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Class 12
Chemistry

Chapter 9

Halogenoalkanes

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Chap:9 Halogenoalkanes

Halogenoalkanes are also called alkyl halides. They are denoted by R-X. They have general formula $C_nH_{2n+1}X$

Aromatic (Halogenoarenes) e.g:-

Alkyl halides :- (R-X) When one hydrogen atom of alkane is replaced by halogen atom (X) compound formed are called alkyl halides

Classification:-

1) Primary alkyl halides (1°-R-X)
2) Secondary alkyl halides (2°- R-X)
3) Tertiary alkyl halides (3°-R-X)

1- **Primary alkyl halides:-** Alkyl halides in which halogen atom is bonded with primary carbon are called primary alkyl halides.

Primary carbon:- Carbon atom which is directly bonded with one other or no other carbon atom.

E.g :-

Pri-propyl chloride (C.N)

OR 1- chloropropane (IUPAC)

2- **Secondary alkyl halides:-** Alkyl halides in which halogen atom is bonded with secondary carbon are called secondary alkyl halides.

Secondary carbon:- Carbon atom which is directly bonded with two other carbon atoms.

E.g:-

sec-hexyl chloride (C.N)

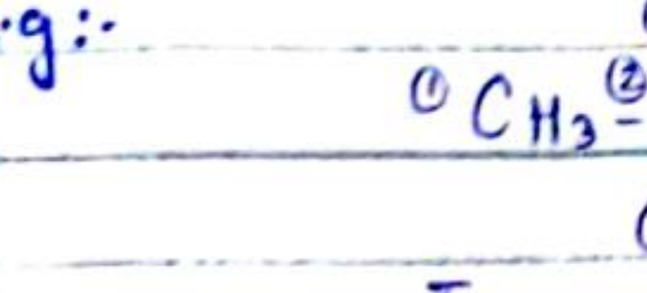
or

3- chloro hexane (IUPAC)

3. Tertiary alkyl halides:- Alkyl halides in which halogen atom is bonded with tertiary carbon are called tertiary alkyl halides.

Tertiary carbon:- Carbon atom which is directly bonded with three other carbon atoms

