

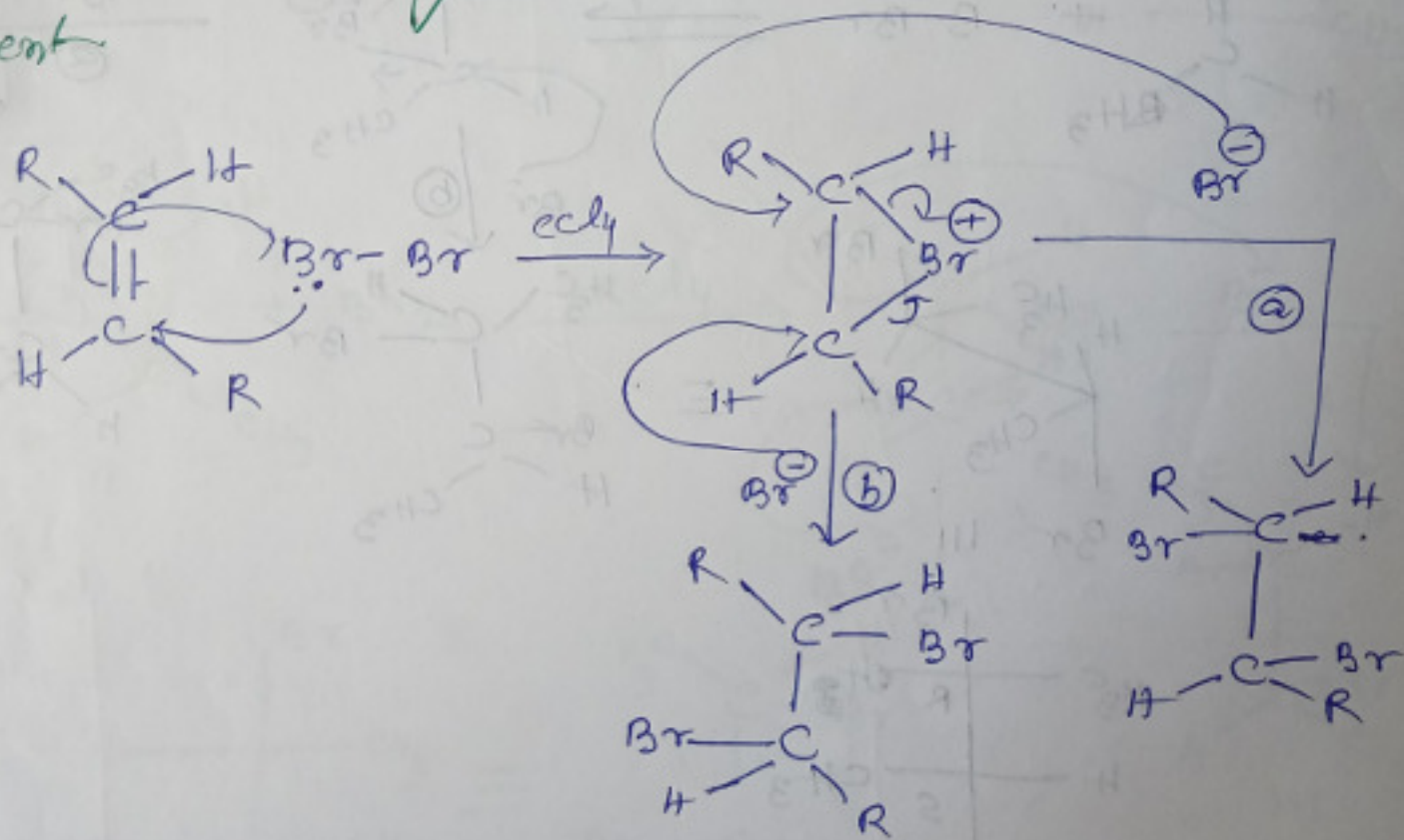
Electrophilic and radical addition to C=C multiple bonds:-

Halogenation of alkene:-

Addition of Br or Cl to $C=C$ readily takes place through electrophilic attack to form vicinal dibromide or vicinal dichloride. Halogenation of alkene is two step process and takes place by two ways.

(i) Halogenation in presence of non polar solvent.

(ii) Halogenation in presence of polar solvent.

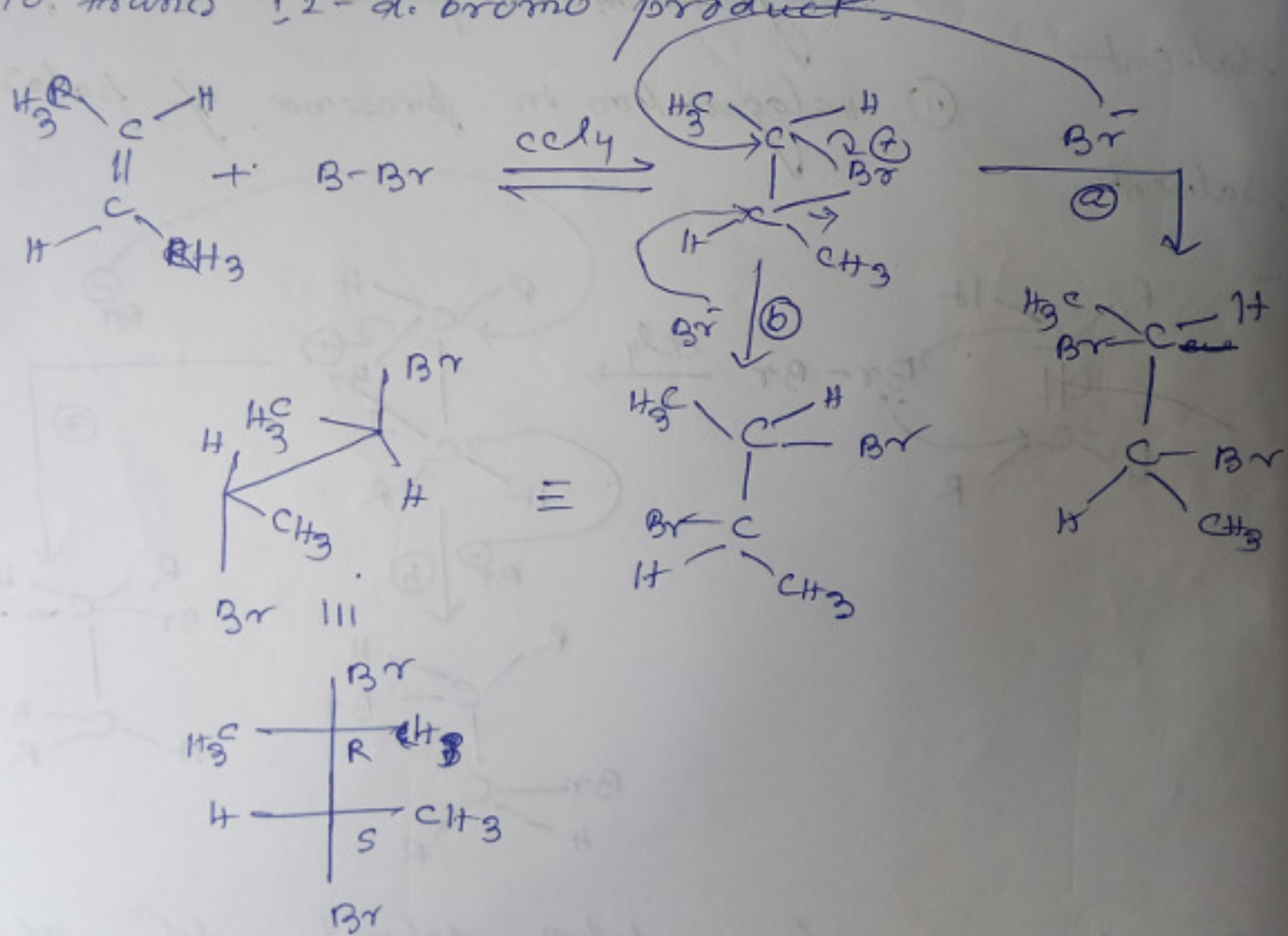


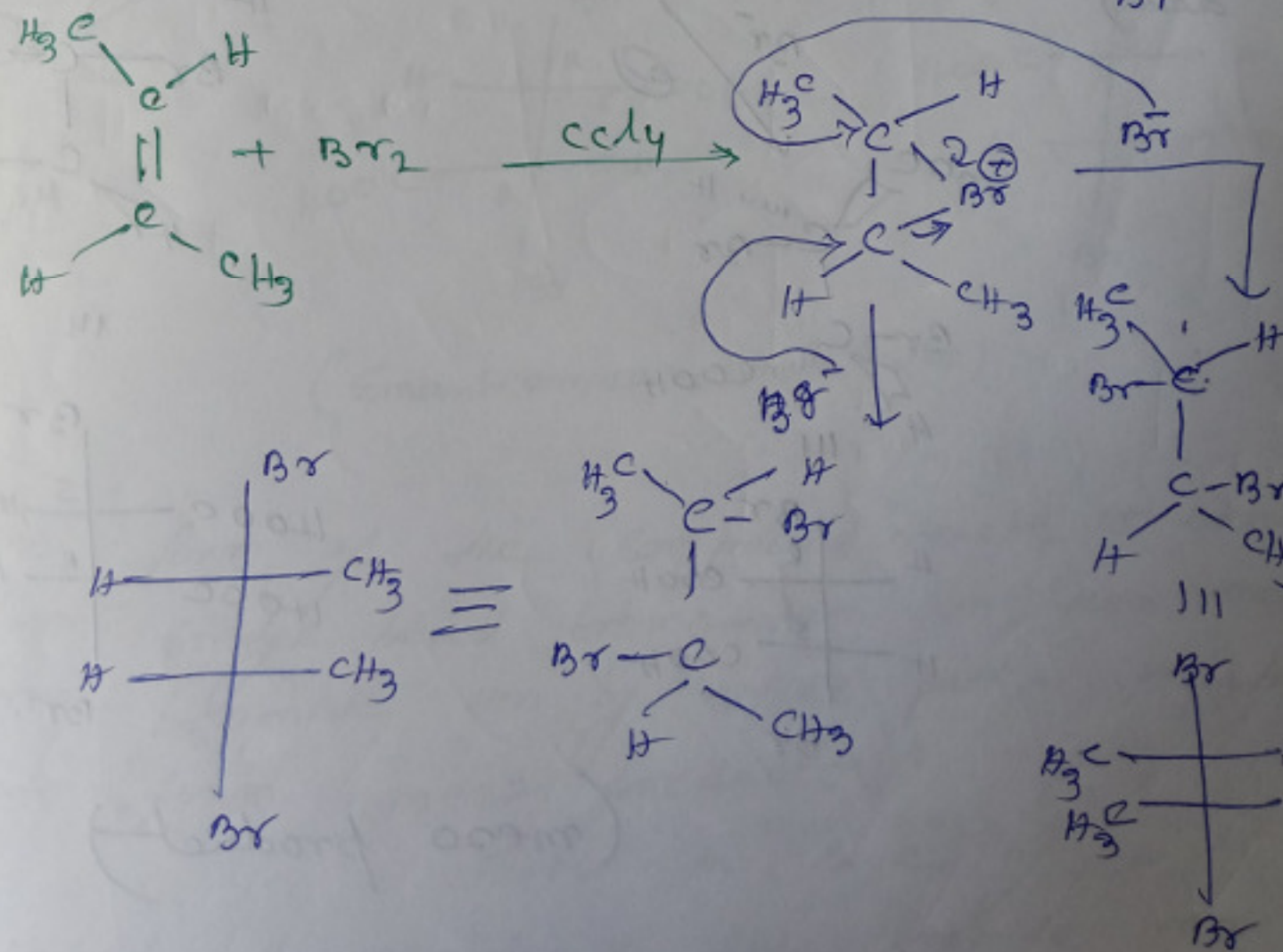
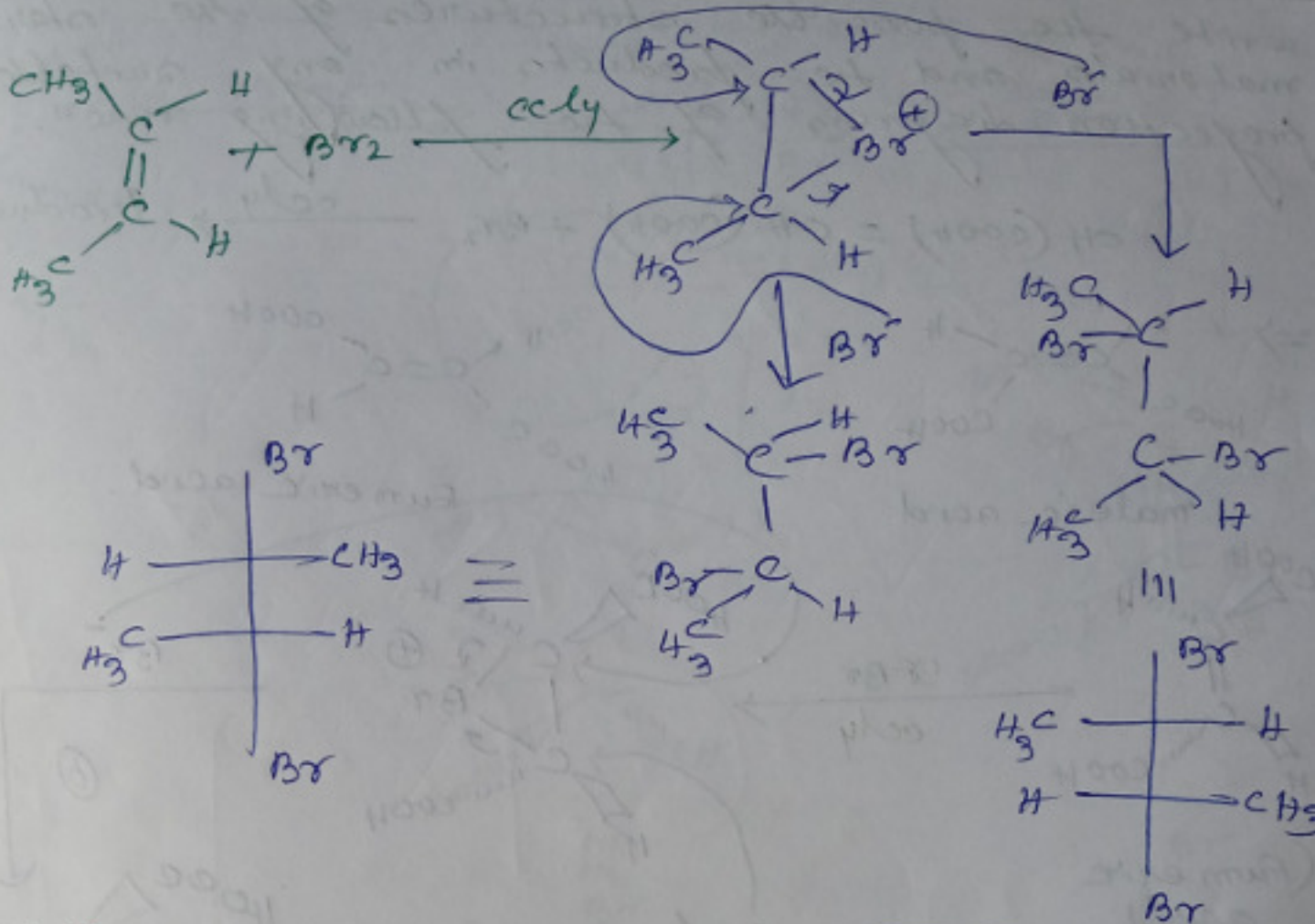
In presence of nonpolar solvent addⁿ of $-Br$ to $C=C$ takes place through trans mech^m. i.e. bromination of alkene in CCl_4 gives only trans 1,2-dibromo alkane and hence the reaction is stereospecific which can be explained

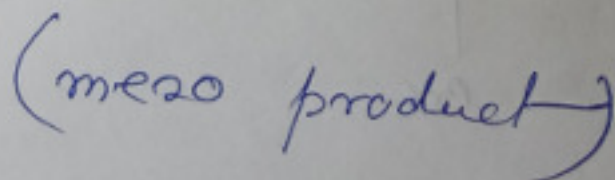
by following two steps mechanism.

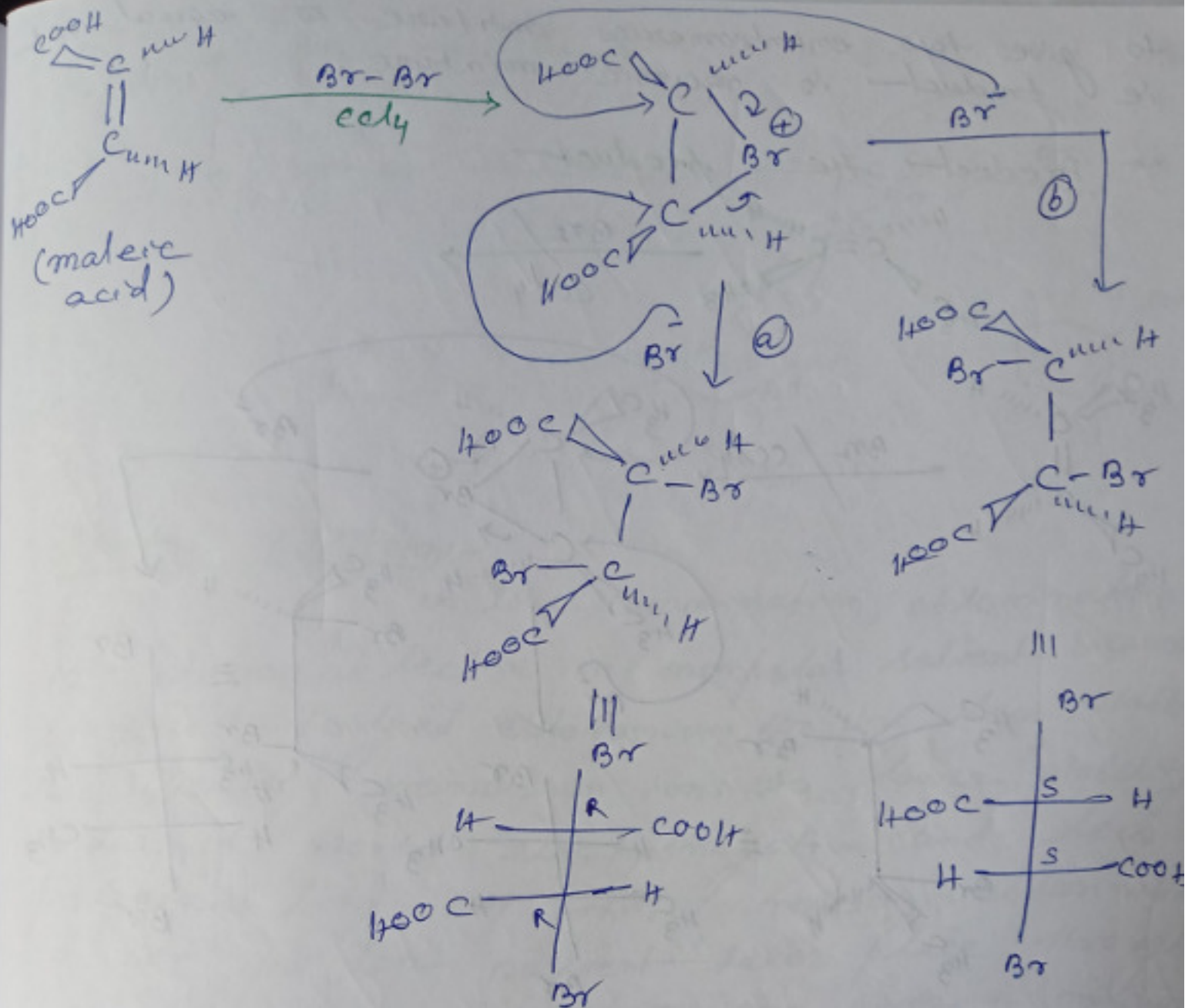
step-I in the initial step alkene reacts with bromine to form cyclic bromonium ion (bridged bromonium ion).

step-II in the final step nucleophilic bromide ion attacks to the cyclic bromonium ion from the opposite side of the ring, leading to trans 1,2-dibromo product.





$$\text{CH}(\text{COOH}) = \text{CH}(\text{COOH}) + \text{Br}_2 \xrightarrow{\text{CCl}_4} \text{Products.}$$


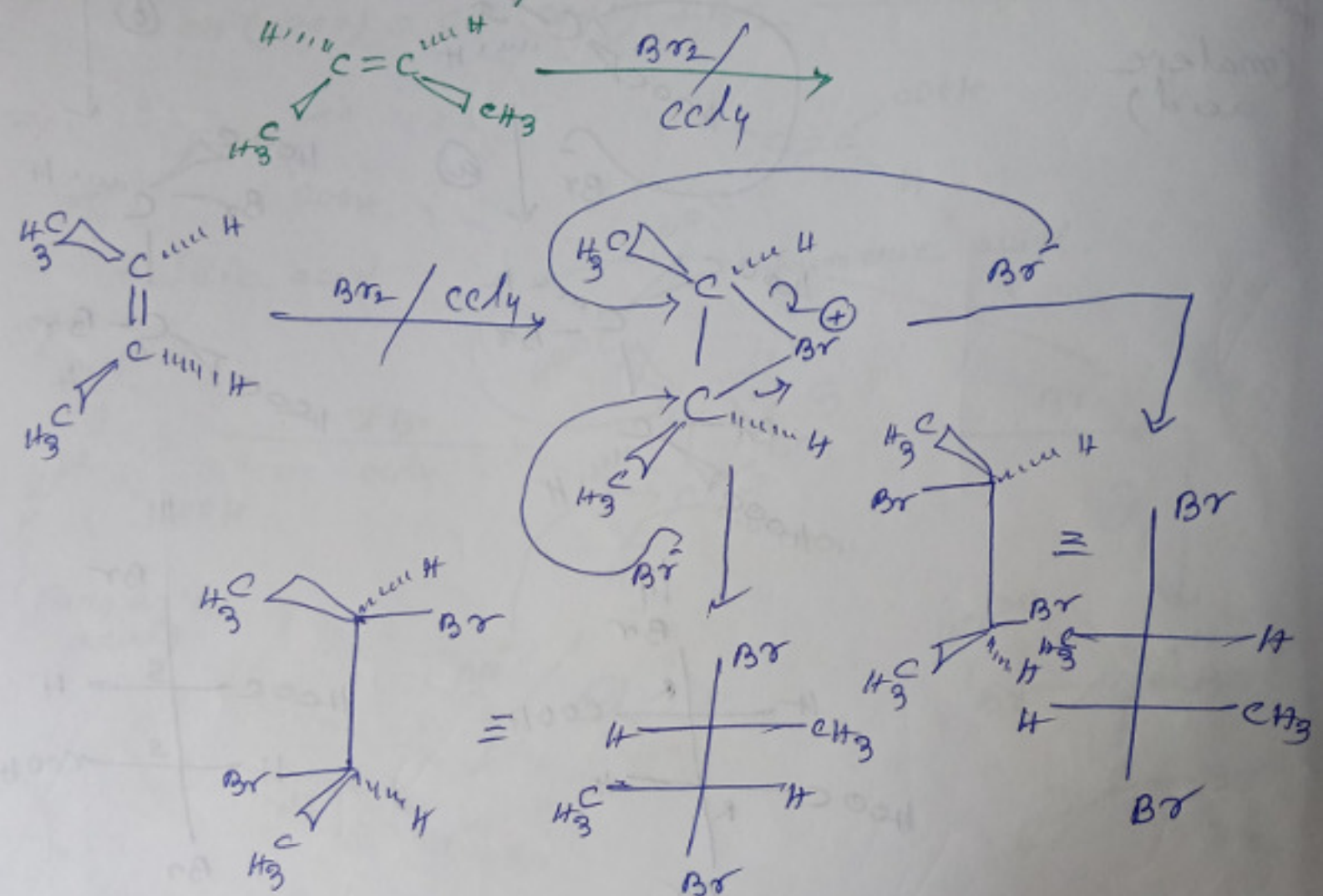


Trans form of the compound reacts to bromine to form bridge head bromonium ion, then reacts to free bromide ion by either path a or path b to form meso product.

