

# CHEMISTRY ASSIGNMENT

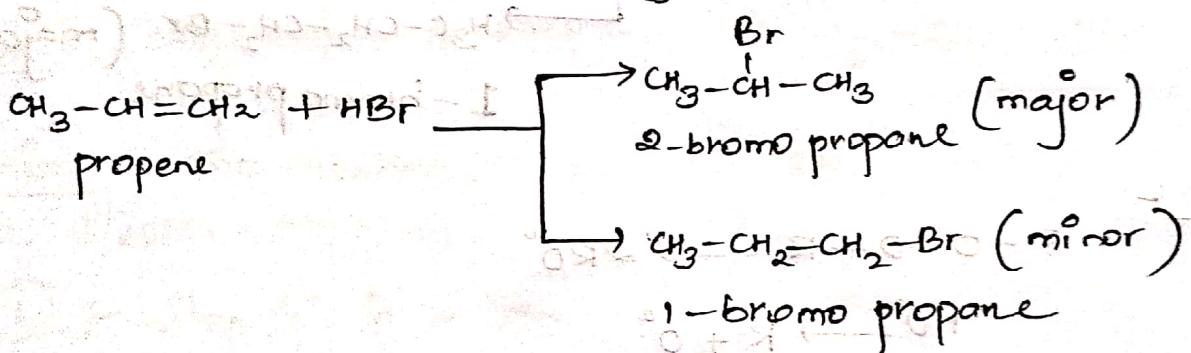
- ① Write Markovnikov's and anti-Markovnikov's rule with suitable examples.

Markovnikov's and anti-Markovnikov's rule is based on electrophilic addition reaction mechanism, and anti-Markovnikov's rule is based on free radical addition reaction mechanism.

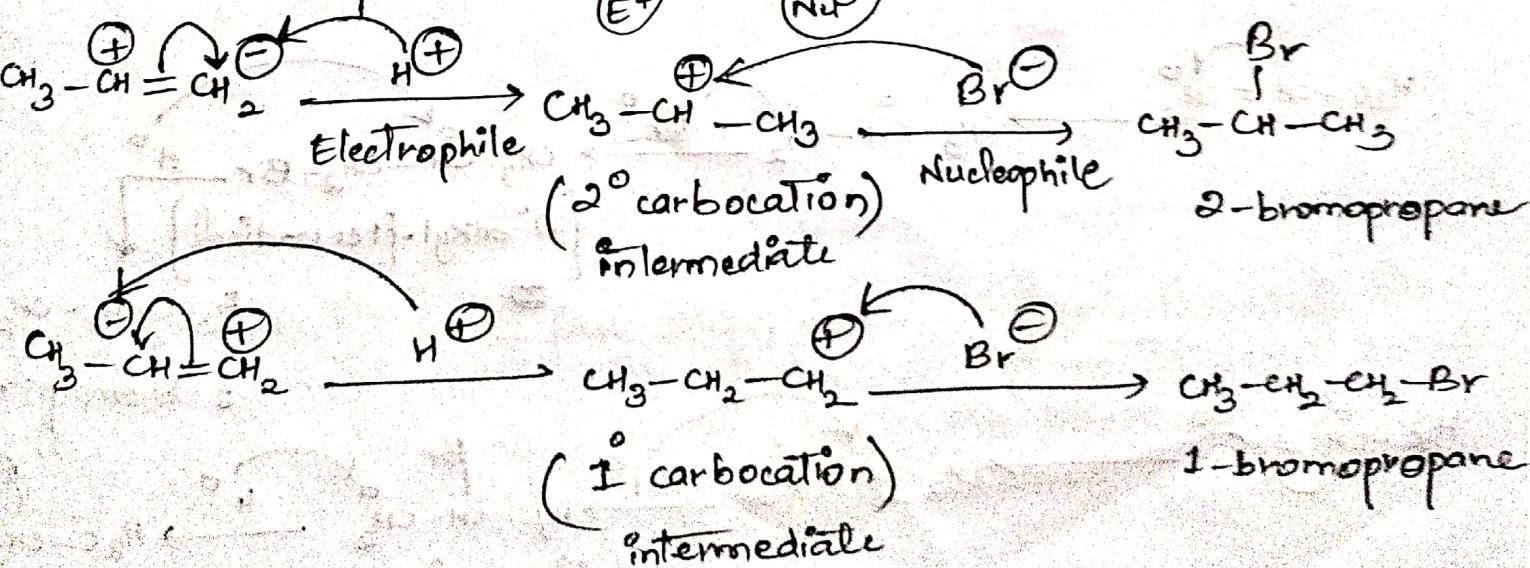
## Markovnikov's Rule

Markovnikov's rule predicts the regiochemistry of  $HX$  in addition to unsymmetrical alkenes.

The halide component of  $HX$  bonds preferentially at the more highly substituted carbon, whereas the hydrogen prefers the carbon which already contains more hydrogens.

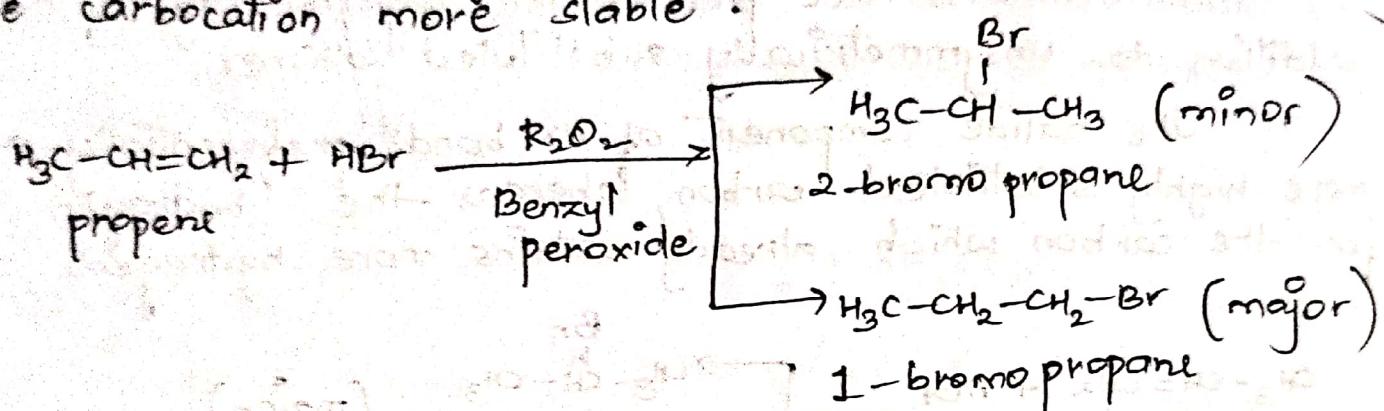


Mechanism :-  $\text{H}-\text{Br} \rightarrow \text{H}^+ + \text{Br}^-$  (heterolysis)

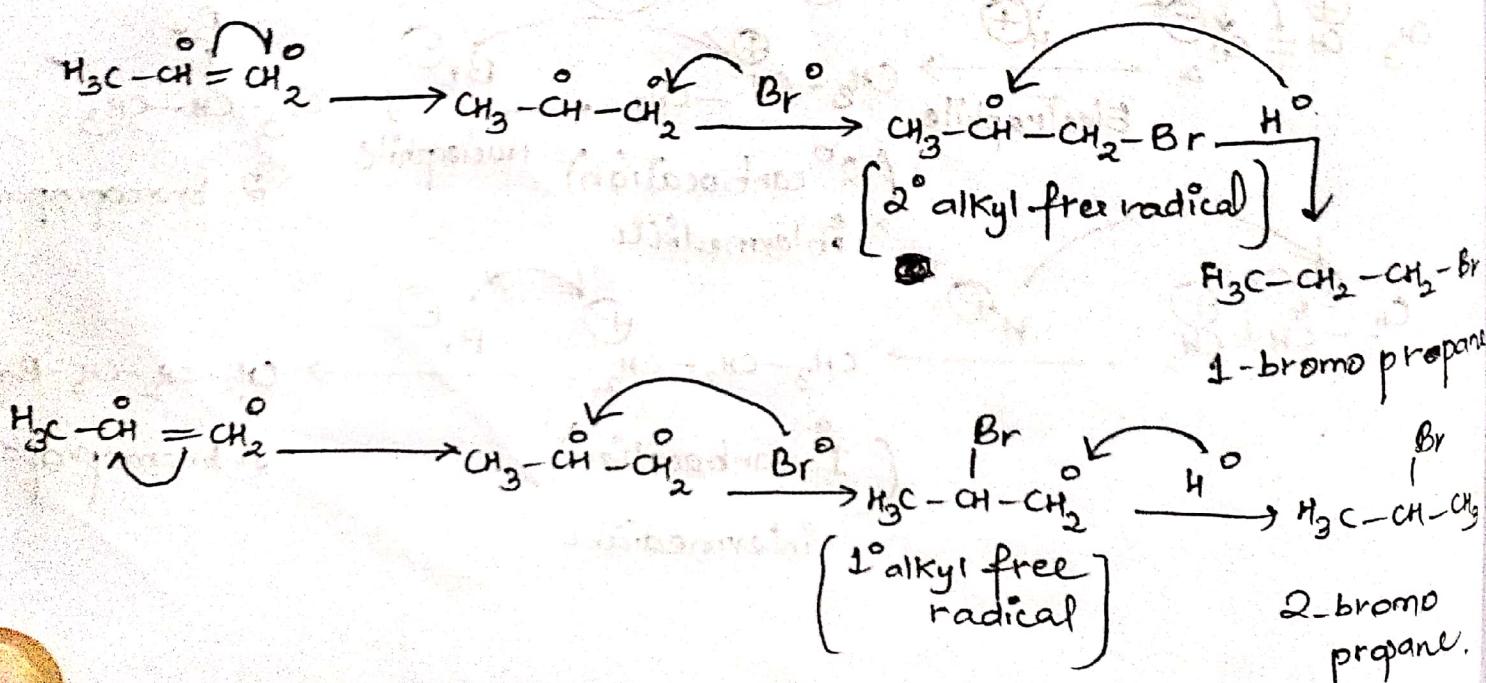
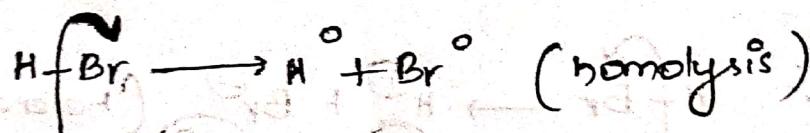


## Anti-markovnikov's rule :-

Anti-markovnikov's rule describes the regiochemistry where the substituent is bonded to a less substituted carbon, rather than the more substituted carbon. This process is quite unusual, as carbocations which are commonly formed during alkene, or alkyne reactions tend to favor the more substituted carbon. This is because substituted carbocation allow more hyperconjugation and induction to happen, making the carbocation more stable.



## Mechanism:-

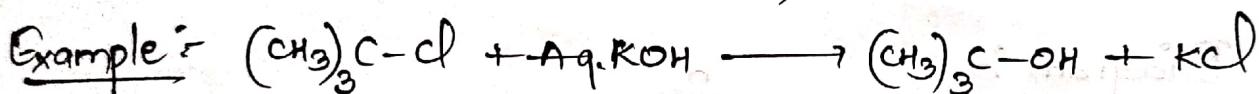
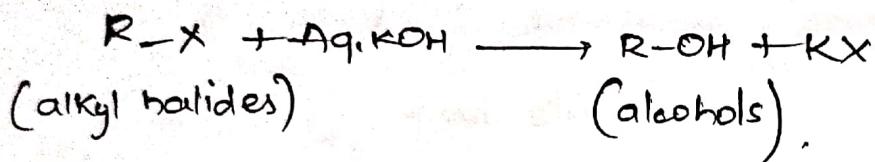


Q) Discuss and explain  $S_N^1$  reaction mechanism and stereochemistry of the reaction.

$S_N^1$  reaction is based on nucleophilic substitution reaction mechanism.  $S_N^1$  is unimolecular nucleophilic substitution reaction. It is commonly seen in tertiary alkyl halides.

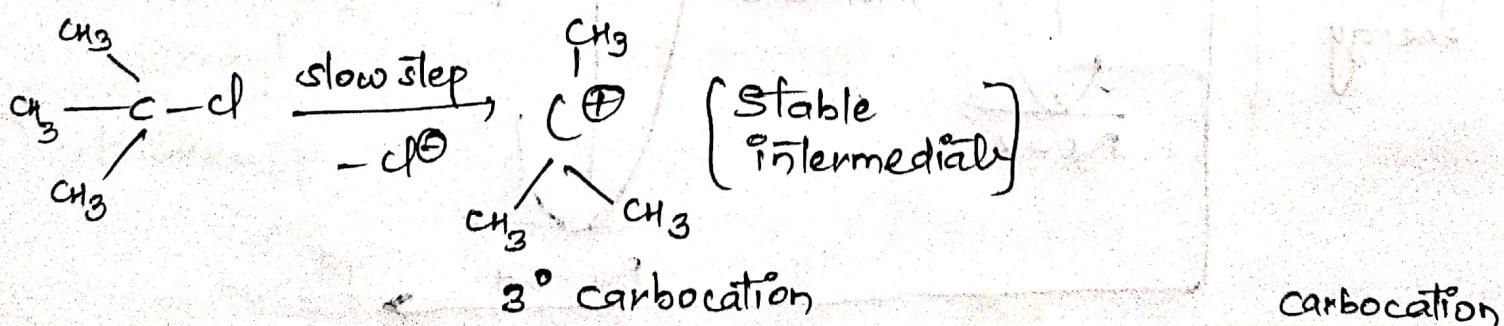
$$\text{Here, } r \propto [R-X] \Rightarrow r = k[R-X]$$

$$r = \frac{dx}{dt}$$

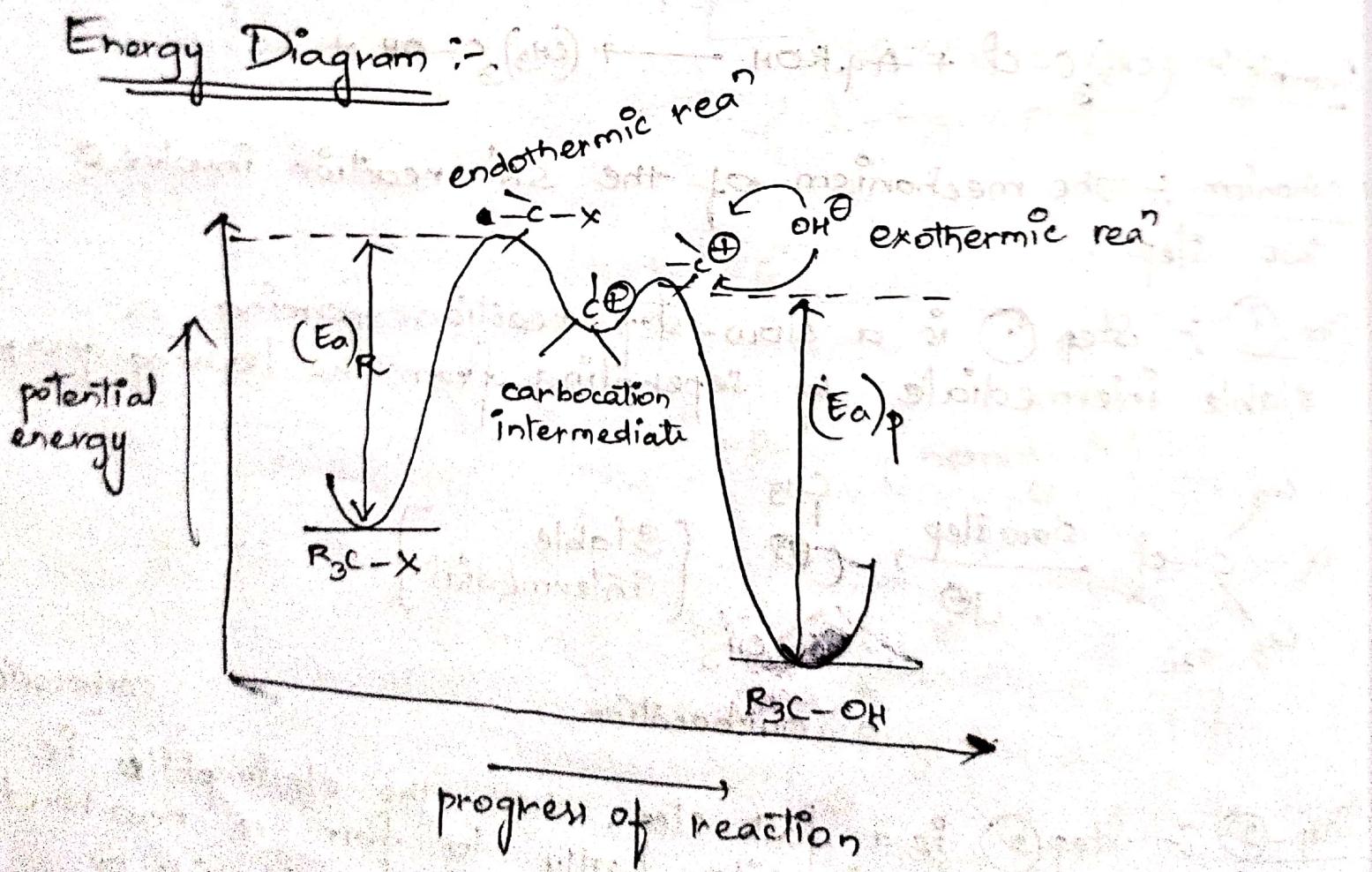
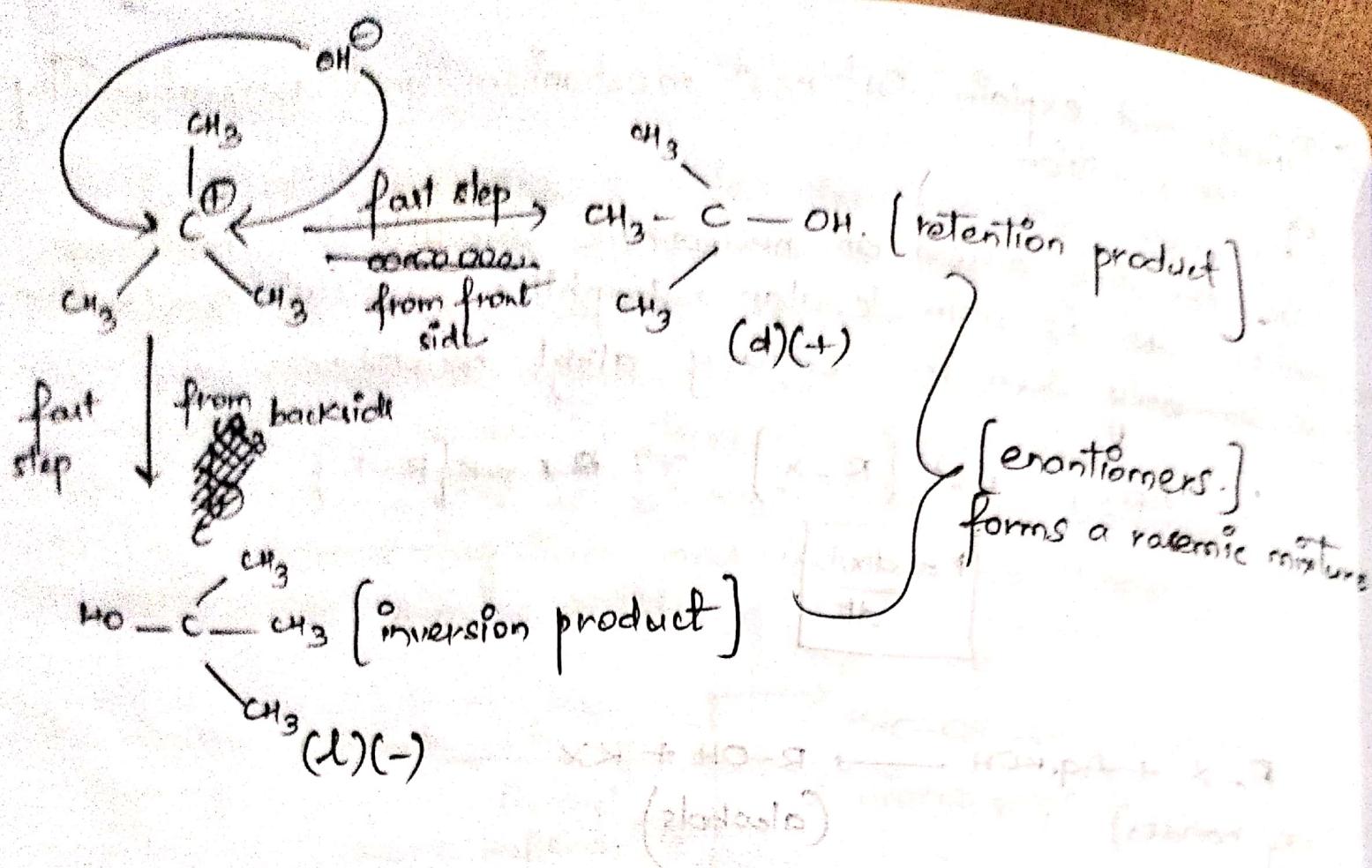


Mechanism :- The mechanism of the  $S_N^1$  reaction involves two steps.

Step ① :- Step ① is a slow-step reaction forming a stable intermediate by separating from the leaving group.

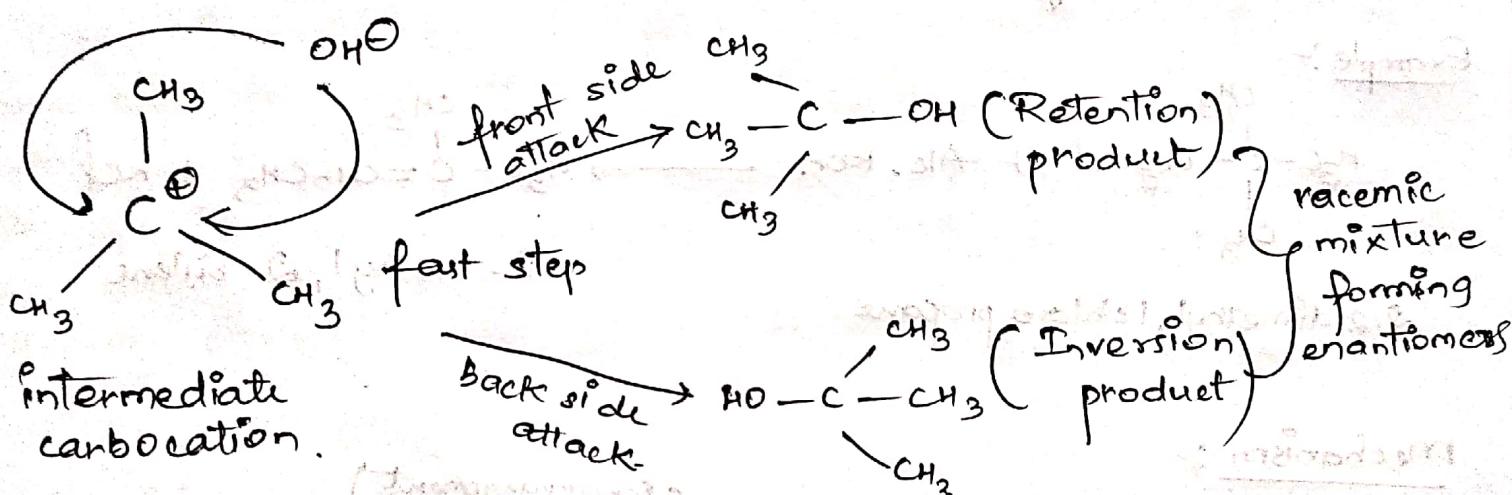


Step ② :- Step ② is a fast step, where the electrophile is attacked by the nucleophile fastly to form a new bond. The nucleophile may attack from the back side or front side which results in racemic mixture.



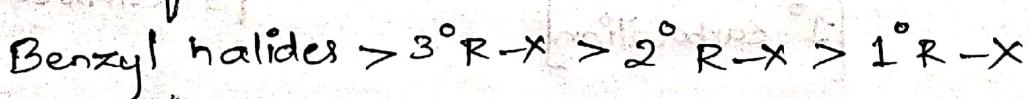
## Stereochemistry of $\text{S}^{\text{N}}\text{I}$ reaction :-

The carbocation intermediate formed in the reaction's rate determining step is an  $\text{sp}^2$  hybridised carbon with trigonal planar molecular geometry. This allows two different ways for the nucleophilic attack, one on either side of the planar molecule. If neither way is preferentially favored, these two ways occur equally, yielding a racemic mixture of enantiomers.

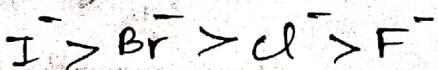


## Factors affecting on $\text{S}^{\text{N}}\text{I}$ :-

i) Nature of alkyl halides ( $\text{R}-\text{X}$ )



ii) Nature of leaving group.



iii) Nature of nucleophile :- weak  $\text{Nu}^-$  is preferable in  $\text{S}^{\text{N}}\text{I}$

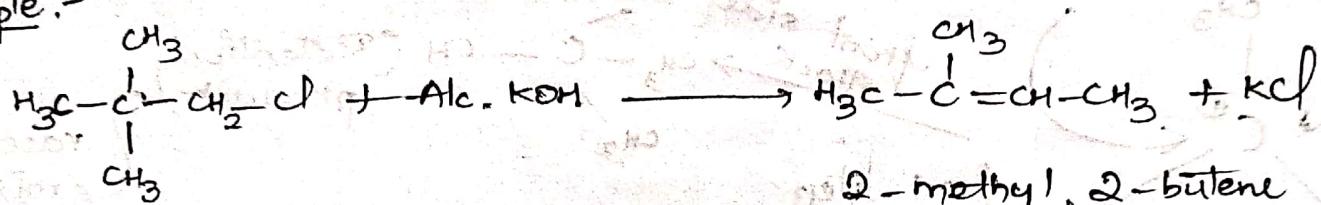
iv) Conc. of nucleophile :- low concentrated  $\text{Nu}^-$  is preferred in  $\text{S}^{\text{N}}\text{I}$  reaction

v) Nature of solvents :- protic solvents are used in  $\text{S}^{\text{N}}\text{I}$

③ What is Saytzeff's rule and explain it by taking one example.

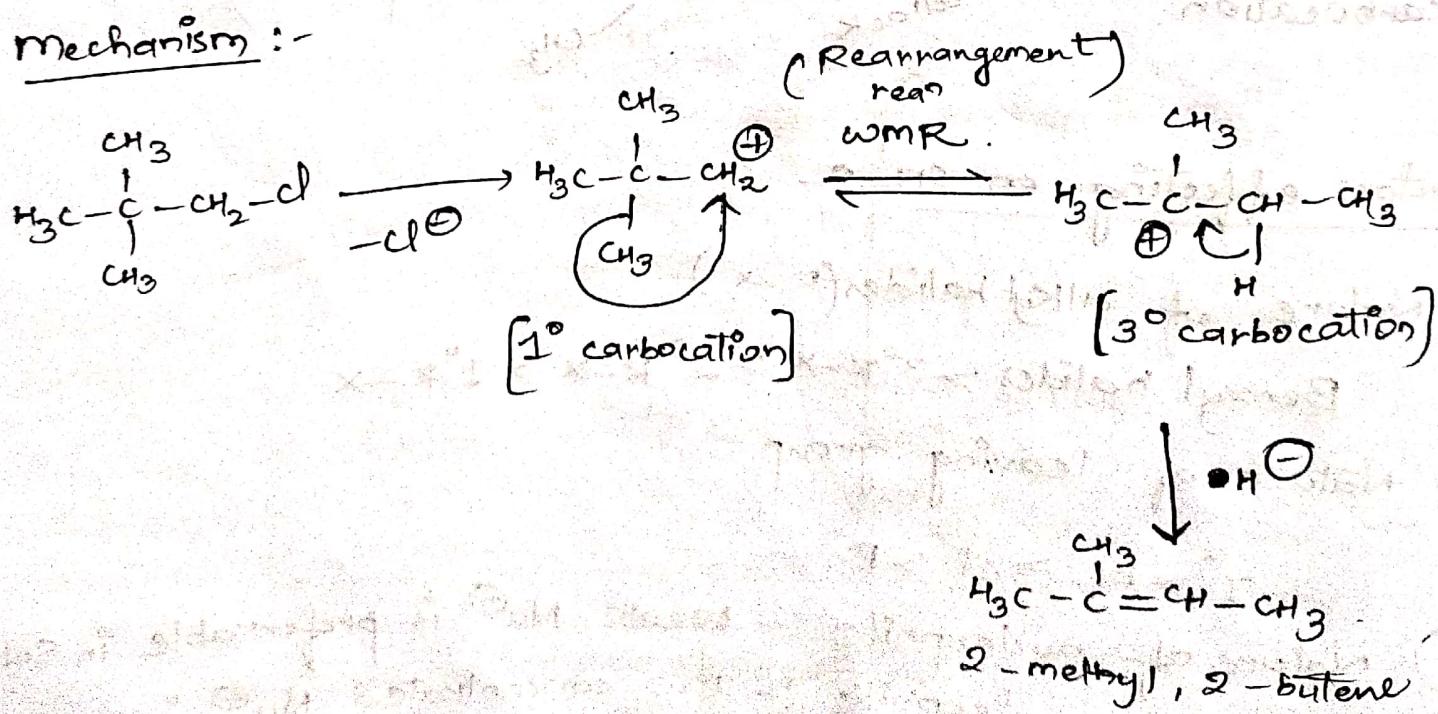
Saytzeff's rule :- Certain haloalkanes can undergo elimination in two different ways giving a mixture of two products. In such reaction, the preferred product is the more highly substituted alkenes (i.e. the alkene having lesser number of hydrogens on the double bonded carbon atoms). This generalisation is known as Saytzeff's rule.

