

Alcohol Preparation (from alkene).

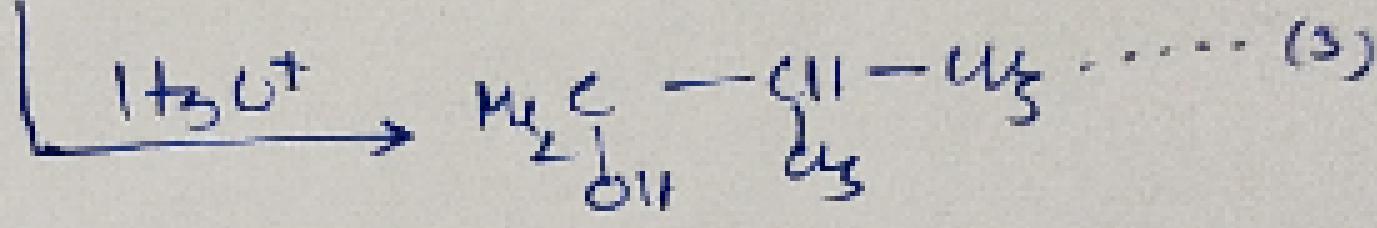
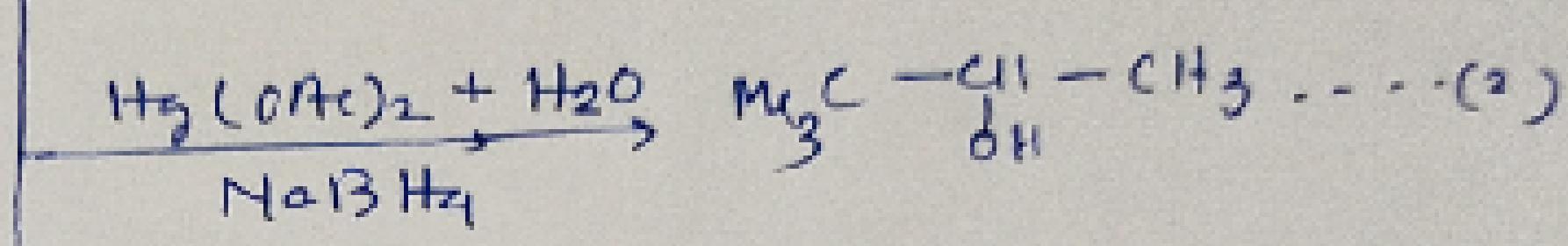
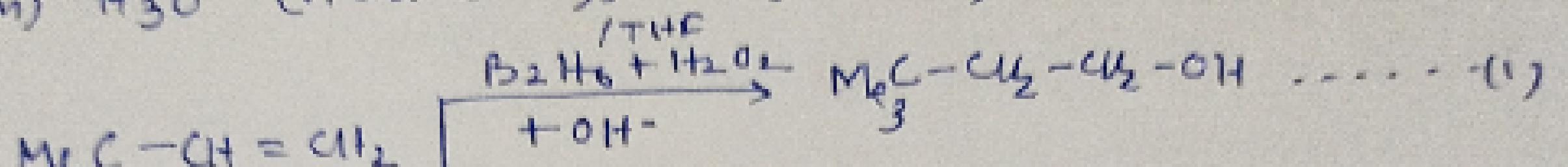
i) H₃BO (Hydroboration oxidation reaction)

the reagent used is $B_2H_6 + H_2O_2 + OH^-$
(THF)

ii) OMDM (oxymercuration & demercuration)

the reagent used is $Hg(OAc)_2$ [mercuric acetate]
+ H₂O + NaBH₄.

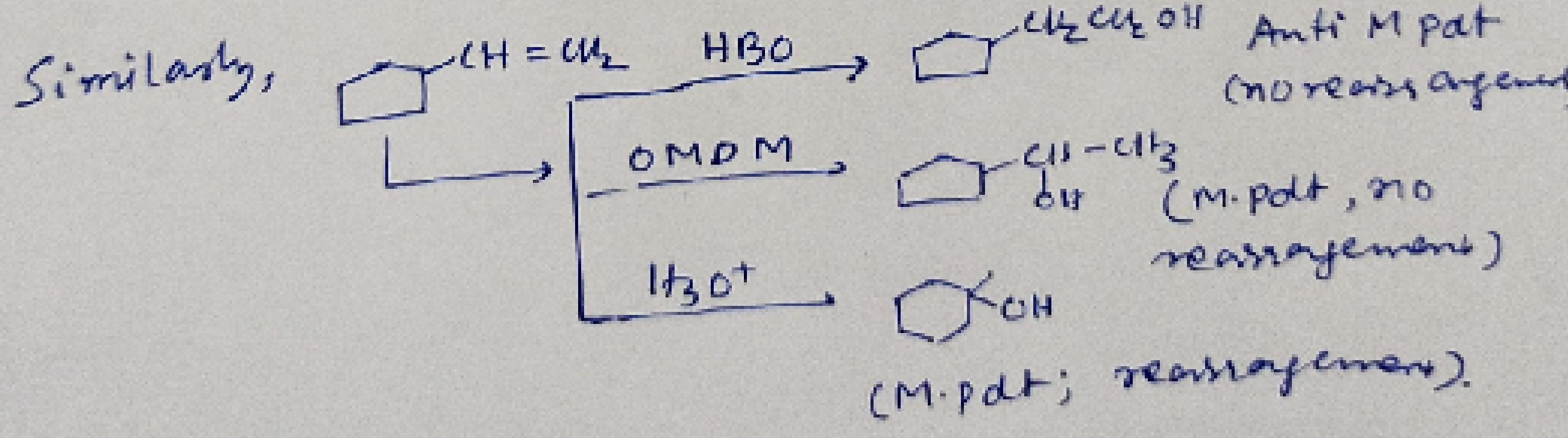
iii) H₃O⁺ (Acid Catalysed hydration).



(+) Product formed in (1) is anti markovnikov product
without any rearrangement.

Product formed in (2) is Markovnikov product
without any rearrangement.

Product formed in (3) is Markovnikov product
with rearrangement (C⁺ is formed as intermediate)

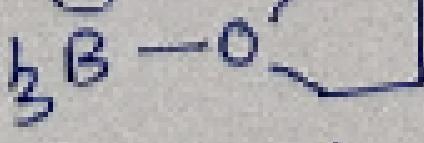


Mechanism using H₃BO.

Using THF: B₂H₆ undergoes symmetrical cleavage

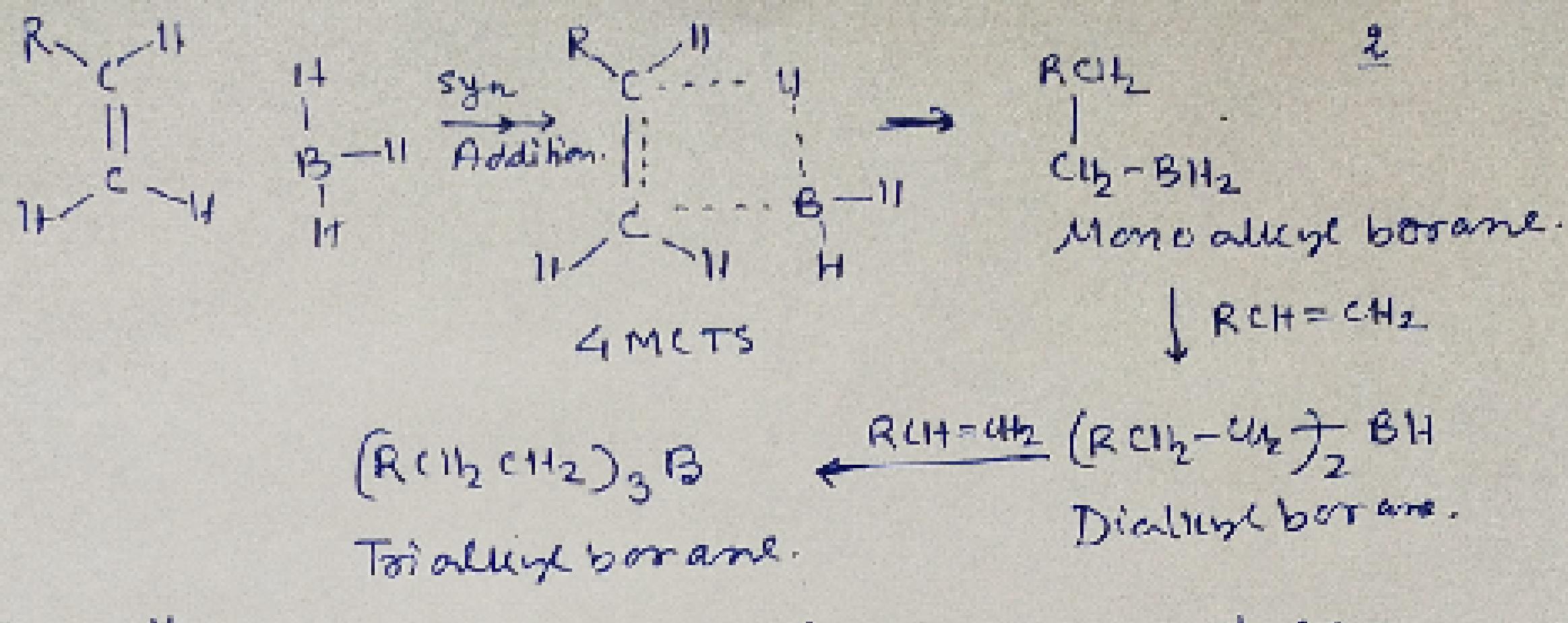
using THF: B₂H₆ undergoes symmetrical cleavage

(solvent)

