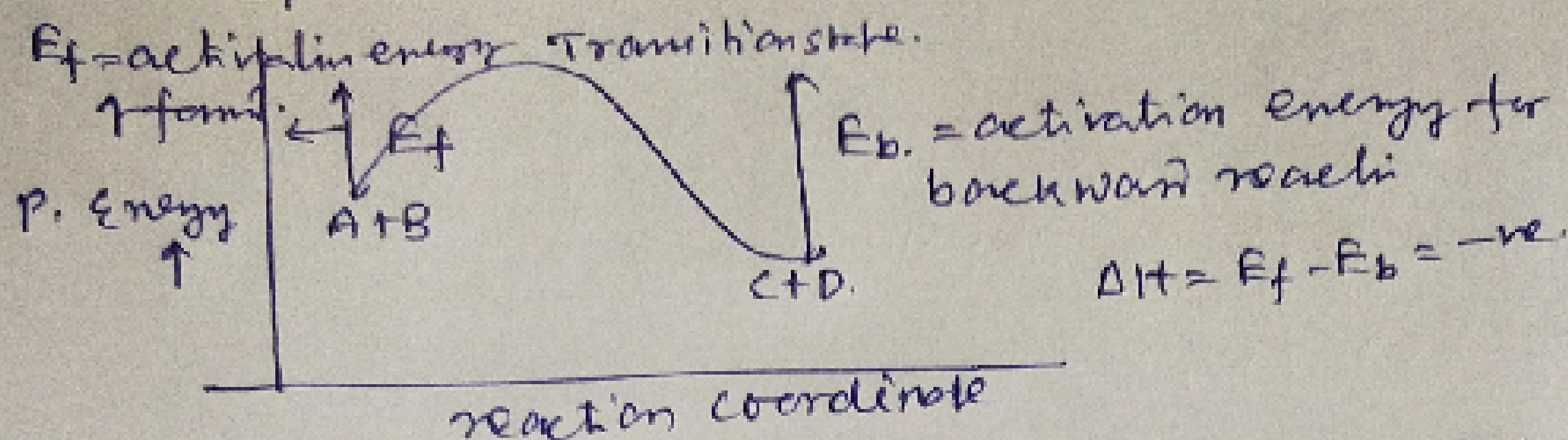
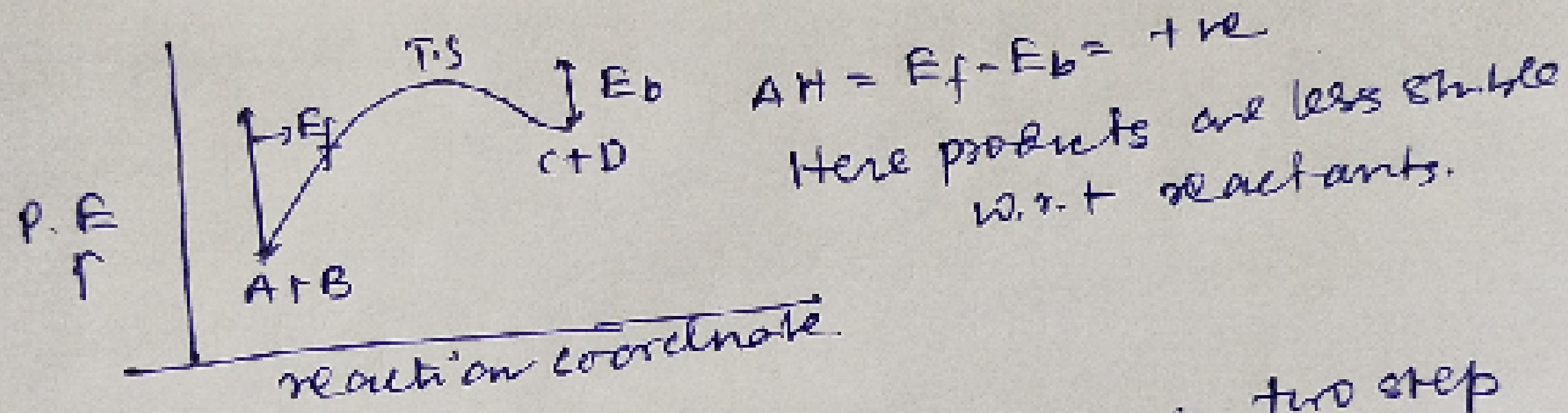


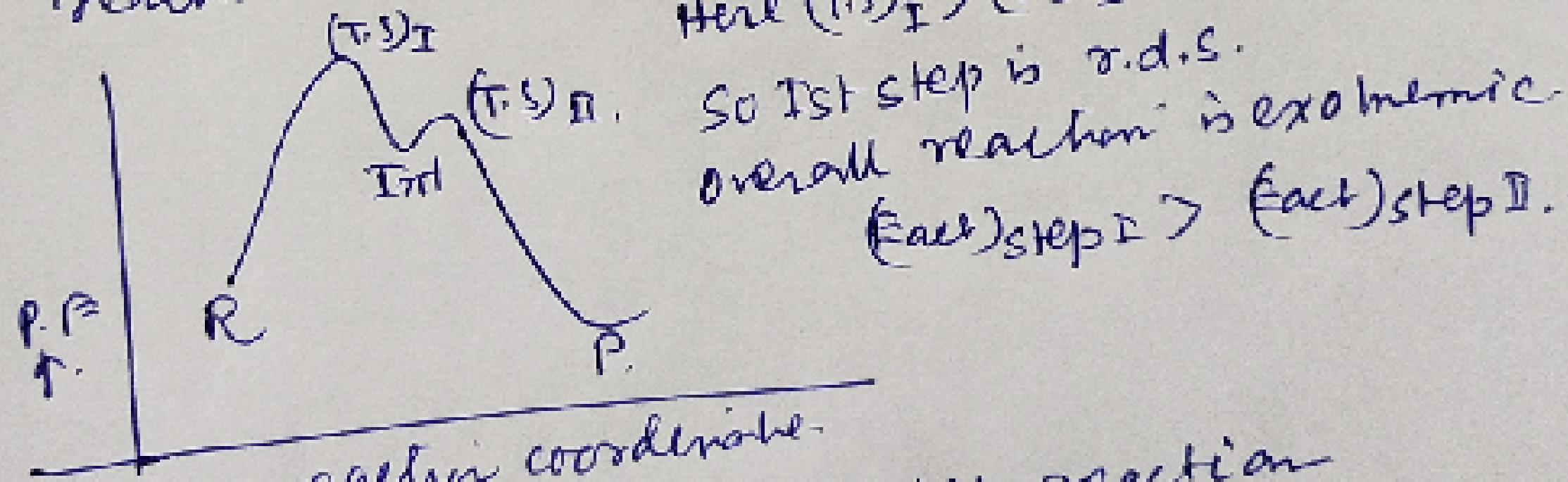
(I) Energy diagram for a reversible one step exothermic reaction $A + B \rightarrow C + D$. ①



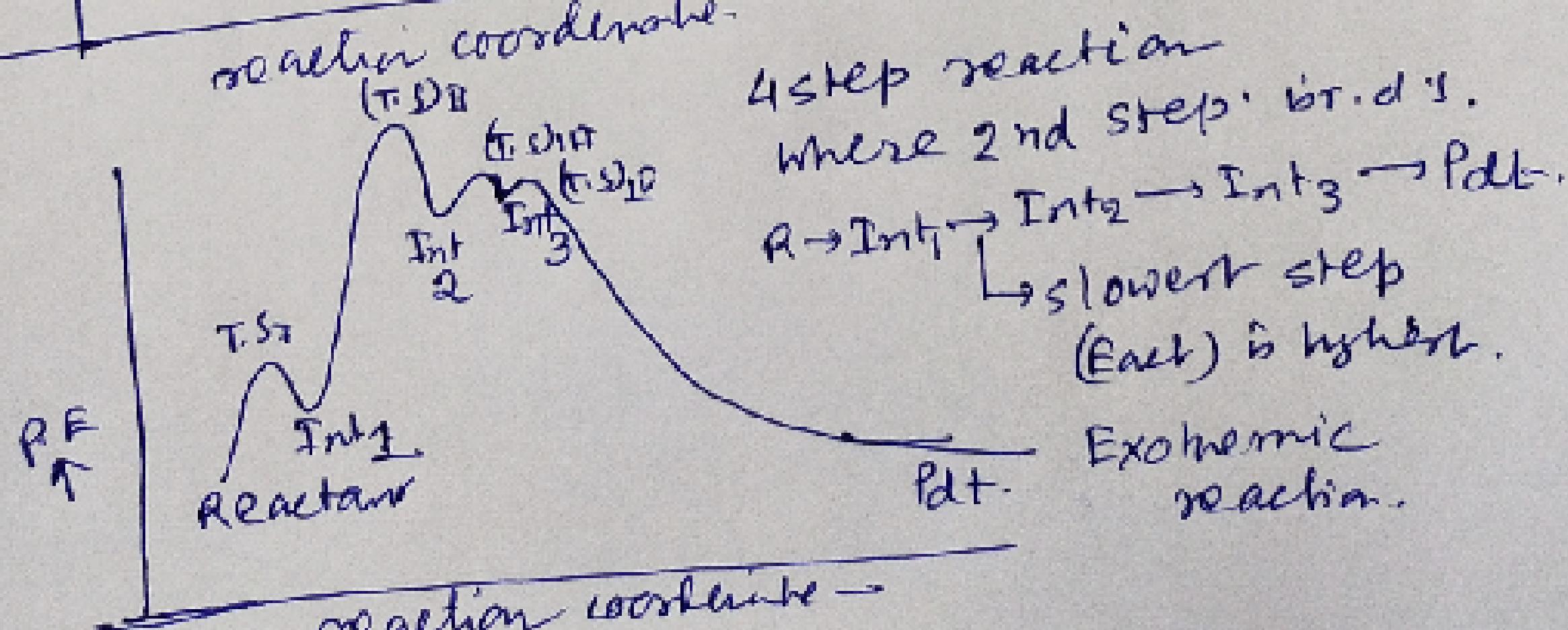
(II) Energy diagram for a reversible one step endothermic reaction. $A + B \rightarrow C + D$.



(III) Energy diagram for an exothermic two step reaction where 1st step is slow (rate determining)



(IV)

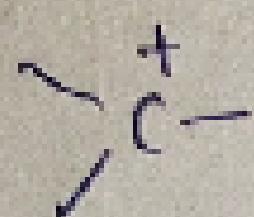


(2)

Reaction involving carbocation.

Carbocation

Reactions:



reaction intermediate.

formal charge: +1 Octet incomplete

No. of bonds: 3. very unstable.

No. of lone pair: 1. Electron deficient

Hybrid orbital number: 3.

Hybrid orbital type: sp^2

shape: Trigonal planar.

Properties:

- i) Carbocation has a tendency to undergo rearrangement provided new carbocation is more stable w.r.t previous carbocation. This is achieved by following way

a) 1,2 shift of alkyl / H⁺ ion

b) Ring expansion c) Ring contraction.

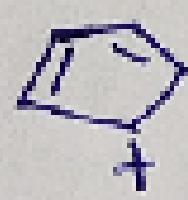
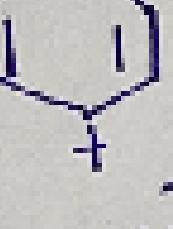
ii) Stability of carbocation:

a) $\text{CH}_3^+ > \text{C}_2\text{H}_5^+ > \text{C}_3\text{H}_7^+ > \text{C}_4\text{H}_9^+$

$\text{CH}_3^+ > \text{C}_2\text{H}_5^+ > \text{C}_3\text{H}_7^+ > \text{C}_4\text{H}_9^+$
2p-2p 2p-3p 2p-4p
overlap.

b) $\text{CH}_2-\text{CH}_3^+ > \text{CH}_2=\text{CH}^+ > \text{H}(\equiv \text{C})^+$

c) $\text{Ph}_3\text{C}^+ > \text{Ph}_2\text{CH}^+ > \text{PhCH}_2^+$

d)  <  <  [Tropylium ion is more stable than triethyl carbocation].

e) $\text{CH}_3^+ > \text{CH}_2-\text{OH}^+ > \text{CH}_2-\text{Cl}^+ > \text{CH}_2-\text{C}_2\text{H}_5^+ > \text{CH}_2-\text{C}_3\text{H}_7^+$

f)  >  > 

g)  < $\text{CH}_2=\text{CH}^+$ < $\text{CH}_3-\text{C}(=\text{O})^+$ $\leftrightarrow \text{CH}_3-\text{C}(=\text{O})^+$
very unstable octet complete.

