Nucleophilic substitution reaction (S_N) : Due to electronegativity difference the $-\overset{|}{\underset{|}{C}}-X$ bond is polarised bond. $\left(-\overset{|\delta+}{\underset{|}{C}}-\overset{\delta-}{X}\right)$

Thus the C-atom of the $\overset{\delta+}{C}-\overset{\delta-}{X}$ bond becomes centre to attack by a nucleophile $(\overset{\ominus}{Nu})$.

$X^{\ominus}$ ion from R—X molecule is substituted by a $\overset{\ominus}{Nu}$. i.e.S_N reaction are the most common reactions in R—X.

$$R—X + \overset{\ominus}{Nu} \longrightarrow R—Nu + X^{\ominus}$$

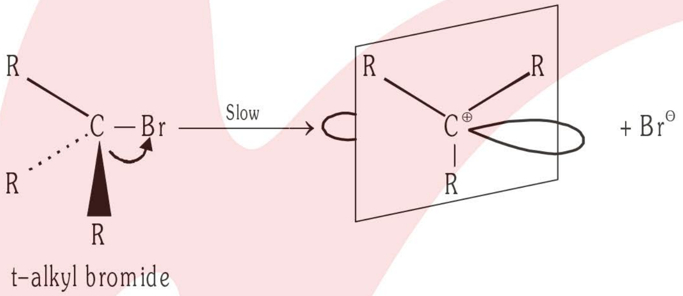
Two mechanisms are observed in S_N reaction :

(a) $S_{N}1$ mechanism (b) $S_{N}2$ mechanism

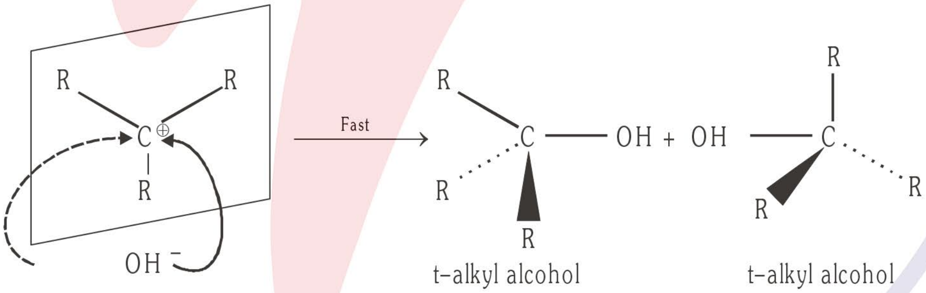
Mechanism of $S_{N}1$ and $S_{N}2$:

$S_{N}1$ ***Mechanism*** : $S_{N}1$ stands for uni molecular nucleophilic substitution. The mechanism involves two steps. Consider the hydrolysis of tert. butyl bromide with aqueous NaOH.

Step 1: The alkyl halide ionises to give a planar corbonium ion. The corbonium ion is planar because the central positively charged carbon is sp^2 hybridized.



Step-2 : The nucleophile can attack the planar carbonium ion from either side to give the product.



(i) Ionisation is the rate determining step because it is the slow step. In other words, the rate at which alcohol is formed depends upon the concentration of tertiary alkyl halide alone.

∴ Rate = $K[R_3C—Br]$

It is obvious that the reaction follows first order kinetics, therefore reaction is called $S_{N}1$.

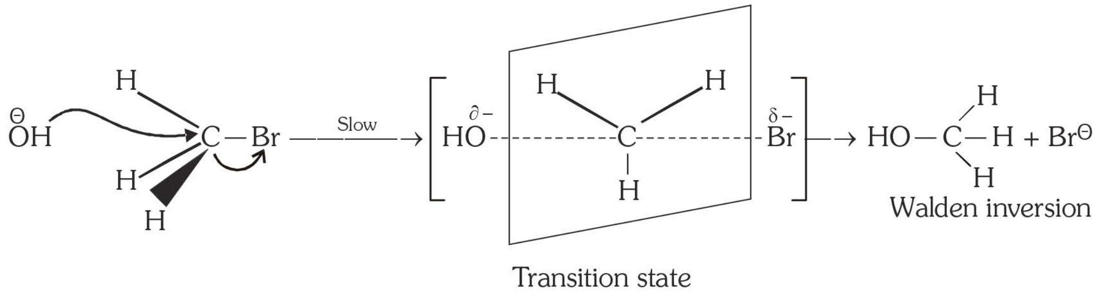
(ii) The reactivity order for $S_{N}1$ reaction $\propto$ stability of carbocations formed by halides.