But in case of cis compound, it reacts to free bromide ion by path a and path b at equal rate

to give two enantiomeric mixture or equal amt
ie product is racemic mixture.

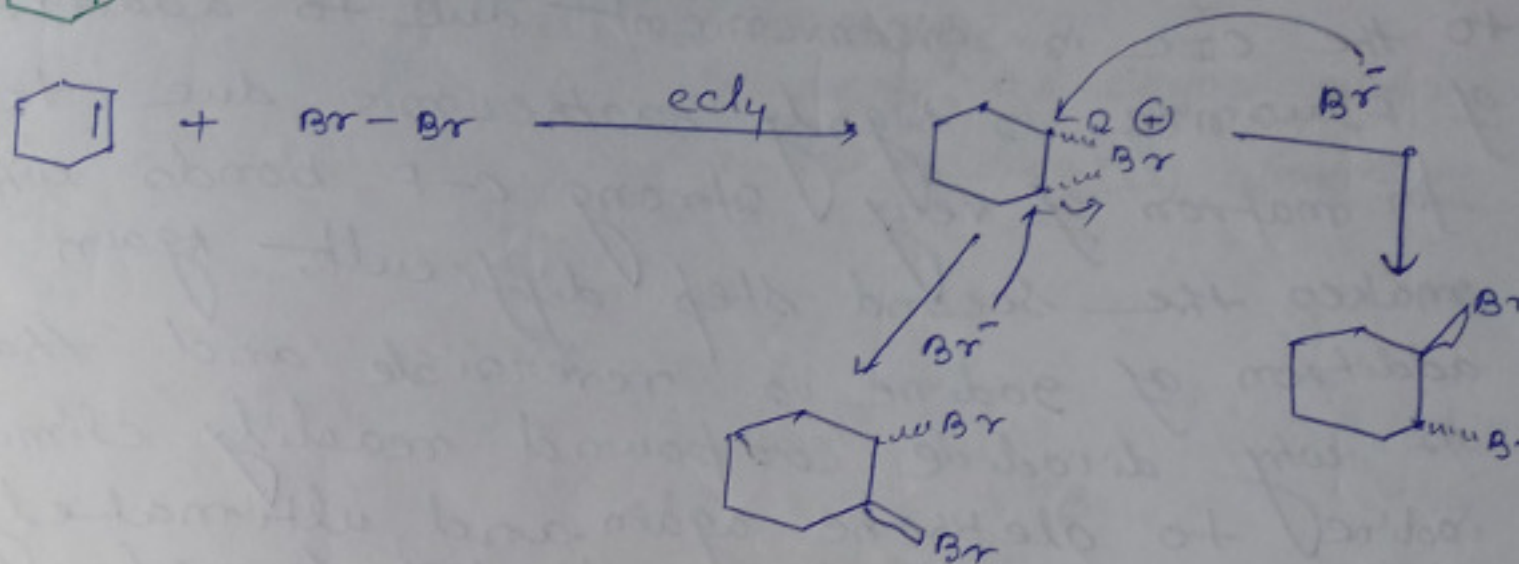
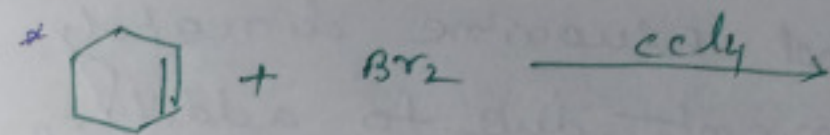
** Predict the product



(Enantiomeric mixture)

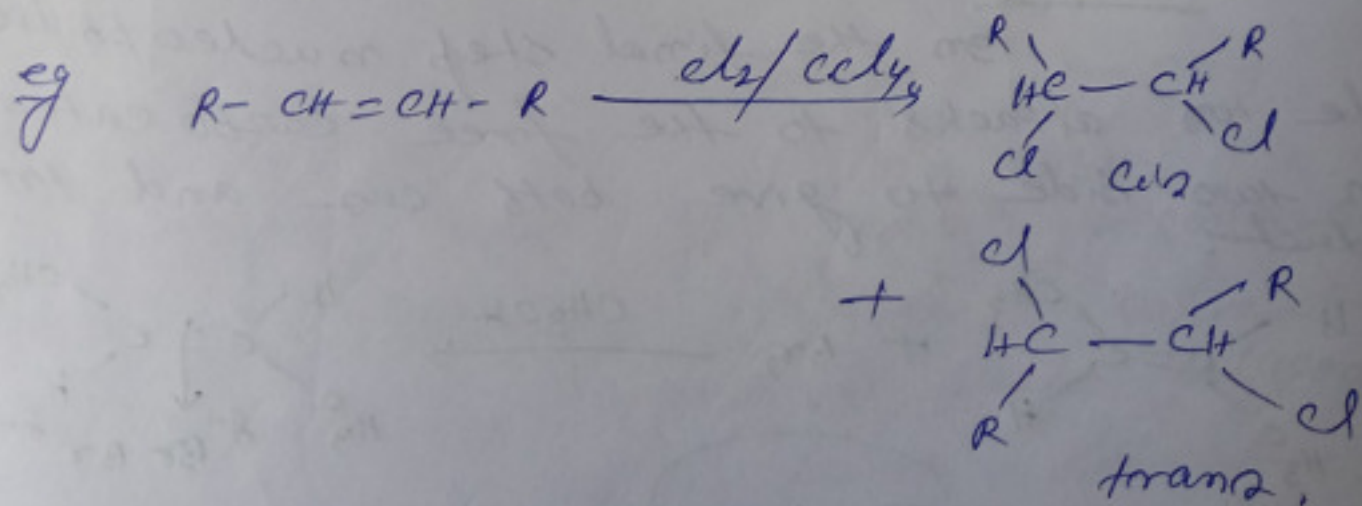
(Racemic product)

1st step bromonium is formed and then
in next step free bromide ion reacts
to the bromonium ion to form enantiomeric
products.



chlorine addition:-

unlike bromination, chlorination is stereoselective in nonpolar solvent because so called bridged chloronium ion is less stable than cyclic bromonium ion. Its lower stability is due to more electronegative and less polarisability. For this reason chlorination in non polar solvent takes place through free carbocation formation and gives a mixture of cis and trans dichloro derivatives.



Addition of iodine and Fluorine directly to the $C=C$ is inconvenient due to addition of Fluorine is highly exothermic due to formation of very strong $C-F$ bonds which makes the second step difficult. again addition of iodine is reversible and that is why diiodide compound readily eliminates iodine to olefine again and ultimately no addition product will be formed.

Halogenation of alkene in polar solvent:-

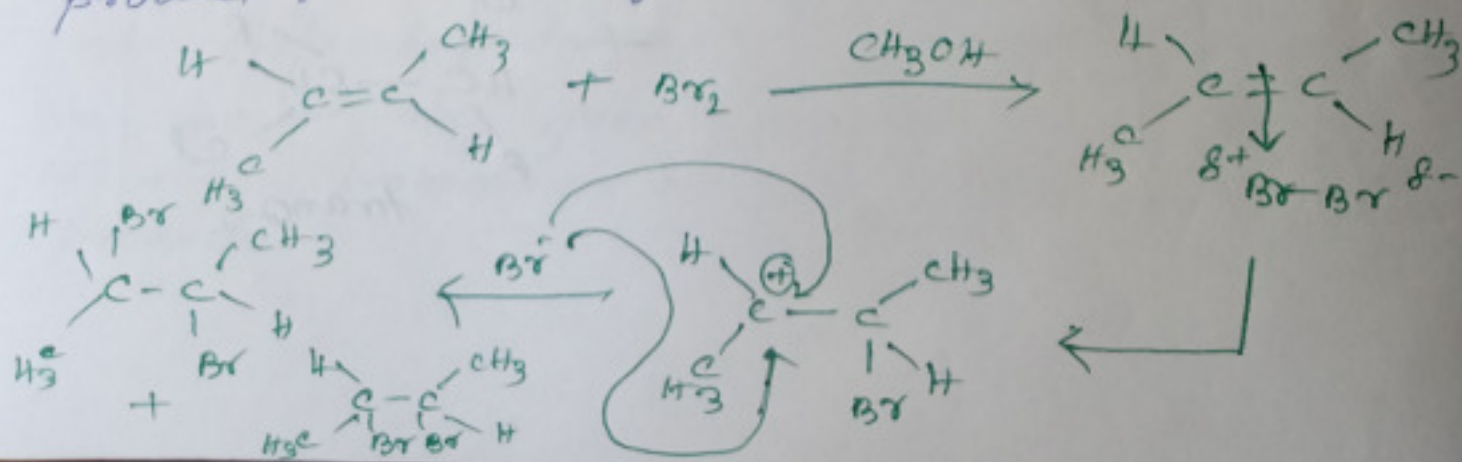
Halogenation of alkene in polar solvent gives both cis and trans addition products, these two products can be explained by the following two step mechanism.

Step-I

on the initial step by the influence of halogen alkene gives probably a free carbocation

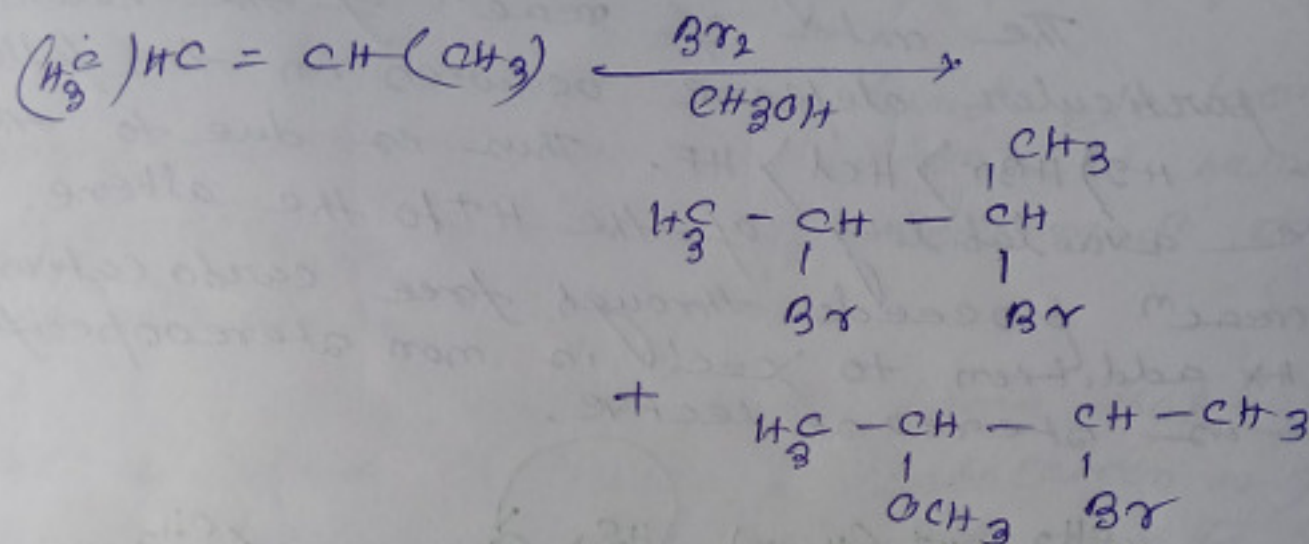
Step-II

on the final step nucleophilic halide ion attacks to the free carbocation from two side to give both cis and trans product.

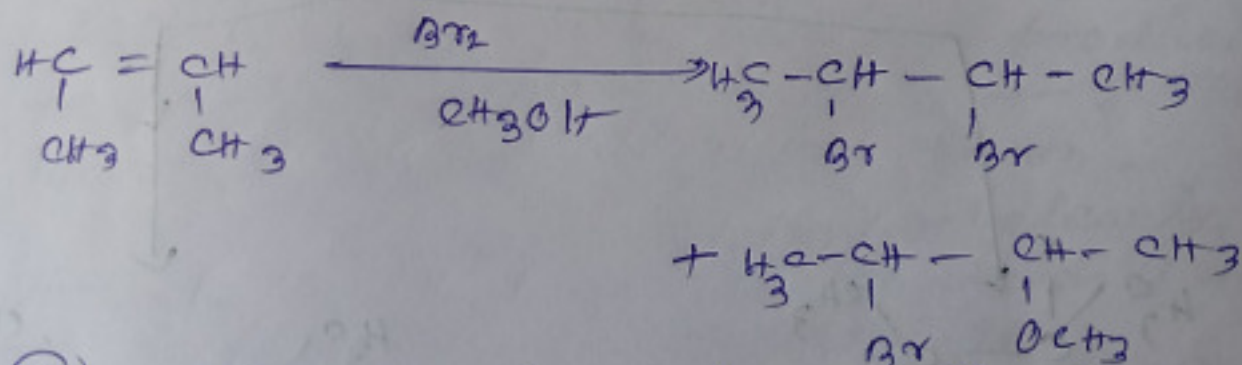


evidence in favour of carbocation intermediate formation in polar solvent.

① Alkene ^{on reaction with} halogen in presence of CH_3OH gives both dihaloalkane and halomethoxy alkane.



Again on reaction with halogen in presence of aqueous sodium nitrate gives both dihaloalkane and nitro haloalkane.



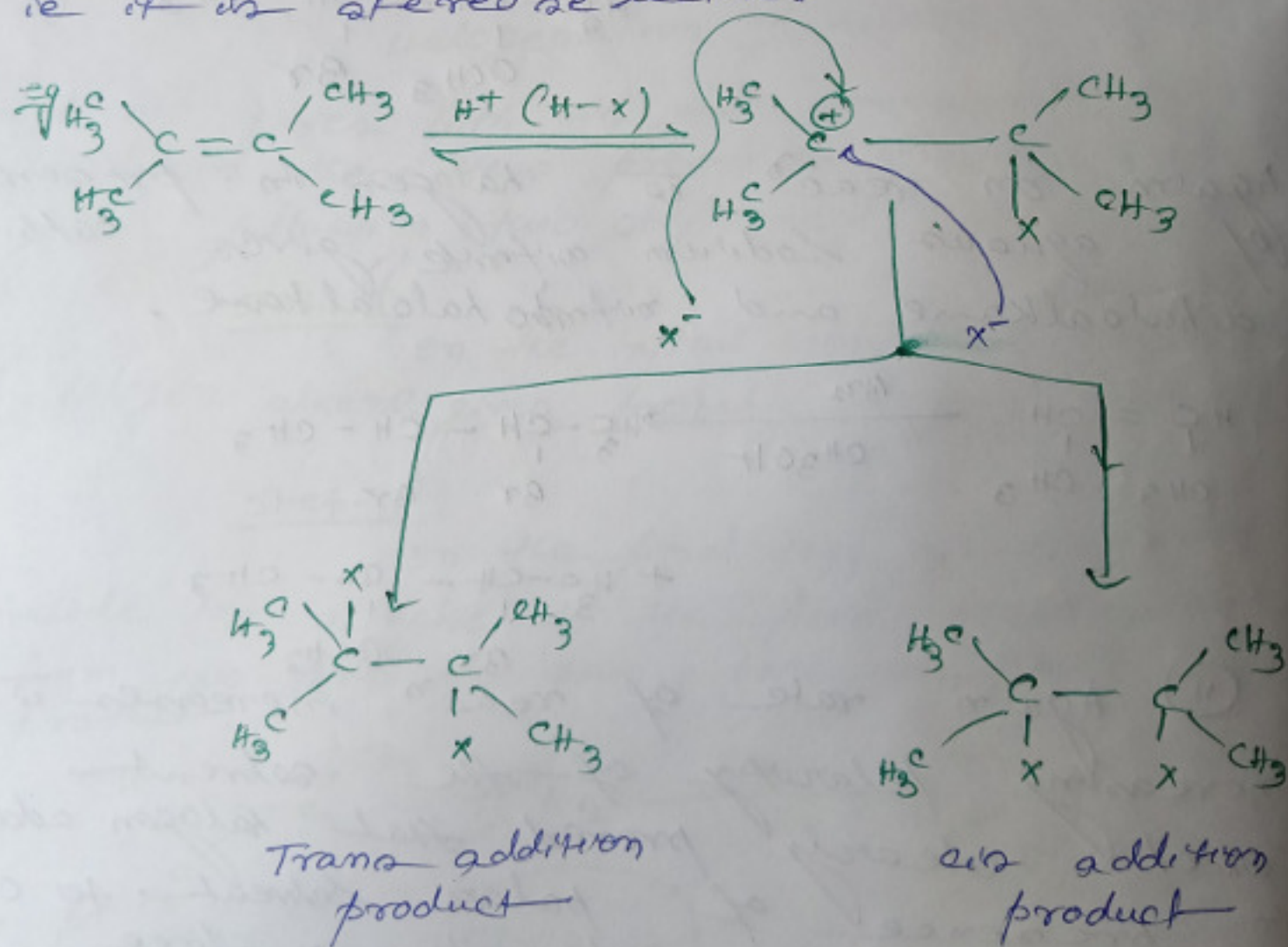
② Again rate of reaction increases with increasing polarity of the solvent which clearly proved that halogen addition in presence of polar solvent to carbon multiple bond proceeds through free carbocation intermediate.

H-X addition to $\text{C}=\text{C}$:-

H-X addition to an alkene is usually carried out in acetic acid or in other polar solvent like CH_2Cl_2 but not in water, because in aqueous medium hydration of alkene is the major product.

The rate of reaction of the haloacid for a particular alkene occurs in the following order - $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$. This is due to the relative availability of the H^+ to the alkene.

This reaction proceeds through free carbocation hence HX addition to $\text{C}=\text{C}$ is non stereospecific i.e. it is stereoselective.