z) Carbocation acts as diamagnetic

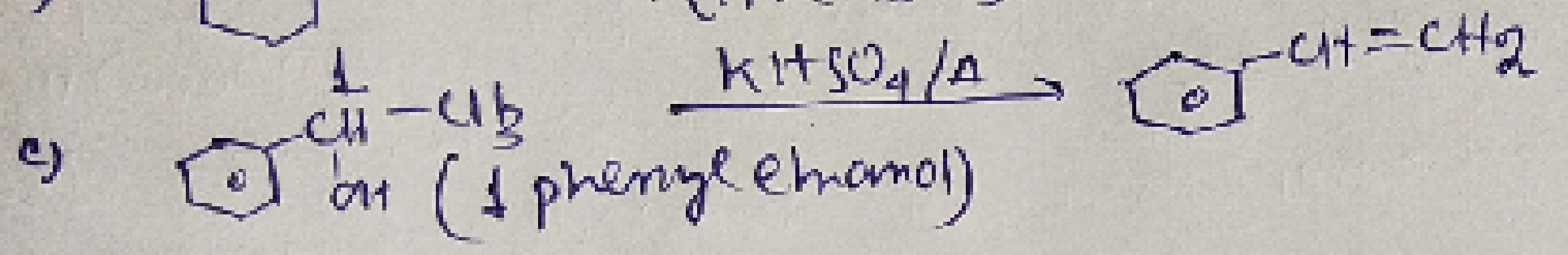
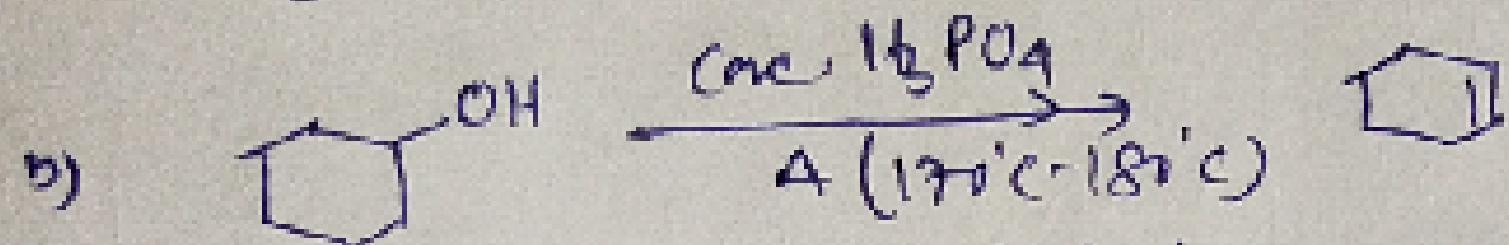
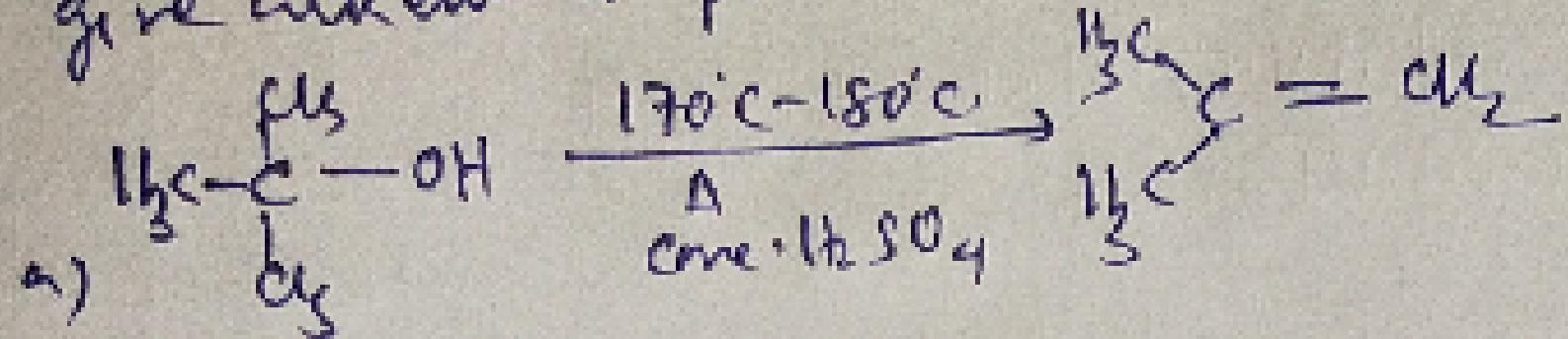
z) Carbocation is formed by heterolytic bond cleavage

z) It reacts with nucleophile.

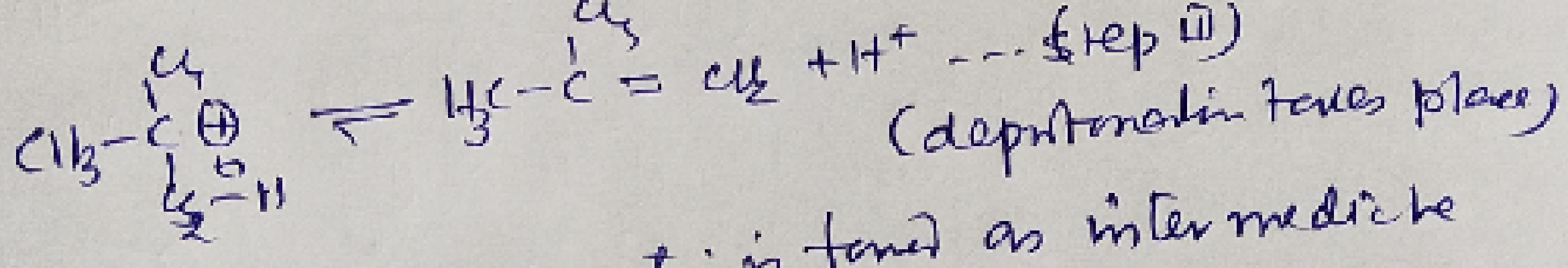
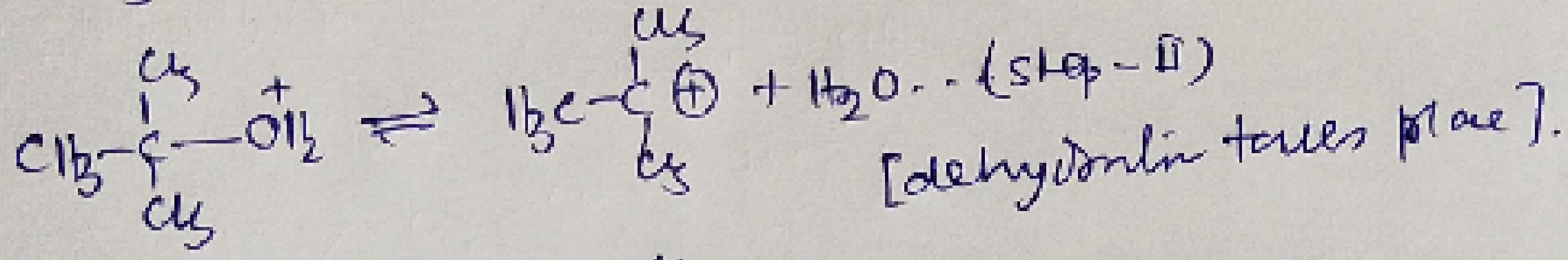
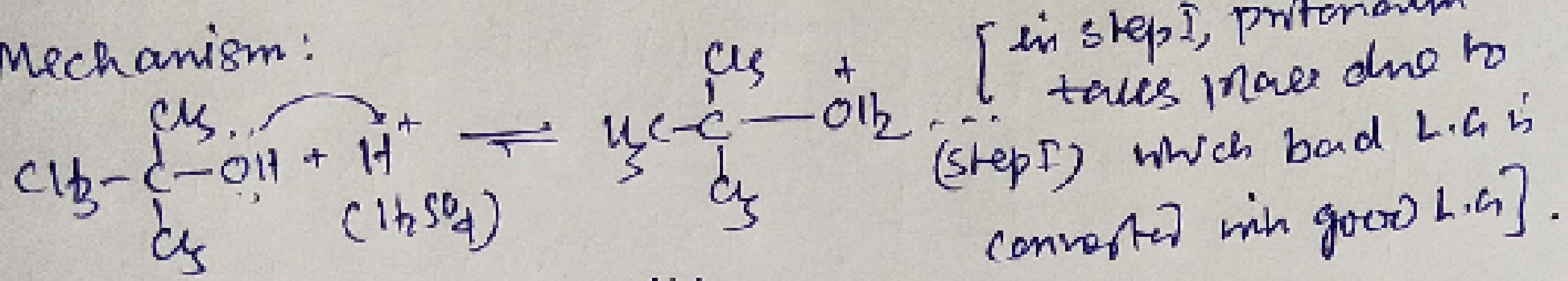
(2)

Dehydration of Alcohol: (Acid Catalysed)

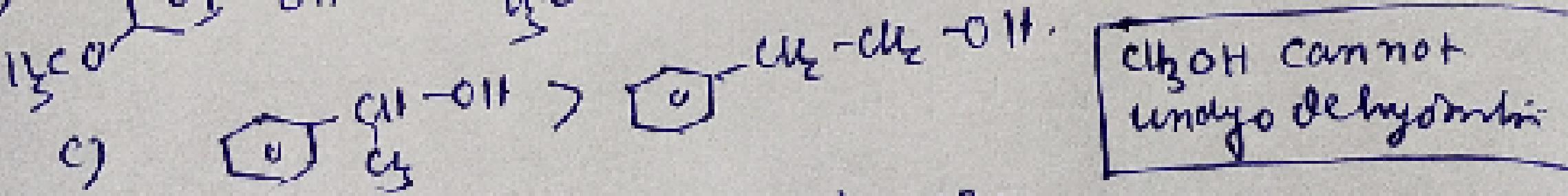
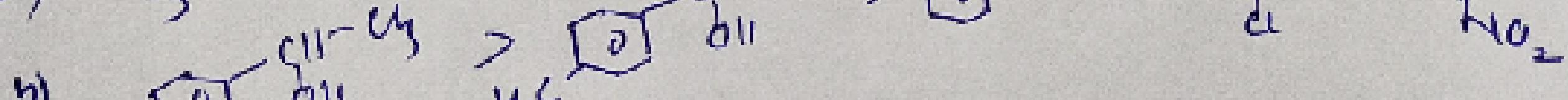
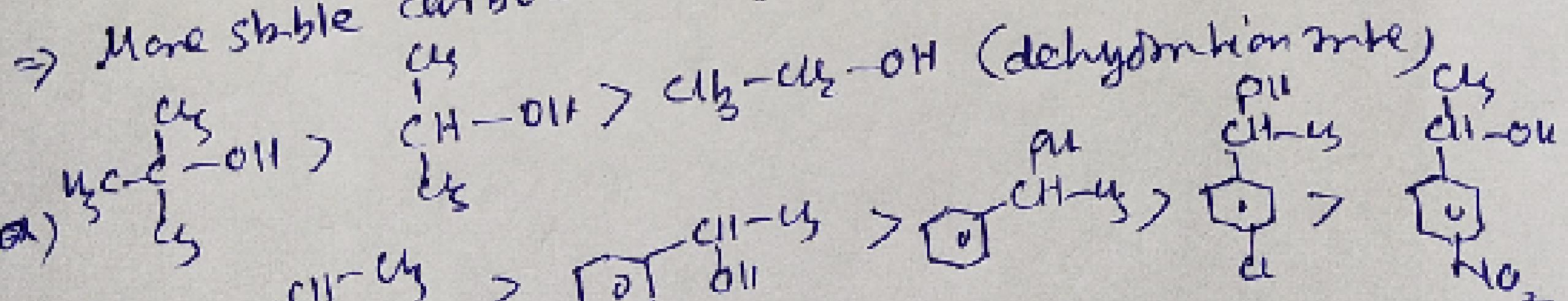
Alcohols in presence of conc. H_2SO_4 / KHSO_4 / conc. H_3PO_4 at high temperature undergoes elimination reaction to give alkene as product.



Mechanism:



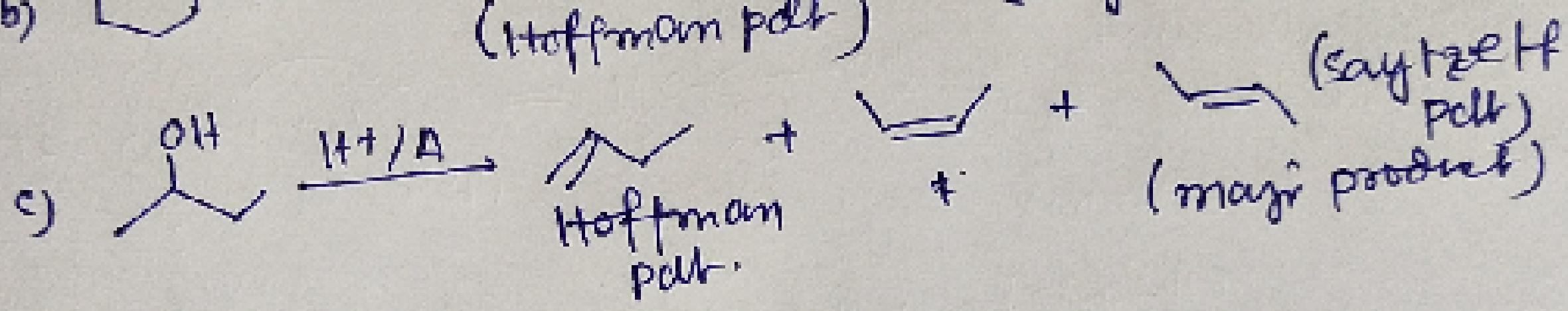
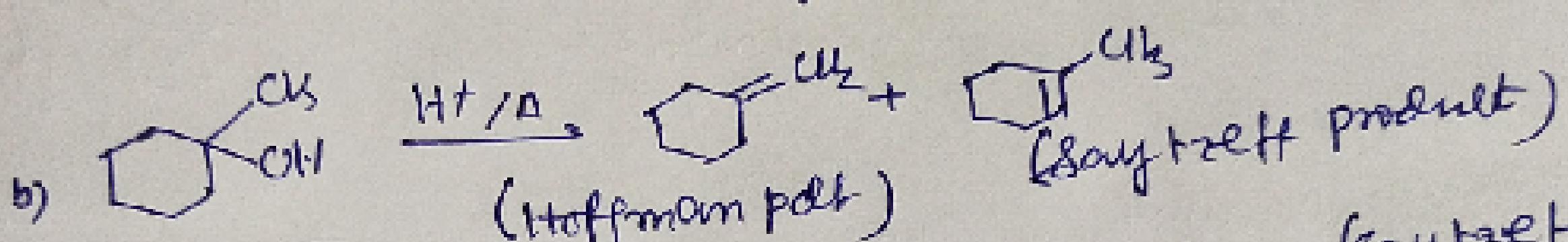
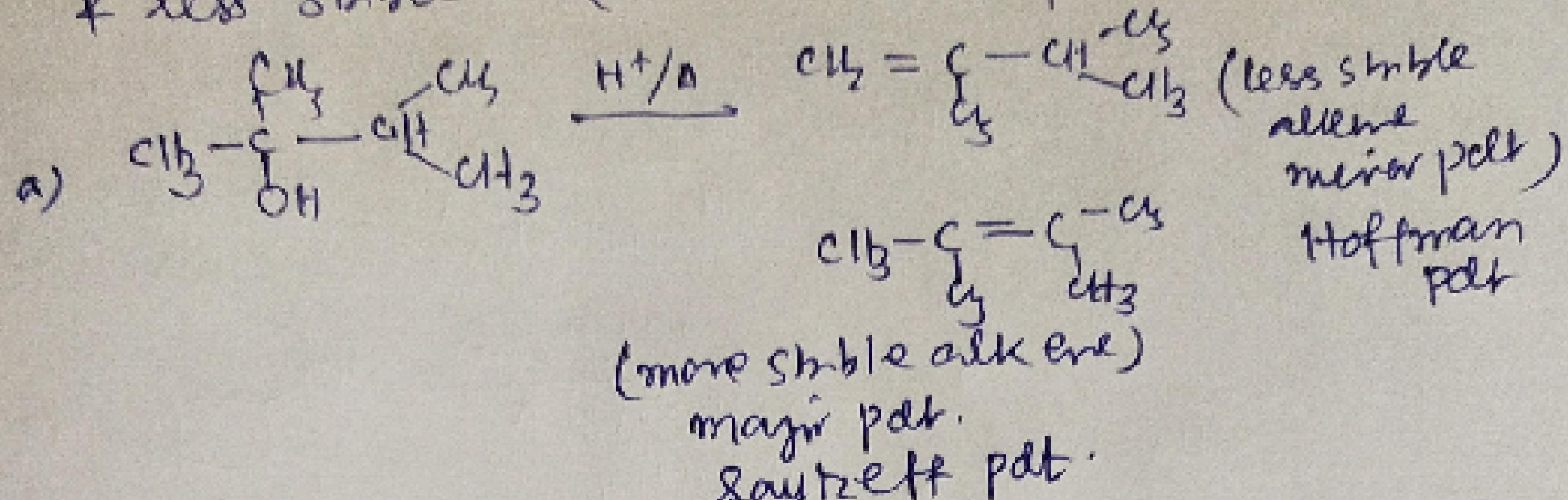
\Rightarrow 2nd step is rate, carbocation further is the reaction.



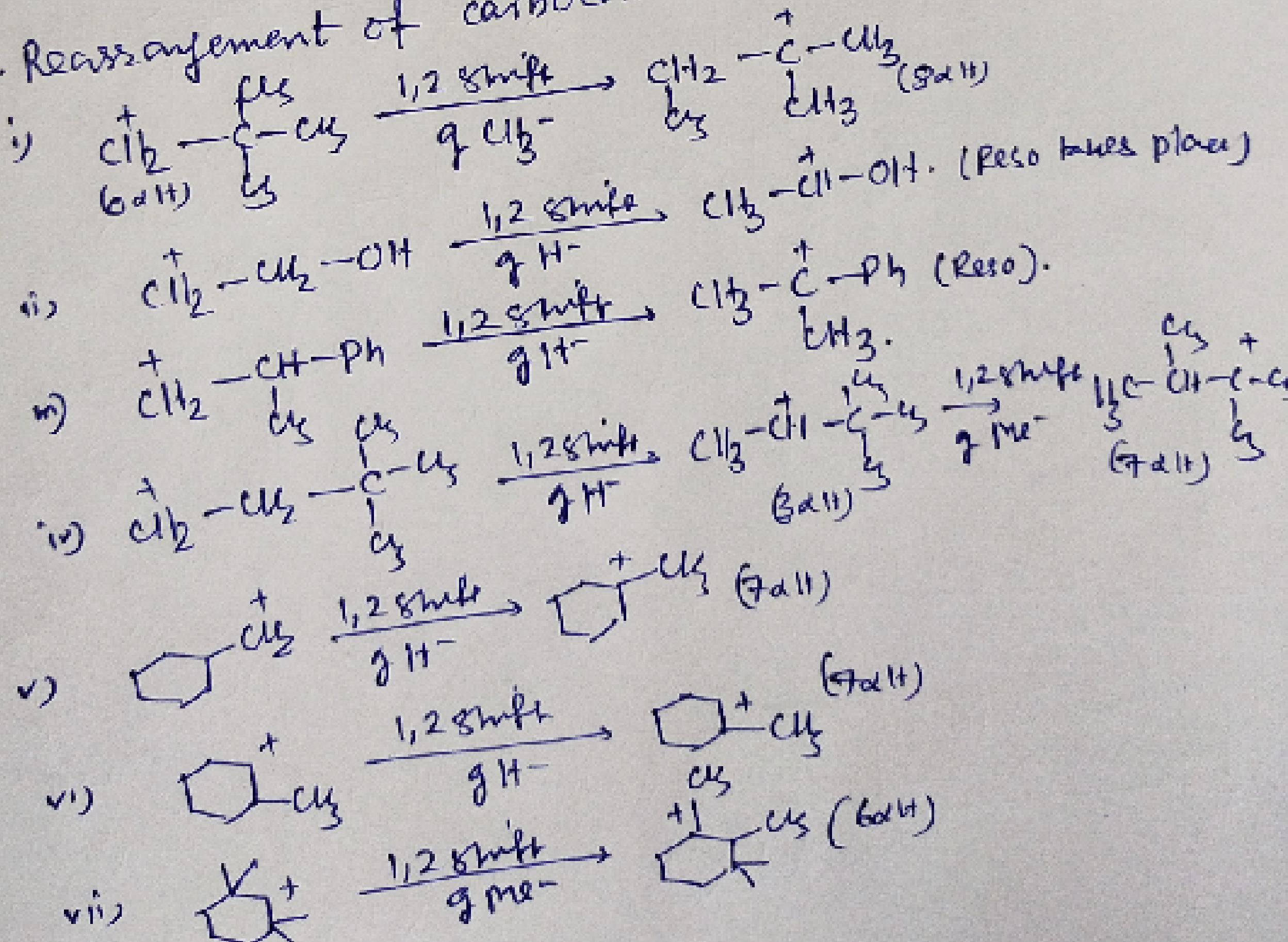
$\boxed{\text{CH}_3\text{OH} \text{ cannot undergo dehydrogenation}}$

i) $3^\circ \text{ Alcohol} > 2^\circ \text{ Alcohol} > 1^\circ \text{ Alcohol}$.

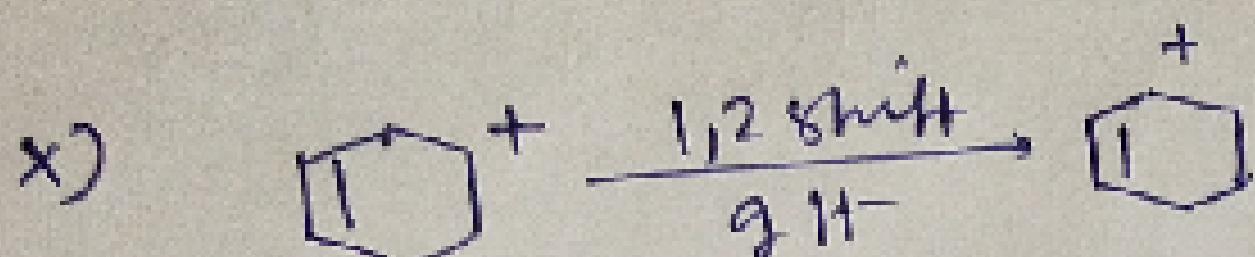
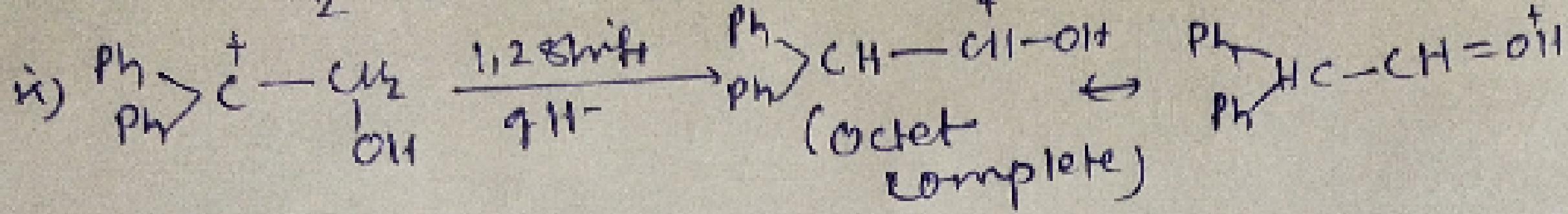
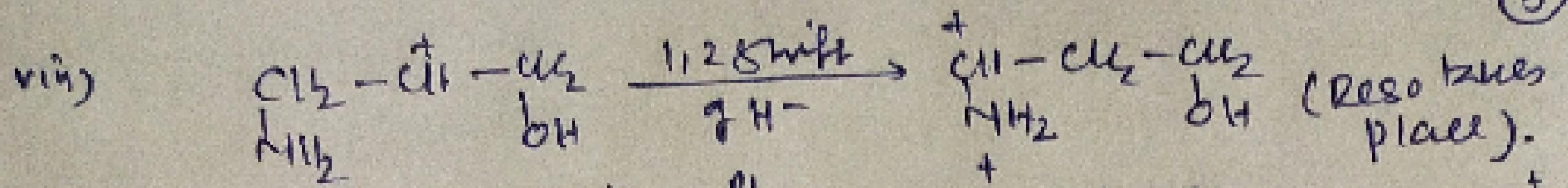
During product (alkene) formation if more than one alkene is formed, then more stable alkene is major product. (A)
 & less stable alkene is minor product.



