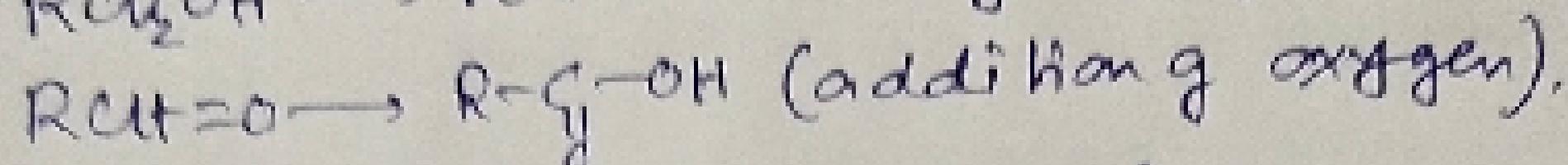
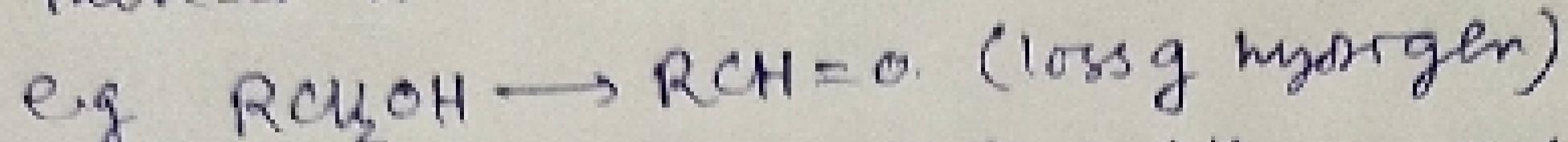


1.

Oxidation:

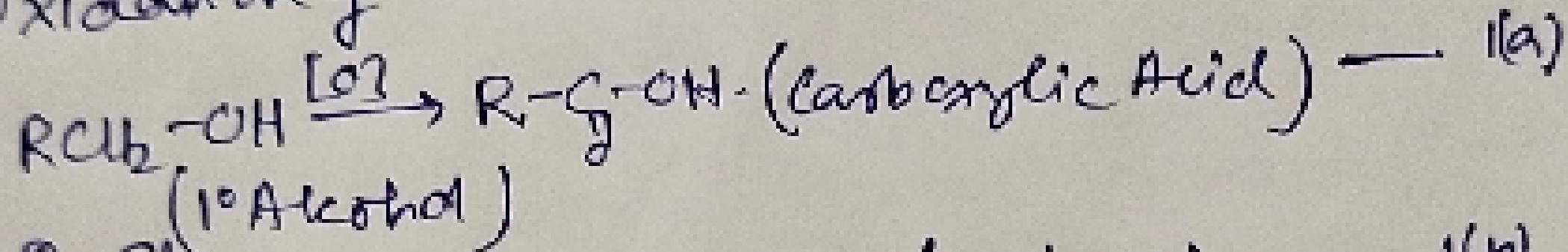
Oxidation: It is a process where hydrogen is lost or oxygen is added during reaction.

Also loss of e⁻ if takes place to a certain reactant then it is called reactant is oxidised.

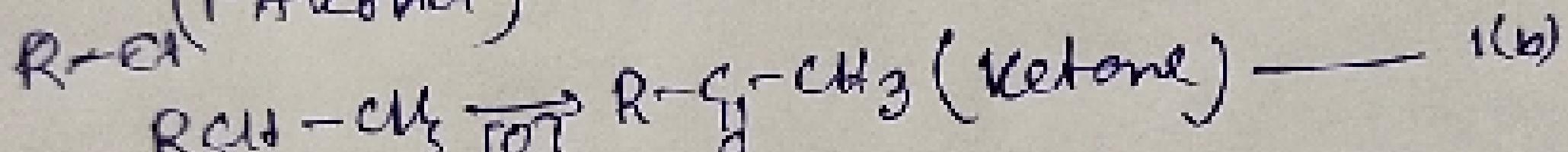


All above three reactions are examples of conversion of oxidation.

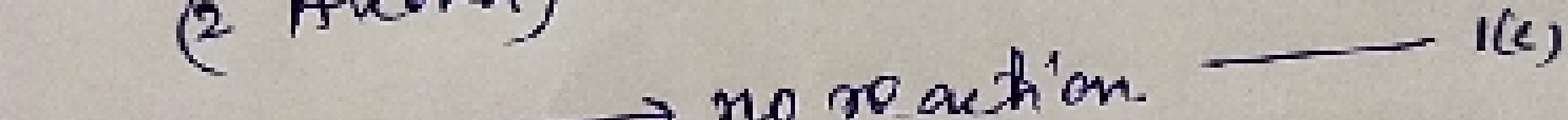
Oxidation of Alcohol:



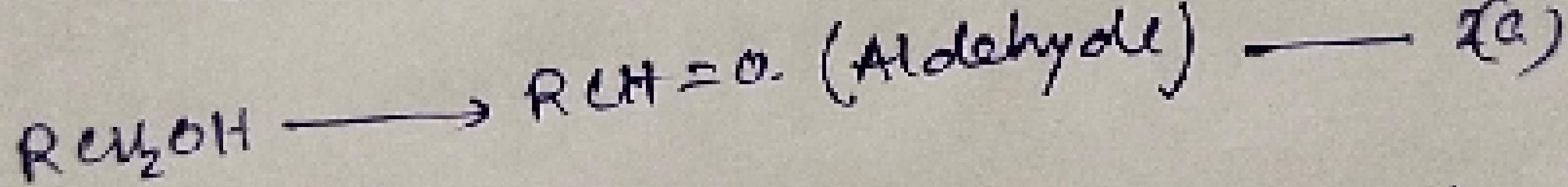
(1° Alcohol)



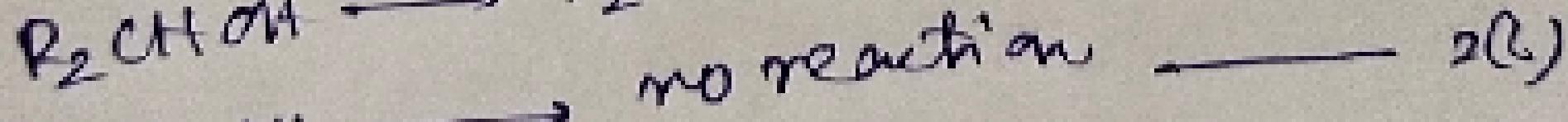
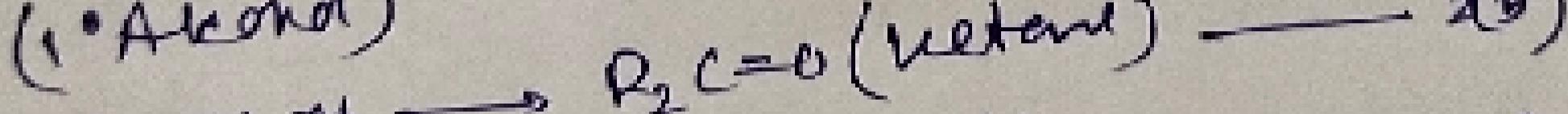
(2° Alcohol)



3° alcohol [because no H is present on carbon]



(1° Alcohol)



3° Alcohol can not be oxidised.

3° Alcohol can not be oxidised.

Concept of oxidising agent:

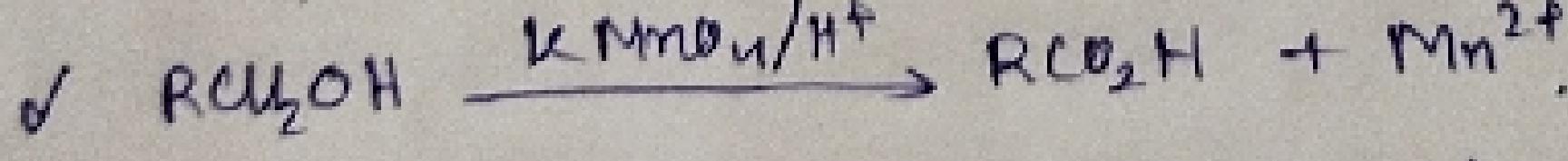
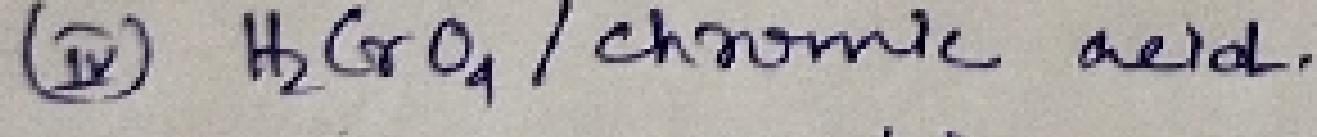
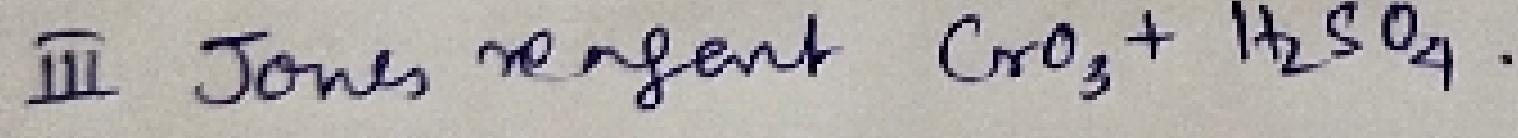
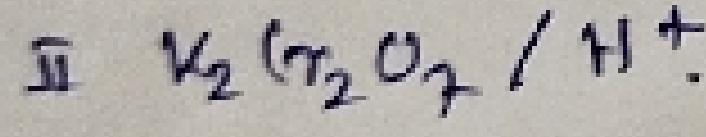
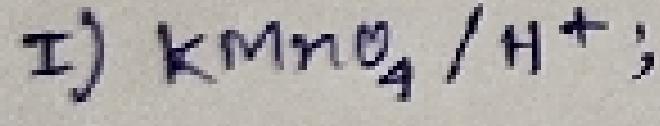
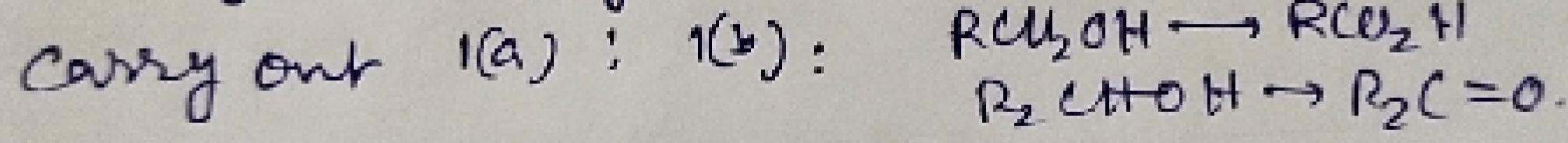
- i) If any compound having central atom with higher oxidation state, it definitely can act as oxidising reagent.

e.g.: KMnO_4 ; $\text{K}_2\text{Cr}_2\text{O}_7$; HNO_3 ; H_2O_2

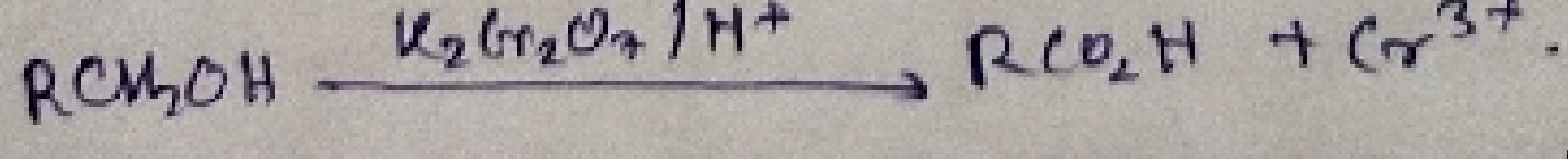
- ii) Also compound with element higher positive oxidation state can act as oxidising reagent.
 MnO_2 ; SeO_2 (oxide of manganese, selenium)
- iii) X_2 can act as oxidising reagent.
 & oxidising power order $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.
- iv) O_2 / O_3 can act as oxidising reagent.
 O_2 is strongest oxidising reagent; O_3 is second strongest oxidising reagent after F_2 .
- v) Compounds having peroxy linkage can give nascent oxygen, so it can act as oxidising agent.