∴ reactivity order of halides ($S_{N}1$) varies as follows :

Benzyl halide > Allyl 3°halide > Allyl 2° halide > Allyl 1° halide > 3°halide > 2° halide > 1° halide > methyl halide.

(iii) Remember that in case alkyl halide is optically active, $S_{N}1$ reactions lead to racemisation.

$S_{N}2$ mechanism : $S_{N}2$ stands for bimolecular nucleophilic substitution. In this type of nucleophilic substitution reaction, bond making and bond breaking process occur simultaneously.



(i) Reactivity of alkyl halides in S_N2 substitution is governed by steric factors. The bulkier the group, that less reactive it will be.

(ii) Reactivity order of alkyl halide varies as follows :

allyl halide > CH_3X > 1°halide > 2°halide > 3° halide

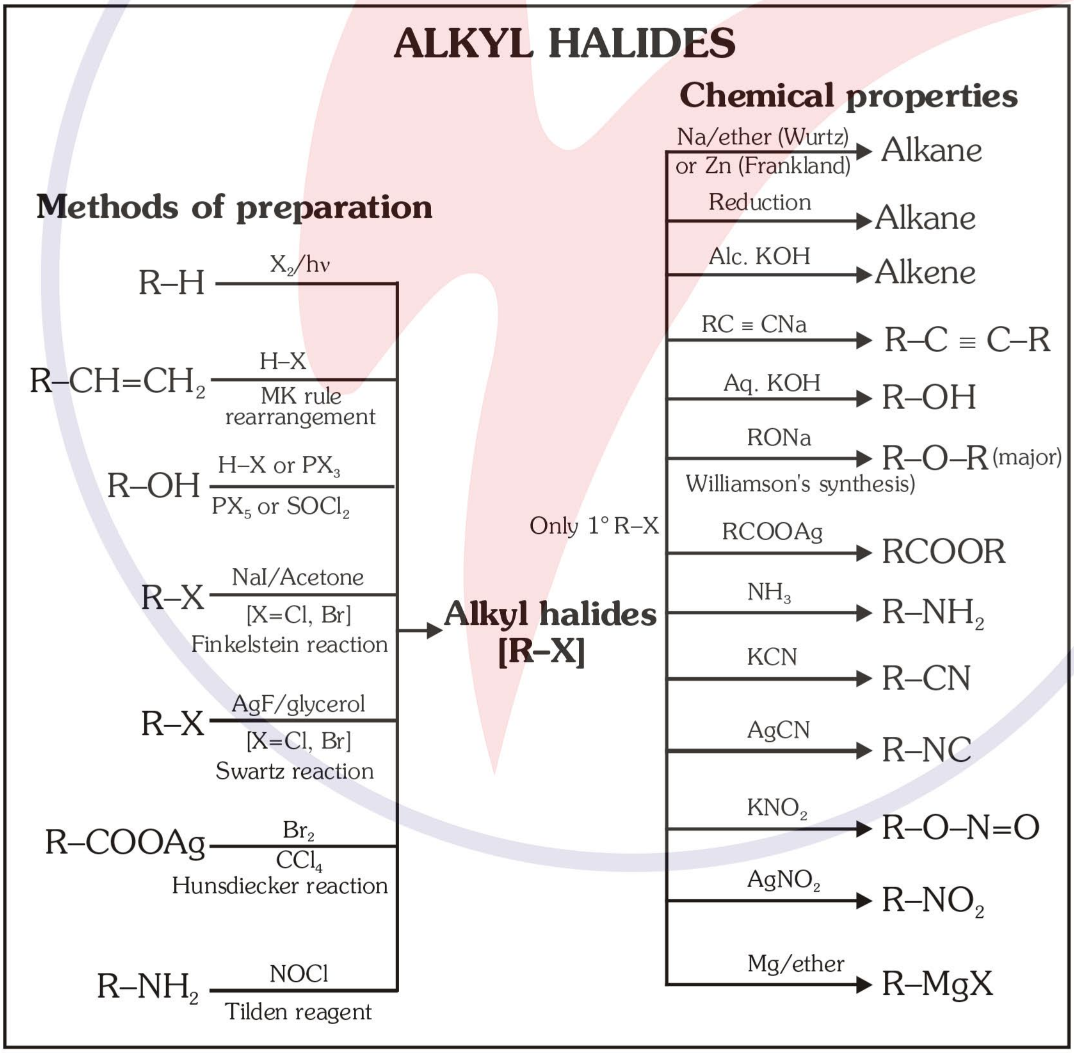
(iii) The order of reactivity among 1° alkyl halides is : **CH_3X > C_2H_5X > C_3H_7X** etc.

