Alkene

- → contains Carbon Carbon double bond
- → general formula (C_nH_{2n})
- → C - atom → sp^2
- → C - C → strong 'σ' → weak 'π'
- e.g Ethene

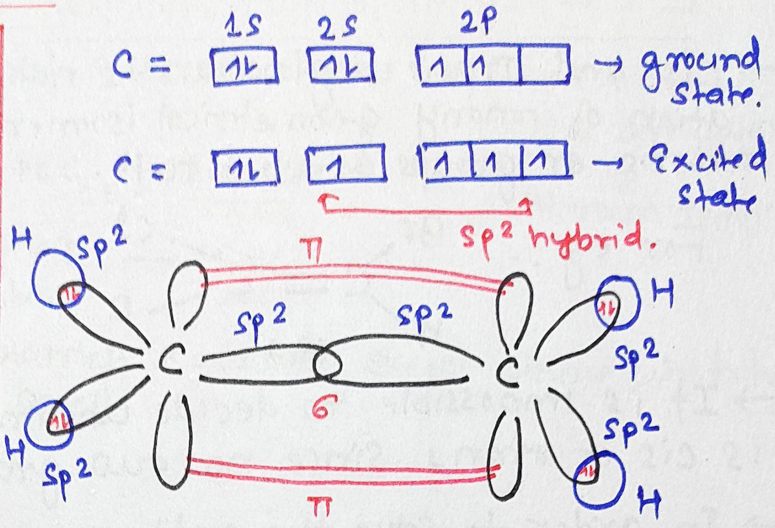


fig:- orbital picture of alkene

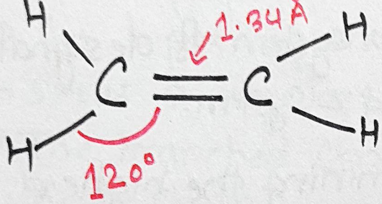
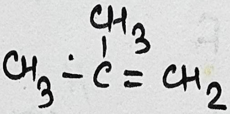


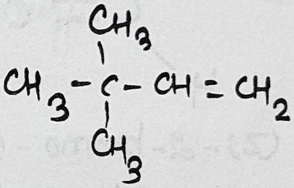
fig:- Structure of ethylene.

Nomenclature

$CH_2 = CH_2$
Ethene or ethylene

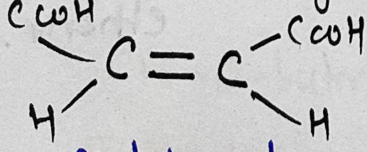
$CH_3 - CH = CH - CH_3$
2-butene


$CH_3 - \overset{CH_3}{\overset{|}{C}} = CH_2$
2-methylpropene (isobutene)

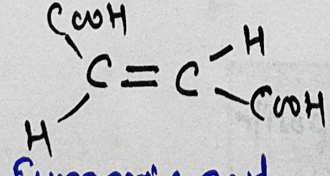

$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - CH = CH_2$
3,3-dimethyl-1-butene.

Geometrical Isomerism

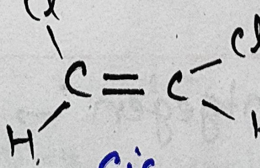
→ The isomer which have same structural formula but differ in their spatial arrangement of the groups around the double bond are known as geometrical isomers and the phenomenon is known as geometrical isomerism.



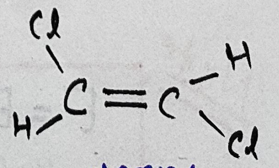
maleic acid (Cis)



Fumaric acid (trans)



Cis 1,2-dichloroethene

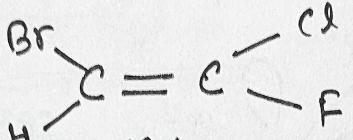


trans 1,2-dichloroethene

E & Z System of Nomenclature

→ Cis and trans degination is not able to give the configuration of many geometrical isomers having different four atoms or groups attached to it.

For e.g :-

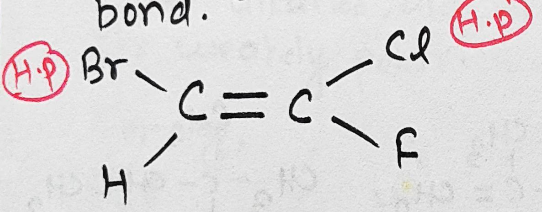


(A)

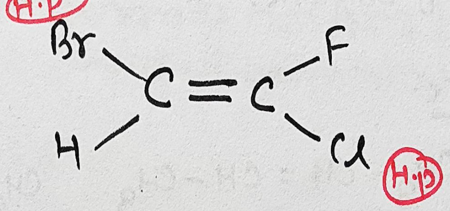
→ It is impossible to decide wheather above structure (A) is cis or trans since no two groups are same.

→ In order to solve the problem a new system of designation Configuration has been adopted called E & Z system.

→ The E & Z nomenclature is give determining the higher priority of different atoms attached to carbon carbon double bond.

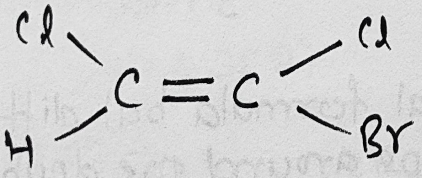


(Z)-2-bromo-1-chloro-1-fluroethene

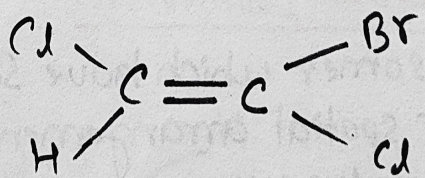


~~(E)-2-bromo-1,2 chloro~~

(E)-2-bromo-1-chloro 1-fluroethene



(E)-1-bromo-1,2-dichloroethene.



(Z)-1-bromo-1,2-dichloro ethene.

Note.

E = Entgegen → opposite

Z = Zussamin → Same.

physical properties

① physical state → first 3 lower alkenes i.e, ethene, propene, butene are gases
⇓
At room tempr.

→ C_5 to C_{15} → liquids

→ higher members → Solid

→ are colourless & odourless except ethene which has pleasent smell.

② Boiling point.

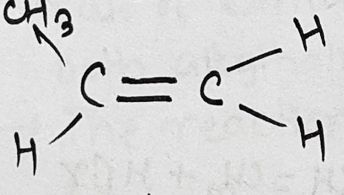
→ The b.p & m.p are higher than that of alkenes.

→ Shows a regular increase with increase molecular weight.

→ The branched chain alkene have lower b.p than the corresponding straight chain.

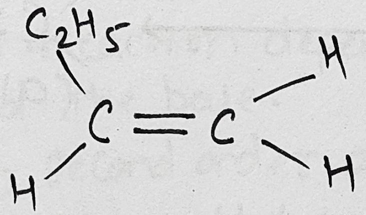
→ Like alkanes, alkynes are generally non polar but certain alkenes are weakely polar due to their unsymmetrical geometry.

For e.g,



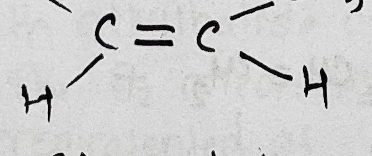
propylene

(μ = 0.35 D)



1-butene

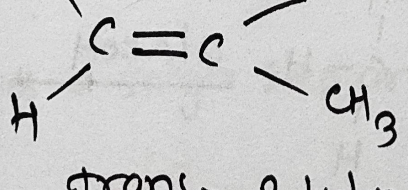
(μ = 0.37 D)



Cis-2-butene

m.p = 139° → Do not fix to the crystalline lattice.

b.p = 4°c



trans-2-butene.

↳ fit to the crystal lattice

m.p = -106°c

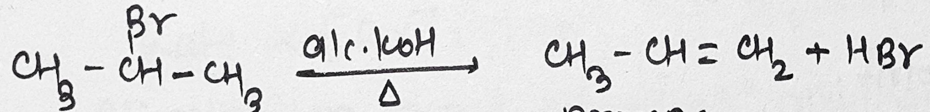
b.p = 1°c.

preparation.

Dehydrohalogenation of alkylhalide

→ The treatment of alkylhalides with alc.KOH yields alkene in such cases a hydrogen halide molecule is eliminated from alkylhalide to produce alkenes and the process is known as dehydrohalogenation.

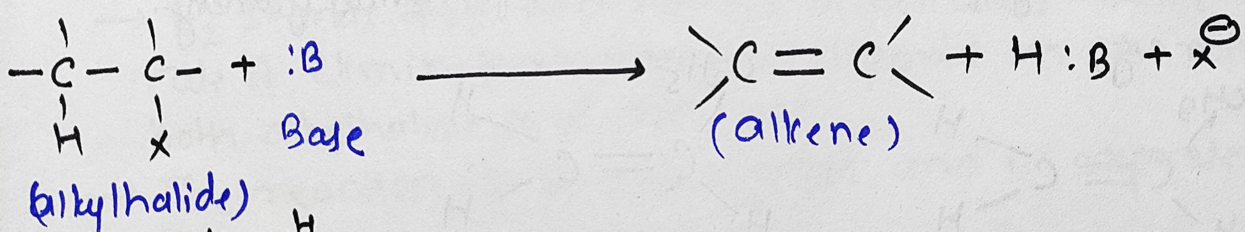
$$CH_3CH_2Br \xrightarrow[\Delta]{alc.KOH} CH_2=CH_2 + HBr$$



$$CH_3-\overset{Br}{CH}-CH_3 \xrightarrow[\Delta]{alc.KOH} CH_3-CH=CH_2 + HBr$$

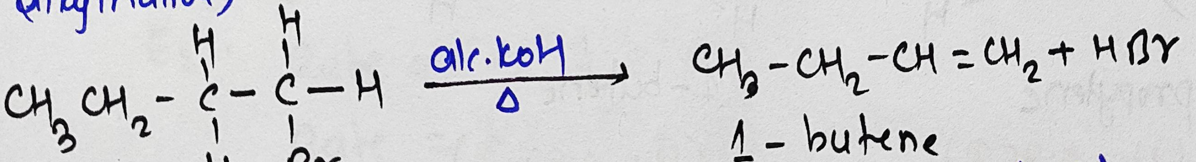
propene

→ From the above reaction it is clear that a proton (hydrogen) is lost from 1st carbon whereas the halide ion is lost from adjacent carbon i.e halide ion is lost from the β-carbon. Hence this type of elimination is also called β-elimination or 1,2-elimination.



