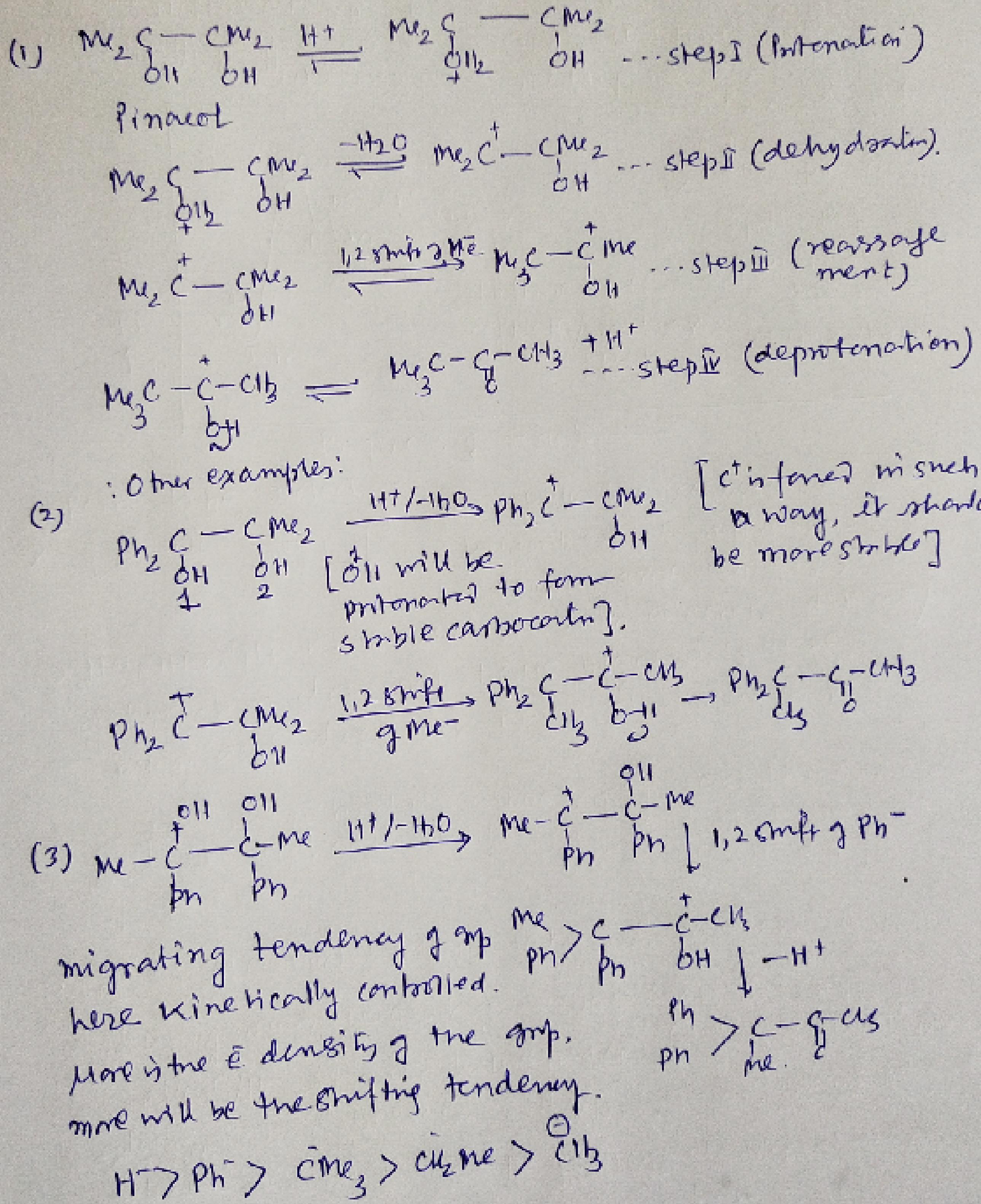
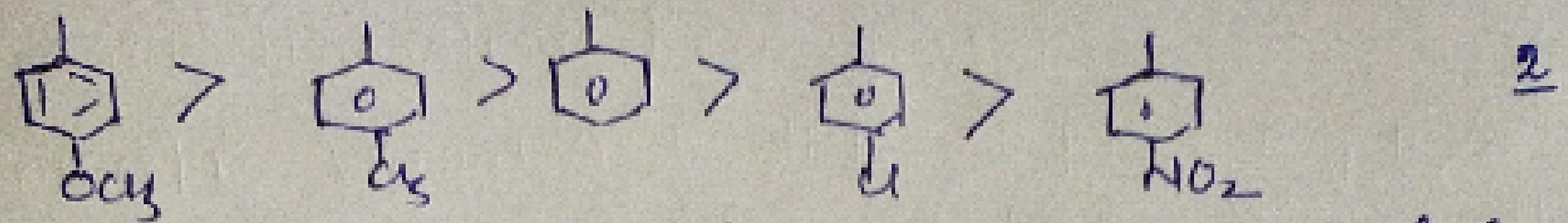


## ①

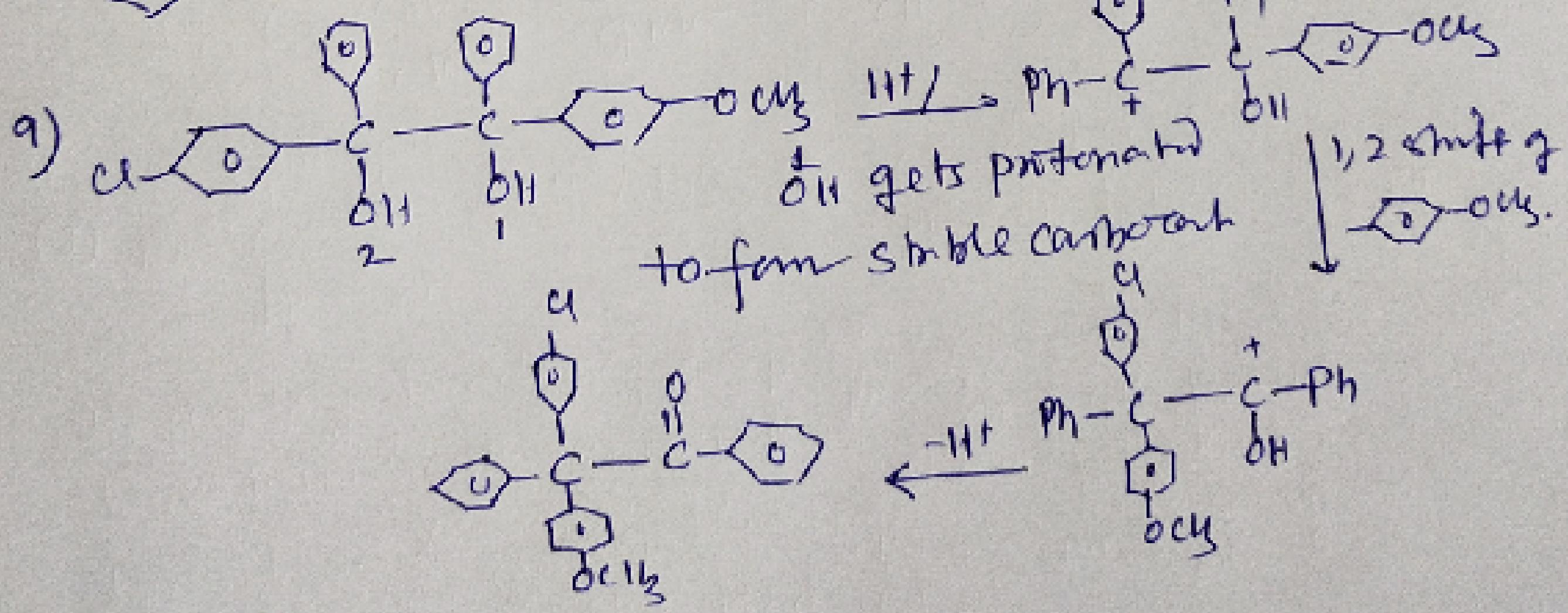
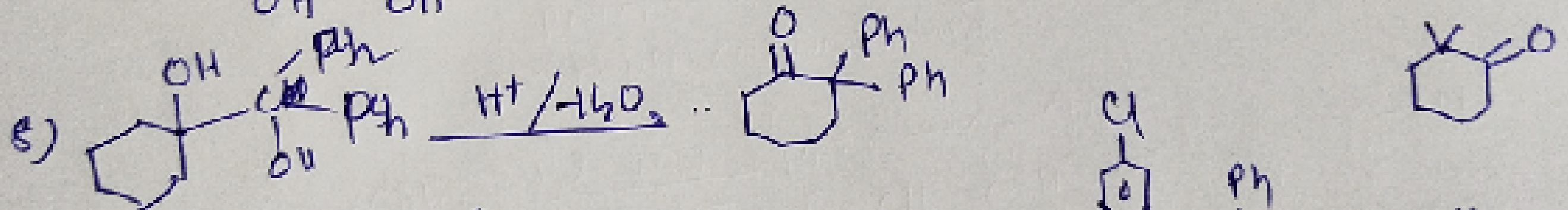
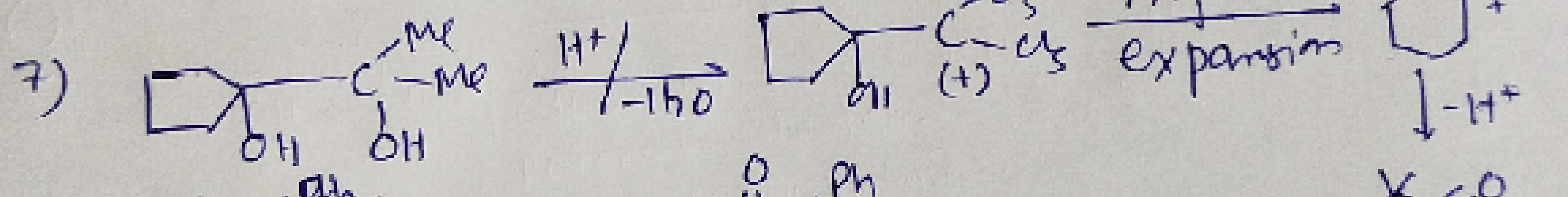
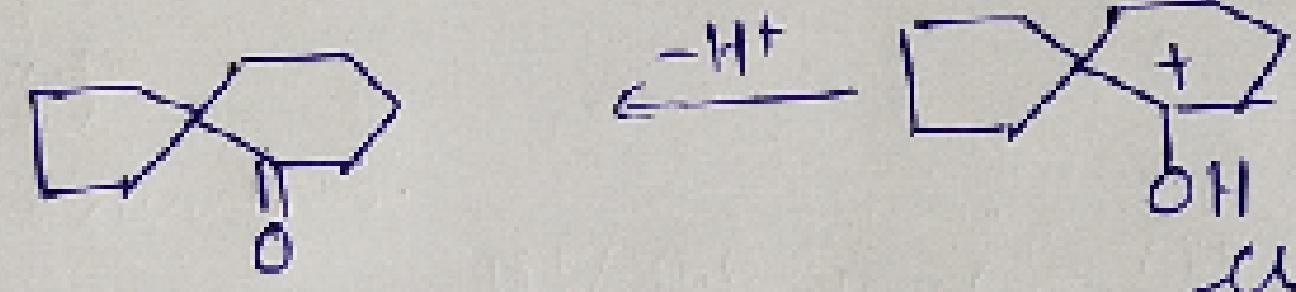
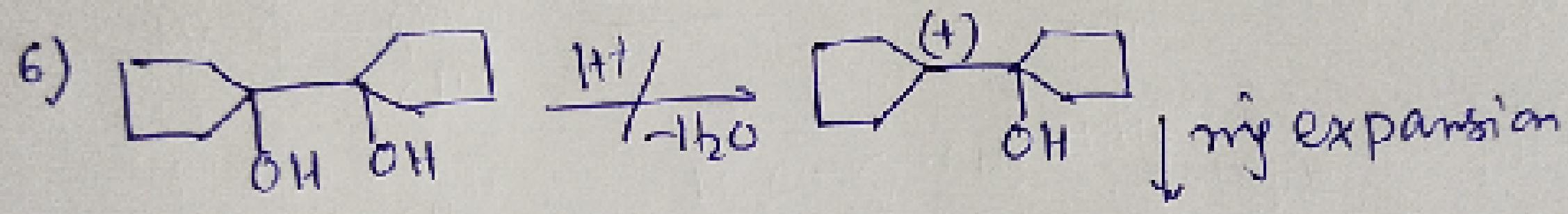
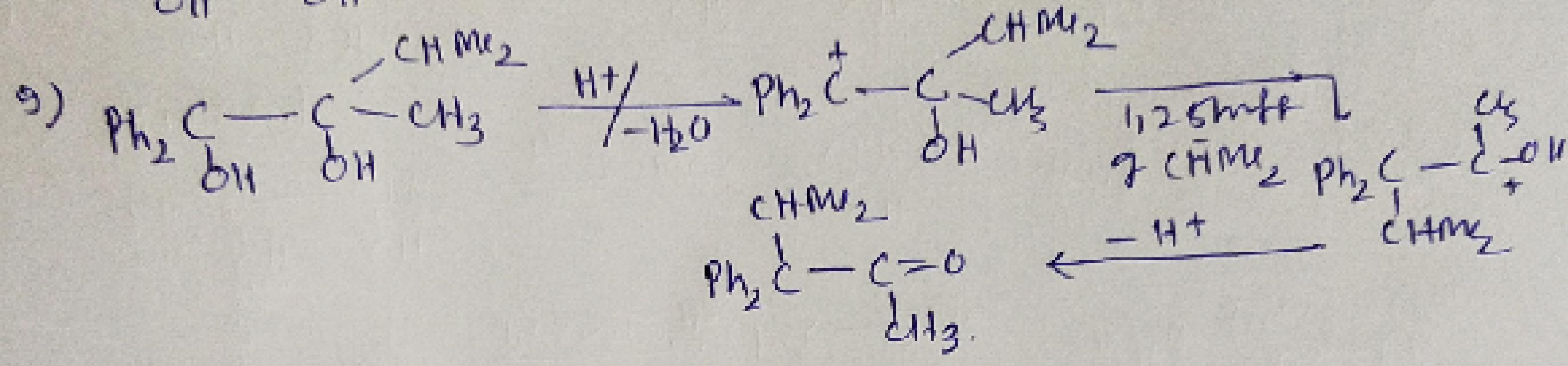
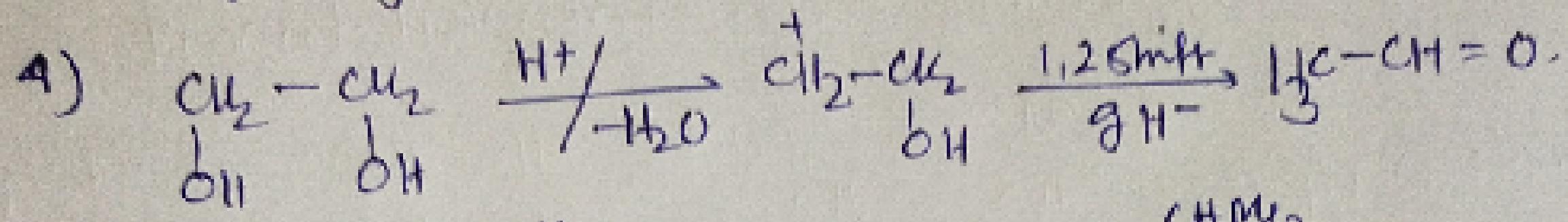
### Pinacol-Pinacolone Rearrangement:

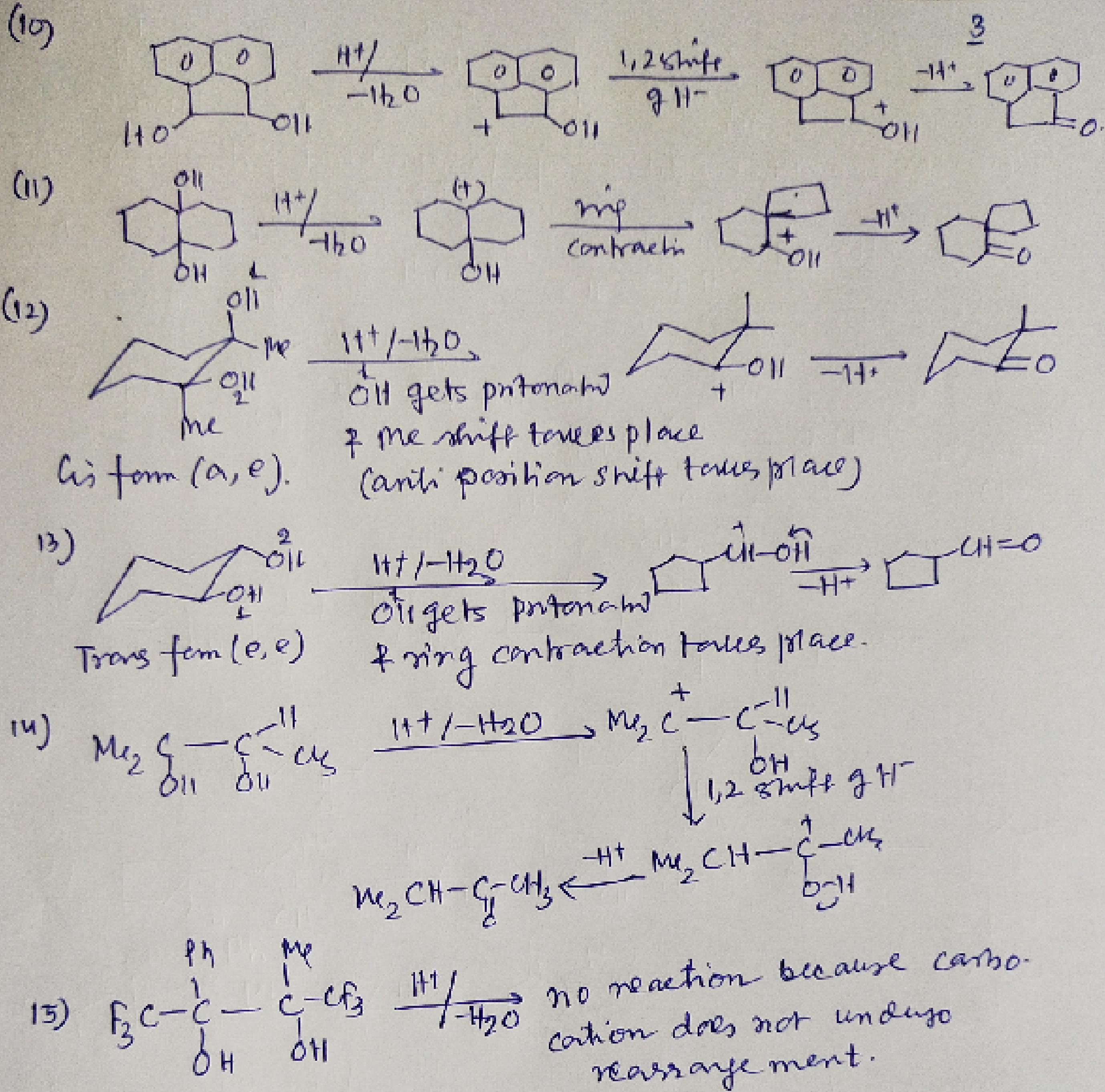
Pinacol is vicinal or 1,2 diol. In presence of  $H^+/\Delta$ , it is converted into ketones/aldehydes. This is called Pinacol-Pinacolone rearrangement.