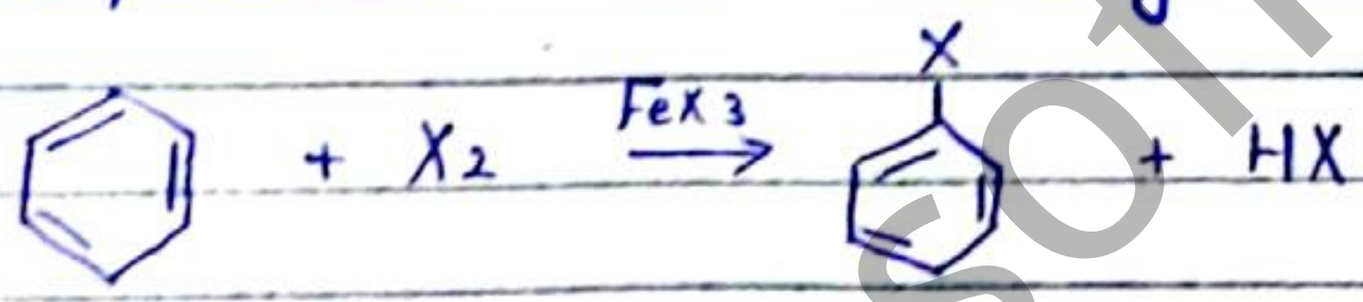
E.g:-

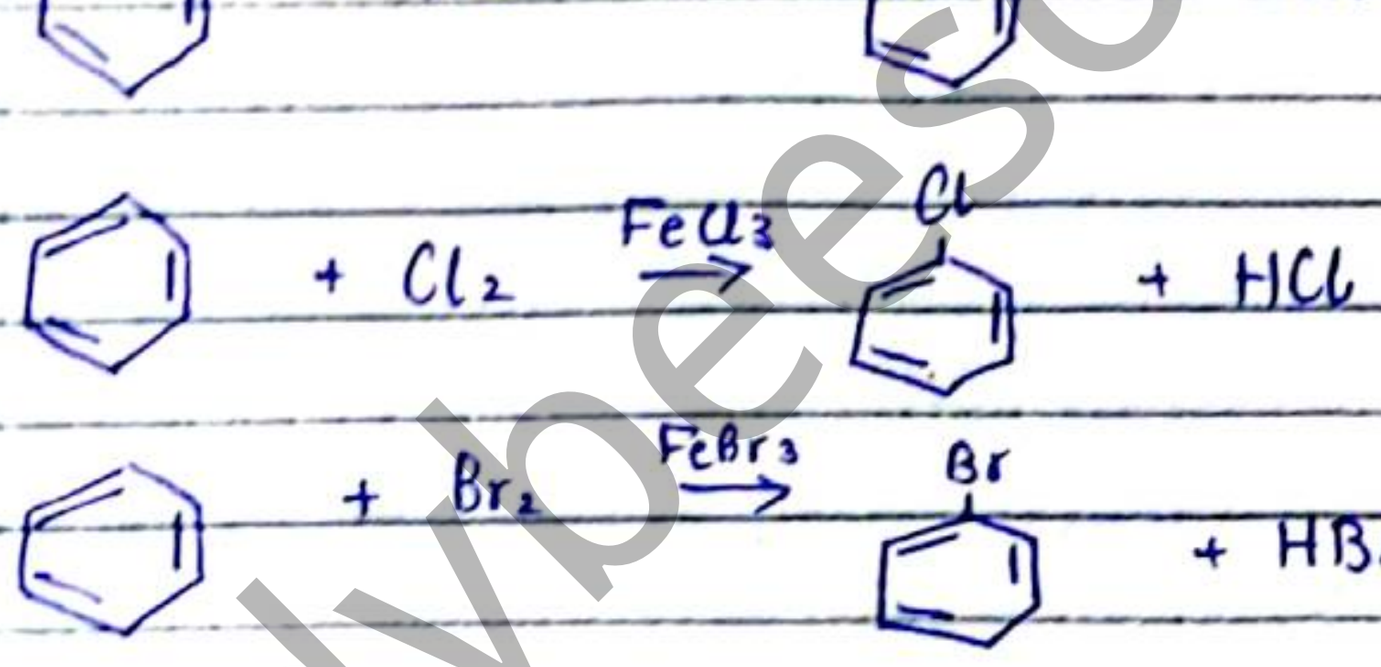


Ter-pentyl chloride (C:N)

2-chloro-2-methyl butane (IUPAC)

Preparation of Halogenoarenes:-





Reactivity of halogenoalkanes:-

Reactivity of halogenoalkanes depend on bond strength or bond energy.

Bond energy:- Amount of energy required to break one mole of bond is called bond energy.

E.gs:-

Bond	Bond Energy
C-F	467 KJ/mol
C-Cl	346 KJ/mol
C-Br	290 KJ/mol
C-I	228 KJ/mol

•> less will be the bond energy and higher will be the reactivity. Reactivity order of alkyl halides is:-

