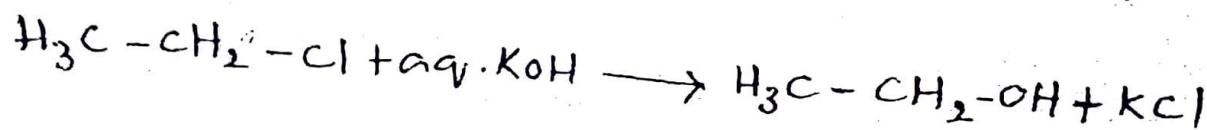
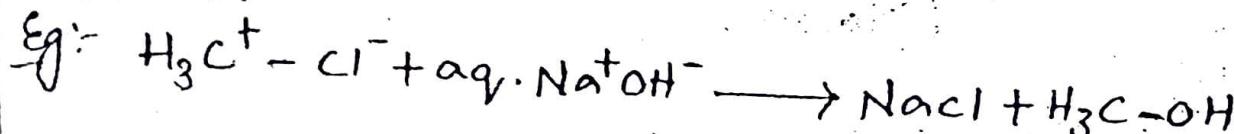


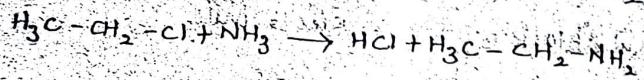
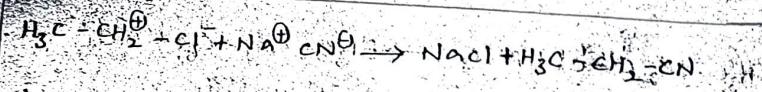
Imp 2) Nucleophilic Substitution Reactions

If the substitution reaction is initiated by the Nucleophile these reaction is known as Nucleophile reaction. Alkyl halides undergoes Nucleophilic Substitution reaction.

For example:- Methyl chloride undergoes basic hydrolysis reaction to form methyl alcohol. In this reaction Substitution of OH group takes place instead of Cl^- .

In this reaction OH^- is nucleophile.





According to Mechanism Nucleophile substitution reactions are divided into two types:-

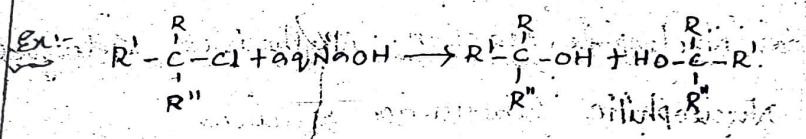
- 1) S_N^1 reactions (unimolecular Nucleophile substitution reaction)
- 2) S_N^2 reactions (bimolecular Nucleophile substitution reaction)

i) S_N^1 reaction: The rate of reaction depends on the only one molecule i.e., concentration of tertiary (3°) alkyl halide is called S_N^1 reaction.

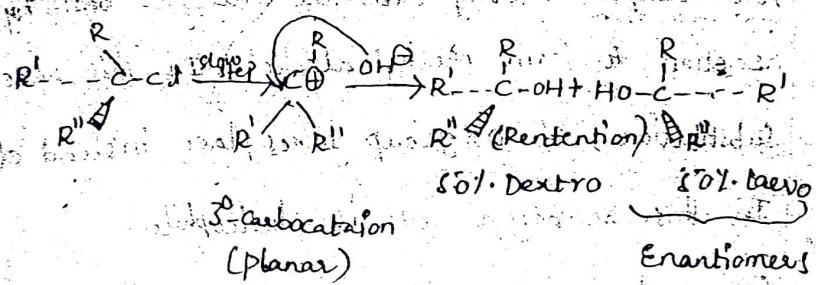
Rate \propto Tertiary 3° -alkyl halides

Generally 3° alkyl halides are giving S_N^1 reaction.

For example:- Basic hydrolysis of tertiary alkyl halide reaction explained on the basis of S_N^1 Mechanism.



Mechanism:



Tertiary alkyl chloride is having 3 alkyl groups, therefore the OH group will not attack to the alkyl group.

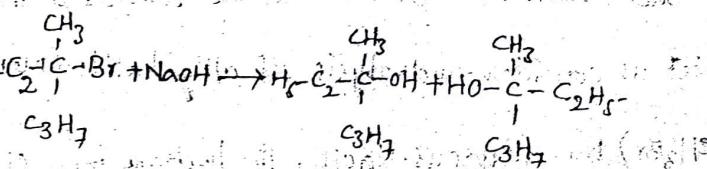
In the First step, C-Cl bond breaking & form 3° alkyl carbonium ion forms a planar structure. Therefore it is rate determining step.

In the Second step 3° alkyl carbonium ion combines with OH Nucleophile forms a product. This step is fast step.

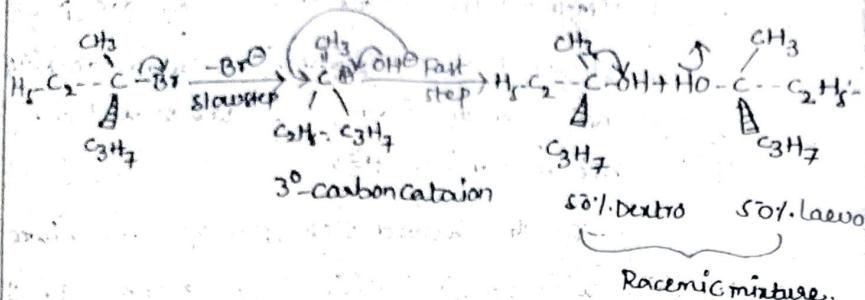
The OH Nucleophile attack on either side to give two forms they are i) Dextro ii) laevo This mixture is known as enantiomeric mixture. In this reaction only one molecule is participating in rate determining step. So, this reaction is called Nucleophilic Substitution unimolecular reaction.

Formation of product is same configuration of the reactant is known as retention product, Inversion of the product is known as Inversion product. (Inversion configuration).

For Example: 1 3-Bromo 3-Methyl Hexane undergoes basic hydrolysis reaction to form and its follow S_N^1 reaction.

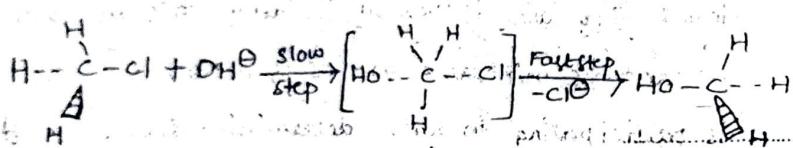


Mechanism



SN_2 reaction:-

Mechanism



If the rate of such reactions depends on the concentration of alkyl halide as well as base nucleophile, it is called S_{N}_2 reaction or bimolecular Nucleophilic Substitution reaction.

$$\text{Rate} \propto [\text{R-X}][\text{Nu}]$$

.. Nu = nucleophile

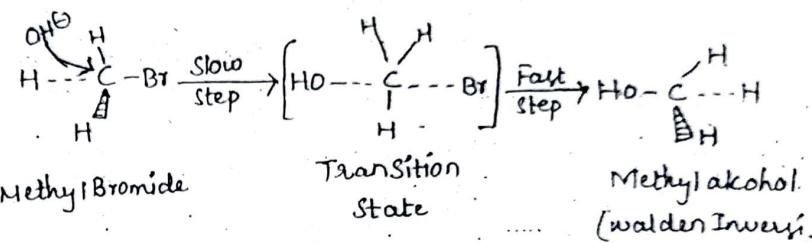
(or)

$$\text{Rate} \propto [\text{CH}_3\text{C}-\text{Br}][\text{OH}^-]$$

Such reactions believed to be completed in one step. Let us consider hydrolysis of alkyl halide (Methyl Bromide, CH_3Br) by aqueous NaOH . The hydroxyl ion starts to share electrons with in the alkyl halide to the opposite

Part of C-Br bond

It forms a transition state in which both OH and Br are partially bonded to the alkyl halide carbon. It is explained by taking example with CH_3Br . Eg: Methyl Bromide (CH_3Br) Basic hydrolysis follows the S_{N}_2 mechanism.



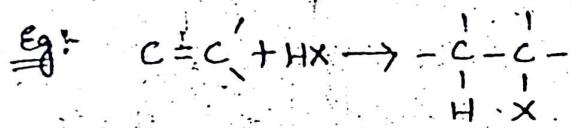
In this reaction, Br^- having negative inductive effect. Therefore, the Nucleophile attacks at carbon centre opposite to the Br^- . Then it forms Transition state. The Transition state converted to products to form Methyl alcohol. In S_{N}_2 reaction when the OH^- attacks backside of the carbon, they change the configuration of molecule i.e., It (attacks) takes inversion like as an umbrella turns inside out in a high wind. The change in configuration often is called walden inversion.

3) Free radicals Substitution reaction: If their atoms are molecules containing single electrons or free electrons are called Free radicals. If the substitution reaction is initiated by Free radical the reaction is known as Free radical substitution reaction.

2 Additional reaction:- Adding two or more than reactants than the reaction is called as addition reaction.

In these reactions atleast 1 π bond is lost. In these addition reaction unsaturated double or triple bonds are becomes as saturated hydrocarbons.

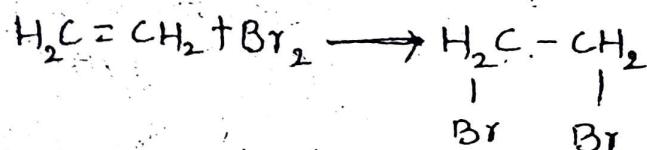
This is opposite to elimination reaction.



According to Mechanism the addition reactions are classified into 3 types :- i) Electrophilic addition reactions
ii) Nucleophilic " "
iii) Free radical " "

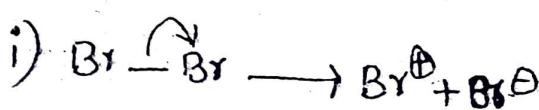
i) Electrophilic addition reactions:- If the addition reaction is initiated by electrophile. These reaction is known as electrophilic addition reaction or when the addition reaction involve the initial attack by an electrophile the reaction is called electrophilic addition reaction.

Eg:- Ethylene ($\text{CH}_2 = \text{CH}_2$) undergoes electrophilic addition reaction with Bromine to form 1,2-Dibromoethane.

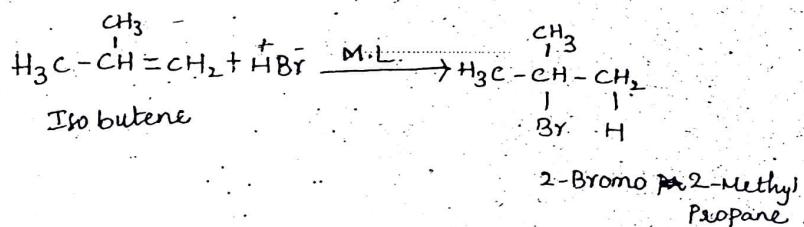


1,2-Dibromoethane.

