

Chemistry by
Prof: JAVED Iqbal Notes

Mulla
MOD
Mehar College Hw

Class

XII

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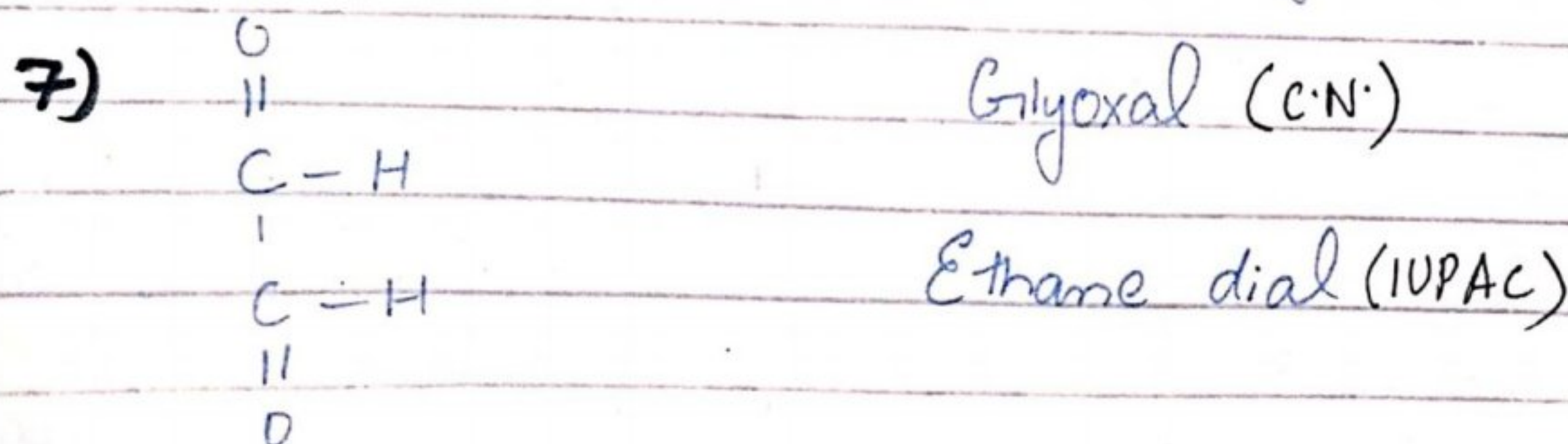
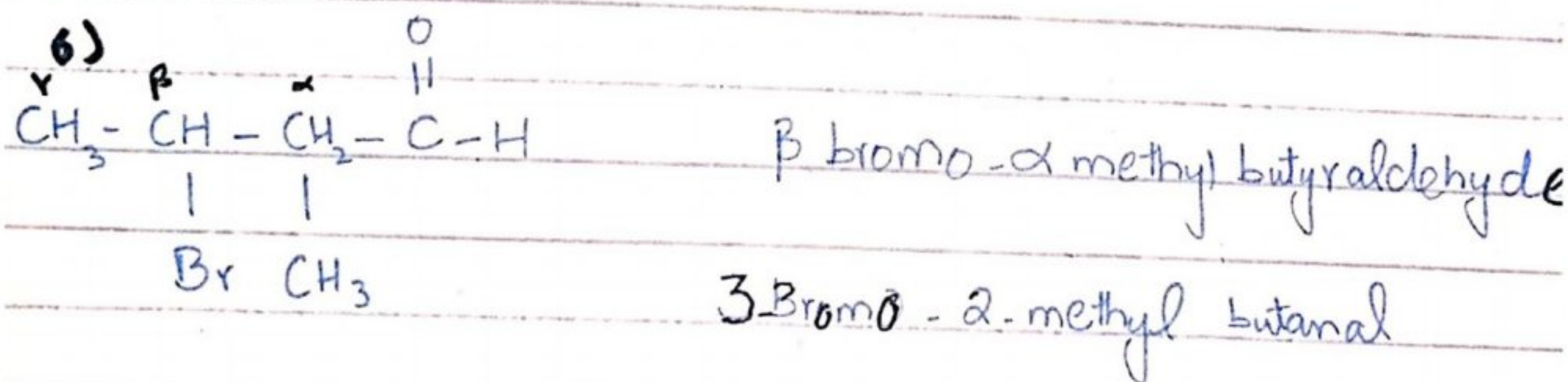
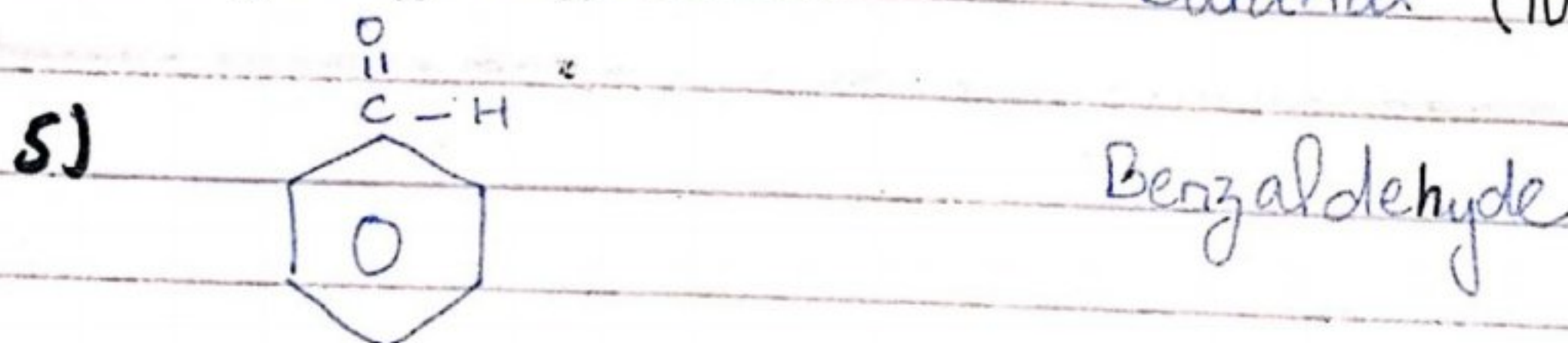
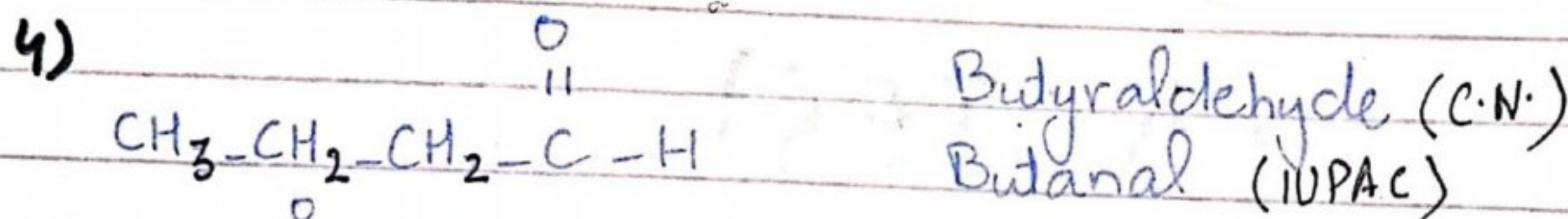
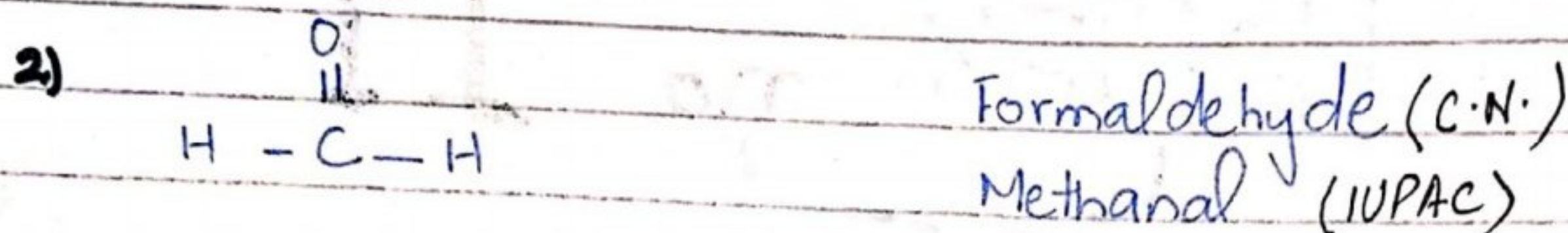
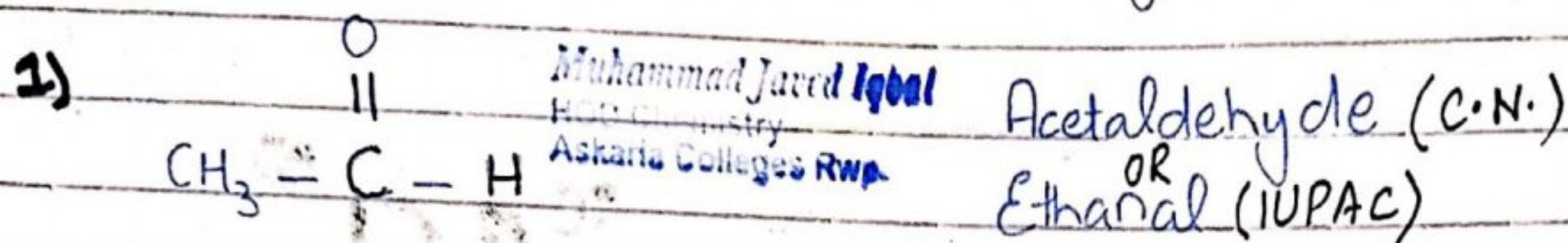
CHAPTER no "19"

(Aldehydes & Ketones)

(NOTES)

Alddehydes $\begin{pmatrix} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{pmatrix}$

When the carbonyl group is directly attached with at least one hydrogen atom, compounds formed are called aldehydes.

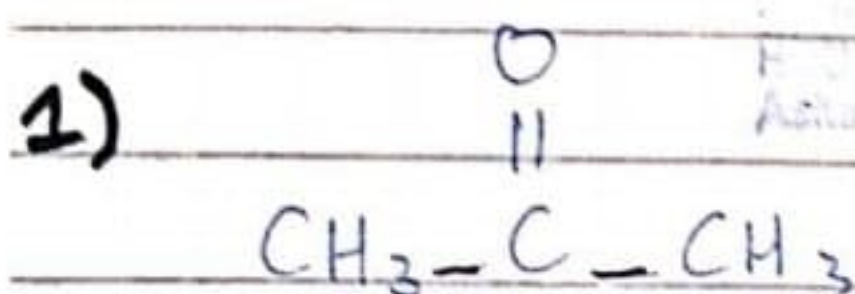


(2)

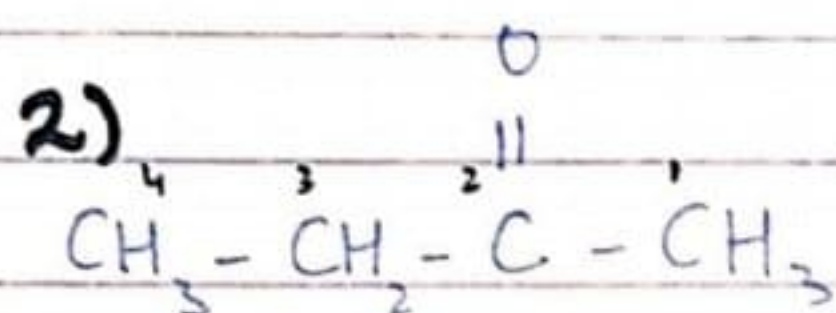
Ketones ($R-\overset{\overset{O}{\parallel}}{C}-R$)

When the carbonyl group is directly bonded with two alkyl groups compound formed are called ketones.

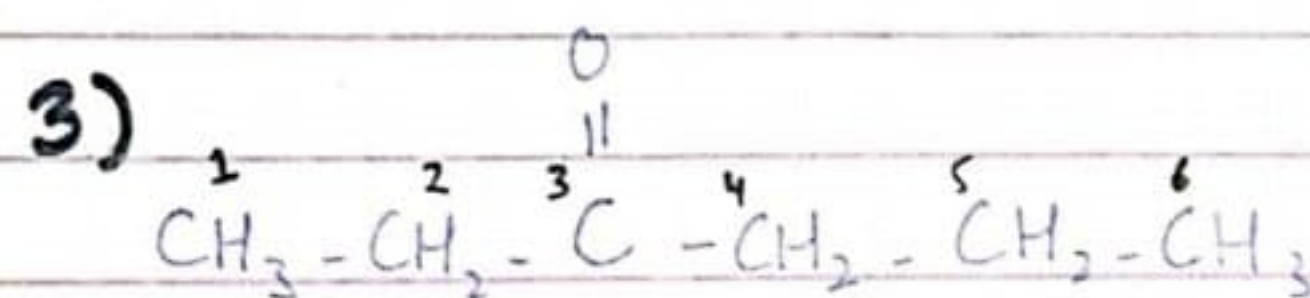
When the alkyl groups attached to carbonyl compounds are same, then it is called symmetrical ketones.



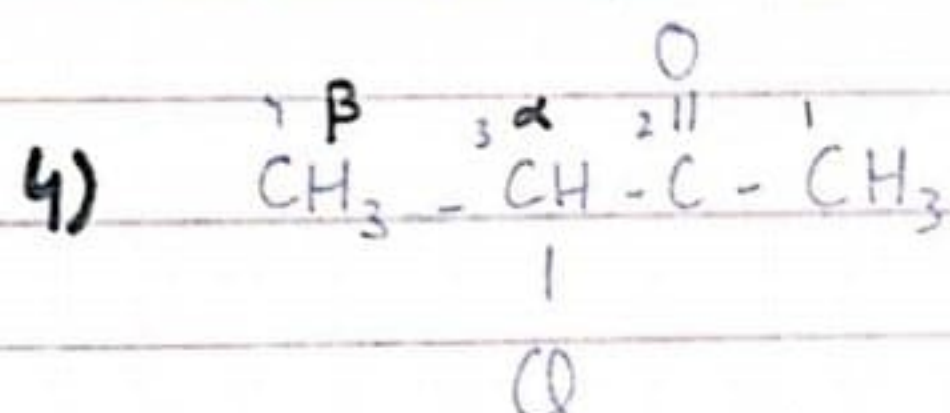
Dimethyl Ketone (C.N.)
Acetone (C.N.)
Propanone (IUPAC)



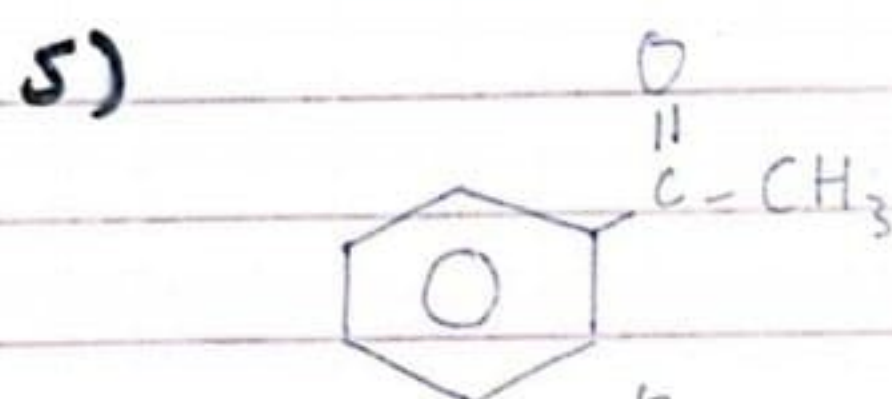
Ethyl methyl Ketone (C.N.)
2-Butanone (IUPAC)



Ethyl Propyl Ketone (C.N.)
3-Hexanone (IUPAC)



α -Chloro ethyl methyl Ketone
3-Chloro-2-butanone (IUPAC)

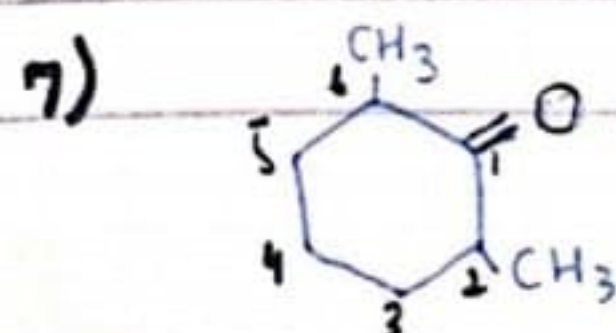


Methyl Phenyl Ketone (C.N.)
Acetophenone (C.N.)



Diphenyl Ketone (C.N.)

Benzophenone (C.N.)



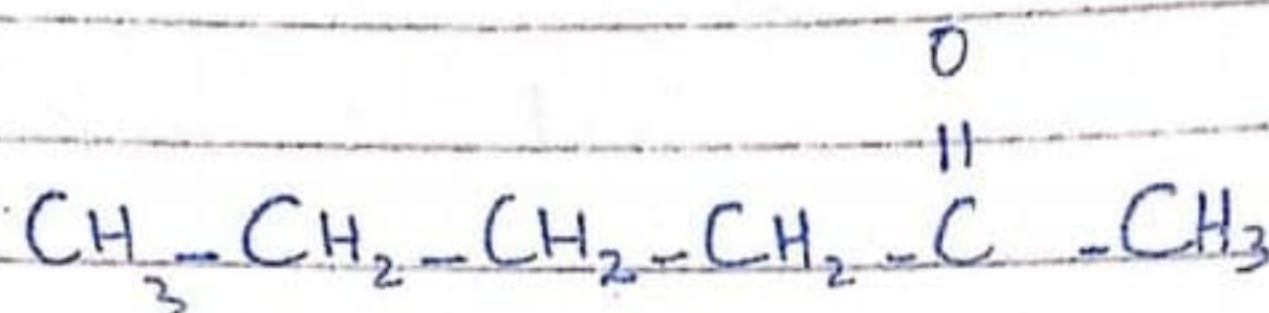
2,6-dimethyl cyclohexanone

(3)

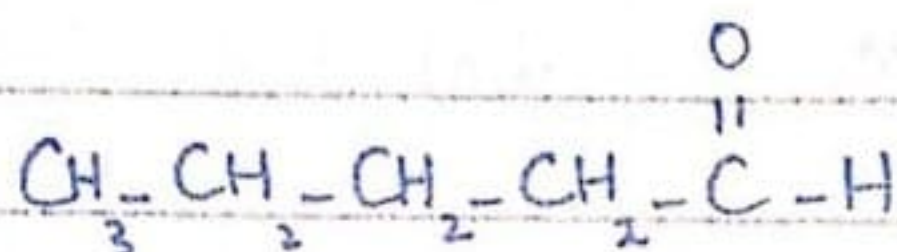
Quick Quiz - 1

Part i) Draw the structures of

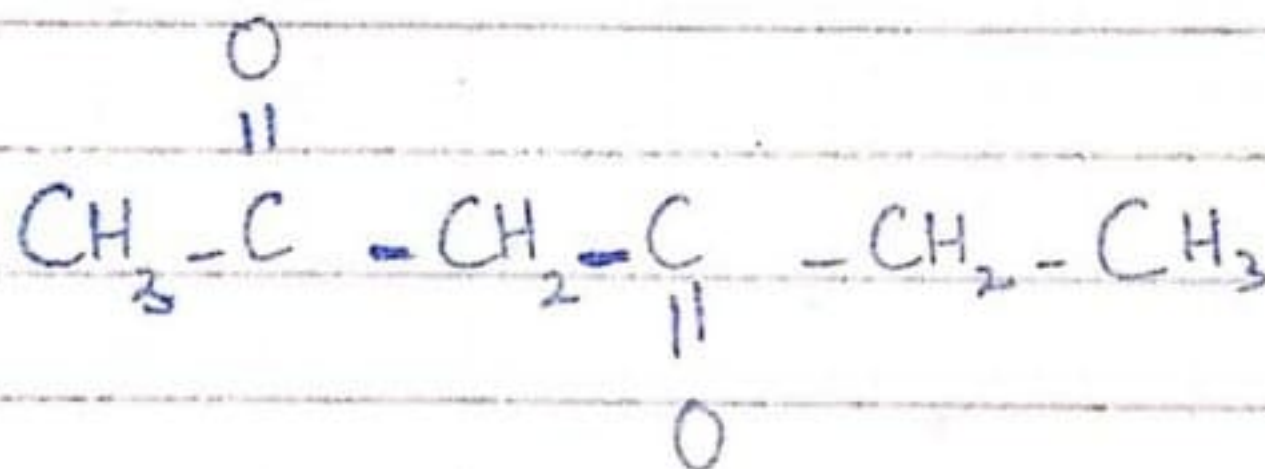
a) 2-hexanone



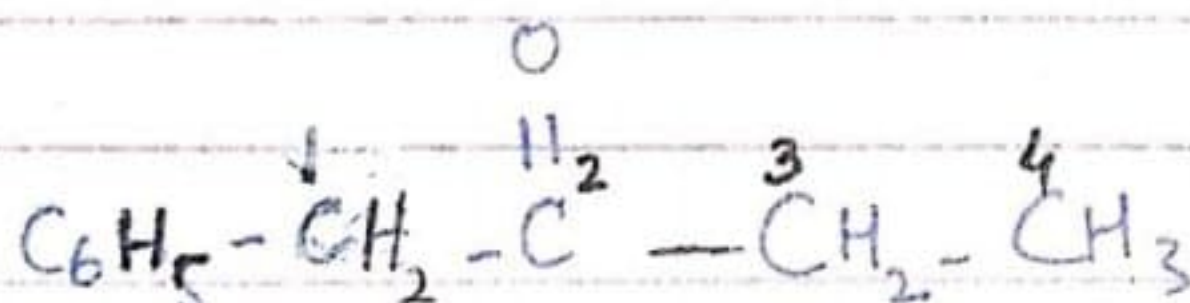
b) Pentanal



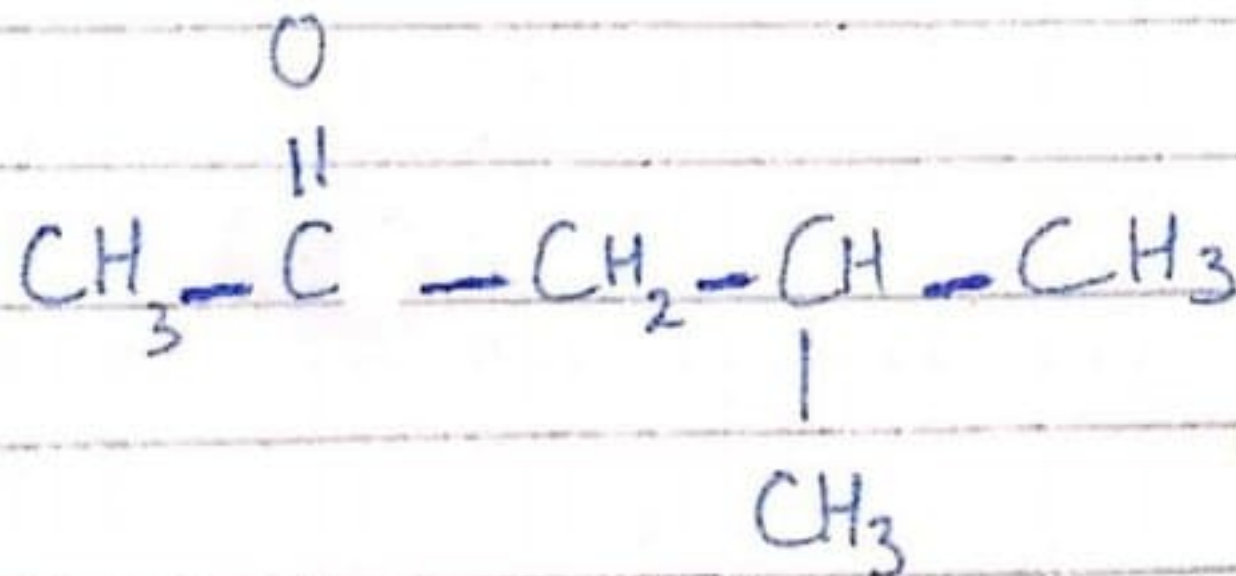
c) 2,4 hexanedione



d) 1 phenyl - 2 - butanone

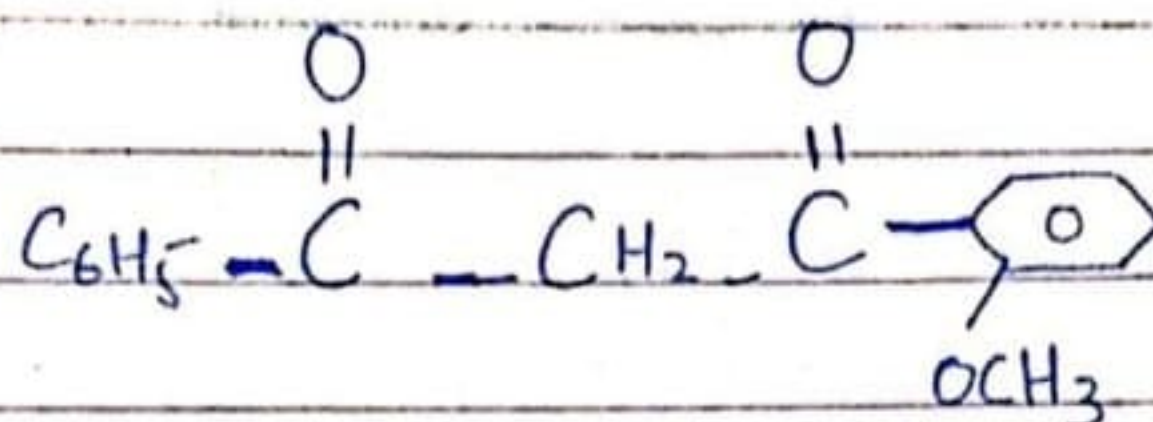


e) 4 methyl - 2 pentanone



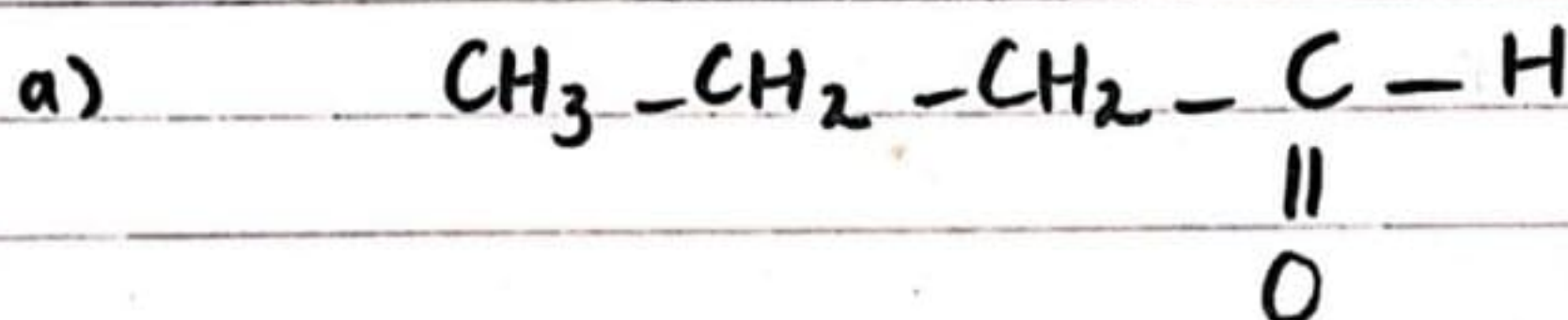
(4)

f) 1 phenyl - 3 - (2-methoxy phenyl) - 1,3 - Propanedione

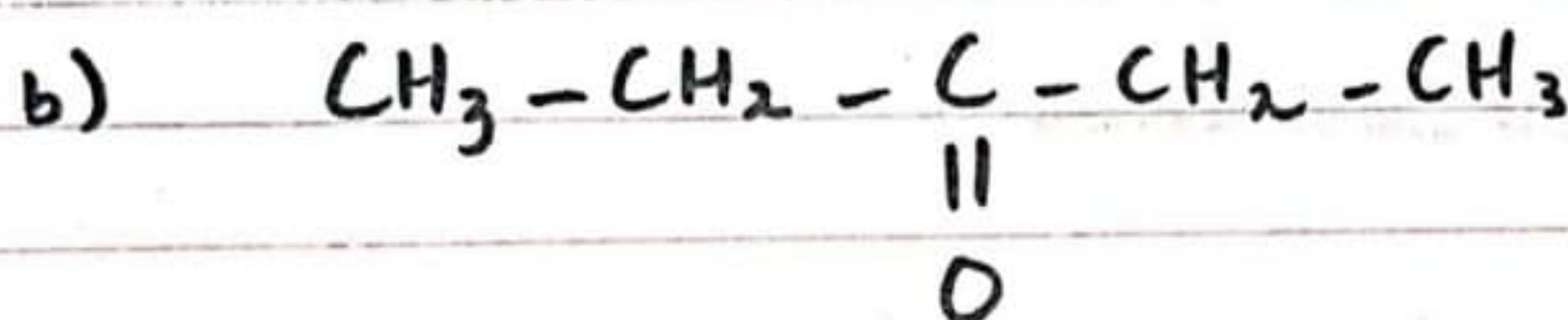


Part ii)

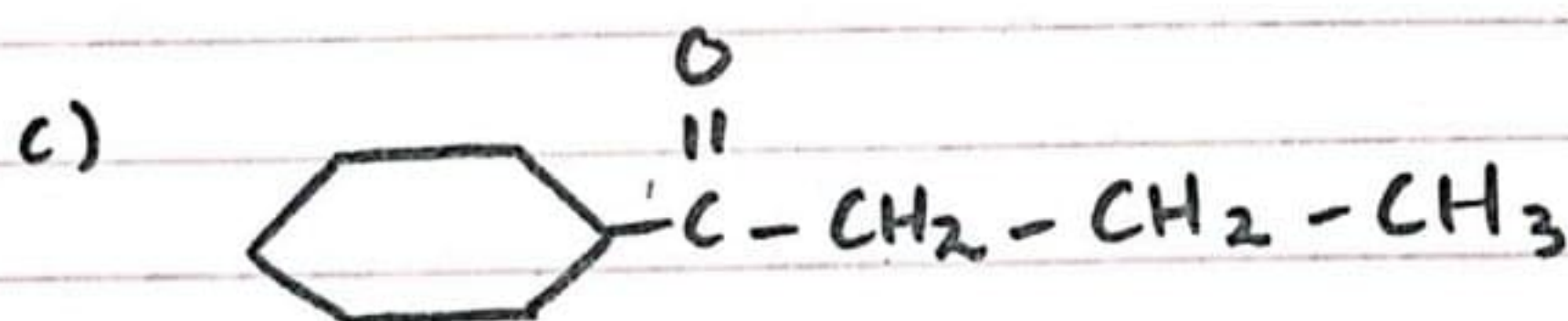
Give IUPAC names of



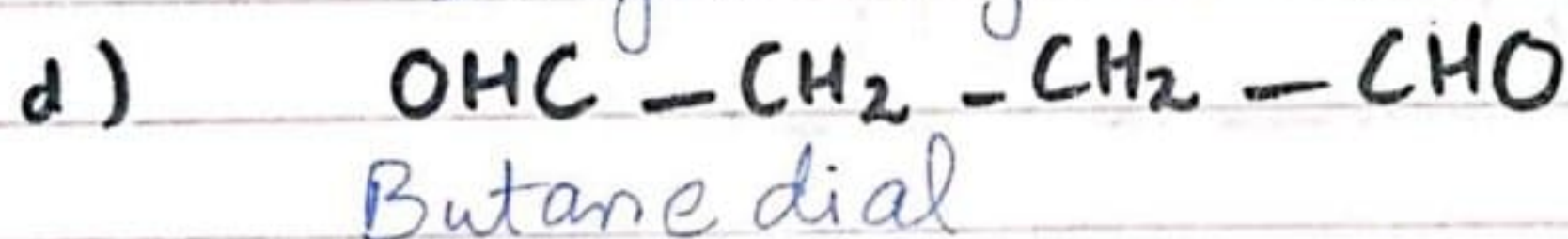
1-Butanal



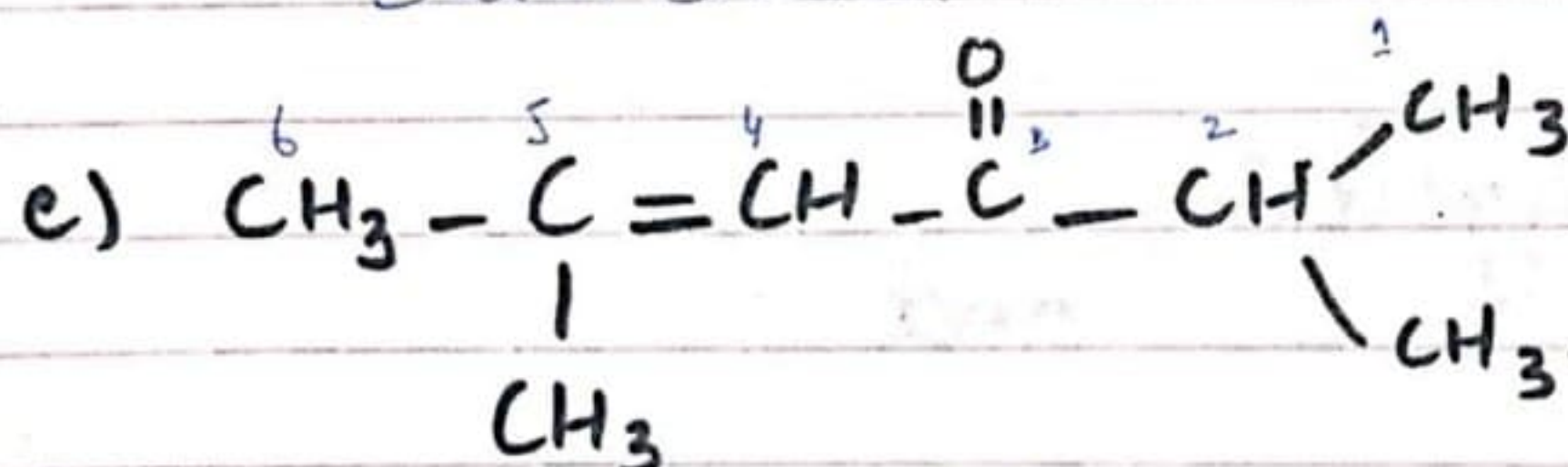
3-Pentanone



1-cyclohexyl butanone



Butane dial



2,5 dimethyl - 4 hexene - 3-one

(5)

Physical Properties

- 1- They have high melting and boiling points as compared to analogous alkanes.
- 2- They have low boiling point as compared to analogous alcohols.
- 3- They are less soluble than alcohols but more soluble than alkanes in aqueous medium.