Remember that in case alkyl halide is optically active, S_N1 reactions lead to Walden inversion.

(iv) For a given alkyl group the order of reactivity is - (for S_N1 and S_N2 both) : **RI > RBr > RCl > RF**

(v) In addition to substitution reaction alkyl halide also undergo elimination reactions to form alkene with the removal of a molecule of hydrogen halide (dehydrohalogenation). In dehydrohalogenation, hydrogen and halogen atoms are eliminated from two adjacent carbon atoms, the reaction also known as β–elimination it may proceed by E^1 or E^2 mechanism (analogous to S_N1 and S_N2 mechanism).

The order of elimination reaction is : **3° halides > 2° halides > 1° halides**



ELIMINATION REACTIONS : These reactions are involve elimination of small molecule from the substrate

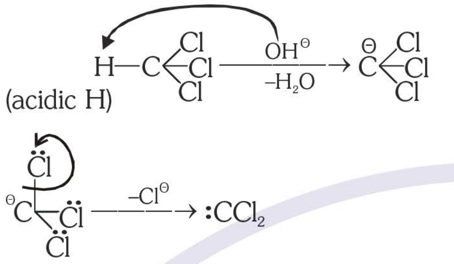
Elimination

- α–elimination or 1, 1–elimination
- β–elimination or 1, 2–elimination

α-Elimination (1, 1-Elimination) : Removal of H and X from one C-atom

Example : $CHCl_3 \xrightarrow{KOH} :CCl_2$ (dichloro carbene)

Mechanism :



α, β Elimination (β-elimination) : Removal of H and X from adjacent C-atoms

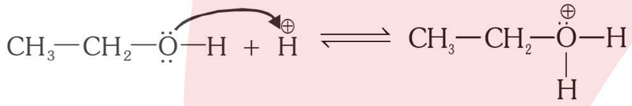
β
- E_1 unimolecular elimination
- E_2 bimolecular elimination

(a) Unimolecular elimination (E_1) :-

$$CH_3-CH_2-OH \xrightarrow[443^{\circ}K]{95\%H_2SO_4} CH_2=CH_2$$

Mechanism of Reaction: The acidic dehydration of alcohol proceeds through the formation of a carbocation intermediate and is explained as follows :

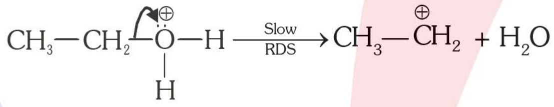
Step I : Alcohol being a Lewis base accepts a proton (H^+) from the acid in a reversible step as follows:



$$CH_3-CH_2-\ddot{O}-H + \overset{\oplus}{H} \rightleftharpoons CH_3-CH_2-\overset{\oplus}{\ddot{O}}(H)-H$$

Ethanol (From acid) Protonated ethanol

Step II : Due to presence of positive charge on electronegative oxygen, its electron accepting tendency increases. As a result C – O bond becomes weak and cleaves as follows :



$$CH_3-CH_2-\overset{\oplus}{O}(H)-H \xrightarrow[RDS]{Slow} CH_3-\overset{\oplus}{C}H_2 + H_2O$$

Ethyl carbocation

This is a slow and is regarded as **rate determining step in E_1 reaction.**

Step III : Base removes Hα (proton) from carbocation and changes it into ethene in a fast step as follows:

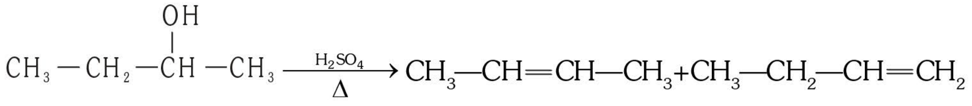
$$H-CH_2-\overset{\oplus}{C}H_2 \xrightarrow[fast]{Base} CH_2=CH_2$$

Ethene

> **Saytzeff rule :** When two possible alkenes are obtained by the elimination reaction then that alkene containing maximum number of alkyl group on double bonded C-atoms is called Saytzeff's product and formed as major product.