Mechanism:-

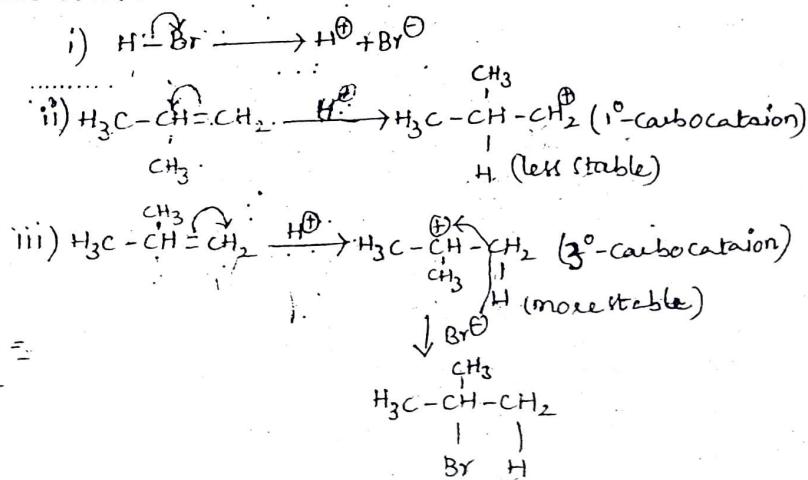


V.I.M Markownikoff's Law: when an asymmetrical reagent like HBr adds to an unsymmetrical double bonds. The positive part of the reagent (electrophile) becomes attached to the double bonded carbon atom which bears the ^{least} number of the hydrogen atoms. This law is known as Markownikoff's Law.



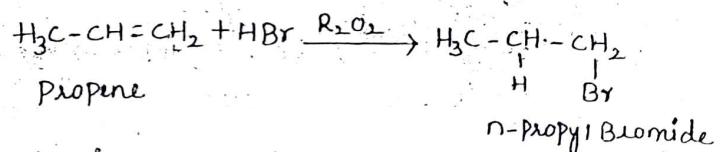
Markownikoff's law is also explained carbonium ion stability. Therefore 3° is more stable than secondary degree 2° and 2° carbonium ion is more stable than 1° carbonium ion: $(3^\circ > 2^\circ > 1^\circ)$

Mechanism:

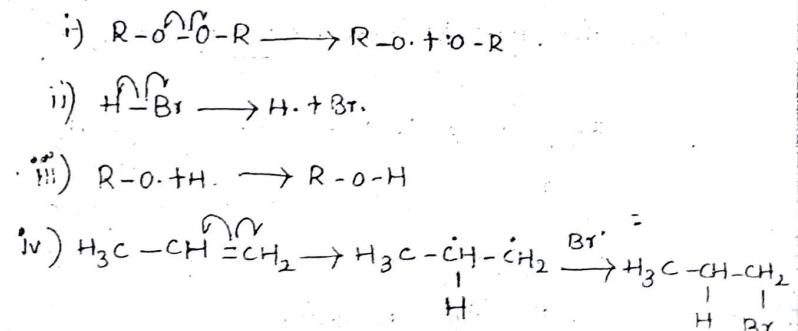


V.I.M Antimarkownikoff's rule (or) Kharash effect: Addition of HBr to unsymmetrical alkenes in presence of Peroxide takes a course opposite to markownikoff's law. This reaction is exactly opposite to Markownikoff's law. Hence it is called as antimarkownikoff's law. This phenomenon of antimarkownikoff addition of HBr caused by the presence of peroxide is known as peroxide effect. It was discovered by Kharash scientist. Therefore it is also known as Kharash law.

For example: when propene reacts with HBr in presence of Peroxide to form n-propyl bromide it can be explained by free radical mechanism.



Mechanism:-



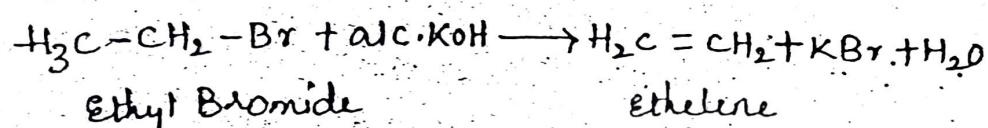
Nucleophilic addition reactions:-

If the addition reaction is

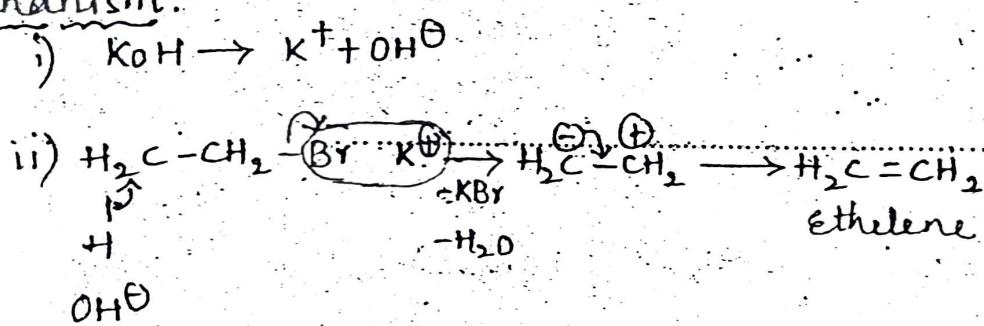
Saturated hydrocarbons becomes unsaturated

Dehydrohalogenation of alkyl halides: Removal of one hydrogen atom and one halogen atom is called Dehydrohalogenation. These reactions followed in presence of alcoholic KOH.

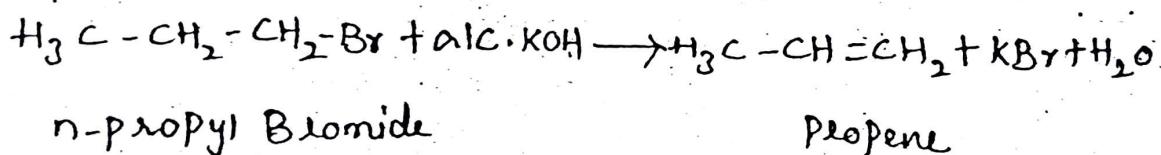
For Ex-1 Ethyl Bromide reacts with alcoholic KOH and undergoes dehydrohalogenation reaction to form Ethylene



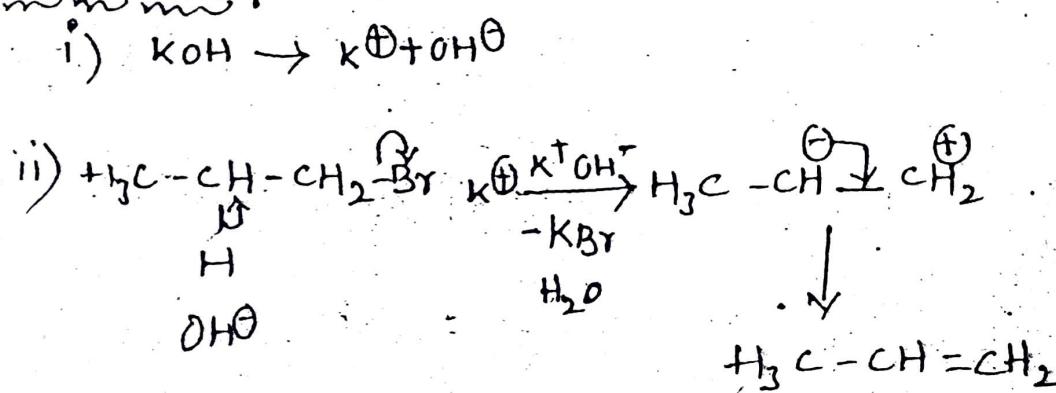
Mechanism:-



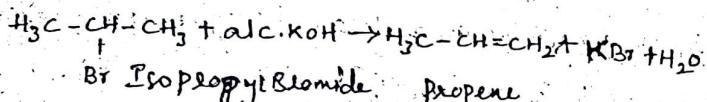
Ex-2 n-propyl Bromide reacts with alco.KOH and undergoes dehydration reaction to form Propene.



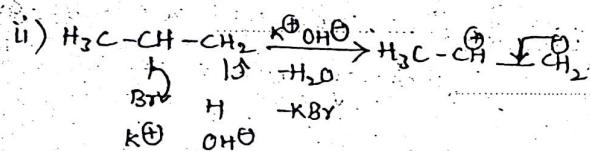
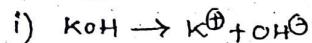
Mechanism :-



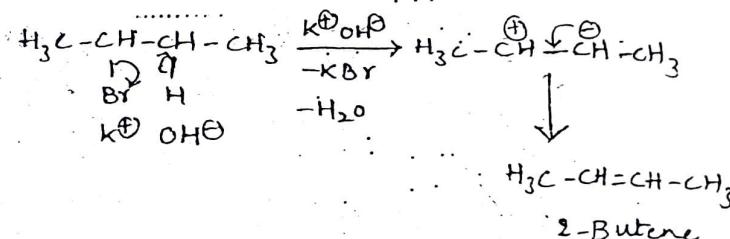
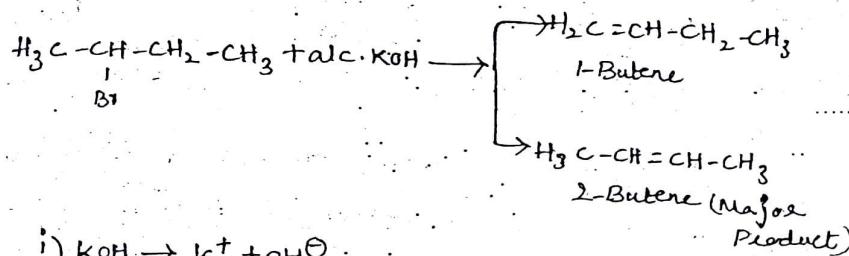
Ex-3 Iso propyl Bromide reacts with alc. KOH and undergoes dehydration reaction to form propene.



Mechanism:



Ex-4 2-Bromo Butane undergoes dehydrohalogenation with alc. KOH to form 1-butene and 2-Butene. But according to Sayteff rule 2-butene forming as a major product.



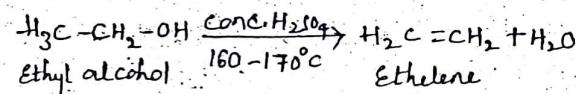
IMP Sayteff rule: Sayteff rule says that there is a possibility of forming 2-alkenes by dehydrohalogenation of alcohols (or) "hydrohalogenation of Alkyl halides"

The hydrogen atom is preferentially eliminated from the carbon atom which contains less number of hydrogen atoms.

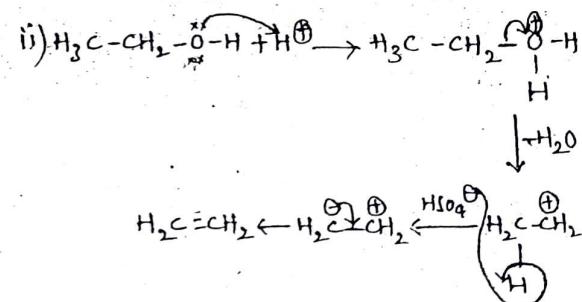
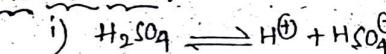
It can be explained in terms of carbonium ion stability.

Dehydration of alcohols :- Elimination of water molecules from alcohol is called dehydration of alcohols. Dehydration is taking in presence conc. H_2SO_4 .

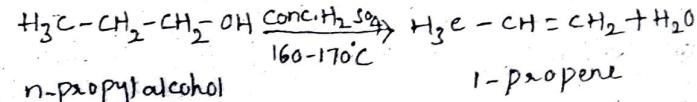
ForEx-1 Ethyl alcohol undergoes dehydration reaction with conc. H_2SO_4 at ~~160~~ $160-170^\circ\text{C}$ to form Ethene.



Mechanism:

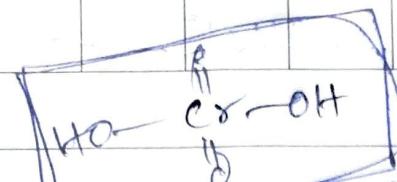


ForEx-2 n-propyl alcohol undergoes dehydration reaction with conc. H_2SO_4 at $160-170^\circ\text{C}$ to form 1-propene.



