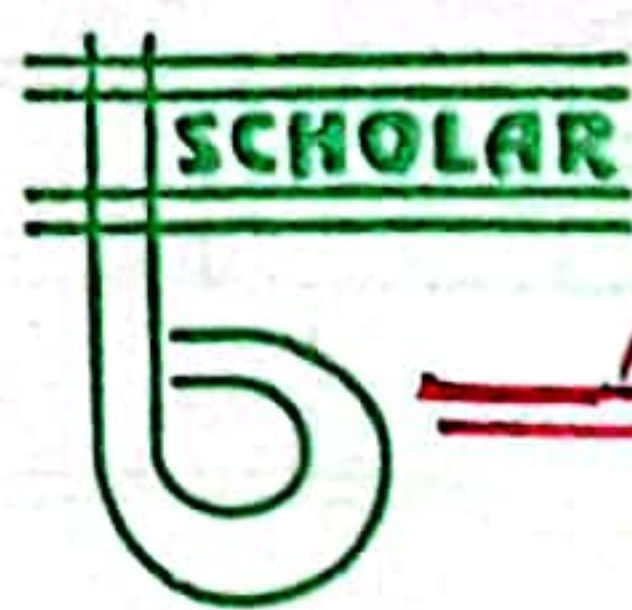


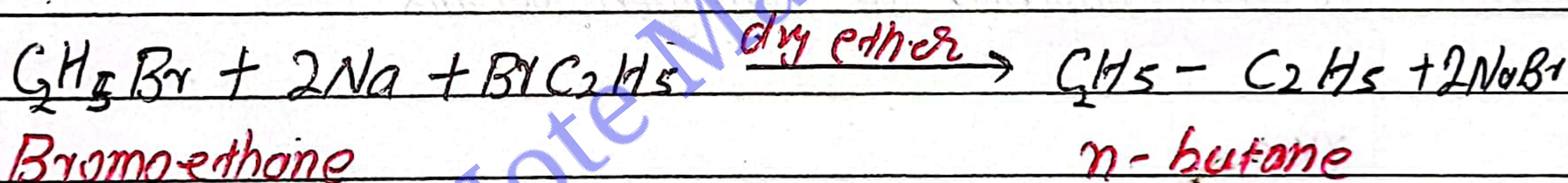
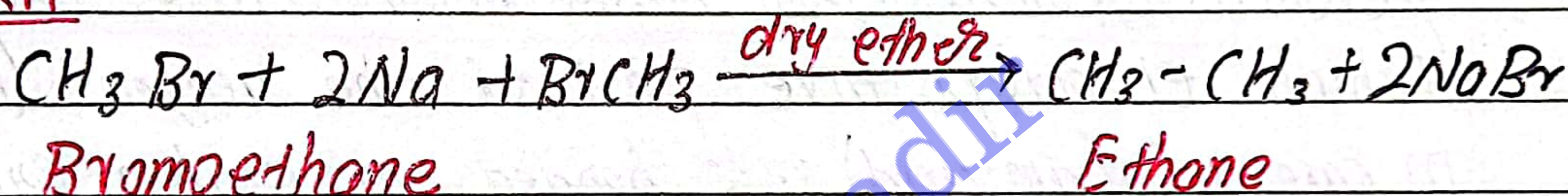


Haloalkane and Haloarene

1. Wurtz Reaction

→ Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide. This reaction is known as Wurtz reaction.

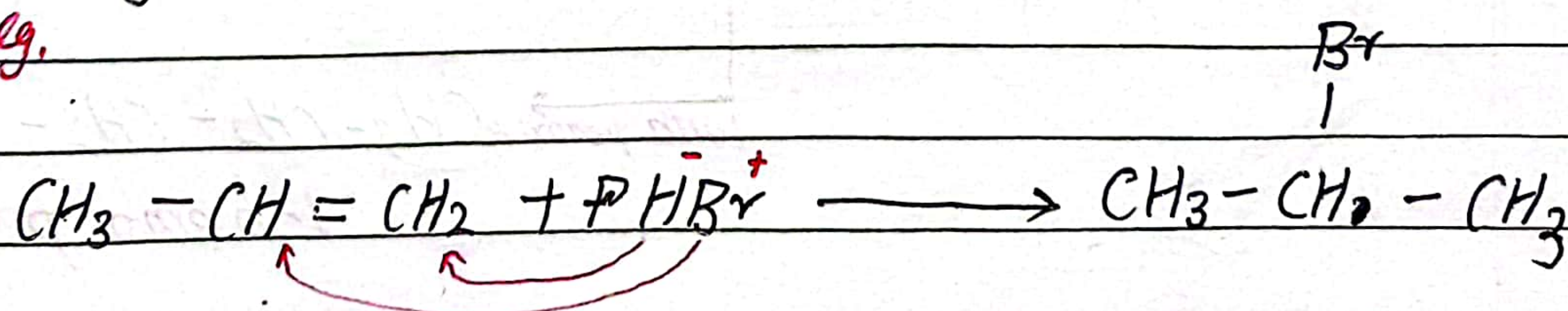
Rxn

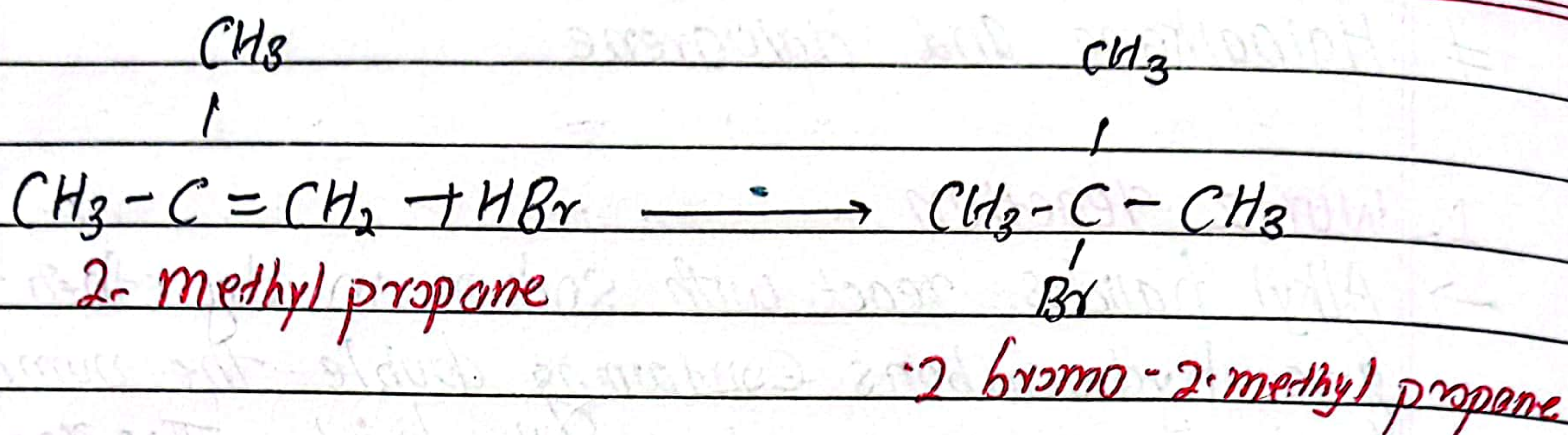


2. Markovnikov's addition (reaction)

→ According to this, when unsymmetrical reagent is added to the unsymmetrical alkene, (-ve) part of the reagent goes to that doubly-bonded carbon atom which contain less number of hydrogen atom and (+ve) part goes to the next doubly-bonded carbon atom.

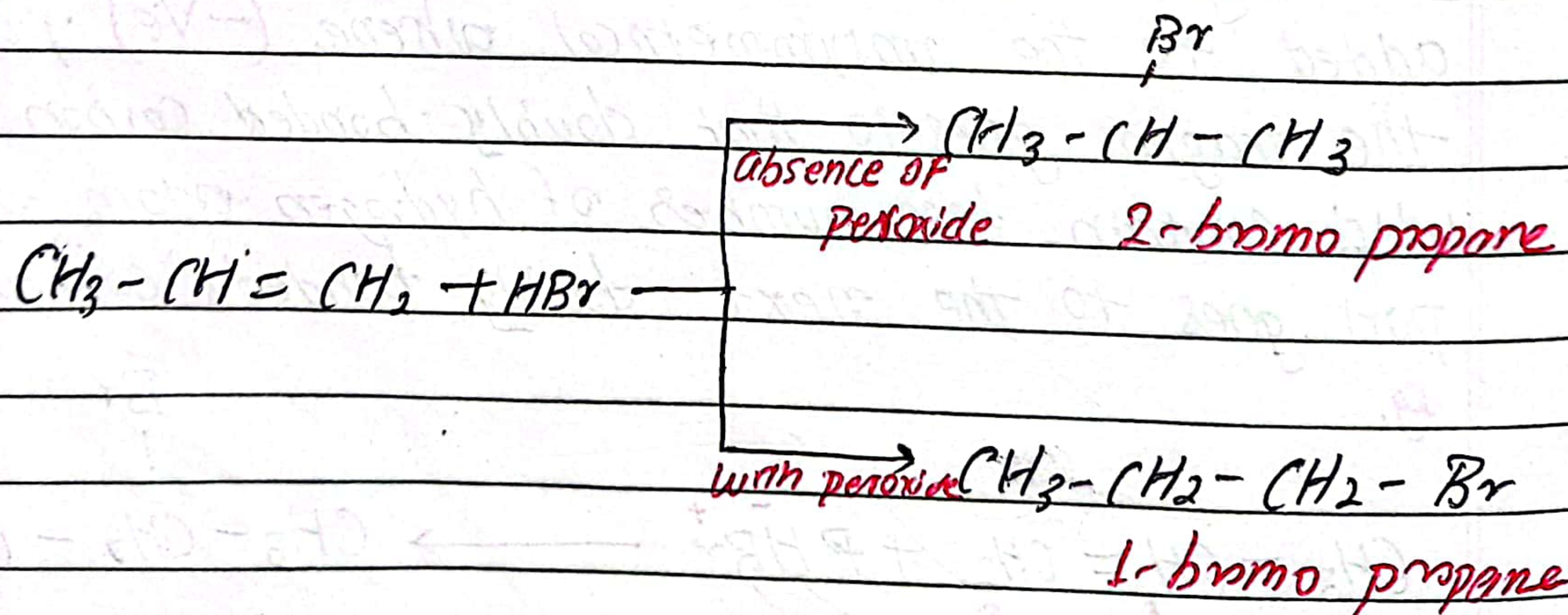
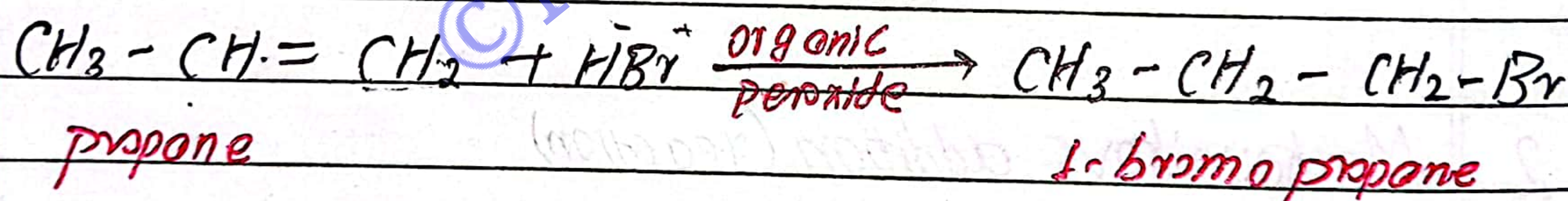
eg.





