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Class: S. Y. B. Sc, Paper-II course-302
Sem.-III (First term)

Name of Paper: Inorganic and organic Chemistry

According to the new revised syllabus of Savitribai Phule University from June 2020

Name of Teacher: Prof. Kolekar S.S.

Topic-Alkyl and Aryl halides

Alkyl and Aryl halides

The halogen derivative of alkane -The one or more number of hydrogen atoms of alkane are replaced by halogen atom or atoms

e.g. R-H + X2 → R-X + HX

Classification of halogen derivatives

The halogen derivatives are classified as mono, di, tri, tetra halogen derivatives. It depend upon the number of halogen atoms are present in the molecule

1) Mono- halogen derivatives e.g methyl bromide CH_3Br, Ethyl chloride CH_3-CH_2 Cl
2) Di halogen derivatives – Ethylene dichloride CH_2-CH_2Cl
3) Trihalogen derivatives- Chloroform $CHCl_3$
4) Tetrahalogen derivatives-Carbon tetrachloride CCl_4

The alkyl halide – When one of hydrogen of alkane is replaced by the halogen atom, the monohalogen derivative of alkane is known as alkyl halide

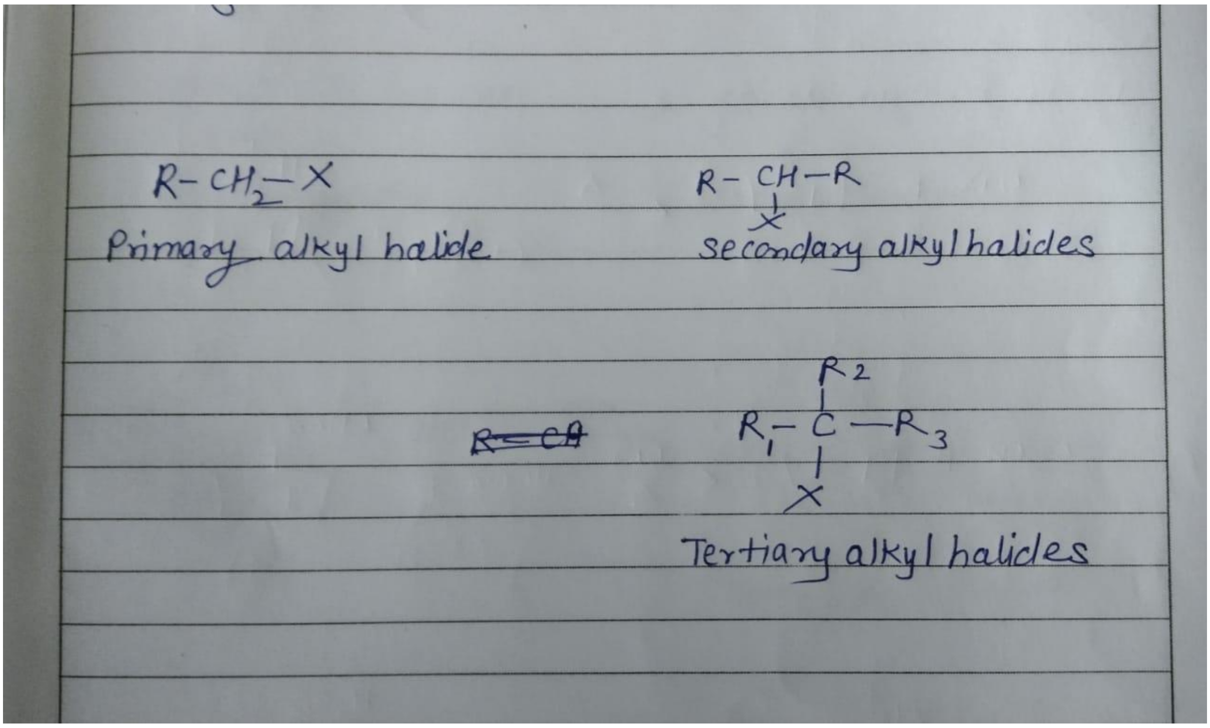
The general molecular formula of alkyl halide CnH2n+1 X and represented by RX where X is halogen may be -Cl, -Br, -I, -F and R = alkyl group the functional group is halogen atom

The classification of the alkyl halide is primary, secondary and tertiary alkyl halide is carried out as per nature of the carbon atom

Primary alkyl halide – When -X halogen attach to the primary carbon atom $R-CH_2-CH_2-X$ e. g. ethyl bromide

Secondary alkyl halide -When -X halogen attach to the secondary carbon atom R_2CH-X e. g. Isopropyl bromide

Tertiary alkyl halide -When -X halogen attach to the tertiary carbon atom R_3C-X e. g. T-butyl bromide



$R-CH_2-X$

Primary alkyl halide

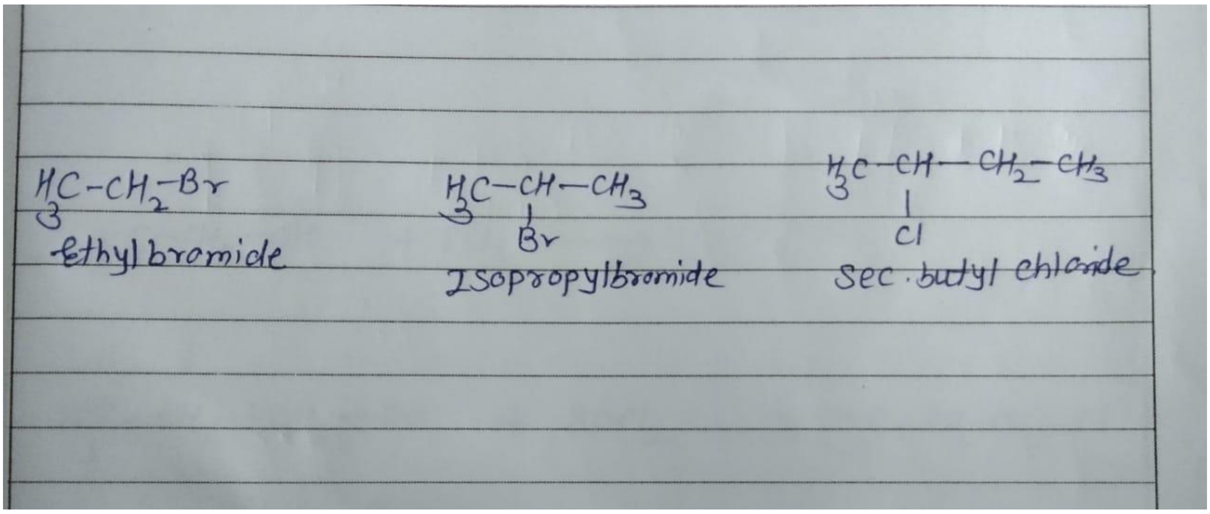
$\underset{X}{R-\overset{}{CH}-R}$

secondary alkyl halides

~~R–CH~~

$$R_1-\underset{X}{\overset{R_2}{C}}-R_3$$

Tertiary alkyl halides



H_3C-CH_2-Br

Ethyl bromide

$H_3C-\underset{Br}{CH}-CH_3$

Isopropylbromide

$H_3C-\underset{Cl}{CH}-CH_2-CH_3$

Sec. butyl chloride

Preparation of alkyl halide

From alcohol-

The alcohol is treated with conc. aq acid or dry hydrogen halide gas, it gives the product alkyl halide

