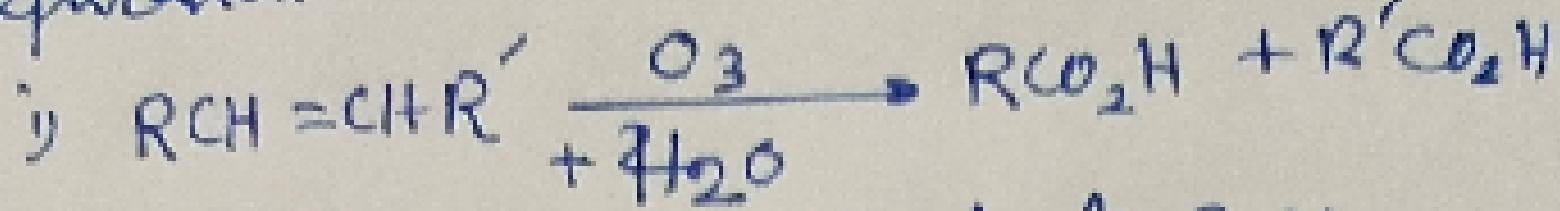


: CARBOXYLIC ACID:

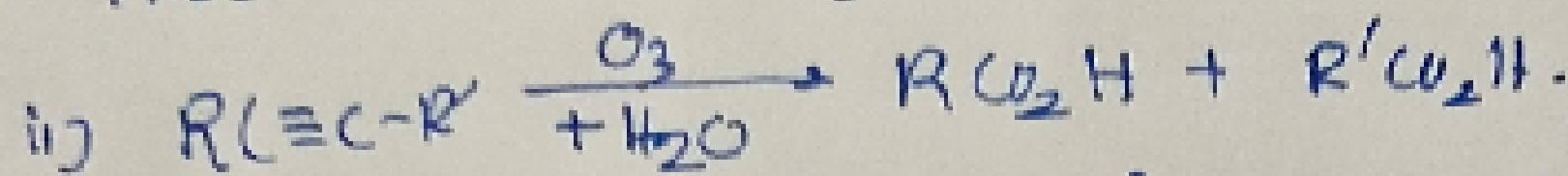
L

Preparation:

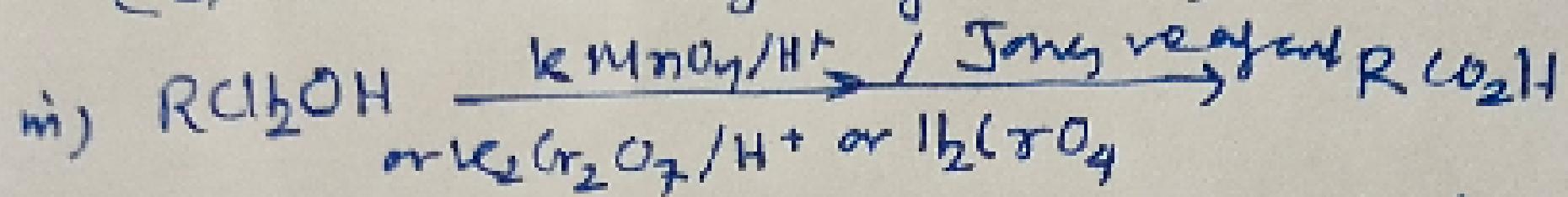


(Oxidative ozonolysis of alkene)

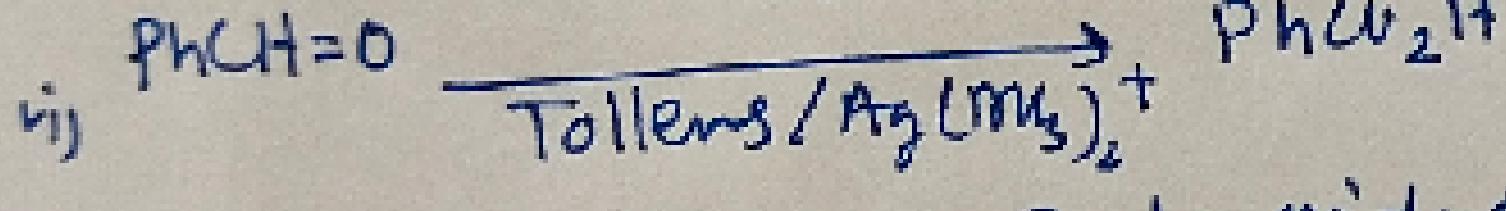
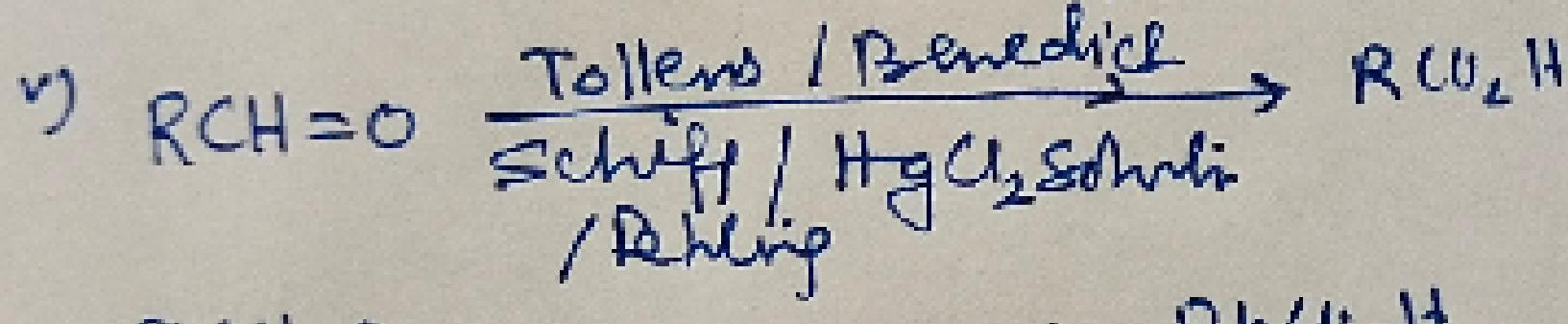
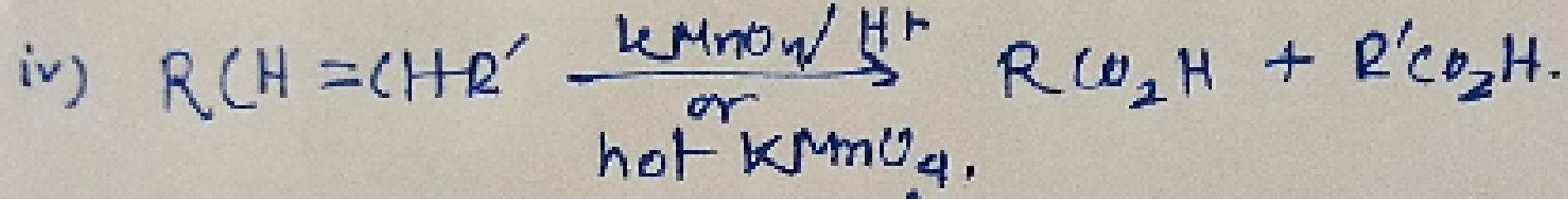
Also we can use $\text{O}_3 + \text{H}_2\text{O}_2$; $\text{O}_3 + \text{RCO}_3\text{H}$.



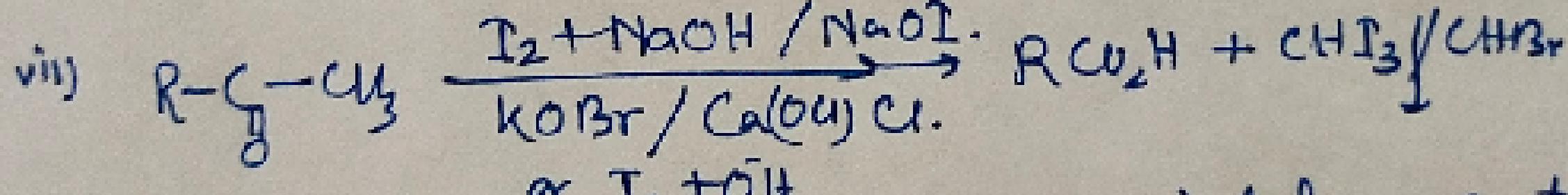
(Oxidative ozonolysis of alkyne)



They all acts as strong oxidising reagent

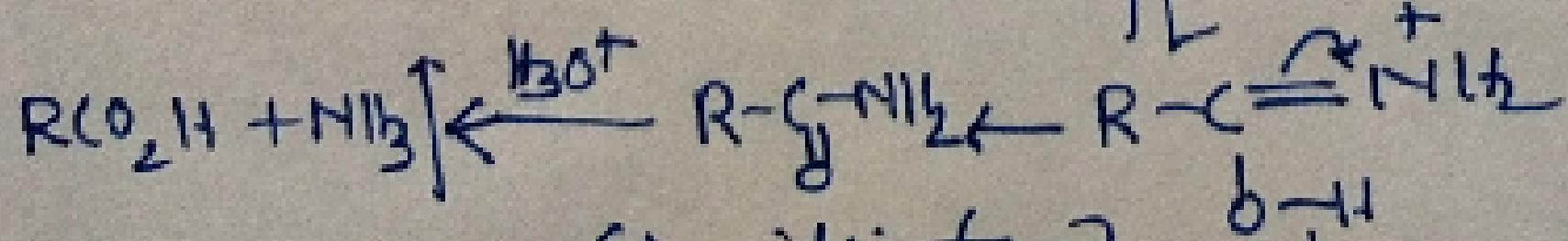
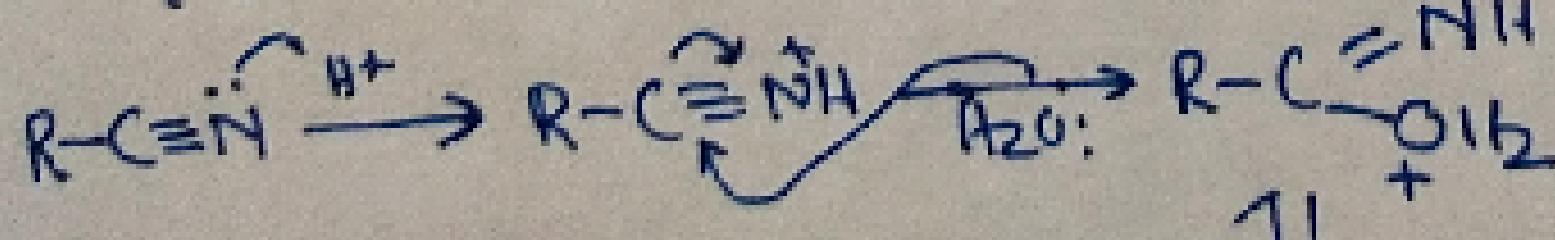
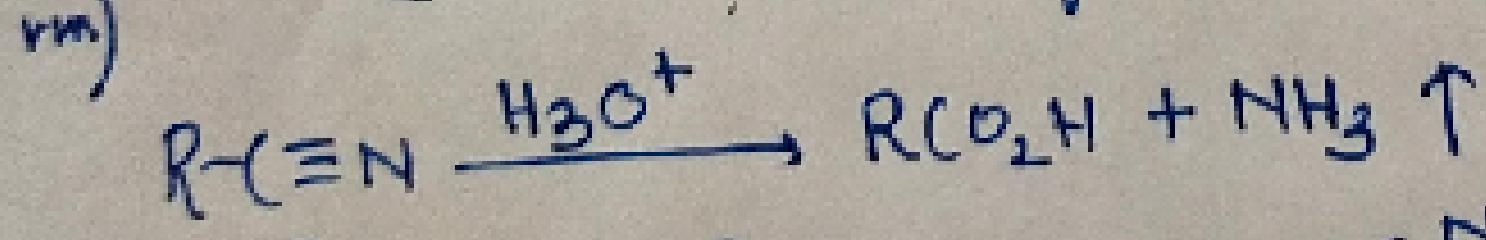


fehling can not be used to oxidise Benanaldehyde

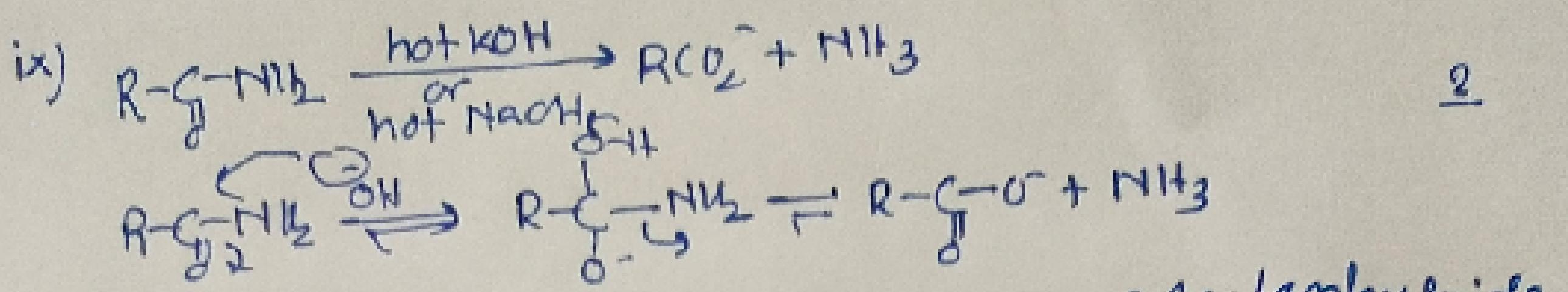


for $\text{I}_2 + \text{NaOH}$, The reaction is called iodofom reaction.

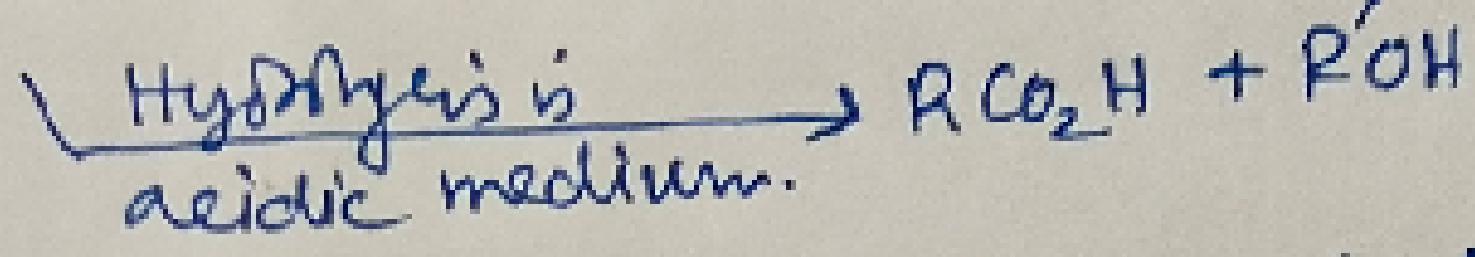
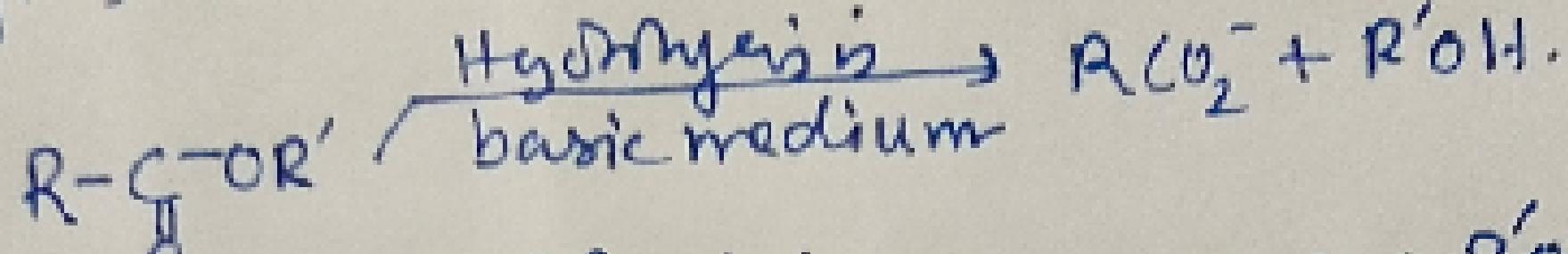
It is example of step down reaction.



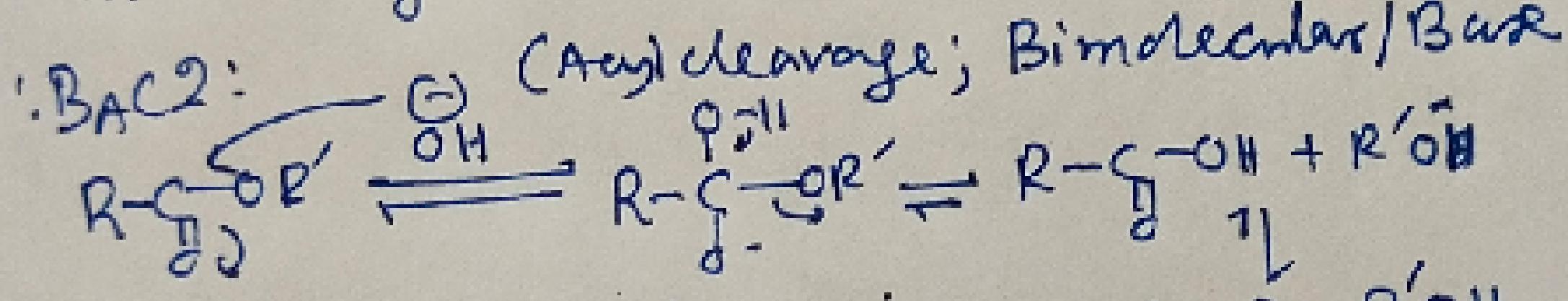
(Amide is formed as partial hydrolysis)



(x) Hydrolysis of acid derivative e.g. ester/ anhydride gives carboxylic acid as product.



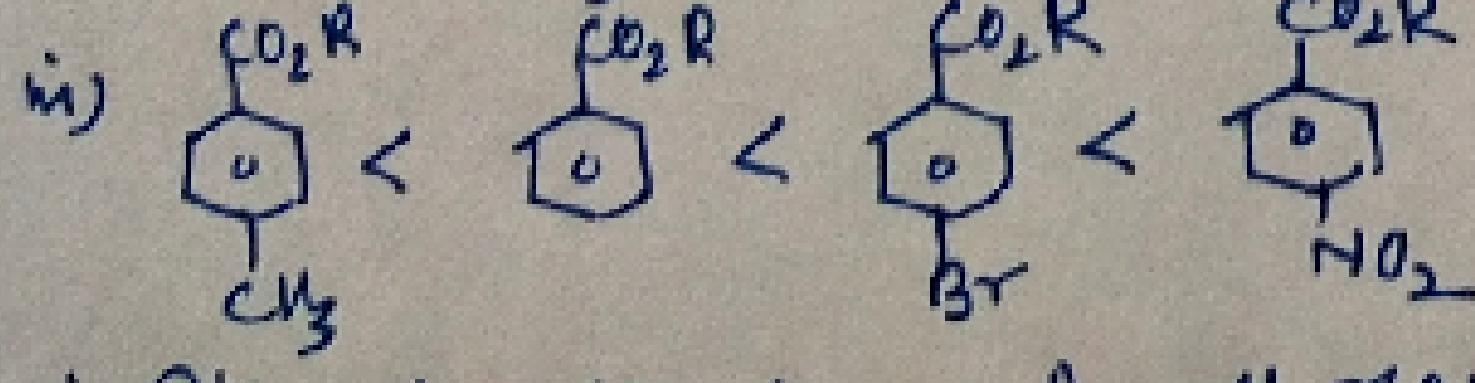
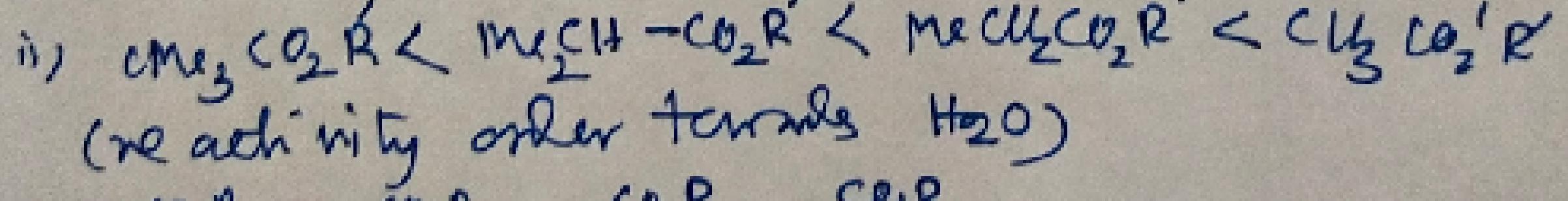
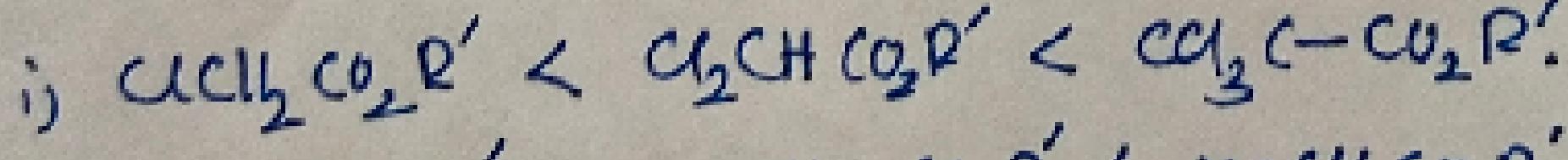
Hydrolysis in basic medium are carried out in two ways; i) Acyl cleavage ii) Alkyl cleavage.



\Rightarrow 3 step process. 1st step is r.d.s

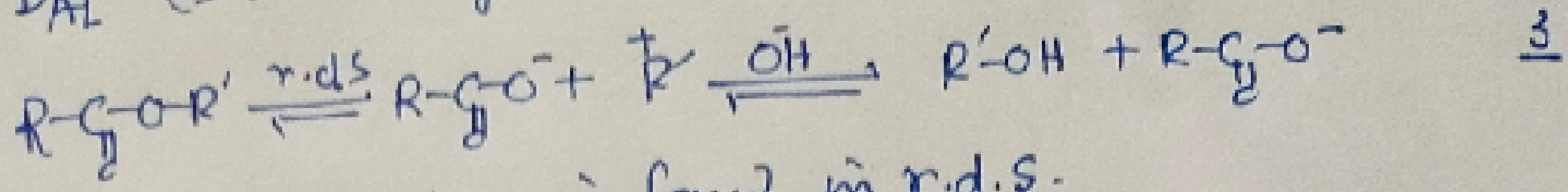
\Rightarrow rate = $k[\text{ester}][\text{OH}^-]$. 2nd order kinetics
2 bimolecular mechanism.

More $\delta+$ charge on carbon increases hydrolysis rate & more steric crowding around carbon decreases hydrolysis rate.



iv) It's very common; As all steps are not reversible then backward reaction (esterification) can not take place in basic medium.

B_{AT}¹ (Base catalyst; alkyl cleavage; Unimolecular)



→ Hence carbonation is forced in r.d.s.

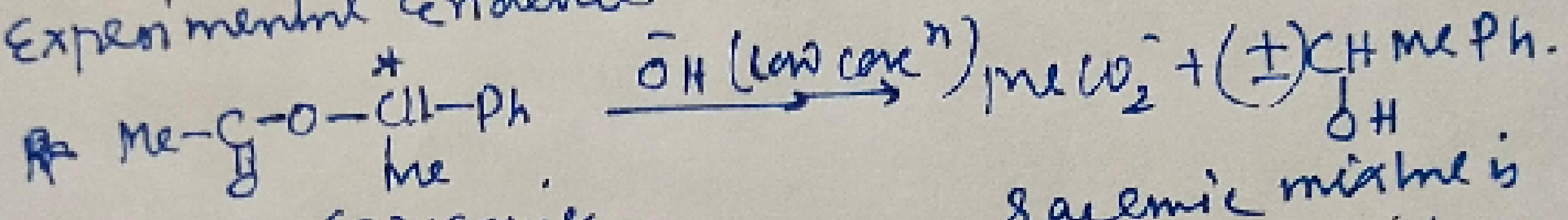
⇒ Here carbocation is formed when it is stable.

a) R^+ is only formed when H_2 is present
- this kind of mechanism takes place for

so this type of mechanism.

2) very specific.
- specific) cut in mild caseⁿ of Otitis.

\Rightarrow reaction is carried out
Experimentally Evidence.

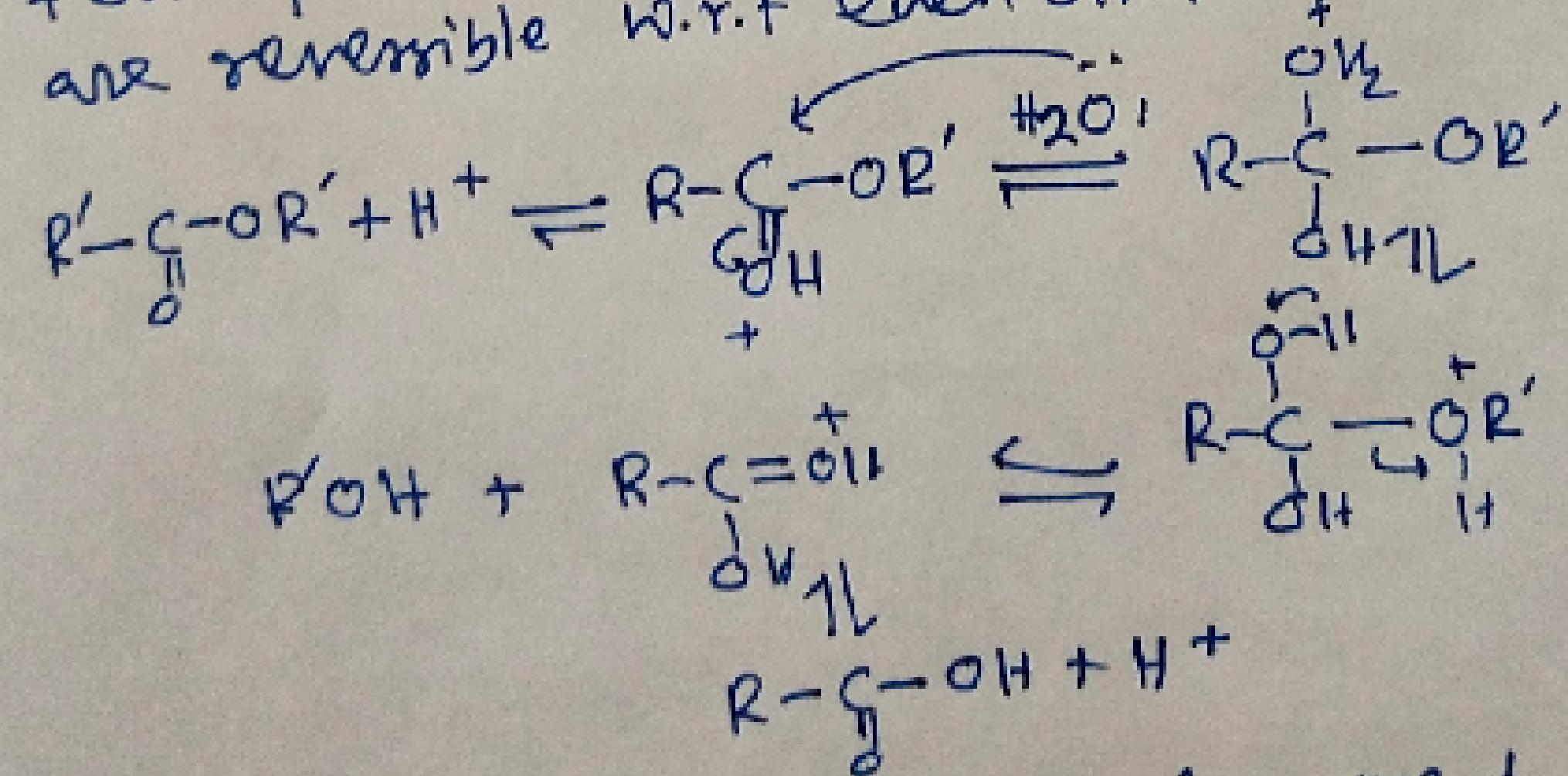


8+
Galvin's method is
found which indicates the
mechanism is BA1.