Example:-



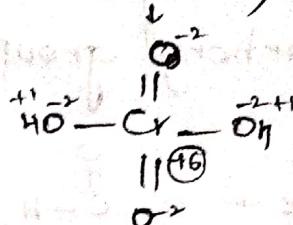
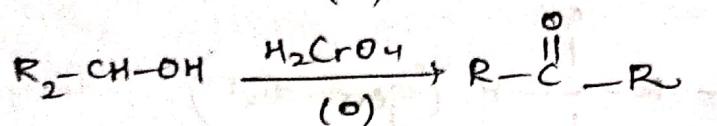
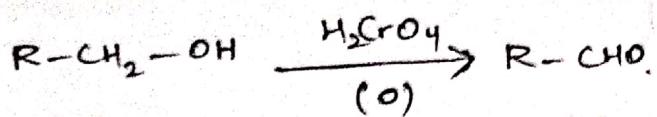
2,2 dimethyl, 1-chloro propane.

Mechanism :-

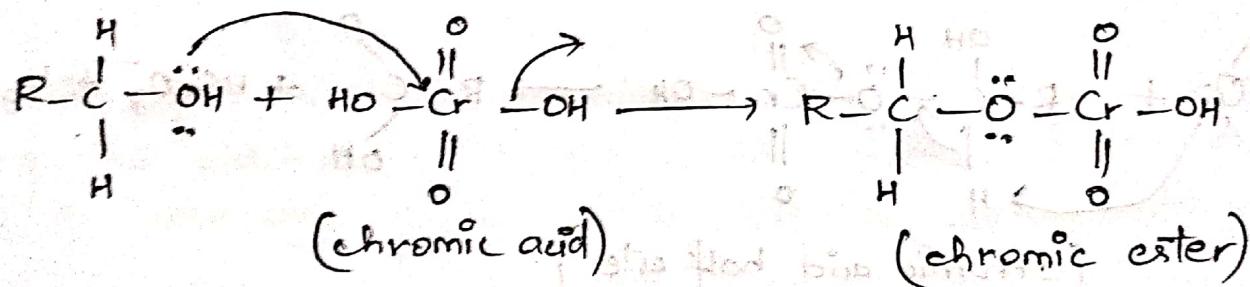


(4) How the alcohols are oxidised with chromic acid? Explain in detail with mechanism.

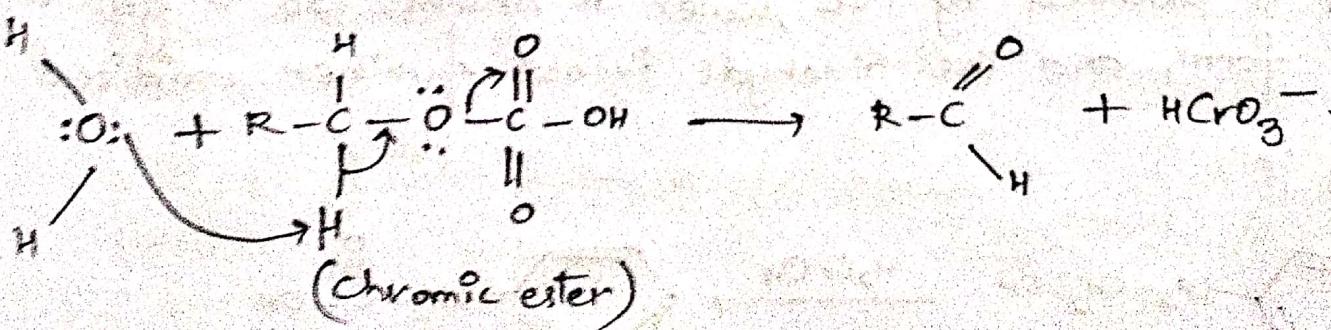
### Oxidation of alcohols with chromic acid ( $H_2CrO_4$ )



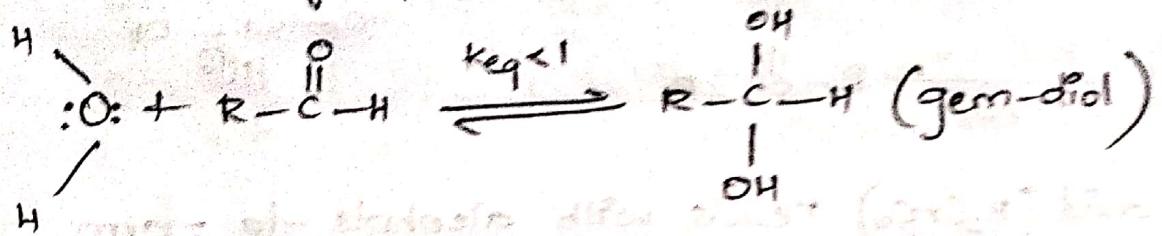
Chromic acid ( $H_2CrO_4$ ) reacts with alcohols to form a chromic ester in which the alcohol oxygen atom bridges the carbon and chromium atoms. The ester forms by nucleophilic attack of the alcohol oxygen atom on the chromium atom. This reaction is analogous to an  $SN_2$  reaction with a  $-OH$  group of chromic acid as the leaving group.



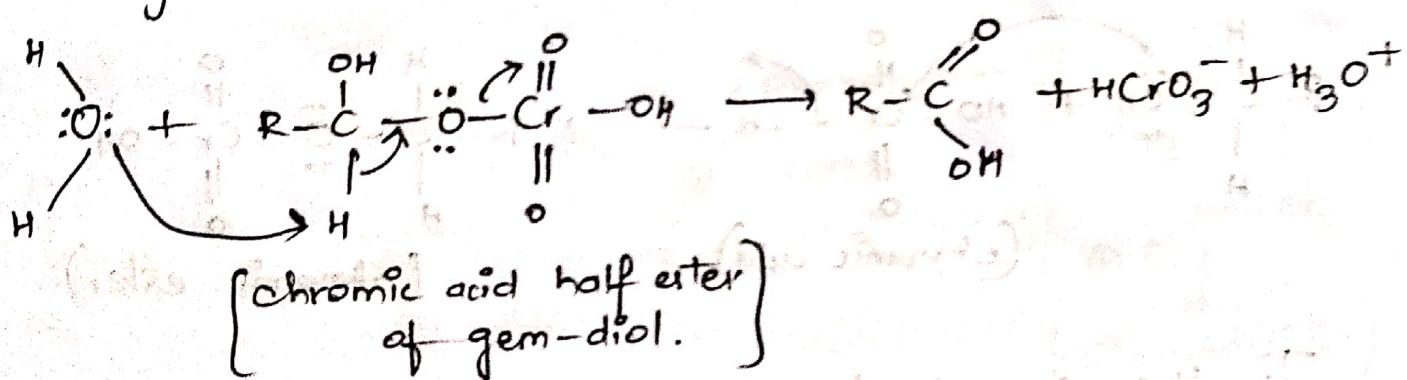
In the second step of the reaction, water extracts a hydrogen atom from the alcohol carbon; the  $\text{O-H}$  pair in the C-H bond acts as a nucleophile, and the O-Cr bond in the chromic ester breaks to form a carbon-carbon double bond.



In an aqueous acid solution, chromic acid converts aldehydes to carboxylic acids. Before this second occurs, the aldehyde reacts with water to give a 1,1-diol called a gem-diol. gem-diol result from an addition reaction to the carbonyl group.

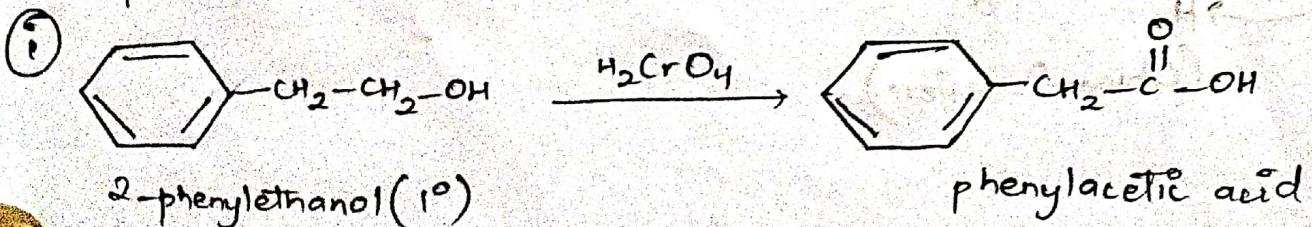


The gem-diol is an alcohol. One of its hydroxyl groups is oxidized by way of a chromic half-ester in the same manner as alcohols. The resulting component retains the hydroxyl group of the original chromic half-ester and is a carboxylic acid.

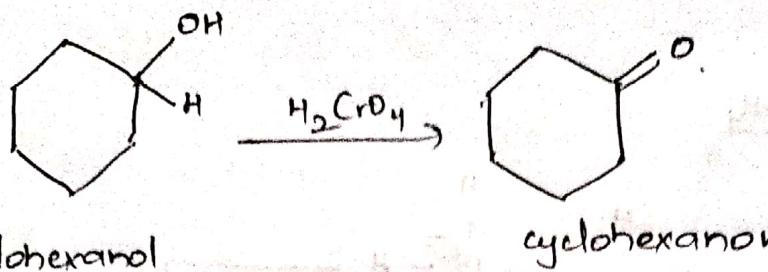


gem-diols form in low concentration in equilibrium with the aldehyde. However, when they are converted into chromic acid half-esters and oxidised, they continue to form until the oxidation is complete. When a primary alcohol is oxidised by PCC, water is absent. So, a gem-diol cannot form, and the aldehyde is not further oxidised.

Example :-



(ii)

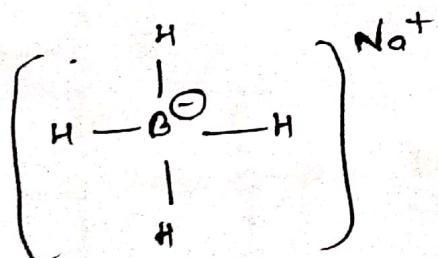


cyclohexanone

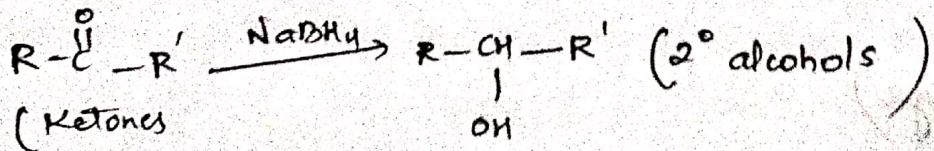
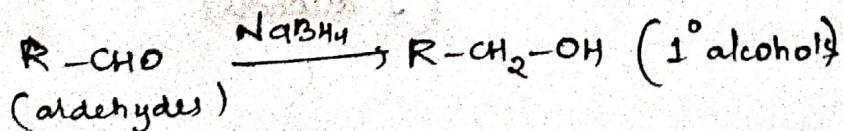
Q How the carbonyl compounds reduced with  $\text{NaBH}_4$ .  
Explain with mechanism.

The most useful reagents for reducing aldehydes and ketones are the metal hydride reagents, most common metal hydride reagents are sodium borohydride ( $\text{NaBH}_4$ ) and lithium aluminium hydride ( $\text{LiAlH}_4$ ). These reagents contain a polar metal-hydrogen bond that serves as a source of the nucleophile hydride  $\text{H}^-$ .  $\text{LiAlH}_4$  is stronger than  $\text{NaBH}_4$  because the Al-H bond is more polar than the B-H bond.

Reduction of aldehydes and ketones with  $\text{NaBH}_4$  involves treating the aldehyde or Ketone with  $\text{NaBH}_4$ ; followed by water or some other proton source affords an alcohol.

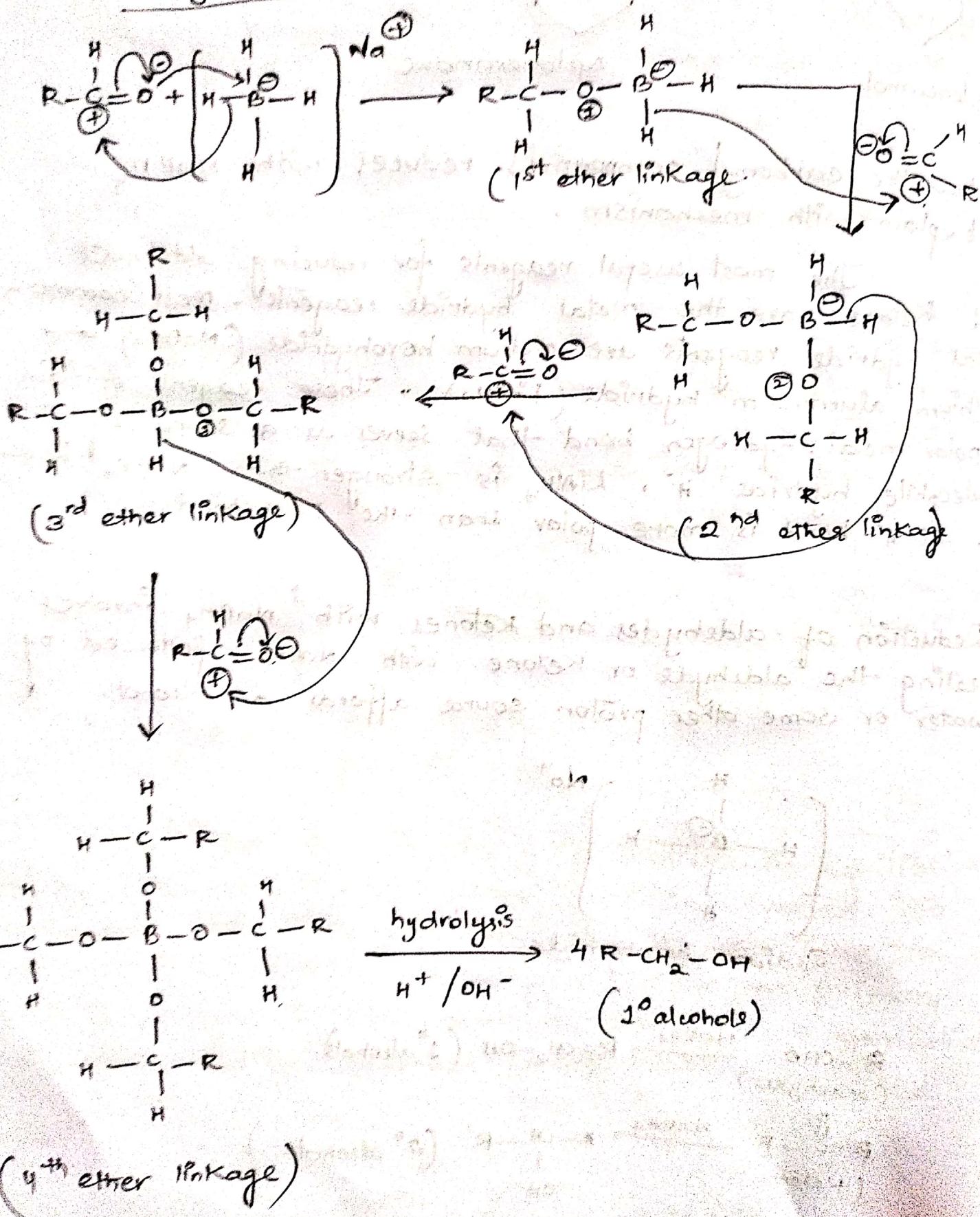


Sodium borohydride

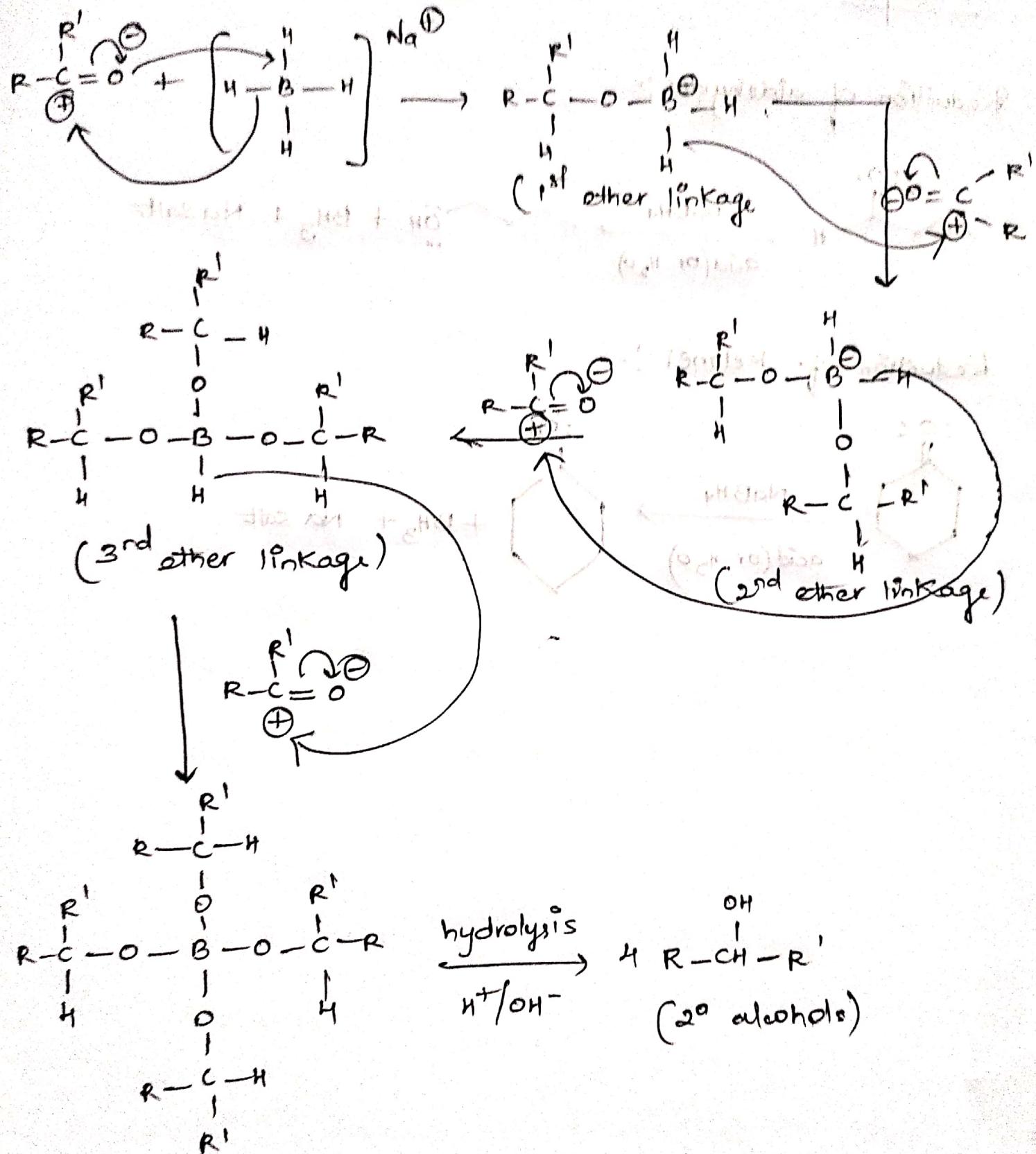


## Mechanism :-

aldehydes with  $\text{NaBH}_4$ .

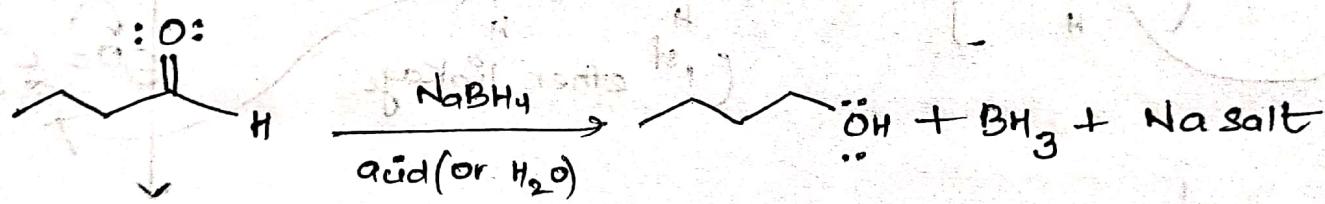


## Ketones with NaBH<sub>4</sub>

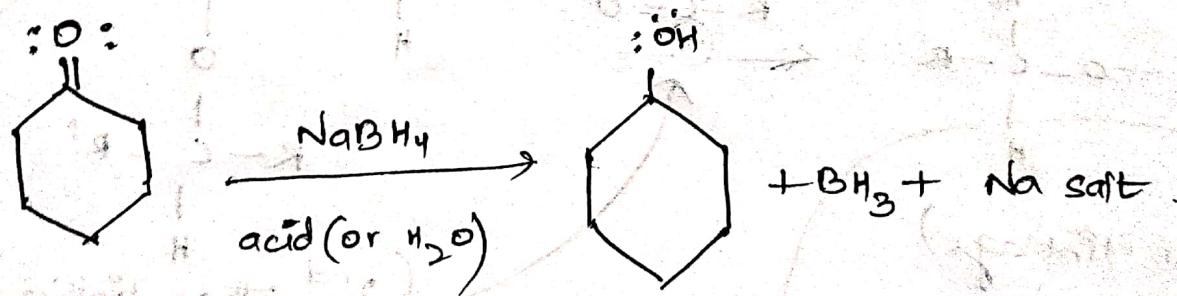


Example :-

Reduction of aldehydes :-



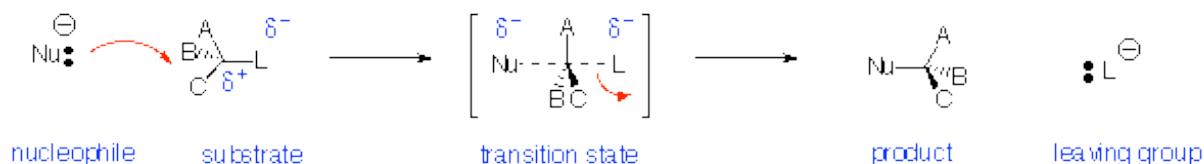
Reduction of ketones :-



## **SN2 , SN1 , E2 , & E1: Substitution and Elimination Reactions**

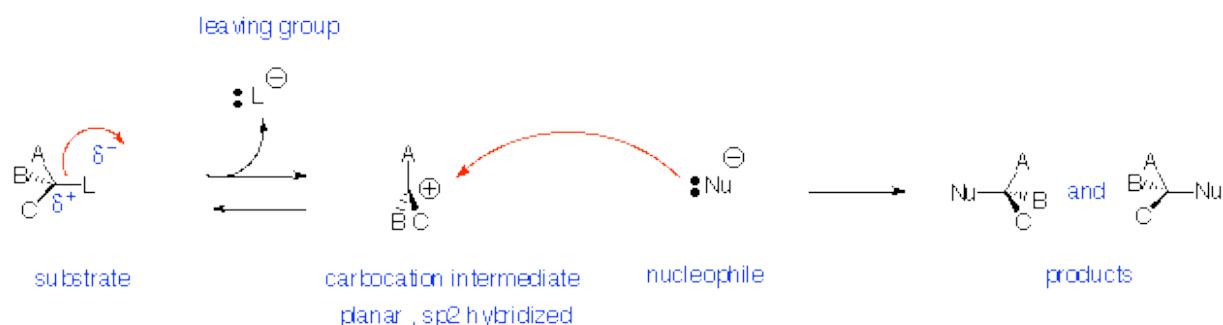
- Nucleophilic Substitution Reactions (SN2 and SN1) replace a leaving group with a nucleophile (Nu: or Nu: - )
- Elimination Reactions (E2 and E1) generate a double bond by loss of " A+ " and " B: - "
- They may compete with each other

### **Nucleophilic Substitution Reactions - SN2 Reaction:**



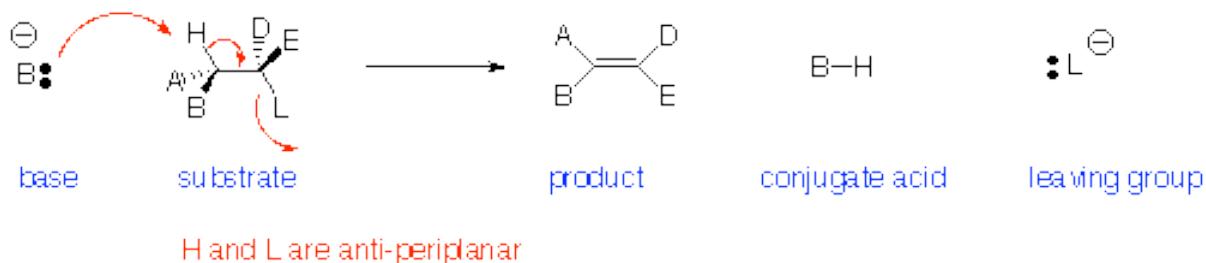
- **Reaction is:**
  - Stereospecific (Walden Inversion of configuration)
  - Concerted - all bonds form and break at same time
  - Bimolecular - rate depends on concentration of both nucleophile and substrate
- **Substrate:**
  - Best if **primary** (one substituent on carbon bearing leaving group)
  - works if secondary, fails if tertiary
- **Nucleophile:**
  - Best if more reactive (i.e. more anionic or more basic)
- **Leaving Group:** Best if more stable (i.e. can support negative charge well):
  - TsO- (very good) > I- > Br- > Cl- > F- (poor)
  - RF, ROH, ROR, RNH<sub>2</sub> are NEVER Substrates for SN2 reactions
  - Leaving Groups on double-bonded carbons are never replaced by SN2 reactions
- **Solvent:** Polar Aprotic (i.e. no OH) is best.
  - For example dimethylsulfoxide (CH<sub>3</sub>SOCH<sub>3</sub>), dimethylformamide (HCON(CH<sub>3</sub>)<sub>2</sub>), acetonitrile (CH<sub>3</sub>CN).
  - Protic solvents (e.g. H<sub>2</sub>O or ROH) deactivate nucleophile by hydrogen bonding but can be used in some case

## Nucleophilic Substitution Reactions – SN1 Reaction:



- **Reaction is:**
  - Non-stereospecific (attack by nucleophile occurs from both sides)
  - Non-concerted - has carbocation intermediate
  - Unimolecular - rate depends on concentration of only the substrate
- **Substrate:**
  - Best if tertiary or conjugated (benzylic or allylic) carbocation can be formed as leaving group departs
  - never primary
- **Nucleophile:**
  - Best if more reactive (i.e. more anionic or more basic)
- **Leaving Group:**
  - Same as SN2
  - best if more stable (i.e. can support negative charge well)
  - Examples: TsO $^-$  (very good) > I $^-$  > Br $^-$  > Cl $^-$  > F $^-$  (poor)
  - However, tertiary or allylic ROH or ROR' can be reactive under strongly acidic conditions to replace OH or OR
- **Solvent:**
  - Same as SN2
  - Polar Aprotic (i.e. no OH) is best
  - Examples: dimethylsulfoxide (CH<sub>3</sub>SOCH<sub>3</sub>), dimethylformamide (HCON(CH<sub>3</sub>)<sub>2</sub>), acetonitrile (CH<sub>3</sub>CN).
  - Protic solvents (e.g. H<sub>2</sub>O or ROH) deactivate but can be used in some cases

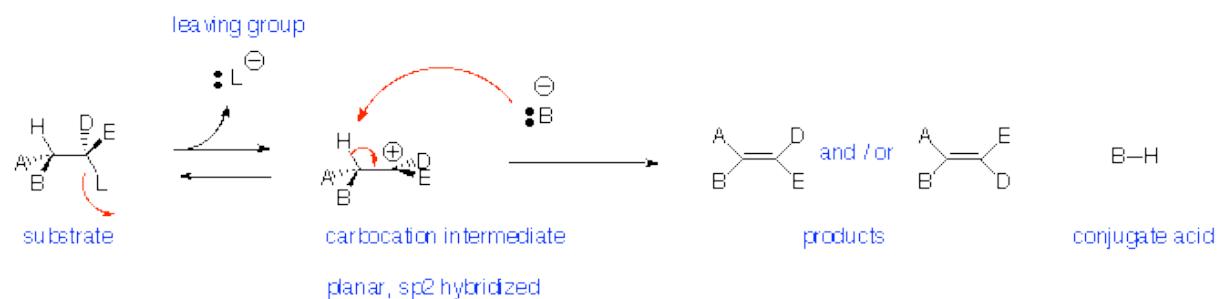
### Elimination Reactions - E2 Reaction:



- **Reaction is:**

- Stereospecific (Anti-periplanar geometry preferred, Syn-periplanar geometry possible)
- Concerted - all bonds form and break at same time
- Bimolecular - rate depends on concentration of both base and substrate
- Favoured by strong bases

### Elimination Reactions – E1 Reaction:



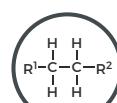
- **Reaction is:**

- Non-stereospecific- follows Zaitsev (Saytseff) Rule
- Non-concerted - has carbocation intermediate - favoured for tertiary leaving groups
- Unimolecular - rate depends on concentration of only the substrate
- Does NOT occur with primary alkyl halides (leaving groups)
- Strong acid can promote loss of OH as  $H_2O$  or OR as HOR if tertiary or conjugated carbocation can be formed

# FUNCTIONAL GROUPS IN ORGANIC CHEMISTRY

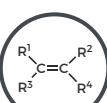
Functional groups are the characteristic groups in organic molecules that give them their reactivity. In the formulae below, R represents the rest of the molecule and X represents any halogen atom.