Oxidation of Alcohol: The reagent used are classified as two types.

a) Strong oxidising reagents which



during reaction purple/pink colour of KMnO_4 is changed to colourless solution of Mn^{2+}



Also during reaction orange colour of $\text{K}_2\text{Cr}_2\text{O}_7$ is changed to green colour of Cr^{3+}

vii) Halogen molecule. ($\text{Cl}_2/\text{Br}_2/\text{I}_2$).

viii) $\text{TiCl}_4 + \text{DMSO} + \text{NaHCO}_3$.

(ix) Cu/Δ (specific use)

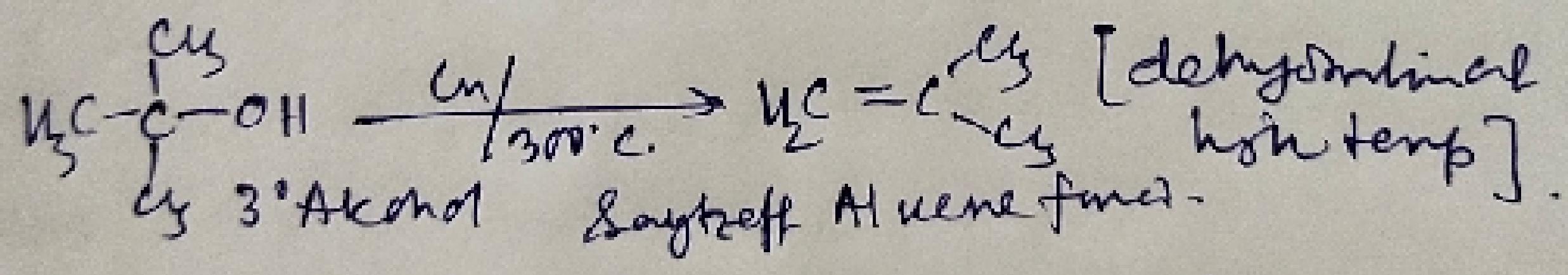
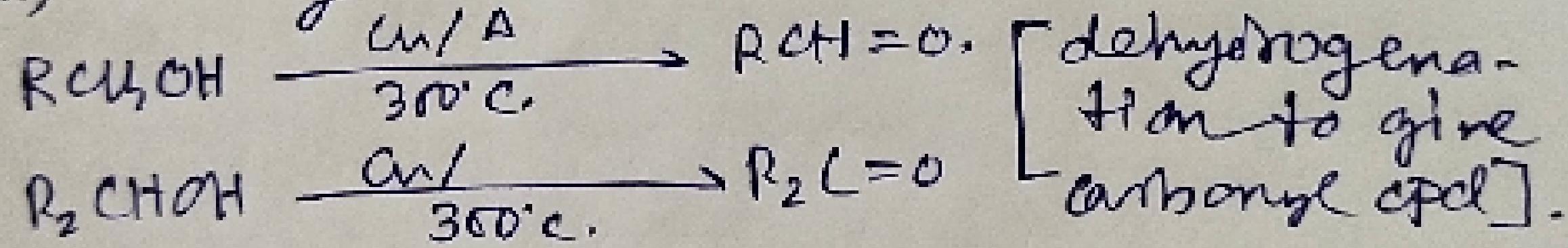
(x) MnO_2 (specific use).

Points to be noted:

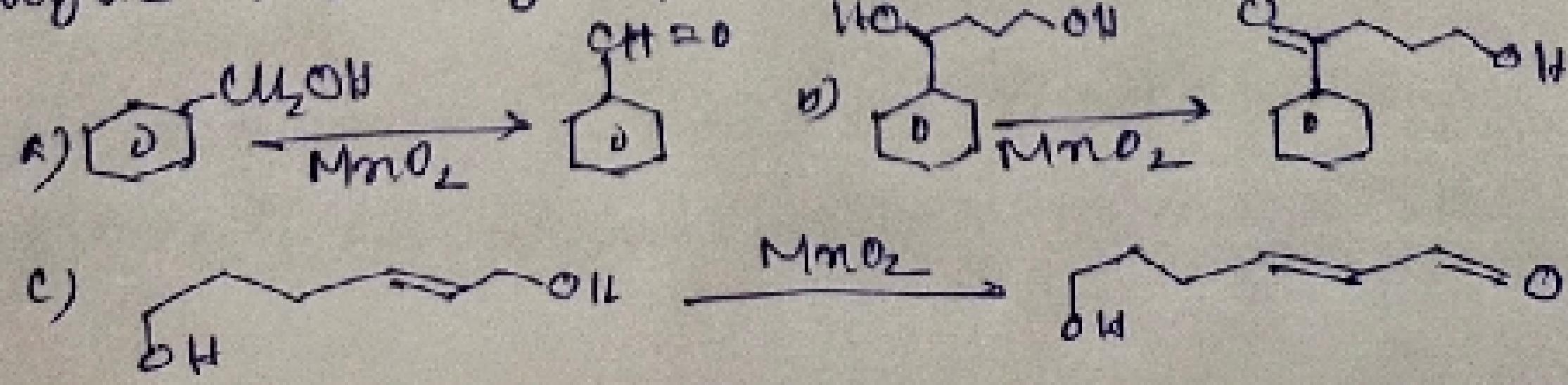
a) CrO_3 in aqueous medium $\rightarrow (\text{CrO}_3 \text{ in nonaqueous medium})$
 (oxidising power)

b) NBS, by giving bromine oxidises 1° Alcohol \rightarrow Aldehyde.
 $\& 2^\circ$ Alcohol \rightarrow Ketone

c) Cu/Δ is little bit different from other mild oxidising reagent in the sense it also reacts with 3° Alcohol, but this time instead of dehydrogenation, actually dehydration takes place.



d) MnO_2 oxidises not all 1° Alcohol & 2° Alcohol.
 It will only oxidise 1° Alcohol & 2° Alcohol
 provided alkoholic $-\text{OH}$ group is present at
 allylic or benzylic position.



4



during reaction, yellow colour solution of H_2CrO_4 is changed into green colour solution of Cr^{3+} . So 1° Alcohol & 2° Alcohol gives +ve test with
 i) $KMnO_4, H^+$ but 3° Alcohol gives -ve test. So
 ii) $K_2Cr_2O_7, H^+$ using any of three 3 reagents we can differentiate
 iii) H_2CrO_4 . 1° Alcohol vs 3° alcohol.
 or
 2° Alcohol vs 3° Alcohol.

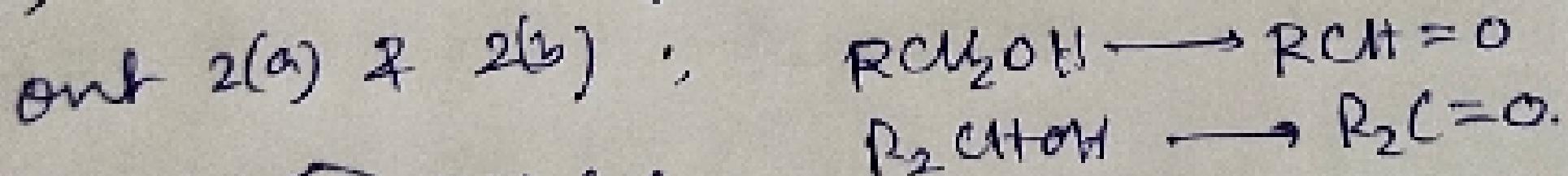
Q. 1 propanol & tertiary butyl alcohol can be differentiated by

- a) $KMnO_4, H^+$ b) $H_2Cr_2O_7, H^+$ c) H_2CrO_4 , d) all.

Q. Which one of the following alcohol can not be oxidised by K_2CrO_4 .

- a) Ethanol b) Isopropane Alcohol c) Tertiary butyl alcohol d) Allyl alcohol. e) 1 hexanol.

Q. (b) Weak oxidising reagents which carry



I) PCC $\text{P}_2\text{Cr}_3^{\oplus} \cdot HCl \cdot (SO_4)_2$
 Pyridinium chloro chromate.

II) CrO_3 in glacial acetic acid / acetone

III) Collin's reagent. 2mole $\text{Cr}_2O_7^{\oplus} \cdot C_6H_5Cl_2$

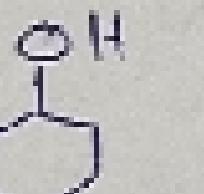
IV) Sarett's reagent. $\text{Cr}_2O_7^{\oplus} \cdot C_6H_5Cl_2$

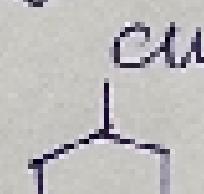
V) NBS.

VI) PDC (Pyridinium dichromate) (All are nonaq. medium)

5

- a)  p) When reacts with CrO_3 , H^+ , carboxylic acid is formed.

b)  Q) give the test with FeCl_3 .

c)  R) When react with HBr , alkyl bromide is formed.

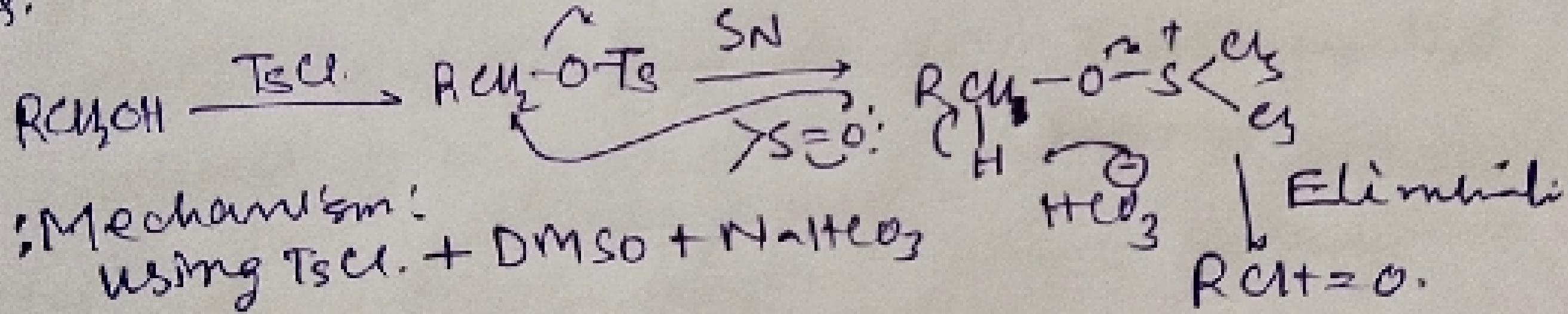
d)  S) When reacts with $\text{K}_2\text{Cr}_2\text{O}_7$, ketone is formed.