• Acid Catalysed Hydrolysis: $\text{Ac}_2\text{: Acyl cleavage}$

- Acid catalysed hydrolysis

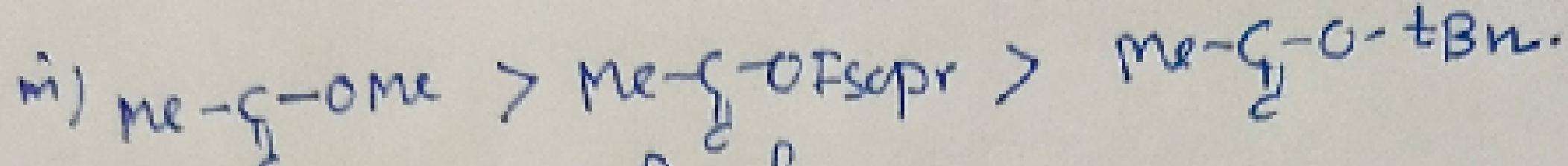
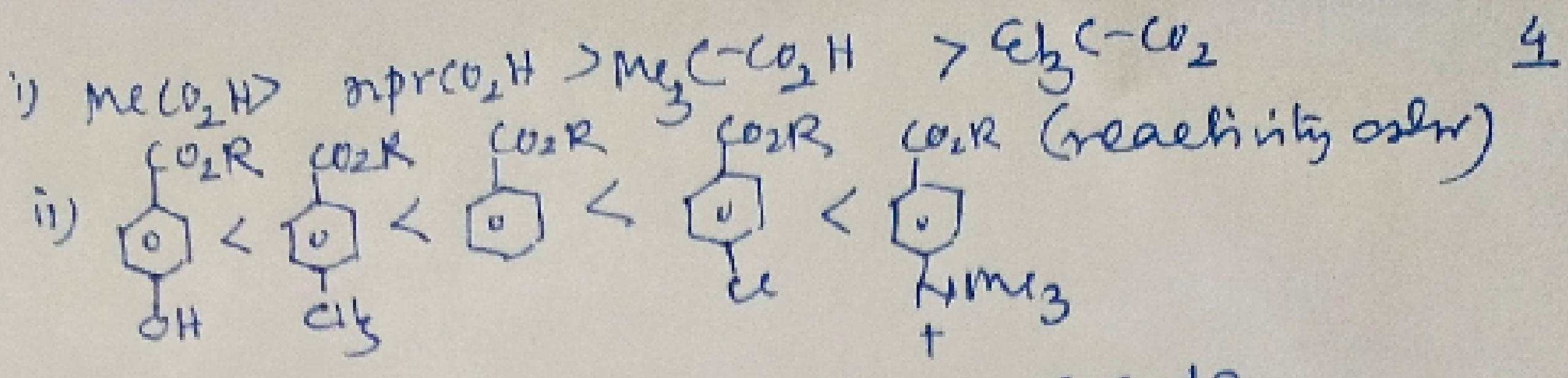
In acidic medium, acid catalysed hydrolysis & esterification both take place because all steps are reversible w.r.t each other.



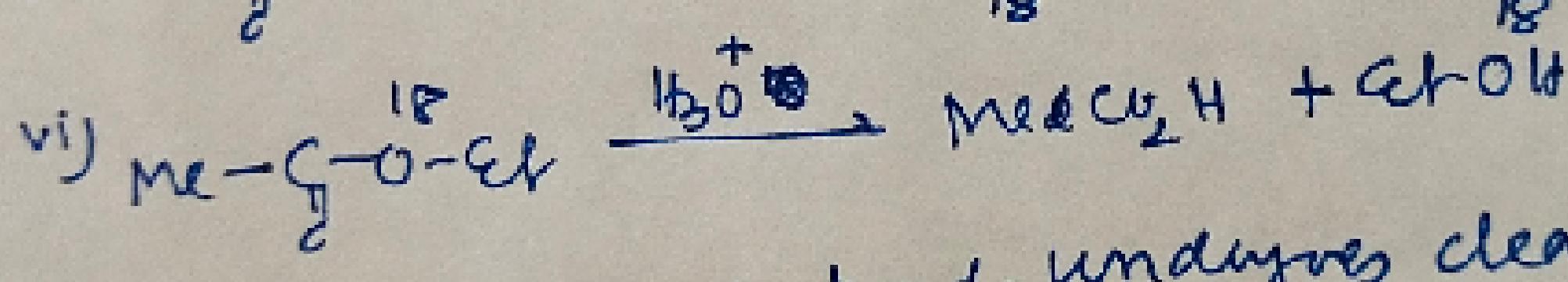
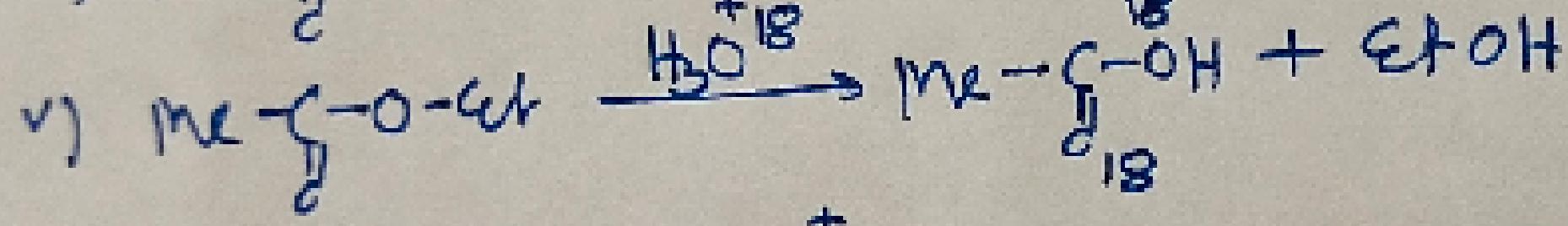
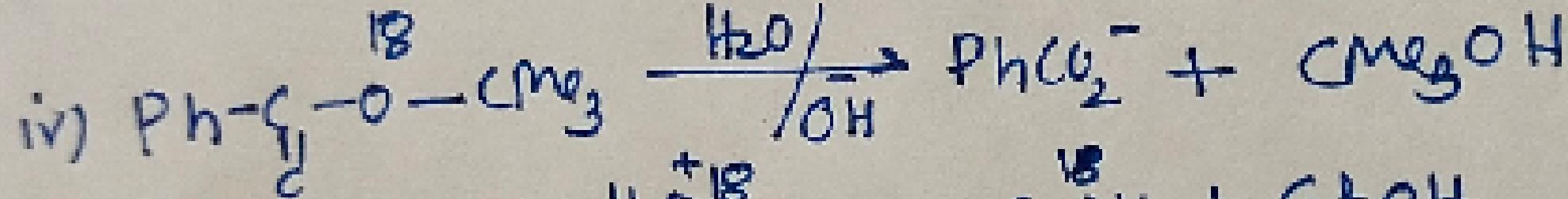
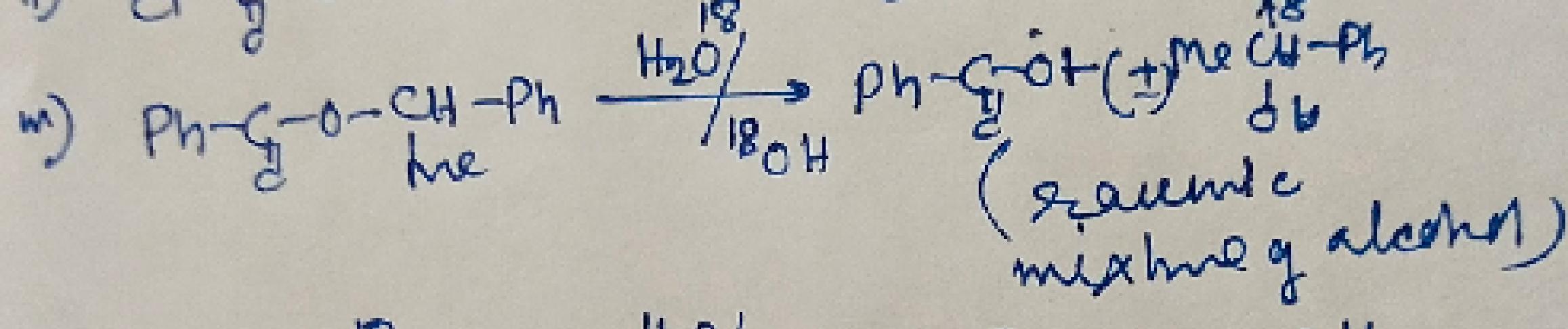
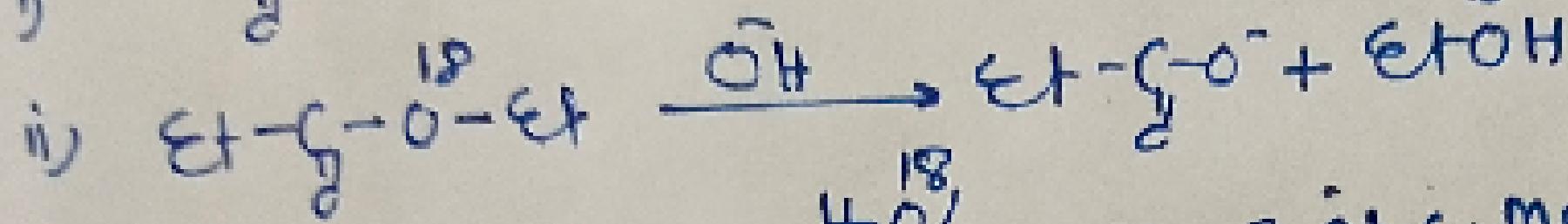
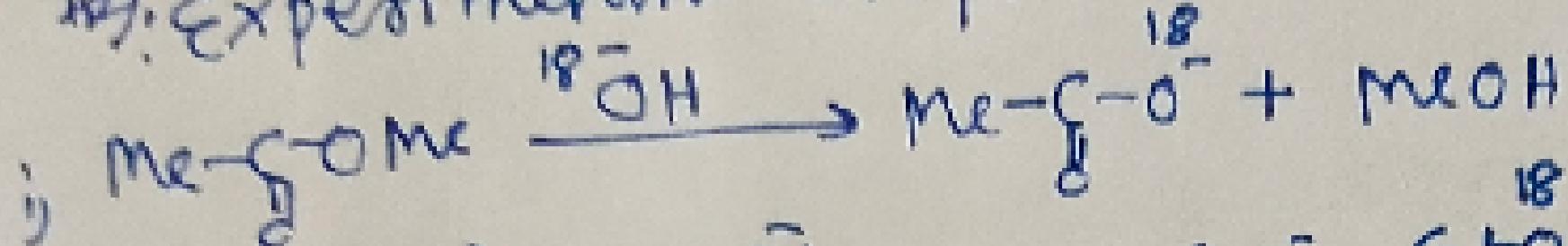
\Rightarrow 2nd order in $\text{O}_2\text{d.s.}$ / Bimolecular mechanism.
 \Rightarrow At low concn of H_2O_2 .

\Rightarrow growing in water , H_2O is a base
 \Rightarrow $\text{rate} = k[\text{ester}][\text{H}_3\text{O}^+]$. At high concn'g of H_2O ;

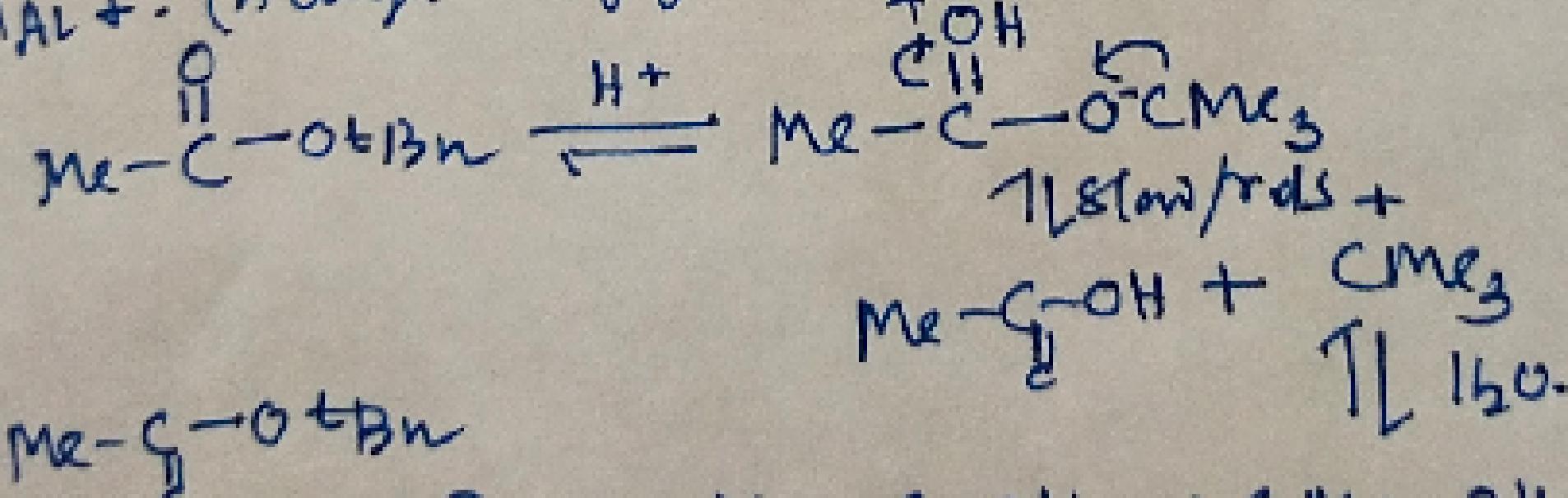
\Rightarrow $\text{Rate} = k[\text{ester}] [\text{H}_3\text{O}^+]$.
 It is pseudo 1st order reaction.



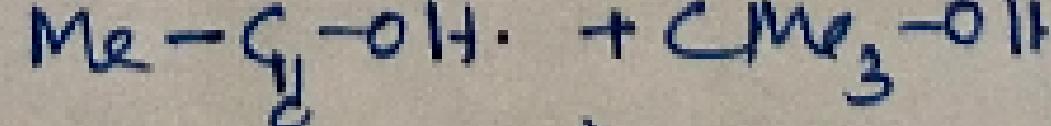
iv) Experimental Proof:



: A.R.T: (Alkyl-oxygen bond undergoes cleavage)



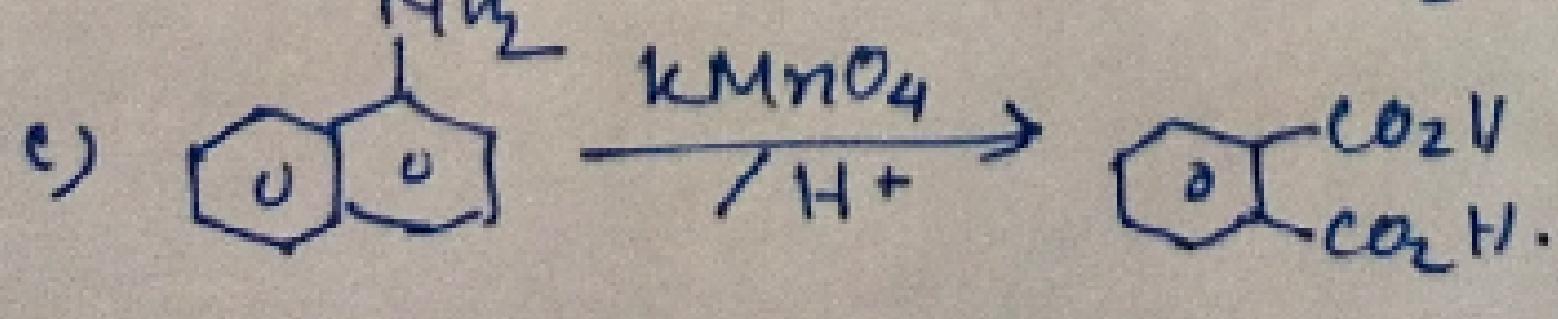
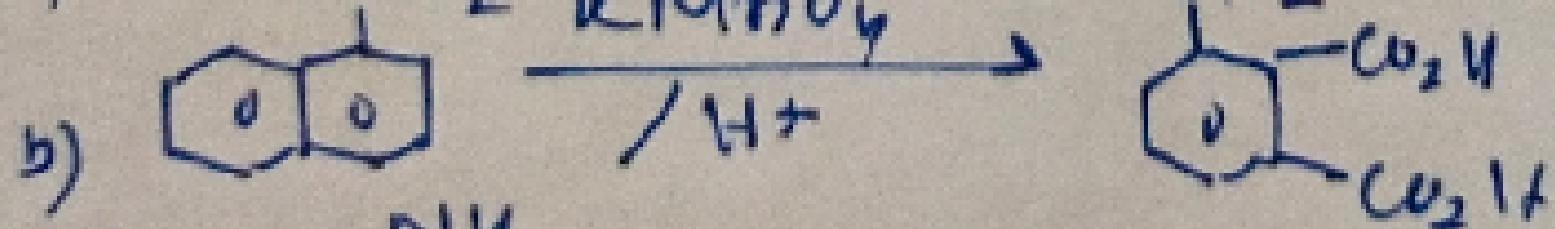
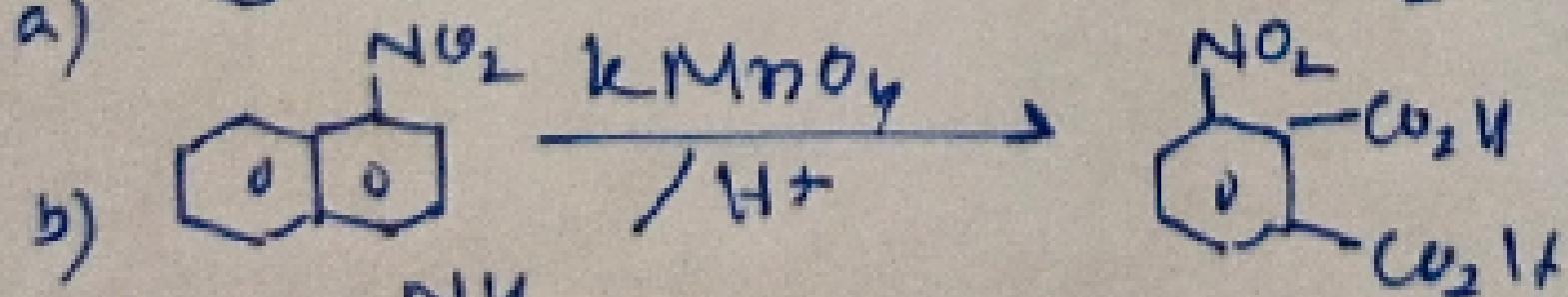
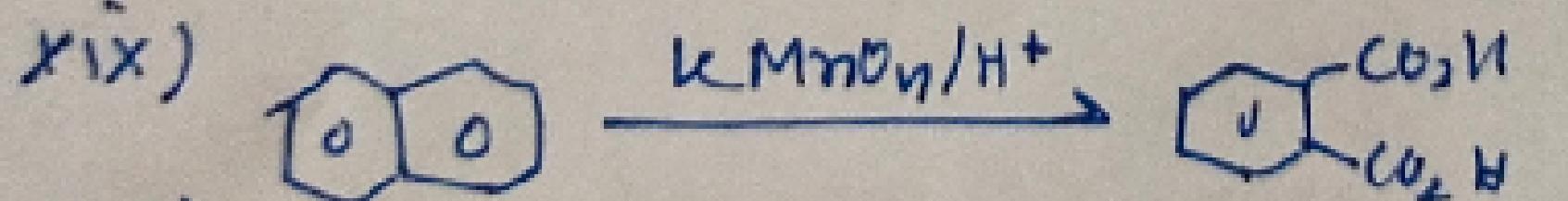
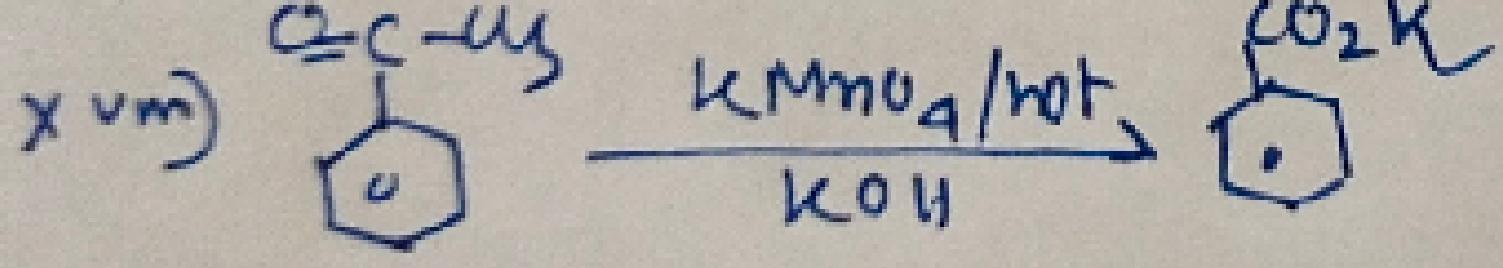
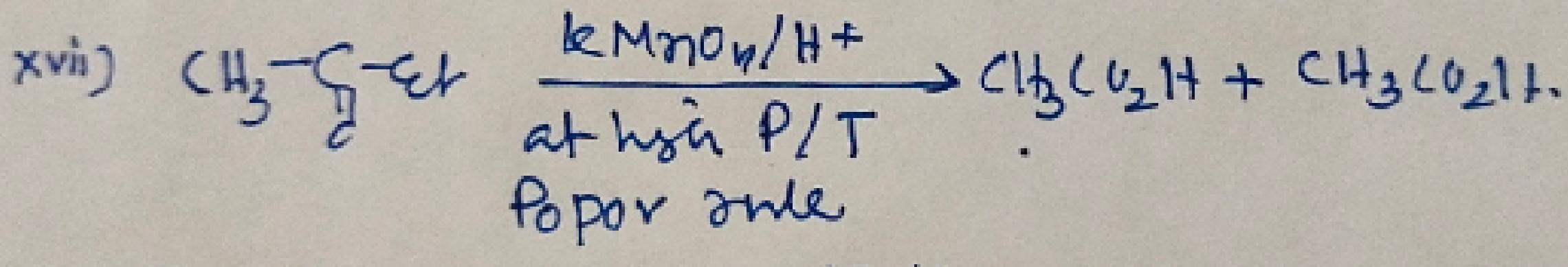
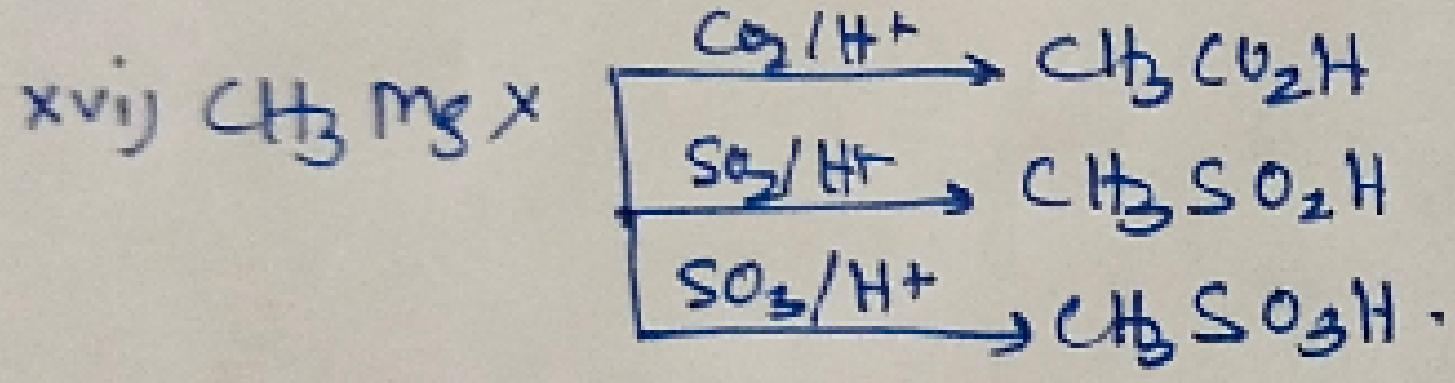
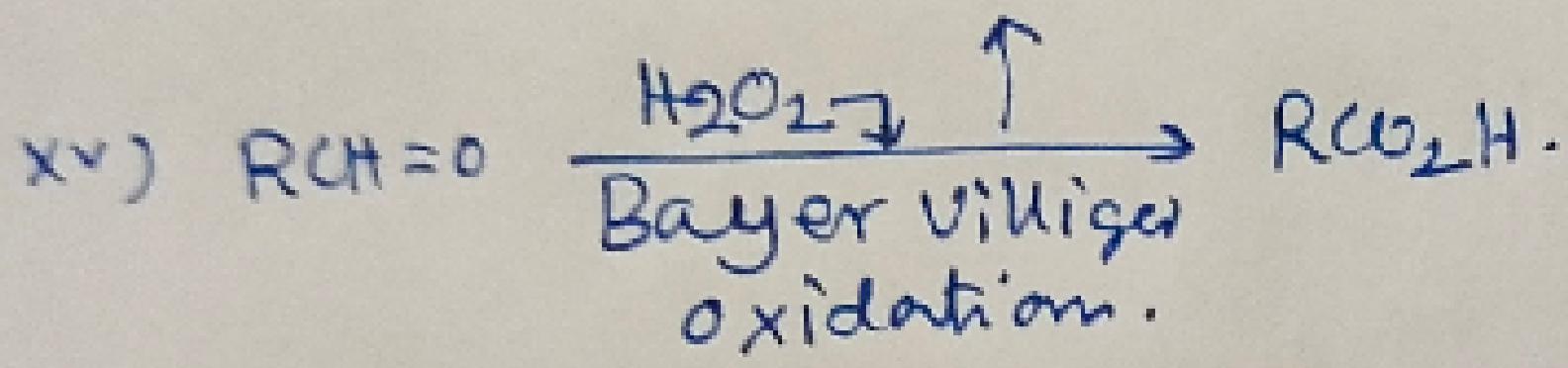
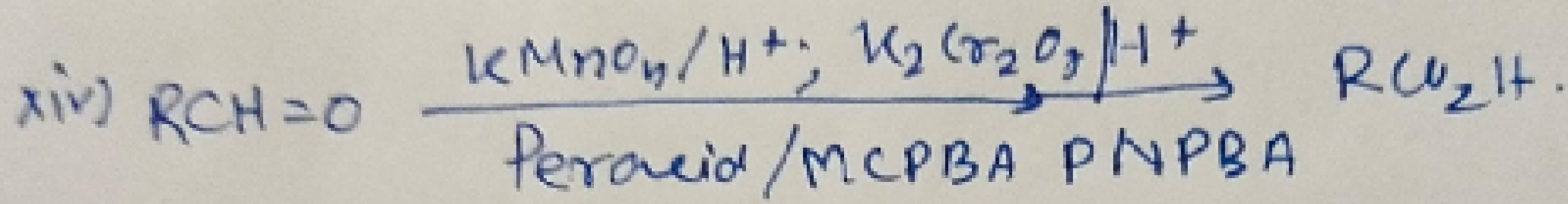
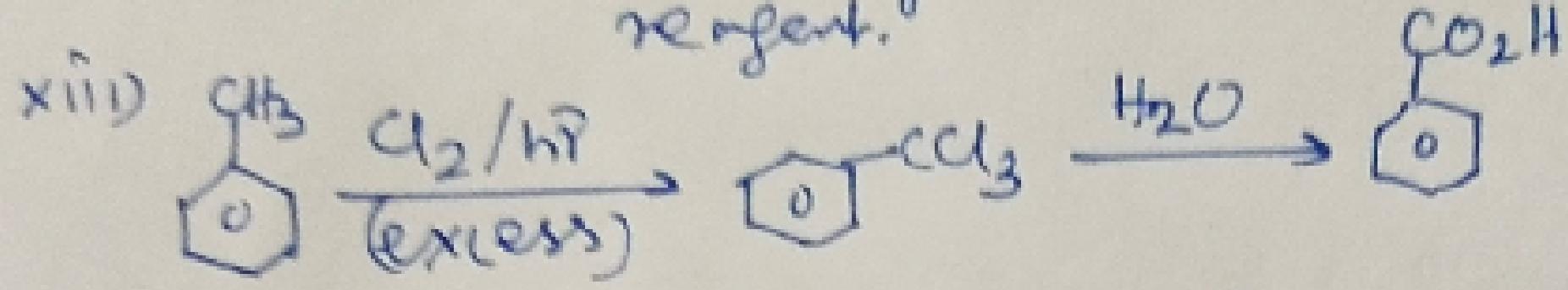
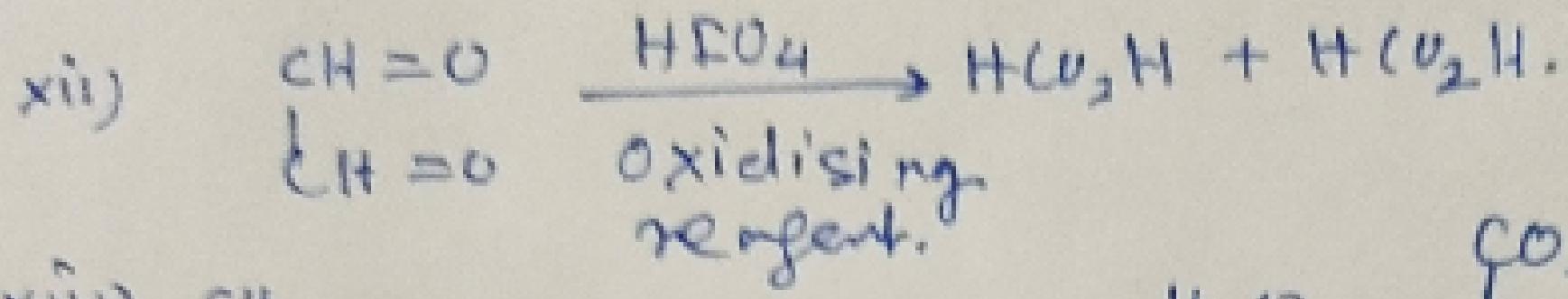
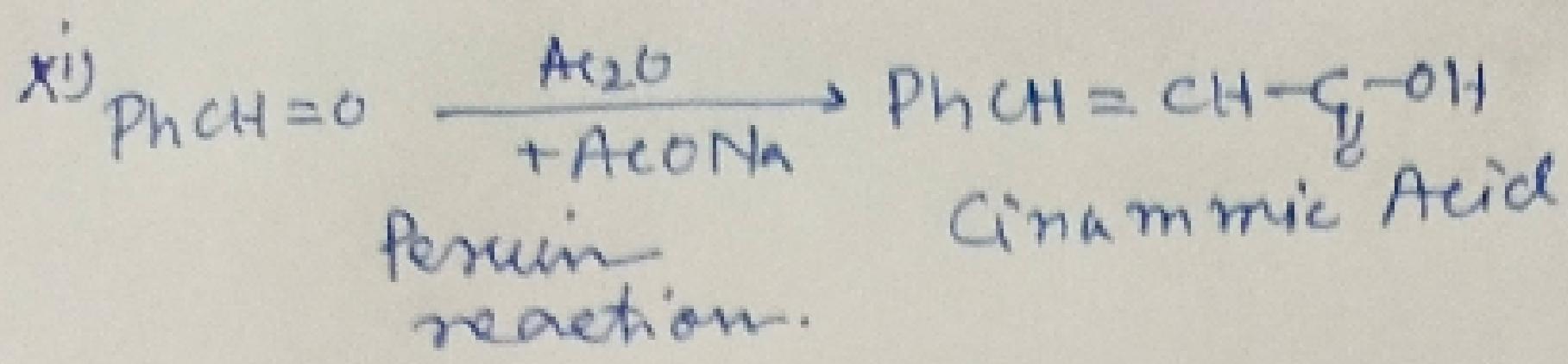
if carried