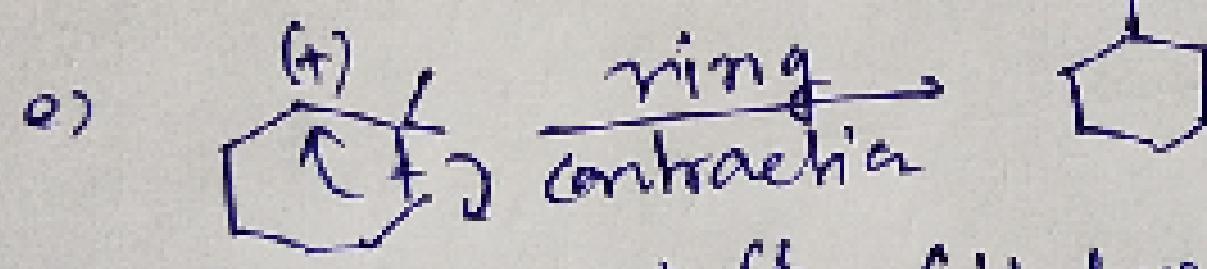
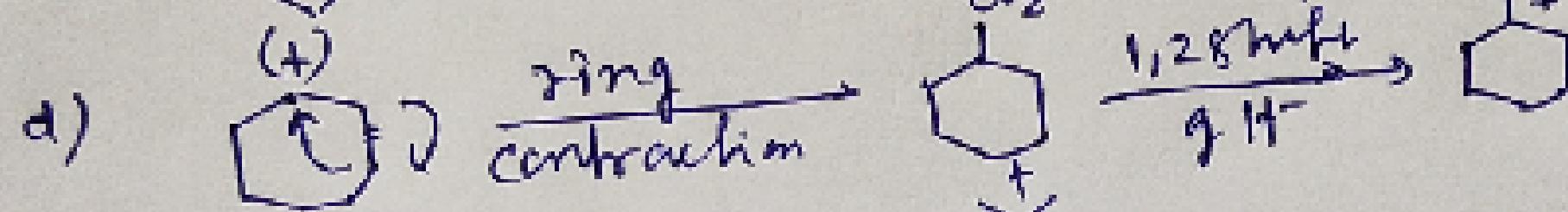
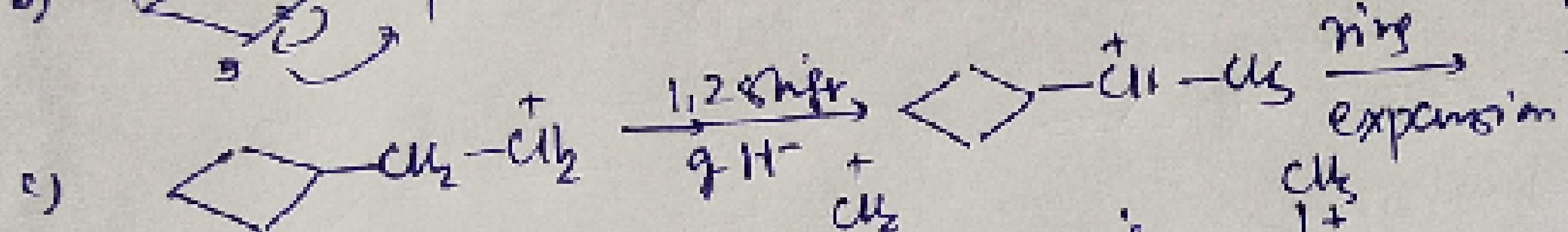
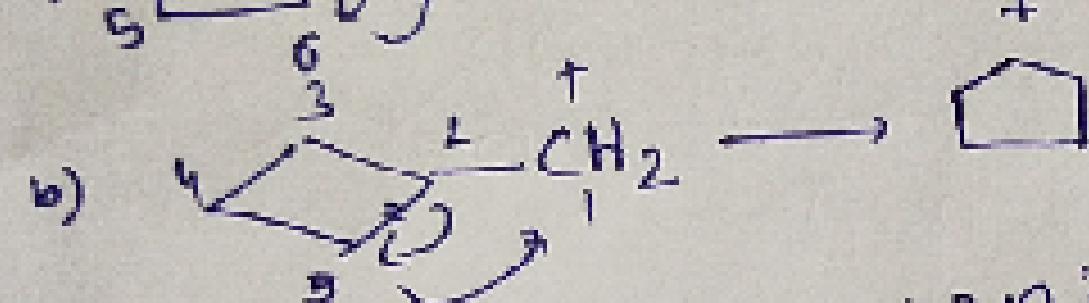
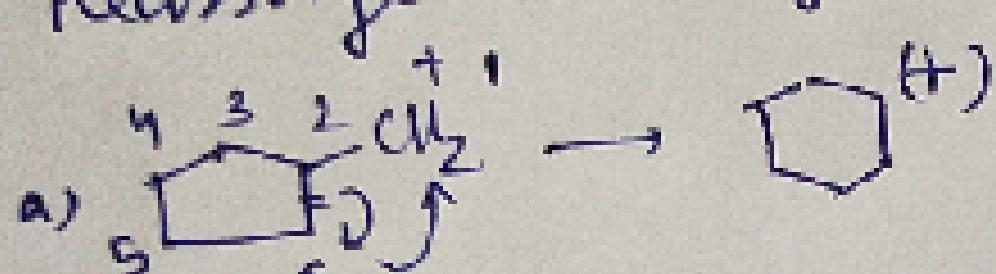
: Rearrangement of carbocation:



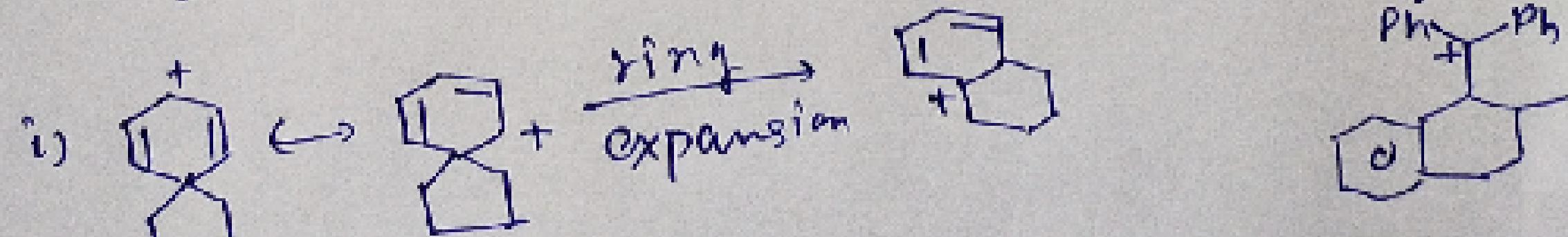
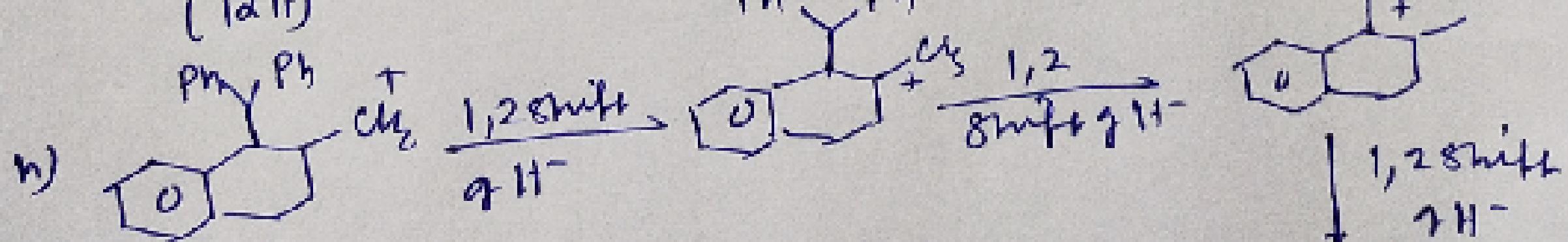
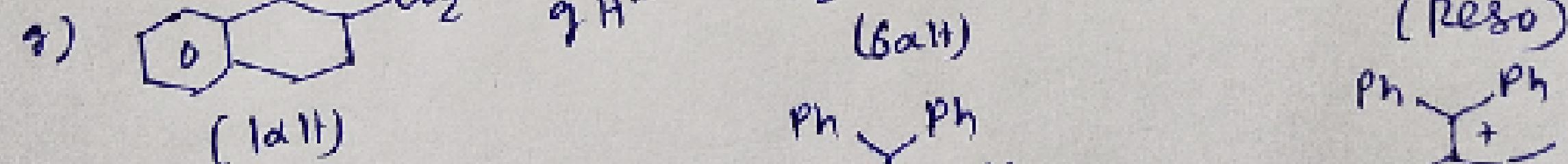
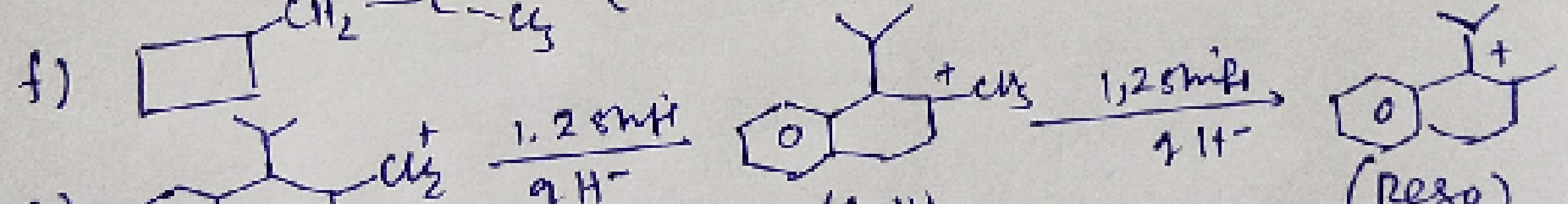
(5)

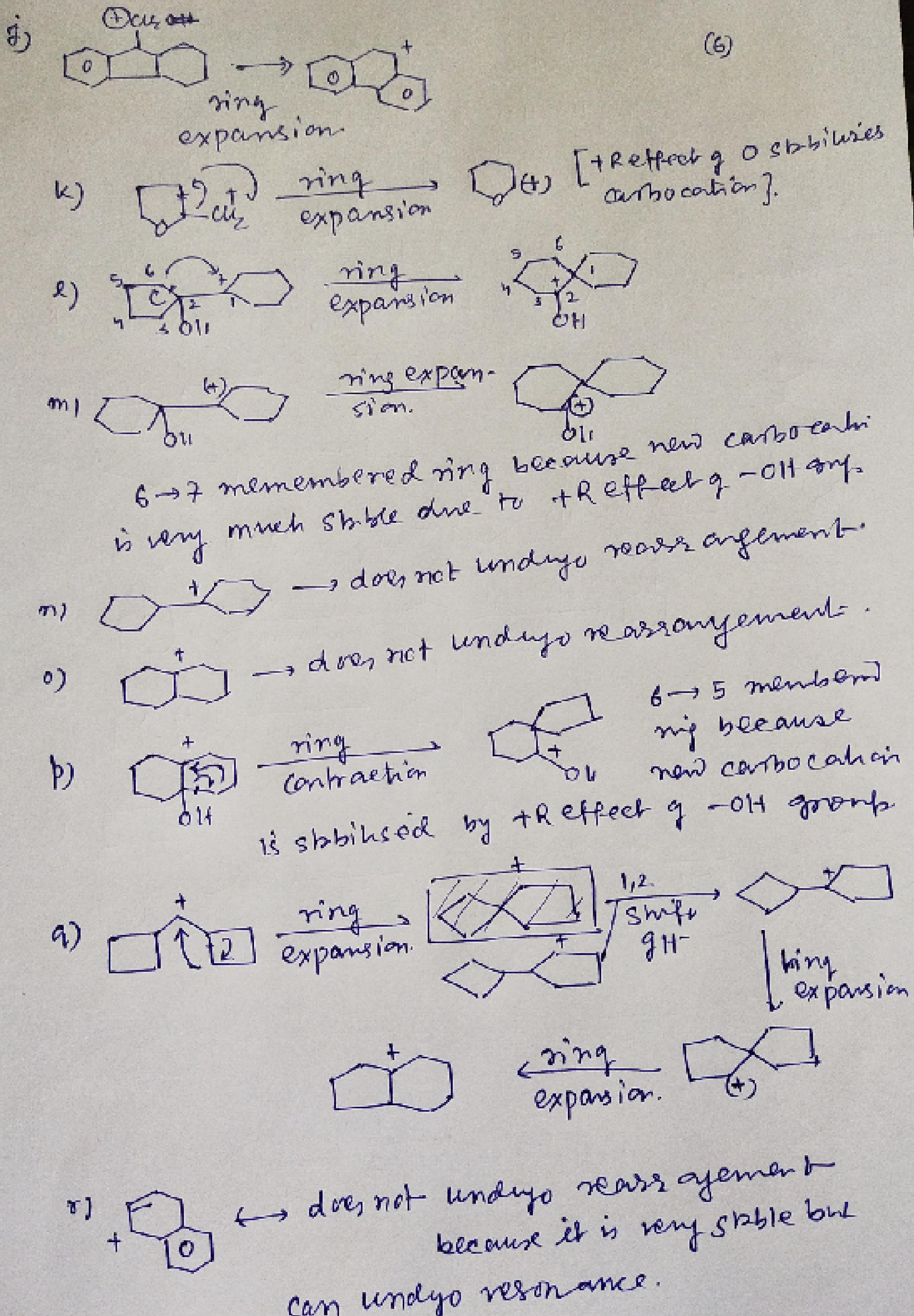


Rearrangement by ring expansion/ring contraction:



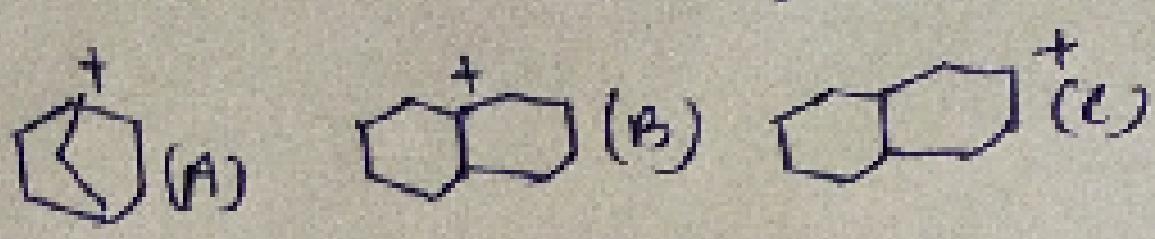
(it does not undergo rearrangement)





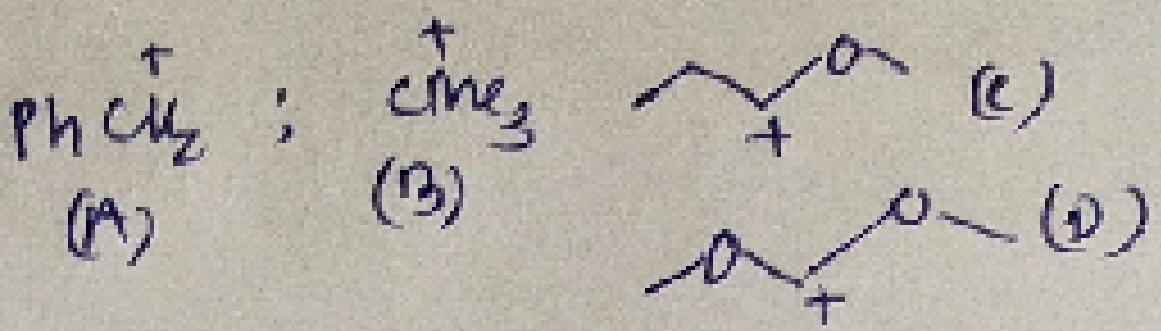
Some other examples & questions:

Q) Stability order of carbocation

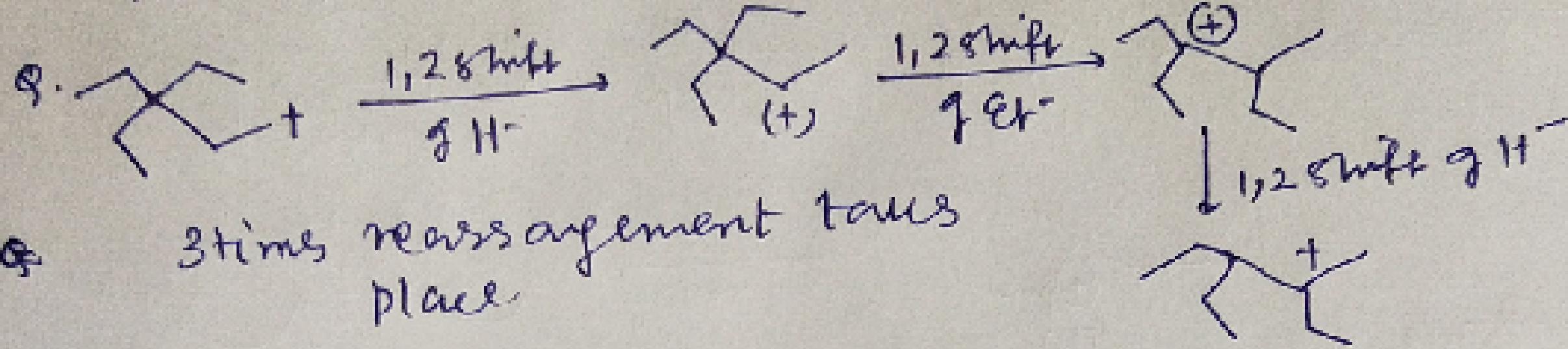


Ans: $B > C > A$

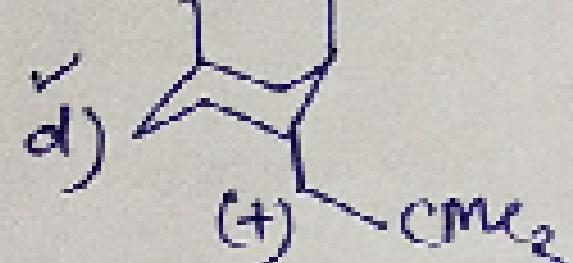
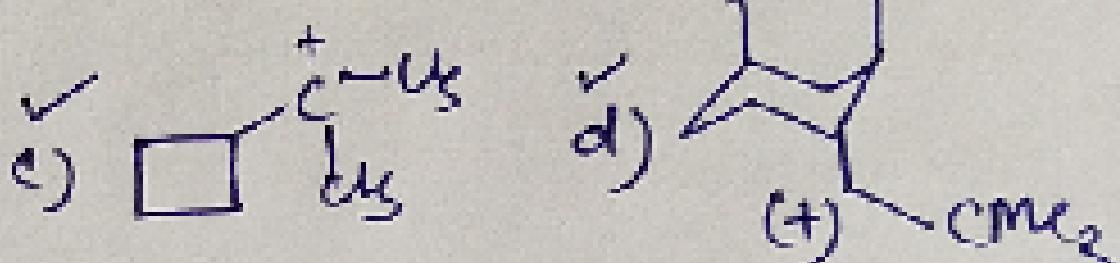
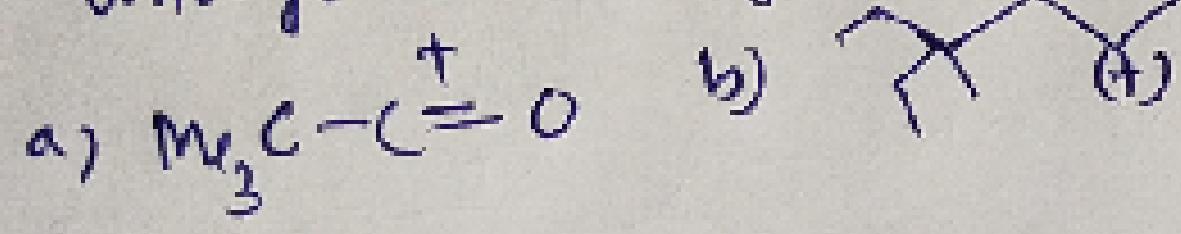
Q) Stability order of carbocation



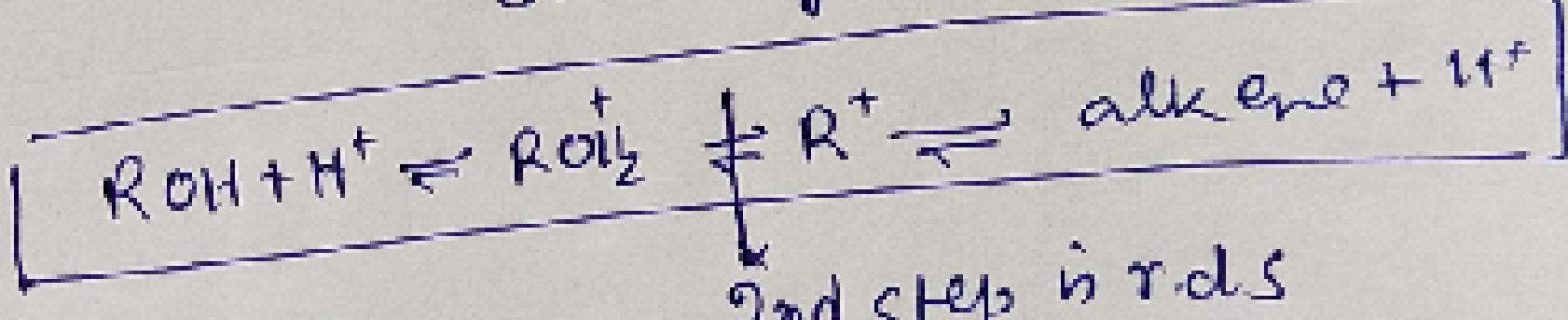
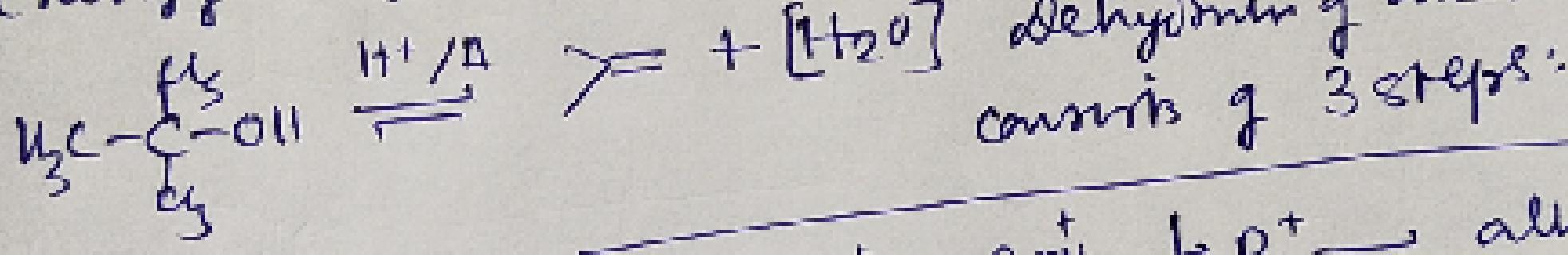
Ans: $D > C > B > A$