The tertiary alcohol reacts faster than secondary alcohol towards halo acid while the secondary alcohol react faster than primary alcohol towards halo acid

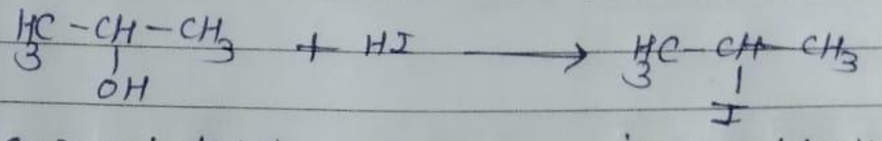
The reactivity of alcohol towards HX is tertiary alcohol > Secondary alcohol > primary alcohol >CH3-OH

From alcohol- The alcohol is allowed to react with PCl_3, PCl_5, $SOCl_2$ gives the alkyl chloride

$C_2H_5OH + HCl \xrightarrow[Zncl_2]{Anhyd.} C_2H_5-Cl + H_2O$

Ethanol

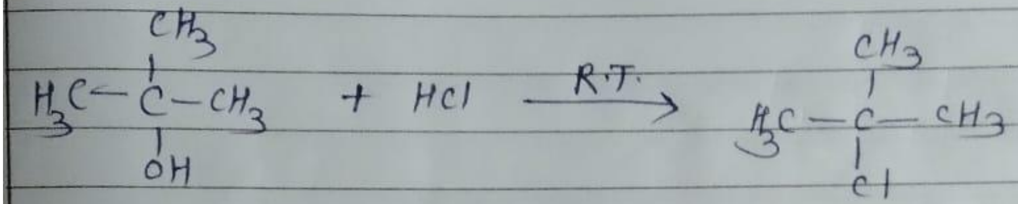
Ethyl chloride.



$$H_3C-\underset{\underset{OH}{|}}{CH}-CH_3 + HI \longrightarrow H_3C-\underset{\underset{I}{|}}{CH}-CH_3$$

isopropyl alcohol.

isopropyl iodide



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3 + HCl \xrightarrow{R.T.} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{cl}{|}}{C}}-CH_3$$

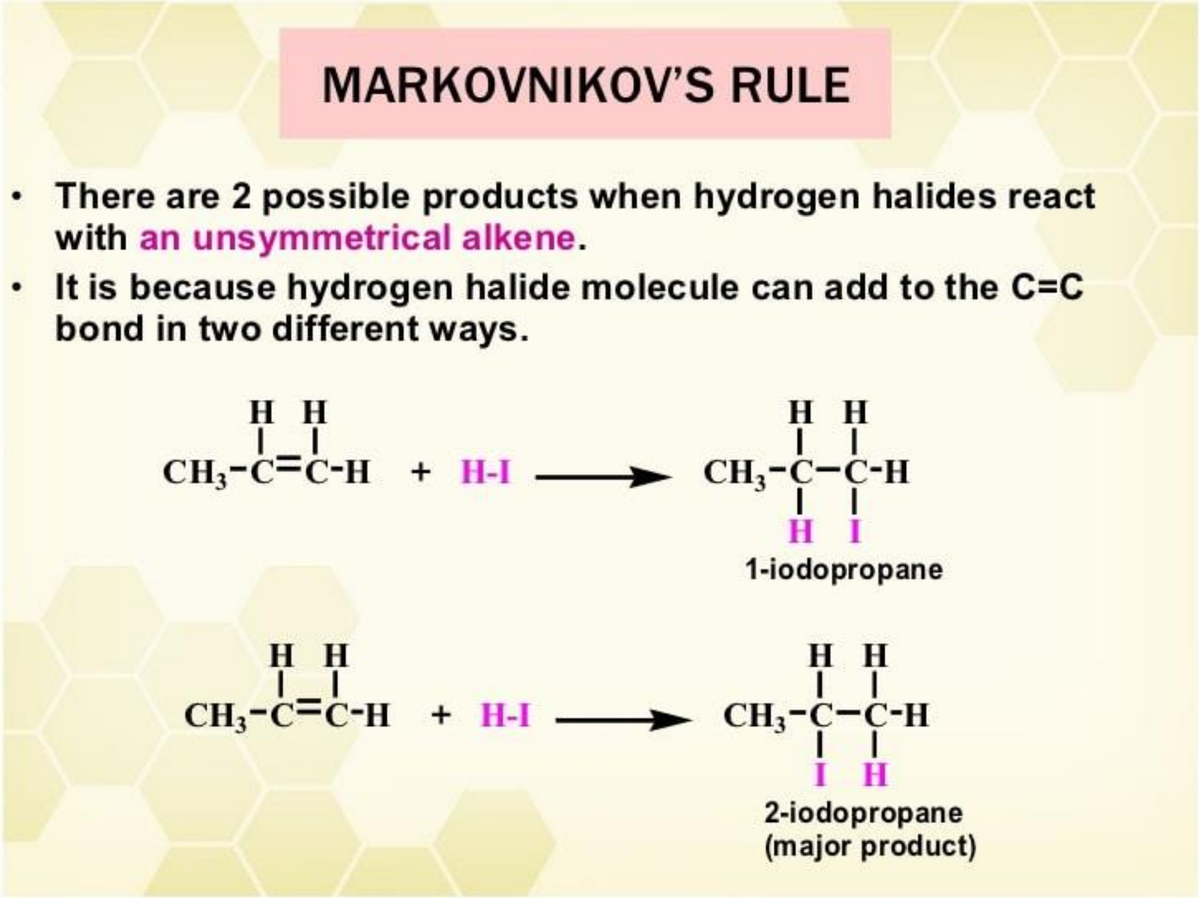
Tert-bytyl chloride.