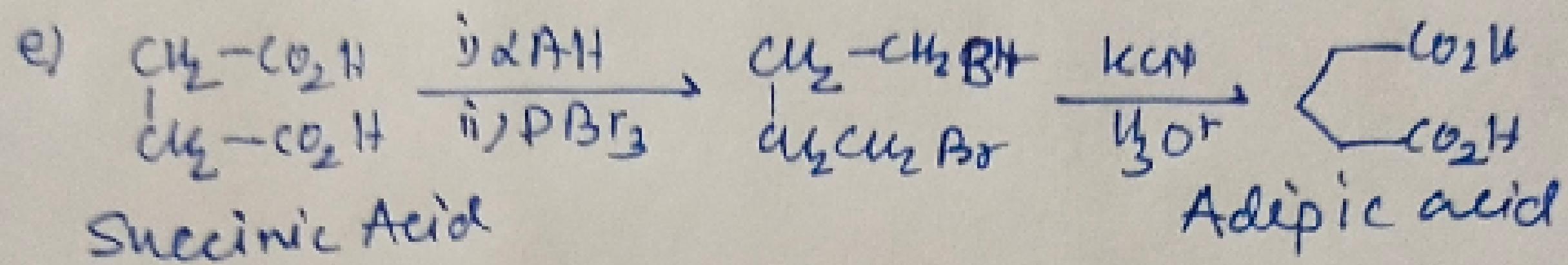
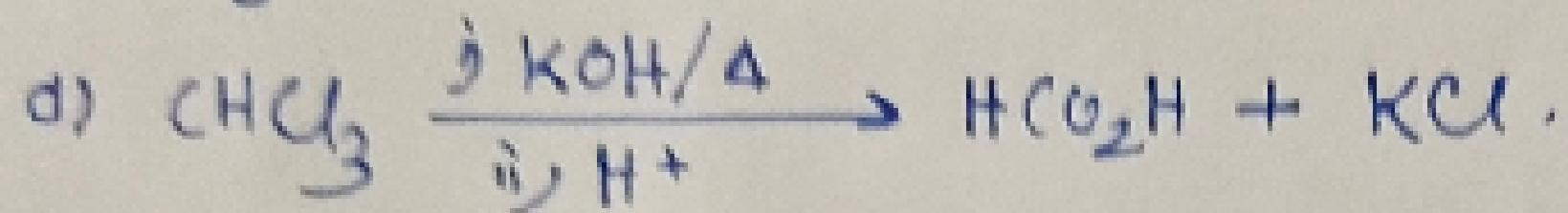
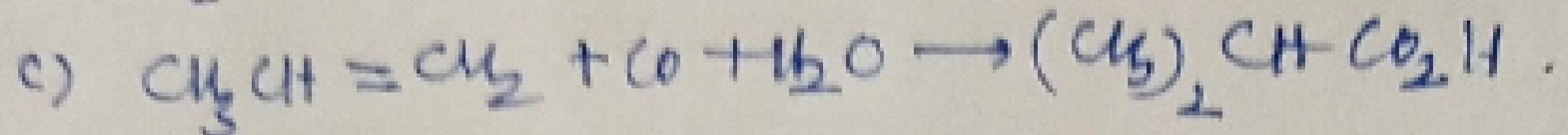
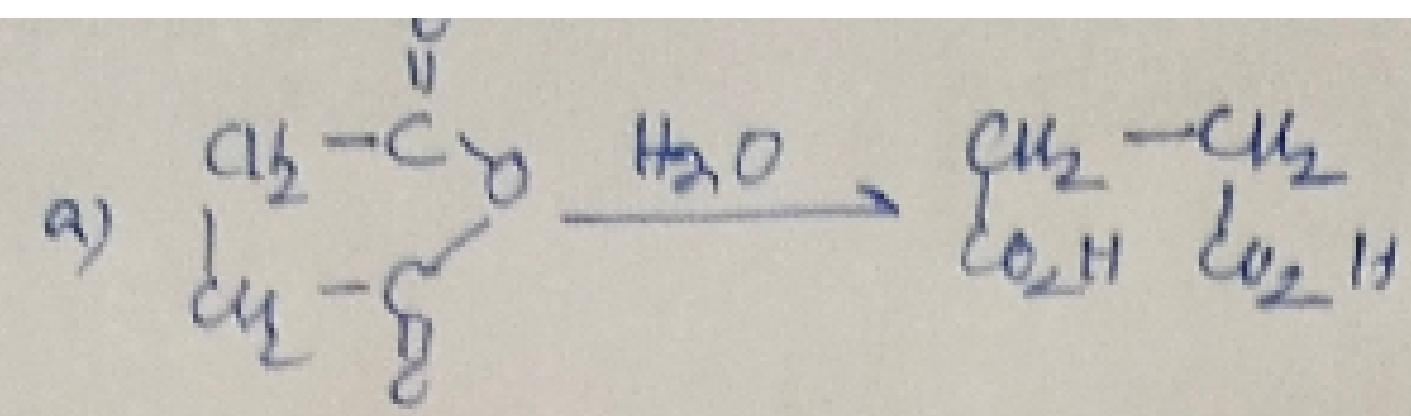


out H_2O^{18} / in presence of H^+ , then

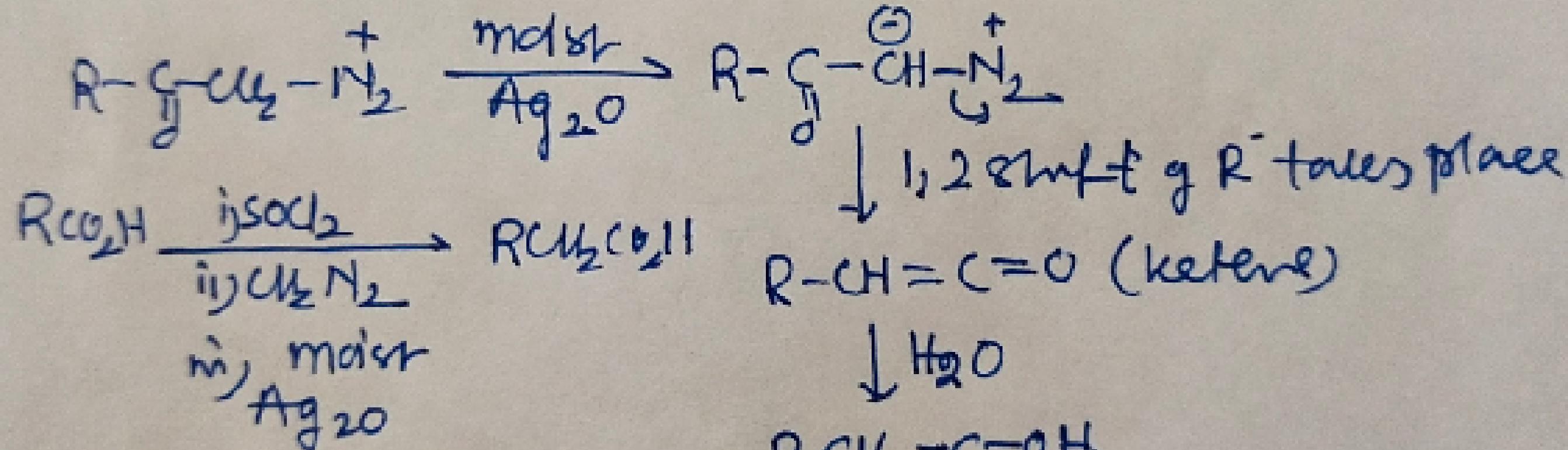
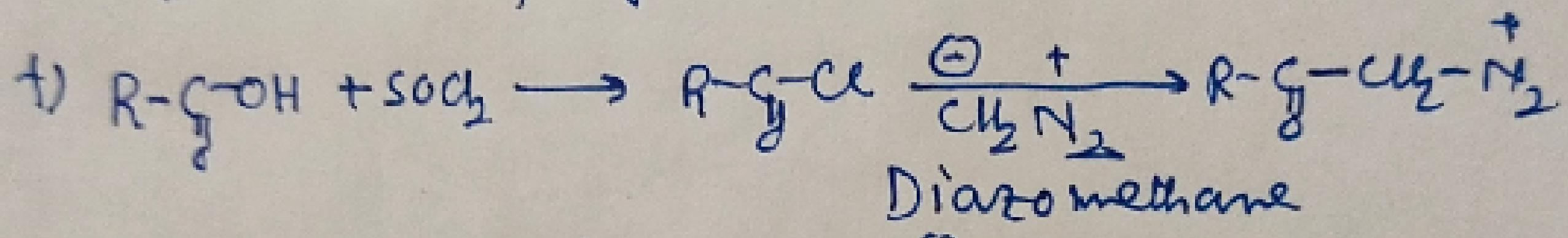
^{18}O will be in the form of alcohol.

Which indicates the mechanism involves O-alkyl cleavage.

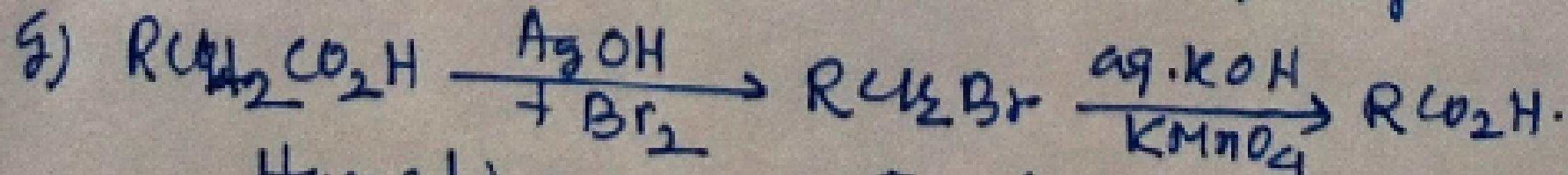
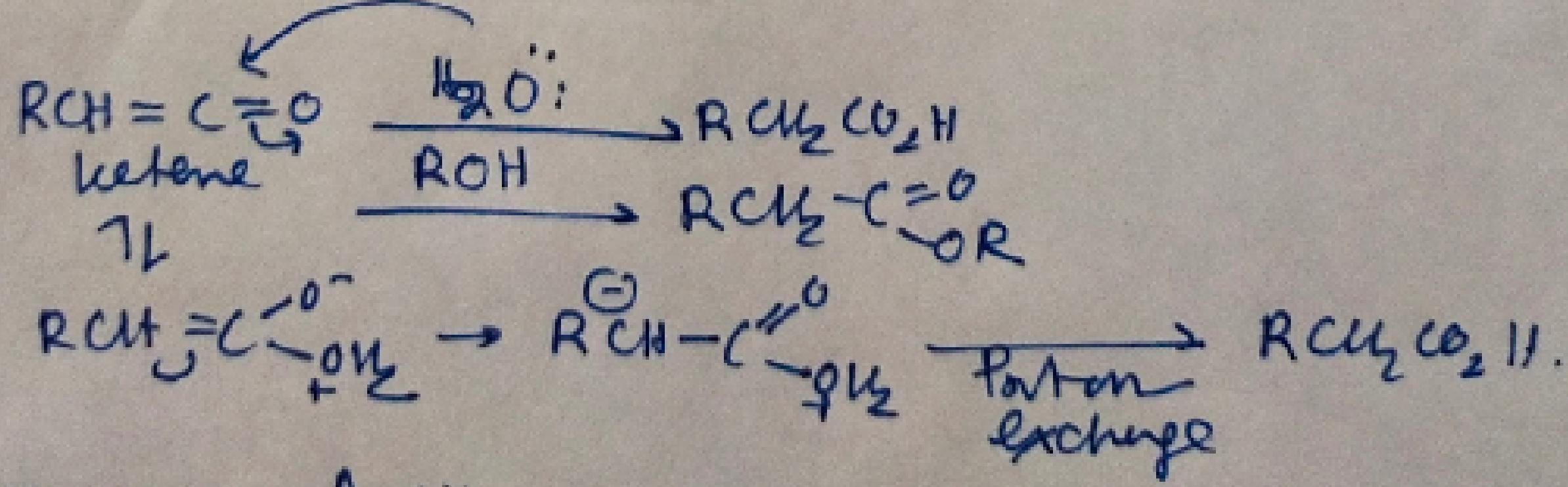




It is example of step up reaction.



It is also example of
step up reaction (Arndt Eistert synthesis)

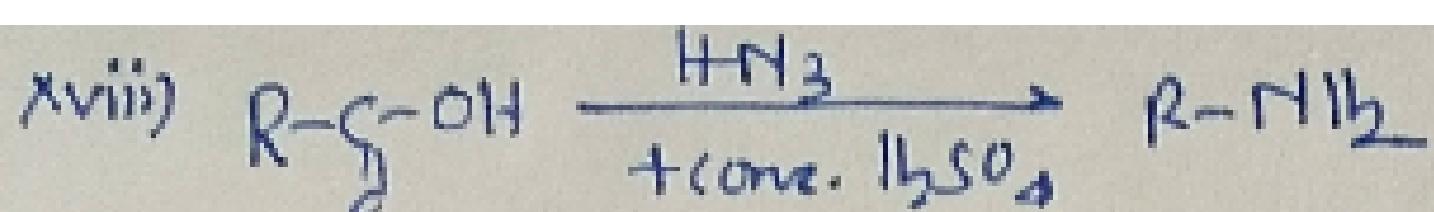


Hunsdicker reaction (step down reaction)

: Reaction of Carboxylic acid:

7

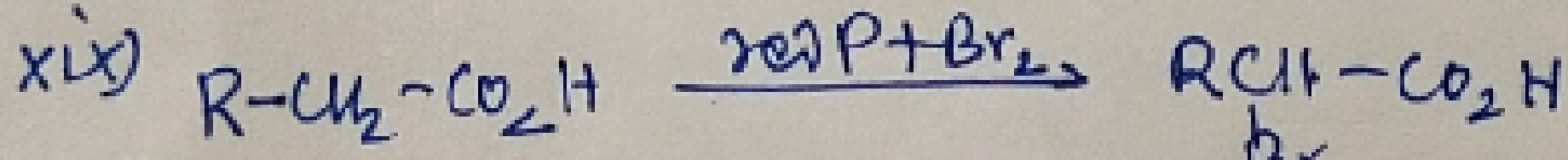
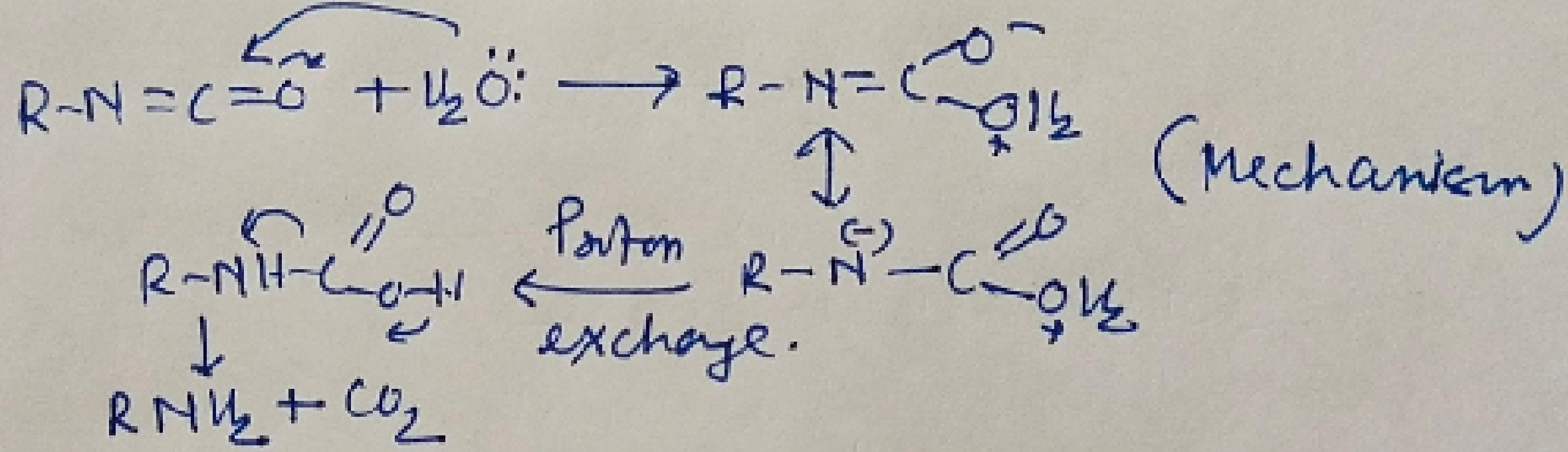
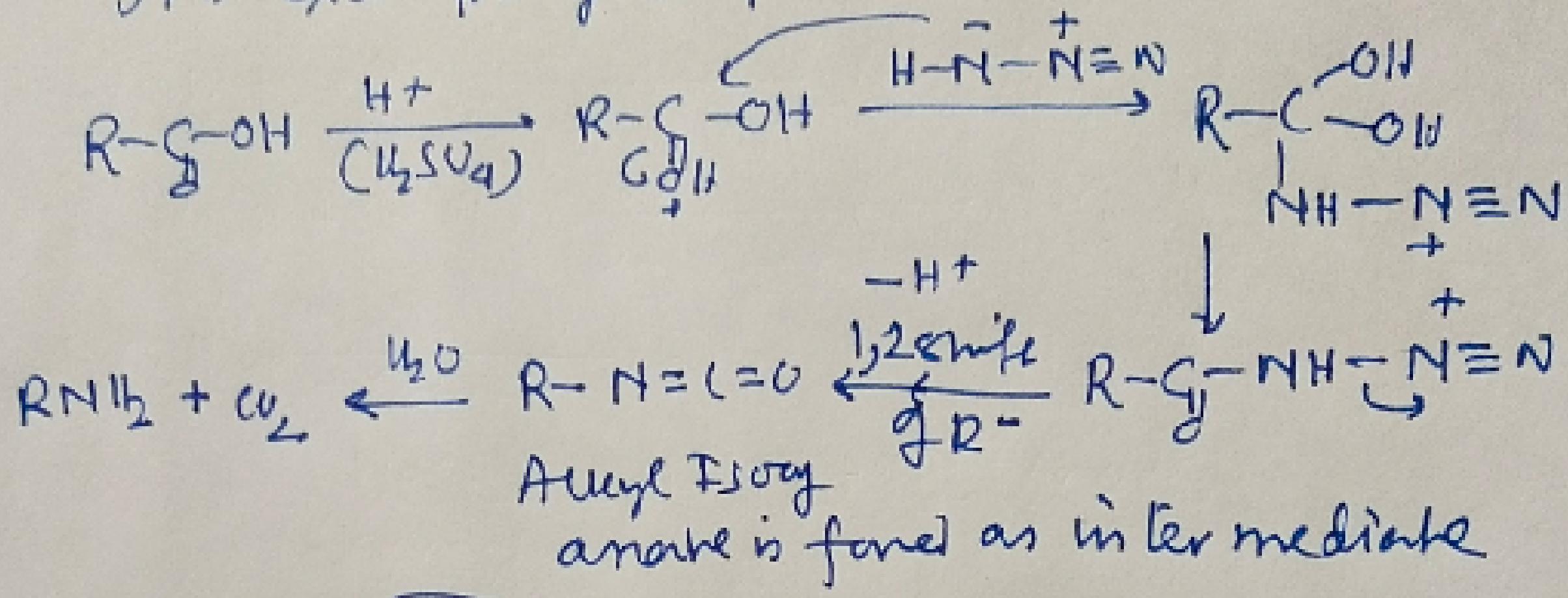
- i) $\text{RCO}_2\text{H} + \text{Na} \rightarrow \text{RCO}_2\text{Na} + \frac{1}{2}\text{H}_2\uparrow.$
- ii) $\text{RCO}_2\text{H} + \text{NaOH}/\text{KOH} \rightarrow \text{RCO}_2\text{Na}/\text{RCO}_2\text{K} + \text{H}_2\text{O}.$
- iii) $\text{RCO}_2\text{H} + \text{Ca(OH)}_2 \xrightarrow[\text{distillation}]{\text{dry}} \text{R}-\text{C}_2^-\text{R}.$
- iv) $\text{RCO}_2\text{H} + \text{Ca(OH)}_2 \xrightarrow[\text{distillation}]{\text{dry}} \text{H}-\text{C}_2^-\text{H}$
- v) $\text{RCO}_2\text{H} \xrightarrow[\text{+CaO}/\Delta]{\text{NaOH}} \text{R}\text{I} + \text{Na}_2\text{CO}_3.$
- vi) $\text{RCO}_2\text{H} \xrightarrow[\text{Electrolysis}]{\text{NaOH}(4)} \text{R}-\text{R} + \text{CO}_2 \text{ (Anode)}$
- vii) $\text{RCO}_2\text{H} + \text{Ba(OH)}_2 \xrightarrow[\text{distillation}]{\text{dry}/\Delta} \text{R}-\text{C}_2^-\text{R}$
- viii) $\text{RCO}_2\text{H} + \text{SOCl}_2 \rightarrow \text{RCOCl}.$
- ix) $\text{RCO}_2\text{H} + \text{NaHCO}_3 \xrightarrow{\text{H}_2\text{O}} \text{RCO}_2\text{Na} + \text{CO}_2 + \text{H}_2\text{O}$
 [This reaction is used to identify carboxylic acid]
- x) $\text{RCO}_2\text{H} + \text{NH}_3 \rightarrow \text{RCO}_2\text{NH}_2 \xrightarrow{\Delta} \text{RCO NH}_2 + \text{H}_2\text{O}$
- xi) $\text{RCO}_2\text{H} + \text{NH}_3 \xrightarrow[\text{Conc. H}_2\text{SO}_4]{\Delta} \text{RCO NH}_2 \xrightarrow{\text{P}_2\text{O}_10} \text{RCN}.$
- xii) $\text{RCO}_2\text{H} + \text{EtOH} \xrightarrow[\text{H}^+/\text{H}_2\text{O}]{\Delta} \text{RCO}_2\text{Et} + \text{H}_2\text{O}.$
- xiii) $\text{R}-\text{C}_2^-\text{OH} + \text{RCO}_2\text{H} \xrightarrow{\Delta} \text{R}-\text{C}_2^-\text{O}-\text{C}_2^-\text{R}$
- xiv) $\text{RCO}_2\text{H} \xrightarrow[\text{R}_2\text{NH}]{\text{RNH}_2} \text{RCO NR}_2 + \text{H}_2\text{O}$
 $\xrightarrow[\text{R}_2\text{NH}]{\text{R}_2\text{NH}} \text{R}_2\text{CO NRR}_2 + \text{H}_2\text{O}$
- xv) $\text{RCO}_2\text{H} \xrightarrow[\text{Na/CuO/H}_2\text{O}]{\text{CH}_3\text{OH}} \text{RCO}_2\text{OH}$
- xvi) $\text{RCO}_2\text{H} \xrightarrow{\text{PCl}_3 + \text{H}_2\text{S}} \text{R Cl}_3.$
- xvii) $\text{RCO}_2\text{H} + \text{SOCl}_2 \rightarrow \text{RCOCl} \xrightarrow[-78^\circ\text{C}]{\text{DIBALHII}} \text{RCO}_2\text{H}$
 $\xrightarrow{\text{MgCl}_2} \text{RCOCH}_3.$



101

This reaction is called Schmidt Reaction

It is example of step down reaction.

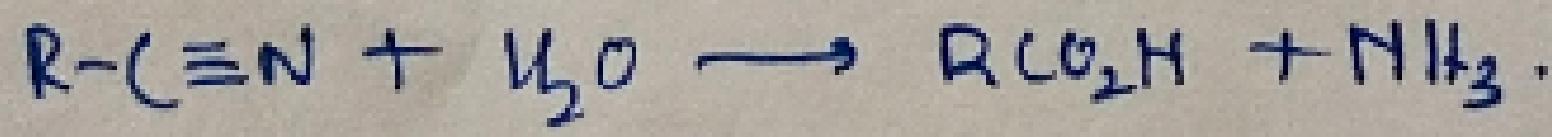
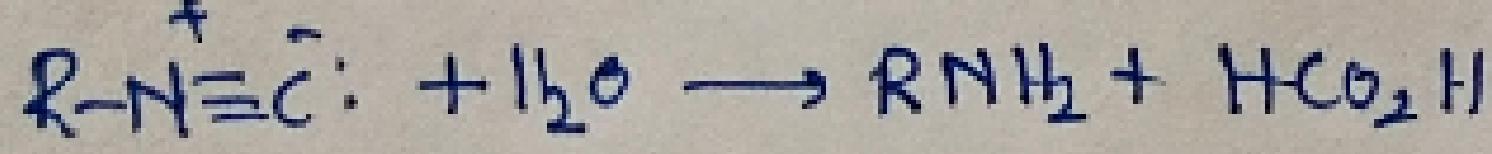


Acid

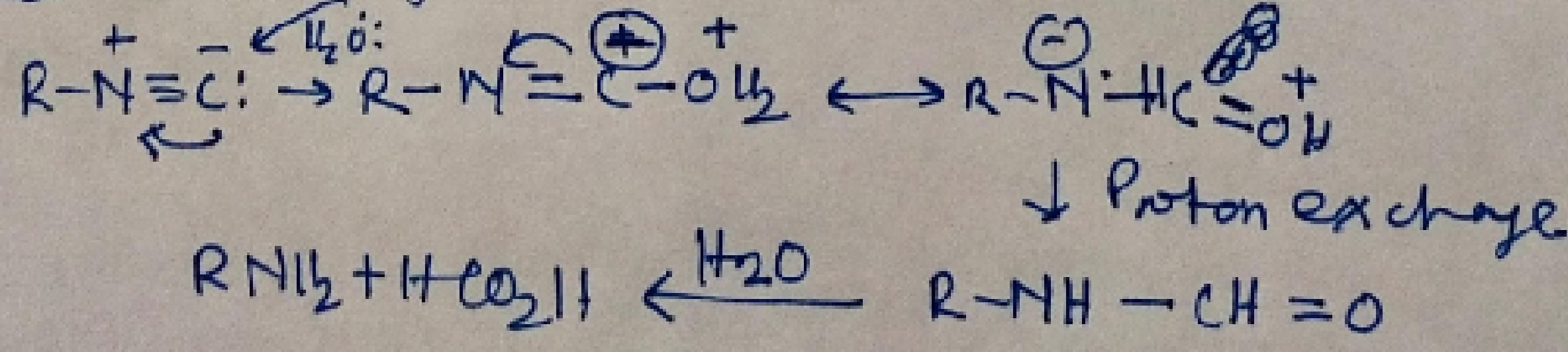
α -bromo/nalo carboxylic acid.

This reaction is called as

Hell-Volhard-Zelinsky reaction.