● Hydrocarbons ● Halogen-containing groups ● Oxygen-containing groups ● Nitrogen-containing groups ● Sulfur-containing groups ● Phosphorus-containing groups



**ALKANE**

Naming: -ane  
e.g. ethane



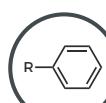
**ALKENE**

Naming: -ene  
e.g. ethene



**ALKYNE**

Naming: -yne  
e.g. ethyne



**ARENÉ**

Naming: -yl benzene  
e.g. ethyl benzene



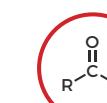
**HALOALKANE**

Naming: halo-  
e.g. chloroethane



**ALCOHOL**

Naming: -ol  
e.g. ethanol



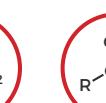
**ALDEHYDE**

Naming: -al  
e.g. propanal



**KETONE**

Naming: -one  
e.g. propanone



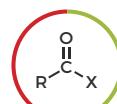
**CARBOXYLIC ACID**

Naming: -oic acid  
e.g. ethanoic acid



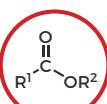
**ACID ANHYDRIDE**

Naming: -oic anhydride  
e.g. ethanoic anhydride



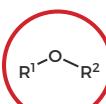
**ACYL HALIDE**

Naming: -oyl halide  
e.g. ethanoyl chloride



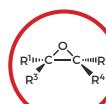
**ESTER**

Naming: -yl -oate  
e.g. ethyl ethanoate



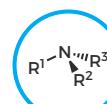
**ETHER**

Naming: -oxy -ane  
e.g. methoxyethane



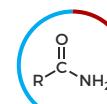
**EPONIDE**

Naming: -ene oxide  
e.g. ethene oxide



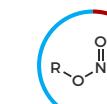
**AMINE**

Naming: -amine  
e.g. ethanamine



**AMIDE**

Naming: -amide  
e.g. ethanamide



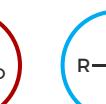
**NITRATE**

Naming: -yl nitrate  
e.g. ethyl nitrate



**NITRILE**

Naming: -yl nitrile  
e.g. ethyl nitrile



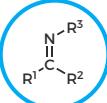
**NITRO**

Naming: nitro-  
e.g. nitromethane



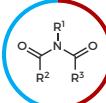
**NITROSO**

Naming: nitroso-  
e.g. nitrosoethane



**IMINE**

Naming: -imine  
e.g. ethanimine



**IMIDE**

Naming: -imide  
e.g. succinimide



**AZIDE**

Naming: -yl azide  
e.g. phenylazide



**CYANATE**

Naming: -yl cyanate  
e.g. methyl cyanate



**ISOCYANATE**

Naming: -yl isocyanate  
e.g. methyl isocyanate



**AZO COMPOUND**

Naming: azo-  
e.g. azoethane



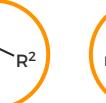
**THIOL**

Naming: -thiol  
e.g. methanethiol



**SULFIDE**

Naming: sulfide  
e.g. dimethyl sulfide



**DISULFIDE**

Naming: disulfide  
e.g. dimethyl disulfide



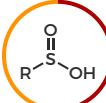
**SULFOXIDE**

Naming: sulfoxide  
e.g. dimethyl sulfoxide



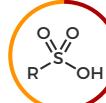
**SULFONE**

Naming: sulfone  
e.g. dimethyl sulfone



**SULFINIC ACID**

Naming: -sulfinic acid  
e.g. benzenesulfonic acid



**SULFONIC ACID**

Naming: -sulfonic acid  
e.g. benzenesulfonic acid



**SULFONATE ESTER**

Naming: -yl sulfonate  
e.g. methylmethanesulfonate



**THIOCYANATE**

Naming: thiocyanate  
e.g. ethylthiocyanate



**ISOThiocyanATE**

Naming: isothiocyanate  
e.g. ethylisothiocyanate



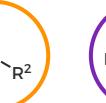
**THIAL**

Naming: -thial  
e.g. ethanethial



**THIOKETONE**

Naming: -thione  
e.g. propanethione



**PHOSPHINE**

Naming: phosphine  
e.g. methylphosphine



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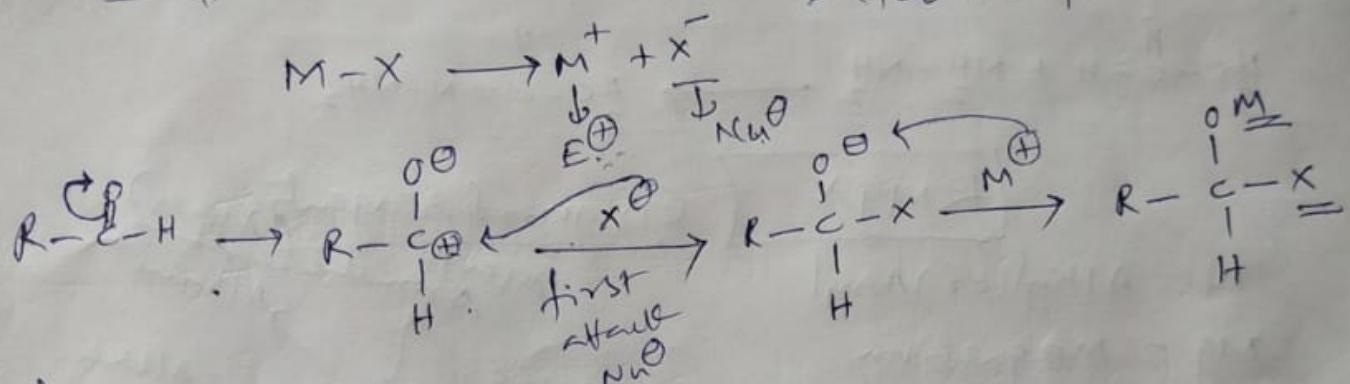
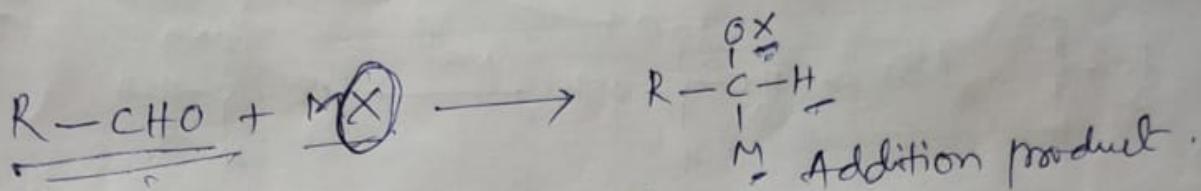
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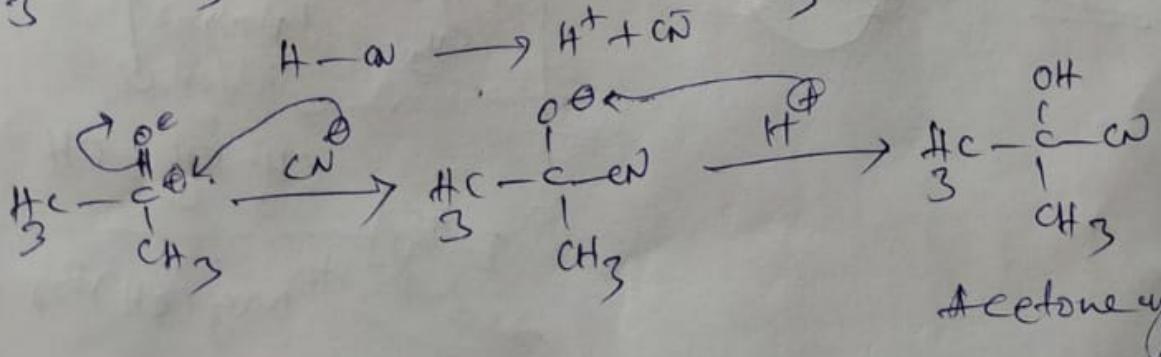
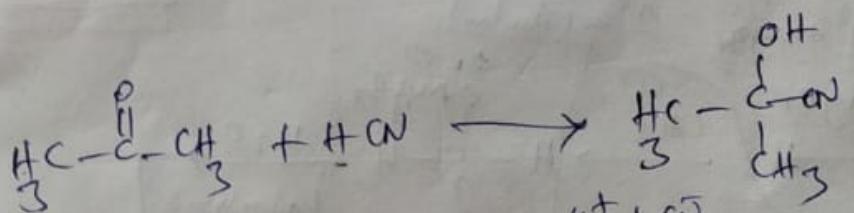
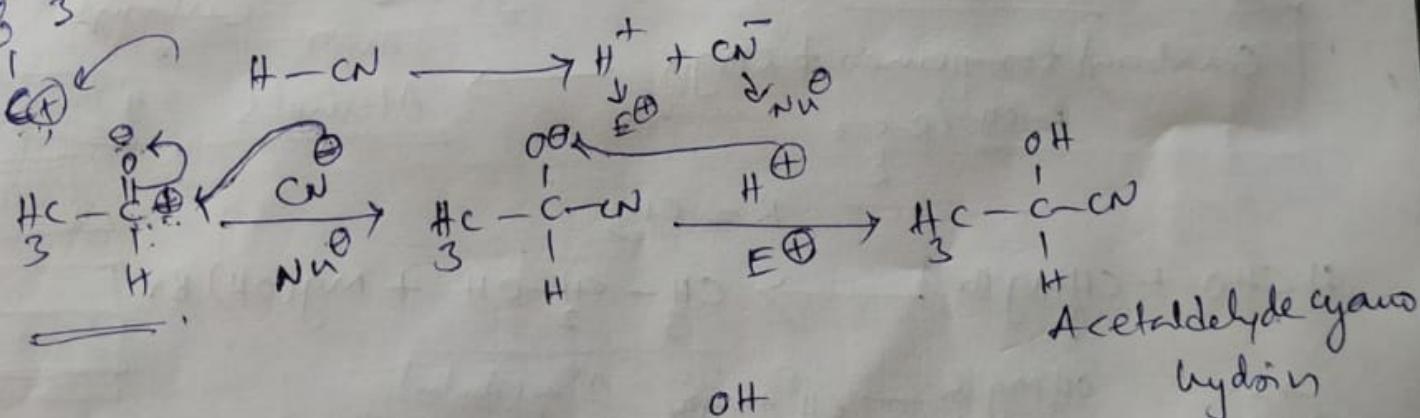
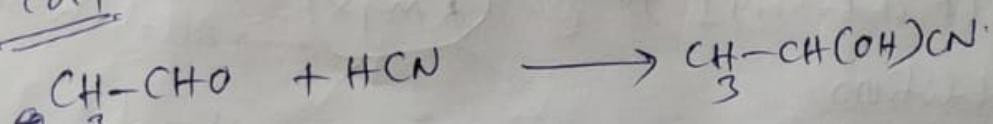
(Ex) Q

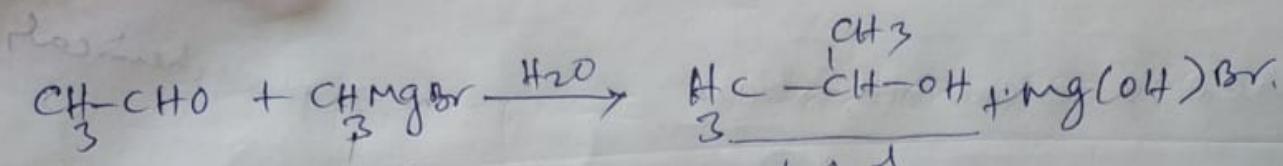
## Nucleophilic Addition reactions

Initial attack is group is nucleophile.  
Carbonyl compounds:  $\text{CHO}$  &  $\text{C=O}$

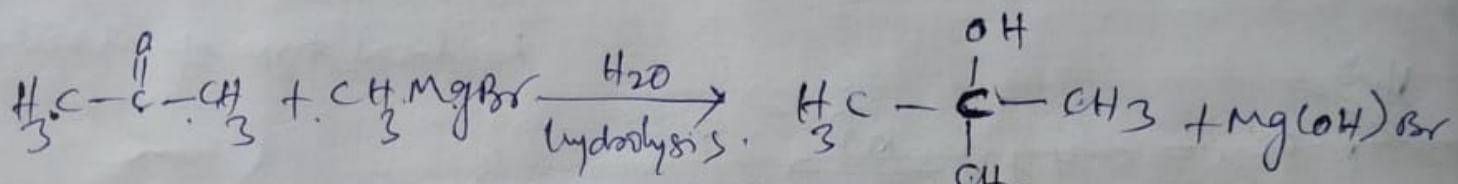
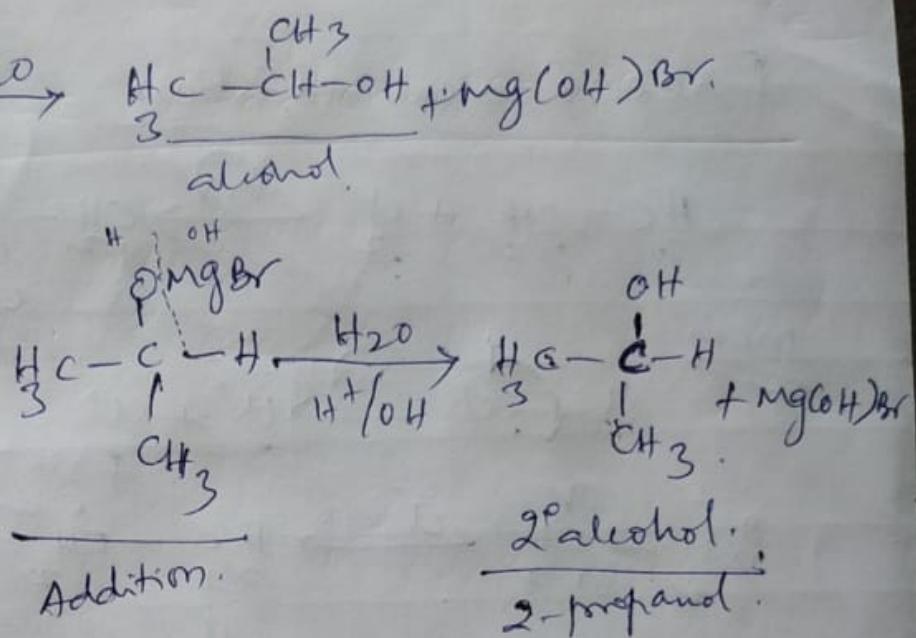
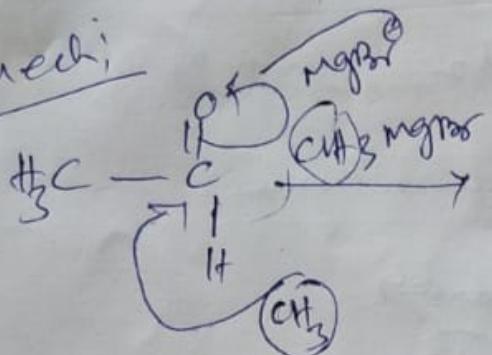


Ex:

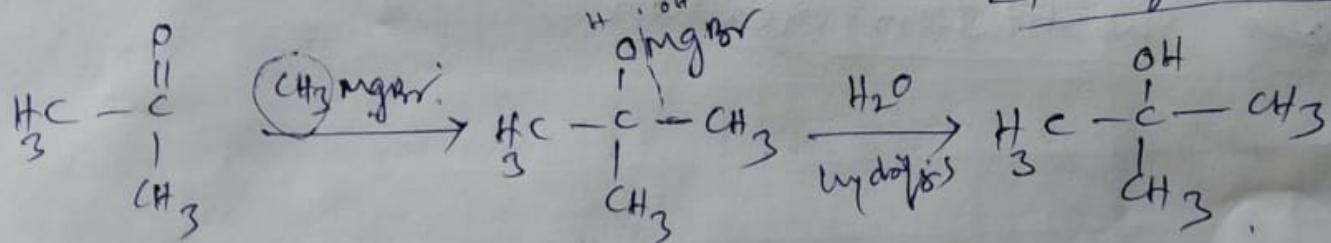




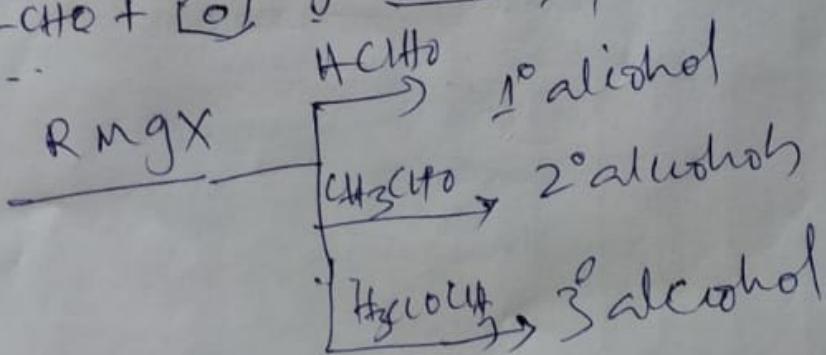
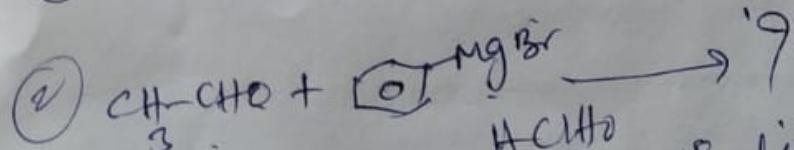
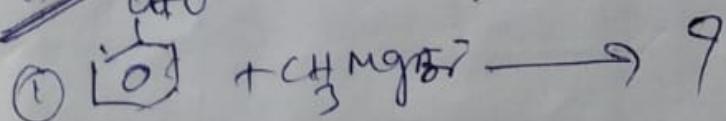
Mechi:



Mechi:

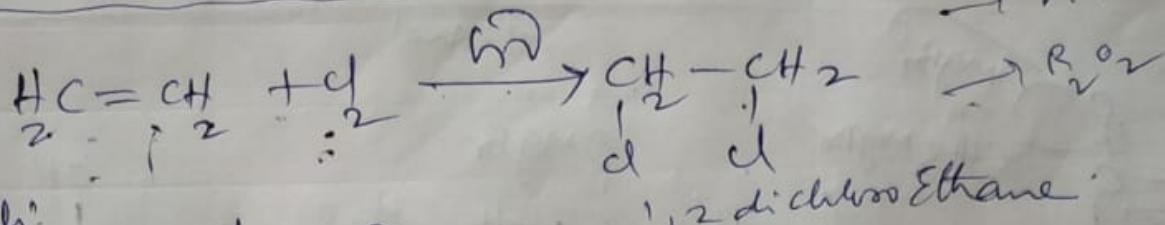


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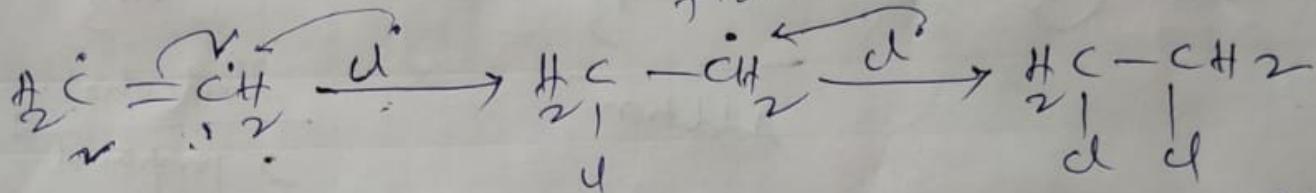
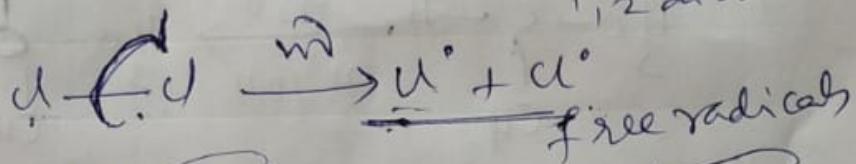


## Free Radical Addition:

→ photo chemically  
→ hν

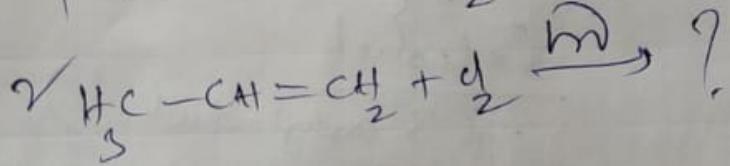
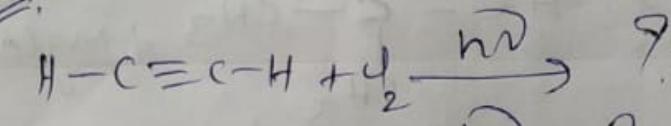


Mech:

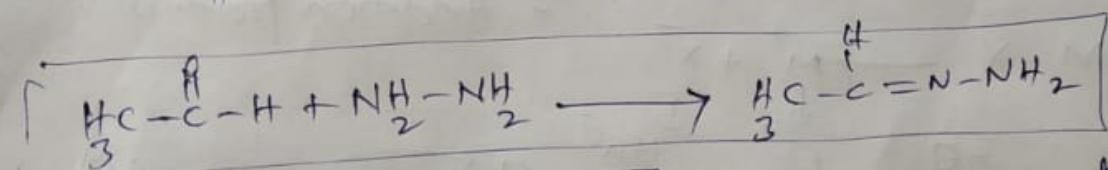
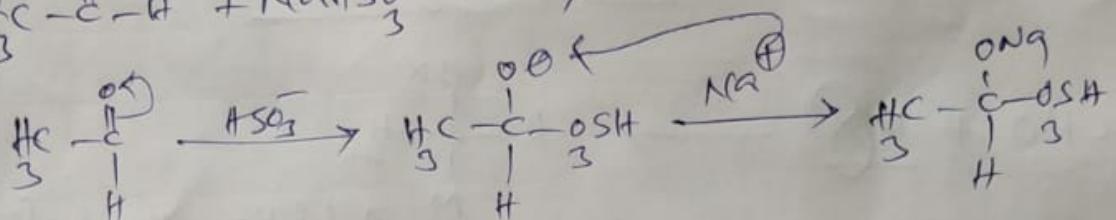
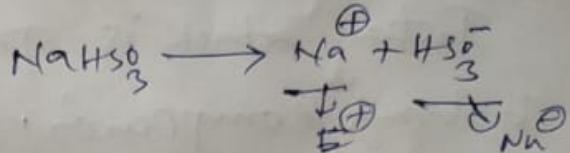
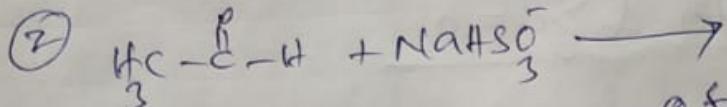
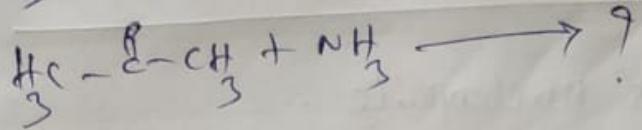
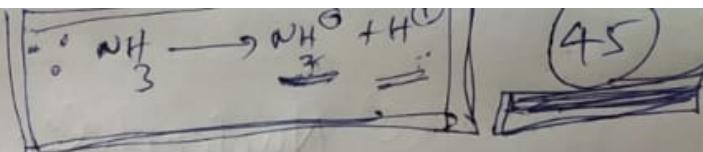
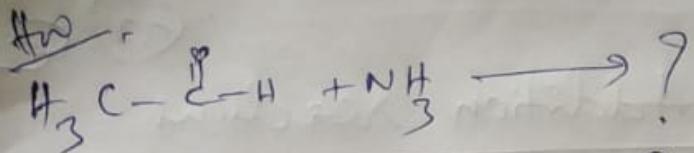


Radical type of reaction

Ques:



~~Ques~~ substitution reaction.



$\text{RMgX}$

Grignard reagent  
(Arenes)  
Alkyl Aromatic  
Alkene

$\text{R} = \text{Alkyl} \text{ (or) } \text{Aryl}$

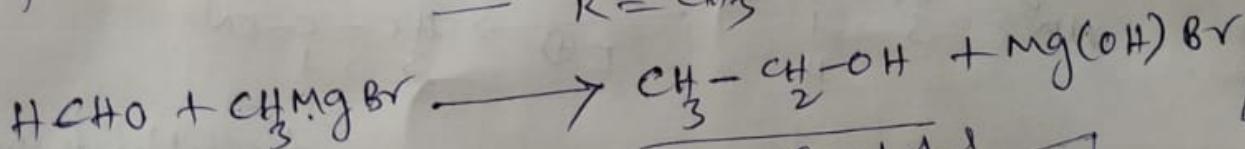
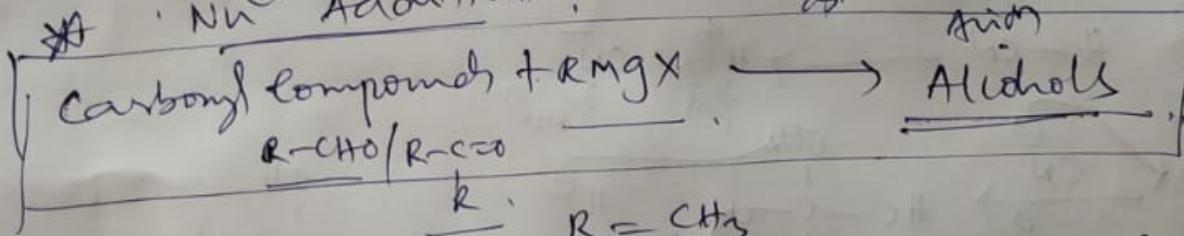
$\text{Mg} = \text{Magnesium}$

$\text{X} = \text{Halide (F, Cl, Br or I)}$

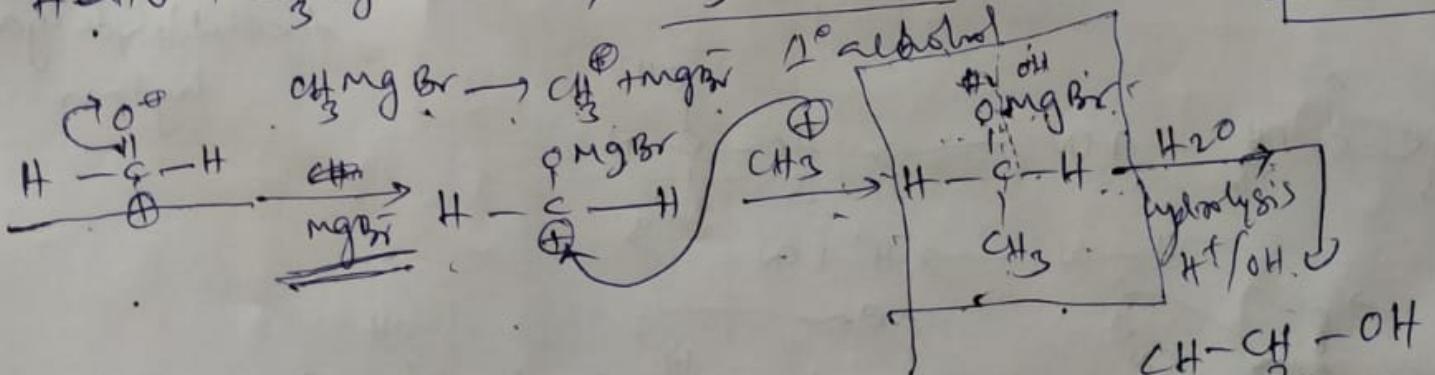
$\text{NN}^\ominus$  Addition.