Q. Which of the following carbocation can undergo rearrangement?

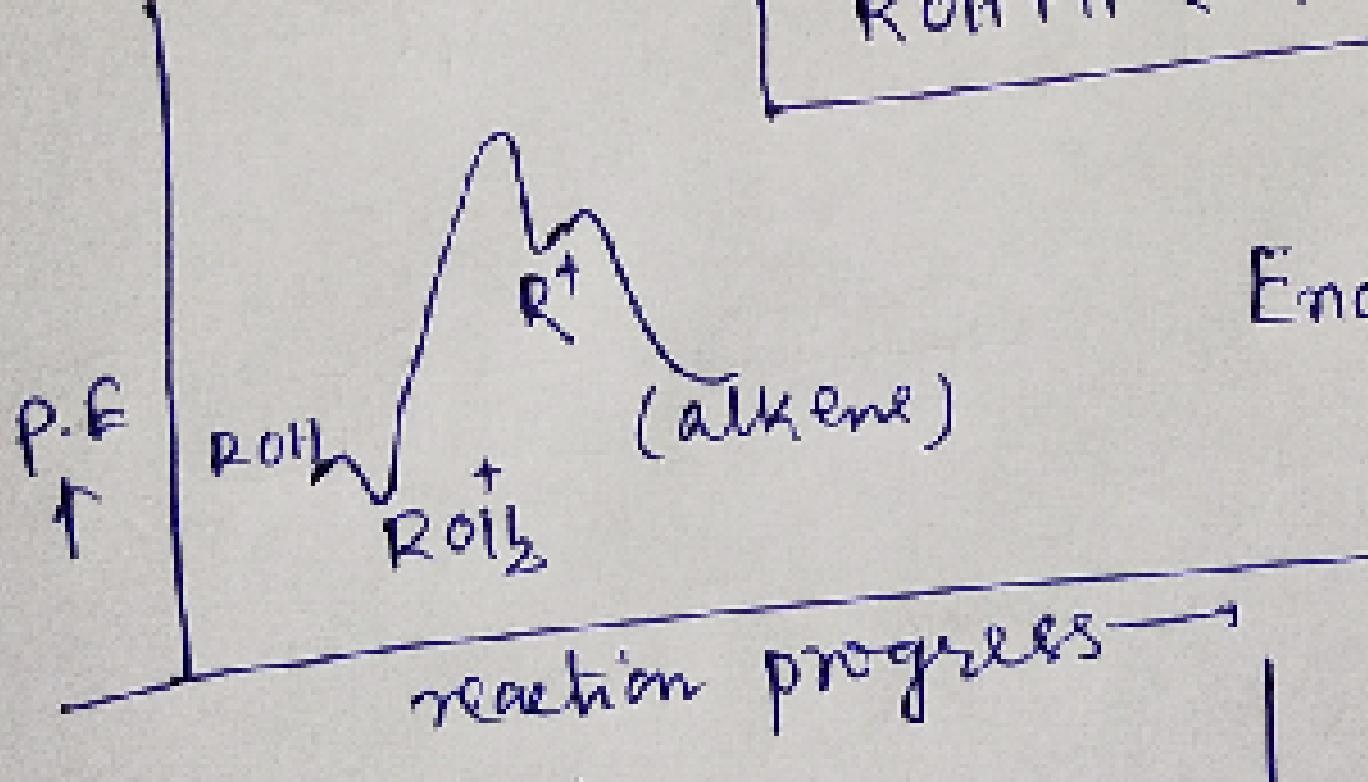


Q. Energy diagram for the reaction:

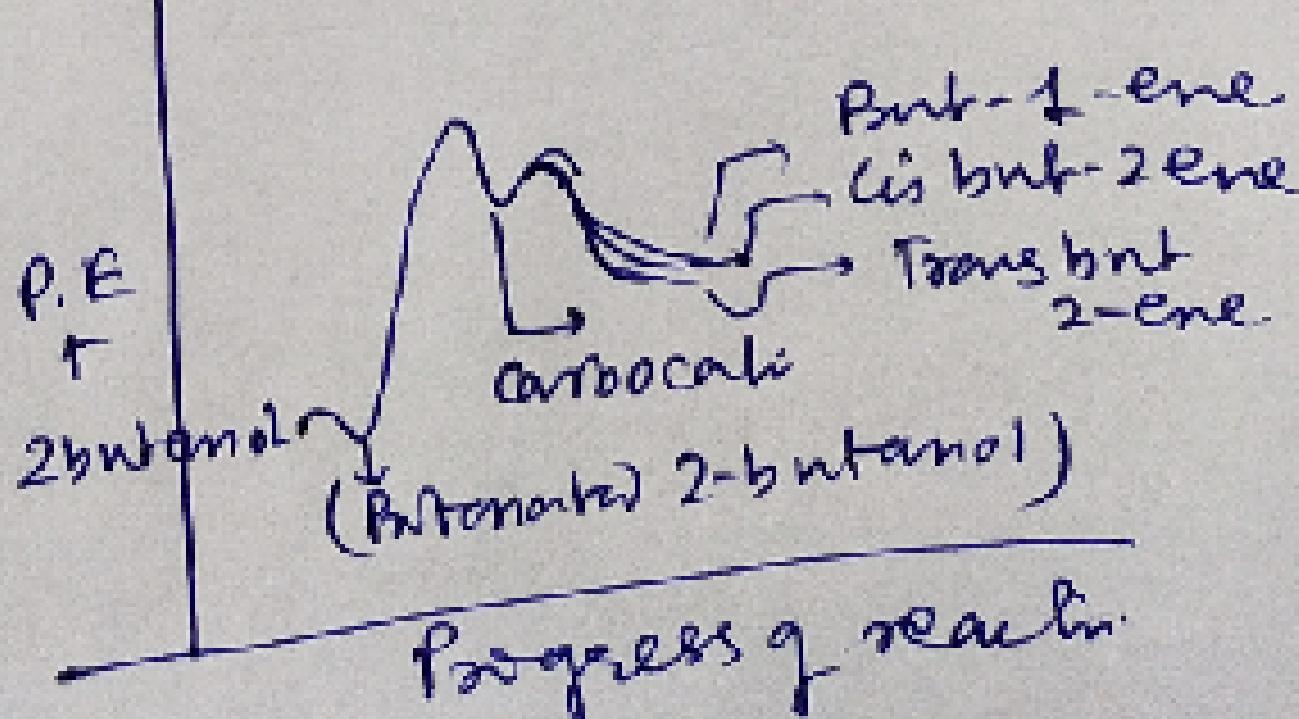


2nd step is r.d.s

Endothermic reaction

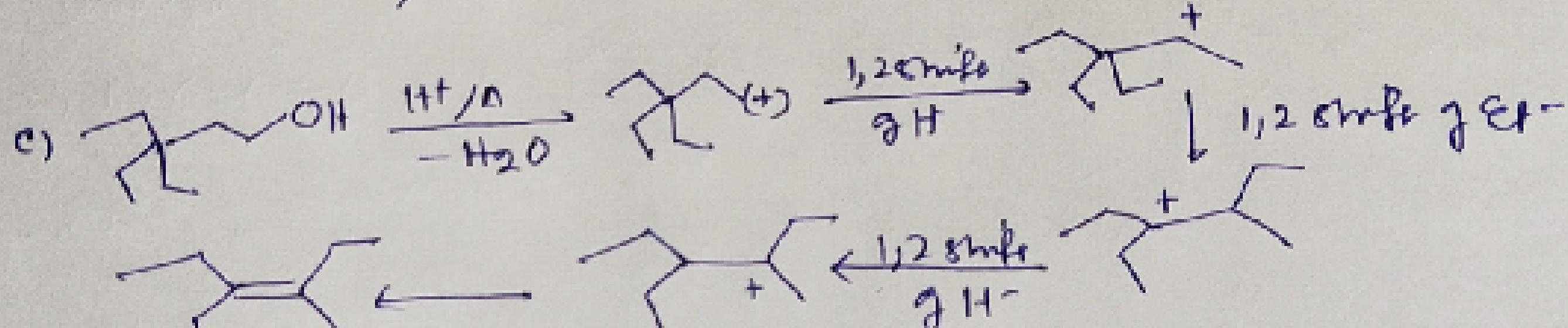
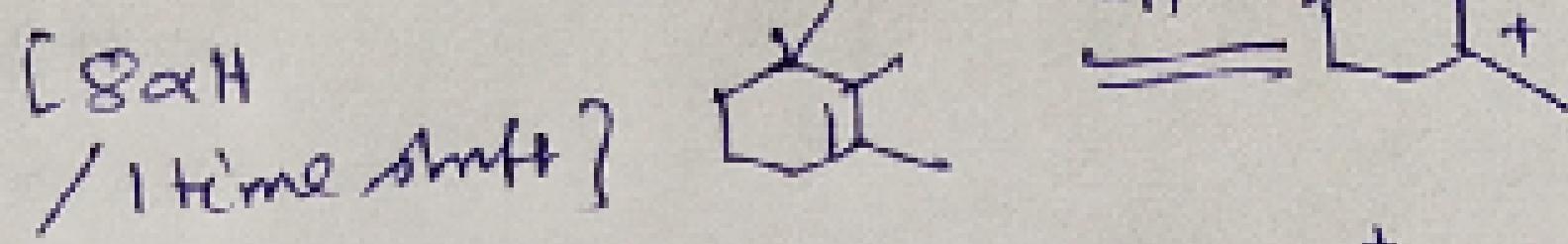
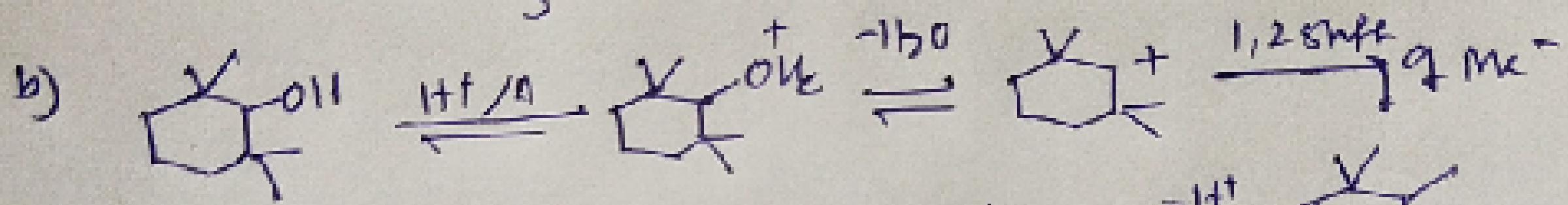
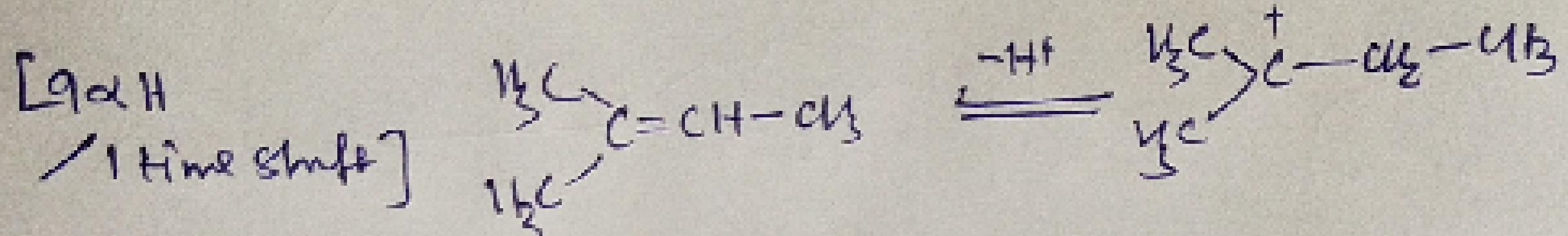
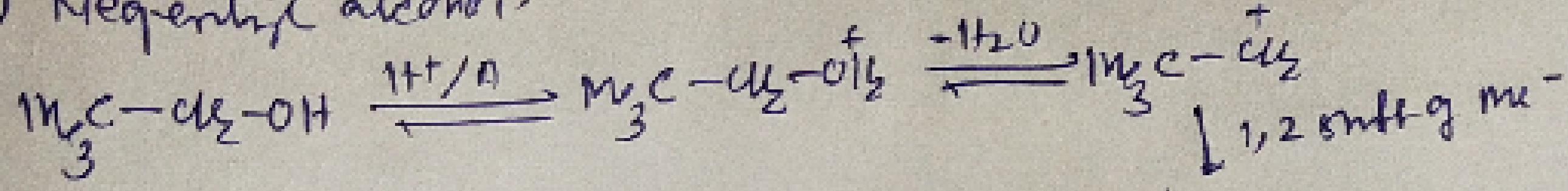


2bntanol $\xrightarrow{\text{H}^+}$
1bnten + cis bnt2ene
+ Trans bnt2ene
(3 products) Write down
energy diagram.

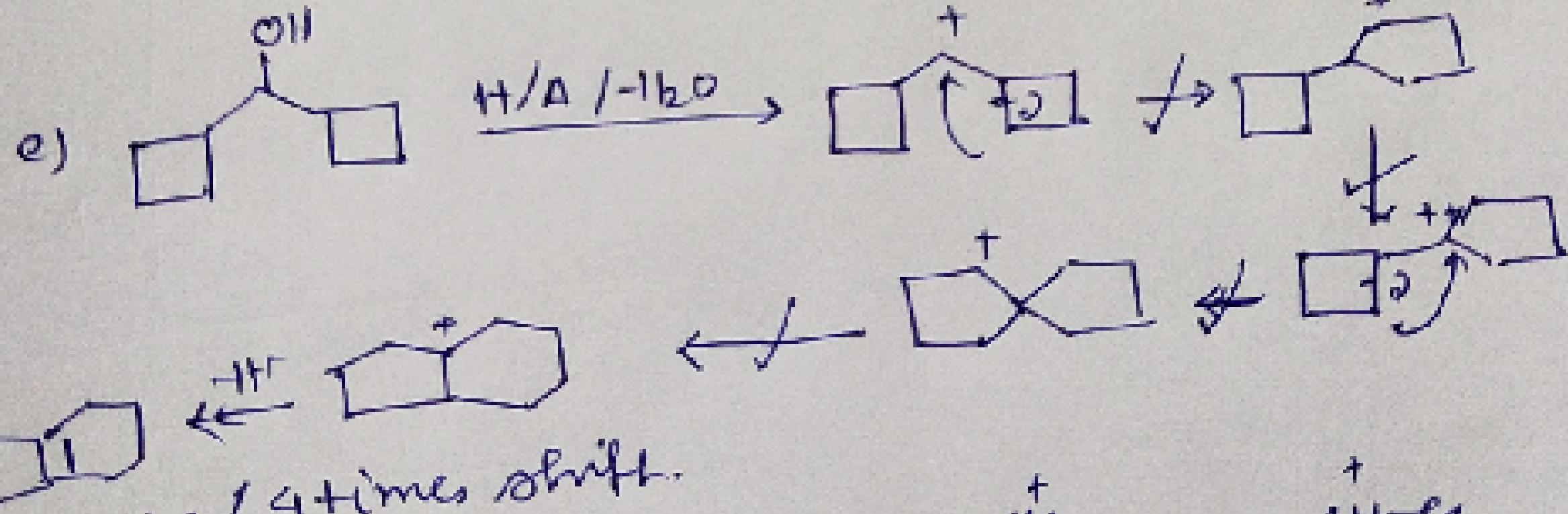
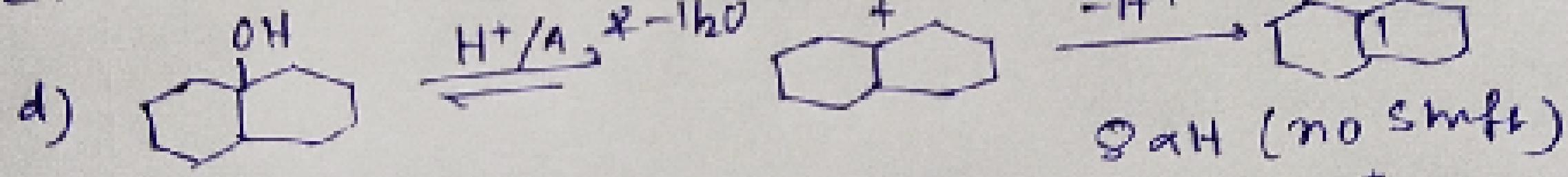


Q. What is the no. of α hydrogen in final major product (B) & no. of shifts (times) made during reaction mechanism.

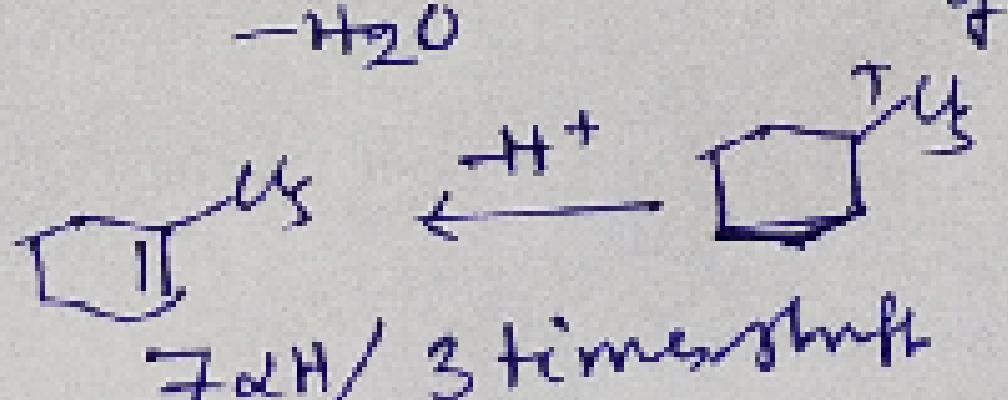
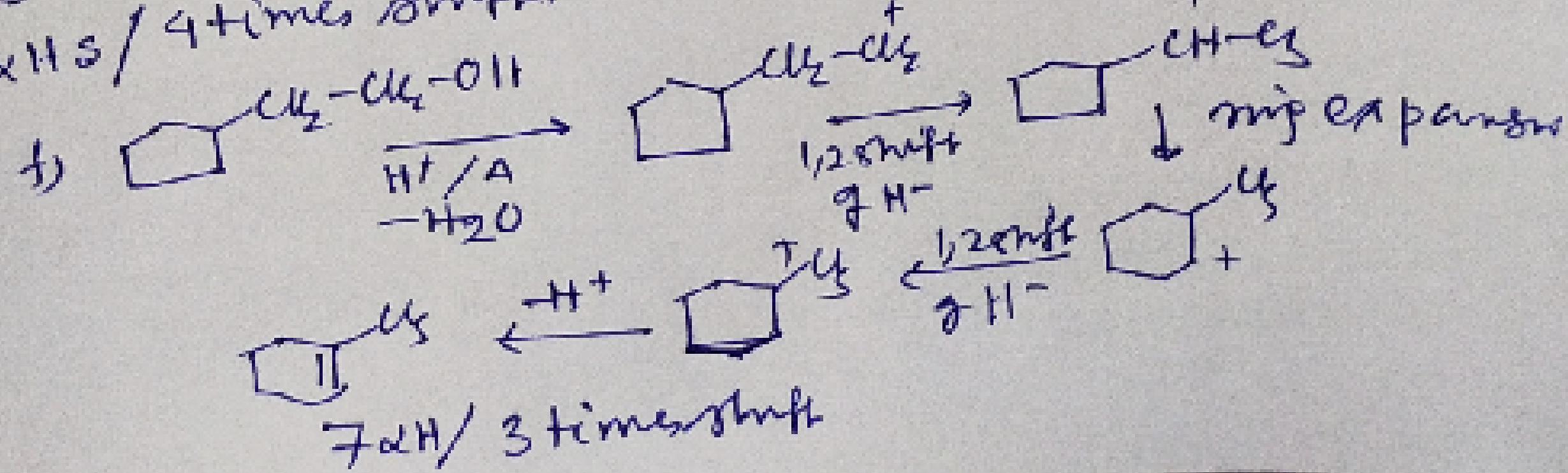
a) Neopentyl alcohol.



