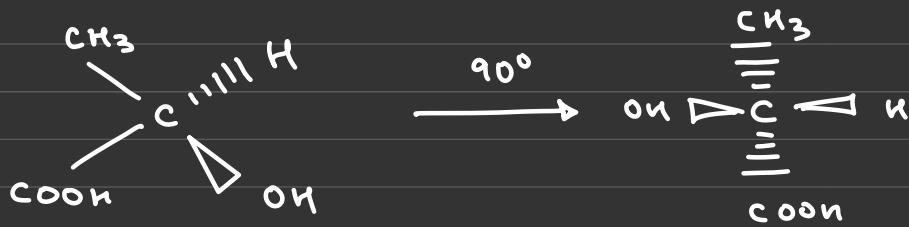
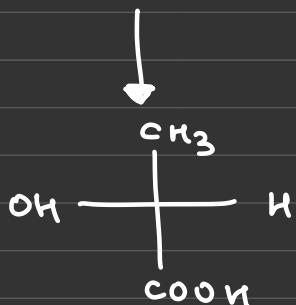


• Fischer, Newman and Sawhorse projection

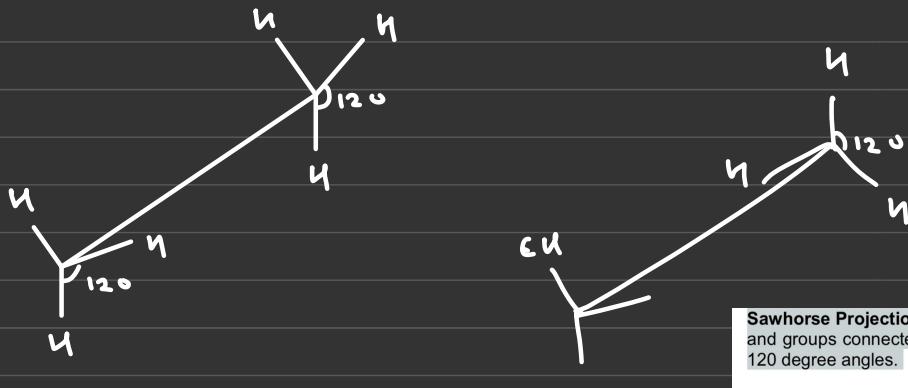
① Fischer


Fisher Projection:

- A Fischer projection is a convention used to depict a three dimensional structure in two dimensions without destroying the stereochemical information, i.e., absolute configuration, at chiral centers.
- In a Fischer projection, the longest chain is drawn vertically.
- The four bonds to a chiral carbon make a cross, with the carbon atom at the intersection of the horizontal and vertical lines.
- The two horizontal bonds are pointing toward the viewer.
- The two vertical bonds are directed away from the viewer.



② Sawhorse



eclipsed

staggered

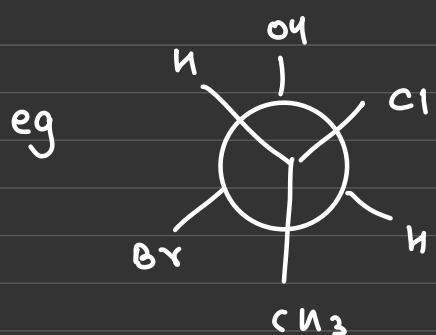
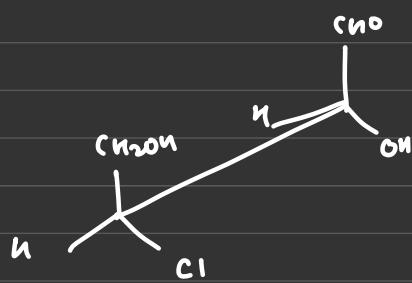
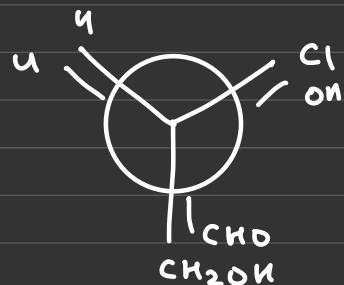
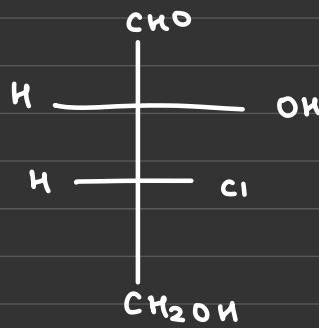
③ Newman



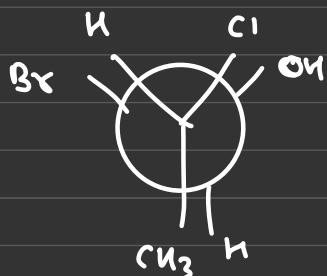
eclipsed

staggered

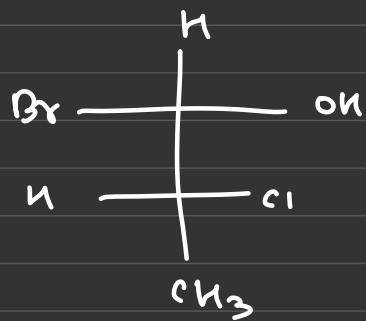
Conversion



Soln first convert to eclipse



Then Fischer



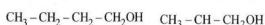
• Isomerism

Geometrical isomerism

Geometrical isomerism is a form of stereo isomerism describing the orientation of functional groups within a molecule. **restricted rotation, spatial arrangement of atoms**

Definition

When two molecules only differ by the three-dimensional position of the substituents around one or more atoms, they are called optical isomers and this phenomenon is called optical isomerism.

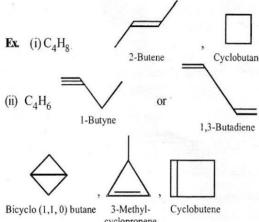


n-Butyl alcohol Isobutyl alcohol

These two butyl alcohols are chain isomers.

Ring chain isomerism :

They can also be considered as functional isomers.



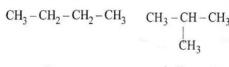
I. STRUCTURAL ISOMERISM

Structural isomers possess the same molecular formula but different structures; however, the term constitutional isomerism is a more modern term of structural isomerism. It arises because of the difference in the sequence of covalently bonded atoms in the molecule without reference to space. It is sub-classified into following types.

(a) Chain Isomerism (Skeleton or Nuclear Isomerism) :

The different arrangement of carbon atoms gives rise to chain isomerism. Chain isomers possess different lengths of carbon chains (straight or branched). Such isomerism is shown by each and every family of organic compounds.

(i) Butane : C_4H_{10}



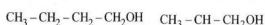
n-Butane has the chain of four carbons, while isobutane has three. Hence they are chain isomers.

(ii) Pentane : C_5H_{12}



n-Pentane, isopentane and neopentane possess the chain of five, four and three carbons, respectively. Hence they are chain isomers.

(iii) Butyl alcohol : $\text{C}_4\text{H}_9\text{OH}$

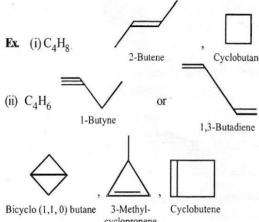


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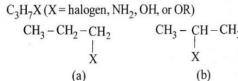


(b) Position Isomerism :

Position isomerism is shown by the compounds in which there is difference in the position of functional group, multiple bond or substituent along the same chain length of carbon atoms.

Ex.

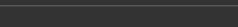
(i) Molecular formula : $\text{C}_3\text{H}_7\text{X}$ (X = halogen, NH_2 , OH , or OR)



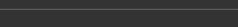
(ii) Molecular formula : $\text{C}_2\text{H}_6\text{O}$



(iii) Molecular formula : $\text{C}_3\text{H}_6\text{O}_2$



(iv) Molecular formula : $\text{C}_4\text{H}_8\text{O}_2$



360

In these structures, three carbon atoms form a chain, and X is joined at the end in (a), while at the middle carbon in (b).

(a) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{OH}$ & $\text{CH}_3 - \text{CH}(\text{CH}_3) - \text{CH}_2\text{OH}$ Position isomers

1-Propanol 2-Propanol

(b) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$ & $\text{CH}_3 - \text{CH}(\text{NH}_2) - \text{CH}_2 - \text{CH}_3$ Position isomers

1-Aminopropane 2-Aminopropane

(ii) Molecular formula : C_4H_6

$\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$ and $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$

1-Butene 2-Butene

(iii) Chlorotoluene, $\text{C}_6\text{H}_5\text{Cl}$ exists in three isomeric forms: ortho, meta and para.

CH_3 CH_3 CH_3

o-Chlorotoluene *m*-Chlorotoluene *p*-Chlorotoluene

CHEMISTRY

(iv) Molecular formula : CH_3NO_2

O

$\text{CH}_3 - \text{N} \longrightarrow \text{O}$ and $\text{CH}_3 - \text{O} \rightarrow \text{N}$

Nitromethane Methyl nitrate

Dinitro Nitro

(d) Metamerism :

This type of isomerism is due to unequal distribution of substituents on either side of the polyvalent functional group. Members belong to the same homologous series.

Ex.

(i) Diethyl ether and methyl propyl ether

$\text{CH}_3\text{OCH}_2\text{OCH}_3$ $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$

Diethyl ether Methyl propyl ether

(ii) Diethyl amine and methyl propyl amine

$\text{CH}_3\text{CH}_2 - \text{NH} - \text{CH}_2\text{CH}_3$ $\text{CH}_3\text{CH}_2\text{CH}_2 - \text{NH} - \text{CH}_3$

Diethyl amine Methyl propyl amine

(e) Tautomerism :

Tautomerism is a special type of functional group isomerism which arises due to the migration of H -atom as proton from a polyvalent atom to other polyvalent atom with reshuffling of p bond.

(i) Such isomers are directly and readily interconvertible under ordinary conditions, and the isomers are called tautomers.

(ii) Tautomers exist in dynamic equilibrium.

(iii) They have no separate existence under ordinary conditions like other isomers mentioned above.

(v) The other names of tautomerism are 'desmotropism' or 'prototropy'.

Keto-enol tautomerism :

(i) When the tautomers exist in the two forms viz keto & enol. Such type of isomerism is called keto-enol tautomerism.