$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}- + :B \longrightarrow \;>C=C<\; + H:B + X^{\ominus}$$

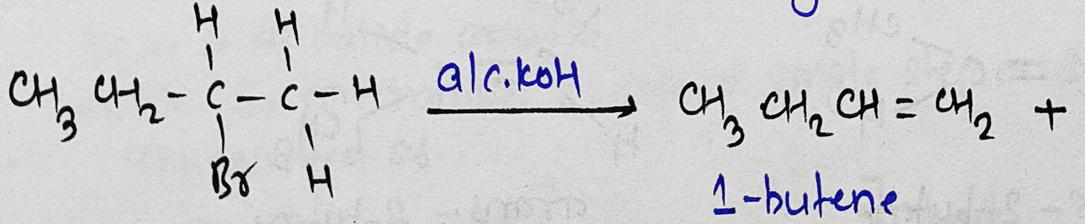
(alkylhalide) Base (alkene)



$$CH_3CH_2-\underset{H}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-H \xrightarrow[\Delta]{alc.KOH} CH_3-CH_2-CH=CH_2 + HBr$$

1-butene

(only one product).



$$CH_3CH_2-\underset{Br}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H \xrightarrow{alc.KOH} CH_3CH_2CH=CH_2 +$$

1-butene (19%)

According to saytzeff rule. ⇐ $CH_3CH=CH-CH_3$

2-butene (81%)

Kinetics of dehydrohalogenation

→ Like nucleophilic substitution, elimination rxn can proceed by two different mechanism i.e E_1 & E_2.

→ Elimination reaction of almost all alkylhalides with concentrated soln of base follow second order kinetics. i.e the rate of formation of alkene depends upon the concn of both alkylhalides & base.

Rate ∝ [Rx][Base] → E_2 mechanism.

→ Elimination rxn of 1°, 2° & 3° alkylhalides with lower concentrated solution of base follows first order kinetics i.e rate of formation of alkene depends only on the concn of alkylhalides.

E_2 Mechanism

→ E_2 stands for elimination bimolecular. When the rate of elimination reaction depends on the concn of both alkylhalide and the base.

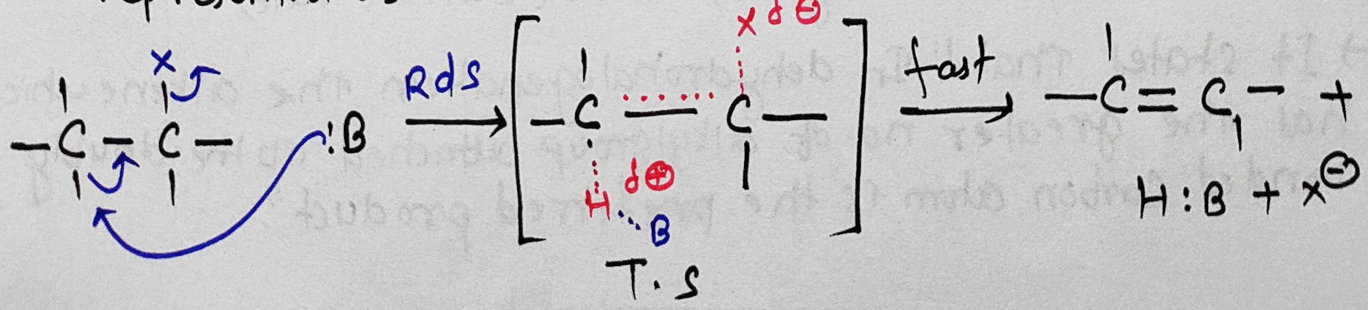
→ The reaction is of second order and is represented as E_2.

$$\text{Rate} \propto [Rx][Base]$$

$$\text{Rate} = k[Rx][:B]$$

→ The rate determining step involves the participation of both alkylhalide and base.

→ The E2 mechanism involves a single step and can be represented as.



→ Here the base abstracts the proton (β-hydrogen) & simultaneously a halide ion departs to give a double bond.

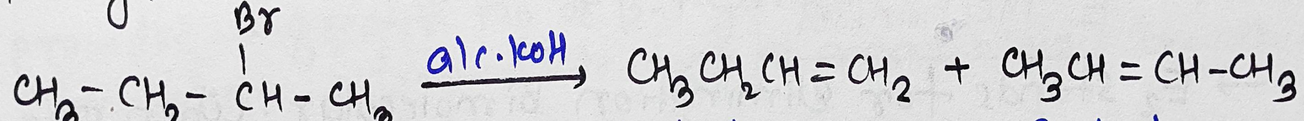
→ In this process, at first a T.S is formed in which partial bond exist between base and β-hydrogen and α-carbon & halogen.

→ Finally the base abstracts the proton & at the sametime the halide ion departs to give alkene.

Orientation and Reactivity

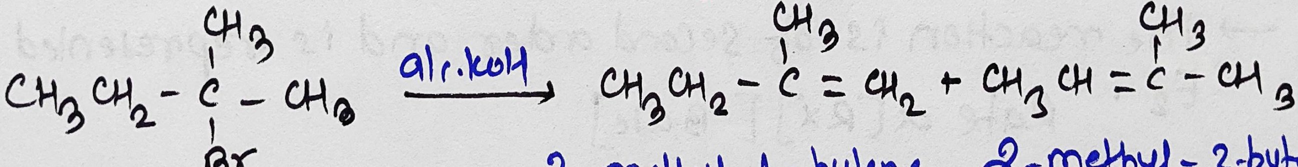
→ when elimination reaction is carried out in an ~~unsymmetrical~~ unsymmetrical alkylhalide, a mixture of all possible alkenes are obtained.

For eg:



$$CH_3-CH_2-\overset{\overset{Br}{|}}{C}H-CH_3 \xrightarrow{alc.KOH} CH_3CH_2CH=CH_2 + CH_3CH=CH-CH_3$$

Sec. butyl bromide — 1-butene (19%) — 2-butene (81%)



$$CH_3CH_2-\overset{CH_3}{\underset{Br}{C}}-CH_3 \xrightarrow{alc.KOH} CH_3CH_2-\overset{CH_3}{C}=CH_2 + CH_3CH=\overset{CH_3}{C}-CH_3$$

2-bromo-2-methyl butane — 2-methyl-1-butene (29%) — 2-methyl-2-butene (71%)

→ In such cases, the orientation i.e formation of major product is governed by the rule given by Alexander Saytzeff and is known as Saytzeff rule (zaitsev rule).

→ It states that " In dehydrohalogenation the alkene which has the greater no. of alkylgroup attached to the doubly bonded carbon atom is the preferred product".

the ease of formation of alkene is in the order ;

$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 : RHC=CHR > RHC=CH_2$
$> H_2C=CH_2$

Also, the value of heat of combustion & hydrogenation show the alkyl substituted alkene have the higher stability. Here it is clear that the ease of formation & the stability of alkene follow the same order.

So the Saytzeff rule may be stated as the more stable alkene, the faster it is formed.

→ The reactivity of alkylhalides in E2 dehydrohalogenation is in the order :

3° alkylhalide > 2° alkylhalide > 1° alkylhalide.

As the branching of carbon carrying halogen atom provides a greater no. of β-hydrogen for attack by base, Elimination is favoured leading to more highly branched alkene i.e more stable.

E$_1$ Mechanism

→ E$_1$ Stands for Elimination unimolecular. when the rate of an elimination reaction depends upon the concⁿ of the alkylhalide only and independent of base.

→ This reaction is of 1st order and is represented by E$_1$.

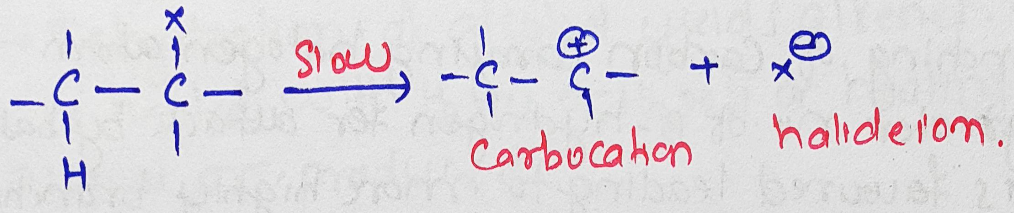
$$R \propto [Rx]$$

$$R = k[Rx]$$ → 1st order kinetics.

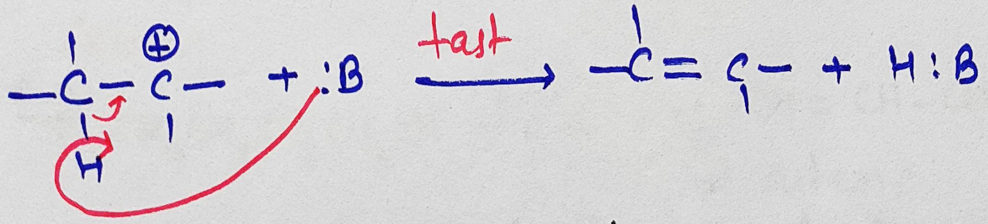
→ The rate determining step involves the participation of alkylhalide only.

→ The mechanism of this type of Elimination involves two steps.

Step (I) In this step, the alkylhalide gets dissociated into halide ion and carbocation.

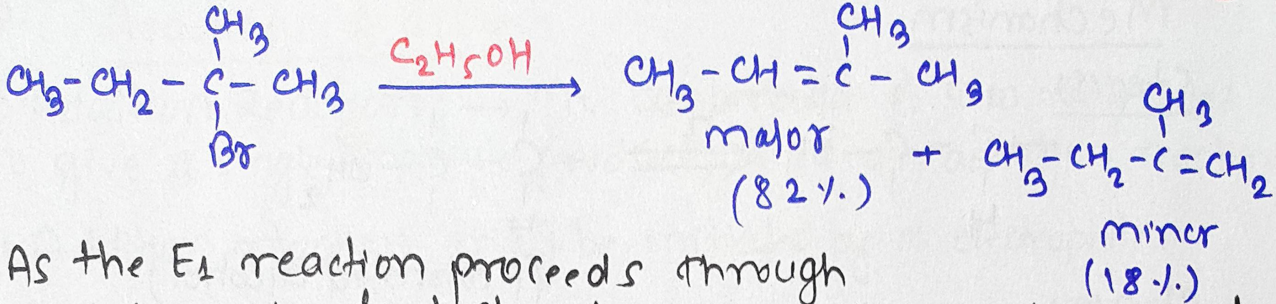


Step (II) In this step Carbocation rapidly loses a proton to base forming the alkene.