$\text{RMgX}$

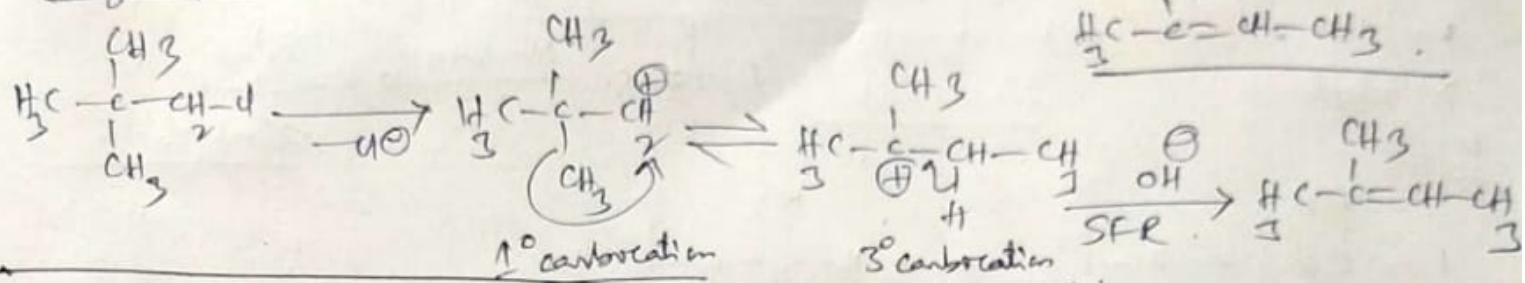
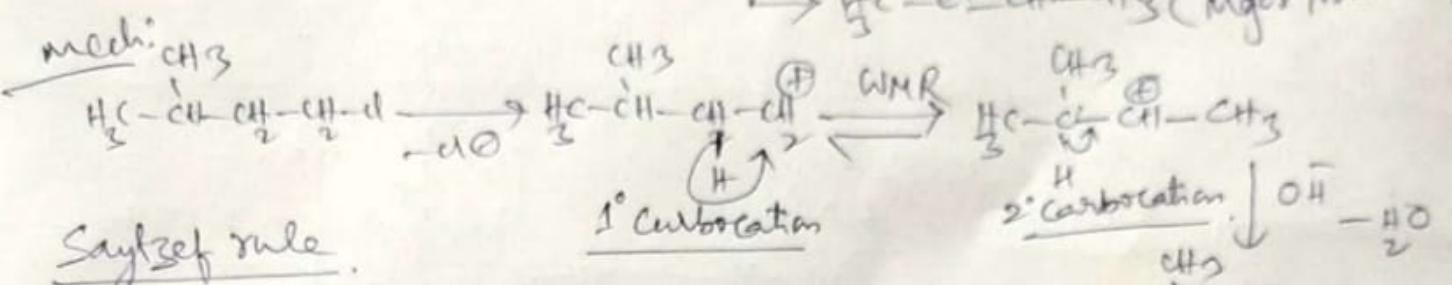
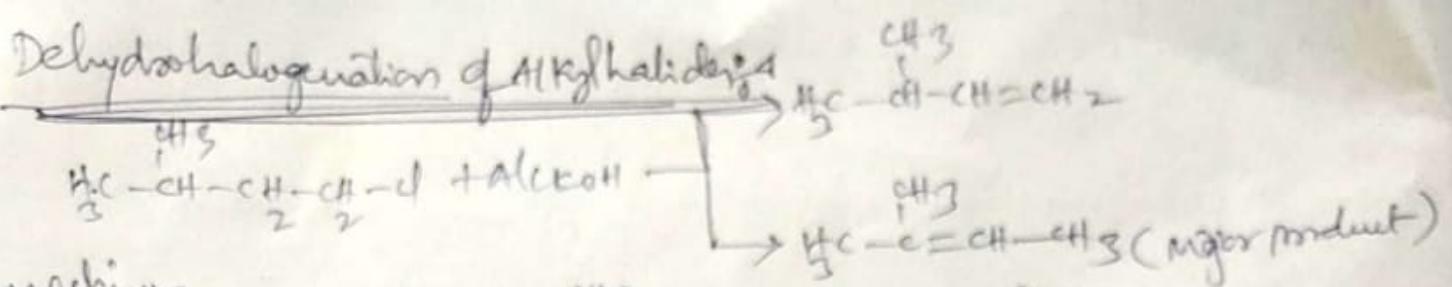
- amine  $\longrightarrow$  Alkane
- ester  $\longrightarrow$  Alcohol
- carbonyl  $\longrightarrow$  Alcohol
- acid  $\longrightarrow$  Alcohols



Zom

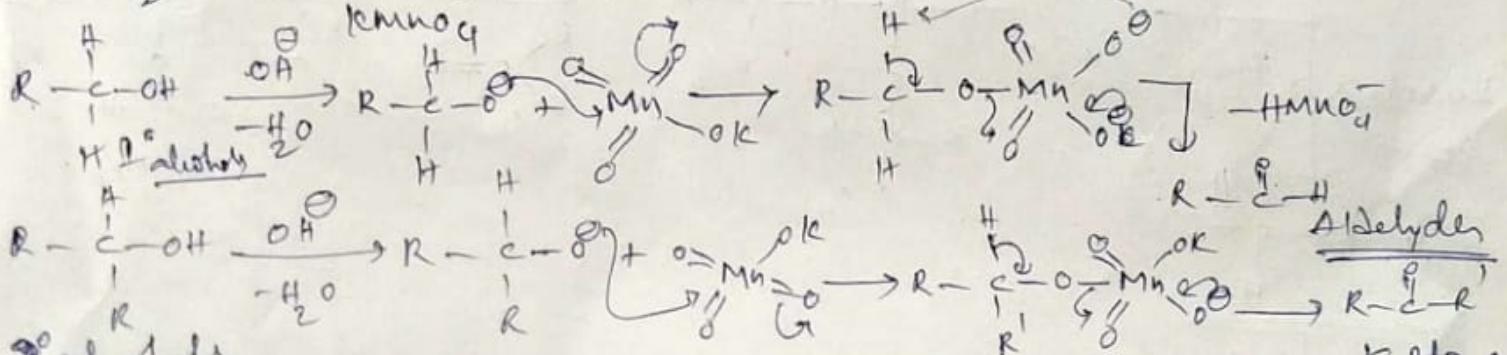
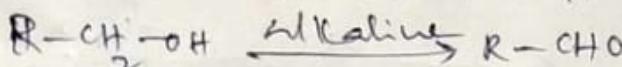
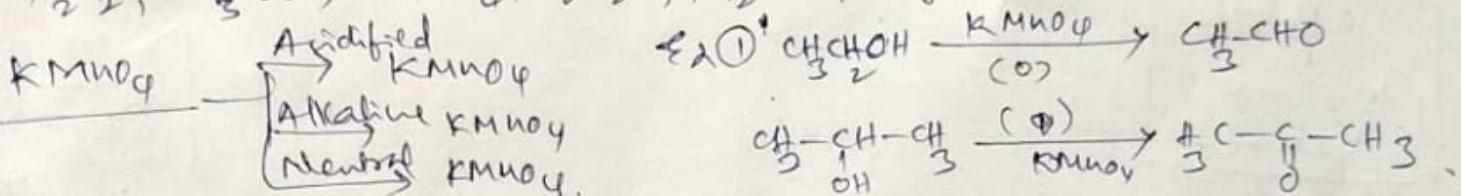


Ethyl alcohol +  $\text{Mg(OH)}\text{Br}$

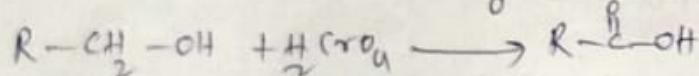
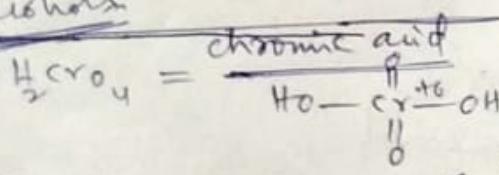


### Oxidation - reactions

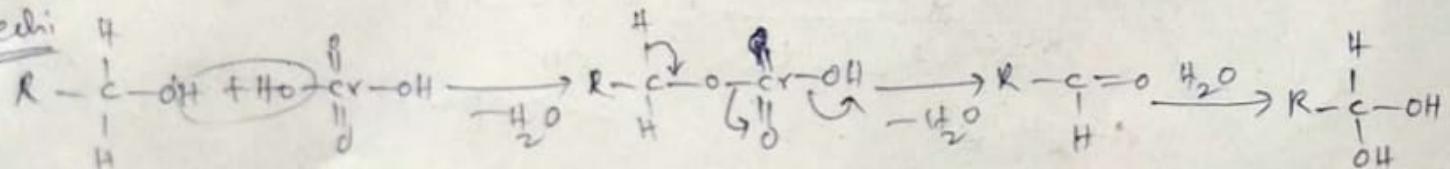
1)  $\text{H}_2\text{O}_2$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{HgCrO}_4$ , Py + PDC, MCPBA.



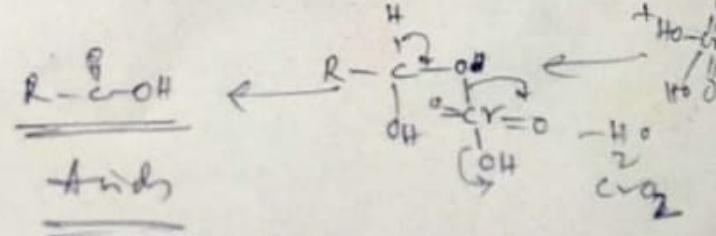
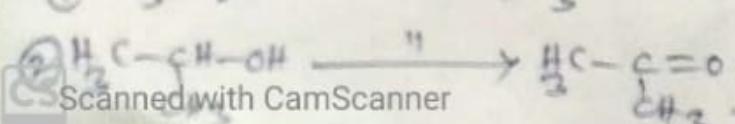
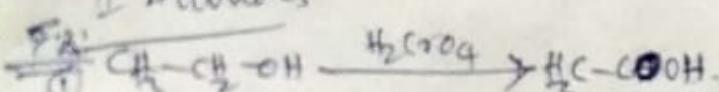
### 2° alcohols



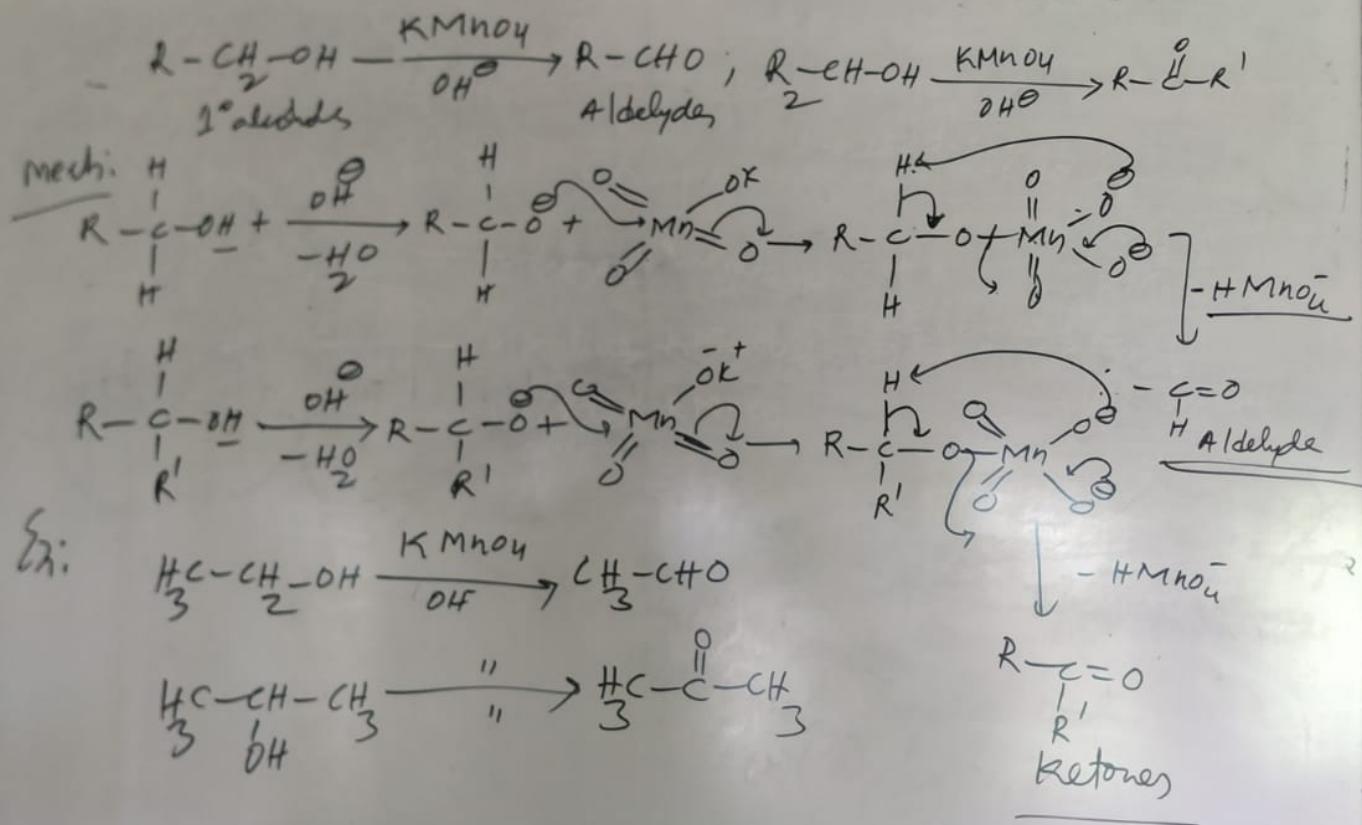
### MeOH



### 2° Alcohols

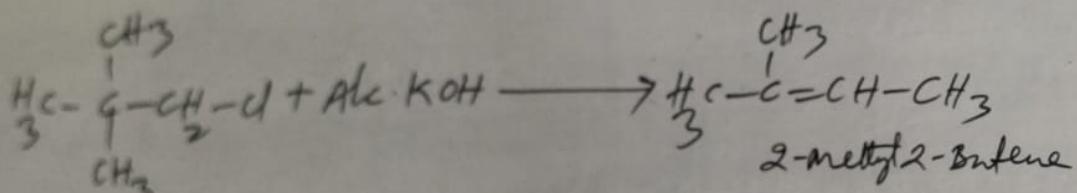


## Oxidation reactions

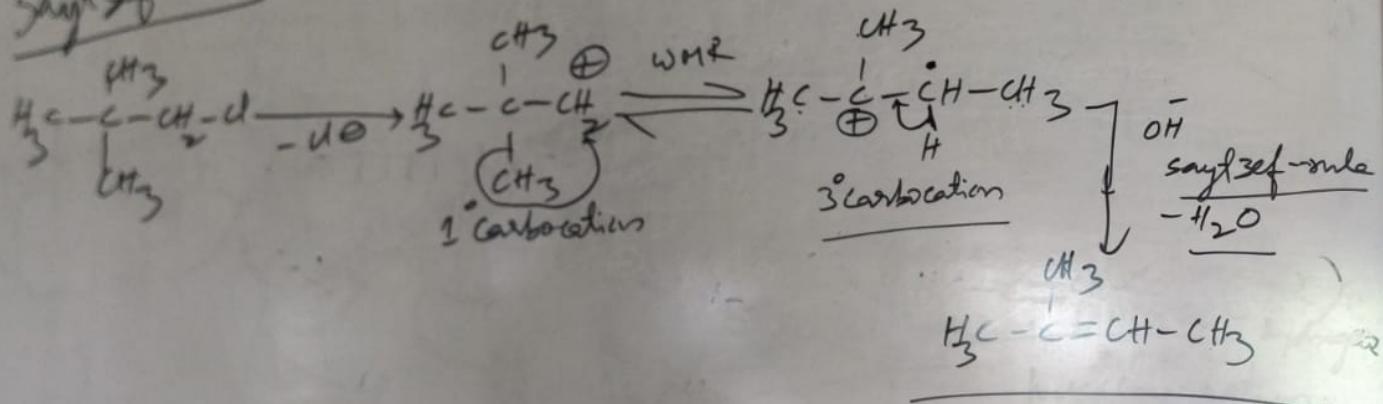


2020/4/16 11:11

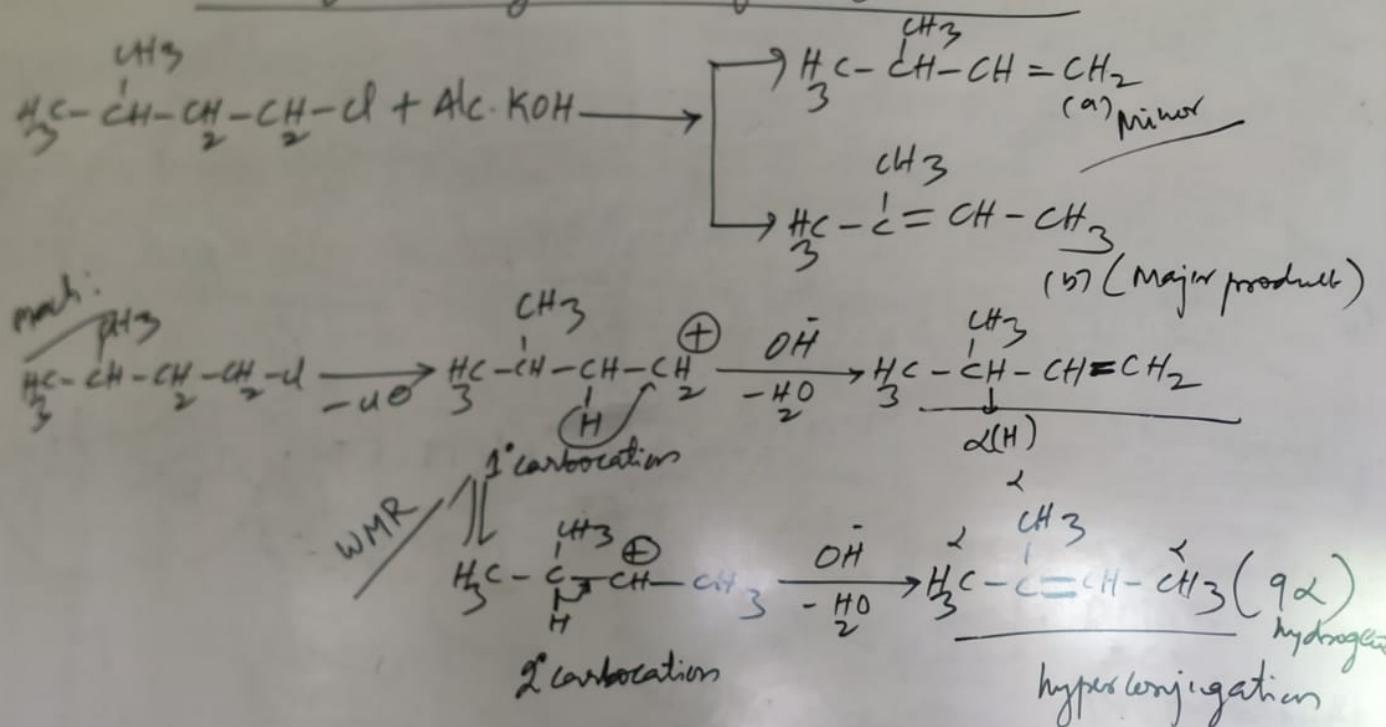
## Dehydrohalogenation of Alkyl halides



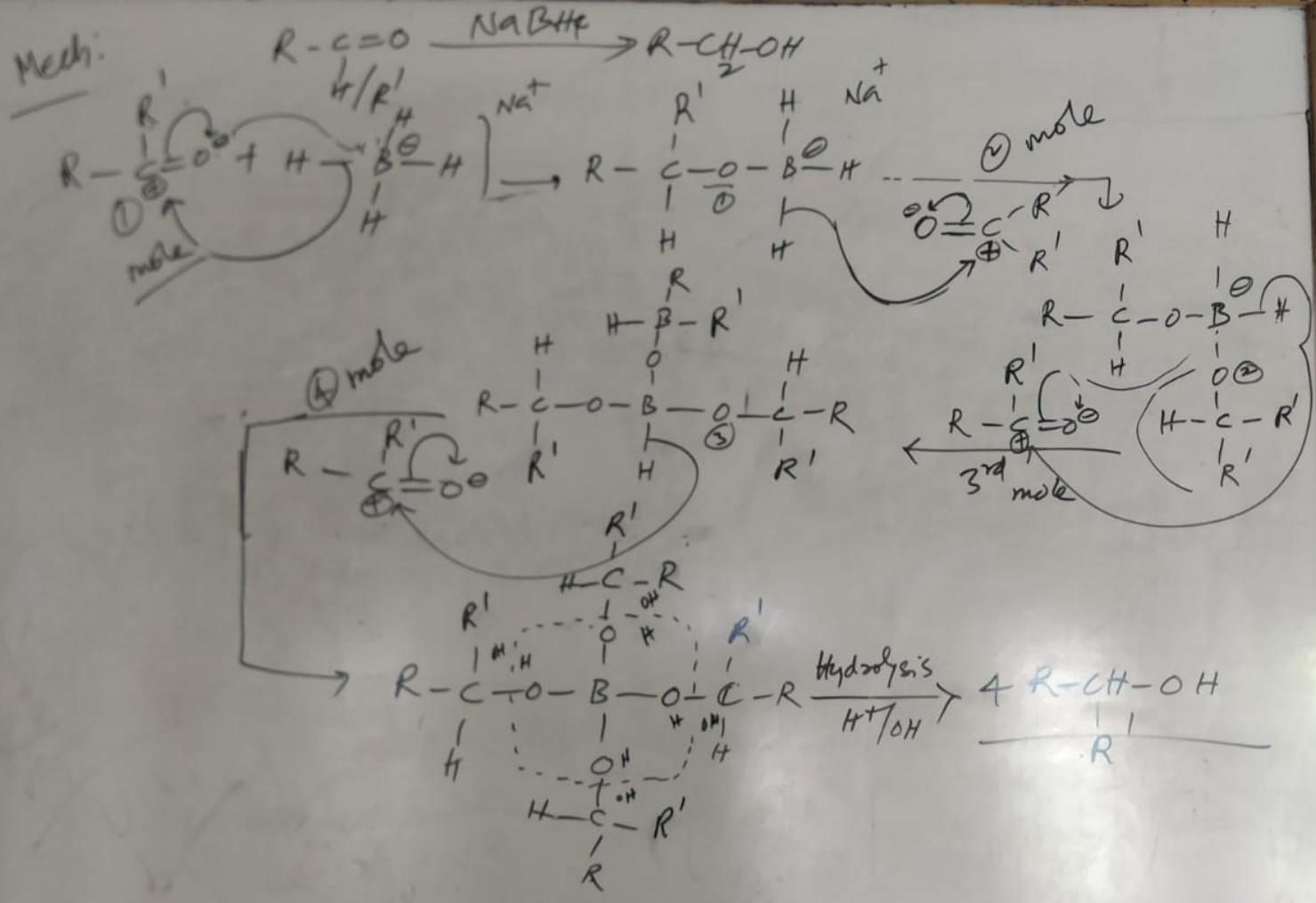
Saytzeff rule:



## Dehydrohalogenation of Alkyl halides

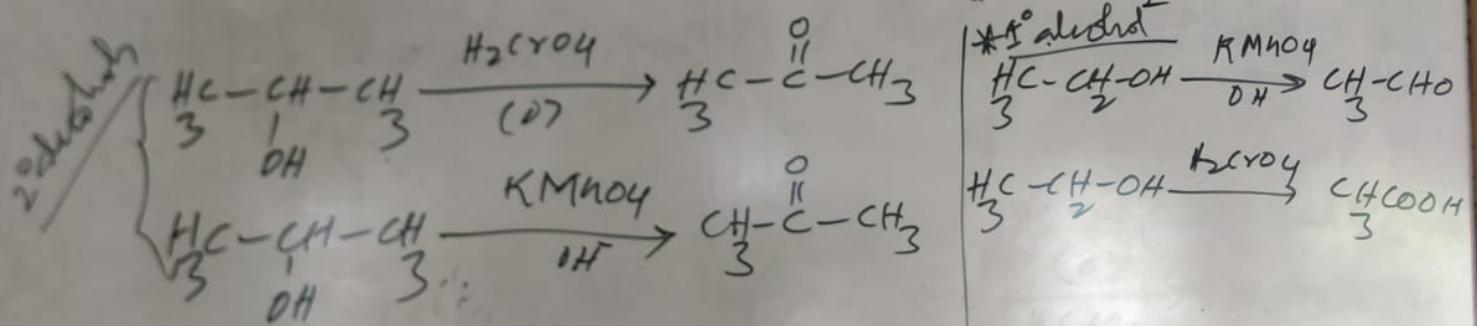
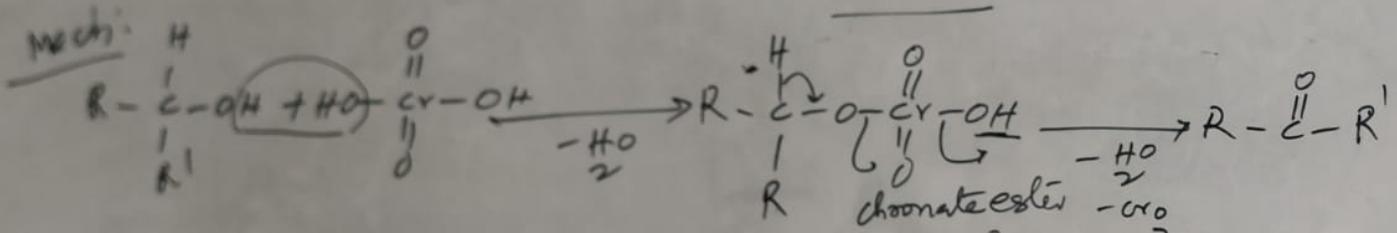
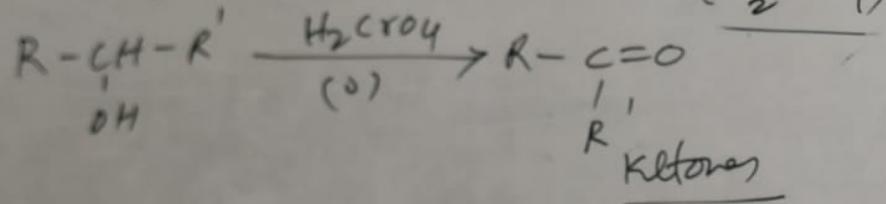