+) SO_3 in anhydrous form (MgCl_2)

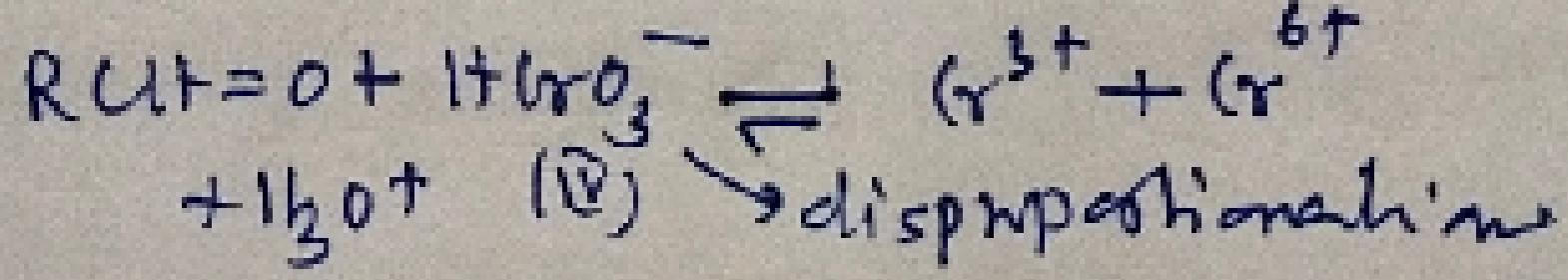
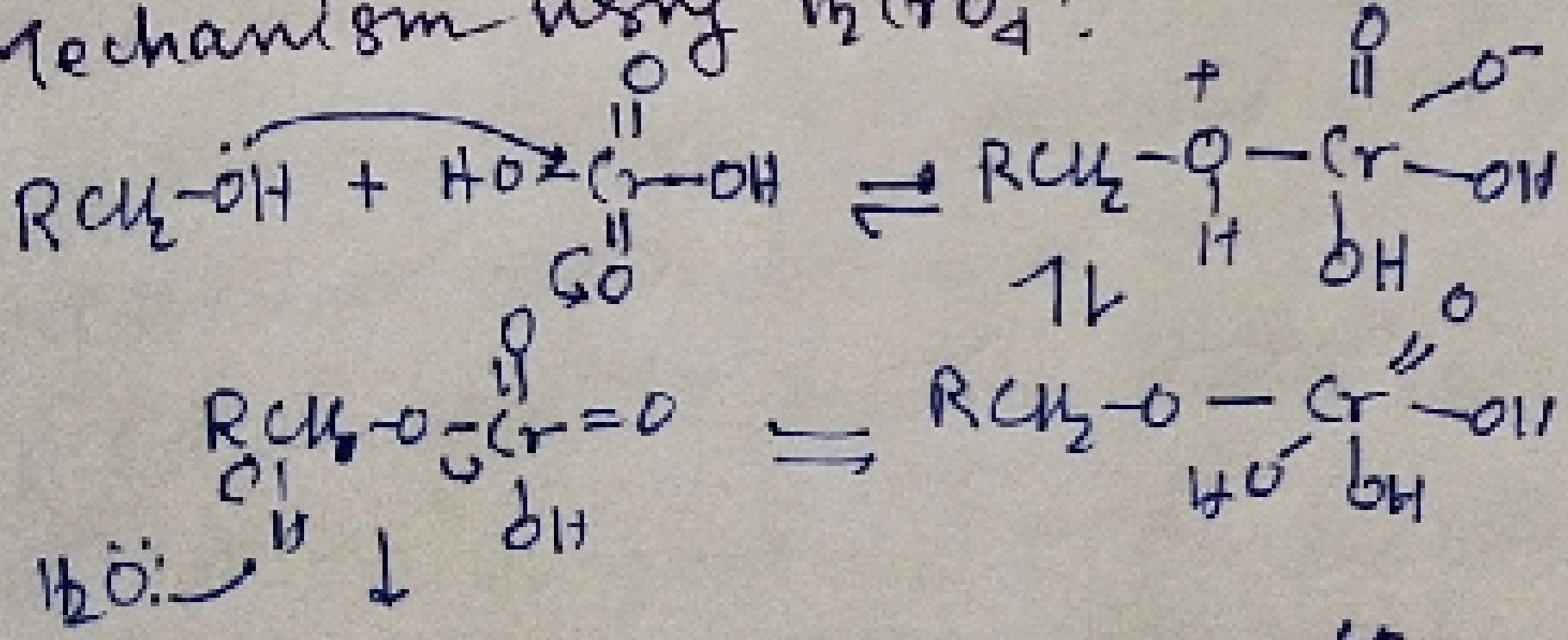
$A \rightarrow R$, $B \rightarrow R, S$ will give aldehyde
 $C \rightarrow P, R, T$, $D \rightarrow O$.

Q. When tertiary butanol or butanol are separately treated with few drops of KMnO_4 , purple colour disappears & a p. brown ppt is formed for one alcohol. Which one it is?

1



Mechanism using H_2CrO_4 .



Points to be noted in mechanism:

6

- i) The step where C-H bond breakage takes place is r.d.s. So this reaction shows kinetic isotope effect.
- ii) reactivity order $\text{RCH}_2\text{OH} > \text{RCD}_2\text{OH}$.
- iii) In presence of H_2O (aq. medium), at first 1° alcohol is converted into aldehyde which give gemdiol & is further oxidized to $\text{R}-\text{C}(=\text{O})-\text{OH}$.
- iv) In non-aqueous medium gemdiol can not be formed so can't be further oxidized. So final product is $\text{RCH}=\text{O}$.
So CrO_3 in acetone } non-aqueous medium
 CrO_3 in CH_2Cl_2 } acts as mild oxidising reagent
- For $\text{CrO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CrO}_4$ aq. medium.
 $\text{CrO}_3 + \text{conc. H}_2\text{SO}_4$ (Jones reagent) } acts as strong oxidising reagent.
- v) for 2° alcohol, ketone is formed. $\text{R}_2\text{CHOH} \rightleftharpoons \text{R}_2\text{C}(=\text{O})$.
ketone forms also gemdiol. $\text{R}_2\text{C}(=\text{O}) \rightleftharpoons \text{R}_2\text{C}(\text{OH})_2$
(in aqueous medium)
but due to non availability of H with carbon, it can not be further oxidized.
- ⇒ Slightly basic medium KMnO_4 also acts as strong oxidising reagent. This time it gives brown ppt of MnO_2 . $\text{RCH}_2\text{OH} + \text{KMnO}_4 \xrightarrow{\text{O}_2\text{H}} \text{RCO}_2\text{K} + \text{MnO}_2 \downarrow$
 RCO_2H .
(Carboxylic acid)

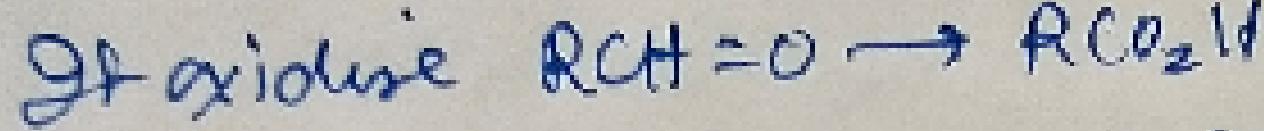
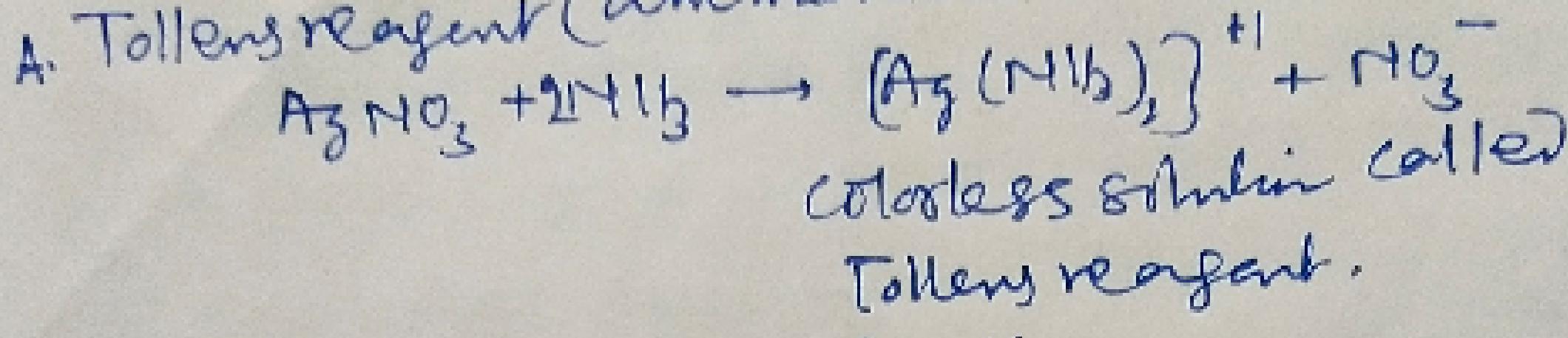
I

Oxidation Aldehyde:

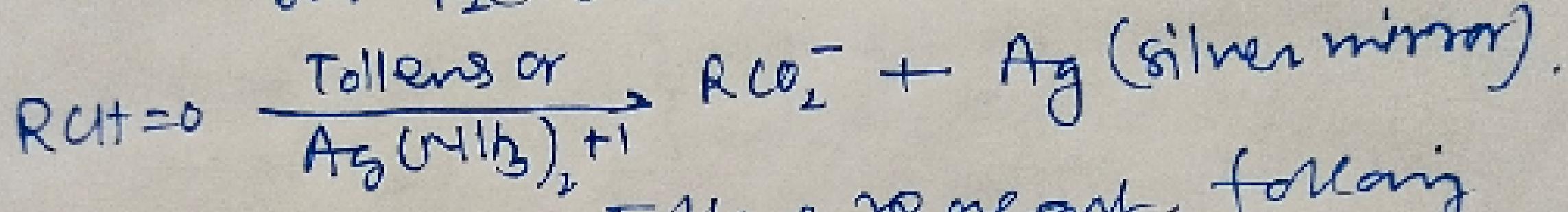
The following reagents are used to oxidise RCHO to carboxylic acid. They can not oxidise ketone because it is very difficult to oxidise ketone at room temp.

examples:

A. Tollens reagent (ammoniacal AgNO_3 ; $\text{Ag}(\text{NH}_3)_2^+$)

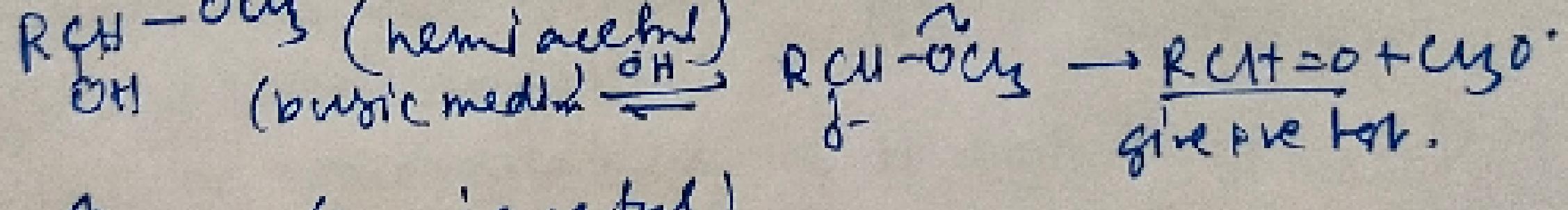


but $\text{R}_2\text{C=O}$ can not be oxidised.

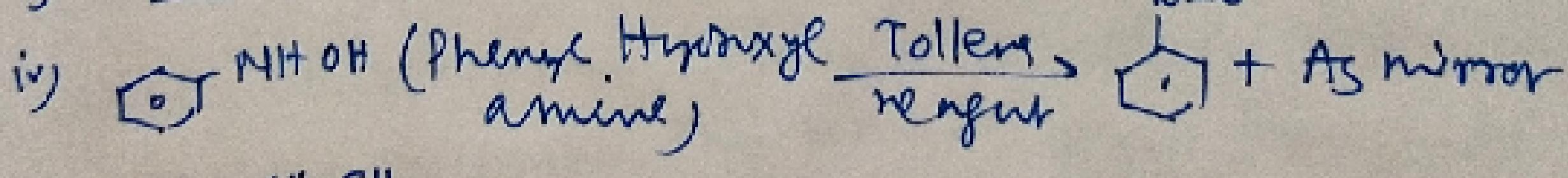


Also in presence of Tollens reagent, following reagents give silver mirror test.

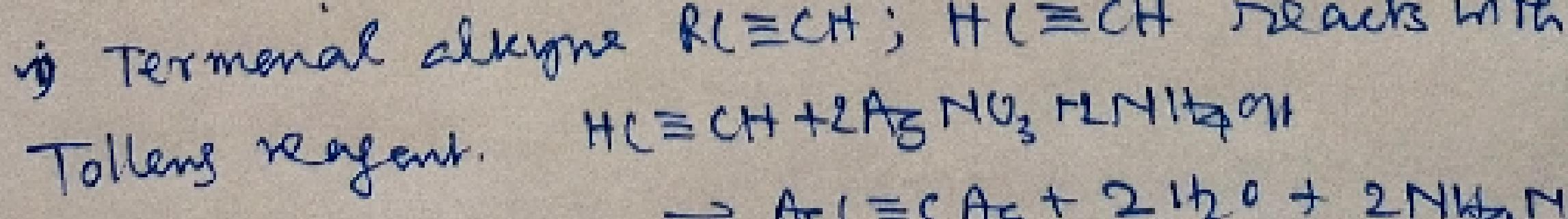
- i) $\text{H}-\text{C}_2\text{H}_3-\text{OH}$ (only monocarboxylic acid which has reducing power due to presence of $-\text{CH=O}$ linkage)
- ii)

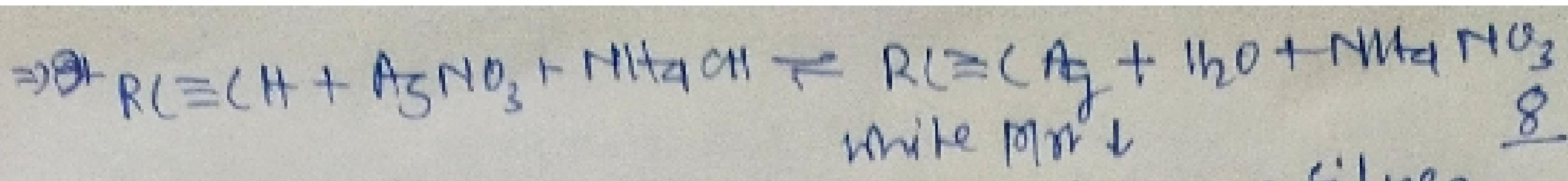


- iii) $\text{C}_5\text{H}_9\text{OH}$ (hemiacetal).