(ii) It was discovered by the scientist 'Knorr' in 1911 in acetoacetic ester.

(iii) Keto means the compound has a keto group $>\text{C}=\text{O}$, and the enol form has both double bond and OH (hydroxyl) group joined to the same carbon.

Keto form Enol form

$\text{H} \quad \text{O}$

$\text{||} \quad \text{||}$

$-\text{C} = \text{O} - \text{C} - \text{H} \rightleftharpoons -\text{C} = \text{C} - \text{O} - \text{H}$

Keto form Enol form

(Ex.)

(i) Molecular formula : $\text{C}_2\text{H}_4\text{O}$

$\text{CH}_3 - \text{CH}_2 - \text{OH}$ and $\text{CH}_3 - \text{O} - \text{CH}_3$

Propanol Dimethyl ether

(Ethol) (Eter)

(ii) Molecular formula : $\text{C}_3\text{H}_6\text{O}_2$

$\text{CH}_3 - \text{CH}_2 - \text{COOH}$ and $\text{CH}_3 - \text{C} - \text{O} - \text{CH}_3$

Propanoic acid Methyl acetate

(Acid) (Ester)

(iii) Molecular formula : $\text{C}_4\text{H}_8\text{O}_2$

$\text{CH}_3 - \text{CH}_2 - \text{C} - \text{H}$ and $\text{CH}_3 - \text{C} - \text{CH}_2 - \text{OH}$

Acetaldehyde Vinyl alcohol

(Acetol) (Ethyleneglycol)

(iv) Molecular formula : $\text{C}_4\text{H}_8\text{O}_2$

$\text{CH}_3 - \text{CH}_2 - \text{COOCH}_3$ and $\text{CH}_3 - \text{C} - \text{O} - \text{CH}_3$

Acetone Isopropyl alcohol

Chem notes conti...

Metamerism

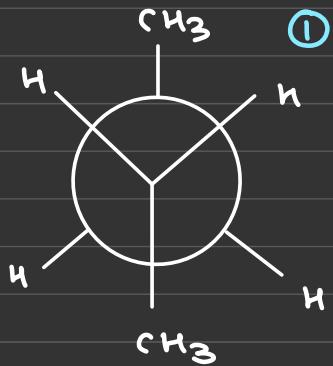


Only possible in polyvalent C chains

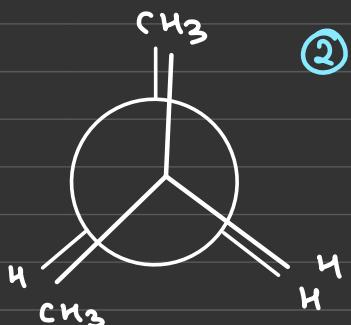
→ basically the parent alkane chain changes
unlike functional isomerism



• Conformations of n-butane

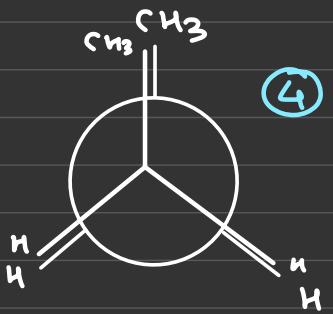


60°
Rotate the
front Carbon

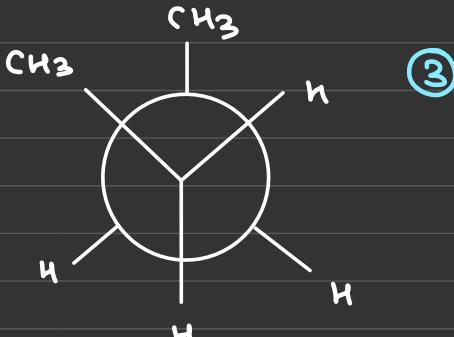
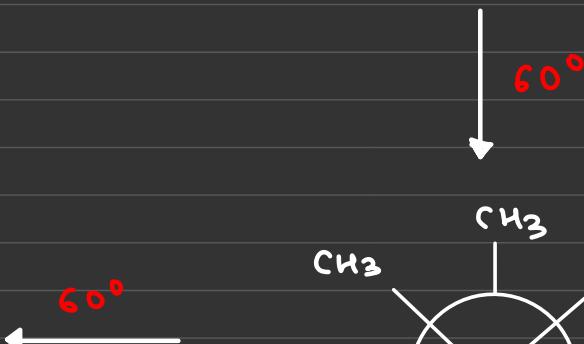


(Anti-
staggered)

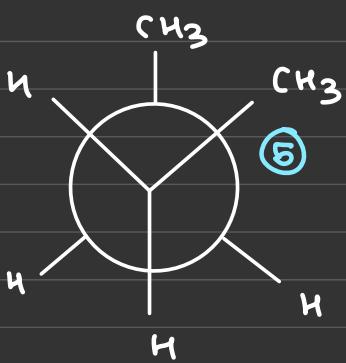
(Partially eclipsed)



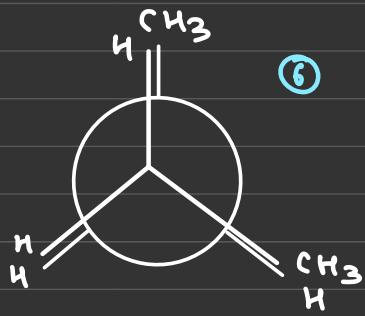
(eclipsed)



(staggered Gauche)

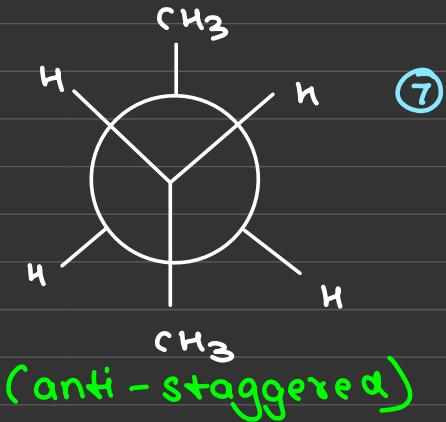
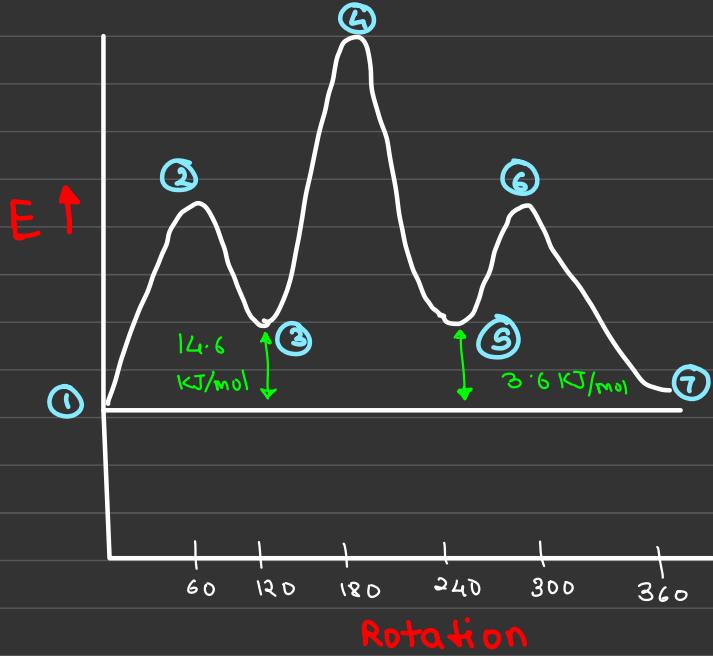


(staggered gauche)



(partially eclipsed)

• Energy diagram :-



(anti - staggered)

Remember, energy $\propto \frac{1}{\text{stability}}$

* eclipsed conformer has more energy coz heavy bonds together

∴ energy order

Fully eclipsed > Staggered gauche > partially eclipse > Anti staggered

Stability order

Fully eclipsed < Staggered gauche < partially eclipse < Anti staggered

- Optical Activity

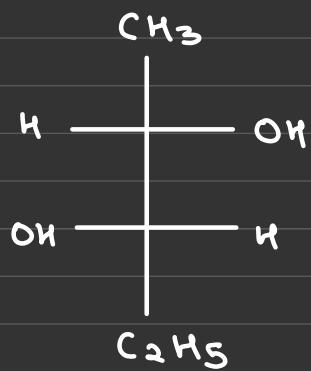
Criteria :-

- i) should have a chiral carbon
- ii) no plane of symmetry
- iii) no centre of symmetry
- iv) non-superimposable mirror images

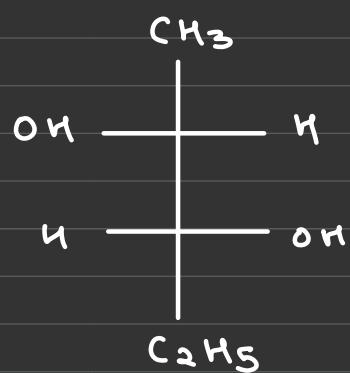
Enantiomers : non-superimposable mirror images of each other

Diastereomers : non-identical, non-superimp. mirror images.

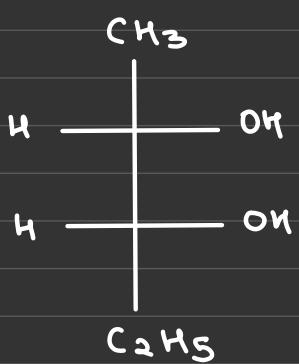
eg:-



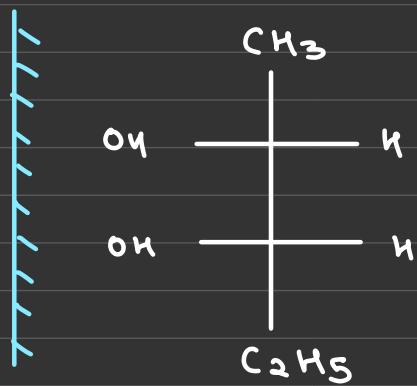
(A)



(B)



(C)



(D)

Note :-

A - B = enantiomers

C - D = enantiomers

A - C = diastereomers

B - D = diastereomers

- Configurations

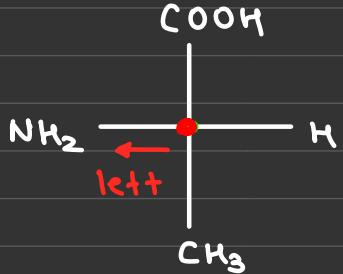
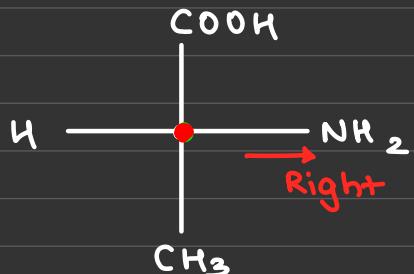
Configuration

Absolute Conf.