★ R-I > R-Br > R-Cl > R-F

Reactivity $\propto \frac{1}{B.E}$

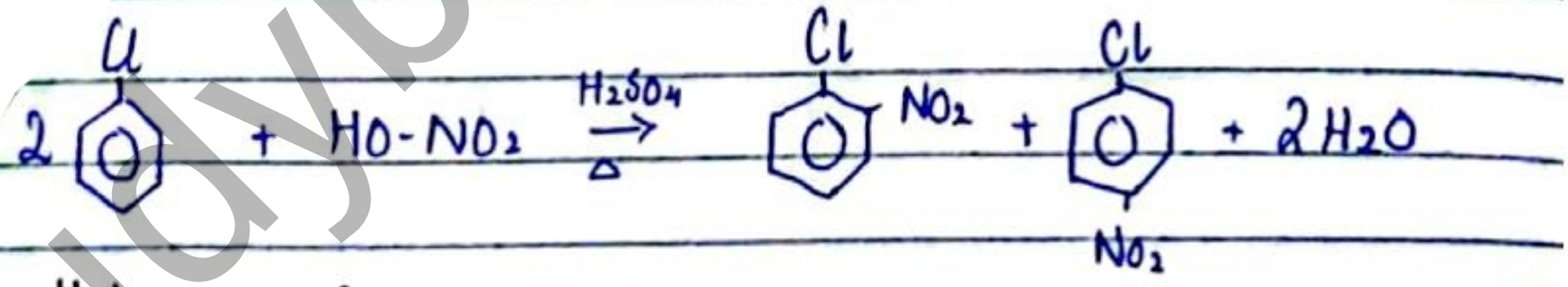
• Reaction of halogenoalkanes are nucleophilic substitution reactions.

General reaction:-

$$CH_3-CH_2-CH_2-X + N\bar{u} \rightarrow CH_3-CH_2-CH_2-Nu + X^-$$

•> Halogenoalkanes are more reactive than halogenoarenes.

Reason:- Because in halogenoarenes carbon is sp^2 hybridized & it result in shorter bond length of carbon-chlorine bond. Moreover, due to delocalization of lone pair of chlorine to benzene ring, halogenoareres are more stable and less reactive.



Halogenoarene

Reactions of alkyl halides or Halogenoalkanes:-

1) Nucleophilic Substitution reactions (SN Reactions)
2) Elimination reactions (E-reactions)

Nucleophilic Substitution reaction (SN Reactions)

Reaction in which halogen atom of alkyl halide is replaced by strong nucleophile such rxn are called nucleophilic substitution reactions.

$$\bar{N}u + R-X \longrightarrow R-Nu + \bar{X}$$

Strong nucleophile Substrate Product Leaving group

1- **Substrate :-** (S) Alkyl halide molecule on which a nucleophile attacks is called substrate (S).

2- **Nucleophile :-** ($\bar{N}u$)

-> Nucleophile means nucleus loving.

-> Substance which is electron rich is called nucleophile.

-> It may be neutral or negatively charged.

E.g :- Cl^-, $\bar{O}H$, $\bar{C}N$, $\ddot{N}H_3$, $\ddot{P}H_3$, $H_2\ddot{S}$, $H_2\ddot{O}$

3- **Leaving Group ($\bar{L}G$)** It is also called nucleophile.

-> Group which depart from the molecule is called leaving group.

-> Good leaving group :- $\bar{Cl}$, $\bar{Br}$, I^-, CH_3COO^-

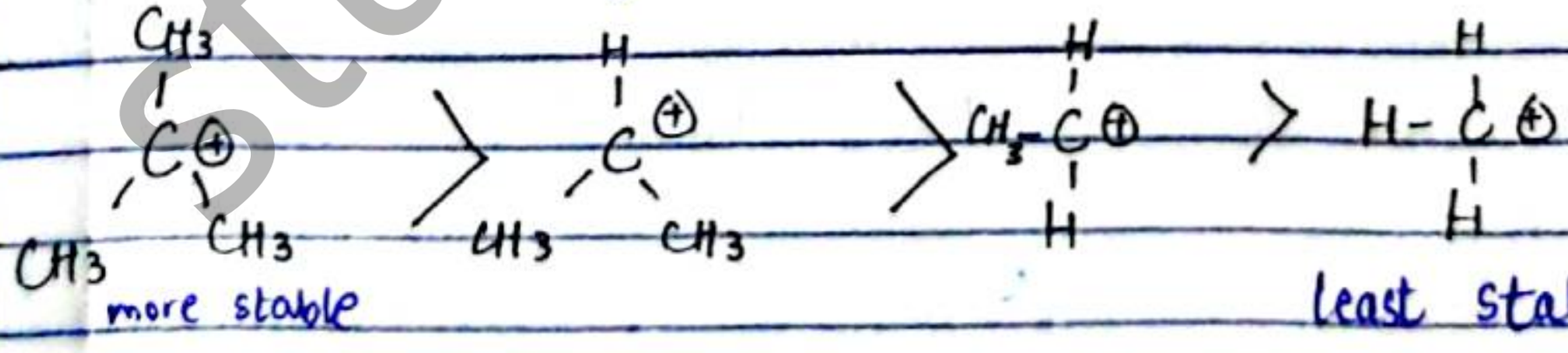
-> Poor leaving group :- $\bar{O}H$, $\bar{N}H_2$, $\bar{O}R$