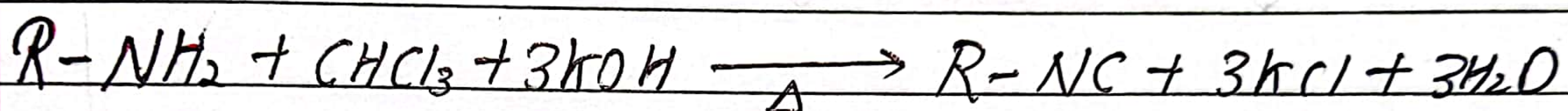
3 **Anti-Markovnikov's rule** (peroxide effect or Kharasch effect)
 → Addition of hydrogen bromide in presence of organic peroxide follows Anti-Markovnikov's rule, according to which electropositive part of the reagent (**hydrogen in case of HBr**) gets bonded to carbon containing lesser number of hydrogen atoms

rxn

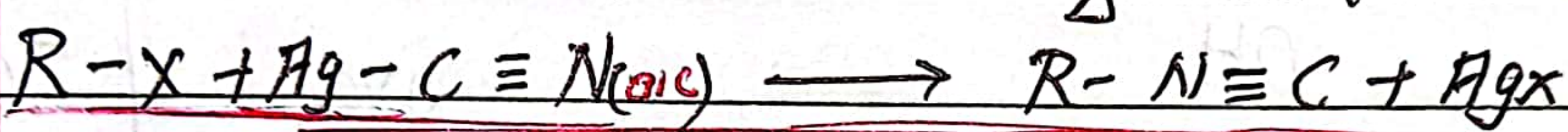


4 Carbylamine reaction

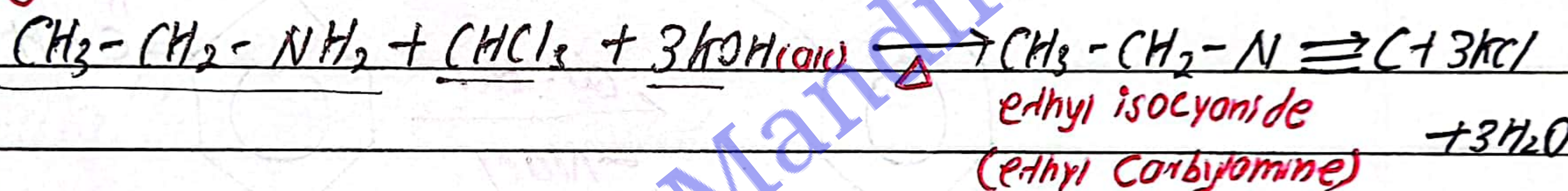
→ Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides (Carbylamine) which are foul smelling substances. This reaction is known as Carbylamine reaction.



another

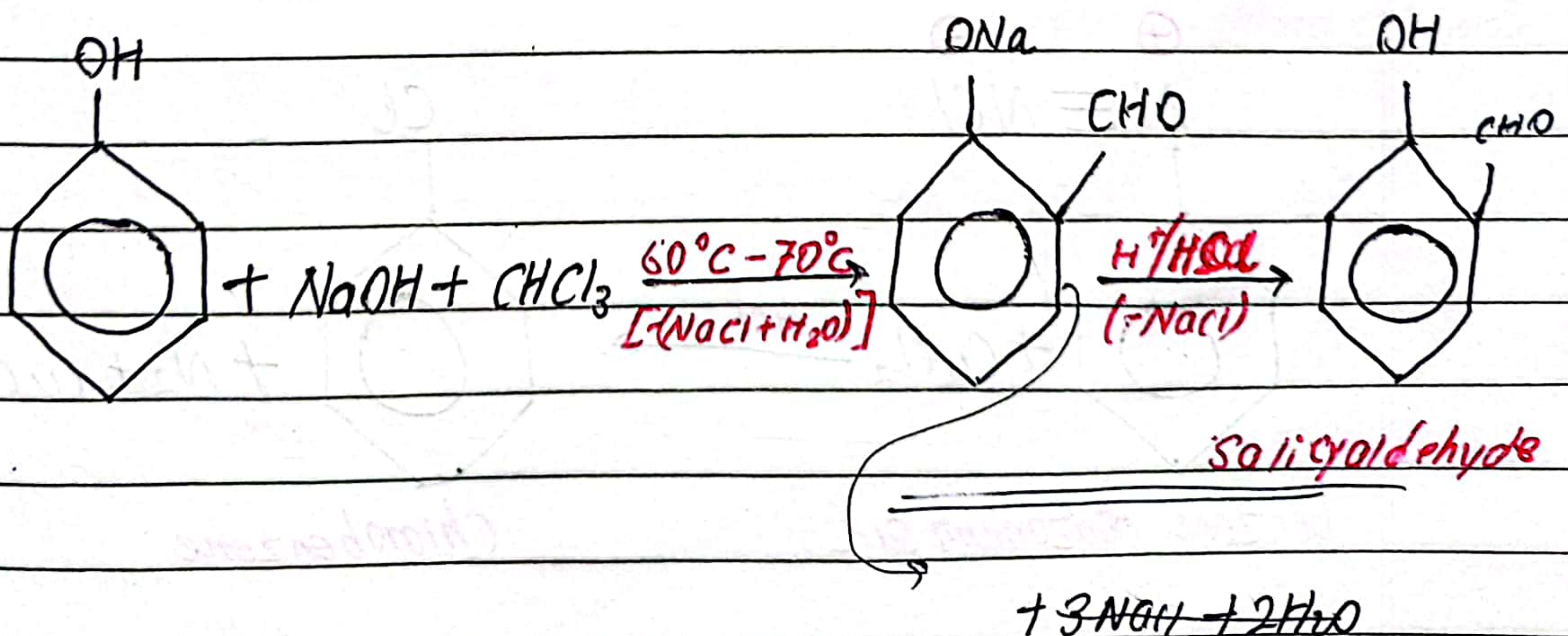


eg.



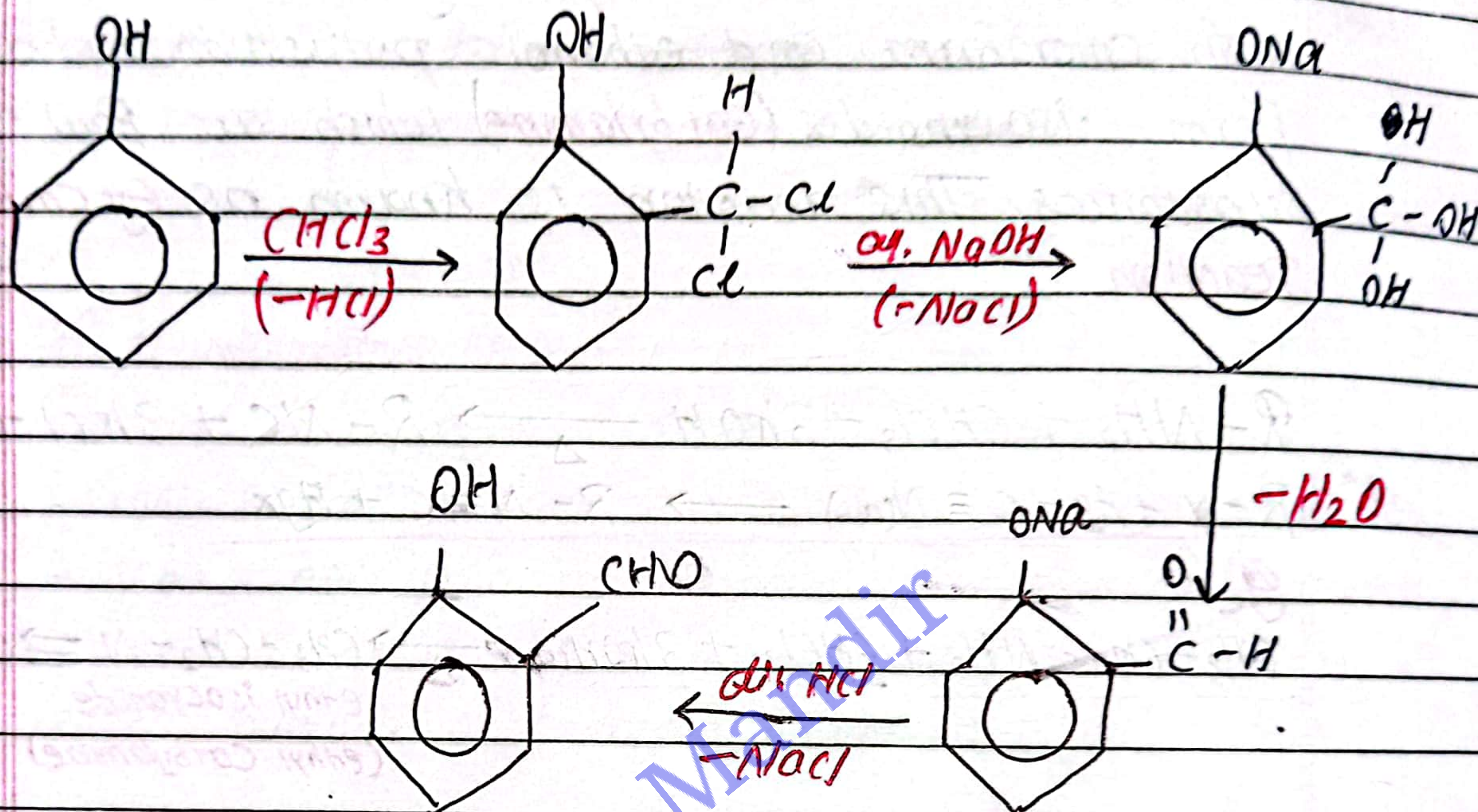
5 Reimer-Tiemann reaction (Action with phenol)

→ On the treating with phenol with chloroform in the presence of sodium hydroxide, a -CHO group is introduced at ortho position of benzene ring resulting salicylaldehyde. This reaction is known as Reimer-Tiemann reaction.