R-S Conf.
Cahn- Ingold Conf.

Relative Conf.
(D, L)

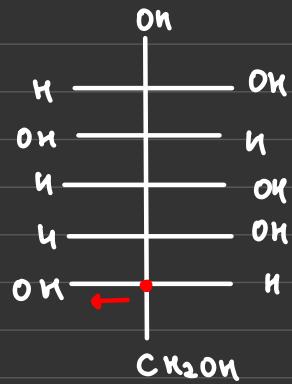
- Relative Conf.



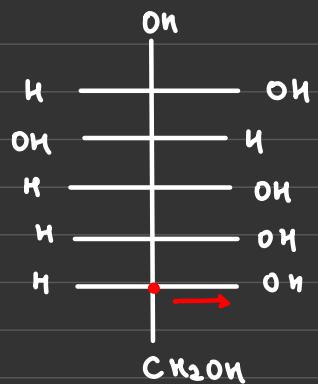
(D)

(L)

If the functional grp at the lowest chiral carbon is at left then L and Right then D



(L)



(D)

Thurs

- Symmetry elements

- ① identity

Rotating by 180 degree or 360°

- ② Proper Axis of Rotation (C_n)

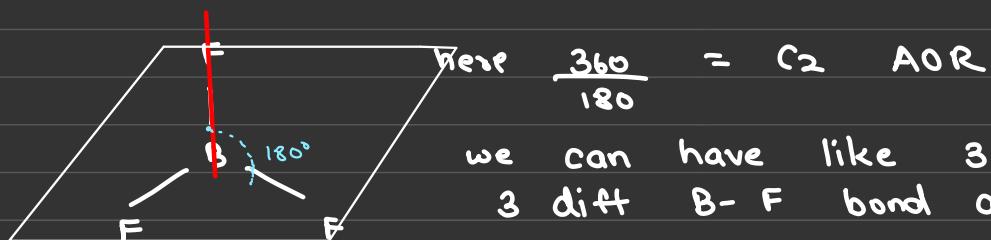
If u rotate a molecule by $360/n$ do get same structure has proper axis of rotation (n)

eg BF_3



$$\text{here } \frac{360}{120} = 3 \therefore C_3 \text{ AOR}$$

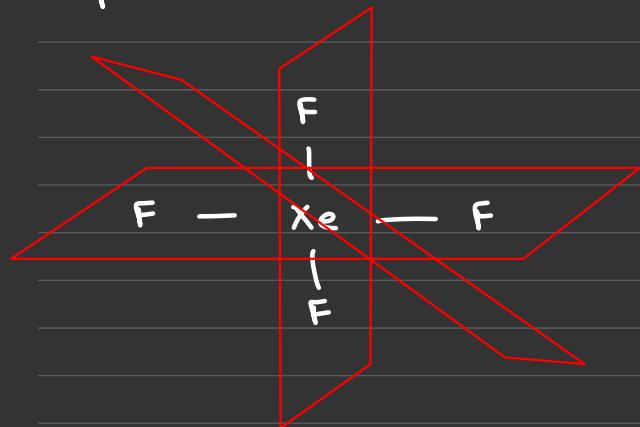
Also, one more axis



\therefore there are more C_2 than C_1 , so C_2 is principle axis of rotation

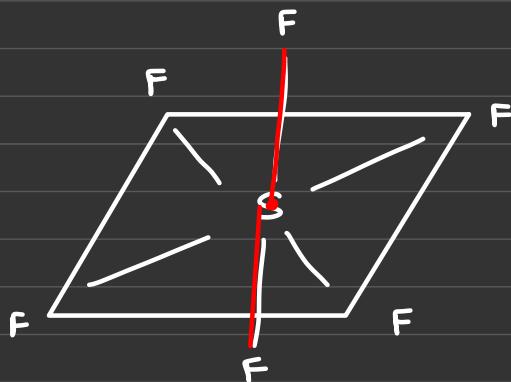
③ Plane of symmetry (σ)

An img. plane which divides the molecule in two eq. parts is called POS



④ Centre of symmetry (i)

Centre of symmetry is an img pt. , such that a line drawn from any atom to a pt and if the line is extented and it u meet the same atom at eq. dist



⑤ Improper axis of rotation ($S_n = C_n \cdot \sigma$)

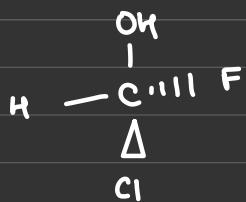
eg



- R-S configuration

Note :- Chiral centre : An atom which has all diff grps connected to it is called chiral centre

eg

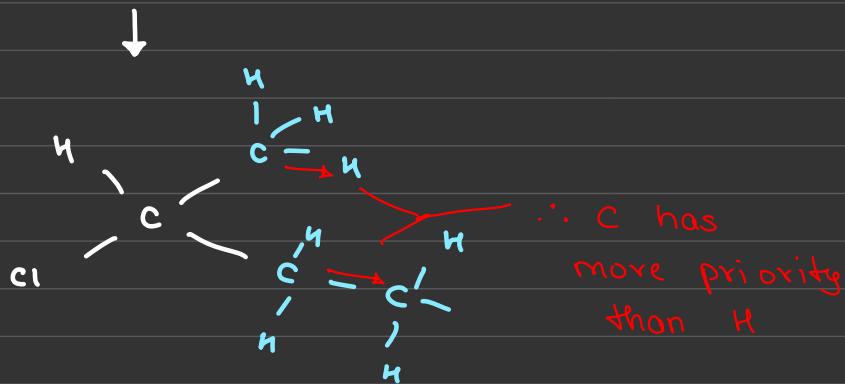
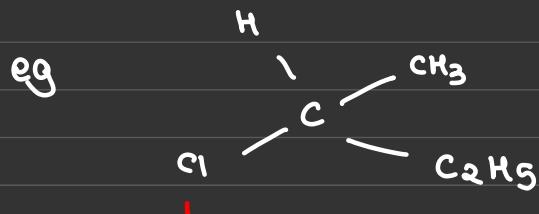


- Priority order

- ① Check the Atomic no. of the atom directly connected to the chiral atom, atom whos has higher atomic no. has high priority



- ② If two or more atoms that are bond to chiral centre are same the give priority to group based on next set of atoms



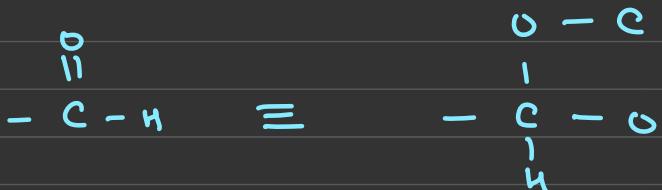
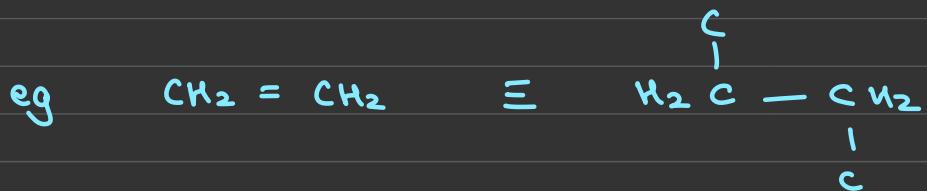
② a) If two atoms have substituents of same priority then higher priority is assigned to the atom with more no. of subs.



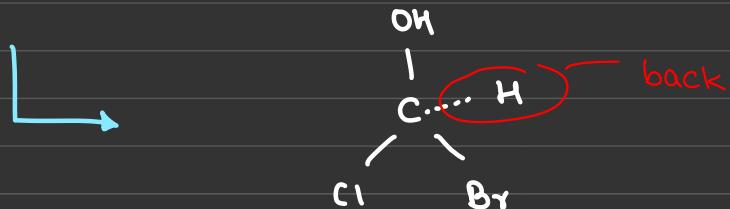
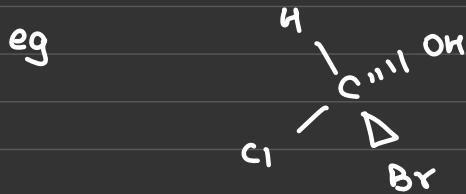
b) A larger group may not necessarily have more priority over small grp



③ Atom participating in $= / \equiv$ bonds are considered to be bonded to an equivalent no. of similar atoms by single bond



④ Orient the space in such a way that lowest priority grp is directed away from the remaining 3 will be projected towards us.