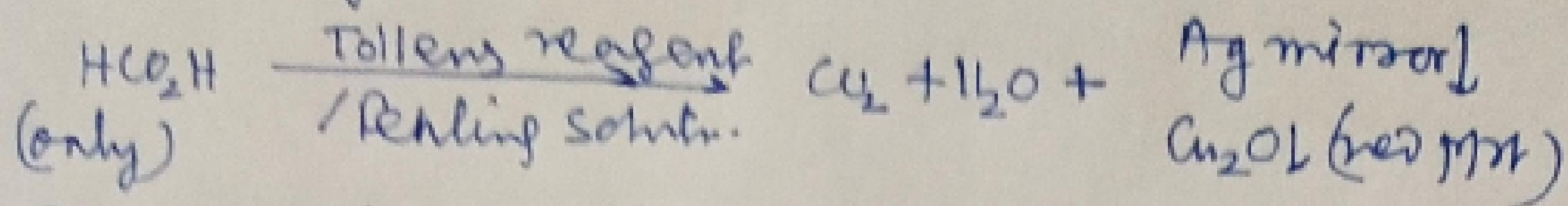


Mechanism for Ist reaction:

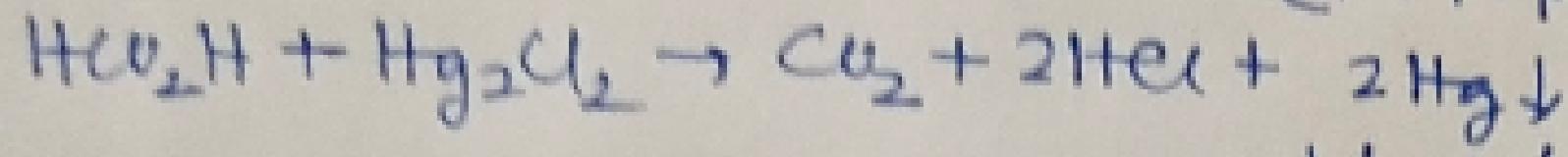
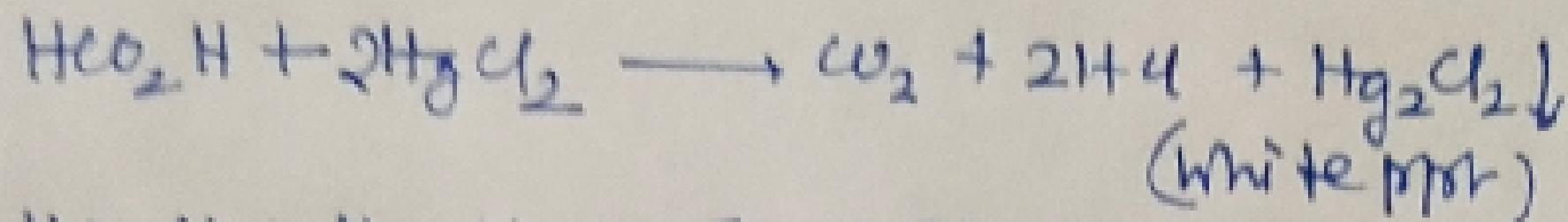


9

Detection of carboxylic acid

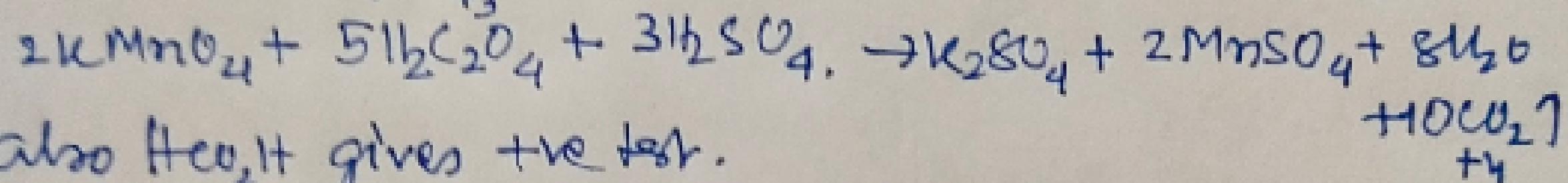
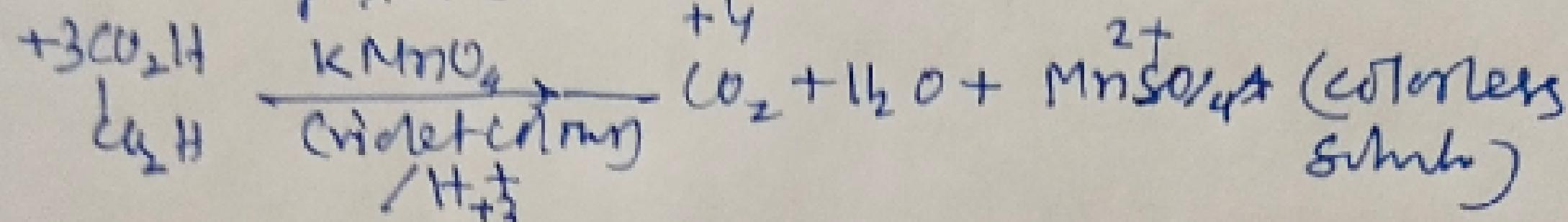


Only HCO_2H (among all carboxylic acid giving +ve test).

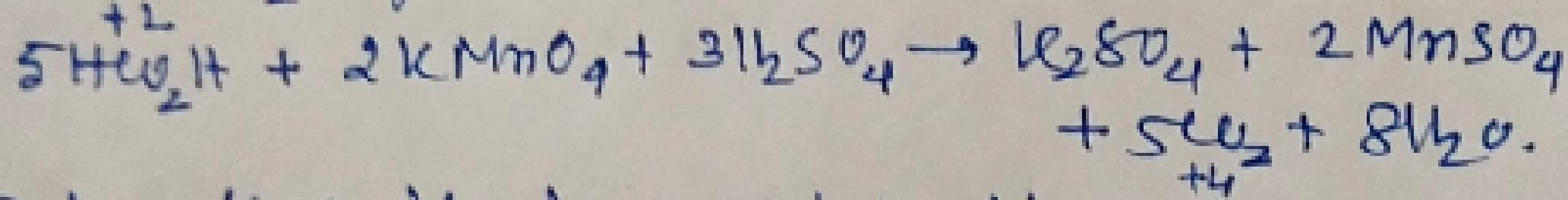


black/brown ppt.

Detection of oxalic acid



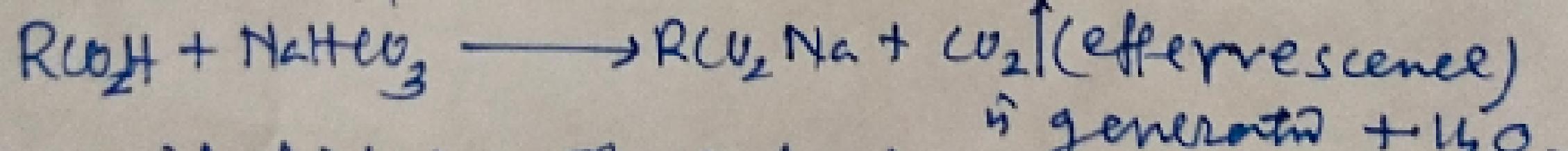
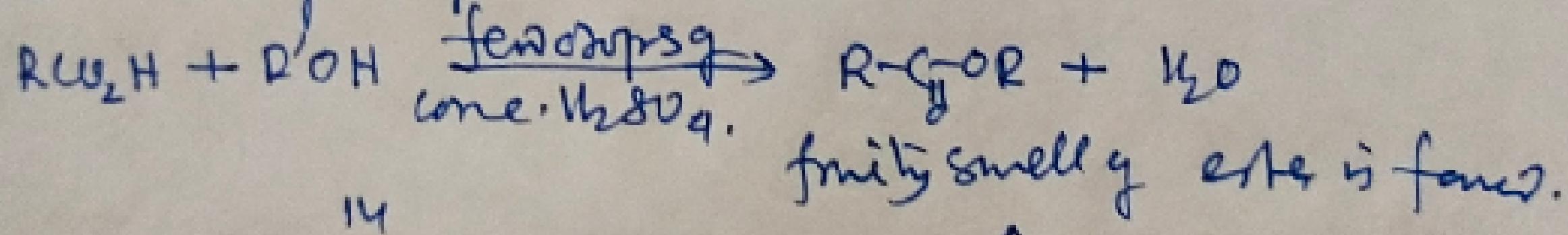
also HCO_2H gives +ve test.



But oxalic acid gives -ve test with

Tollens / Fehling / HgCl_2 soln.

Detection of any acid



The acid which are stronger than

NaHCO_3 give the test.

i) Any carboxylic / sulphonic acid. ($-\text{CO}_2\text{H}/-\text{SO}_3\text{H}$ resp.)

ii) Ascorbic Acid i) squamic acid. (c) picric acid

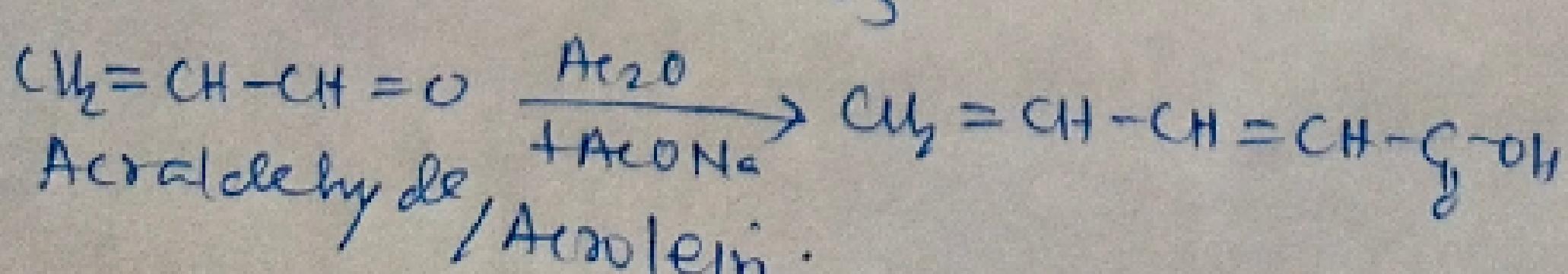
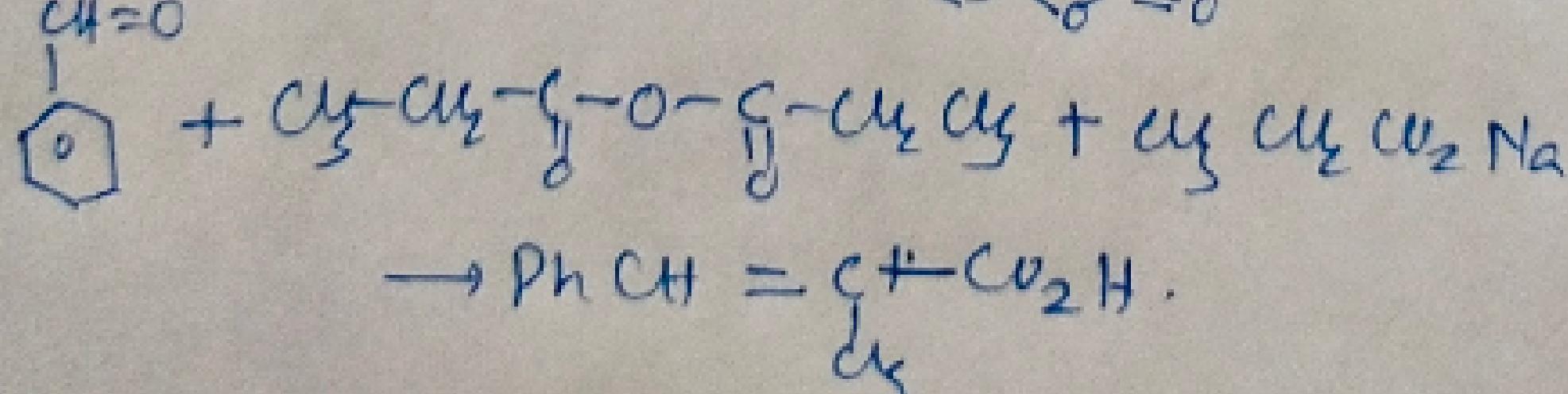
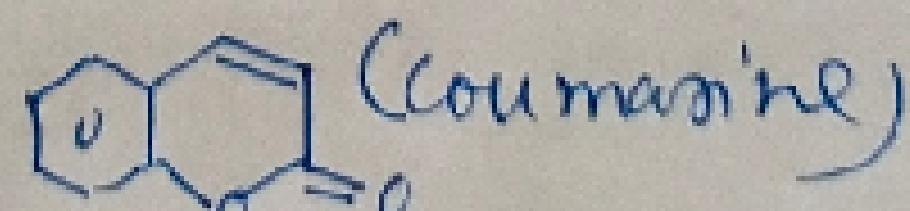
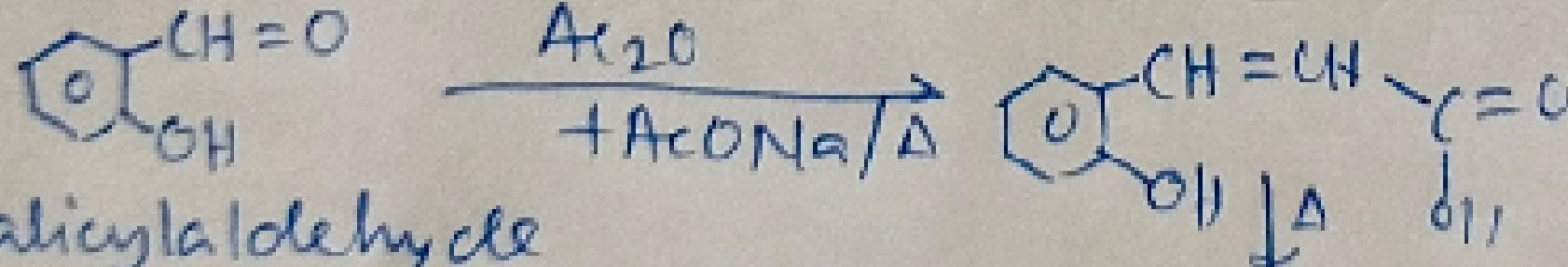
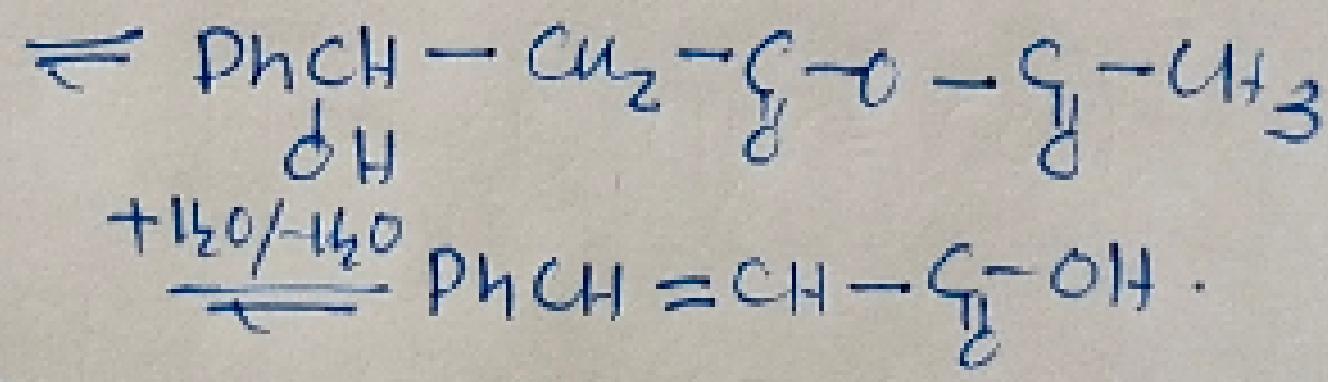
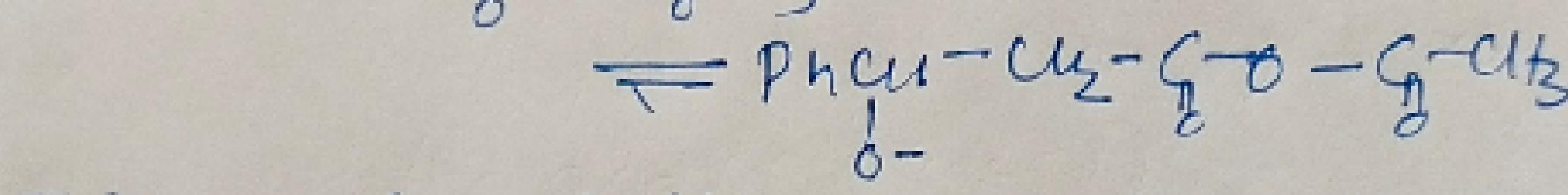
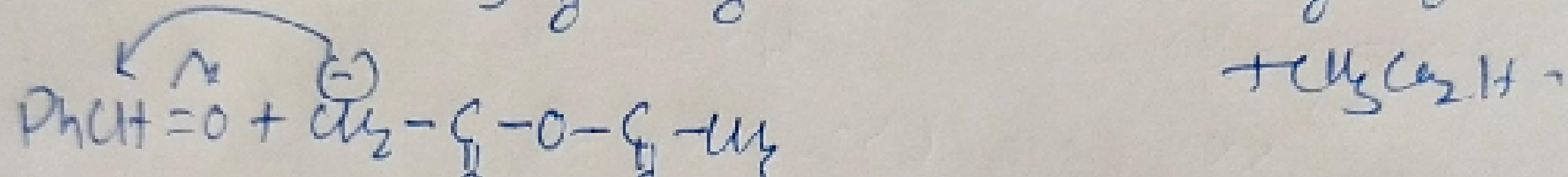
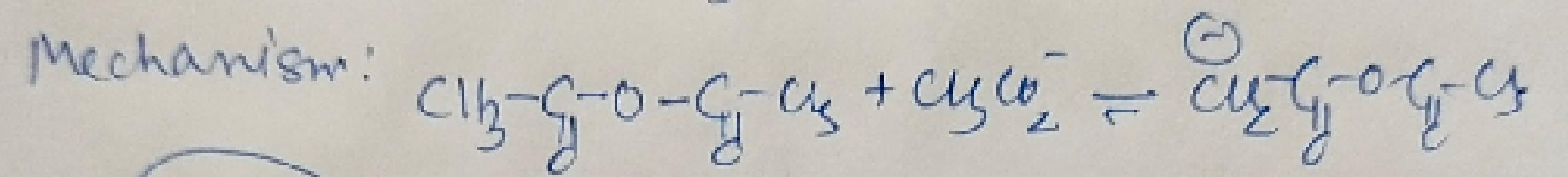
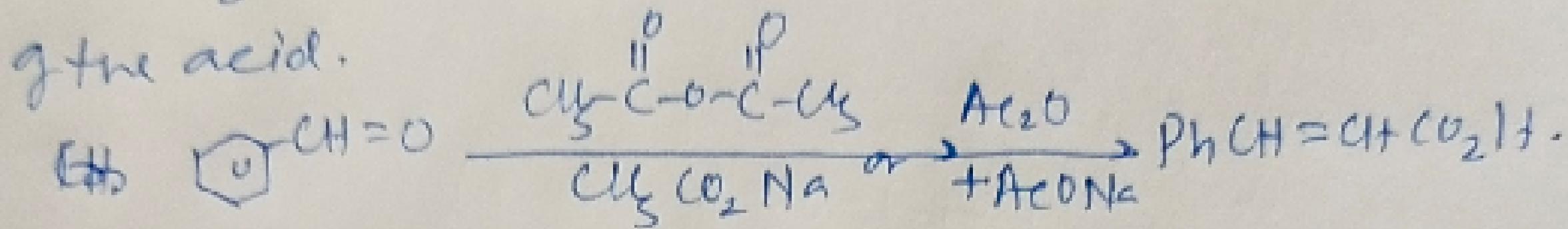
iii) not having $-\text{CO}_2\text{H}$, but gives +ve test with NaHCO_3 .

Carboxylic acid (PhOH) gives -ve test.

a) Cinamic acid ($\text{PhCH=CH-CO}_2\text{H}$) +ve test

b) Aspirin $\text{C}_6\text{H}_5\text{CO-C}_6\text{H}_4-\text{CO-C}_6\text{H}_3(\text{OH})_2$

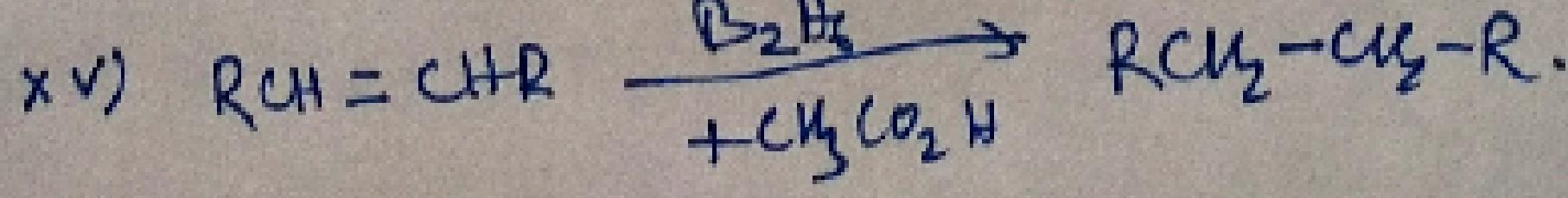
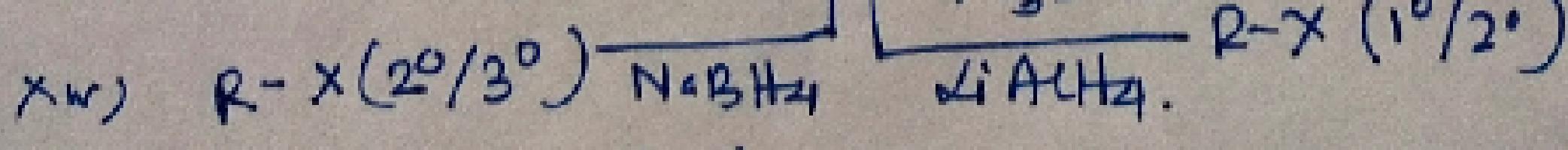
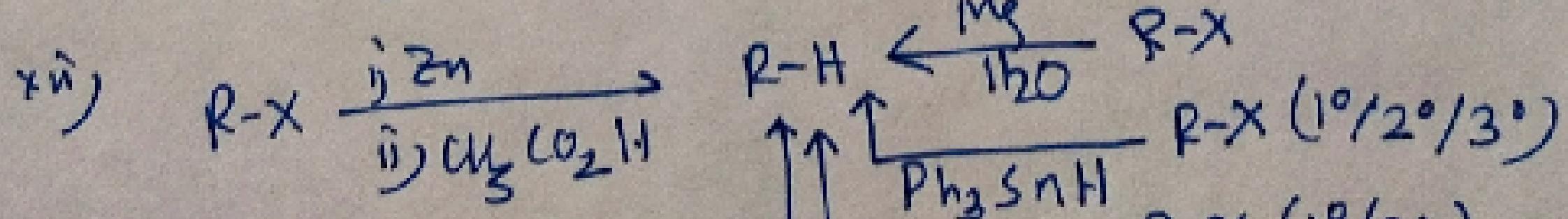
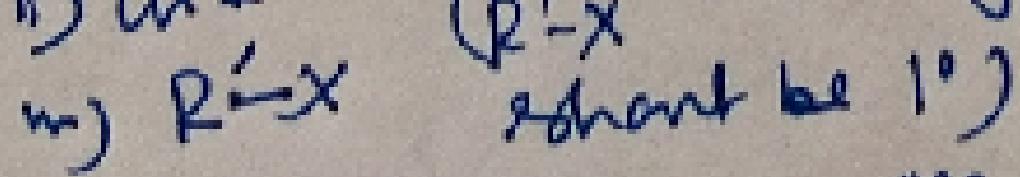
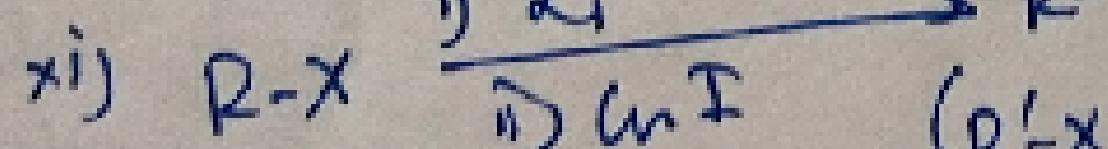
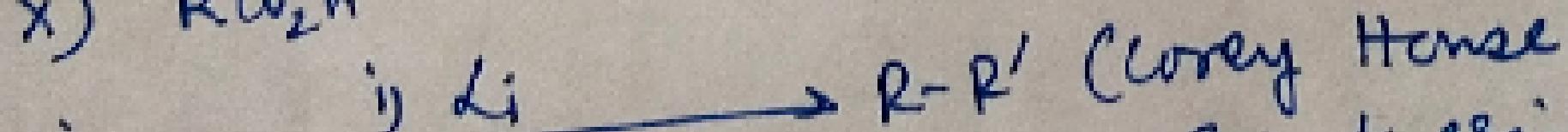
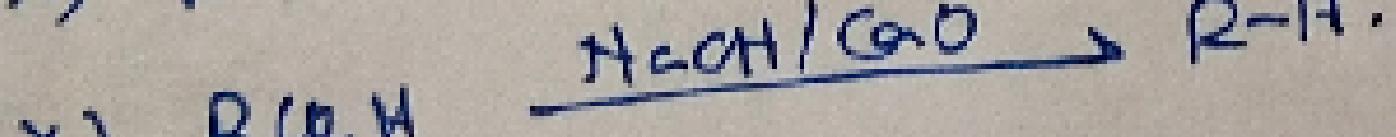
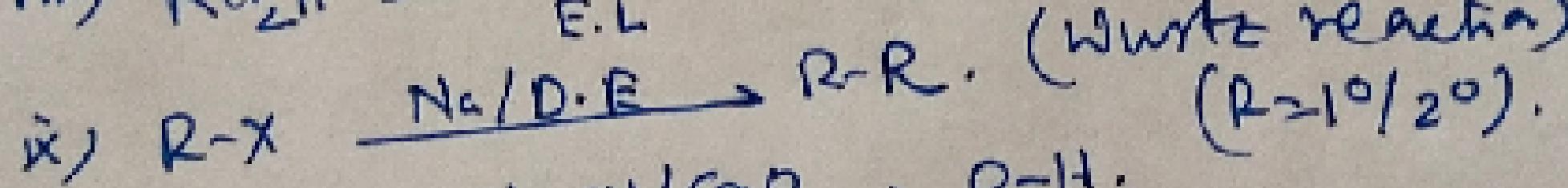
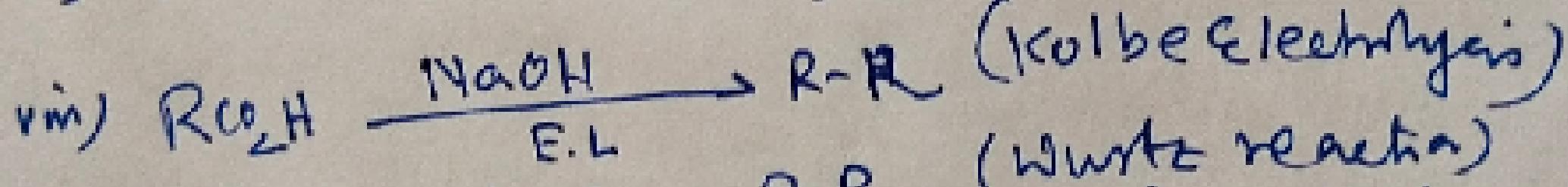
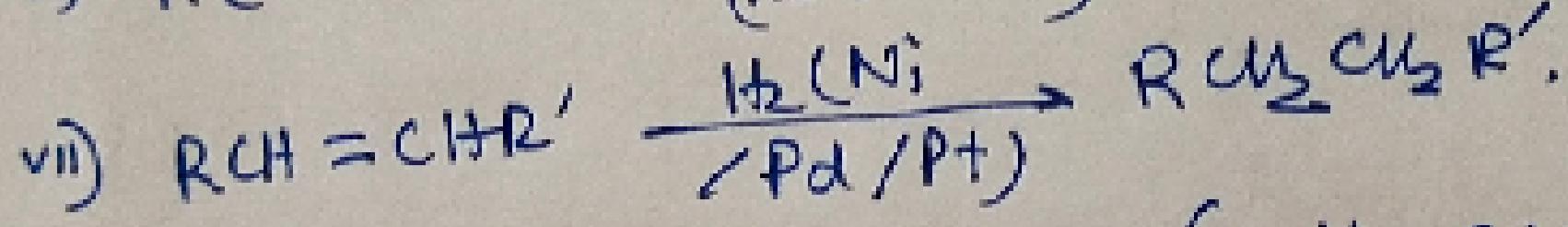
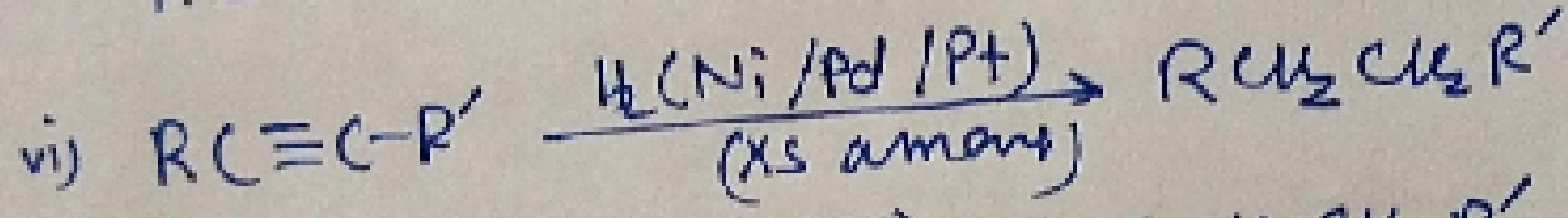
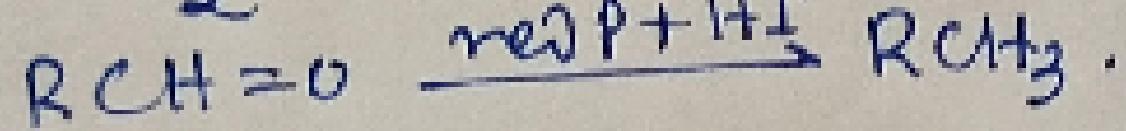
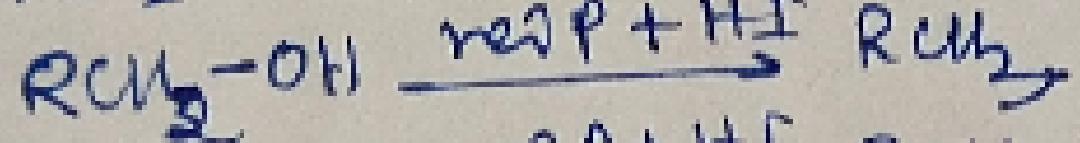
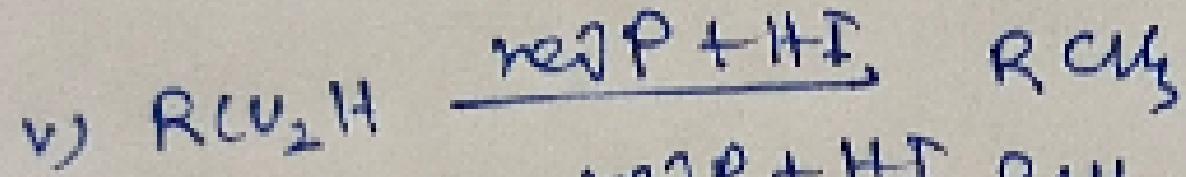
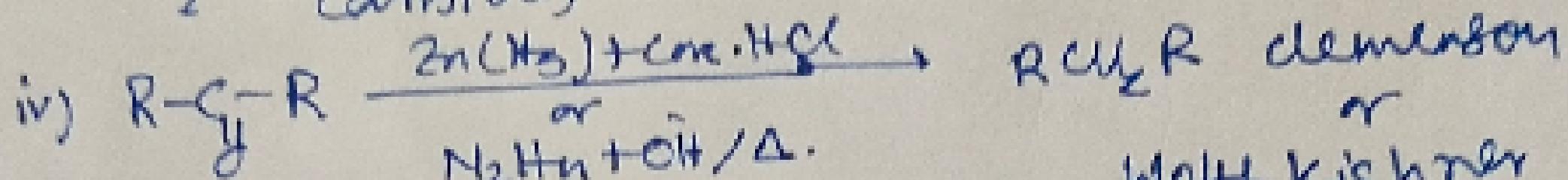
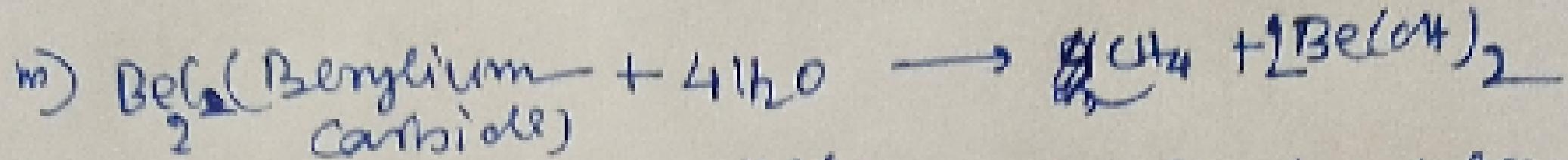
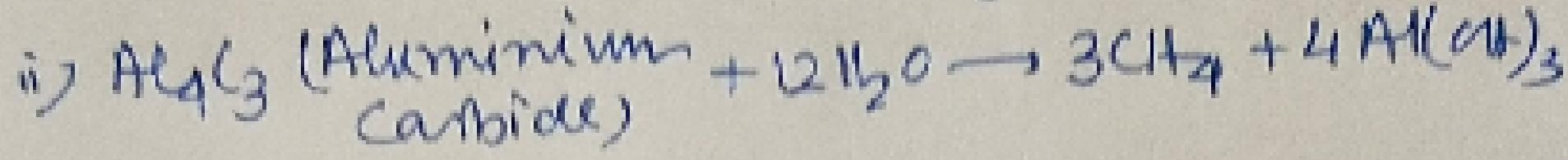
: Perkin Reaction: The Perkin reaction is an organic ¹⁰ Bonn dehydrogenation reaction developed by William Henry Perkin that is used to make cinnamic acid. It gives an α,β unsaturated aromatic acid by aldol condensation of an aromatic aldehyde & an acid anhydride, in the presence of an alkali salt of the acid.