Signature

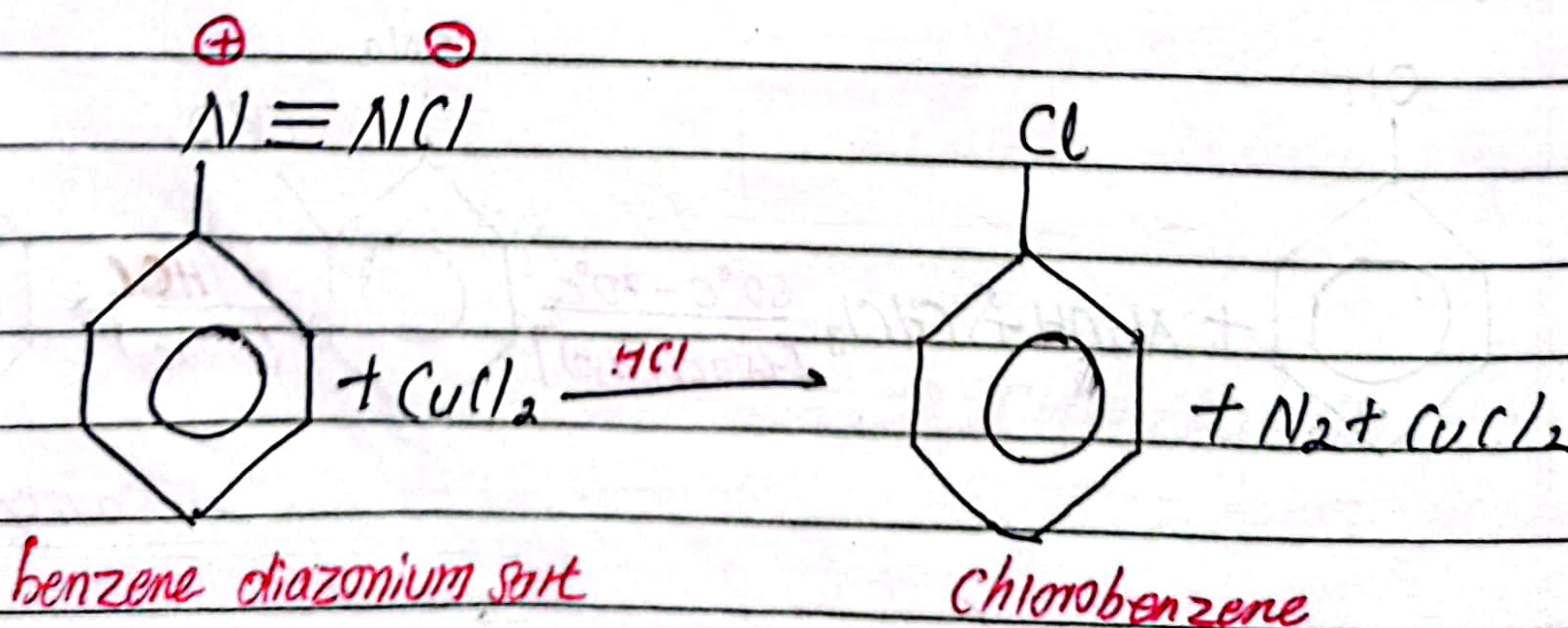
This reaction is considered as,

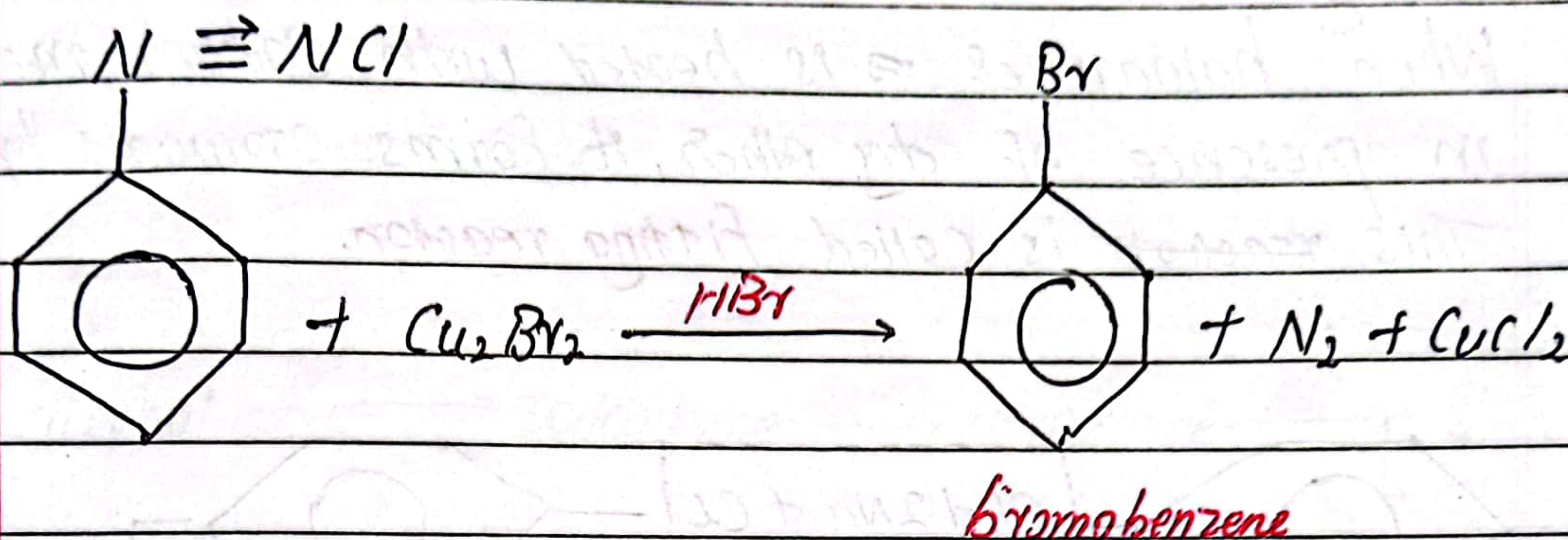


• Haloarene

6 Sand meyer's reaction (from diazonium salt)

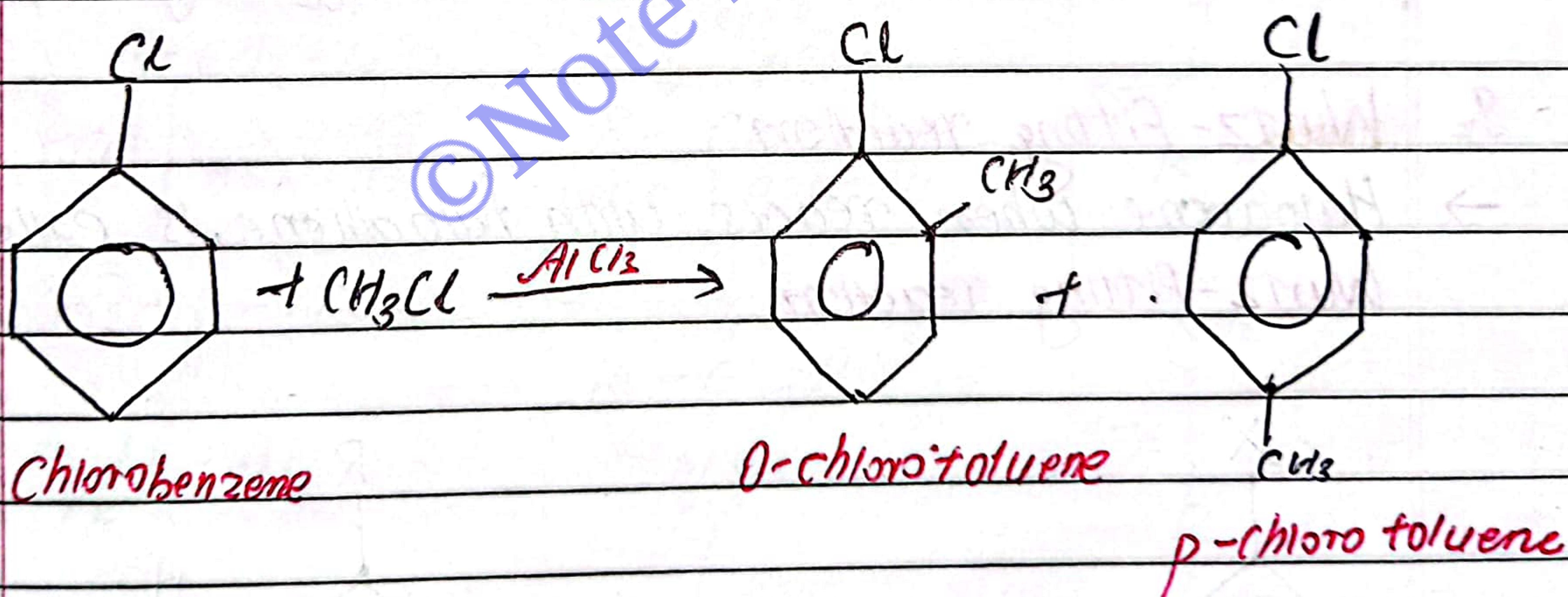
→ When diazonium salt is treated with cuprous halide in presence of a halo acid, then haloarene is obtained



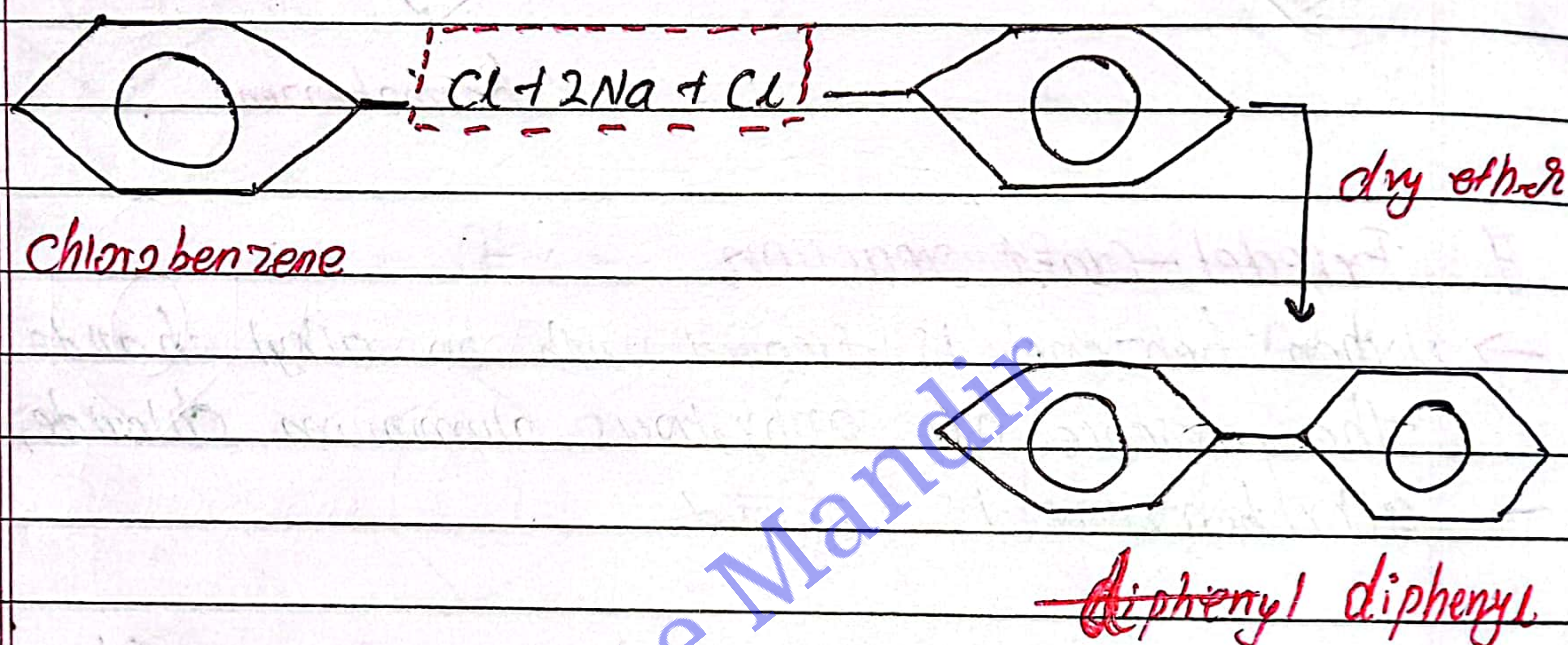


7 Friedel-Craft reaction

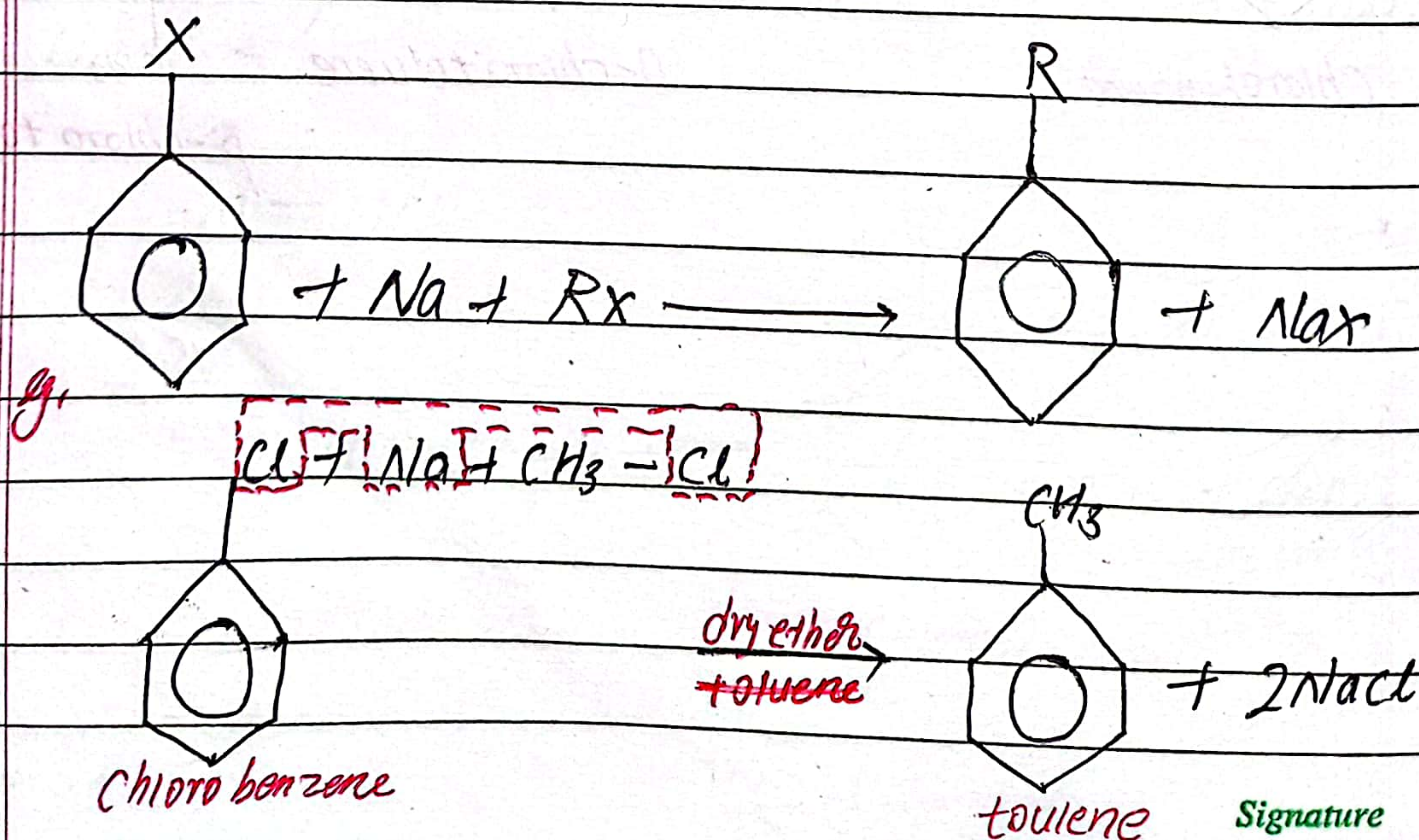
→ When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, alkylbenzene is formed.



- 8 **Fitting reaction** (Action with sodium metal)
 → When haloarenes $\Rightarrow$ is heated with sodium metal in presence of dry ether, it forms aromatic hydrocarbon. This ~~reaction~~ is called **Fitting reaction**.



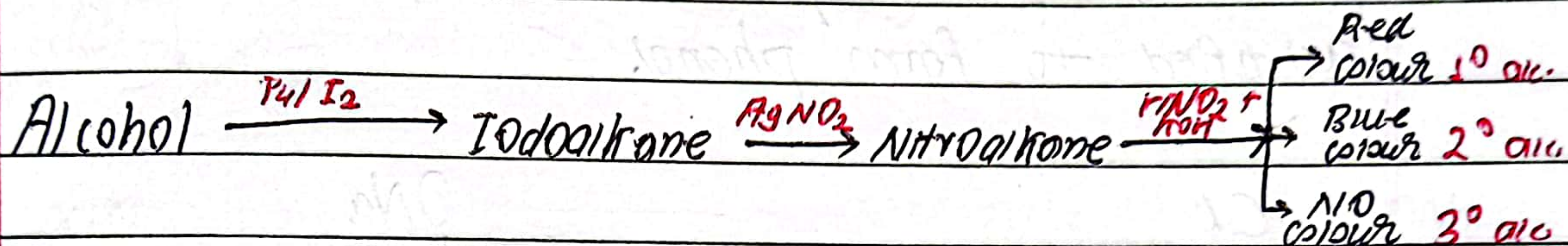
9. **Wurtz-Fitting reaction**
 → Haloarene when reacts with haloalkene, is called **Wurtz-Fitting reaction**