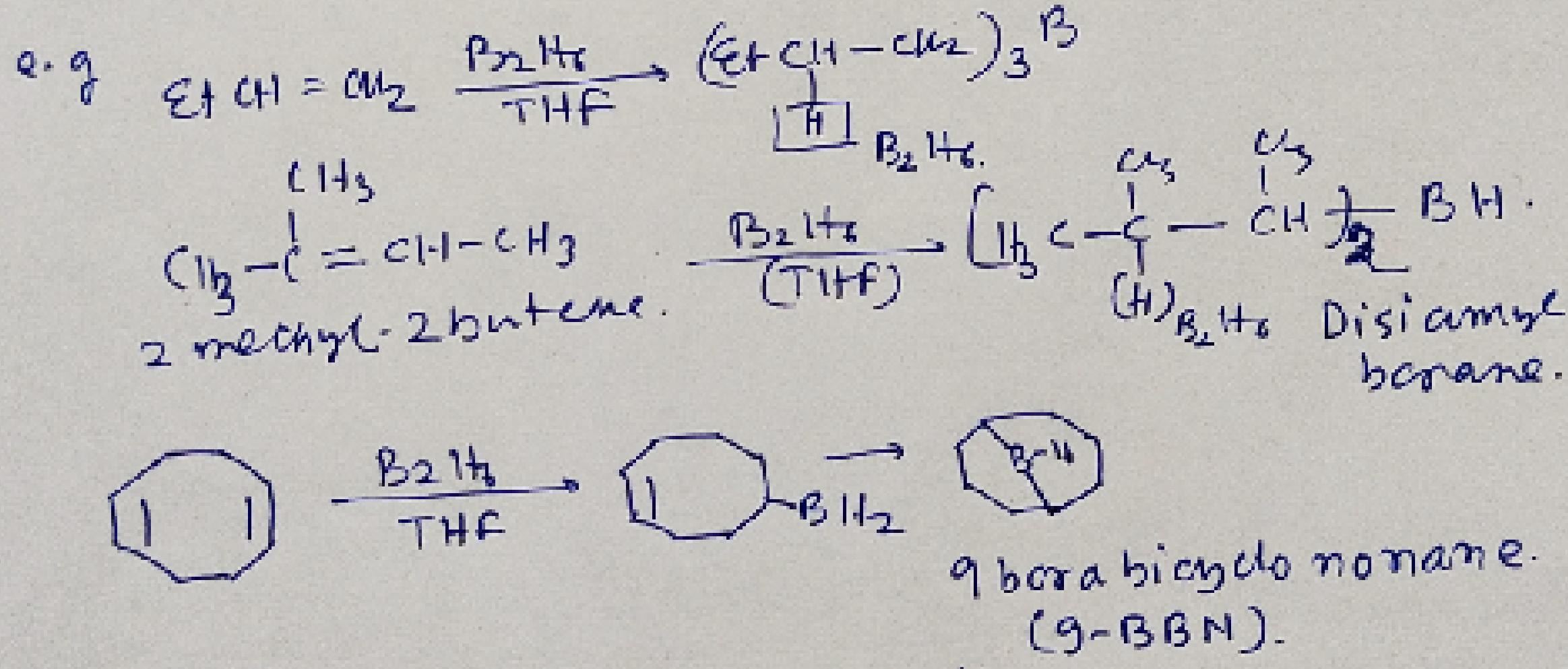


This adduct combines with RCH=CH₂.

& alkene attacking monomeric B₂H₆ e.g. B₂H₅

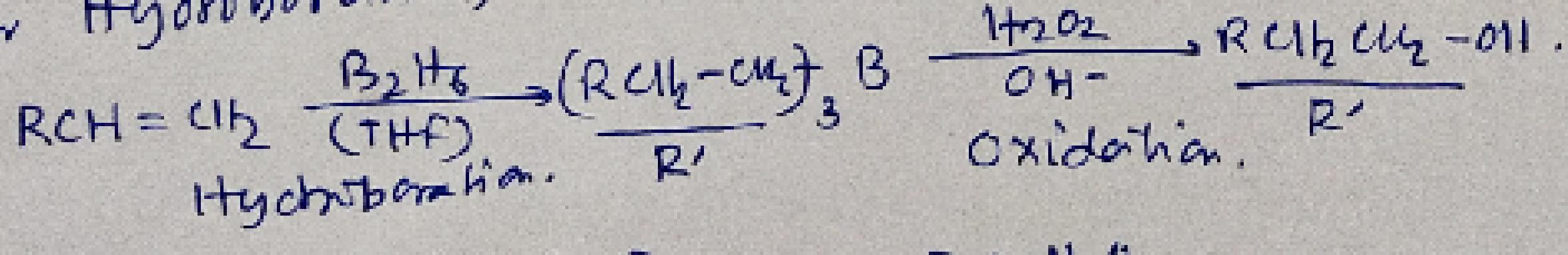


Generally, if no. of carbon in alkene ≤ 4 , then final product is trialkyl borane; if $4 < n \leq 8$, then dialkyl borane is the final product & if no. of carbon in alkene is more than 8, then monoalkyl borane is the final pd.



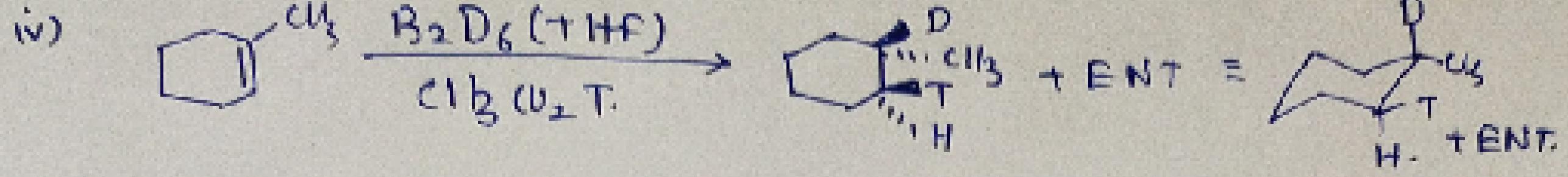
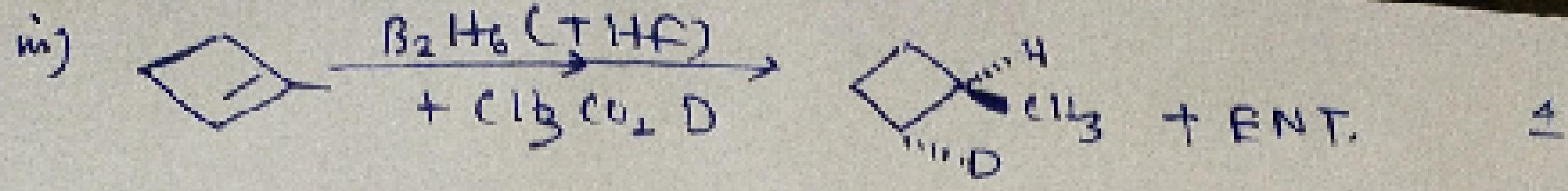
All are example of Hydaboration where Hg B₂H₆ is added to de the carbon which is more sterically crowded. It is example of Markovnikov addition.

After Hydroboration, oxidation takes place.
With Cr_2O_7 or Hg_2O_2 .

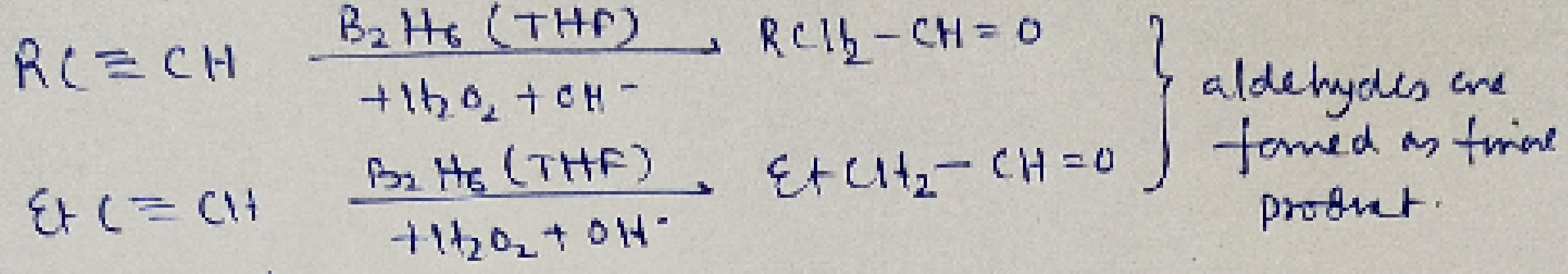


Mechanism: $\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO-O}^- + \text{H}_2\text{O}$

acts as attacking. \leftarrow (Strong nucleophile
nucophilic). [Hydroperoxide
ion].

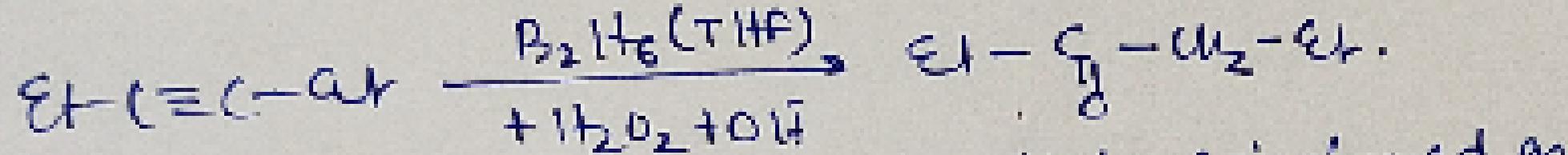


HBO of alkyne:



(Terminal Alkyne)