Orientation and Reactivity

→ As in E$_2$ Elimination, orientation in E$_1$ reaction follows the saytzeff rule i.e when there is possibilityies of more than one alkene, then the alkene which is more highly branched is the preferred product.



$$CH_3-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}-CH_3 \xrightarrow{C_2H_5OH} \underset{\substack{\text{major}\\(82\%)}}{CH_3-CH=\overset{\displaystyle CH_3}{C}-CH_3} + \underset{\substack{\text{minor}\\(18\%)}}{CH_3-CH_2-\overset{\displaystyle CH_3}{C}=CH_2}$$

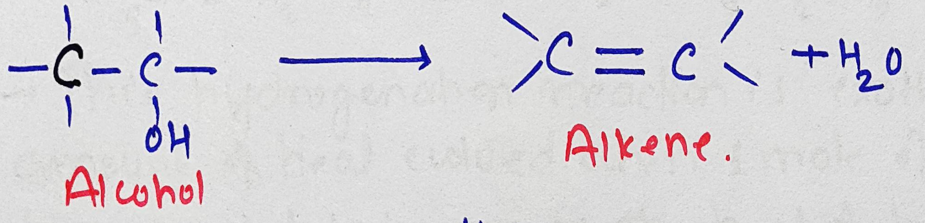
→ As the E_1 reaction proceeds through two steps, the first step determines the reactivity and the second step determine the orientation.

Since the reactivity of E_1 reaction depends upon the step (I) of the mechanism i.e formation of carbocation, thus order of reactivity is;

3° alkylhalide > 2° alkylhalide > 1° alkylhalide.

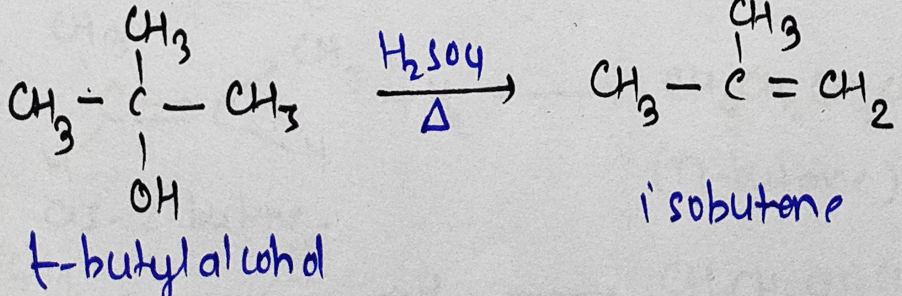
By dehydration of alcohol

→ Dehydration of alcohol yields alkenes. When alcohols are heated with H_2SO_4 or H_3PO_4 or heating with Al_2O_3 alkenes are produced.



$$\underset{\text{Alcohol}}{-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{OH}{C}}-} \longrightarrow \underset{\text{Alkene.}}{>C=C<} + H_2O$$

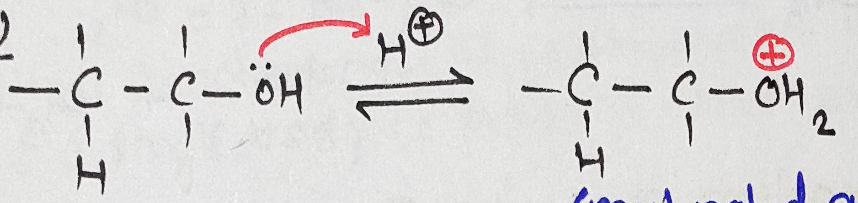
e.g $CH_3CH_2CH_2CH_2OH \xrightarrow[\Delta]{H_2SO_4} \underset{\substack{\text{2-butene}\\\text{(major)}}}{CH_3-CH=CH-CH_3} + \underset{\substack{\text{1-butene}\\\text{(minor)}}}{CH_3CH_2CH=CH_2}$



$$\underset{\text{t-butylalcohol}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH_3} \xrightarrow[\Delta]{H_2SO_4} \underset{\text{isobutene}}{CH_3-\overset{\displaystyle CH_3}{C}=CH_2}$$

Mechanism.

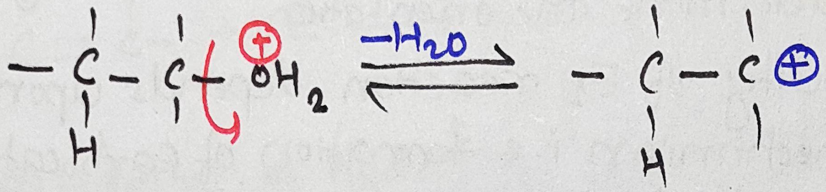
Step (I)



$$-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{|}{C}}-\ddot{O}H + H^{\oplus} \rightleftharpoons -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{|}{C}}-\overset{\oplus}{O}H_2$$

(protonated alcohol)

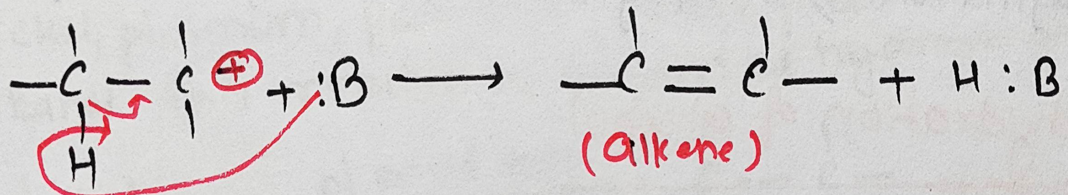
Step (II)



$$-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{|}{C}}-\overset{\oplus}{O}H_2 \underset{}{\overset{-H_2O}{\rightleftharpoons}} -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{|}{C}}^{\oplus}$$

(Carbocation)

Step (III)



$$-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{|}{C}}^{\oplus} + :B \longrightarrow -\overset{|}{C}=\overset{|}{C}- + H:B$$

(alkene)

Reactions of alkene

① Addition Reaction :→ The combination of two molecules to give a single molecule product called an addition reaction.

→ Addition reaction may be initiated by a electrophile.

$$-\overset{|}{C}=\overset{|}{C}- + yz \longrightarrow -\underset{y}{\overset{|}{\underset{|}{C}}}-\underset{z}{\overset{|}{\underset{|}{C}}}-$$ (addition product)

ⓐ Addition of hydrogen (hydrogenation)

→ Alkenes add hydrogen in the presence of catalyst such as nickel, platinum, paladium under pressure to give corresponding alkanes. This reaction is known as hydrogenation.

$$-\overset{|}{C}=\overset{|}{C}- + H_2 \xrightarrow{pt\ or\ pd\ or\ Ni} -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{H}{\overset{|}{\underset{|}{C}}}-$$ (alkane)

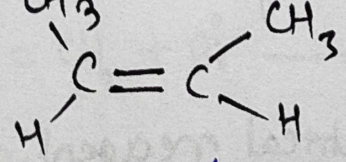
eg $CH_2=CH_2 + H_2 \xrightarrow{pt} CH_3CH_3$ (Ethane)

$CH_3CH=CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_3$ (propane).

→ This hydrogenation reaction is exothermic & the amount of heat evolved when 1 mole of an alkene is hydrogenated is known as the heat of hydrogenation.

→ Almost all the alkenes produce about 13 kilocalorie per mol of heat during hydrogenation.

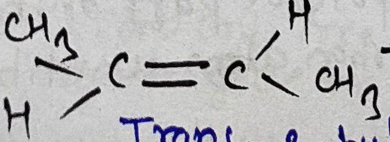
eg



$+ H_2 \longrightarrow CH_3CH_2CH_2CH_3 + 28.6\ kCal\ mol^{-1}$.

(n-butane)

cis-2-butene.



$+ H_2 \longrightarrow CH_3CH_2CH_2CH_3 + 27.6\ kcal\ mol^{-1}$.

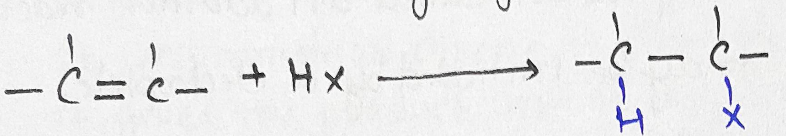
(n-butane)

Trans-2-butene. → Lower the heat of hydrogenation of alkane the more stable it is.

(more stable.

(B) Addition of hydrogenhalide (Hx)

→ Alkene add to hydrogen halide readily to give alkylhalides.

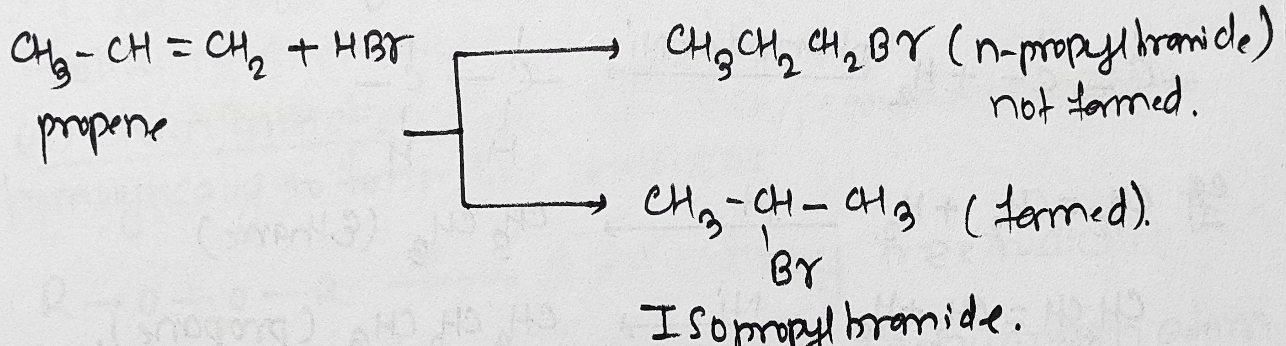


$$-\overset{|}{C}=\overset{|}{C}- + Hx \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}-$$

alkene (X = Cl, BrorI) alkylhalide

→ The reaction is carried out by passing the dry gaseou hydrogen halide to the alkene.

e.g $CH_2=CH_2 + HBr \xrightarrow{CH_3COOH} CH_3CH_2Br.$
Ethyl bromide.



$CH_3-CH=CH_2 + HBr$
propene

→ $CH_3CH_2CH_2Br$ (n-propyl bromide) not formed.

→ $CH_3-\underset{Br}{\underset{|}{CH}}-CH_3$ (formed).
Isopropyl bromide.

→ However in this case of unsymmetrical alkene, there is possibility of forming two products.

→ But only one ~~of~~ product is formed in actual practise.