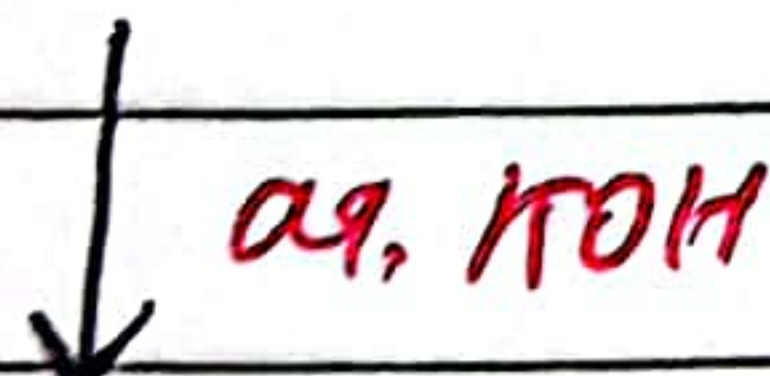
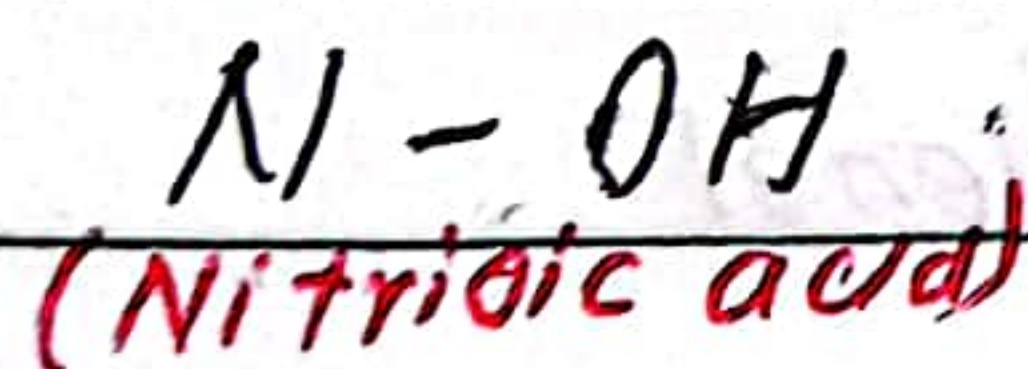
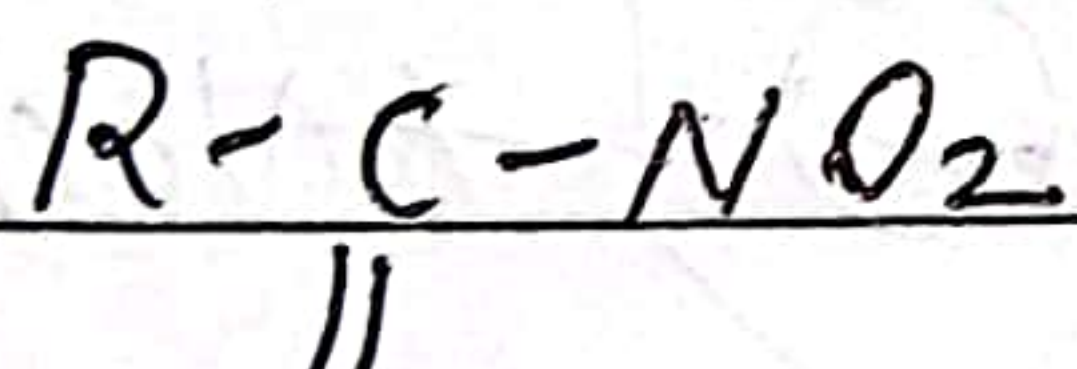
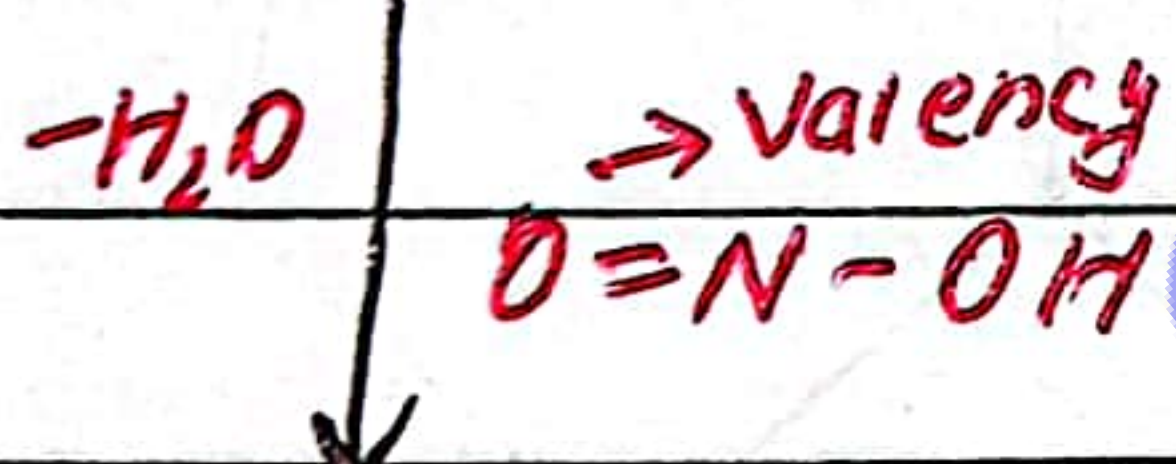
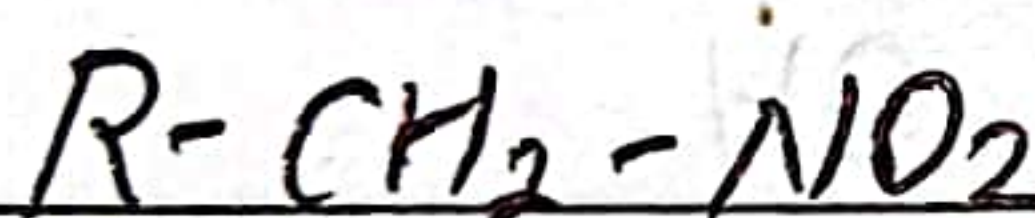
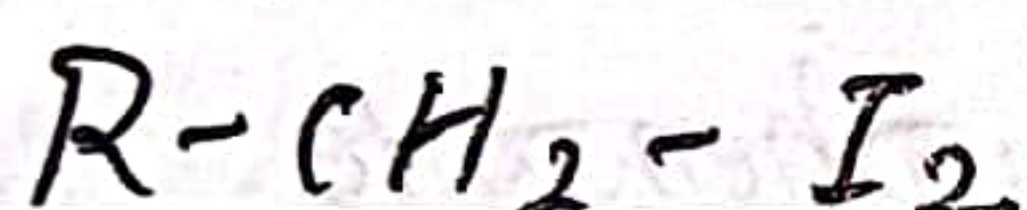
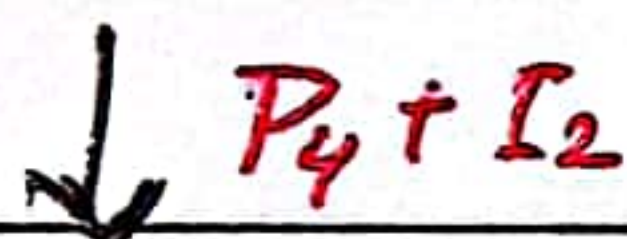
Alcohols and Phenols

10 Victor Mayer Method

→

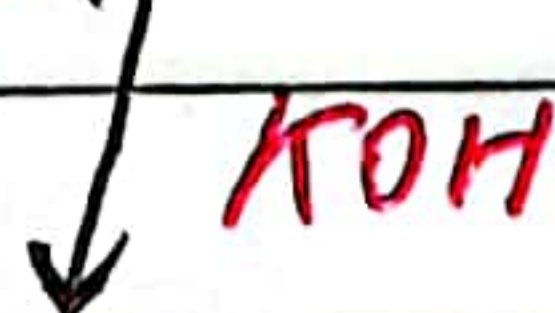
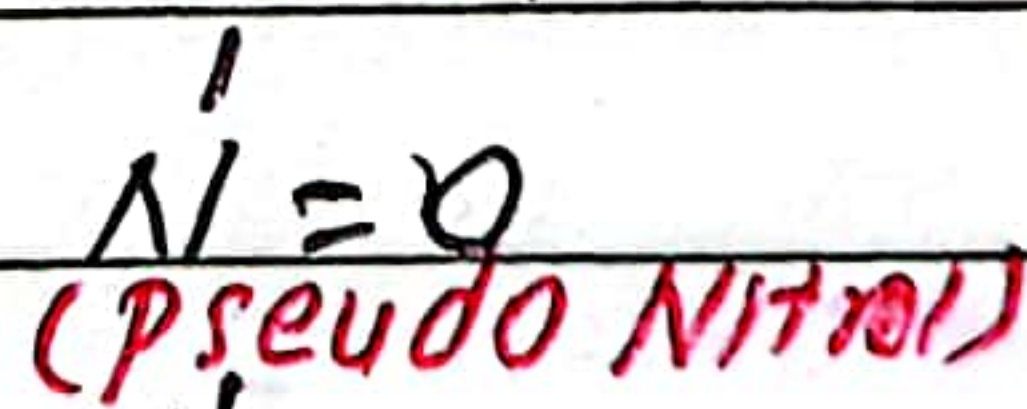
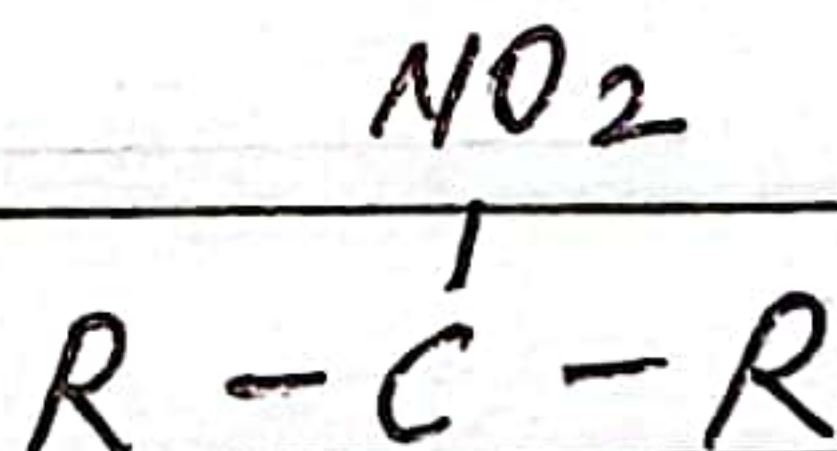
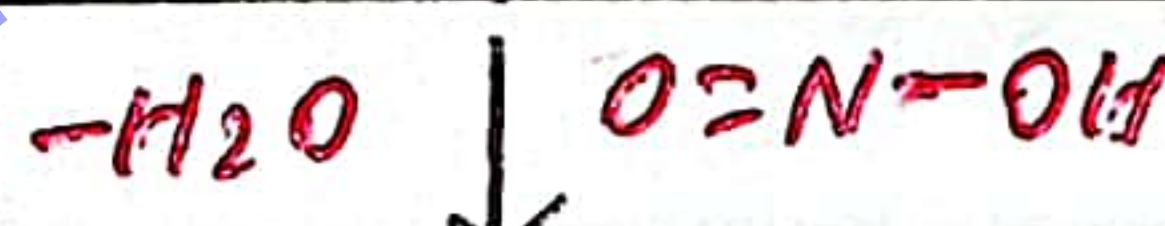
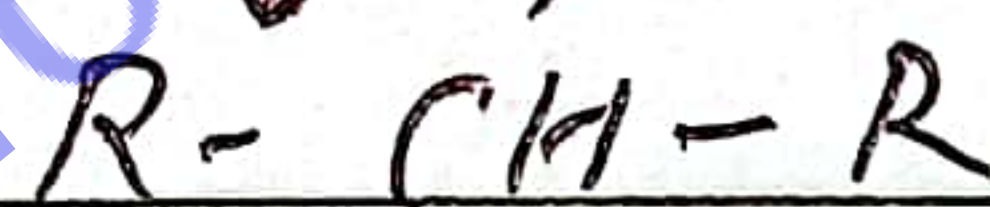
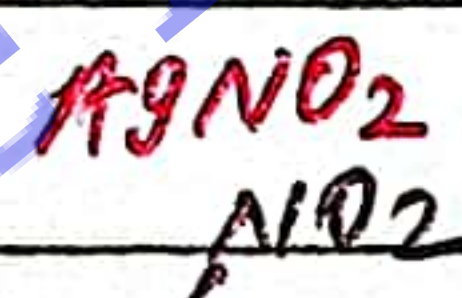
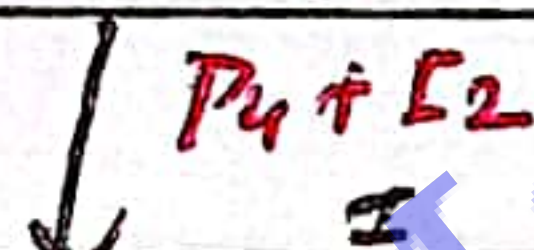
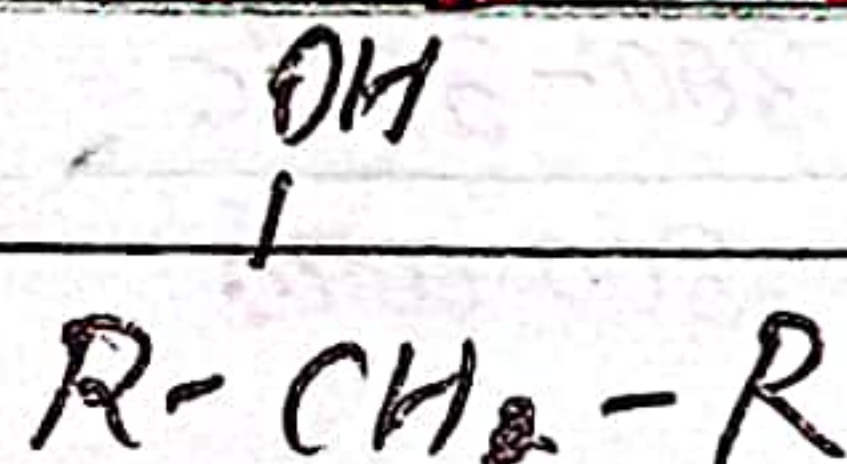