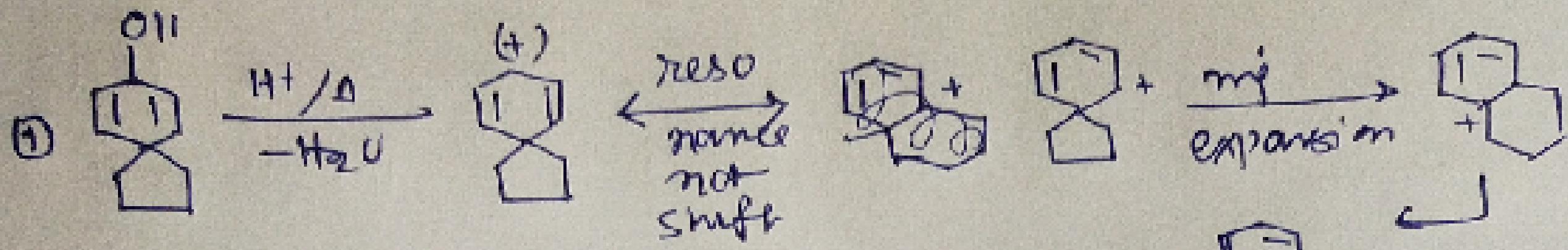
[9αH / 3 times shift]



$8\alpha\text{Hs} / 4 \text{ times shift.}$



Q. What is the mechanism of dehydrogenation of following alcohols & comment on aromaticity of final product. (9)



⇒ If 0 shift, then dehydrogenation of alcohol is 3 step process.

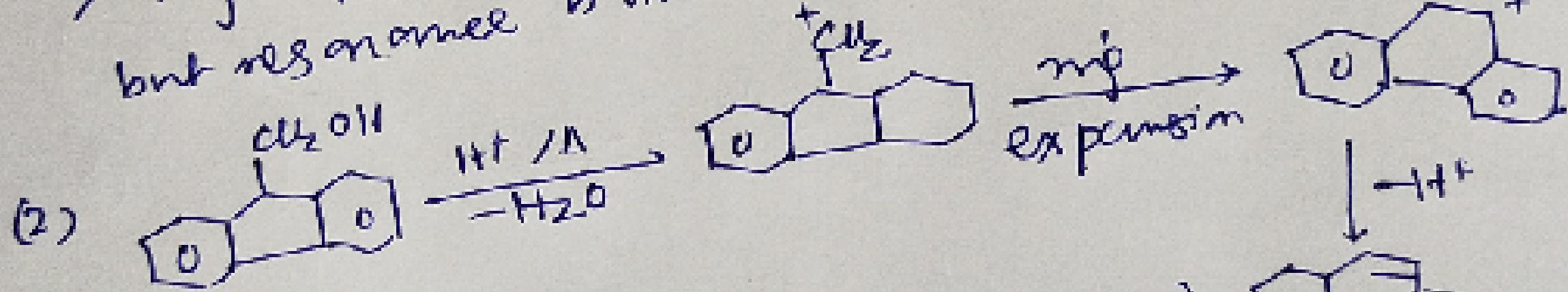
⇒ If single shift takes place, then dehydrogenation of alcohol is 4/step process.

⇒ If 2/3 turns shift takes place during rearrangement of carbocation then dehydrogenation of alcohol is 5/6 step process.

⇒ If n. is the total no. of steps in the chemical reaction, then n is the total no. of transition state.

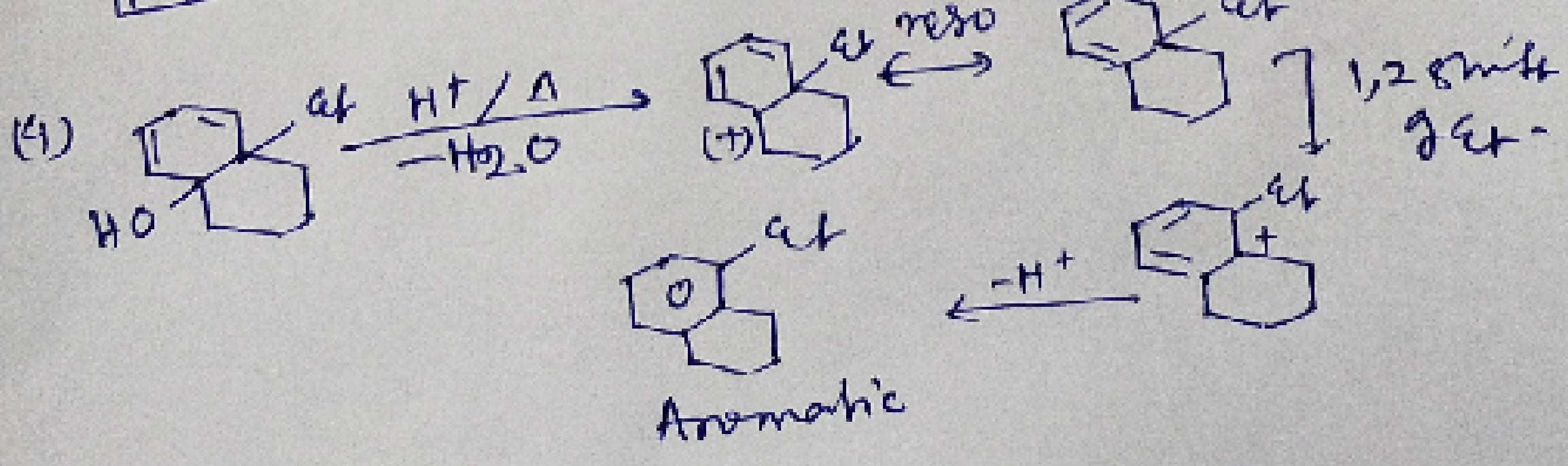
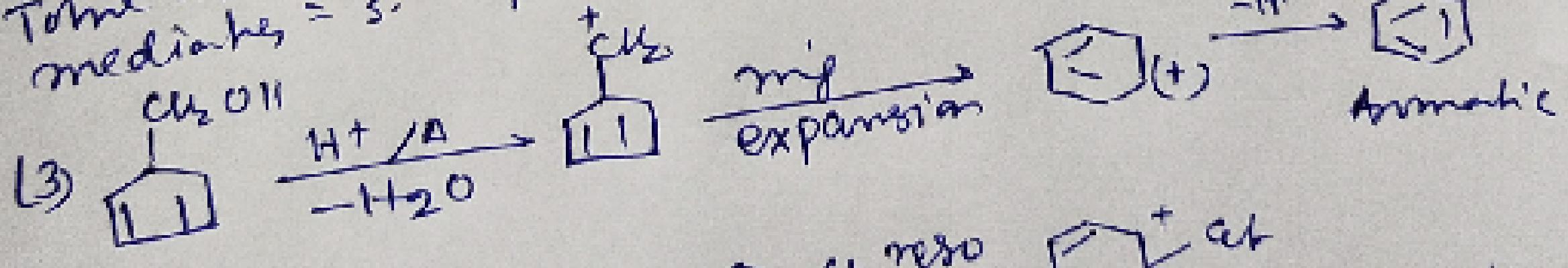
then $(n-1)$ is the total no. of intermediates.

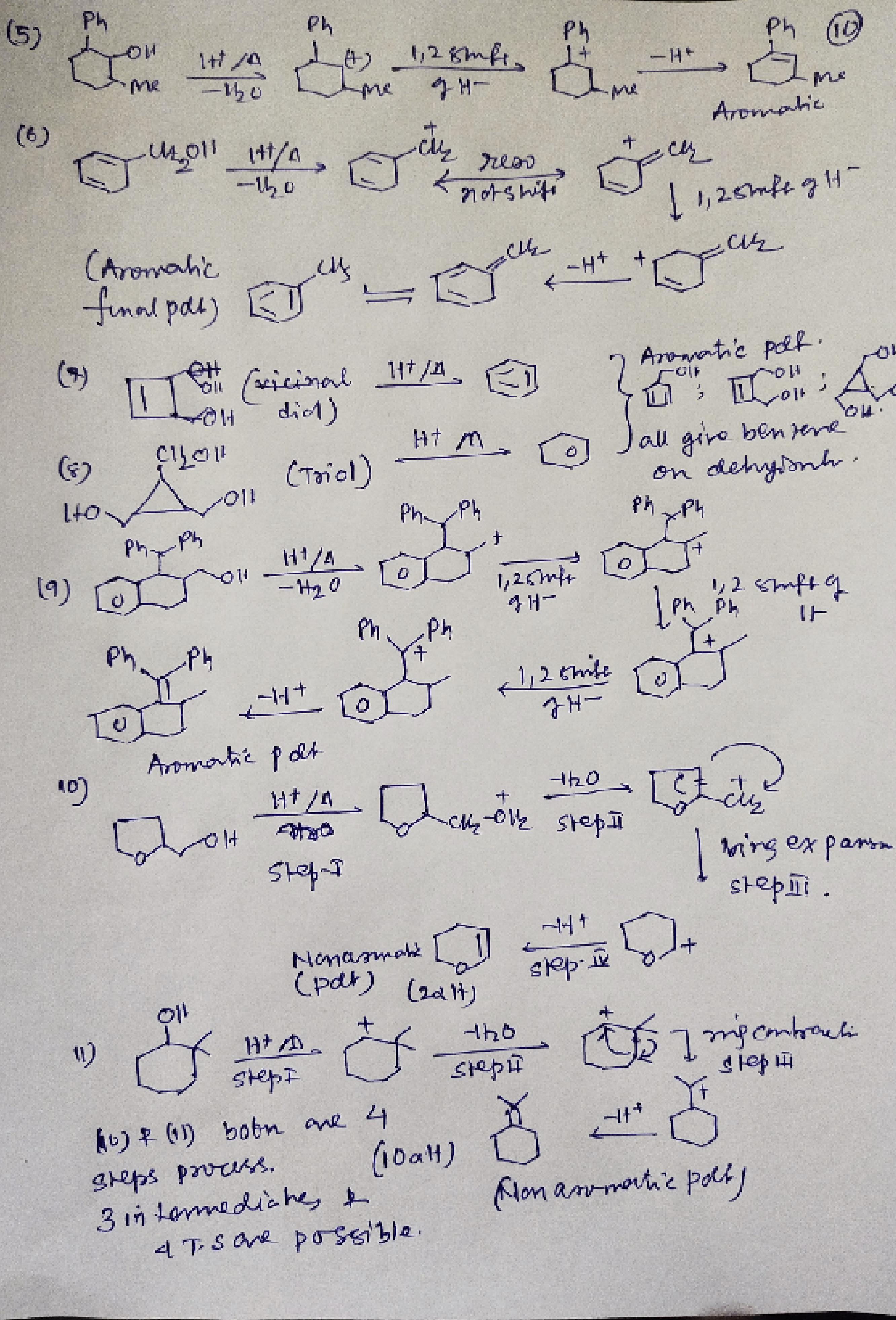
⇒ mig expansion/contraction is considered as step. /shift. but resonance is not considered as step.



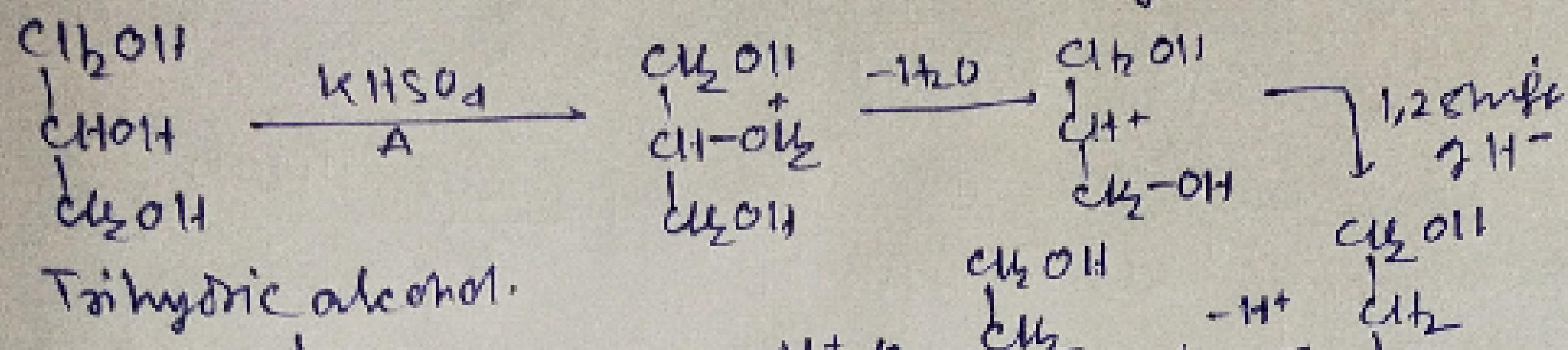
Total steps = 4.