- iv) $\text{CH}_3-\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}=\text{CH}_3$ α -hydroxy ketone gives +ve tollens test.





Terminal alkyne ~~so~~ does not give +ve silver mirror test with terminal alkyne. Tollen's reagent but gives white colour ppt with Tollen's reagent. Nonterminal alkyne does not react with Tollen's reagent. So Tollen's reagent is useful to distinguish

- i) Aldehyde vs ketone.
- ii) Terminal alkyne vs nonterminal alkyne.
- iii) HCO_2H vs any monocarboxylic acid other than HCO_2H .

B. Fehling Solution:

It is a mixture of Fehling A & Fehling B solution.

Fehling B \Rightarrow Sodium potassium tartarate HCOO^-Na^+

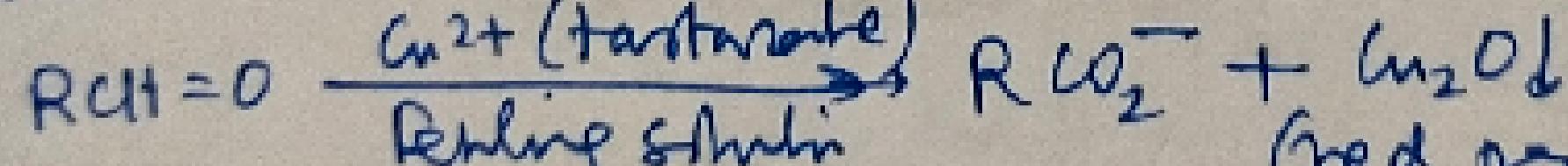
Fehling A \Rightarrow Aqueous solution of CuSO_4 . Cu_2K^+ .

During reaction Cu^{2+} (tartarate) complex is formed which is deep blue colour (blue called)

Fehling Solution:

It acts as oxidising reagent oxidises aldehyde

$\text{RCH=O} \rightarrow \text{RCO}_2\text{H}$. But ketone can not be oxidised.

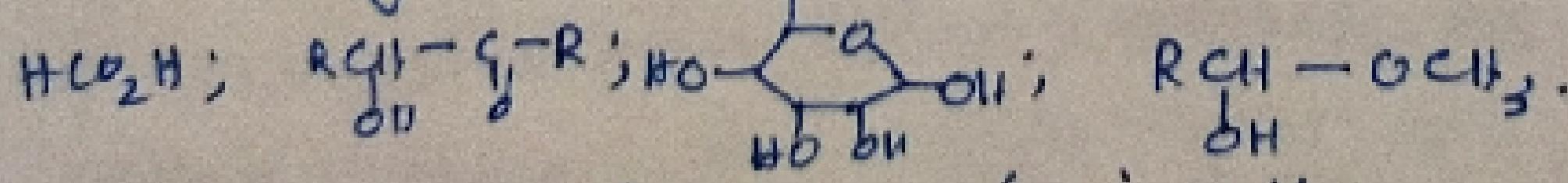


(red precipitate)

Points to be noted:

\Rightarrow Aromatic aldehydes, PhCH=O ; $\text{C}_6\text{H}_5\text{CHO}$ gives -ve Fehling test but +ve Tollen's test.

So oxidising power Tollen's reagent $>$ Fehling soln.



also give +ve Fehling test. (use Tollen's reagent).

Glucose & Fructose give both +ve Fehling & Tollen's test.

9

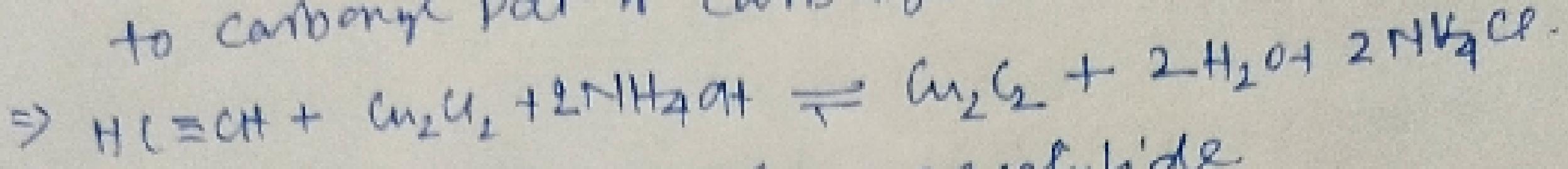
Points to be noted:

Fehling gives -ve test with terminal & nonterminal

aldehyde

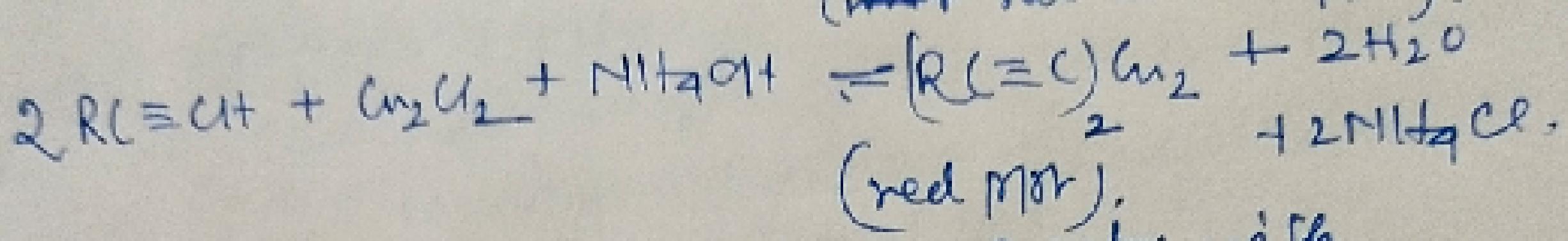
\Rightarrow aldehyde can not oxidise any alcohol

\Rightarrow Tollens & Fehling can not oxidise any carbonyl group or carboxylic acid



(cuprous acetylidide)

(~~red~~ red colour ppt).



(red ppt).

\Rightarrow Nonterminal alkyne can not react with cuprous acetylidide/chloride in ammoniacal medium.

to distinguish 1 butyne vs 2 Butyne.

i) $\text{AgNO}_3 + \text{NH}_4^+$ ✓ ✗

ii) $\text{Cu}_2\text{O}_2 + \text{NH}_4^+$ ✓ ✗

iii) R_2Mg ✗ ✗

iv) NaBH_4 ✓ ✗

v) NaNH_2 ✓ ✗

vi) white ppt.

for terminal alkyne +ve test.

vii) red ppt.

for nonterminal alkyne
-ve test.

viii) gas evolution $\text{RH} \uparrow$

ix) gas evolution $\text{H}_2 \uparrow$

x) gas evolution $\text{NH}_3 \uparrow$.

Other exception: i) glycoxal gives -ve tollens & Fehling test.

i) Tartaric acid gives +ve test. $\text{CO}_2\text{H}-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CO}_2\text{H}$
(Tollens).

ii) 

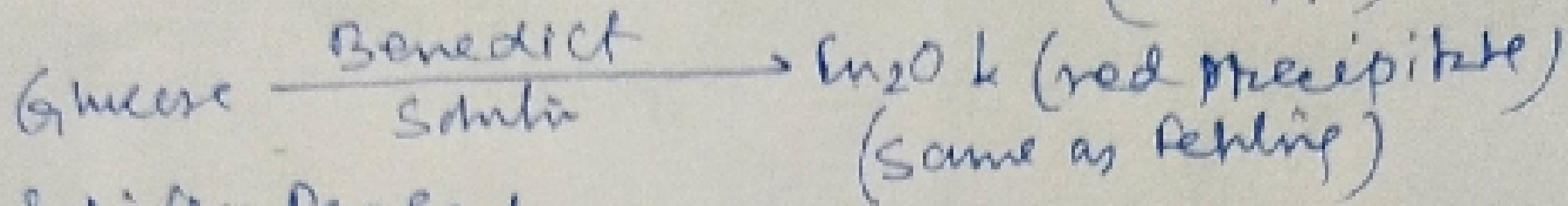
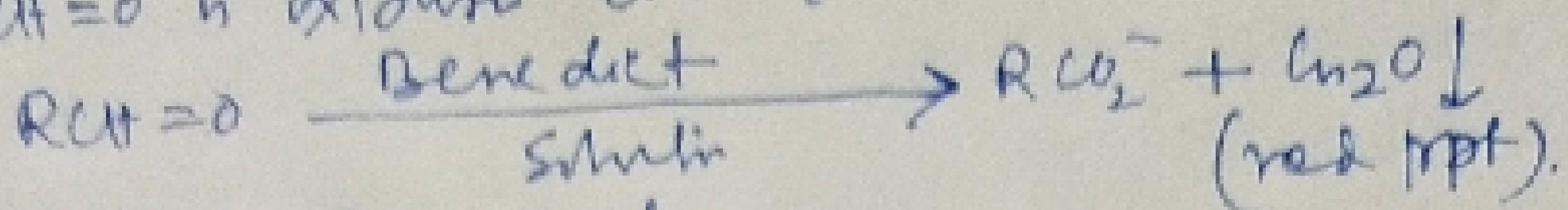
(Quinone) + 2Ag^+ -complex \rightleftharpoons  + 2H^+ + Ag (mirror)

C: Benedict's solution:

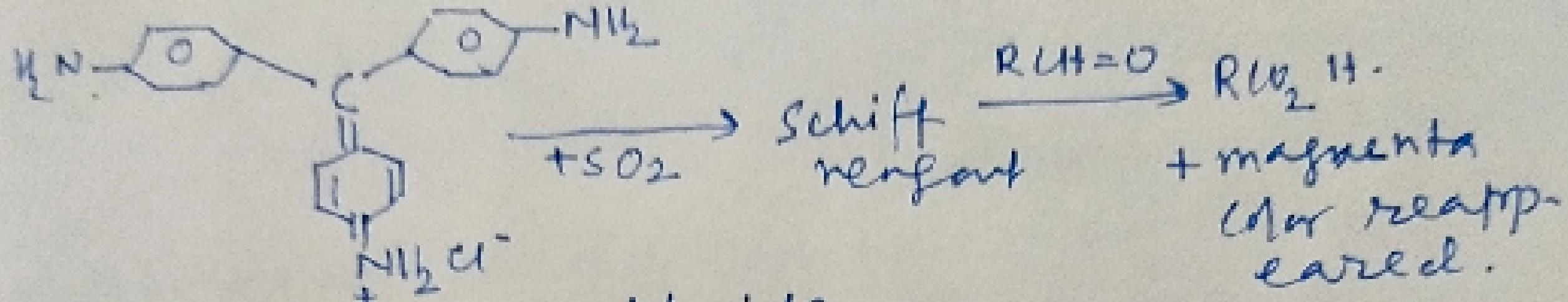
It is Cu^{2+} (citrate) solution. [Sodium Citrate + NaOH + CuSO_4]

RCit=O is oxidized but $\text{R}_2\text{C=O}$ is not.