Marks Obtained

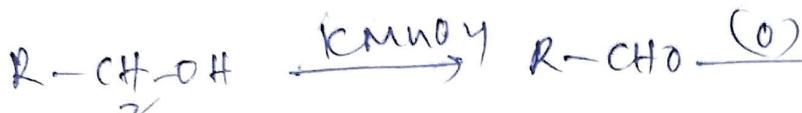
Total Marks (in words)



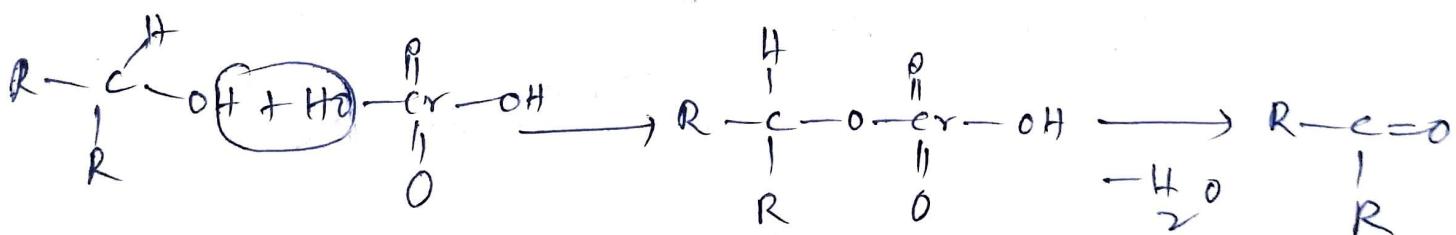
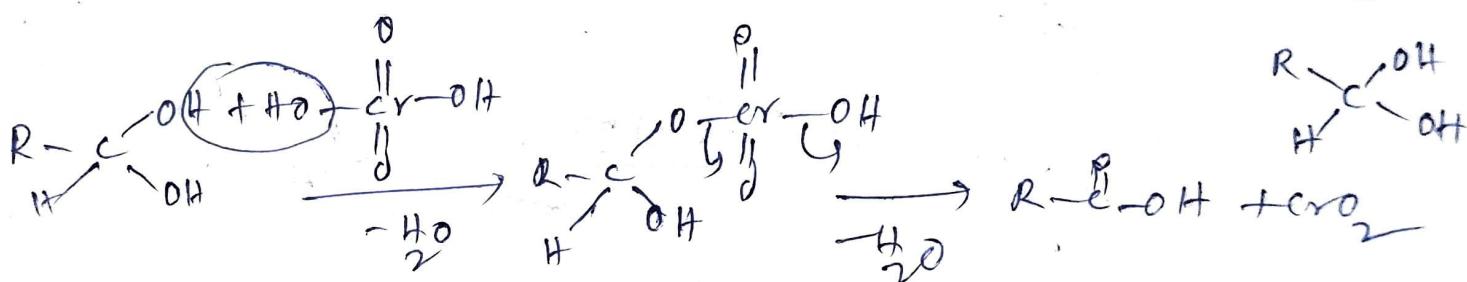
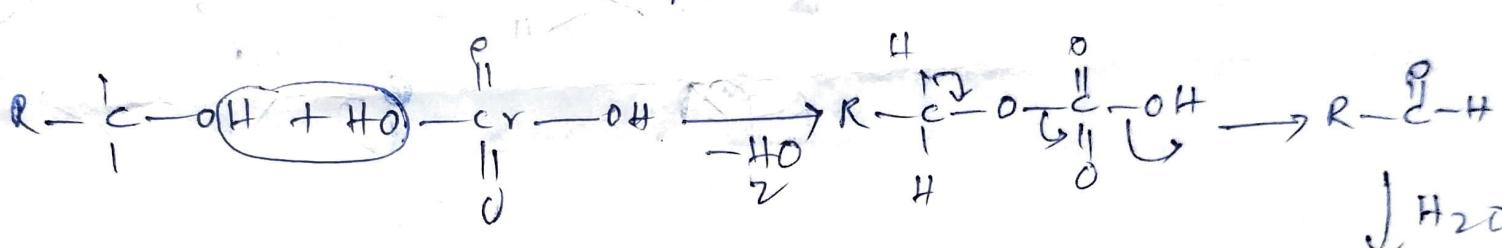
oxidation reactions

Quesn

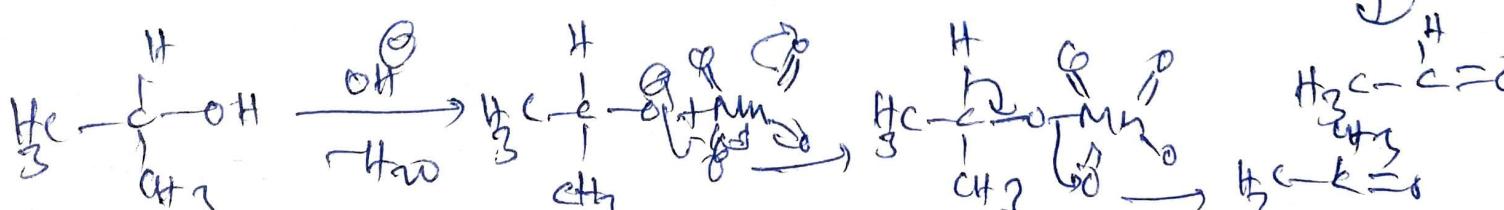
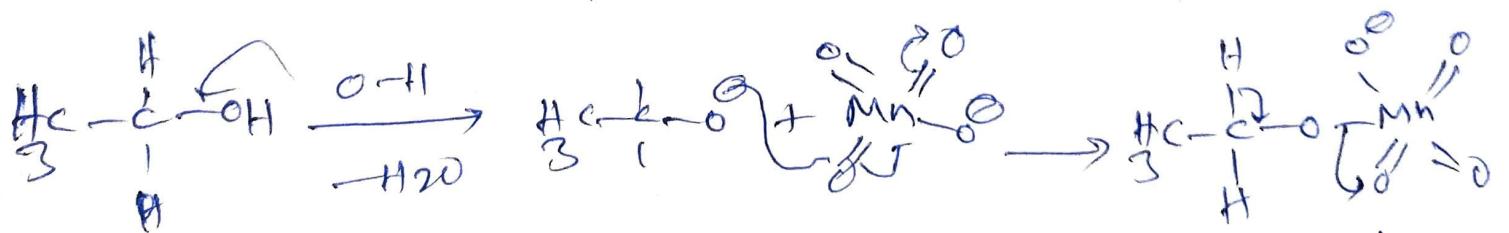
KMnO₄

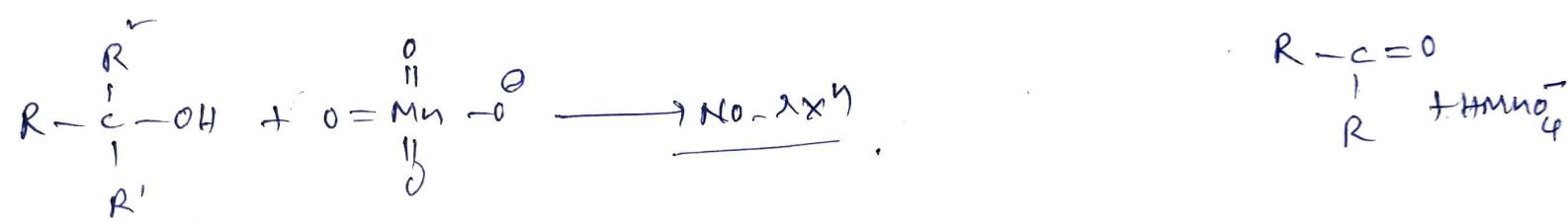
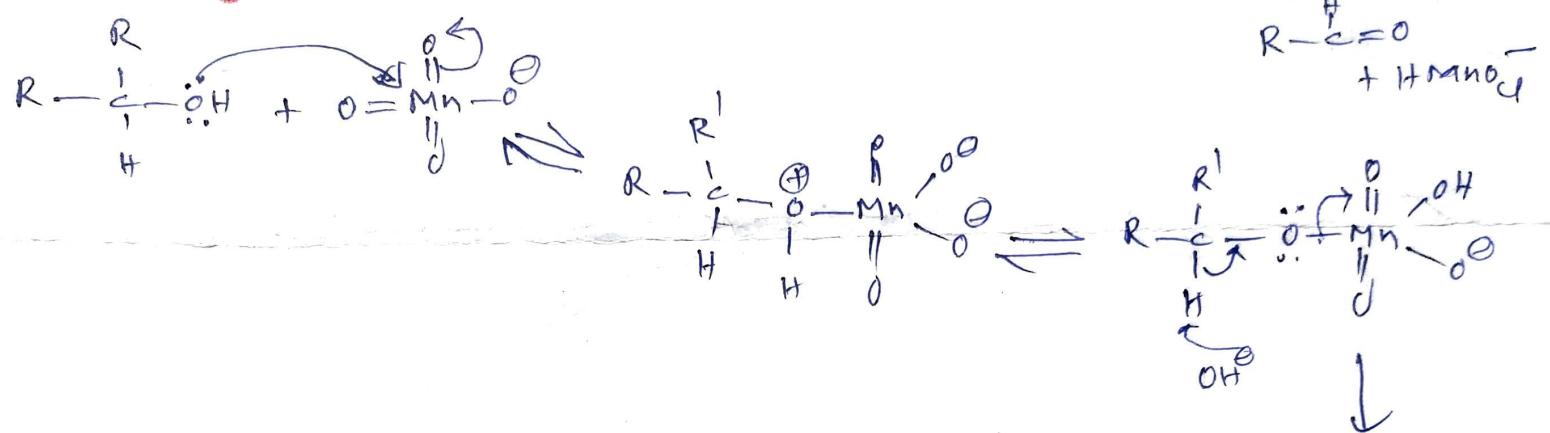
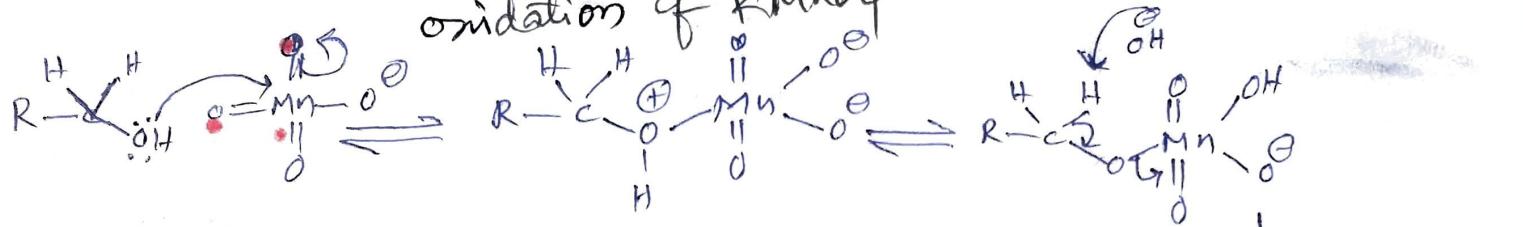


Johner - $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}_4 + \text{Ac}$
Sarett - $\text{Cr}_2\text{O}_7^{2-} + \text{Hg} + \text{Dm}$