Structure

The carbonyl group consists of an O-atom bonded to a carbon atom via double bonds and sp^2 hybridized.



PREPARATIONS Of

Aldehydes

and

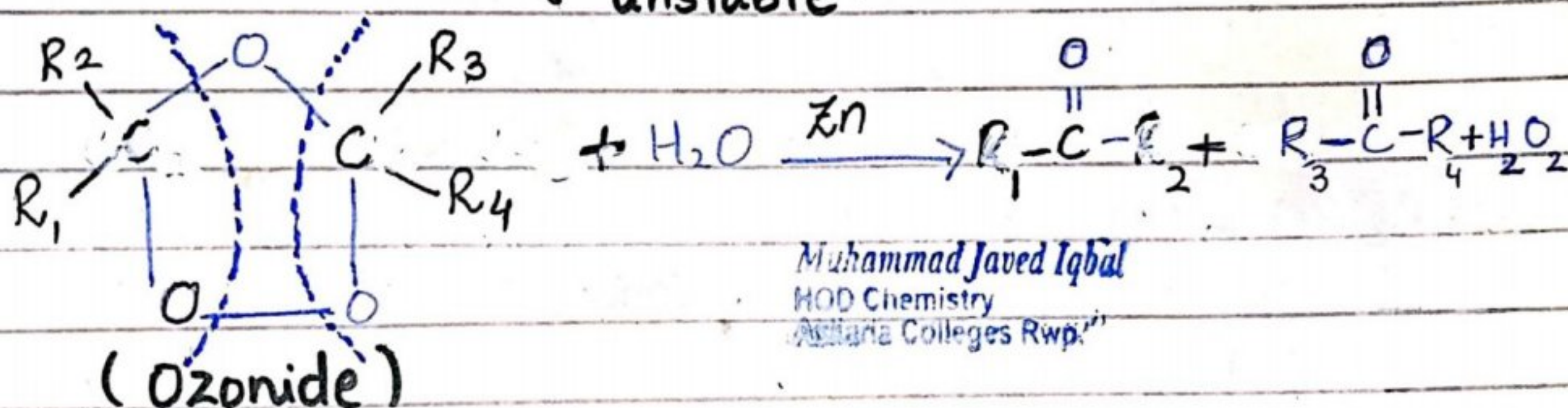
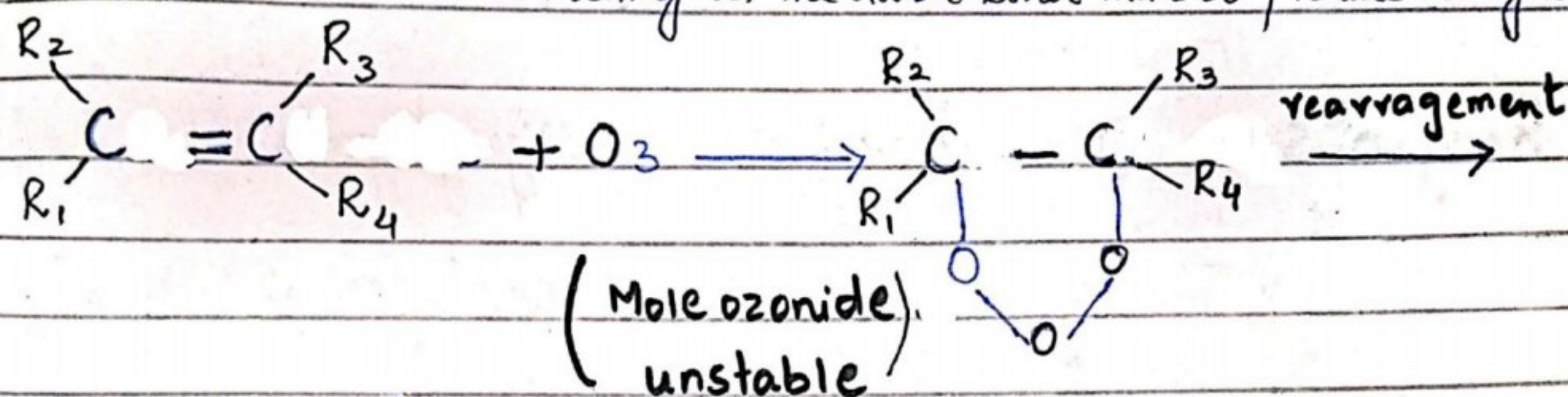
Ketones

(6)

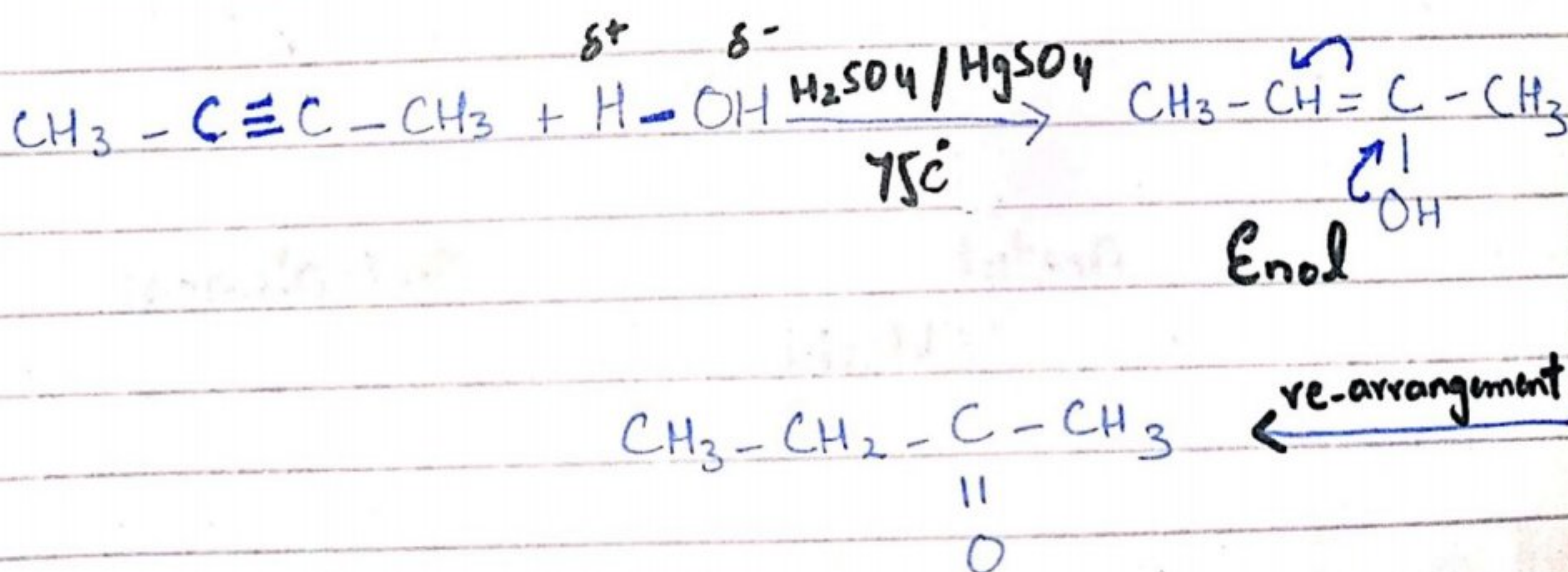
1) Ozonolysis of Alkene :- (v.v.v Imp)

1- This reaction is used to locate the position of double bond in alkene.

2- if alkene has no branching at the double bond than it produce aldehydes



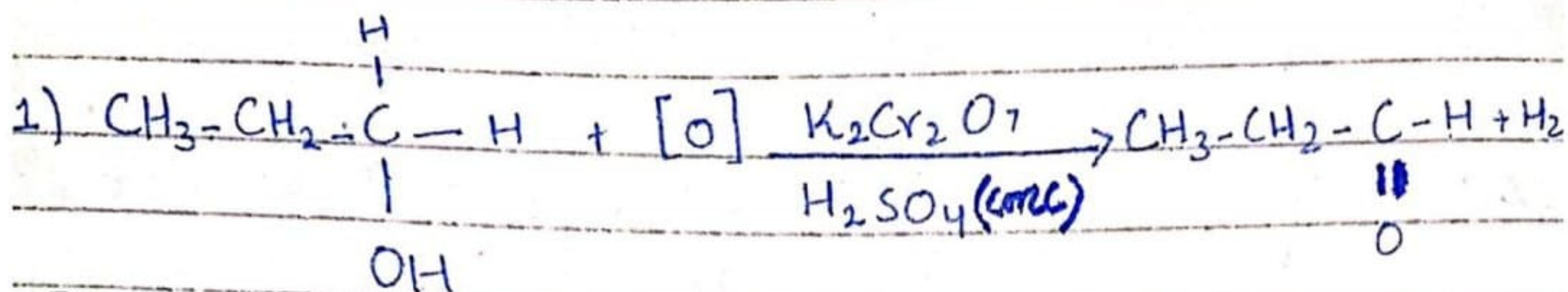
2) Hydration of Alkyne :-



3) Oxidation of Alcohols :-

→ Primary alcohols are oxidised into aldehydes.

→ Secondary alcohols are oxidised into ketones.

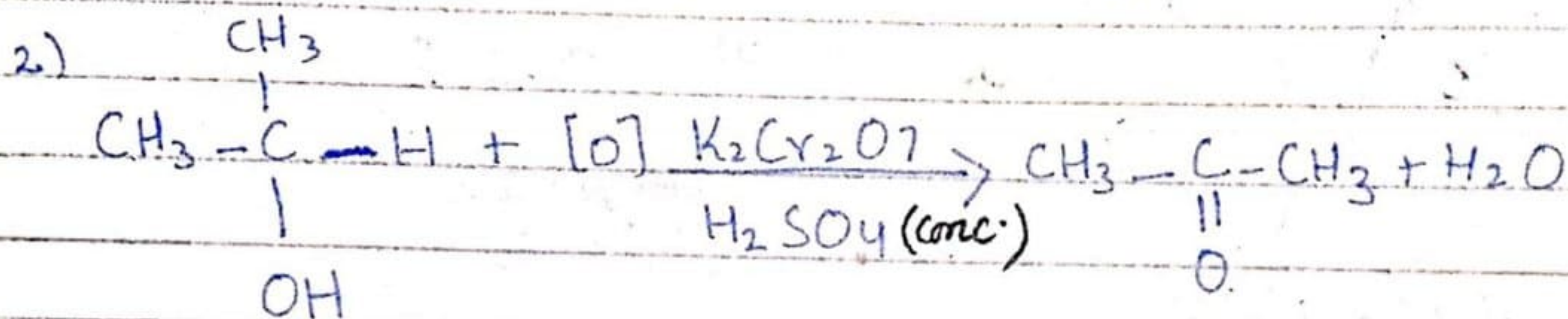


Reagents:- (For Information) oxidizing agents

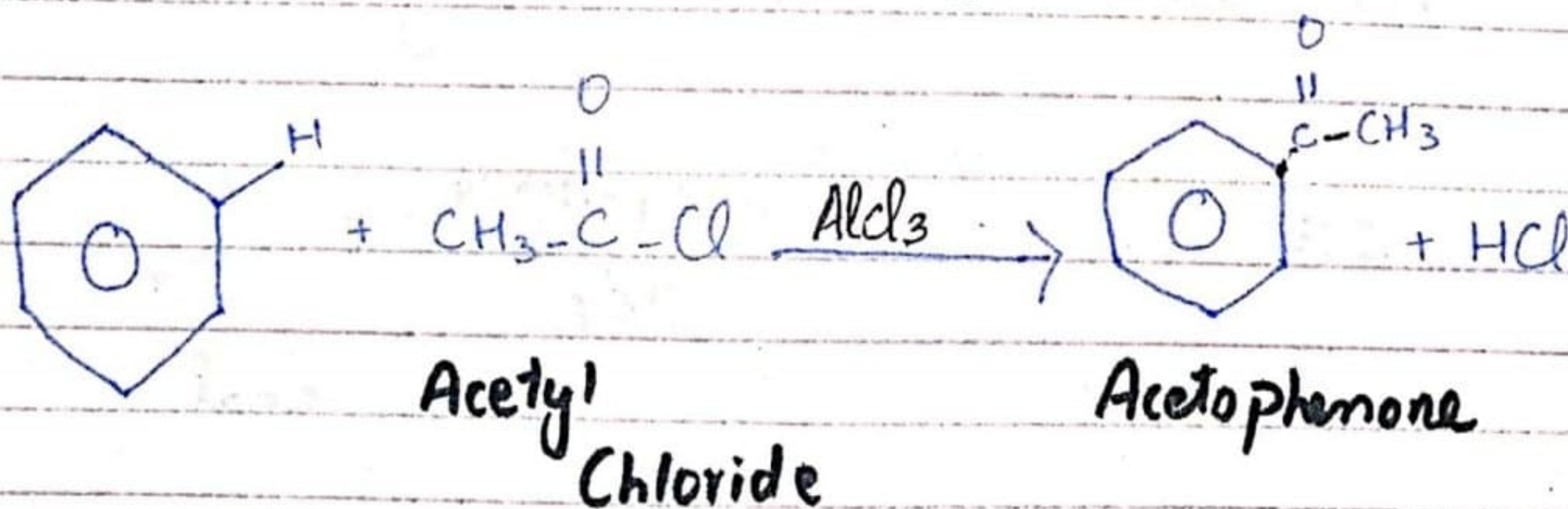
1) $\text{H}_2\text{SO}_4 / \text{K}_2\text{Cr}_2\text{O}_7$

2) John's Reagent ($\text{CrO}_3 + \text{dil. H}_2\text{SO}_4 + \text{Acetone}$)

3) Sarret Reagent ($\text{CrO}_3 + \text{Pyridine}$)



4) Friedel Craft Acylation:-

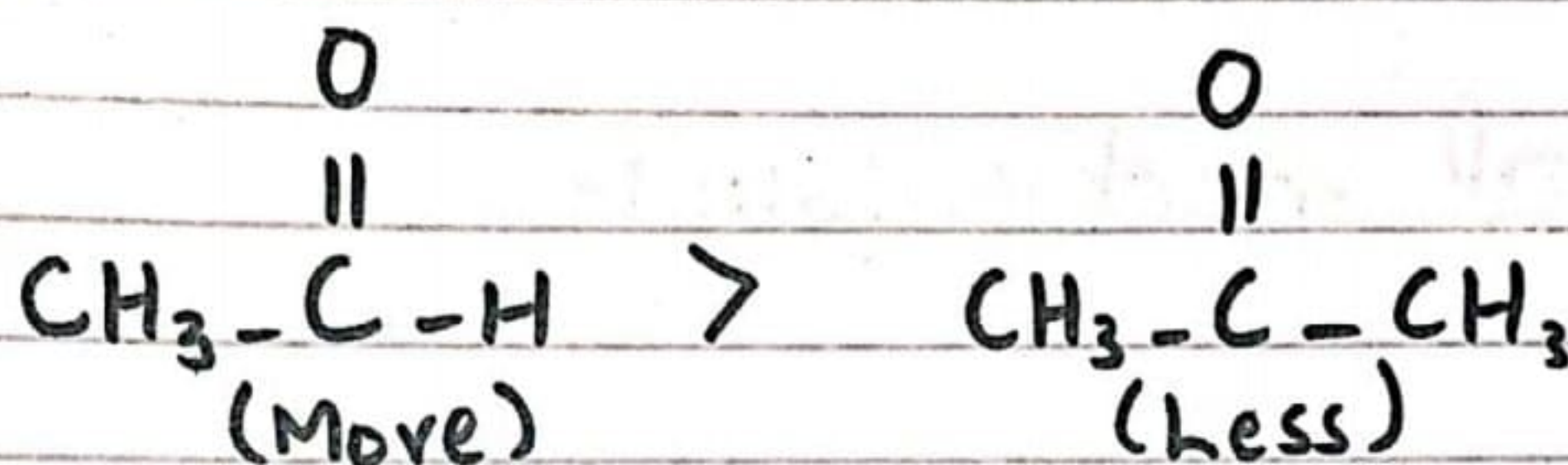


(Answer of
Long question
(1) (1)

Reactivity

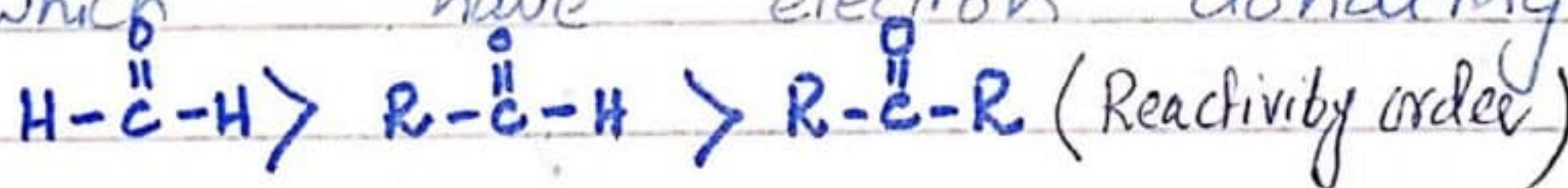
The carbonyl compounds are reactive due to following reasons :-

1. The C-O bond is polar.
2. It has π bonds.
3. The aldehydes are more reactive than ketone.



This is because in aldehyde the carbonyl compound is more polar than ketone.

In ketone carbonyl compound is less polar due to two alkyl groups (R) which have electron donating effect.



REACTIONS OF CARBONYL:-



COMPOUNDS

i) Nucleophilic addition :-

There are two types of nucleophilic addition reactions.

- 1) Base catalysed nucleophilic addition reactions.
- 2) Acid catalysed nucleophilic addition reactions.

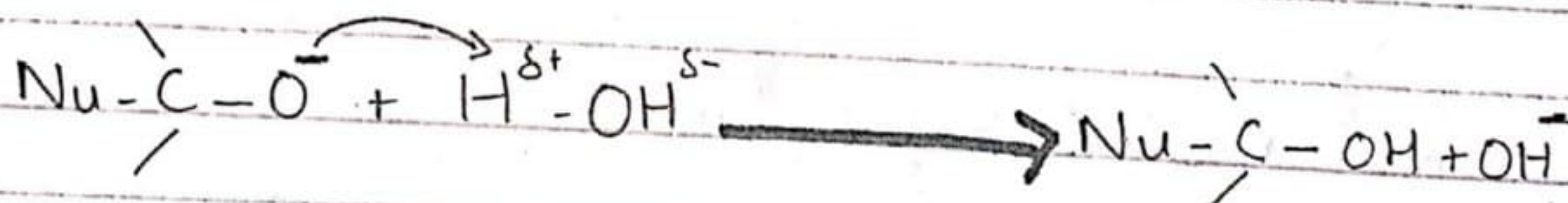
1) Base Catalysed Nu^- addition reaction:

General mechanism: Exercise Q: no 2(ii)
Ans.

Step 1:



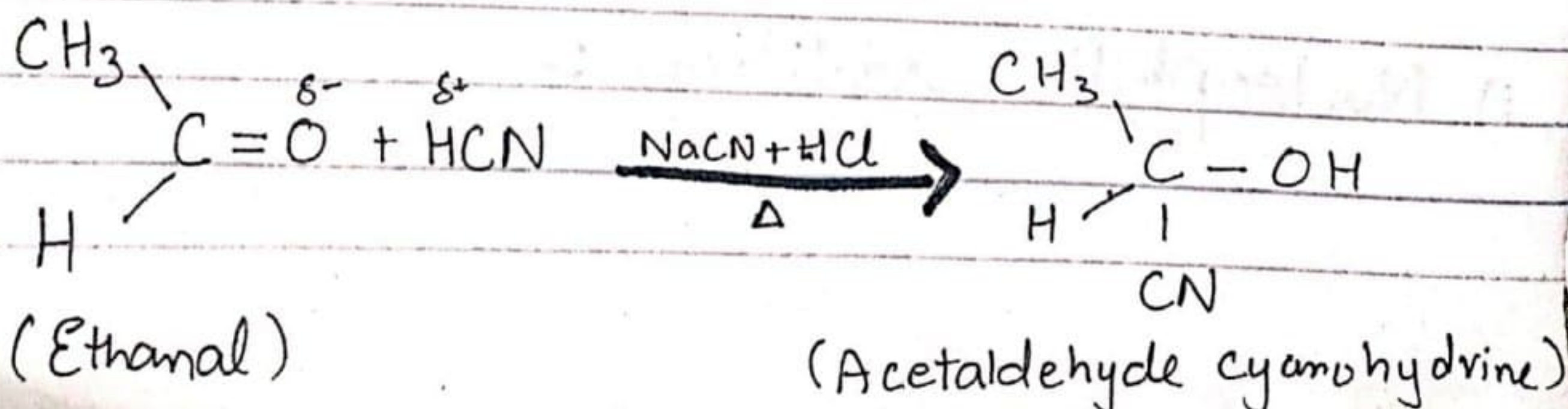
Step 2:

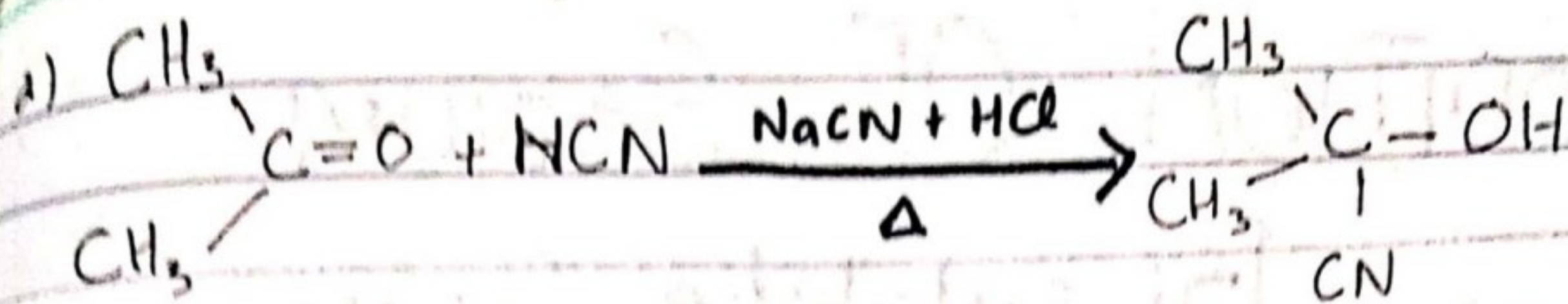


There are 5 types of base catalysed nucleophilic addition reactions.