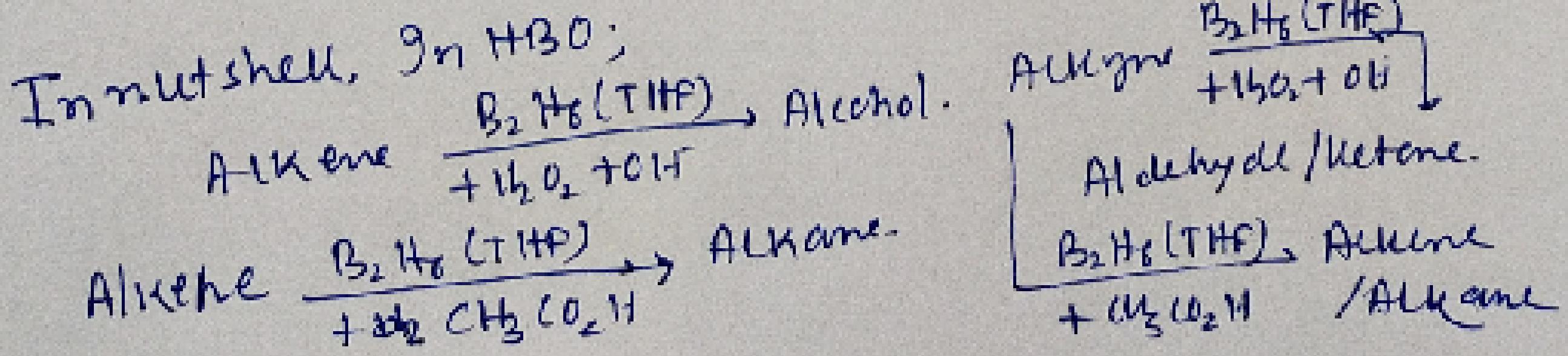
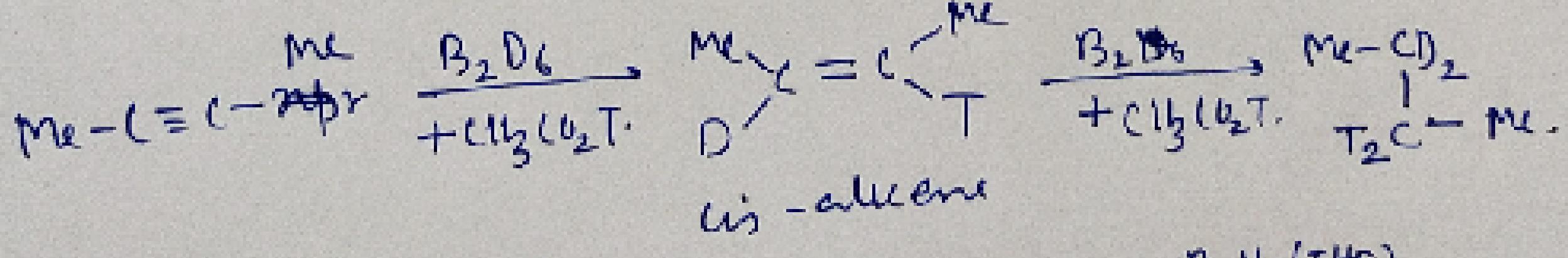
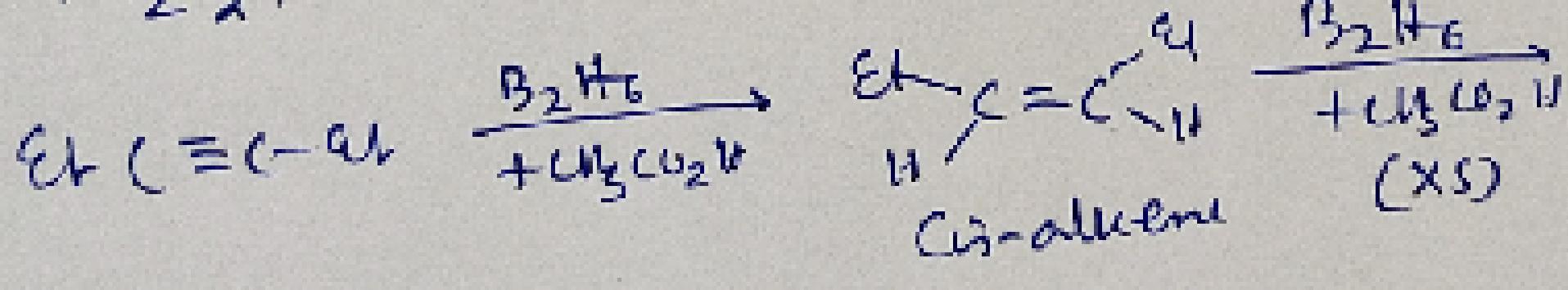
They are all example of anti-Markovnikov product.



Ketone is formed as final product.
Non-terminal alkyne

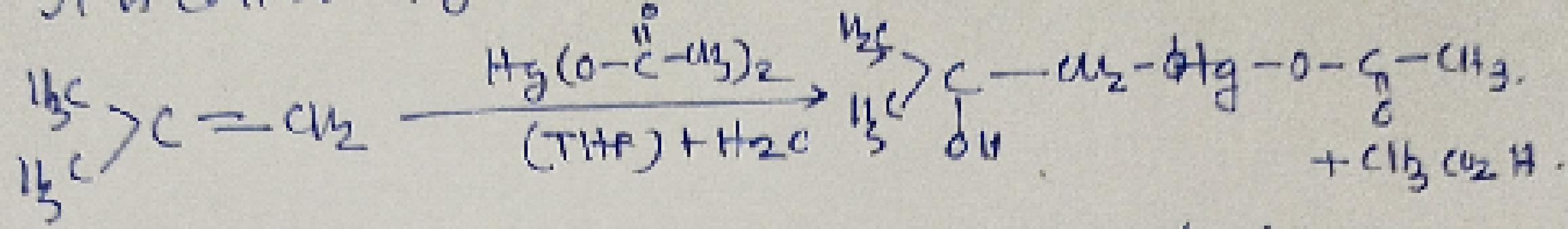
(Enol is formed as intermediate in HBO of alkyne using $B_2H_6(THF) + H_2O_2 + OH^-$ which is converted into corresponding keto/aldehyde form).

If we use $B_2H_6(THF) + Cl_3CO_2H$ instead of $B_2H_6(THF) + H_2O_2 + OH^-$, the product formed will be alkene / alkane.

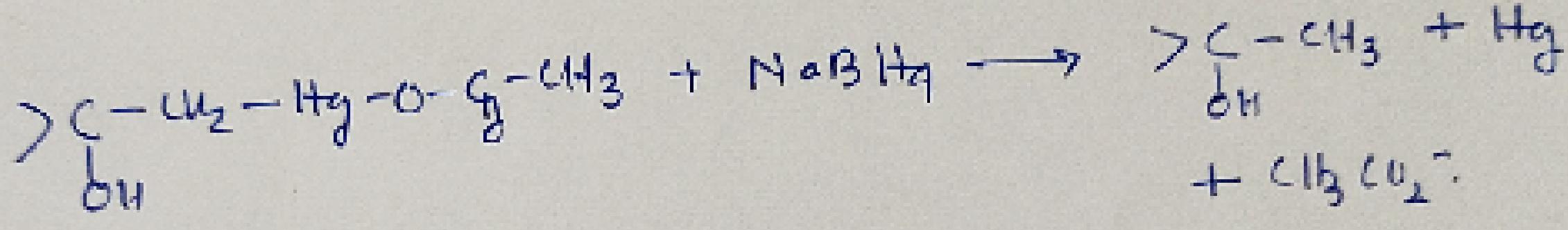


: OMDM: A useful laboratory procedure for synthesising alcohols from alkene in a two step reactions called ⁵
Oxymercuration - Demercuration.

Alkene reacts with mercuric acetate in a mix of THF & water to produce (hydroxy alkyl) mercury compound. It is called oxymercuration.



These (hydroxy alkyl) mercury compounds can be reduced to alcohols with NaBH₄. (Sodium borohydride)



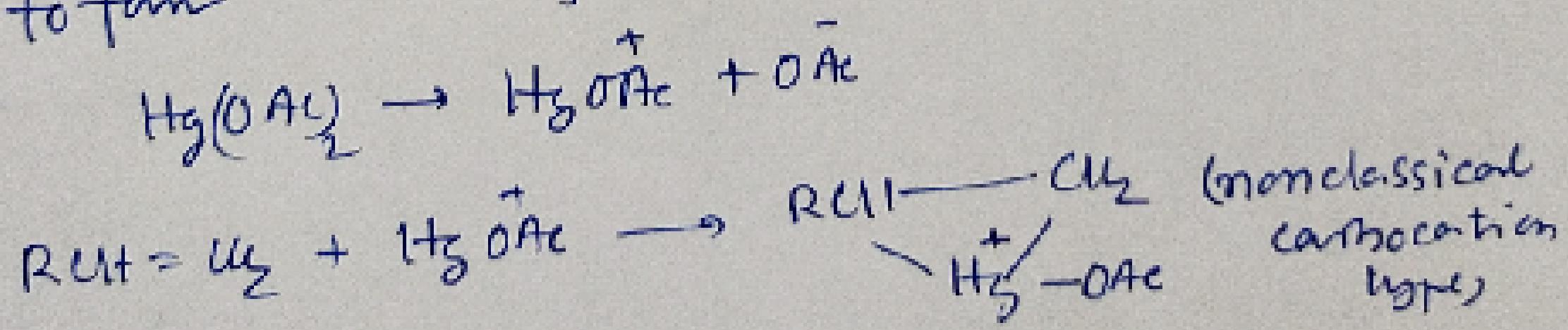
Here NaBH₄ reduce the acetoxymercury group

(Hg-O-C(=O)) & replace it with H. This is called demercuration. Hg change its oxidation state from +2 to 0.

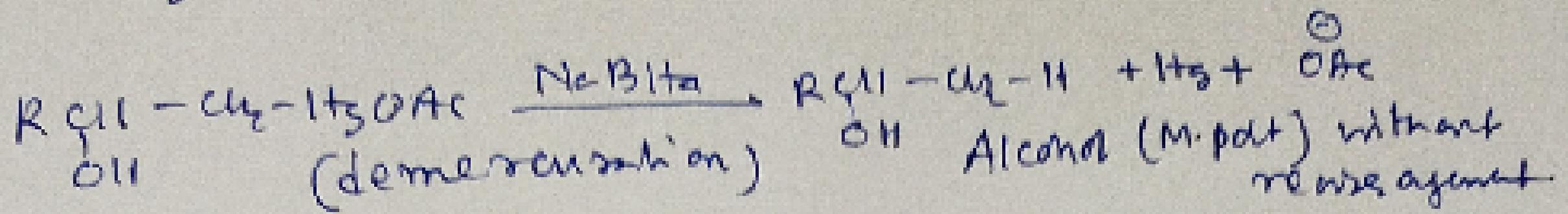
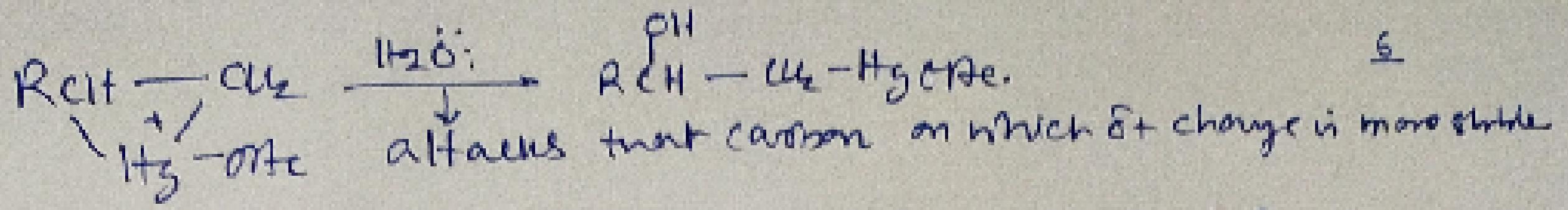
Both the steps are very rapid at room temperature. The overall reactions give alcohol in very high yield (> 90%).