$H_3C-CH_2-OH + PCl_3 \longrightarrow H_3C-CH_2-Cl$

$H_3C-CH_2-CH_2-OH + SOCl_2 \longrightarrow H_3C-CH_2-CH_2-C$

From alkene- The alkene contains carbon double bond carbon when allow to react with halo acid like HCl, HBr, HI it undergoes the hydrohalogenation reaction gives alkyl halide When alkene is unsymmetrical allow to react with HX acid it gives two product one is major and other is minor

Markovnikoff's rule- The addition of HX across the carbon double bond carbon is carried out, then negative part of HX is X^- is added to the carbon atom which carries the less number of hydrogen atoms



MARKOVNIKOV'S RULE

- There are 2 possible products when hydrogen halides react with an unsymmetrical alkene.
- It is because hydrogen halide molecule can add to the C=C bond in two different ways.

$$CH_3-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H + H\text{-}I \longrightarrow CH_3-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{I}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H$$

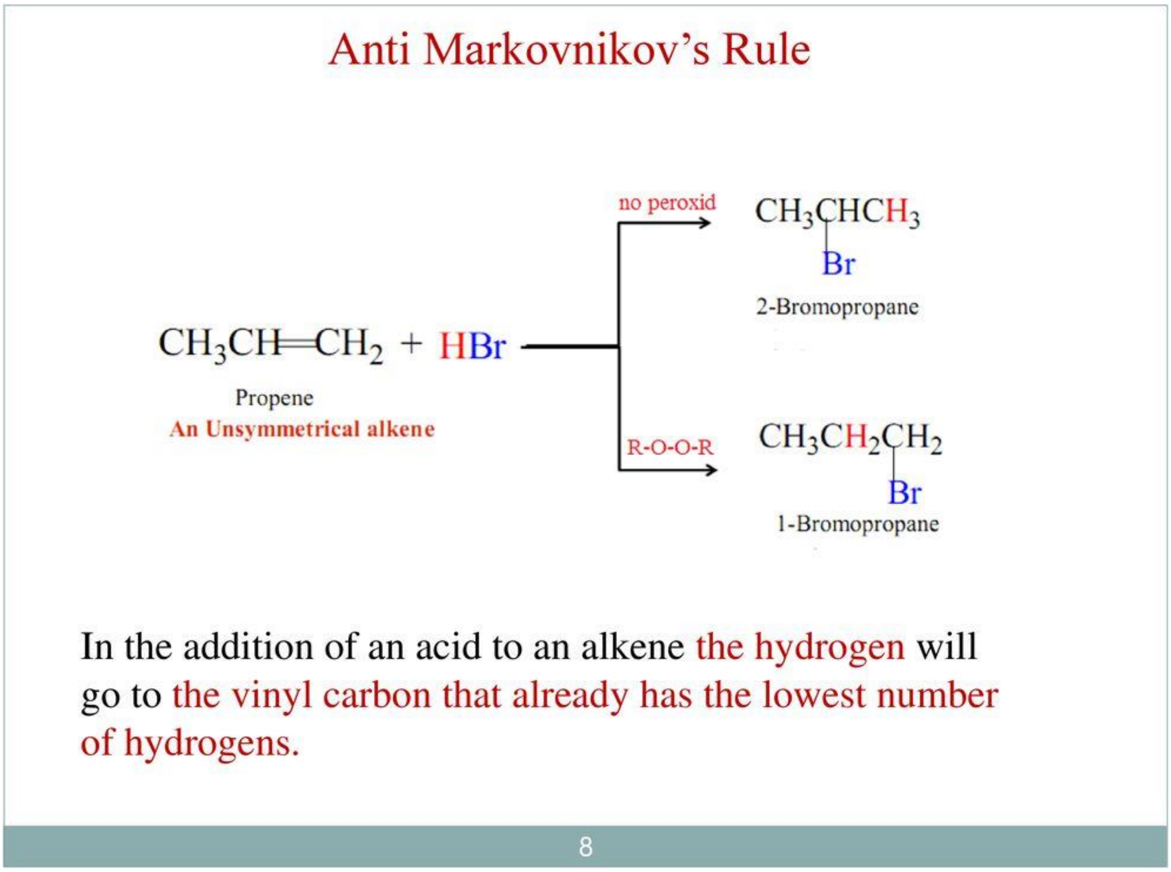
1-iodopropane

$$CH_3-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H + H\text{-}I \longrightarrow CH_3-\underset{I}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H$$

2-iodopropane
(major product)

Anti- Markovnikoff's rule- It is also called as peroxide effect The addition of HX across the carbon double bond carbon is carried out, then negative part of HX is X- is added to the carbon atom which carries the more number of hydrogen atoms

The peroxide effect is carried out by using benzoyl peroxide, Hydrogen peroxide and it is shown by HBr and not by HCl and HI



Anti Markovnikov's Rule

$$CH_3CH{=}CH_2 + HBr \xrightarrow{\text{no peroxid}} CH_3\underset{Br}{C}HCH_3$$

$$CH_3CH{=}CH_2 + HBr \xrightarrow{R\text{-}O\text{-}O\text{-}R} CH_3CH_2\underset{Br}{C}H_2$$

Propene

An Unsymmetrical alkene

2-Bromopropane

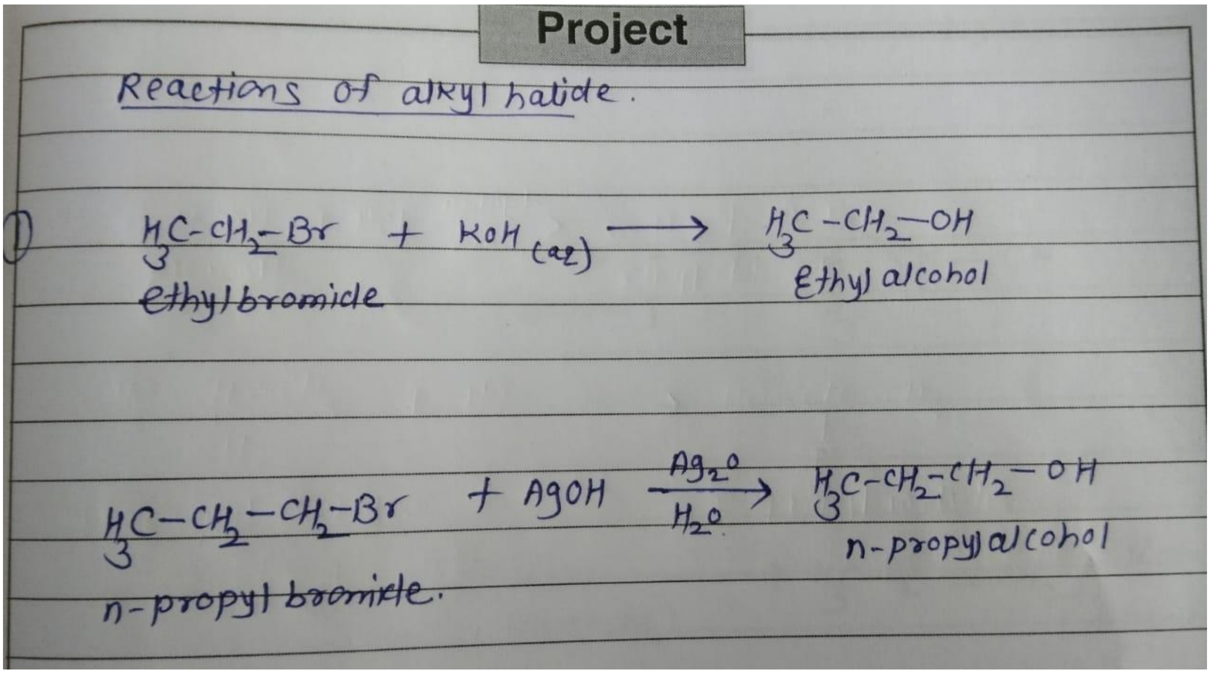
1-Bromopropane

In the addition of an acid to an alkene the hydrogen will go to the vinyl carbon that already has the lowest number of hydrogens.