Type

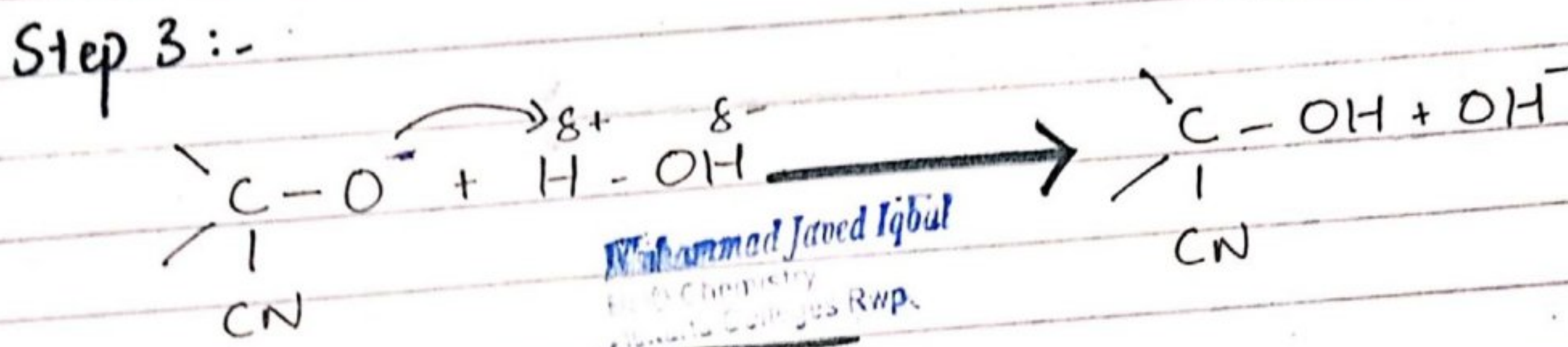
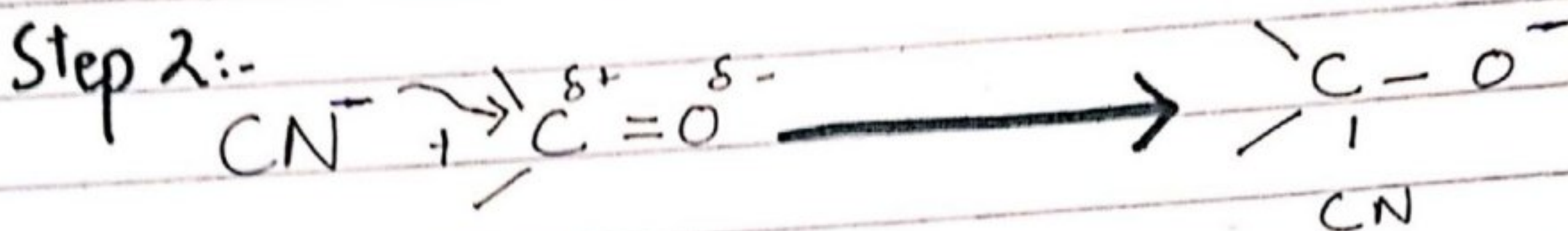
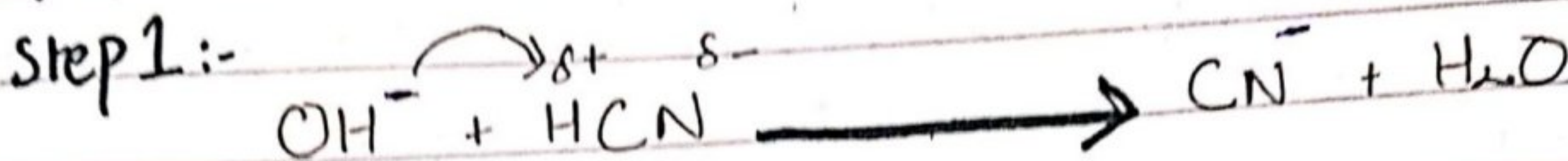
1) ADDITION OF HCN:-





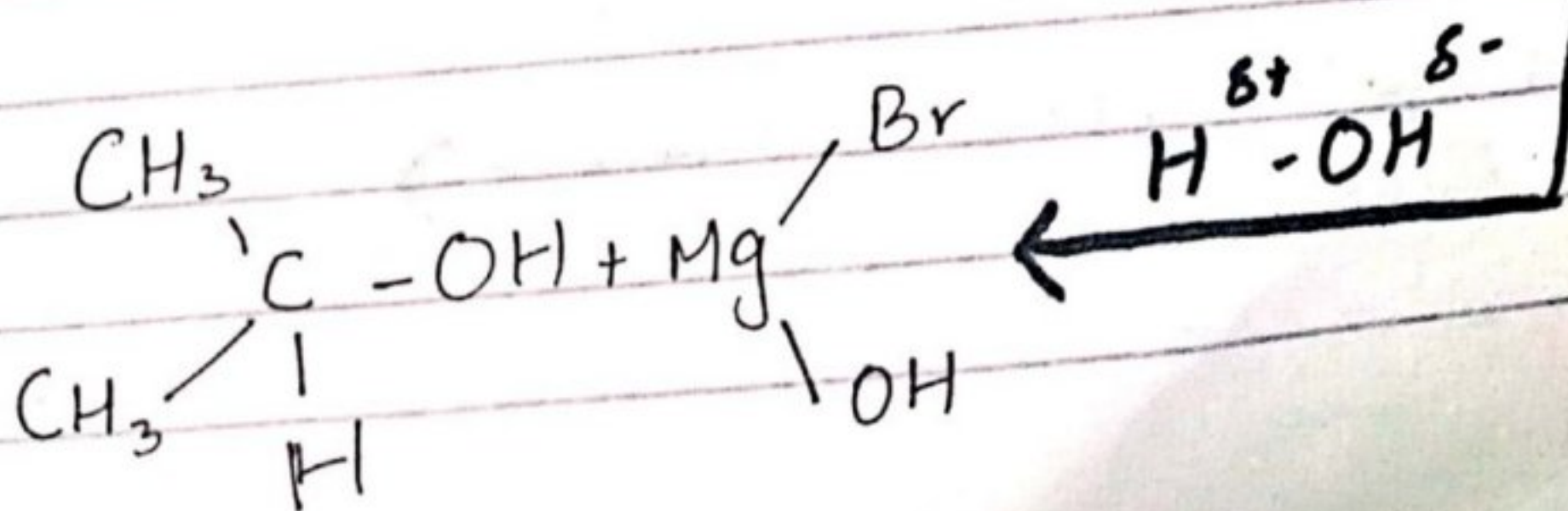
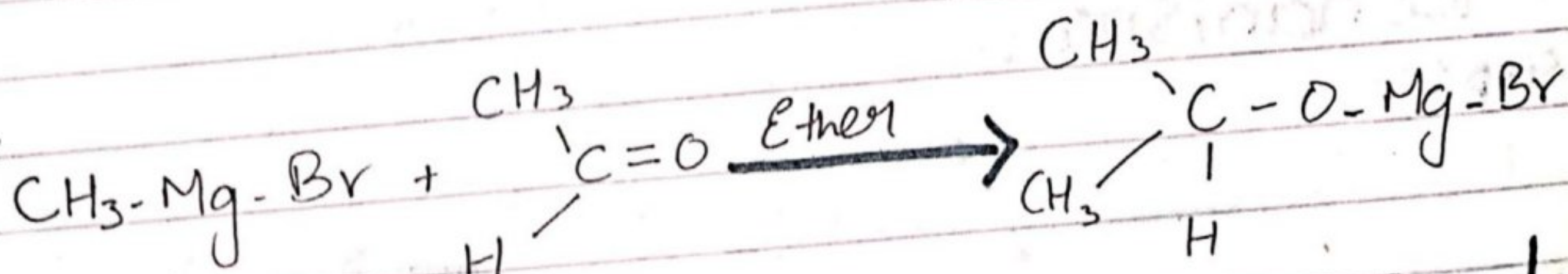
(Acetone cyanohydrine)
(2-Hydroxy-2-methylpropanenitrile)

Mechanism:- (also Ans of exercise Qno 3) iii



Type

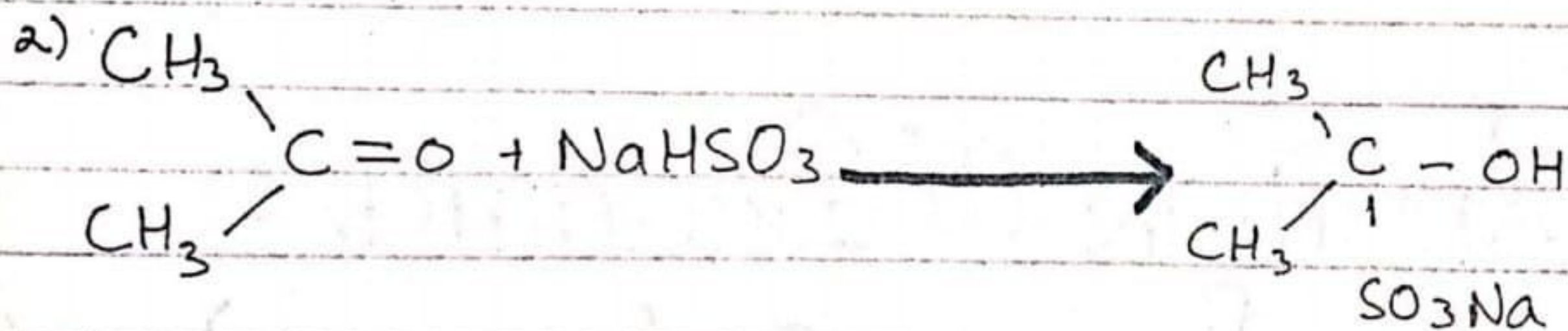
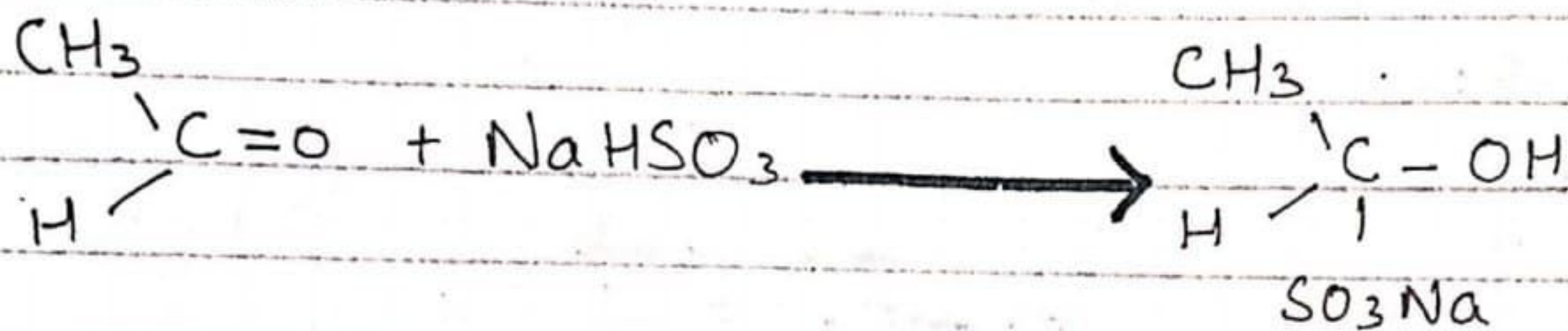
2) ADDITION OF GRIGNARD'S REAGENT (R-Mg-X)



3) ADDITION OF SODIUM Bi.sulphite (NaHSO_3)

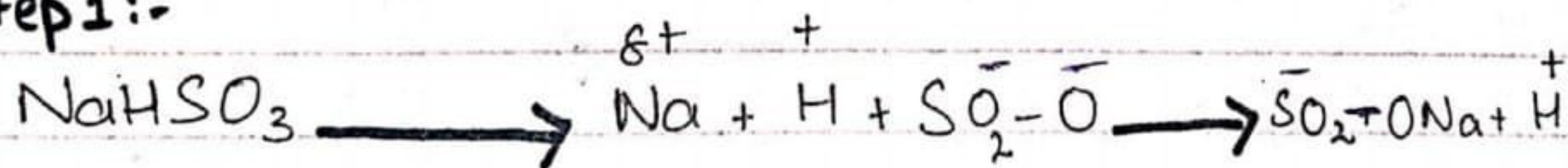
- Aldehyde and small methyl ketone reacts with sodium bisulphite to produce white ppt of addition product
- It is used to distinguish between carbonyl and non-carbonyl compounds.

1)

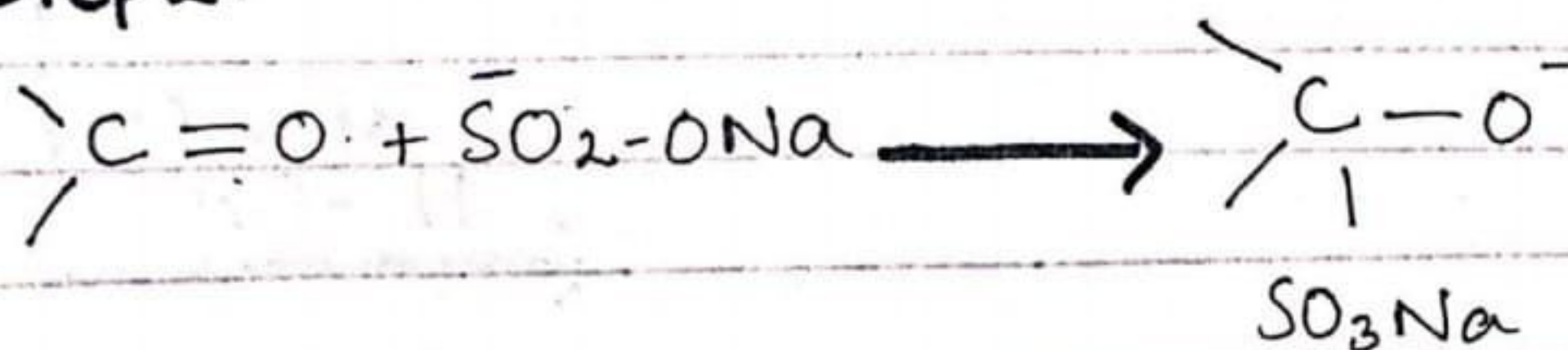


Mechanism :- (Answer of short question (XI)(10))

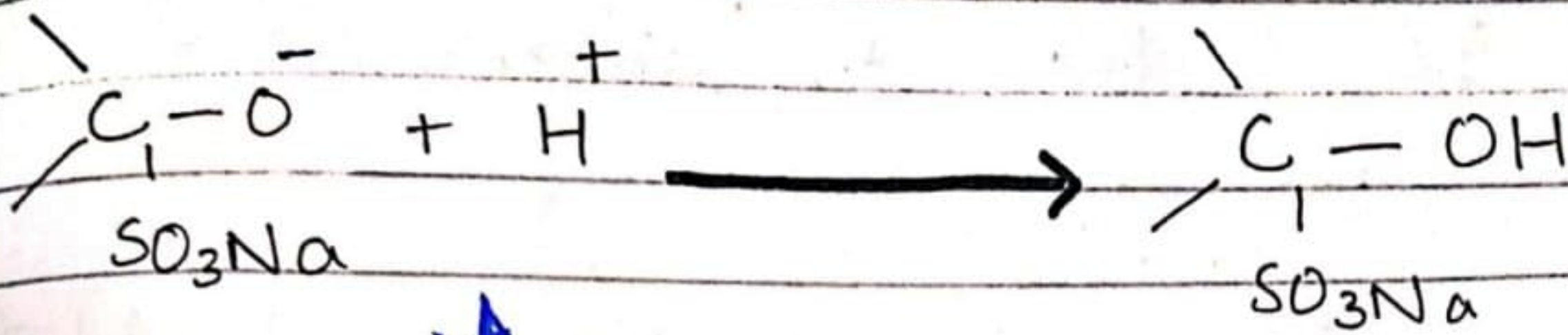
Step 1:-



Step 2:-

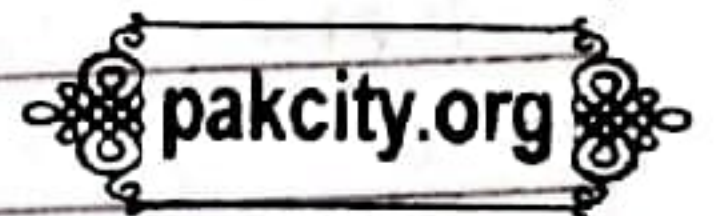


step 3 :-



(4)

CONDENSATIONS REACTIONS



Def:- The reactions in which two molecules may be same or different combine with each other to form new molecule with or without elimination of small molecule like water or ammonia are called condensation reactions.

TYPES :- There are two types
i) Aldol Condensation
ii) Cannizzaro's Reaction

Short Question
(9) (10) Ans

ALDOL CONDENSATION

1) Aldehydes and ketones having

α -hydrogen undergoes aldol condensation.
 2- Formaldehyde does not undergo aldol condensation due to absence of α -hydrogen.

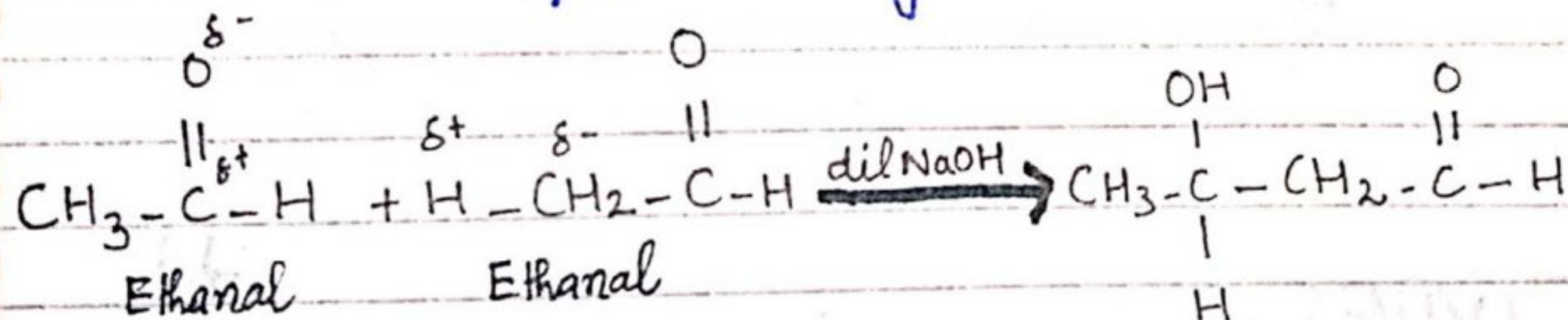
3- The product formed is called aldol because it contains aldehyde and Alcohol two functional group within same molecule.

4- Aldol condensation takes place in presence of dil NaOH or $\text{Ba}(\text{OH})_2$.
 Na_2CO_3 or NaHCO_3

Types :- Aldol condensation occurs b/w .

- 1) Between two aldehyde (identical or different)
- 2) Between two ketone (identical or different)
- 3) Between aldehyde and ketone

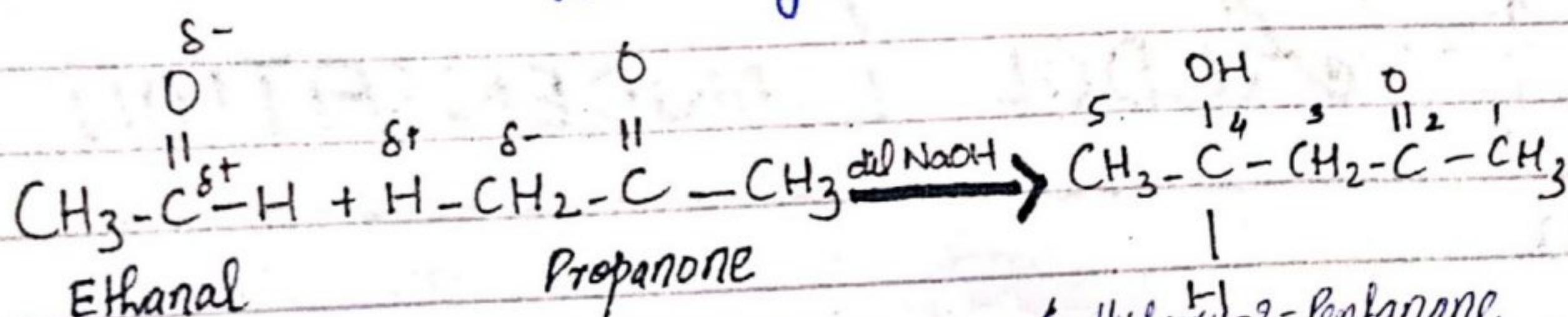
1) Condensation b/w two aldehydes:-



(Aldol)

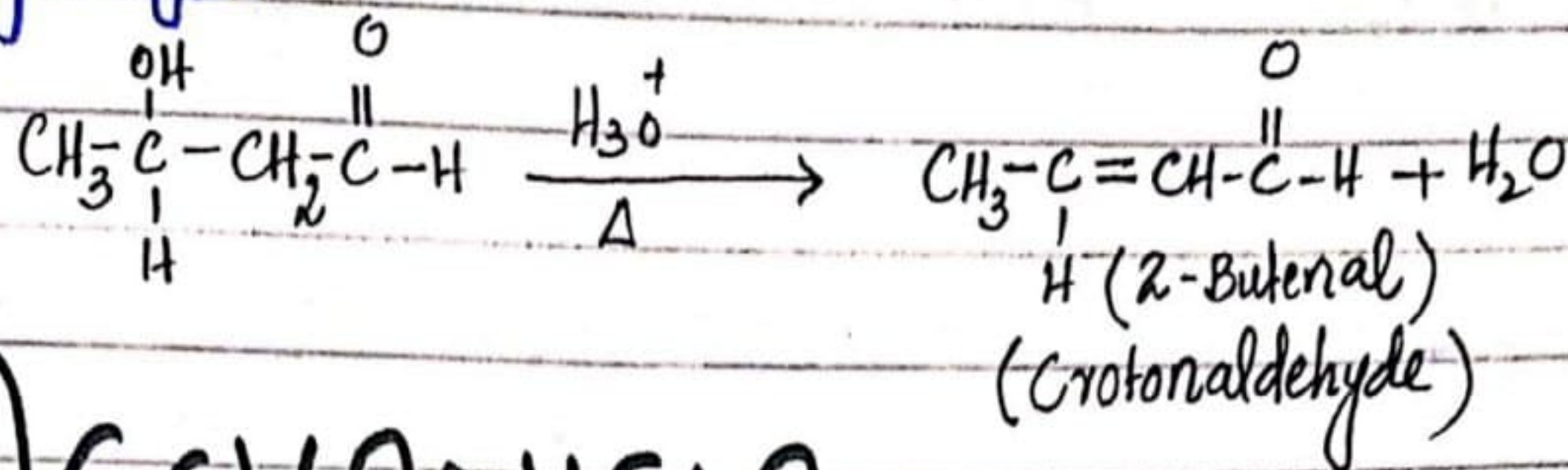
(3-hydroxy butanal)

2) Condensation b/w aldehyde and ketone:-



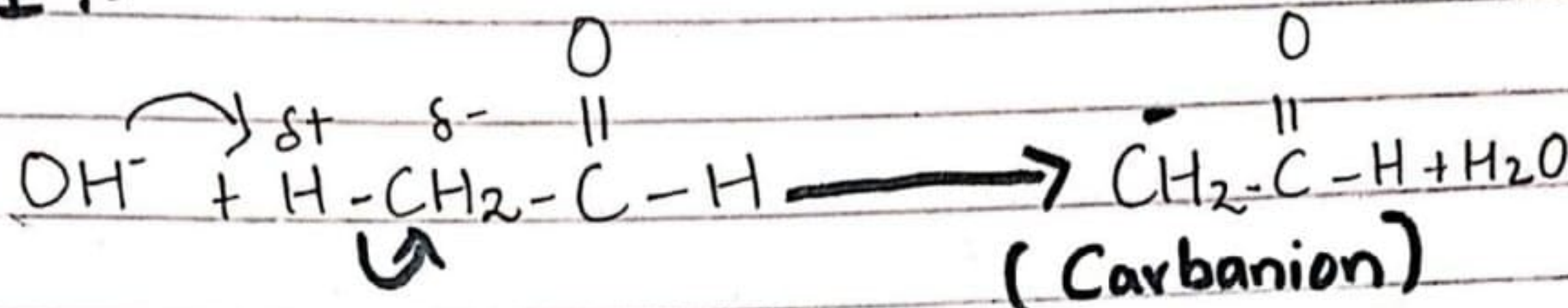
4-Hydroxy-2-Pentanone
 (Ketol)

Acidic hydrolysis:-

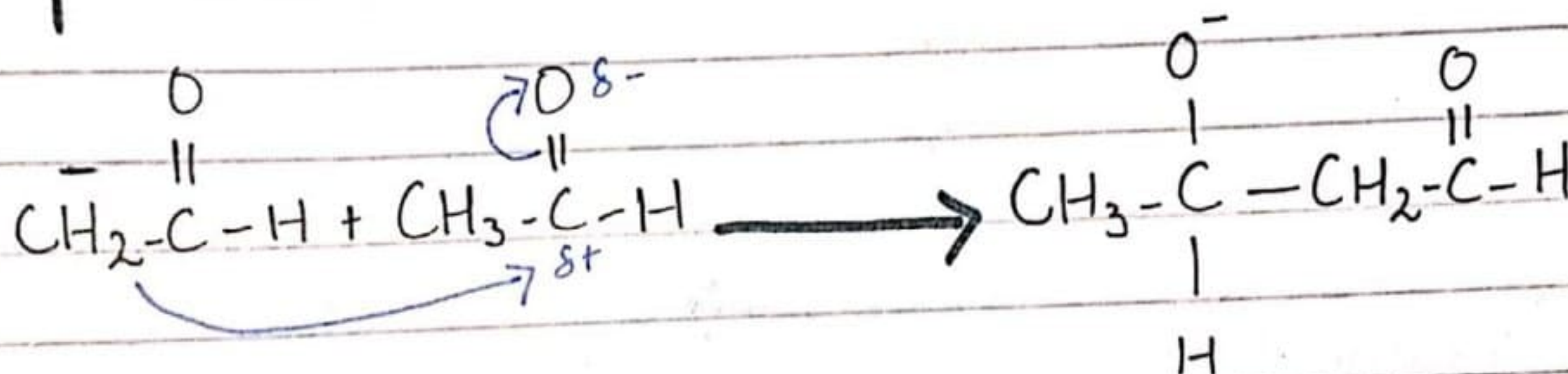


MECHANISM :-

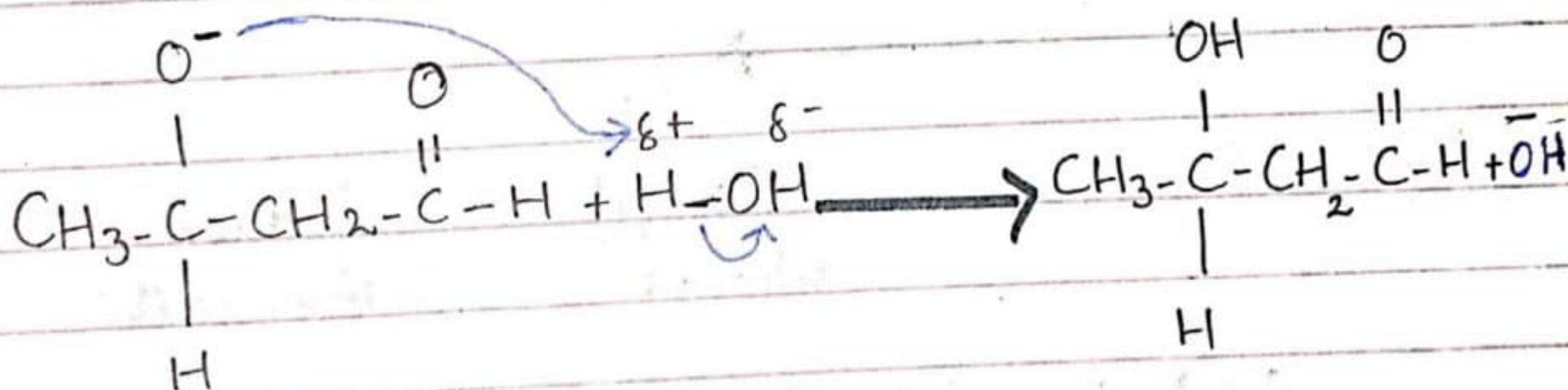
Step 1 :-



Step 2 :-



Step 3 :-



2- CANIZZARO'S

REACTIONS

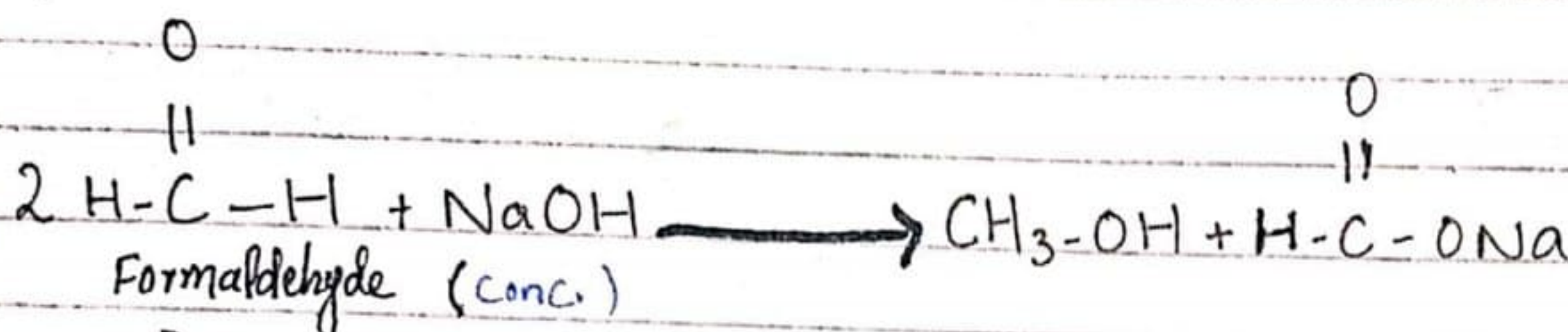
(Long Q no 8 Ans)

- Aldehydes having no α -hydrogen undergo Cannizzaro's reaction.

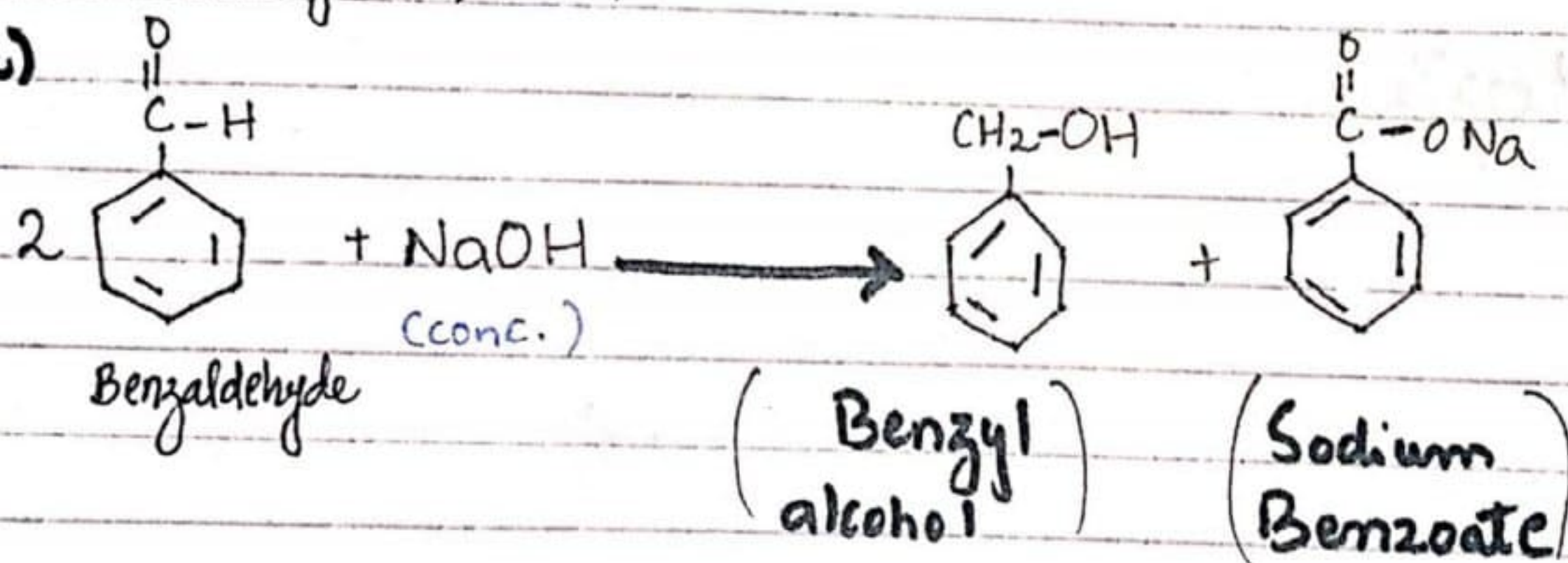
- This reaction is disproportionation reaction because one molecule of aldehyde is reduced into alcohol and other molecule is oxidized to sodium salt of carboxylic acid.