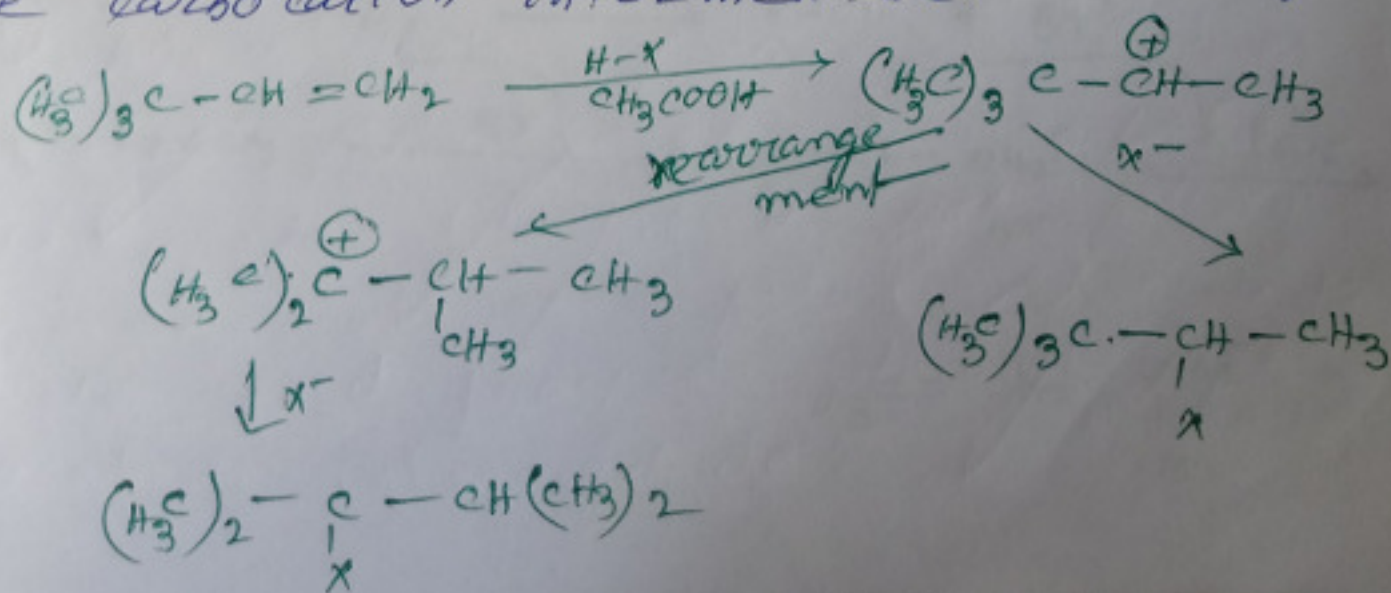
evidence in favour of carbocation intermediate in H-X addition to $>C=C<$.
 electron ^{with drawing} group retards the H-X addition if they attached to $C=C$ and that is why tetra chloro ethylene does not react w/ H-X due to extreme unstability of the carbocation involved.

on the other hand electron releasing group favours the H-X addition and hence this $(H_3C)_2C=CH_2$ shows a faster reaction w/ H-X than $H_2=CH_2$.

The above facts prove that during H-X addition probably a carbocation is formed. A suitable substrate adds to H-X w/ rearrangement along w/ normal fashion.

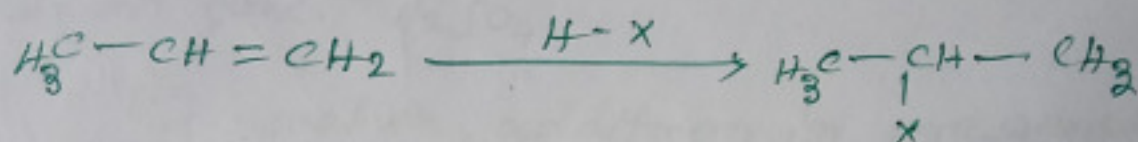
eg $(H_3C)_3C-CH=CH_2$ does not add to H-X w/ normal fashion that means it does not give only $(H_3C)_3C-CH_2-CH_3$ but $(CH_3)_2-C-CH_2-CH_3$ is also obtained as a major product due to rearrangement of incipient 2° carbocation to more stable 3° carbocation.

This observation clearly proved that H-X addition to $C=C$ proceeds through free carbocation intermediate.

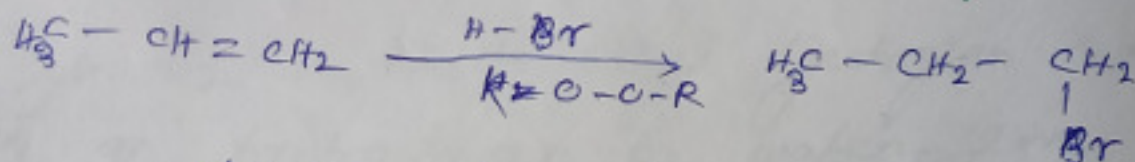


Merkonikoff's rule! -

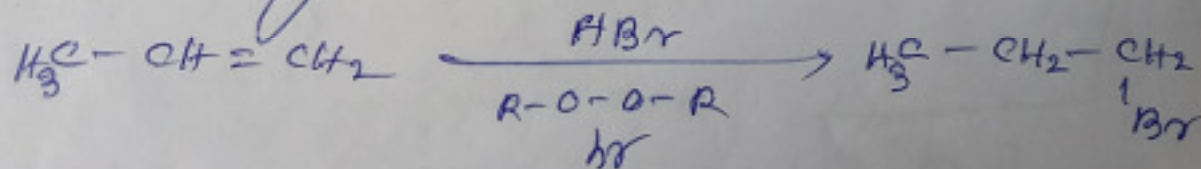
The Org part of addendum (H-X) addition to the carbon atom of unsymmetrical alkene is joined to the ^{carbon to} least no of H atom, i.e. more substituted end of $C=C$. This rule is totally empirical but may be explained theoretically on the basis of the stability of carbocation involved.



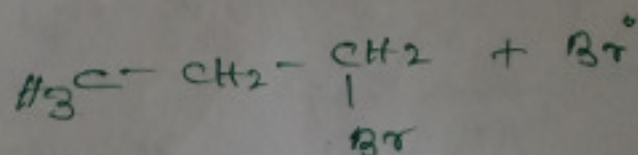
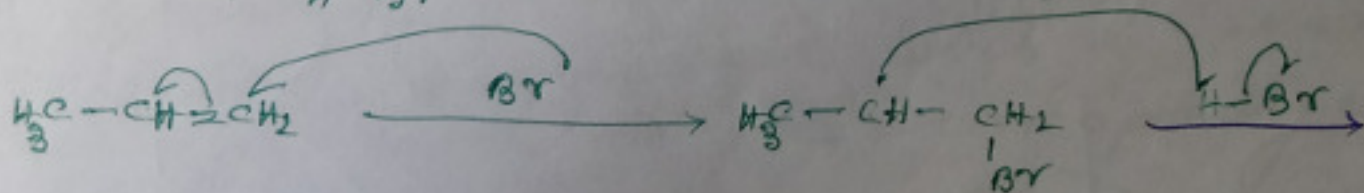
Addition of H-X in presence of organic peroxide



Addition of HCl or Hg in presence of peroxide occurs according to Markonikoff's rule but in case of HBr, it occurs opposite type of reaction through free radical mechanism.



mech^m:



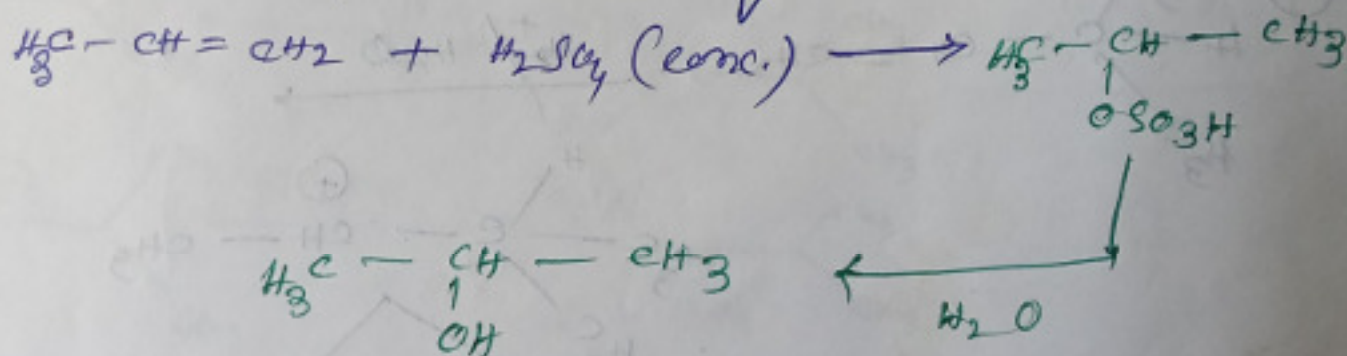
on case of HCl , formation of $\text{Cl}^\cdot$ is not thermodynamically favourable (as $\text{H}-\text{Cl}$ bond is stronger than that $\text{H}-\text{Br}$). And in case of H_2 , $2^\cdot$ is readily obtained but it immediately combined with another $2^\cdot$ to form H_2 . Hence $2^\cdot$ free radical is not ~~formed~~ available of this type of reacⁿ.

Water addition to >C=C< :-

Due to lower reactivity of alkene and alkyne, water does not add to alkene or alkyne normally. For addition of water, a catalyst is required like H_2SO_4 , Hg^{2+} . Addition of water to an alkene occurs in accordance to Markovnikov's rule in presence of dil or conc. H_2SO_4 .

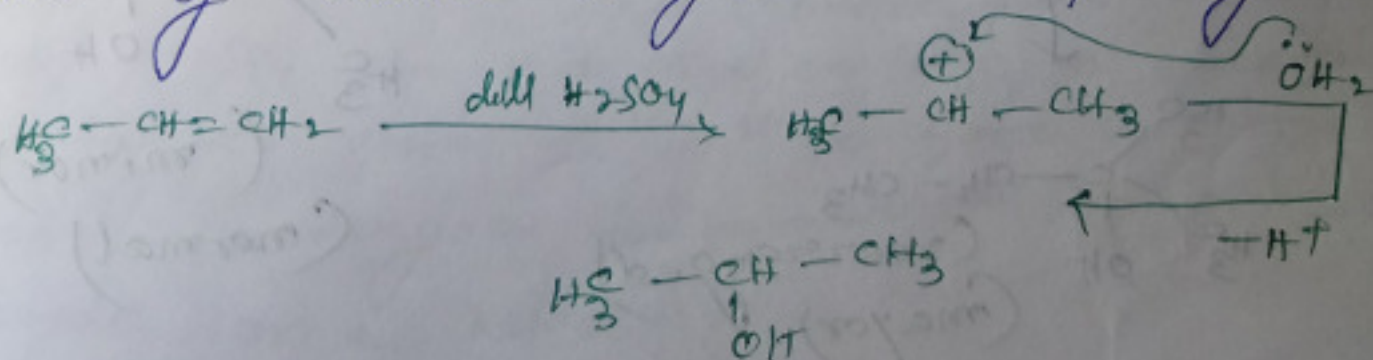
(i) water addition in presence of conc. H_2SO_4 :-

Alkene on treatment with conc. H_2SO_4 forms initially alkyl hydrogen sulphate which on hydrolysis by water gives Markovnikov's alcohol predominantly.

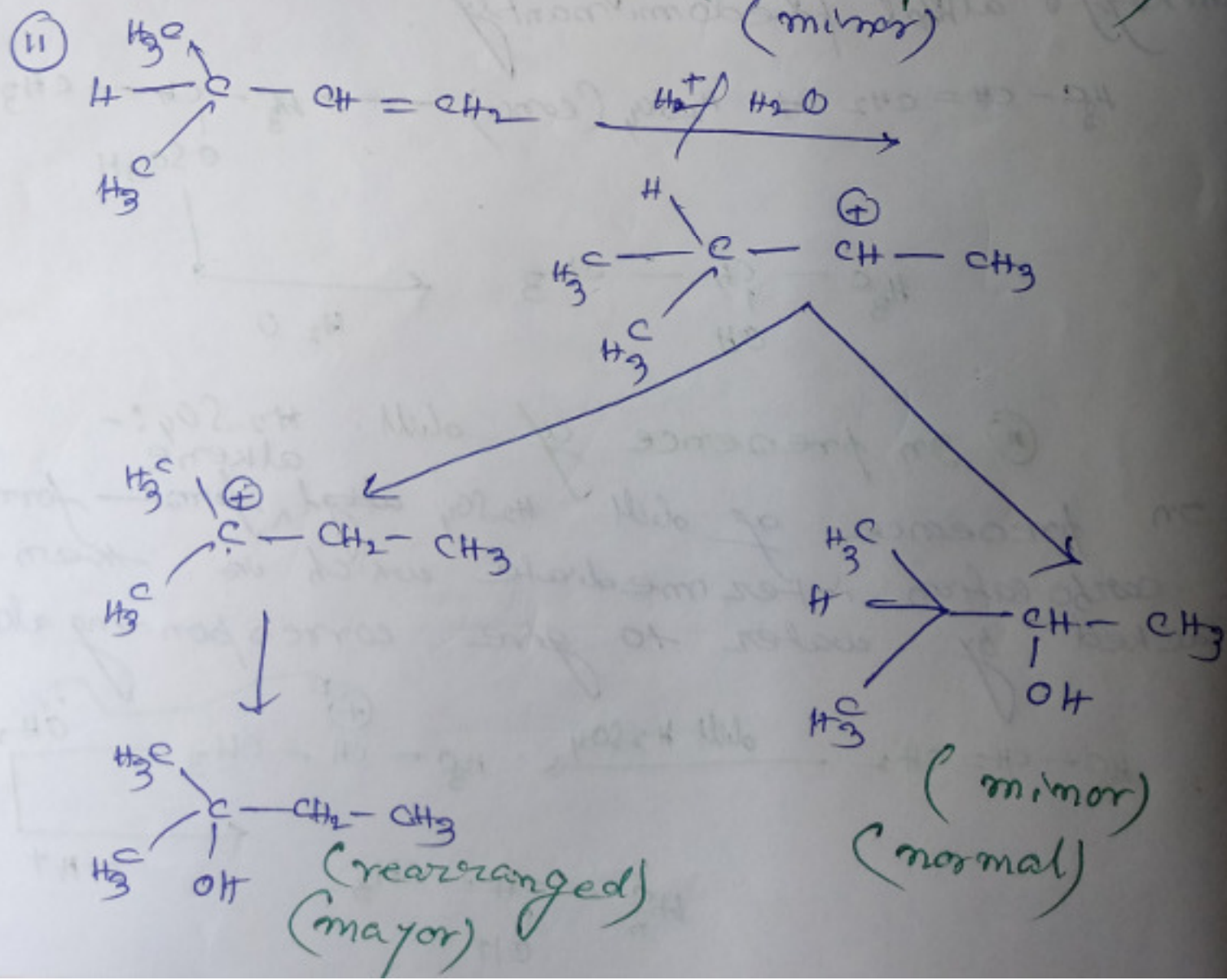
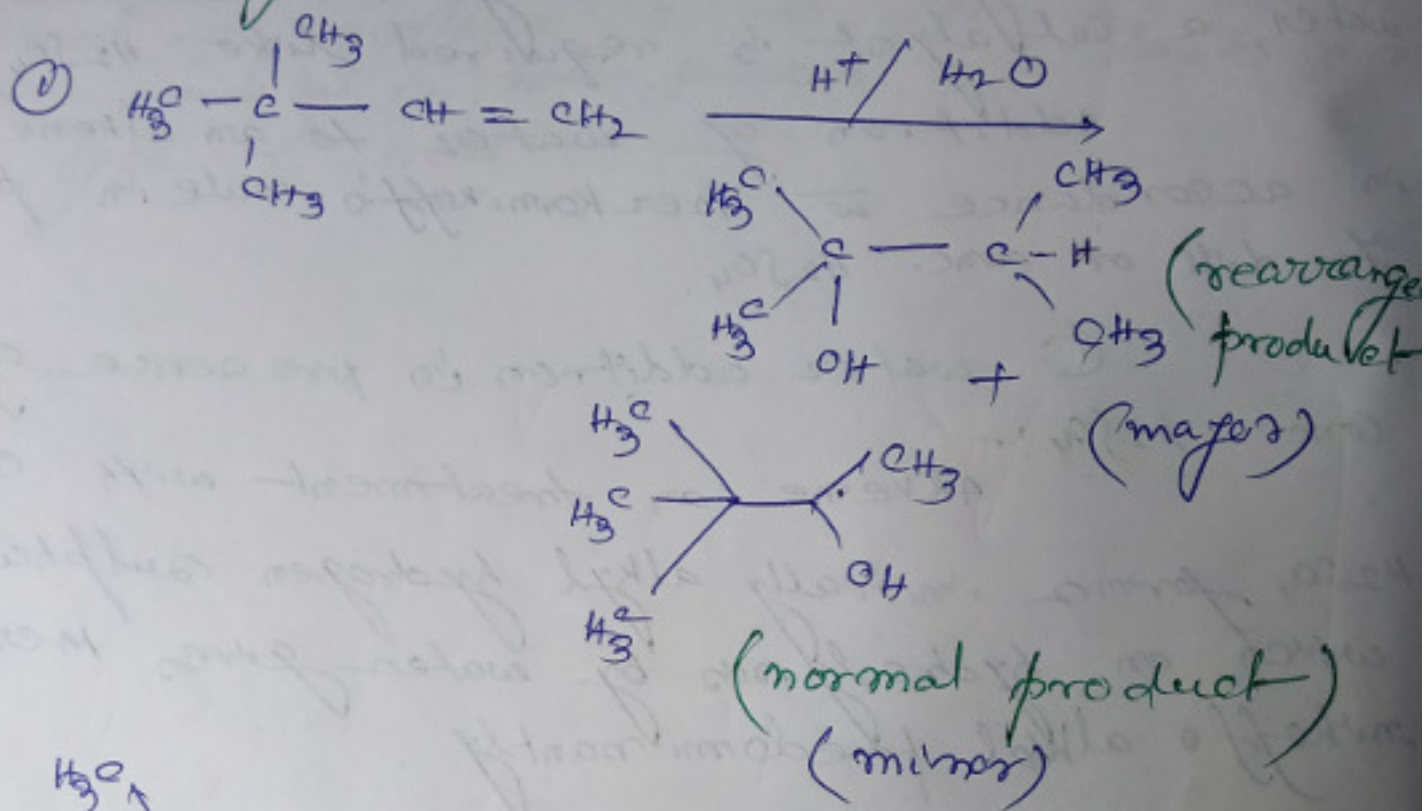


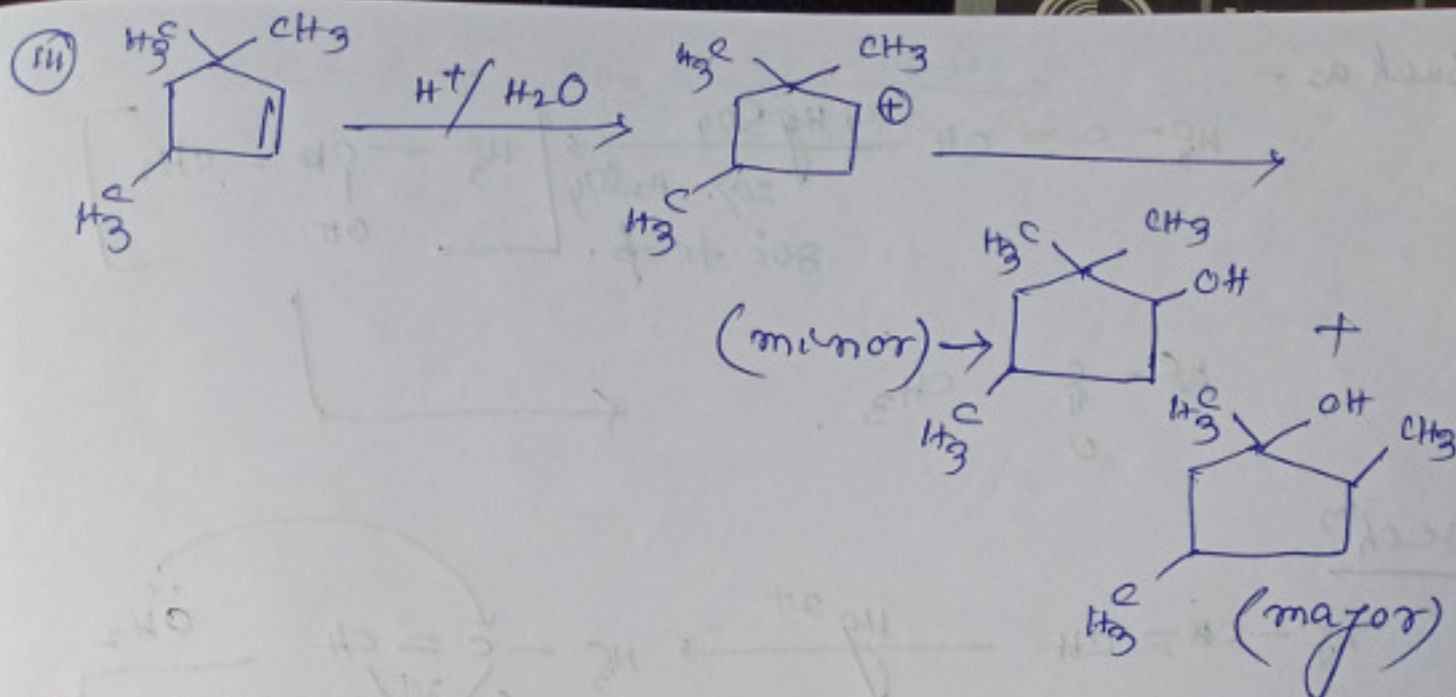
(ii) in presence of dil. H_2SO_4 :-

on presence of dil H_2SO_4 alkene forms a carbocation intermediate which is then attacked by water to give corresponding alcohol.