(migrating tendency of  $p$ -substituted phenyl group)

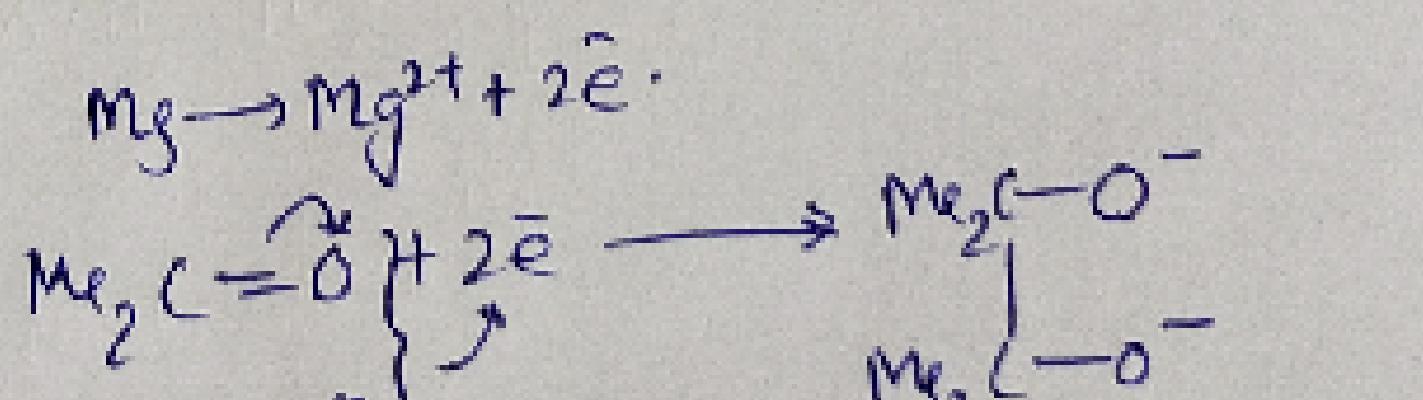




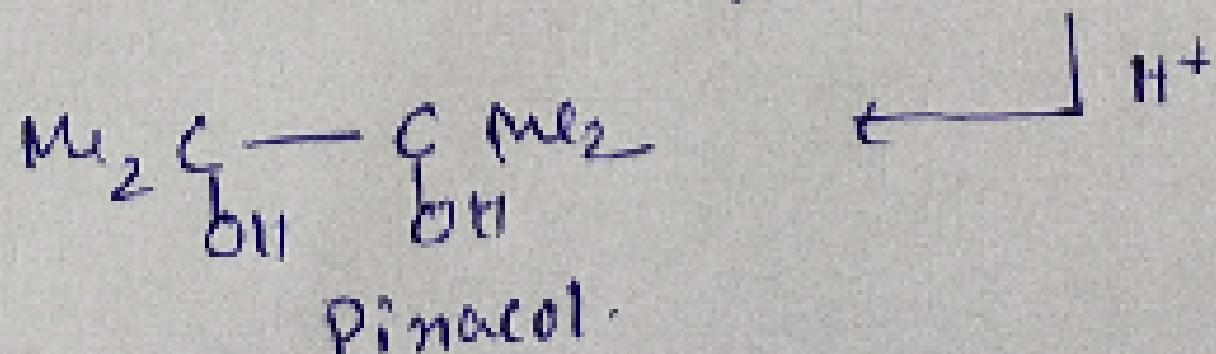
: Pinacol formation:

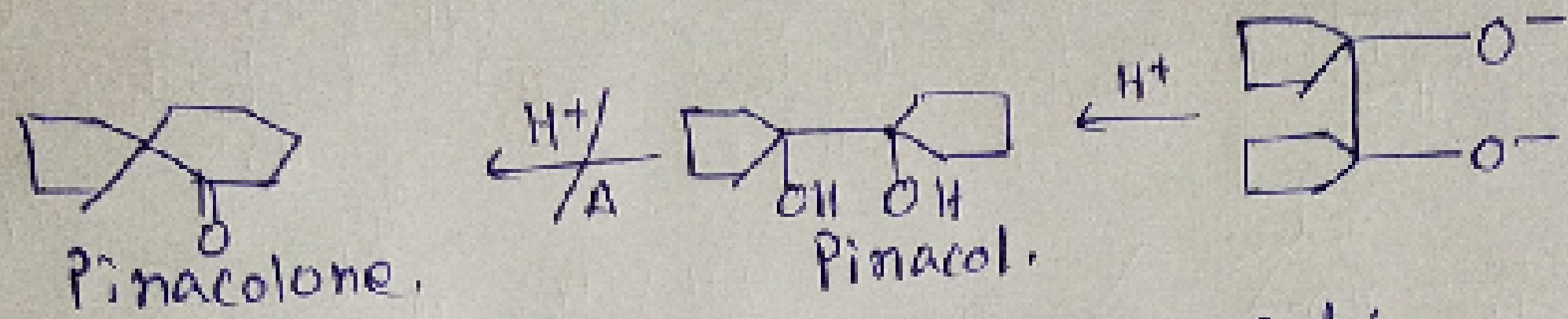
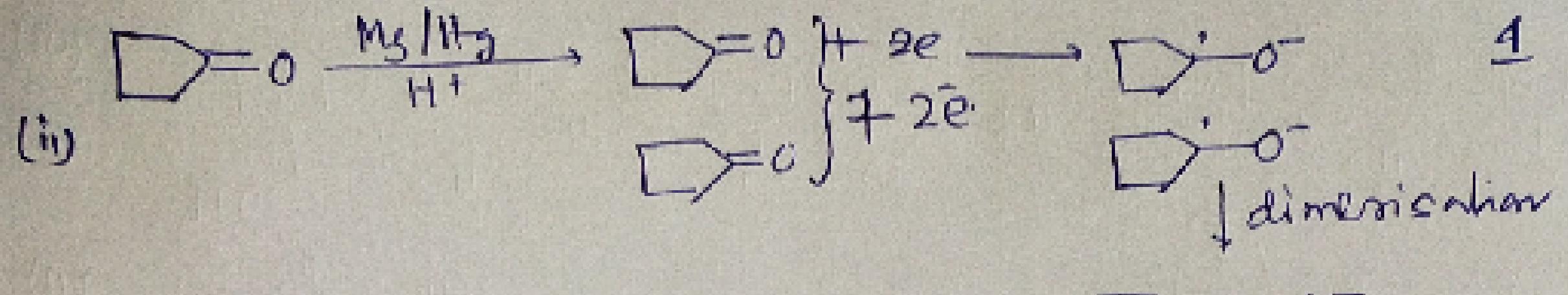
i)  $\text{Me}_2\text{C=O} \xrightarrow{\text{i) Mg(Hg)}}$   
ii)  $\text{H}^+$

$\Rightarrow$  Here Mg is e<sup>-</sup> donor  
 $\Rightarrow$  It is example of redox reaction.

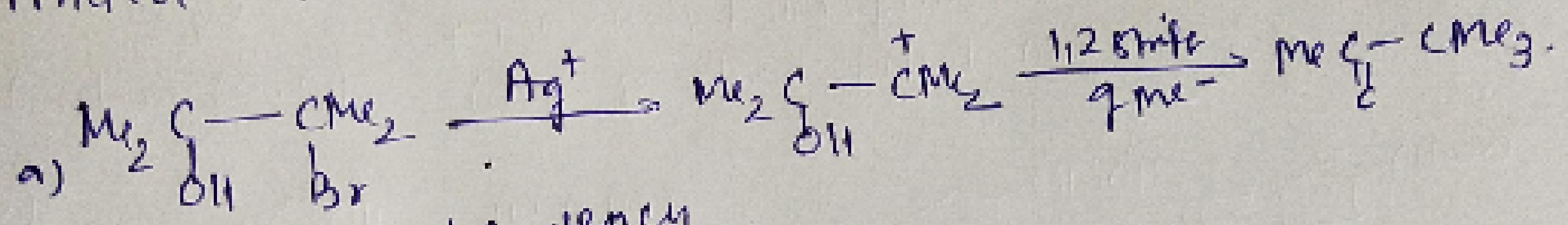


dimersisation takes place



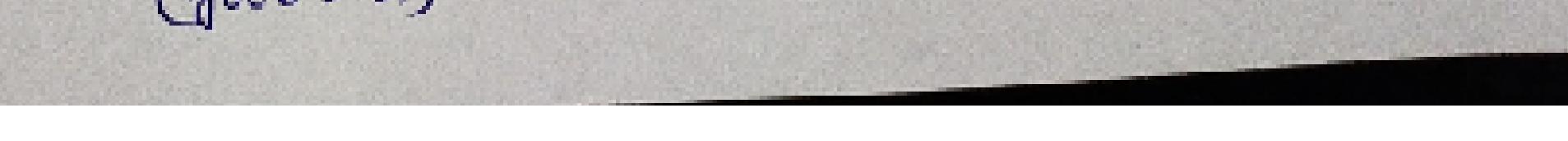
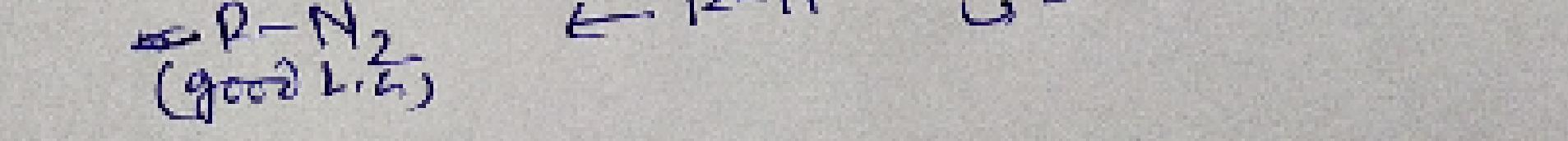
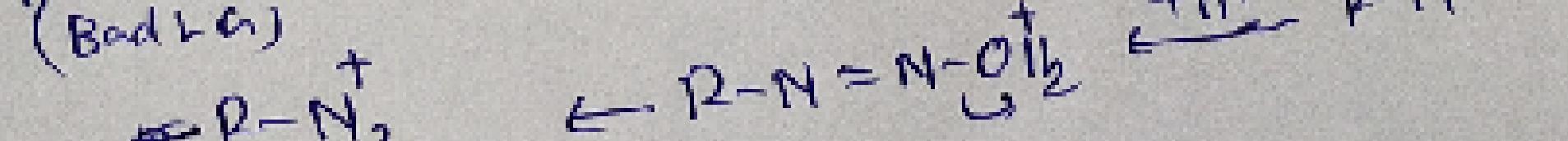
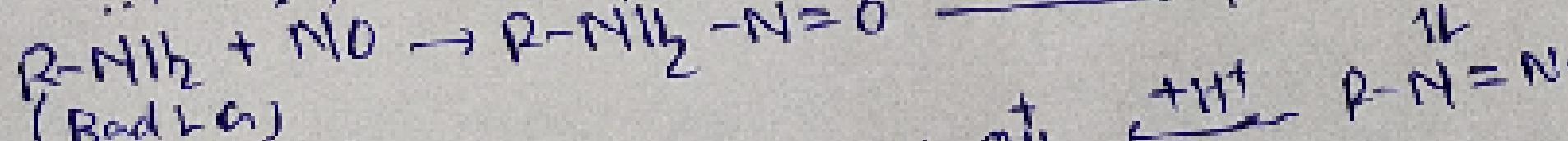
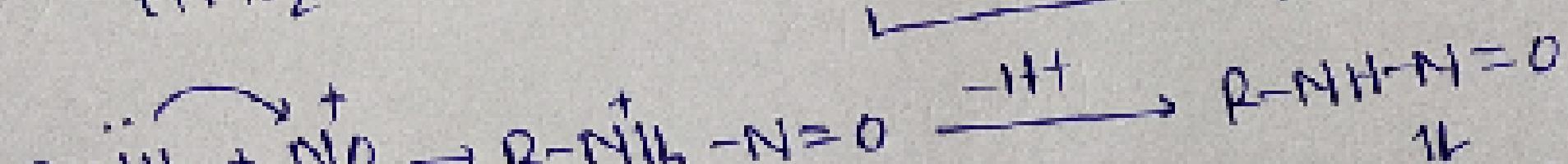
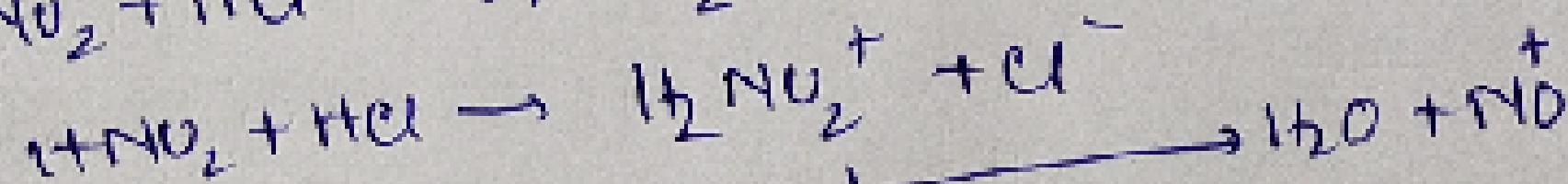
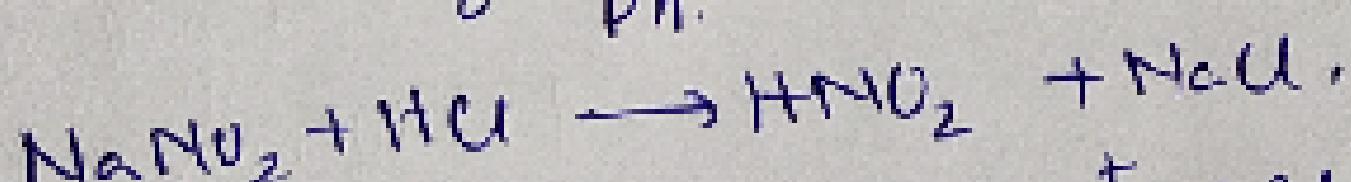
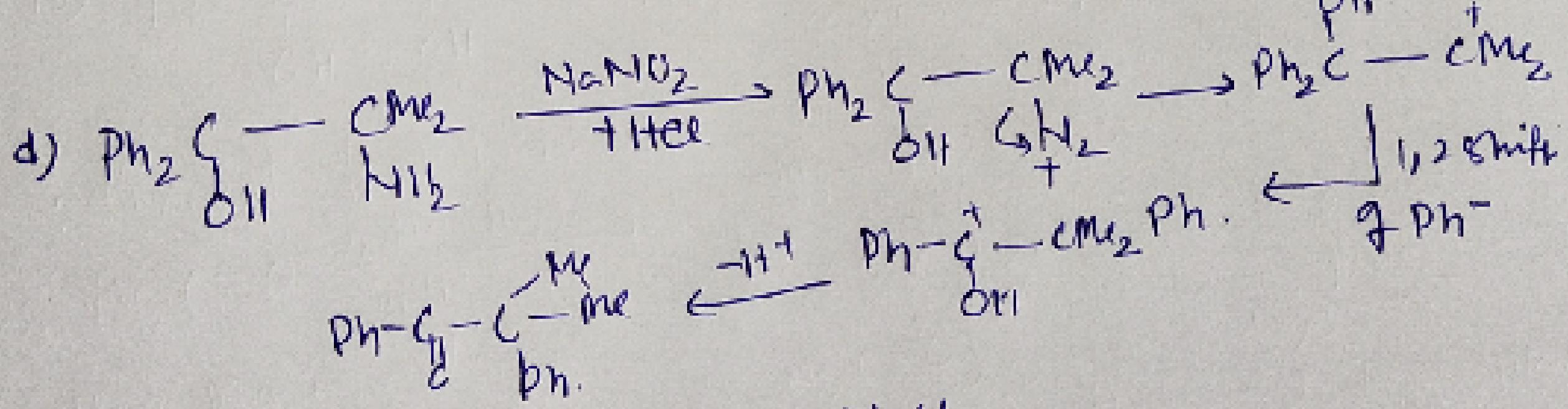
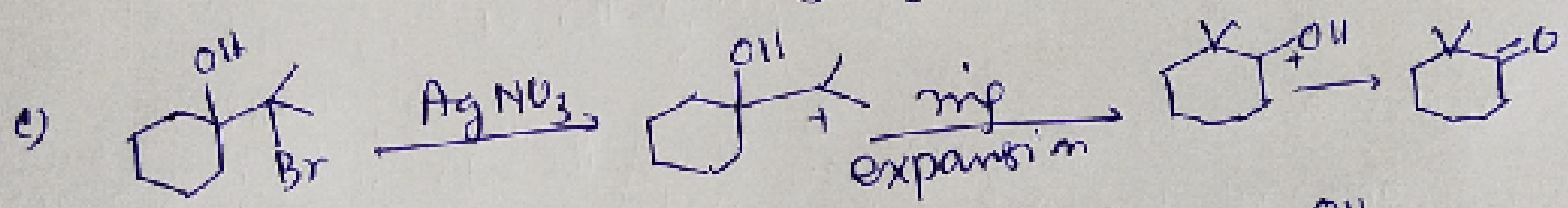
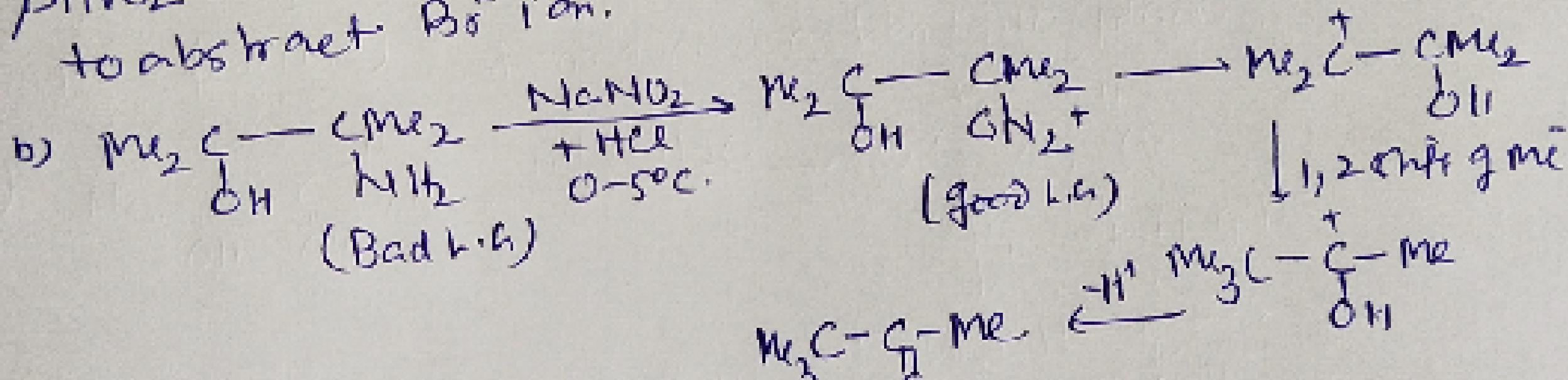