Note : The alkene having less number of alkyl groups on double bonded C-atoms is called Hofmann's product.

Example : (i)



$CH_3-CH_2-\overset{OH}{CH}-CH_3 \xrightarrow[\Delta]{H_2SO_4} CH_3-CH{=}CH-CH_3 + CH_3-CH_2-CH{=}CH_2$

2–butanol

main product 2–butene 80% (Saytzeff's product)

1–butene 20% (Hoffmann's product)

(ii) $CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[\Delta]{H_2SO_4} CH_3-CH{=}CH-CH_3 + CH_3CH_2CH{=}CH_2$

1–butanol

2–butene80% Main product

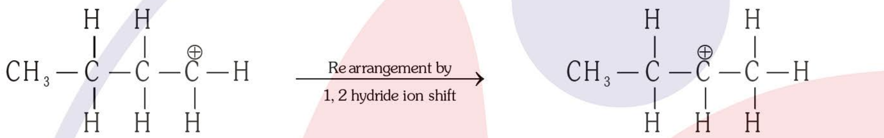
1–butene 20%

Mechanism : Acid catalyzed dehydration of alkanols proceeds via the formation of more stable carbonium ion.

$$CH_3CH_2CH_2-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H + \overset{\oplus}{H} \longrightarrow CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2$$

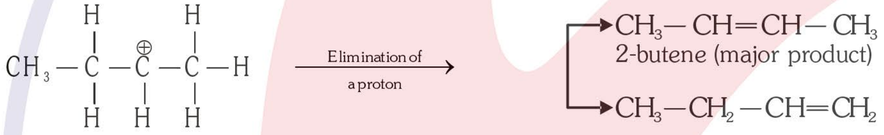
$$CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2 \longrightarrow CH_3CH_2CH_2-\overset{\oplus}{C}H_2 + H_2O$$

Primary Carbonium ion



1° Carbonium

2° Carbonium more stable



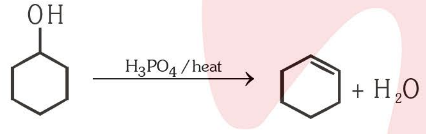
$CH_3-CH{=}CH-CH_3$

2-butene (major product)

$CH_3-CH_2-CH{=}CH_2$

1–butene (minor product)

(iii)



Cyclohexanol Cyclohexene

Reactivity order of acidic dehydration of alcohols is : 3° > 2° > 1° R–OH

- Rate of reaction ∝ [substrate]
- Molecularity of reaction = 1 (So reaction is called as E_1)
- In reaction intermediate carbocation is formed, so carbocation rearrangement is possible.

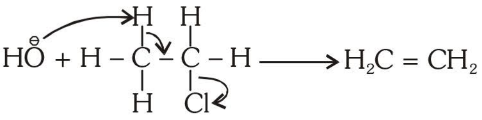
(b) Bimolecular elimination (E_2) :

Example :

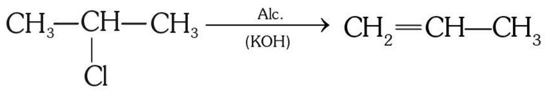
(i) Dehydrohalogenation of halides by alcoholic KOH/NaNH$_2$:

$$CH_3-CH_2-Cl + KOH_{(alc.)} \longrightarrow CH_2 = CH_2 + KCl + H_2O$$

Mechanism :

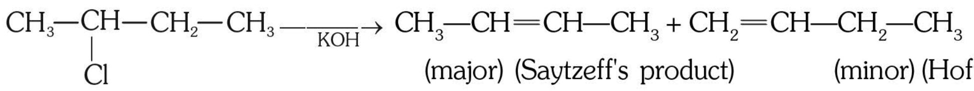


- Rate of reaction α [substrate] [base]
- Order of reaction = 2 (So reaction is E_2)
- In E_2 reaction intermediate (carbocation) is not formed. So there will be no carbocation rearrangement.