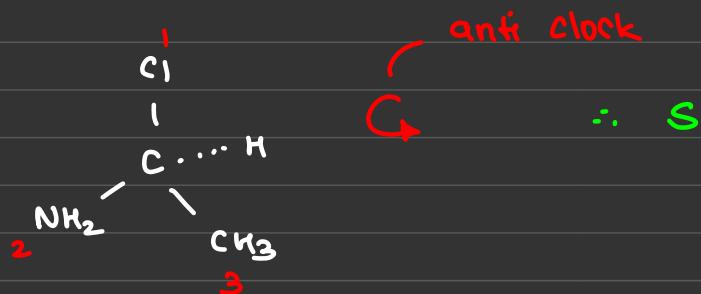
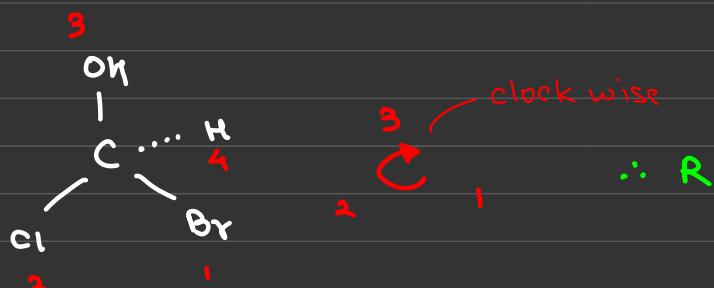


* ⑤ If the 3 groups projected to us are ordered from higher priority to lower

if direction is clock wise then R

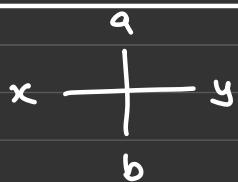
" " anti clock " S

eg



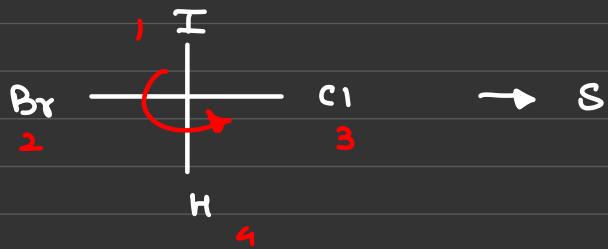
- R-S in Fischer projection

Note :-

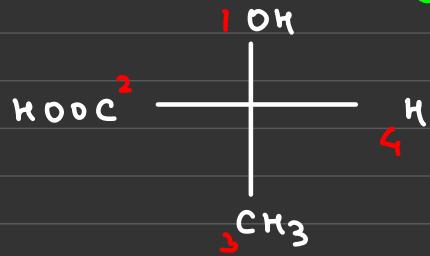


here a, b are back
x, y towards us

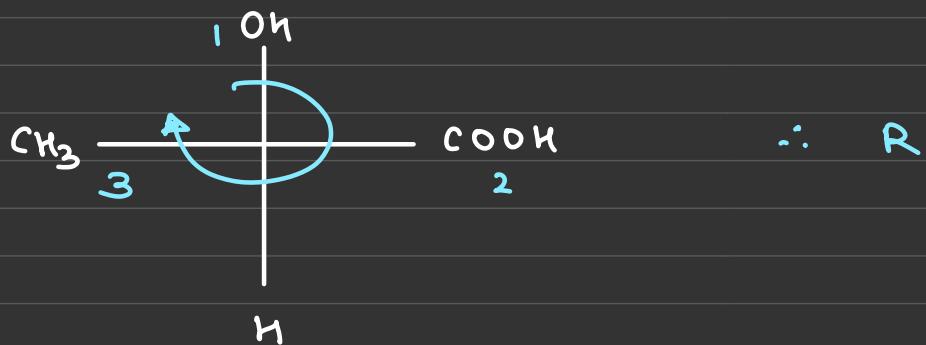
Case - 1] H at bottom



Case - 2] H at right

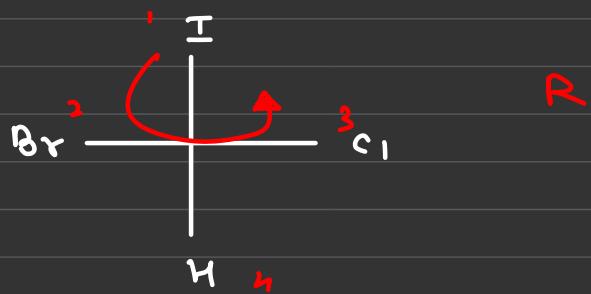
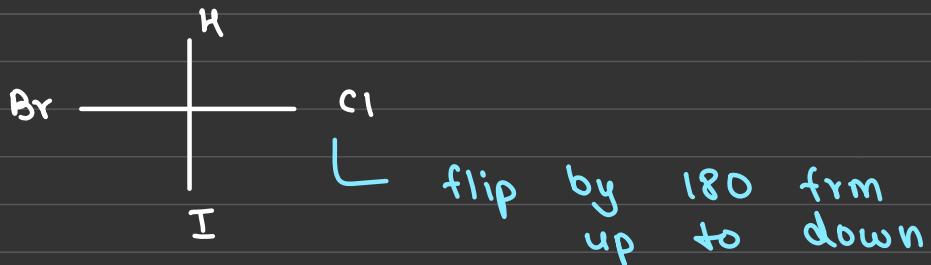


here lower priority grp H is at from , ∴.
take it back by rotating 3 atoms keep
the position of remaining 1 atom same



similar for H at left side case

Case - 3] H at top



Rxn list

1. Free - radical (Mech)
2. S_N1 (Mech)
3. S_N2 (Mech)
4. Electrophilic Sub Rxn
5. Addition
6. Free radical (Peroxide) (Mech)
7. Nucleophilic Add" (Mech)
8. Oxidation & Reduction
9. E₁ & E₂ (Mech)
10. Ring Opening
11. Zaitsev
12. Dieckman
13. Aspirin & Paracetamol.

• Substitution Reaction

① Free Radical substitution

 single e⁻

eg Chlorination of methane



if excess Cl₂

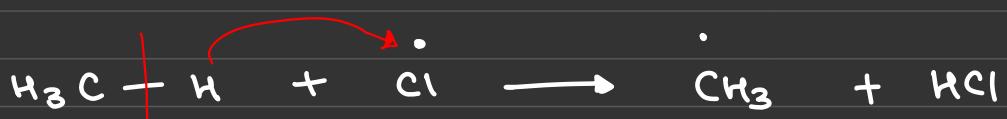


Mechanism :-

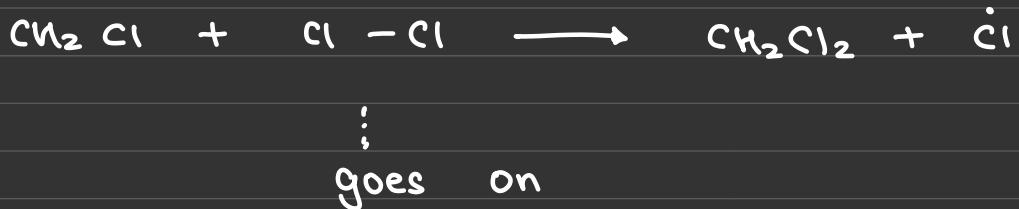
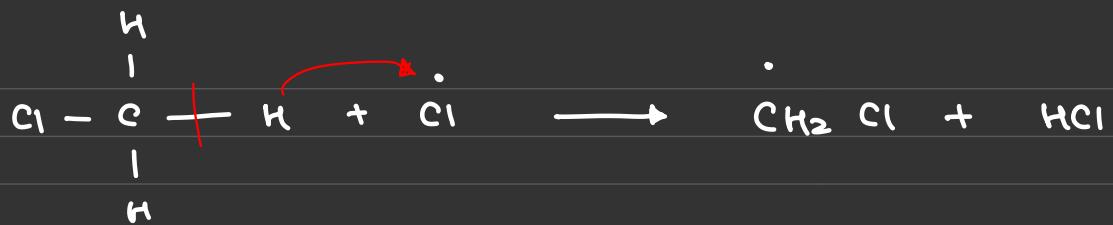
① Initiation



② Propagation



and the process goes on till CCl₄



② Termination

② Substitution Reaction ($\text{S}_{\text{N}}2$)

i) $R \propto [\text{Substrate}]^{1/2} [\text{Nu}]$

ii) Second order kinetics

iii) Single-step rxn

iv) Inversion of Conf. (Walden inversion)