Mechanism: Hg(OAc)₂ dissociates to form Hg⁺OAc & OAc⁻.

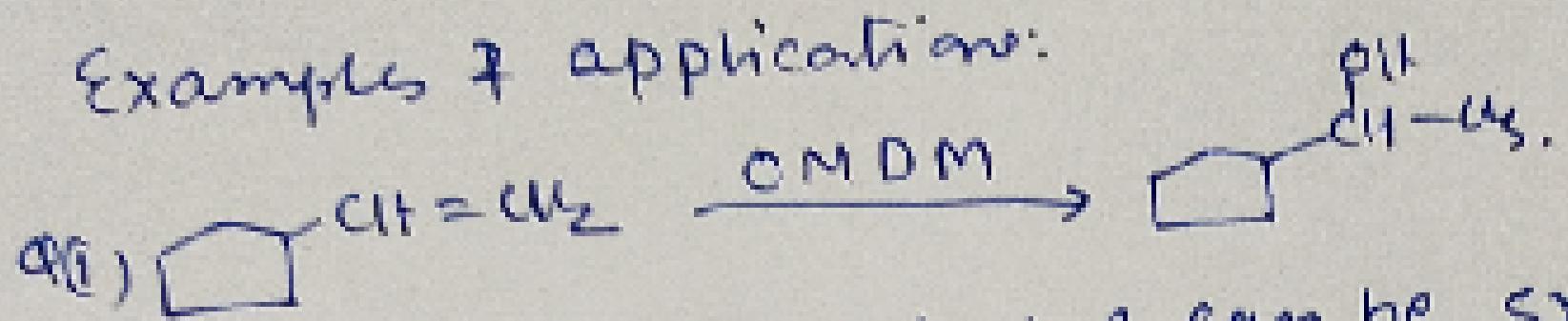
The attacking electrophile Hg⁺OAc is attacked by alkene to form the following intermediate.



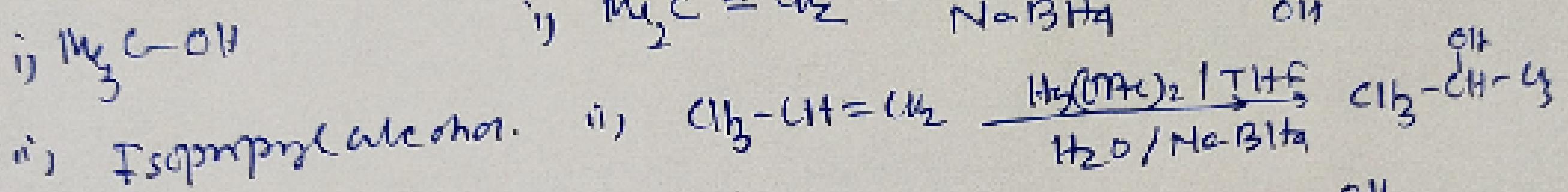
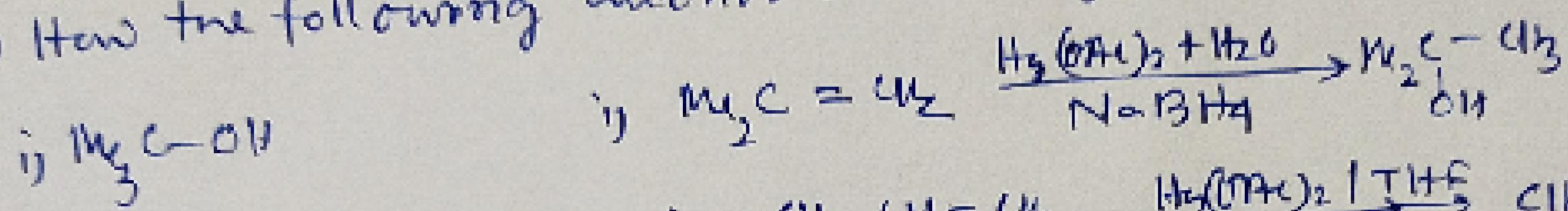
The charge on carbon is large enough to account for Markovnikov addition but not large enough for a rearrangement to occur.



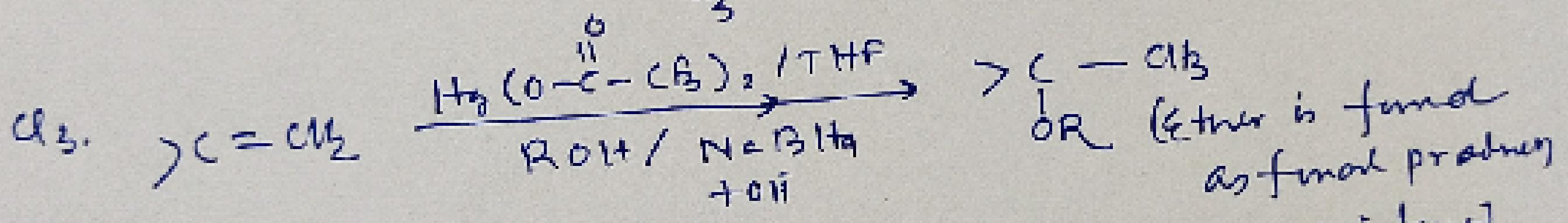
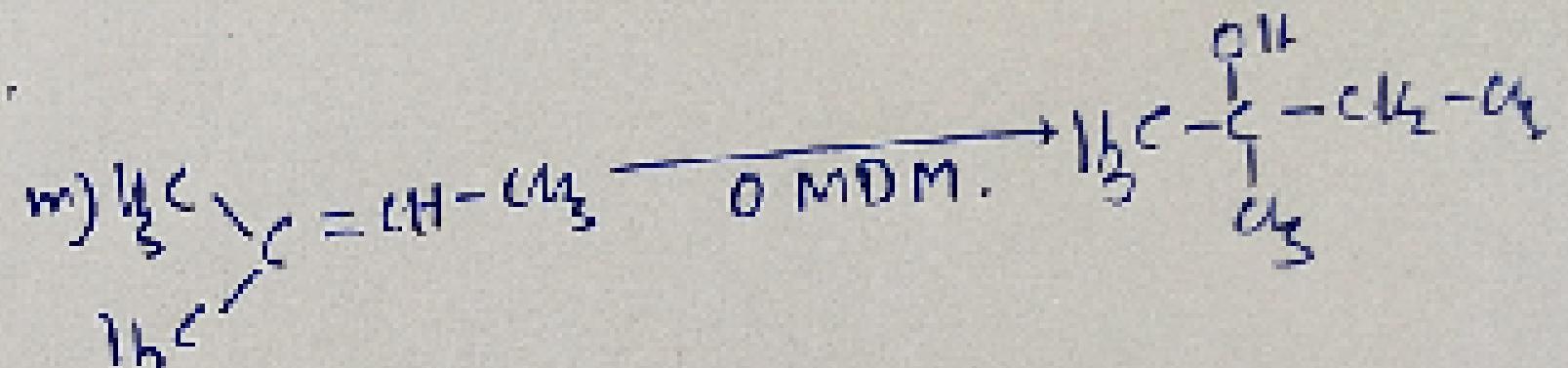
Examples & applications:



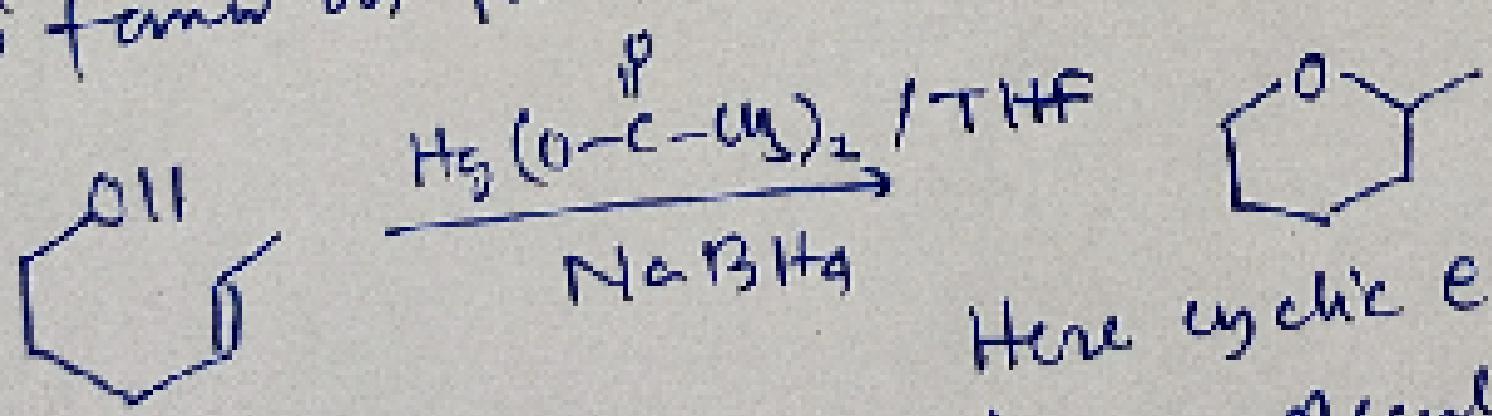
Q2.) How the following alcohol can be synthesised?



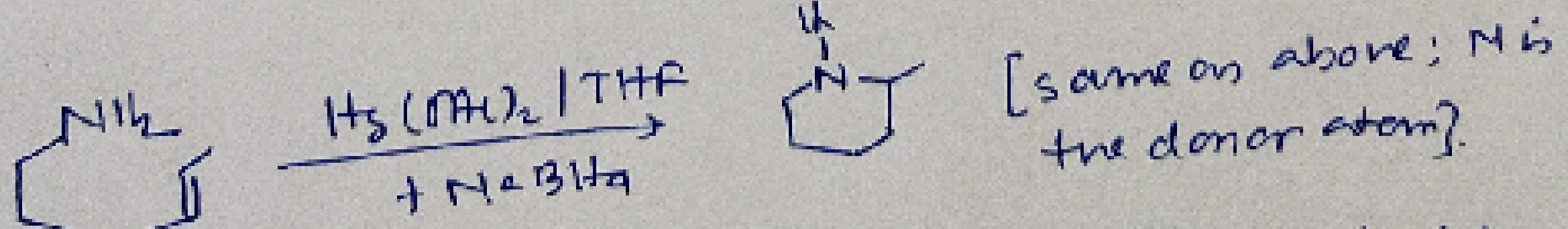
m) 2-Methyl 2-butanol.