- The reaction takes place in presence of 50% NaOH (conc. NaOH)

1)



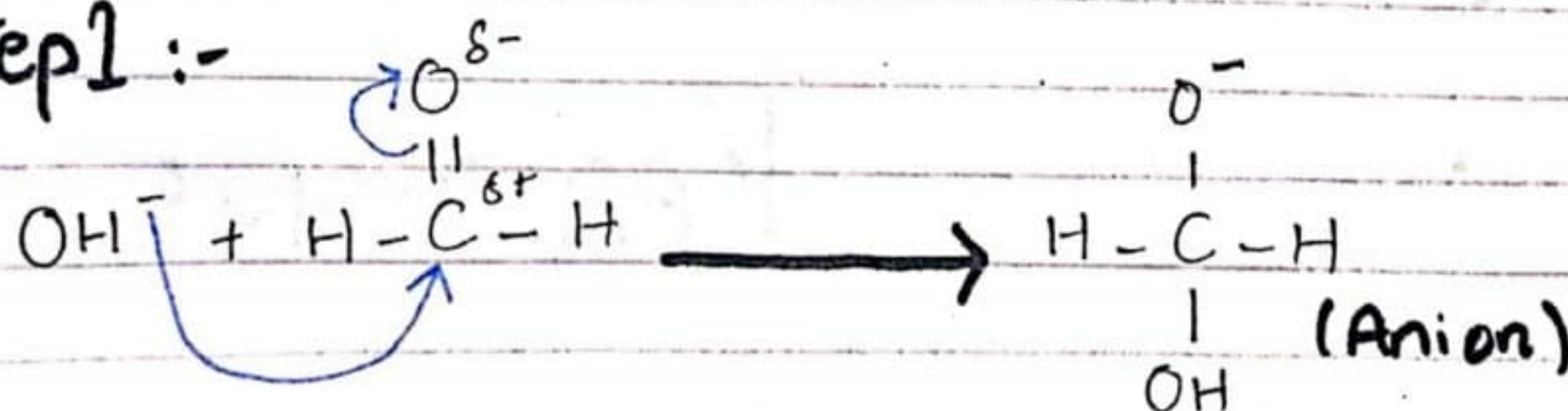
2)



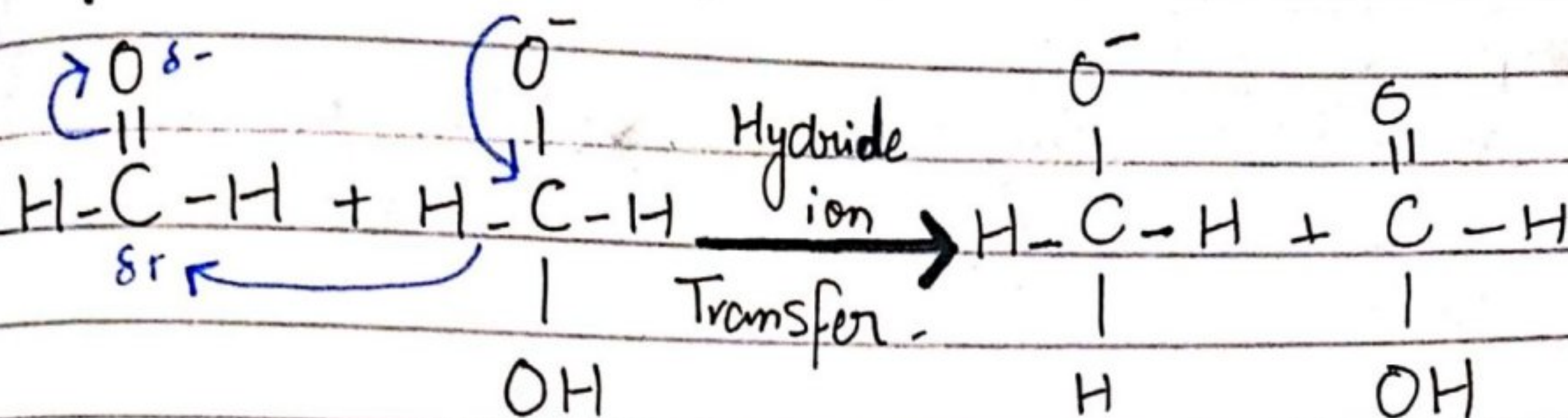
MECHANISM

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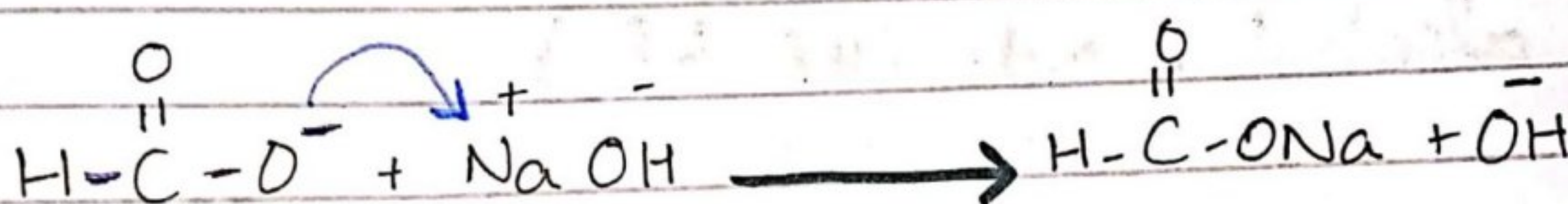
Step 1 :-



Step 2:-



Step 3:-



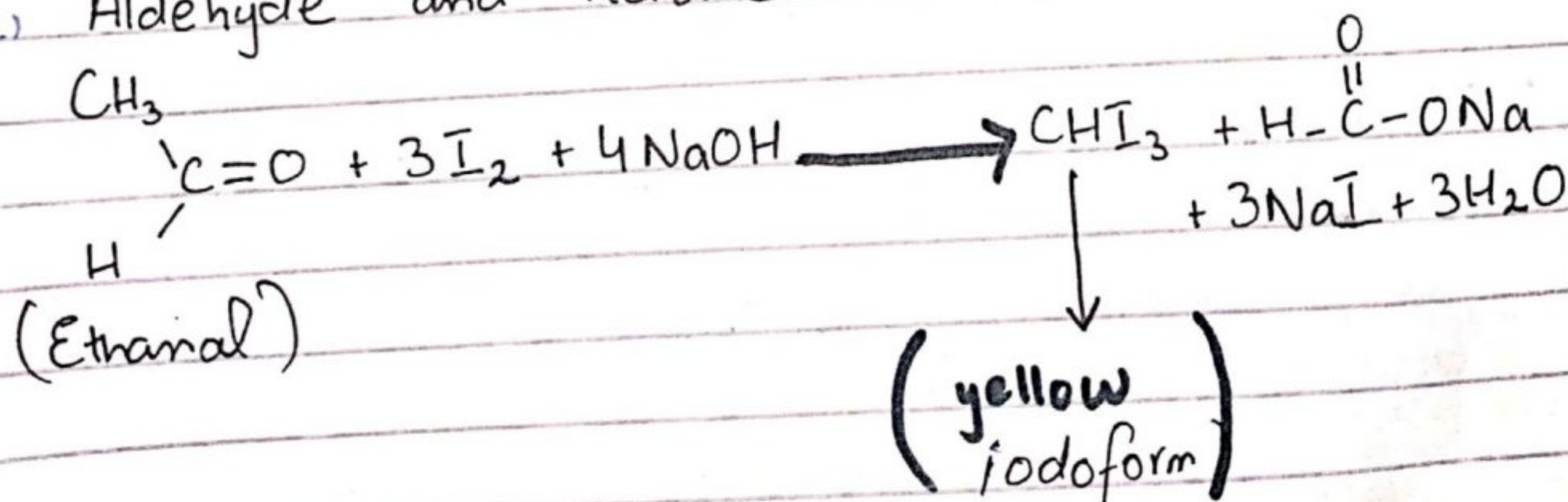
Answer of exercise Q no 6:

5)

HALOFORM REACTIONS

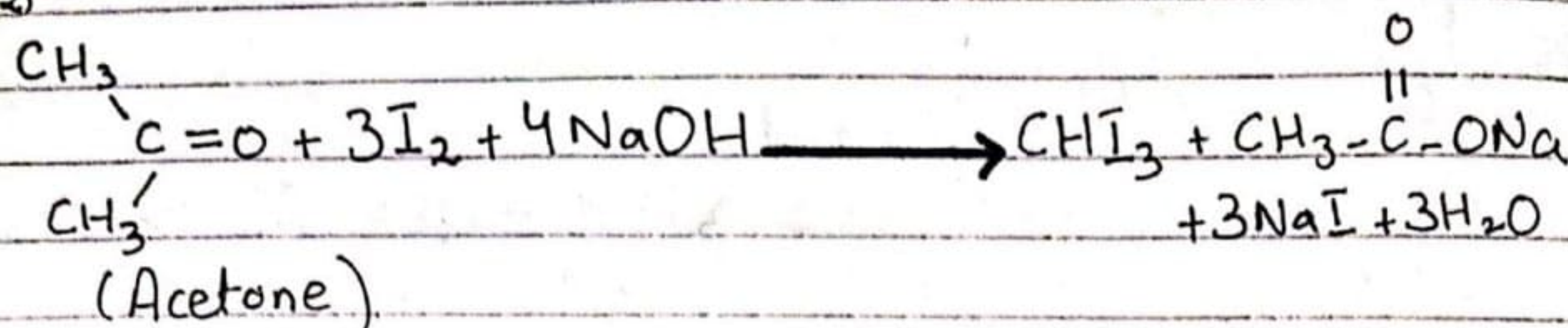
Only ~~acet~~acetaldehyde and methyl ketone reacts with halogen in the presence of NaOH, haloform is obtained.

1) Aldehyde and Ketone:- code (34 33)

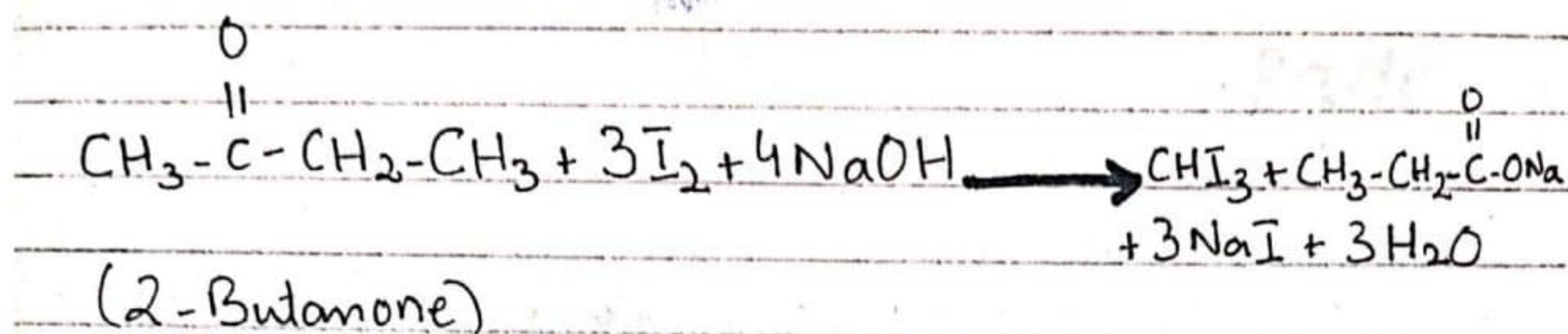


(17)

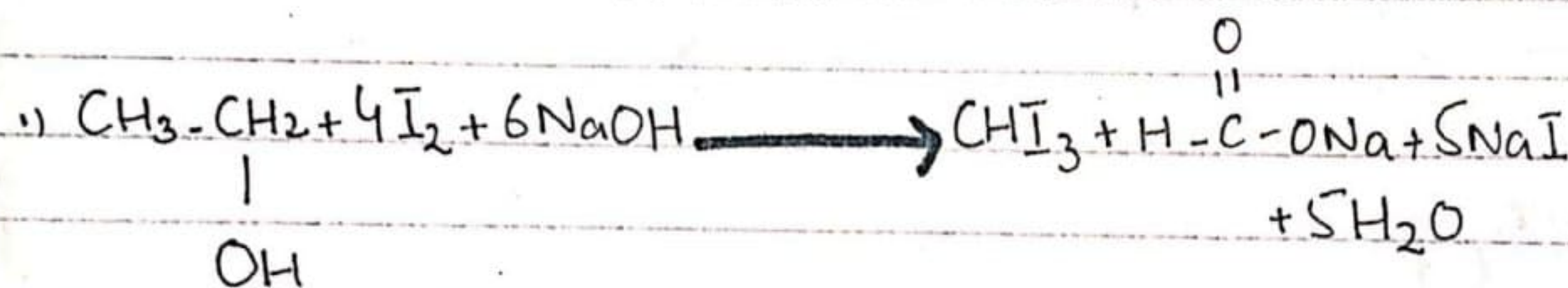
2)



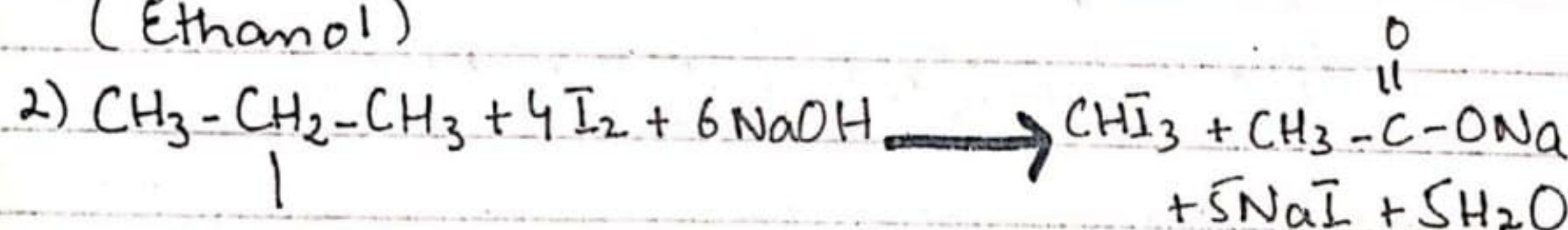
3)



Sec. alcohol :- code (46 55) (Short question 7 Ans)



(Ethanol)



(2-propanol)

IODIFORM TEST :-



- It is used to distinguish b/w acetaldehyde and other aldehyde.

- It is used to distinguish b/w methyl ketone and other ketone.

- It is used to distinguish b/w ethyl alcohol and other primary alcohol

- It is used to distinguish b/w secondary alcohol containing OH group on second carbon and other secondary alcohol.

Five Types of Questions can be made :-

Q1:- How will you distinguish b/w acetaldehyde and formaldehyde?

Q2:- How will you distinguish b/w methanal and ethanal?

Q3:- How will you distinguish b/w 2-pentanone and 3-pentanone?

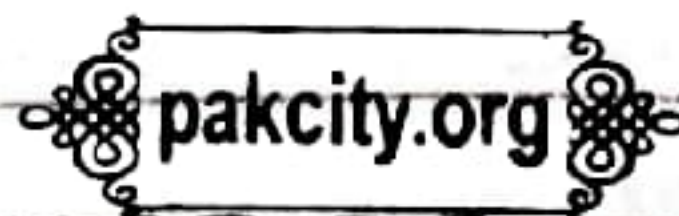
Q4:- How will you distinguish b/w acetophenone and benzophenone?

Q5:- How will you distinguish b/w 2-pentanol and 3-pentanol?

2.)

ACID CATALYZED

Nucleophilic Addition

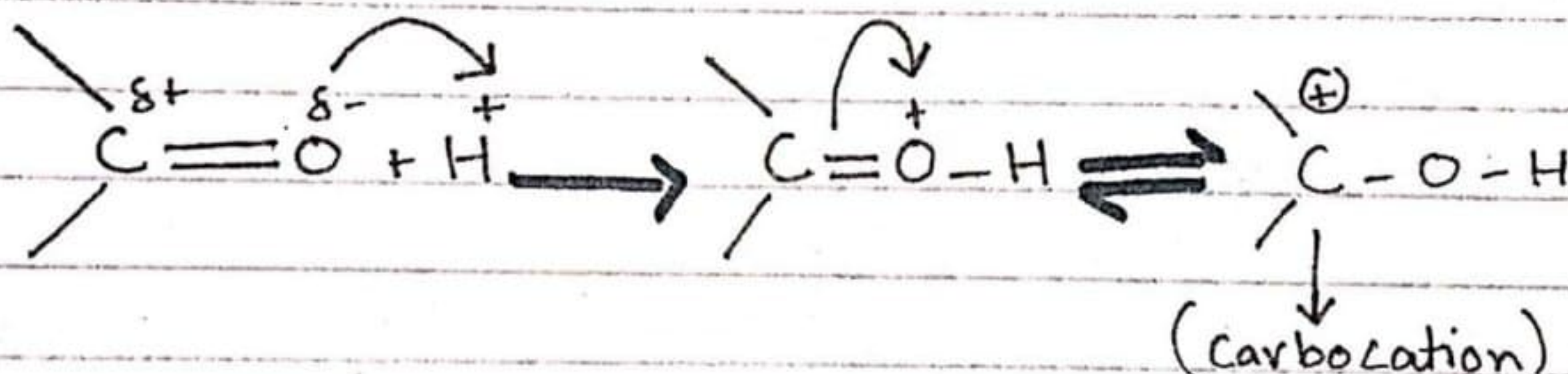


Ans of exercise q no 2 :-

Q:- Write general mechanism of acid catalysed nucleophilic addition reaction of carbonyl compounds?

Ans :-

Step 1 :-



Step 2 :-



TYPES :-

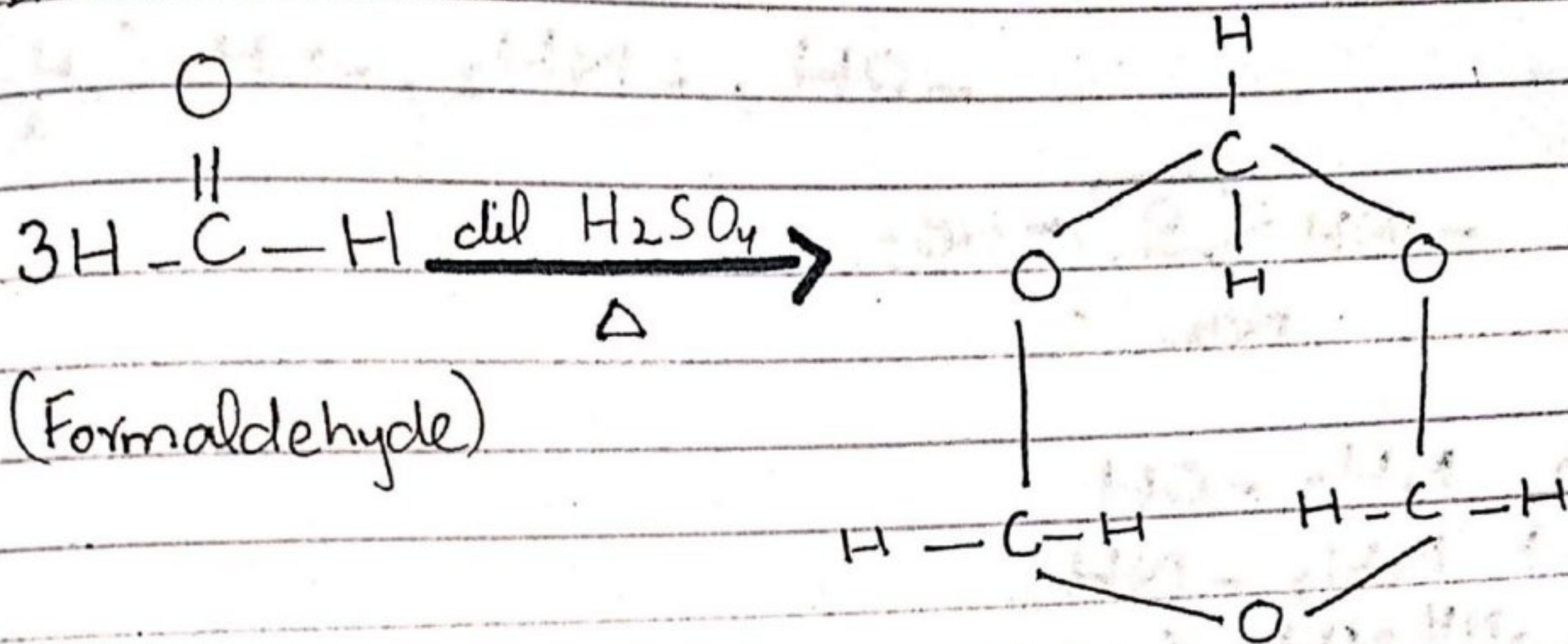
There are 3 types of acid catalysed nucleophilic addition.

reactions.

1) POLYMERIZATION REACTIONS :-

(Short question VIII(8))
Ans)

1)



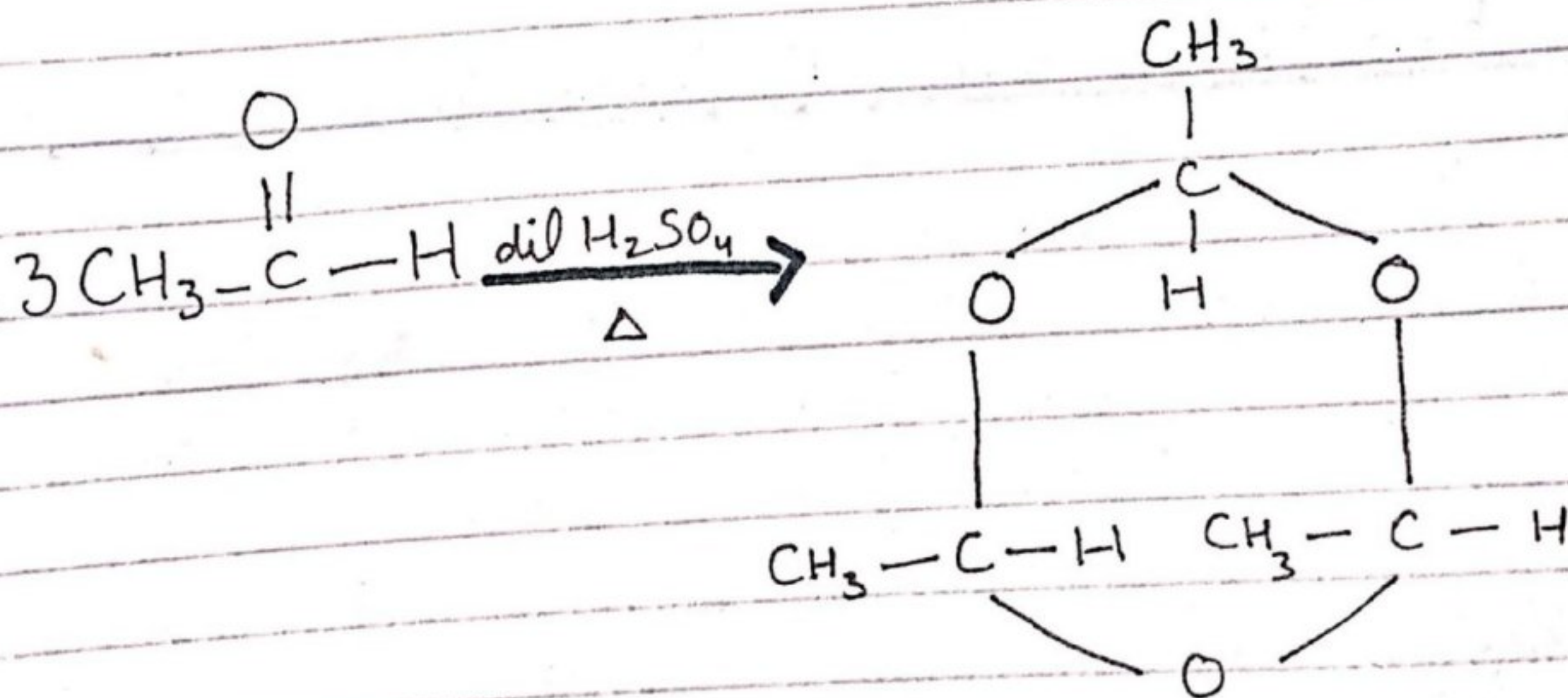
(Formaldehyde)

(Meta formaldehyde)

or

(Trimer of methanal)

2)



(Trimer of methanal)

or

(Paraldehyde)

(21)

2) ADDITION OF AMMONIA DERIVATIVES

The general formula of ammonia derivatives is

where G is NH_2-G
 $-OH, -NH_2, -NH-C_6H_5,$

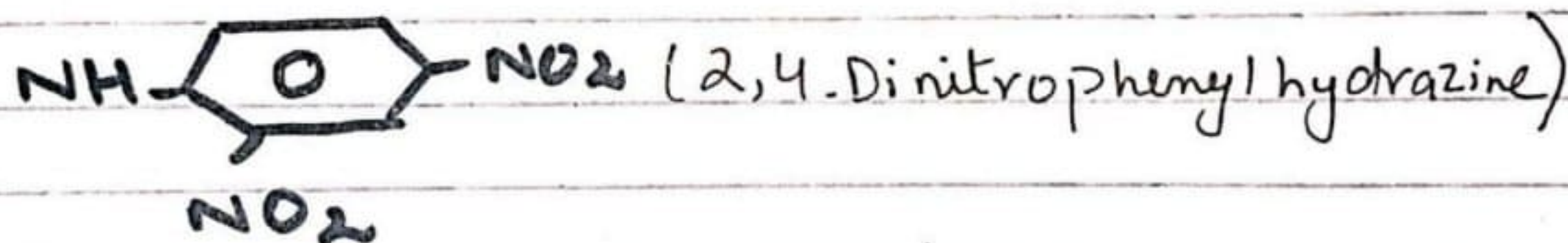


1) NH_2-OH (Hydroxyl amine)

2) NH_2-NH_2 (Hydrazine)

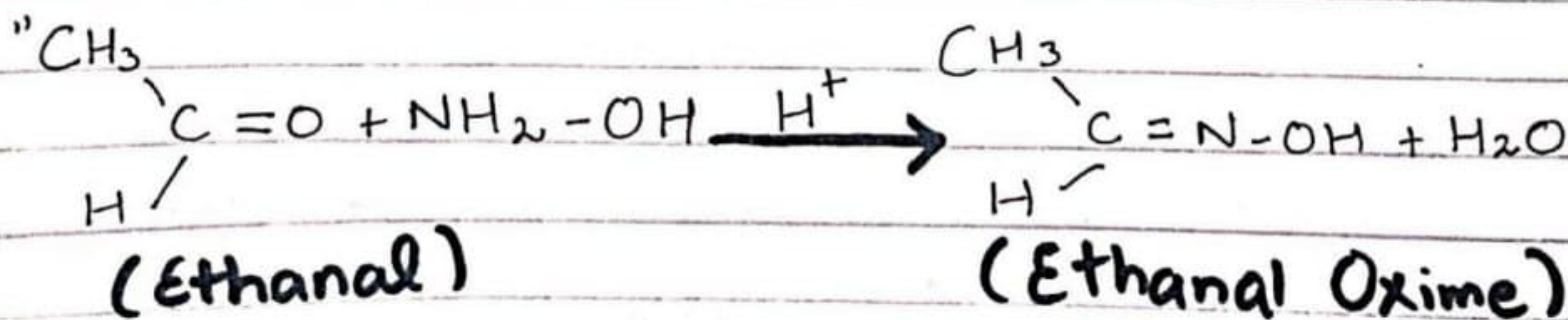
3) $NH_2-NH-C_6H_5$ (Phenyl hydrazine)

4)

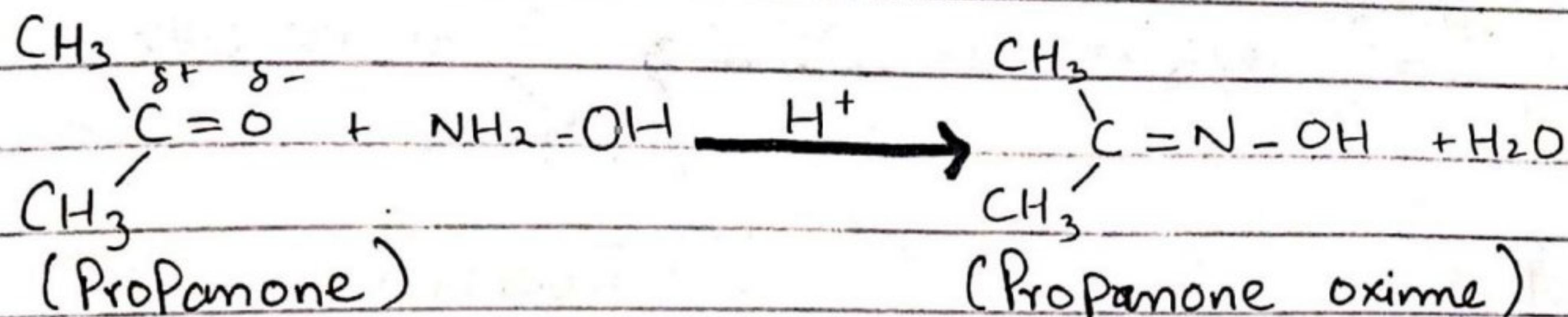


i) Reaction with Hydroxyl amine (NH_2-OH)

When carbonyl compound is reacted with hydroxyl amine in the presence of acid as an catalyst, then oxime is obtained.