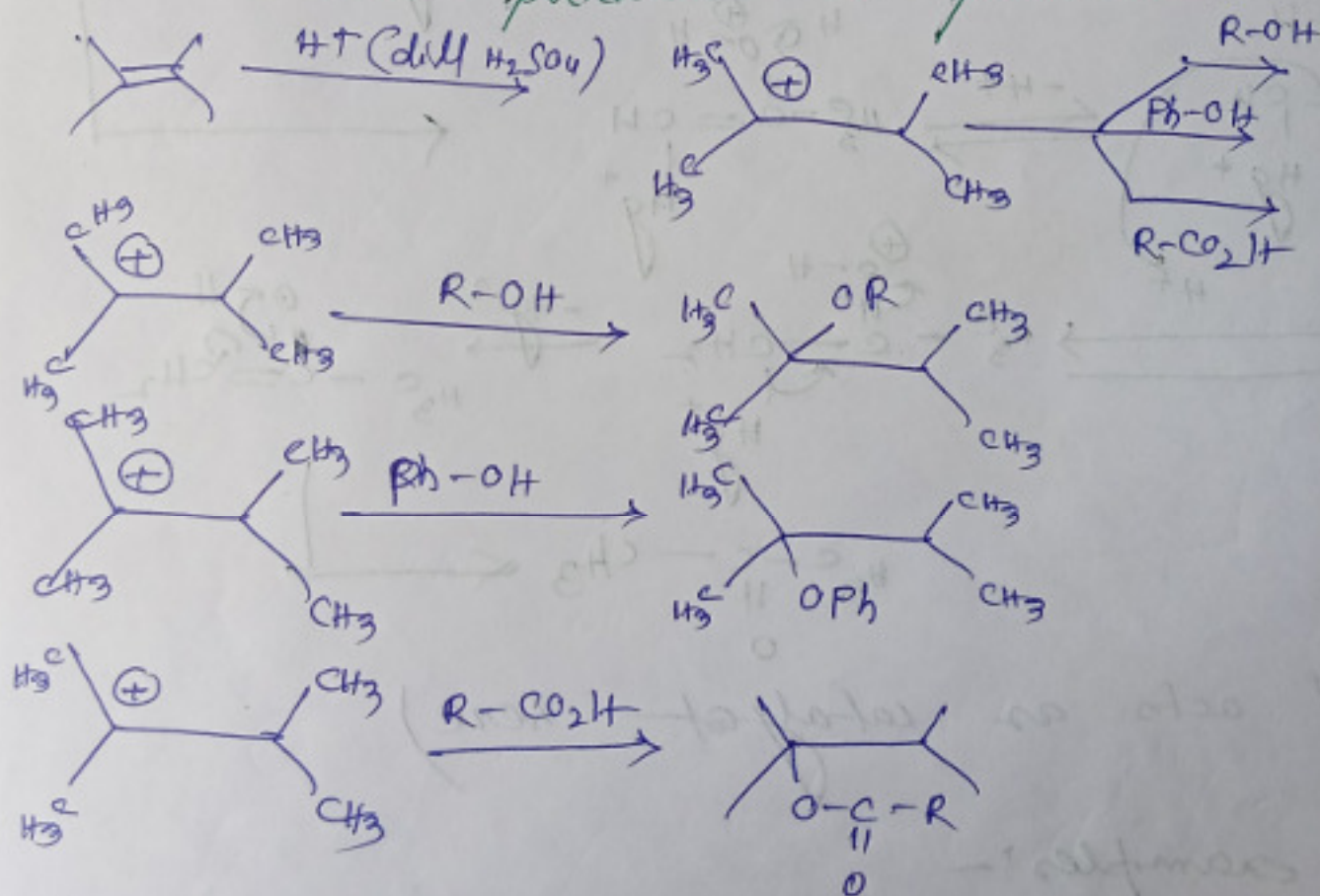


NOTE Addition of water to an alkene may undergo rearrangement to isomeric alcohol through rearrangement shown below.



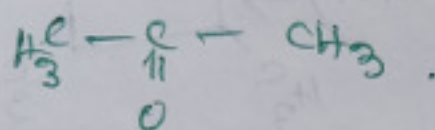


Predict the product to probable mechanism:-



Addition of water to $-C \equiv C-$:-

water adds to alkyne in 20% H_2SO_4 at $80^\circ C$ temperature in presence of catalytic amt of Hg^{2+} to form an enol which undergoes tautomerism to give aldehyde or a ketone.

$$\text{H}_3\text{C}-\text{C}\equiv\text{CH} \xrightarrow[\substack{20\% \text{ H}_2\text{SO}_4 \\ 80^\circ\text{C temp.}}]{\text{aq HgSO}_4} \left[\text{H}_3\text{C}-\underset{\substack{| \\ \text{OH}}}{\text{C}}=\text{CH}_2 \right]$$


mech^{on}

$$\text{H}_3\text{C}-\text{CH}=\text{CH} \xrightarrow{\text{Hg}^{2+}} \text{H}_3\text{C}-\text{C}(\text{Hg}^+)=\text{CH}-\text{OH}_2^+$$

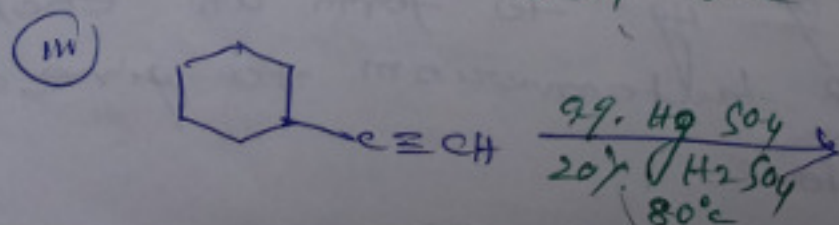
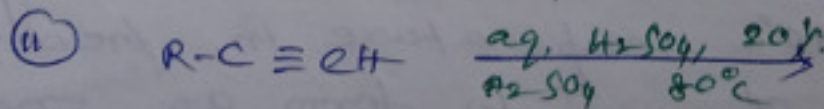
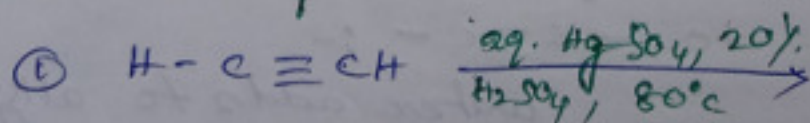
$$\text{H}_3\text{C}-\text{C}(\text{Hg}^+)=\text{CH}-\text{OH}_2^+ \xrightarrow{-\text{H}^+} \text{H}_3\text{C}-\text{C}(\text{Hg}^+)=\text{CH}-\text{OH}^+$$

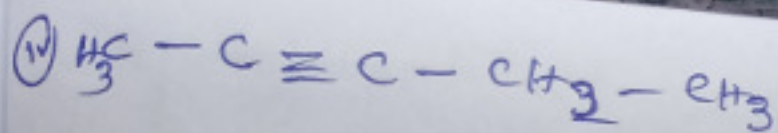
$$\text{H}_3\text{C}-\text{C}(\text{Hg}^+)=\text{CH}-\text{OH}^+ \xrightarrow{-\text{Hg}^{2+}} \text{H}_3\text{C}-\text{C}(\text{OH})=\text{CH}_2$$

$$\text{H}_3\text{C}-\text{C}(\text{OH})=\text{CH}_2 \xrightarrow{\text{H}^+} \text{H}_3\text{C}-\text{C}(\text{OH})-\text{CH}_3$$

(Hg^{2+} acts as catalyst here)

some examples! -





aq. HgSO_4
20% H_2SO_4 , 80°C

Hydrogenation:-

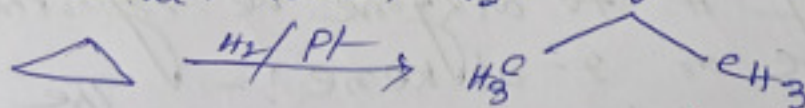
Hydrogenation of alkenes or alkynes requires very high temperature. commonly used catalysts for hydrogenation are finely divided Pt, Ni, Pd, Raney Ni and Ru, Rh.

Catalytic hydrogenation is sometimes called **heterogeneous catalyst reaction** because it involves different types of phases like solid (cat), gas (H_2 and substrate) and liq. (solvent and substrate).

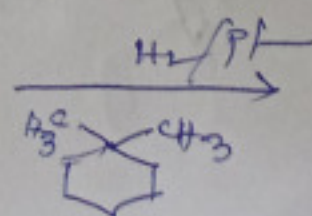
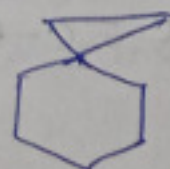
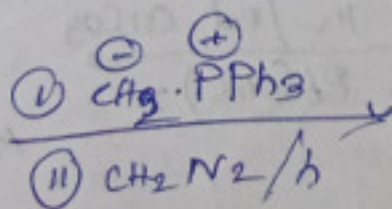
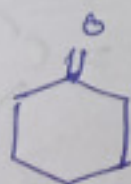
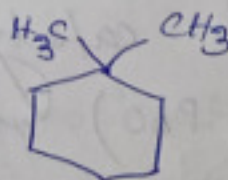
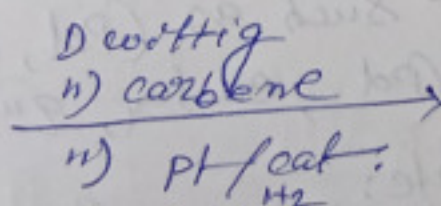
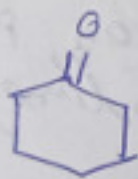
The catalytic hydrogenation is syn addition process as the H atoms add from the same side of $C-C$ multiple bond. But due to stepwise addition, very small percentage may be trans addition product.

Hydrogenation of alkane:-

Cycloalkanes which have strain in ring, can be reduced catalytically by the cleavage of $C-C$ bond. Such as-



Provide specific reagents for the following reaction:-



reagent

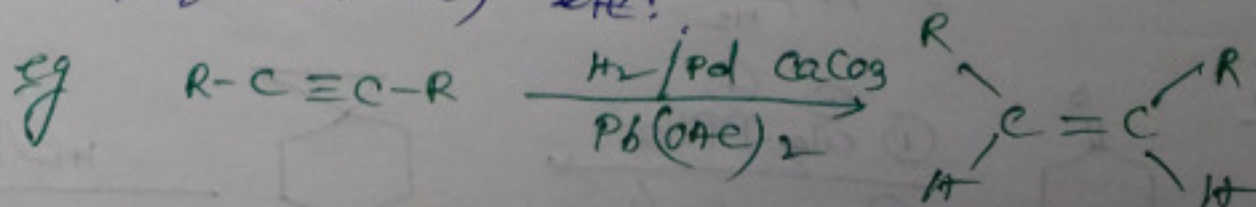
Hydrogenation of alkyne to alkene:-

Since alkynes have more labile π electrons than alkenes π electron, for this reason hydrogenation of alkyne is more faster and more exothermic than the catalytic hydrogenation of alkene.

Depending upon the condition and the catalyst involved, one or two molar equivalent of H will be added to a $C \equiv C$ bond, when a Pt ($Pd/M/Ru/Rh$ etc) catalyst is used, the alkynes are generally react to two molar equivalent H to give alkane.

Hydrogenation of an alkyne to alkene can be done by using special catalyst or reagent. The hydrogenation of alkyne can not be stopped through alkene stage until the catalyst being poisoned by $BaSO_4$, CaO_2 , quinoline or by using Ni_2B / by Na or lithium in liq NH_3 or amine ($1^\circ/2^\circ$).

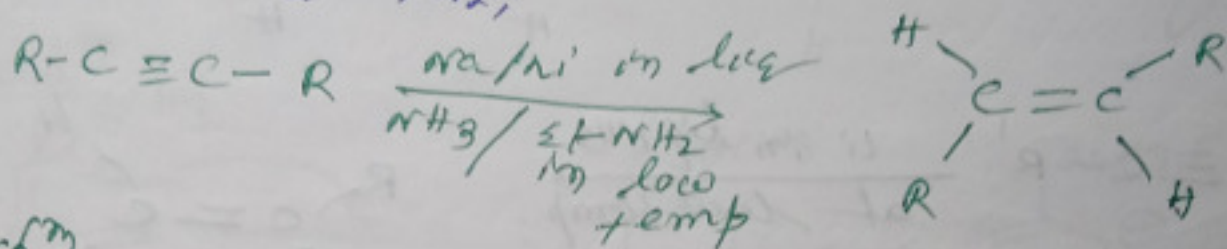
syn addition of H to alkyne i.e. synthesis of cis alkene or Z-alkene:- The catalysts which permit hydrogenation of an alkyne to Z-alkene (cis alkene) are Ni_2B (Brown's cat) and Lindler's catalyst such as ($Pd, CaO_2, Pb(OAc)_2$) or ($Pd, BaSO_4, quinoline$) or ($Pd, CaCO_3, quinoline$) etc:



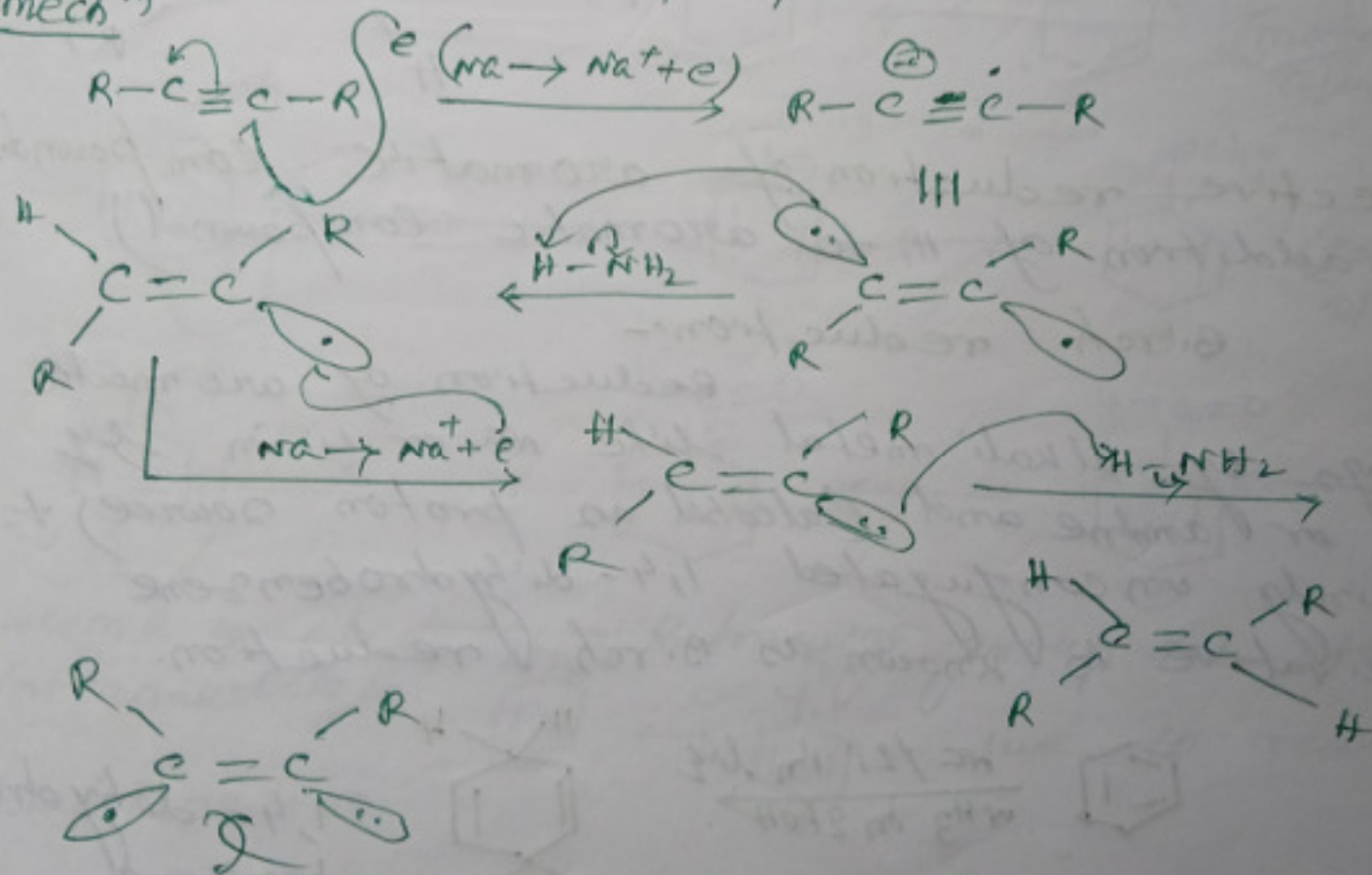
trans addition of C-C multiple bond:-

The trans addition of H to the triple bond occurs when alkynes are reduced by Li or Na in liq NH_3 or ethyl amine at low temp. This reduction is called dissolving metal reduction. By this reduction alkyne give trans or E alkene.

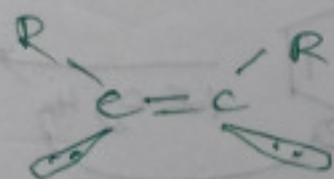
Such as,



mech^m

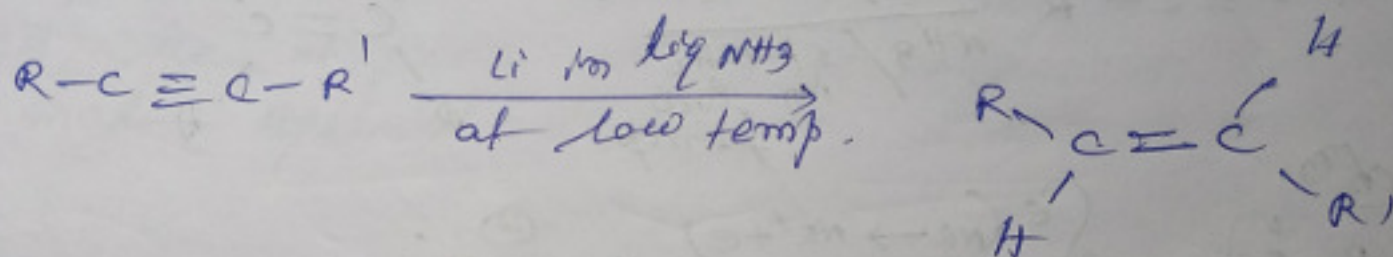
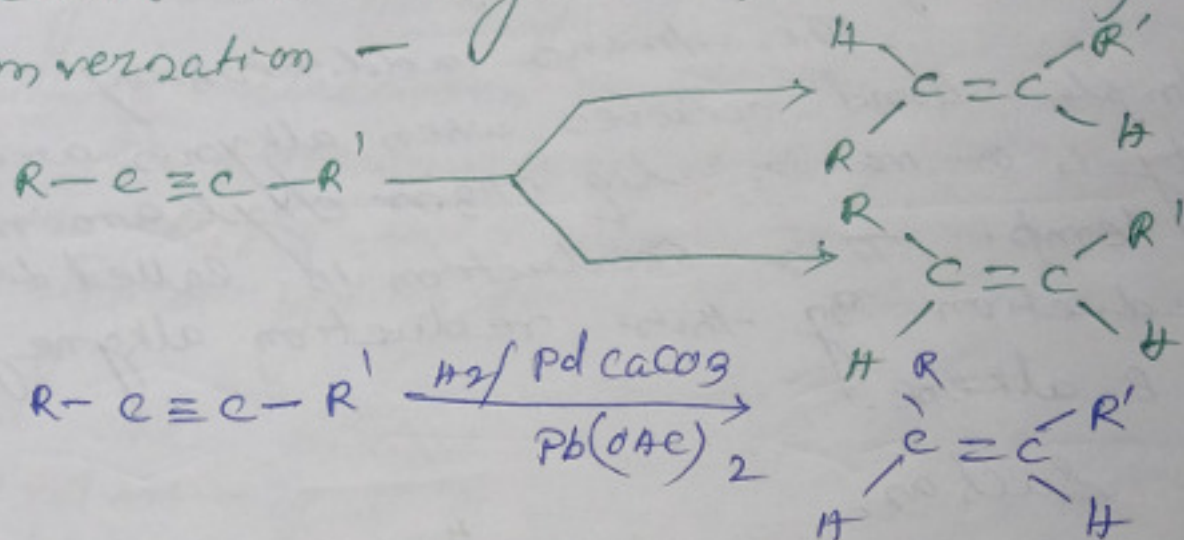


This is why cis product is not obtained



It is not possible as $\ominus$ ve charge in consecutive carbon atom is not possible.