For 1° alcohol



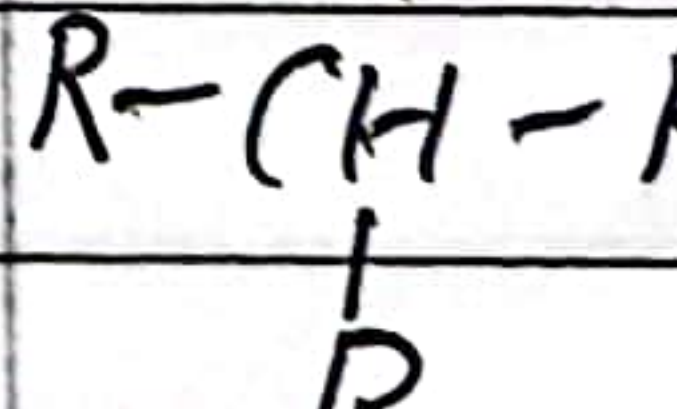
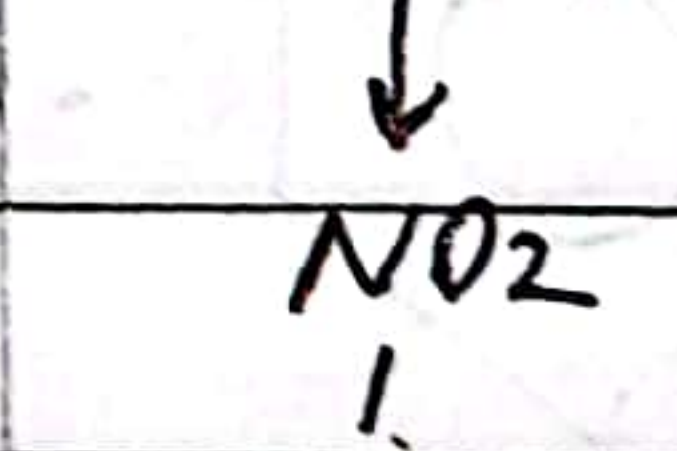
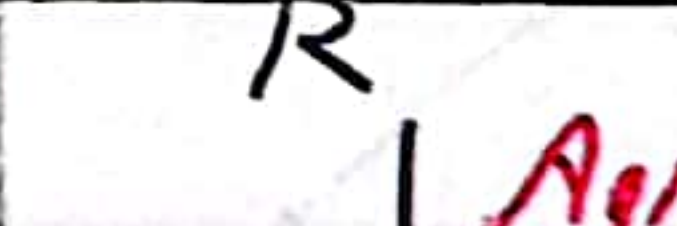
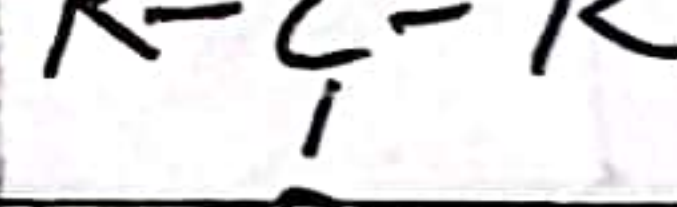
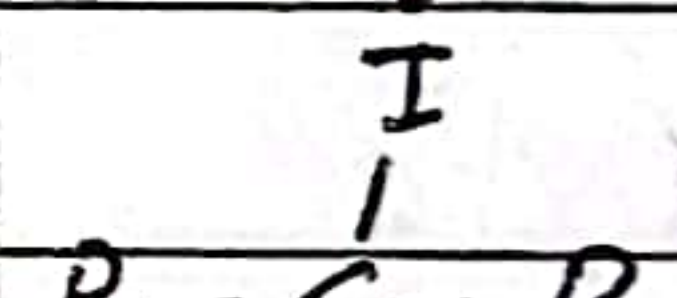
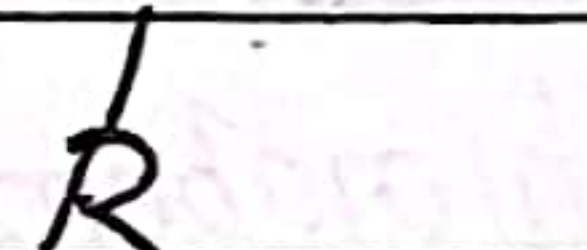
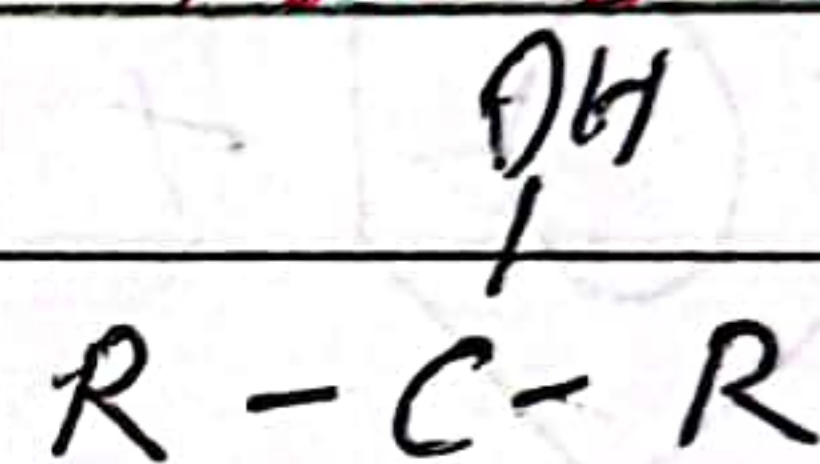
Blood red colour

For 2° alcohol



Blue colour

For 3° alcohol



NO reaction

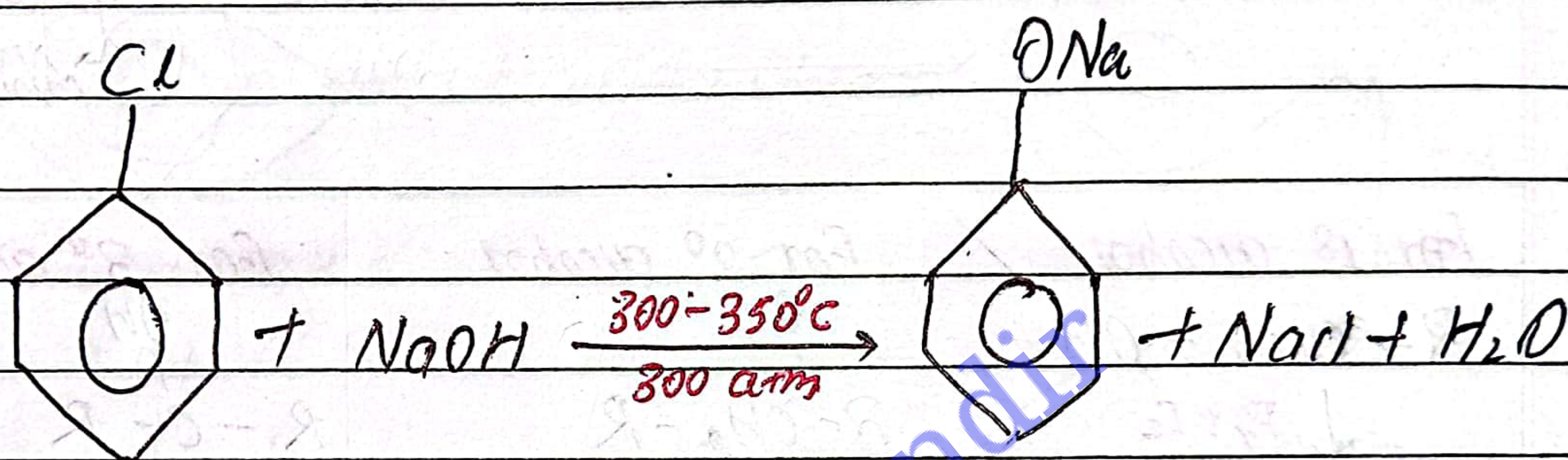
↓ KOH

Colourless

Phenols

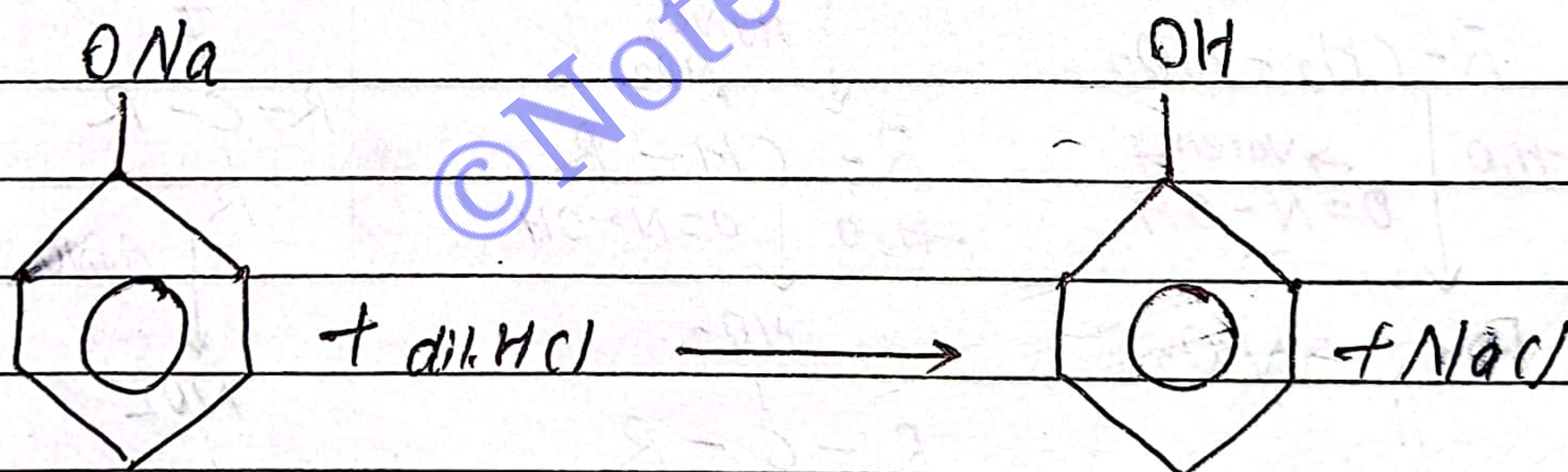
II Dow's process (from haloarenes)

→ When chlorobenzene is heated with 10% caustic soda solution at $300-350^{\circ}\text{C}$ and 300 atmospheric pressure, sodium phenoxide is formed which is acidified to form phenol.



