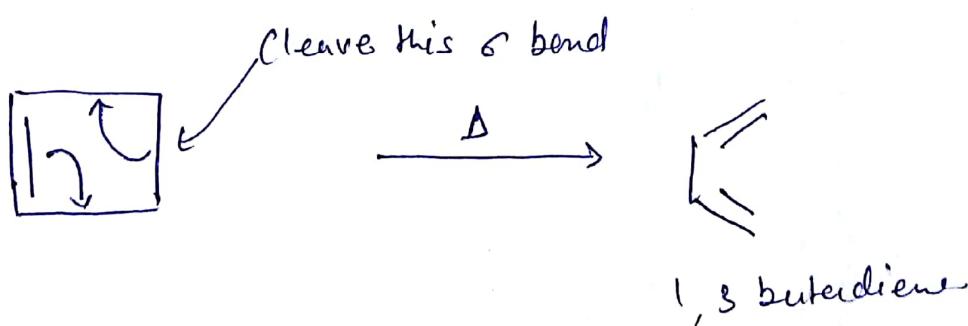
and the less substituted carbon is the site of nucleophilic attack, leading to what we will refer to a product.

Acidic opening - When solvolysis occurs in acidic methanol, the reaction occurs by a S_N^1 mech. and the more substituted carbon



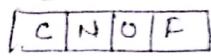
is the site of attack.

→ An electrocyclic ring opening reaction is a reaction in which a σ bond of a cyclic reactant is cleaved to form a conjugated product with one more π bond.



* Solvolytic:- Solvolytic is a type of nucleophilic substitution or elimination, where the nucleophile is a solvent molecule.

Preparation of Paracetamol



Mildgesics : — Reduce pain
 Antipyretics — Reduce fever } uses of paracetamol