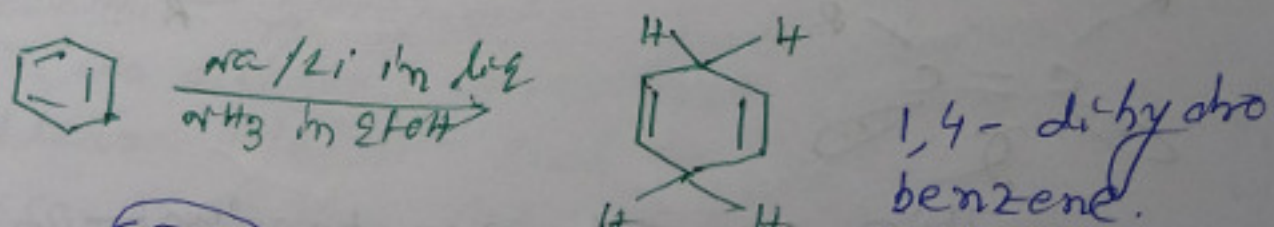
Predict the reagents for the following conversion -



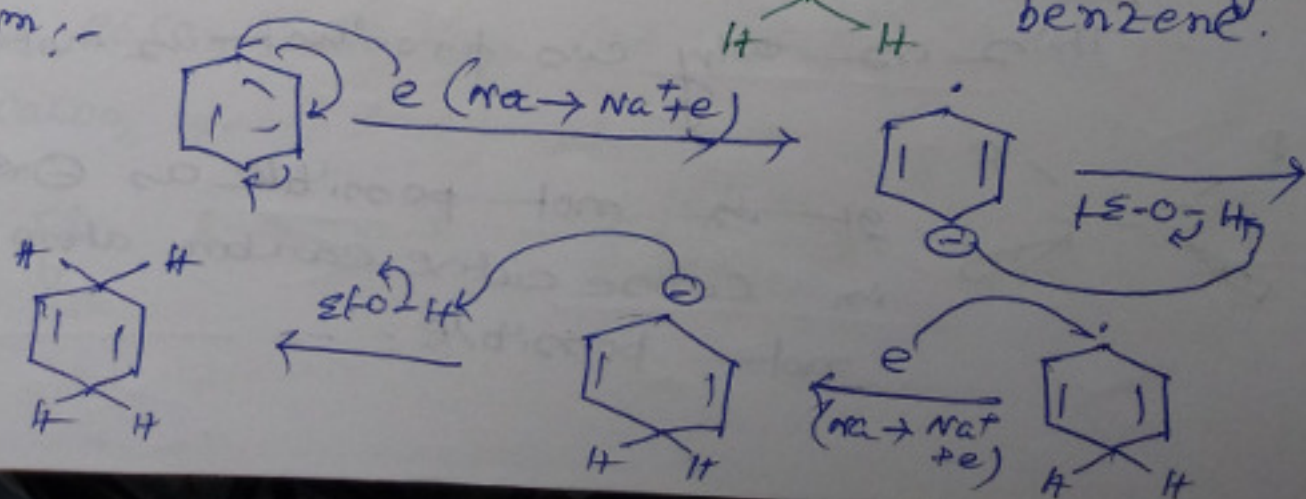
Selective reduction of aromatic compounds:
(1,4 addition of H to aromatic compound)

Birch reduction:-

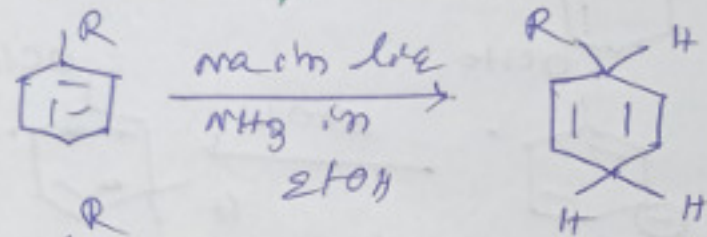
Reduction of aromatic rings by alkali metal like Na or Li in liq NH_3 or amine and (alcohol as proton source) to mainly unconjugated 1,4-dihydrobenzene derivative is known as Birch reduction.



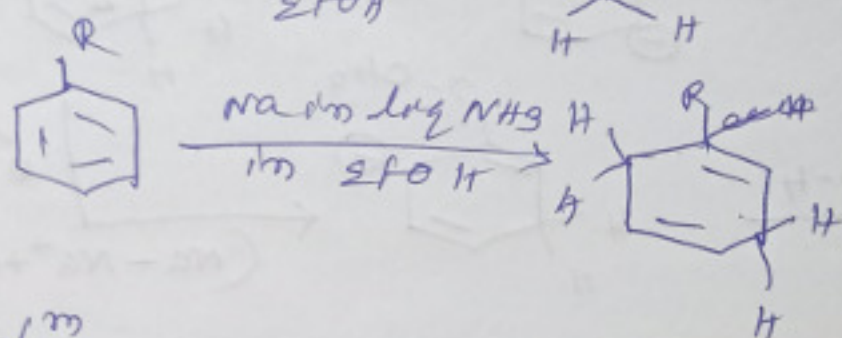
mech^m:-



selectivity of Birch reduction in substituted aromatic compounds:-

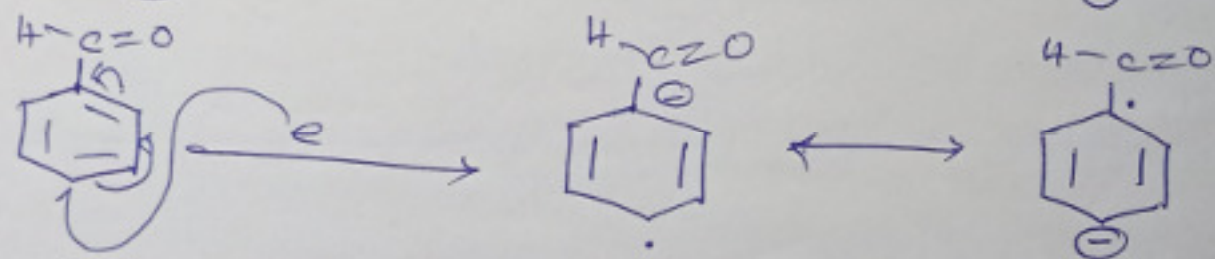
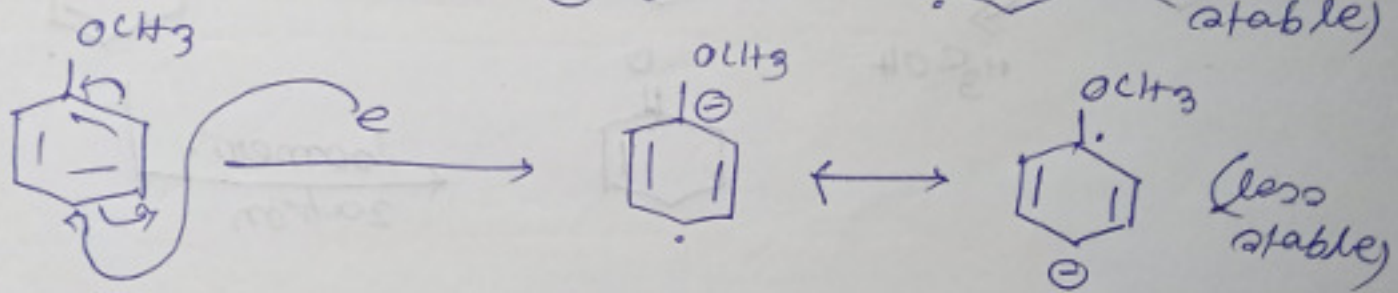
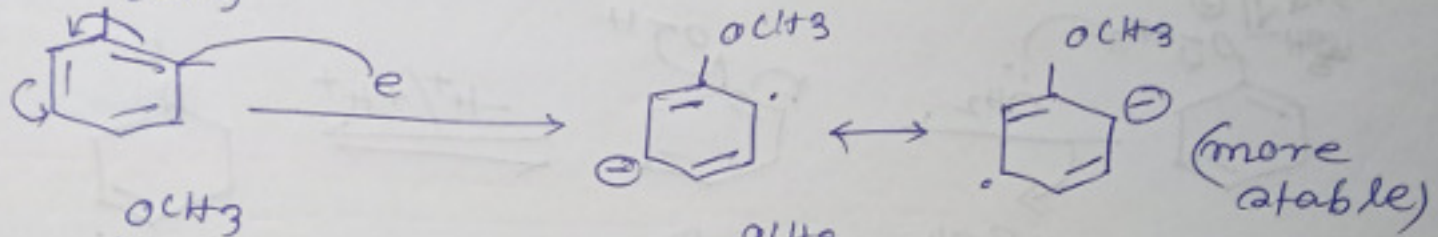


(when R is electron withdrawing group)



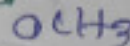
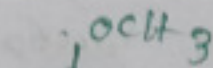
(when R is electron releasing group)

mechanism

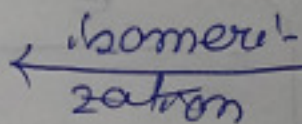
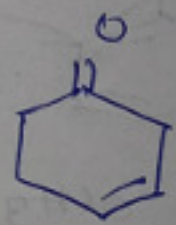
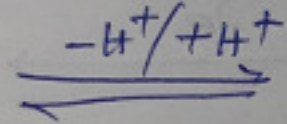
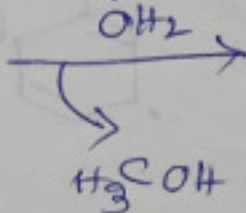
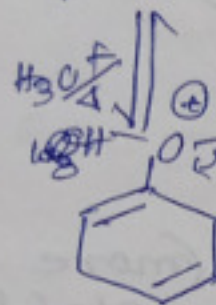
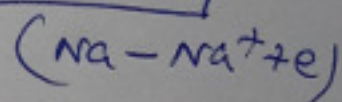
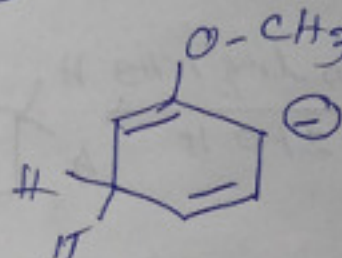
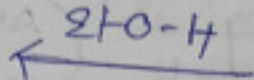
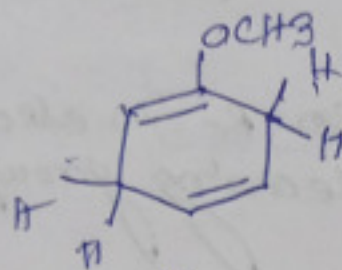
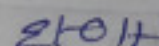
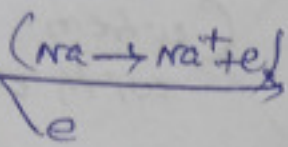
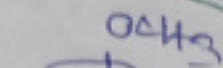


when R is electron withdrawing group the stable intermediate is due to resonance stabilization.

convert

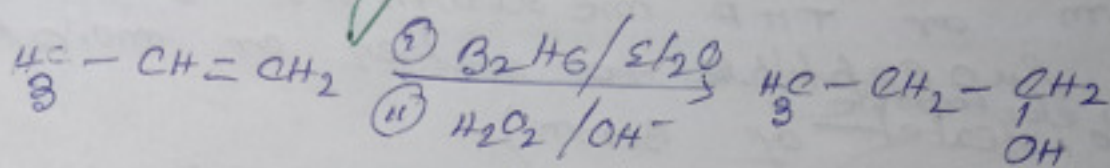


$\Rightarrow$



Hydroboration

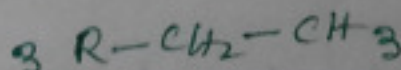
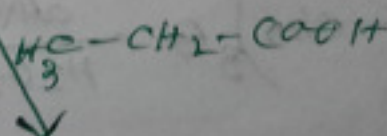
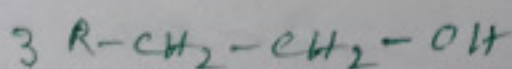
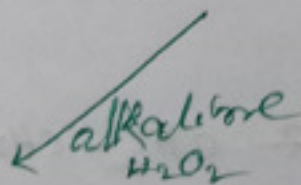
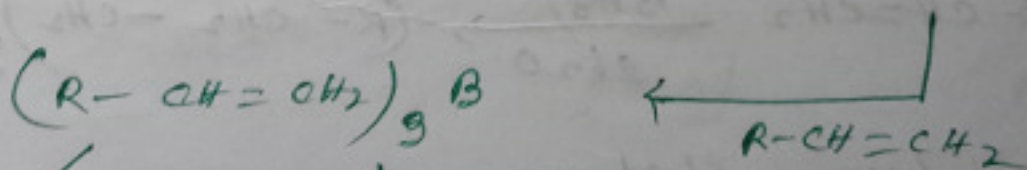
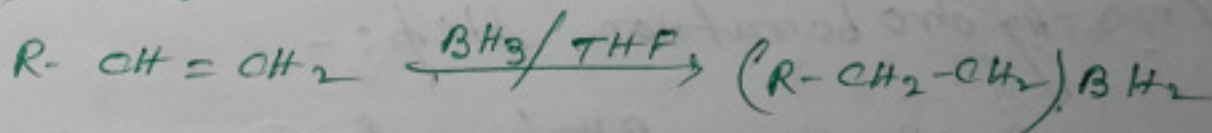
Hydroboration and hydroboration oxidation:-



Preparation of anti-Markovnikov's alcohol from alkene:-

Diborane is the composition of two BH_3 units, BH_3 is an electron deficient species due to the electronic sextet of borane and while, basically it involves the addition of BH_3 to $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$ triple bond to form alkyl or alkenyl borane, which on undergoes oxidation to give alcohol and enol respectively or alkyl borane on protonolysis by carboxylic acid gives alkane.

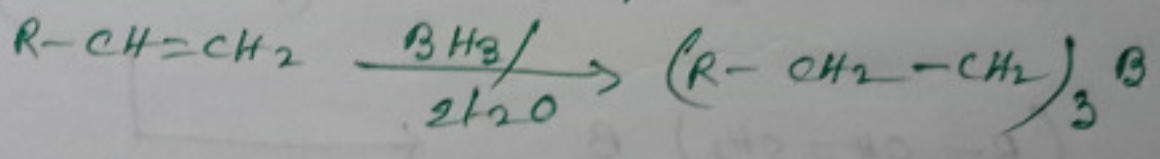
Such as.



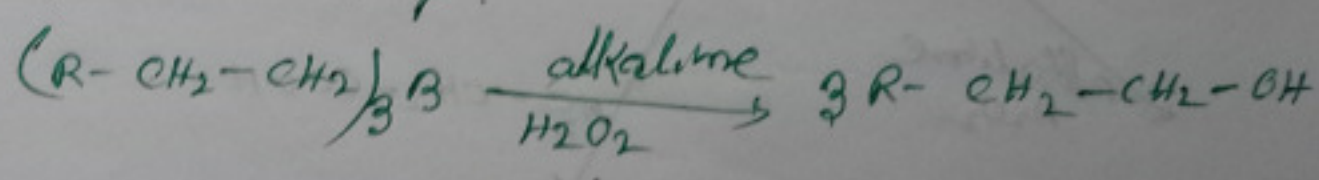
The addition of BH_3 is stereospecifically cis and occurs from less hindered site of the double bond, the reaction is carried out in ether medium or THF medium as BH_3 is very much susceptible to water or moisture (due to ^{electrophilic} ~~seal~~ of Boron).

A concerted mechanism proposed as follows in which Boron attached to less hindered site or less substituted end of C-C multiple bond along to simultaneous transfer of hydride (H^-) ion to the more substituted end of C-C multiple bond through cyclic transition state to form mono alkyl borane which undergoes ^{same} reaction to two another molecules of alkene to form trialkyl borane. Thus trialkyl borane then on oxidation by alkaline H_2O_2 (which is known as hydroboration oxidation reaction) to form anti-Markovnikov's alcohol.

i) Hydroboration Step:-

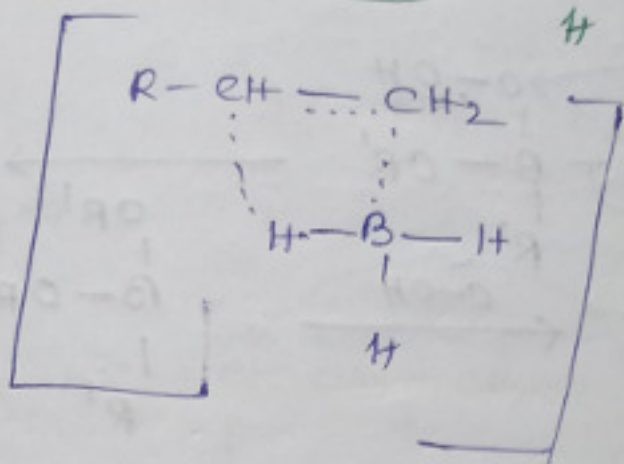
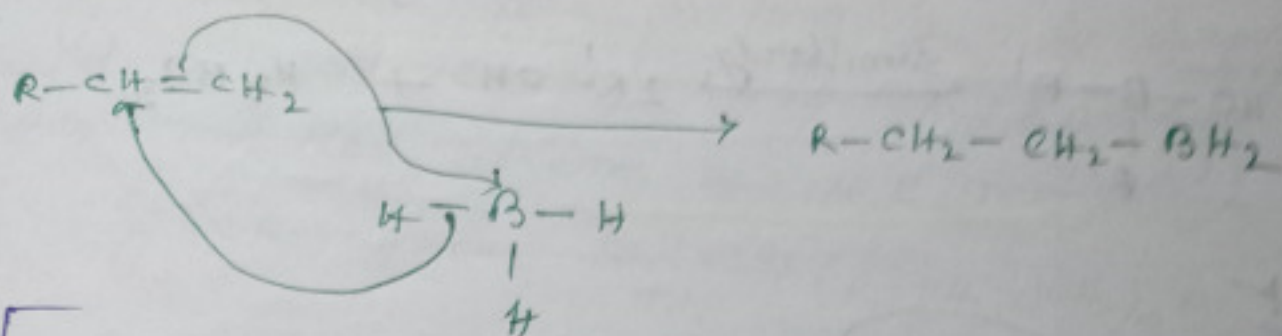


ii) oxidation Step:-

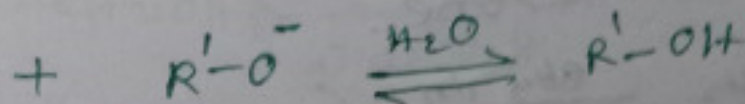
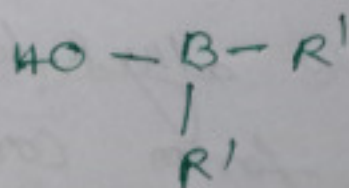
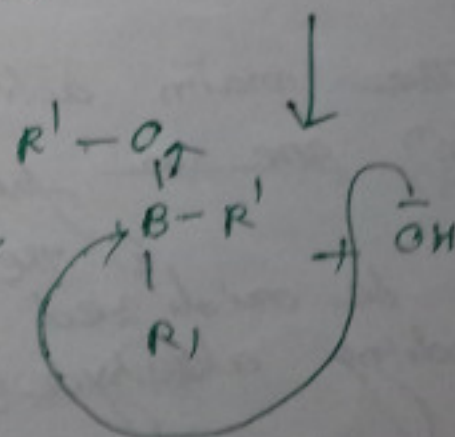
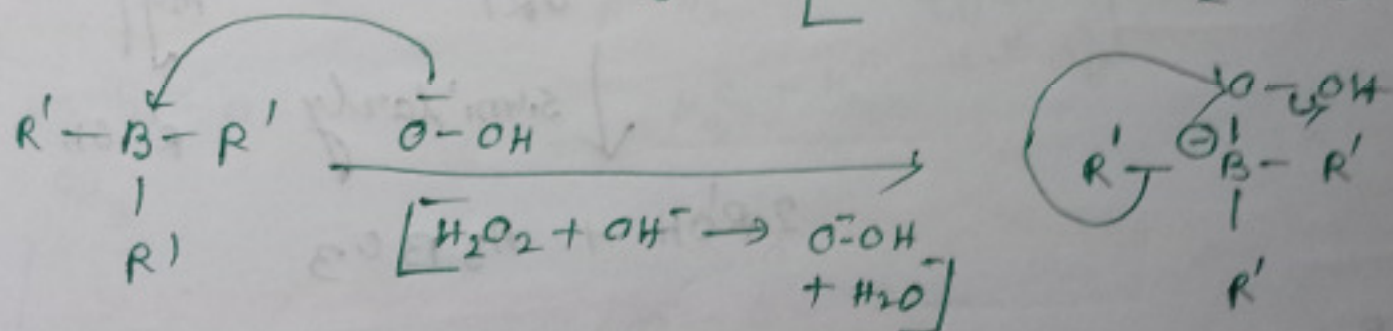
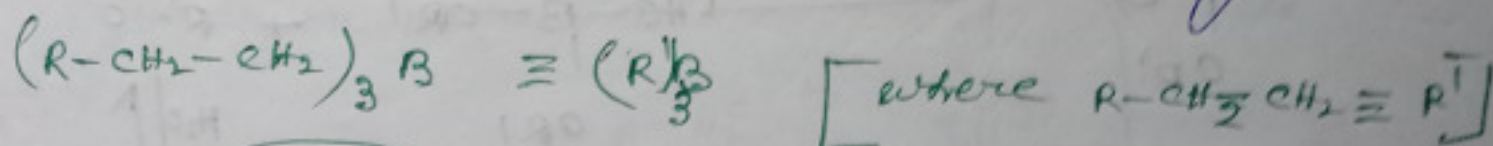
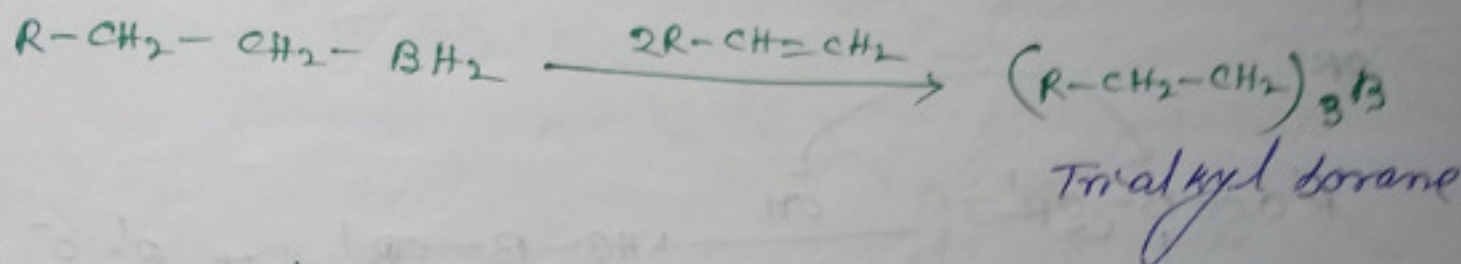


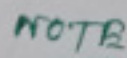
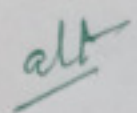
Hydroboration oxidation reaction.

mech^m

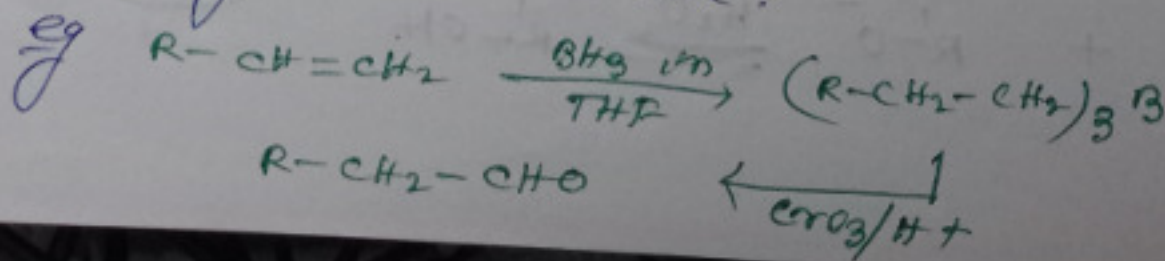


cyclic transition state.

