

Module No 10

S3. Sto-1.

Introduction to Reaction involving substitution Reaction.

S_N^1 :- Unimolecular Nucleophilic Substitution Reaction.

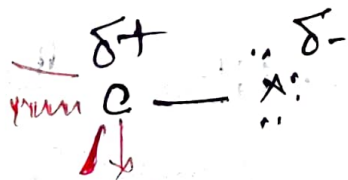
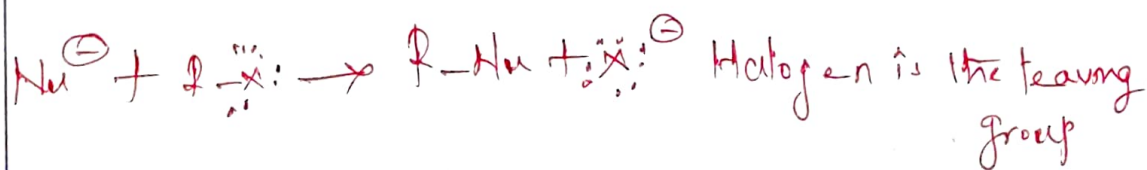
A Nucleophile is any Negative ion or any Neutral molecule that has at least one unshared electron pair.

In general



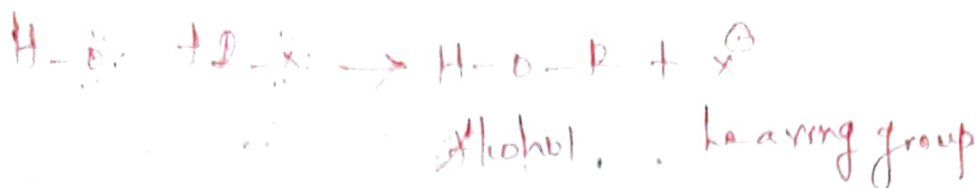
Nucleophile substrate product leaving group

A substitution Reaction taking place between the Halogen and the ^{Alkyl} Halides the one which is cleaved with the electron pairs are called leaving group and the reaction is named as Nucleophilic substitution rxn.

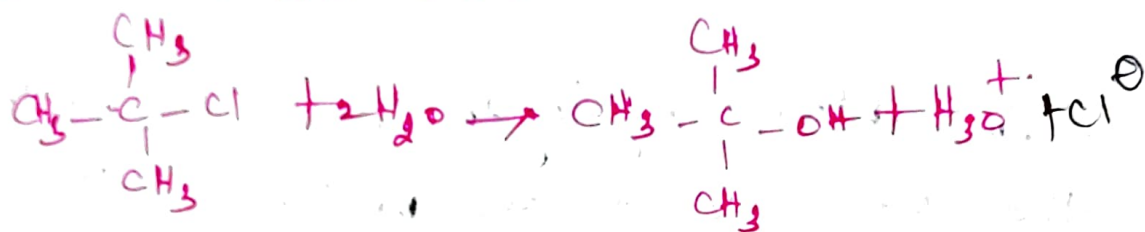


Positive centre at the Nucleophile reacts.

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



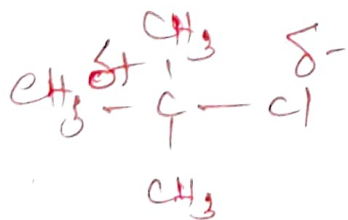
Mechanism for S_N1 Reaction



Step 1: First step is the slowest step: - Rate determining step

* Tert-butyl chloride ionizes and becomes tert-butyl cation and chloride ion as a leaving group

* In the transition state the carbon-chlorine bond gets broken and ions are beginning to develop.

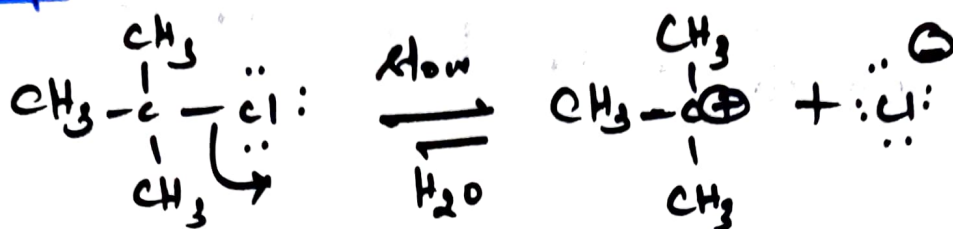


The solvent water molecule stabilizes these ions by solvation. order of the S_N1 reactivity