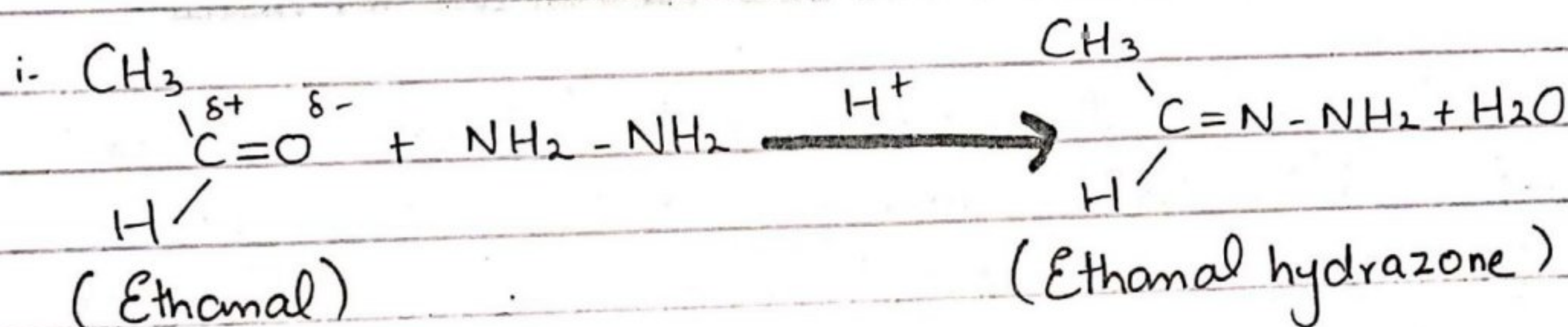


ii)

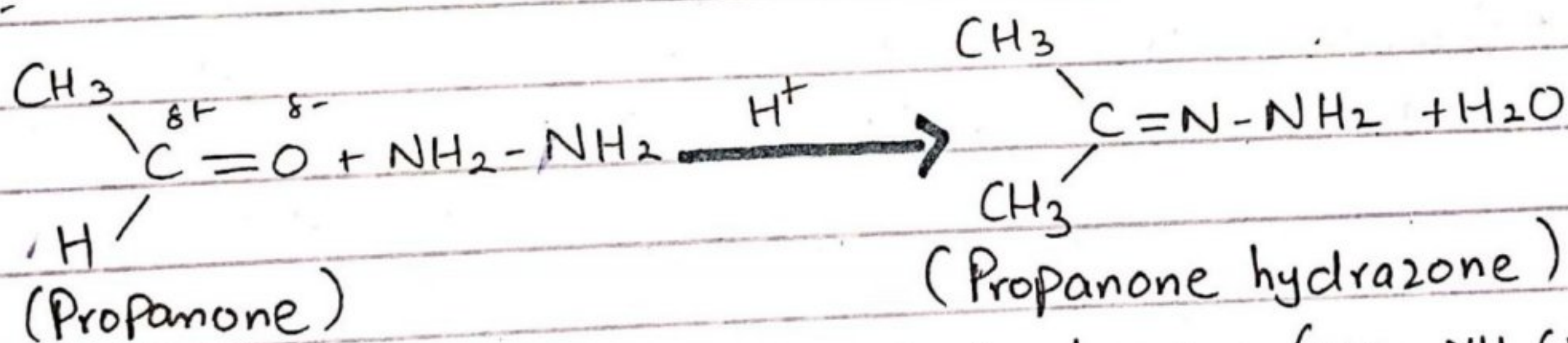


ii. Reaction with hydrazine (NH₂-NH₂)

When carbonyl compounds are reacted with hydrazine in the presence of catalyst, then hydrazone is obtained.

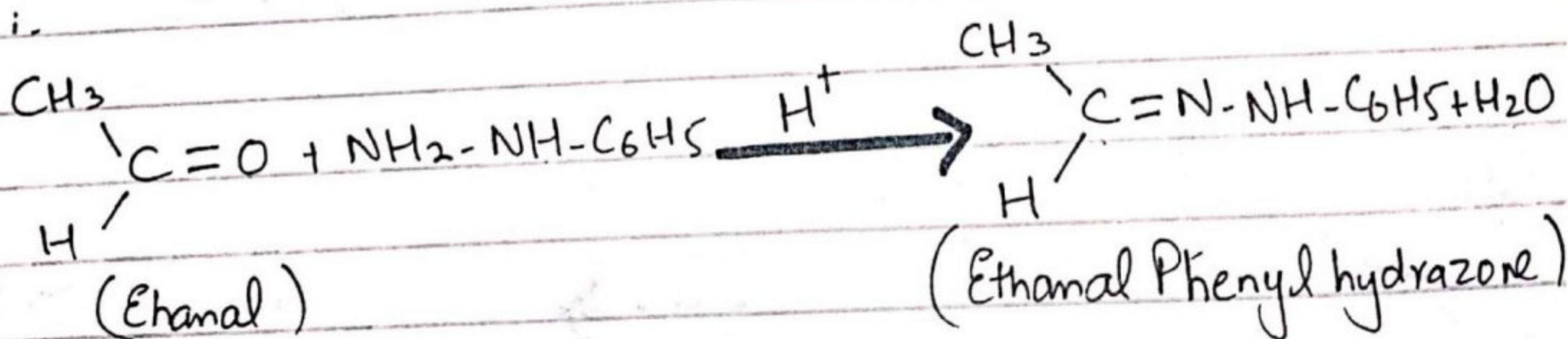


ii-

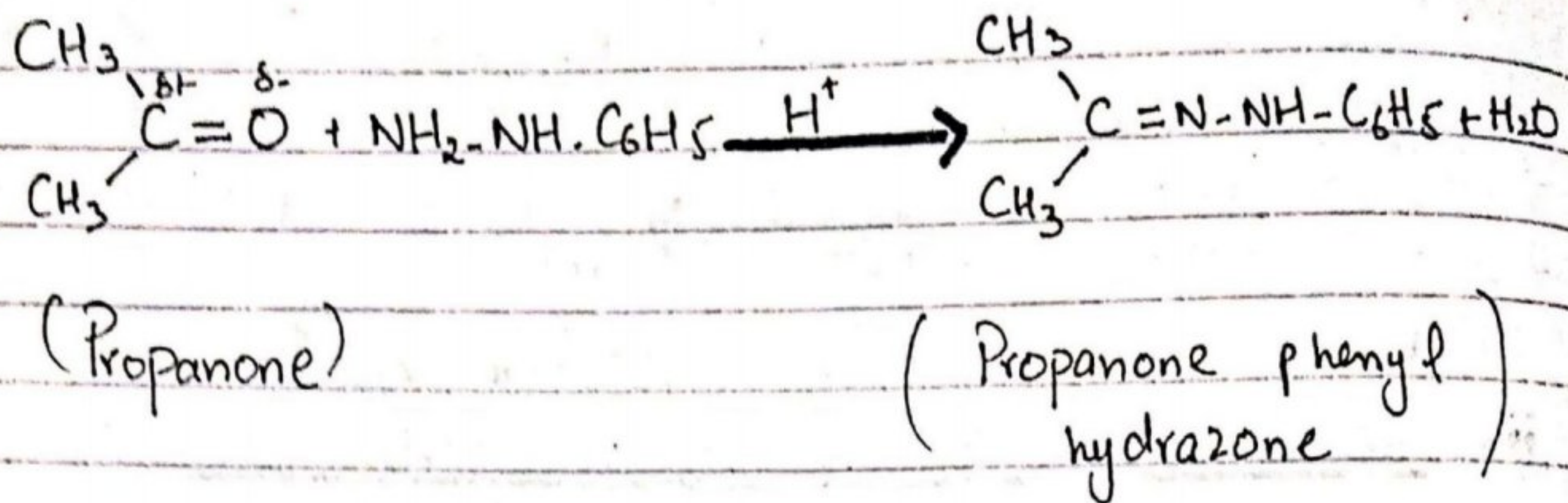


iii) Reaction with phenyl hydrazine (NH₂-NH-C₆H₅)

When carbonyl compounds are reacted with phenyl hydrazine in the presence of catalyst, phenyl hydrazone is obtained.



ii-

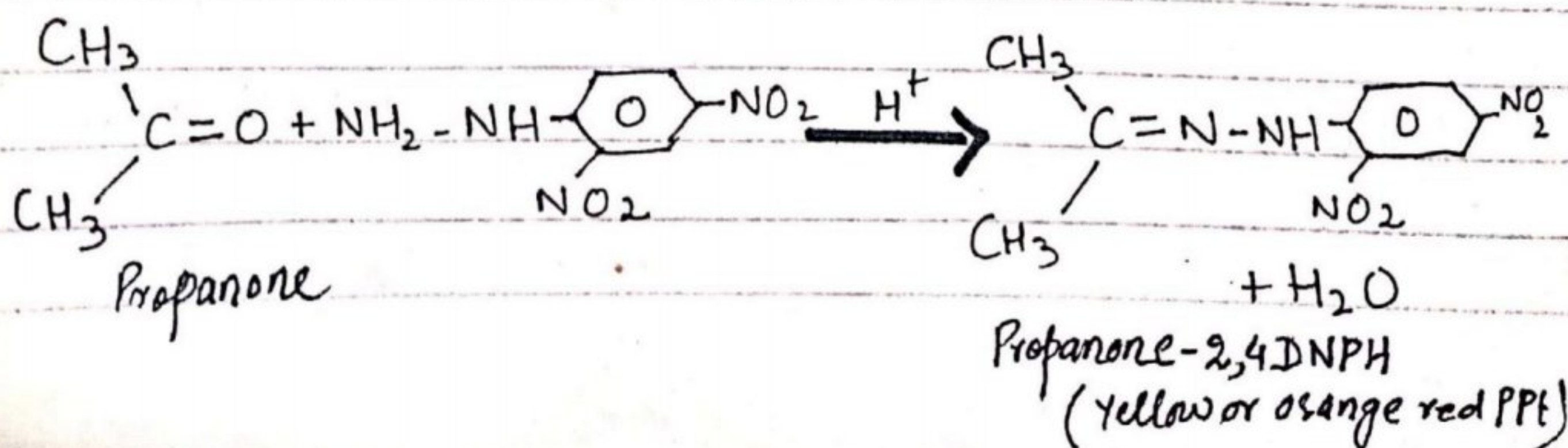
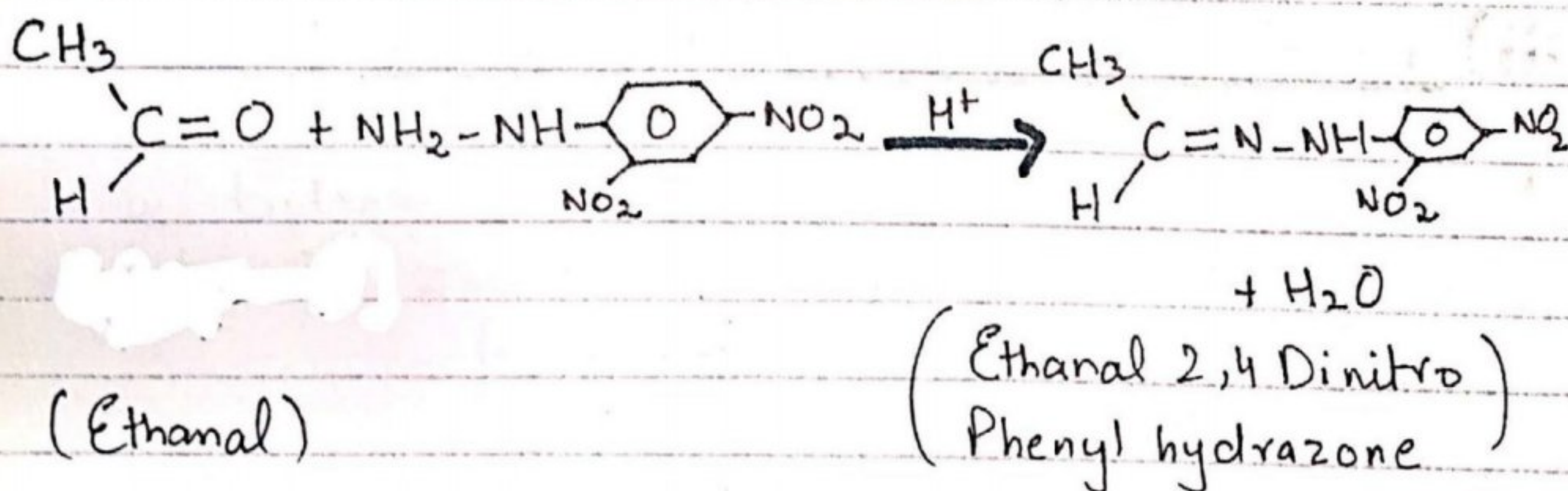


iv- Reaction with 2,4 Dinitrophenyl hydrazine

or Identification test for carbonyl compound

When aldehydes and ketones are reacted with 2,4 Dinitrophenyl hydrazine the presence of acid as catalyst yellow and orange red ppt of 2,4 Dinitrophenyl hydrazone is obtained this test is used to distinguish between carbonyl and non-carbonyl compounds.

i-



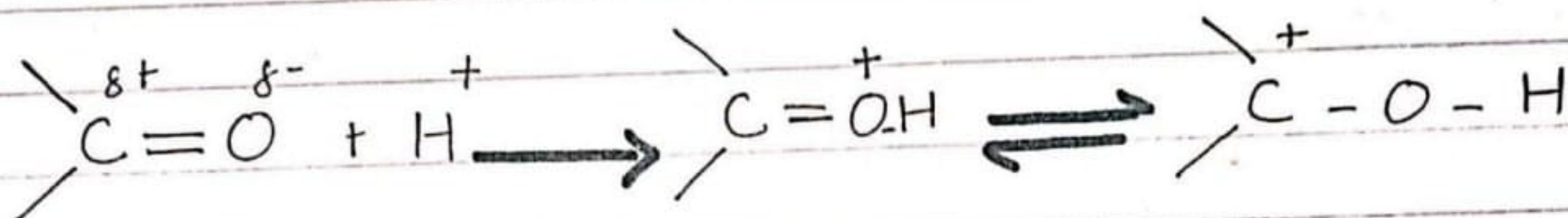
Propanal $\longrightarrow$ Propanone 2,4 Dinitrophenyl
hydrazone

Ques. (Long Ques? Ans)

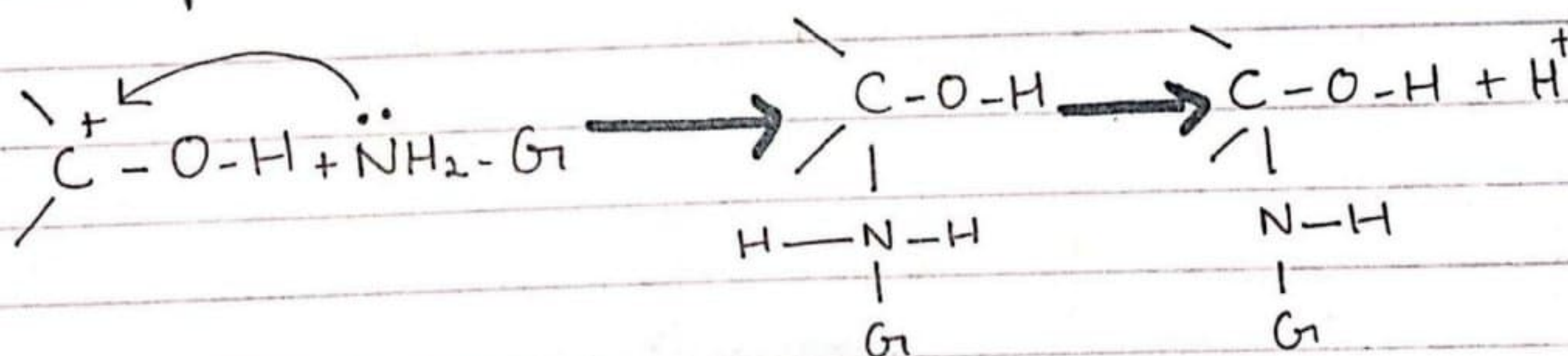
MECHANISM OF ADDITION of AMMONIA DERIVATIVES

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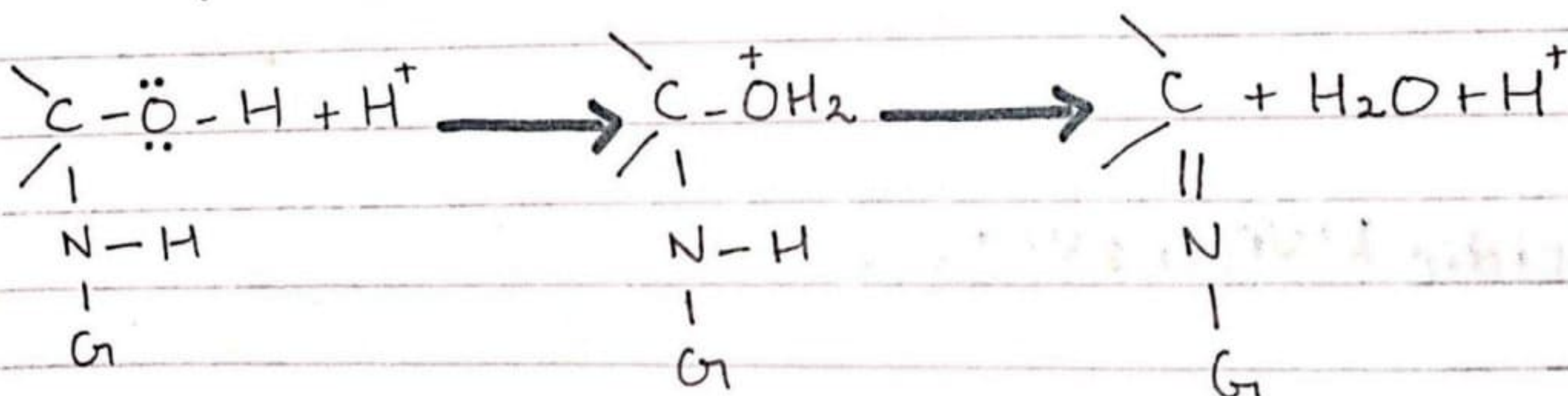
Step 1 :-



Step 2 :-



Step 3 :-



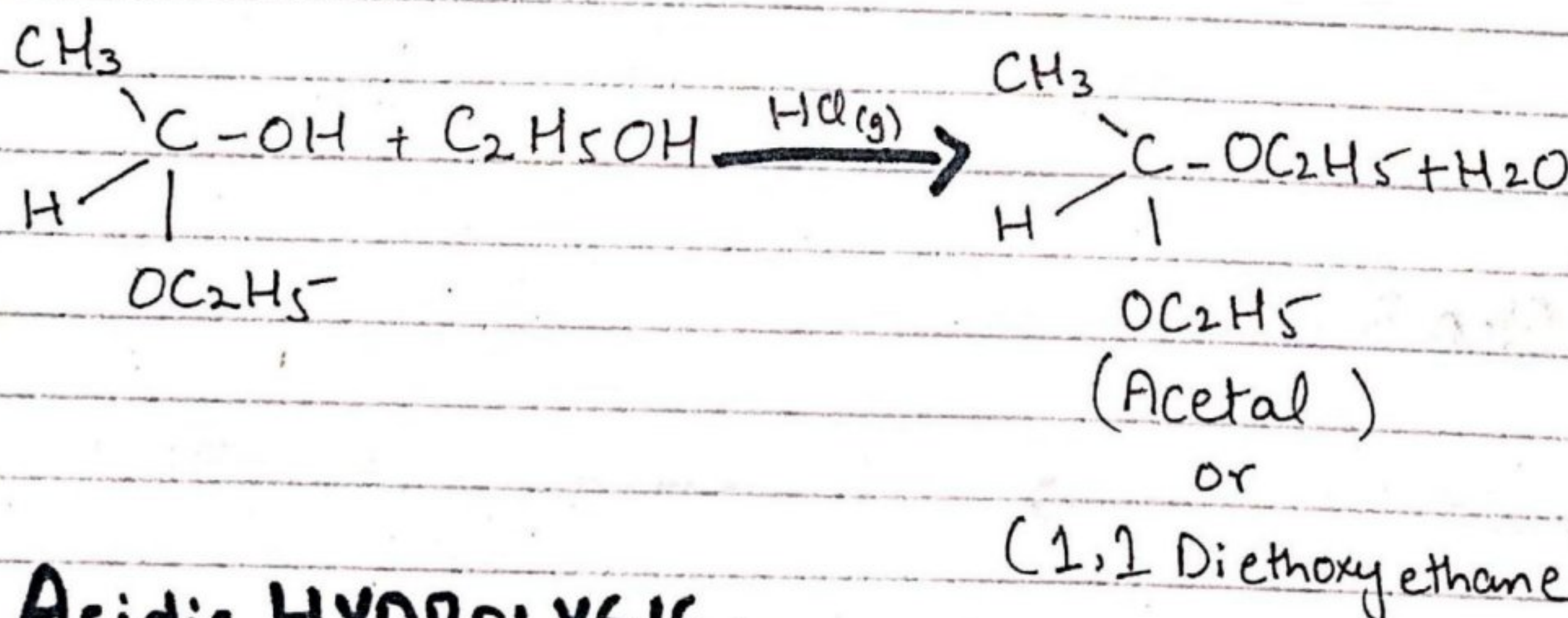
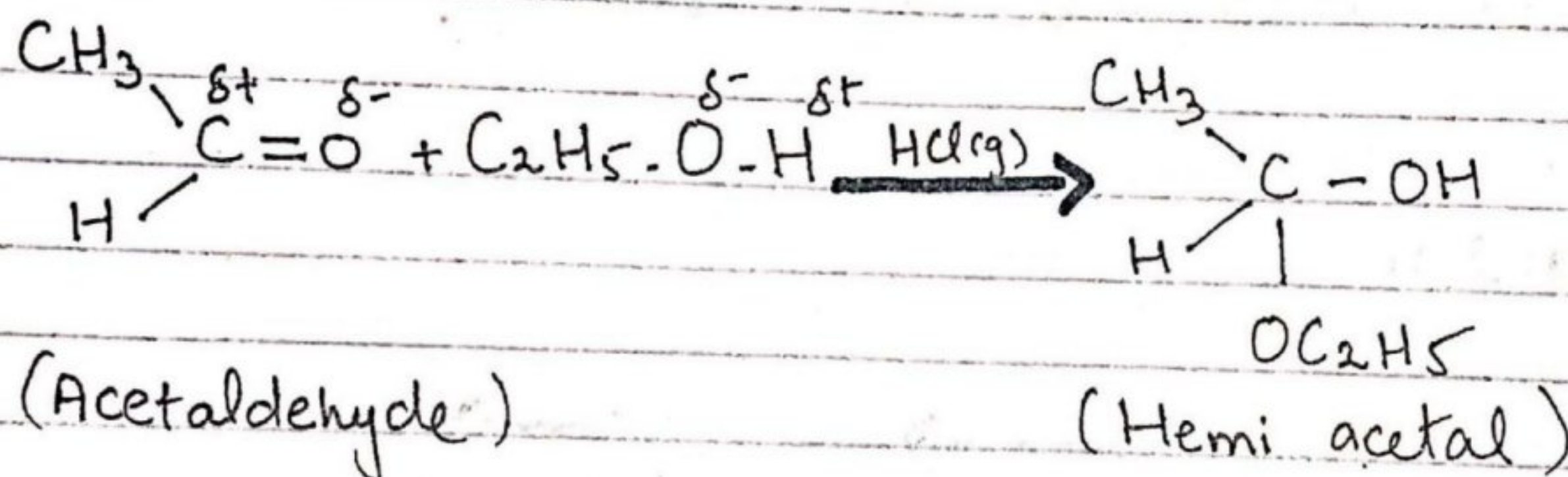
3) ADDITION OF ALCOHOL ::

(IN ALDEHYDES ONLY)

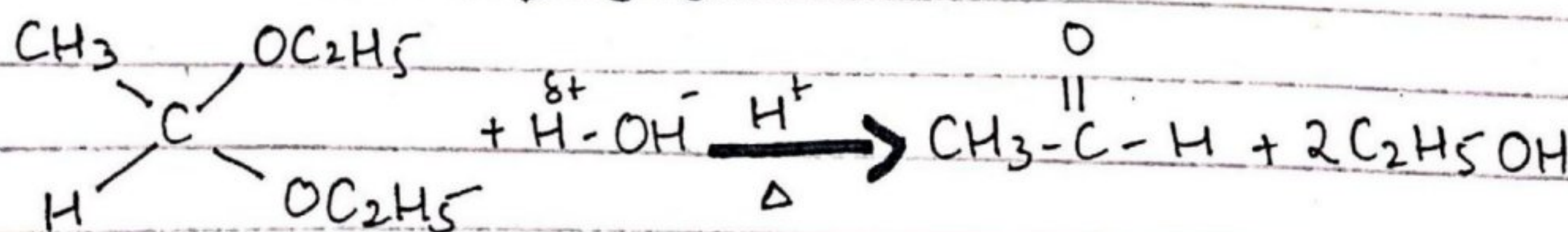
When the aldehydes are reacted with alcohol in the presence of HCl gas as a catalyst, acetals are obtained.

Uses :- These acetals are used as a strong protecting group against strong oxidizing agents.

On acidic hydrolysis these acetals are converted into corresponding aldehydes.



Acidic HYDROLYSIS :-



REDUCTION REACTIONS

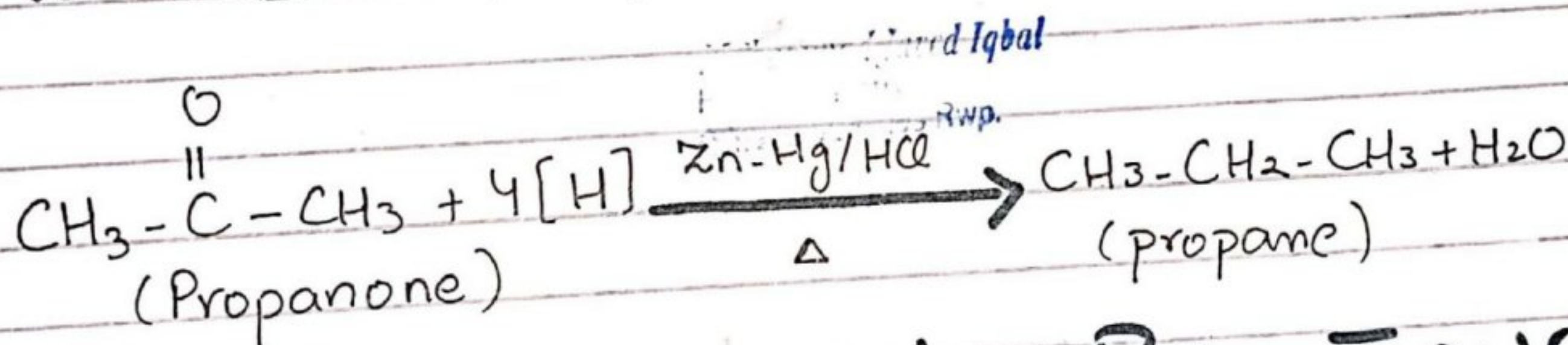
i) Clemmensen's and Wolf Kishner reduction reactions

Methods of preparation of alkanes

a)

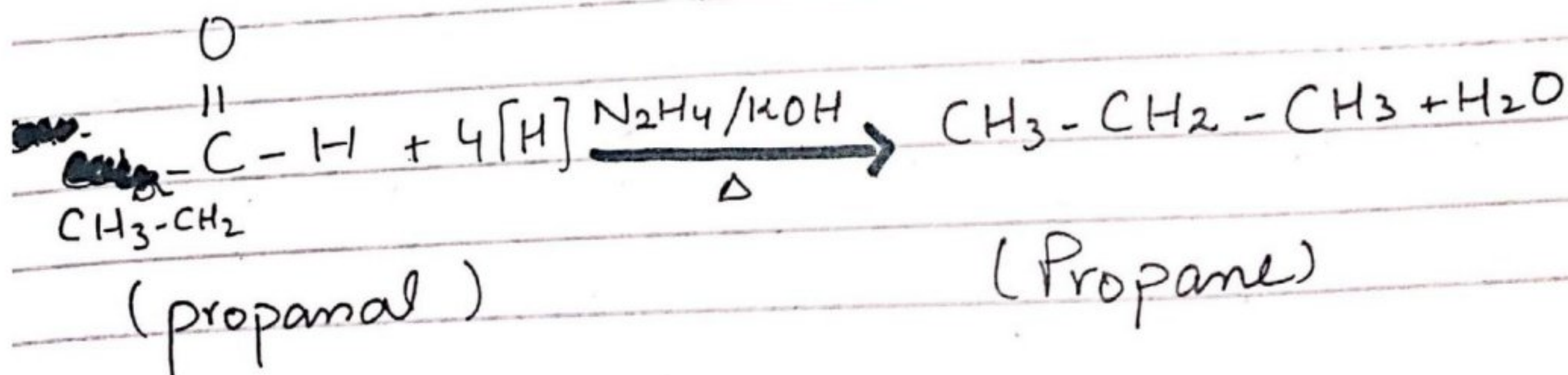
CLEMMENSEN'S REDUCTION:-

When the carbonyl compounds are reacted with zinc amalgam in the presence of HCl, alkane is obtained. It is used for reduction of ketones.



b) WOLF KISHNER'S REACTIONS:-

When carbonyl compounds are reacted with hydrazine ($\text{NH}_2 - \text{NH}_2$) in the presence of KOH as catalyst, alkanes are obtained. It is used for reduction of aldehydes.



(27)

ii) Hydride ion reduction of Ketones and aldehydes or

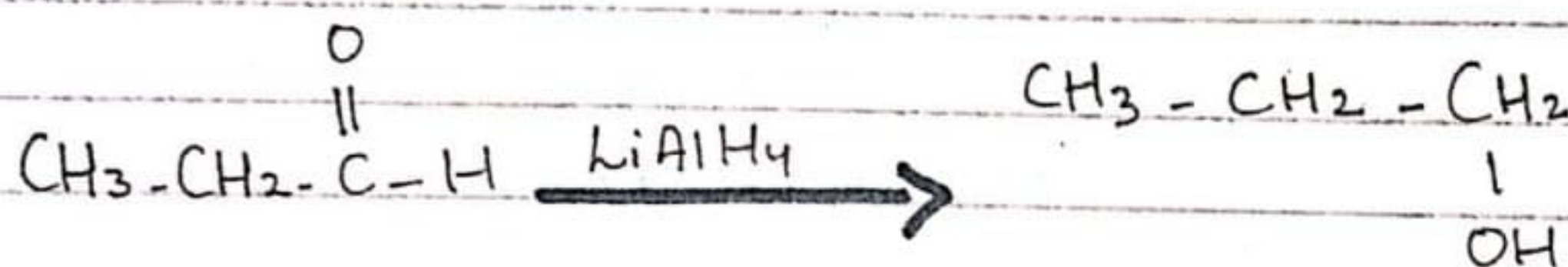
Catalytic reduction with sodium
Boro hydride (NaBH_4)

Aldehydes are reduced into primary alcohols and ketones are reduced into secondary alcohols. LiAlH_4 is stronger reducing agent than NaBH_4 .