Reactions of alkyl halide –

1)Hydrolysis of alkyl halide – Alcohol formation

The alkyl halide undergoes the hydrolysis by refluxing it with aq. alkali solution like KOH or NaOH or on heating with moist silver oxide it gives the alcohol



Project

Reactions of alkyl halide.

① $H_3C-CH_2-Br + KOH_{(aq)} \longrightarrow H_3C-CH_2-OH$

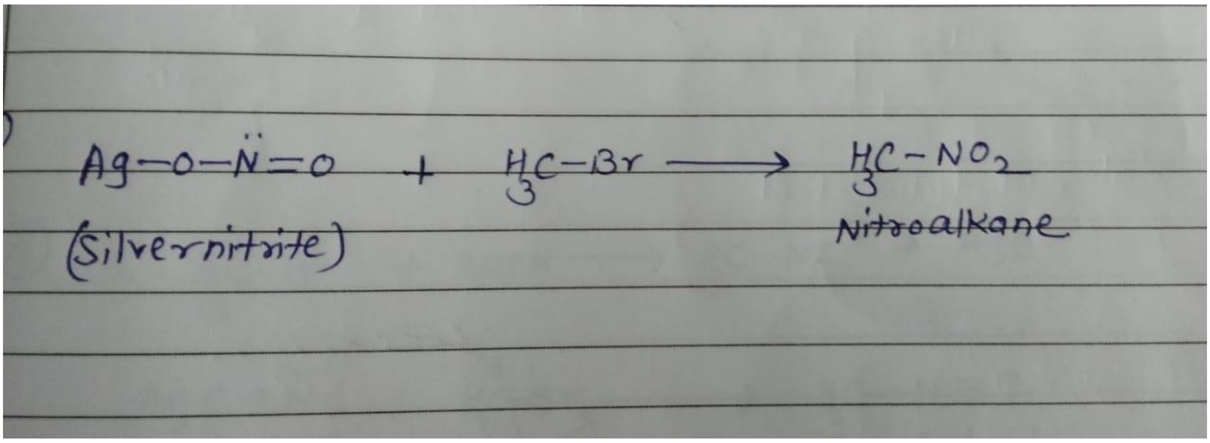
ethyl bromide Ethyl alcohol

$H_3C-CH_2-CH_2-Br + AgOH \xrightarrow[H_2O]{Ag_2O} H_3C-CH_2-CH_2-OH$

n-propyl bromide. n-propyl alcohol

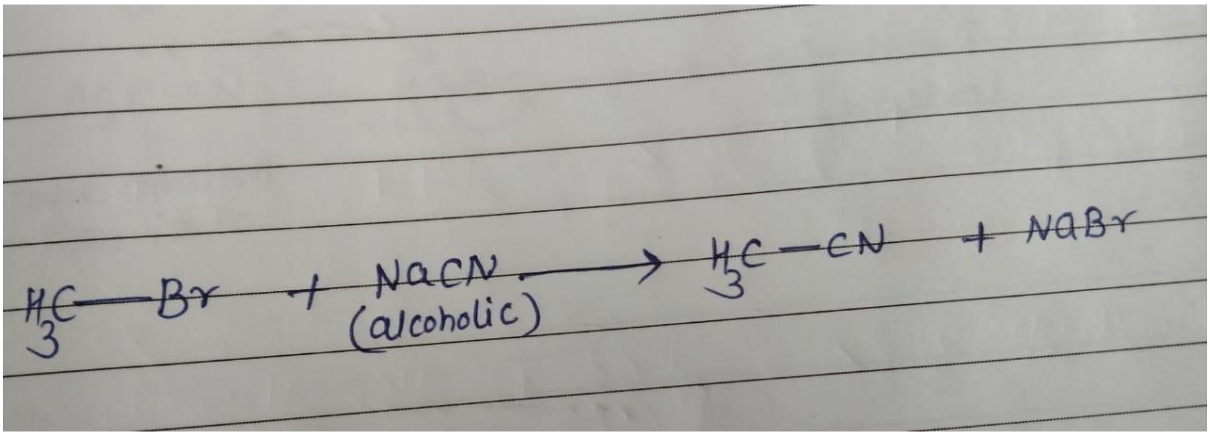
2) Formation of Nitro-alkane –

The alkyl halide reacts with aq. alcoholic solution of sodium nitrite or potassium nitrite or silver nitrite gives nitro alkane