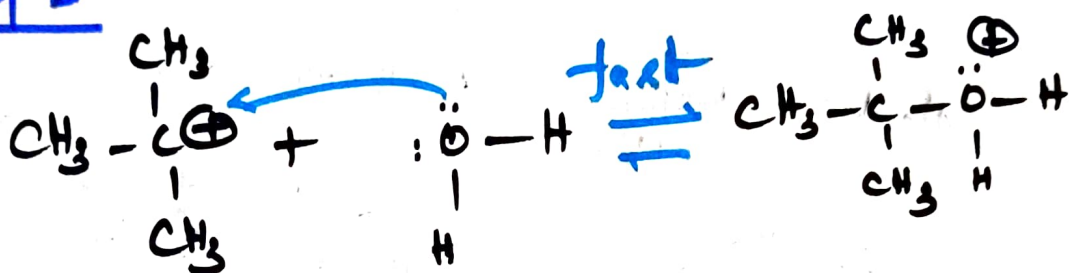
Benzyl, allyl, $3^\circ > 2^\circ > 1^\circ$ > methyl halides

Mechanism

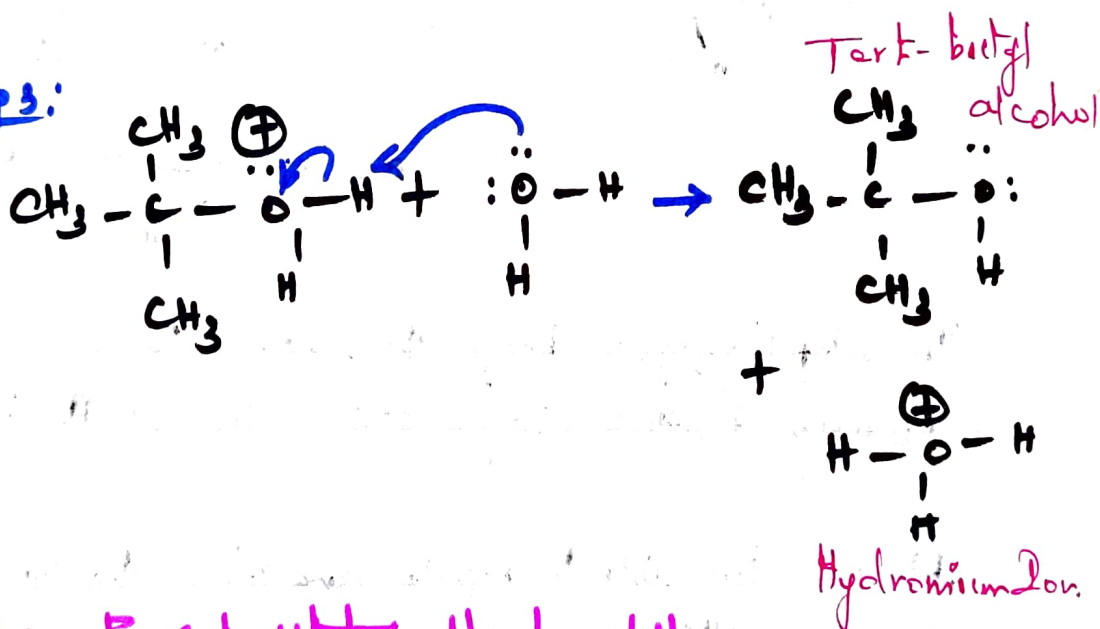
Step 1:



Step 2:

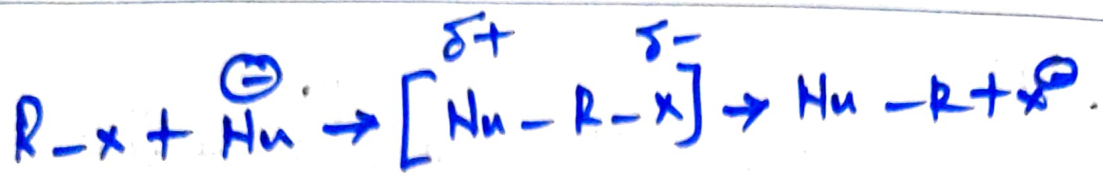


Step 3:

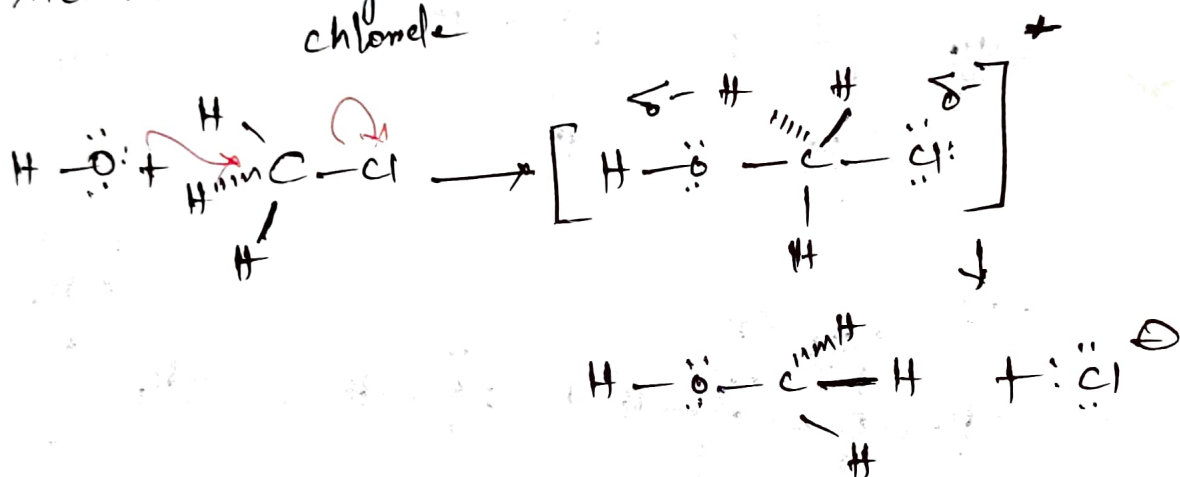
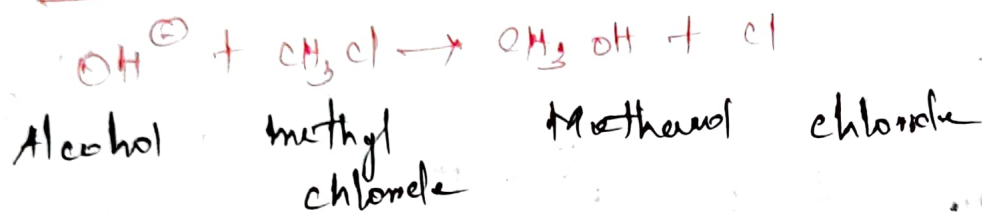


S_N2 :- [Substitution Nucleophilic bimolecular Reaction]

S_N2 proceeds via one step reaction. The nucleophile attacks the substrate carbon simultaneously pushing out the leaving group in a concerted fashion.



General Reaction



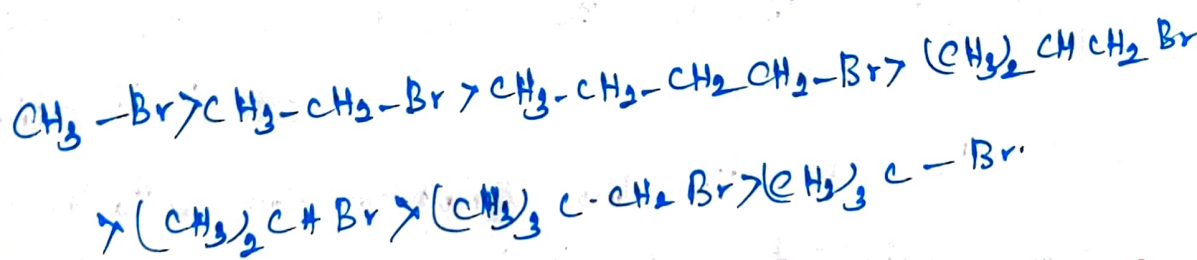
In step 1 oxygen brings the shared pair of e^- to the partially positive charge carbon atom at the backside

chlorine atom able to migrate and takes the lone pair of electrons with itself.

In the transition state New Carbon-oxygen bond is formed and the carbon-chlorine bond gets broken then the configuration of the Carbon atom begins to invert

Elimination Reaction

Effects of Substituents on the Rate of S_N2 Reaction

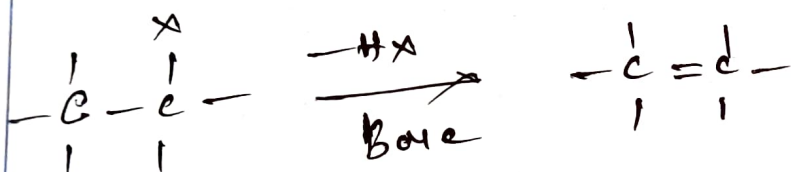


Class of Halide: methyl $> 1^\circ > n\text{-butyl} > \text{isobutyl } (1^\circ) > 2^\circ > \text{tert-pentyl} > 3^\circ$