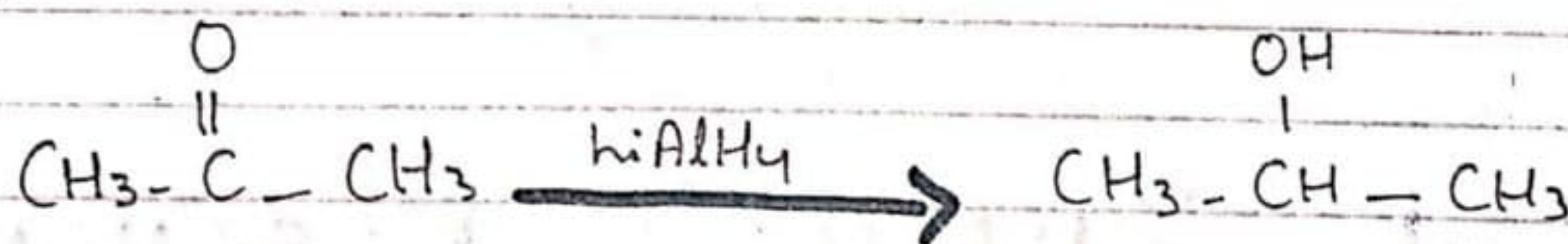
Reducing agents :- 1. LiAlH_4
2. NaBH_4



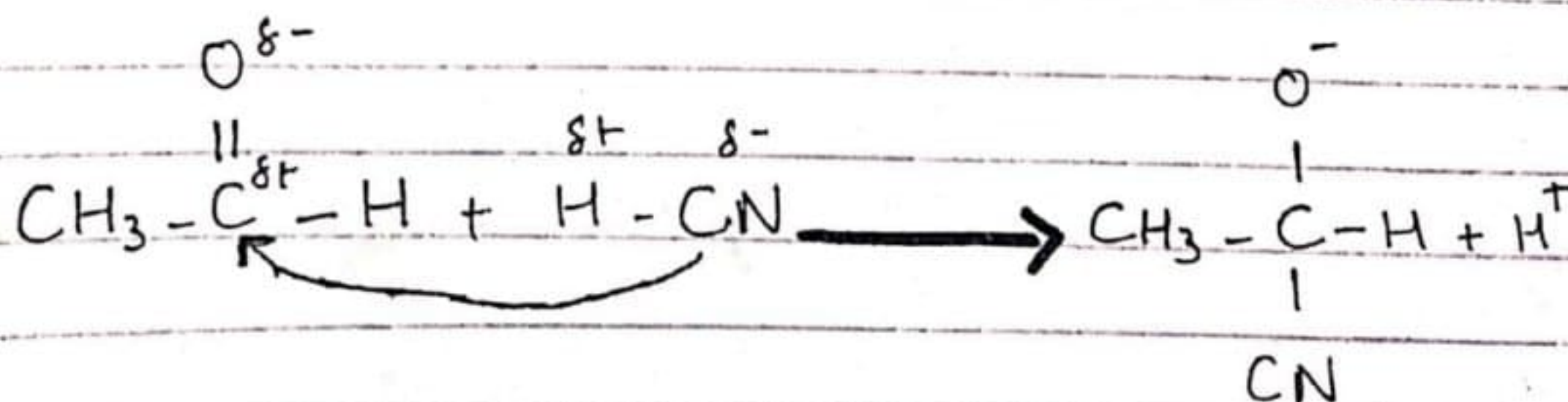
i-

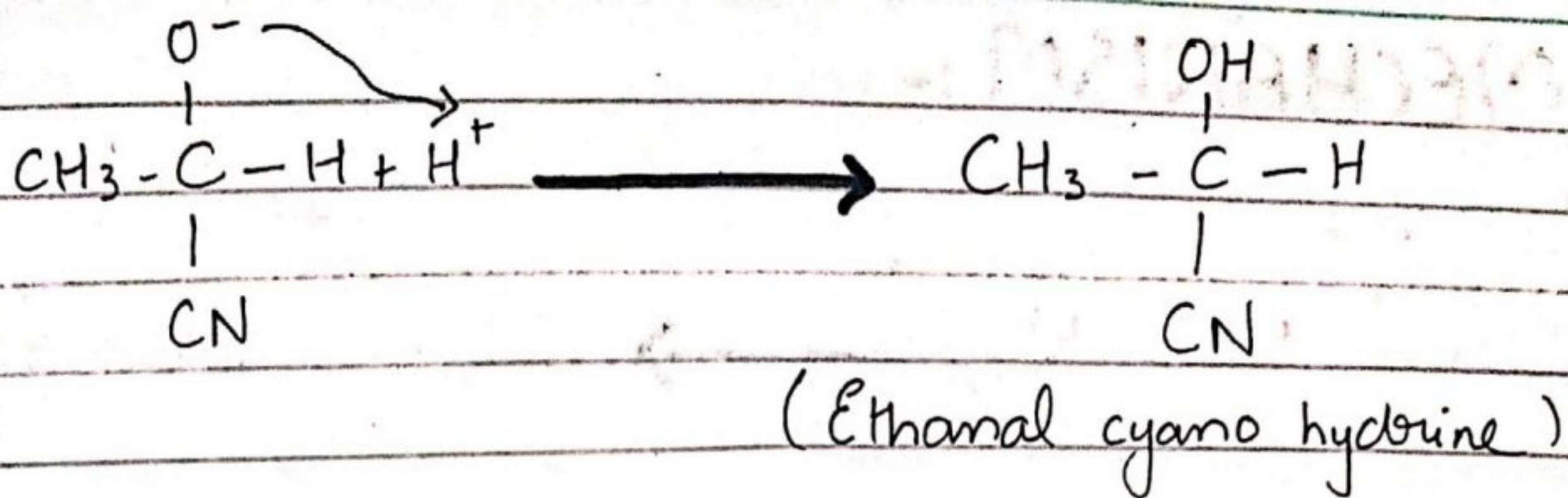


ii-



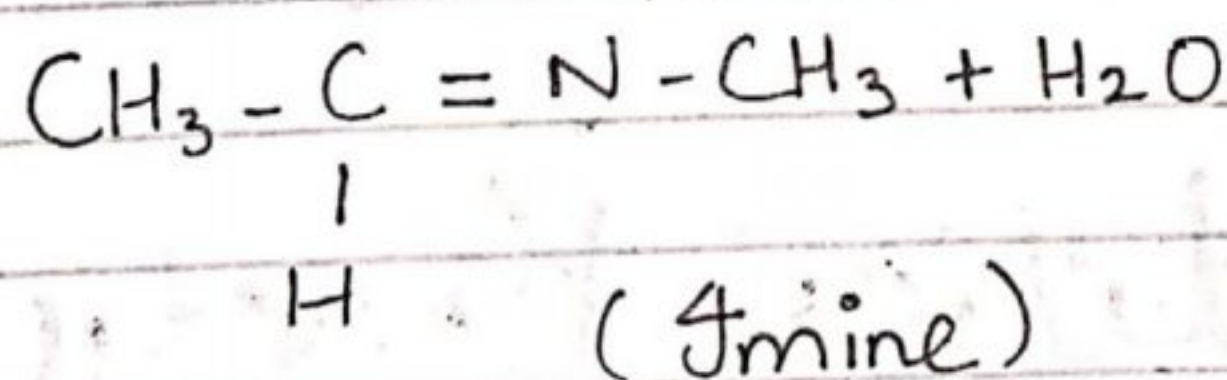
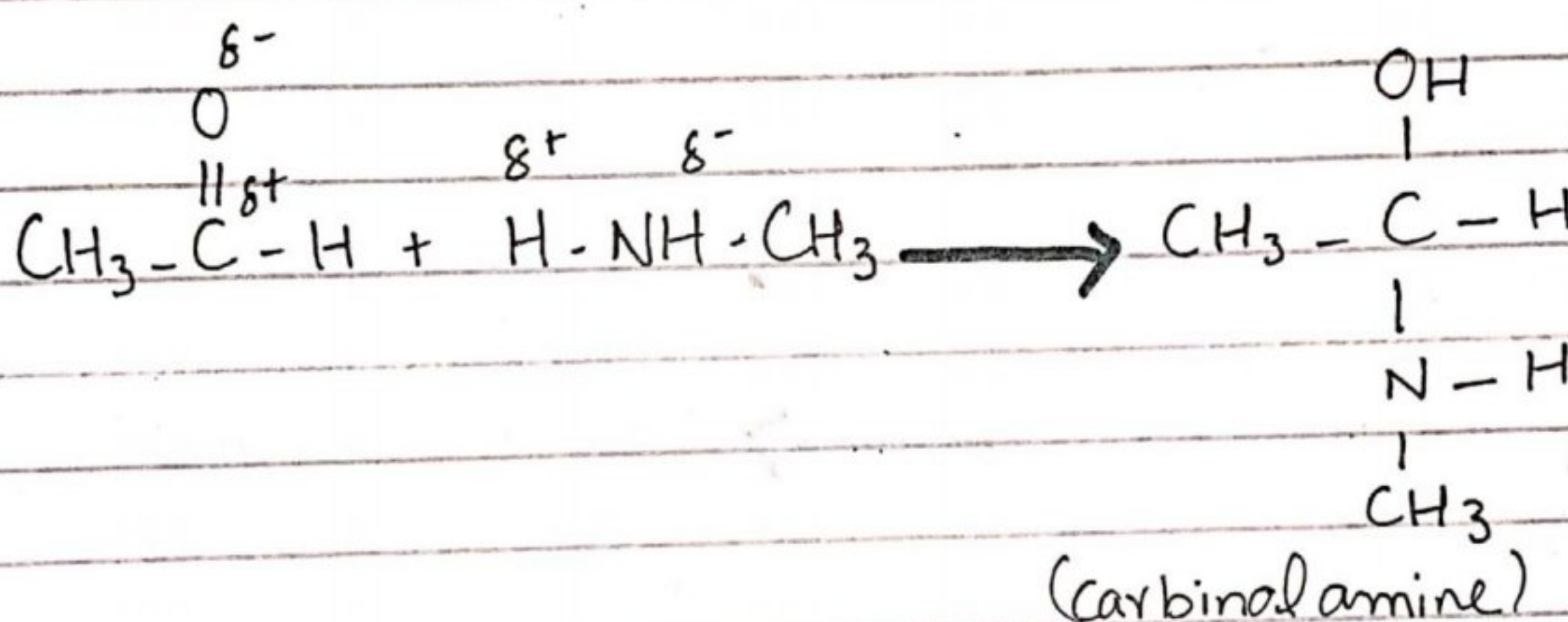
iii - Using Carbon Nucleophile (Nu^-):.



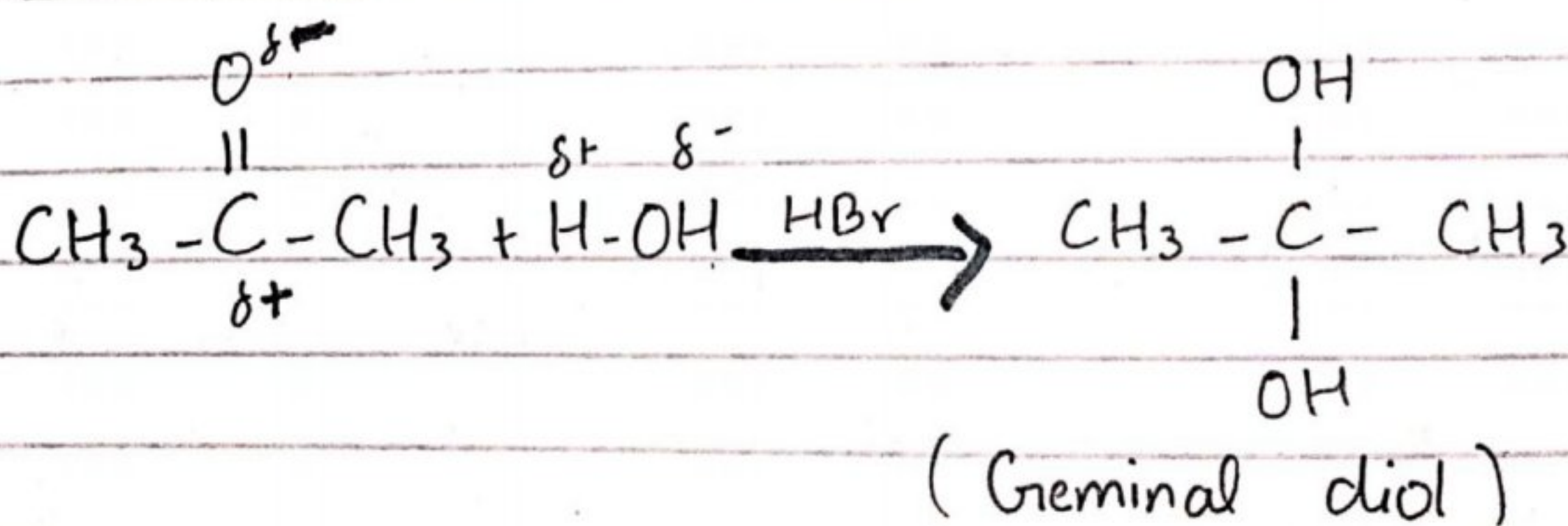


iv.

USING NITROGEN Nu

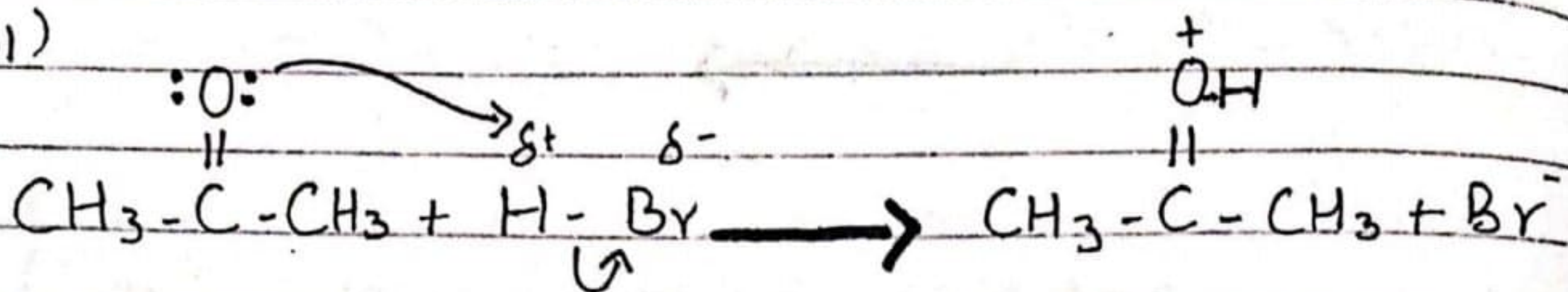


v:- Using Oxygen Nucleophiles :-

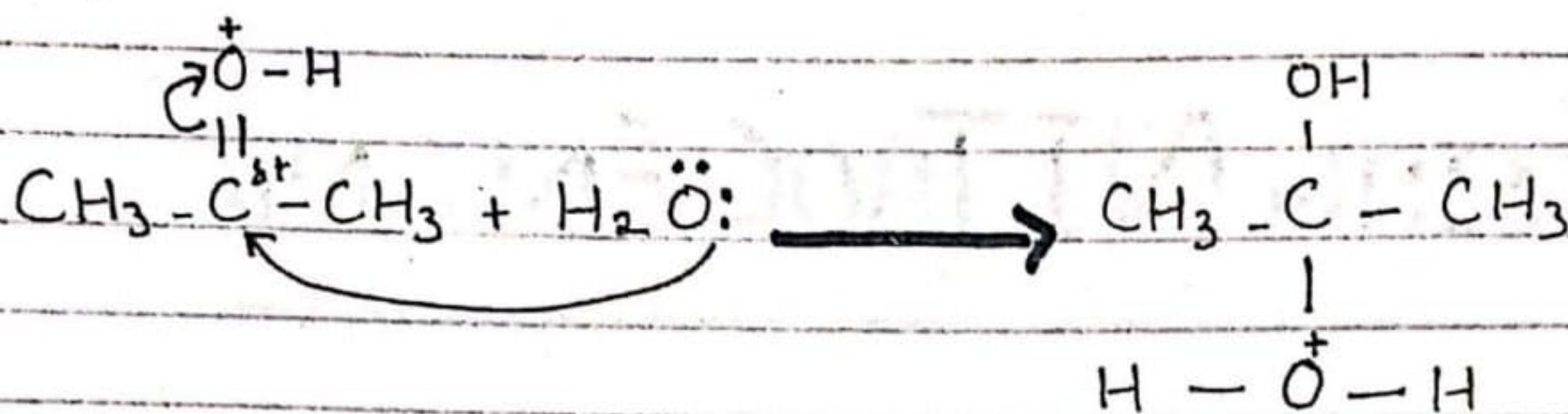


MECHANISM:-

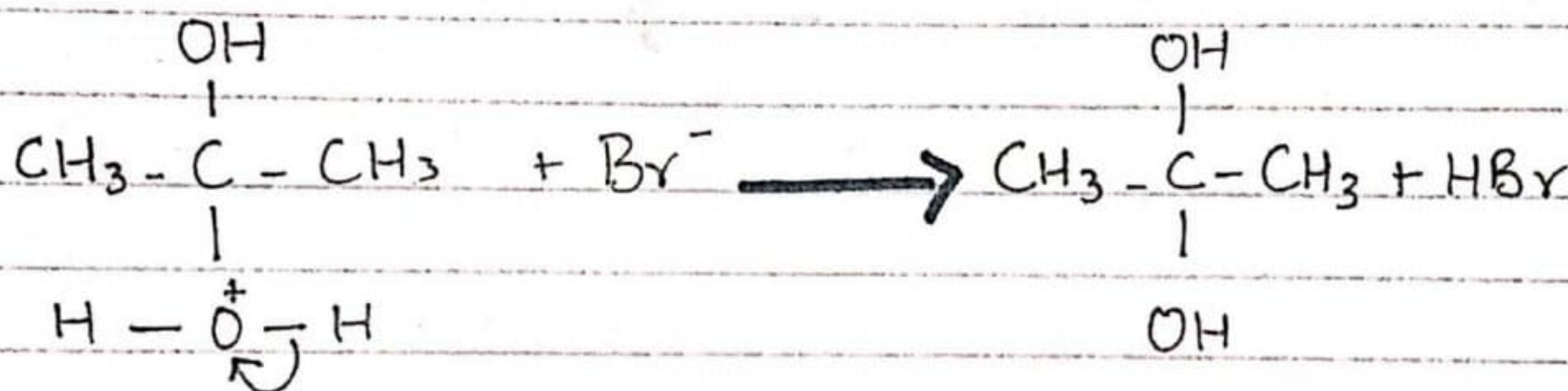
Step 1)



Step 2



Step 3 :-



*

Oxidation Reactions

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i) Oxidation of ALDEHYDE :-

Aldehydes are oxidized into their corresponding carboxylic acid in presence of strong oxidizing agent as well as mild oxidizing agent.

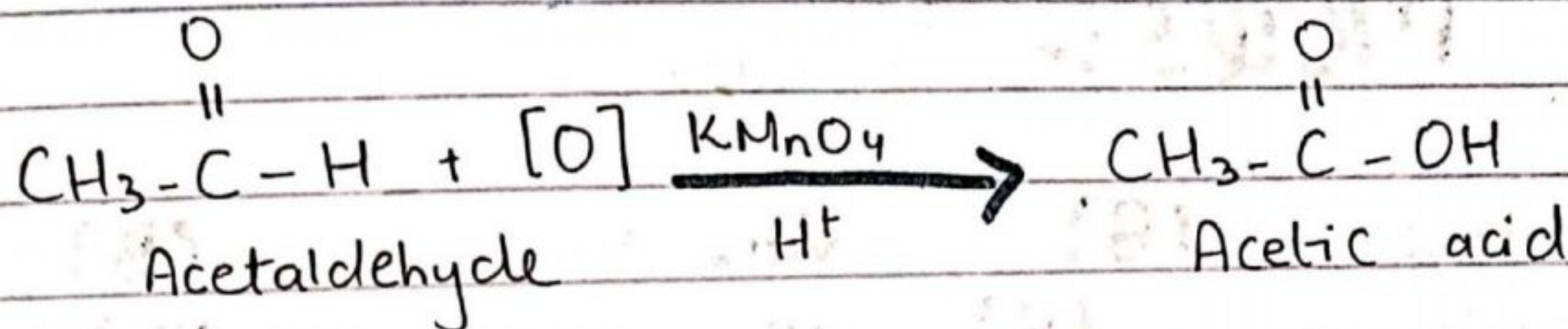
Strong Oxidizing agents

- 1- $K_2Cr_2O_7 / H_2SO_4$
- 2- $KMnO_4 / H_2SO_4$
- 3- Dil. HNO_3

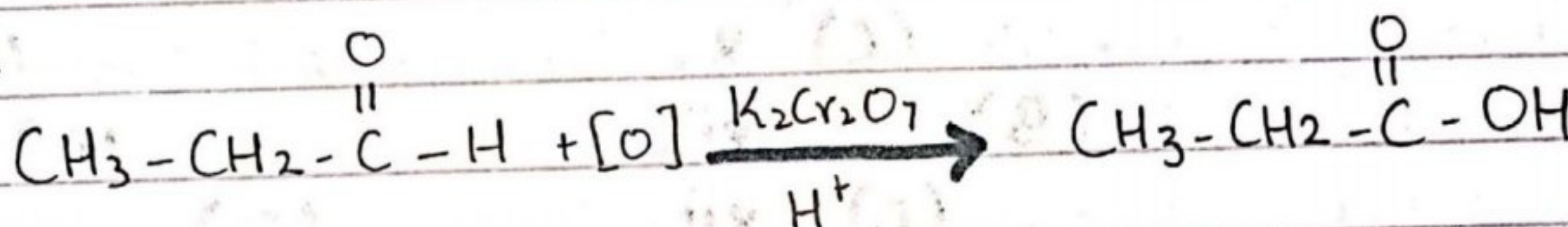
Mild oxidizing agents

- 1- Tollen's Reagent
($AgNO_3 + NH_4OH$)
- 2- Fehling's solution test
- 3- Benedict's solution test

i-



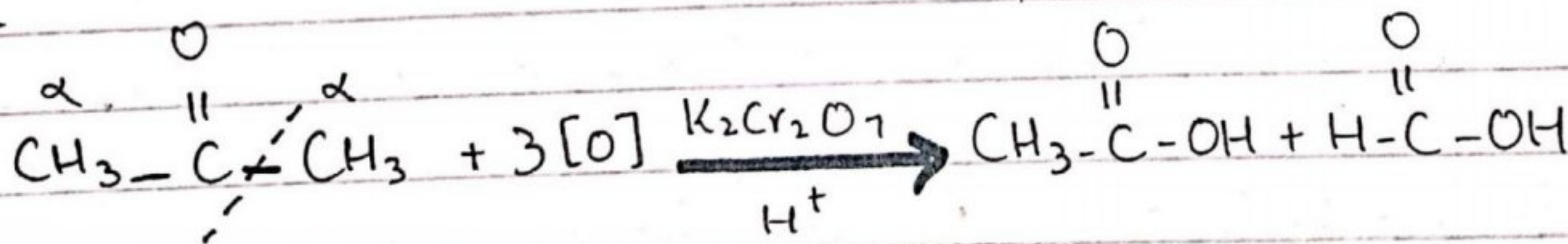
ii-



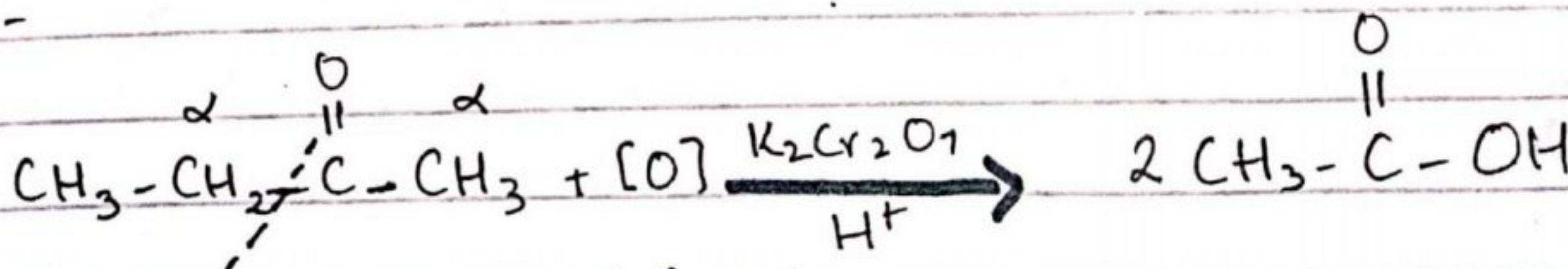
ii- Oxidation of Ketones

Ketones does not oxidize with mild oxidizing agent because high energy is required to break carbon-carbon bond. However, ketones are oxidized in presence of strong oxidizing agent and form mixture of carboxylic acid. Reaction proceed with oxidative cleavage.

i-



ii-



END

EXERCISE

Q₁: MCQs:- (answers)

i - sp^2 hybridized (B)

ii - Secondary alcohol (B)

iii - Nucleophilic addition (C)

iv - Acetaldehyde (B)

v - Grignard Reagent (A)

vi - pri - alcohols (A)

vii - 3-pentanone (D)

viii - Aldehydes Only (B)

ix - Acetaldehyde (B)

x - Having no α -hydrogen (A)

xi - Phenyl hydrazone (B)

xii - $C_nH_{2n}O$ (A)

xiii - Yellow (C)

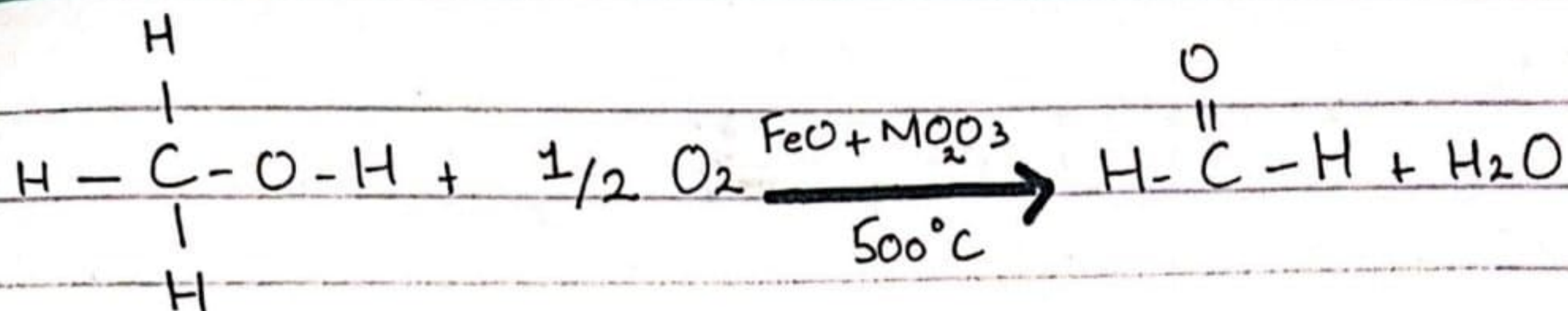
Q₂. Give brief answers of following questions?

(Part i)

Q: How is formaldehyde prepared industrially?

Ans. Industrial preparation of formaldehyde (Formalin):
or methanal:-

Formaldehyde is manufactured by passing an mixture of methanol vapours and air over iron oxide - molybdenum oxide or Ag catalyst at 500°C .



Formaline is a mixture of 40% formaldehyde, 8% methyl alcohol and 52% water.

(Part ii)

Q:- Describe briefly nucleophilic addition mechanism to carbonyl compounds?

Ans:- Both mechanism of acid catalysed and base catalysed nucleophilic addition is written.

Base catalysed is on page no # 9

Acid catalysed is on page no # 19

(Part iii)

Q

What is the mechanism of HCN addition to carbonyl compound?

Ans:

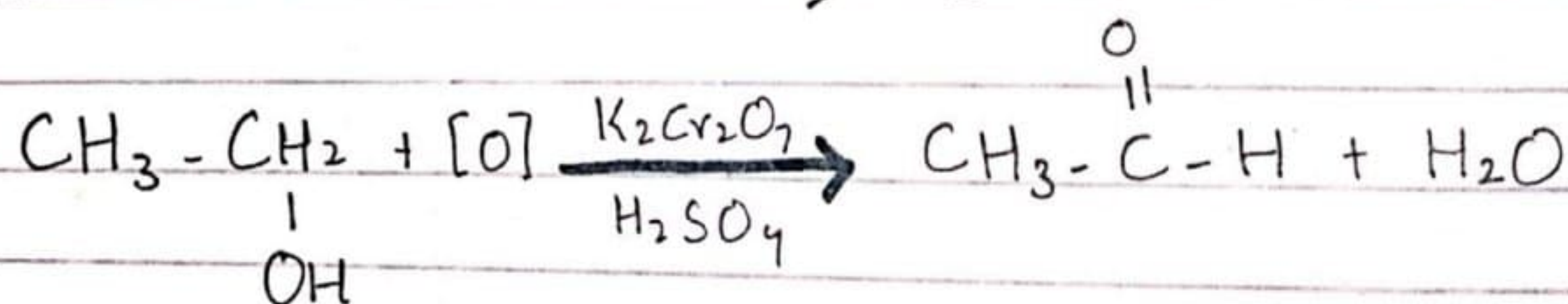
Ans is on page no # 10

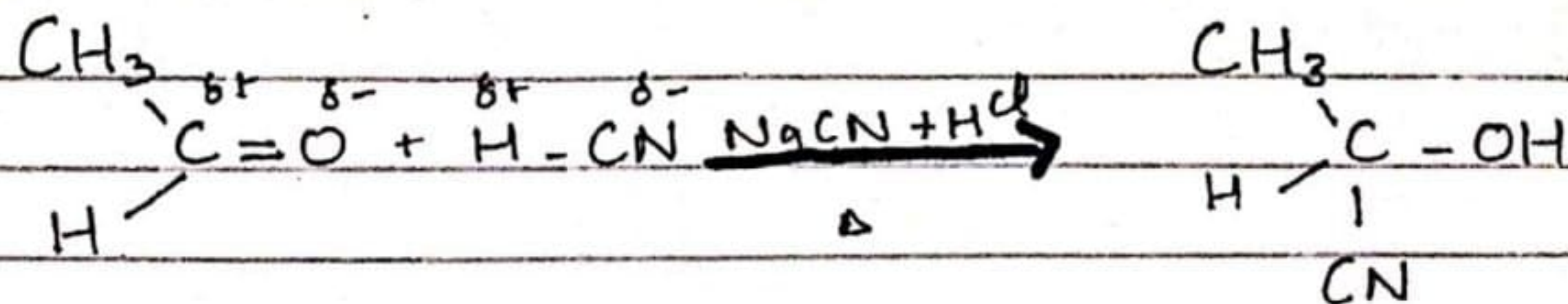


(Part iv)

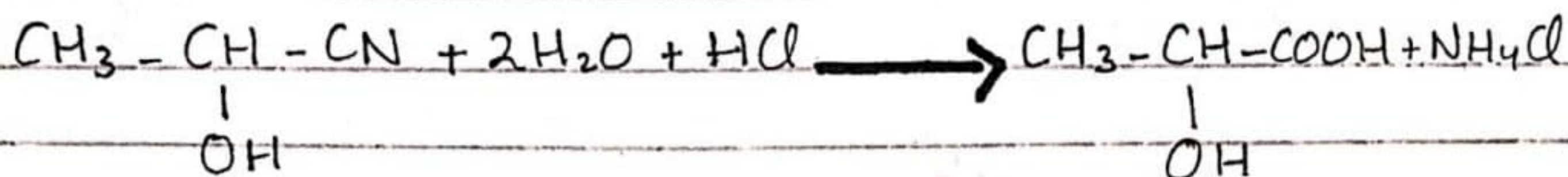
Q How is ethanal converted to lactic acid?