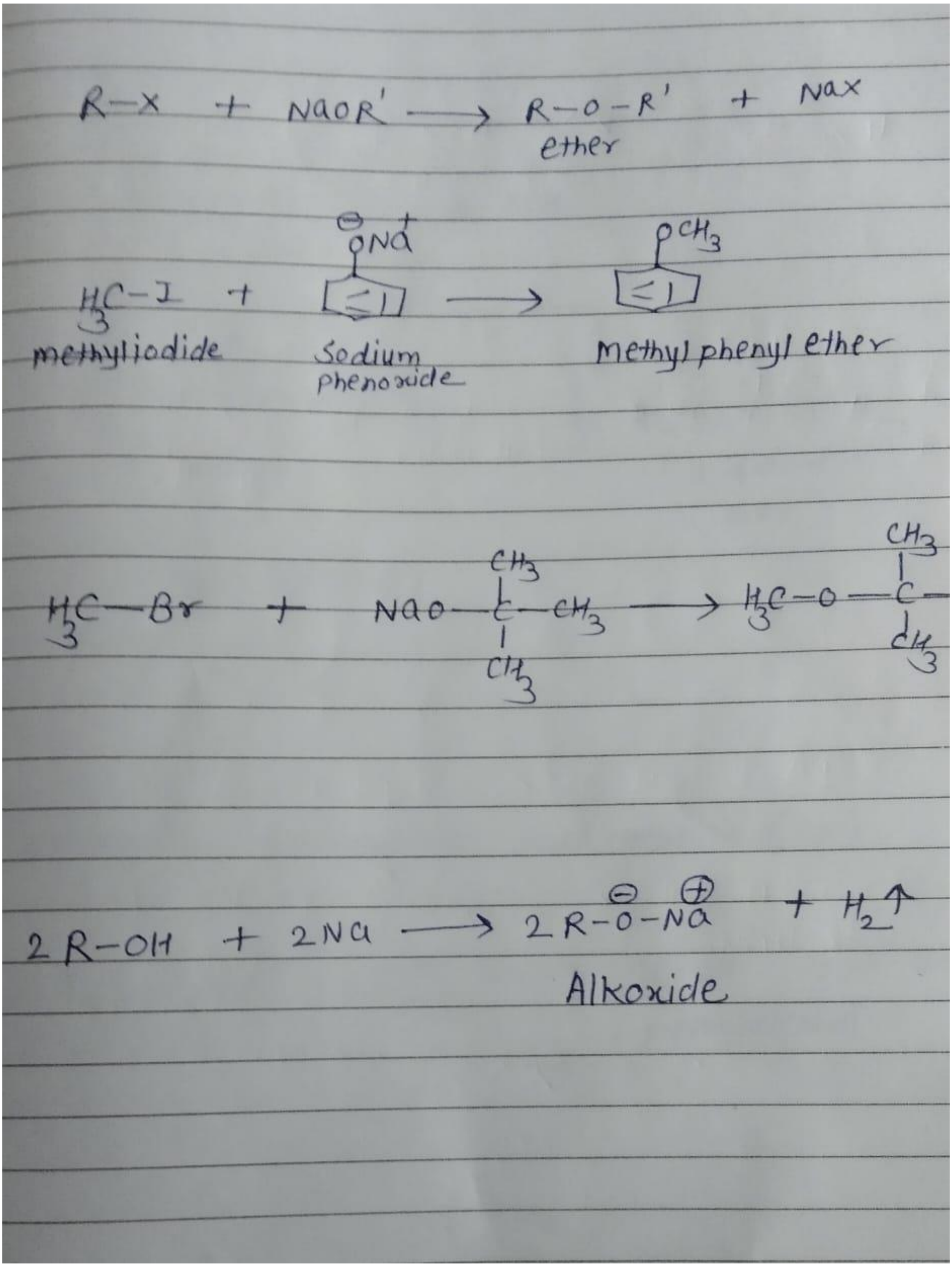
3) Formation of Alkyl Isonitrile-

The alkyl halide reacts with aq. alcoholic solution of silver cyanide it gives nitro alkane



4)Williamsons ether synthesis – The symmetrical as well as unsymmetrical ether can be prepared by Williamsons ether synthesis method, it is most convenient method to prepare the symmetrical as well as mixed ether

The alkyl halide is allow to react with sodium alkoxide or sodium phenoxide gives ether



$R{-}X + NaOR' \longrightarrow R{-}O{-}R' + NaX$

ether

$H_3C{-}I$ + Sodium phenoxide ($\overset{\ominus}{O}\overset{+}{Na}$ on the benzene ring) $\longrightarrow$ Methyl phenyl ether (OCH_3 on the benzene ring)

methyliodide

Sodium phenoxide

Methyl phenyl ether

$H_3C{-}Br + NaO{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_3 \longrightarrow H_3C{-}O{-}\underset{CH_3}{\overset{CH_3}{C}}{-}$

$2R{-}OH + 2Na \longrightarrow 2R{-}\overset{\ominus}{O}{-}\overset{\oplus}{Na} + H_2\uparrow$

Alkoxide

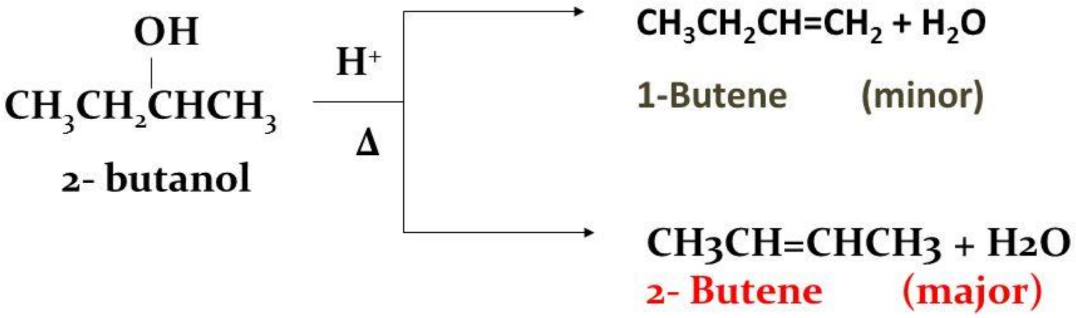
5) Formation alkene – The alkyl halide undergoes the elimination reaction with treated with the alcoholic KOH it gives alkene, the dehydrohalogenation is take place by elimination of halogen atom from α position and hydrogen atom from β position. This reaction is called as 1,2 elimination or β elimination

When alkyl halide contains two β- hydrogen atoms then elimination is take place gives the two products.

The more substituted alkene will obtain as major product according to the Saytzeff rule