2020/4/16 10:38



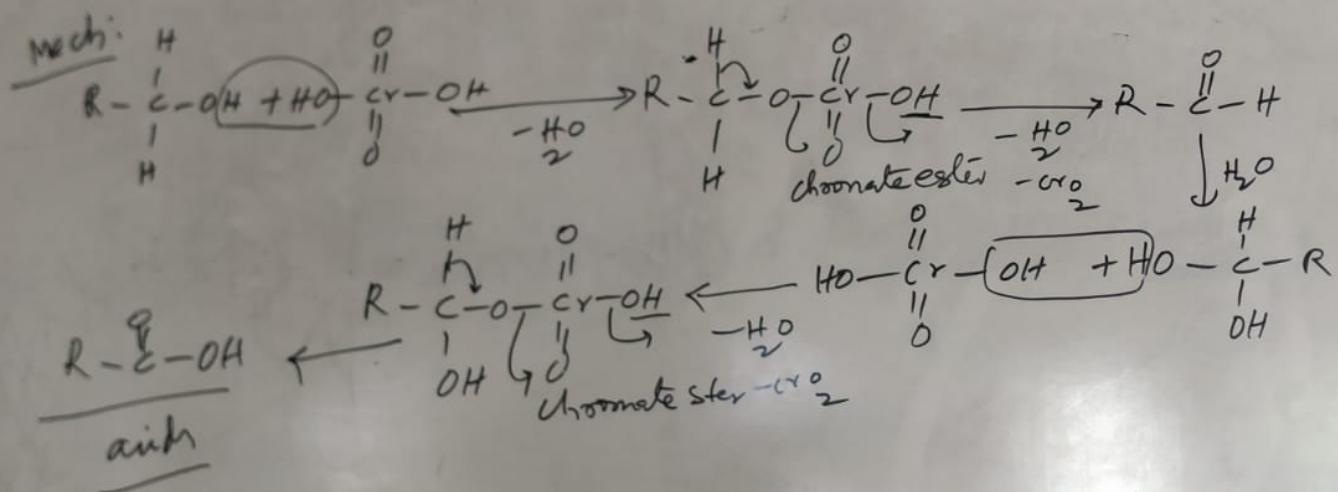
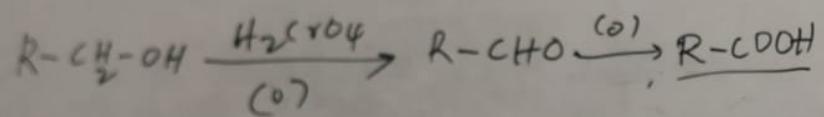
2020/4/17 10:58

Oxidation with chromic acid ( $H_2CrO_4$ )



2020/4/17 10:27

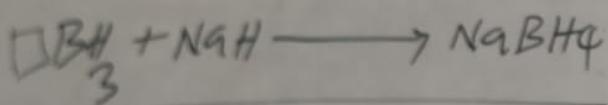
oxidation with chromic acid ( $\text{H}_2\text{CrO}_4$ )



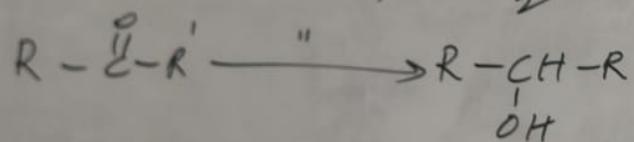
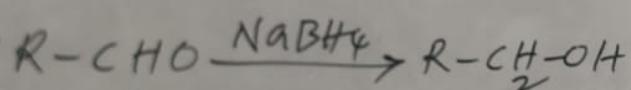
2020/4/17 10:17

## Reduction:

→ Addt<sup>n</sup> of hydrogens  
 (or)  
 → removal of oxygen



Red<sup>n</sup> of  $\text{NaBH}_4$



→ Reduction-agents

→ Ni / pd / pt

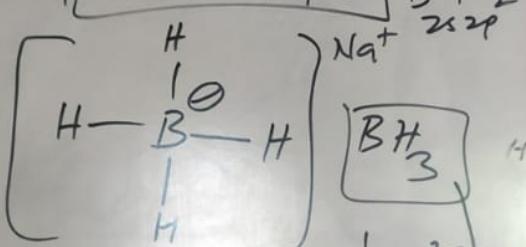
→ M-LigandH<sub>3</sub>

→ Pd-BaSO<sub>4</sub> / Quinoline

→ EtOH / Amylalcohol

→ NaBH<sub>4</sub>

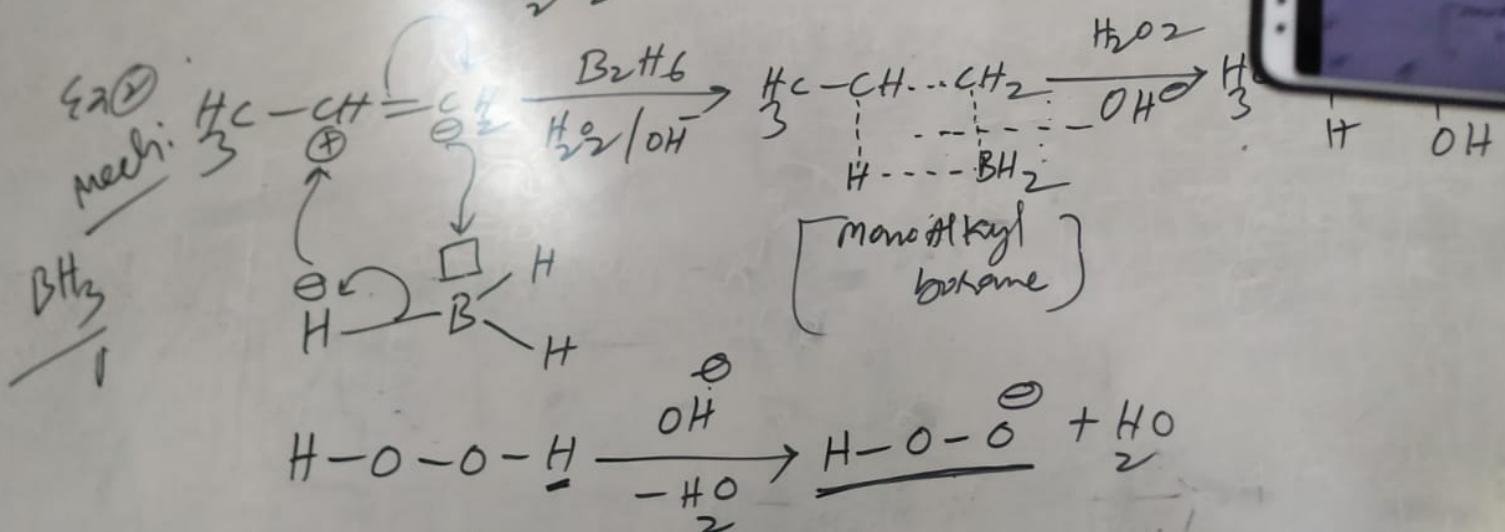
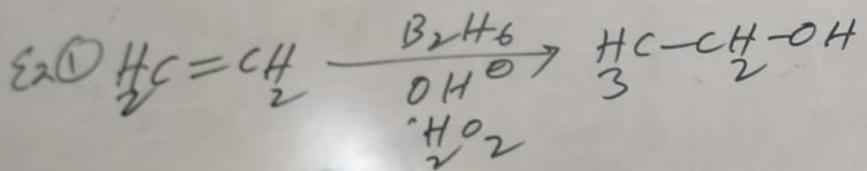
→ di AlH<sub>4</sub>.



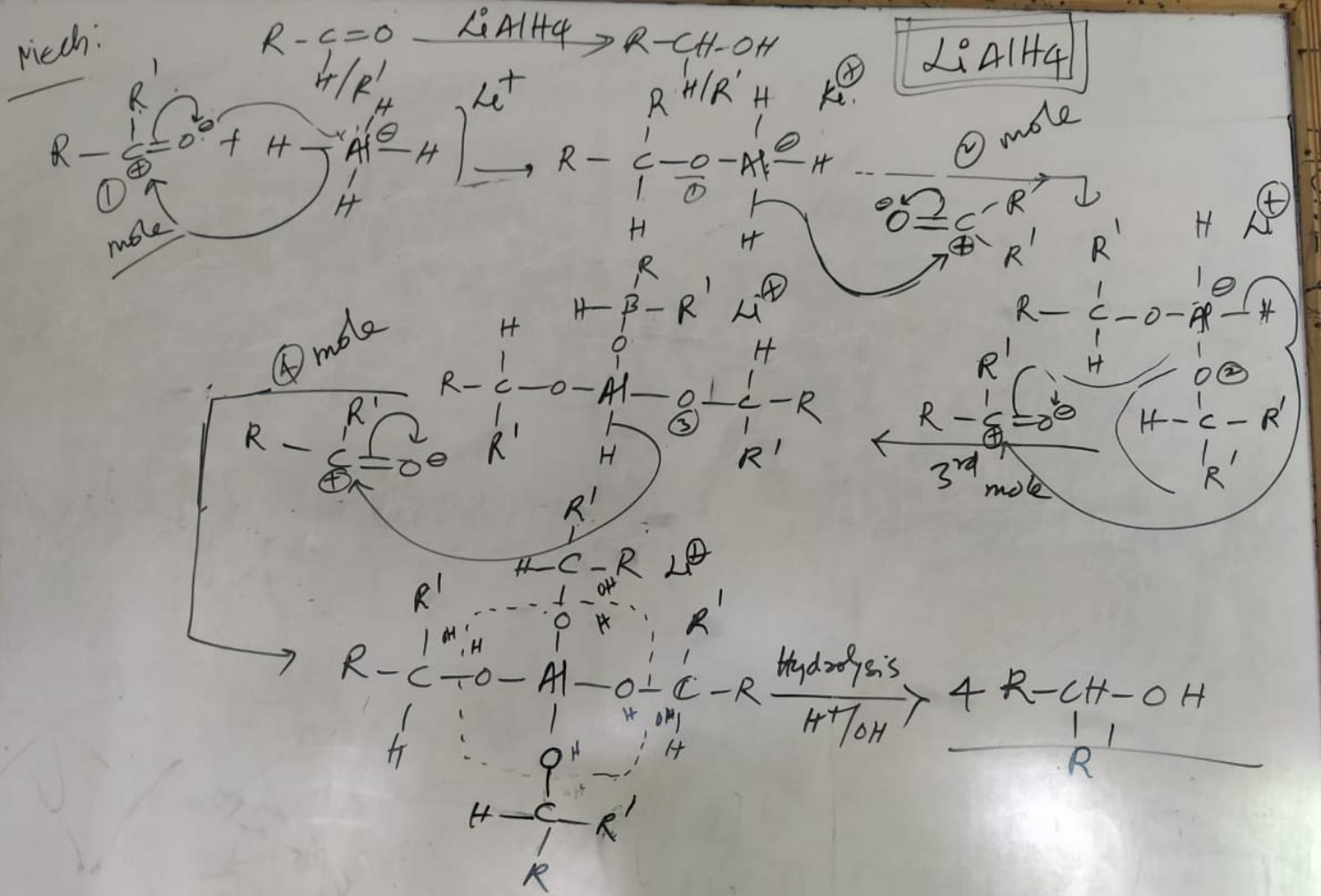
2020/4/17 10:36

P3

## Hydroboration of olefins:

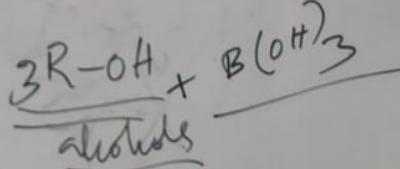
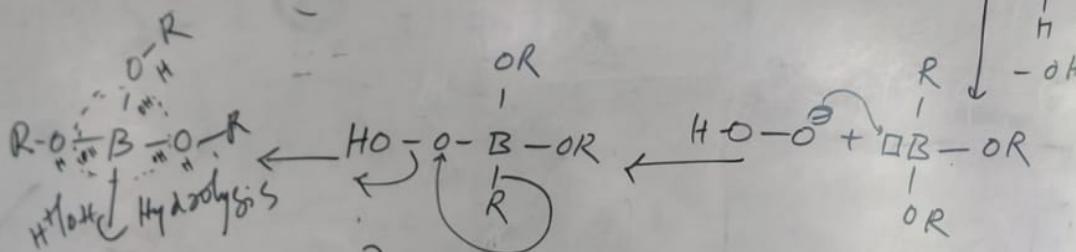
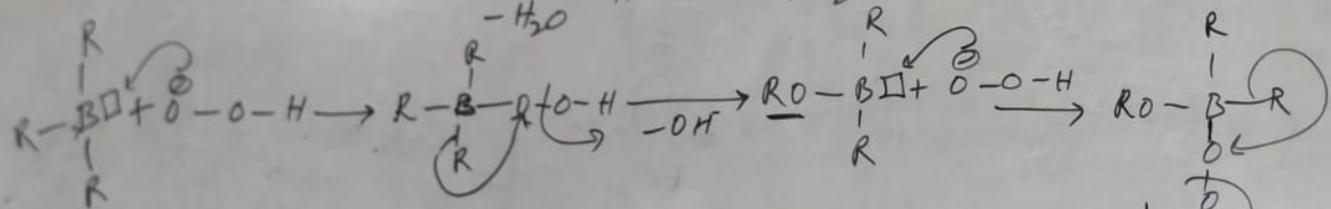
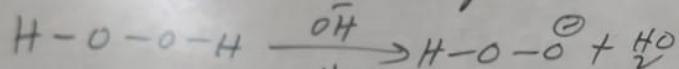
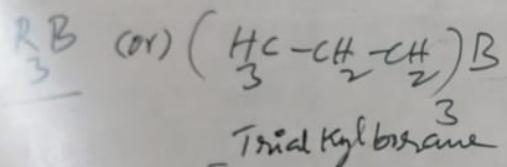
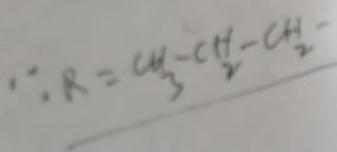
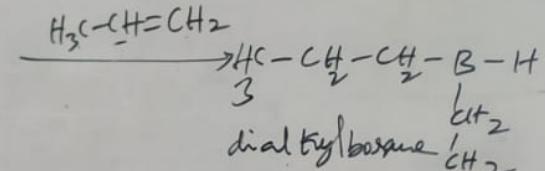
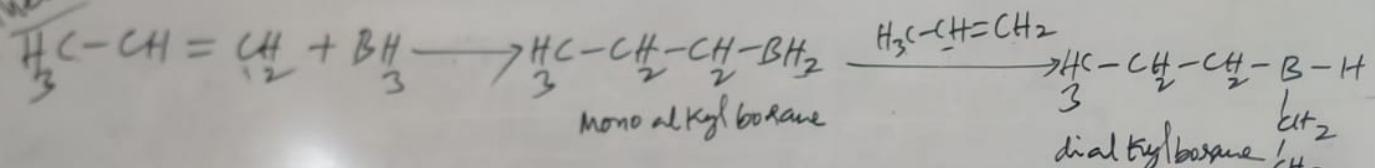


2020/4/18 10:32

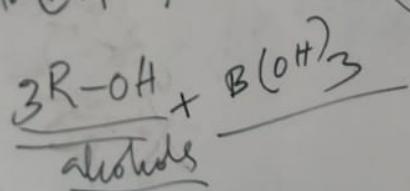
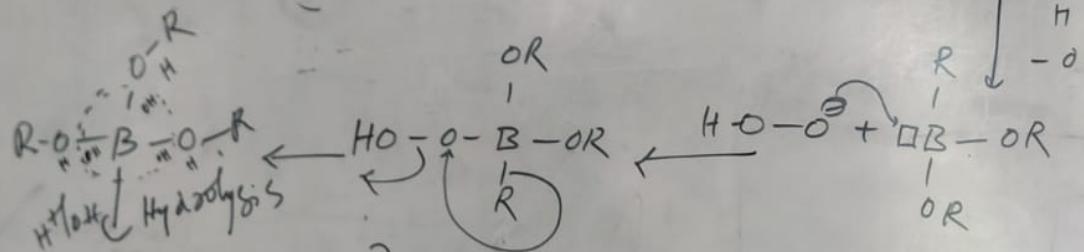
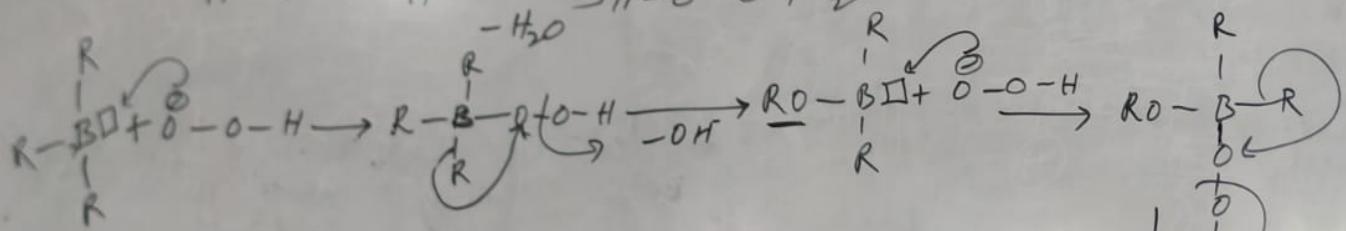
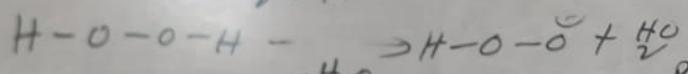
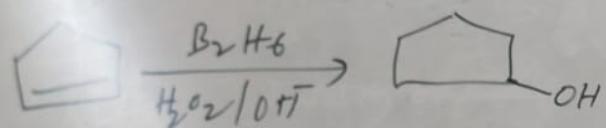
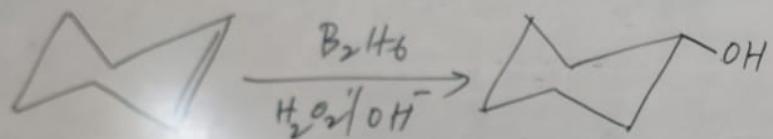


2020/4/18 10:01

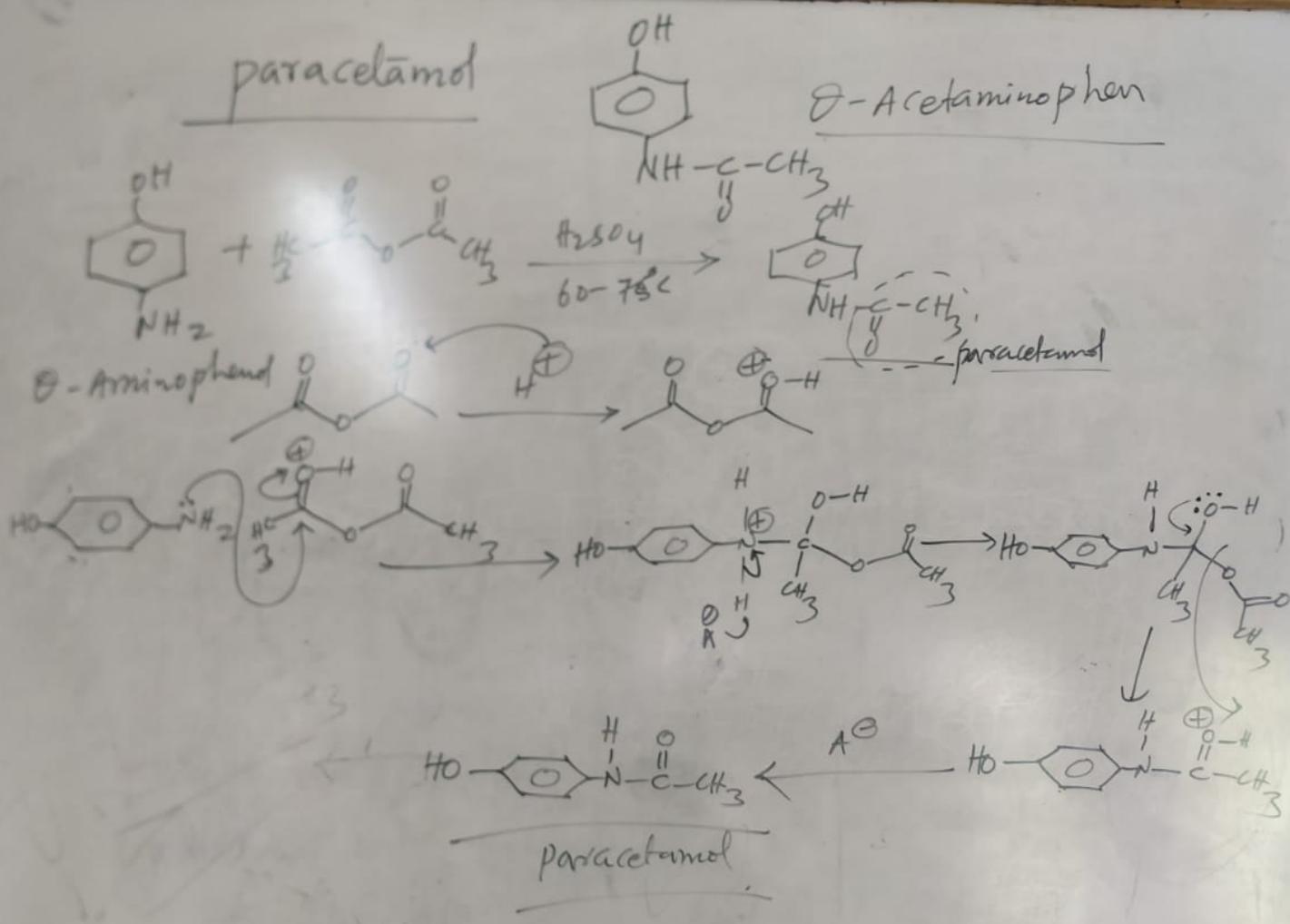
mech:



2020/4/18 10:48

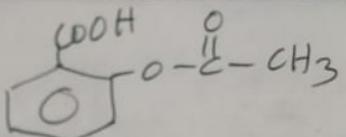


2020/4/18 10:53



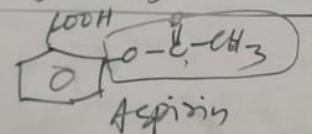
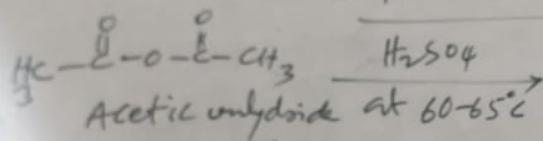
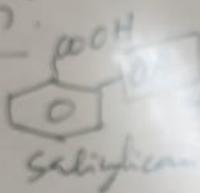
2020/4/18 11:37

## Aspirin

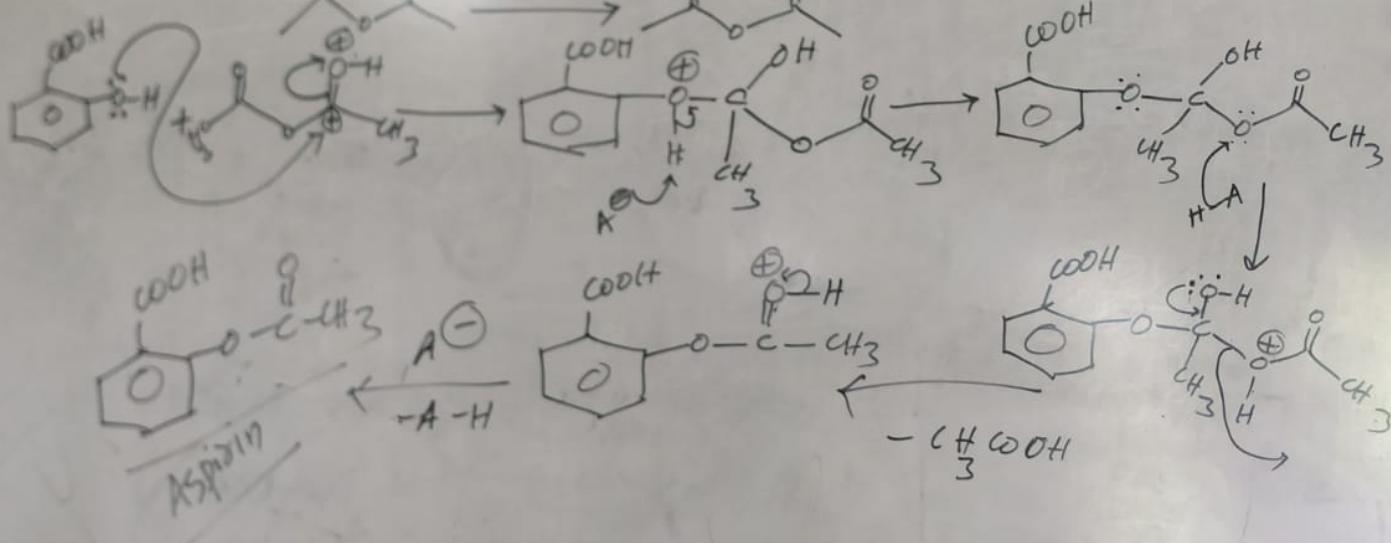


IUPAC: ortho-Acetyl Salicylic acid

preparation:

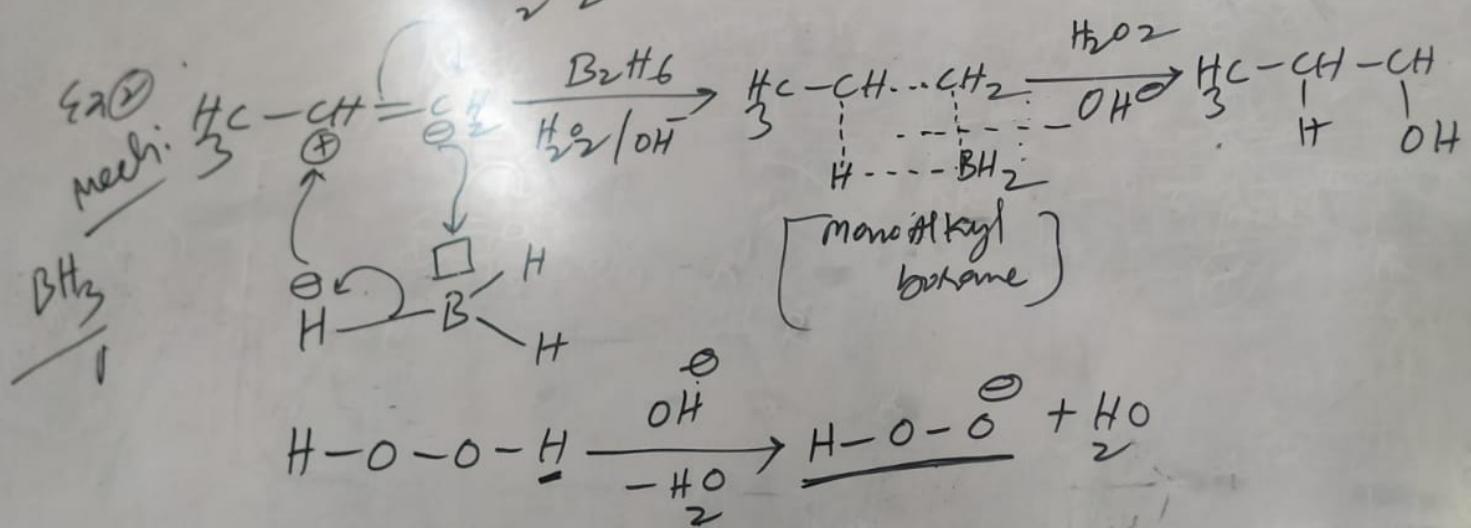
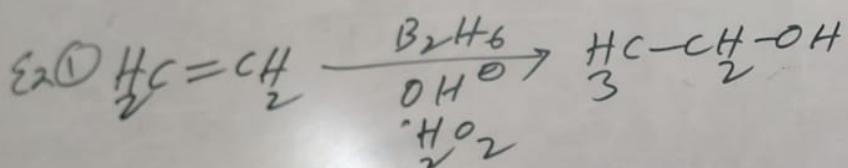


mech:



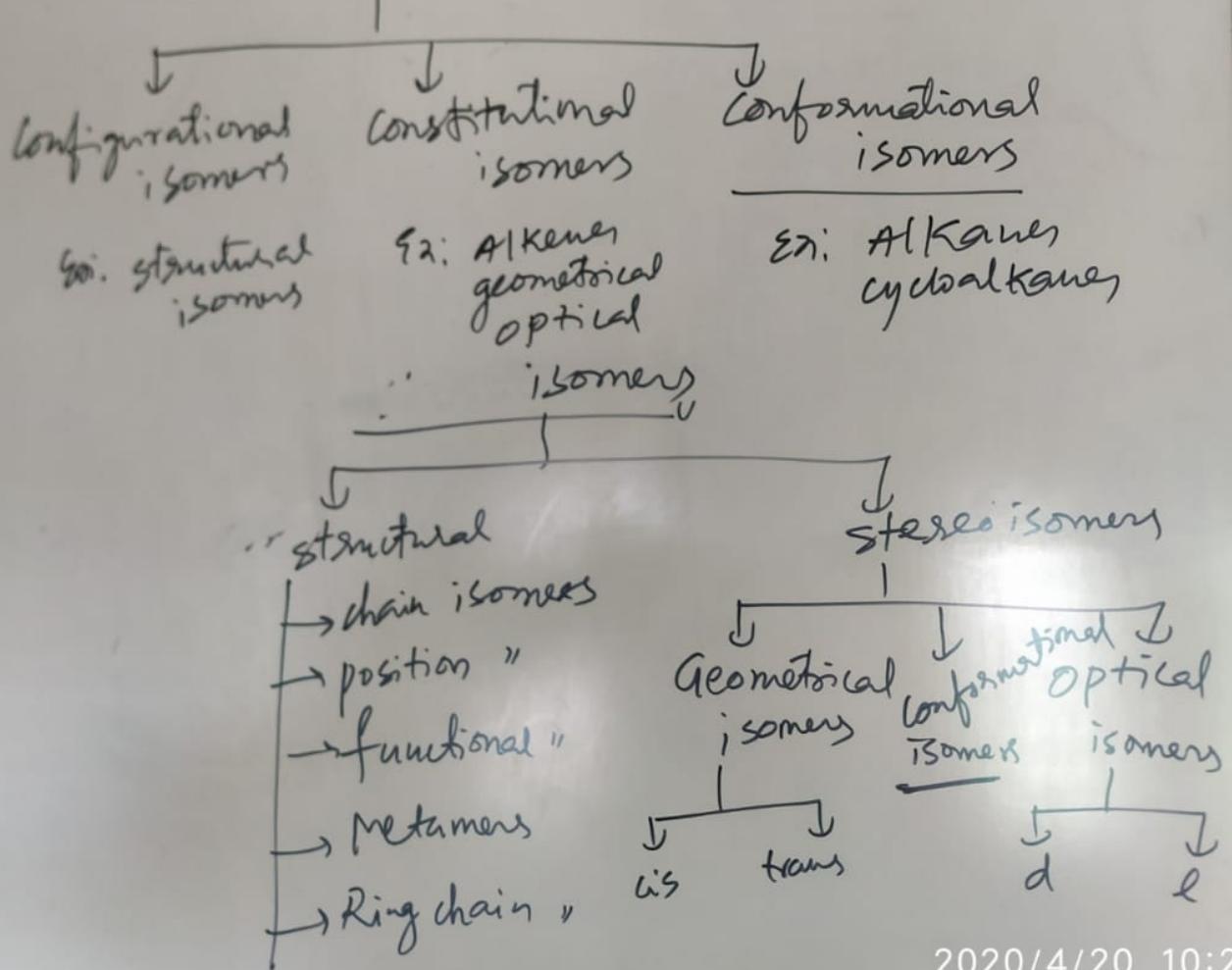
2020/4/18 11:11

## Hydroboration of olefins:



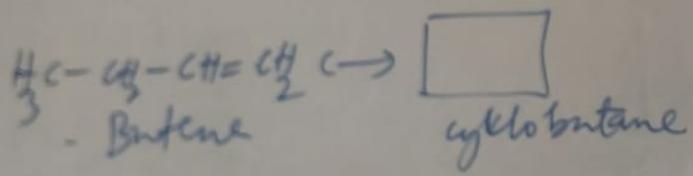
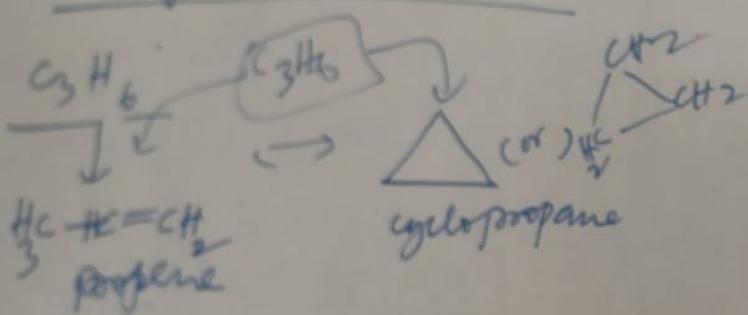
2020/4/18 10:32

# Stereochemistry



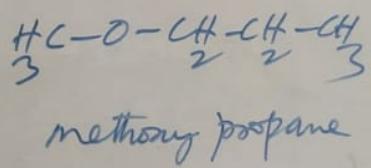
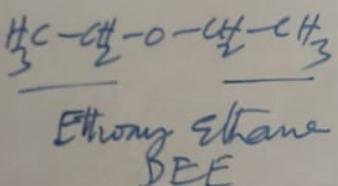
2020/4/20 10:25

### Ring chain isomerism

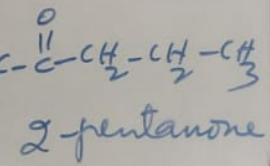
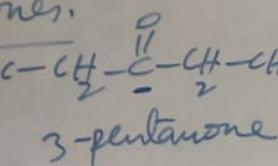


### Metamerism:

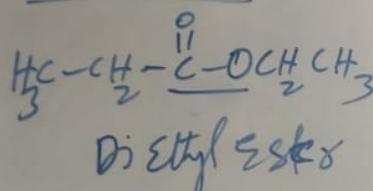
① In ethers:  $\text{R}-\text{O}-\text{R}$



② Ketones:



③ Esters:

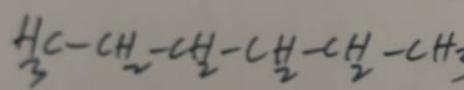
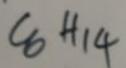


2020/4/20 11:05

## structural isomers

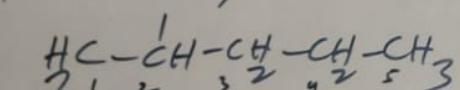
## (ii) chain isomerism

Heane

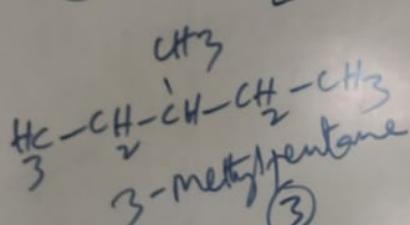


n-Heptane

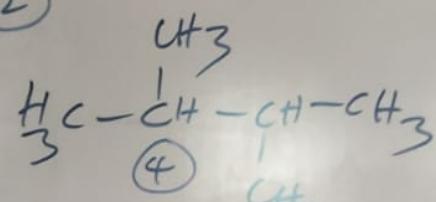
1



$\nearrow$  2-methylpentane (iso-Heptane)

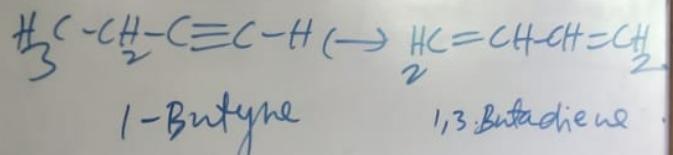
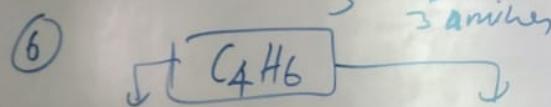
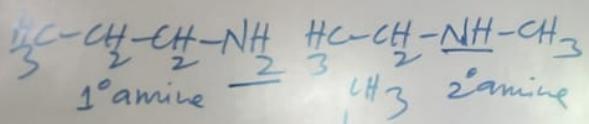
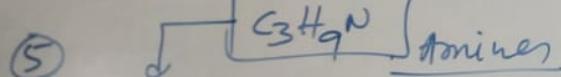
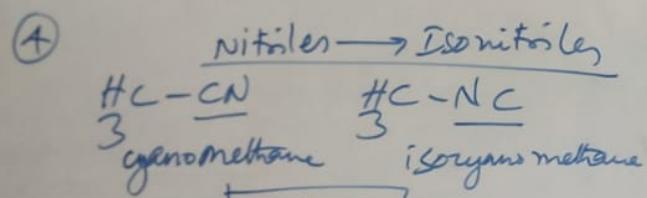
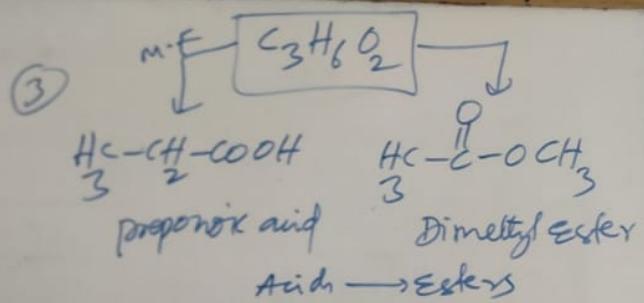
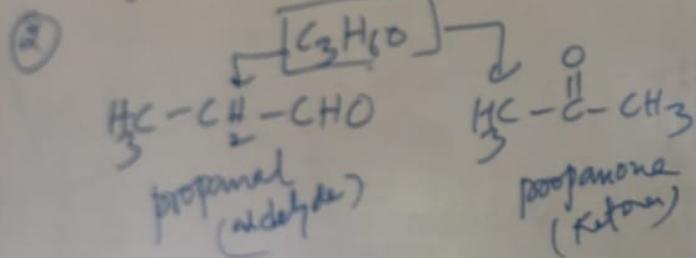
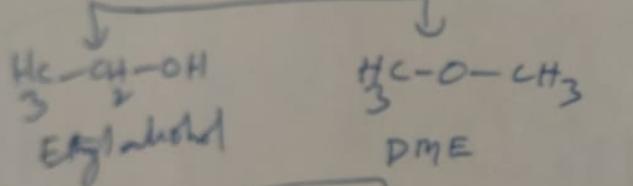
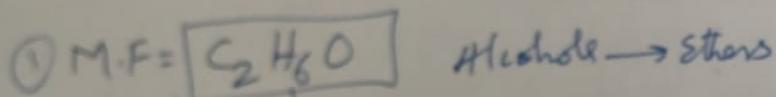


<sup>2</sup>  
3-methylper  
(3)



2,3 dimethylbutane  
(Neohexane)

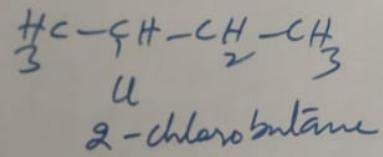
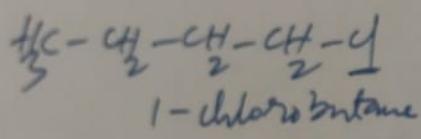
### Functional isomers:



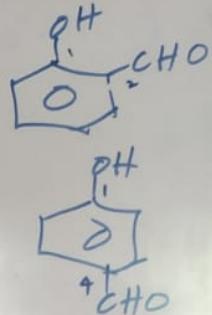
2020/4/20 10:56

## structural isomers

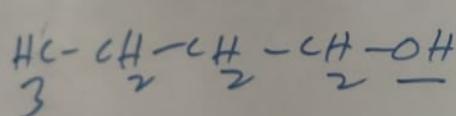
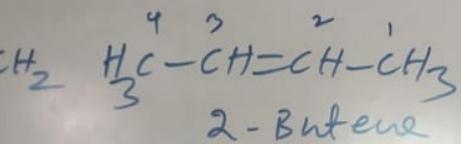
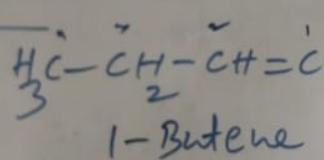
position isomers:  $C_4H_9Cl$



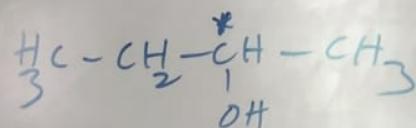
- hw
- 1 Alkenes
  - Alkynes
  - Alkyl halides
  - Alcohols
  - Carbonyl compounds



$C_4H_8$



1-Butanol

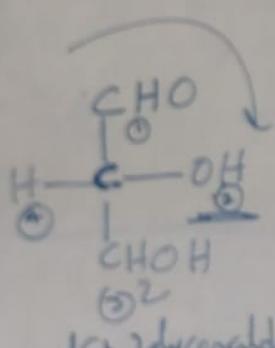
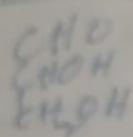


2-Butanol

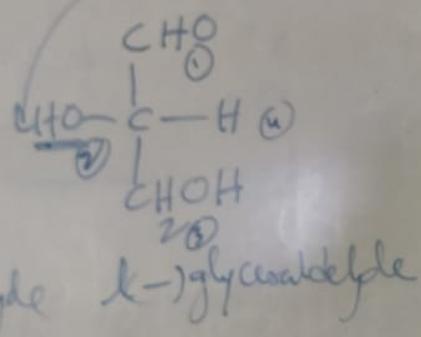
2020/4/20 10:40

## optical isomerism

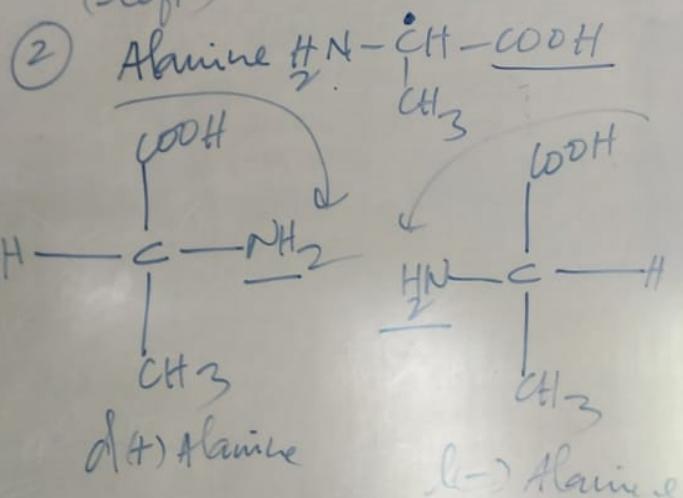
① glyceraldehyde



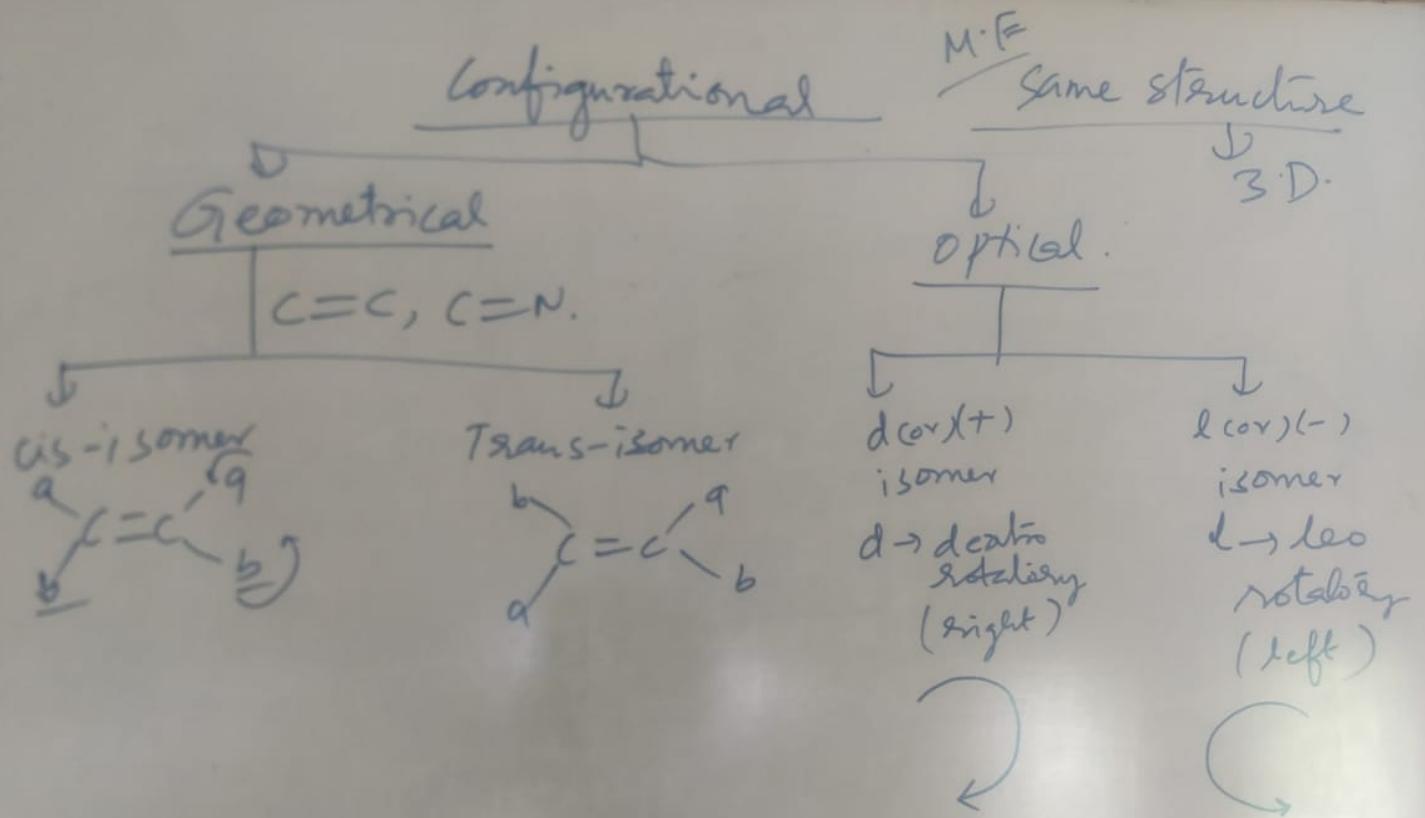
dextrorotatory  
d → dextro (right)



l (levorotatory)  
l = leo (left)

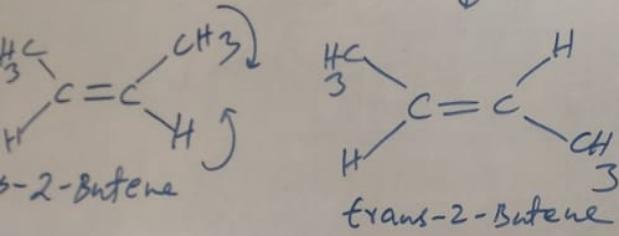
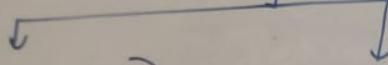
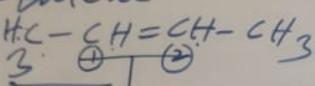


2020/4/21 10:51

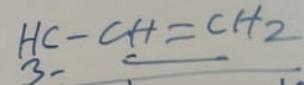
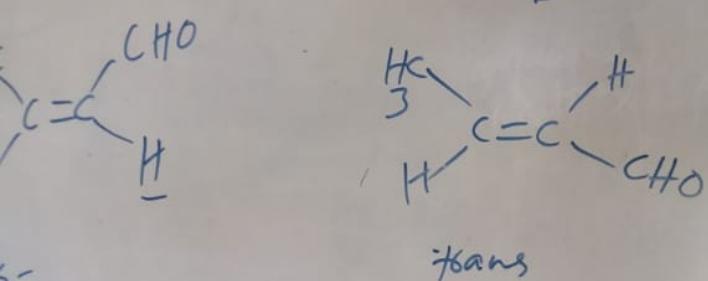
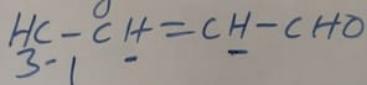


2020/4/21 10:11

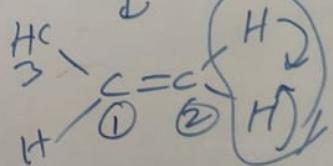
Ex(1) 2-Butene



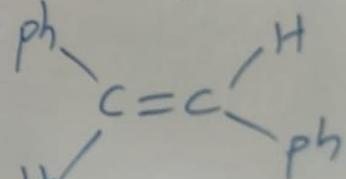
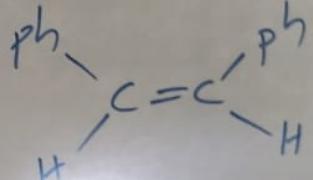
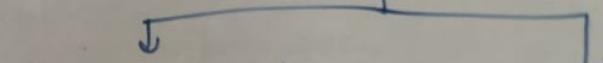
Ex(2) Octanaldehyde



No-geometrical



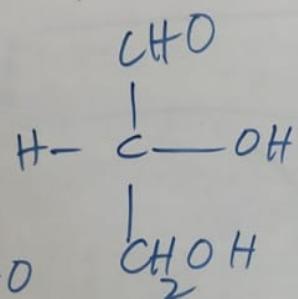
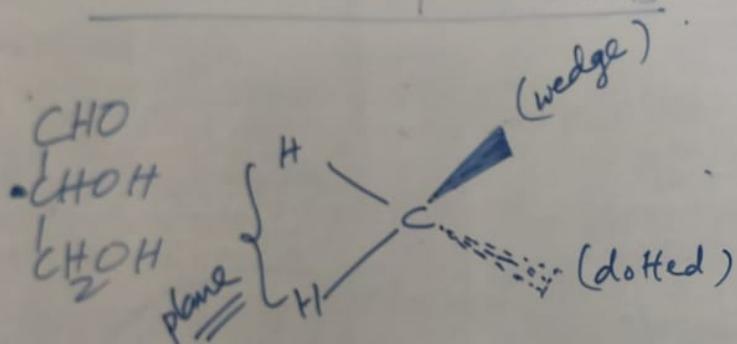
Ex(3) Stilbene  $\text{Ph}-\text{CH}=\text{CH}-\text{Ph}$



PPS: They differ B.pt, m.pt, solubility, refractive index

## Molecular Representations

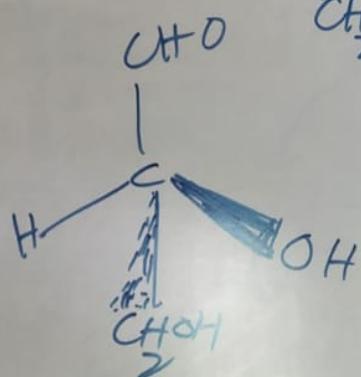
Any



1) Fischer projections

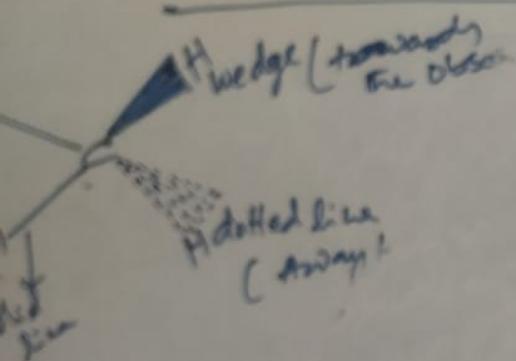
2) Newmann "

3) Sawhorse "

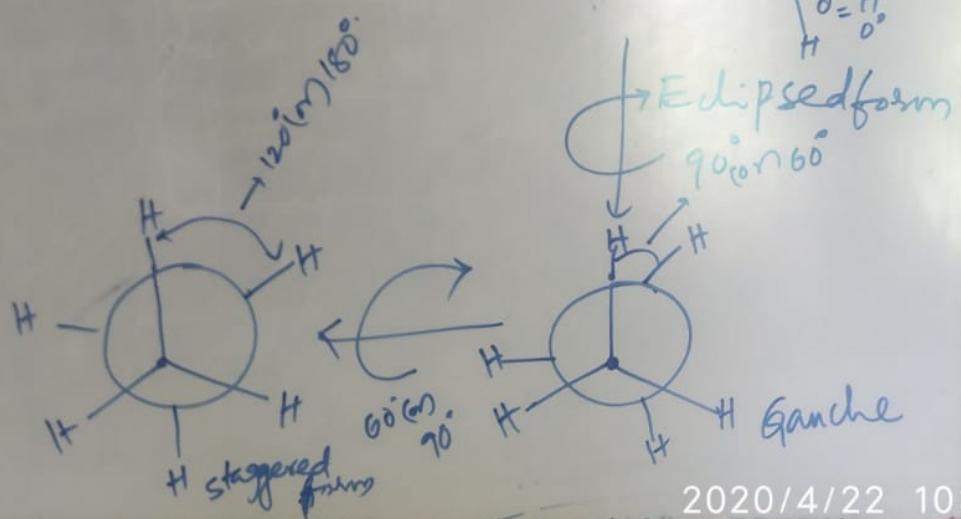
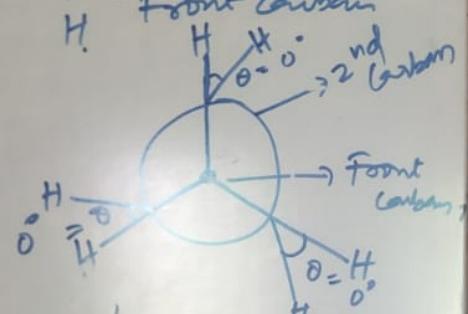
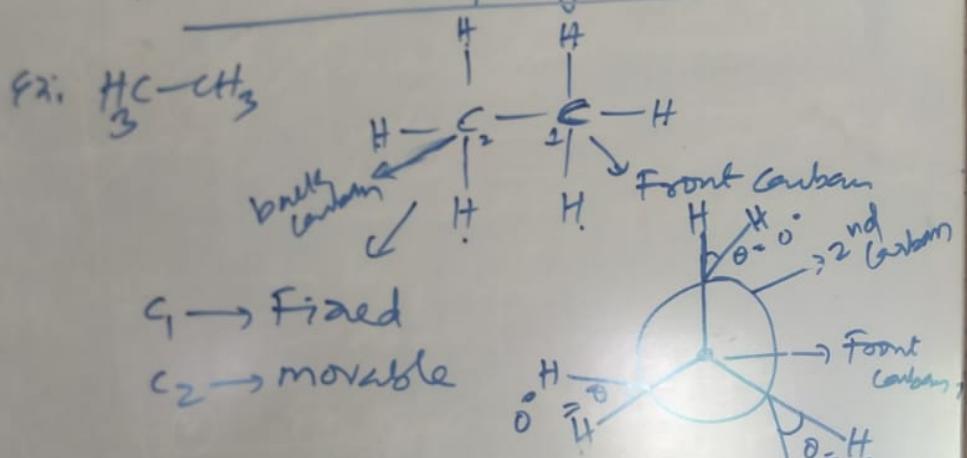


2020/4/21 11:02

## Molecular Representations of organic molecules

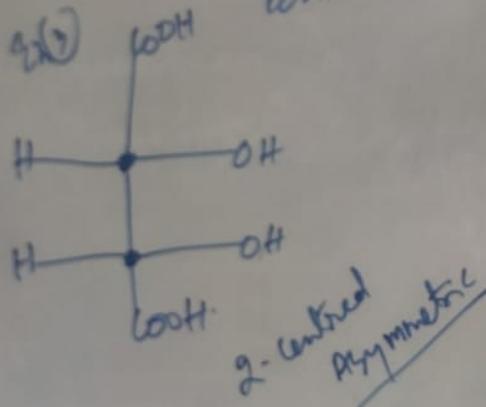
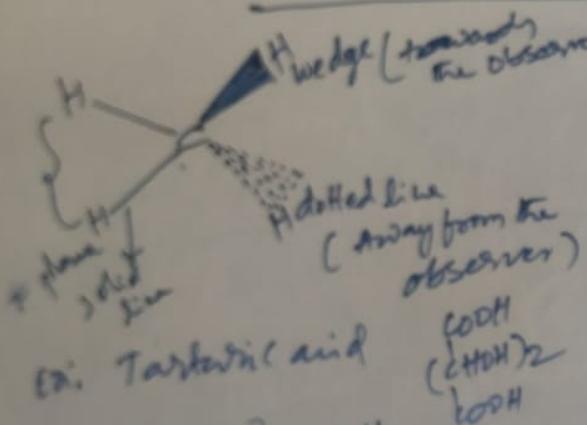


### b) Newmann projection



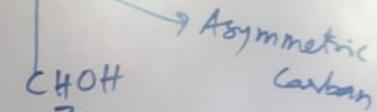
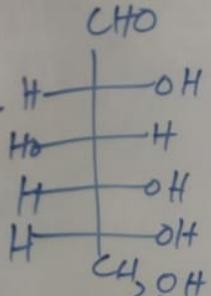
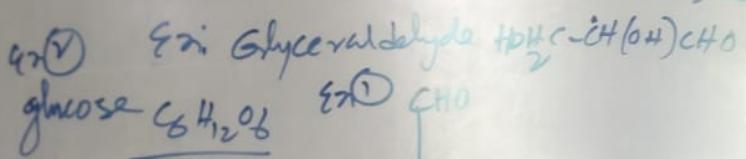
2020/4/22 10:42