So in OMDM, if we use $\text{Hg(OAc)}_2 / \text{H}_2\ddot{\text{O}}$, alcohol is formed as final product but if we use $\text{Hg(OAc)}_2 / \text{P}_2\text{O}_5$, ether is formed as final product. This reaction is regioselective.



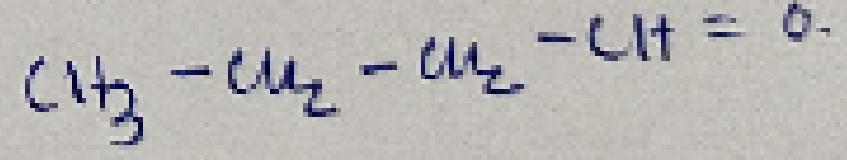
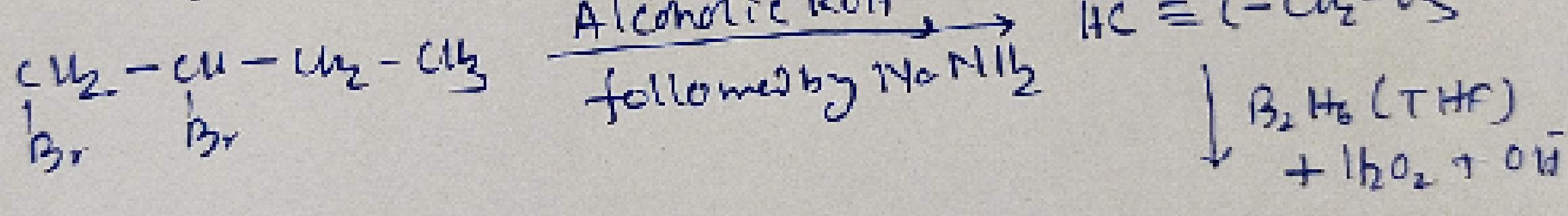
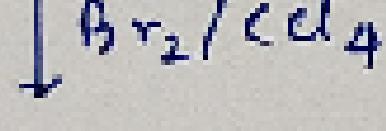
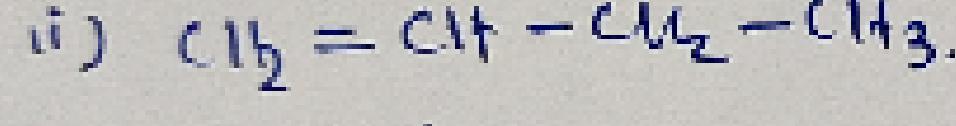
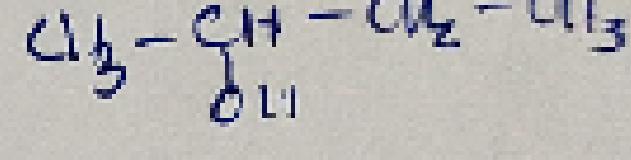
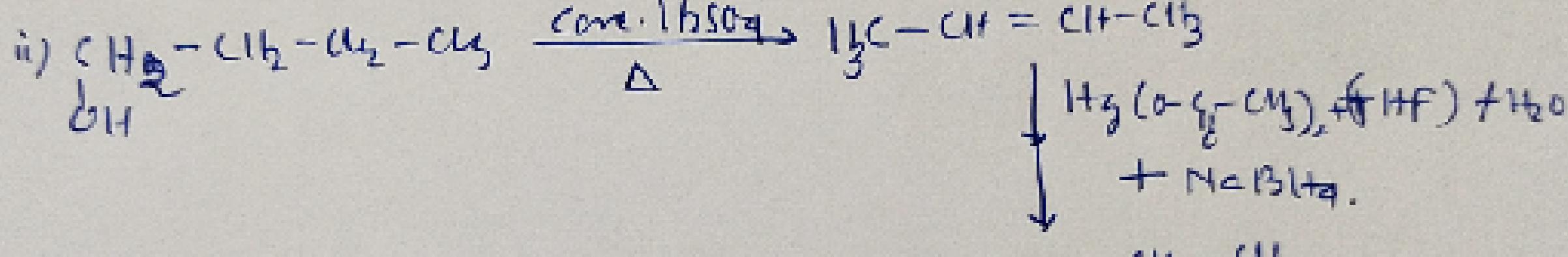
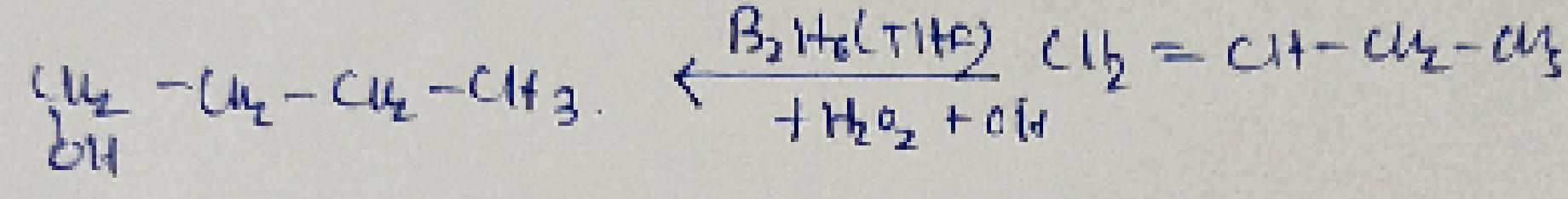
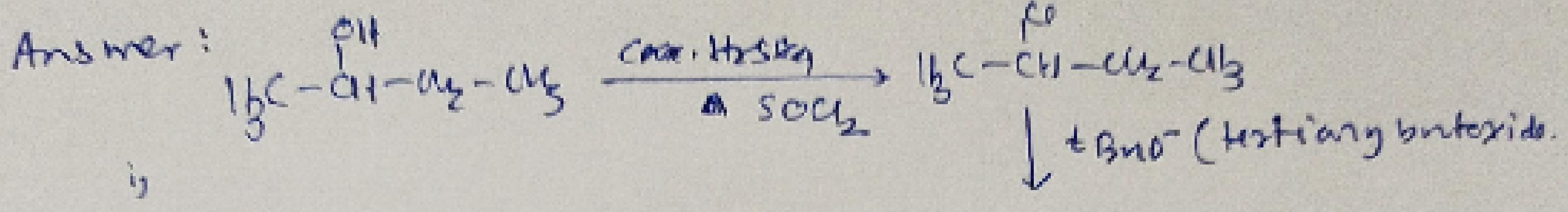
Here cyclic ether is formed by intramolecular attack by OH on $\text{C}_6\text{H}_5\text{O}^-$



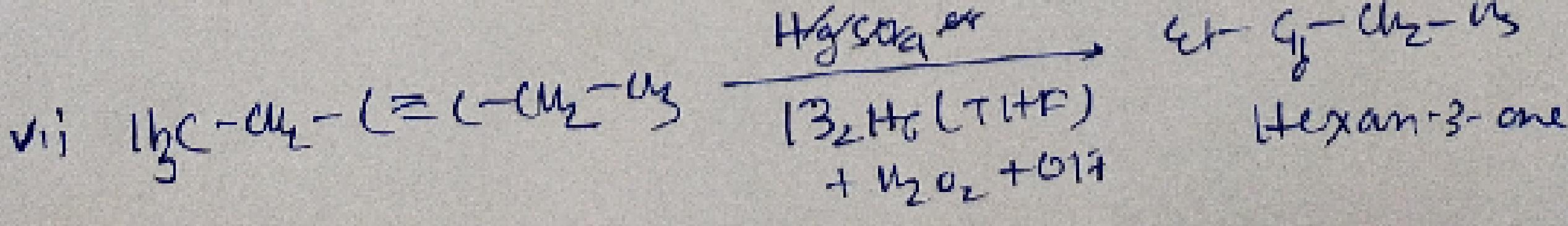
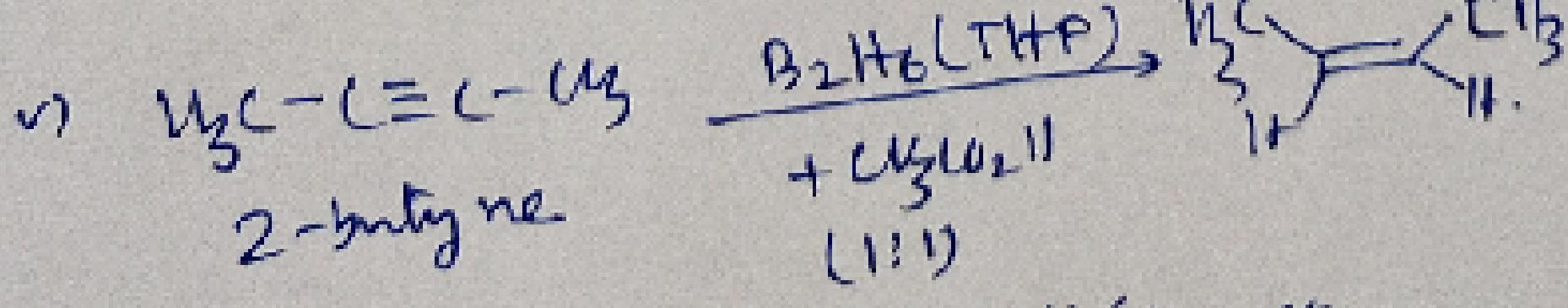
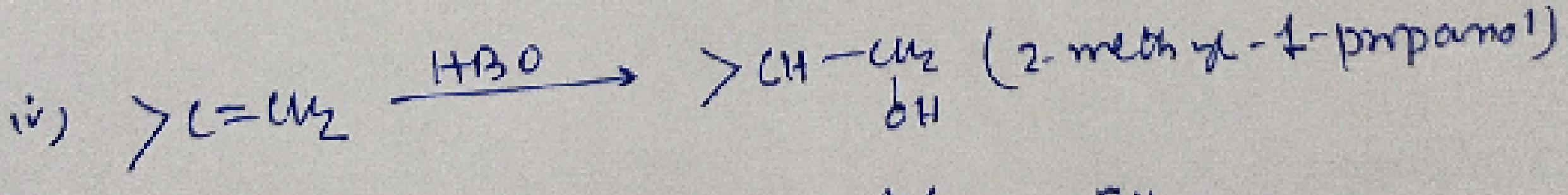
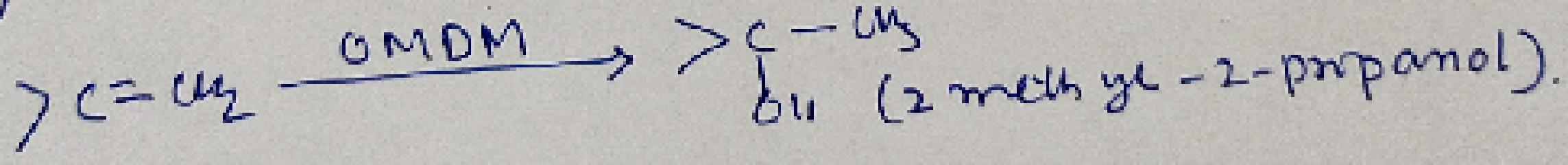
H_3O^+ (Acid catalysed hydration) addition to (=C system) is already discussed in carbo cation topic.