10



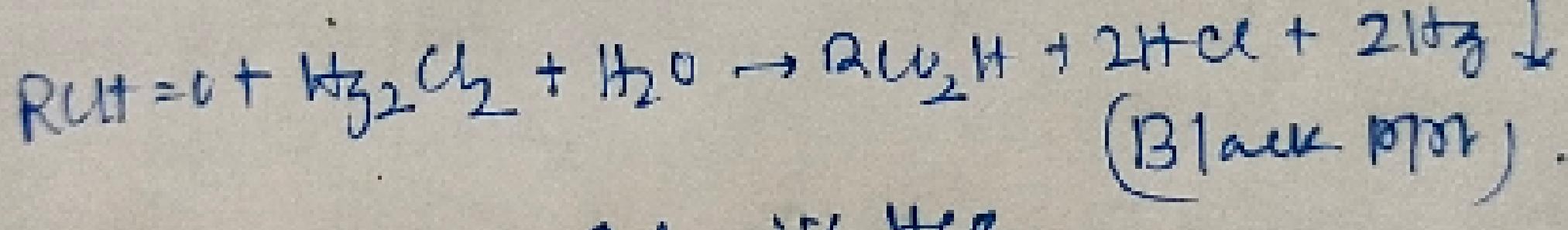
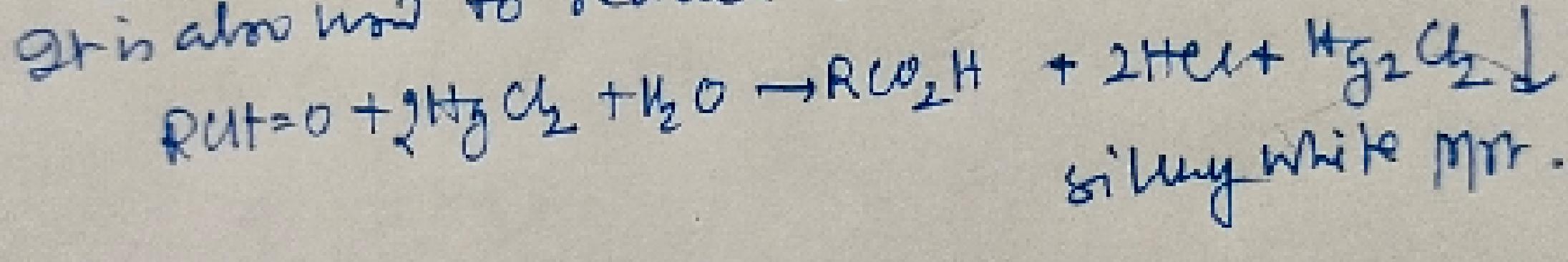
D. Schiff's Reagent.



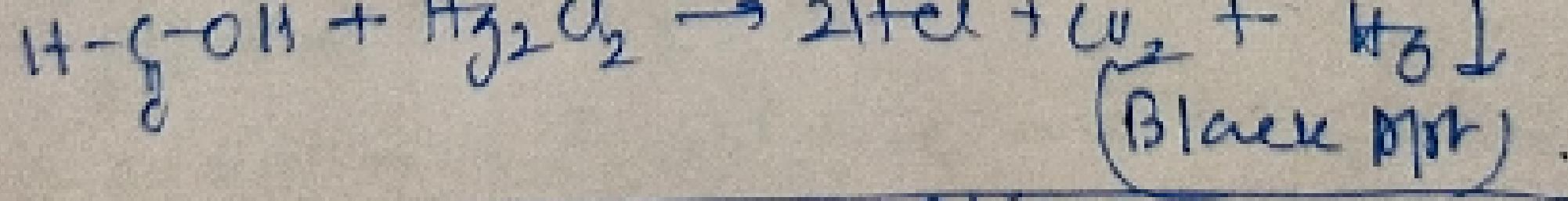
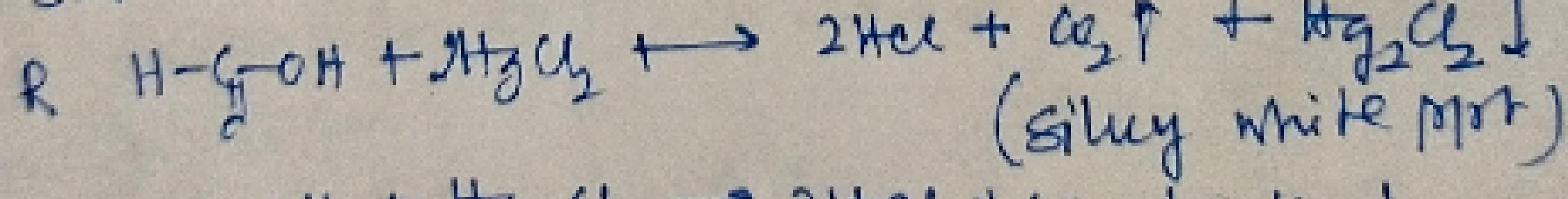
(magenta color / very red)

E. HgCl_2 solution. (mercuric chloride)

It is also used to reduce RCit=O but not ketone.



It is also used to react with HCO_2 but not other monocarboxylic acid.

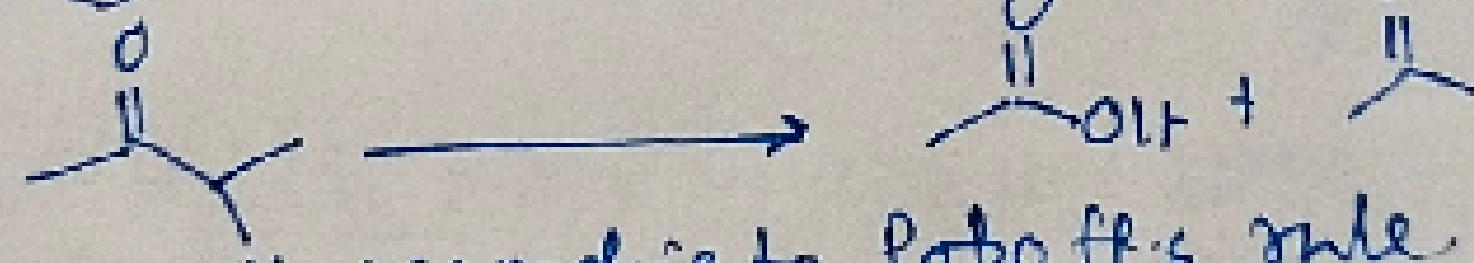
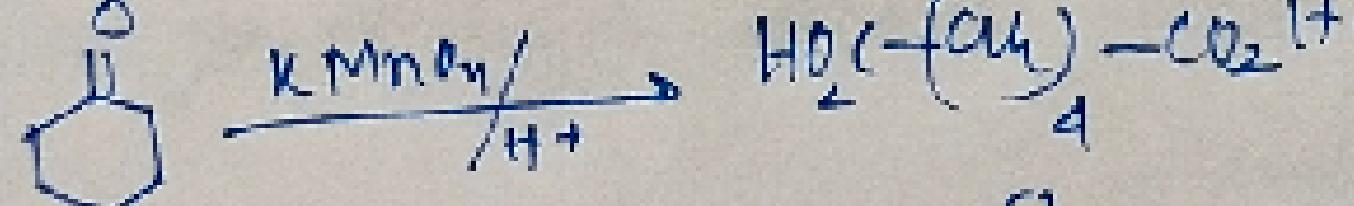
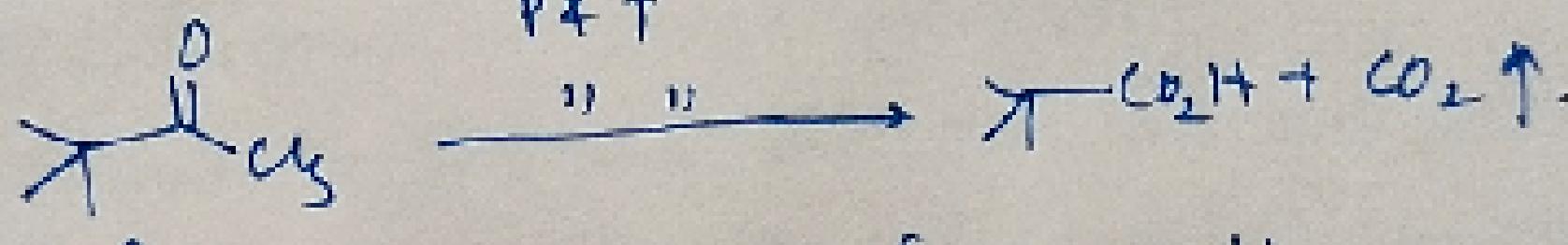
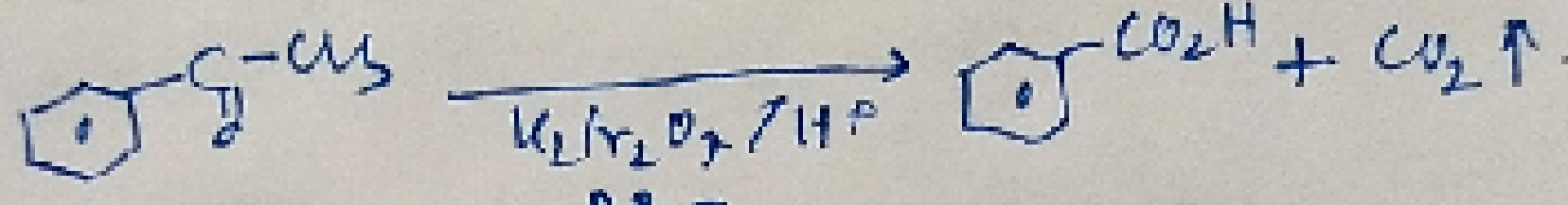
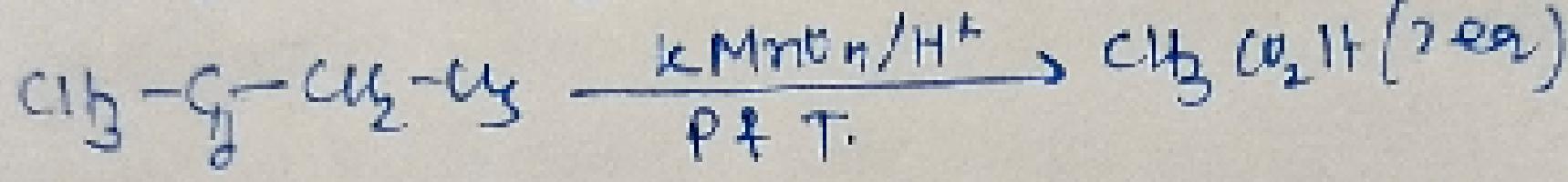
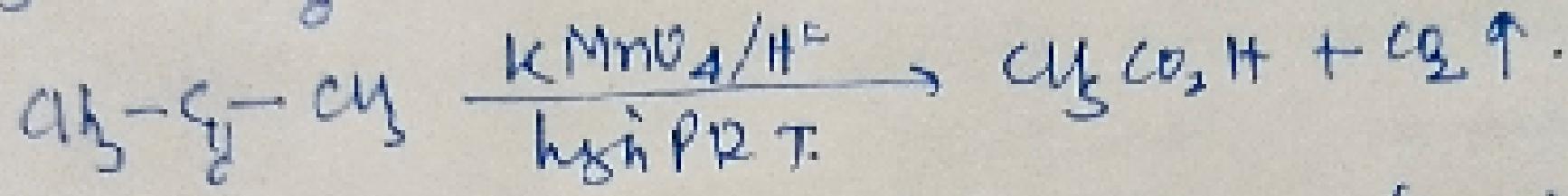
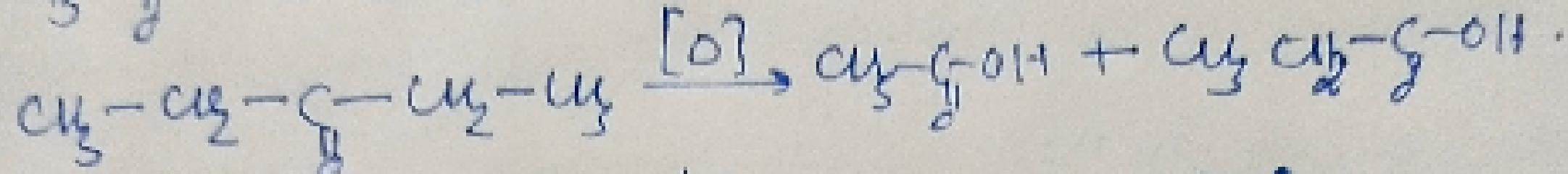
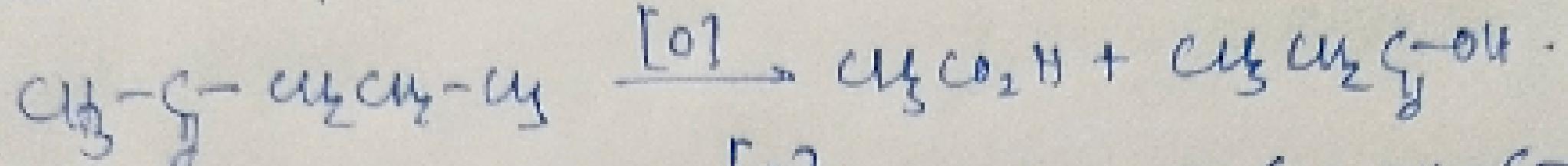


Oppenauer Oxidation: $\text{R}_2\text{CHOH} \xrightarrow[\text{Hg}_2\text{Cl}_2 = \text{O.}]{\text{Al(OBu)}_3} \text{R}_2\text{C=O.}$

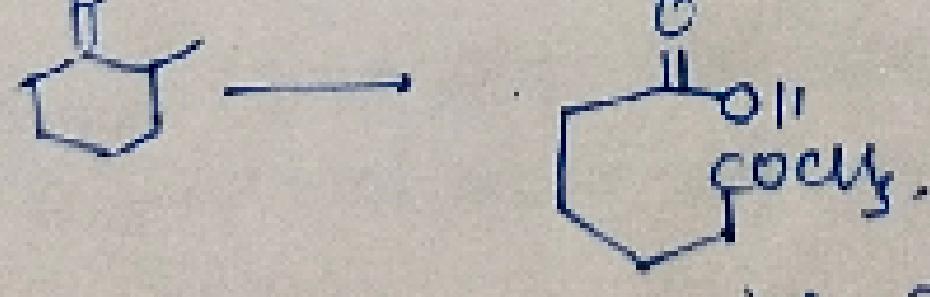
$\text{Al(OBu)}_3 \Rightarrow$ Aluminium tert-butoxide. $\text{RCitOH} \xrightarrow{\text{Hg}_2\text{Cl}_2 = \text{O.}} \text{RCit=O.}$
Acetone or any other ketone is used
as solvent. It oxidizes 1° alcohol \rightarrow Aldehyde; 2° alcohol \rightarrow ketone

Oxidation of Ketone:

Ketones are generally oxidised under vigorous conditions, i.e. strong oxidising agents & at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.