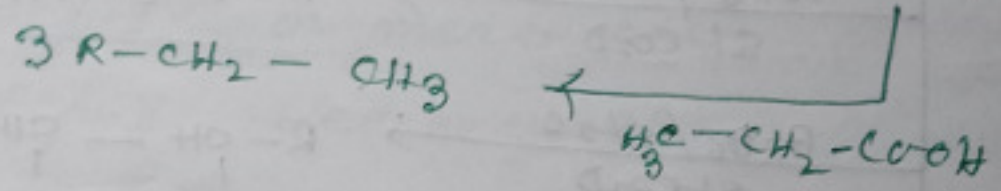
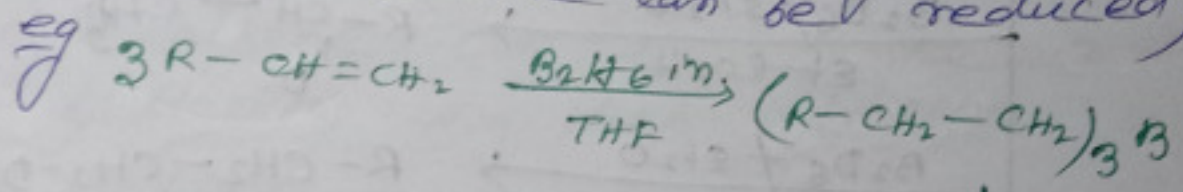




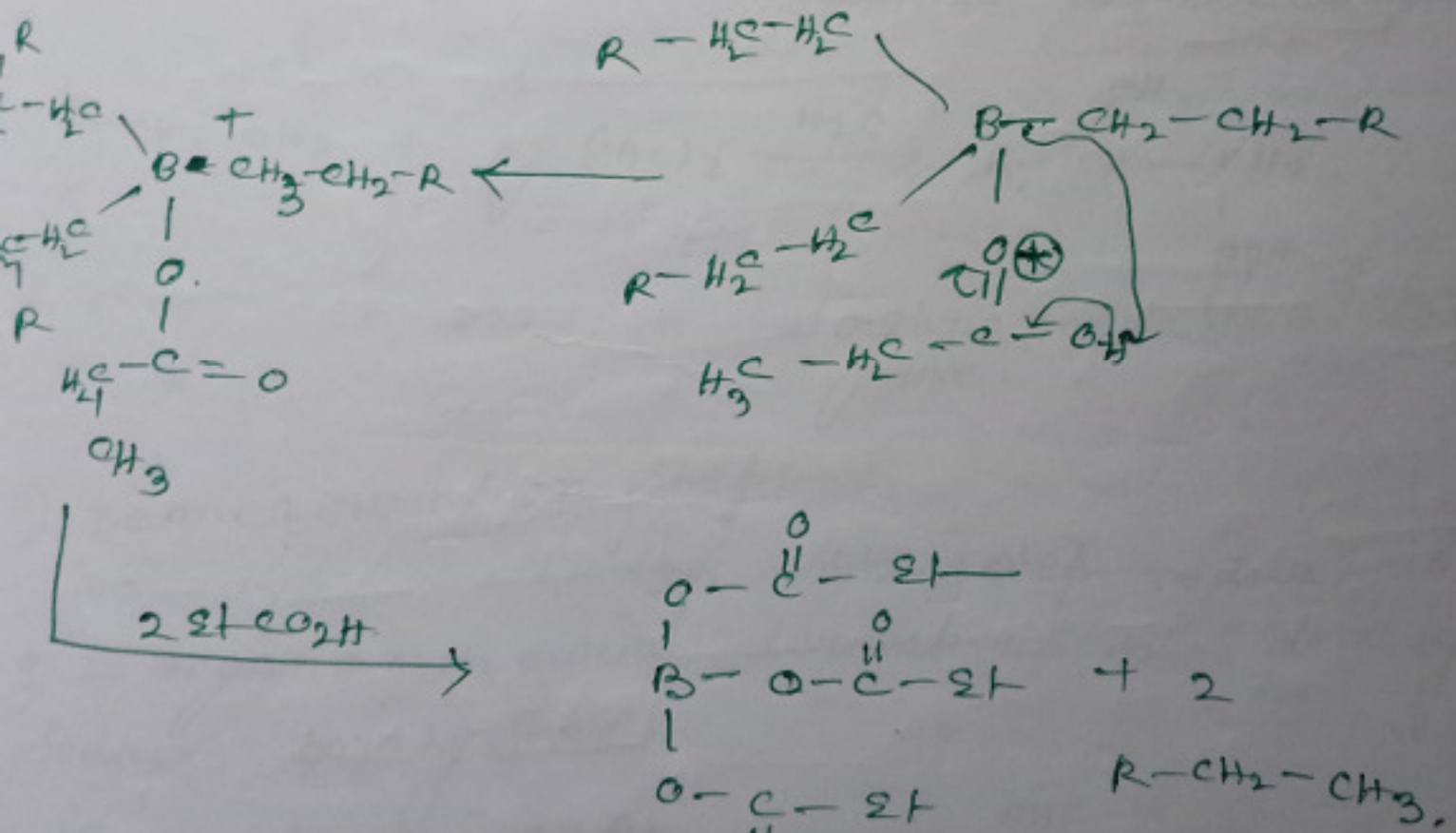
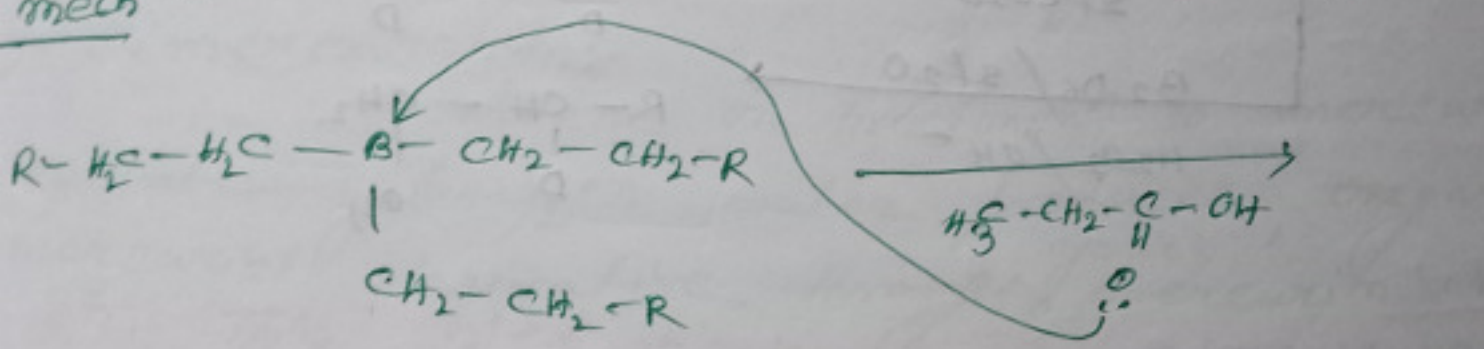
can be oxidized by CrO_3/H^+ to form corresponding aldehyde or ketone.



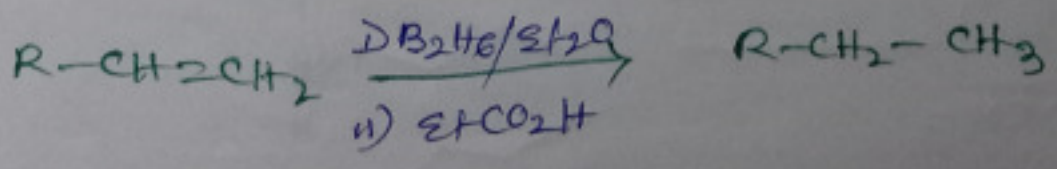
ii) Alkyl borane on protolysis by carboxylic acid to give corresponding hydrocarbon (by this method alkene can be reduced)

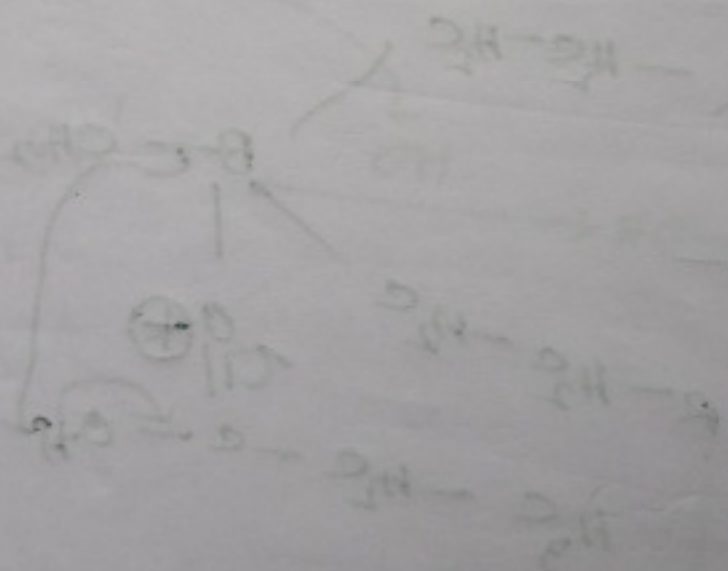
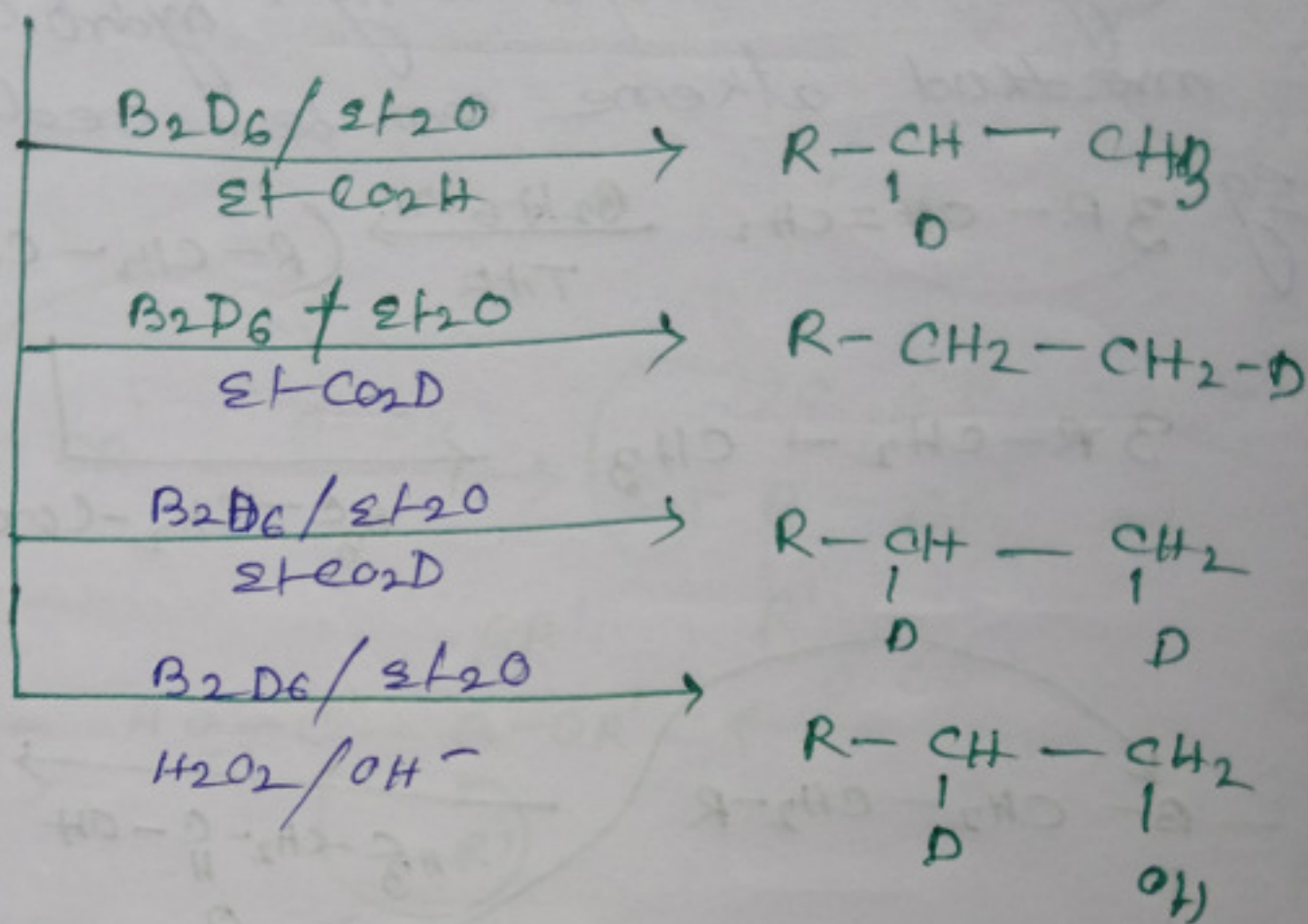
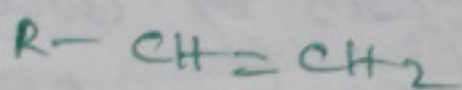


mech^m



convert





Preparation of merkmikoff's alcohol from unsymmetrical alkene:-

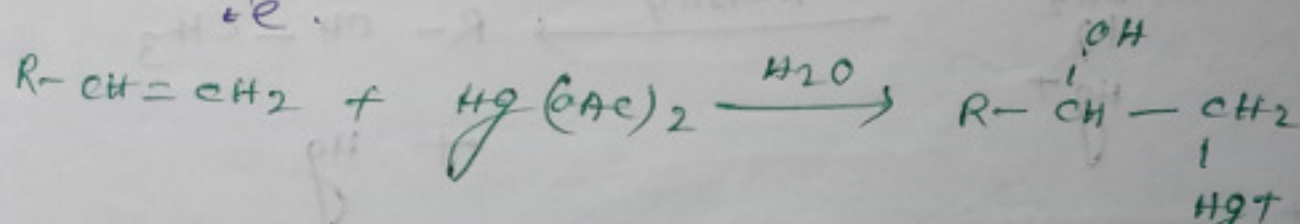
merkmikoff's alcohol from unsymmetrical alkene can be synthesized by the following two step process.

i) step-I - omercuriation

ii) step-II - demercuriation.

i) omercuriation:-

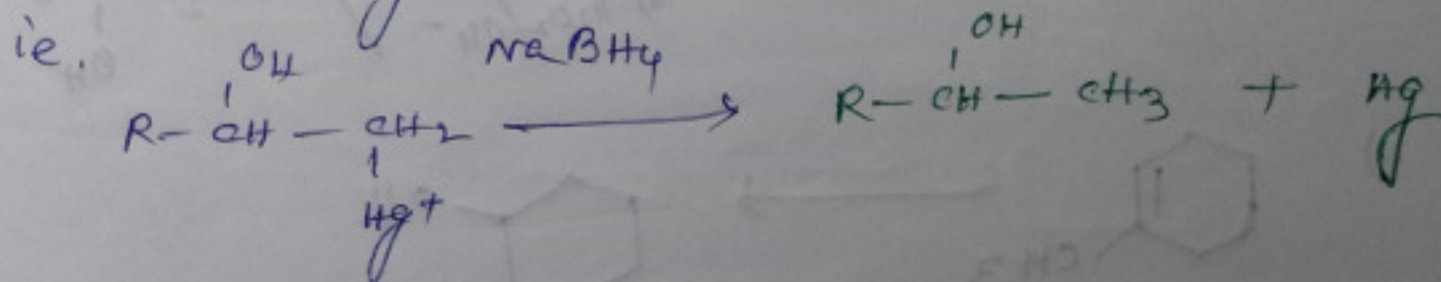
Alkene on treatment to mercuric acetate, $Hg(OAc)_2$ in water produces omercurial derivative through ^{cyclic} mercurinium ion. This step is known as omercuriation.
i.e.



organo mercurial derivative.

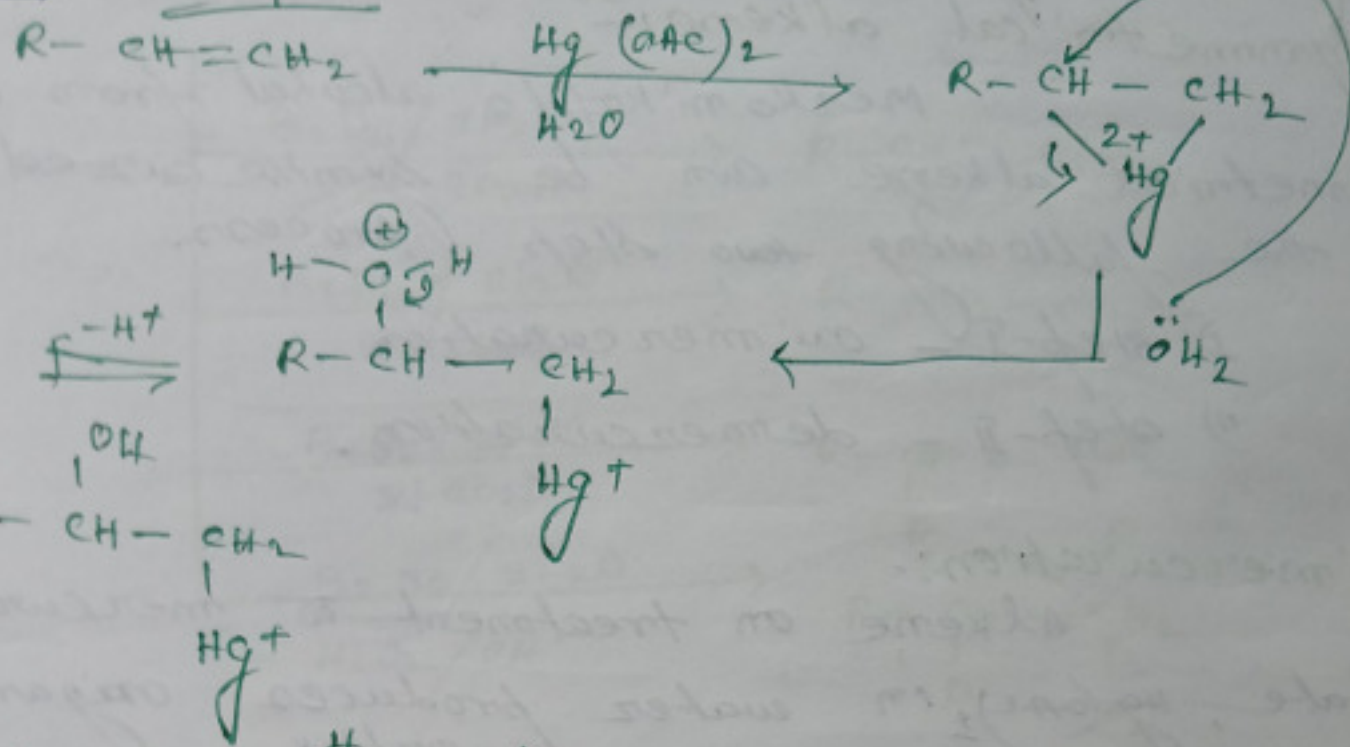
ii) Demercuriation Step:-

in this step reduction of organo mercurial derivative is done by sodium borohydride.