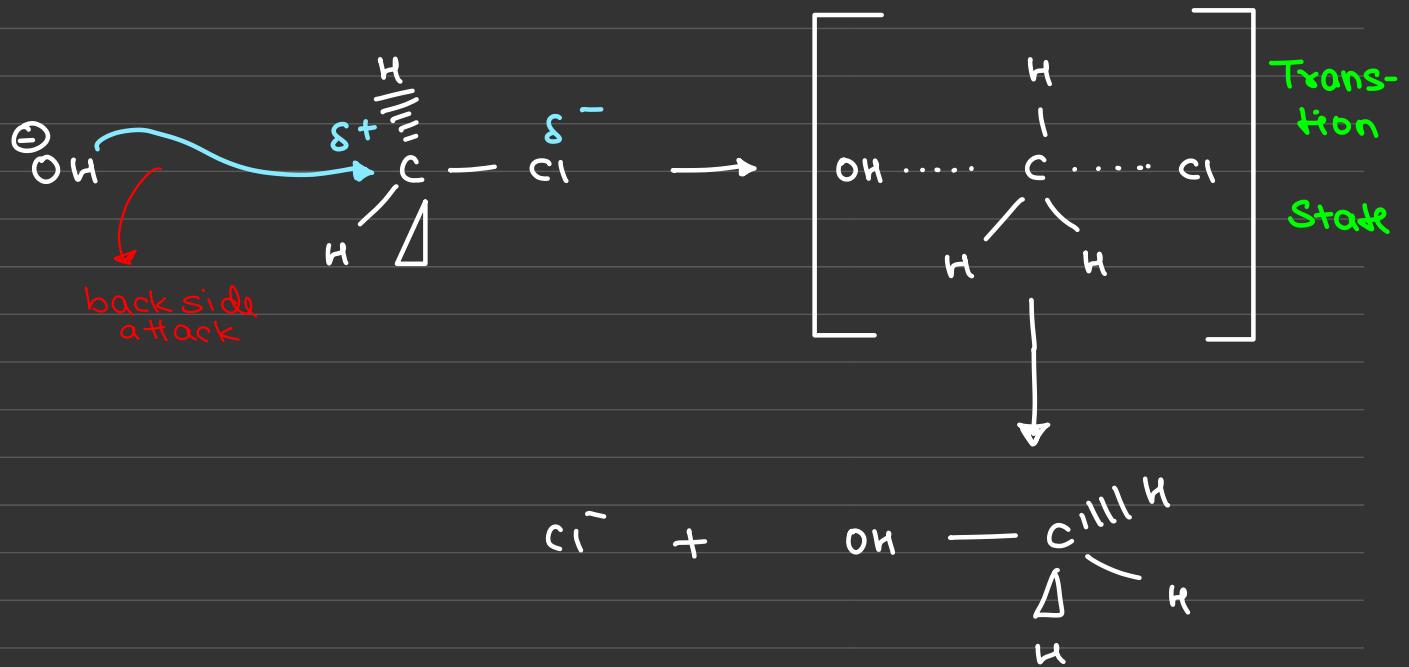
↳ if reactant is R
then product is S

v) Back side attack of Nucleophile



Mechanism





Factors affecting rate

i) Nature of substrate

$$1^\circ \text{C} > 2^\circ \text{C} > 3^\circ \text{C}$$

i.e primary > secondary > tertiary

ii) Nature of nucleophile

Strong base strong nucleophile

$$\text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$$

iii) Nature of leaving grp

poor base is good leaving grp

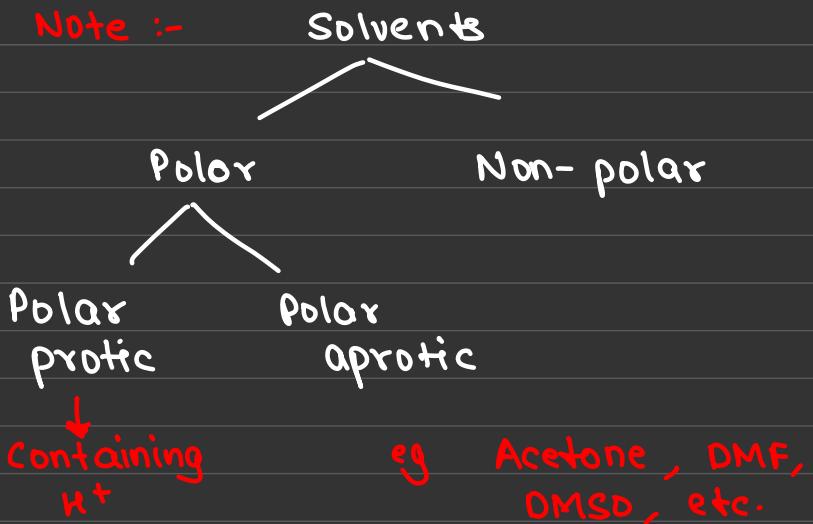
i.e opp order

$$\text{OH}^- < \text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$$

iv) Nature of Solvent

SN_2 favours Polar Aprotic Solvent

Note :-

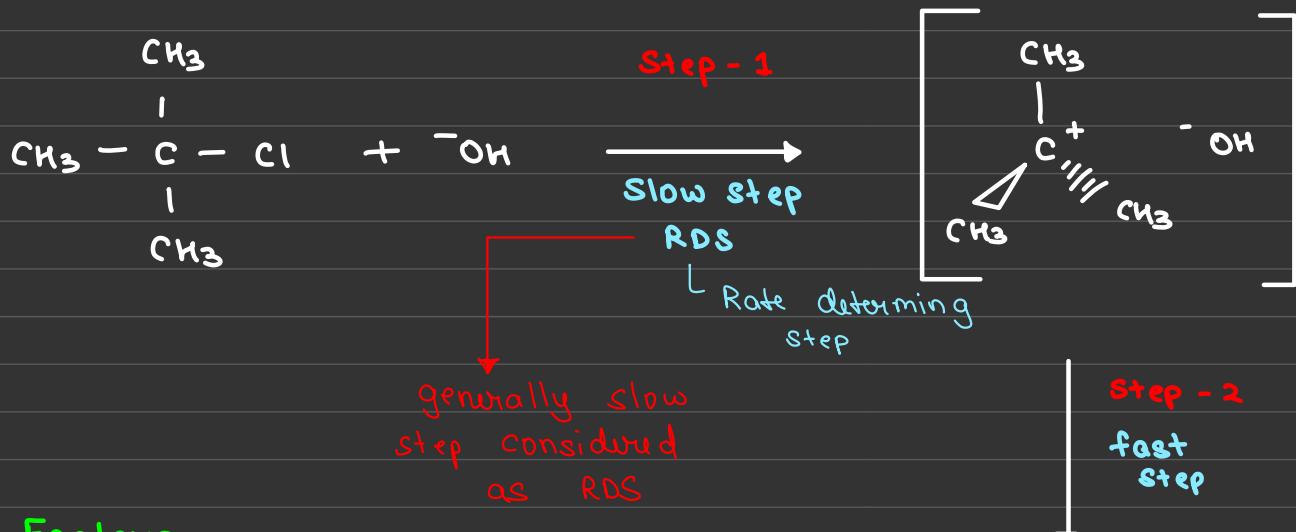


Friid

③ S_N^1

- Unimolecular
- Two step
- Rate \propto [Substrate]
- 1st Order kinetics

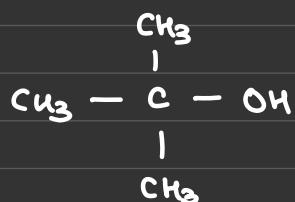
Mechanism



Factors

① Nature of substrate

$$3^\circ \text{ C} > 2^\circ \text{ C} > 1^\circ \text{ C}$$



② Nature of solvent

Both protic & Aprotic

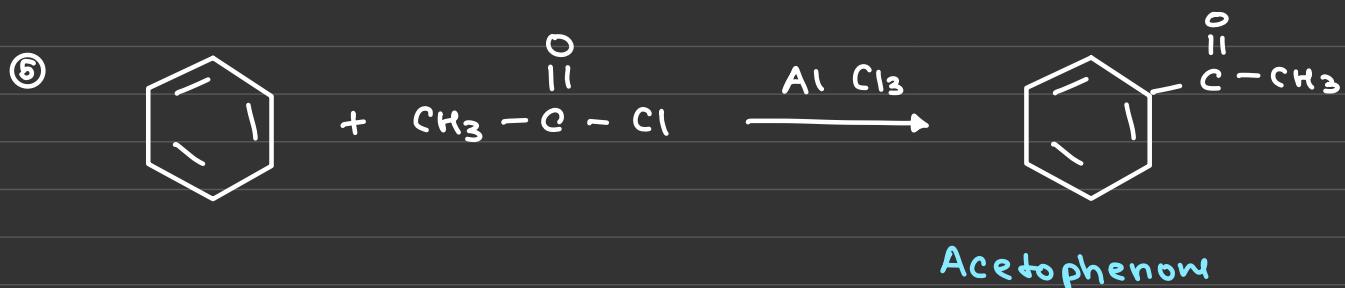
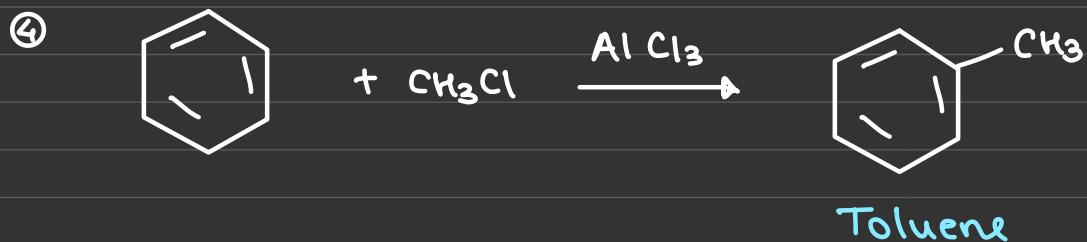
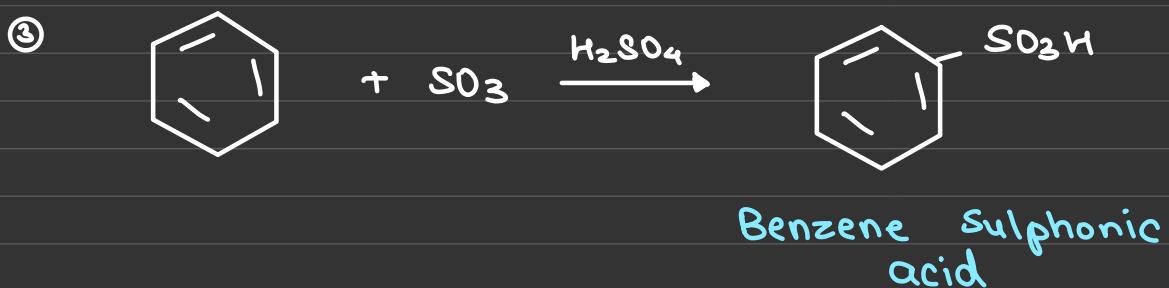
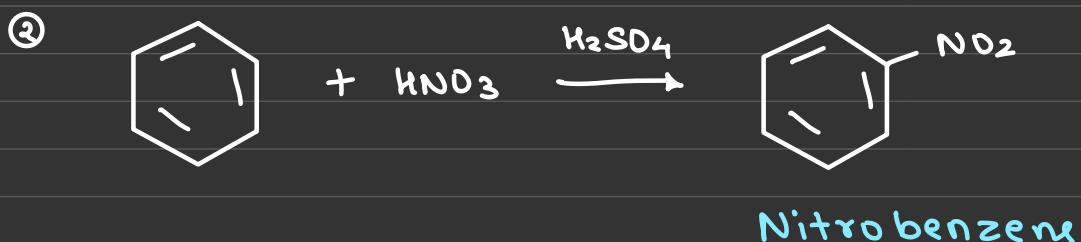
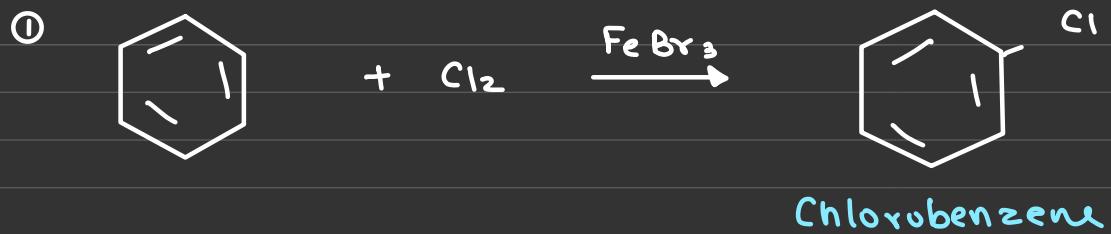
③ Nature of leaving grp

Poor base is good leaving grp



④ Electrophilic Substitution rxn

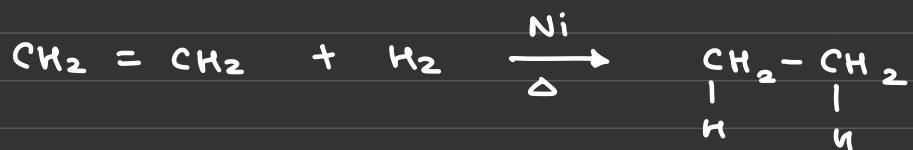
* No mechanism , Only examples



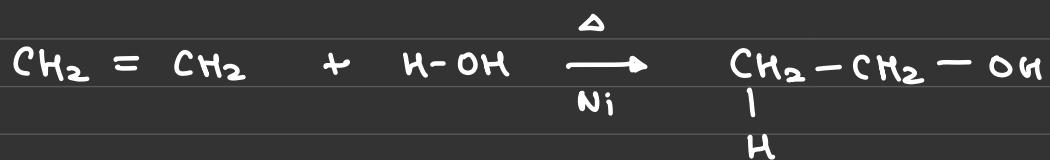
⑤ Addition Reaction (Markonikov's add")

In case of addition of unsymmetrical reagent to unsymmetrical alkene, the most electro-ve part of the reagent goes to the most substituted carbon.