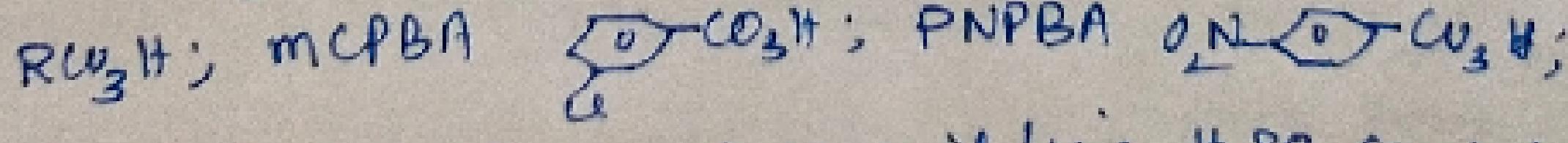


These are all according to Popoff's rule.

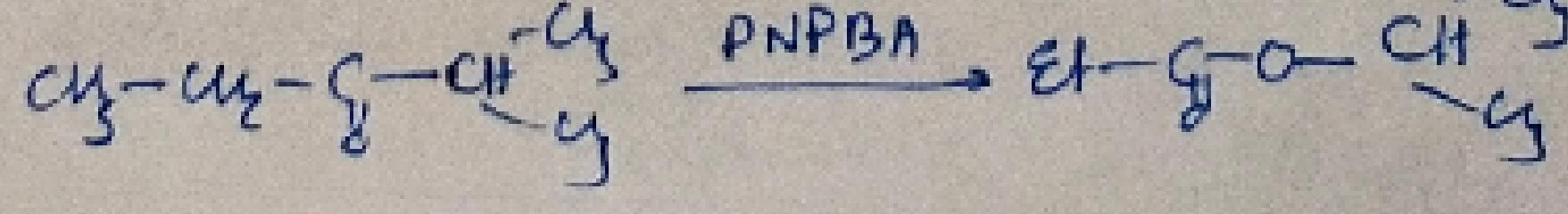
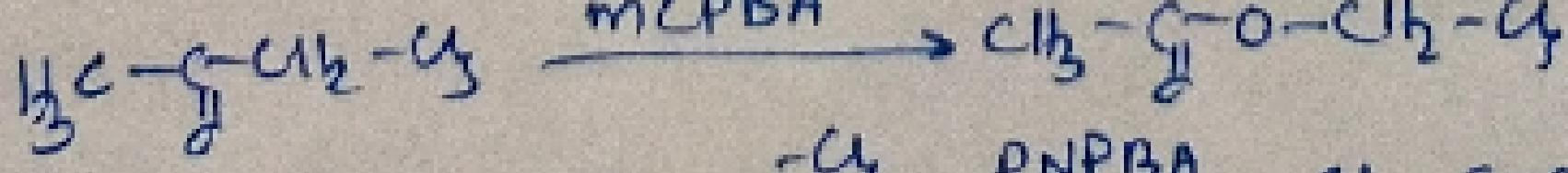


Sometimes ketone can be oxidised to ester.

The reagent used for this purpose is Any per acid.



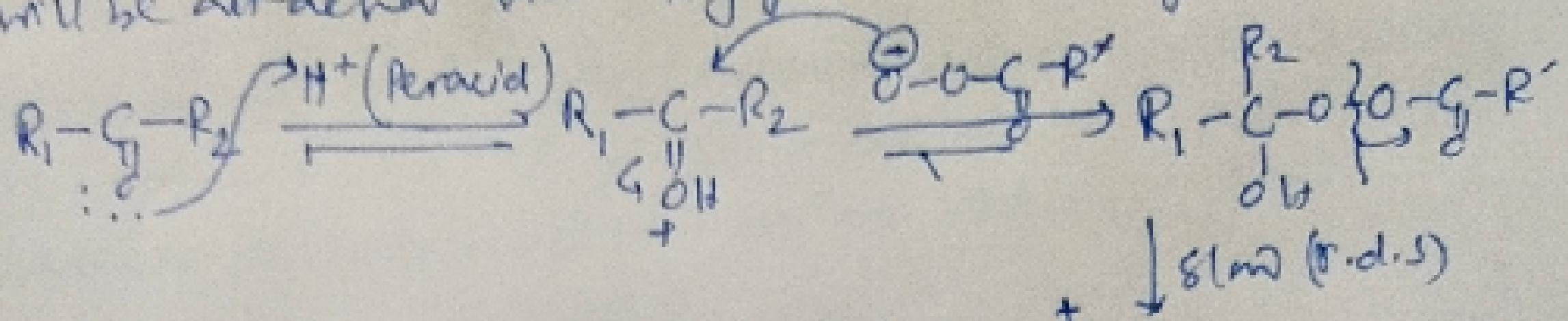
Also H_2O_2 or in organic peracid like $\text{H}_2\text{S}_2\text{O}_8$ can be used.



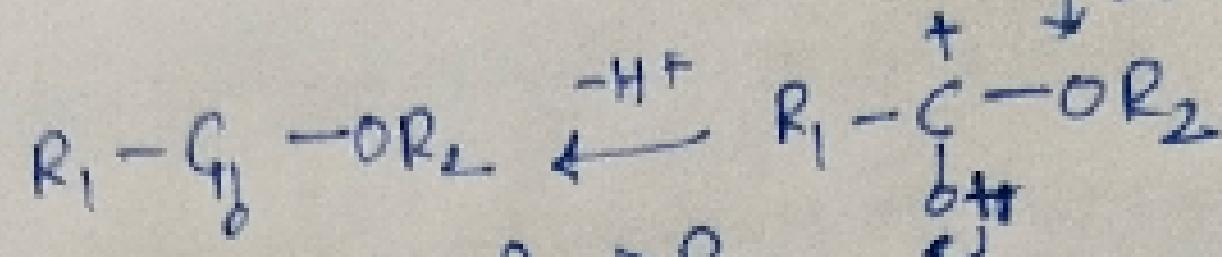
This is called Baeyer-Villiger Oxidation.

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The group(alkyl) which has more migrating tendency will be attached with oxygen in ester system.



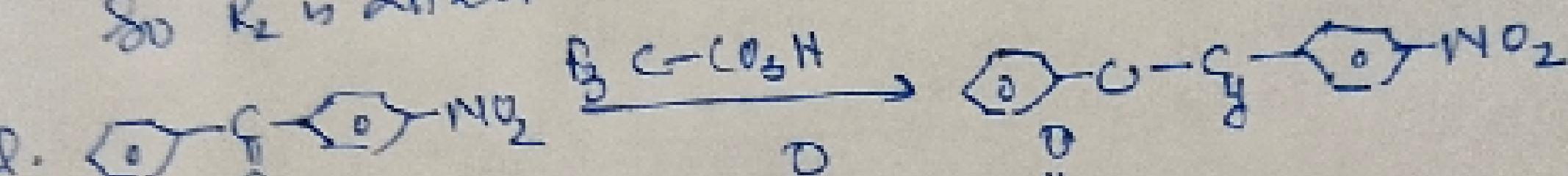
\downarrow 81% (F.d.s)



Here migrating alkene $\text{R}_2 > \text{R}_1$.

So R_2 is attached with oxygen system.

Q. 1)



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b)

c)

d)

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So, Reagents used to oxidise $\text{RCH}=\text{O} \rightarrow \text{RCO}_2\text{H}$ are 13
 listed below. $(\text{R}=\text{C}_6\text{H}_5)$ $(\text{R}=\text{CH}_3)$

- i) $\text{KMnO}_4 / \text{H}^+$ or any fm.
- ii) $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+$ or neutral $\text{K}_2\text{Cr}_2\text{O}_7$.
- iii) H_2O_2 / chromic acid
- iv) Tollen's reagent.
- v) Fehling solution [not applicable for aromatic aldehydes].
- vi) Benedict solution [not applicable for aromatic aldehydes].
- vii) Schiff reagent.
- viii) HgCl_2 solution.
- ix) H_2O_2 or any peracid.
- x) Nitric acid (HNO_3). [aqueous soln].

Reagents used to oxidise $\text{R}-\text{C}_2\text{H}_3-\text{R} \rightarrow \text{RCO}_2\text{H}$ (or mixture of acids)

- i) KMnO_4 / high P & T. [extreme condition] $\text{CO}_2 + \text{acid}$
- ii) $\text{K}_2\text{Cr}_2\text{O}_7$ / high P & T [only] $\text{Ketone} + \text{acid}$.

Reagents used to oxidise $\text{R}-\text{C}_2\text{H}_3-\text{R} \rightarrow \text{Et}-\text{C}_2\text{H}_3-\text{OEt}$.
 Reagents used to oxidise ketone \rightarrow ester.

- i) MCPBA
- ii) PNPBA
- iii) $\text{CH}_3\text{CO}_2\text{H} / \text{C}_6\text{H}_5\text{CO}_2\text{H} / \text{PhCO}_2\text{H}$ [Perbenzoic acid].
- iv) H_2O_2
- v) $\text{H}_2\text{S}_2\text{O}_8$ (Caro's acid)

Reagents used to oxidise having keto methyl

group. i, $\text{H}_3\text{C}-\text{C}_2\text{H}_3 \rightarrow \text{CH}_3\text{C}(=\text{O})\text{H}$ All are examples
 are noted. ii, $\text{CH}_3-\text{C}_2\text{H}_3-\text{CH}_3 \rightarrow \text{CH}_3-\text{CH}_2\text{CO}_2\text{H}$ Step down
 below. iii, $\text{PhC}_2\text{H}_3 \rightarrow \text{PhCO}_2\text{H}$ reaction].

This is known as haloform reaction.