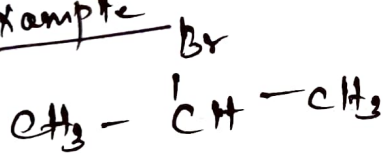
Elimination Reaction

* The elimination reaction is the reverse of the addition reaction

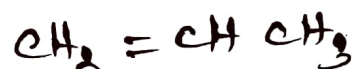
* In these reaction two group containing atoms attached to the adjacent carbon atom of the substrate molecule are eliminated to form a multiple bond.



example



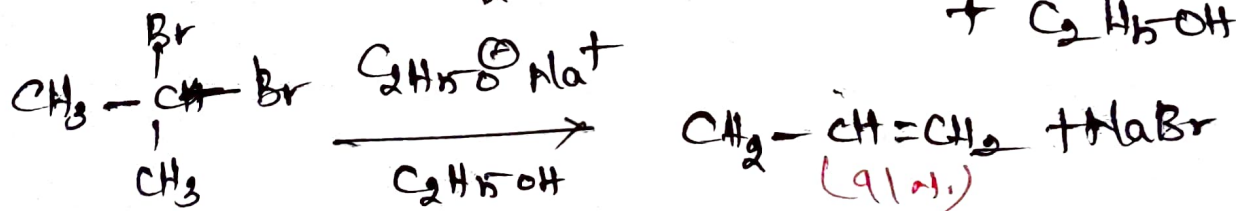
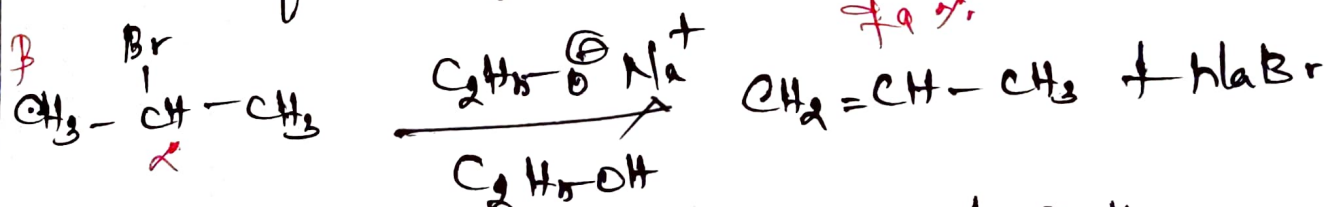
2-Bromo propane



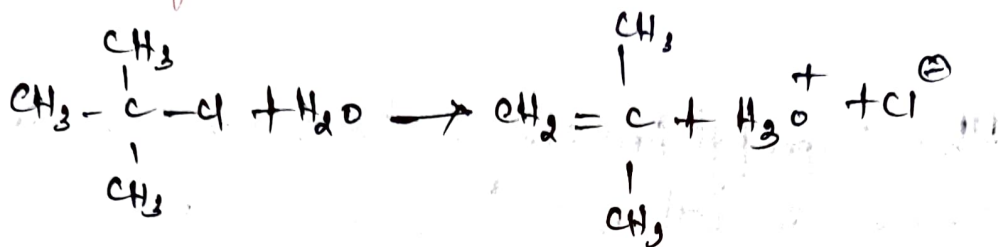
Propene

(Dehydro Bromination)

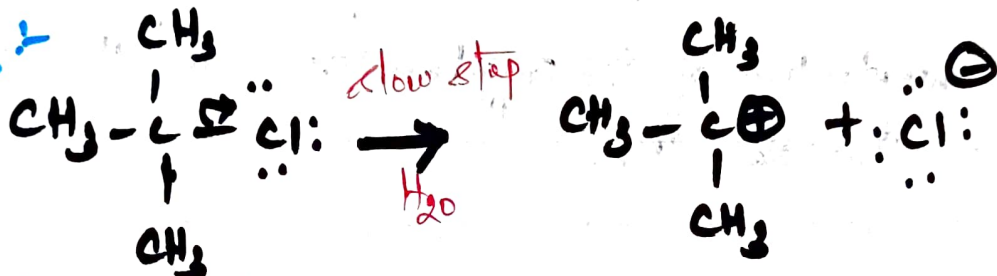
When an alkyl halide treated with a strong Base leads to form Dehydro Halogenation.