## (3D) Molecular Representations of organic molecules



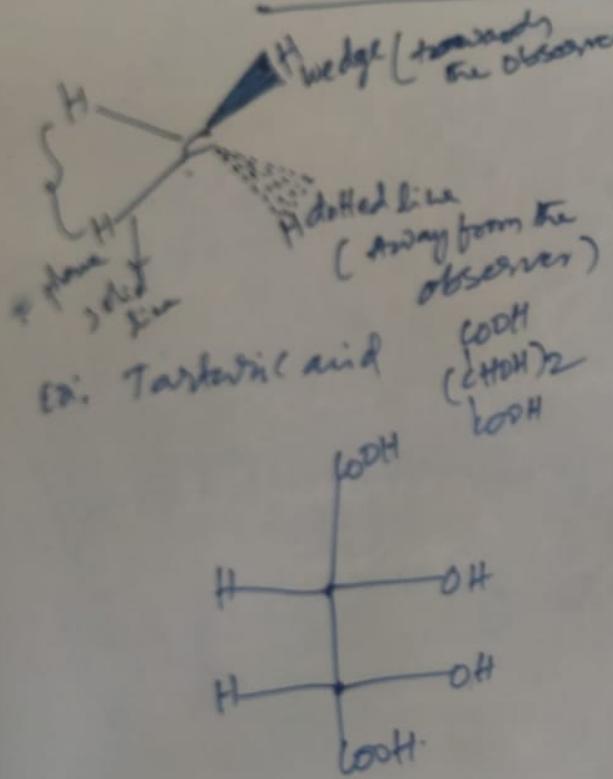
### a) Fischer projections:

- dot → centre atoms (asymmetric)
- base      } horizontal lines
- more oxidised gp on top.
- less/unoxidised gp at bottom
- remaining gp are on horizontal lines



2020/4/22 10:25

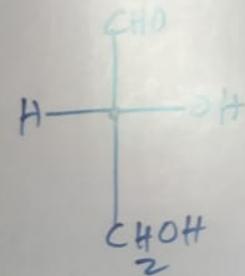
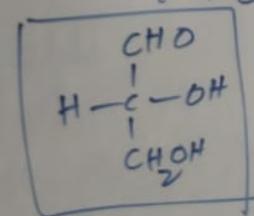
## (3D) Molecular Representations of organic molecules



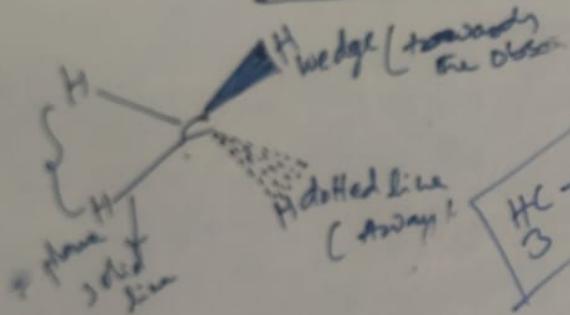
### a) Fischer projections:

→ centre atoms (asymmetric)  
 base      } horizontal lines  
 → more oxidised gr on top.  
 → less/unoxidised gr at bottom  
 → remaining gr are on horizontal lines

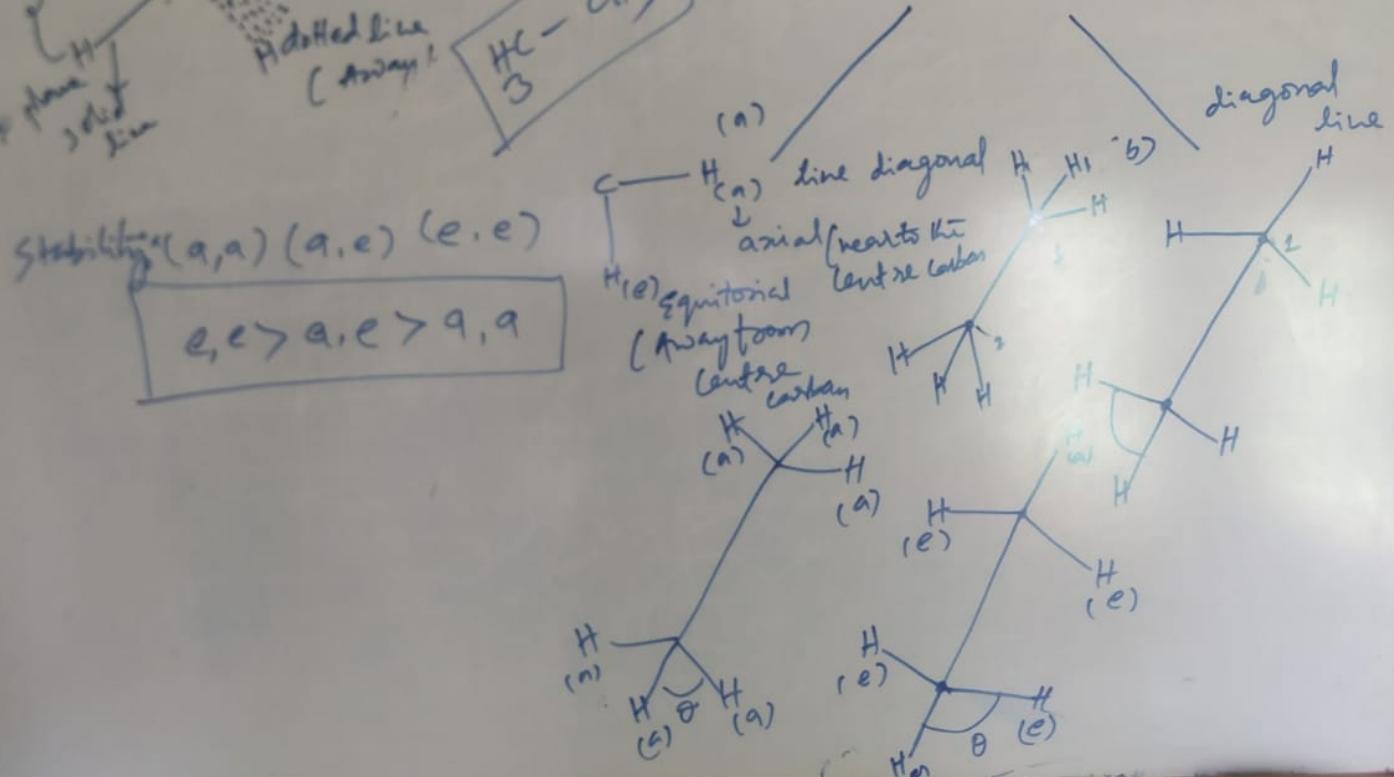
Ex: Glyceraldehyde  $\text{HO}_2\text{C}-\text{CH}(\text{OH})\text{CHO}$



## (3D) Molecular Representations of organic molecules



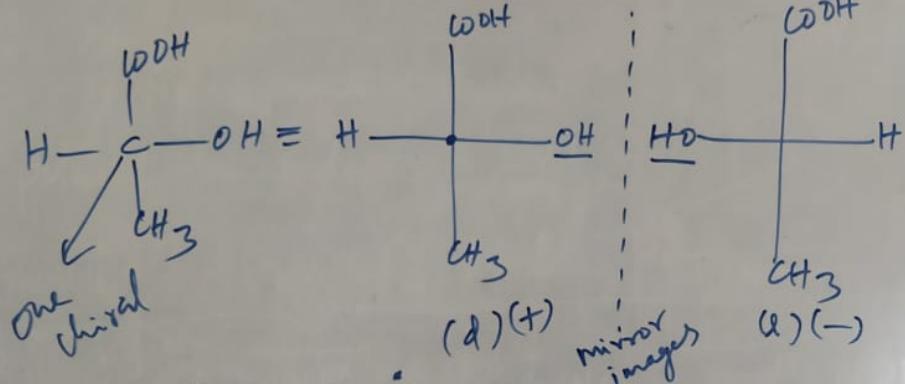
### c) Sawhorse projection



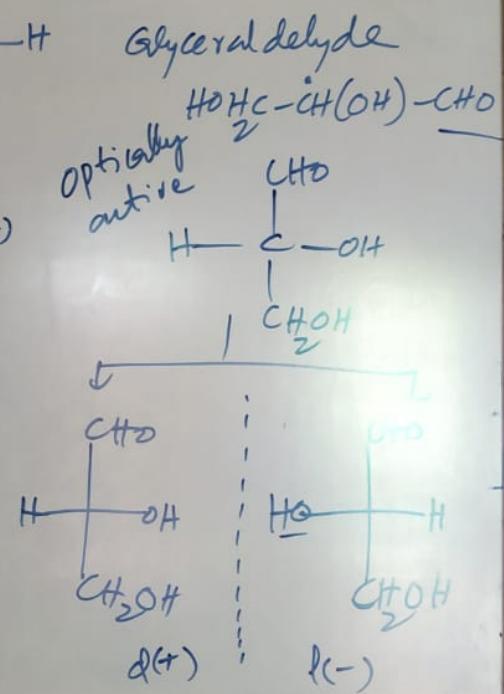
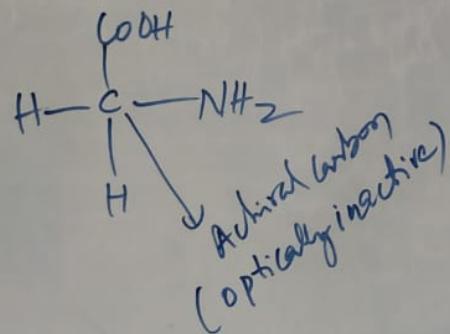
2020/4/22 10:50

## Optical isomerism of molecules having one chiral centre

Q2(i) Lactic acid  $\text{HC}-\overset{\text{D}}{\underset{\text{L}}{\text{CH}}}(\text{OH})-\overset{\text{D}}{\underset{\text{D}}{\text{COOH}}}$  optically active  $2^h = \frac{2^l}{2^l} = 2$   
 $\therefore n = \text{no. of chiral}$



Q2(ii) Glycine  $\text{H}_2\text{N}-\overset{\text{D}}{\underset{\text{D}}{\text{CH}}}-\text{COOH}$



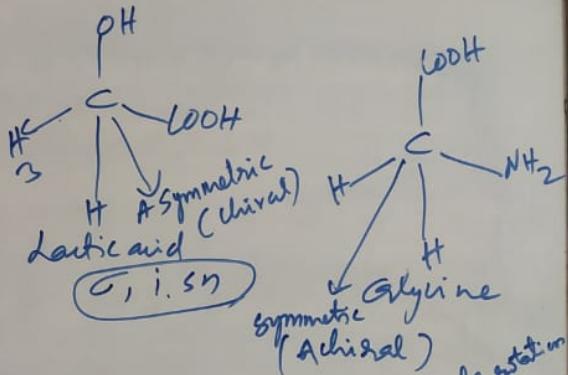
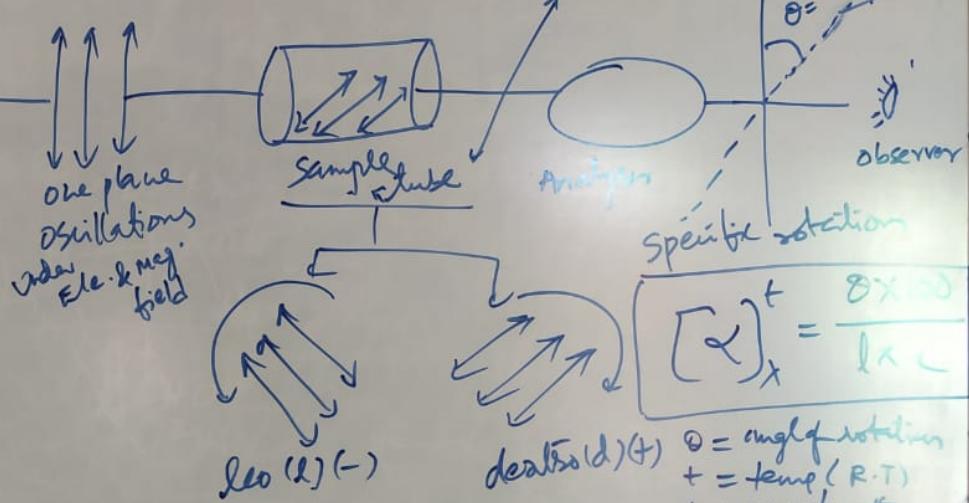
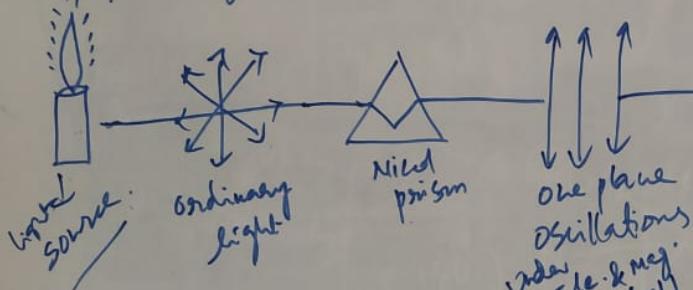
2020/4/23 10:57

## Optical activity

depends:

- (1) Asymmetric carbon (chiral carbon)
- 2) PPL
- 3) NO-Symmetry of elements

plane of plane polarised light (PPL)



$$[\alpha]_D^T = \frac{\theta \times 10}{l \times c}$$

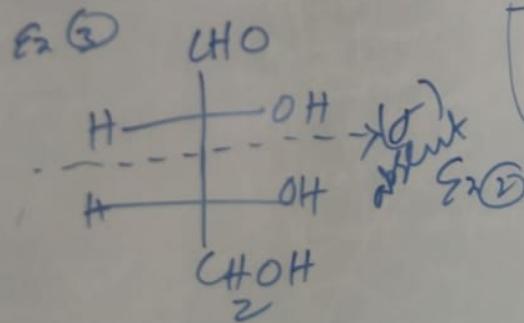
Definitions:  
 $\theta$  = angle of rotation  
 $T$  = temp (R.T)  
 $\lambda$  = wavelength  
 $l$  = length of tube  
 $c$  = conc of soln

2020/4/23 10:41

## (3D) Molecular Representations of organic molecules

### Symmetry of elements

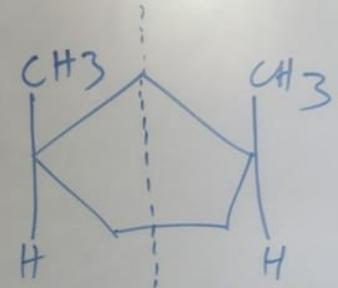
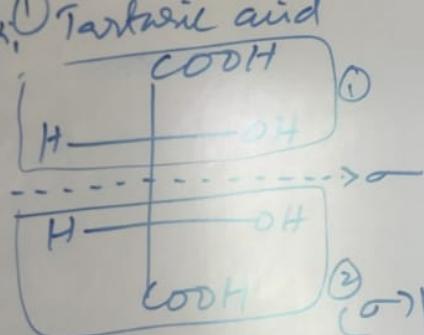
1. plane of symmetry ( $\sigma$ )
2. Centre of symmetry (i)
3. Axis of symmetry ( $S_n$ )



symmetry = two equal halves

### a) plane of symmetry

Ex: ① Tartaric acid

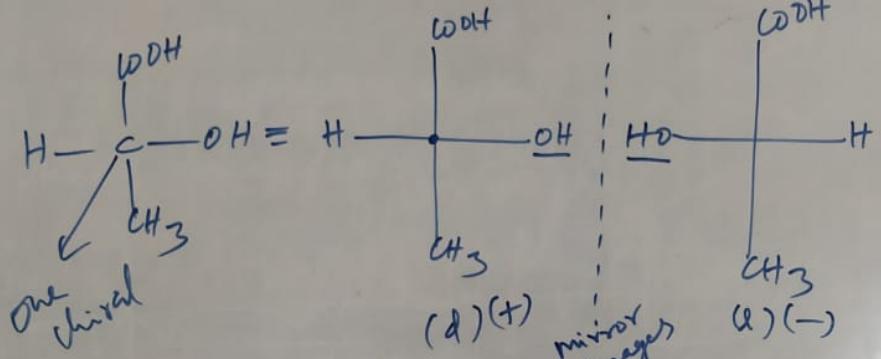


2020/4/22 11:01

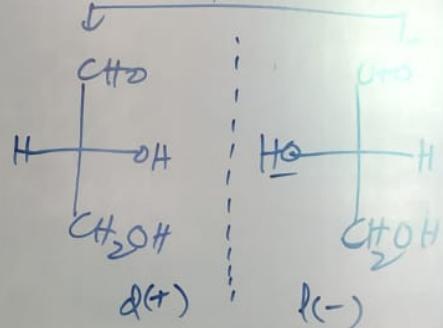
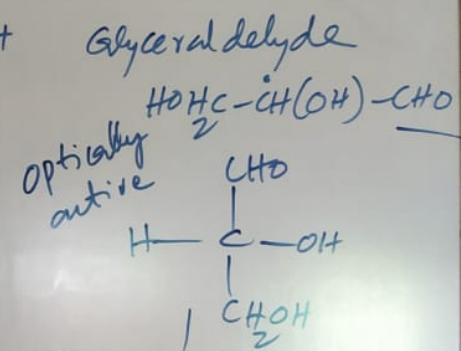
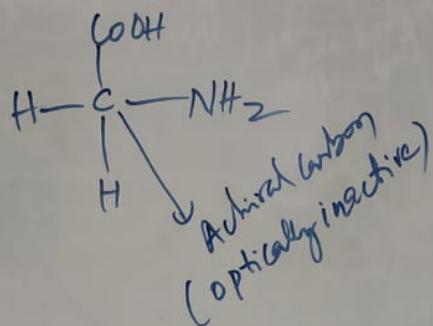
### Optical isomerism of molecules having one chiral centre

Q1 Lactic acid  $\text{HC}-\text{CH}(\text{OH})-\text{COOH}$  optically active

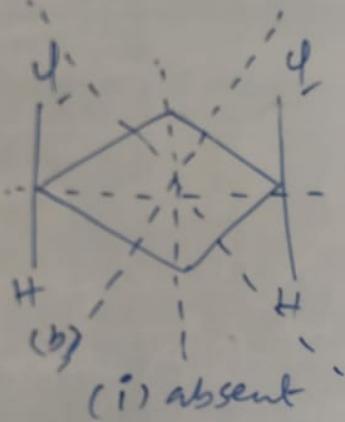
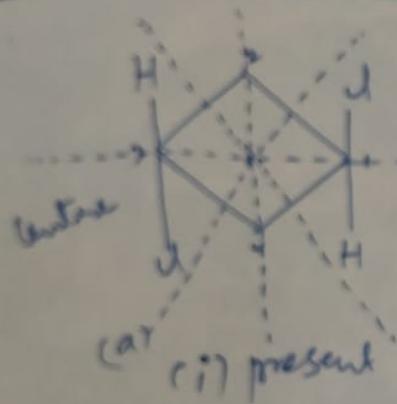
$$2^n = \frac{2^1}{2} = 2 \\ \therefore n = \text{no. of chiral}$$



Q2 Glycine  $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$

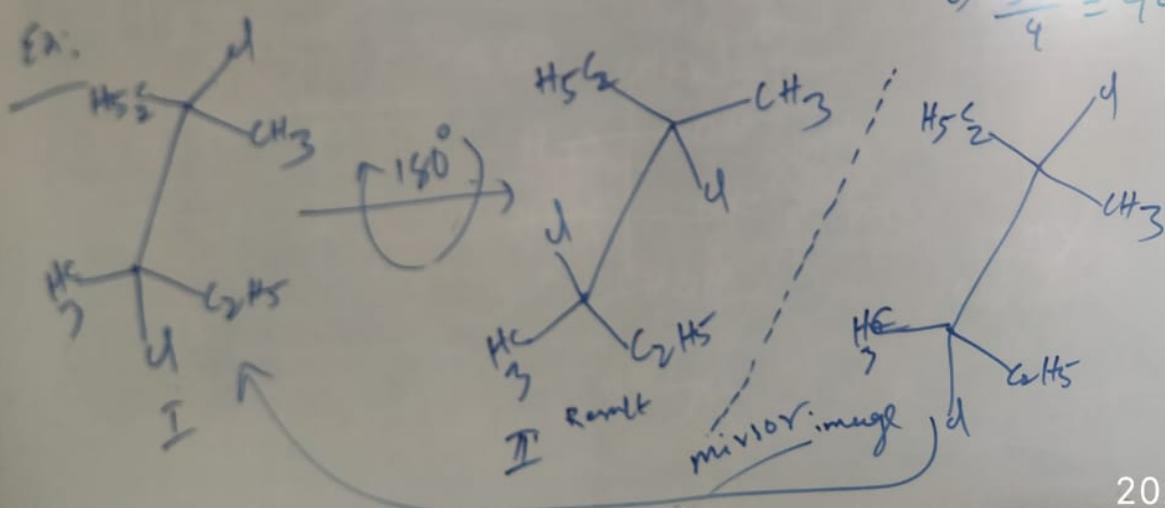


## 2) Centre of Symmetry



## 3) Axis of Symmetry

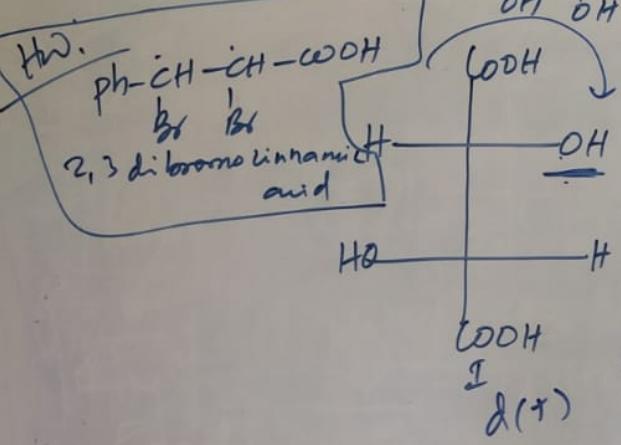
- $\frac{360^\circ}{n}$  (no. of fold axis of symmetry)
- $\frac{360^\circ}{2} = 180^\circ$  (two-fold axis of symmetry)
  - $\frac{360^\circ}{3} = 120^\circ$  (three-fold axis of symmetry)
  - $\frac{360^\circ}{4} = 90^\circ$  (four-fold axis of symmetry)



2020/4/23 10:18

## Optical isomerism of Compounds containing two chiral centres

e.g. Tartaric acid  $\text{HOOC}-\overset{\text{OH}}{\underset{\text{OH}}{\text{CH}}}-\overset{\text{COOH}}{\underset{\text{OH}}{\text{CH}}}-\text{COOH}$



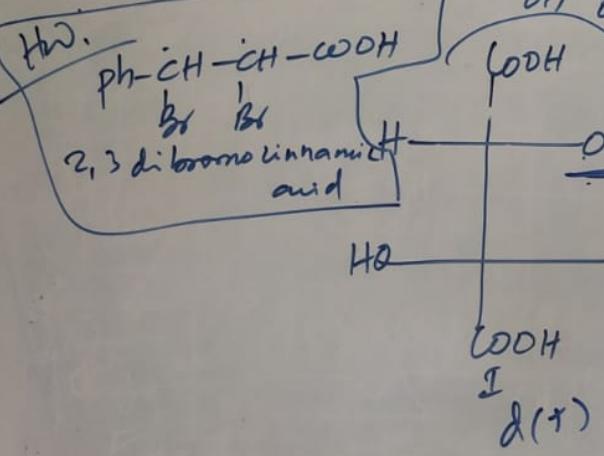
Enantiomers properties:

- Same phys. props like B.pt density, M.pt, M, solubility
- Same chemical thermodynamic PPs.
- Both are optically active with same extent of specific rotation
- They can pass PPL in opp. directions but same extent
- They differ in biological properties

2020/4/24 10:35

## optical isomerism of Compounds I & II

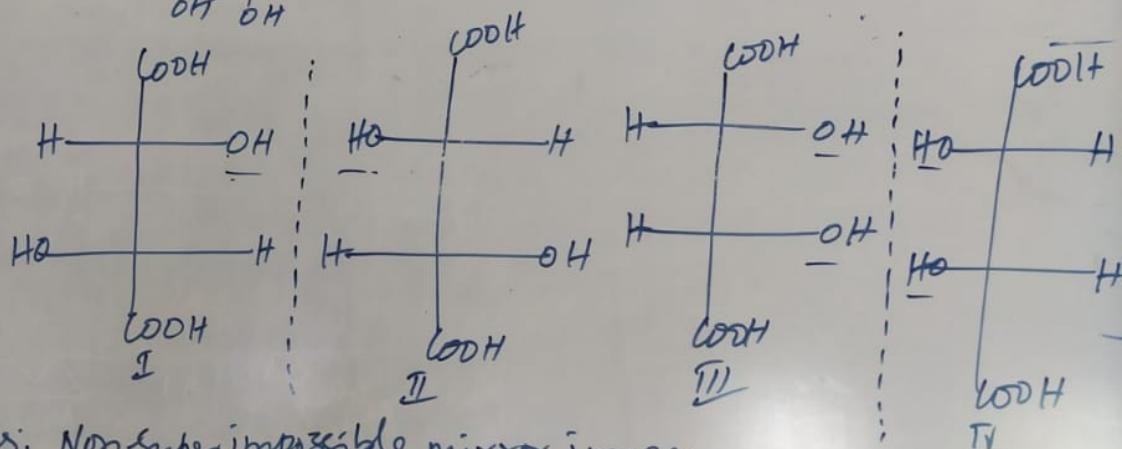
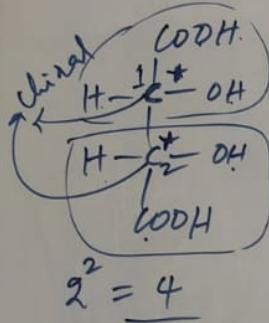
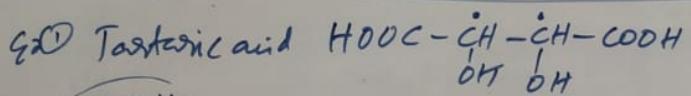
Eg) Tartaric acid HOOC-CH(OH)-CH(OH)-COOH



Diastereomers:  
properties:

- they diff. in phys. props like B.pt density, M.pt, M, solubility
- same chemical props
- they diff. specific rotation with diff. extent of rotation
- they diff. in biological PPs

## optical isomerism of Compounds containing two chiral Centres



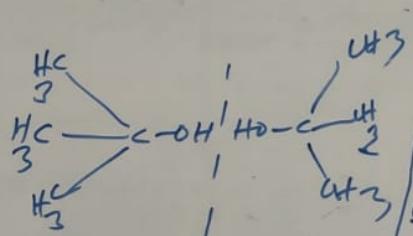
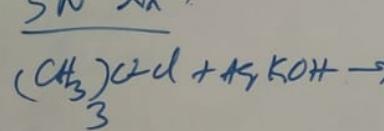
Enantiomers: Non-superimposable mirror images

I & II }  
 III & IV } → Enantiomers

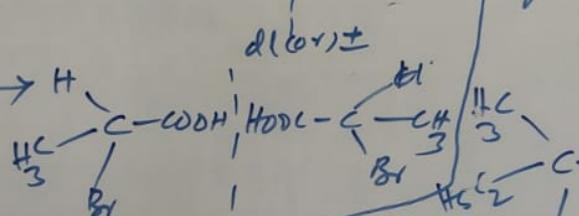
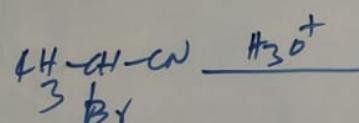
Diastereomers: Non-mirror images I & III  
 II & IV

PPTn of R-M

(1) SN' Nixn



(2)



Resolution of racemic modifications

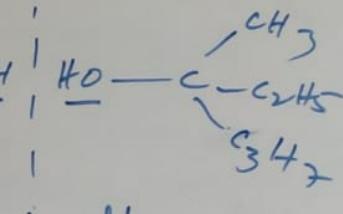
- R.M  
method
- 1) physical method
  - 2) Biological method
  - 3) Chemical method

Enantiomers

90:10
25:75
50, 50

Racemic mixtures (R.M)