(11)

Hydrocarbons:

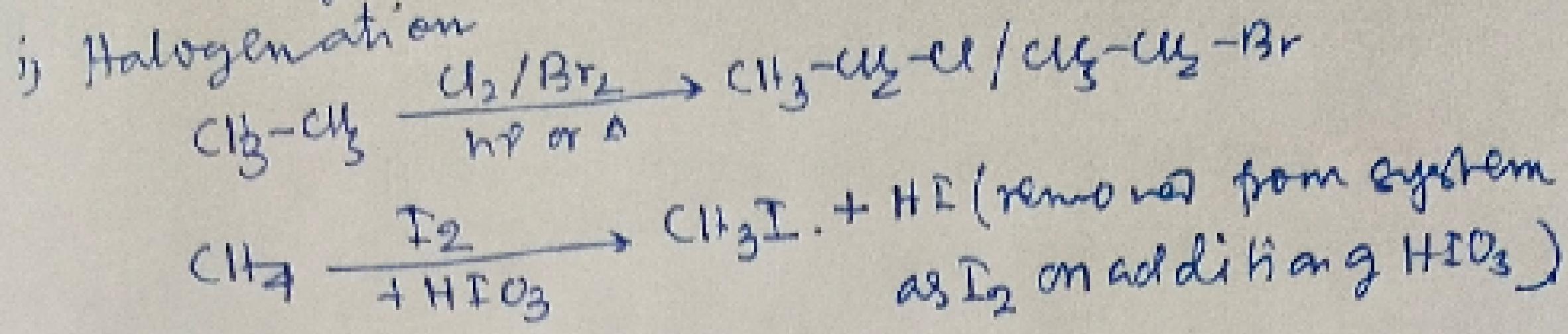
Alkane: Preparation: i) $\text{Rmex} + \text{H}_2\text{O}/\text{RCOOH}/\text{RCl}_2\text{H} \dots \rightarrow \text{R}-\text{H}$
 (any acid having acidic H)



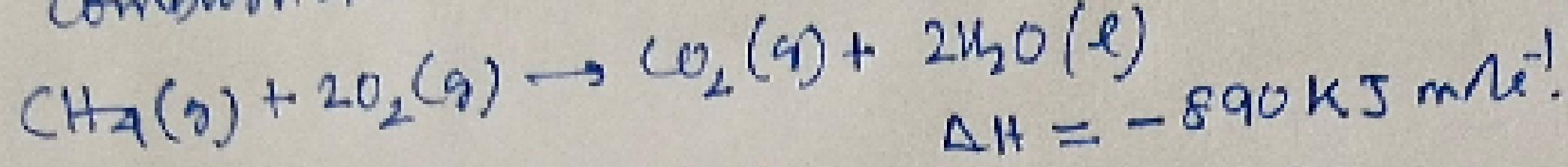
(12)

: Reaction of Alkane:

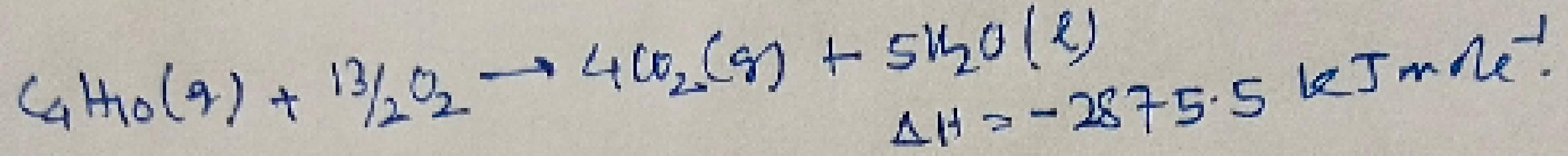
i) Halogenation



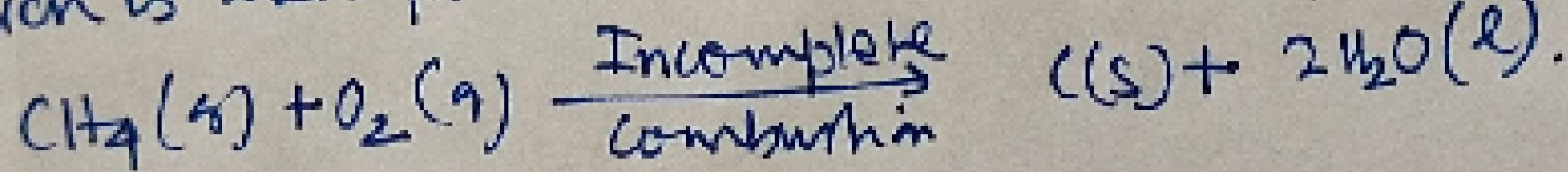
ii) Combustion:



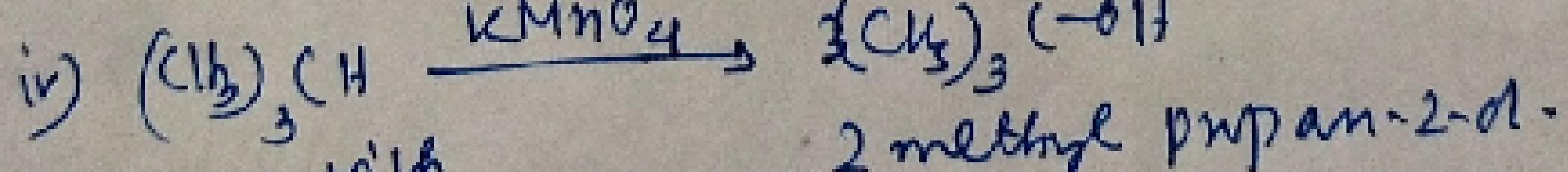
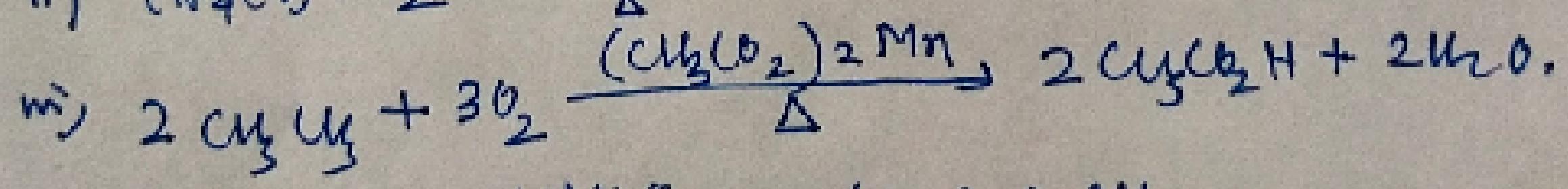
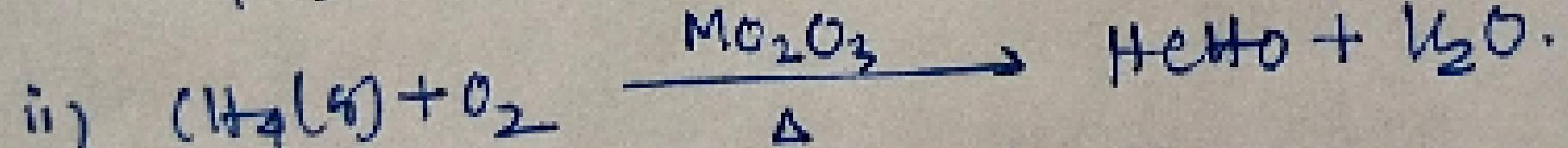
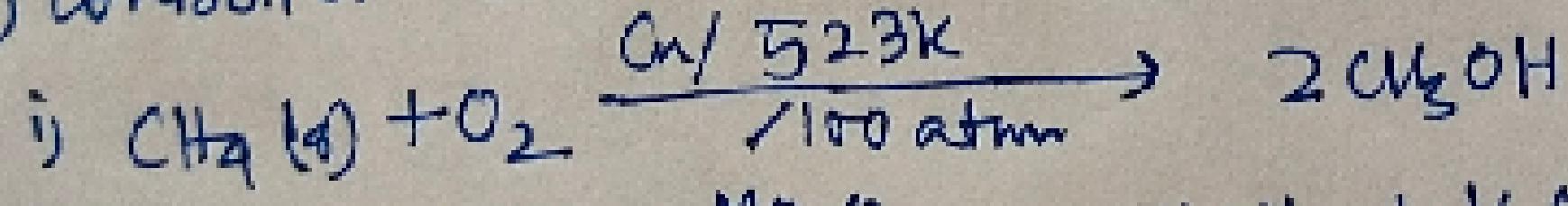
$$\Delta H = -890 \text{ kJ mol}^{-1}$$



There are all examples of complete combustion.
During incomplete combustion with insufficient amount of air or oxygen, carbon black is formed which is used for manufacture of black pigment.

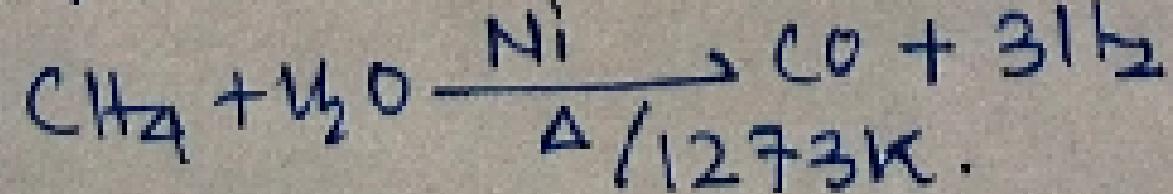


iii) Controlled Oxidation:



Alkane with tertiary hydrogen will be only oxidized.

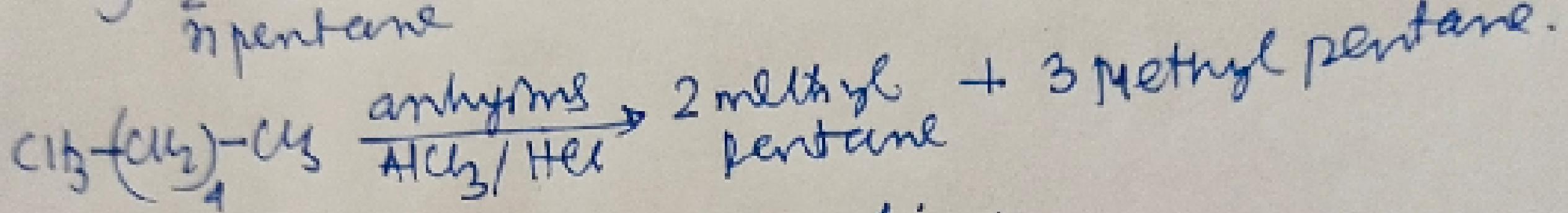
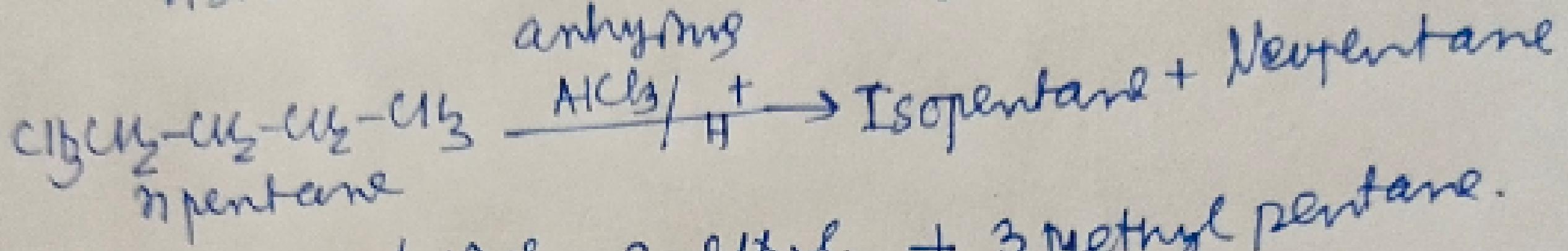
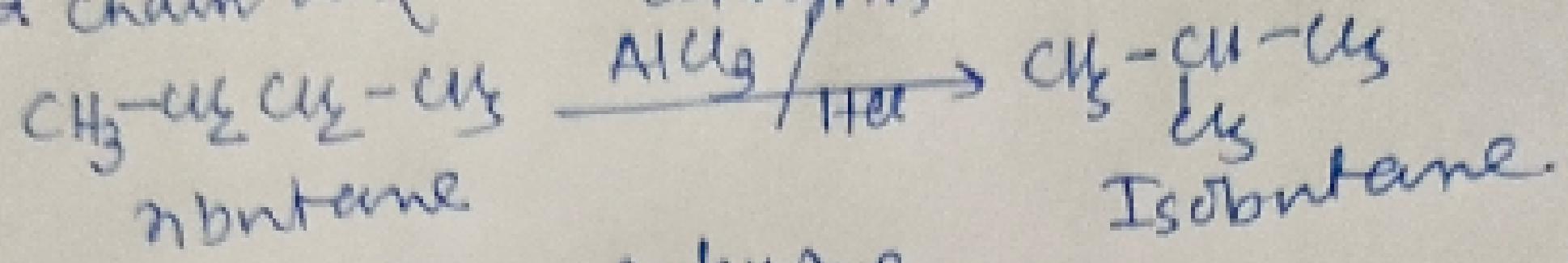
iv) Reaction with Steam:



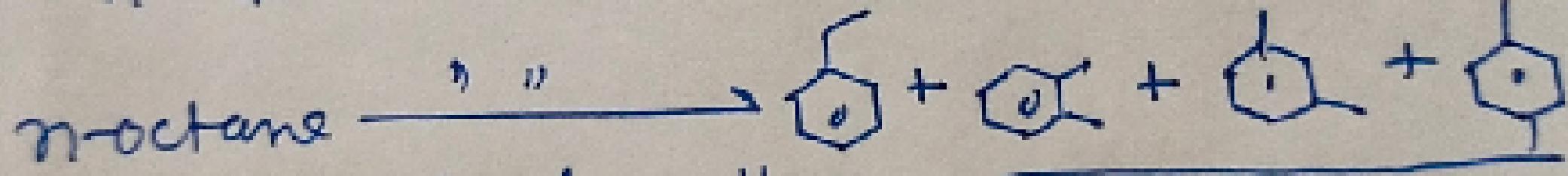
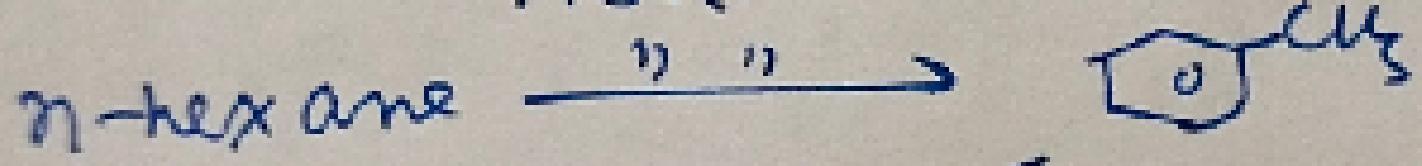
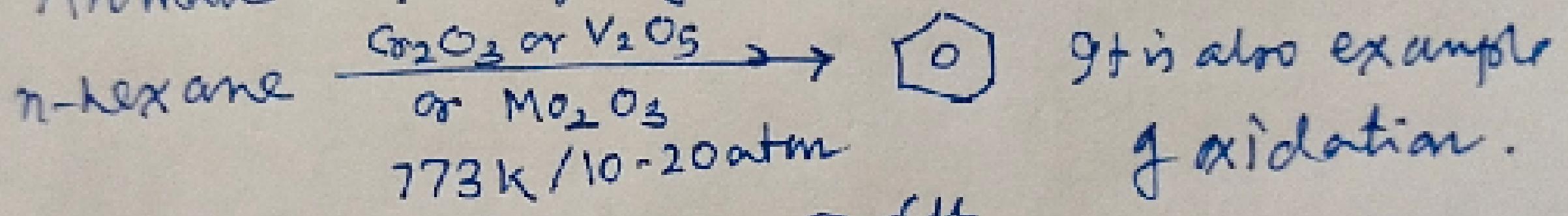
This is used to prepare dihydrogen gas.

(v) Isomerisation:

n-alkane on heating in presence of anhydrons ¹³
AlCl₃ & HCl gas (very less amon) isomericise to branched
al chain alkanes. anhydrons



(vi) Aromatisation/dehydrogenation:



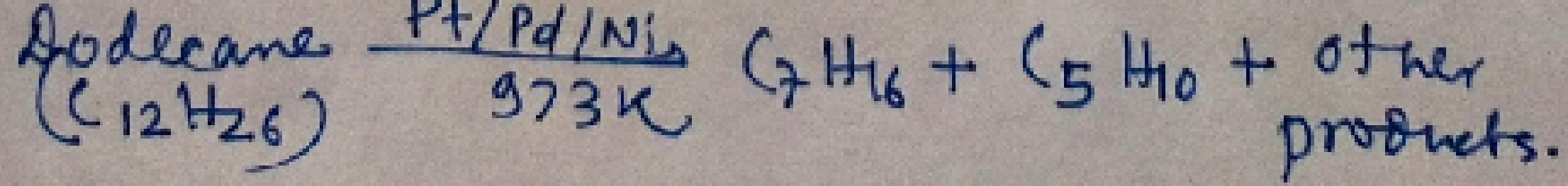
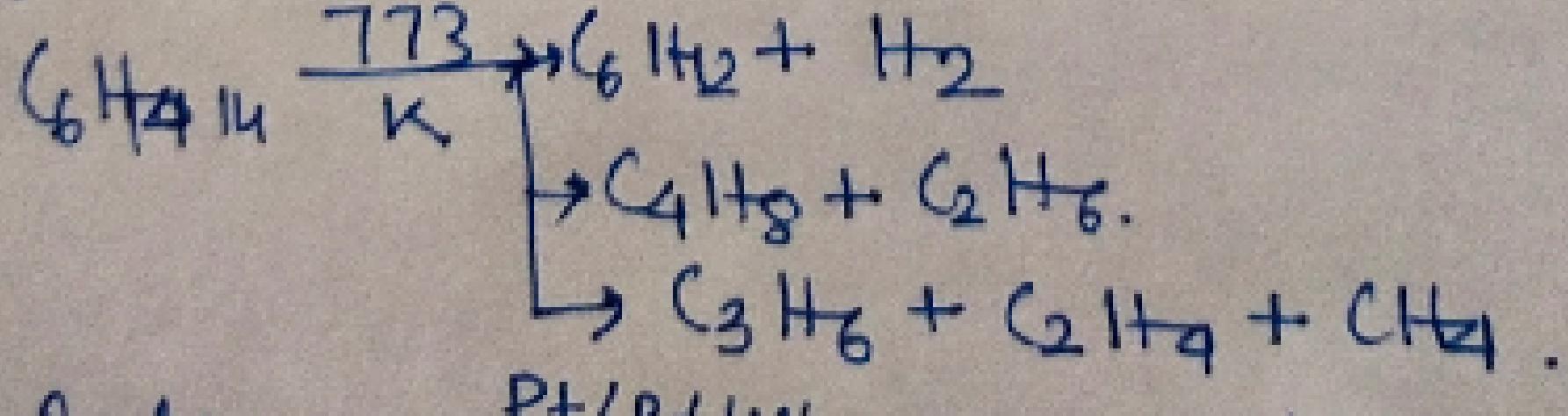
This reaction is also called catalytic cracking/reforming.

vii) Pyrolysis:

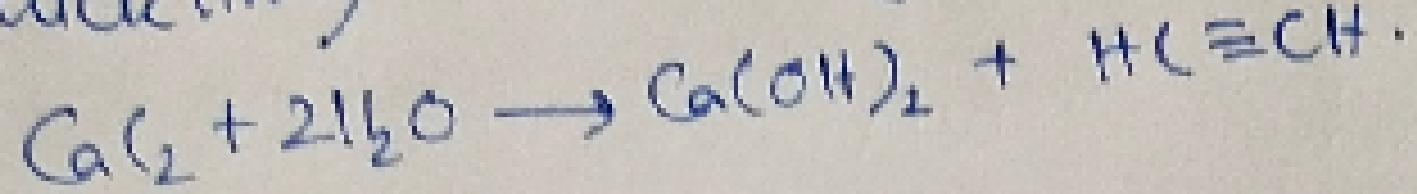
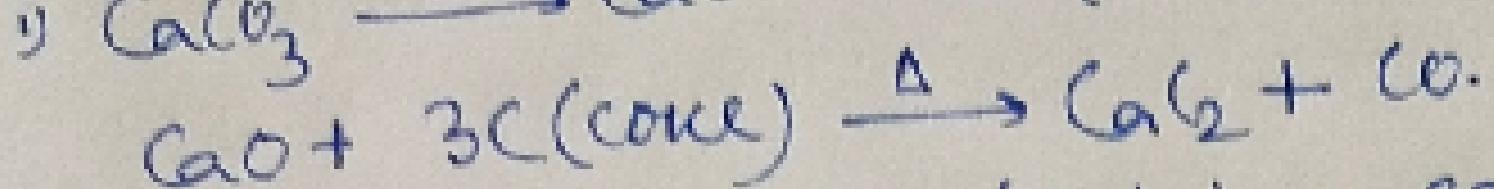
Higher alkanes on heating to higher temperature

decomposes to lower alkanes, alkenes etc.