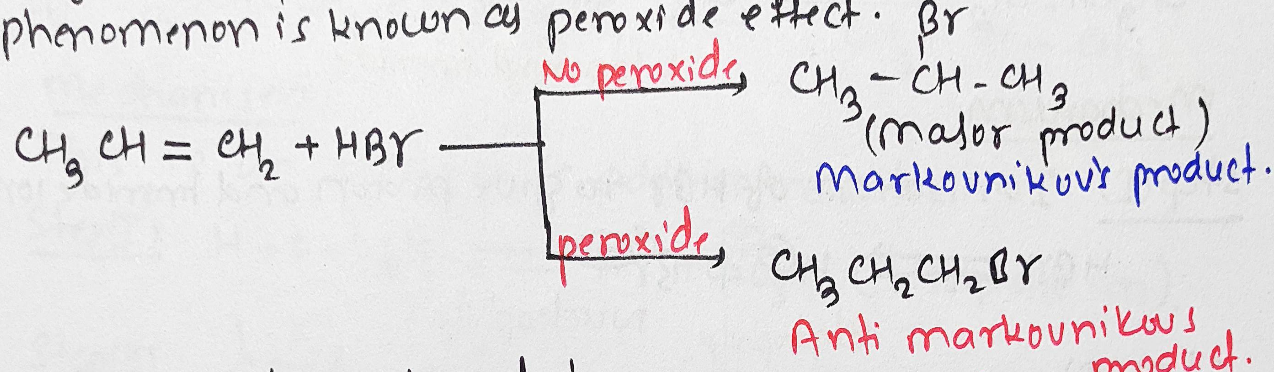
→ The predominant formation of the above product is in accordance with markovnikov's rule. which governs the addition of unsymmetrical reagent to unsymmetrical alkenes.

Markounikov's rule

→ It states that " when an unsymmetrical reagent adds to ~~the~~ an unsymmetrical alkene the positive part of the reagent goes to that doubly bonded Carbon atom which bears greater no. of hydrogen.

Addition of hydrogen bromide (peroxide Effect)

→ In 1933, American chemist named M.s kharasch discovered that when hydrogen bromide (HBr) is added to unsymmetrical alkene in the presence of organic peroxide, it gives the product anti to the Markounikov's rule. This phenomenon is known as peroxide effect.



$$CH_3CH=CH_2 + HBr \xrightarrow{\text{No peroxide}} CH_3-\overset{Br}{\overset{|}{C}}H-CH_3$$

(major product)
Markounikov's product.

$$CH_3CH=CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2Br$$

Anti markounikovs product. (major).

→ This can be explained by following mechanism.

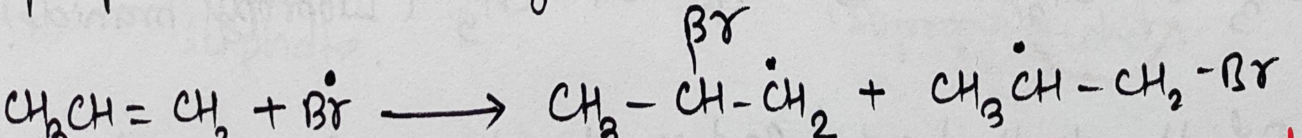
(A) Chain initiation step :- Step (I) In this, peroxide dissociates homolytically to form free radicals.

$$R-O-O-R \xrightarrow{\Delta} 2\,R\dot{O} \text{ (alkoxy free radicals).}$$

Step (II) Alkoxy free radical abstract the hydrogen atom from HBr to generate bromide free radicals.

$$R\dot{O} + H-Br \longrightarrow ROH + \dot{Br}$$

(B) Chain propagation step :- The bromide free radical attacks propene molecule to give more stable free radicals.



$$CH_3CH=CH_2 + \dot{Br} \longrightarrow CH_3-\overset{Br}{\overset{|}{C}}H-\dot{C}H_2 + CH_3\dot{C}H-CH_2-Br$$

1° free radical (least stable).

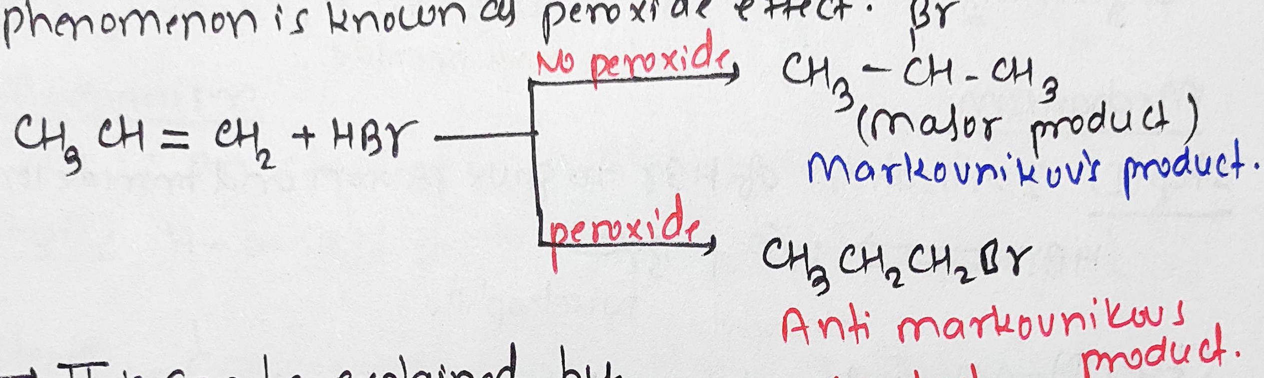
2° free radical (more stable)

The Secondary free radical then react with another HBr molecule to give the product.

$$CH_3-\dot{C}H-CH_2Br + HBr \longrightarrow CH_3CH_2CH_2Br + \dot{Br} \text{ (1-bromo propane)}$$

Addition of hydrogen bromide (peroxide Effect)

→ In 1933, American chemist named M.S kharasch discovered that when hydrogen bromide (HBr) is added to unsymmetrical alkene in the presence of organic peroxide, it gives the product anti to the Markovnikov's rule. This phenomenon is known as peroxide effect.



$$CH_3CH=CH_2 + HBr \xrightarrow{\text{No peroxide}} CH_3-\overset{Br}{\overset{|}{C}}H-CH_3$$

(major product) Markovnikov's product.

$$\xrightarrow{\text{peroxide}} CH_3CH_2CH_2Br$$

Anti markovnikovs product. (major).

→ This can be explained by following mechanism.

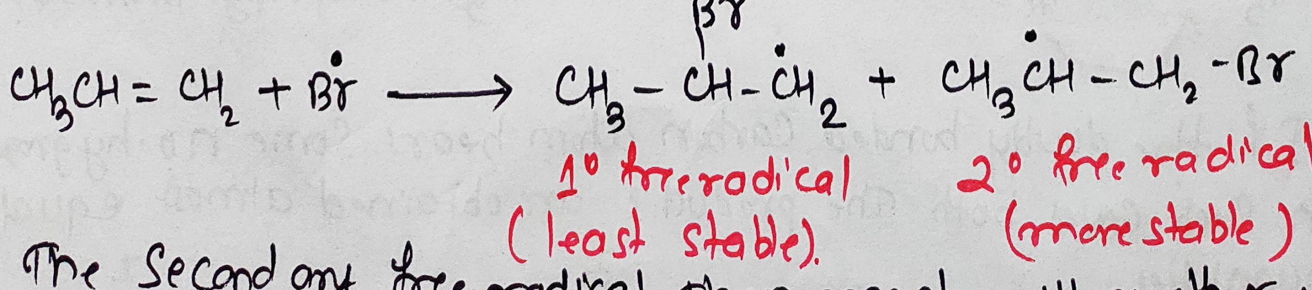
(A) **Chain initiation step** :- Step(I) In this, peroxide dissociates homolytically to form free radicals.

$$R-O-O-R \xrightarrow{\Delta} 2RO^{\bullet} \text{ (alkoxy free radicals).}$$

Step(II) Alkoxy free radical abstract the hydrogen atom from HBr to generate bromide free radicals.

$$RO^{\bullet} + H-Br \longrightarrow ROH + Br^{\bullet}$$

(B) Chain propagation step :- The bromide free radical attacks propene molecule to give more stable free radicals.



$$CH_3CH=CH_2 + Br^{\bullet} \longrightarrow CH_3-\overset{Br}{\overset{|}{C}}H-\dot{C}H_2 + CH_3\dot{C}H-CH_2-Br$$

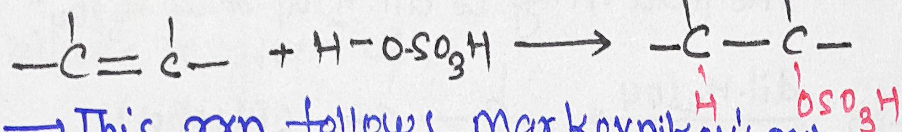
1° free radical (least stable). 2° free radical (more stable)

The Secondary free radical then react with another HBr molecule to give the product.

$$CH_3-\dot{C}H-CH_2Br + HBr \longrightarrow CH_3CH_2CH_2Br + Br^{\bullet}$$ (1-bromo propane)

Addition of H_2SO_4

→ Alkene react with cold and conc. H_2SO_4 to give alkyl hydrogen Sulphate.

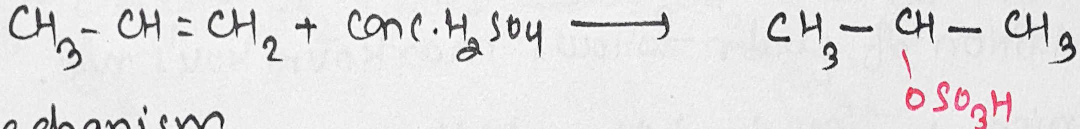


$$-\overset{|}{C}=\overset{|}{C}- + H-OSO_3H \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{OSO_3H}{\overset{|}{C}}-$$

(alkyl hydrogen sulphate)

→ This rxn follows markovnikov's rule.

eg



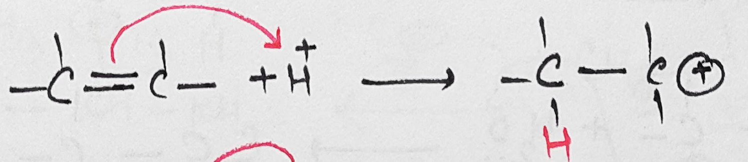
$$CH_3-CH=CH_2 + \text{conc.}\,H_2SO_4 \longrightarrow CH_3-\underset{OSO_3H}{CH}-CH_3$$

Mechanism

This is an electrophilic addition reaction.

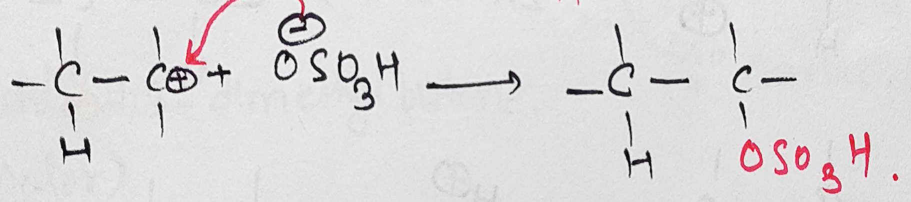
Step(I) $H-O-SO_3H \rightleftharpoons H^{\oplus} + \overset{\ominus}{O}SO_3H$ (bisulphate ion).