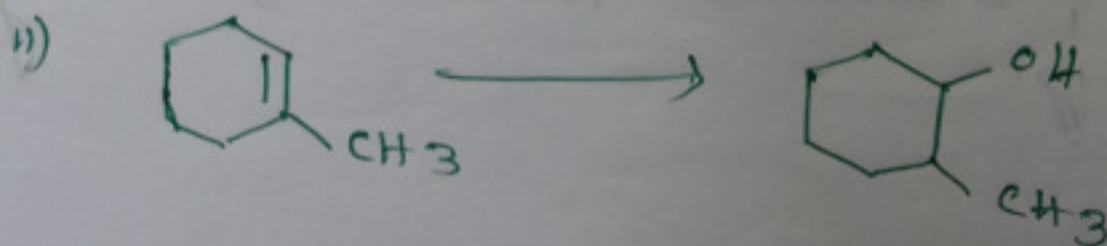
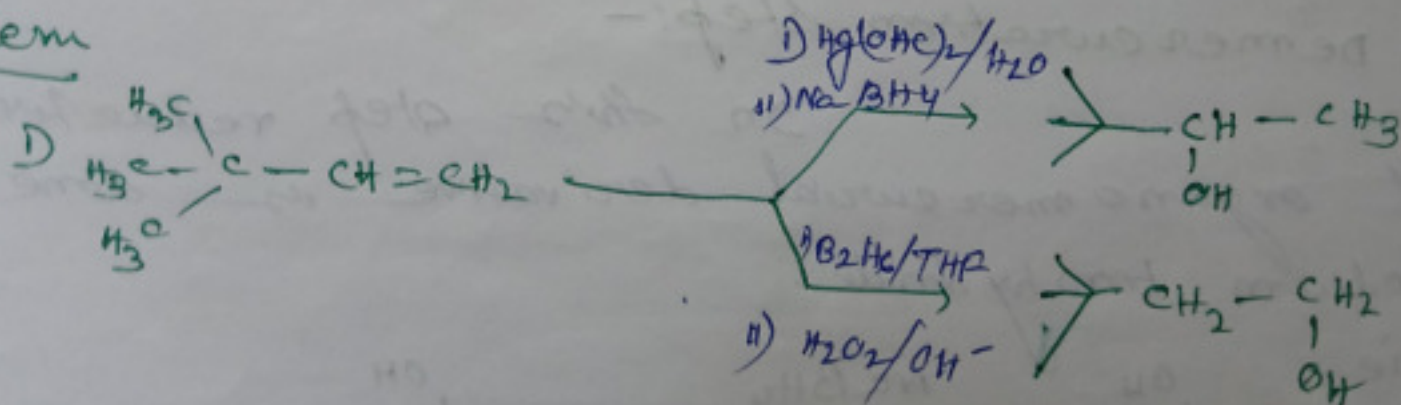
mech^m

Step-I



$[Hg^{2+}] \xrightarrow{\text{here}} Hg$, hence Hg acts as reagent

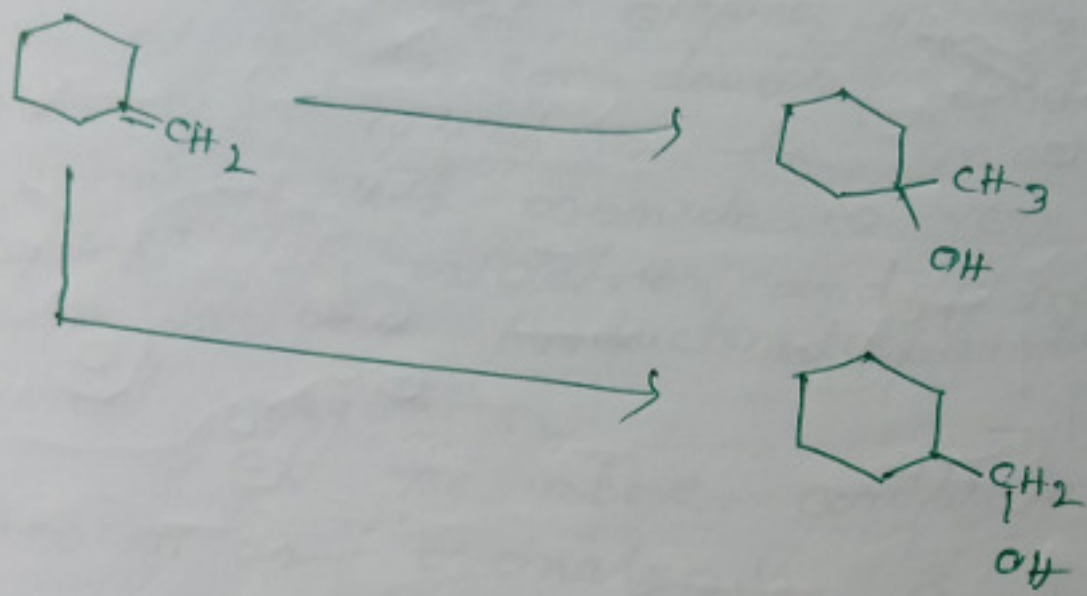
Problem



iii)



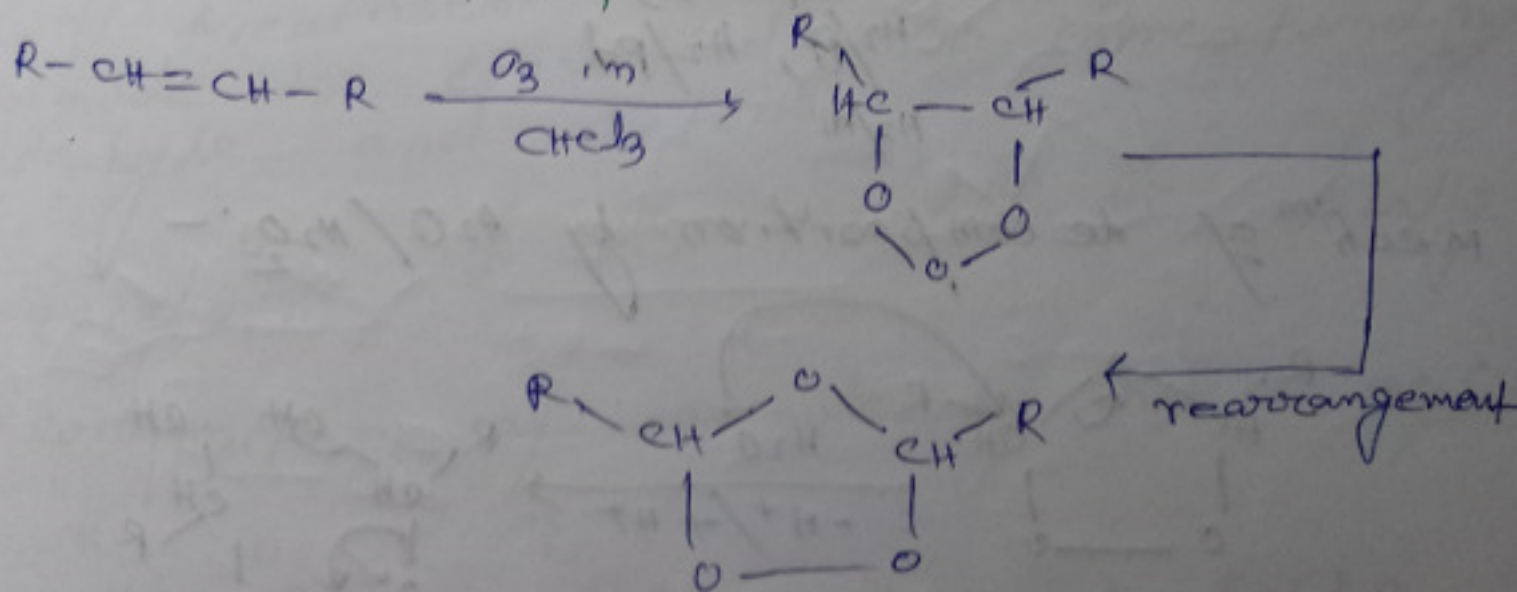
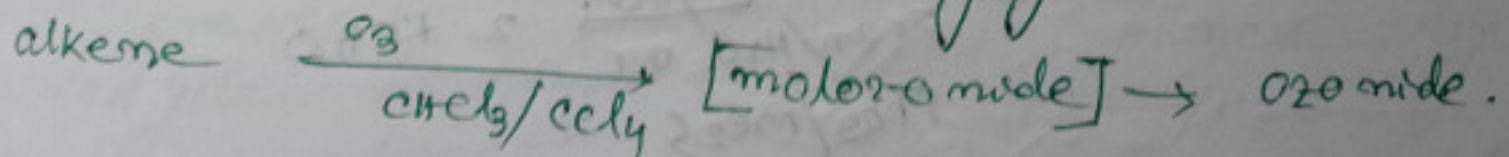
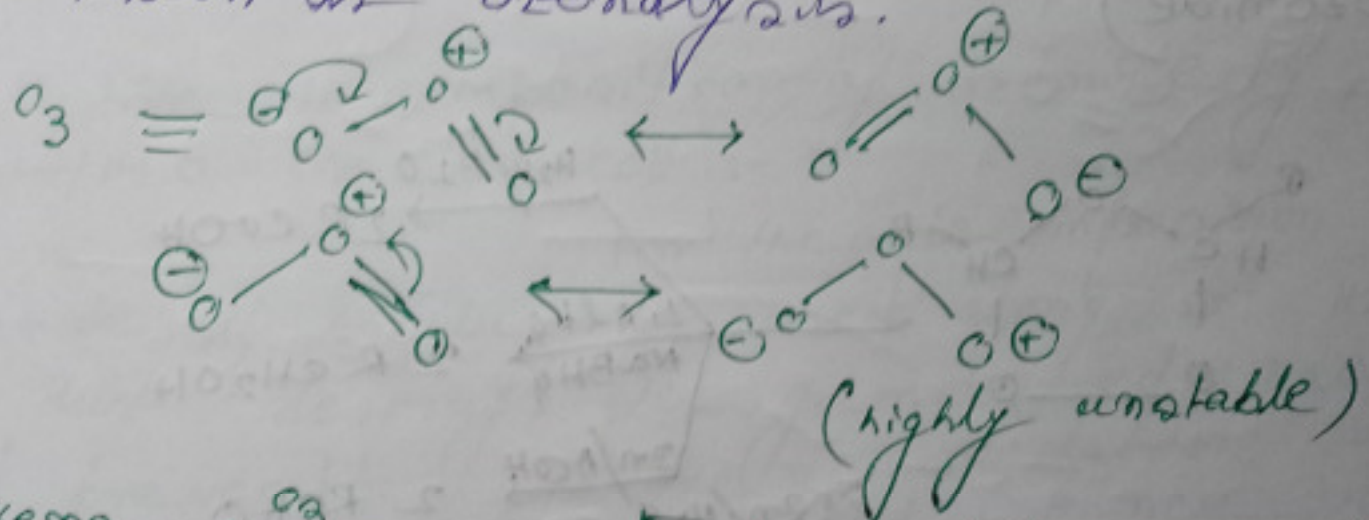
iv)



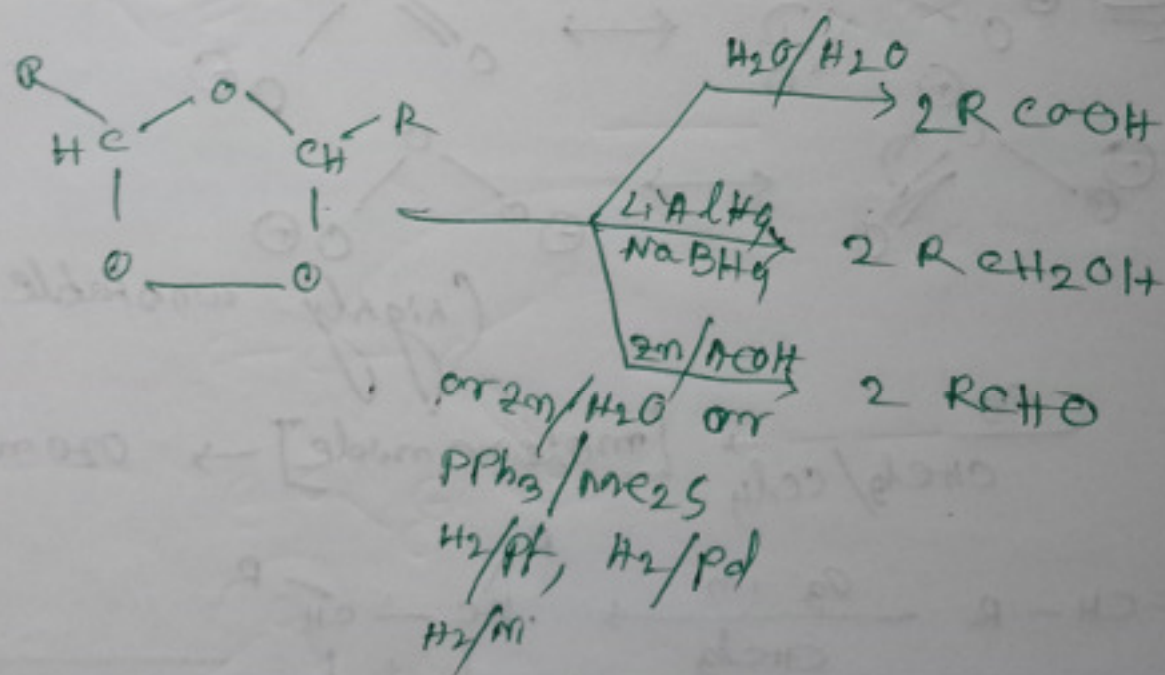
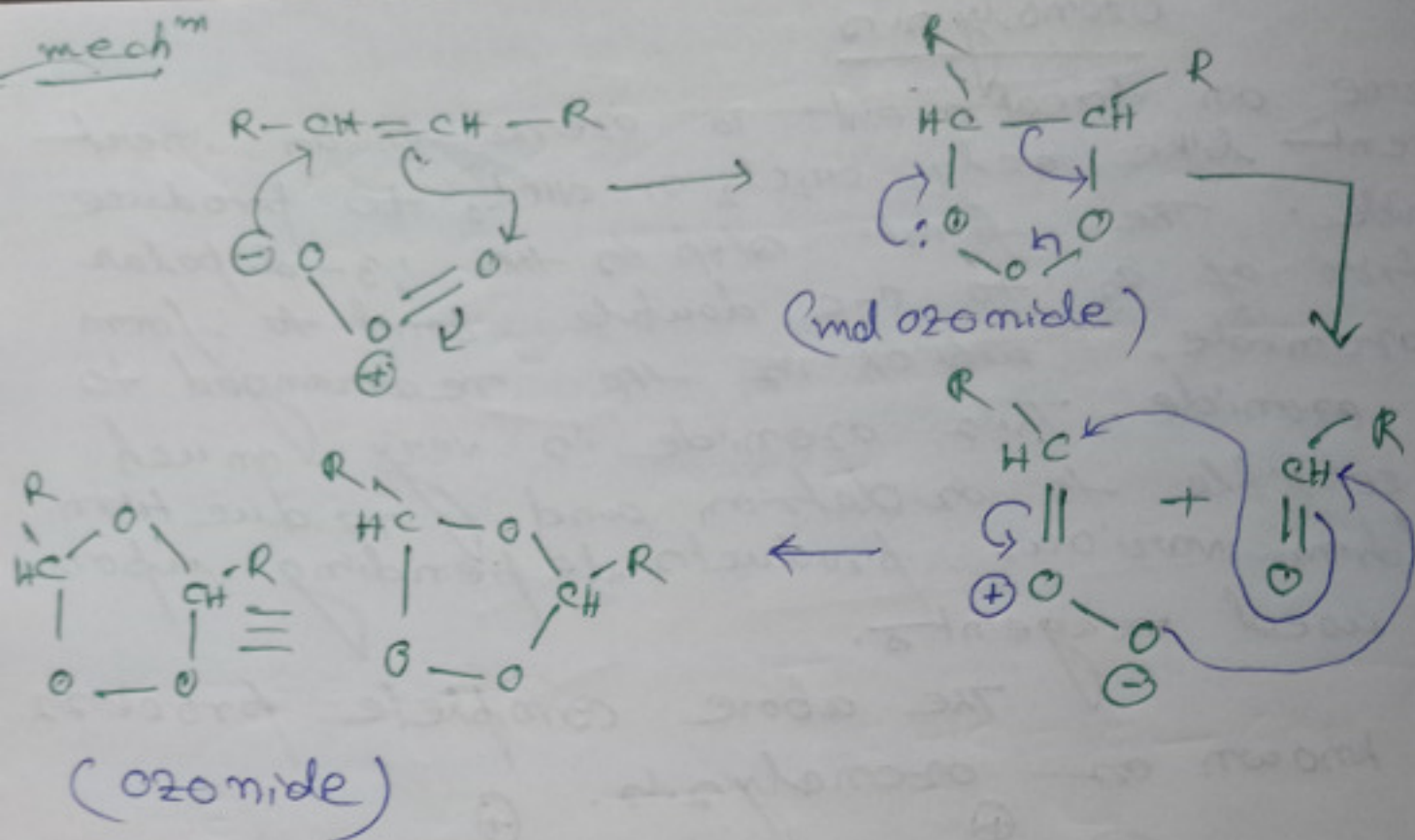
Ozonolysis

Alkene on treatment with ozone in an inert solvent like CCl_4 , CH_2Cl_2 or CHCl_3 to produce ozonide. The first step is the 1,3-dipolar addition of O_3 to C-C double bond to form molarozonide, which is then rearranged to form ozonide. This ozonide is very much susceptible to oxidation and reduction to form various products depending upon the used reagents.

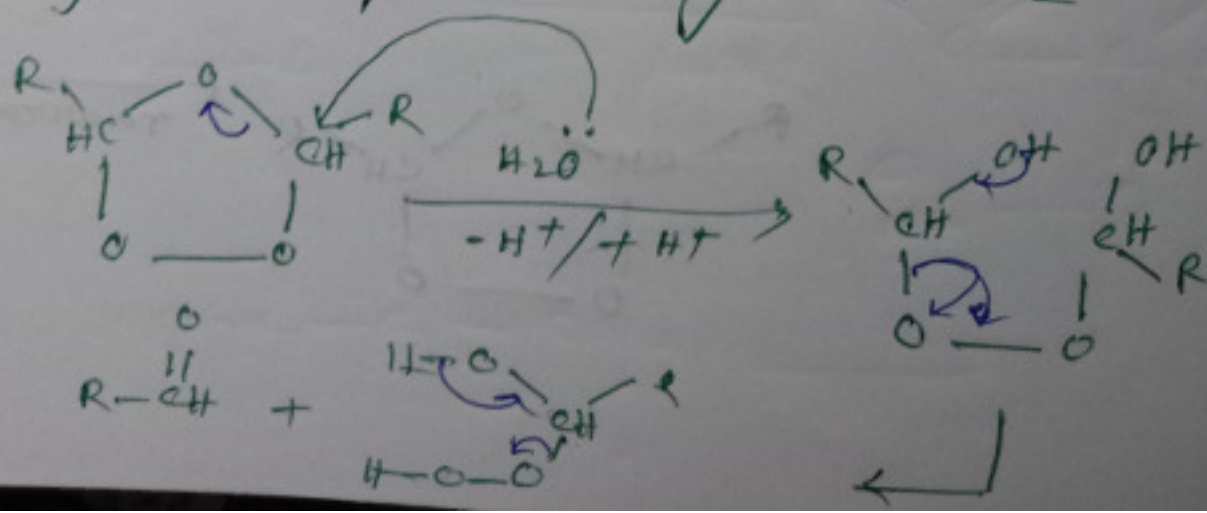
The above complete process is known as ozonolysis.

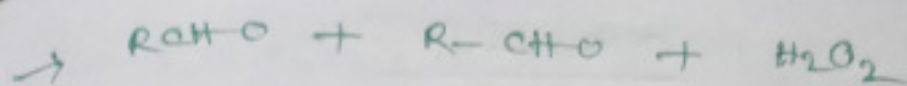


mech^m

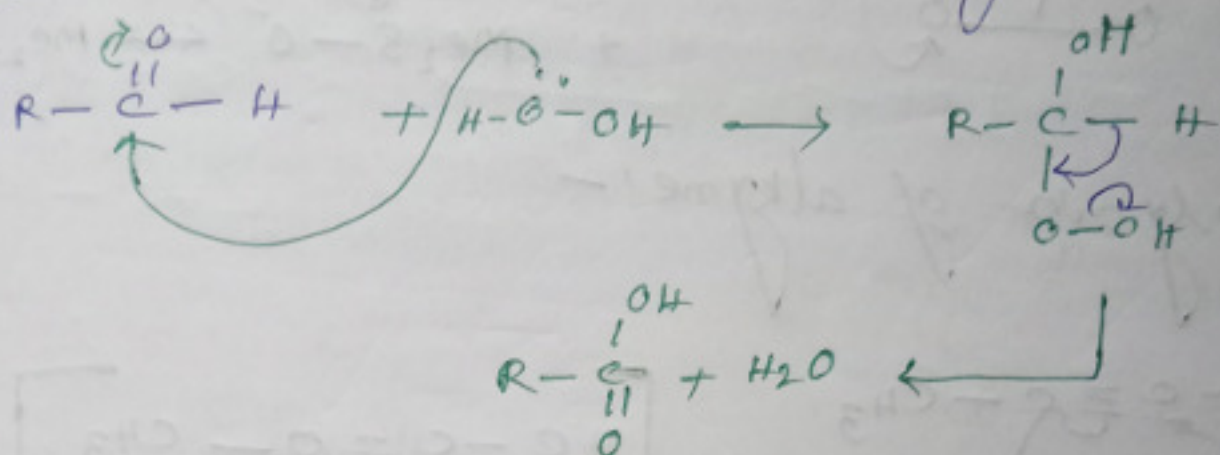


mech^m of decomposition by H_2O/H_2O :-





This aldehyde then oxidized by generated H_2O_2 to form carboxylic acid by following mech^m.