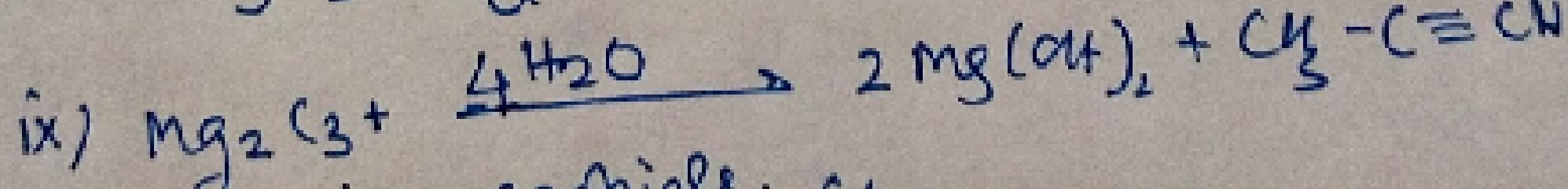
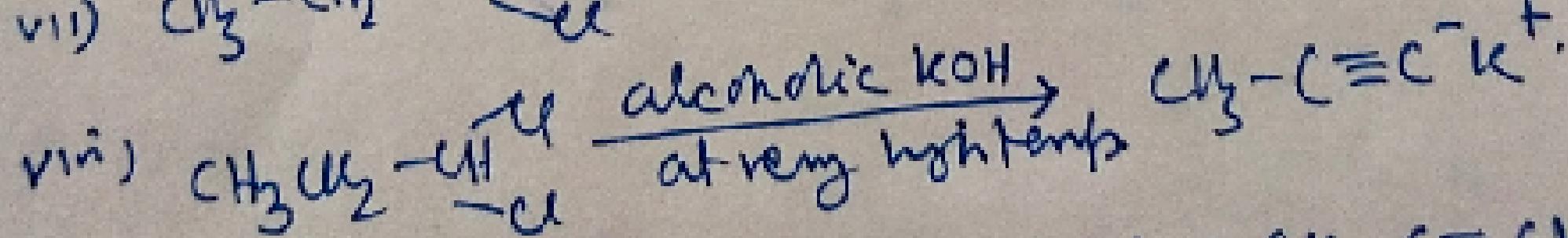
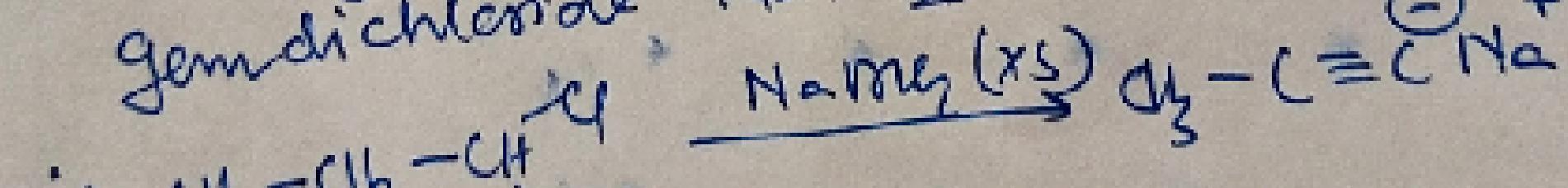
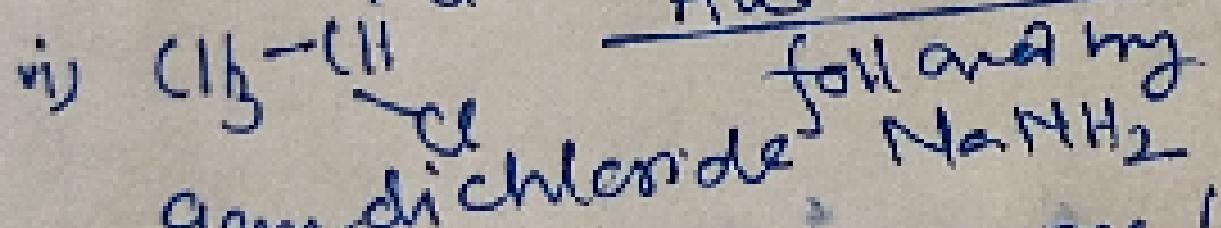
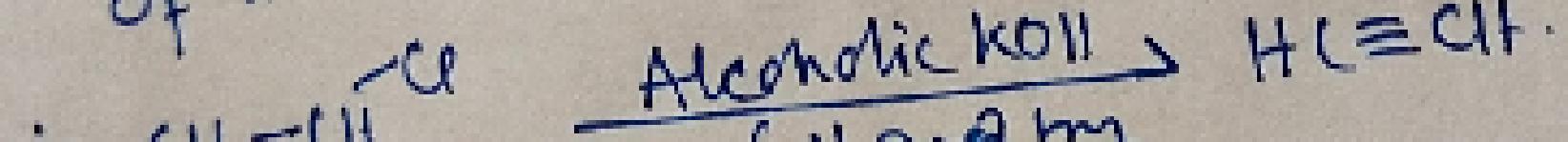
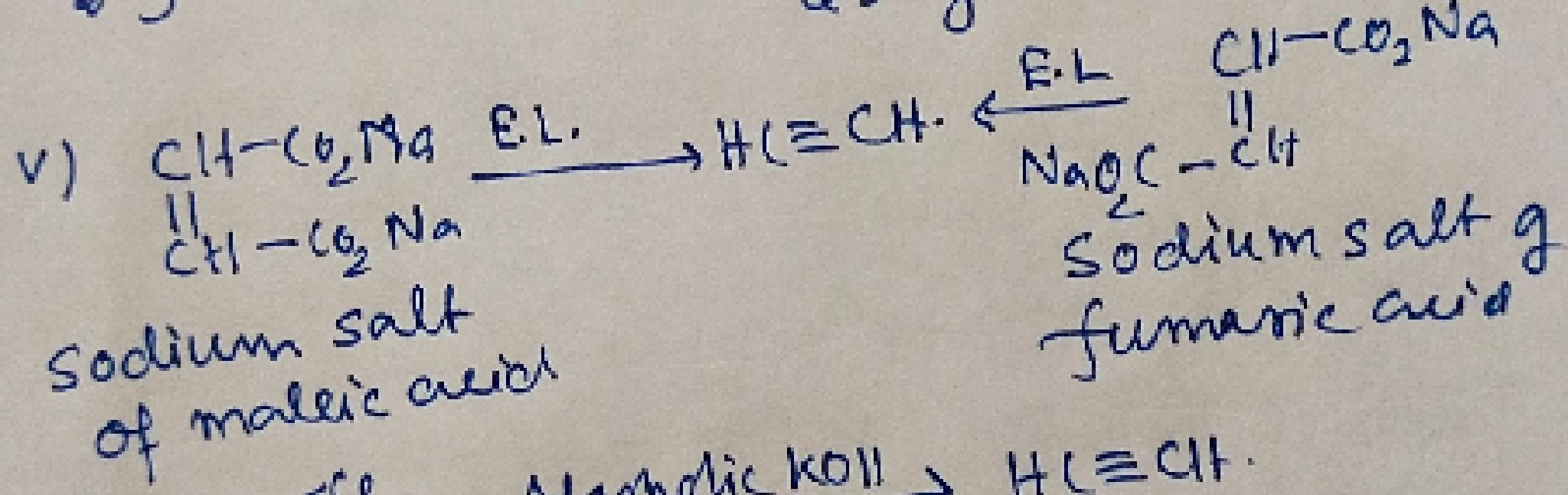
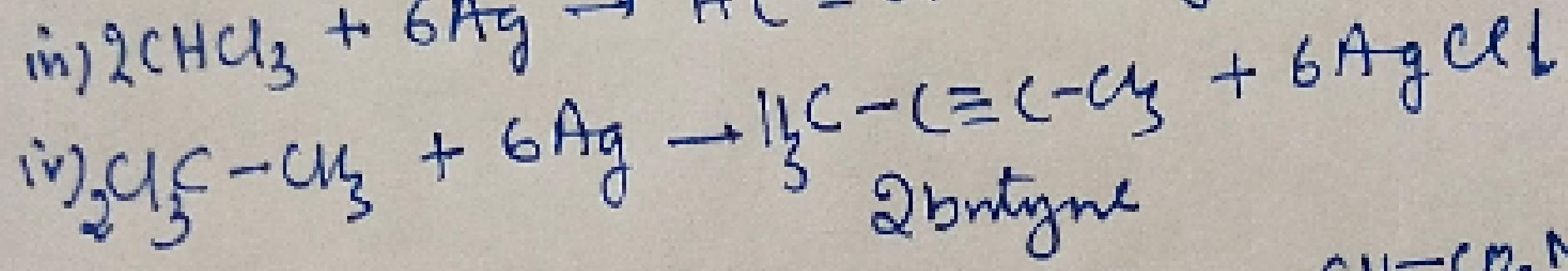
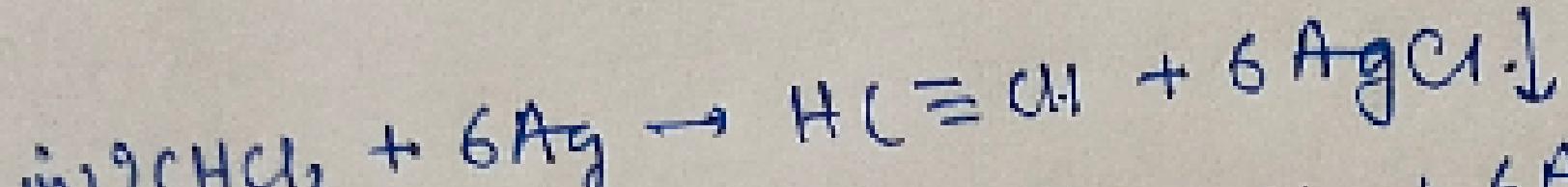
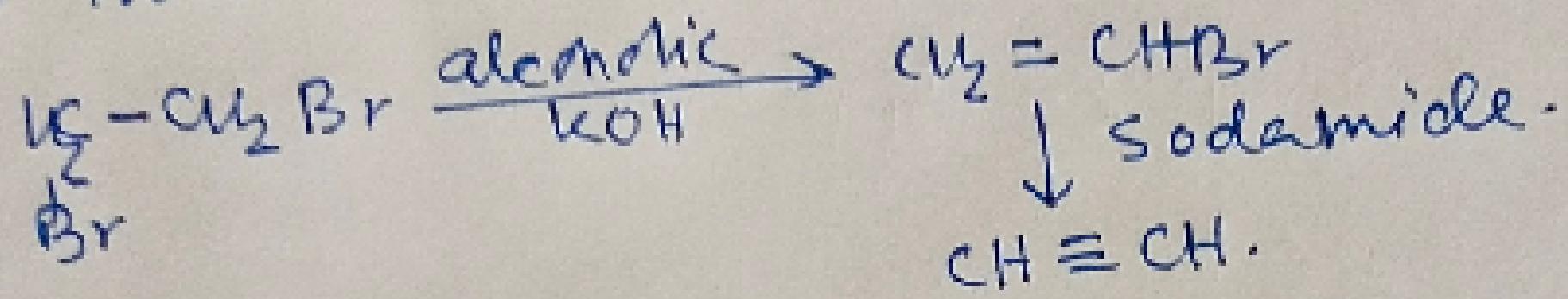
Such a decomposition reaction smaller fragments
by applying heat is called Pyrolysis/cracking.



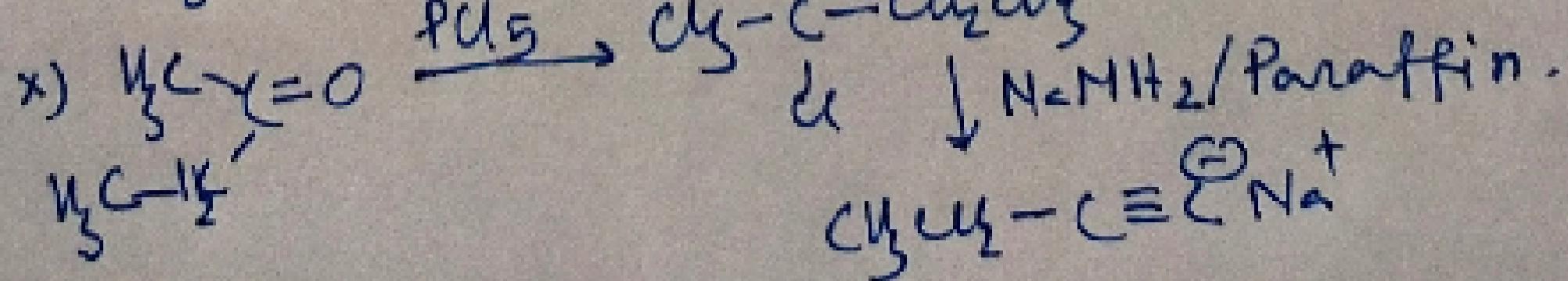
Acyne; Preparation:

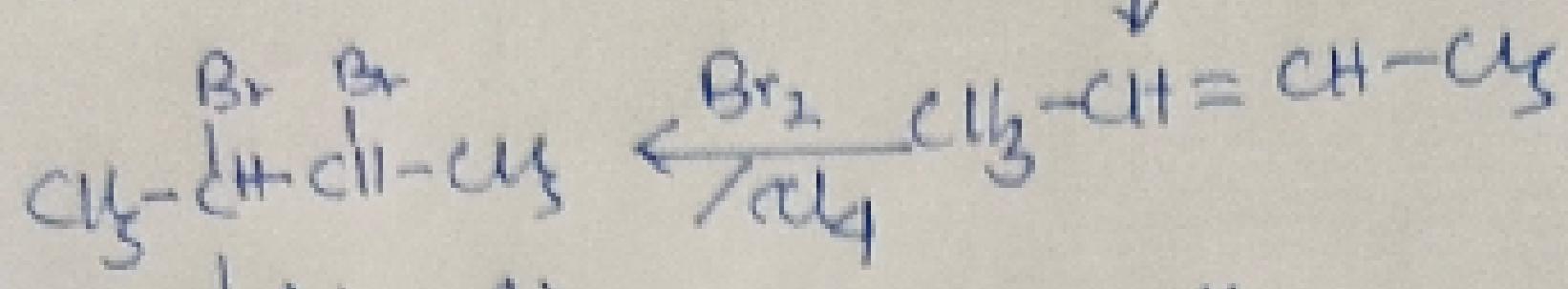
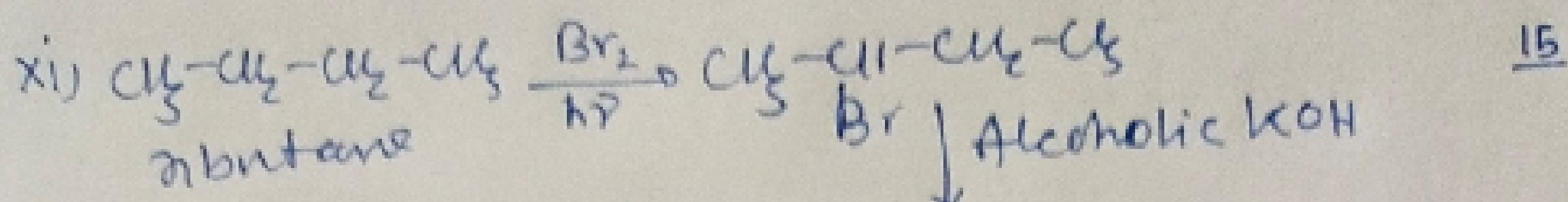


ii) From vicinal dihalide.

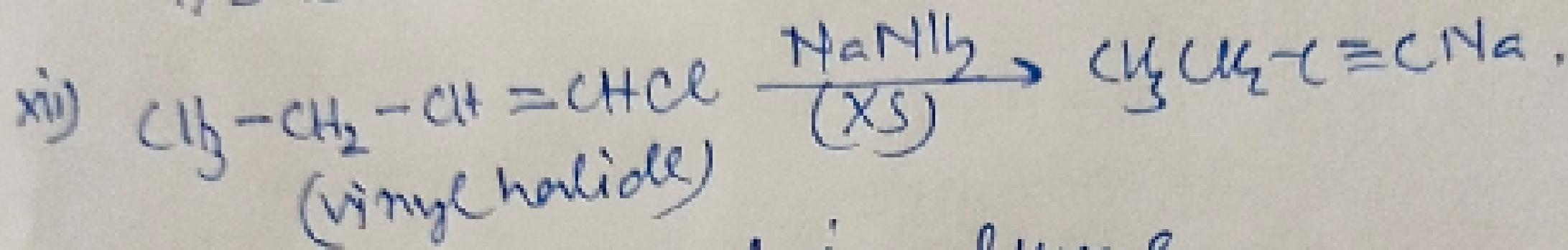
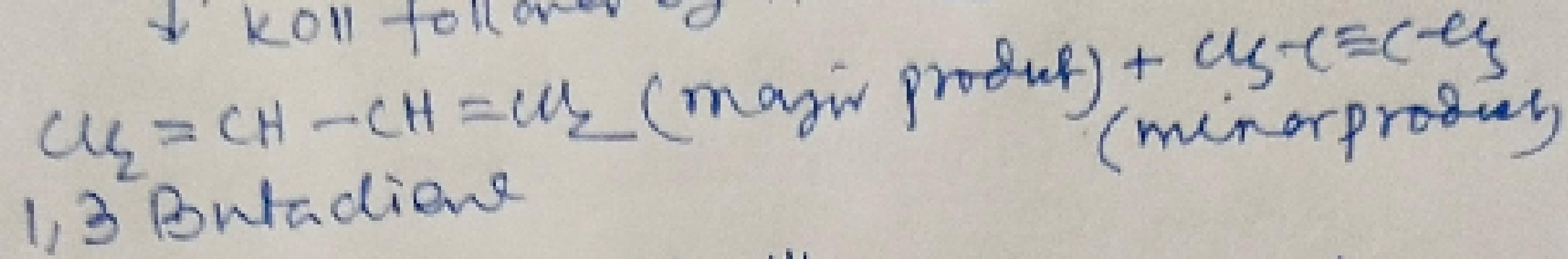


Magnesium carbide. 4

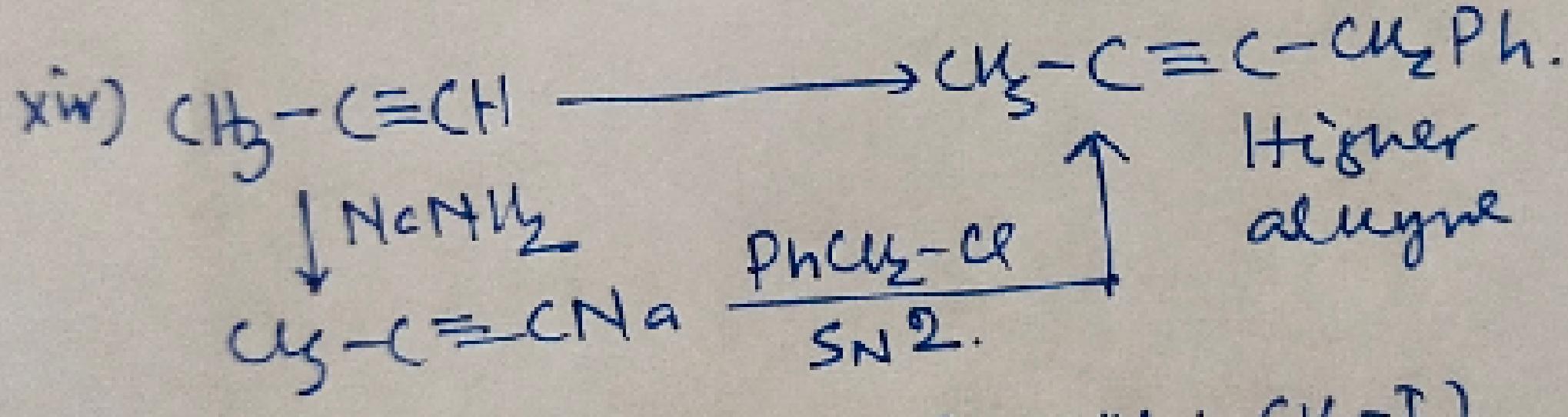
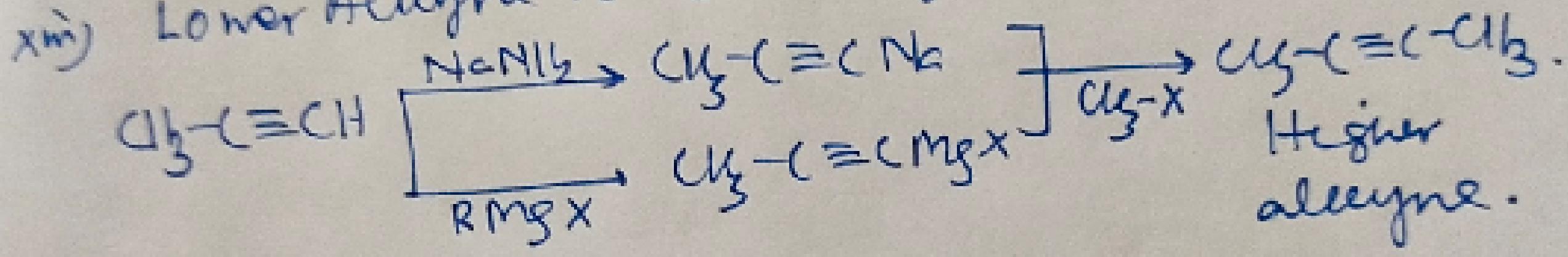




\downarrow Alcoholic KOH followed by NaNH_2



xiv) Lower Alkyne to higher alkyne.



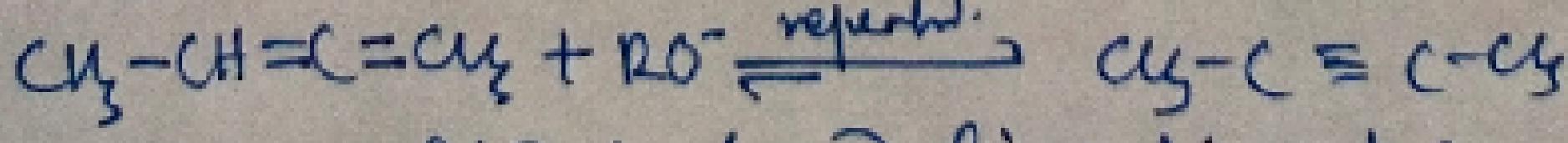
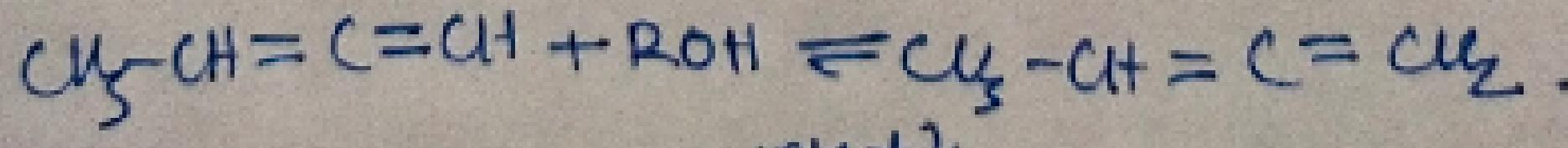
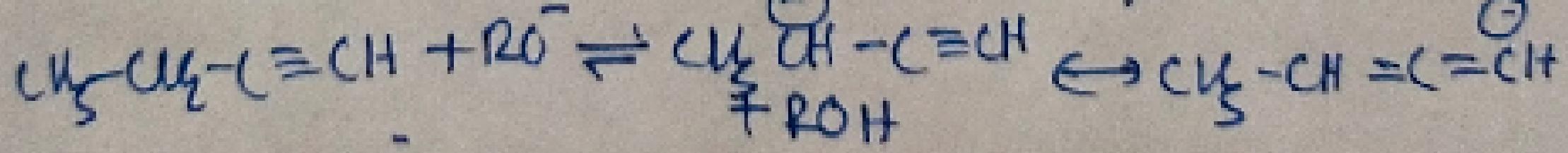
xvi) Iocytne \rightarrow 2-monoyne (NaNH_2 ; CH_3-I).

xvii) Terminal alkyne to nonterminal alkyne.



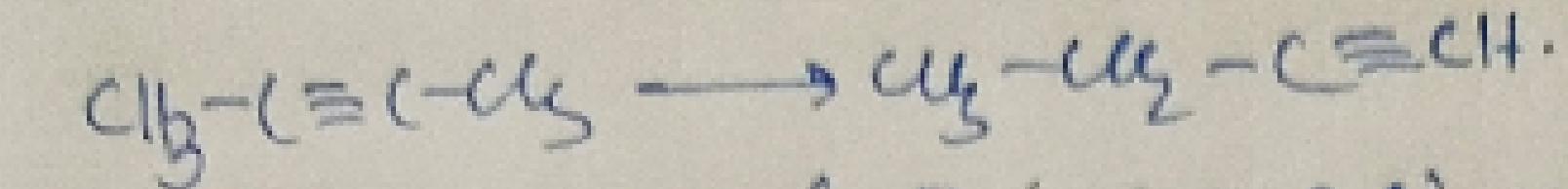
The reagent used here: alcoholic KOH/ Δ

or $\text{EtO}^-/\text{high temperature}$

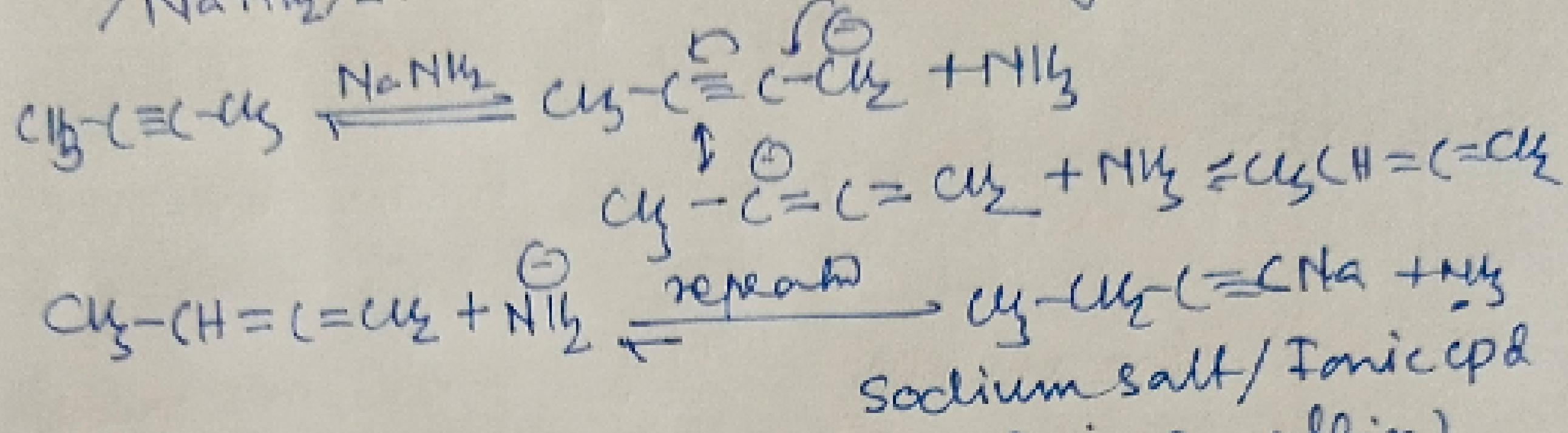


Eqn^m is shifted to forward direction because 2-butyne is more stable than 1-butyne.

Non-terminal alluvium → Terminal Alluvium. 16



The reagent used for this conversion NaNH_2 /Paraffin or
 NaNH_2/Δ .

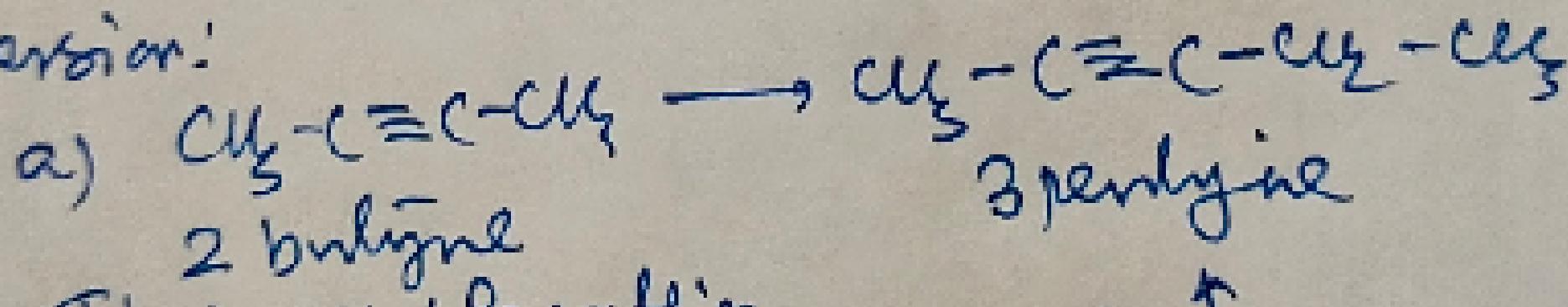


(precipitated in organic solvent like Paraffin).
Also at low temp. NH_3 gas is liberated, so equilibrium
is shifted to forward direction.

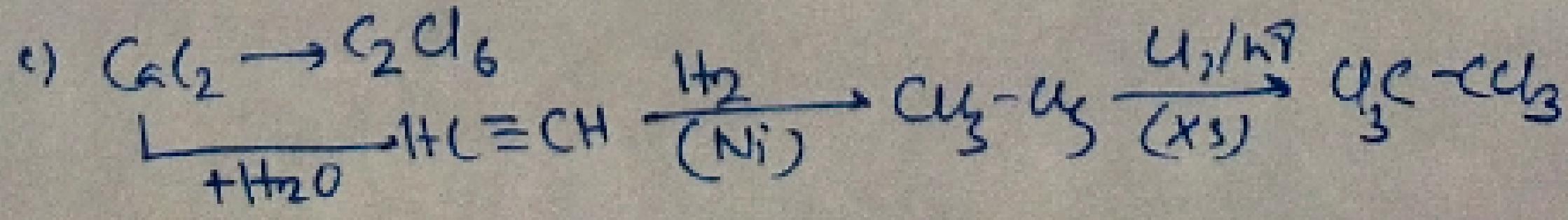
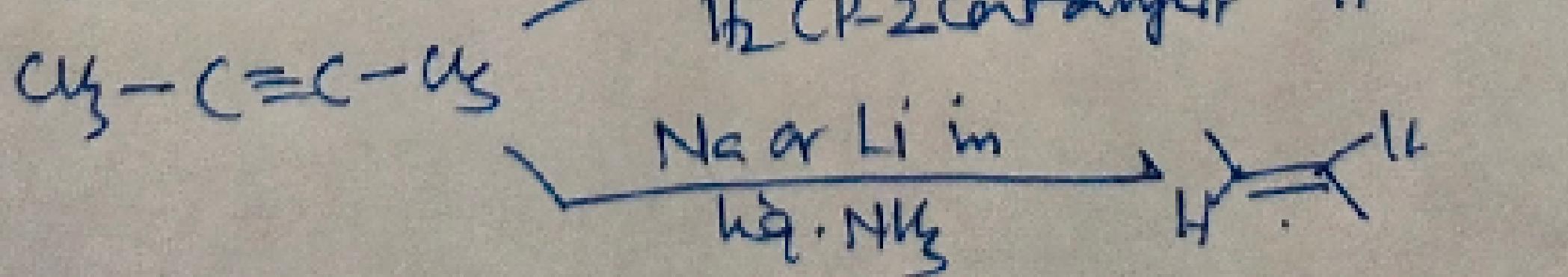
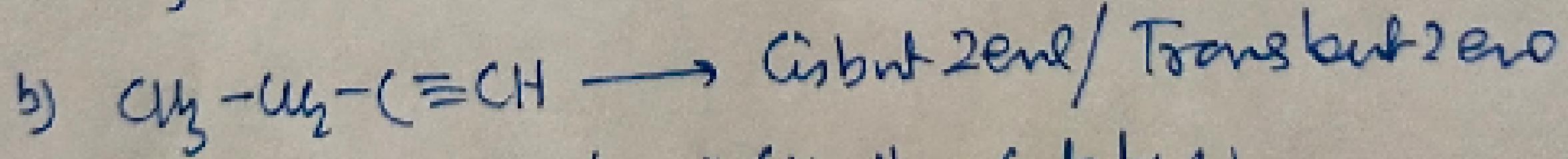
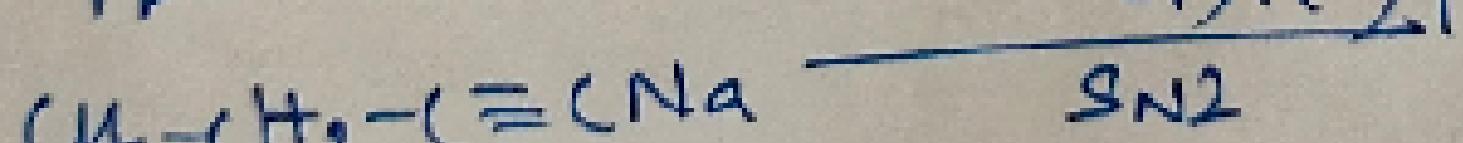
is oxygen to form the intermediate carbonyl group of the reaction.