Step(II)



$$-\overset{|}{C}=\overset{|}{C}- + \overset{+}{H} \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}^{\oplus}$$

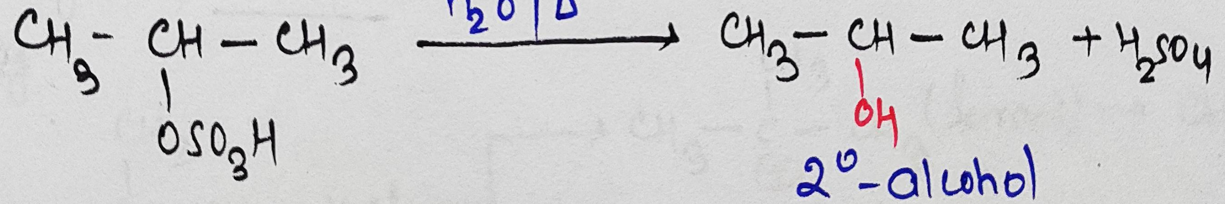
(Carbocation)



$$-\underset{H}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}^{\oplus} + \overset{\ominus}{O}SO_3H \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{OSO_3H}{\overset{|}{C}}-.$$

The hydrogen sulphate on hydrolysis yield alcohols. ~~for~~.

eg



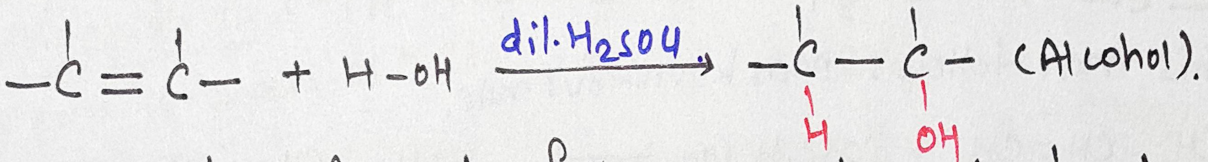
$$CH_3-\underset{OSO_3H}{CH}-CH_3 \xrightarrow{H_2O\,/\,\Delta} CH_3-\underset{OH}{CH}-CH_3 + H_2SO_4$$

Isopropyl hydrogen sulphate.

2^0-alcohol
isopropyl alcohol.

Addition of water. (hydration)

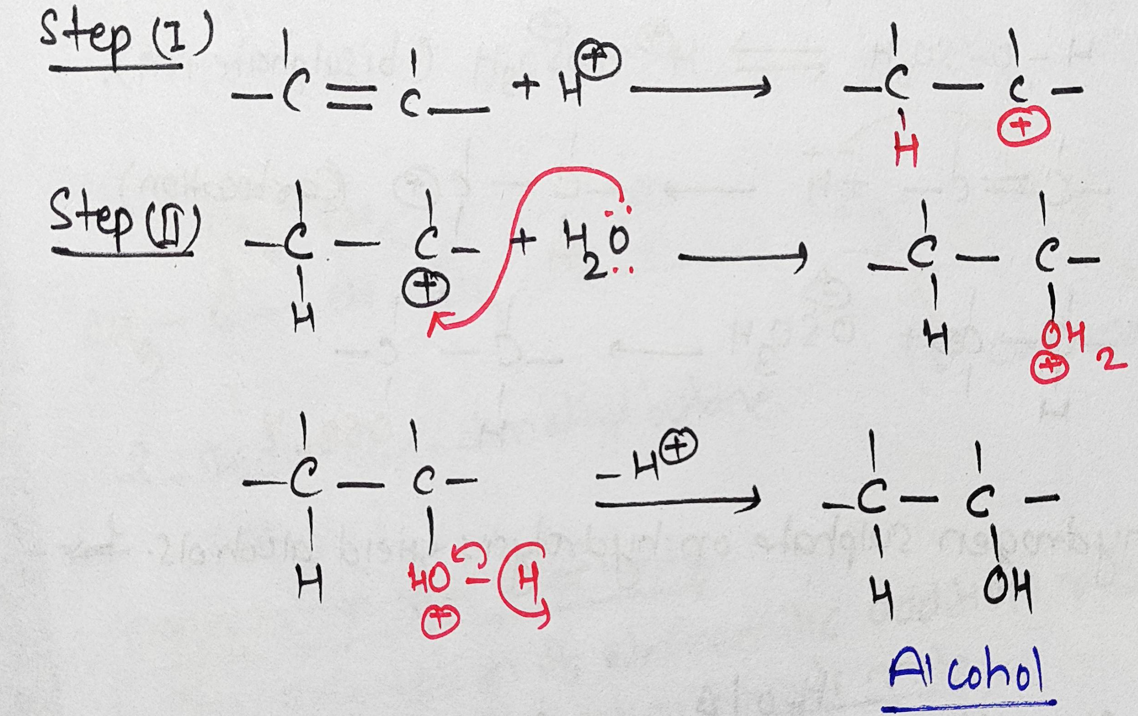
→ The addition of water molecule to alkene take place only in the presence of acid. The acid may be dil. H_2SO_4 or dil. H_3PO_4.



$$-\overset{|}{C}=\overset{|}{C}- + H-OH \xrightarrow{dil.\,H_2SO_4} -\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \text{ (Alcohol).}$$

↳ Addition of water follows markovnikov's rule.

Mechanism :- Electrophilic addition.



Step (I)

$$-\overset{|}{C}=\overset{|}{C}- + H^{\oplus} \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{\oplus}{\overset{|}{C}}-$$

Step (II)

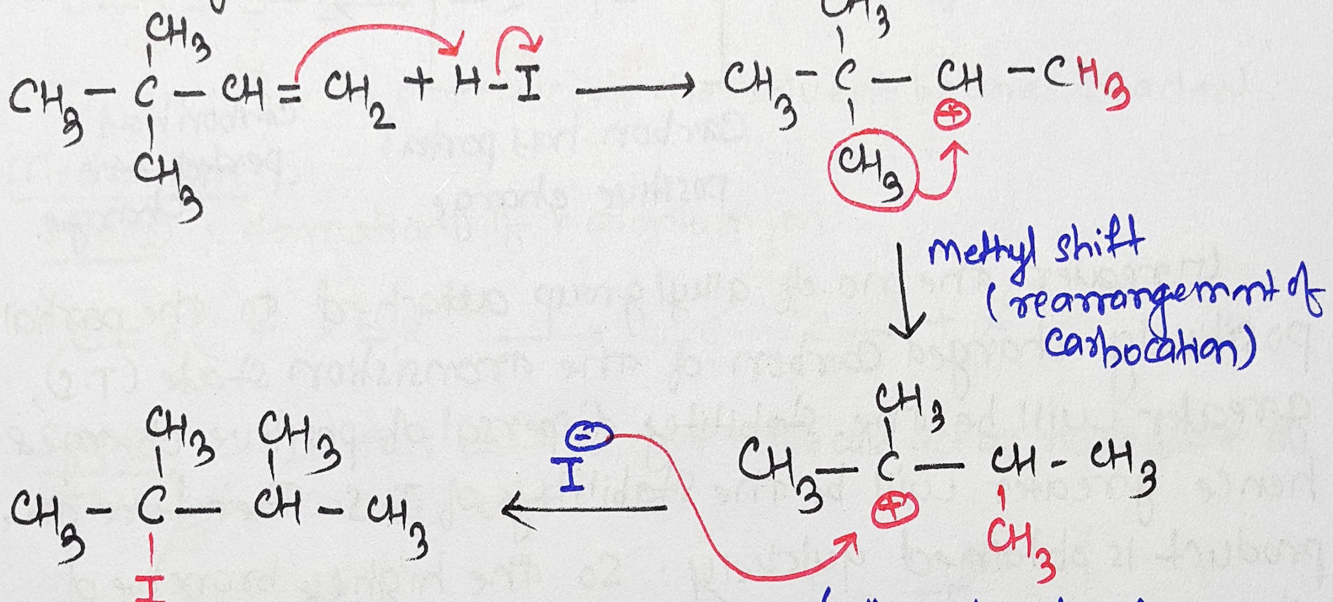
$$-\underset{H}{\overset{|}{C}}-\underset{\oplus}{\overset{|}{C}}- + H_2\ddot{O} \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{\overset{\oplus}{O}H_2}{\overset{|}{C}}-$$

$$-\underset{H}{\overset{|}{C}}-\underset{H\overset{\oplus}{O}-H}{\overset{|}{C}}- \xrightarrow{-H^{\oplus}} -\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$$

Alcohol

Electrophilic addition (mechanism, orientation & reactivity)

Mechanism :- The mechanism of electrophilic addition in alkene is given as;



methyl shift (rearrangement of carbocation)

(3° carbocation)

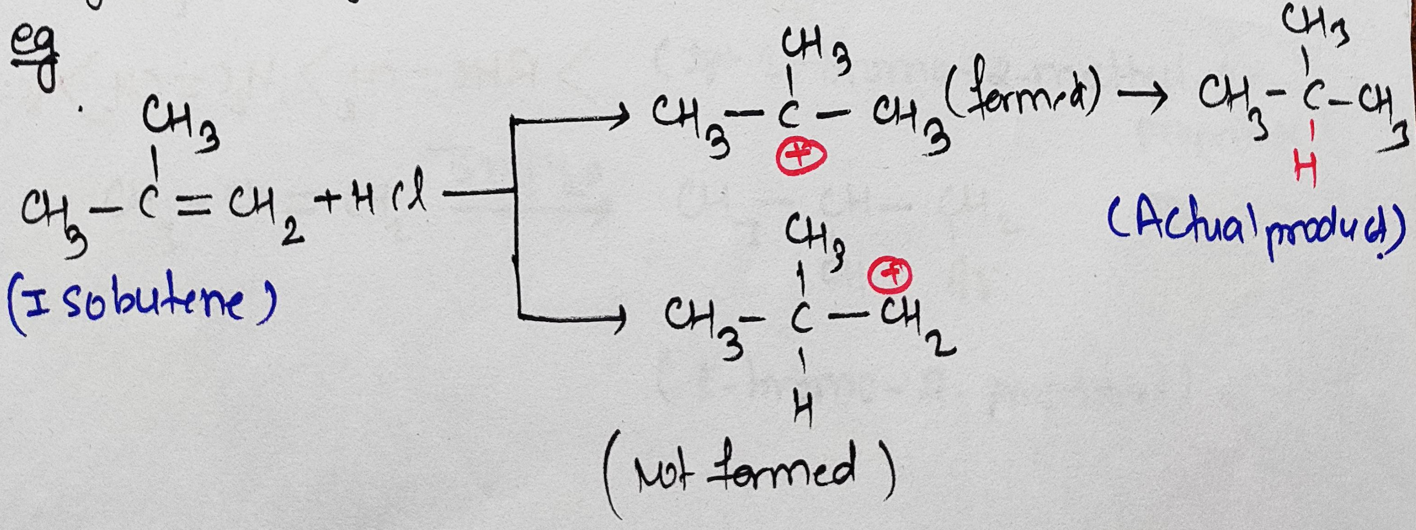
2-Iodo-2,3-dimethyl butane.