Mechanism of E₁ Reaction

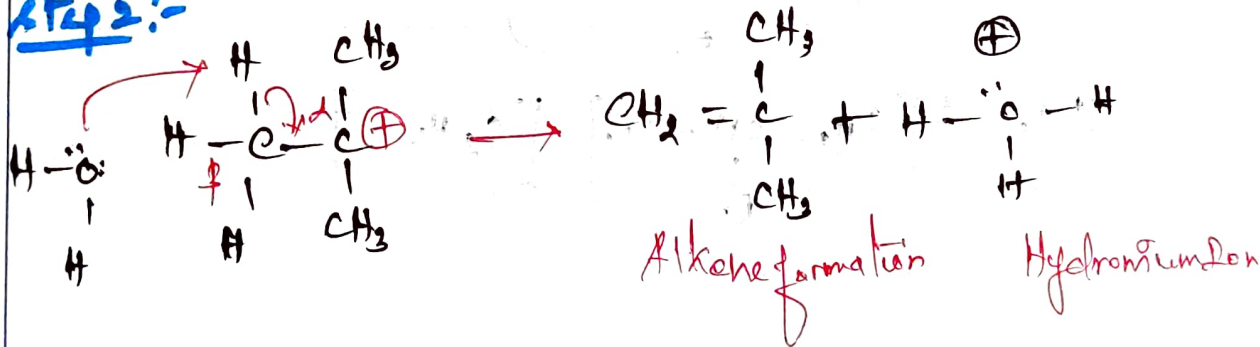


Step 1:-



Tert-butyl chloride

Step 2:-



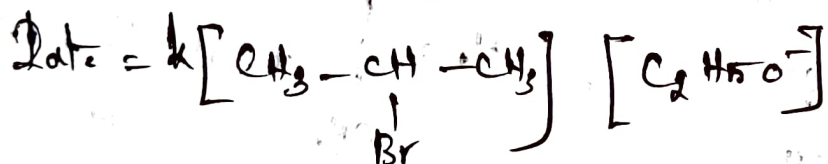
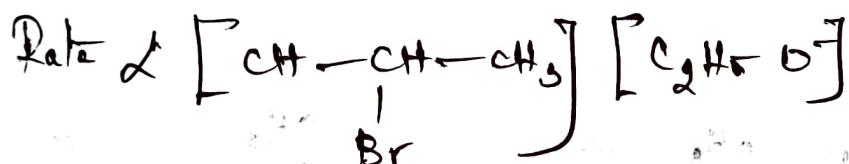
Removal of the hydrogen halide from the alkyl halide group is termed as Dehydrohalogenation

E₂ elimination

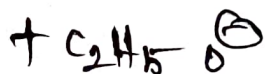
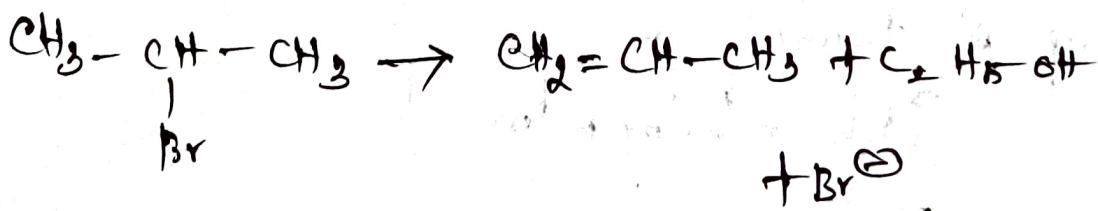
When isopropyl bromide is heated with sodium ethoxide in ethanol to form propene.

The reaction rate depends upon the concentration of $\text{t-Bu propyl bromide}$ and the concentration of Bromide Ion.

The rate of the equation follows the first order kinetics and overall it's second order reaction.



Mechanism for E_2 Reaction



* E_2 reaction always follow from elimination

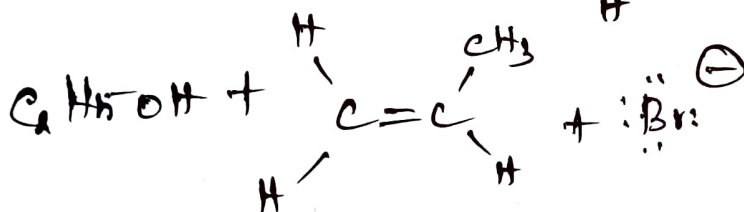
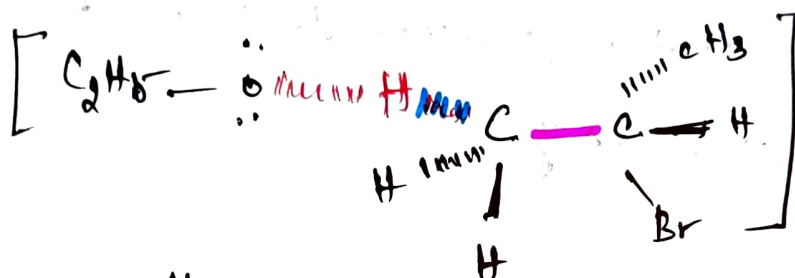
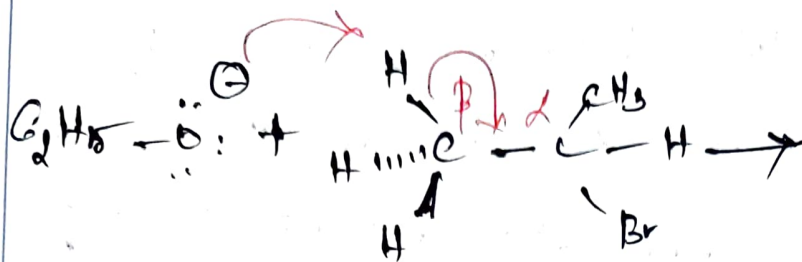