: pinacol-Pinacolone type rearrangement:



Bilwer salt has tendency  
to abstract  $\text{Br}^-$  ion.

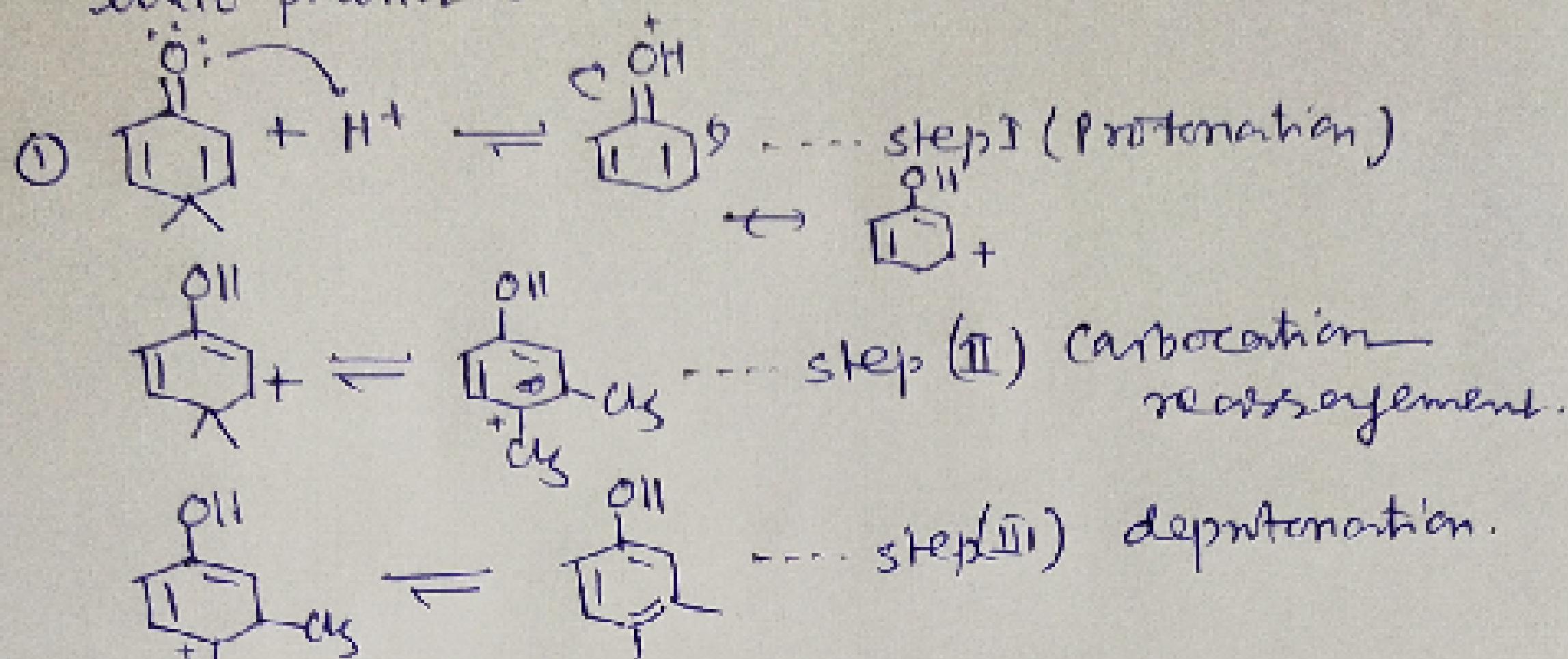
(Bad L.G.)



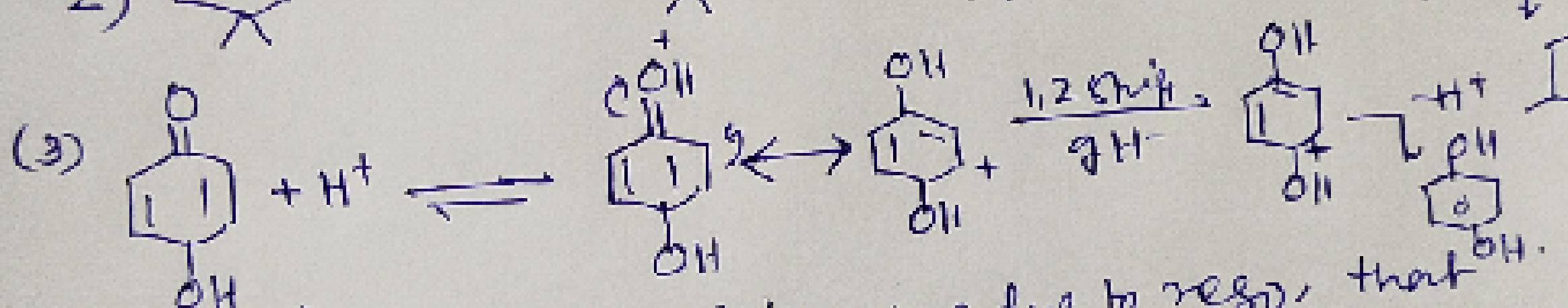
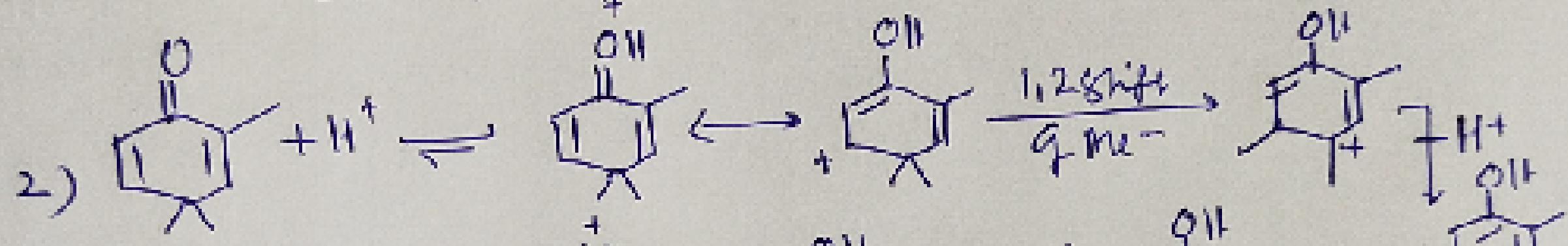
## Dieneone-Phenol rearrangement.

5

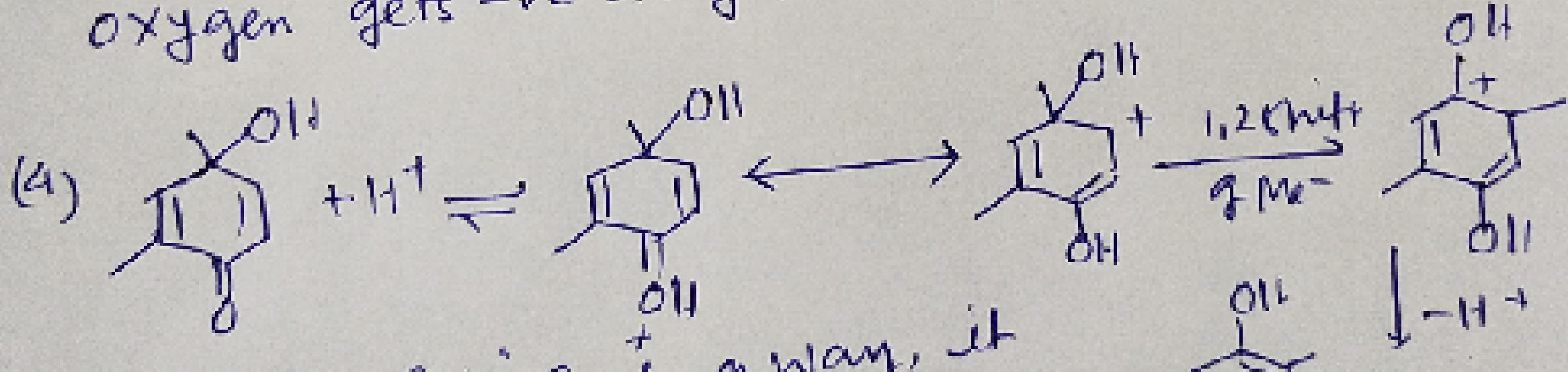
Here dienone system in presence of  $H^+$  is converted into phenol derivative.



Ques : Other examples:



[Here  $\text{O}=\text{O}$  gets protonated because due to reso, that oxygen gets -ve charge, so it is more e rich]



Pdt is formed in such a way, it should be stable (sterically less crowded).

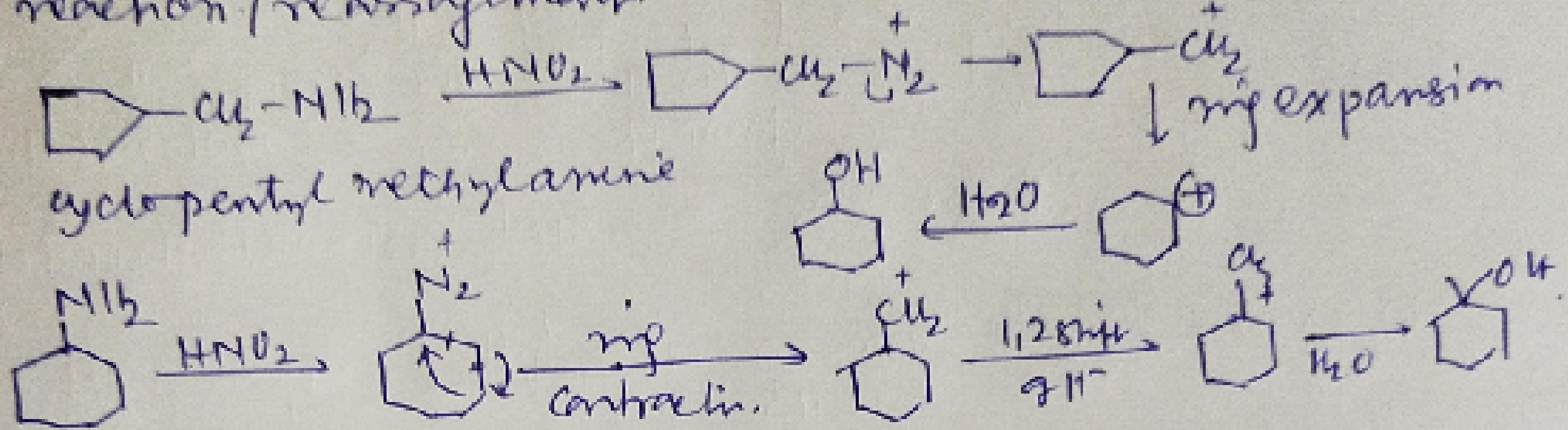
In question(4)  $\text{C}^+$  is not formed  $\left[ \begin{array}{c} \text{O}^{\text{H}} \\ | \\ \text{C}^+ \\ | \\ \text{OH} \end{array} \right]$  because it leads to less stable Pdt

[more sterically crowded product  $\rightarrow$

## Demjanov Reaction:

6

The isomerisation of acyclic rings involving ring expansion & ring contraction of cycloalkyl methyl amine respectively by the action of  $\text{HNO}_2$  or  $\text{NaNO}_2 + \text{HCl}$  is known as Demjanov reaction/rearrangement.



cycloheptyl amine

→ Diazotisation: formation of diazonium ion

$\text{R}-\text{NH}_2 \rightarrow$  carbocation is formed as intermediate.

⇒ 1° Amine here converted into alkene.

⇒  $\text{NO}^+$  is generated as electrophile.

⇒  $\text{R}-\text{N}_2^+$  (alkyl diazonium ion) is formed as intermediate.

⇒  $\text{R}-\text{N}_2^+$  (alkyl diazonium ion) is formed as product.