In both the reaction products is C_6H_6 Maximum no. of atoms present in one plane = 6.

Conversion

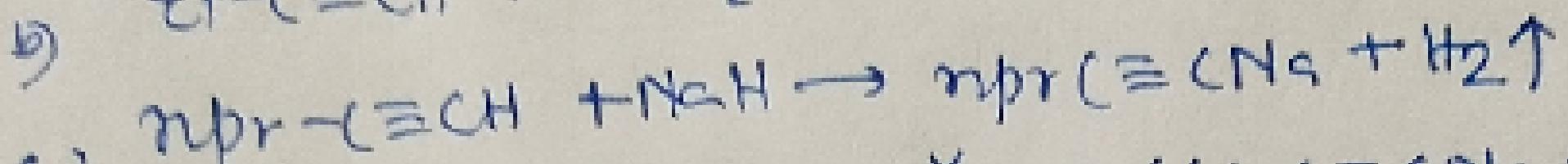
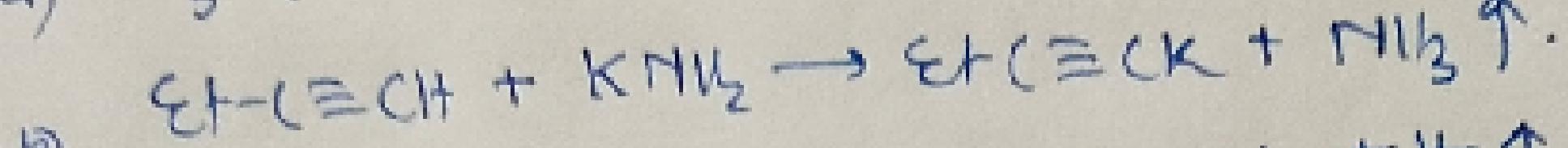
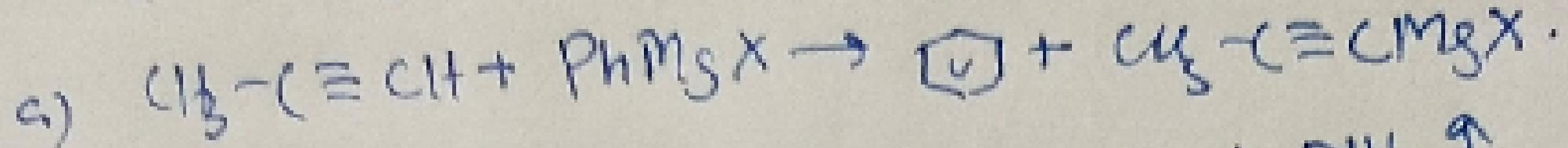


Tl NaNO₃/Paraffin. Ex(I)

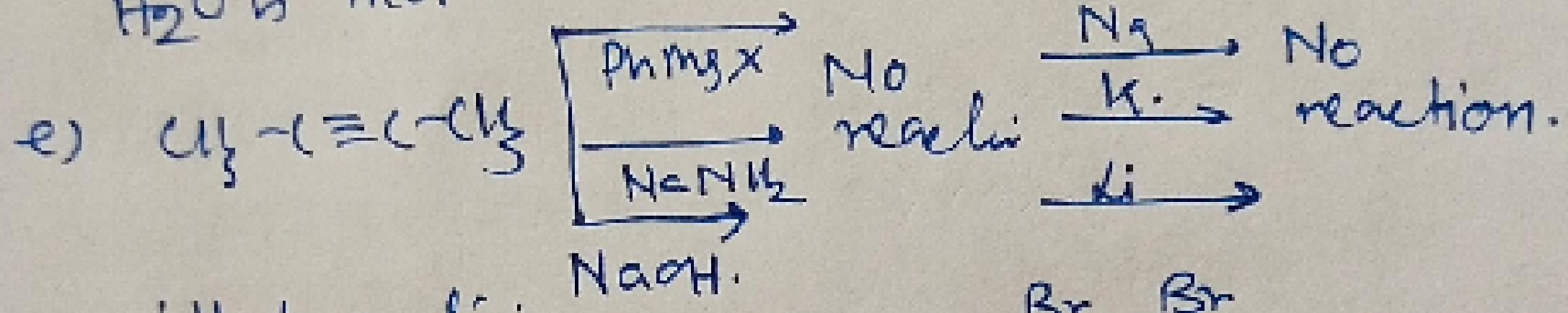


: Reaction of alkyne:

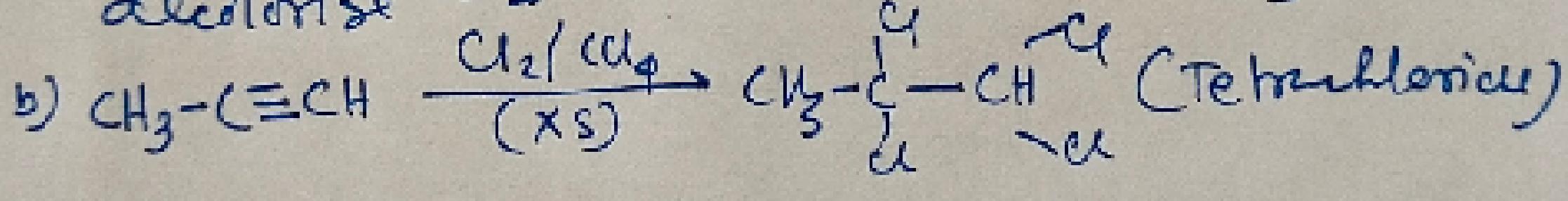
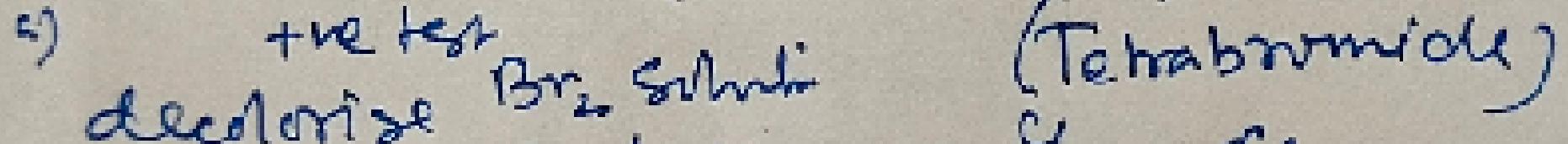
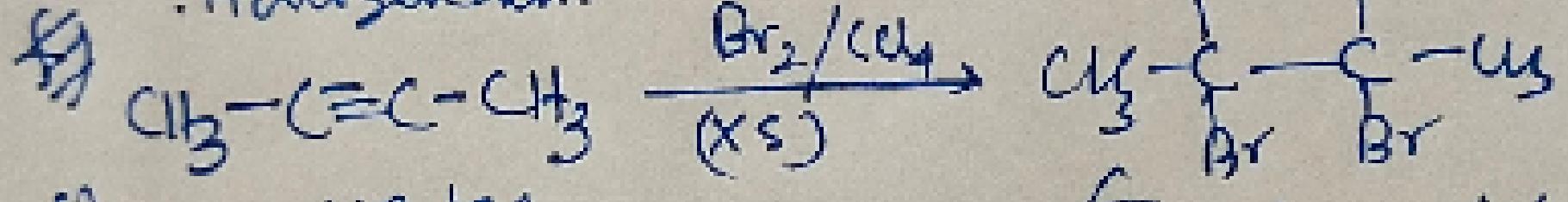
Acetyne has some acidic character. Nonterminal (terminal) alkyne is not acidic in nature.



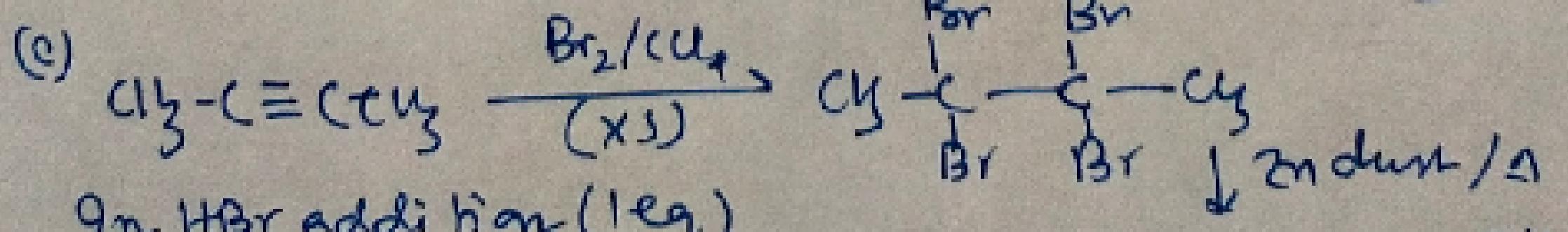
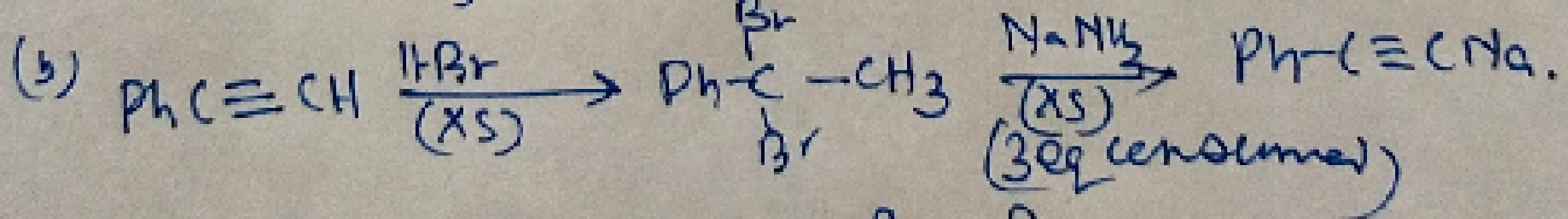
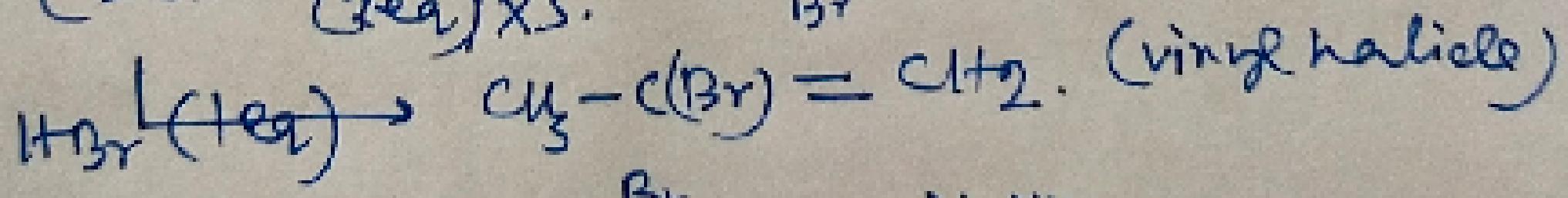
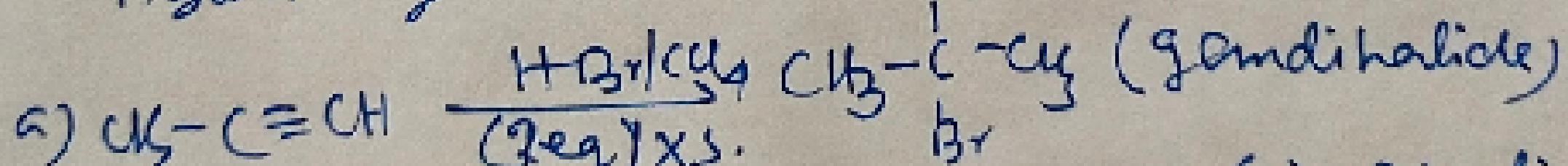
e) It does not react with NaOH/KOH because H_2O is more acidic than alkyne.



f) : Halogenation:

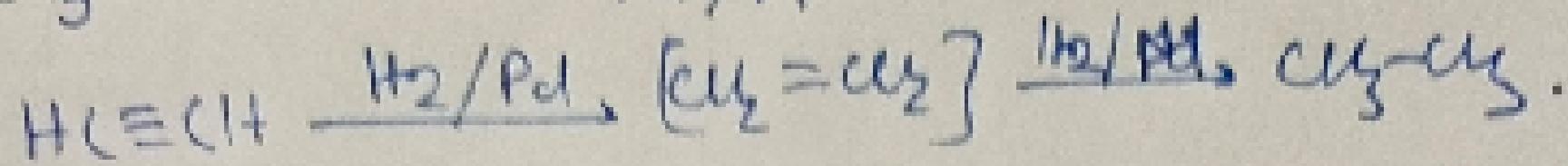
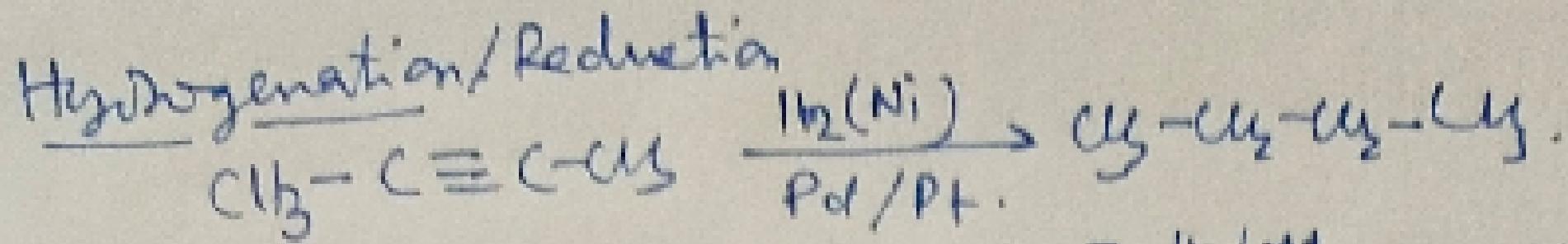


Hydrohalogenation:



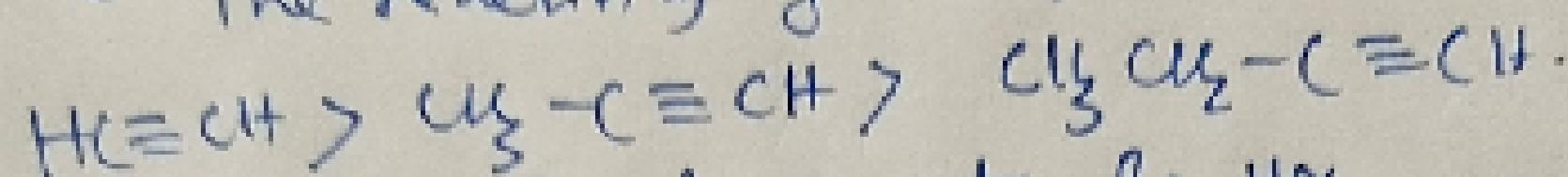
In HBr addition (1 eq)
vinyl cation is formed as intermediate $\text{CH}_3\text{C}\equiv\text{C}^+\text{CH}_3$.

18

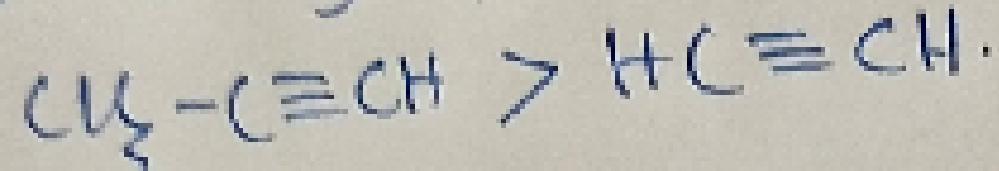


The reactivity $\text{HC}\equiv\text{CH} > \text{CH}_3-\text{C}\equiv\text{CH} > \text{CH}_3-\text{C}\equiv\text{C}$
of alkyne towards hydrogenation.

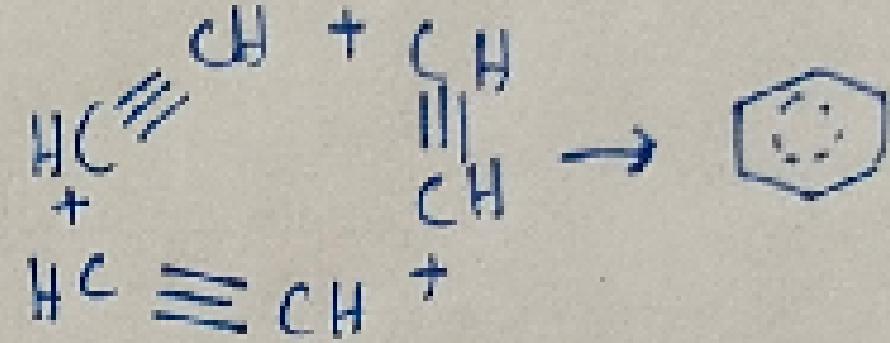
H_2 The reactivity of alkyne towards basic



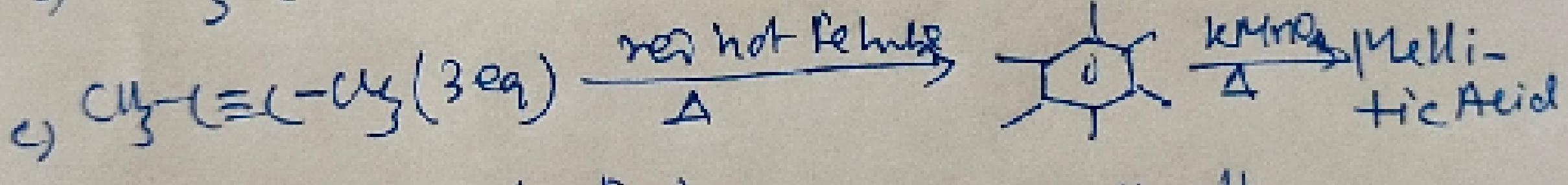
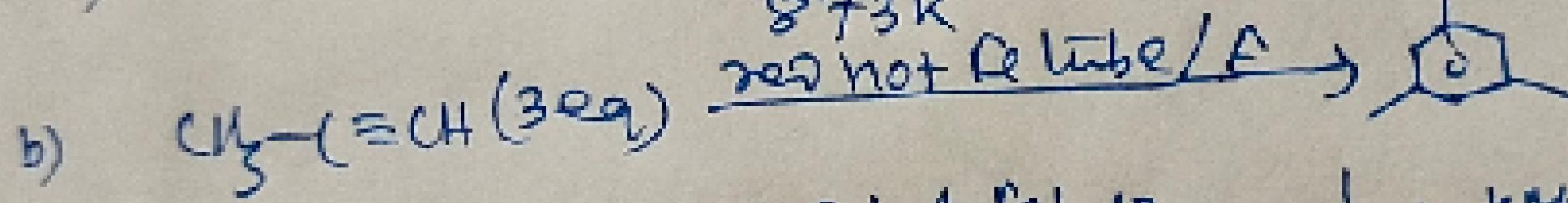
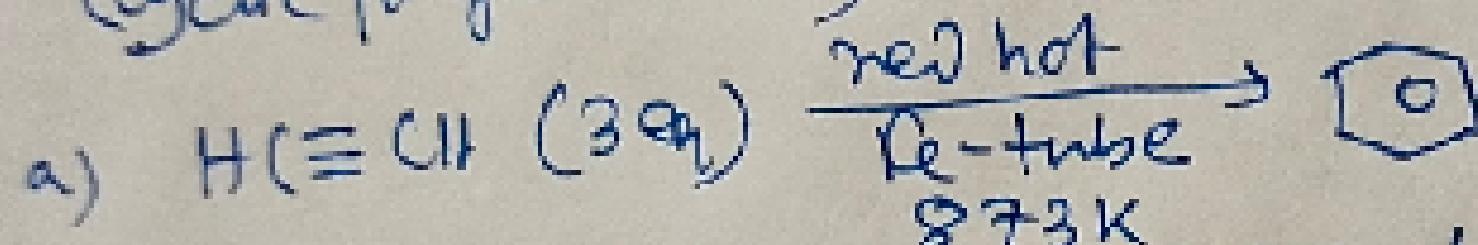
The reactivity of alkyne towards HX .



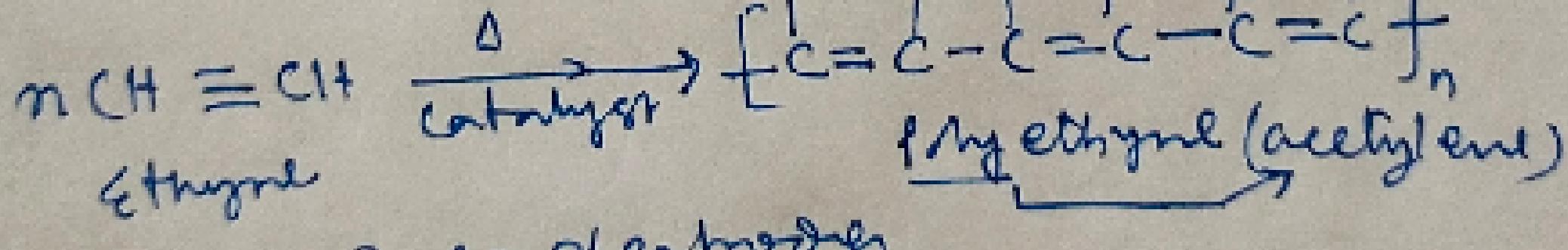
: Polymerisation: $\begin{cases} \xrightarrow{\text{cyclic}} \\ \xrightarrow{\text{linear}} \end{cases}$



(cyclic polymerisation)

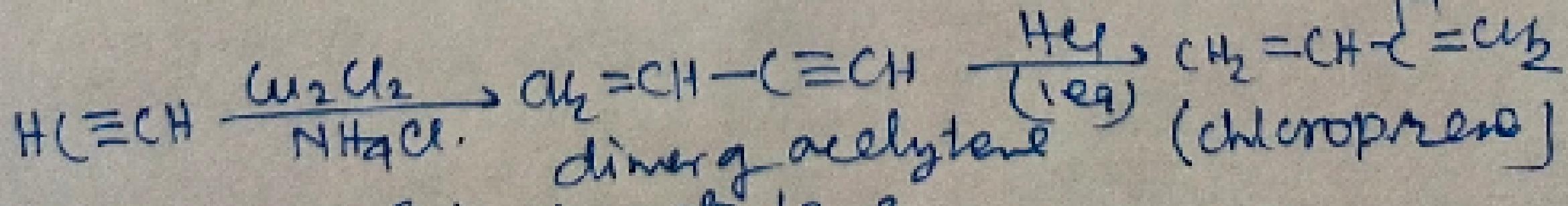
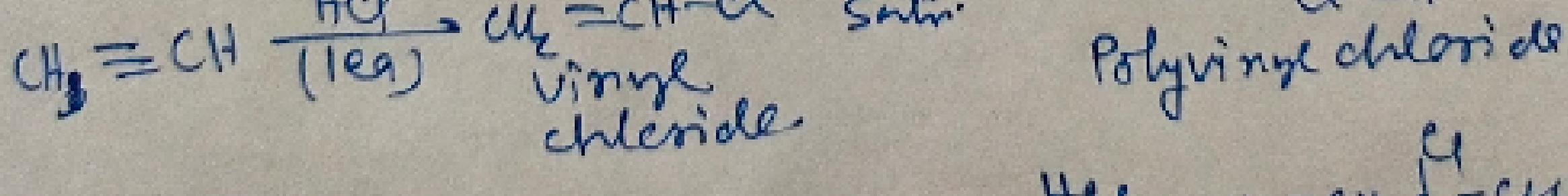
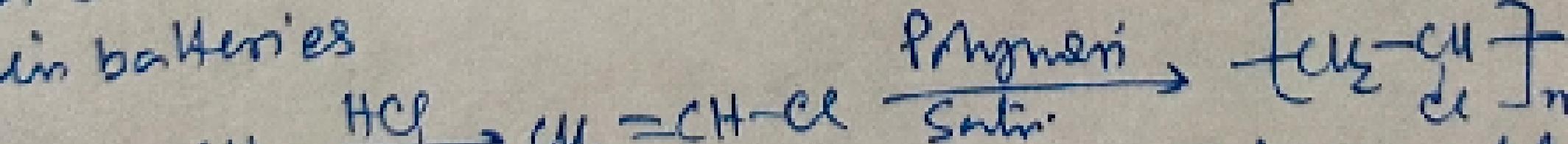


(Linear Polymerisation)

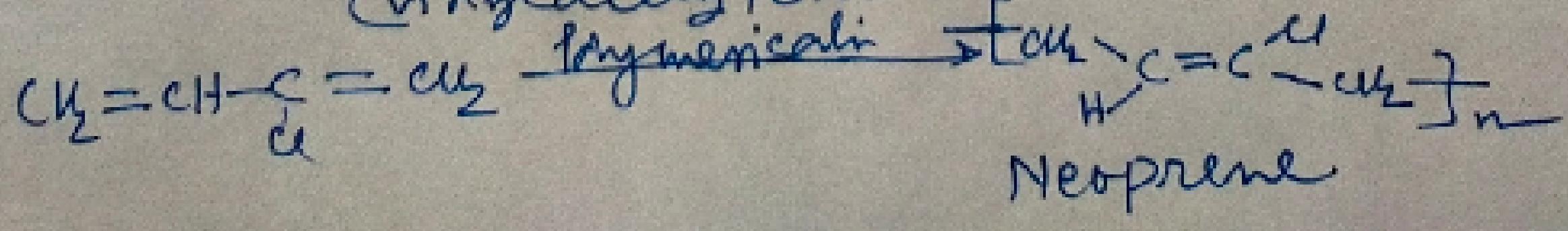


It can be used as electrodes

in batteries

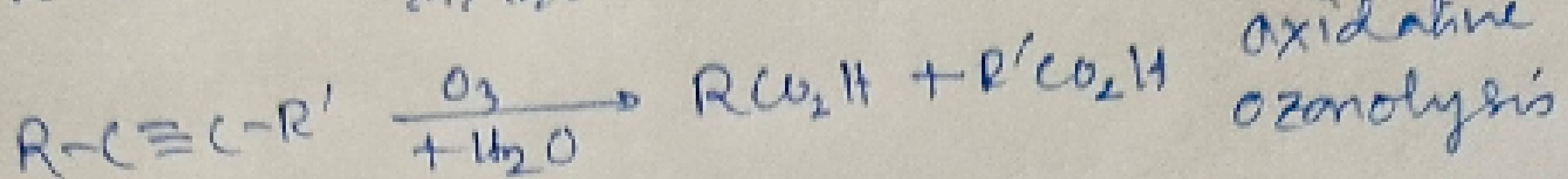
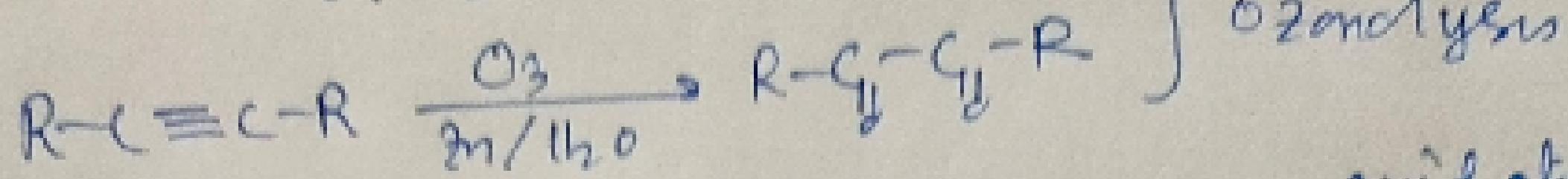


(vinylacetylene)