Equimolar mixture of (1:1) of Enantiomers are called R.M



± and 1  
(+) → d  
(-) → l  
(+) (L) (D) (1:1)  
Equimolar

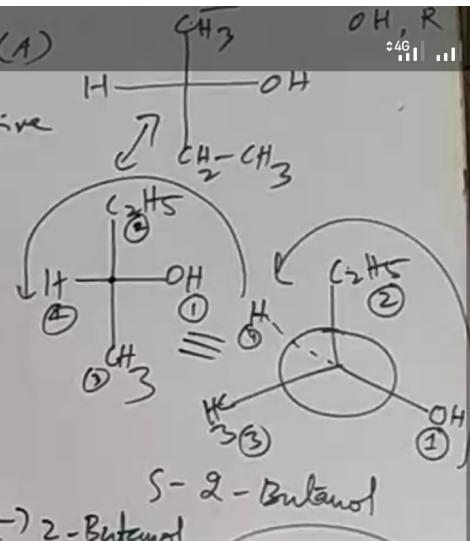
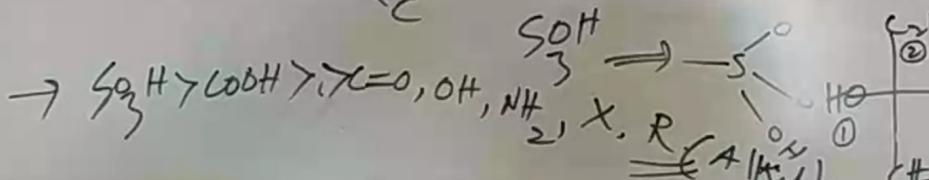
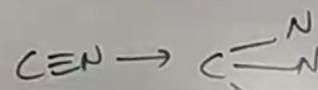
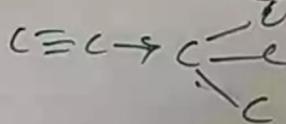
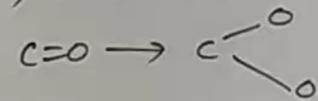
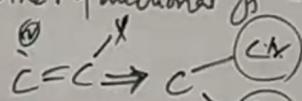
10:52

→ If At. No. give same given priority towards At. Mass (A)

→ TWO substituents present same (functional gp) give large chain (more At. M)

→ Same functional gp (Alkyl) → second carbon

→ Other functional gp  $C=C$ ,  $C\equiv C$ ,  $C\equiv N$ ,  $C=O$



(-)-2-Butanol

You

G

$\text{R} \rightarrow$  Neans = right side  
 $\text{S} \rightarrow$  Senester = left side

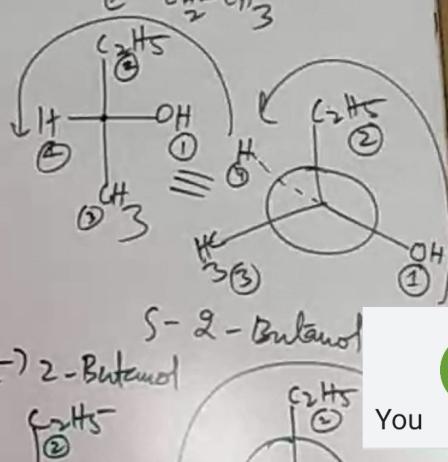
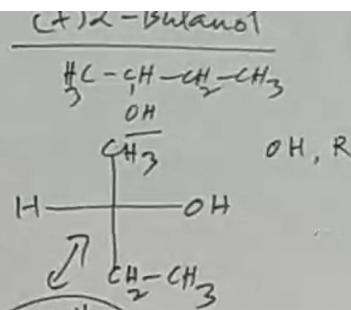
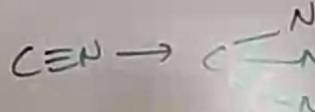
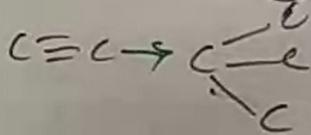
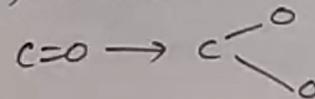
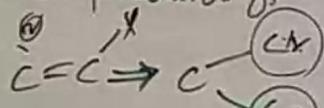
Rules: (1) Priority first  $\rightarrow$  At. No. ( $\Sigma$ )

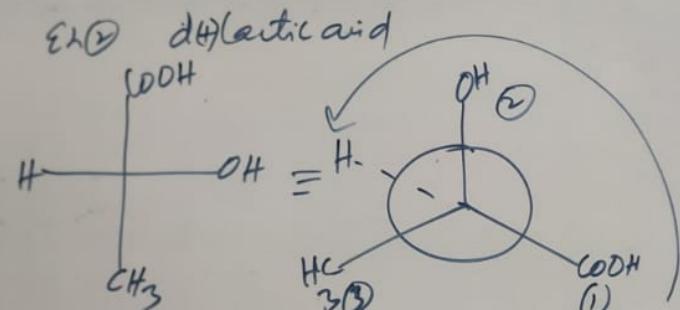
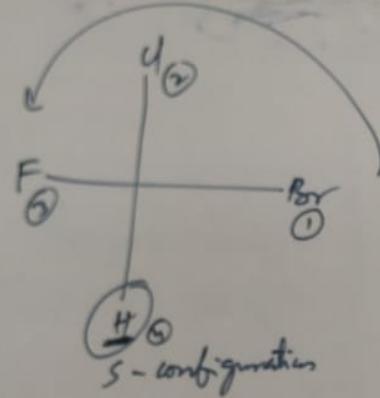
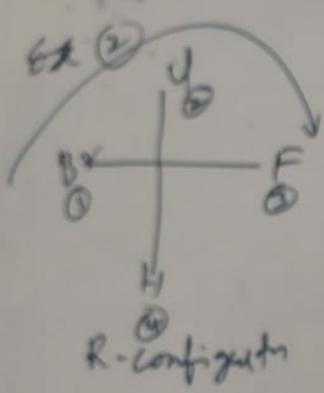
$\rightarrow$  If At. No. are same given priority towards At. Mass (A)

$\rightarrow$  Two substituents present same (functional group) give large chain (more At. Mgt.)

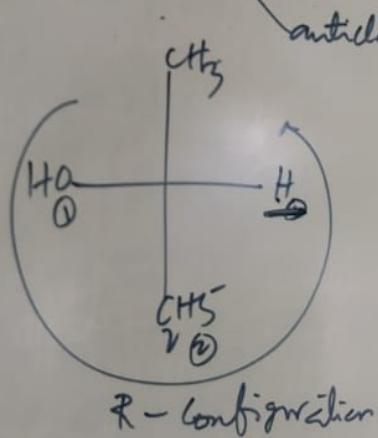
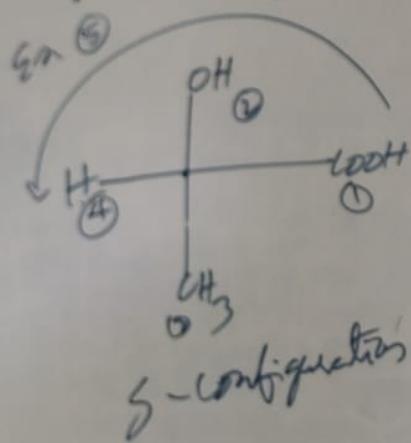
$\rightarrow$  Same functional group (At. Mgt.)  $\rightarrow$  second carbon

$\rightarrow$  other functional groups  $\text{C}=\text{C}$ ,  $\text{C}=\text{E}$ ,  $\text{C}=\text{N}$ ,  $\text{C}=\text{O}$





If the least priority gp as horizontal



clockwise  $\rightarrow$  S-(-)anti acid

anticlock  $\rightarrow$  R

H-W

L.S Nomenclature

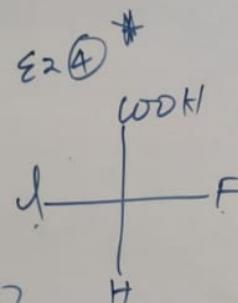
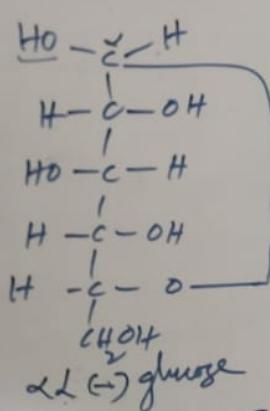
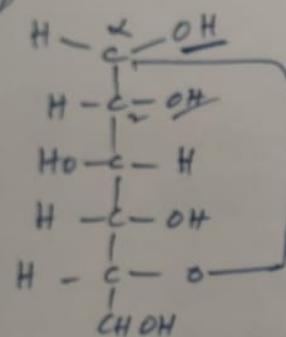
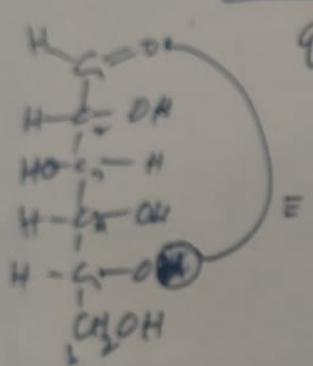
1) Alanine

2) glyceric acid

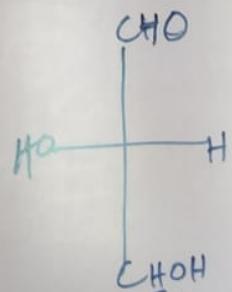
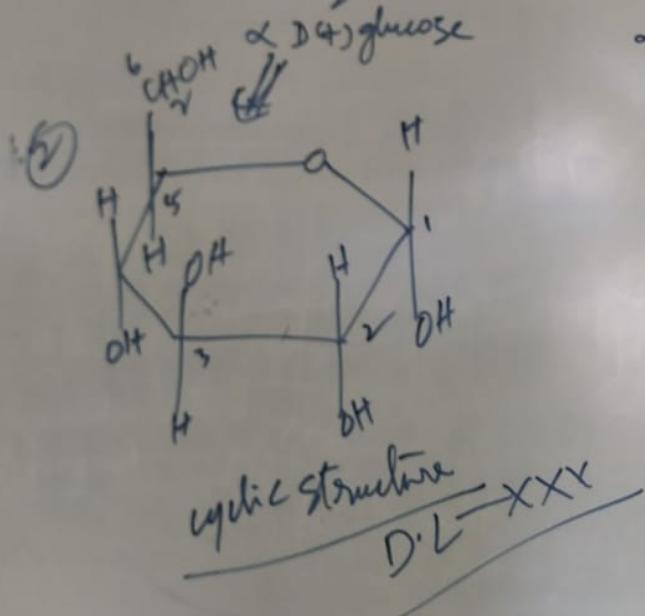
3) Mandelic acid

4) 2-chlorobutane

Glucose :  $C_6H_{12}O_6$



(1) two E.N groups present on horizontal line - D.L not applicable



2020/4/25 10:29

## Greek R,S Nomenclature

R → Rectus = right side  
 S → Seneser = left side

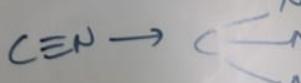
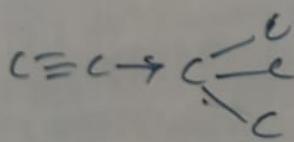
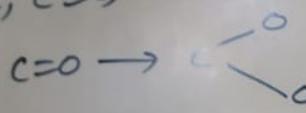
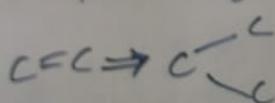
Rules: (1) Priority first → At. No (Z)

→ If At. No. give same given priority toward At. Mass (A)

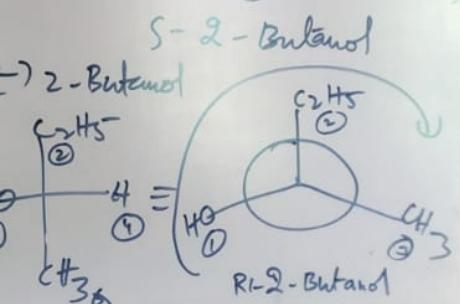
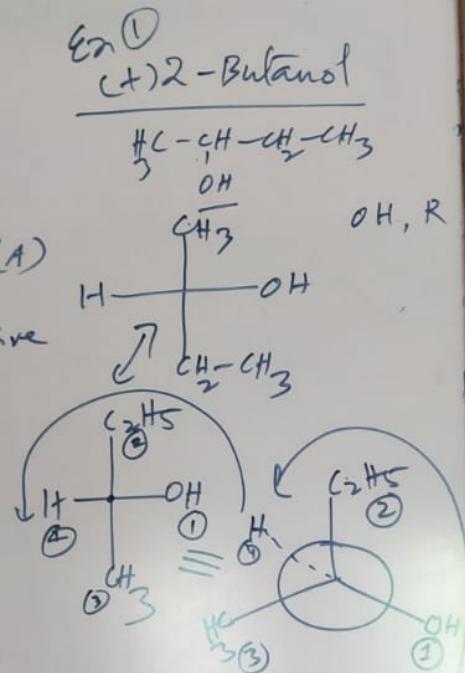
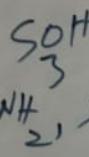
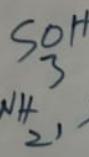
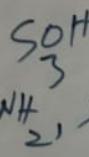
→ Two substituents present same functional gr. give large chain (more At. No.)

→ Same functional gr. (At. No.) → second carbon

→ other functional gr. C=C, C=O, C≡N, C=O



→  $S_3^+H > COOH > i>C=O, OH, NH_2, X, R$



2020/4/25 10:48

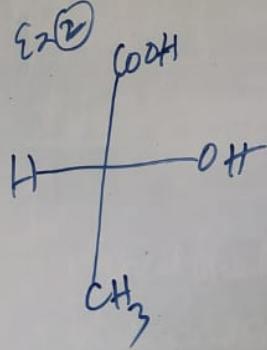
## Configuration

Absolute configuration

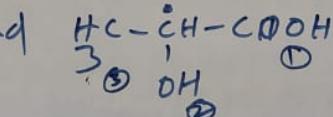
Ex: one chiral centre

Ex: R, S Nomenclature

Ex: lactic acid



d(+) Lactic acid



l(-) Lactic acid

Relative Configuration

Ex: one or more chiral centres

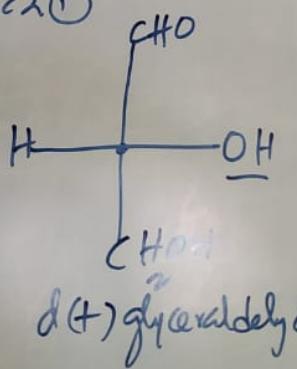
Ex: D,L Nomenclature

cont: CHO, CN, OH etc  
etc ph, etc

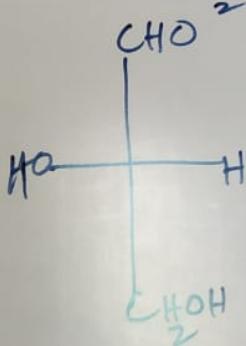
## D, L Nomenclature

Compound should be in Fischer projection  
more oxidised gp should be on top  
on oxidised gp. 1 " " at bottom  
remaining gp " " at horizontal rows  
More E.N on right side → dextro (+) (d)  
More E.N on left side → levo (-) (l)

Ex ①



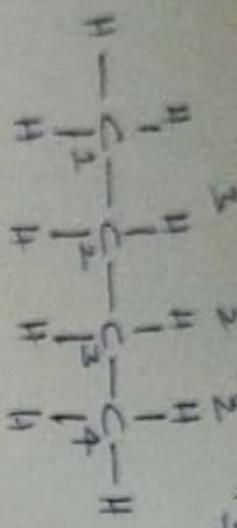
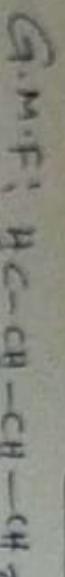
d(+) glyceraldehyde



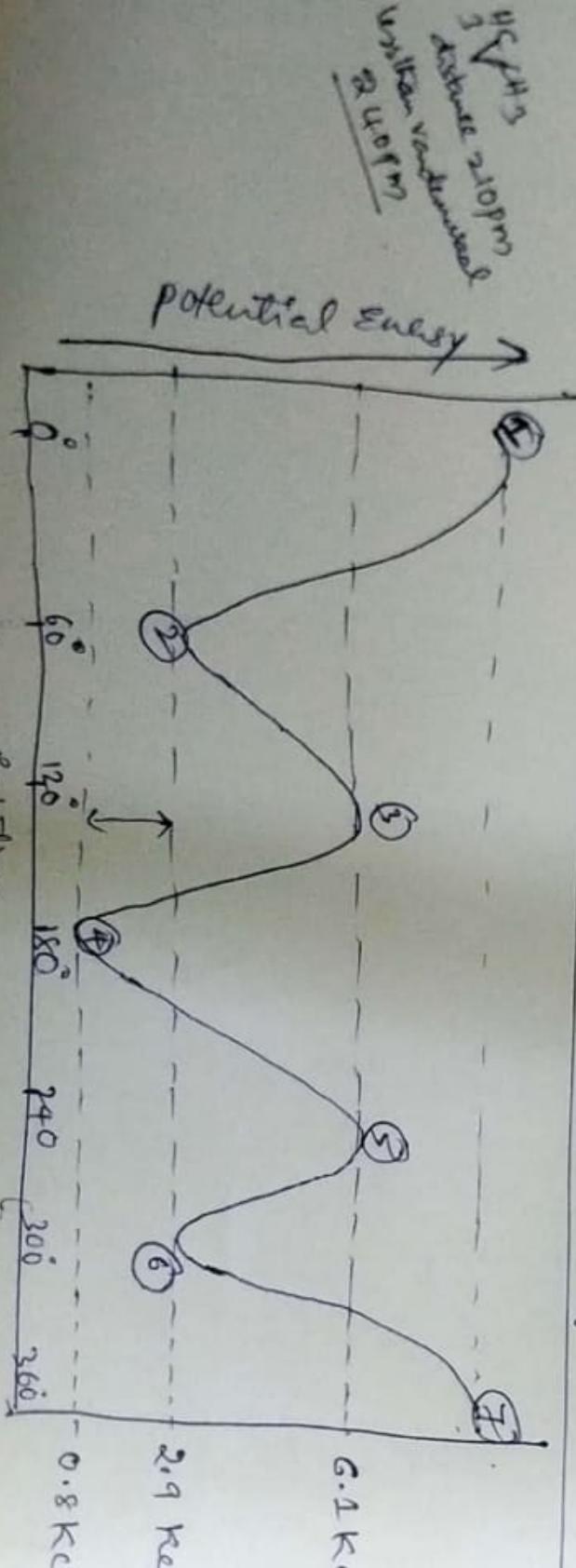
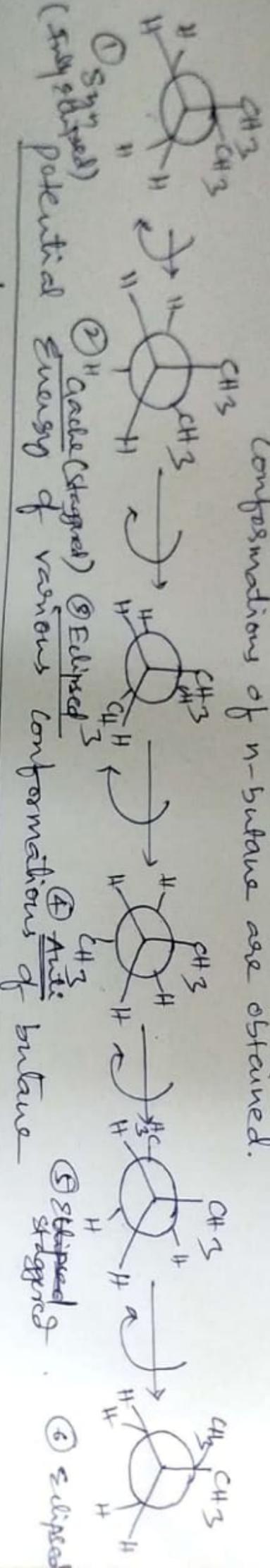
l(-) glyceraldehyde

2020/4/25 10:14

## Conformational Analysis of n-Butane



along their bond axis without breaking the bond. In one  $\text{C}_1-\text{CH}_2$ -group is kept stationary and other  $\text{CH}_2-\text{CH}_3$ -group is allowed to rotate through  $360^\circ$  in six steps ( $60^\circ$  each time) then following six conformations of n-butane are obtained.



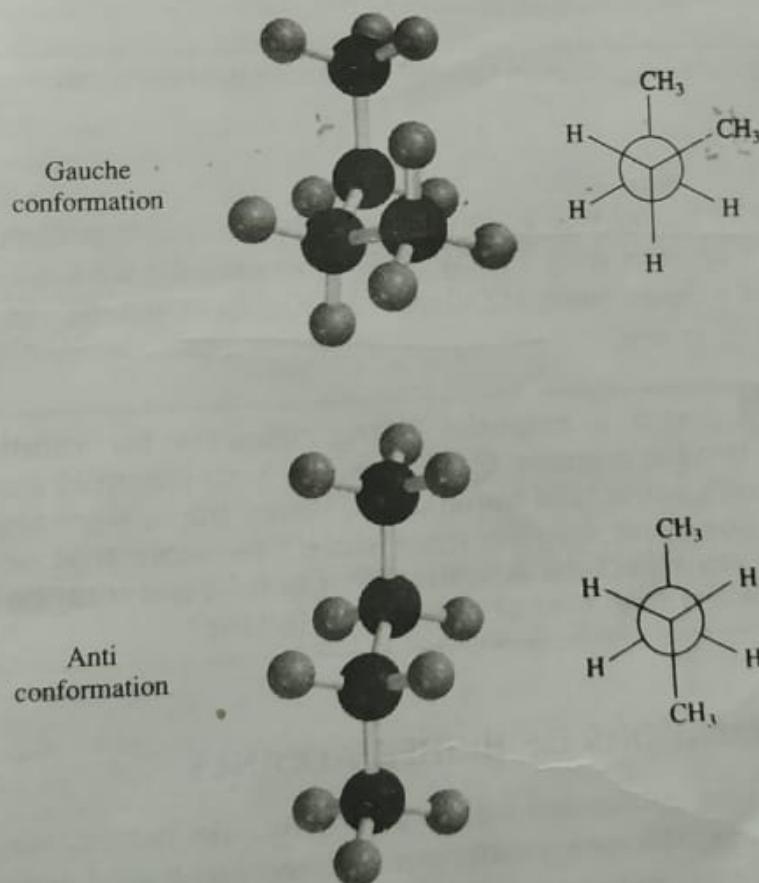
## 3.2 Conformational Analysis of Butane

(lower). The effect of temperature is quite pronounced; an increase of only  $10^{\circ}\text{C}$  produces a two- to threefold increase in the rate of a typical chemical process.

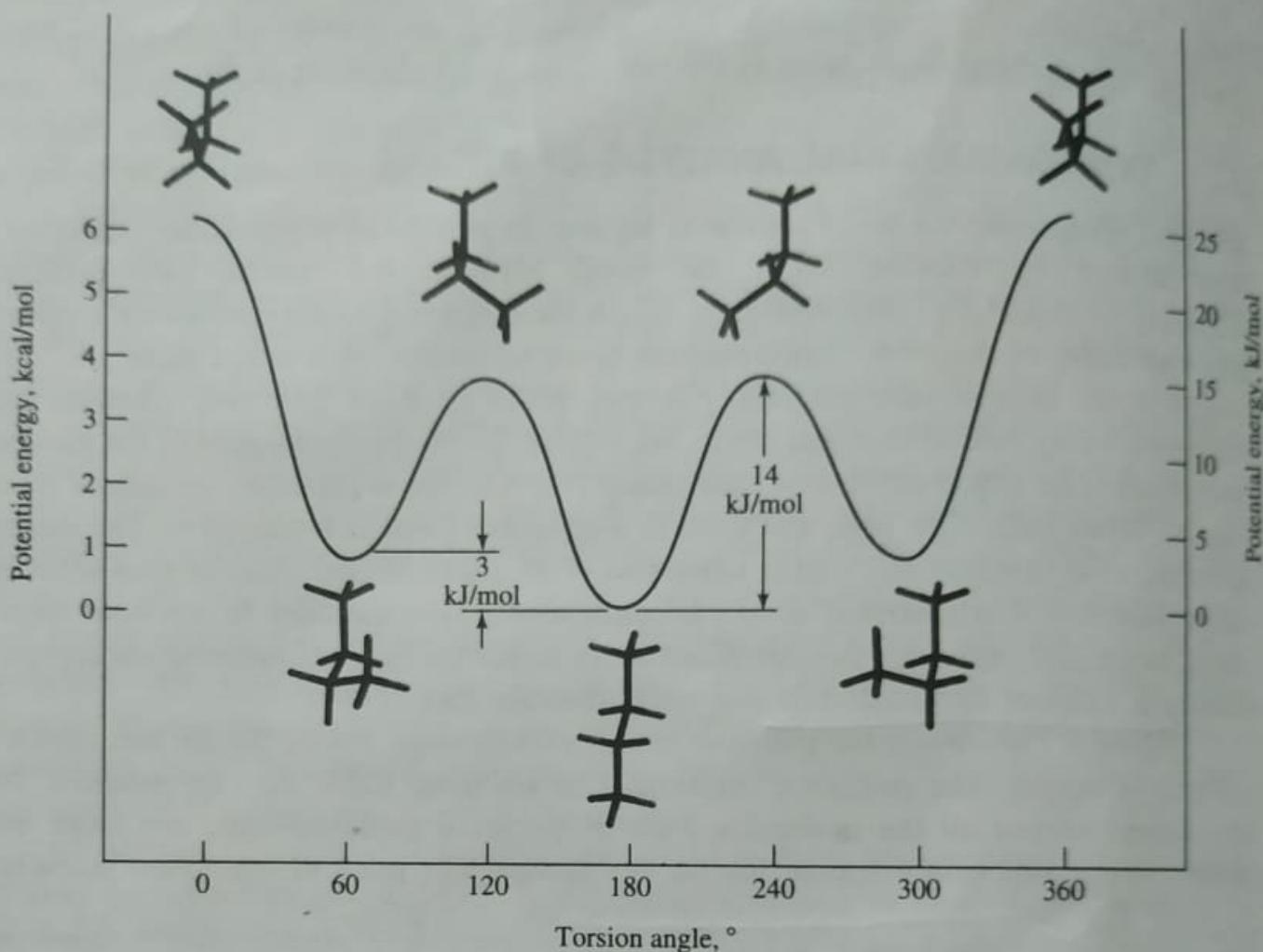
### 3.2 CONFORMATIONAL ANALYSIS OF BUTANE

The next alkane that we will examine is butane. In particular, we consider conformations related by rotation about the bond between the middle two carbons ( $\text{CH}_3\text{CH}_2-\text{CH}_2\text{CH}_3$ ). Unlike ethane, in which the staggered conformations are equivalent, two different staggered conformations occur in butane, shown in Figure 3.6. The methyl groups are gauche to each other in one, anti in the other. Both conformations are staggered, so are free of torsional strain, but two of the methyl hydrogens of the gauche conformation lie within 210 pm of each other. This distance is less than the sum of their van der Waals radii (240 pm), and there is a repulsive force between them. The destabilization of a molecule that results when two of its atoms are too close to each other is called **van der Waals strain**, or **steric hindrance** and contributes to the total steric strain. In the case of butane, van der Waals strain makes the gauche conformation approximately 3.3 kJ/mol (0.8 kcal/mol) less stable than the anti.

Figure 3.7 illustrates the potential energy relationships among the various conformations of butane. The staggered conformations are more stable than the eclipsed. At any instant, almost all the molecules exist in staggered conformations, and more are present in the anti conformation than in the gauche. The point of maximum potential



 **FIGURE 3.6** The gauche and anti conformations of butane shown as ball-and-spoke models (left) and as Newman projections (right). The gauche conformation is less stable than the anti because of the van der Waals strain between the methyl groups.



**FIGURE 3.7** Potential energy diagram for rotation around the central carbon–carbon bond in butane.

energy lies some 25 kJ/mol (6.1 kcal/mol) above the anti conformation. The total strain in this structure is approximately equally divided between the torsional strain associated with three pairs of eclipsed bonds (12 kJ/mol; 2.9 kcal/mol) and the van der Waals strain between the methyl groups.

**PROBLEM 3.3** Sketch a potential energy diagram for rotation around a carbon–carbon bond in propane. Clearly identify each potential energy maximum and minimum with a structural formula that shows the conformation of propane at that point. Does your diagram more closely resemble that of ethane or of butane? Would you expect the activation energy for bond rotation in propane to be more than or less than that of ethane? Of butane?

### 3.3 CONFORMATIONS OF HIGHER ALKANES 2020/4/26 20:25

Higher alkanes having unbranched carbon chains are, like butane, most stable in their