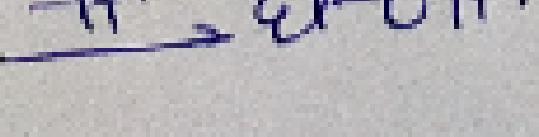
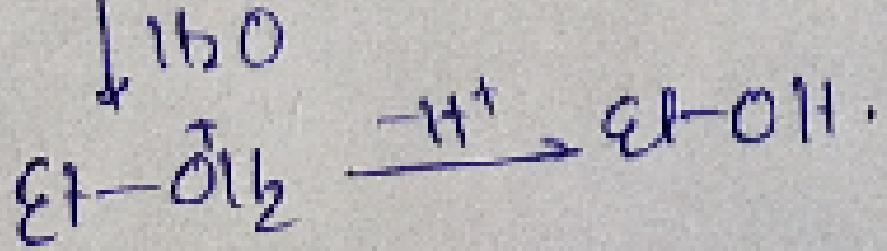
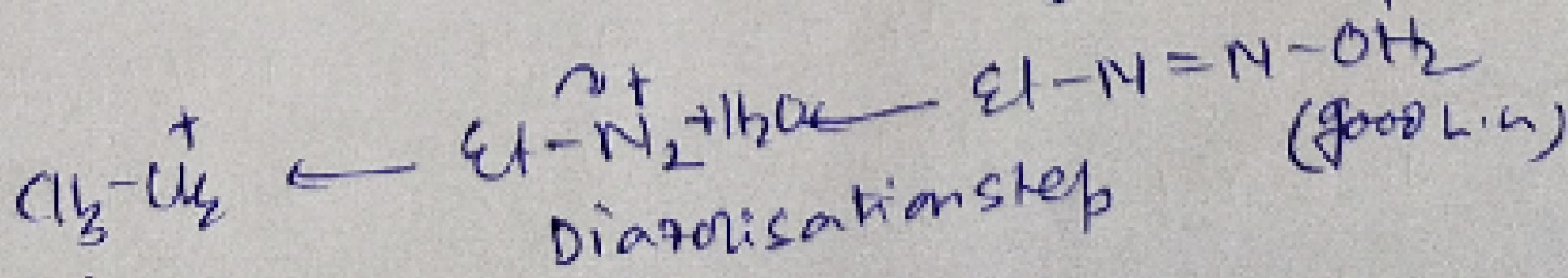
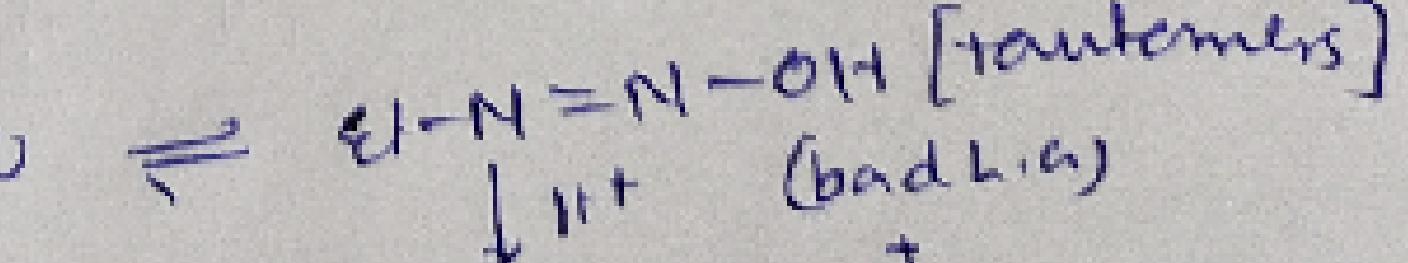
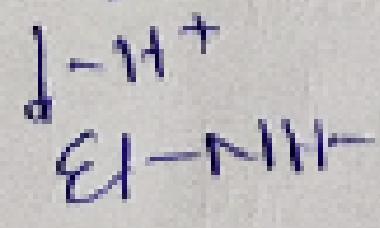
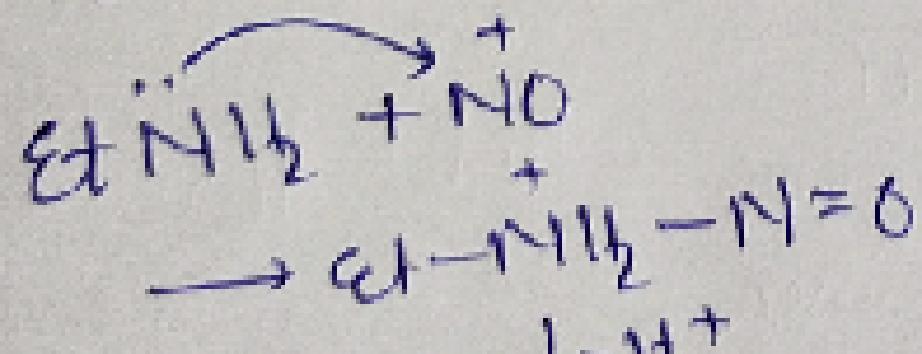
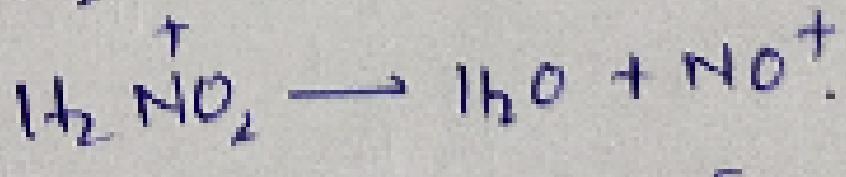
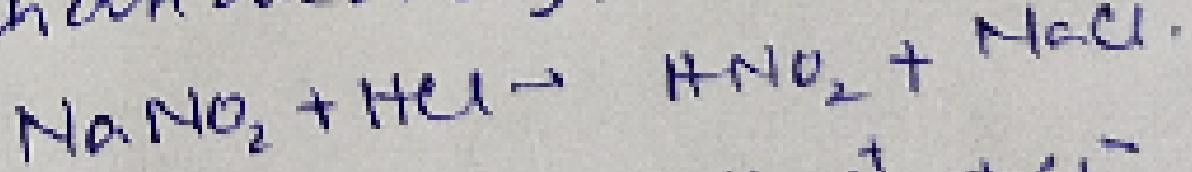
which can't be isolated as major pdt.

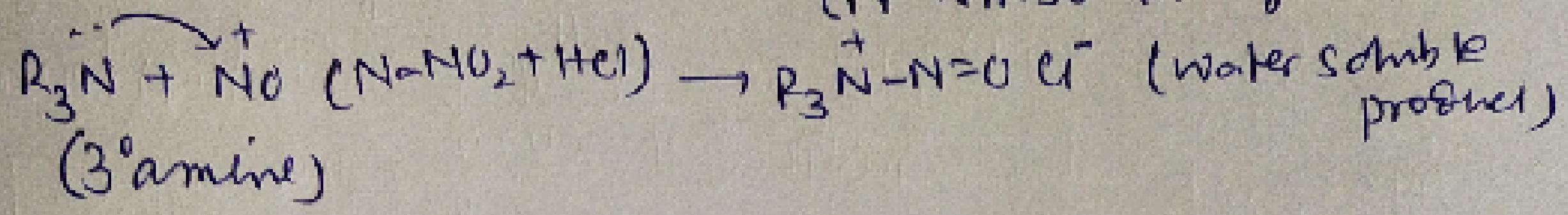
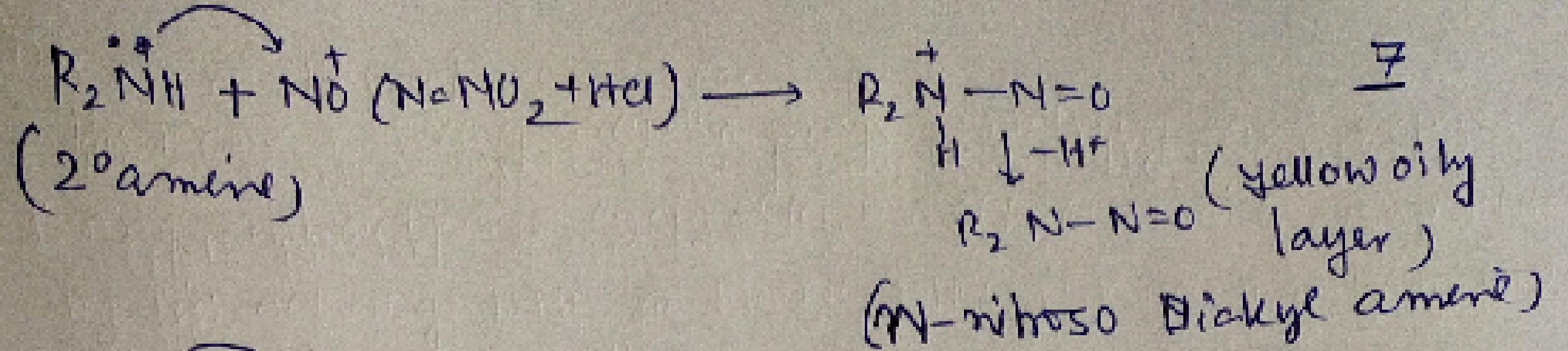
⇒ At high temp. alkene can be formed as major pdt.

⇒ At high temp. alkene can be formed as major pdt.

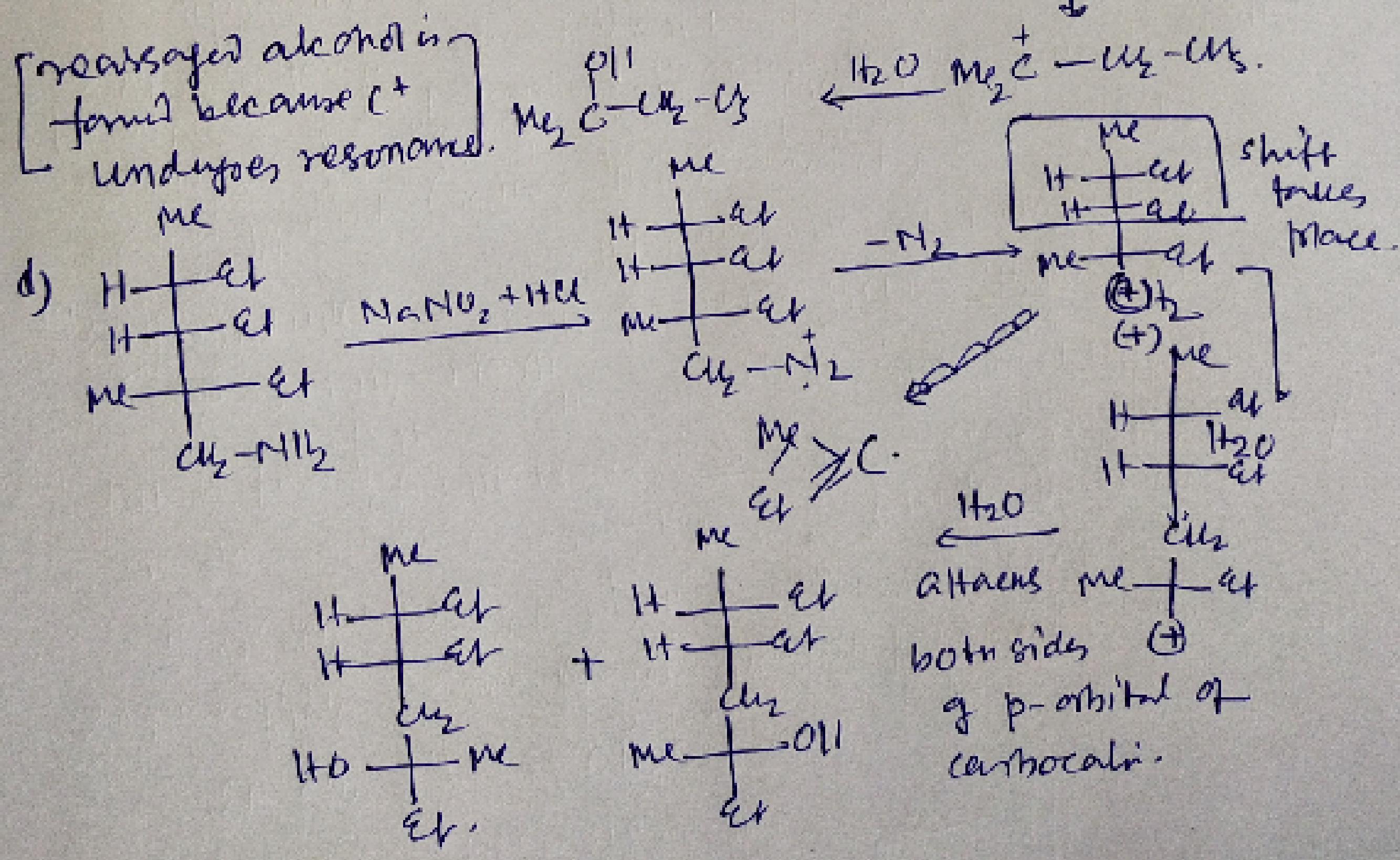
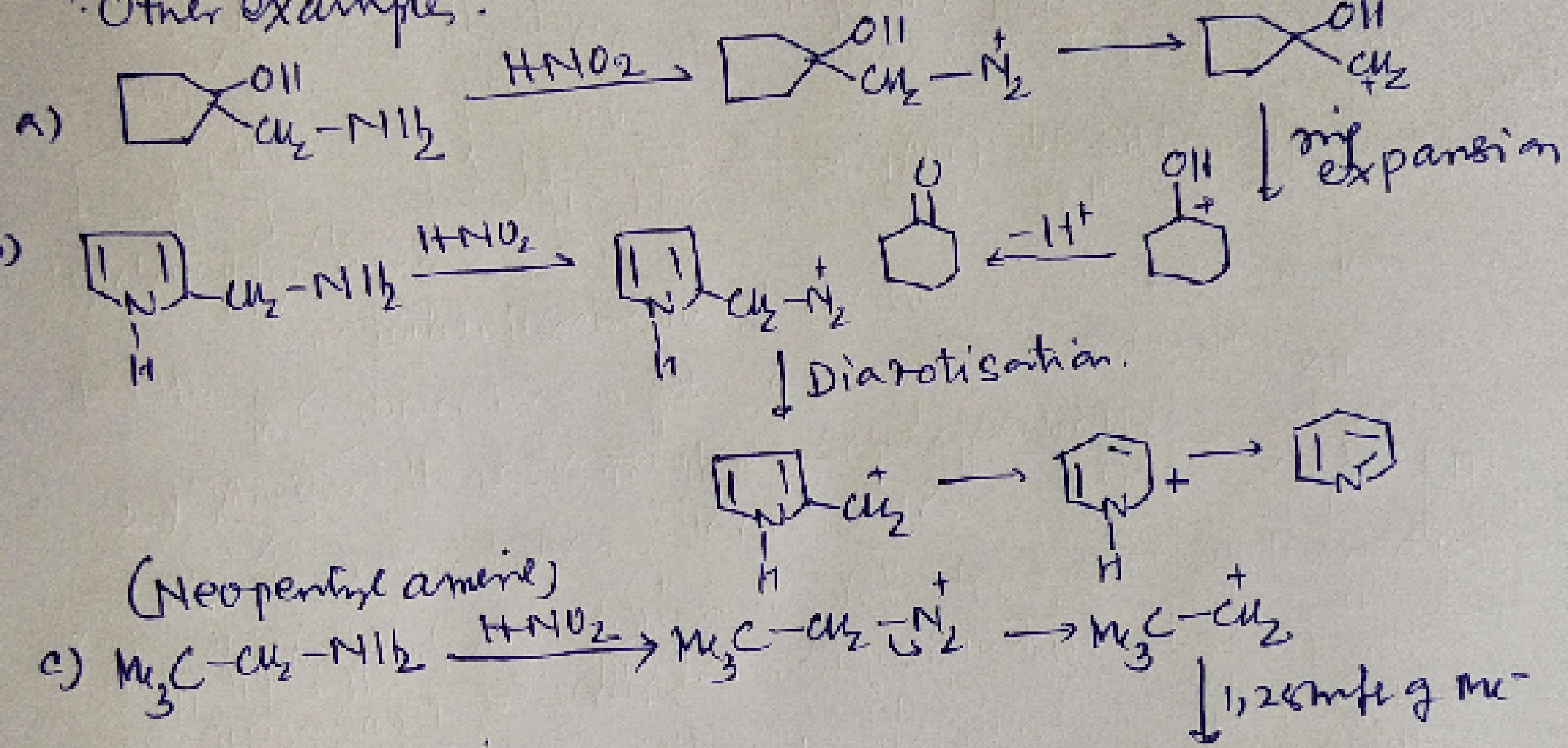
⇒ 2° amine & 3° amine with  $\text{NaNO}_2 + \text{HCl}$  give some

other product (other than alcohol).





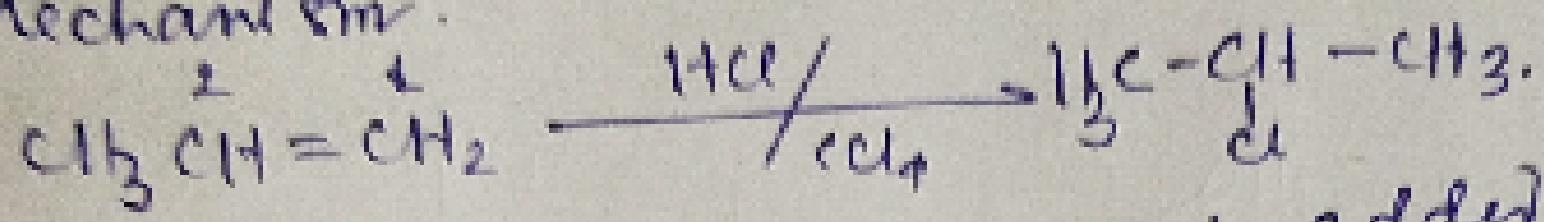
Other examples:



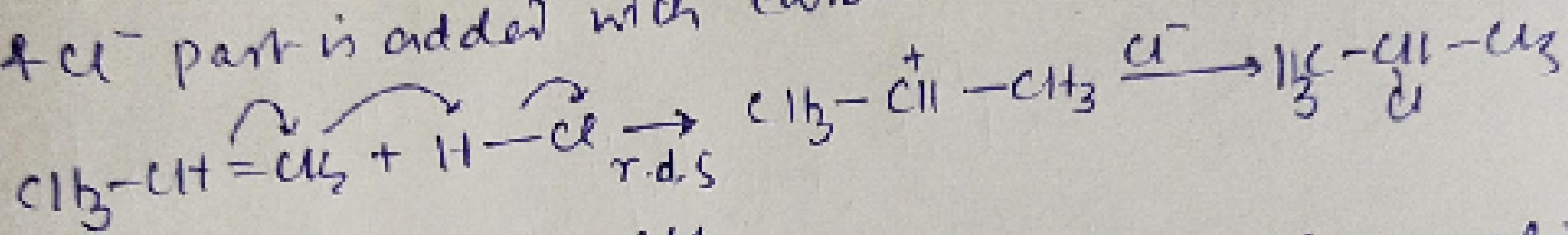
- Electrophilic addition to alkene system (EAS): 8
- Markovnikov's rule is applicable

for nonsymmetrical alkene, when electrophile of the <sup>donor</sup> addendum is added, it will be attached with carbon having more no. of hydrogen atoms directly attached.

Mechanism:



Here HCl, Electrophilic part is added with carbon no. 1.  
 $\text{Cu}^+$  part is added with carbon no. 2.



It's a 2nd step process

1st step is r.d.s., carbocation is formed as intermediate.