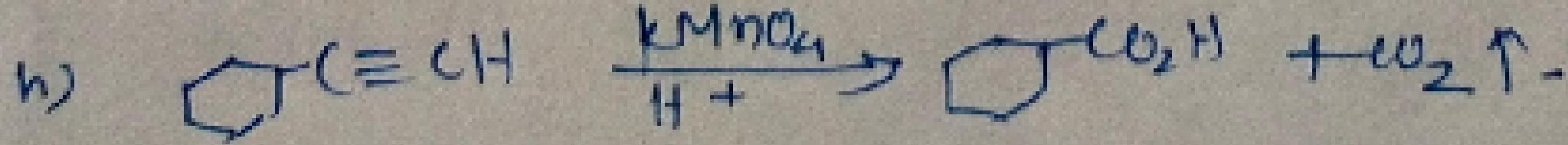
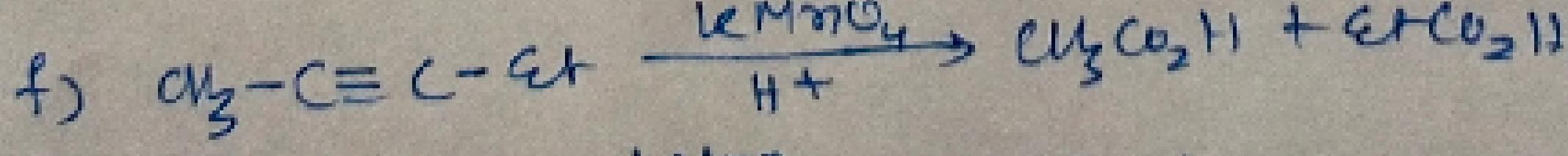
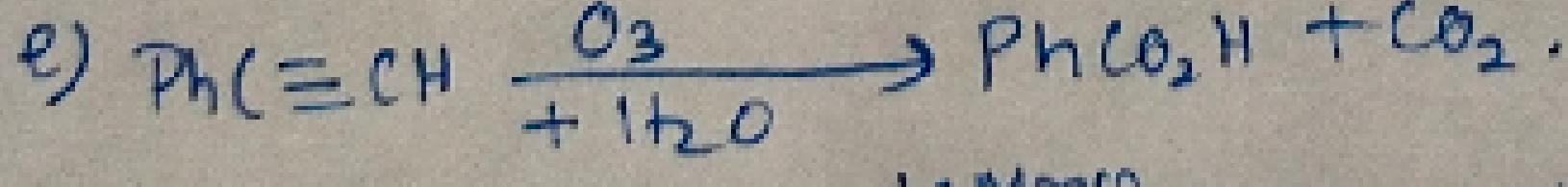
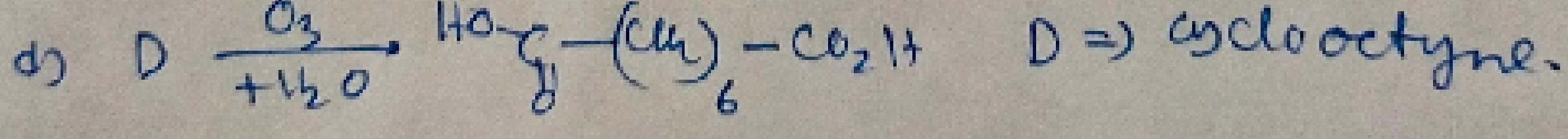
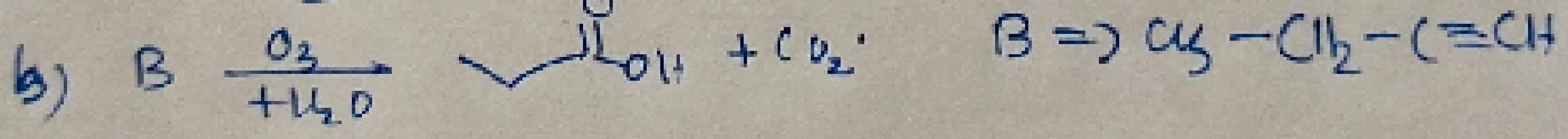
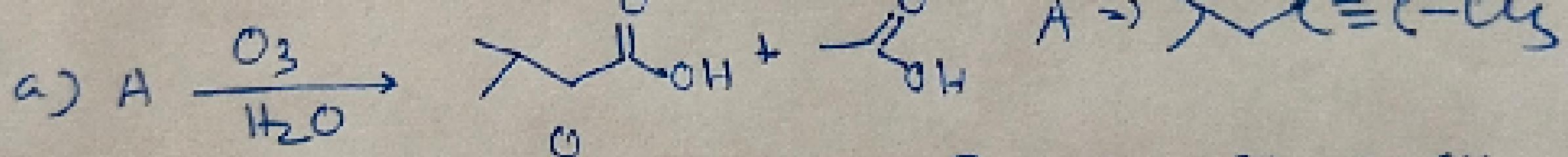
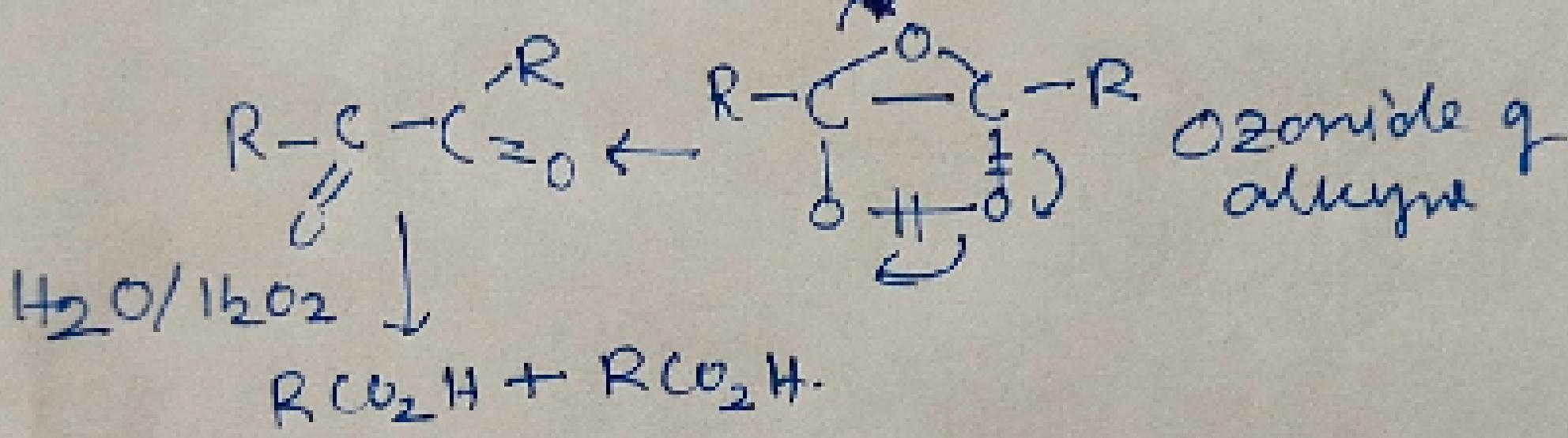
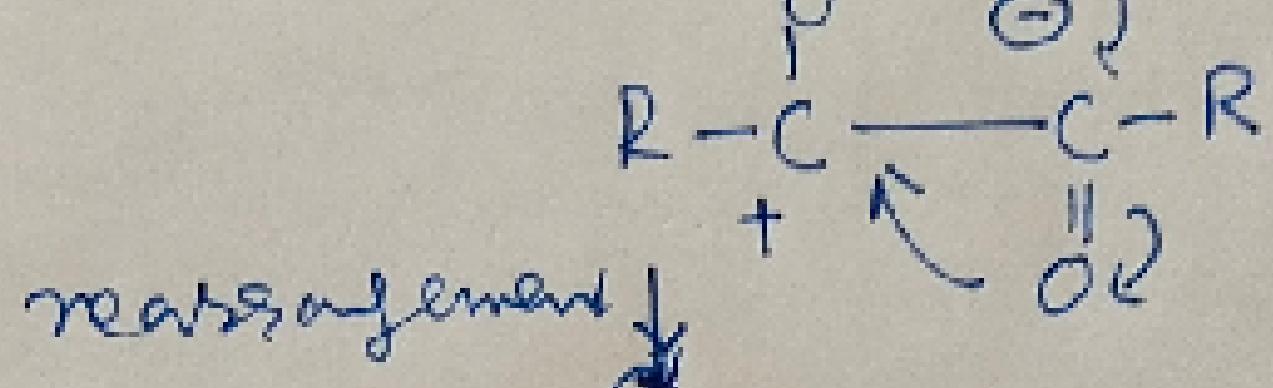
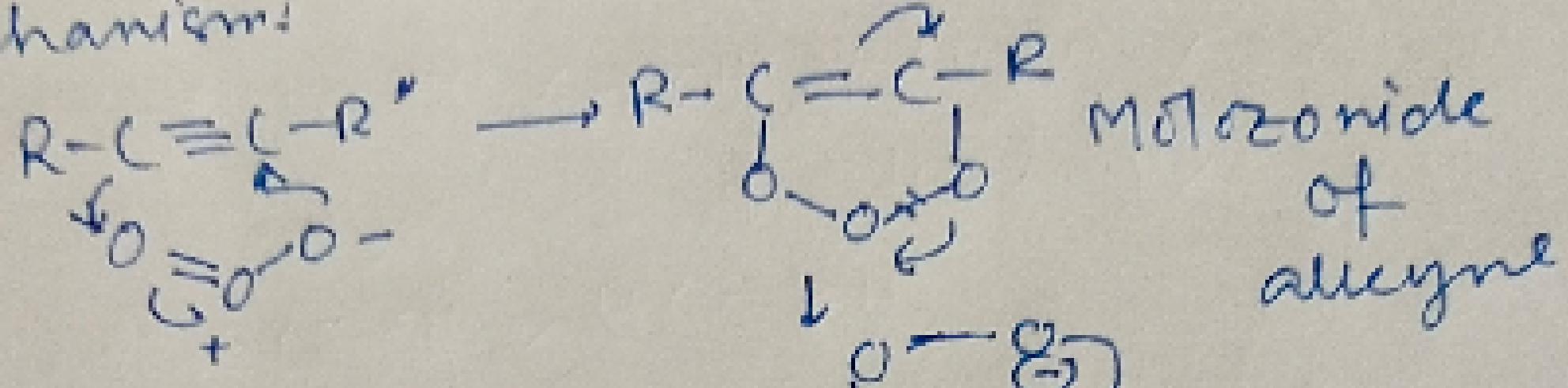


Ozonolysis of alkyne:

19



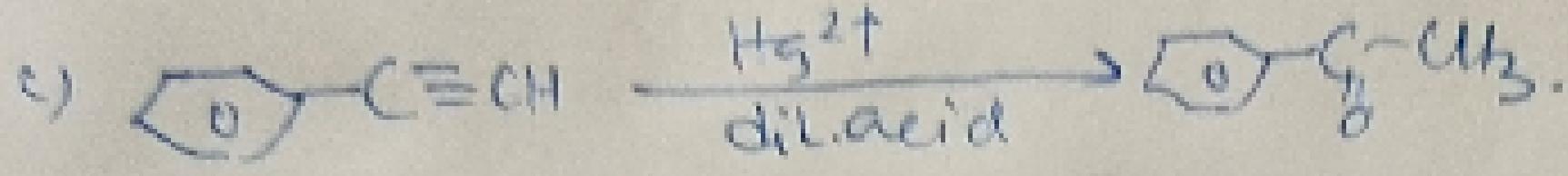
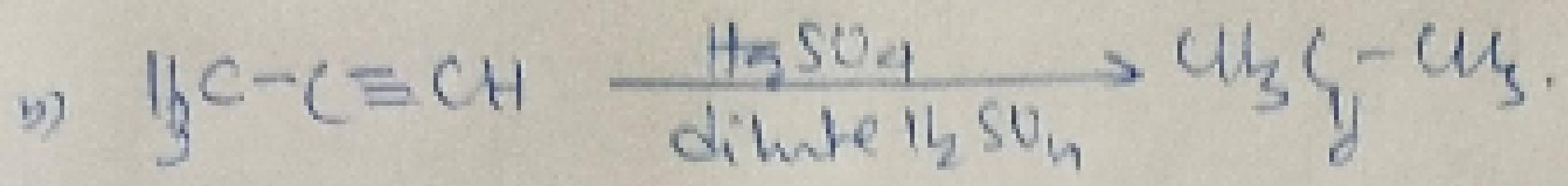
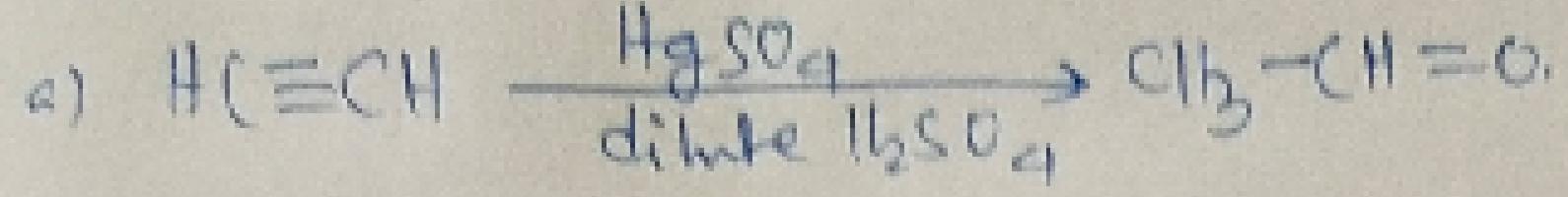
Mechanism:



Reaction KMnO_4/H^+ \equiv oxidative ozonolysis

: Hydrogenation of Acetylene:

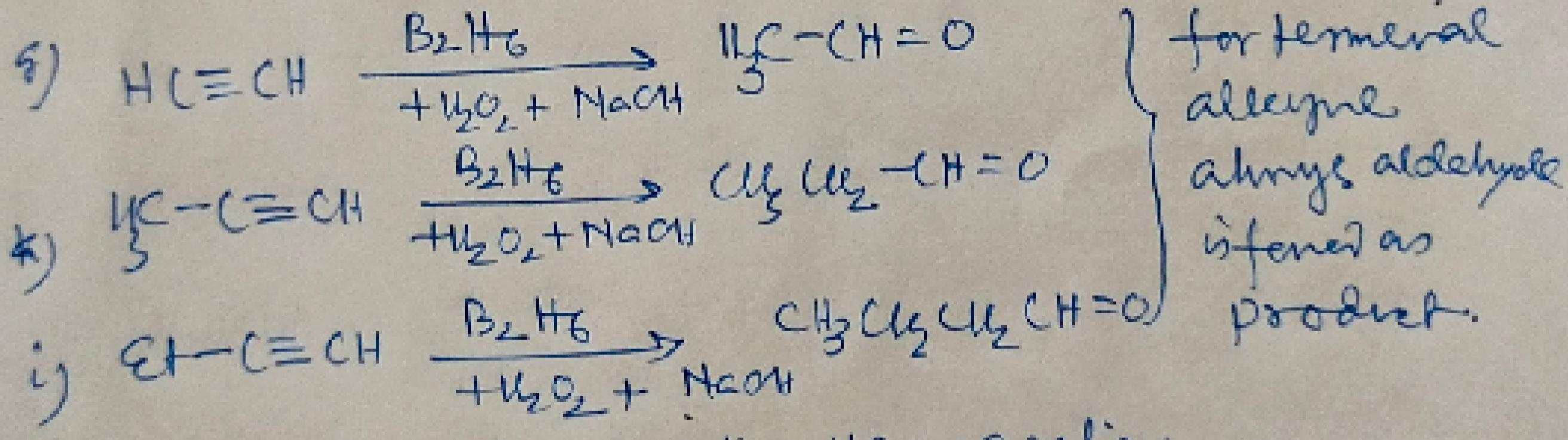
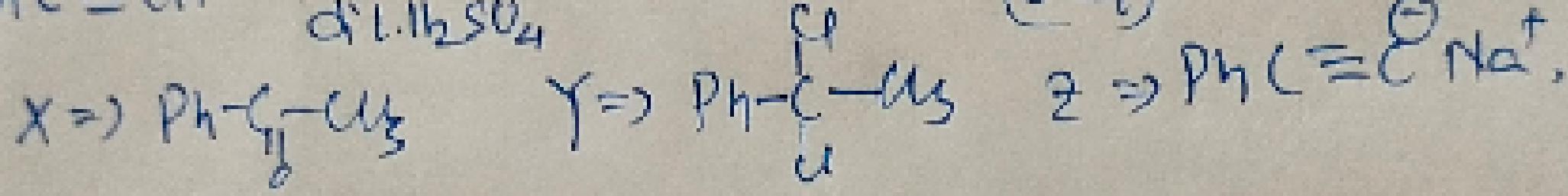
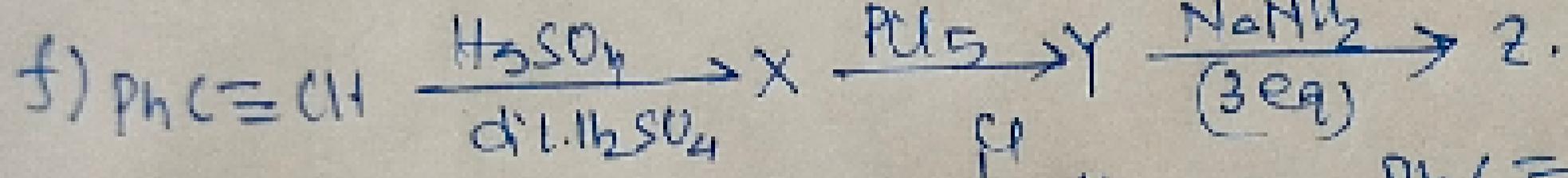
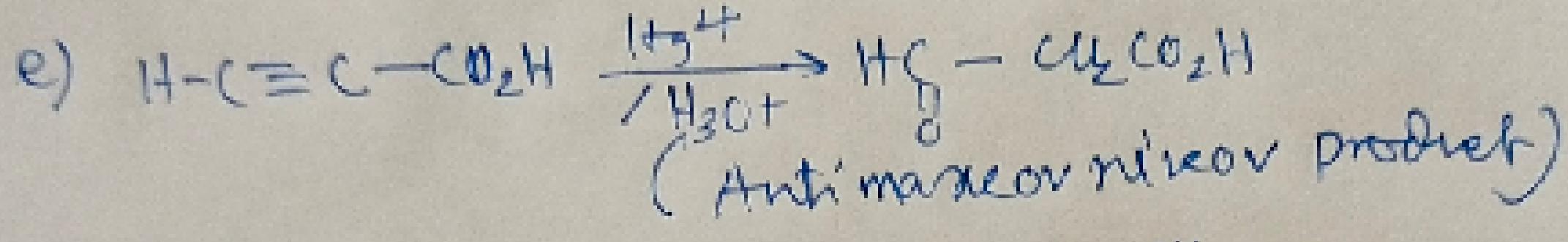
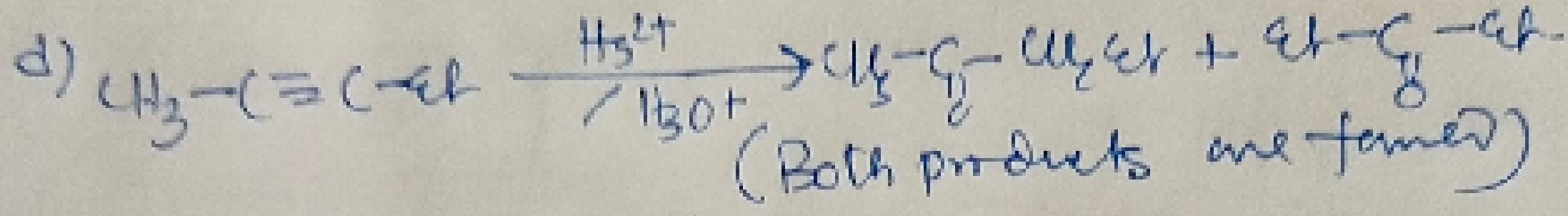
22



The above reaction is called Kucherov reaction.

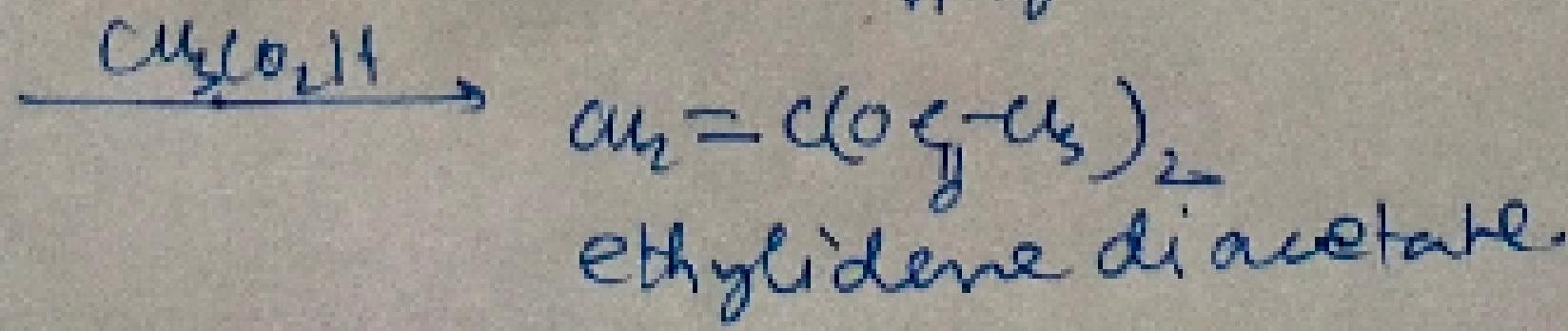
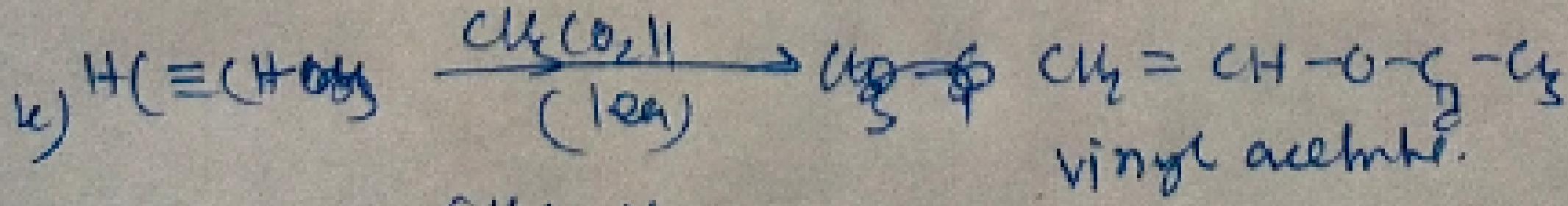
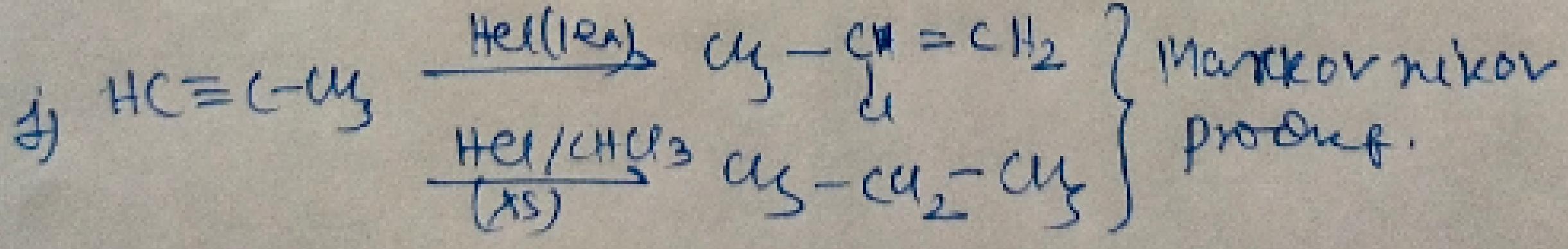
Markovnikov product

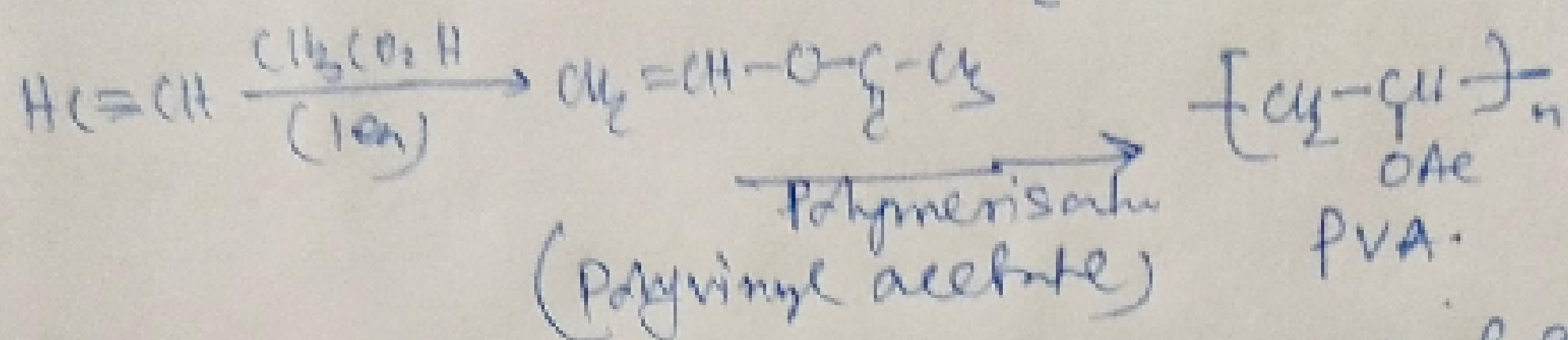
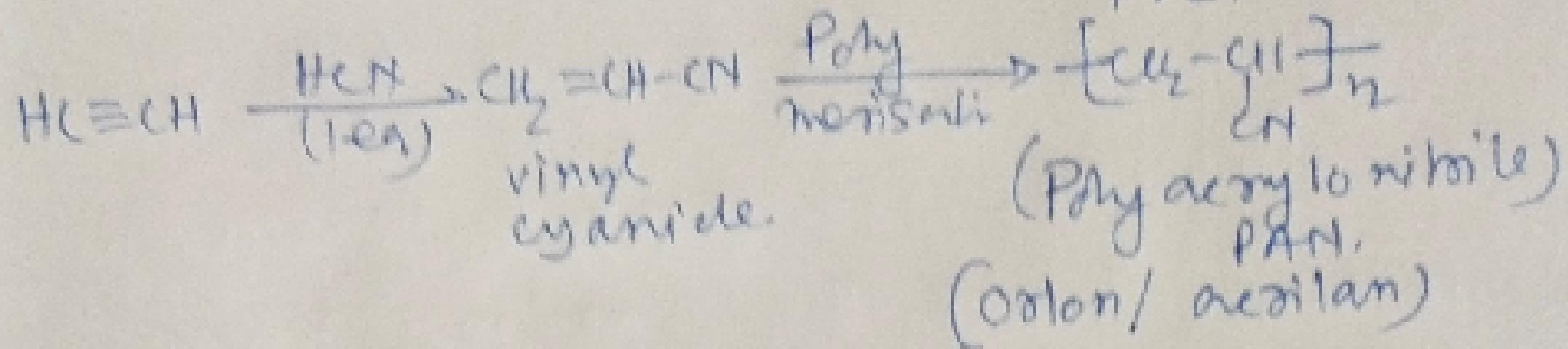
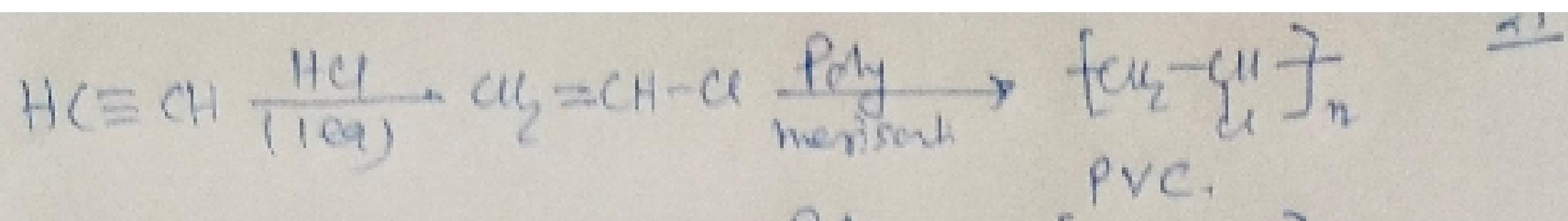
ketone is formed in all acetylene except $\text{H}\equiv\text{CH}$.



The above reaction is called H₃BO reaction.

Antimarkovnikov product is formed.





: Distinguish terminal alkyn & nonterminal alkyne:

	$\text{CH}_3-\text{C} \equiv \text{C}-\text{CH}_3$	$\text{CH}_3-\text{CH}_2-\text{C} \equiv \text{CH}$
NaNH_2	✓ (NH ₃ gas released)	✗
RMgX	✓ (R=CH ₃ , CH ₂ gas released)	✗ ✗
NaH	✓ (H ₂ gas released)	✗ ✗
Na	✓ (H ₂ gas released)	
Cu_2U_2 + NH_3OH	Red ppt.	$\text{CH}_3-\text{CH}_2-\text{C} \equiv \text{CU}$
AsNO_3 + NH_4OH	White ppt.	$\text{CH}_3\text{CH}_2-\text{C} \equiv \text{CAg} \downarrow$