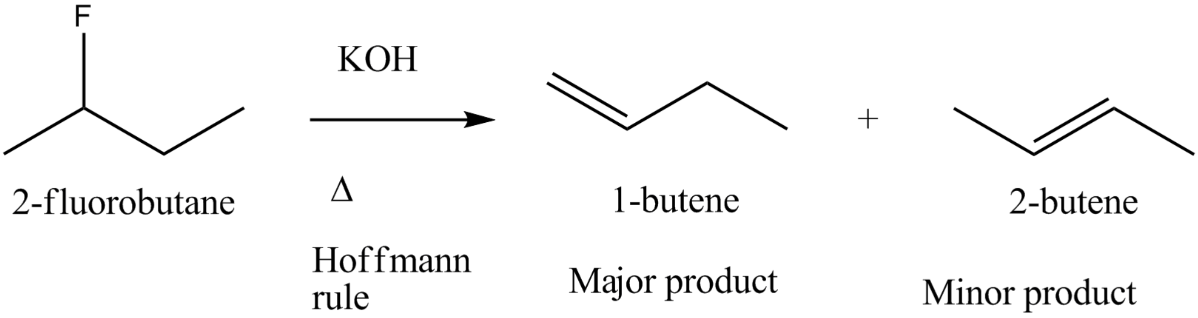
Saytzeff's Rule

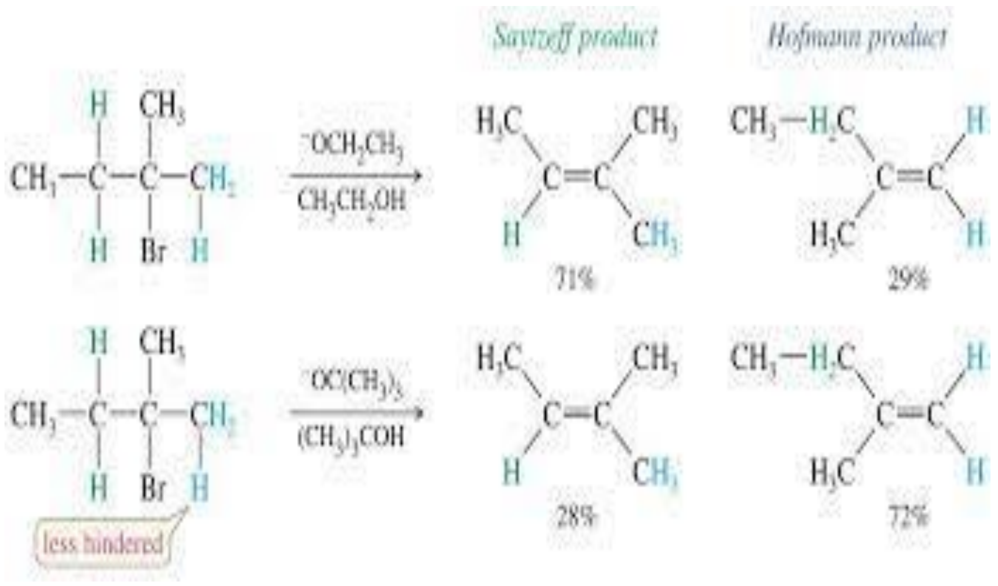
In every instance in which more than one alkene can be formed, the major product is the alkene with the most alkyl substituents attached on the double bonded carbon.



$$CH_3CH_2\overset{OH}{C}HCH_3 \xrightarrow[\Delta]{H^+} CH_3CH_2CH{=}CH_2 + H_2O \quad + \quad CH_3CH{=}CHCH_3 + H_2O$$

The less substituted alkene will obtain as major product according to the Hoffmann rule





1)Aliphatic nucleophilic substitution reaction
SN^1, SN^2, SNi
2) Aliphatic electrophilic substitution reaction
SE
3) Aromatic electrophilic substitution reaction
ArS$_E$

Substitution reaction

The reaction in which an group of atoms or atom in the substrate (i.e. reactant) is replaced by another group of atoms or atom of the reagent used is known as substitution reaction.

R-Y + A-B gives R-A + Y-B

Substrate Reagent Product

Y is said to be the leaving group and A as the incoming group. Y of the substrate is replaced by the A of reagent used.

Substitution reactions are

1)Aliphatic nucleophilic substitution reaction
    SN1, SN2, SNi

2)Aliphatic electrophilic substitution reaction
    SE

3) Aromatic electrophilic substitution reaction
    ArSE

Nucleophilic Substitution Reaction

Aliphatic nucleophilic substitution reaction

SN1, SN2, SNi

Electrophilic Substitution Reaction

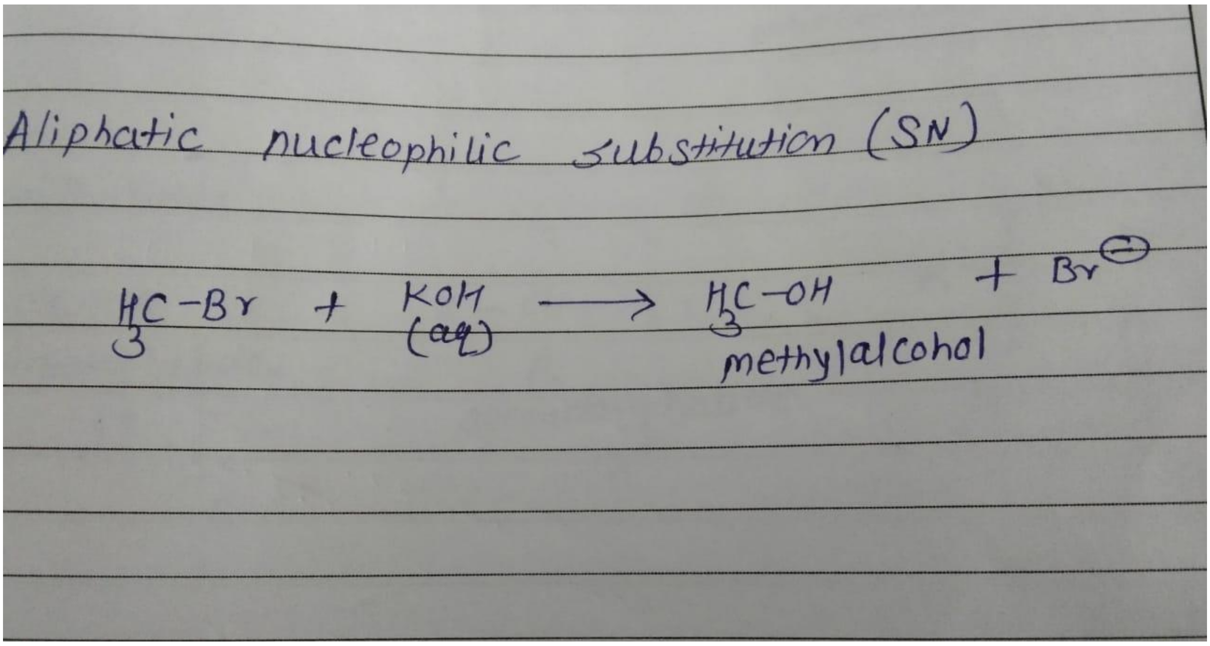
Aromatic electrophilic substitution reaction - ArSE

Aliphatic electrophilic substitution reaction SE

Aliphatic nucleophilic substitution reaction

SN1, SN2, SNi

The electron rich or negatively charged group is called as nucleophile. The nucleophile is attack on the substrate known as attacking group or incoming group and leaving group get departed then reaction is known as nucleophilic substitution.
e.g. Hydrolysis of methyl bromide- The methyl bromide is treated with aq. KOH gives methyl alcohol.
Where Br- is leaving group and OH- is Nucleophile.



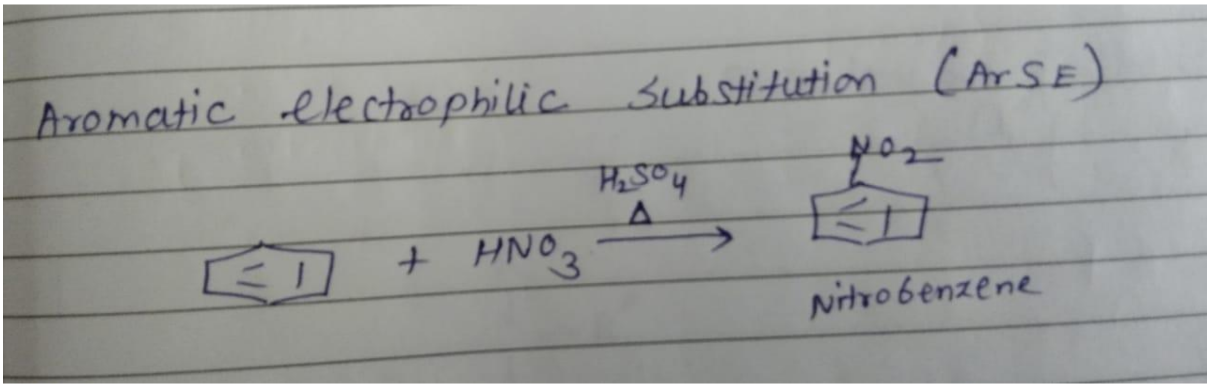
Aliphatic nucleophilic substitution (SN)

$$H_3C-Br + \underset{(aq)}{KOH} \longrightarrow \underset{\text{methyl alcohol}}{H_3C-OH} + Br^{\ominus}$$