Chlorobenzene

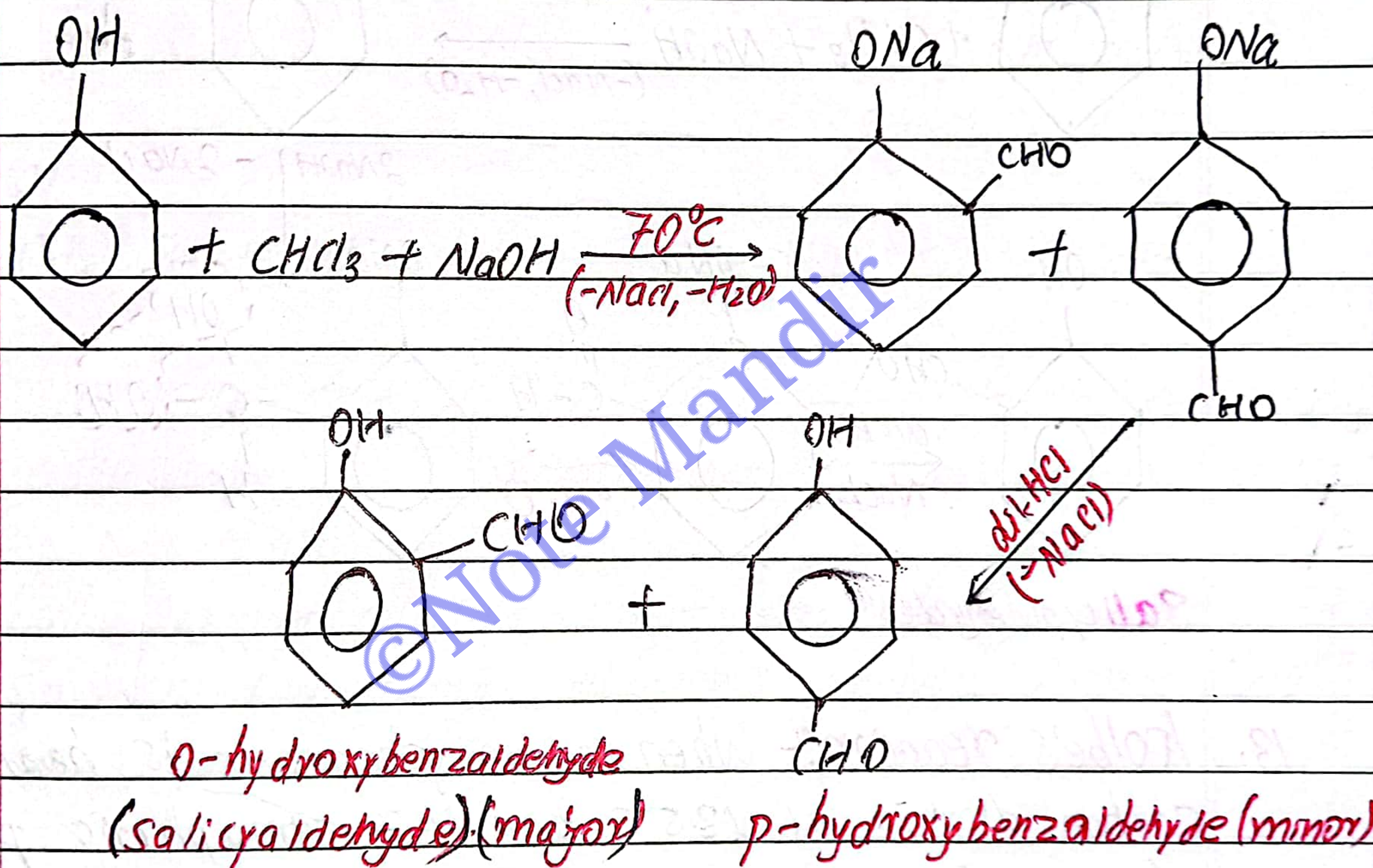
Sodium phenoxide



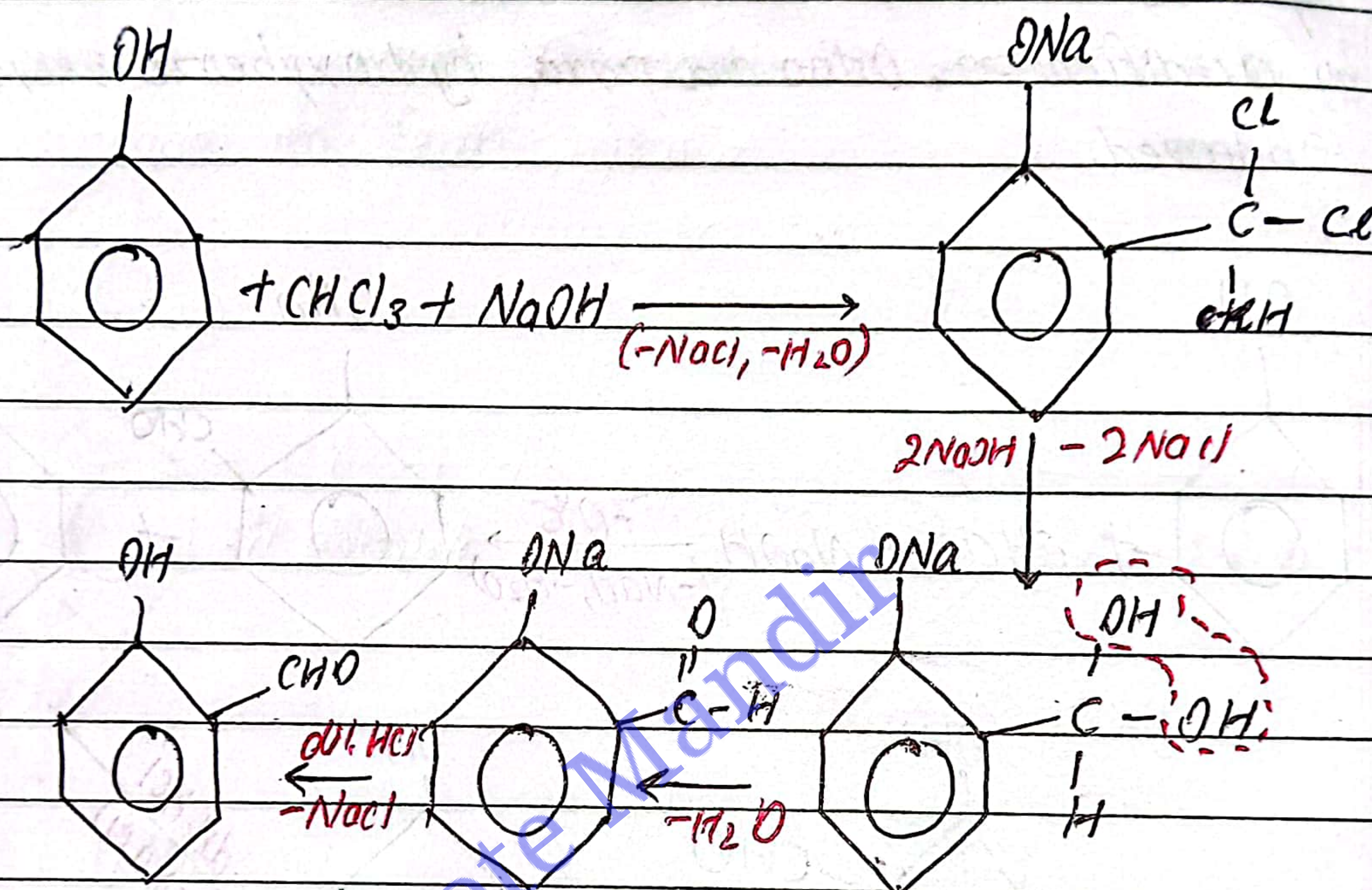
phenol

12 Reimer-Tiemann reaction

→ Phenol when treated with chloroform in presence of aqueous solution of alkali solution at $60-70^{\circ}\text{C}$ followed by acidification, **ortho** and **para** hydroxybenzaldehyde are obtained.

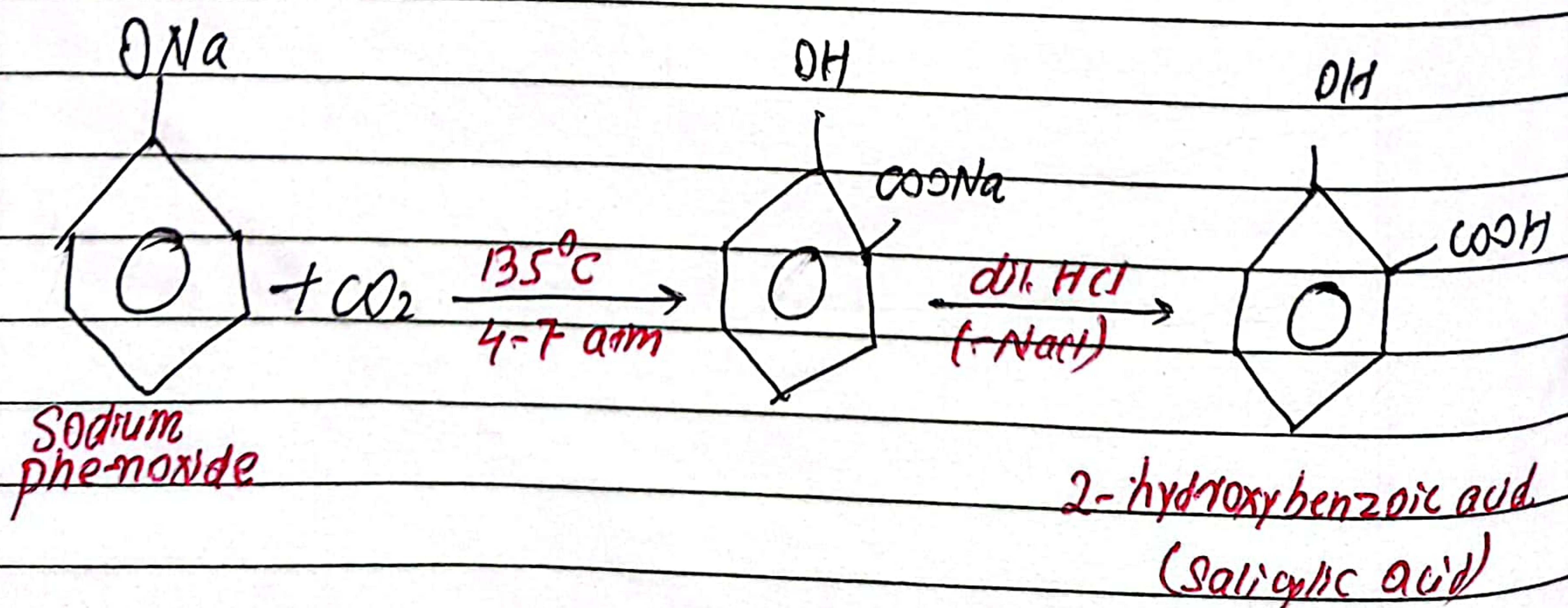


This chemical reaction is considered to occur as following



Salicylaldehyde

13. Kolbe's Reaction:- When sodium phenoxide is heated with carbon dioxide at 135°C and 4-7 atmospheric pressure followed by acidification, it gives salicylic acid.

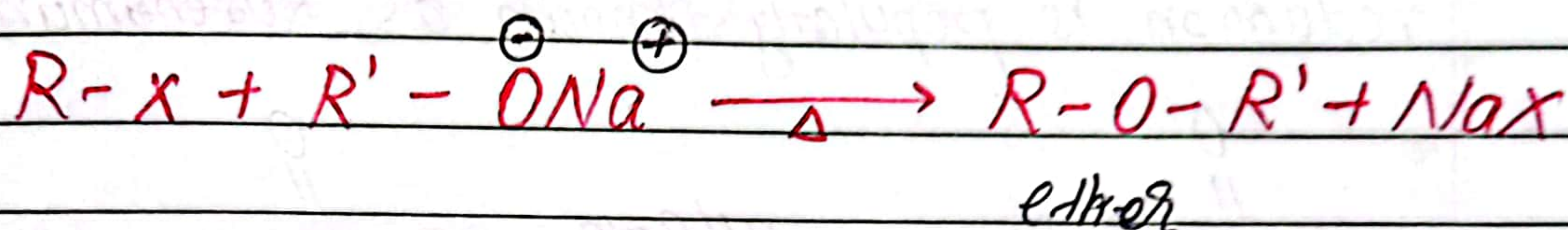


Signature

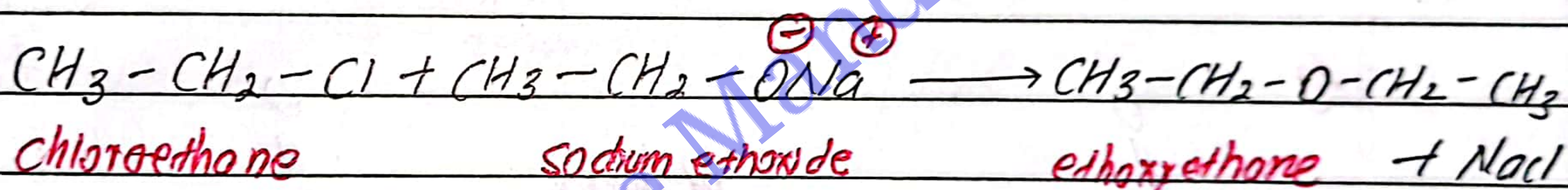
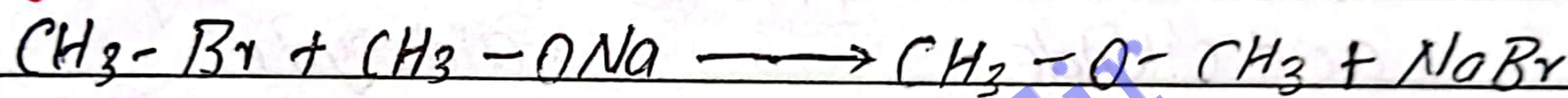
Ethers

14 Williamson's Synthesis

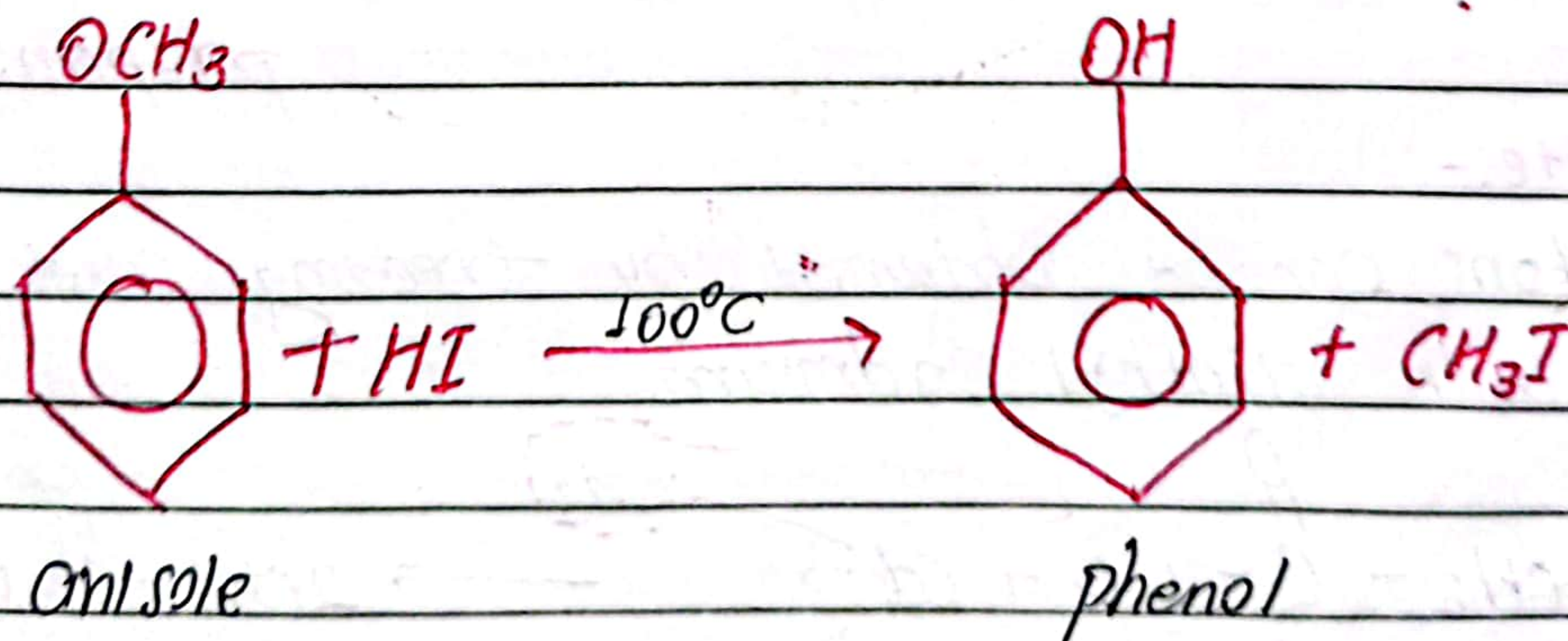
→ Haloalkane when heated with alcoholic sodium alkoxide, it forms ether as a result of nucleophilic substitution of haloalkane



eg.