Illustration for E_2 Reaction

In these reaction like S_N^2 E_2 reaction is a single step process.

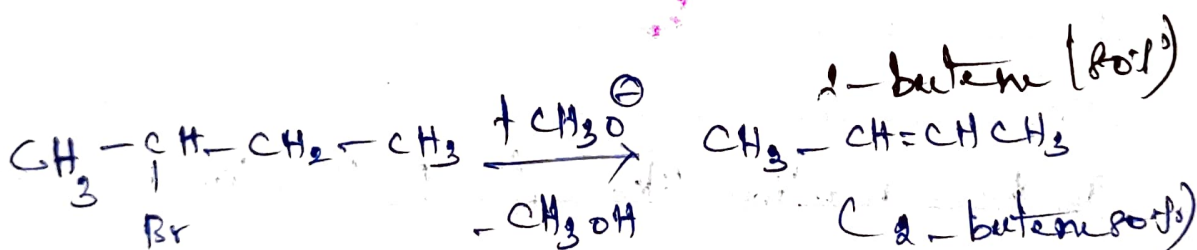
In these reaction the abstraction of the proton from the β -Carbon atom and the releasing of an atom from the α -Carbon atom occurs simultaneously.

Saytzeff Rule: In an unsymmetrical alkene (or) alkyl halide (ex) 2-bromobutane the course of elimination deter

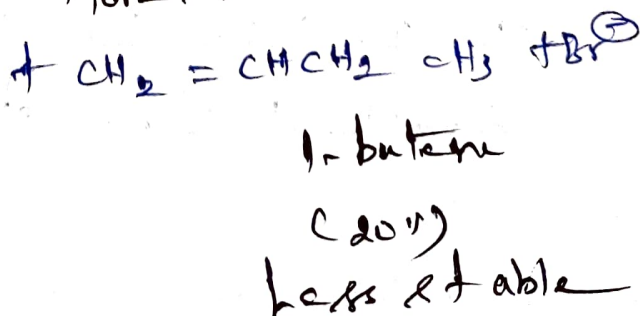
In E_2 elimination - Abstraction of a proton by the base from the β -carbon and the departure of the leaving group along with its bonding pair of electron from the α -carbon occur simultaneously.

The reaction is second order (or Bimolecular)
Rate depends upon the Concentration of the Base and the alkyl halide

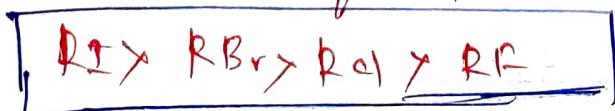
$$\text{Reaction Rate} = k [\text{Base}] [\text{R-X}]$$



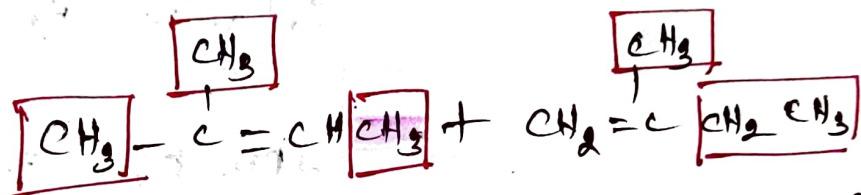
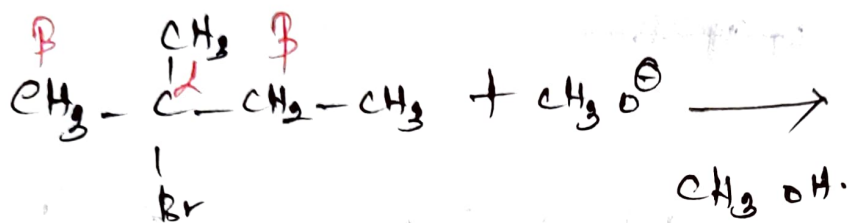
Mixture of E and Z
More stable