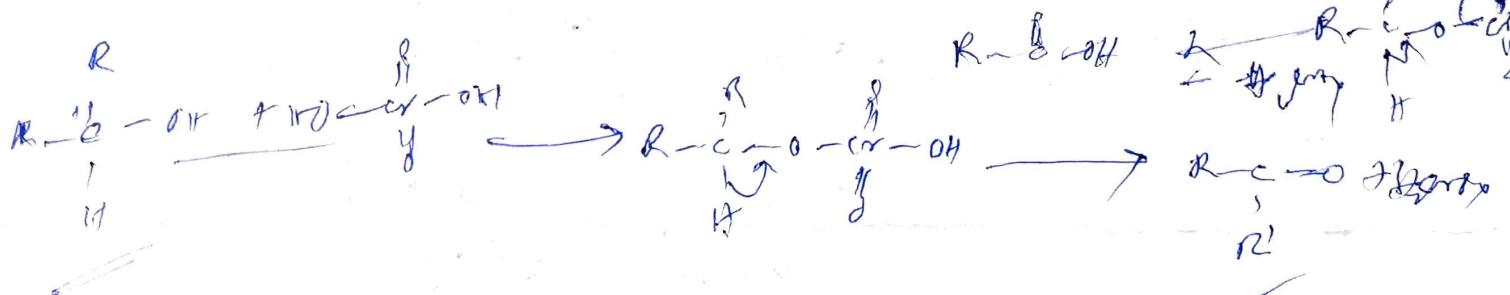
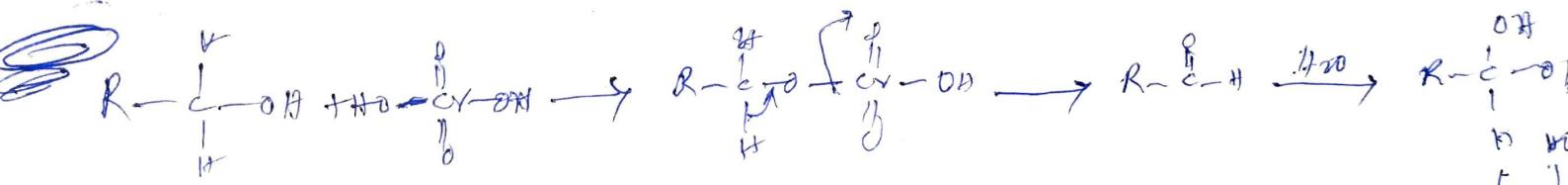


chromate ester

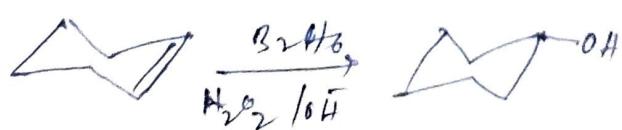
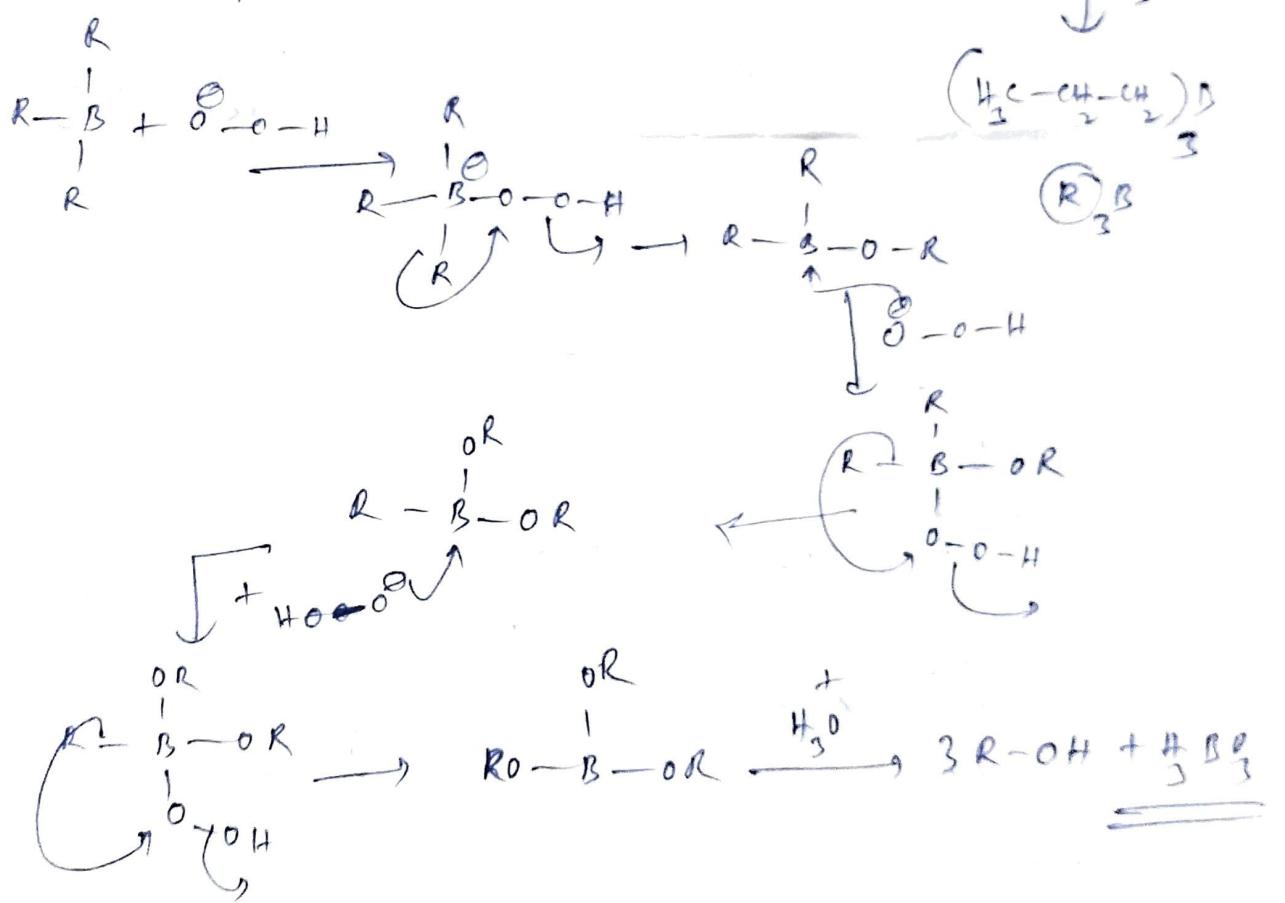
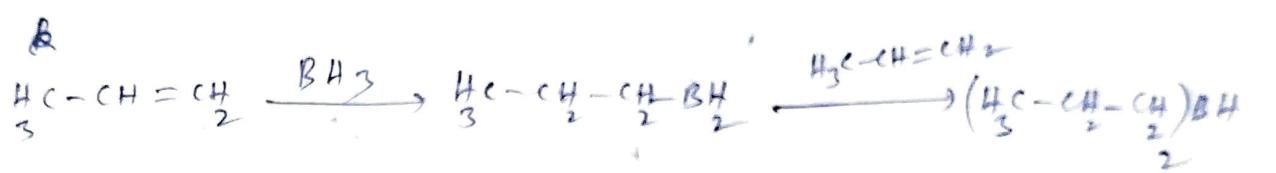
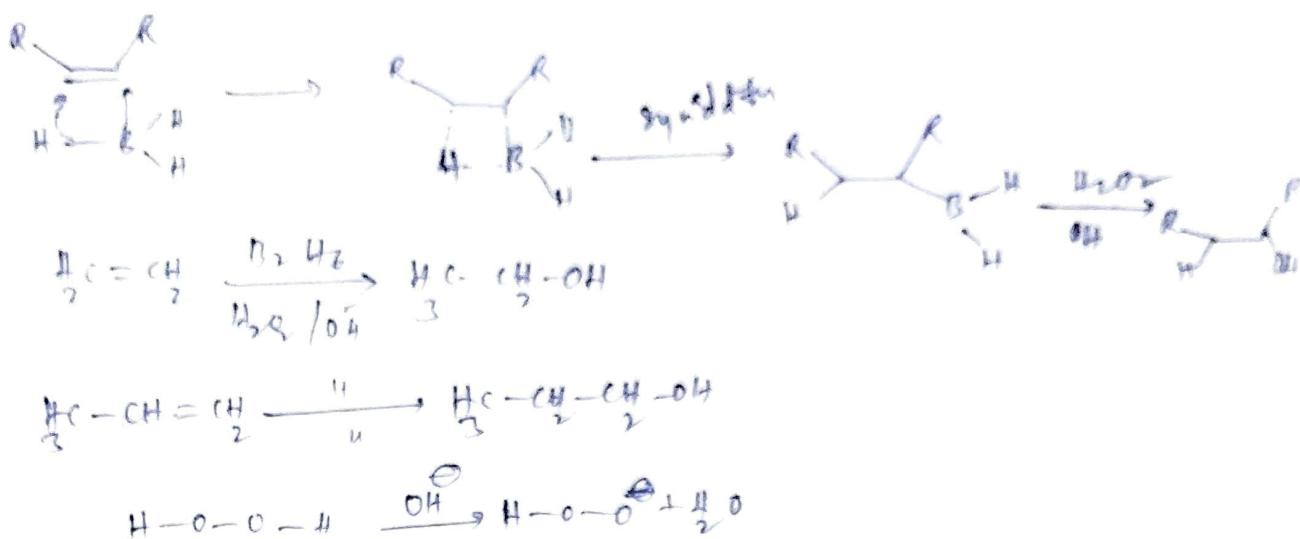