Note :-

Iodide is a good leaving group as well as good nucleophile.

4- **Carbocation :-** or Carbonium ions :- Ion having positive charge on carbon atom is called carbocation.

Relative stability order of carbocation are



Alkyl group are weak electron donor group. Due to more hyper conjugation and inductive effect tertiary Carbocation are more stable. Hyper conjugation and inductive effect is directly proportional to no. of carbon atoms. Inductive effect refers to the reduction of positive charge

density on carbon atom via donation of electrons by alkyl groups.

Nucleophilic Substitution Reaction

There are two types:-

1) Unimolecular nucleophilic Substitution reactions (SN_1 reactions)
2) Bimolecular nucleophilic Substitution reactions. (SN_2 reactions)

SN_1 reactions	SN_2 reactions
1. SN_1 stands for substitution nucleophilic unimolecular	1. SN_2 stands for substitution nucleophilic bimolecular.
2. One molecule take part in rate determining step.	2. Two molecules take part in rate determining step.
3. These reactions are two step mechanism.	3. These reactions are based on single step mechanism.
4. Reaction take place in the presence of polar solvent.	4. Reaction take place in the presence of non-polar solvent.
5. Reaction takes place in the presence of strong as well as weak base.	5. Reaction take place in the presence of strong base.
6. There is 50% inversion of configuration and 50% retention of configuration taking place.	6. There is 100% inversion of configuration taking place.
7. Tertiary alkyl halide undergo SN_1 mechanism due to stability of carbocation.	7. Primary alkyl halide undergo SN_2 mechanism due to less sterric hindrance.

8- Secondary alkyl halide undergo SN_1 mechanism in the presence of polar solvent.	8. Secondary alkyl halide SN_2 mechanism in the presence of non-polar solvent.
9- Primary alkyl halide don't undergo SN_1 due to unstability of carbo cation.	9. Tertiary alkyl halide don't undergo SN_2 due to sterric hindrance.
10- Rate $\propto$ [R-X] Rate = K [R-X] order = 1 (1st order reaction)	10. Rate = K [R-X] [Nu̅] order = 2 (2nd order reaction)

SN_2 Reaction :-

$$R_2-\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{C}}-X + N\bar{u} \rightarrow R_2-\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{C}}\cdot Nu + X^-$$

Mechanism:- or Stereochemical evidence

Step: 1 Formation of Carbocation

$$R_2-\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{C}}-X \underset{\text{polar solvent}}{\overset{\text{slow step}}{\rightleftharpoons}} \overset{\overset{R_1}{|}}{C^{\oplus}}(R_2, R_3) + X^-$$

sp^3 109.5 — $sp^2 = 120^\circ$

3°-carbocation

Step: 2 Attack of nucleophile

$$N\bar{u} + \overset{\overset{R}{|}}{C^{\oplus}}(R_2, R_3) + N\bar{u} \xrightarrow{\text{fast}} Nu-\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{C}}-R_2 + R_2-\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{C}}-Nu$$