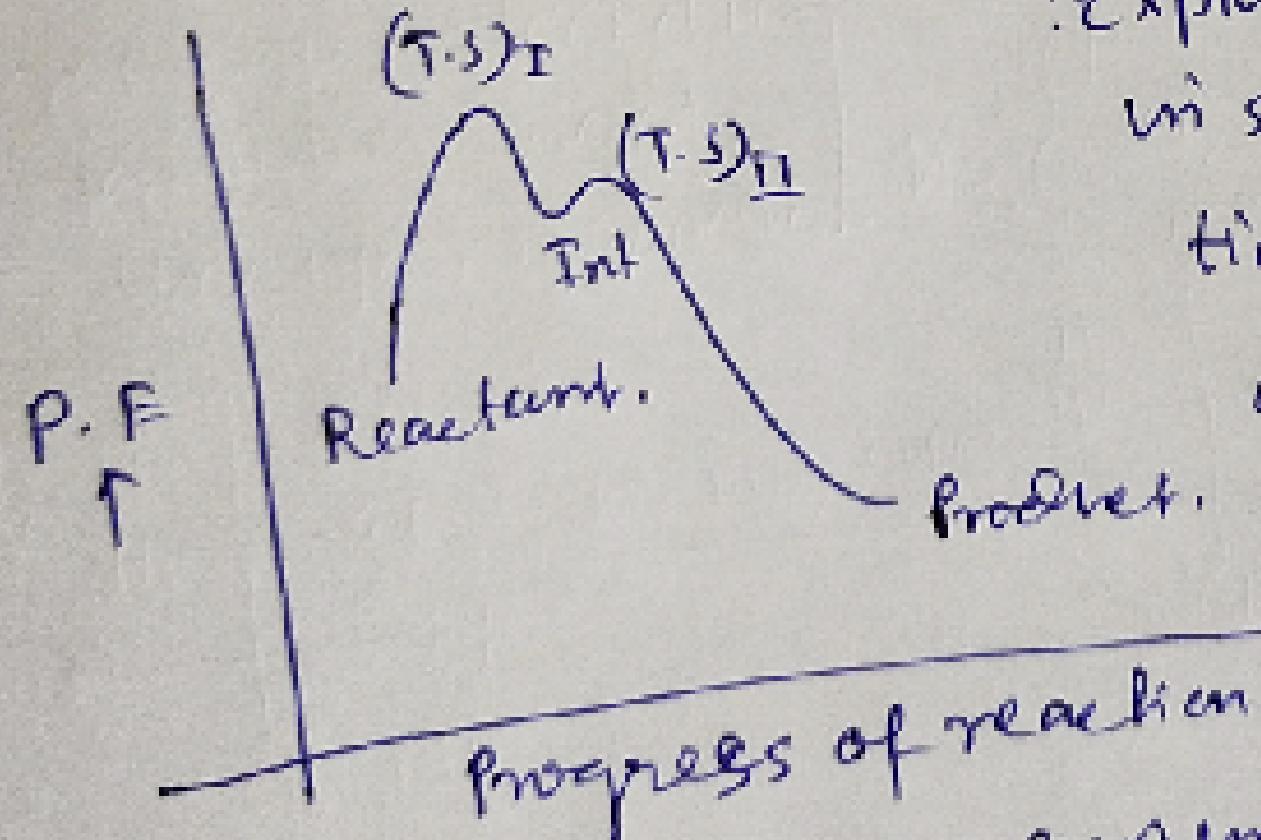
More stable carbocation, faster is the reaction.

Carbocation has a tendency to undergo rearrange-

ment when new C<sup>+</sup> is more stable than previous C<sup>+</sup>

Explanation: At first alkene reacts in such a way so that carbocation formed will be more stable.

after that it will be attacked by X<sup>-</sup> to give the product.

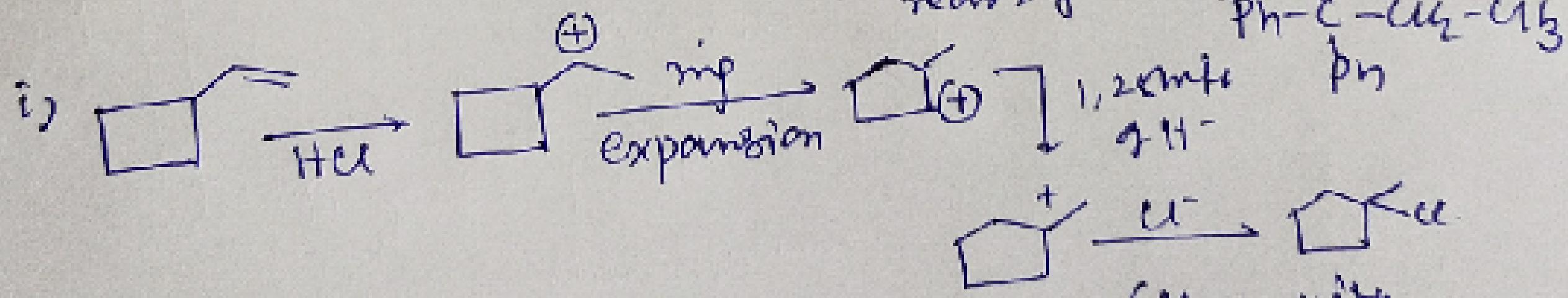
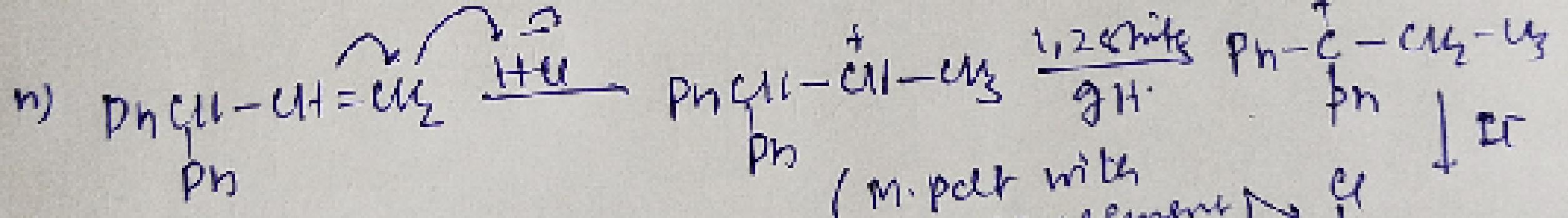
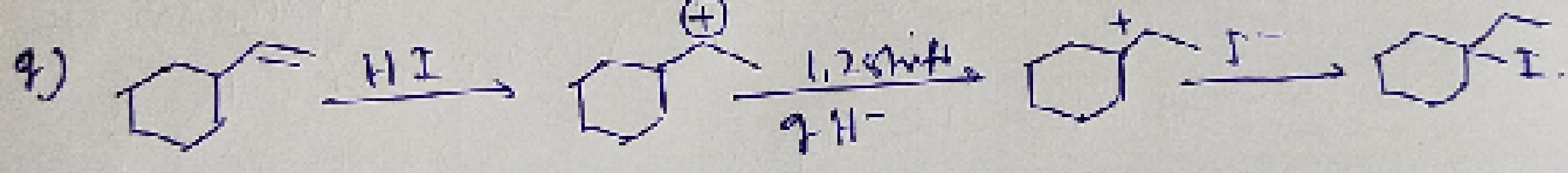
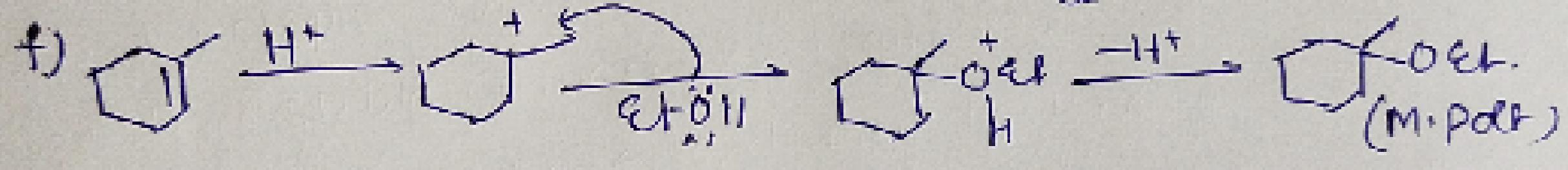
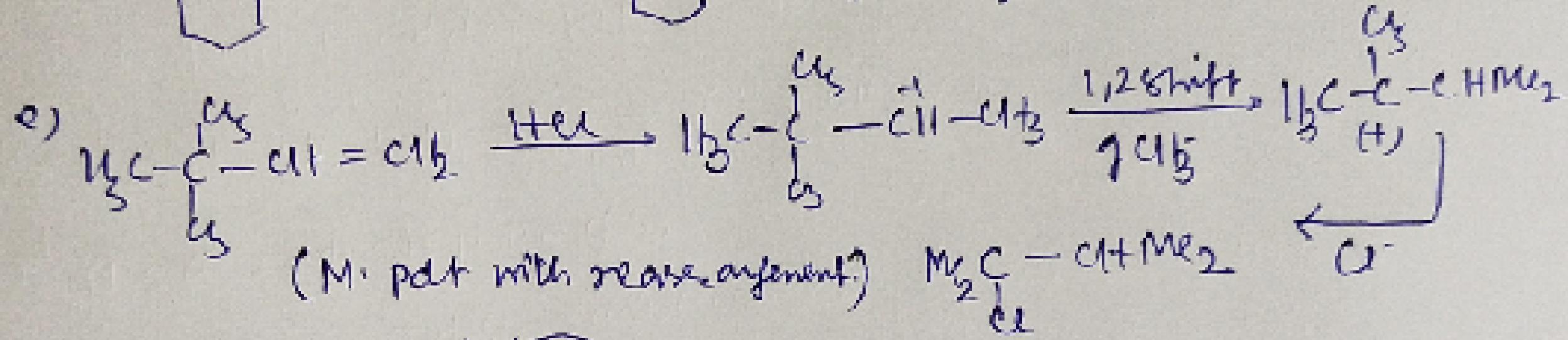
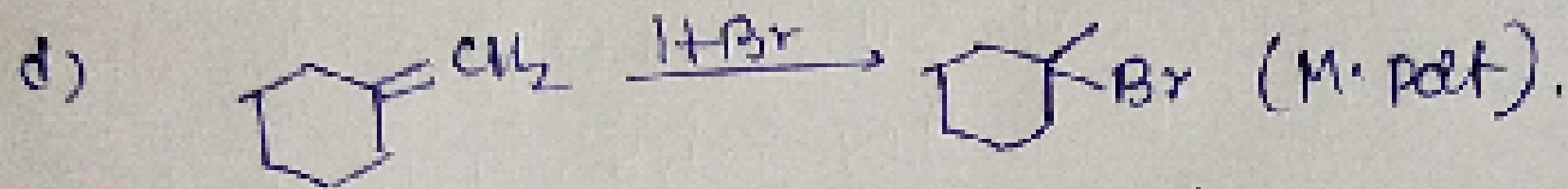
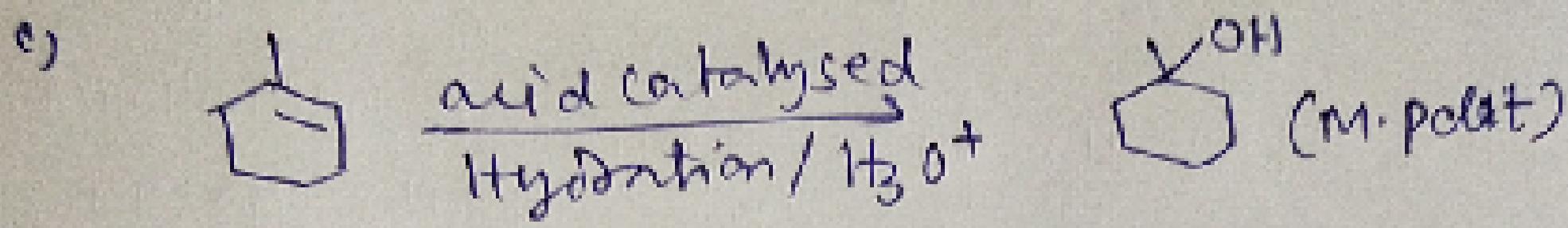
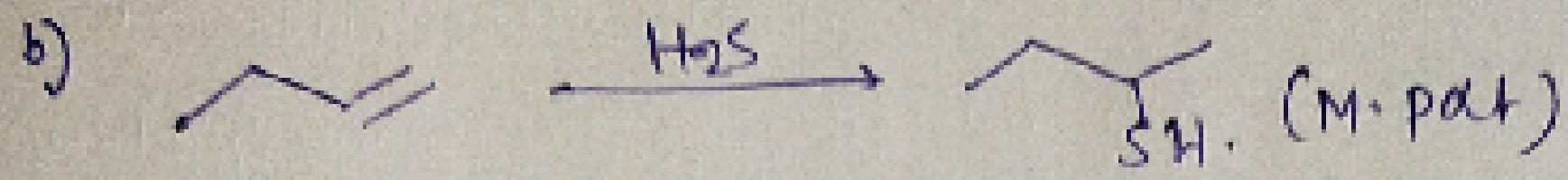
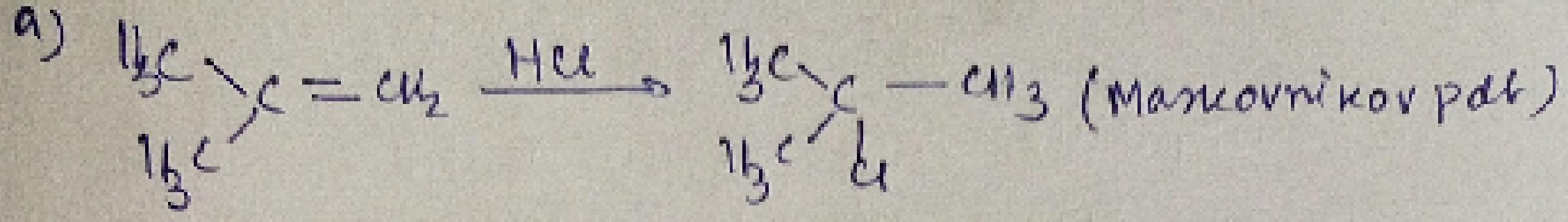


Different E-Nu system:

	E <sup>+</sup>	Nu <sup>-</sup>	H <sub>2</sub> S	H <sup>+</sup>	Nu <sup>-</sup>	H <sup>+</sup> /ROH	H <sup>+</sup>	ROH/RO <sup>-</sup>
H-X	H <sup>+</sup>	X <sup>-</sup>	dil.	H <sup>+</sup>	H <sub>2</sub> O/O <sup>-</sup>	HBr	H <sup>+</sup>	Br <sup>-</sup>
I <sub>Cl</sub>	I <sup>+</sup>	Cl <sup>-</sup>	acid	H <sup>+</sup>			Br <sub>2</sub>	Br <sup>+</sup>
NO <sub>2</sub>	NO <sup>+</sup>	Cl <sup>-</sup>	(H <sub>2</sub> O+H <sup>+</sup> )					Br <sup>-</sup>
H <sub>3</sub> O <sup>+</sup>	H <sup>+</sup>	H <sub>2</sub> O <sup>-</sup>	H <sub>2</sub> S	H <sup>+</sup>	H <sup>-</sup>	H <sub>2</sub> Br	Br <sup>+</sup>	Br <sup>-</sup> or Br <sub>2</sub> Water.

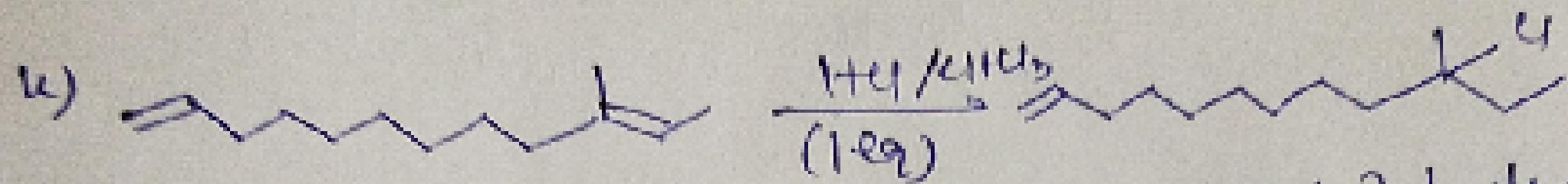
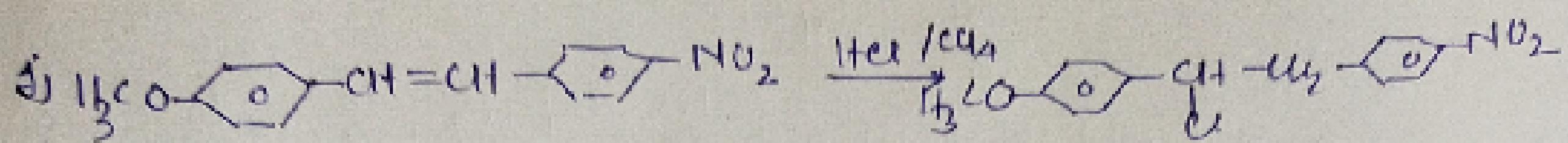
## Examples:

9

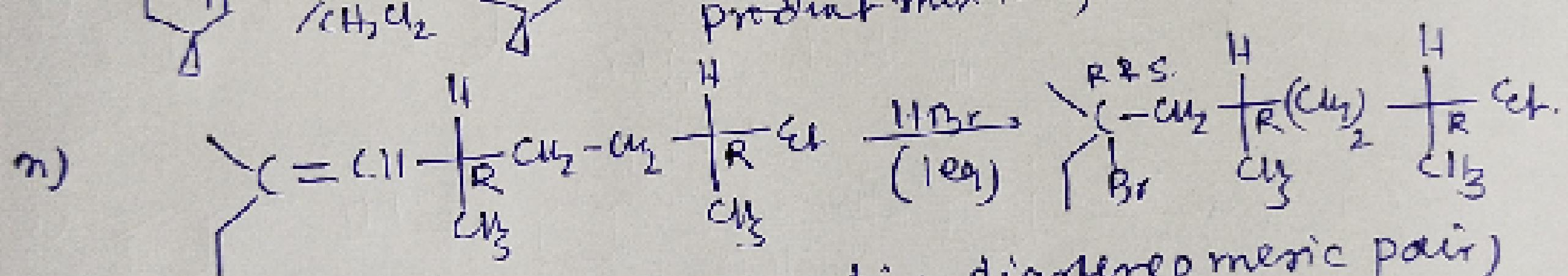
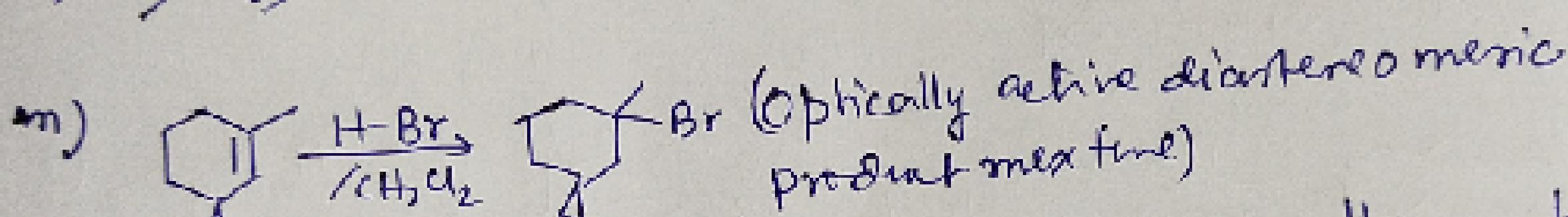
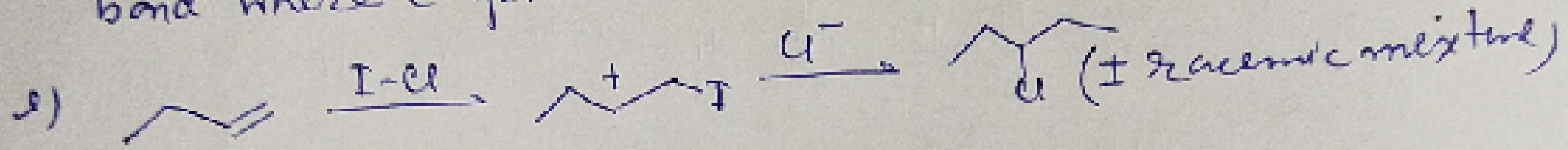


In all cases, carbocation  
is formed in such a way, it  
should be more stable. Then it  
can undergo rearrangement. At last step, nucleophile  
will react with carbocation to give neutral product.