$$CH_3-\underset{\displaystyle |\atop Cl}{CH}-CH_3 \xrightarrow[(KOH)]{Alc.} CH_2=CH-CH_3$$

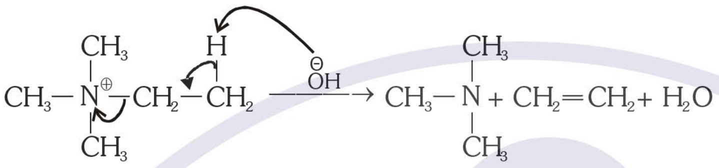
$$CH_3-CH_2-CH_2-CH_2-Cl \xrightarrow[(KOH)]{Alc.} CH_3-CH_2-CH=CH_2$$



$$CH_3-\underset{\displaystyle |\atop Cl}{CH}-CH_2-CH_3 \xrightarrow[KOH]{} CH_3-CH=CH-CH_3 + CH_2=CH-CH_2-CH_3$$

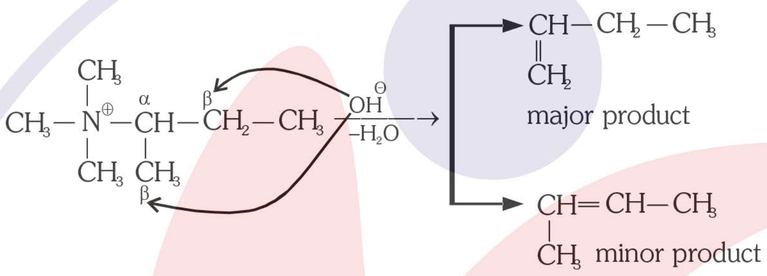
(major) (Saytzeff's product) (minor) (Hoffmann's product)

(ii) Pyrolysis of tetra alkyl ammonium ion :



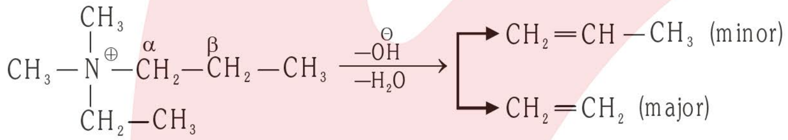
$$CH_3-\overset{\displaystyle CH_3 \atop |}{\underset{\displaystyle | \atop CH_3}{N^{\oplus}}}-CH_2-\overset{\displaystyle H \atop |}{CH_2} \xrightarrow{\overset{\ominus}{O}H} CH_3-\overset{\displaystyle CH_3 \atop |}{\underset{\displaystyle | \atop CH_3}{N}} + CH_2=CH_2 + H_2O$$

Ex.



$$CH_3-\overset{\displaystyle CH_3 \atop |}{\underset{\displaystyle | \atop CH_3}{N^{\oplus}}}-\overset{\alpha}{\underset{\displaystyle | \atop \overset{\beta}{CH_3}}{CH}}-\overset{\beta}{CH_2}-CH_3 \xrightarrow[-H_2O]{\overset{\ominus}{O}H} \begin{cases} \underset{\displaystyle \| \atop CH_2}{CH}-CH_2-CH_3 & \text{major product} \\ \underset{\displaystyle | \atop CH_3}{CH}=CH-CH_3 & \text{minor product} \end{cases}$$

Ex.



$$CH_3-\overset{\displaystyle CH_3 \atop |}{\underset{\displaystyle | \atop CH_2-CH_3}{N^{\oplus}}}-\overset{\alpha}{CH_2}-\overset{\beta}{CH_2}-CH_3 \xrightarrow[-H_2O]{-\overset{\ominus}{O}H} \begin{cases} CH_2=CH-CH_3 & \text{(minor)} \\ CH_2=CH_2 & \text{(major)} \end{cases}$$

Note : Hoffmann's product is formed as major product.

REACTION AT A GLANCE :

S.N.	Class of compounds	Types of reactions
(i)	Alkane	Free radical substitution
(ii)	Alkene, alkyne	Electrophilic addition
(iii)	Alkyl halide	Nucleophilic substitution
(iv)	Aldehyde, ketone	Nucleophilic addition
(v)	Acid and their derivatives	Nucleophilic substitution
(vi)	Aromatic compounds	Electrophilic substitution