Inversion of configuration + Retention of configuration

50% 50%

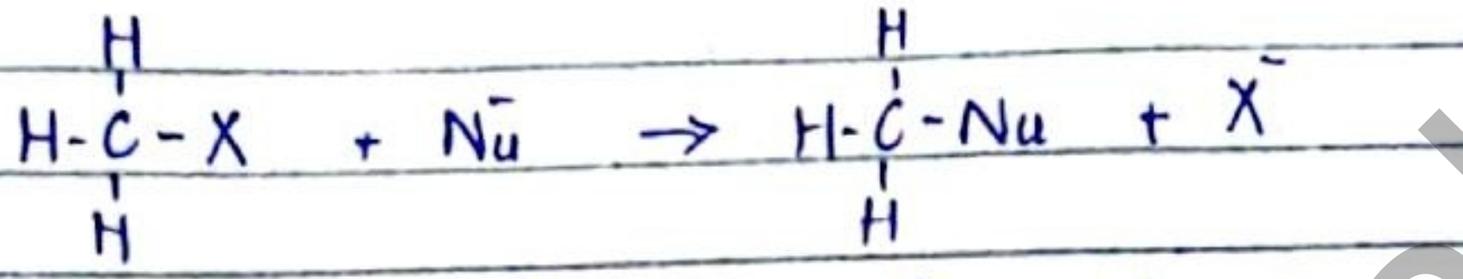
racemic mixture

Kinetic evidence or Kinetic equation

Rate $\propto$ [R-X]

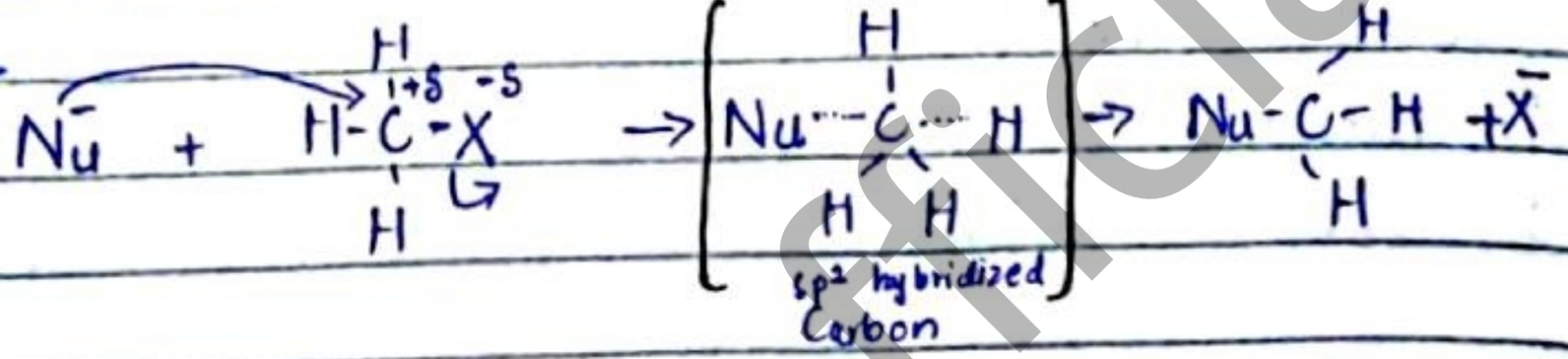
Rate = k [R-X] Order = 1

SN_2 Reaction:-



Mechanism:- or Stereochemical evidence

Step:1



Transition State

Kinetic evidence

Rate $\propto$ [R-X] [Nu^-]

Rate = K [R-X] [Nu^-]

order = 1 + 1 = 2

Predicting SN_1 & SN_2 Mechanism:-

1- The Nature of Electrophile (Alkyl halide):-

- If L.G is attached to 1° -carbon, the electrophile is unhindered the nucleophile can easily attack and SN_2 mech. is favoured. If L.G is attached to 3° carbon, the tertiary carbocation intermediate is stable, and the attack of nucleophiles is sterically hindered, so SN_1 mech. is favoured.

2- The nature of Nucleophile:- Powerful nucleophiles favour SN_2 mechanism for e.g OH^-, CN^-, I^-. While weaker nucleophiles i.e water or alcohol favour SN_1 mechanism.

3- Nature of the Solvent:-

-> Polar aprotic Solvents i.e acetone = SN_2 mechanism

-> Protic solvent = SN_1 mechanism

Elimination Reaction :- V. Imp for Long

Reaction in which atom or group of atom are removed from adjacent carbon atom and molecule become unsaturated such reaction are called elimination reaction.