① Hydrogenation reaction



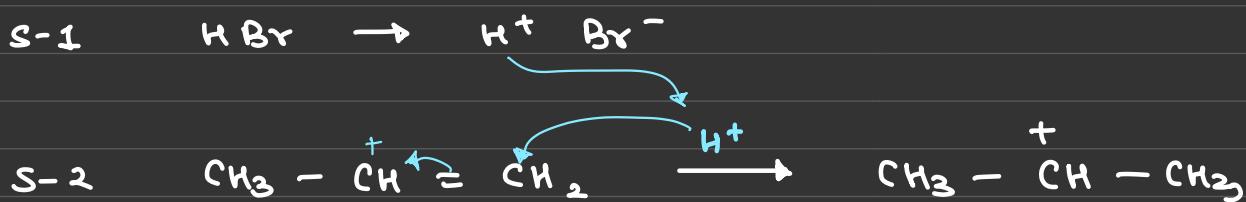
② Hydration



③ Halogenation

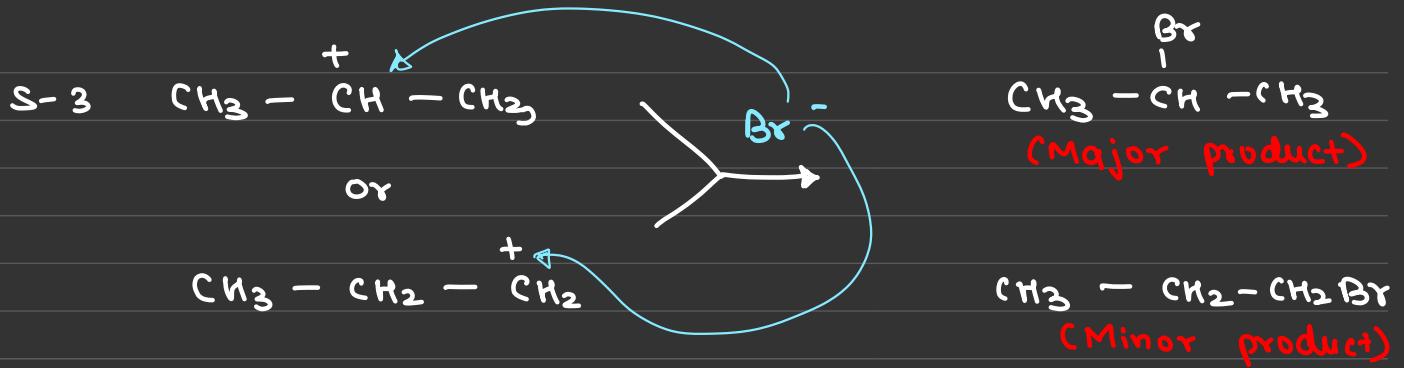


↳ here markonikov rule will apply



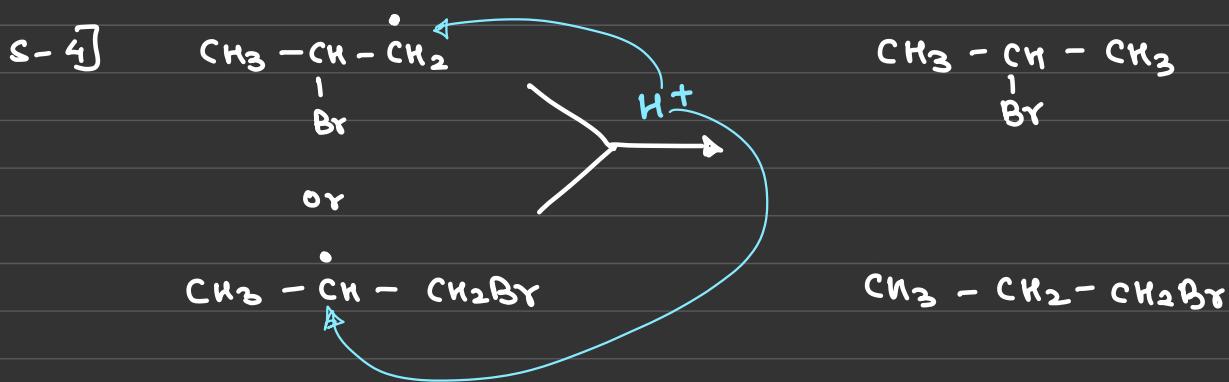
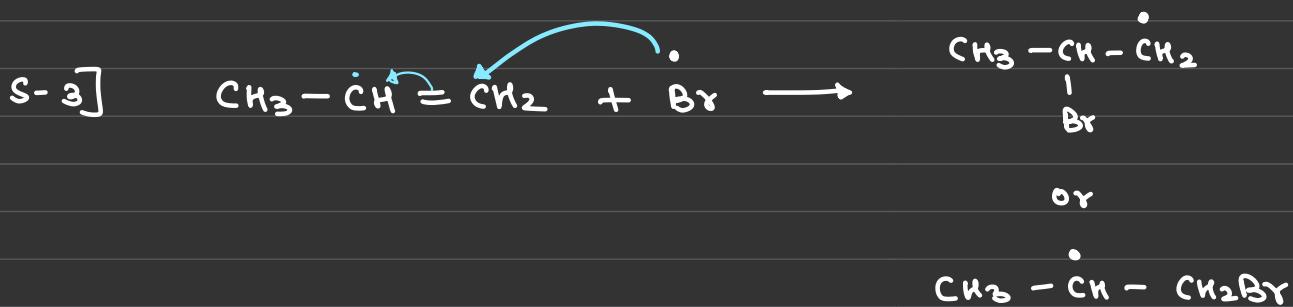
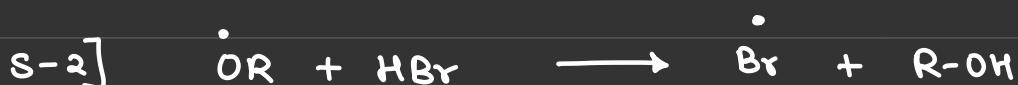
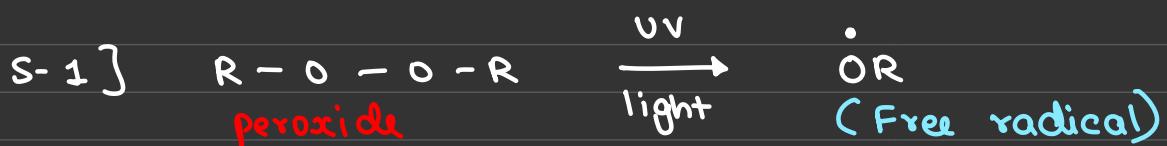
or





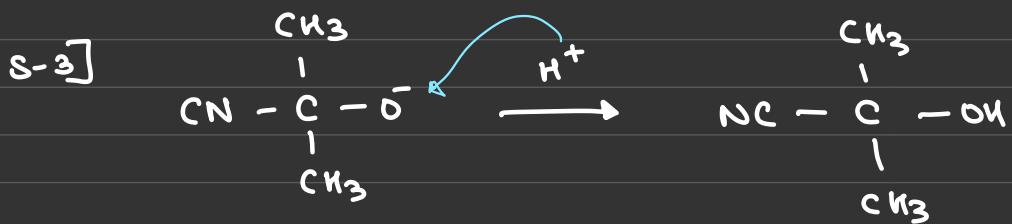
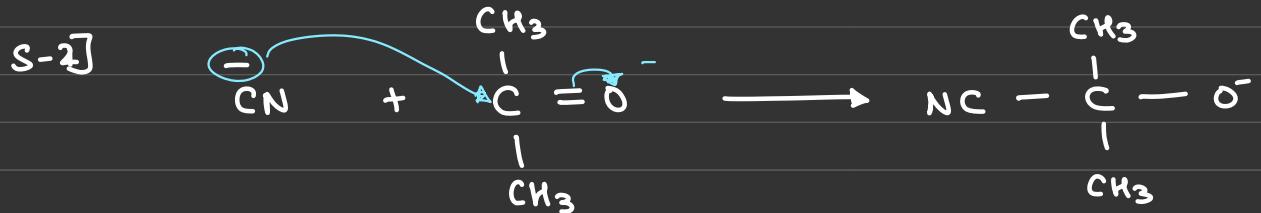
Note : Addⁿ rxns are regioselective as one of two products is stable than other

⑥ Free radical addition (Anti Markonikov)



⑦ Nucleophilic addition

eg Addition of HCN to CH_3CO



Cyanohydrin

• Elimination Reaction

$\text{H}_2\text{O} \rightarrow$ Dehydration

$\text{KX} \rightarrow$ Dehydrohalogenation

base catalysed

$\text{E}^1 + \text{E}^2$

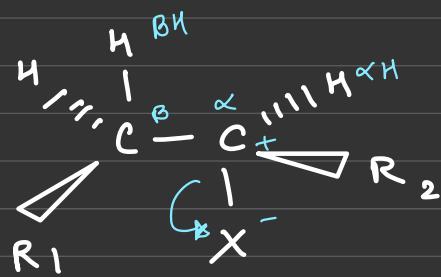
Steps :-

1. Removal of β -H

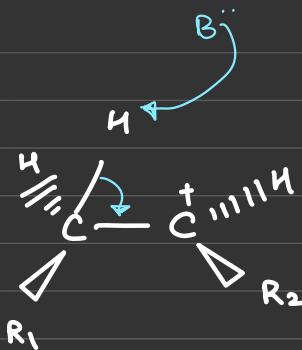
2. formation of $\text{C}=\text{C}$

3. removal of X

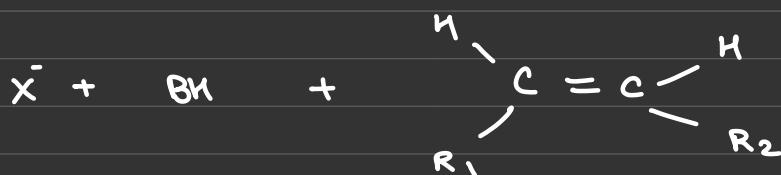
① E'