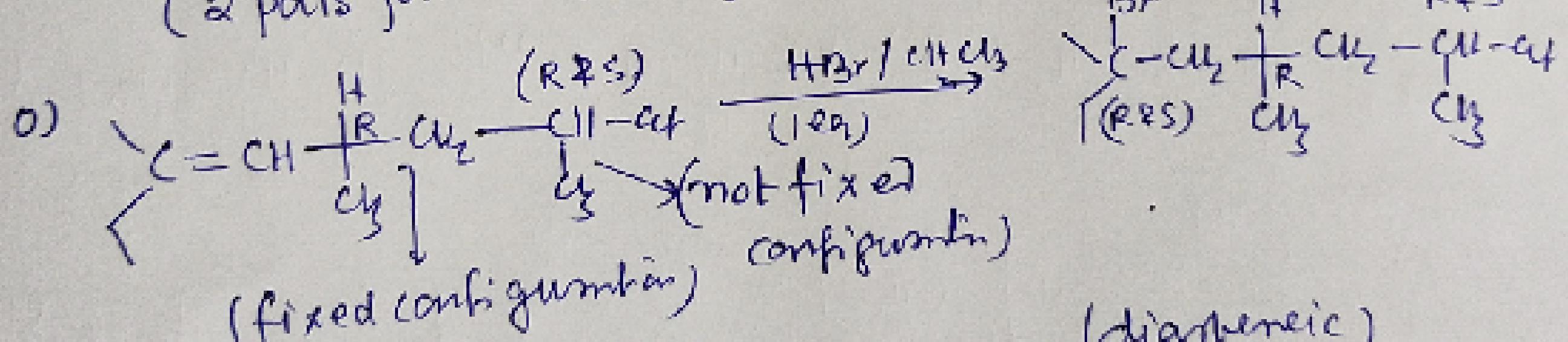
In dehydrohalogenation of alcohol, after generation of carbocation, (10) it undergoes deprotonation to stabilise it. In electrophilic addition reaction after generating carbocation it undergoes attack by nucleophile to stabilise it.



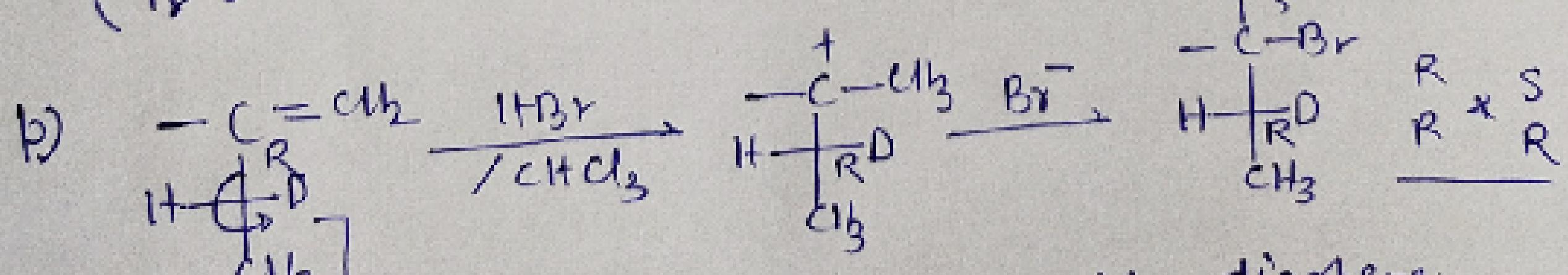
for isolated alkadiene  $H^+$  of HCl is added to that double bond where  $C^+$  formed is more stable



(2 ppts formed optically active diastereomeric pair)



(Total 4 ppts formed optically active) (diastereomeric)



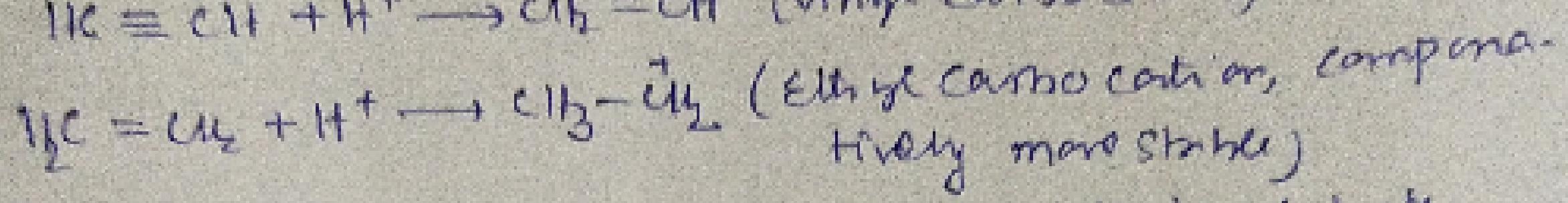
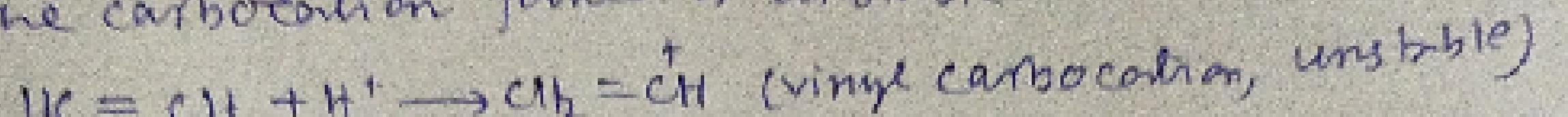
(fixed configuration) (2 optically active diastereomeric pair products one formed)

Order of reactivity of following alkene toward the  $\text{I}^+ (addition)$

$\text{CH}_2\text{Cl}_2 / \text{CHCl}_3 / \text{CH}_3$  all are used as solvent).

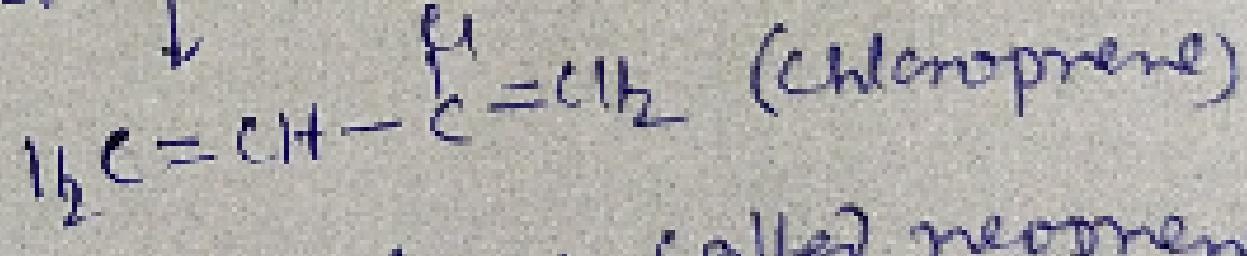
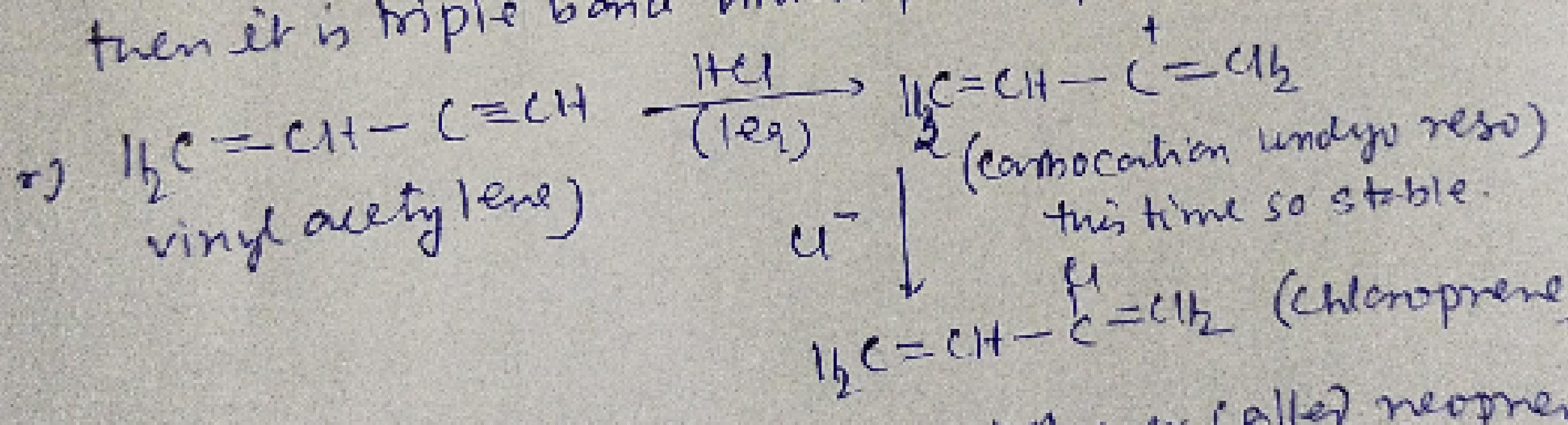


Alkyne is less reactive with respect to alkene because the carbocation formed is unstable.

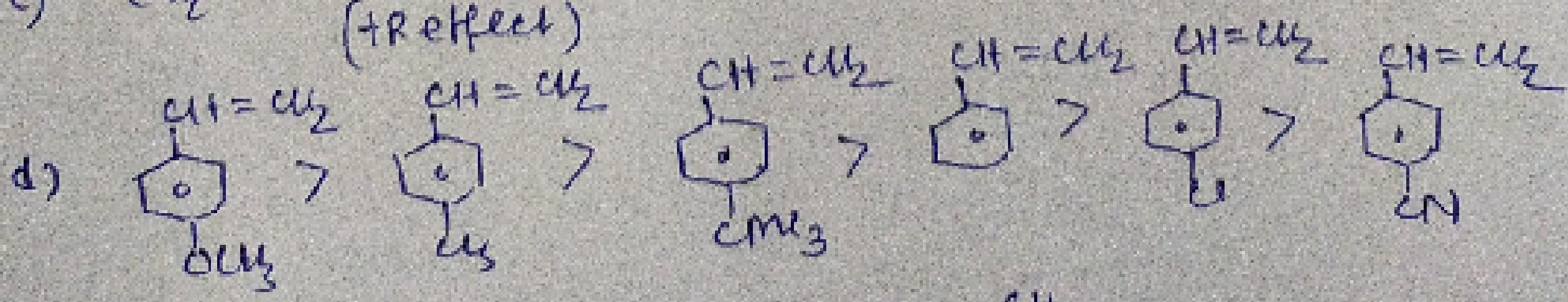
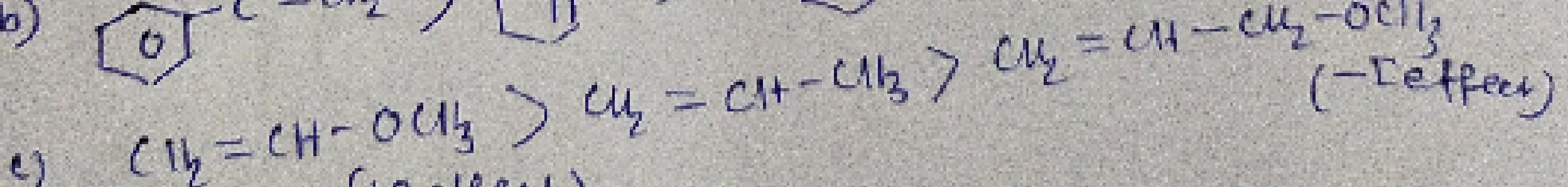
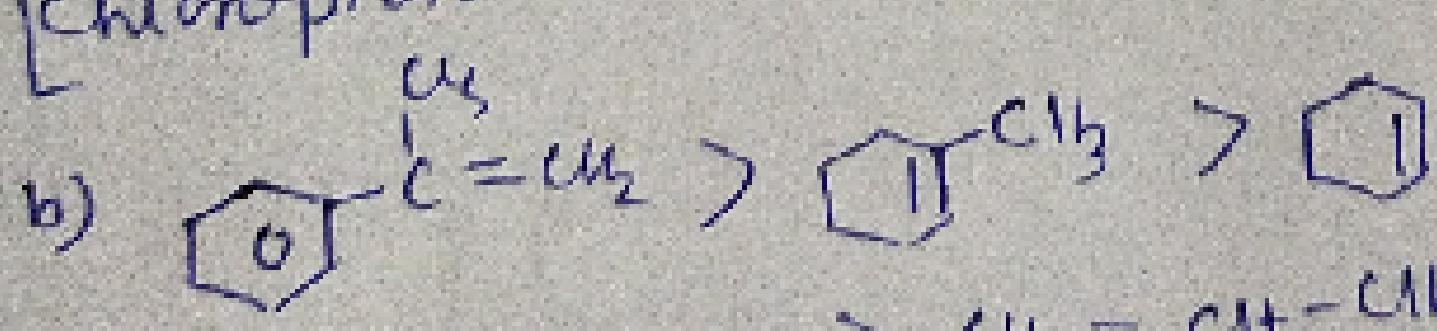


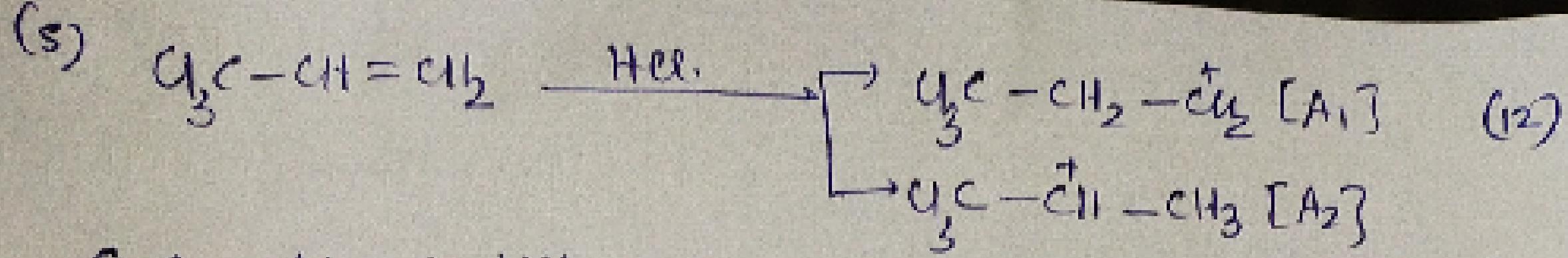
So if a system has double bond & triple bond both then towards  $\text{H}^+$  (ter), at first double bond participates in the reaction. a)  $\text{HC} \equiv \text{C}-(\text{CH}_2)_9-\text{CH}_3 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{H}^+ \text{ (ter)}} \text{H}-\text{C} \equiv \text{C}-(\text{CH}_2)_9-\overset{+}{\text{CH}}-\text{CH}_3$ .

But if triple bond is in conjugation with double bond then it is triple bond which participates in the reaction.