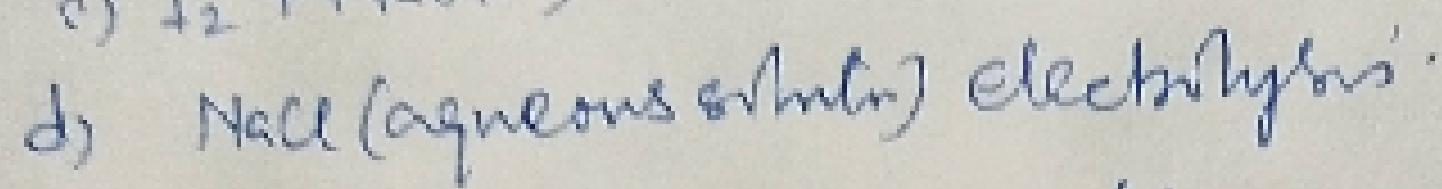
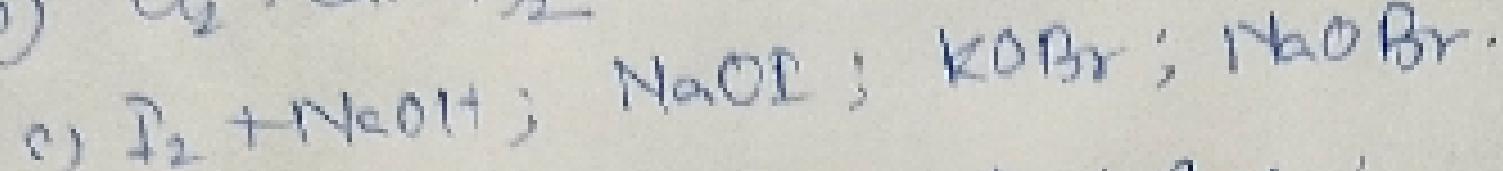
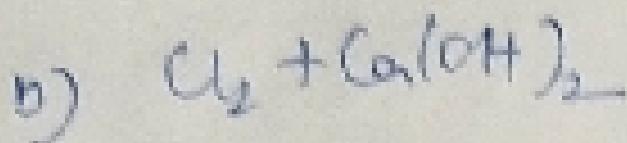
The reagents now are as follows.

14

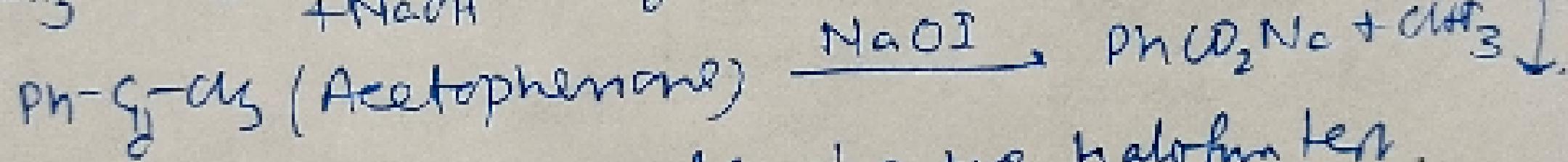
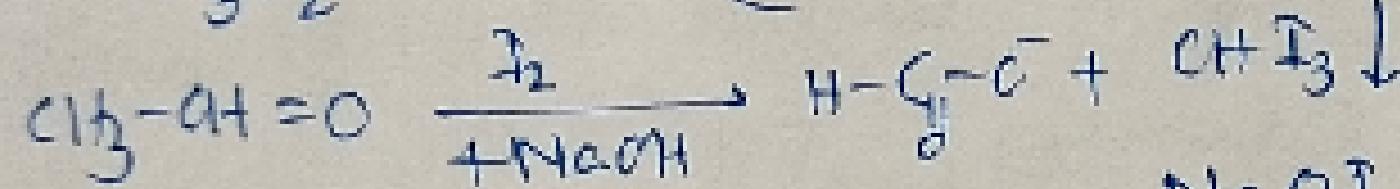
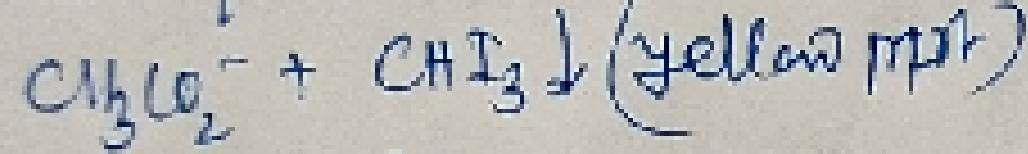
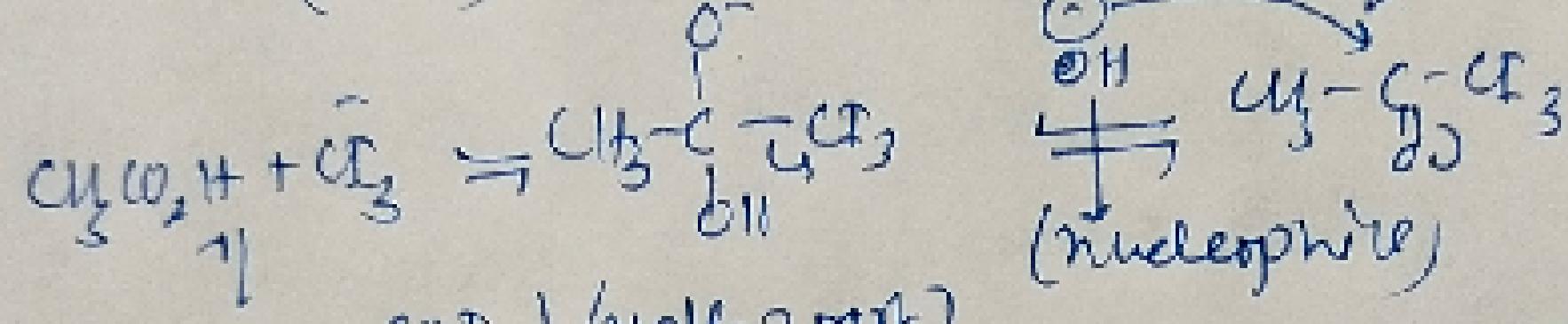
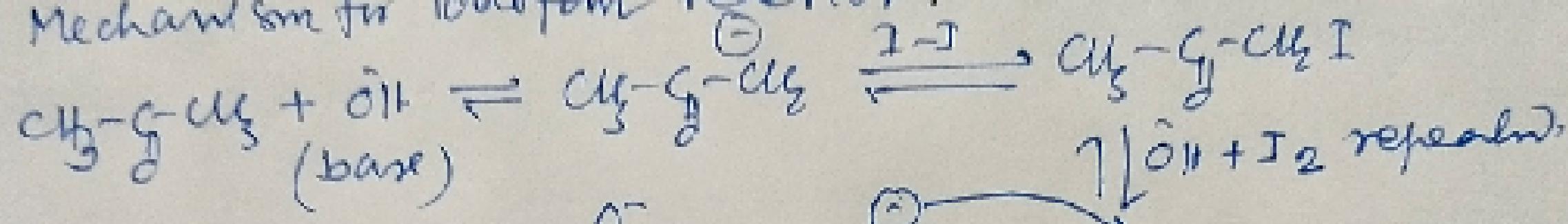


If I_2 is used *the reaction is called iodoform reaction

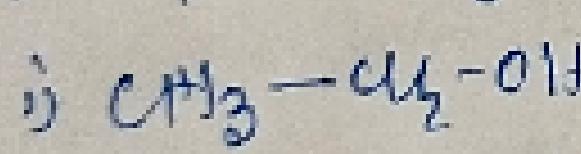
If X_2 is used then it is called halofrom reaction



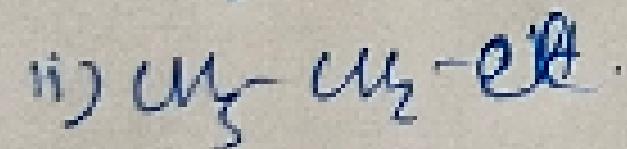
Mechanism for iodoform reaction:



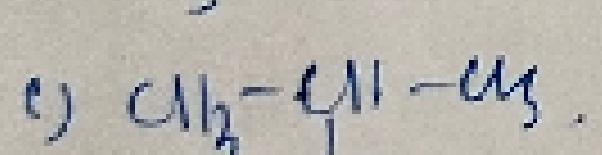
The following compounds give +ve halofrom test.



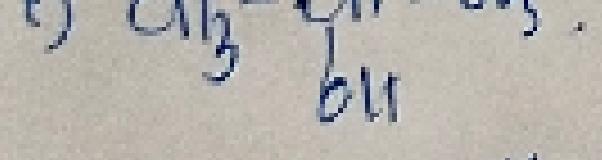
All alcohols having ($Cl_2 + NaOH$)



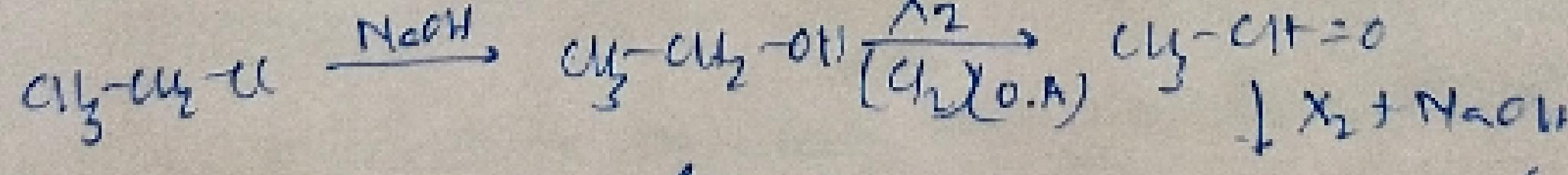
CH_3-OH - group & all carbonyl



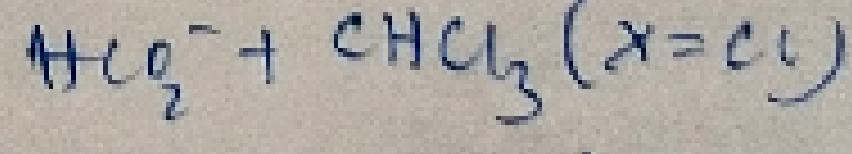
compounds having - $\overset{\underset{|}{\underset{|}{\underset{|}{O}}}}{C}l_2$