1st Step
RDS slow



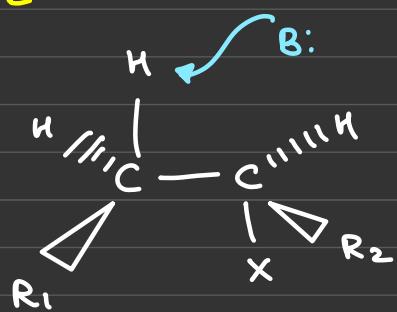
2nd Step
deprotonation



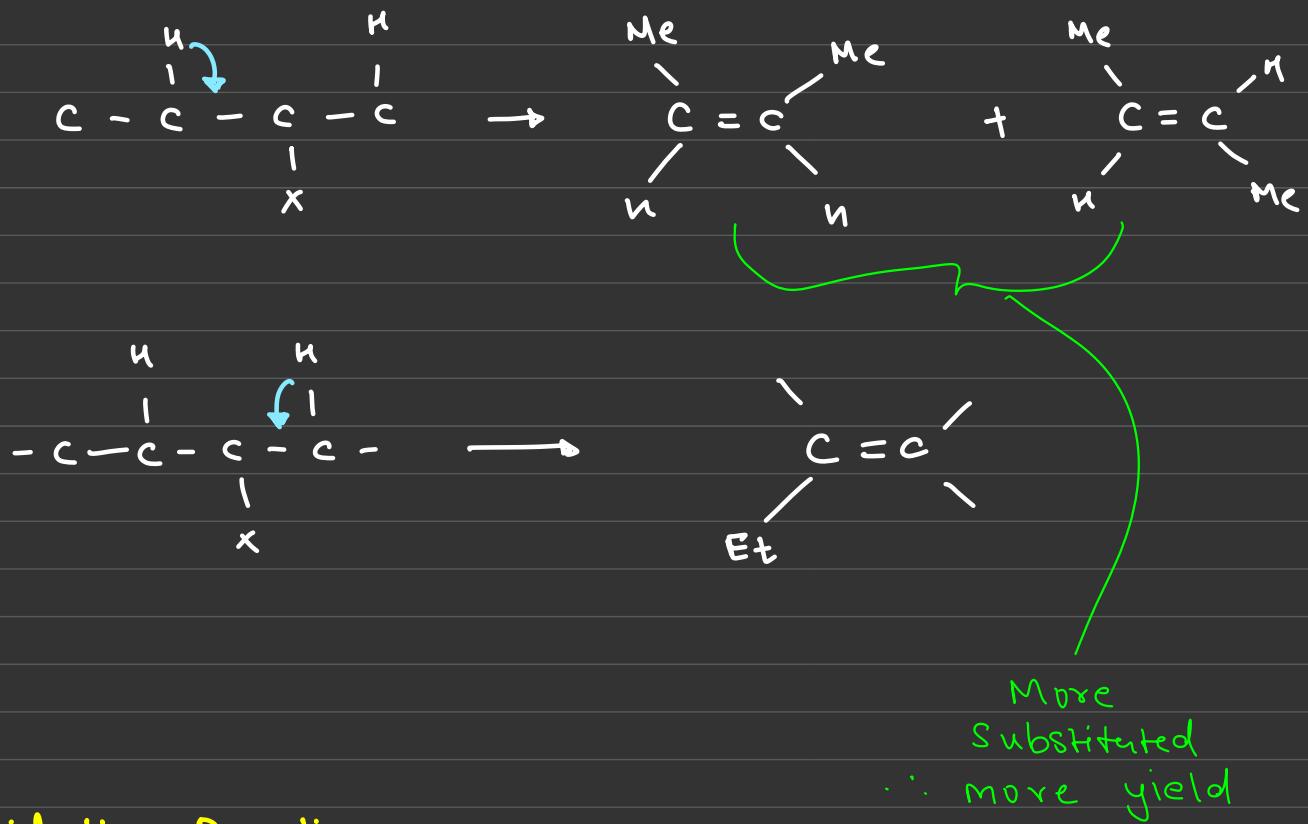
Characteristics :-

1. Two step
2. First order kinetics $R \propto [Rx]$
3. C⁺ intermediate

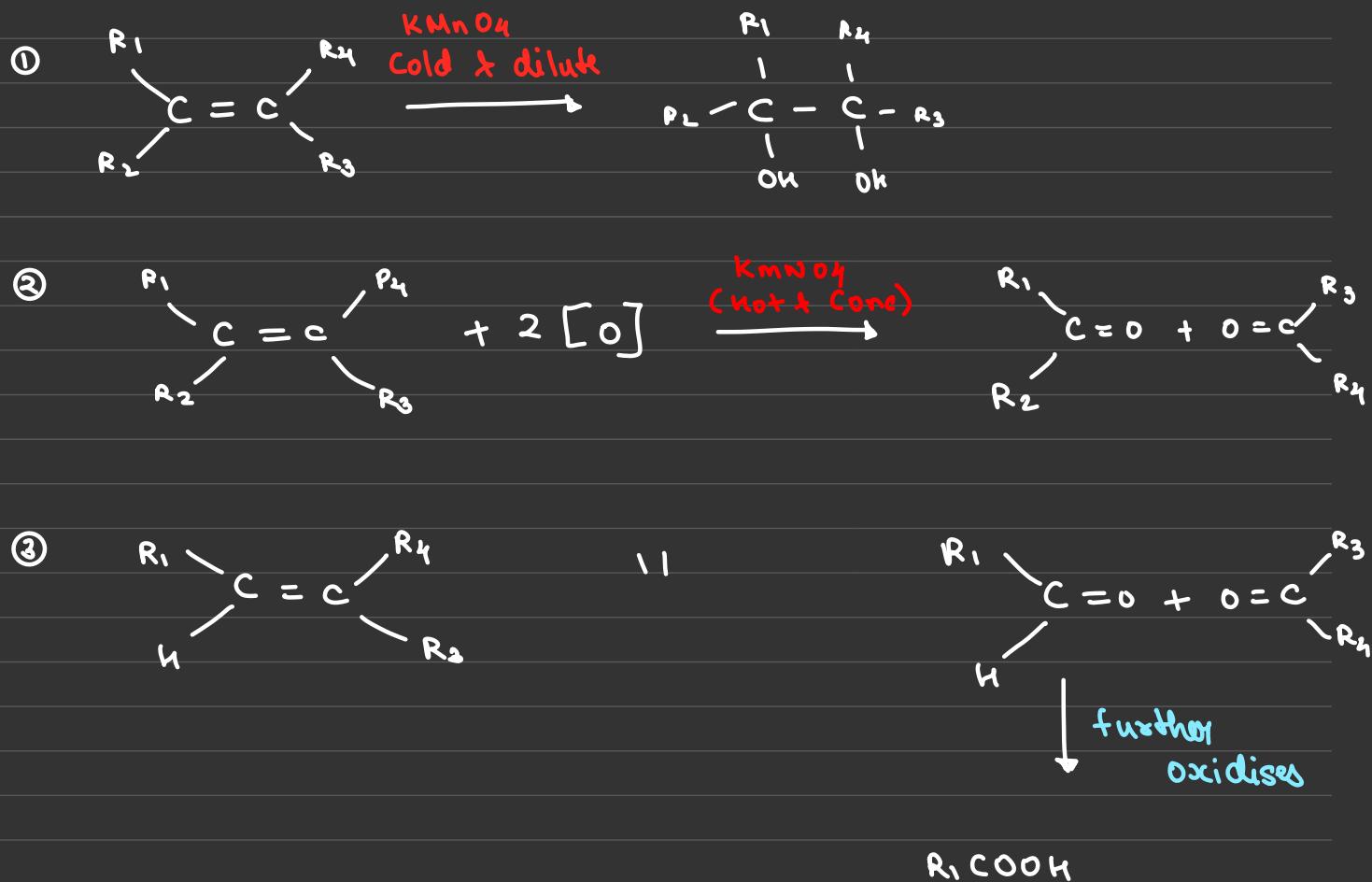
② E²

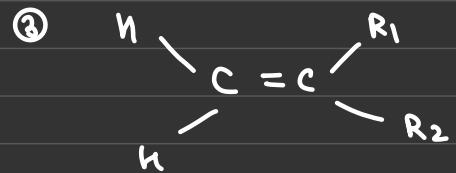


• Zaitsev Rule

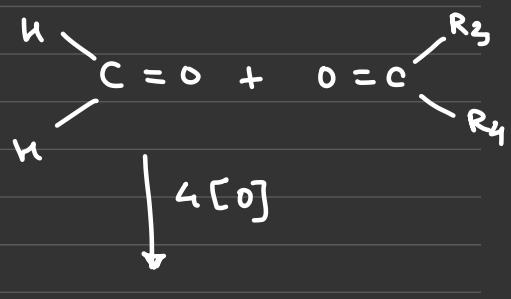


• Oxidation Reactions





11



Note :- K₂C₂O₄

Primary OH → ald → acid

Secondary → Ketone

Tertiary → X

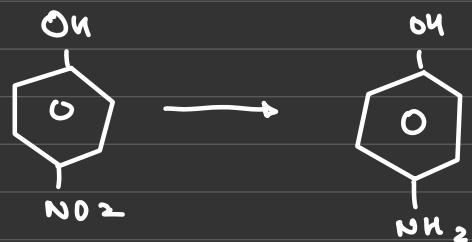
• Reduction

1. Removal of H
2. addition of e⁻
3. gain of 'e'
4. reduction in O.S

Reducing Agents

- ① NaBH₄ (Mild) [does not reduce acids]
- ② LiAlH₄ (Strong)