Electrophilic Substitution Reaction

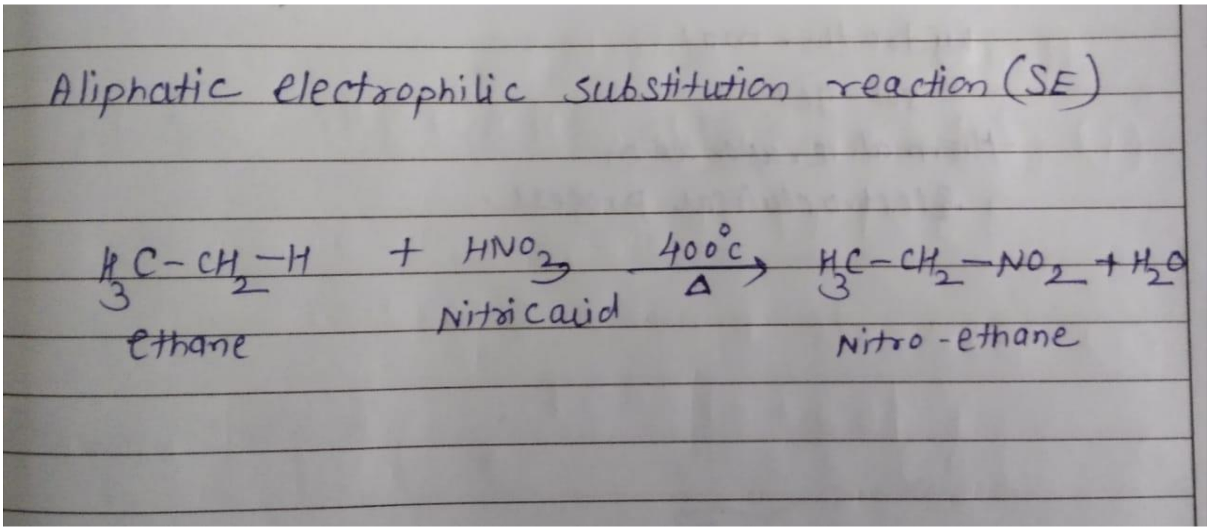
Aromatic electrophilic substitution reaction - ArSE

The electrophile is electron deficient when acts as the incoming group and leaving group like H +get departed then reaction is called as electrophilic substitution reaction.
e.g. Nitration of benzene- When benzene is allow to react with nitrating mix. i.e. CHNO3 and CH2SO4. gives nitrobenzene. Where benzene is substrate and nitronium ion is electrophile



Aliphatic electrophilic substitution reaction SE

The saturated hydrocarbon like alkane undergoes the electrophilic substitution reaction in which hydrogen atom of alkane is substituted by the electrophilic part of the reagent e.g when ethane is treated with conc. nitric acid are heated in vapour phase at 400^0c gives the nitro-ethane



Aliphatic electrophilic substitution reaction (SE)

$$H_3C-CH_2-H + HNO_3 \xrightarrow[\Delta]{400^\circ c} H_3C-CH_2-NO_2 + H_2O$$

ethane

Nitri caid

Nitro-ethane

Nucleophilic Substitution Reaction

Aliphatic nucleophilic substitution reaction of order one

SN1, SN2, SNi

Nucleophilic Substitution Reaction of order one. i.e. SN1

It is nucleophilic substitution reaction follows first order having two step mechanism gives racemic mixture and process is called as racemization. i.e. 50% inversion and 50%

retention. The polar solvent increases the rate of reaction and weak nucleophile favor the reaction. The reactivity sequence is tertiary carbocation> secondary carbocation> primary carbocation., so some time rearrangement may take place.

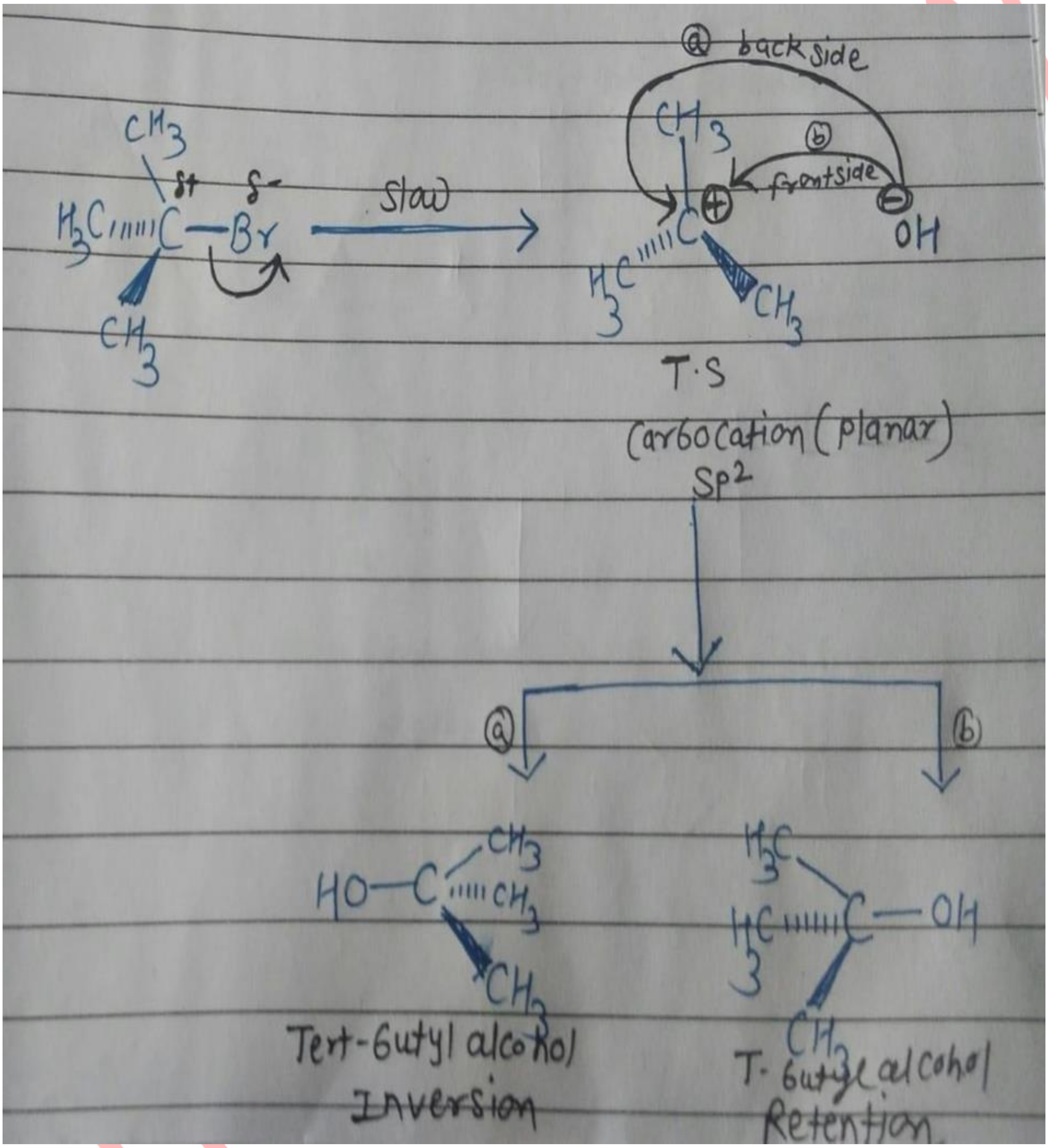
e.g. T. butyl bromide undergoes hydrolysis aq. NaOH to gives tert-butyl alcohol.