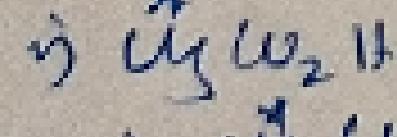
group undergo halofrom reaction



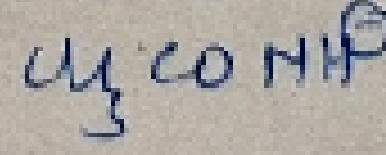
The following compounds



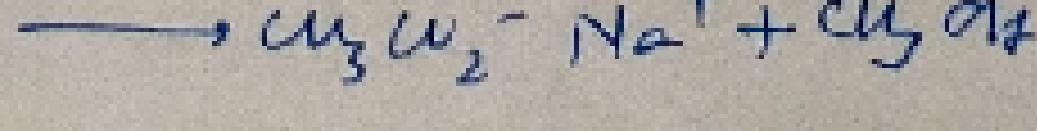
give -ve halofrom test



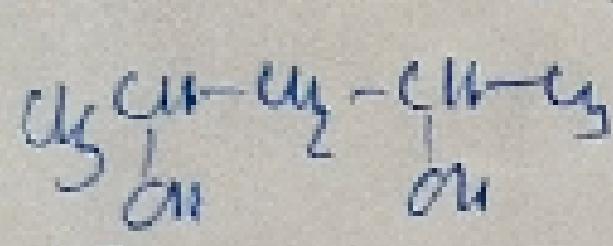
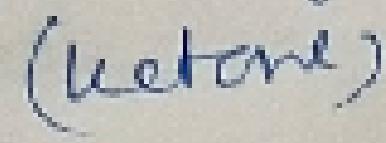
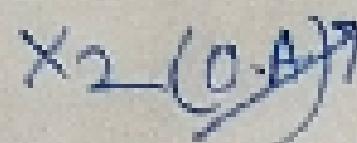
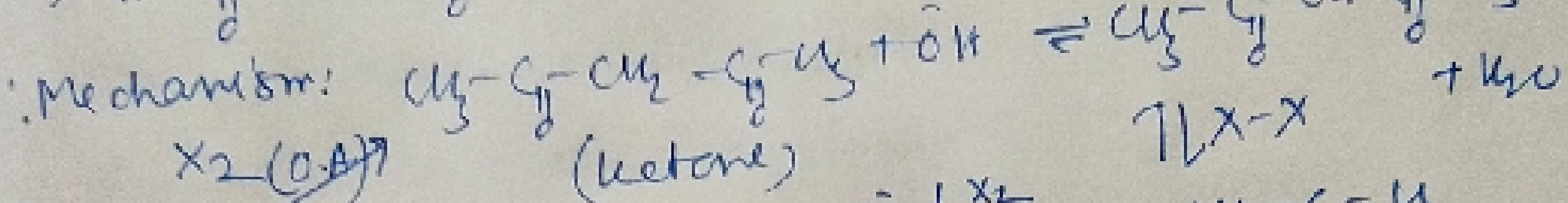
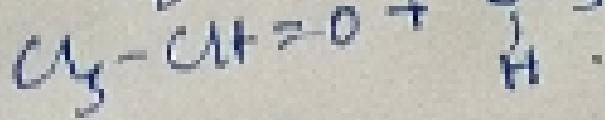
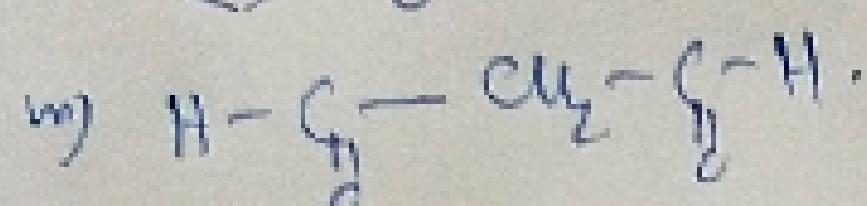
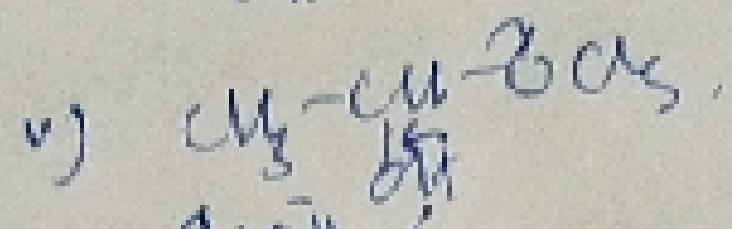
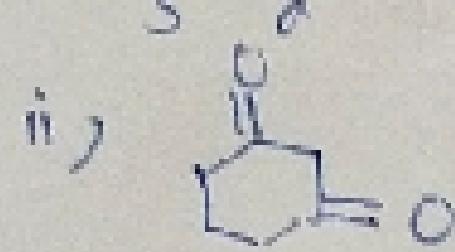
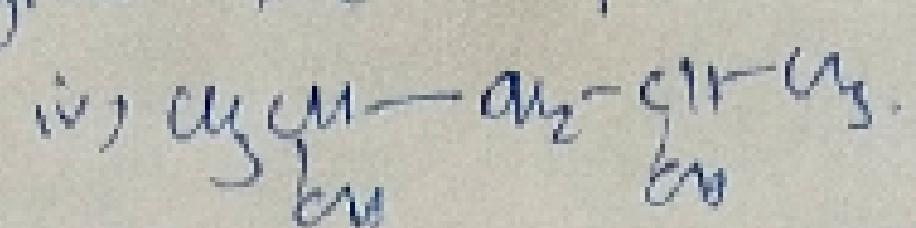
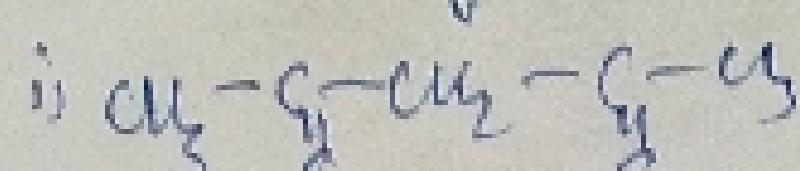
(now as anaesthetic)



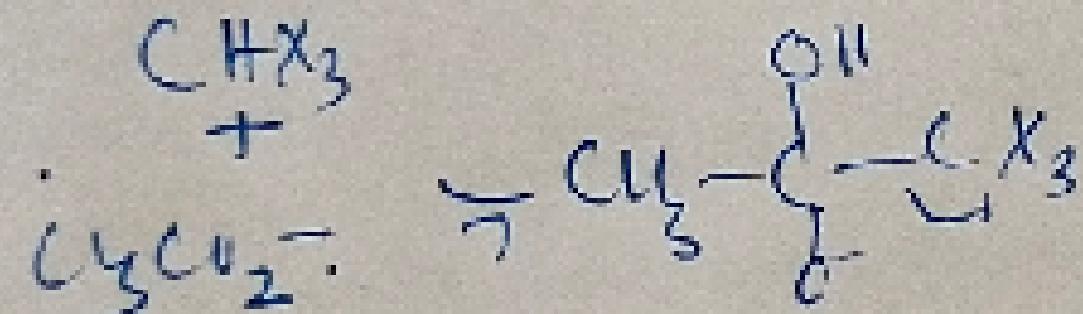
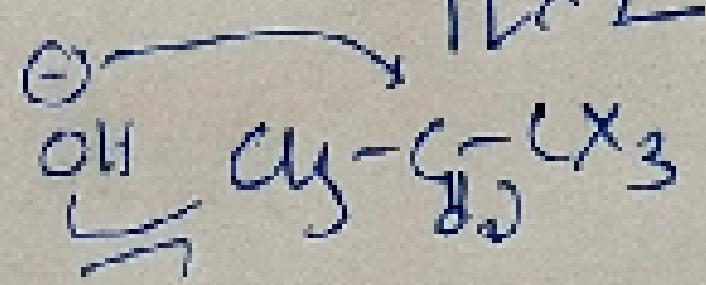
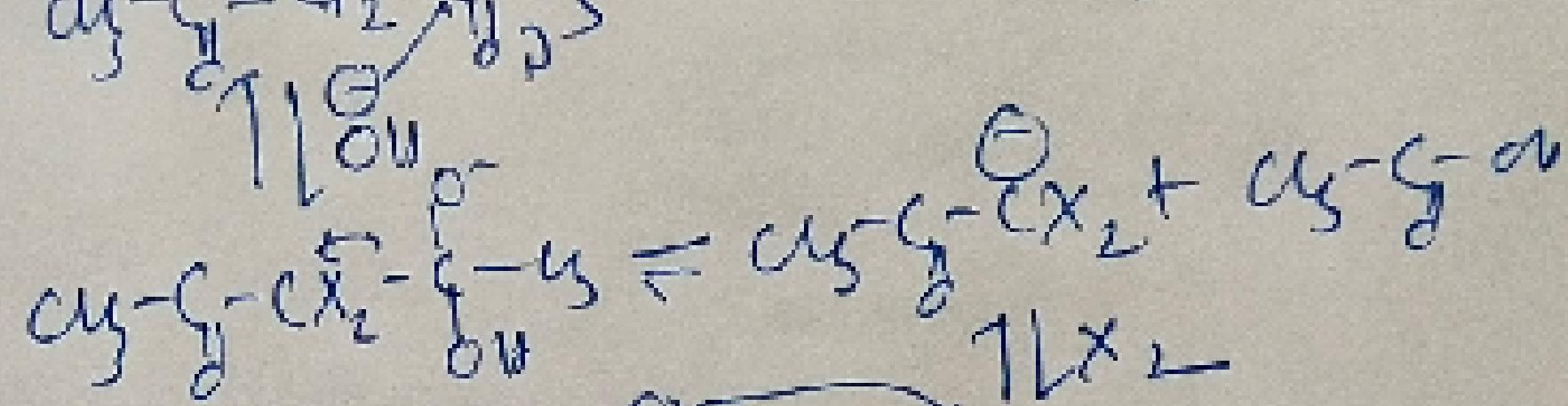
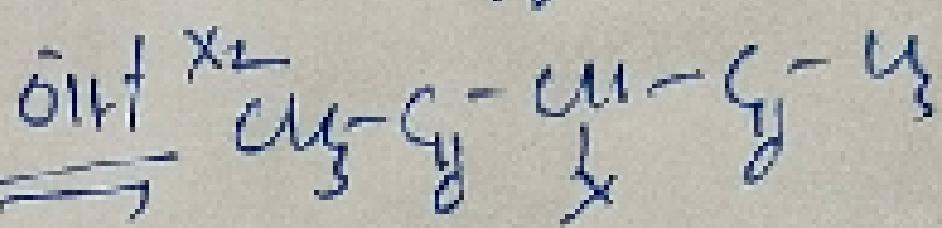
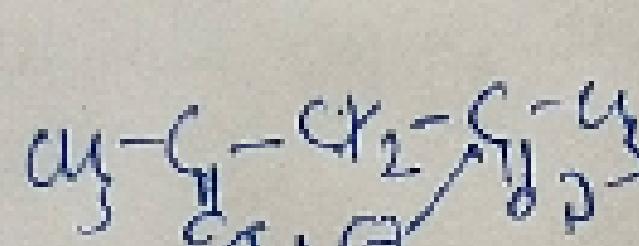
* It is not removed.



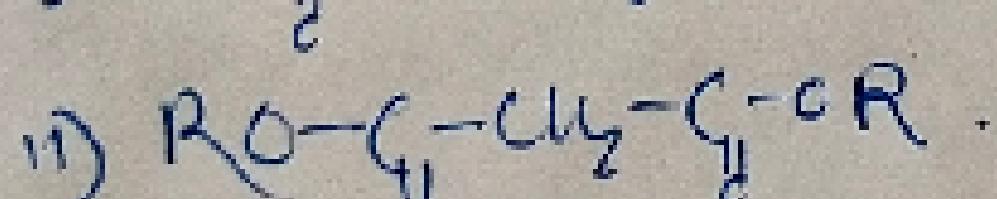
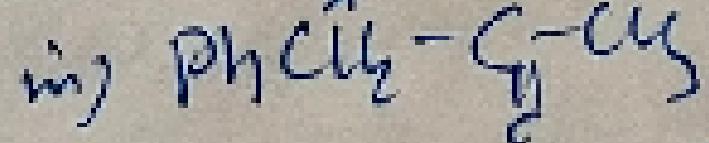
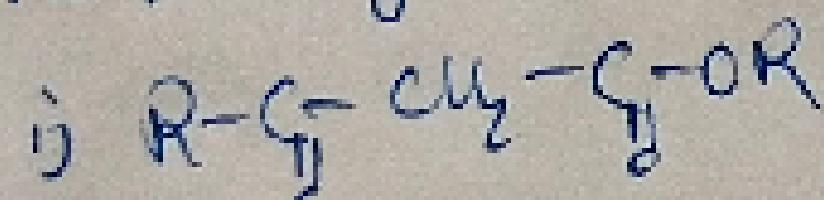
The following compounds give the iodofantet.



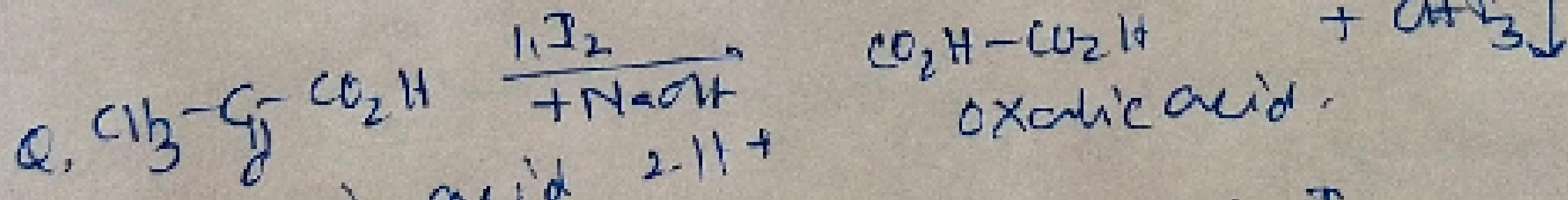
(2° Alkene system)



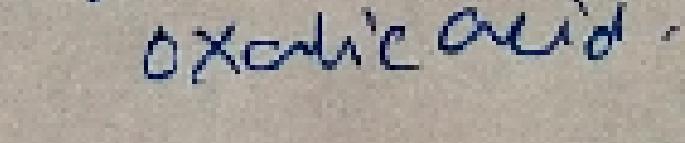
The following compounds give the iodofantet.



involves an reaction
with base *H is
removed.



Pyruvic acid $\xrightarrow{2-\text{H}^+}$



∴ Iodofant reaction is 0th order w.r.t. I_2

⇒ Iodofant reaction is 2nd order; bimolecular rate = $k[\text{OH}^-][\text{RC}_2\text{H}_2]$.

⇒ $\text{CH}_3-\text{C}_2\text{H}-\text{CH}_2-\text{C}_2\text{H}-\text{OR} \rightarrow \text{CH}_3\text{CO}_2\text{H}$ $\text{CH}_3\text{C}_2\text{H}-\text{OR} \rightarrow \text{CH}_3\text{CO}_2\text{H}$.

To distinguish $\text{CH}_3\text{C}_2\text{H}-\text{OR}$ & $\text{CH}_3\text{CO}_2\text{H}$; $\text{CH}_3\text{CO}_2\text{H}$ is weak & strong.

We can use iodofant reaction [weak & strong].