NaBH_4 Rxns



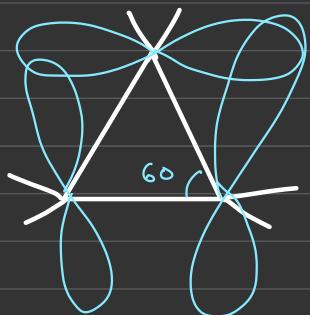
LiAlH_4 (Strong)



• Ring Opening Reactions

best in cyclopropane

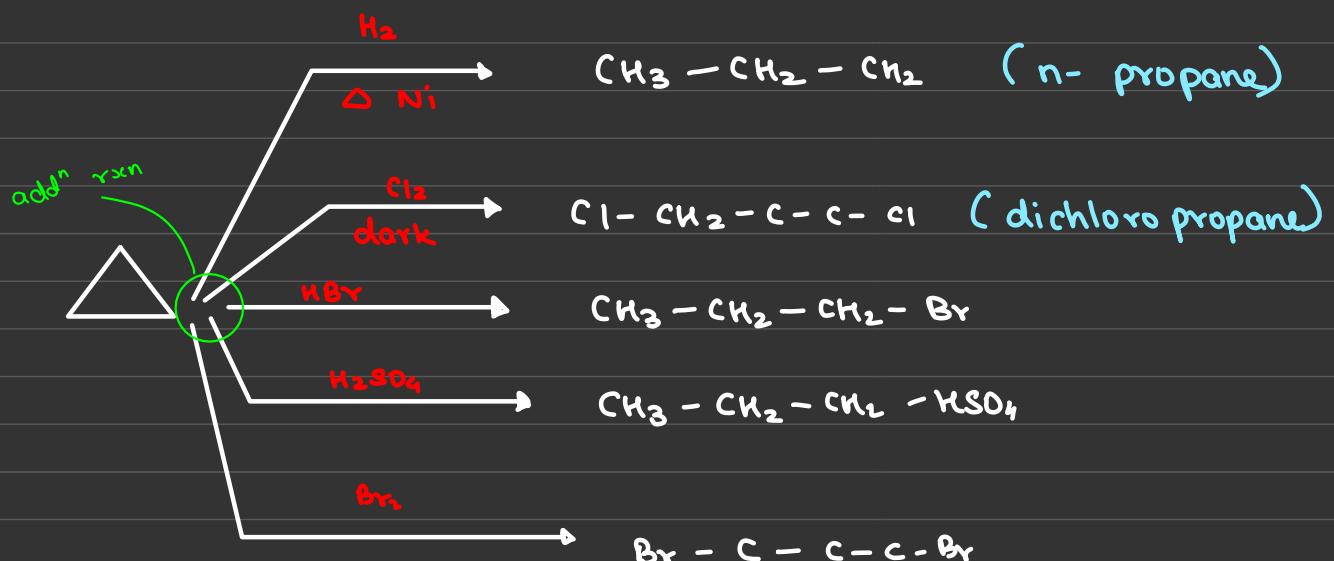
angle strain



Ring Strain

109.5°

Torsional
Strain



In case of higher cycles, the strain is less so cycl. prop n also undergo bending or ring puckering.

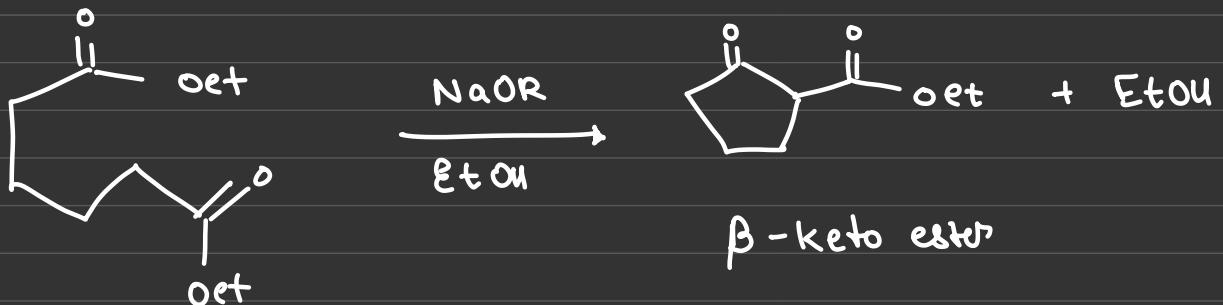
• Cyclization (Dieckmann Condensation)

intramolecular condensation of diester

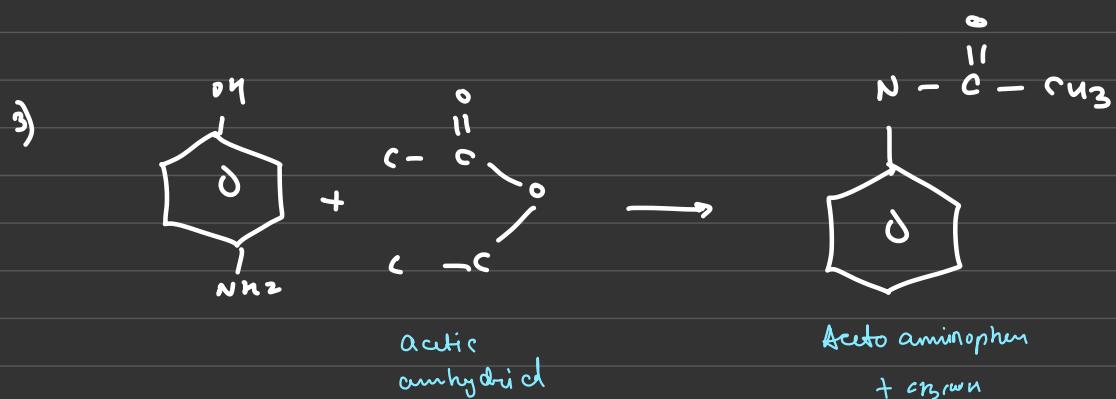
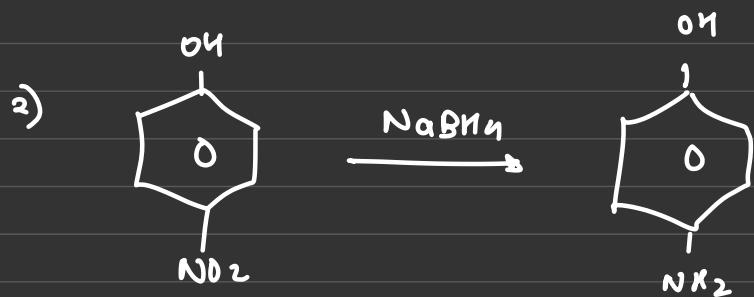
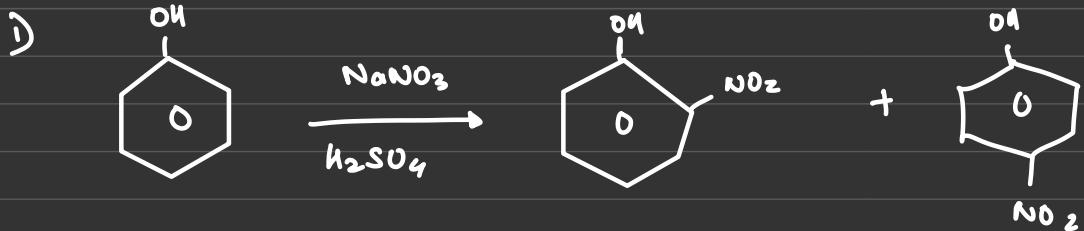
base catalysed

forms 5/6 membered β -keto ester

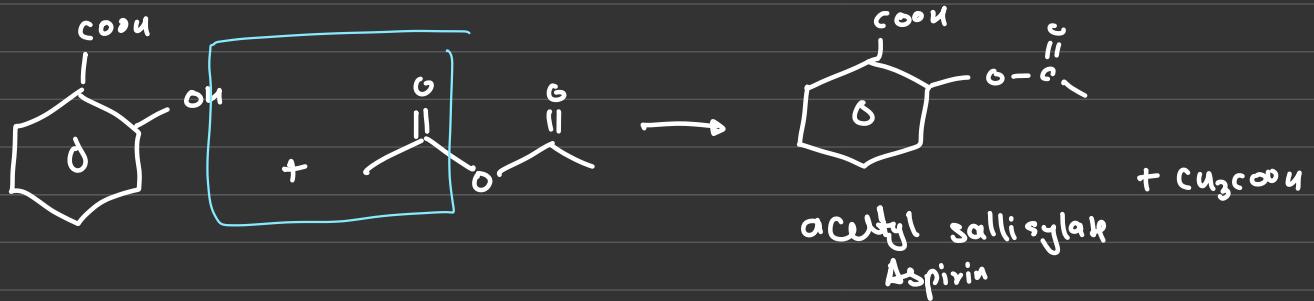
effected in sodium alkoxide & alcoholic solvent



• Paracetamol / Acetaminophen / Panadol / Tyrenol



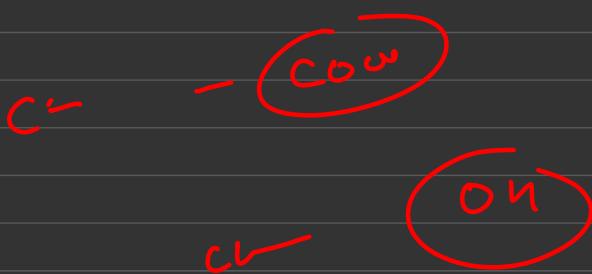
Aspirin



H							He
Li Be							
Na Mg							
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn							
	B C N O F						Ne
	Al Si P S Cl						Ar

Cross link \longrightarrow less soluble

Bifunctional \rightarrow Conde



R

P

Sy

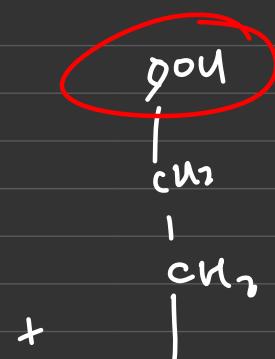
F

T_{Sc}t

Propanoic
ethanol



But a



+



diester

dicarboxylic acid

Hydrox