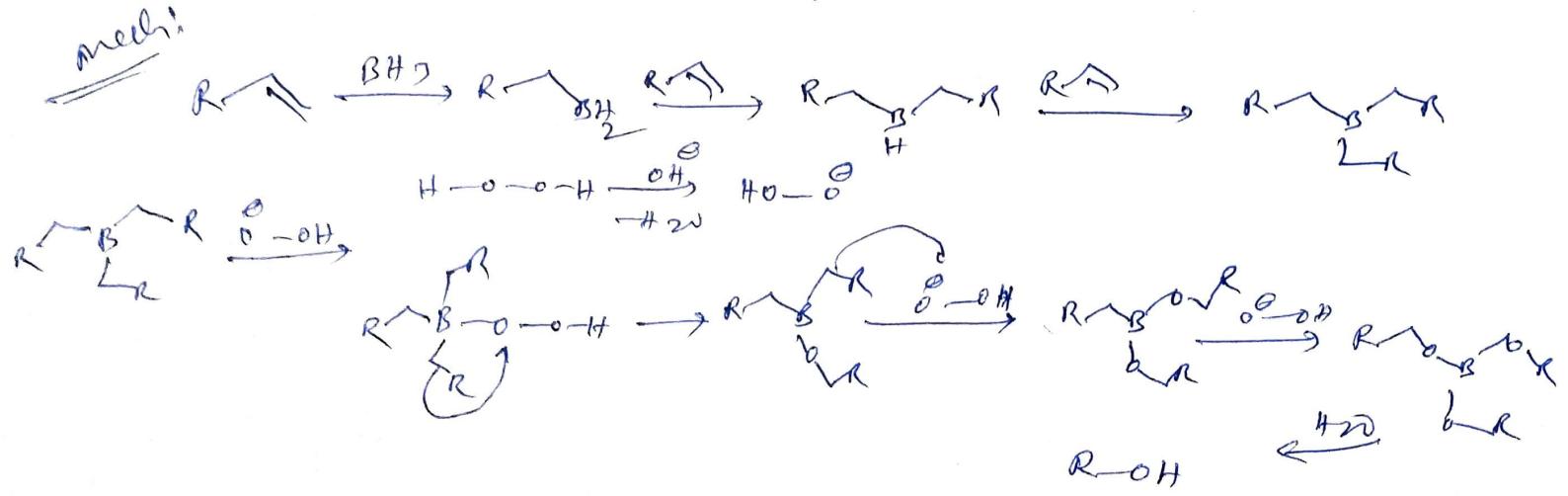
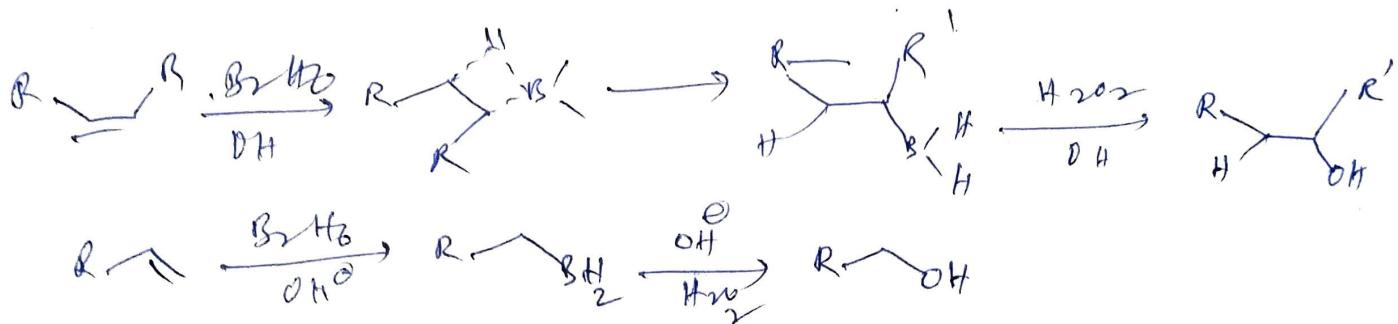
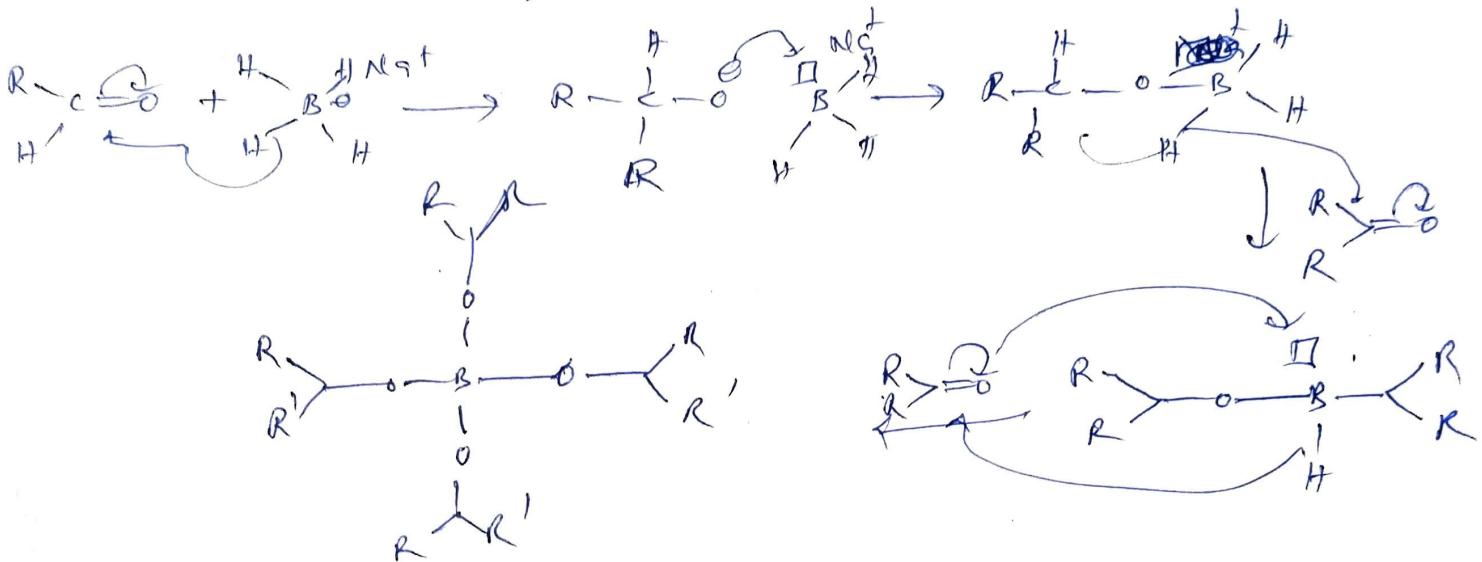
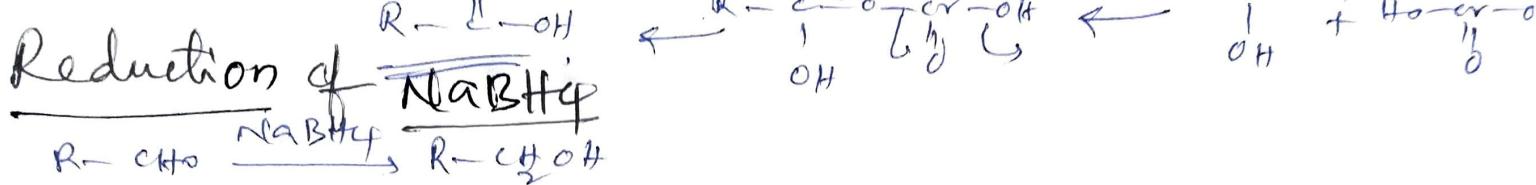


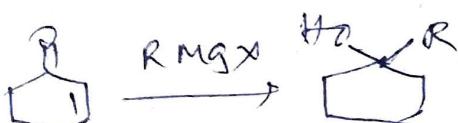
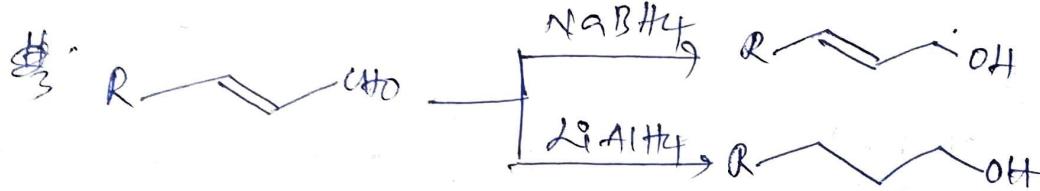
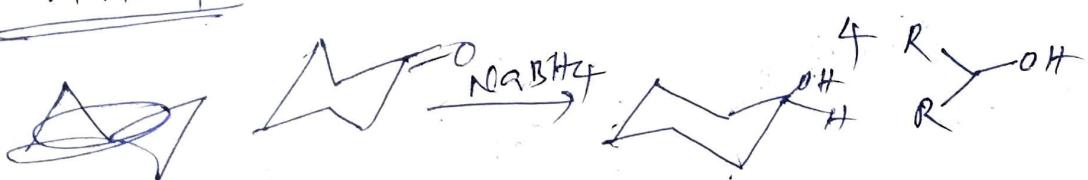
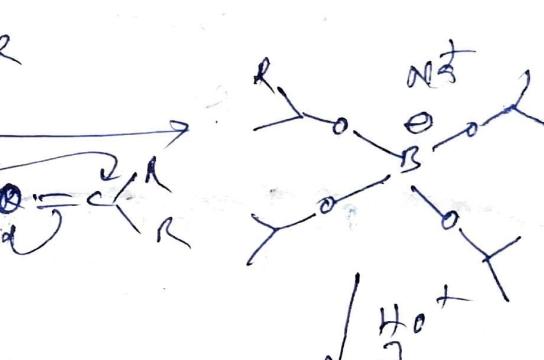
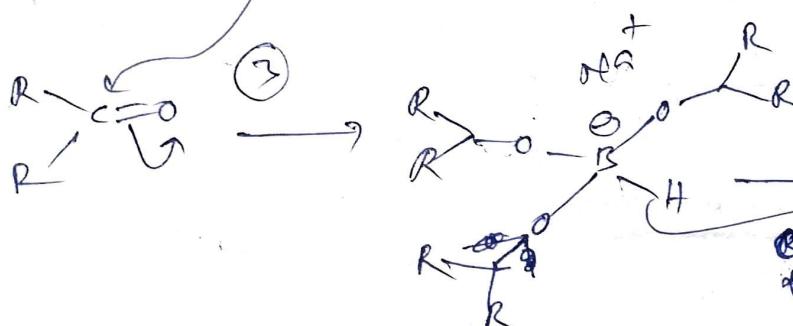
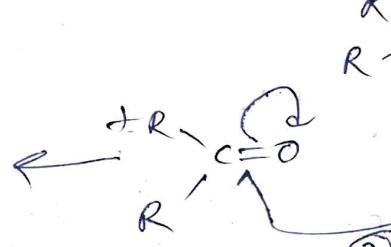
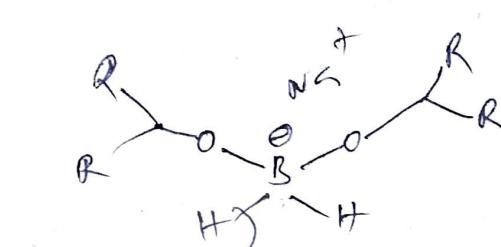
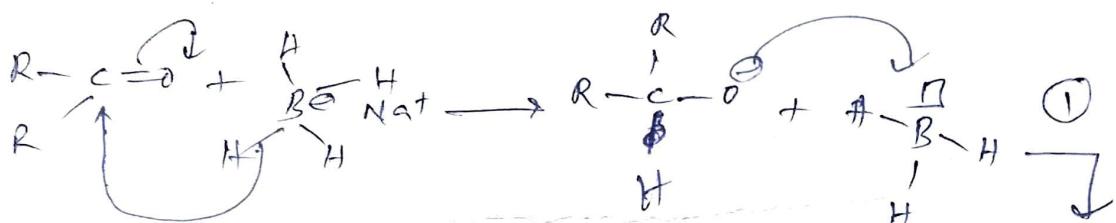
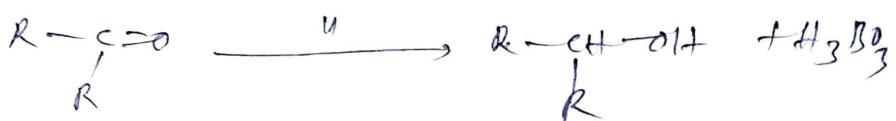
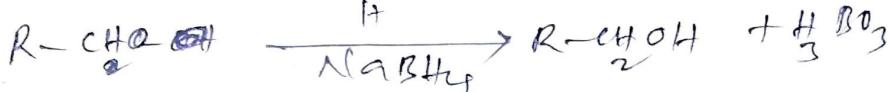
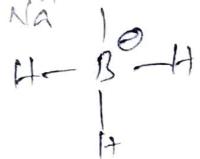
Oxidation with chromic acid



Hydrogenation of olefins







Stereochemistry

Stereo = solid form + volume

Stereochemistry describes physical, chemical and biological properties of molecules with respective to spatial position of groups.

Majority of organic molecules are 3D molecules.

It is not possible to directly show 3D molecules, objects or

2D plane. Some manipulations (or) changes

To show 3D molecule in 2D plane some manipulations (or) changes
in 3D molecule required.

i) wedge representation

Centre atom of molecule connected to different groups with

three different types of covalent bonds.