Kinetics-The kinetics study shows that the rate of the reaction is proportional to tert-butyl bromide only. (i.e. it is first order kinetics) and rate of reaction is independent on concentration of Since the rate of the reaction is dependent only the concentration of T- butyl bromide. Only

T-butyl bromide molecule is take part in slow step and the rate of reaction is independent of the concentration of nucleophile as the attack of nucleophile must be occurring in the fast step

T-butyl bromide undergoes hydrolysis aq. NaOH to gives T-butyl alcohol.

Proposed Mechanism The -R is alkyl group like methyl, -X is leaving group like halogen may be chloride, bromide and nucleophile is OH-


CH3
δ+ δ-
H3C C Br
CH3
slow
ⓐ back side
ⓑ frontside
CH3
⊕ C
⊖ OH
H3C
CH3
T·S
Carbocation (planar)
sp2
ⓐ
ⓑ
HO C CH3 CH3 CH3
Tert-butyl alcohol
Inversion
H3C H3C C OH CH3
T-butyl alcohol
Retention

The SN1 Reaction –

Stereochemistry

Tert- butyl bromide undergoes hydrolysis aq. NaOH to gives tert- butyl alcohol.

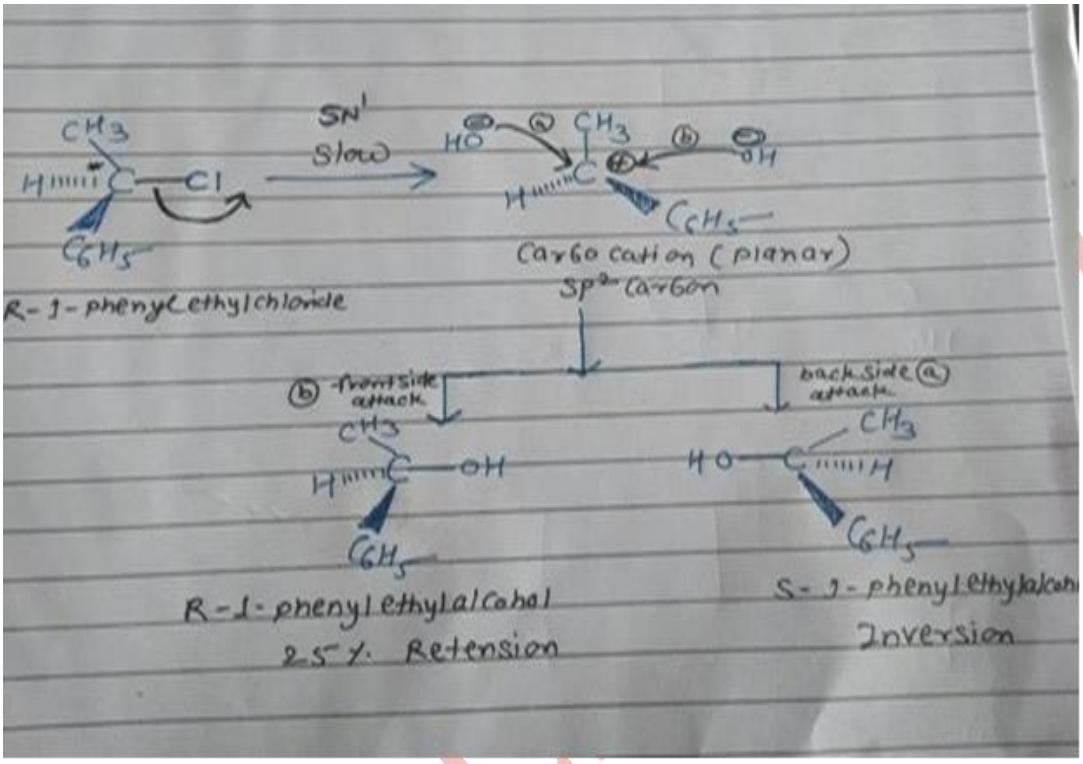
In slow step the C-Br bond might be breaking to carbocation or carbonium ion, the carbonium ion is SP hybridized and planar with bond angle 120^o Once the carbocation is formed, the nucleophile OH- can be attack from back side as well as from front side as it has planer geometry ,theoretically the chances of back side attack and front side attack are equal therefore 50% inversion and 50% retention and the product should be 100% racemic mixture, known as racemization but1experimentally racemization in SN mechanism though not 100% if starting substrate is optically active and product obtain is due to back side and front side attack would be enantiomers of each other. In practice however 100% racemization is rarely observed. the most of the

SN1 reaction occur with varying degree of inversion. The higher degree of inversion indicates that even though the intermediate carbocation is planer, the chances of back side of nucleophile are more than front side attack This mainly due to stability of carbocation and the nucleophilicity of the solvent.

Stability of carbocation- If the stability of the carbocation is extremely stable The carbocation formed quickly and exists for longer time, the front as well as back side attack by nucleophile is possible equally so it shows higher degree of racemization.

If the carbocation is less stable, the leaving group remains in its close vicinity even after dissociation. Due to this it prevents the front side attack and nucleophile favors the backside attack gives higher degree of inversion As the stability of carbocation increases the proportion of racemization increases while as the stability of carbocation decreases percentage of inversion increases.

The nucleophilicity of solvent – For formation of carbocation the energy required is provided by solvent molecules through solvation. If the solvent polarity increases the stability of carbocation increases, it can attack by nucleophile by front as well as back side so has higher degree of racemization.



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