: Application : Conversion:

- i) 2-Butanol \rightarrow 2-butanol.
- ii) 1-Butanol \rightarrow 2-butanol.
- iii) 1-Butene \rightarrow Butanol.
- iv) Isobutene \rightarrow 2-methyl 2-propanol.
- v) Isobutene \rightarrow 2-methyl 2-propano.
- vi) 2-butyne $\xrightarrow[7]{\text{HgSO}_4}$ cis-but-2-ene.
- vii) 3-pentyne hexyne \rightarrow Hexan-3-one.



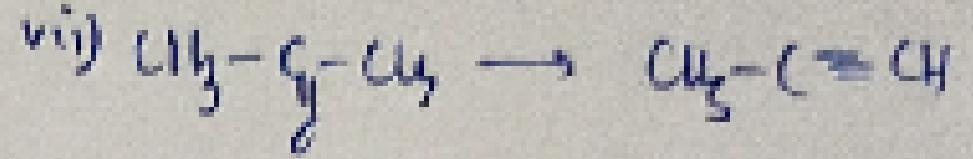
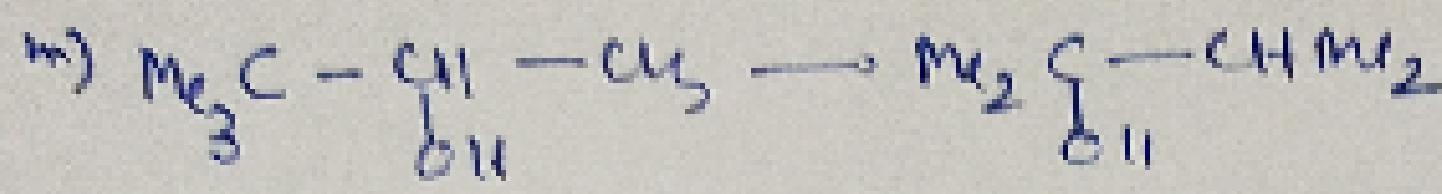
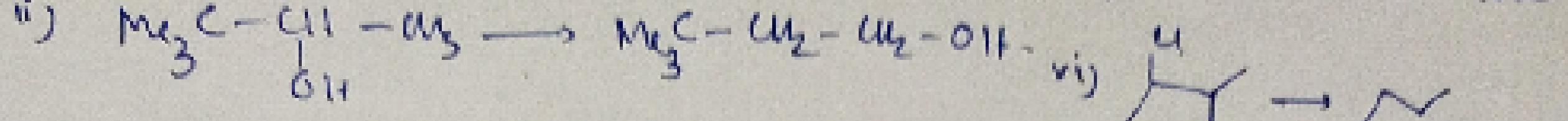
iii)



: Application: find out two reagents for following conversion. 8

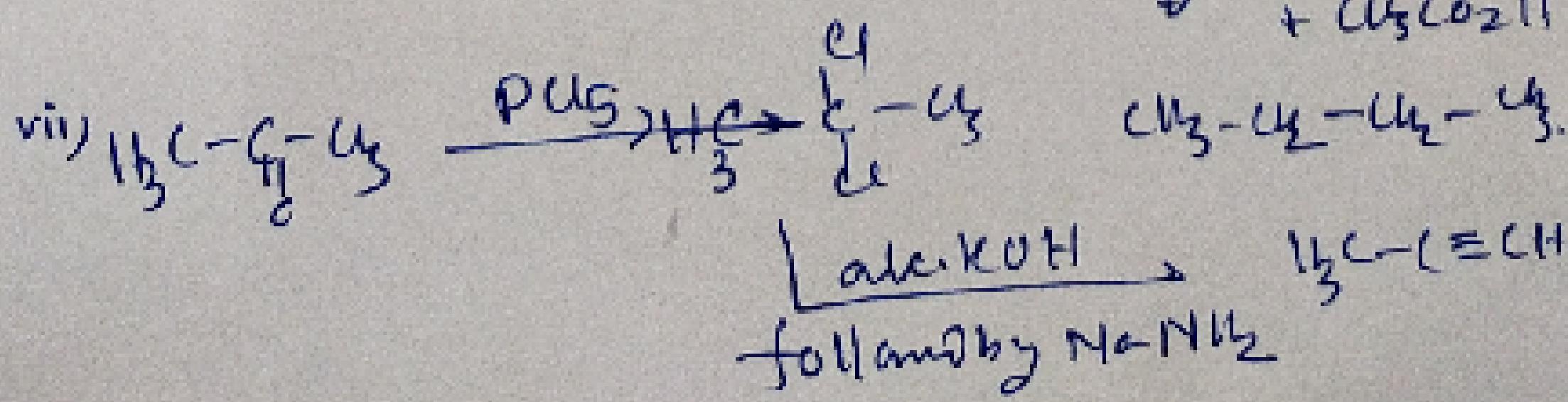
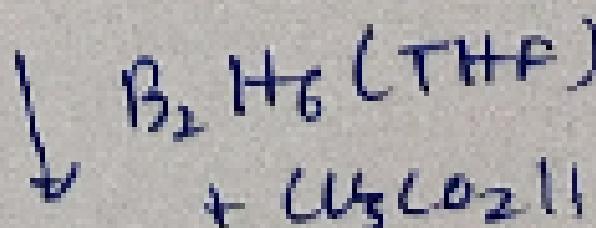
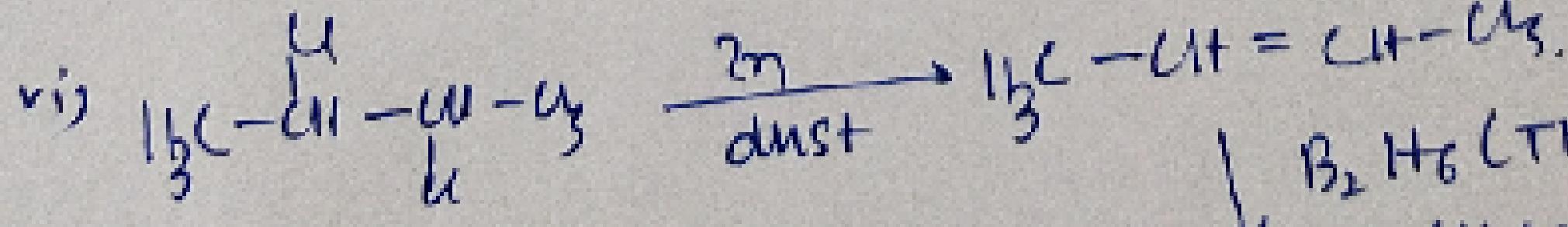
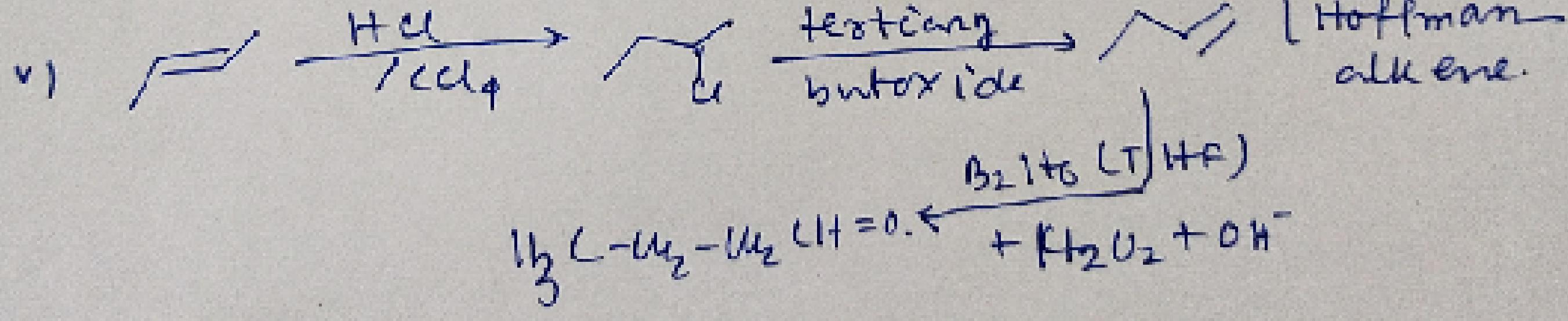
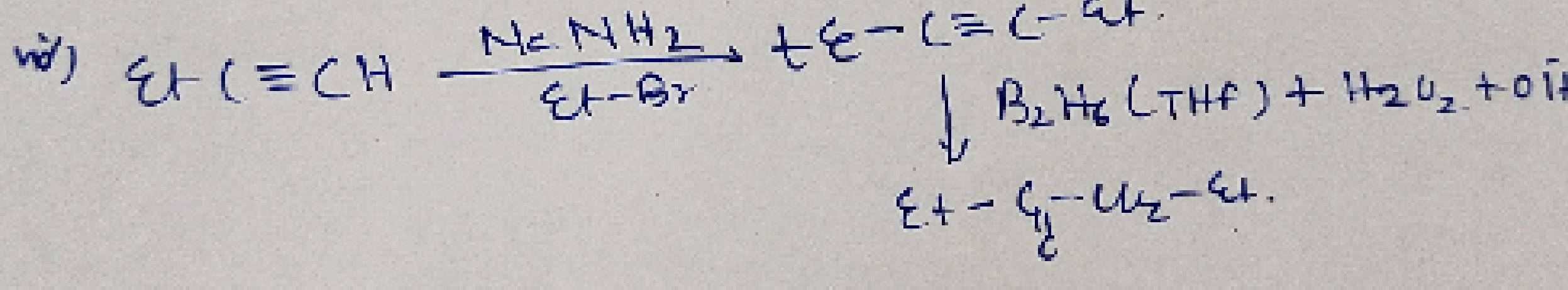
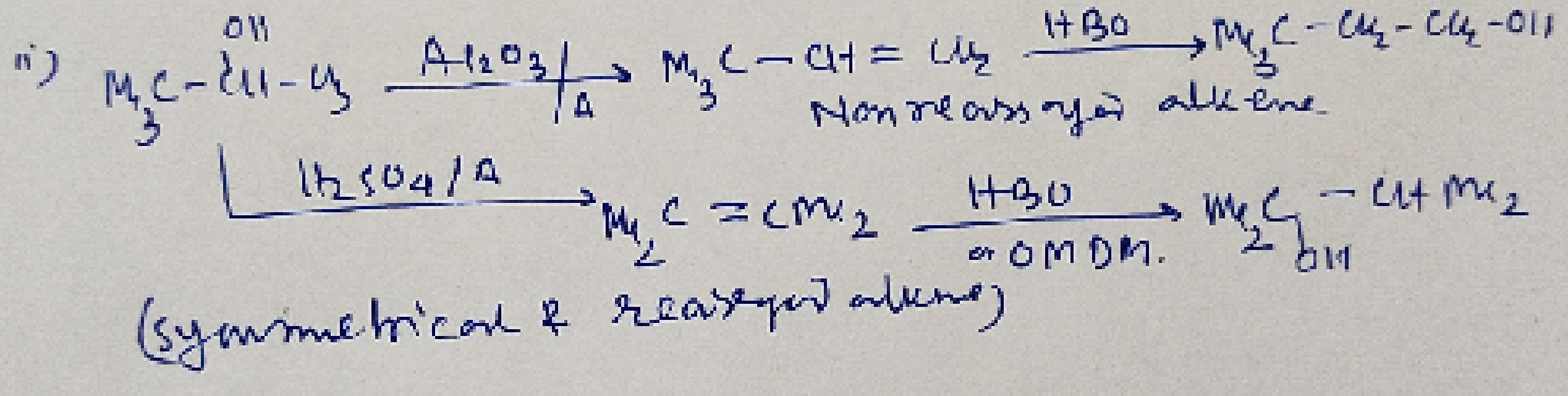
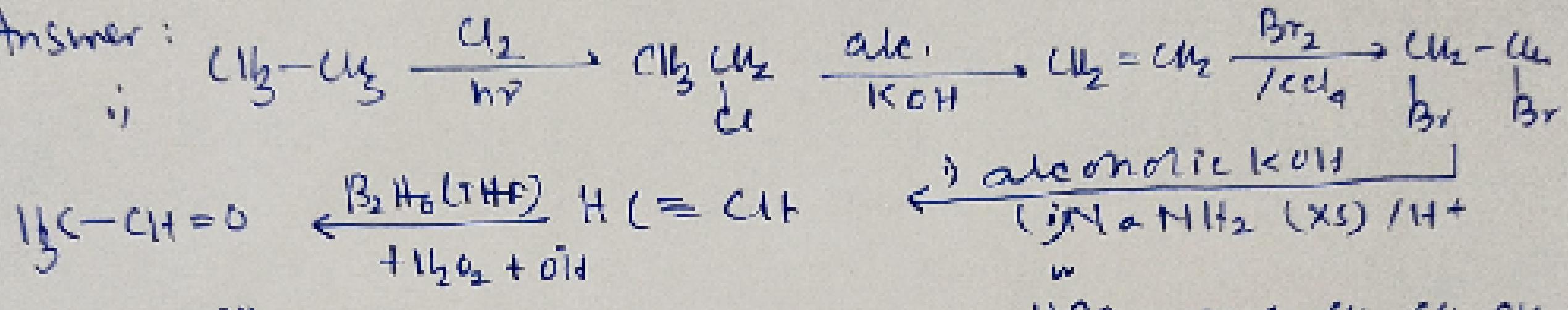