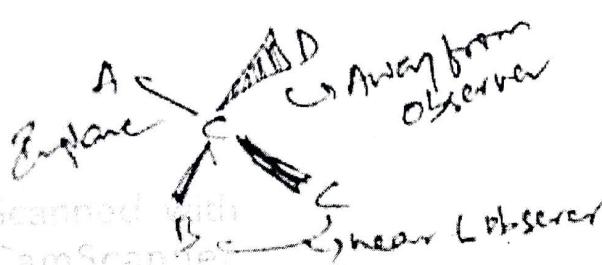
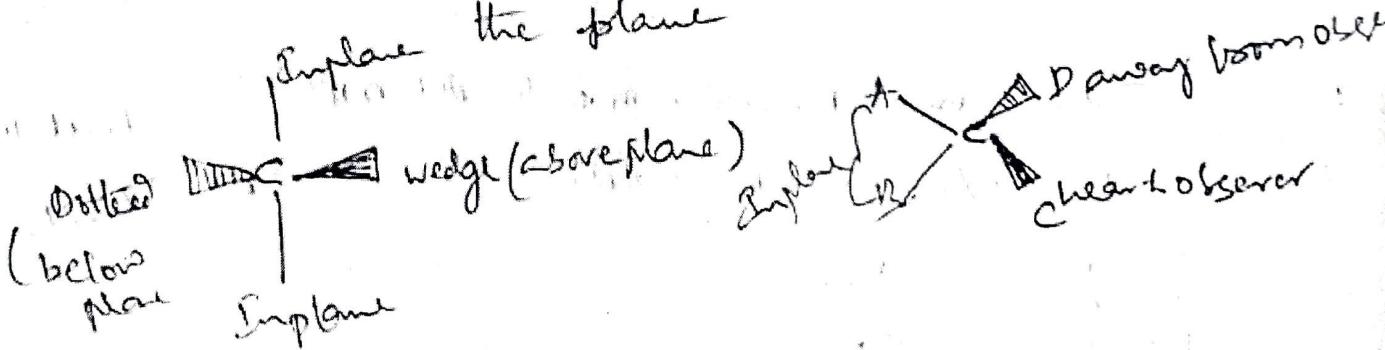
Three different types of covalent bond - represents in the plane

a) — Normal covalent bond - represents in the plane

b) ► Heavy (or) thick covalent bond above the plane which
are near to observer (or) in front of plane

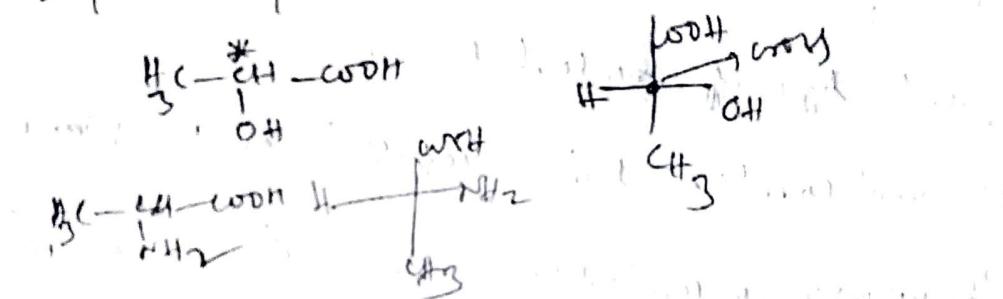
c) / \ / \ / \ (or) - - - Broken or dotted C-B represent - below the
plane (or) away from observer (or) behind

the plane



Fischer projection

- Every F.P. have one vertical line, one or more than vertical line.
- meeting point of vertical and horizontal line is called cross. Cross represents centre atom.
- Arrange the max nof carbonyl on the vertical line
- Keeping highly oxidized carbon at the top vertical line
- In Fischer projection mutual spatial exchange of any three groups is not free. Producers identical one
- only one pair of opt. mutual exchange produces enantiomers
- In Carbohydrate chemistry F.P. very much useful to explain physical and chemical properties.



Newman projection

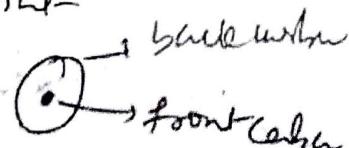
the molecule along C-C bond axis

Center carbon near to observer is the front atom (or) carbon

Center carbon which is away from observer is back carbon

Front carbon must be shown with dot on point

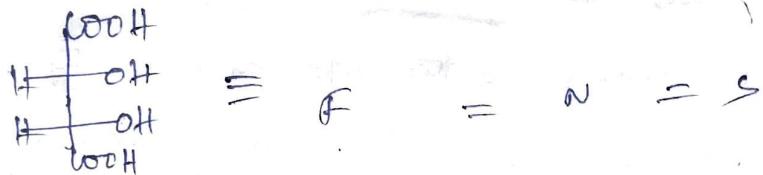
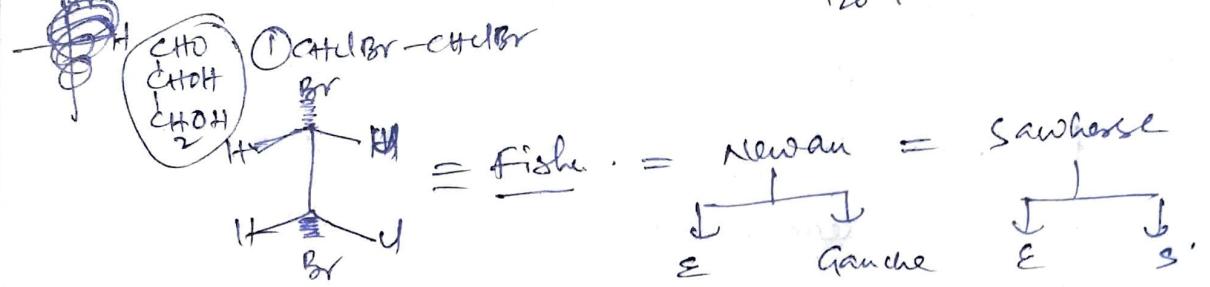
Back carbon shown with circle



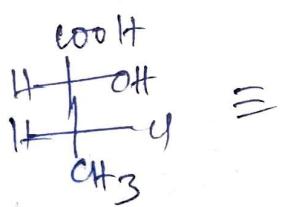
0° - Eclipsed

60° - Gauche

120° - anti



Tartaric acid

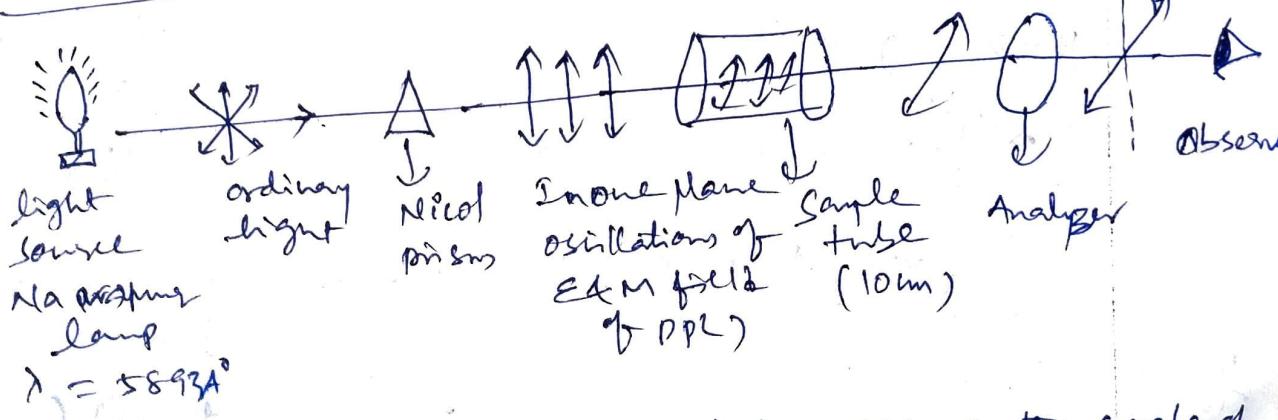


Optical activity

the phenomenon of rotation of the plane of ~~of~~ the polarised light in (+) (or) (-) direction that compound is said to be optically active (or) chiral compound.

Polarized plane light: the light which is confined to a single plane (PPL); the light which is confined to a single plane is known as PPL

Measurement of polarimeter:



Polarimeter; the instrument used to measure the angle of rotation of the plane of polarised light by the chiral centre is called polarimeter.
→ It is used to determination of optical isomers of d (or) l type polarimeters is called.

Polarimeter consists of light source, polarizer, sample tube, analyzer etc. Monochromatic light (lambda) is used to measure the optical activity.

Sample (solvent) is first placed in the path of half light beam and adjust the analyzer to establish a half dark & half white field. This setting is called zero of optical rotation. Now place the test sample in sample tube, the no of degrees that analyzer must be turned to establish the same field corresponds to the optical activity.

In this PPL is rotated clockwise direction is said to be (+) (+) where PPL rotates anti clockwise direction is said to be (-) (-).

$$\text{Specific rotation} [\alpha]_D^t = \frac{\alpha \times 100}{l \times c}$$

$l = 10 \text{ cm}$

$\alpha =$

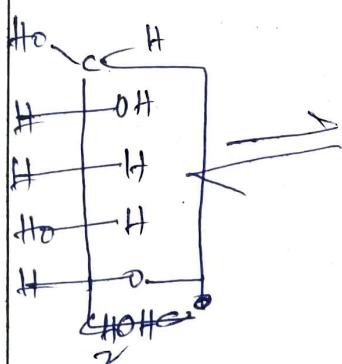
~~l = 10 cm~~

$$(\text{or}) \cdot \frac{\alpha}{l \times c}$$

$c = \text{conc}$

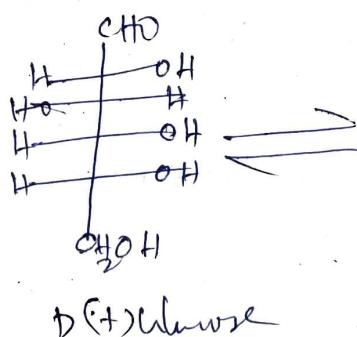
$t = RT(27^\circ\text{C})$

$\alpha = \text{observed angle of rotation}$

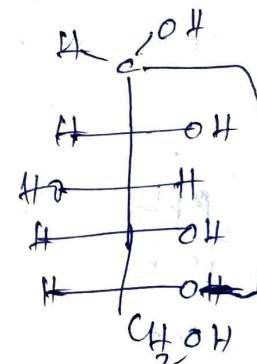


B-D (+) glucose

$$[\alpha]_{H_2O}^{25} = +19^\circ$$



D (+) glucose



D (-) glucose

$$[\alpha]_{H_2O}^{25} = -113$$

$[\alpha]$ depends on

- Nature of substance
- Wavelength of light (λ)
- Conc of soln (1gr/1ml)
- Nature of solvent
- Path length (l) = (10cm)

$$\frac{\Sigma \alpha}{10} = 0.5 \text{ g/mol}$$

$$\text{Molar rotation} = \frac{[\alpha] \cdot \text{molar}}{100}$$

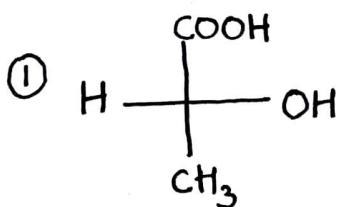
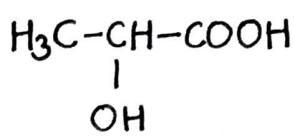
Sol: 5gm of C.P sample is taken in 10cm polarimeter tube. Conc of soln is 5gm/100ml. Temp of the medium.

$$\text{Observed optical rotator } +0.25^\circ \text{ Calculate specific rotation } [\alpha]_D = \frac{0.25}{1 \times 0.5} = 0.5$$

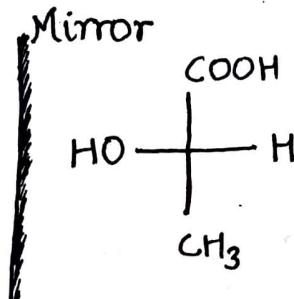
Optical isomerism of molecule having one chiral center

Optical isomerism of lactic acid:-

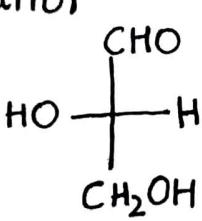
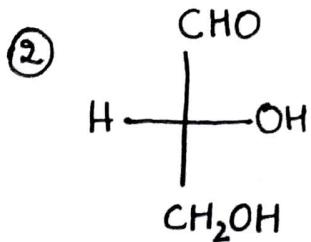
Lactic acid contains one asymmetric centre carbon atom and exist in two optical active forms, which are related to each other as mirror images and one non superimposable.



d(+)-lactic acid



l-(+)-lactic acid



Calculation for optical isomers of one asymmetric carbon = $2^n = 2^1 = 2$

the above two isomers are called $\therefore n=1$
Enantiomers.