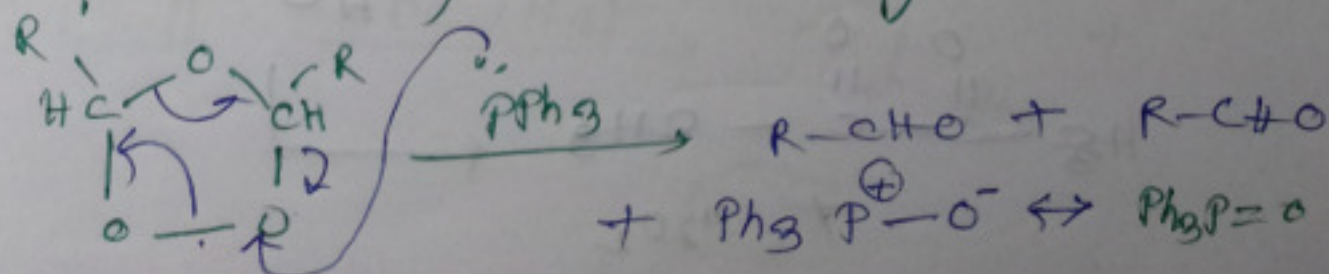


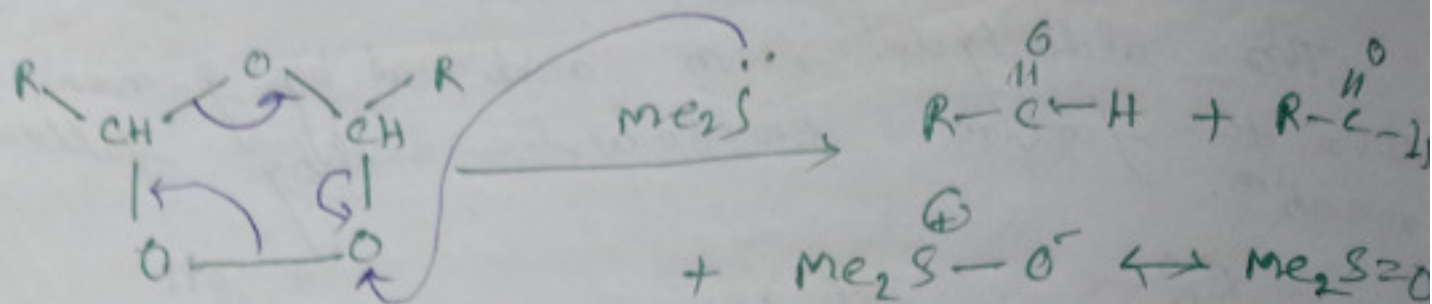
Reductive decomposition of ozonide by Zn dust/ H_2O or Zn/AcOH :-

For the decomposition of ozonide, if Zn dust is used along w H_2O , Zn dust destroys the generated H_2O_2 and prevent further oxidation of aldehyde to carboxylic acid. Hence by the treatment of Zn dust/ H_2O , the ozonide is converted into corresponding aldehyde and ketone.

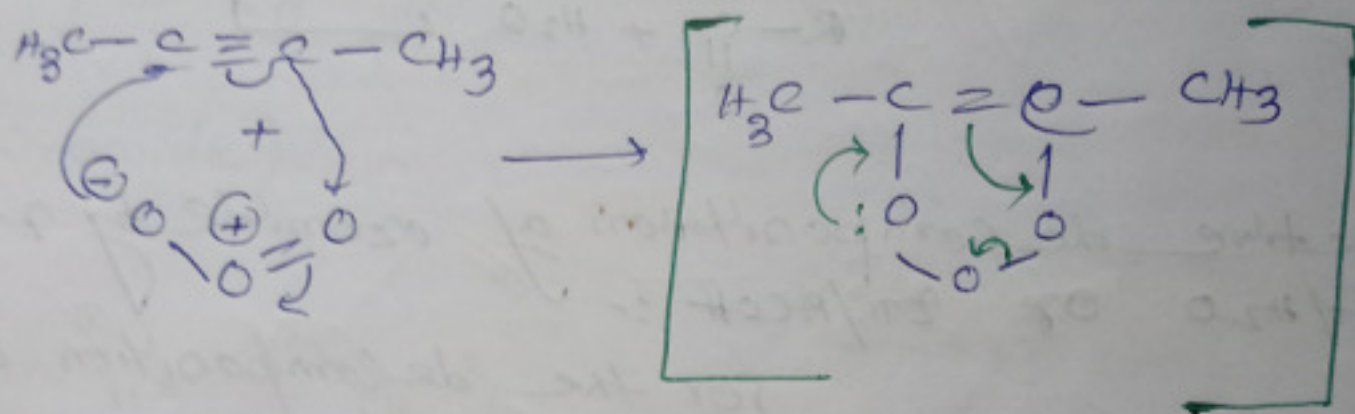
The mech^m is totally uncertain.

Decomposition of ozonide by Ph_3P or Me_2S :

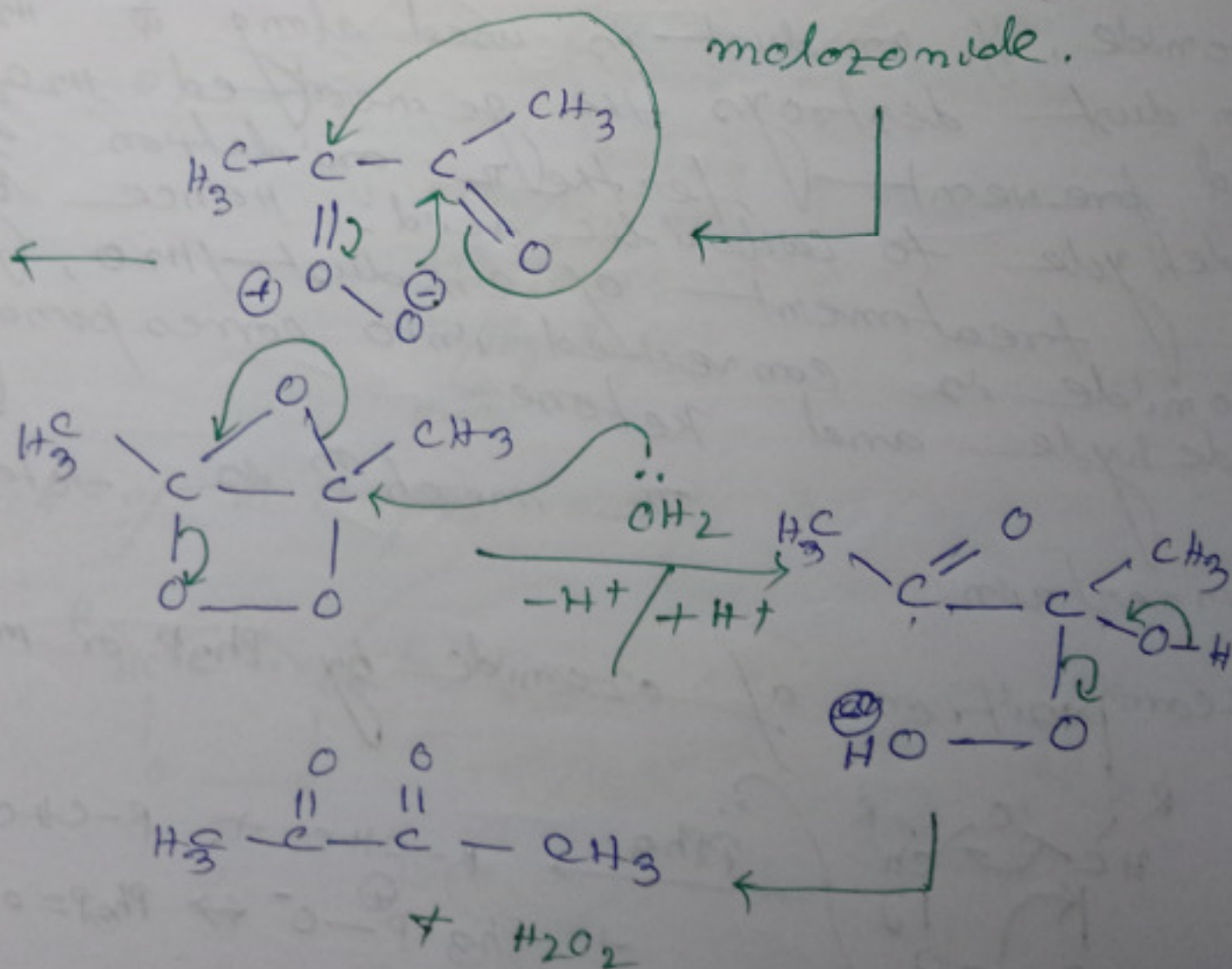


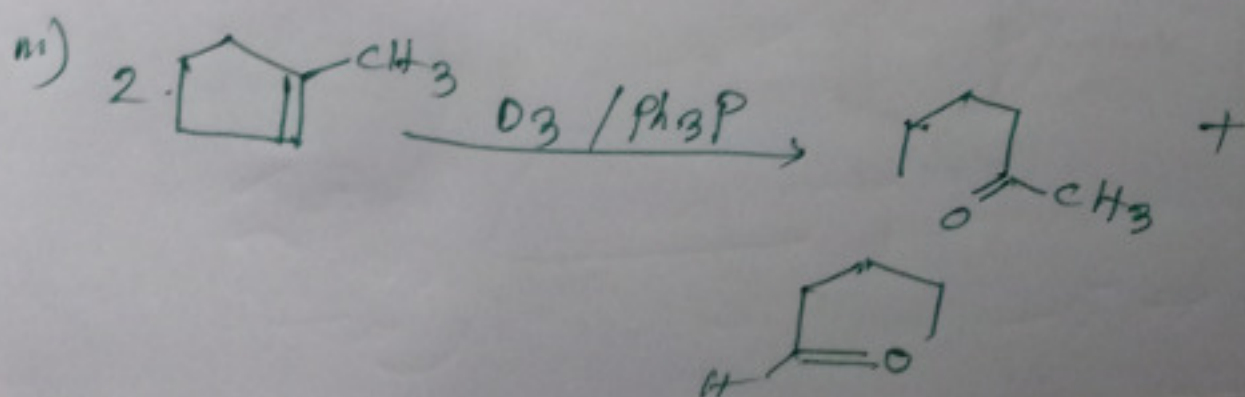
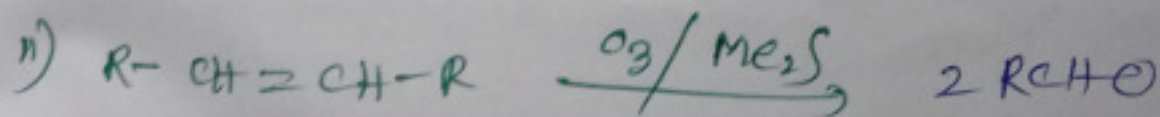
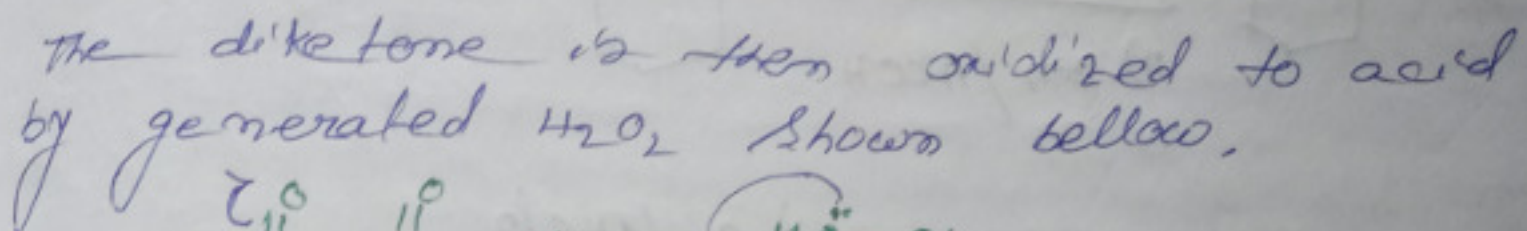


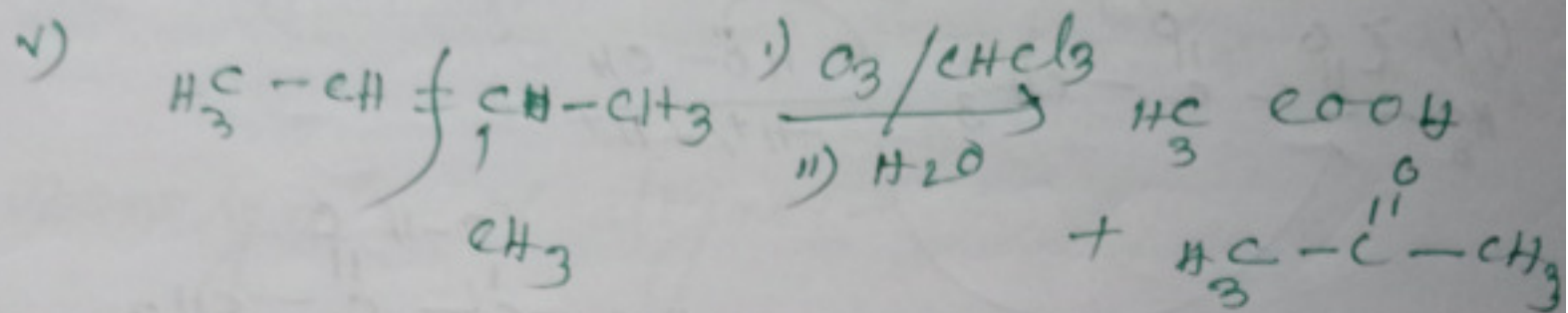
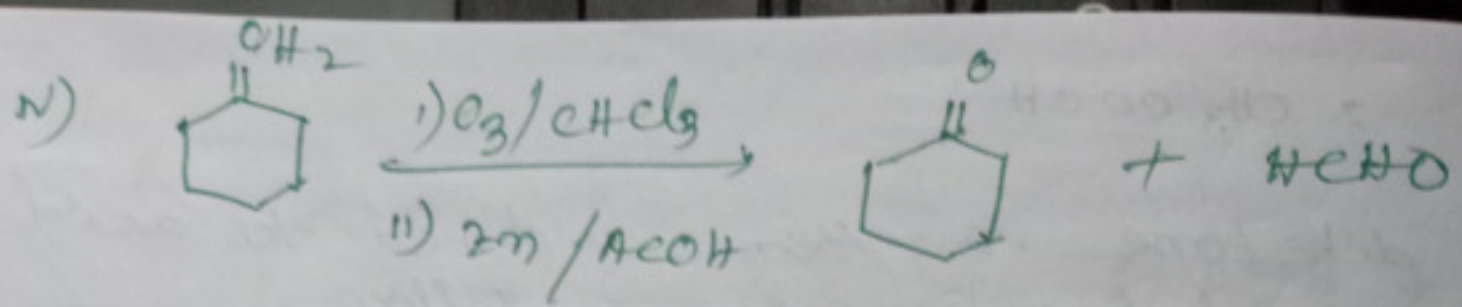
ozonolysis of alkyne:-



moleozonide.

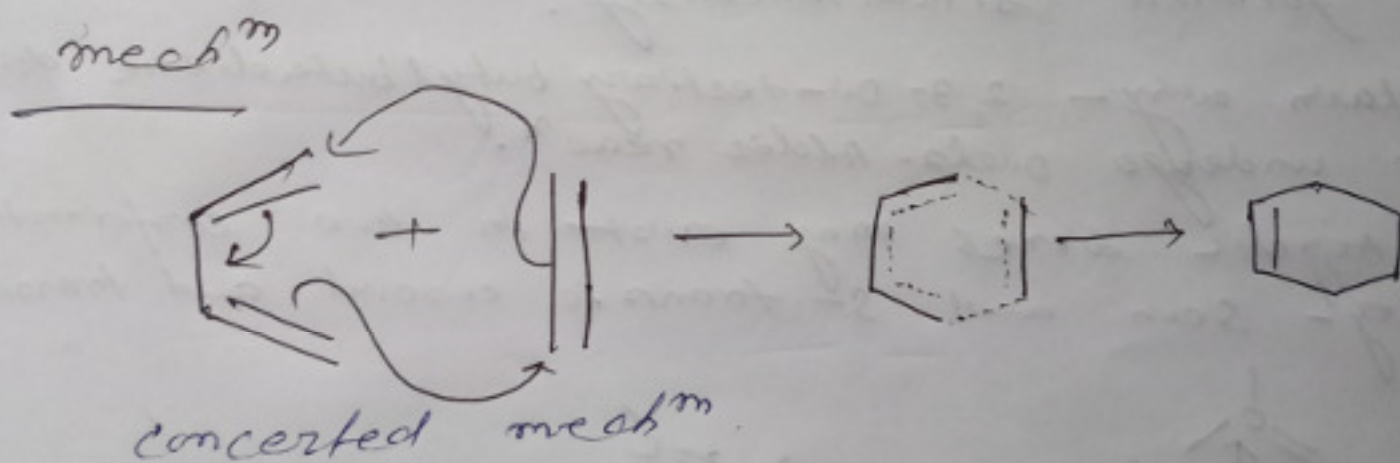
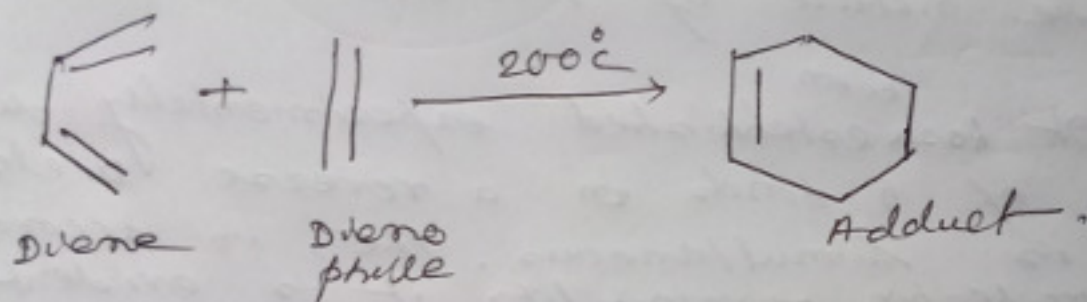




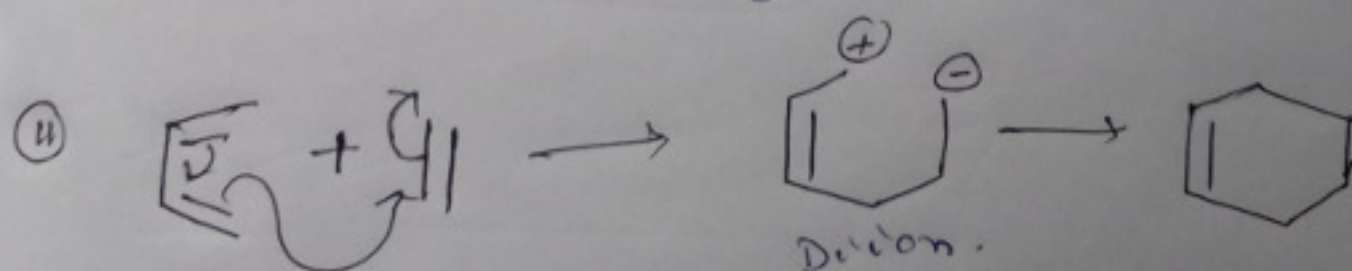
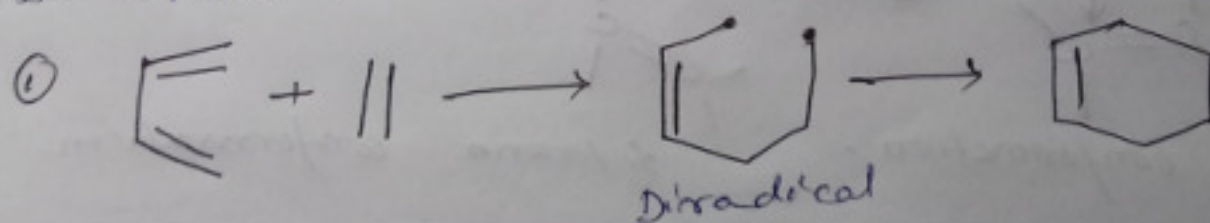


Diels-Alder reactions:-

The reversible and thermal (4+2) cyclo-addⁿ reacⁿ b/w a conjugated diene (a 4 π -electron system) and a compound containing an active multiple bond, called a dienophile (a 2 π electron system) to form a six membered cyclic product (adduct) is known as the Diels-Alder reacⁿ.
The simplest Diels Alder reacⁿ is the reacⁿ of 1,3-butadiene and ethylene to yield cyclohexene.



stepwise mech^m:-



The bulk of evidence suggests that most Diels-Alder reactions occur by the one step cyclic mechanism. The evidence is as follows.

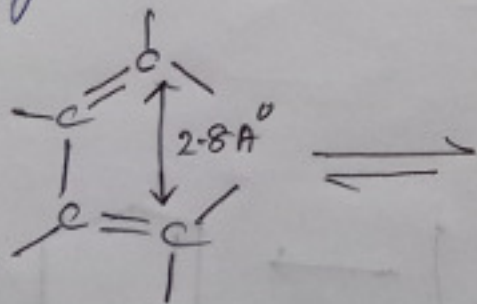
(a) The reaction is stereospecific with respect to both diene and dienophile. A completely free radical or diradical would not be able to retain its configuration.

(b) The reaction depends generally very little on the nature of solvent.

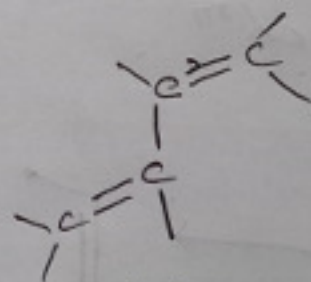
(c) It ^{has} been established experimentally that the cleavage of 5 bonds in a reverse Diels-Alder reaction is simultaneous. Then, in accordance with the microscopic reversibility, it is evident that in the forward reaction the two 5 bonds are formed simultaneously.

Explain why - 2,3-Di-tertiary butyl butadiene does not undergo Diels-Alder reaction.

=> Acyclic dienes may exist in two conformations for eg - s-cis and s-trans i.e. cisoid and transoid



s-cis conformation.



s-trans conformation