(Major)

Orientation and Reactivity

→ The orientation of electrophilic addition reaction of alkene is governed by markovnikov's rule.

eg



(Isobutene)

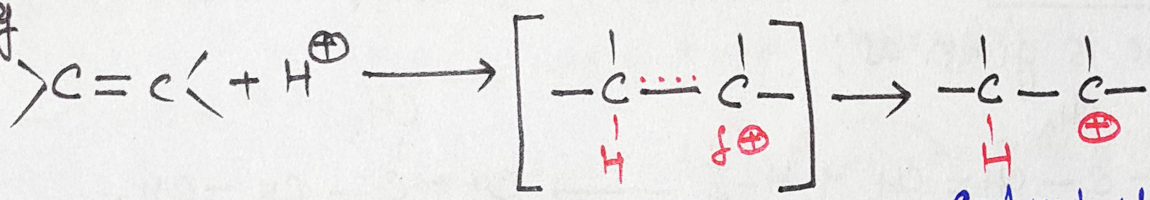
(formed)

(Actual product)

(Not formed)

→ The reactivity of alkenes towords electrophilic alkene can be understood by knowing the stability of carbocation.

eg



$$>C=C< + H^{\oplus} \longrightarrow \left[-\overset{|}{\underset{H}{C}} \cdots \overset{|}{\underset{\delta\oplus}{C}}- \right] \longrightarrow -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{\oplus}{C}}-$$

Carbon has partial positive charge.

Carbon has perfect +ve charge.

Greater the no. of alkyl group attached to the partially positively charged carbon of the transistion state (T.S), greater will be the ~~stability~~ dispersal of positive charge & hence greater will be the stability of T.S. Therefore the product is obtained quickely. So the highly branched alkenes are reactive during the electrophilic ~~substitutia~~ addition.

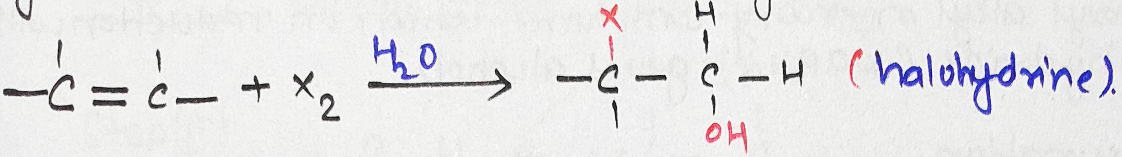
Thus, the decreasing order of reactivity of alkene is.

$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2, RHC=CHR >$ ~~$RHC=CH_2$~~

$> RHC=CH_2 > H_2C=CH_2 > H_2C=CHX$ 101 ?

Halohydrine formation.

→ When alkene is treated with halogen in aqueous soln, it gives halo alcohol, also called halohydridne.



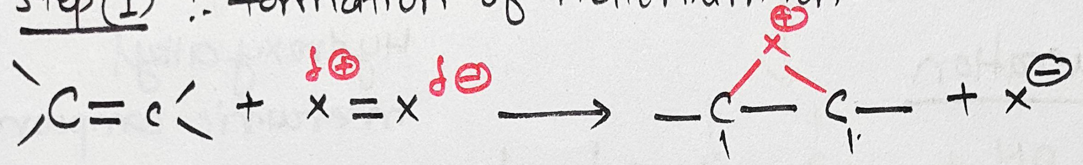
$$-\overset{|}{C}=\overset{|}{C}- + X_2 \xrightarrow{H_2O} -\overset{X}{\underset{|}{\overset{|}{C}}}-\overset{H}{\underset{OH}{\overset{|}{\underset{|}{C}}}}-H$$

(halohydrine).

In this case → molecule of the solvent becomes reactant.

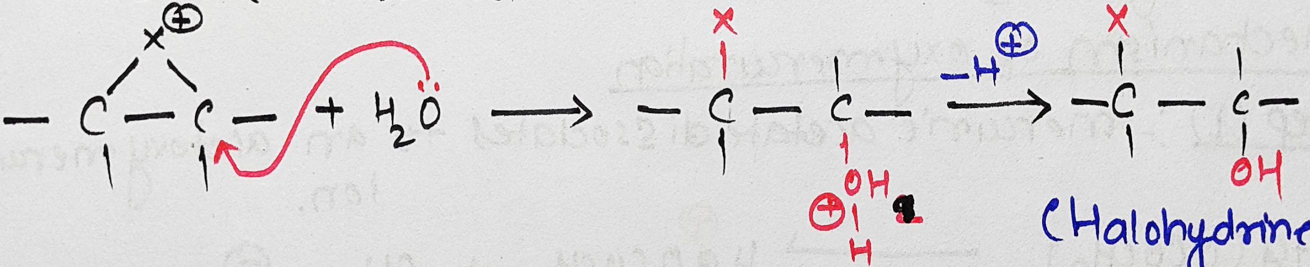
Mechanism :-

Step(I) :- formation of halonium ion.



$$>C=C< + \overset{\delta\oplus}{X}=\overset{\delta\ominus}{X} \longrightarrow -\underset{|}{C}-\underset{|}{C}- \;(\text{bridged by } X^{\oplus}) + X^{\ominus}$$

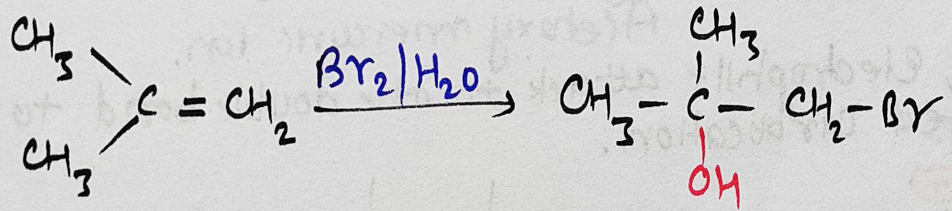
Step(II) :- In this case water molecule act as nucleophile & attacks the carbon atoms.



$$-\underset{|}{C}-\underset{|}{C}- (X^{\oplus}) + H_2\ddot{O} \longrightarrow -\overset{X}{\underset{|}{\overset{|}{C}}}-\underset{\overset{\oplus}{O}H_2}{\overset{|}{\underset{|}{C}}}- \xrightarrow{-H^{\oplus}} -\overset{X}{\underset{|}{\overset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$$

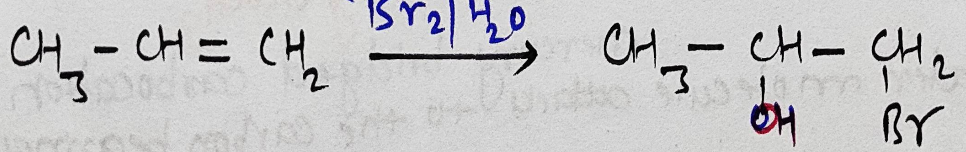
(Halohydrine).

eg



$$(CH_3)_2C=CH_2 \xrightarrow{Br_2|H_2O} CH_3-\overset{CH_3}{\underset{OH}{\overset{|}{\underset{|}{C}}}}-CH_2-Br$$

(~~1g~~ 1-bromo-2-methyl-2-propanol)



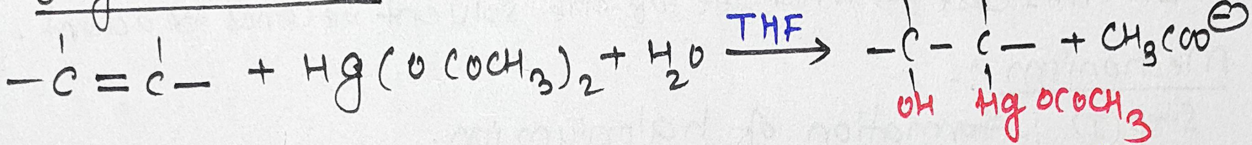
$$CH_3-CH=CH_2 \xrightarrow{Br_2|H_2O} CH_3-\underset{OH}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}$$

(1-bromo-2-proponol).

Oxymercuration-demercuration.

→ when alkene is treated with mercuric acetate in the presence of ~~under~~ water and THF (Tetra hydro furan), it gives hydroxyl alkyl mercury compound which on reduction with sodium borohydride ($NaBH_4$) gives alcohol).

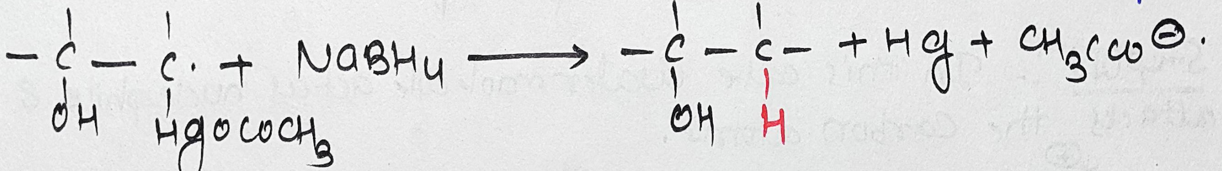
Oxymercuration



$$-\overset{|}{C}=\overset{|}{C}- + Hg(OCOCH_3)_2 + H_2O \xrightarrow{THF} -\underset{OH}{\overset{|}{C}}-\underset{HgOCOCH_3}{\overset{|}{C}}- + CH_3COO^{\ominus}$$

Hydroxy alkyl mercuric compound.

Demercuration



$$-\underset{OH}{\overset{|}{C}}-\underset{HgOCOCH_3}{\overset{|}{C}}\cdot + NaBH_4 \longrightarrow -\underset{OH}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}- + Hg + CH_3COO^{\ominus}.$$

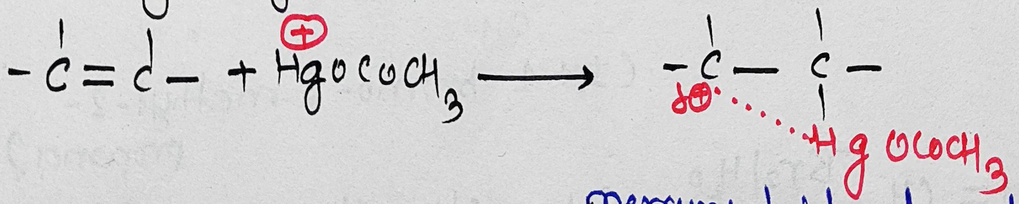
Mechanism of oxymercuration

Step (I) :- mercuric acetate dissociates to an acetoxy mercuric ion.

$$Hg(OCOCH_3)_2 \rightleftharpoons \overset{\oplus}{Hg}OCOCH_3 + CH_3COO^{\ominus}$$

Acetoxy mercuric ion.