Enantiomers:-

Non-superimposable mirror images are called Enantiomers.

Properties:-

Enantiomers have same physical properties like MP, BP, density, solubility and dipole moment.

→ It has same chemical, thermodynamic and spectroscopic property (IR NMR UV)

2

M

- these are optically active.
- They rotate PPL in opposite direction but to the same extent.
- They differ in biological activity.

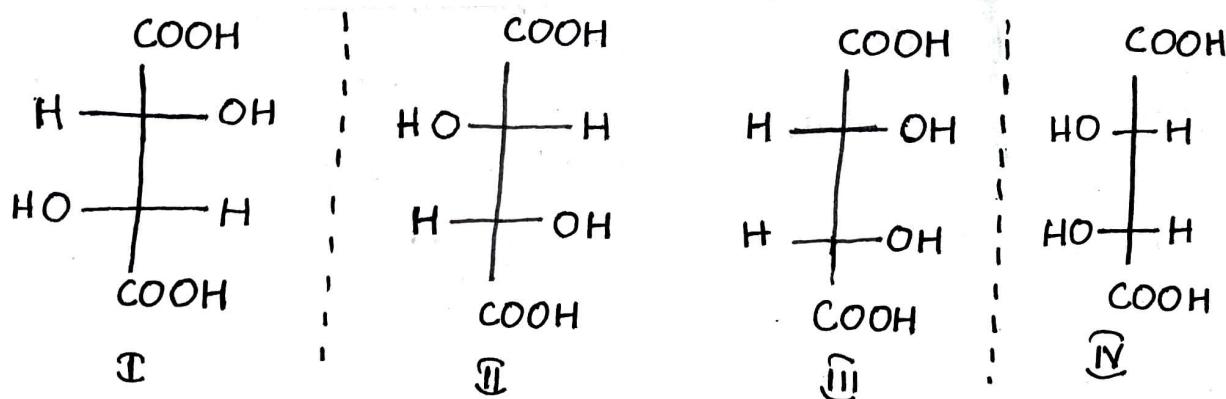
Diastereomers :-

The stereo isomers that are non-mirror images are called diastereomers.

(or)

the isomers that are non superimposable and non mirror images of each other are called diastereomers.

Ex:- Tartaric acid



I & II enantiomers

I & III } → diastereomers
II & IV }

III & IV → mesocompounds
(Homomers)

Properties:-

which are differ in physical properties.

→ These have same chemical properties but differ in rate of rxtn.

→ They differ in specific rotation.

Symmetry of Elements

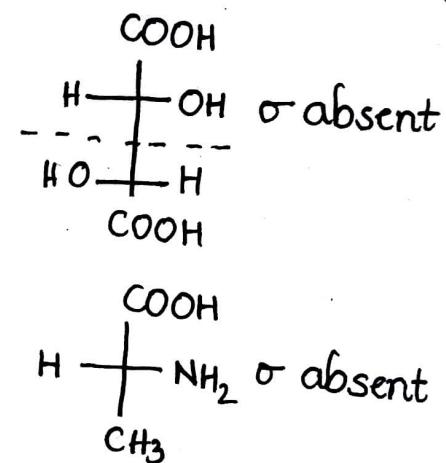
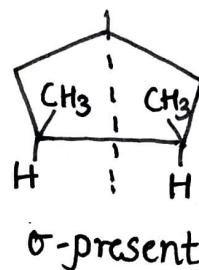
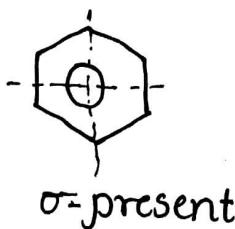
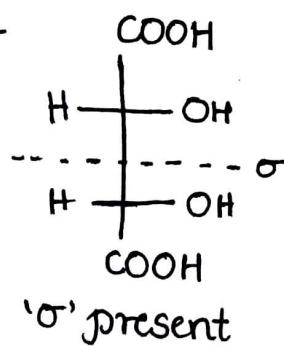
- ① plane of symmetry (σ)
- ② centre of symmetry (i)
- ③ axis of symmetry (C_n)

Plane of symmetry:-

It is defined as a plane which bisects the molecule in two equal and identical symmetrical halves is known as plane of symmetry.

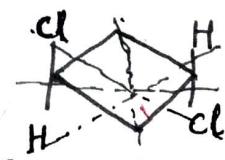
- The molecule having plane of symmetry are symmetric molecule and are optically inactive.
- the molecule having no (or) one dissymmetric and are optically active.

Ex:-

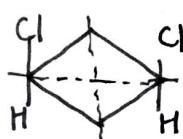


Centre of symmetry (i):-

If all straight lines that can be drawn through the centre of all the molecule meet identical atoms at distance from the centre.



i) present

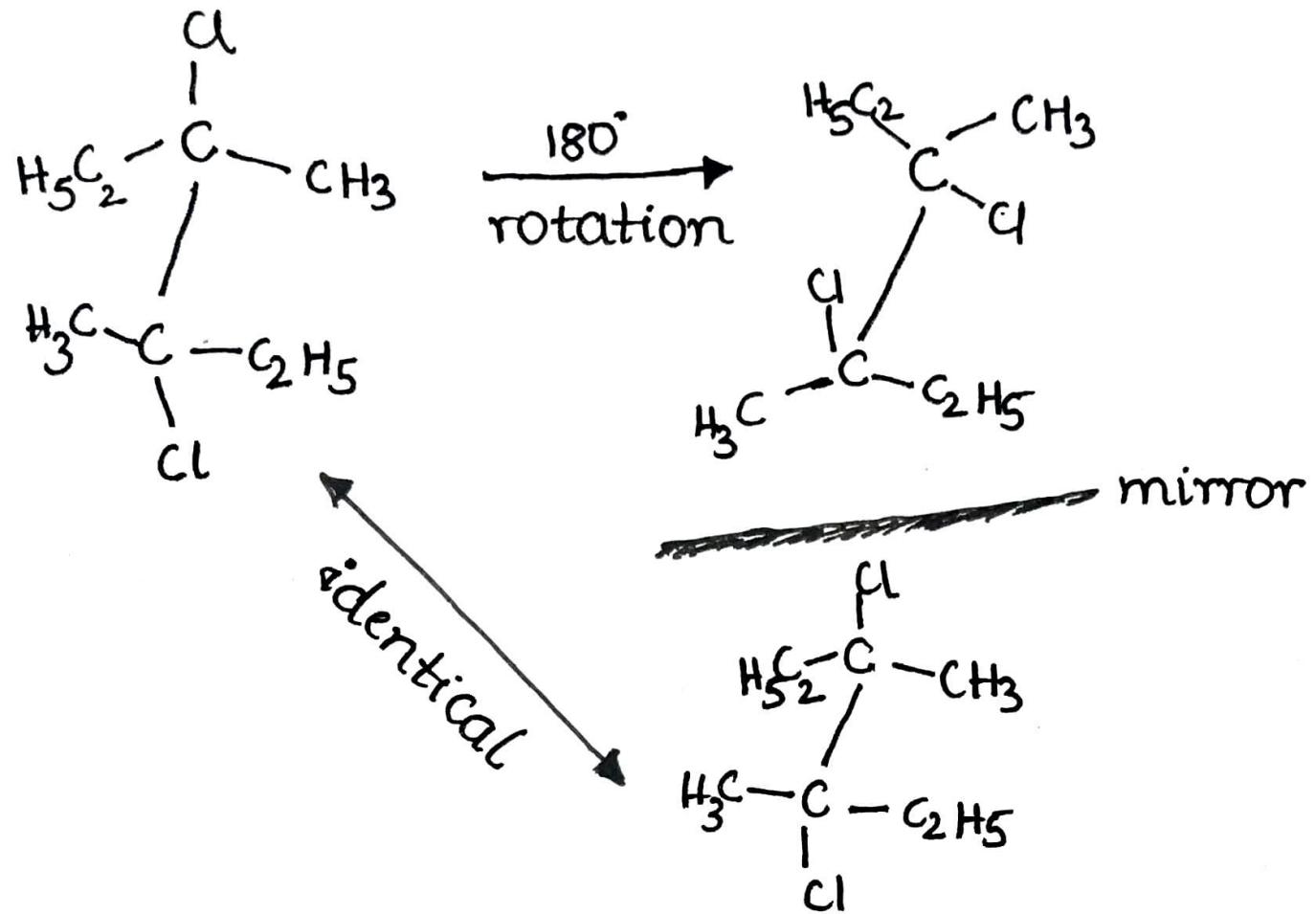


ii) absent

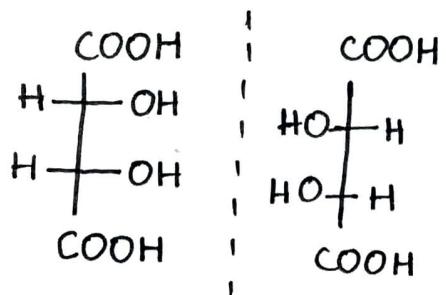
1,4 dichlorocyclobutane

(5)

Axis of symmetry:- It is defined as axis through which the rotation of the molecule by a certain angle results in an arrangement with initial molecule.



Meso compounds:-

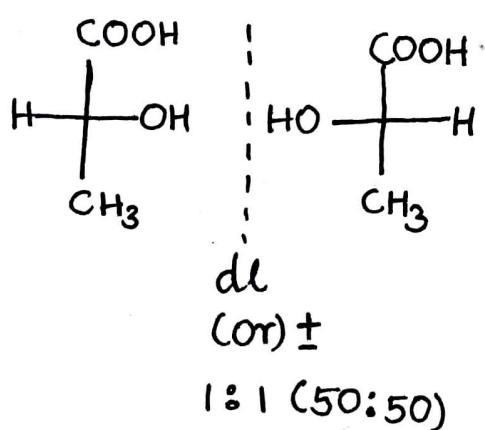


Defined on the compounds containing two (or) more chiral carbon centre, and are optically inactive due to the presence of the plane of symmetry.

→ Optical inactivity of meso compounds is due to Internal compensation. In such compounds the rotation due to one half of the molecule is cancelled by rotation due to another half of the molecule in opposite direction.

Racemic mixtures:-

The equimolar mixture of two enantiomers are called R.M.



Ex:- $\text{S}^{\text{N}}\text{1}$ rxtn.

Separation of enantiomers are called racemic modification.

Lactic acid $\xrightarrow[\text{(R.M)}]{\text{enzyme catalyst}}$ $\xrightarrow[\text{optical pure}]{(+)} \text{lactic acid}$

Symmetry of Elements:-

A molecule which can be divided into two equal halves through their imaginary axis, plane (or) centre is called symmetry.

Configuration: Determination of spatial positions of groups or atoms at asymmetric centre is called as configuration

configuration

Absolute

Relative

Eg: R,S Notation

only at one asymmetric centre orientation of groups in space will be fixed.