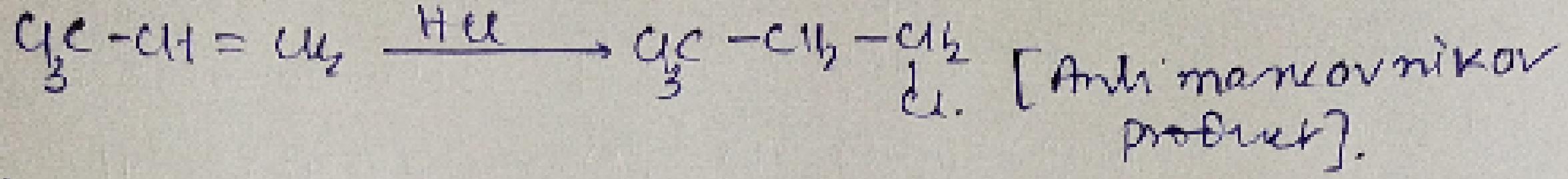


[Chloroprene is used to prepare polymer called neoprene]

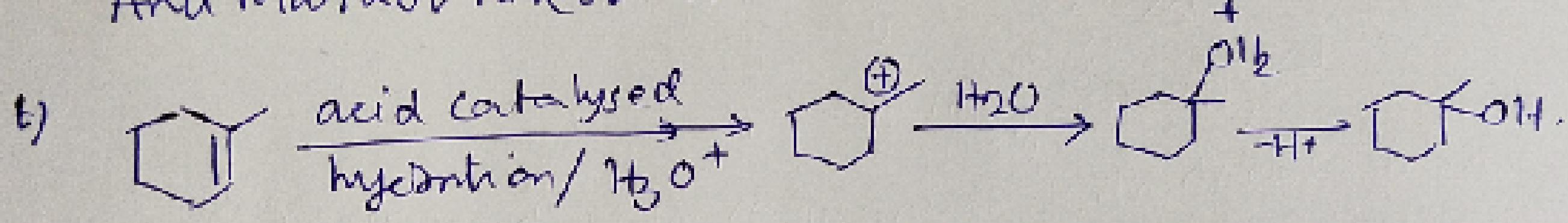




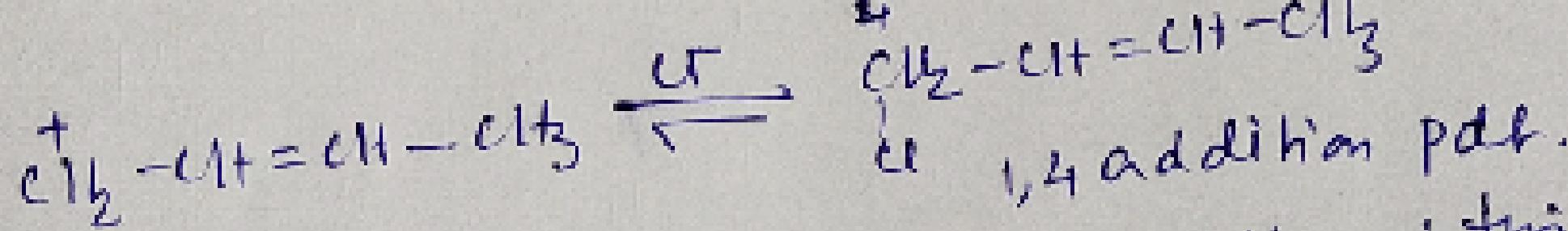
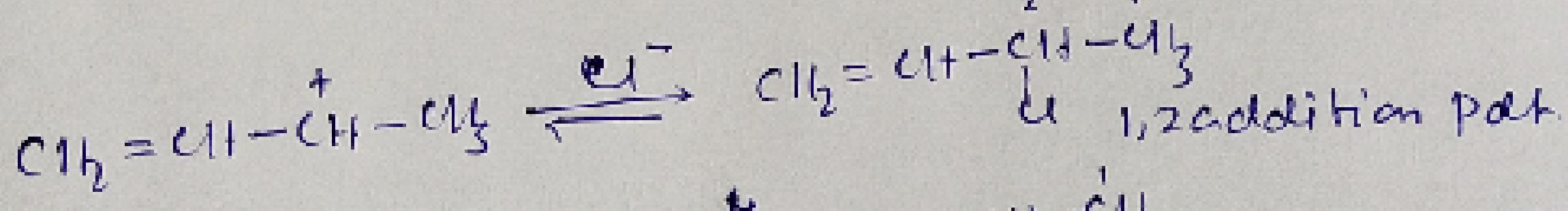
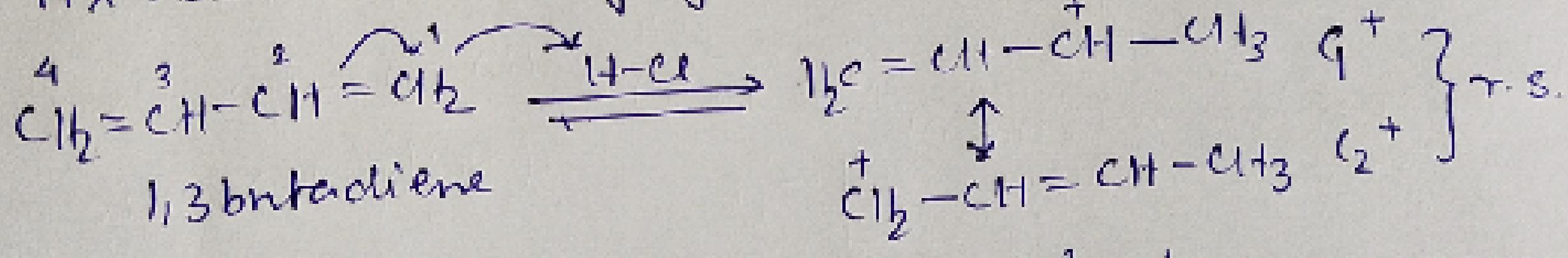
Carbocation stability order  $\text{A}_1 > \text{A}_2$  [ $\text{C}_6\text{H}_5\text{NO}_2 / -\text{CCl}_3 / -\text{CO}_2\text{Et} / -\text{CO}_2\text{H} / -\text{CN}$  having very high electron withdrawing nature  $\rightarrow \text{CCl}_3$  makes  $\text{A}_2$  unstable].



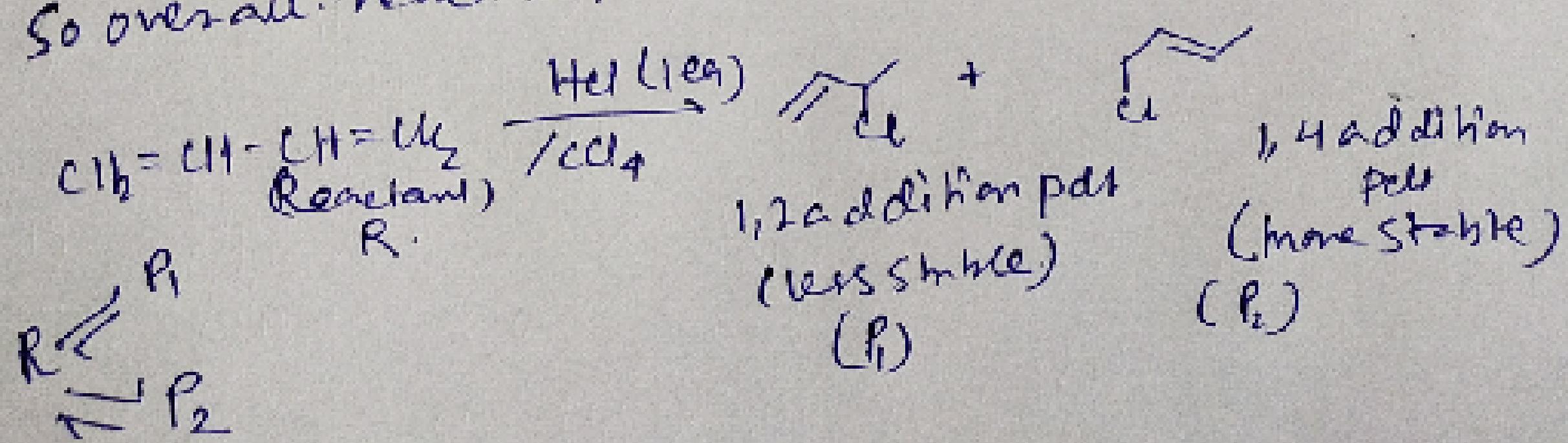
If groups like  $-\text{NO}_2 / -\text{CCl}_3 / -\text{CO}_2\text{Et} / -\text{CO}_2\text{H} / -\text{CN}$  having very high electron withdrawing nature is directly added to  $\text{C}=\text{C}$ , then  $\text{HX} / \text{E-Na}$  addition does not follow Markovnikov Rule. Product obtained is called Anti-Markovnikov product.

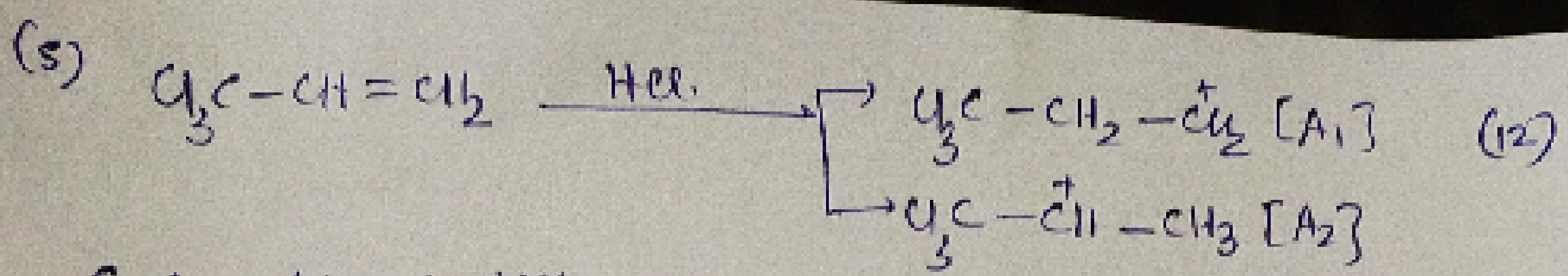


$\text{HX}$  addition to conjugated alkadiene:

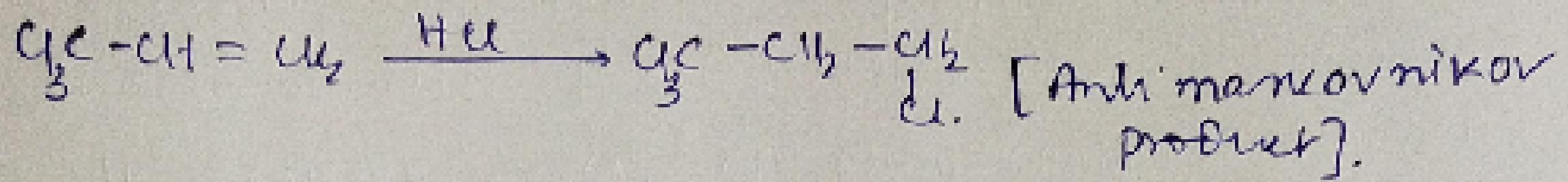


So overall reaction / pdt will be written in this way

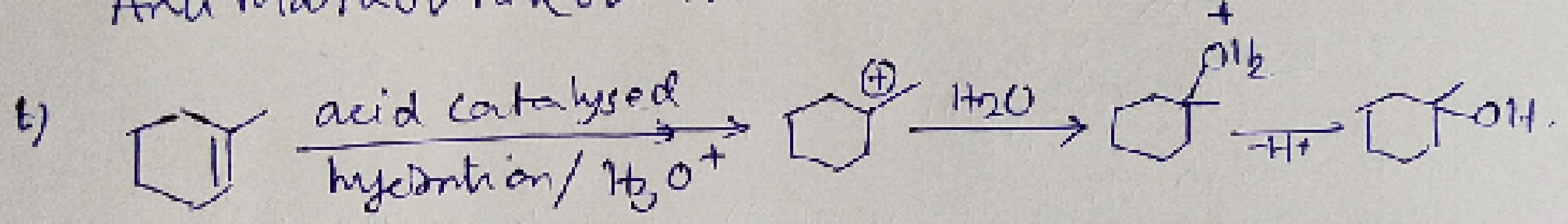




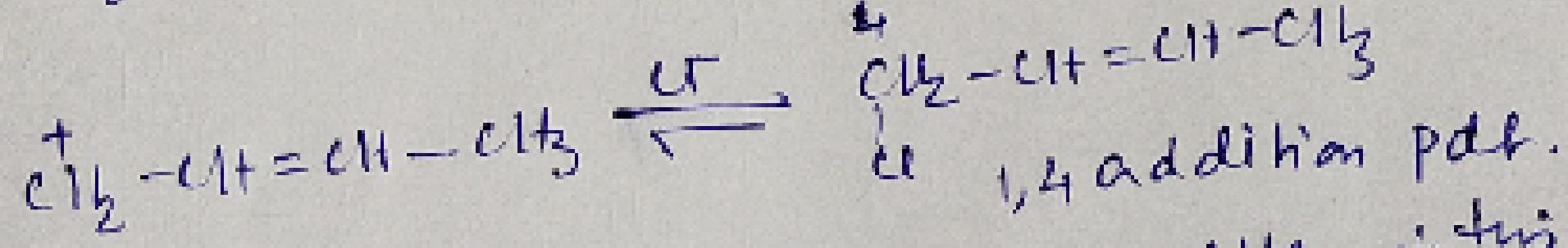
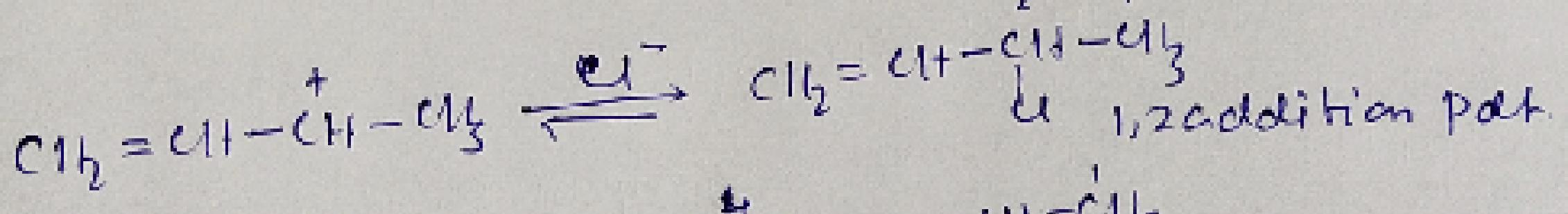
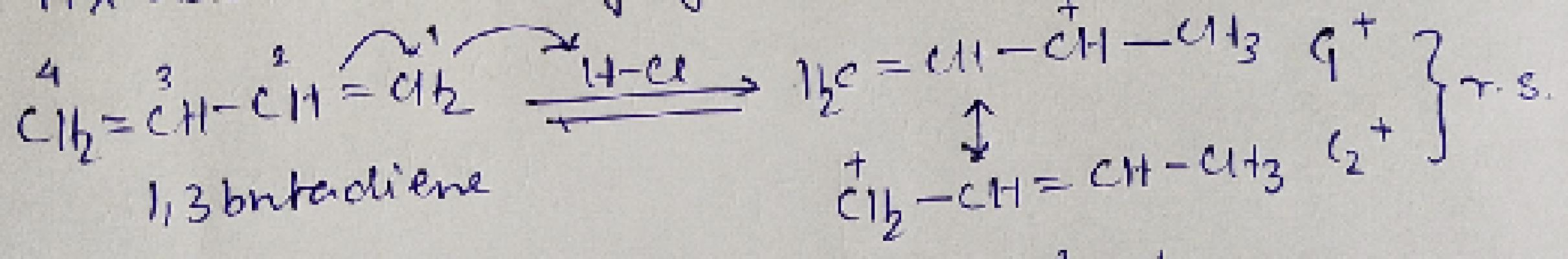
Carbocation stability order  $\text{A}_1 > \text{A}_2$  [  $\delta$  withdrawing nature of  $\text{Cl}_3$  makes  $\text{A}_2$  unstable].



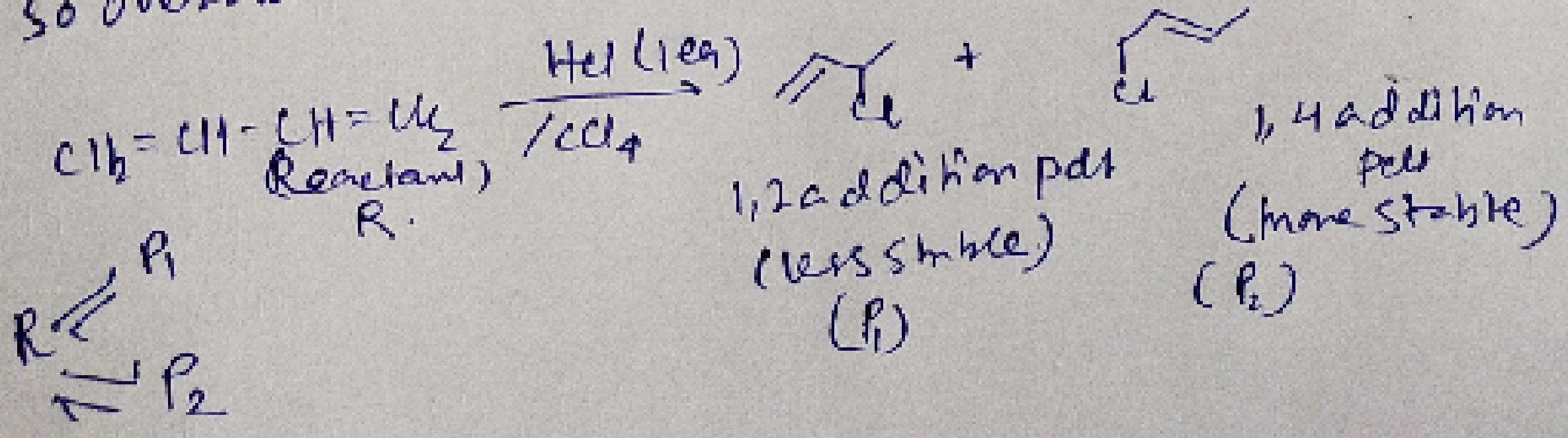
If groups like  $-\text{NO}_2 / -\text{CO}_2\text{Et} / -\text{CO}_2\text{H} / -\text{CN}$  having very high electron withdrawing nature is directly added to  $\text{C}=\text{C}$ , then  $\text{HX} / \text{E-Na}$  addition does not follow Markovnikov Rule. Product obtained is called Anti-Markovnikov product.