Ans:- Ethanol $\longrightarrow$ Lactic acid





(cyano hydrine)



(Lactic acid)



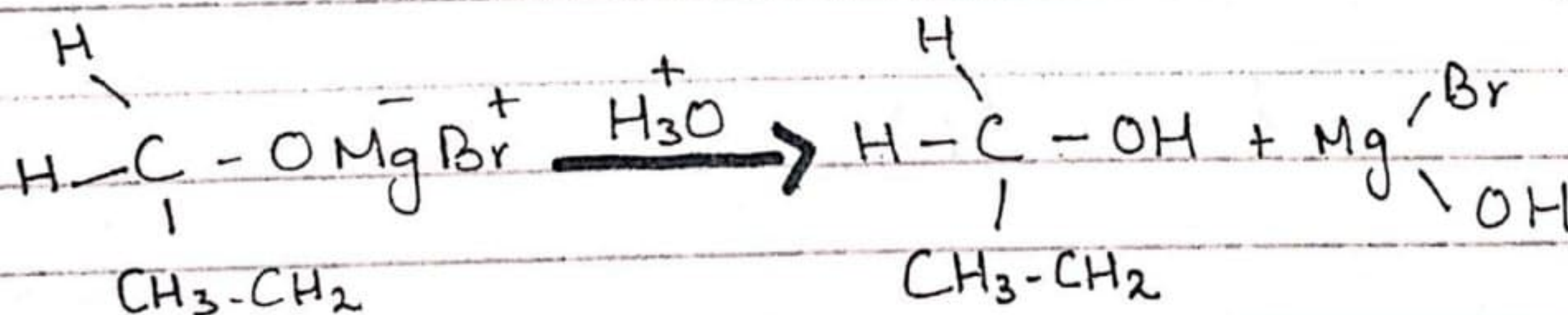
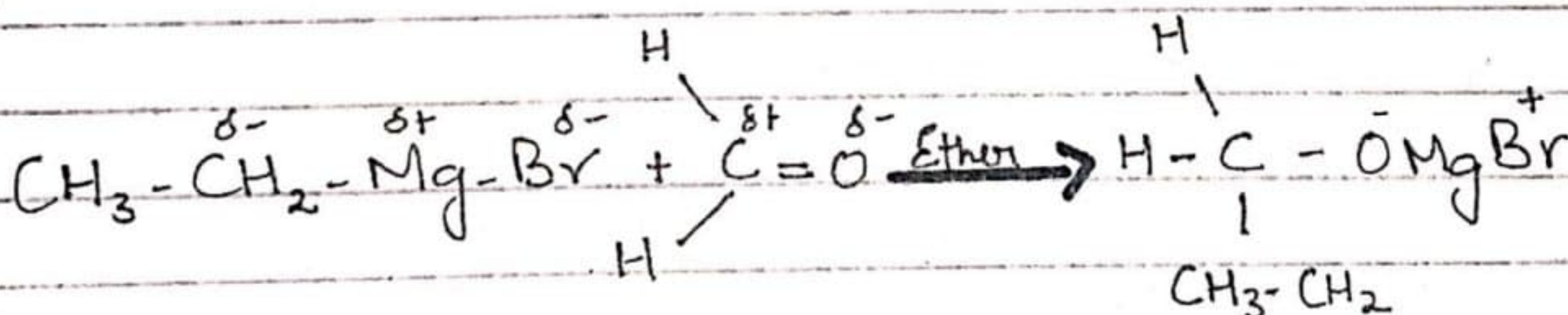
(Part v)

Q:- What is the addition product of grignard reagent to formaldehyde, acetaldehyde and ketone?

Ans:

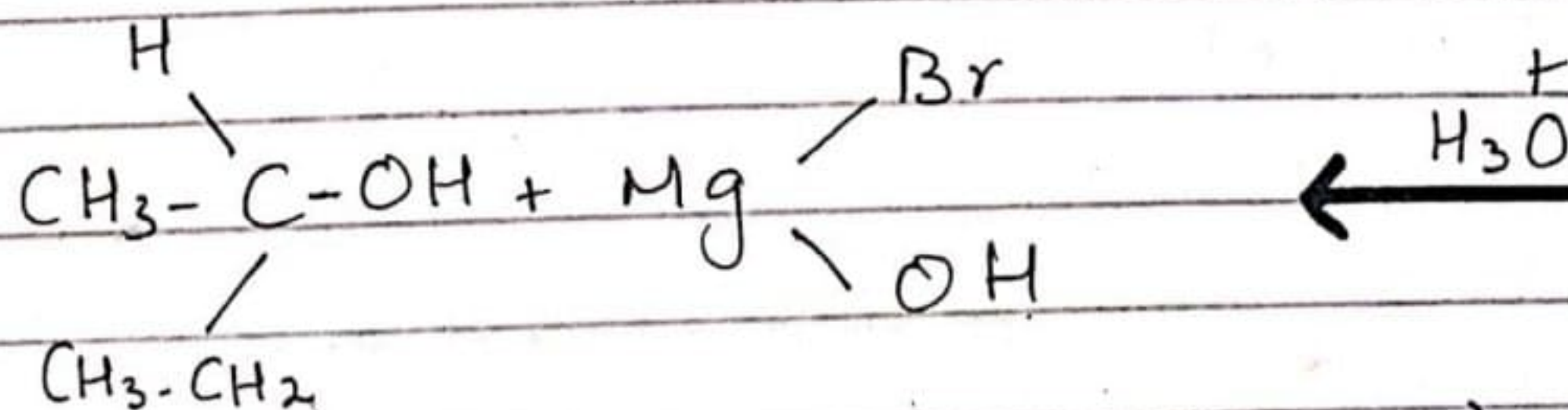
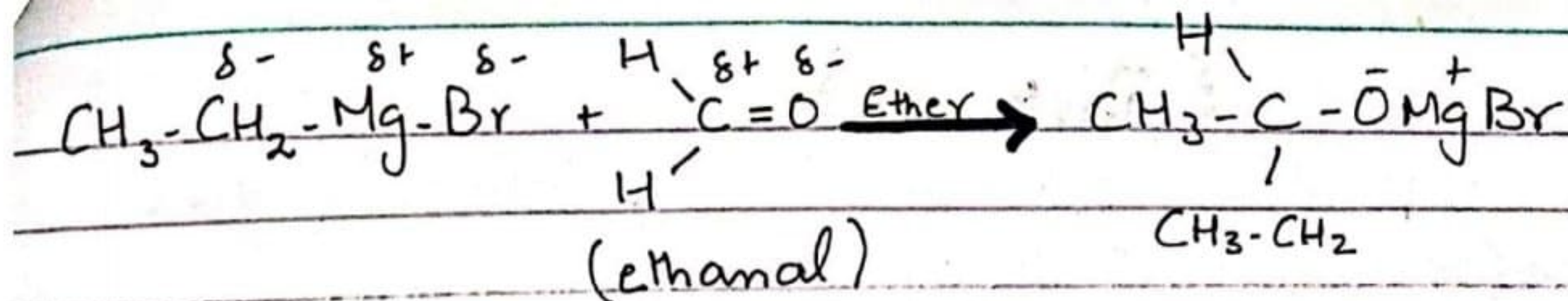
1. GRIGNARD REAGENT TO FORMALDEHYDE :-

i-



1-propanol (Pri. alcohol)

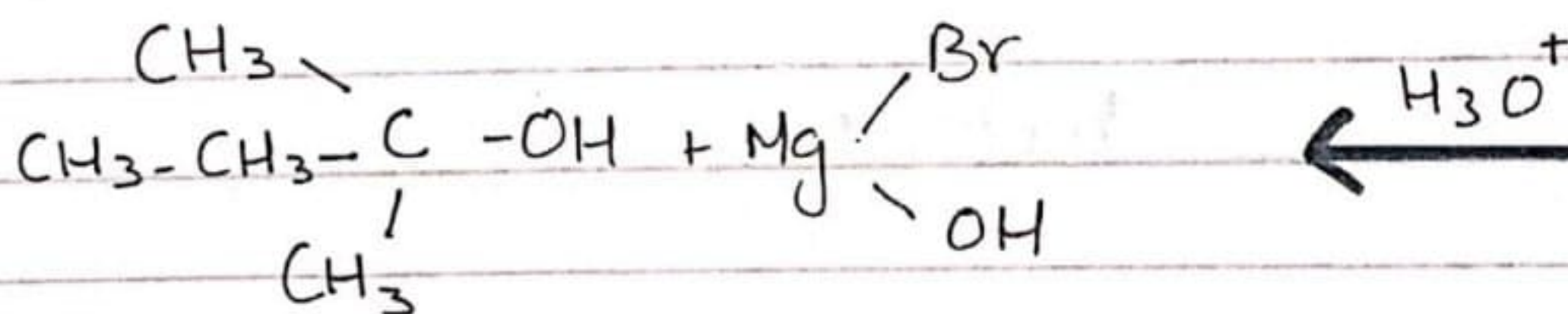
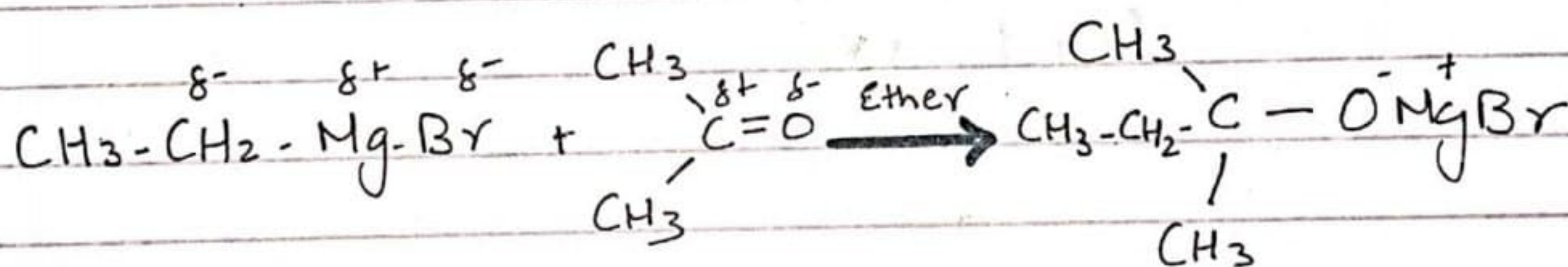
2. GRIGNARD REAGENT TO ACETALDEHYDE



2 Butanol (Sec. alcohol)

iii) GRIGNARD REAGENT

TO KETONE



2 methyl - 2 butanol (Ter alcohol)

(Part vi)

Ans: Q What is Haloform reaction?
See answer on page no # 16

(Part vii)

Q Which type of alcohols undergo iodoform reaction?

Ans.

Secondary alcohols -

See answer on pg # 17



(Part viii)

Q How are methanol and ethanol polymerized?

Ans.

See answer on pg # 20

(Part ix)

Q Why formaldehyde do not give aldol condensation reaction?

Ans.

See answer on pg # 12

(Part x)

Q:- Give the mechanism of addition of sodium bisulphite to ketone?

Ans

Ans is on pg # 11

Q3 Give detailed answer of following questions?

(Part i)

Q:- What is the reactivity of the carbonyl compounds?

Ans.

Ans is on page # 8



(Part ii)

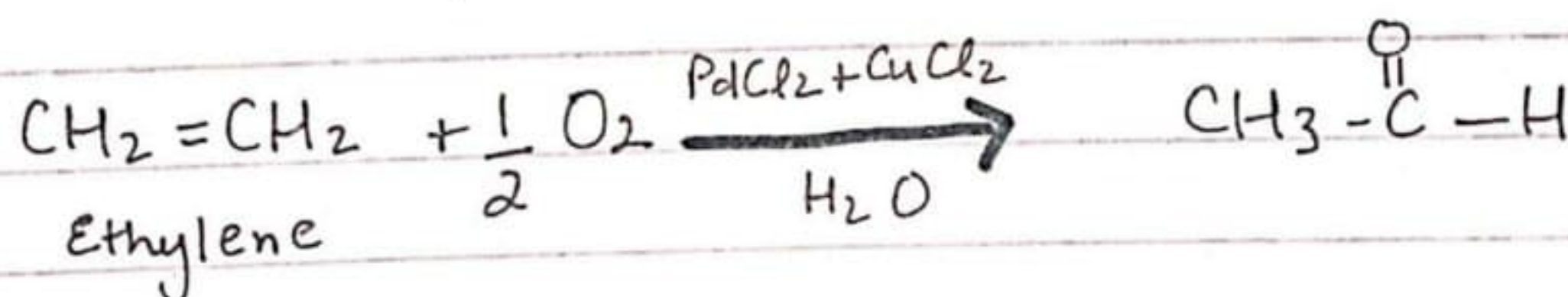
Q How will you prepare formaldehyde and acetaldehyde on industrial scale?

Ans.

i- Preparation of formaldehyde is Ans of short question no (i) on pg # 31

ii-

Industrial preparation of acetaldehyde :-



(Part iii)

Q How formaldehyde reacts with following

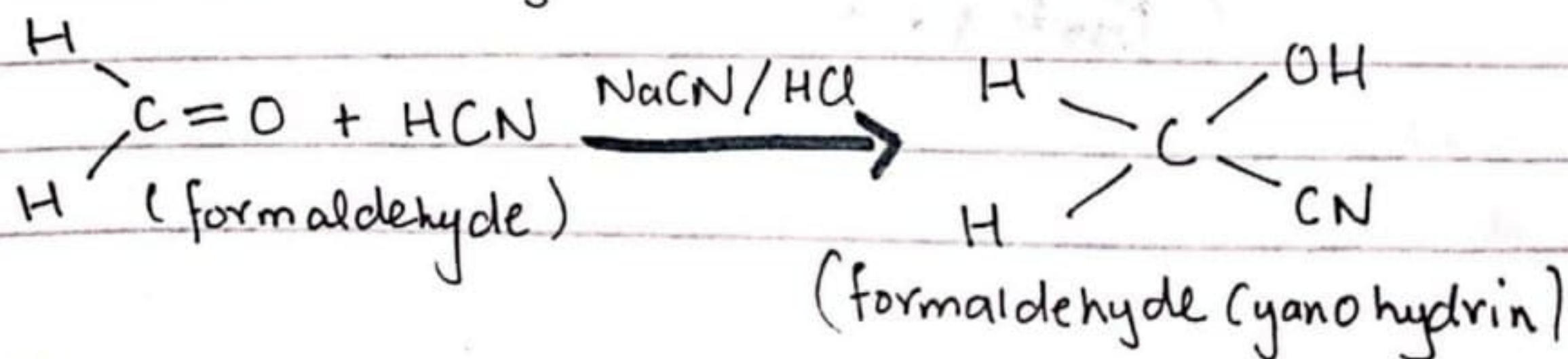
i- HCN

ii- H₂SO₄

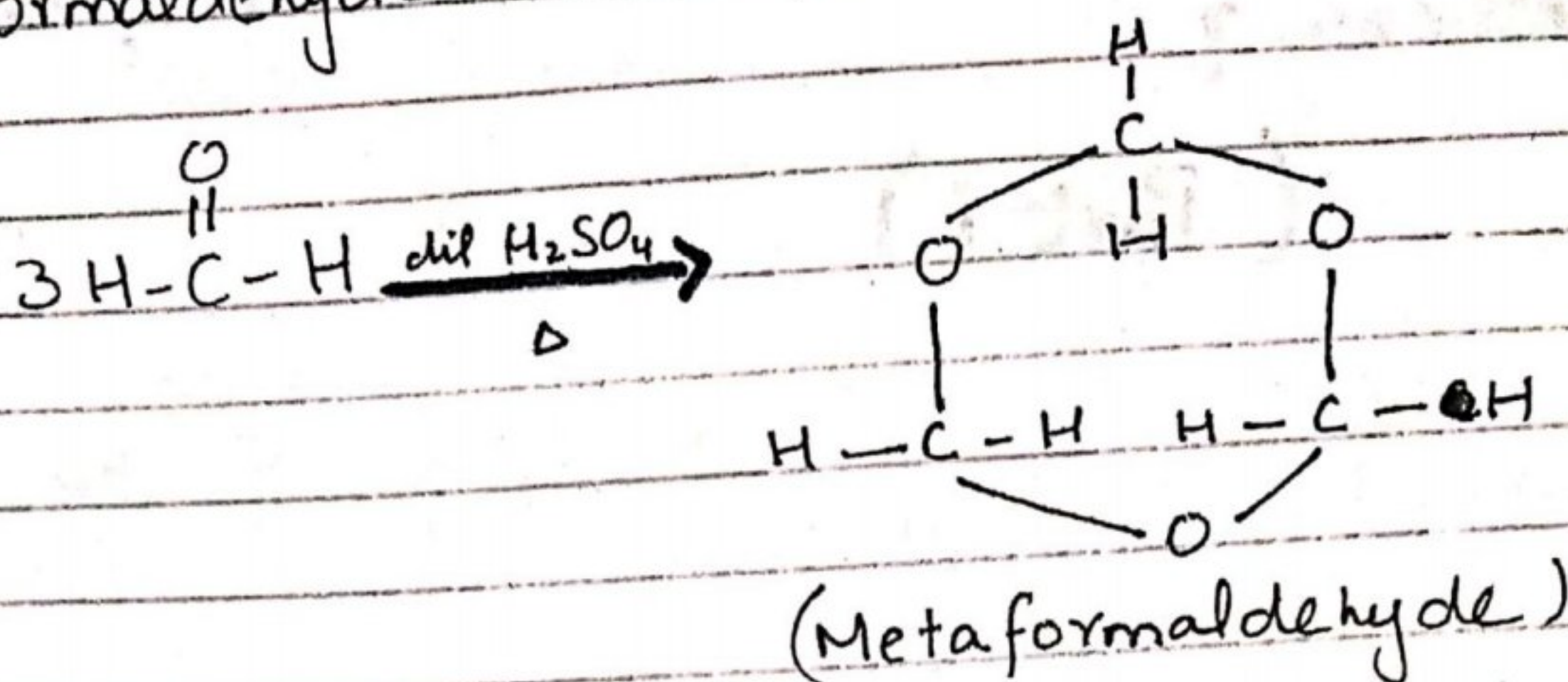
iii- NaHSO₃

Ans :-

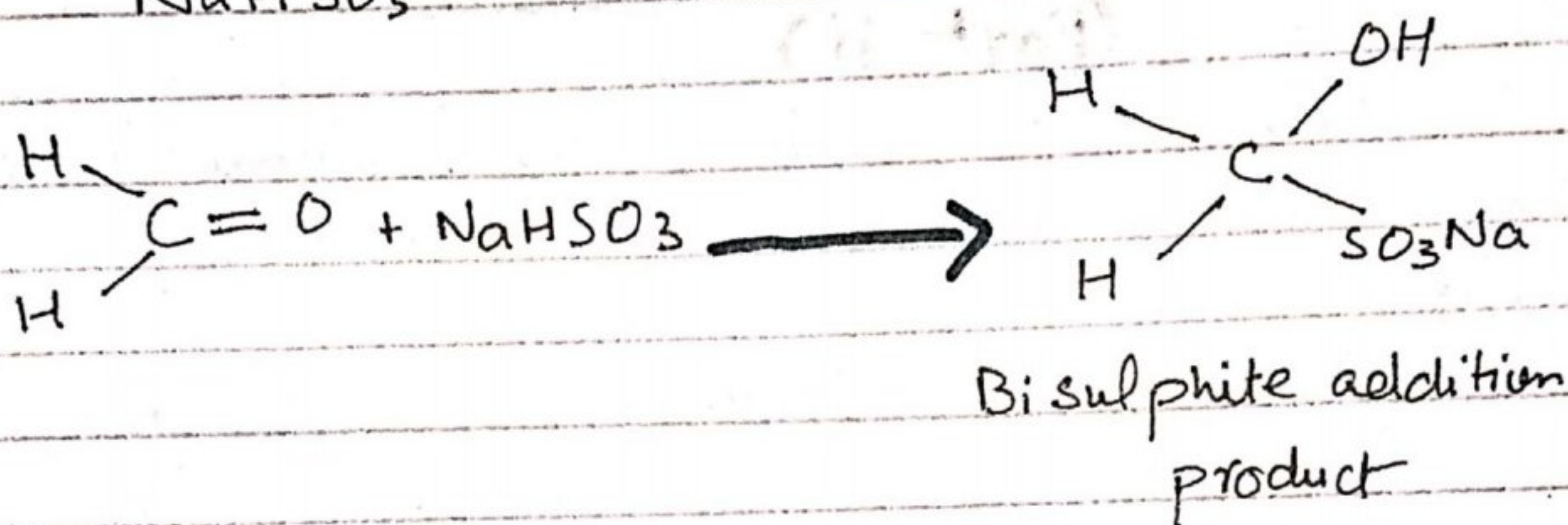
i- Formaldehyde reacts with HCN :-



ii. Formaldehyde reacts with H_2SO_4 .



iii - Formaldehyde reacts with $NaHSO_3$



(Part iv)

Q Define and explain aldol condensation with mechanism?

Ans :- See Ans on page # 12

(Part v)

Q Give detail of haloform reaction? Why it is called so?

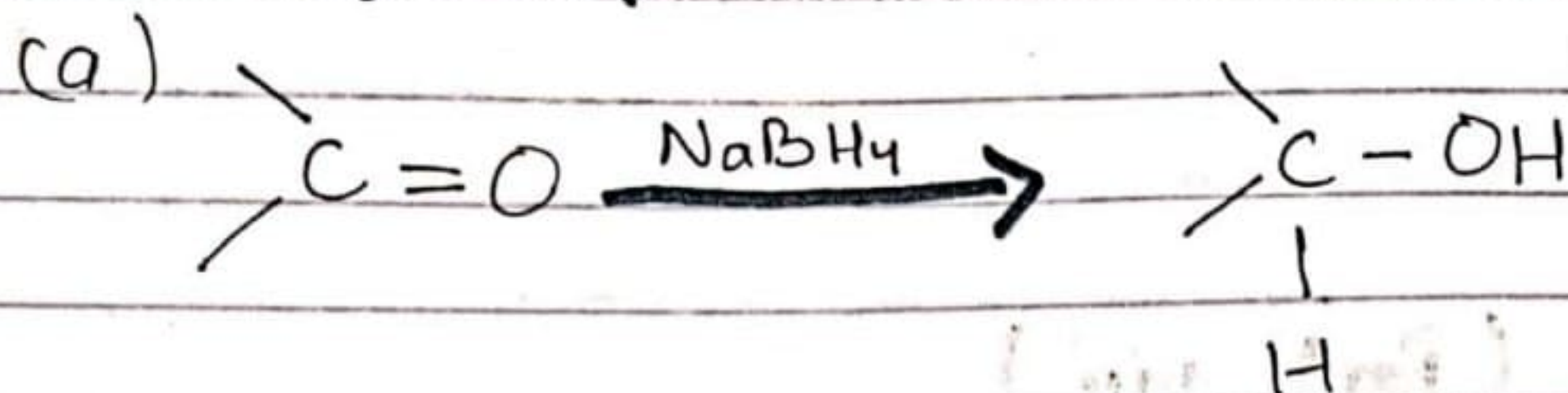
Ans :- See Ans on page # 16

(Part vi)

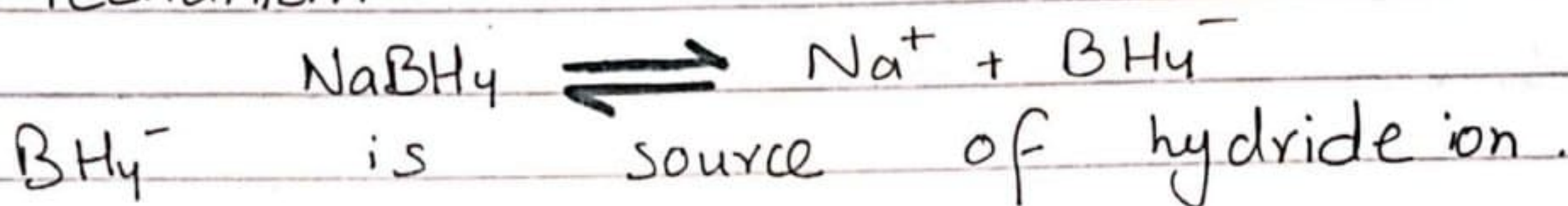
Q Give the following reductions of aldehydes and ketones along with

mechanism? a) NaBH_4 b) catalytic reduction?

Ans: NaBH_4



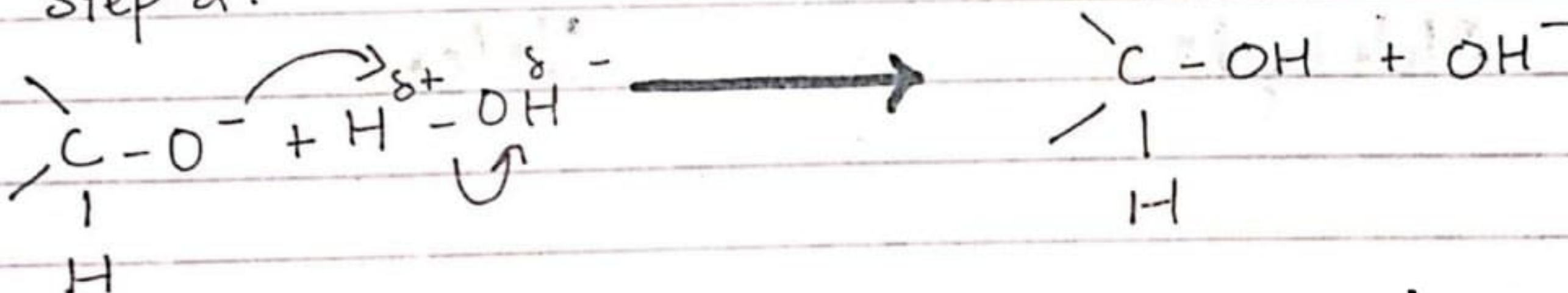
Mechanism:



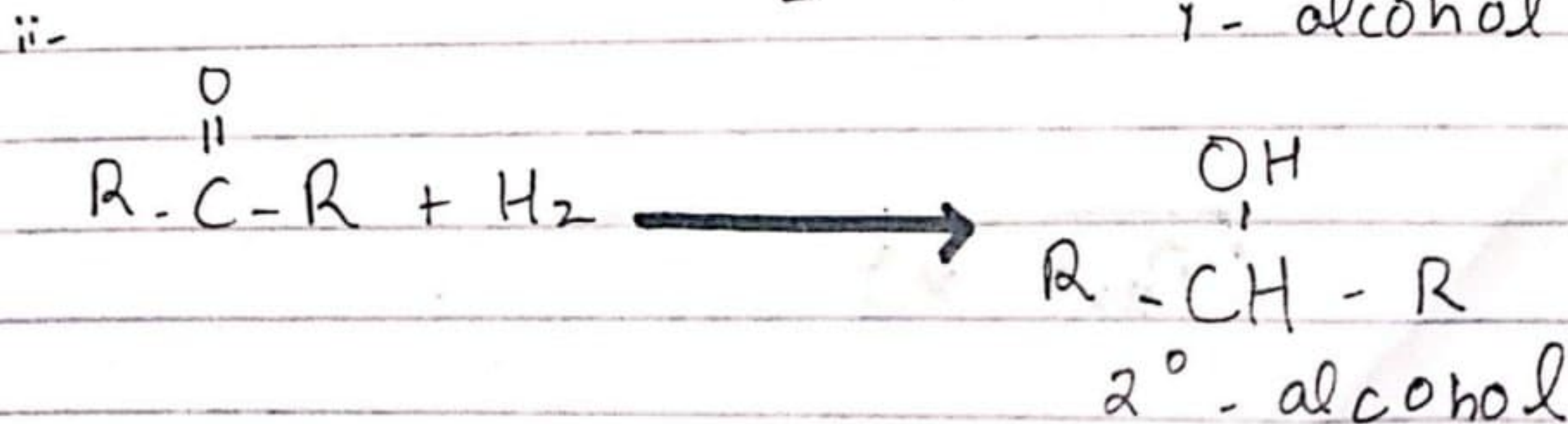
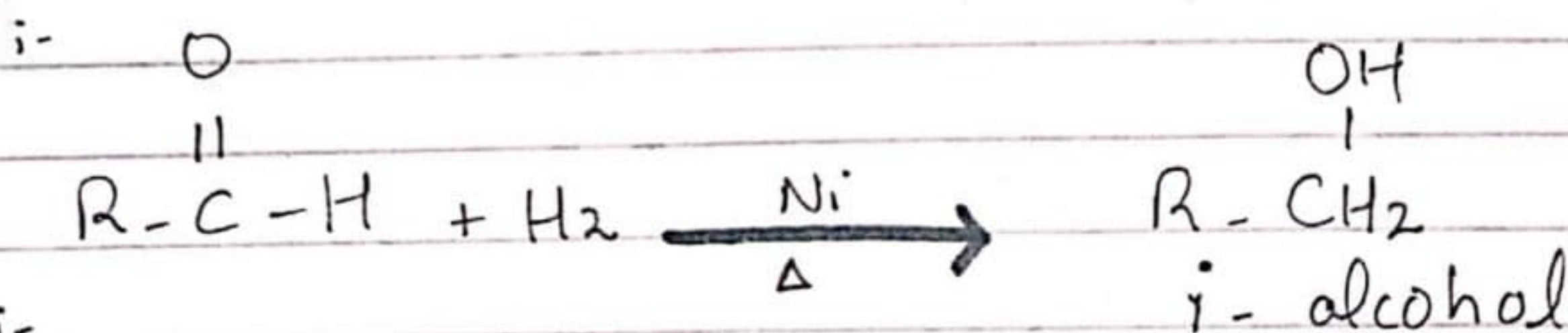
Step 1:-



Step 2:



b) Catalytic reduction:-



(Part vii)

Q What is mechanism for addition of ammonia derivatives of carbonyl group?