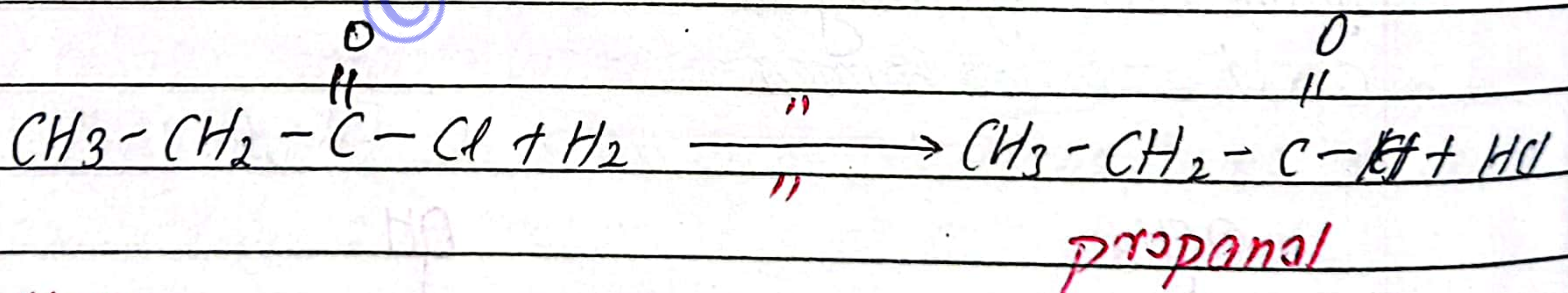
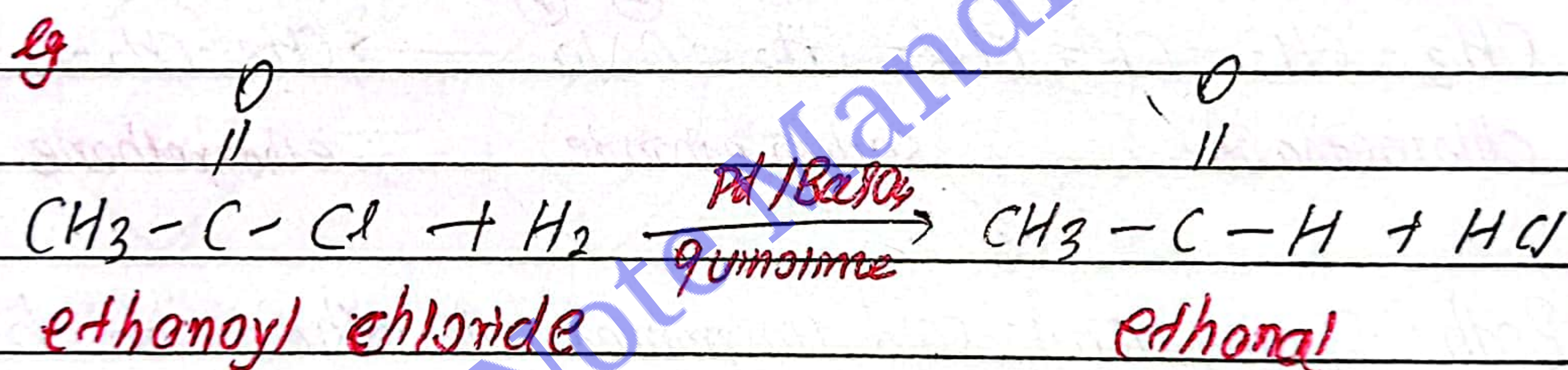
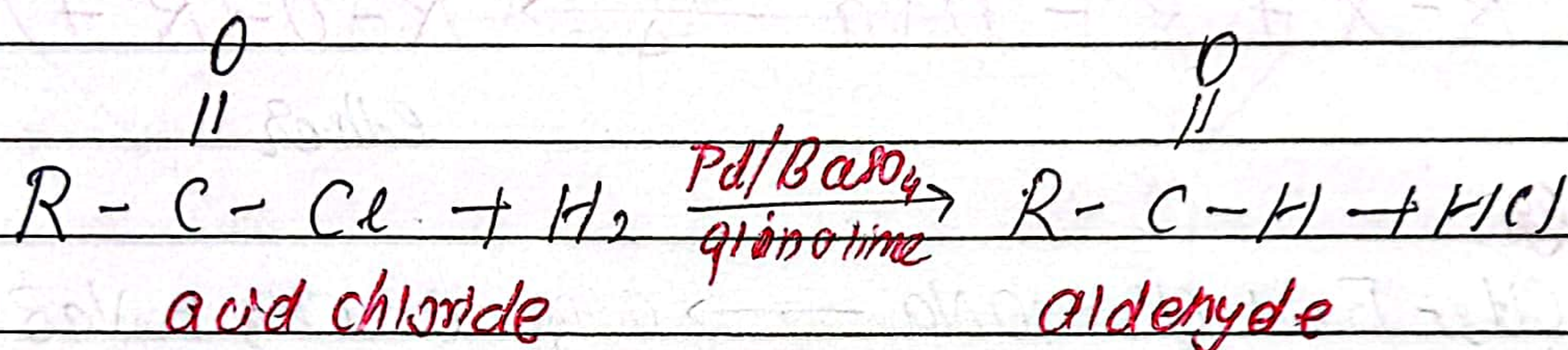
Both symmetrical and unsymmetrical ether can be synthesized by using Williamson's synthesis. Aromatic ether can also be formed.



Aldehyde and Ketones

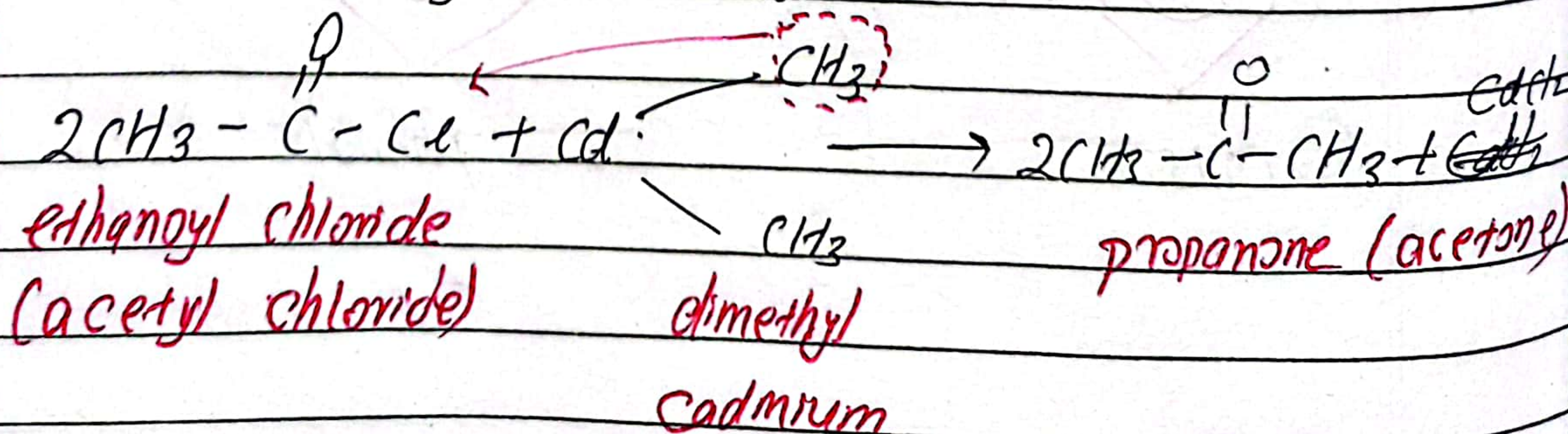
15. Rosenmund reduction (From acid chloride)

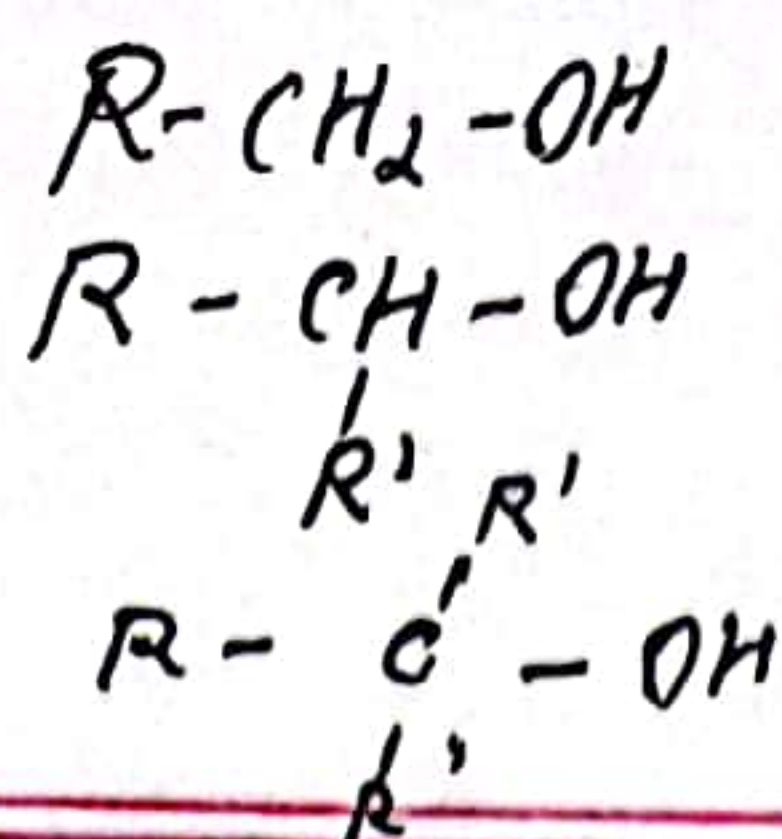
→ In this method hydrogen gas is passed over the boiling solution of acid chloride in presence of palladium metal supported by barium sulphate. This reduction is popularly known as **Rosenmund's reduction**.