β-carbon is necessary for these reactions therefore, they are also called β-elimination reaction.

Types :- There are two types :-

1) Unimolecular elimination reactions (E_1 reactions)
2) Bimolecular elimination reactions (E_2 reactions

E_1 - reactions	E_2 - reactions
1. E_1 stands for elimination unimolecular.	1. E_2 stands for elimination bimolecular.
2. One molecule take part in rate determining step.	2. Two molecules take part in rate determining step.
3. These reactions are two step mechanism.	3. These reactions are based on two step mechanism
4. Tertiary alkyl halides undergo E_1 mechanism.	4. Primary Alkyl halides undergo E_2 mechanism.
5. These reactions are first order.	5. These reactions are second order.

E_1 - reaction :-

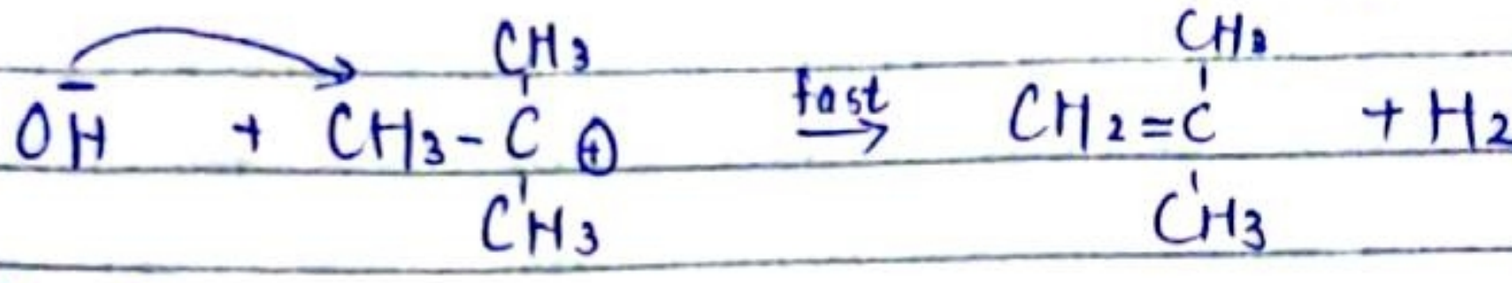
$$CH_3-\underset{\beta}{C}H_2-\underset{\alpha}{C}(CH_3)_2-Br + KOH \xrightarrow{\text{abc}} CH_2=C(CH_3)_2 + H_2O + KBr$$

Mechanism :-

Step : 1 Formation of carbocation

$$CH_3-C(CH_3)_2-\overset{\delta+}{C}H_2-\overset{\delta-}{Br} \rightleftharpoons CH_3-C^{\oplus}(CH_3)_2 + Br^-$$