v) $\swarrow \curvearrowright \rightarrow$ Butanal



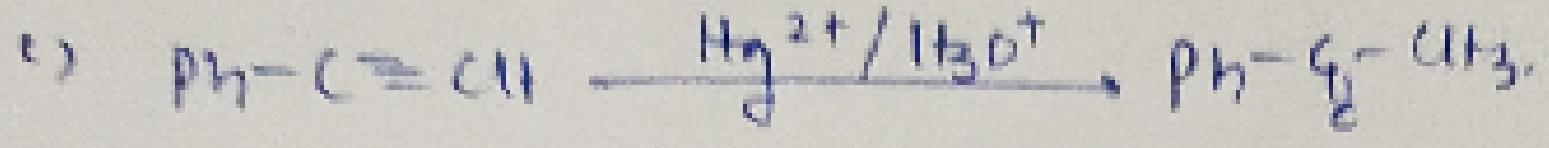
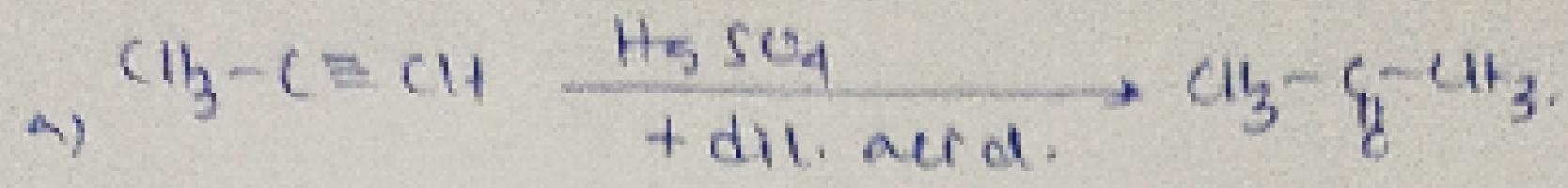
& vice versa.

: Answer:



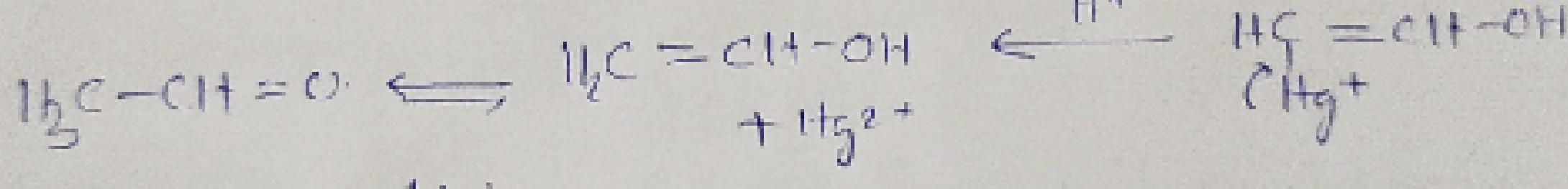
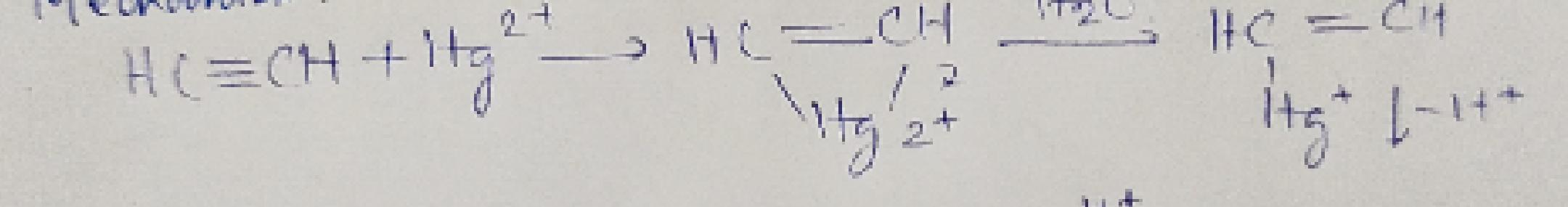
Kucherov Reaction:

Here aldehyde is converted into ketone. Markovnikov product is formed. Only acetylene gives acetildehyde.