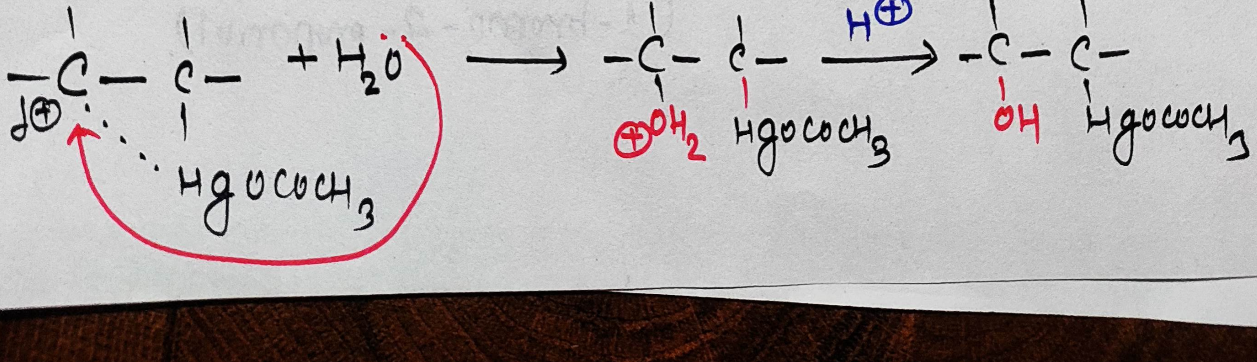
Step (II) : Now, electrophile attack to the double bond to give mercury bridged carbocation.



$$-\overset{|}{C}=\overset{|}{C}- + \overset{\oplus}{Hg}OCOCH_3 \longrightarrow -\underset{\delta\oplus}{\overset{|}{C}}-\underset{HgOCOCH_3}{\overset{|}{C}}-$$

Mercury bridged carbocation.

Step (III) : water molecule attacks to the carbon bearing positive charge.

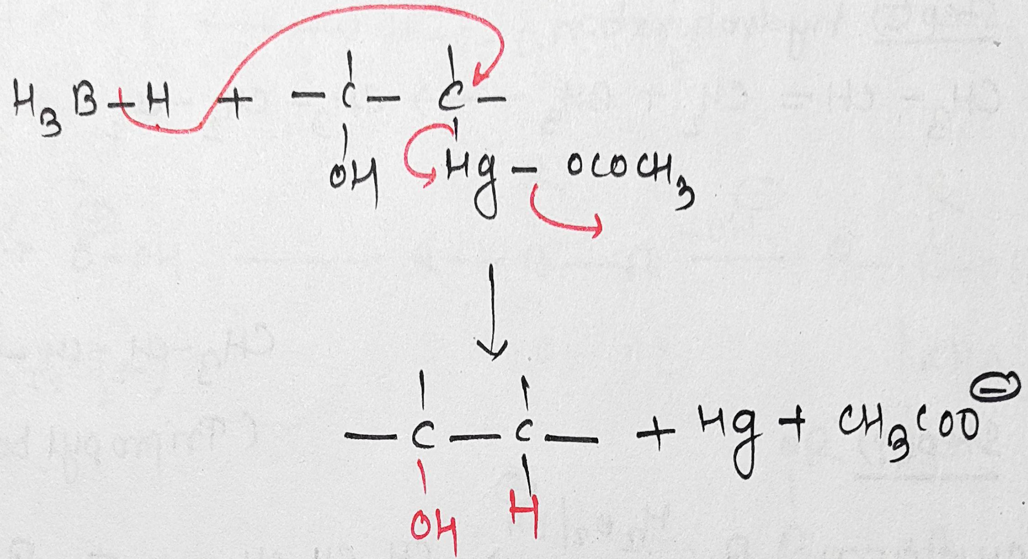


$$-\underset{\delta\oplus}{\overset{|}{C}}-\underset{HgOCOCH_3}{\overset{|}{C}}- + H_2\ddot{O} \longrightarrow -\underset{\oplus OH_2}{\overset{|}{C}}-\underset{HgOCOCH_3}{\overset{|}{C}}- \xrightarrow{H^{\oplus}} -\underset{OH}{\overset{|}{C}}-\underset{HgOCOCH_3}{\overset{|}{C}}-$$

Mechanism of deoxymercuration

Step (I) $NaBH_4 \rightleftharpoons Na^{\oplus} + \overset{\ominus}{B}H_4$

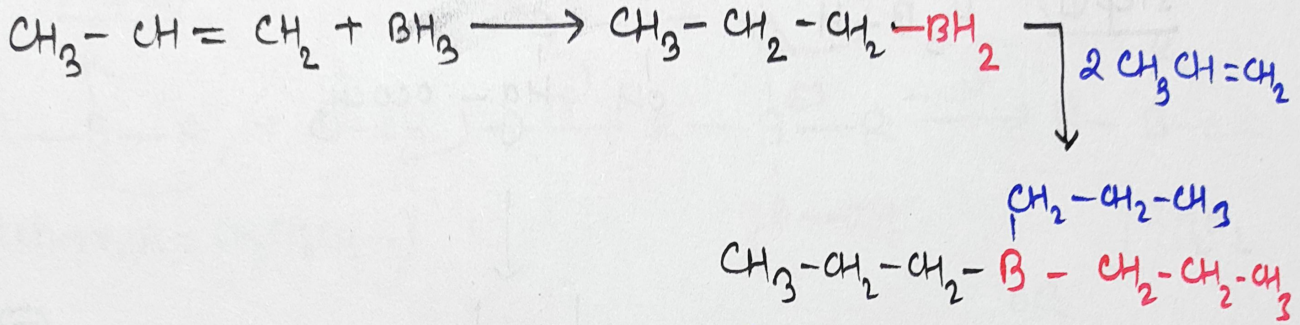
Step (II)



Hydroboration oxidation.

→ Alkene when treated with diborane, it gives trialkyl borane. which on oxidation with alkaline hydrogen peroxide gives alcohol.

Step(I) hydroboration.



$$CH_3-CH=CH_2 + BH_3 \longrightarrow CH_3-CH_2-CH_2-BH_2 \xrightarrow{2\,CH_3CH=CH_2} CH_3-CH_2-CH_2-\overset{CH_2-CH_2-CH_3}{\overset{|}{B}}-CH_2-CH_2-CH_3$$

(Tripropyl borane).

Step(II)

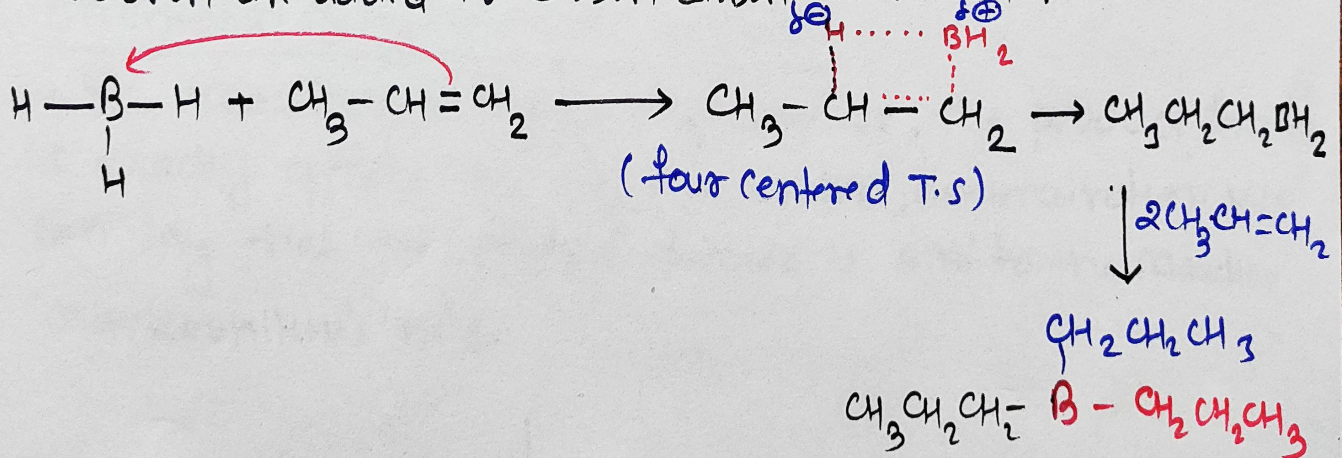
$$(CH_3-CH_2CH_2)_3B \xrightarrow{H_2O_2/\overset{\ominus}{OH}} CH_3CH_2CH_2OH + B(OH)_3$$

propanol.

Mechanism of hydroboration.

→ single step electrophilic addition reaction.

→ formation four centred transistion step in which both hydrogen & boron are added to carbon carbon double bond.



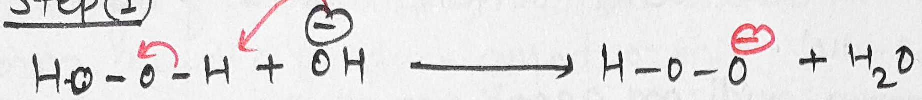
$$H-\underset{\underset{H}{|}}{B}-H + CH_3-CH=CH_2 \longrightarrow CH_3-\overset{\overset{\delta\ominus}{H}\cdots\cdots\overset{\delta\oplus}{BH_2}}{CH\,\text{---}\,CH_2} \longrightarrow CH_3CH_2CH_2BH_2 \xrightarrow{2CH_3CH=CH_2} CH_3CH_2CH_2-\overset{CH_2CH_2CH_3}{B}-CH_2CH_2CH_3$$

(four centred T.S)

(Tripropyl borane.)