Step: 2 Attack of base on β-hydrogen



Kinetic equation:-

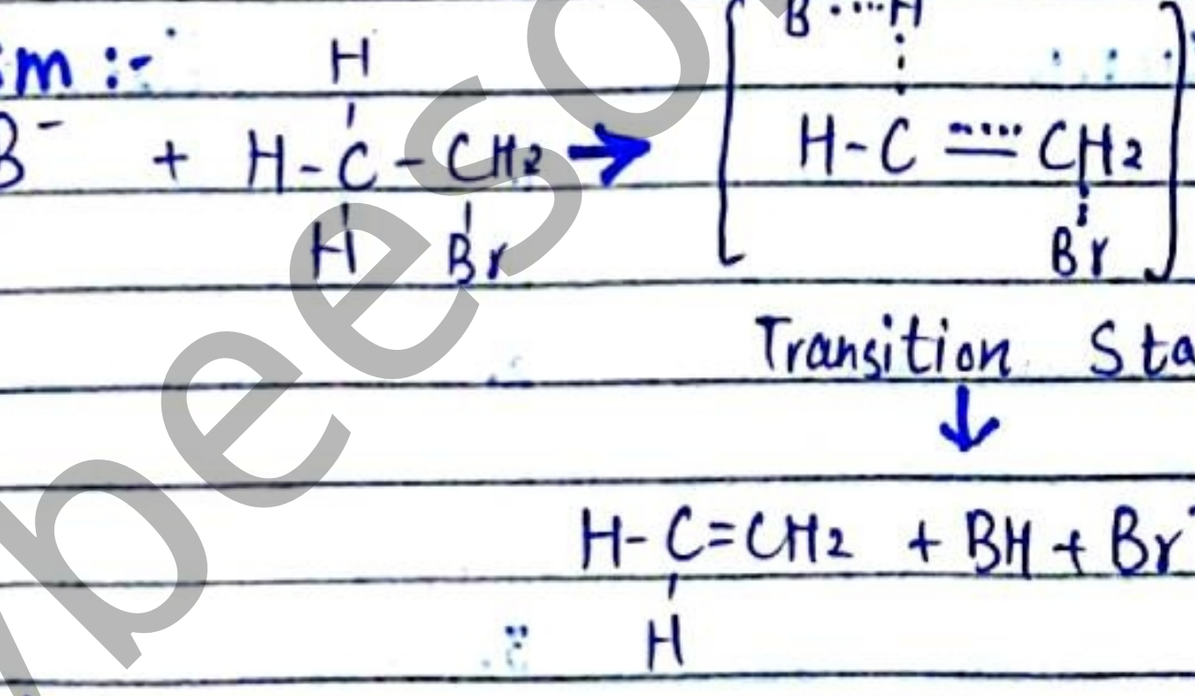
Rate = K [R-X]

order = 1

E_2 Reactions:-

Mechanism :-

Step: 1



Transition State

Kinetic Evidence:-

Rate = K [Base] [R-X] or K [Substrate] [Base]

order = 1+1 = 2

MCQs:-

i. b

ii. b

iii. b

iv. b

v. c

vi. c

vii. a

viii. b

ix. a

The Conditions for SN & E Reactions:-

Primary alkyl halides:- Undergo SN_2

Secondary alkyl halides:- Strong nucleophile / base = SN_2 or E_2

Weak nucleophile / base = SN_1 or E_1

Tertiary alkyl halides:- Weak nucleophiles / base = SN_1 or E_1

Strong base = E_2

Solvent:- Polar protic solvent = SN_1 or E_1

Polar aprotic solvent = SN_2 or E_2

Nucleophile or base:- Good nucleophile that is a weak base, favours SN_2.

Weak nucleophile that is a strong base favours E_2.

Rxn with Aq. $AgNO_3$:-

R-F = No reaction with $AgNO_3$.

R-Cl = $R\text{-}Cl + AgNO_3 \Rightarrow R\text{-}NO_3 + AgCl$

white ppt — Soluble in NH_4OH

R-Br = $R\text{-}Br + AgNO_3 \rightarrow R\text{-}NO_3 + AgBr$

cream ppt — partially soluble in NH_4OH

AgI = $R\text{-}I + AgNO_3 \rightarrow R\text{-}NO_3 + AgI$

yellow ppt — insoluble in NH_4OH

Alkyl Halides and Retrosynthesis:- Alkyl halides are good starting materials to produce organic compounds.

Consider rxn b/w haloalkane & nucleophile

$$R\text{-}X + Nu^- \rightarrow R\text{-}Nu + X^-$$

Starting material for ethanol can be found by retrosynthesis.

$$R\text{-}X \rightarrow R^+ + X^-$$

$$CH_3\text{-}CH_2\text{-}OH \rightarrow CH_3\text{-}CH_2^+ + OH^-$$

So, starting material is $CH_3\text{-}CH_2\text{-}Br$

$$\Rightarrow CH_3\text{-}CH_2\text{-}Br + OH^- \rightarrow CH_3\text{-}CH_2\text{-}OH + Br^-$$