Relative Reactivities of Alkyl Halides



More substituted alkene is the major product in the E elimination reaction

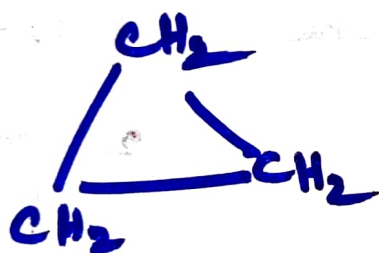


2-methyl-2-butene
70%

+ CH₃OH + Br⁻
2-methyl-1-butene
30%

More substituted alkene is obtained when hydrogen from the β hydrogen of the β -carbon atom that is bonded to the fewest hydrogens.
called Zaitsev's rule

Addition Reaction to $\text{Cl}_2/\text{Br}_2/\text{H}_2$ $\text{H}_2\text{SO}_4/\text{H}_2$ to cyclopropane



Cl_2 / dark $\text{Cl}-(\text{CH}_2)_3-\text{Cl}$ Addition Reaction

$+\text{Br}_2$ $\text{Br}-(\text{CH}_2)_3-\text{Br} \rightarrow$ 1,3-dibromopropane

$+\text{HBr}$ $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{Br}$ 1-bromopropane

$+\text{H}_2/\text{Pt}$
 121°C $\text{CH}_3-\text{CH}_2-\text{CH}_3$ Propane

$+\text{H}_2\text{SO}_4$ $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{H}_2\text{SO}_4$

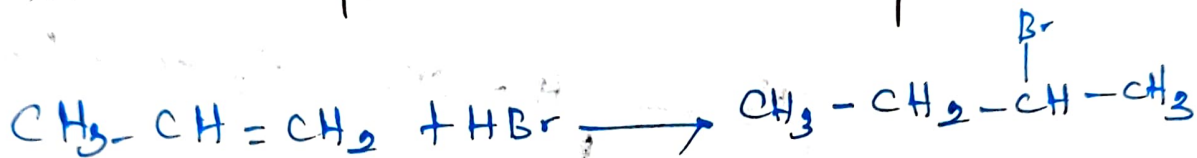
$+\text{KMnO}_4$ No Reaction

HI $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{I}$
 1-Iodopropane

Free Radical Reaction to an Alkene

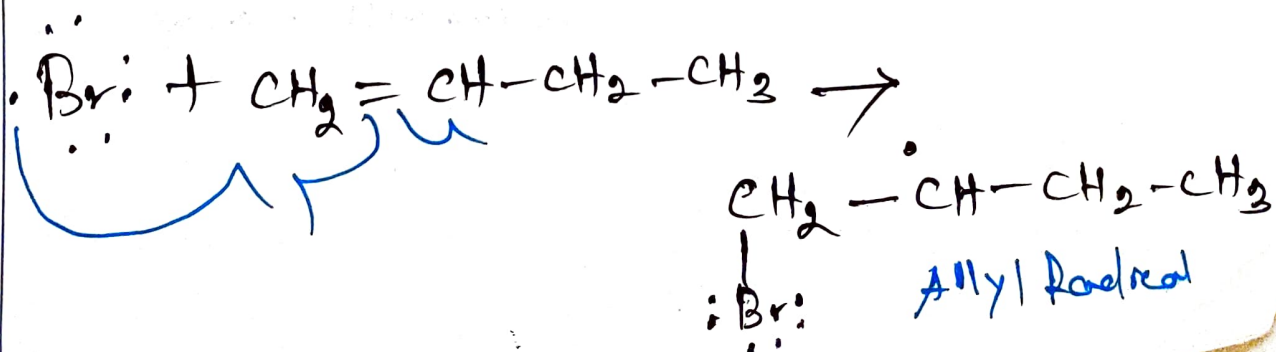
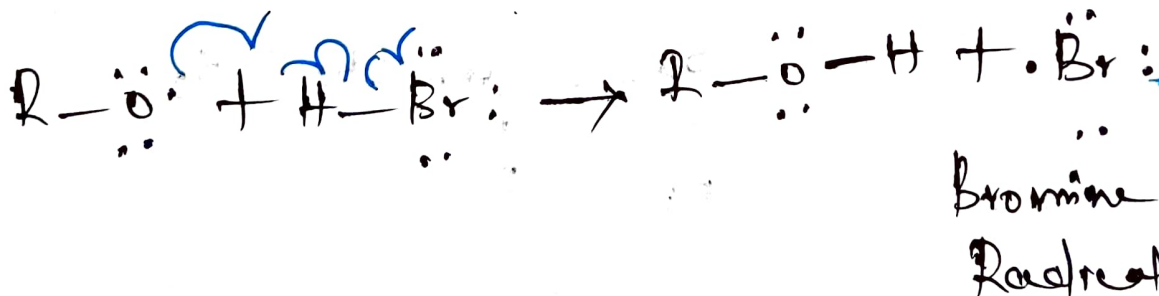
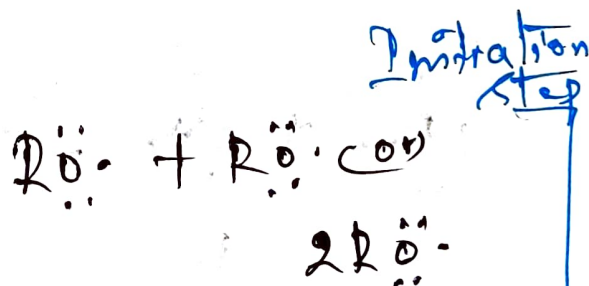
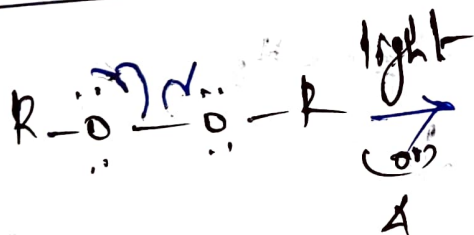
the adding HBr to 1-butene to form 2-bromobutane