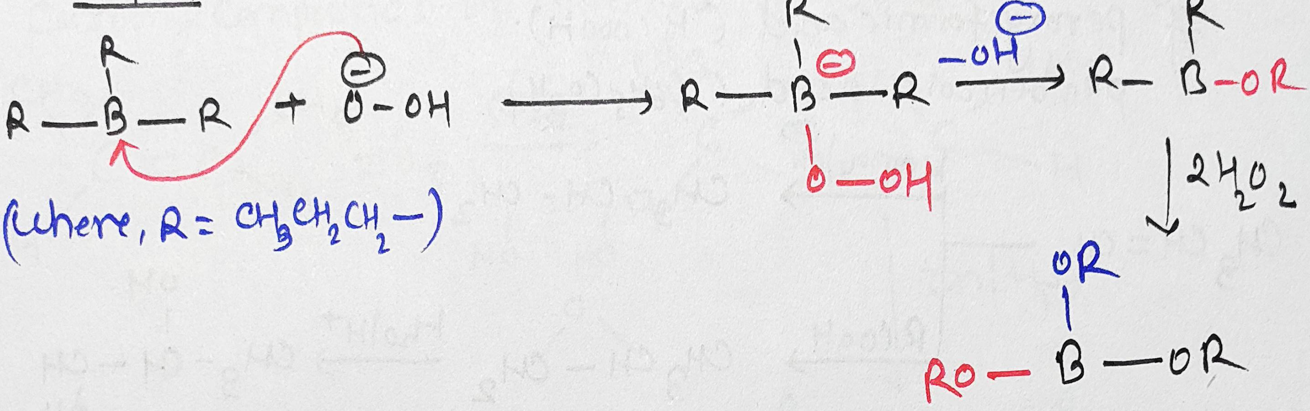
Mechanism of oxidation

Step(I)



$$H-O-\overset{..}{O}-H + \overset{\ominus}{O}H \longrightarrow H-O-\overset{\ominus}{O} + H_2O$$

Step(II)

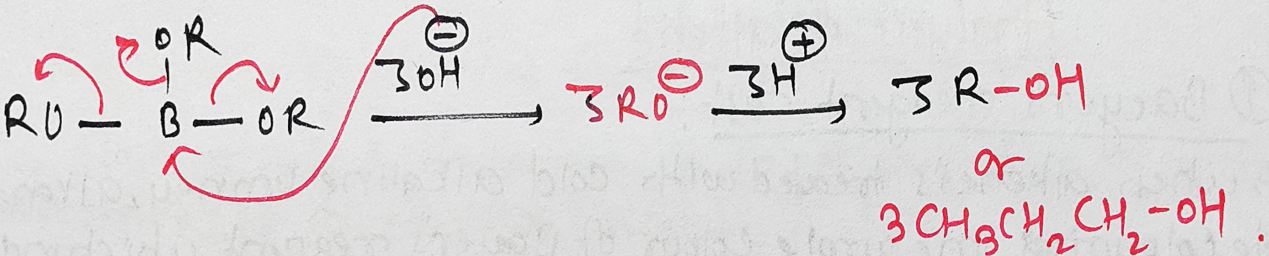


$$R-\overset{R}{\underset{}{B}}-R + \overset{\ominus}{O}-OH \longrightarrow R-\overset{R}{\underset{O-OH}{\overset{\ominus}{B}}}-R \xrightarrow{-OH^{\ominus}} R-\overset{R}{B}-OR \xrightarrow{2H_2O_2} RO-\overset{OR}{B}-OR$$

(where, $R = CH_3CH_2CH_2-$)

(Trialkyl borane).

Step(III)



$$RO-\overset{OR}{B}-OR \xrightarrow{3\overset{\ominus}{O}H} 3RO^{\ominus} \xrightarrow{3H^{\oplus}} 3R-OH$$

or

$3CH_3CH_2CH_2-OH$.

Orientation of hydroboration oxidation.

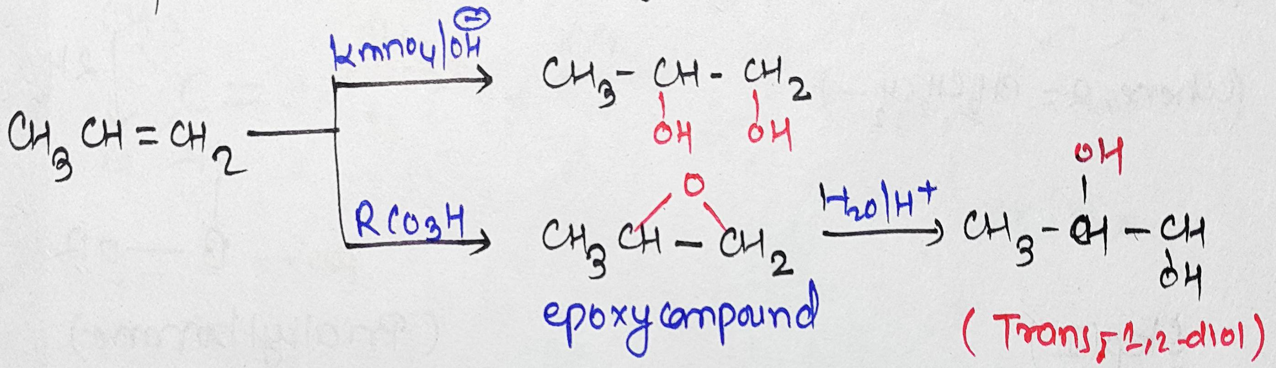
→ The reaction is highly regioselective, the product formed is exactly opposite to oxymercuration, demercuration. We can say that the product formed is anti to the ~~Markov~~ markovnikov's rule.

Hydroxylation (formation of 1,2-diol or glycol)

→ Alkenes when treated with certain oxidizing agents give glycol or 1,2-diol.

→ The most common oxidizing agents are alkaline $KMnO_4$ or peroxyacid ($RCOOOH$);

eg peroxy formic acid ($HCOOOH$)
perbenzoic acid ($C_6H_5CO_3H$).



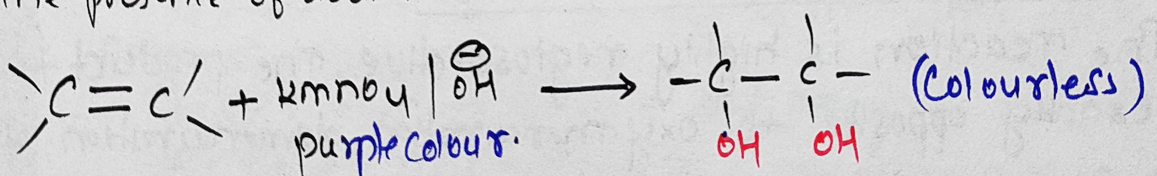
$$CH_3CH=CH_2 \xrightarrow{KMnO_4/\overset{\ominus}{O}H} CH_3-\underset{OH}{CH}-\underset{OH}{CH_2}$$

$$CH_3CH=CH_2 \xrightarrow{RCO_3H} CH_3\overset{O}{CH-CH_2} \xrightarrow{H_2O/H^+} CH_3-\overset{OH}{CH}-\underset{OH}{CH}$$

Analysis of alkene

① Baeyer's reagent test:

→ when alkene is treated with cold alkaline $KMnO_4$, alkene decolourises the purple colour of Baeyer's reagent which indicates the presence of double bond in molecule.



$$>C=C< + KMnO_4/\overset{\ominus}{O}H \longrightarrow -\underset{OH}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$$

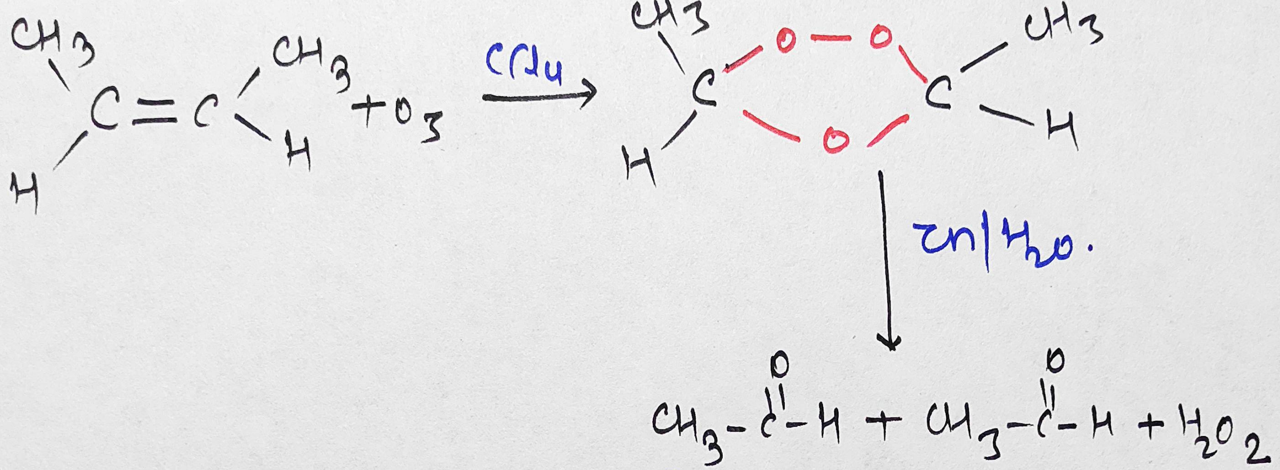
② Bromine test:

→ when alkene is treated with bromine in presence of Carbon tetrachloride (red colour), the red colour of bromine is discharged which indicates the presence of double bond in the molecule.

Ozonolysis:-

→ when ozone is passed through a solution of an alkene in an inert Solvent, it adds across the double bonds to form a cyclic product called ozonid.

→ The ozonide on reduction with $Zn|H_2O$ gives Carbonyl Compounds i.e aldehyde or ketones.



Acetaldehyde.

Application of alkenes to prepare polymers.

→ The process of formation of a polymer from its corresponding monomers is called polymerisation.

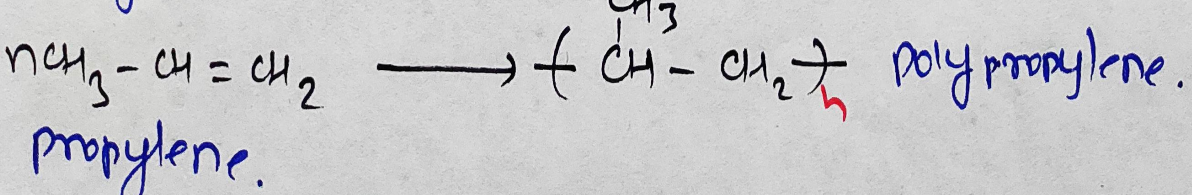
→ Alkene molecules can act as monomer units to form polymers.

→ For a number of ethylene and propylene molecules can simply add to one another to give polyethylene & polypropylene.

$$nCH_2=CH_2 \longrightarrow +CH_2-CH_2+_n$$

(monomer) ethylene

Polyethylene (polymer)



$$nCH_3-CH=CH_2 \longrightarrow +\overset{CH_3}{\underset{|}{CH}}-CH_2+_n$$

propylene.

Polypropylene.