Total intermediates = 3. [Aromatic prod.] (Phenanthrene) Cane

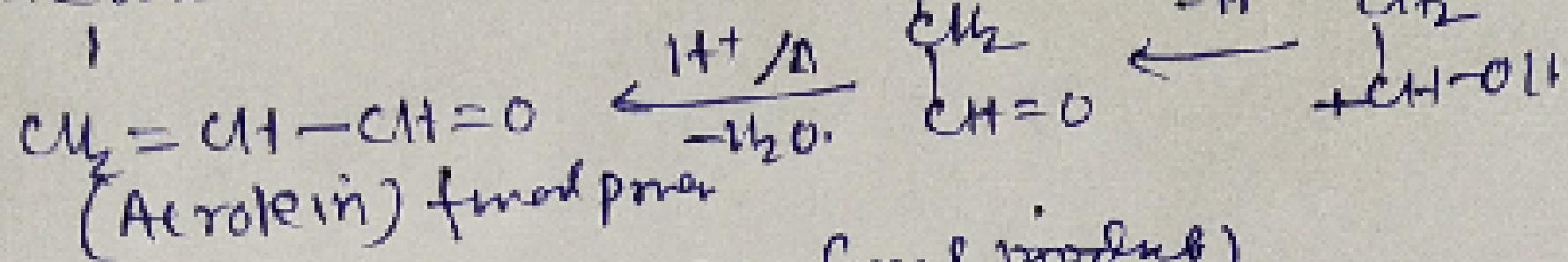




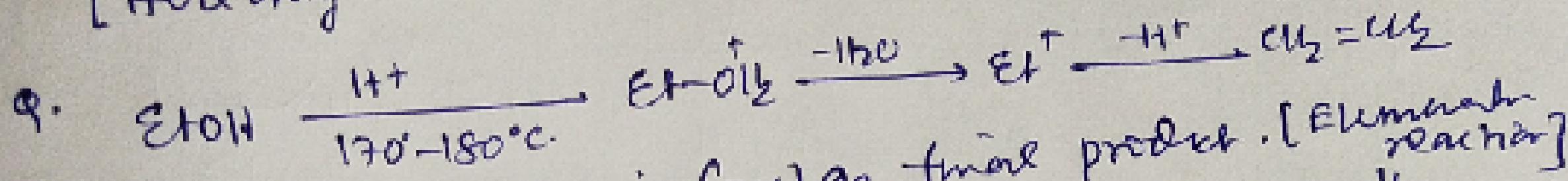
d. What is the major product in the following reaction? (ii)



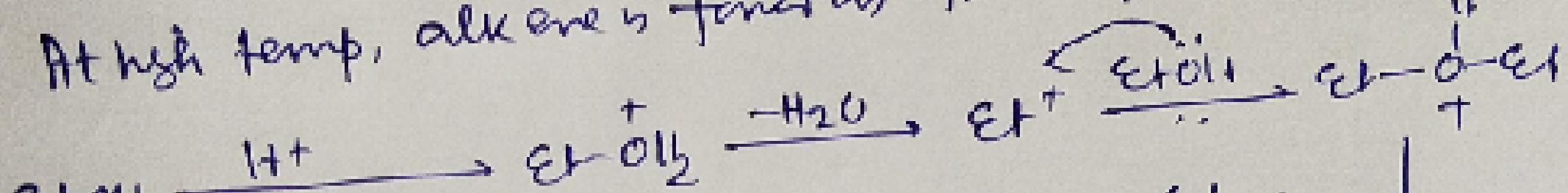
Trihydroic alcohol.



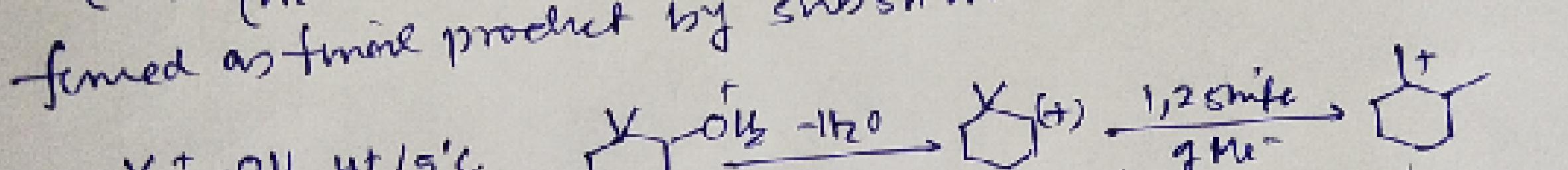
[Here only alkene is not as final product]



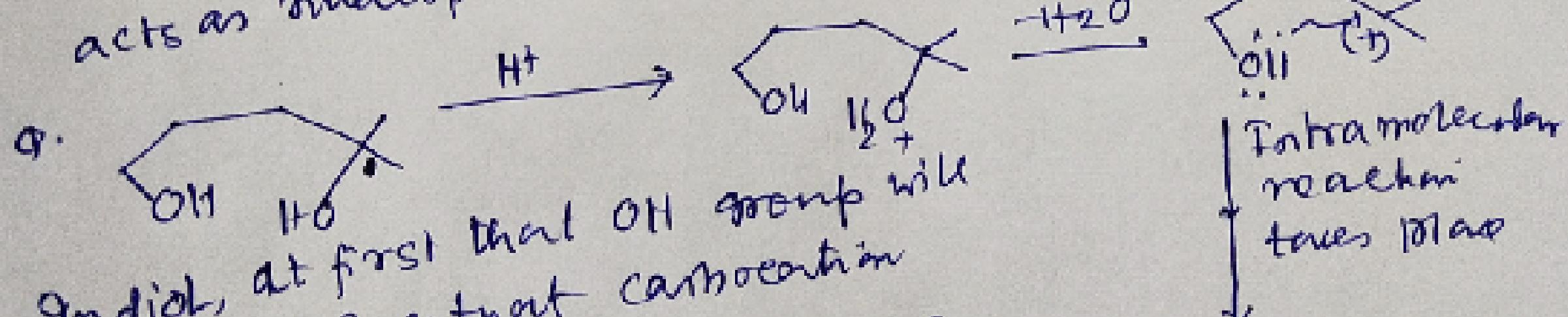
At high temp, alkene is formed as final product. [Elemental reaction]



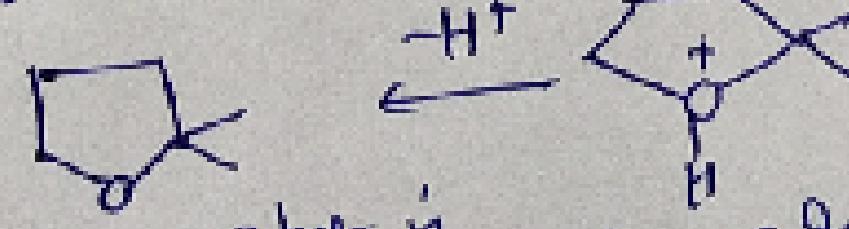
(eg) (At low temp ether is formed as final product by substitution reaction)



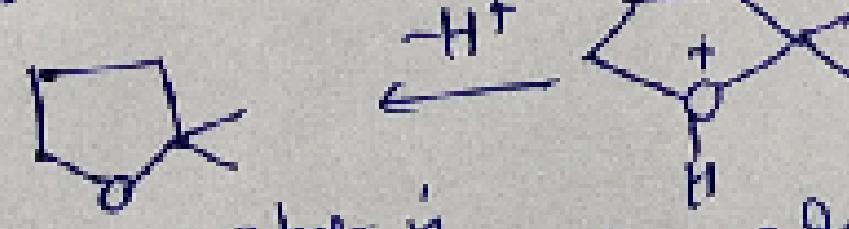
Here at 5°C , in last step deprotonation does not take place, rather H_2O acts as nucleophile & rearranged alcohol is formed as final product.



Indic, at first that OH group will be protonated so that carbocation formed will be more stable because in r.d.s carbocation is formed as intermediate

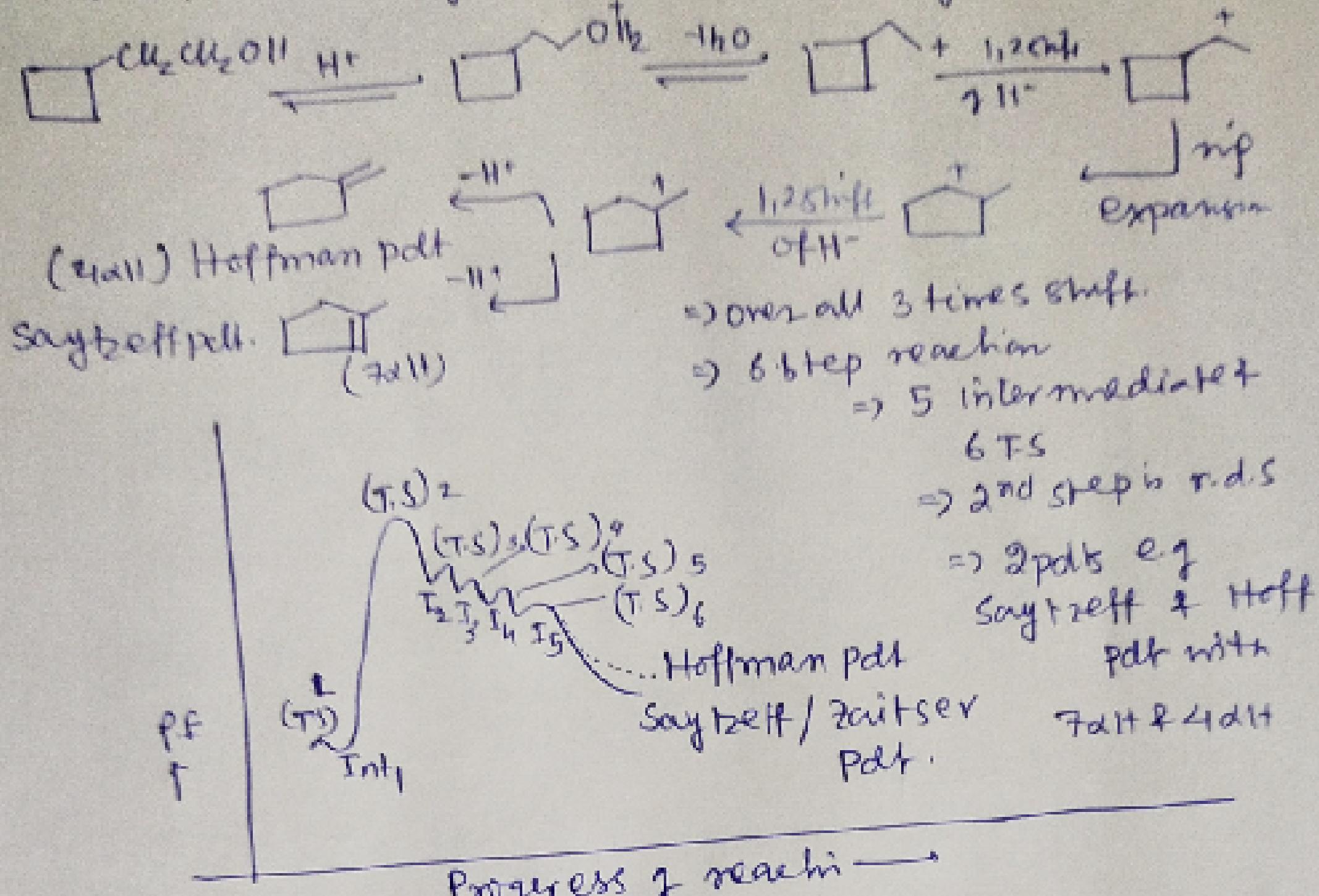


Intramolecular reaction takes place



cyclic ether is formed as final product.

Written down the energy diagram for following reaction (12)



- Points to be noted
- $\Rightarrow \text{C}_6\text{H}_{12} \rightleftharpoons \text{C}_6\text{H}_5^+$ Here both the carbocations are present in equilibrium (almost same amount)
 - $\Rightarrow \text{HCl}, \text{HBr}, \text{HF}$ when reacts with alcohol, alkene dehydrohalogenation does not take place because hydron acid does not have dehydrating property.
 - \Rightarrow zero bridge carbon cation is stable. but this carbocation is very unstable (1/2 bridge).

- \Rightarrow It cannot undergo dehydrohalogenation process.
- \Rightarrow During rearrangement of carbocation, 1,3 shift of aliphatic C-H does not take place (1,2 shift takes place along; π bond between α-C-β C/H breaks, w.r.t C⁺; electron movement α-C → β, β atom develops -ve charge attacks carbocation)