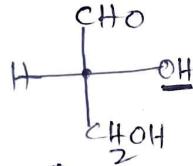
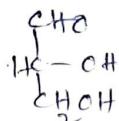
Eg: D,L Nomenclature

Two or more than two asymmetric centres taken into consideration

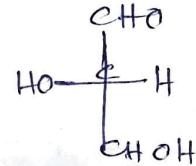
① D,L-Configurations:

- This configuration mainly applicable for Fischer projections
- Highly oxidised groups should be top on the vertical line
- Bottom is preferably carbon / Alkyl groups.
- More electronegative groups lie on right side is called - "D"
- Where as ~~more~~ more E.N group on left side is called - "L"

Eg: Glyceraldehyde

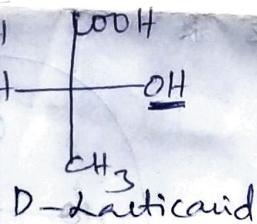
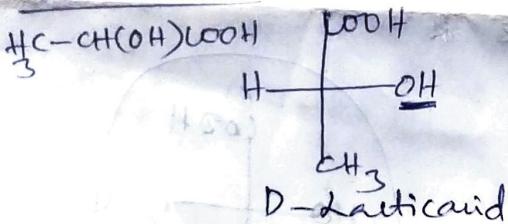


D-Glyceraldehyde

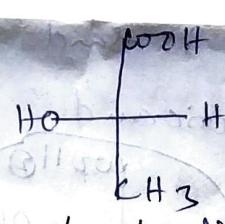


L-Glyceraldehyde

Lactic acid



D-Lactic acid



L-Lactic acid.

Limitations:

- D,L Nomenclature is not applicable, when two electronegative groups on the asymmetric carbon
- D,L Nomenclature is not possible to write cyclic structures

② R,S Nomenclature:

- It is proposed by Cahn, Ingold & Prelog
- It is widely used after asymmetric carbons

R ⇒ Rectus (clockwise) right

R ⇒ Sinister (Anticlockwise) left.

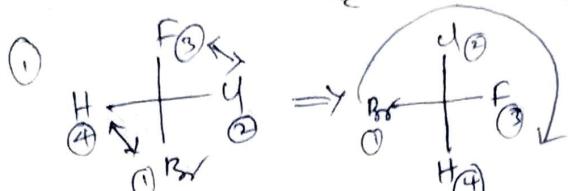
Sequence-rules: The four different groups (or) atoms attached to asymmetric carbon are arranged in priority order.

- Priority of atoms are given with respect to At·No, Afwt.

→ If first atoms are same, give the priority to second atoms

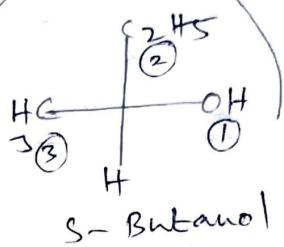
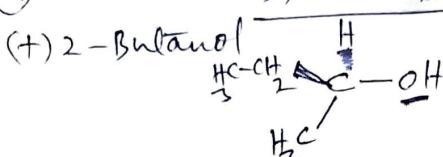
- If second atom is attached by double bond (or) triple bond are

considered as two (or) three single bonds

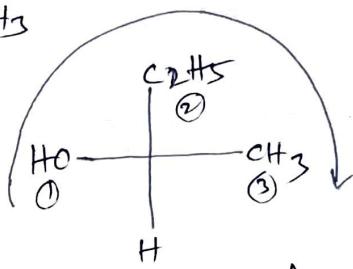
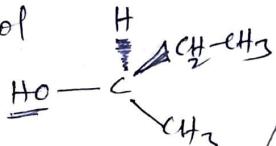


R-configuration

② Butanol D,L to R,S



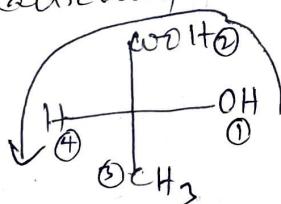
(-) 2-Butanol



③

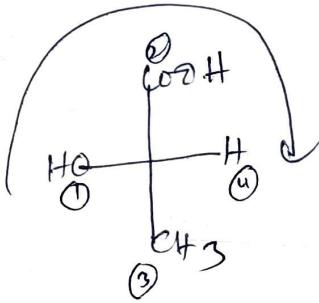
If least priority group present on horizontal line, the clockwise direction is said to be "S" and anti-clockwise direction is said to be "R"

Ex: Lactic acid



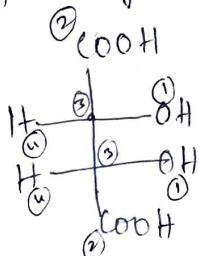
④

R-Lactic acid

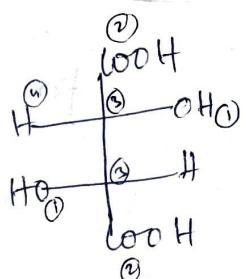


S-Lactic acid

④ If a compound contain two chiral centres, the priority as given below.



2R, 3S Lactic acid

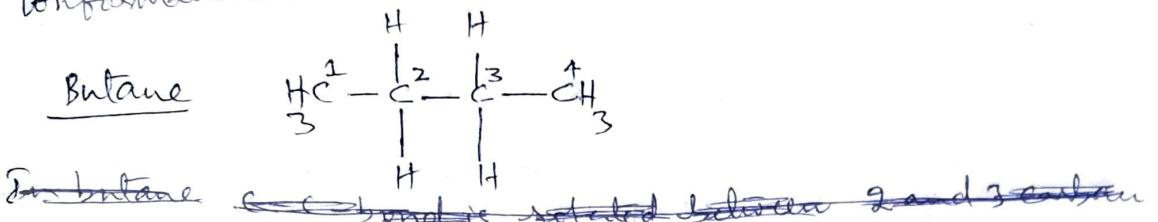


2R, 3R - Lactic acid

Conformational Analysis of n-Butane

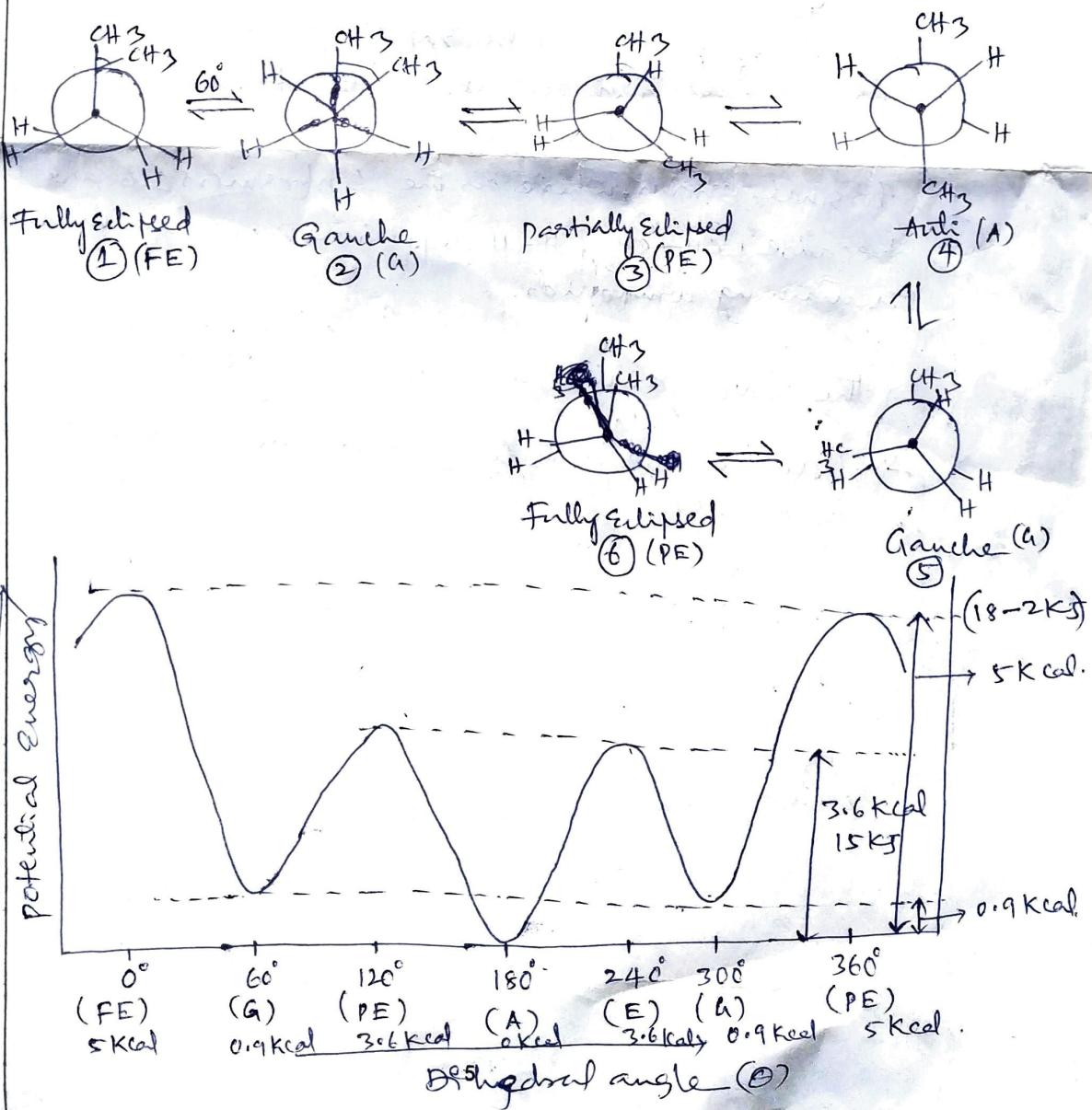
Conformational isomers: The isomers which are obtained due to the rotation of groups (or) atoms around single bond in space are known as conformational isomers.

Conformational isomers are also called (conformers) rotamers.



In butane carbon-carbon free rotation is permits the atoms of 2 and 3 carbons with respect to each other along their bond axis without breaking the bond.

If one CH_2CH_2 -group is kept stationary and other CH_2CH_2 group is allowed to rotate through 360° in six steps, then following six conformations of n-butane are obtained.



Stability: Anti > Gauche > Eclipsed > Fully eclipsed

(4)

(2,3)

(3)

(1,6)

→ conformations of molecule may not have same energy, and Energy for conformations are calculated in Kcal/mole (or) kJ/mole

→ Energy $\propto \frac{1}{\text{Stability}}$ & stability $\propto \frac{1}{\text{Strain (torsional)}}$

→ least energetic anti form (4) is sturtest form

→ Gauche forms (2,3) are slightly less stable than Anti form and the Energy difference between them is 0.9 kcal/mole

→ Fully eclipsed forms (1,6) are less stable than remaining forms due to the presence of torsional strain

Torsional strain: Repulsive interactions between bonds of adjacent atoms which leads to restrict of rotation.

Dihedral angle: (θ) Degree of rotation about C-C bond in a specific conformation of the molecule is called dihedral angle

→ stability of anti can be explained by torsional strain and dihedral angle and energy; In this form $\begin{smallmatrix} 2 \\ \text{CH}_3 \end{smallmatrix} - \begin{smallmatrix} 3 \\ \text{CH}_3 \end{smallmatrix}$ dihedral angle is 180° and it has zero potential also ~~it is~~ it is free of torsional strain, whereas the conformers 1,6 are unstable because $\begin{smallmatrix} 2 \\ \text{CH}_3 \end{smallmatrix} - \begin{smallmatrix} 3 \\ \text{CH}_3 \end{smallmatrix}$, H-H repulsion forces are more than remaining compounds.

→ the two gauche conformations are dynamic enantiomers

→ Gauche and anti conformers are dynamic diastereomers.