$\text{HX}$  addition to conjugated alkadiene:



So overall reaction / pdt will be written in this way



$P_1$  is called kinetically controlled prod. (KCP) (B)

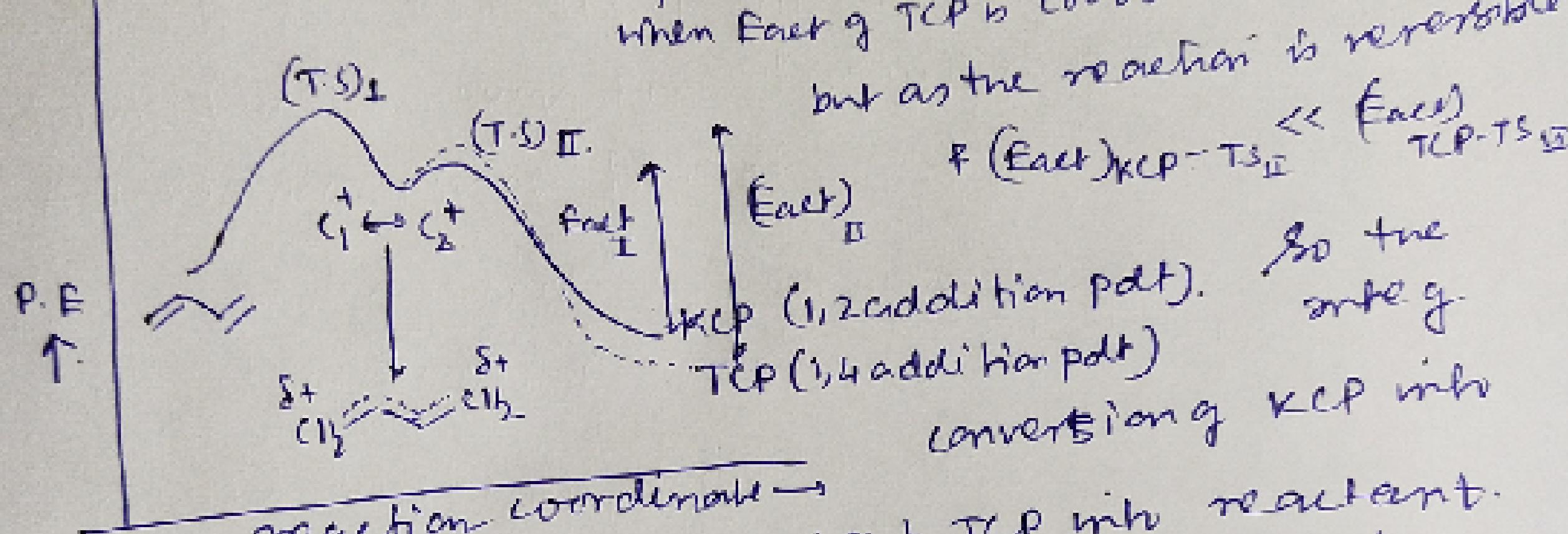
$P_2$  is called thermodynamically controlled prod (TCP)

$P_1$  is formed as major product at very low temp ( $-80^\circ\text{C}$  to  $0^\circ\text{C}$ )

$P_2$  is formed as major product at room temp/ high temp ( $20^\circ\text{C}$  -  $50^\circ\text{C}$ ).

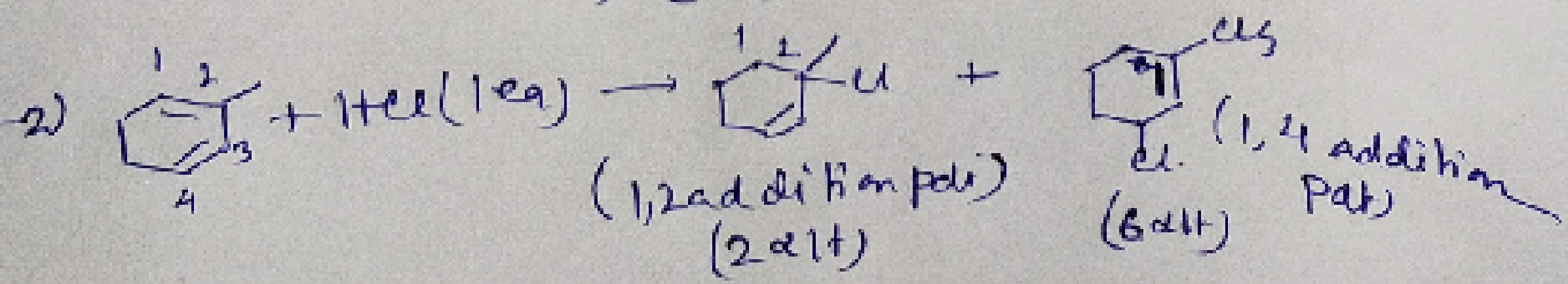
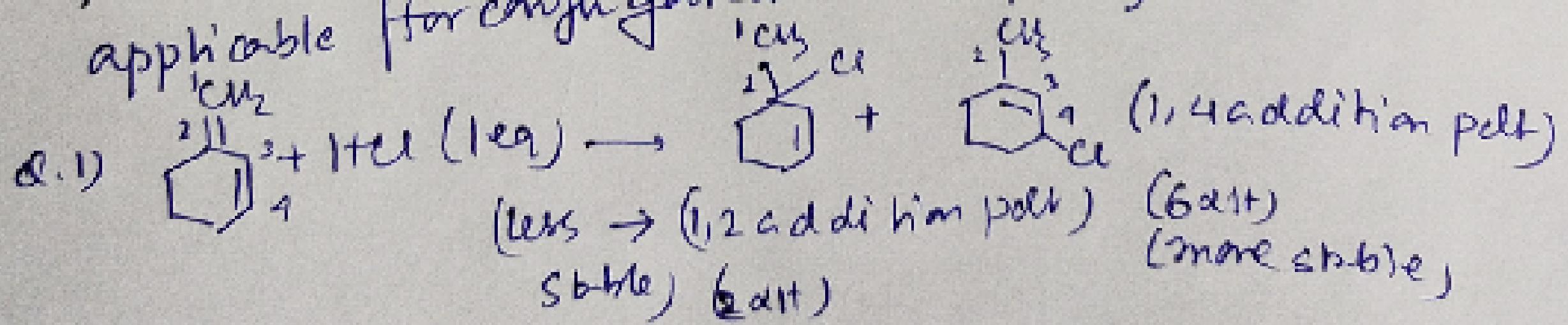
$P_1$  is formed at faster rate so its formation is kinetically governed whereas  $P_2$  is more stable so its formation is thermodynamically governed.

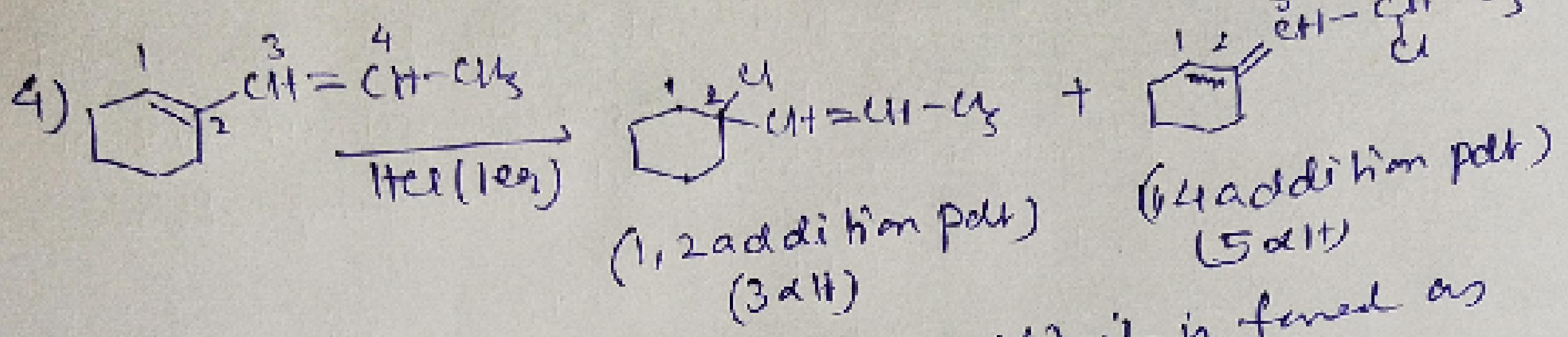
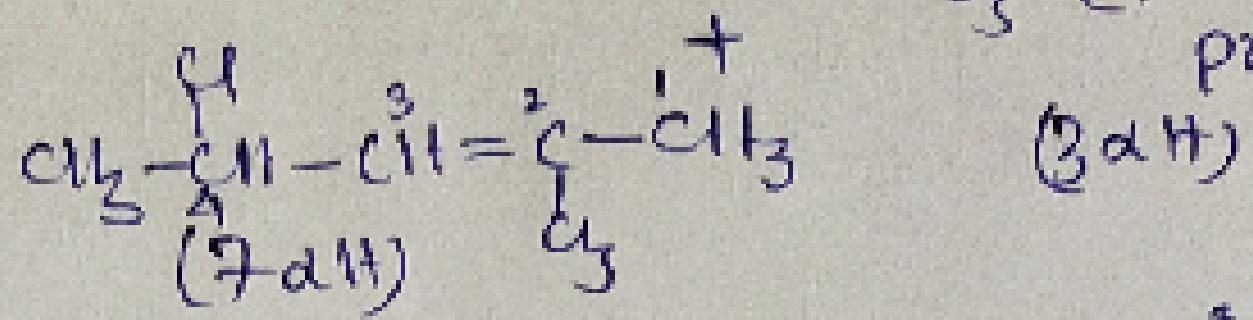
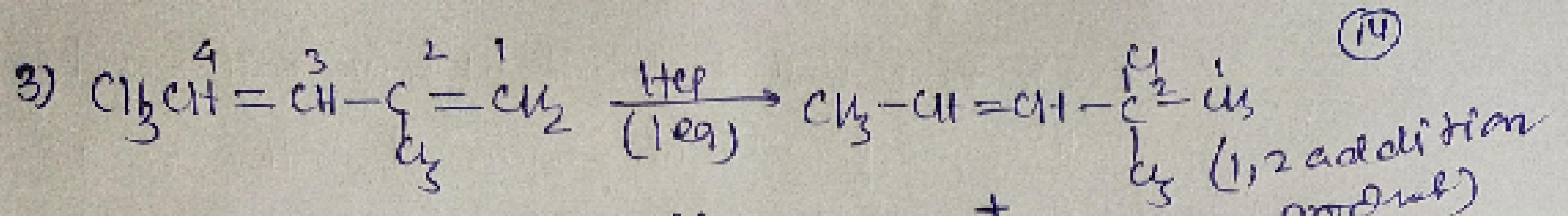
: Energy diagram: At low temp the Ea<sub>act</sub> of KCP is crossed it is formed at faster rate, but a high temp when Ea<sub>act</sub> of TCP is crossed it starts fast but as the reaction is reversible



reactant is much more w.r.t TCP with reactant. So at high temp TCP is accumulated & it becomes the major product. This KCP & TCP concept is applicable when reaction is reversible. If reaction is irreversible then always KCP becomes major product.

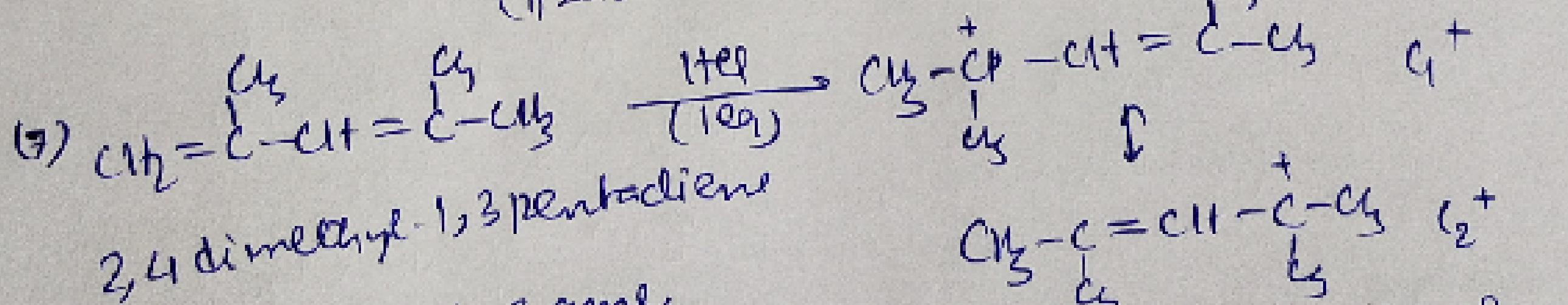
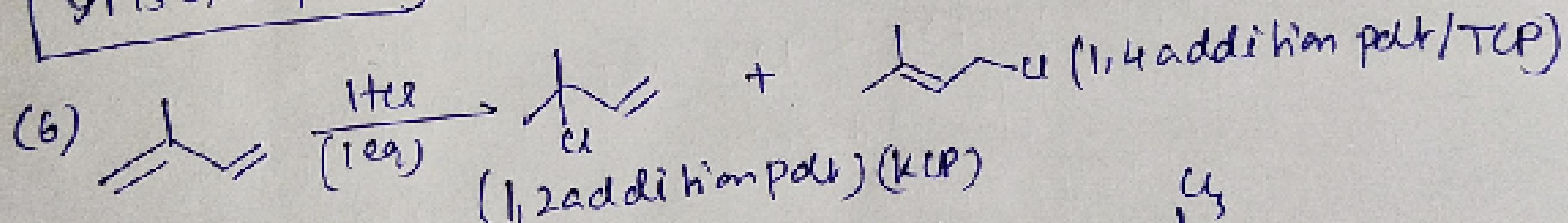
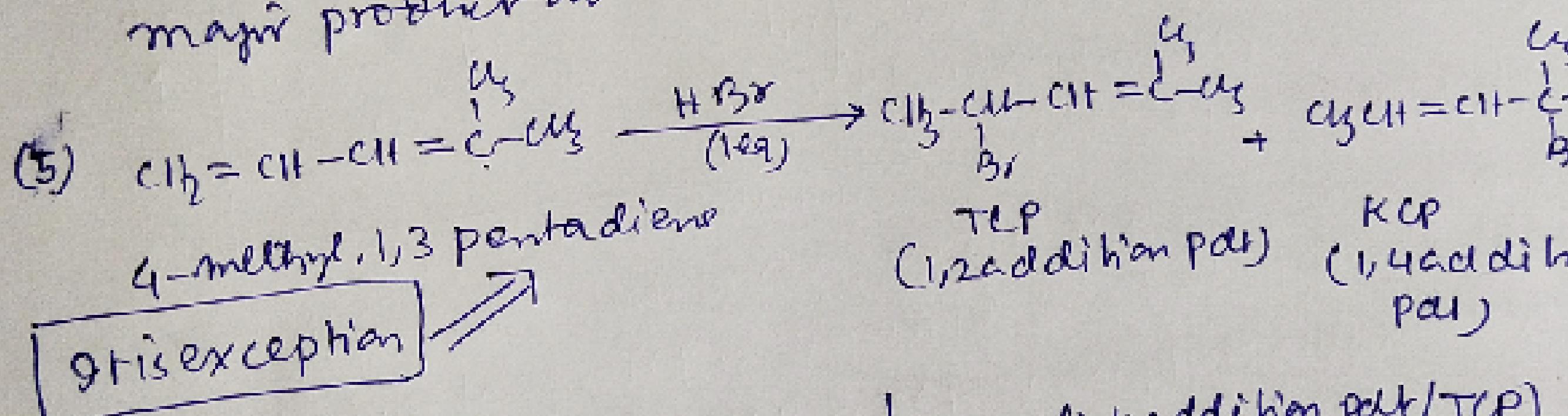
Some other examples where KCP & TCP concept is applicable (for conjugated alkadiene).





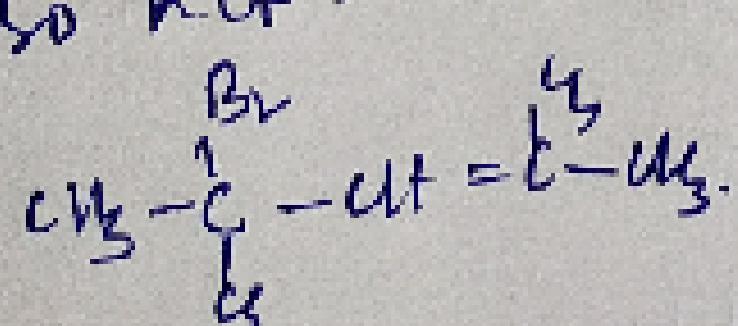
In every case KCP (1,2 addition pdt), it is found as major product at very low temp ( $0^\circ\text{C} \text{ to } -80^\circ\text{C}$ ).

In every case TCP (1,4 addition pdt), it is found as major product at high temperature ( $25^\circ\text{C} \text{ to } 40^\circ\text{C}$ ).



As both R.S is same.

so KCP = TCP (no KCP, not TCP pdt). only 1 pdt



$\boxed{it \text{ is exception}}$