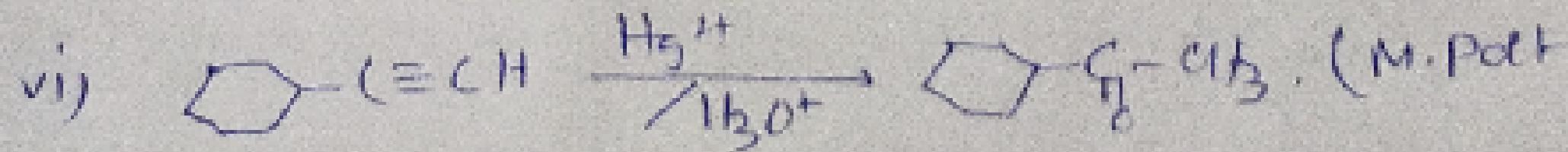
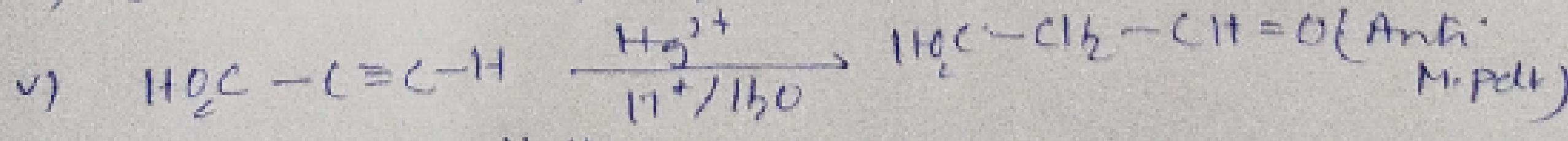
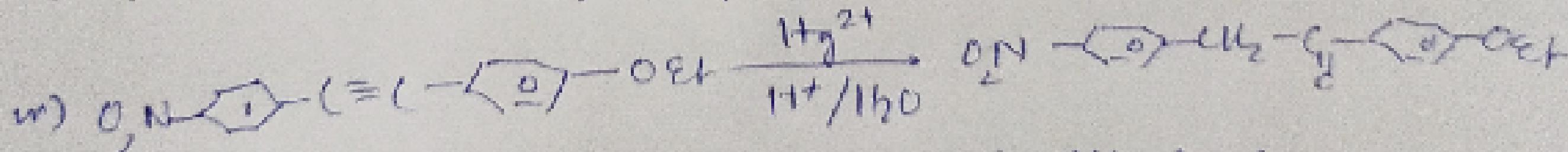
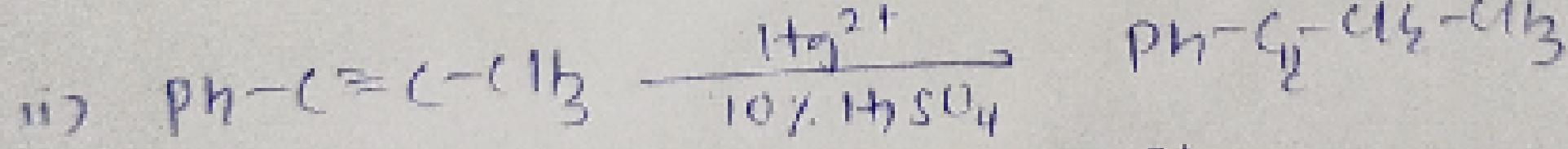
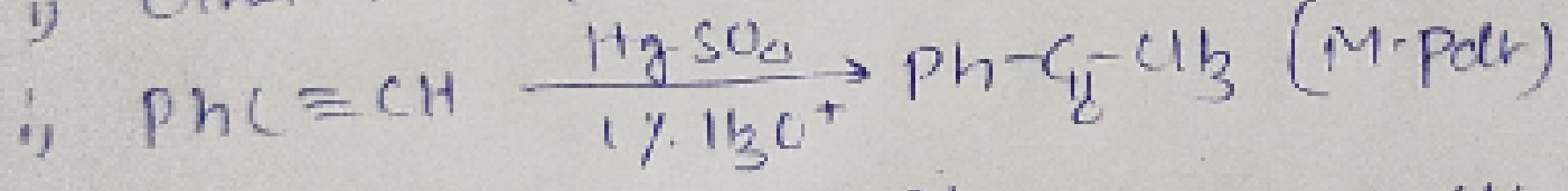


In all the reaction, H_2O addition takes place on that carbon which having more stable partial positive charge and is formed as intermediate. Non-classical carbocation enol is formed as intermediate.

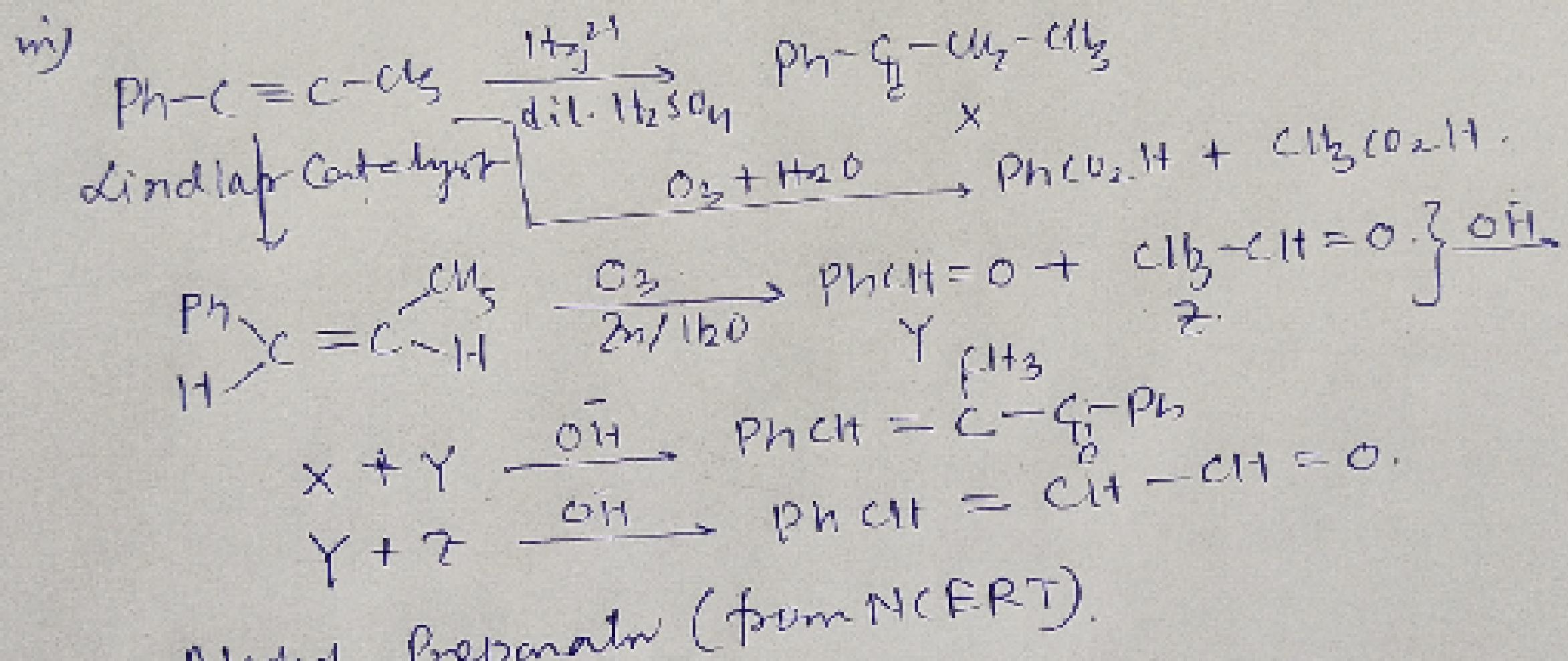
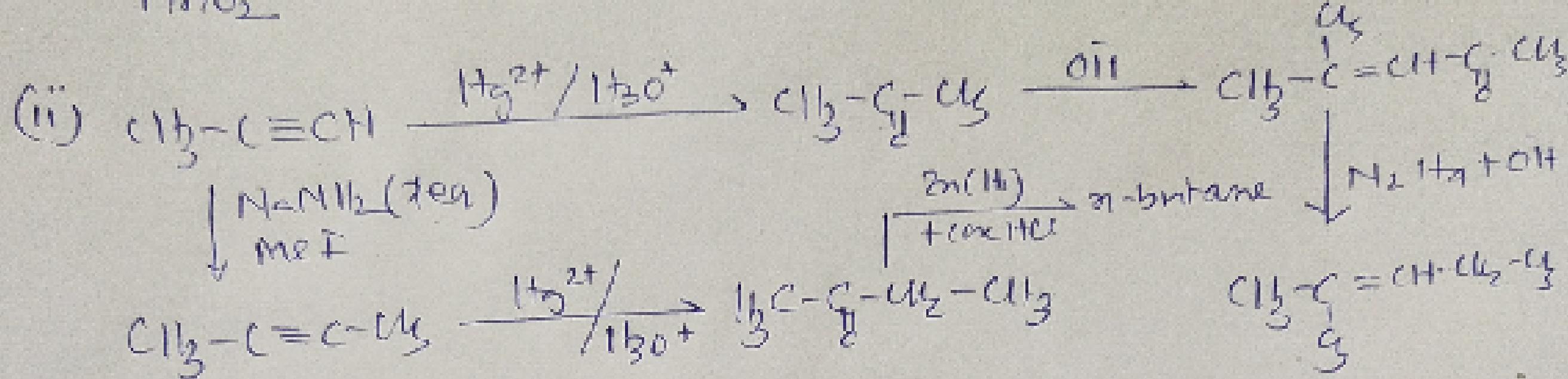
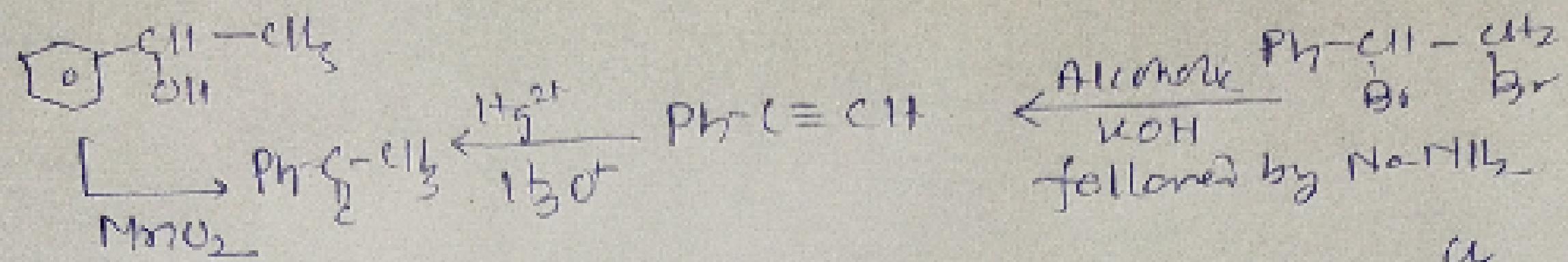
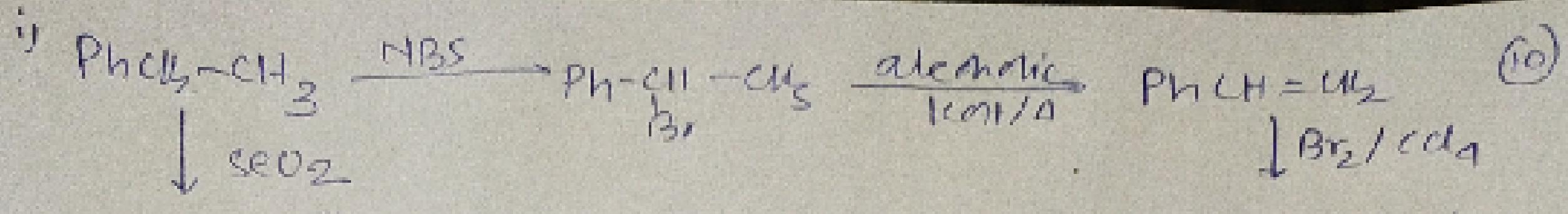
Mechanisms:



ij) Other examples:



[The carbon on which $\delta+$ is more stable will be attached with double bonded oxygen. Another one has two extra H's].



Alcohol Preparation (from NCFRT).