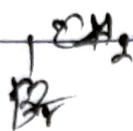
The electrophile H^+ adds to the sp^2 carbon atom



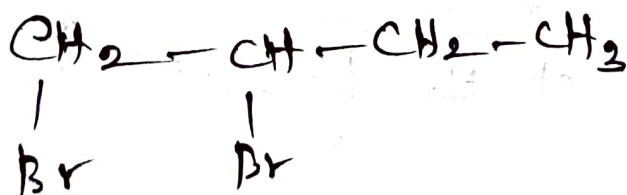
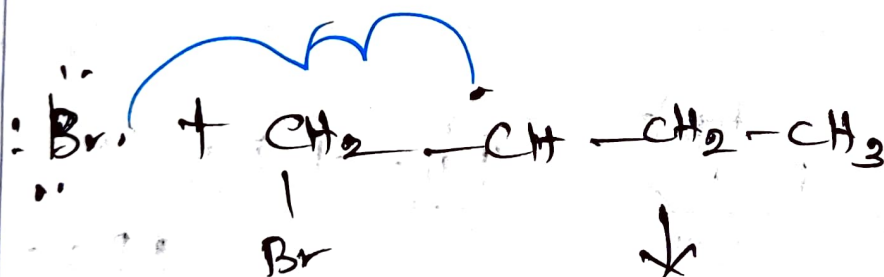
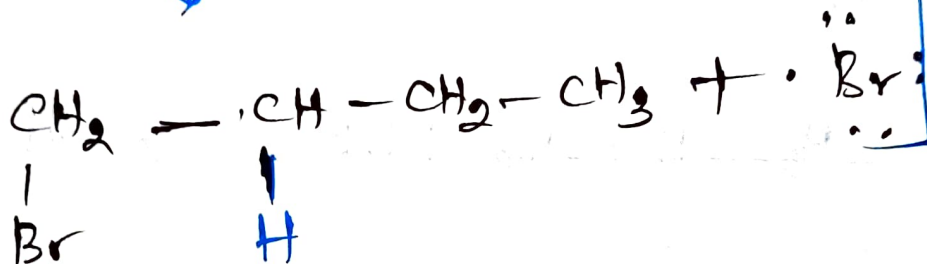
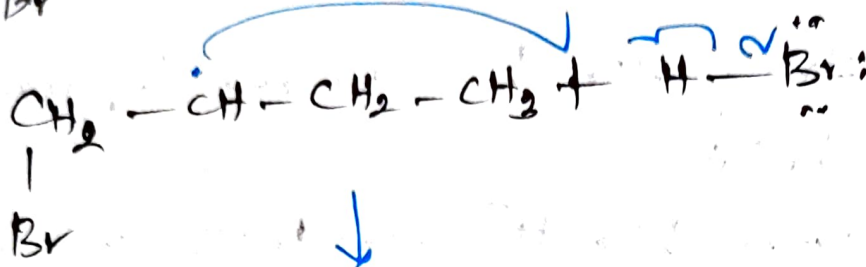
Peroxide adds to the reaction mixture the product of the addition reaction is 2-bromobutane [ROOR]

Mechanism





Propagation step



Termination step