Ans :

Ans is on page # 24

(Part viii)

Q Which type of aldehyde give canizzaro's reaction? Explain the mechanism?

Ans :

Ans is on page # 15

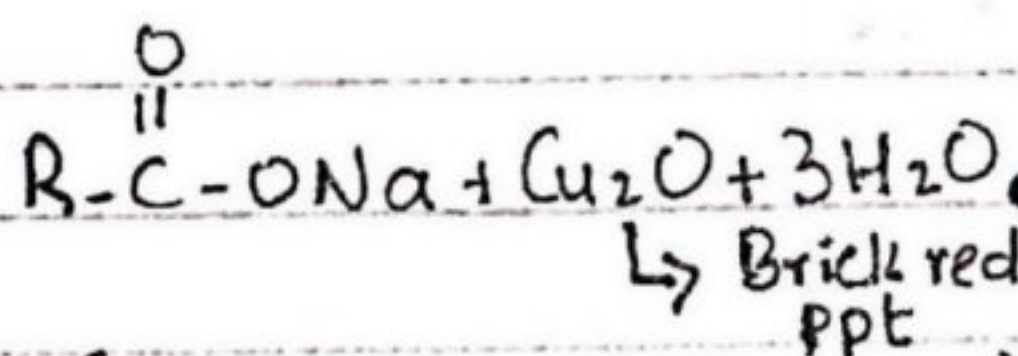
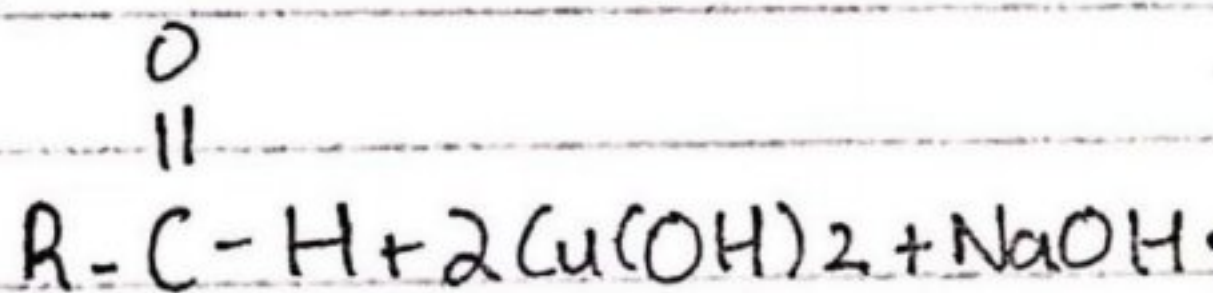
(Part ix)

Q How do you distinguish an ketone and an aldehyde by chemical method?

Ans :

Aldehyde

i)



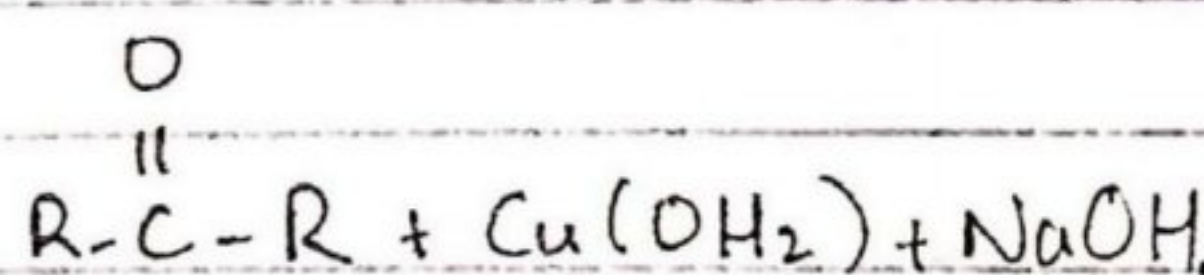
(Fehlings solution)

ii)

Strong oxidizing agent

Ketone

i)



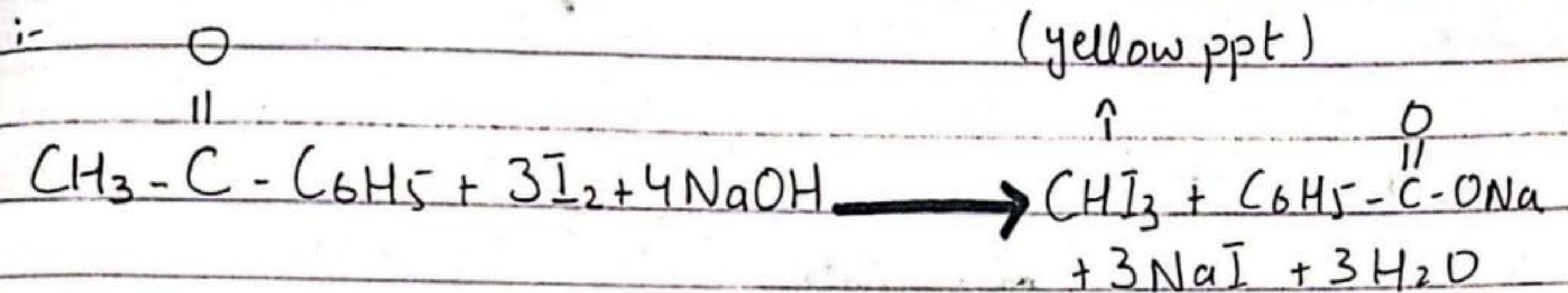
No Reaction

ii. Weak oxidizing agent.

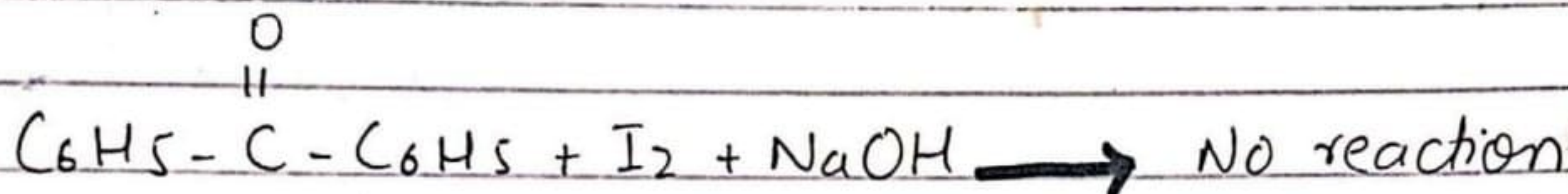
(Part x)

Q How will you differentiate b/w acetophenone and benzophenone?

Ans.



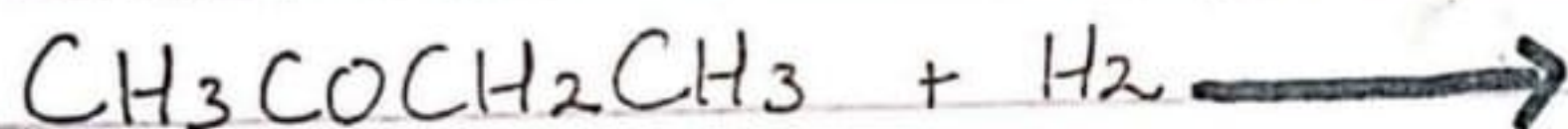
ii.



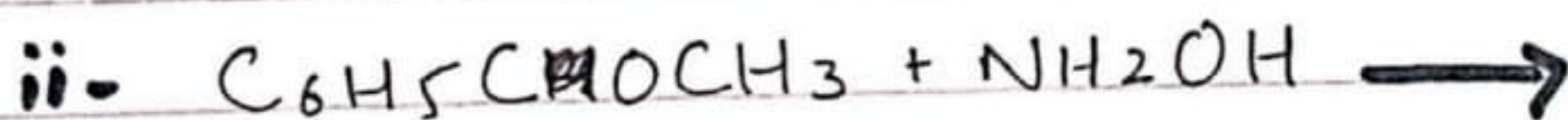
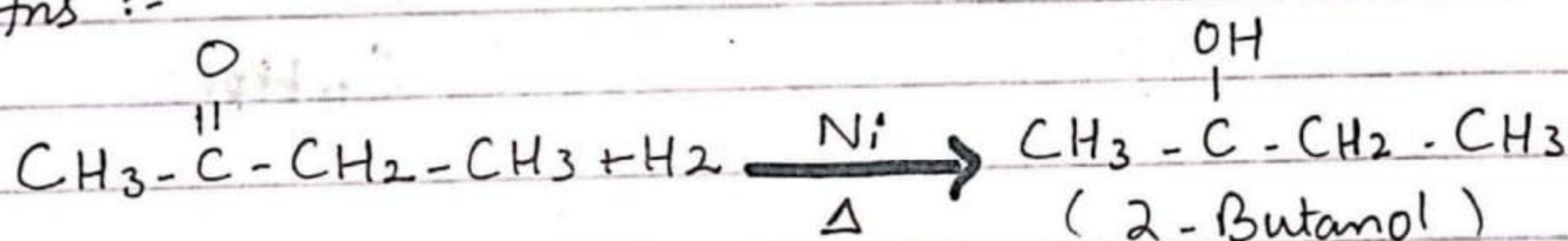
(xi) Skill Activity

Q Predict the formulas of products of following reactions?

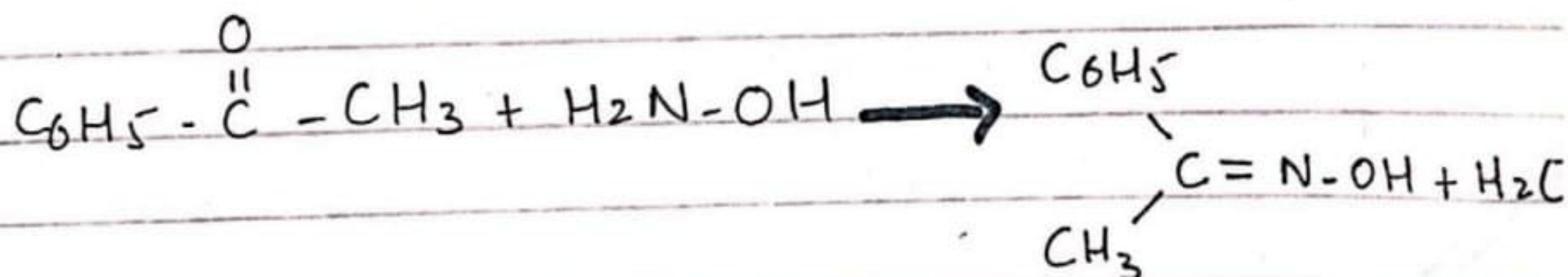
* i)



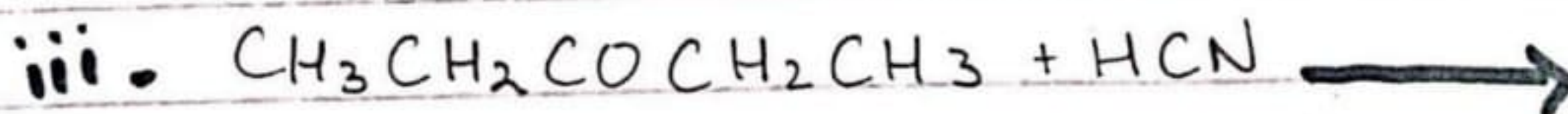
Ans :-



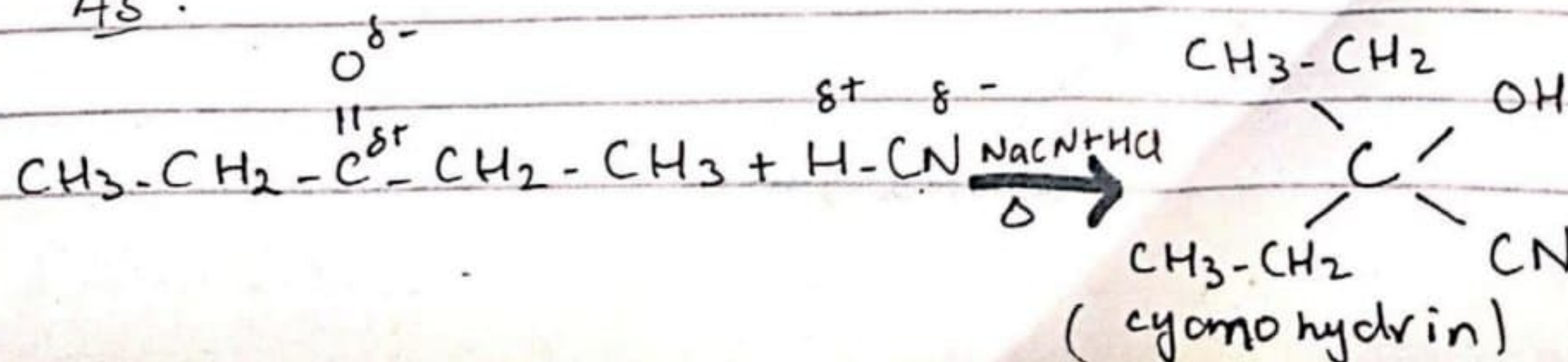
Ans

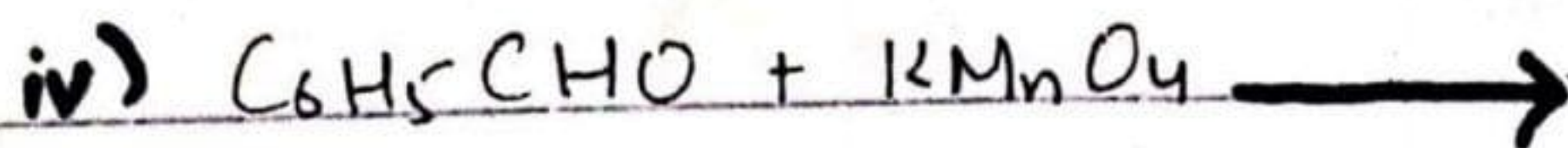


(Acetophenone oxime)

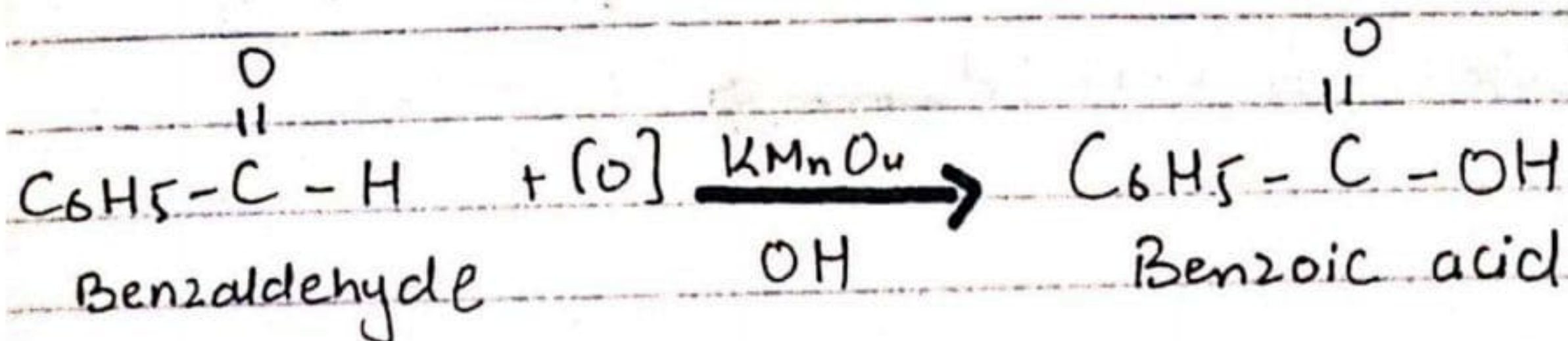


Ans.

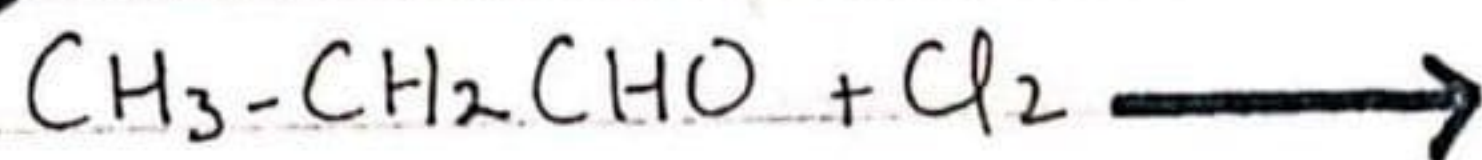




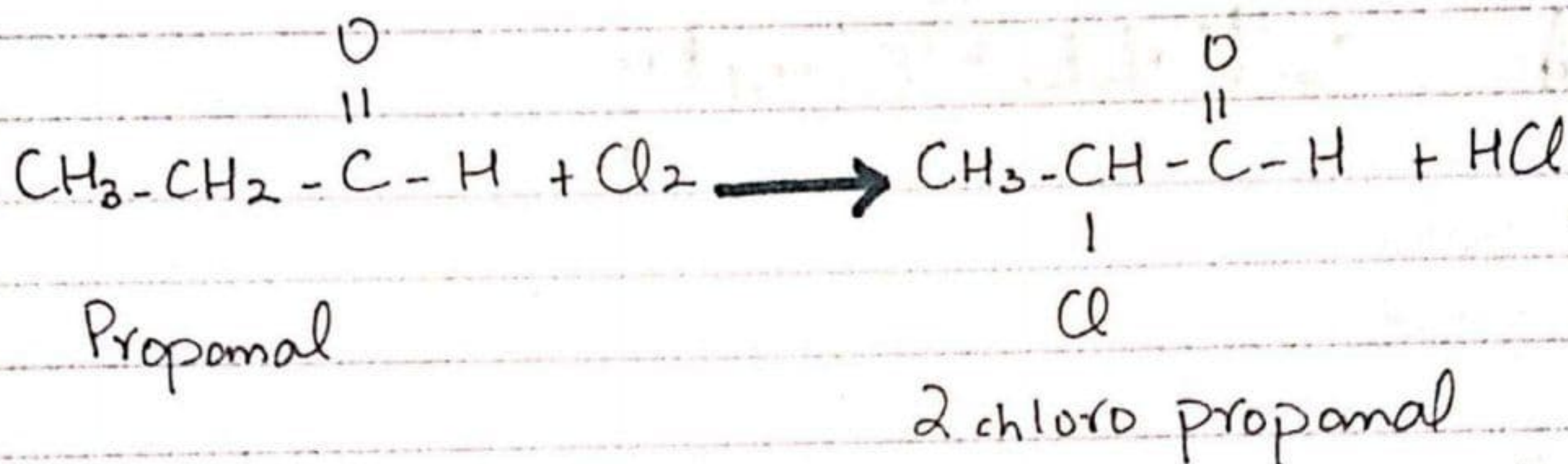
Ans.



v)



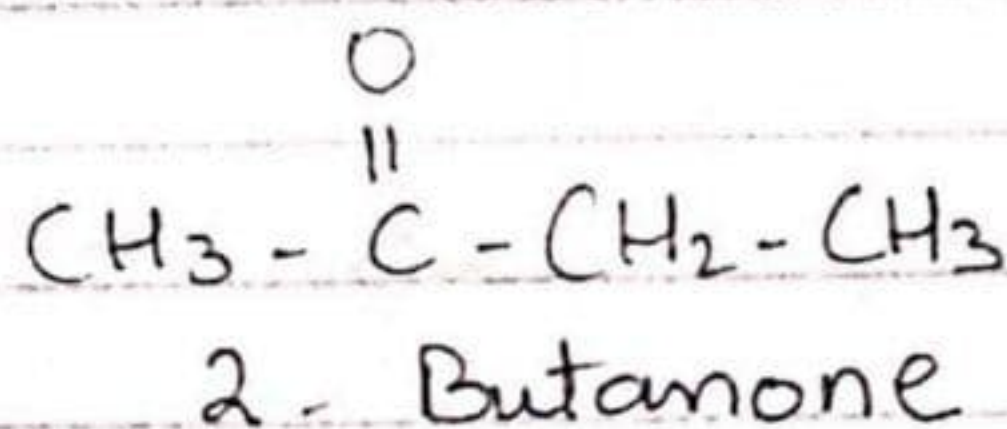
Ans:



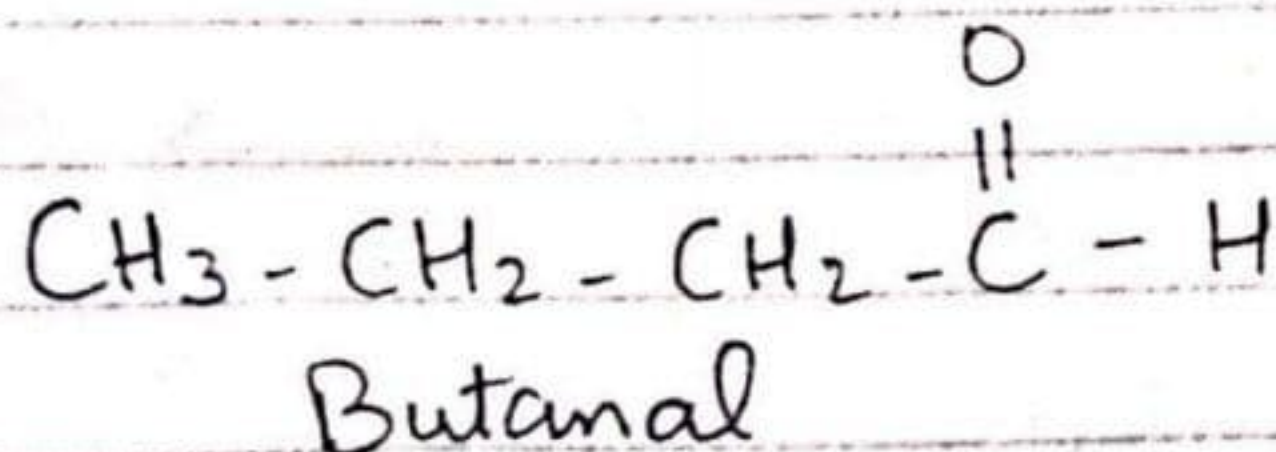
(Part xii)

Q Write structural formulas for all compounds of molecular formula $\text{C}_4\text{H}_8\text{O}$ containing carbonyl group?

Ans: i-



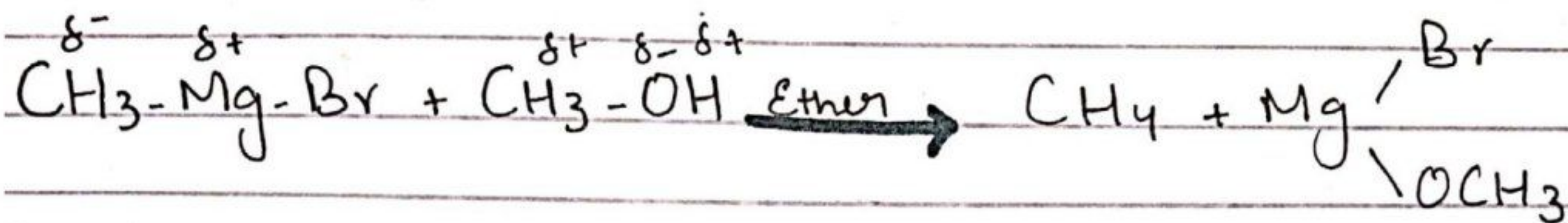
ii-



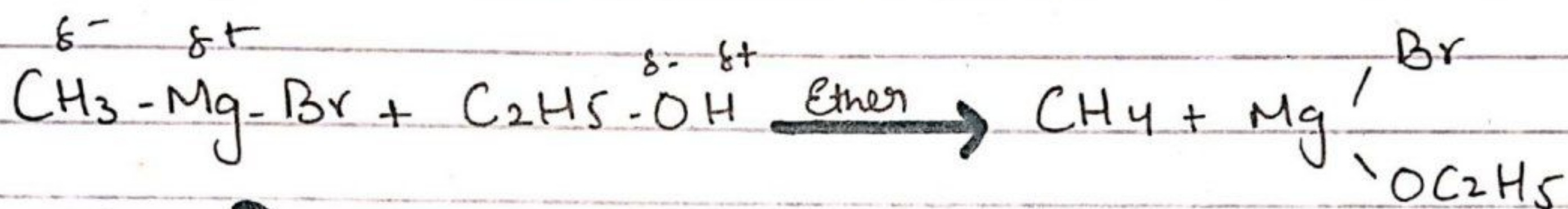
(Part xiii)

Q: Predict the formulas of compound formed when following are treated with Grignard's reagent methyl magnesium bromide followed by water?

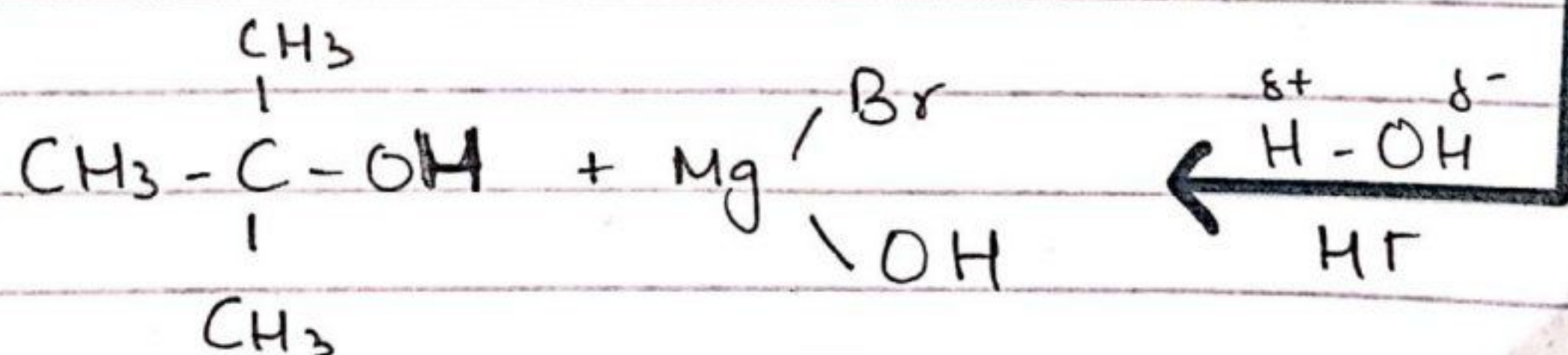
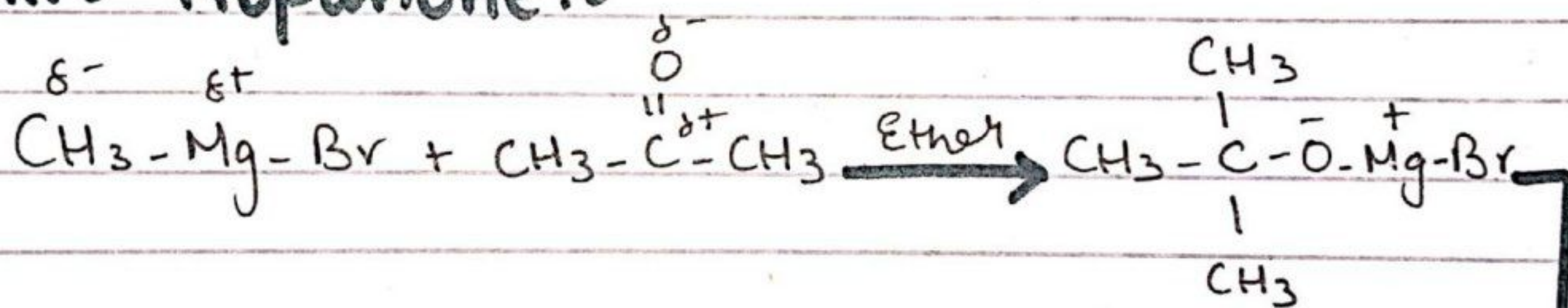
i. Methanol :-



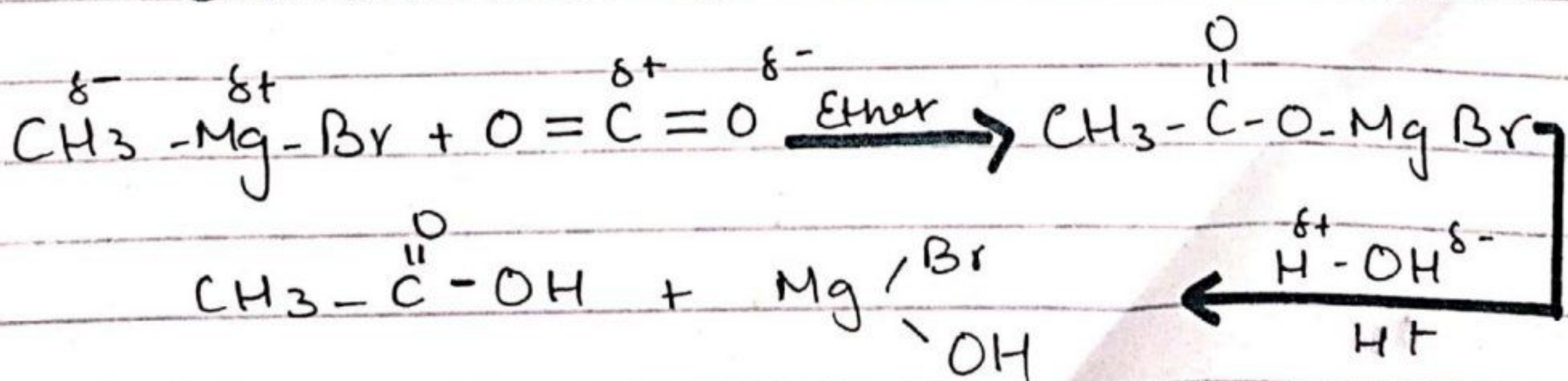
ii. Ethanol :-



iii. Propanone :-



iv. Carbon dioxide (CO₂):-



- x - x -
END 😊