Note:-

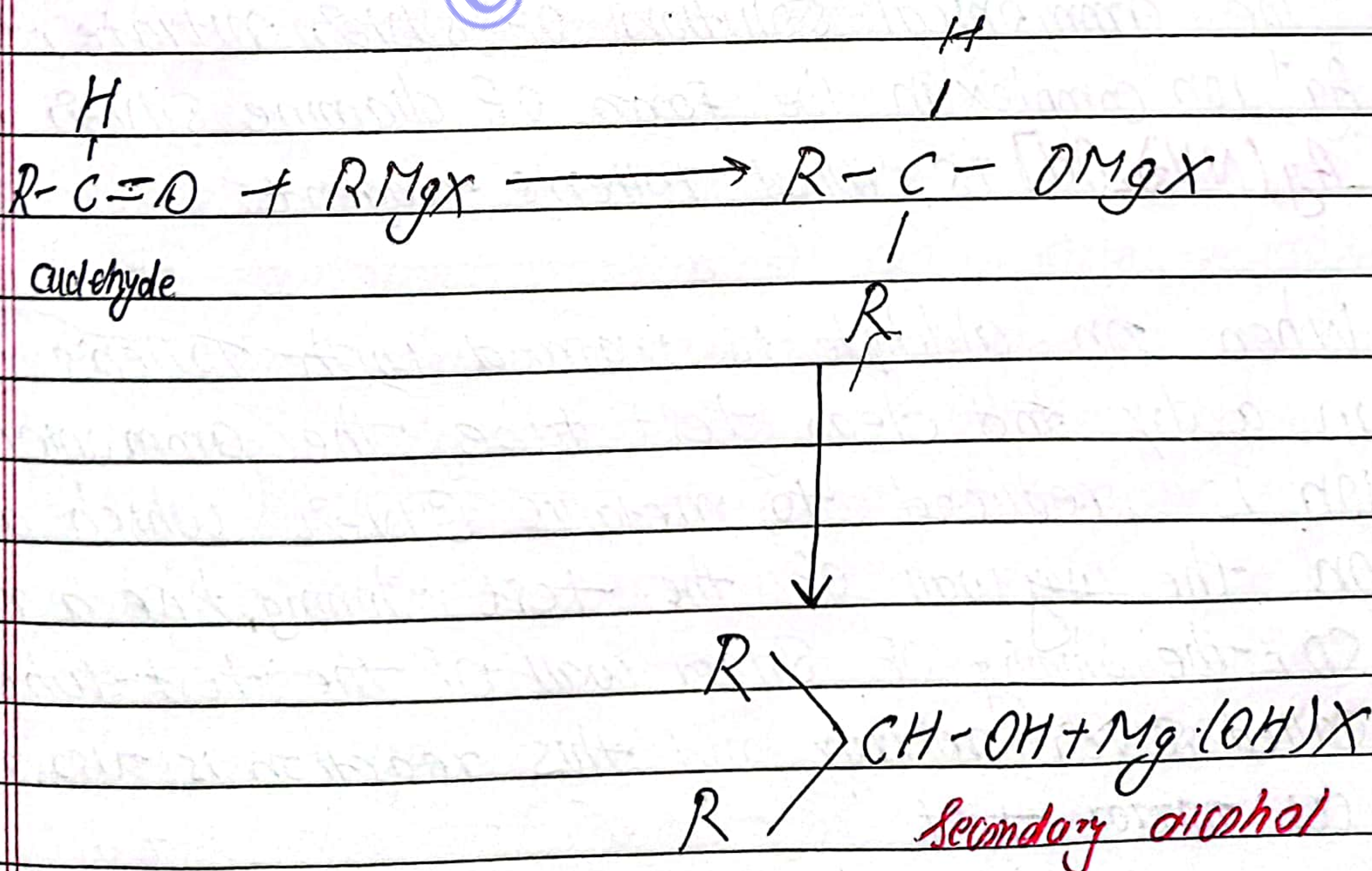
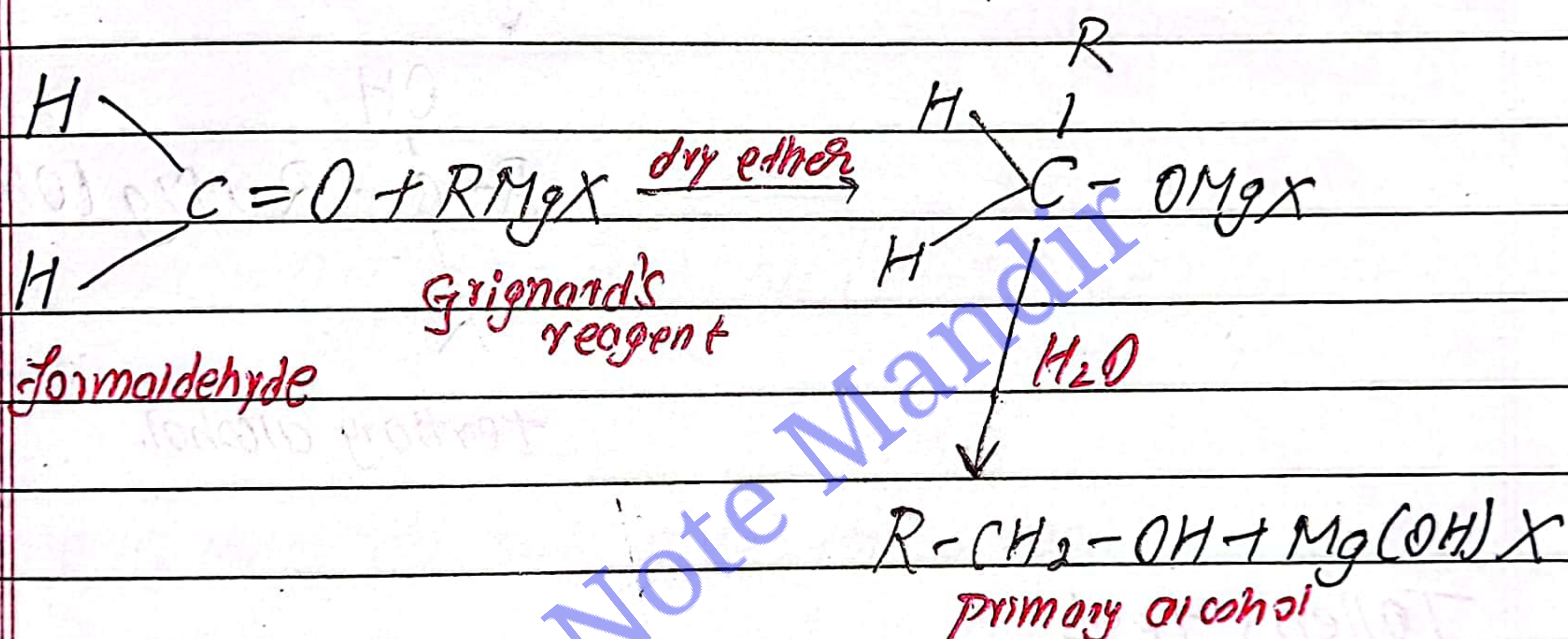
Ketons can be obtained by treating acid chloride or with dialkyl cadmium.



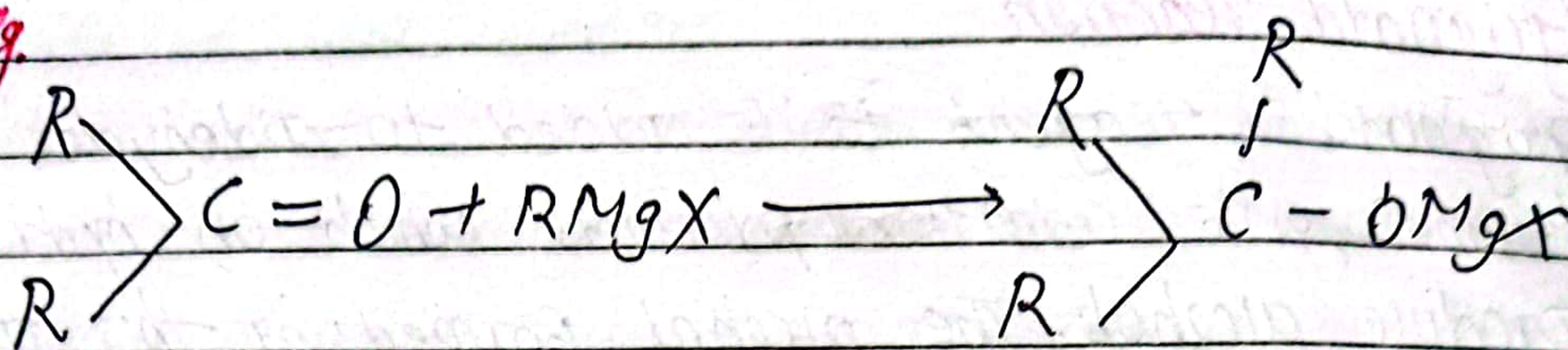


16 Grignard Reaction

→ Grignard's reagent if added to aldehydes or Ketones give additional products which on hydrolysis produce alcohols. The alcohol formed by this process can be primary, secondary or tertiary depending parent aldehydes or ketons.

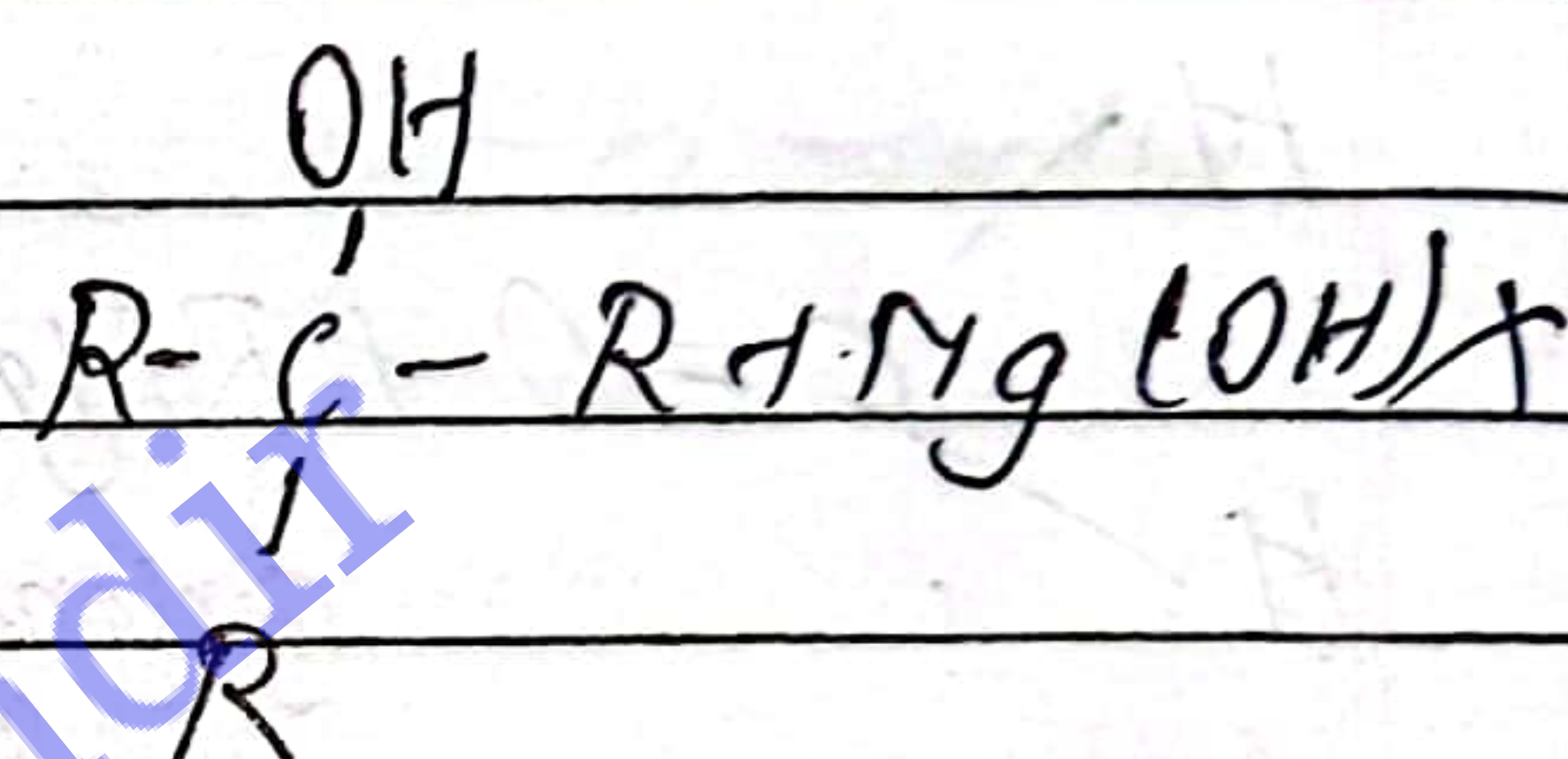


eg.



ketone

H₂O

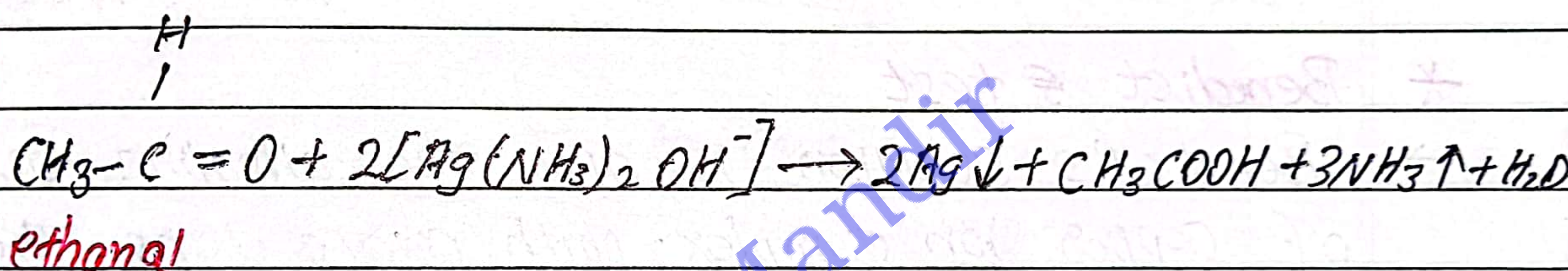
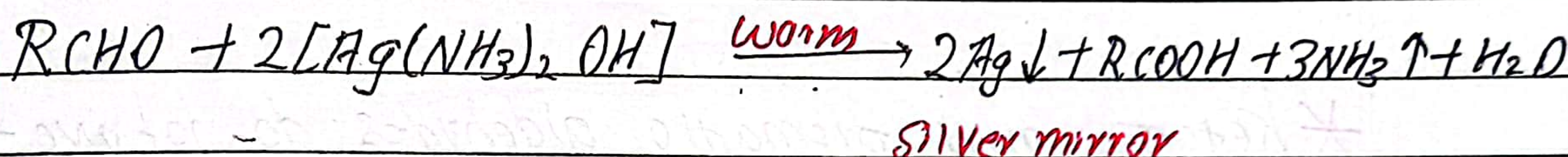
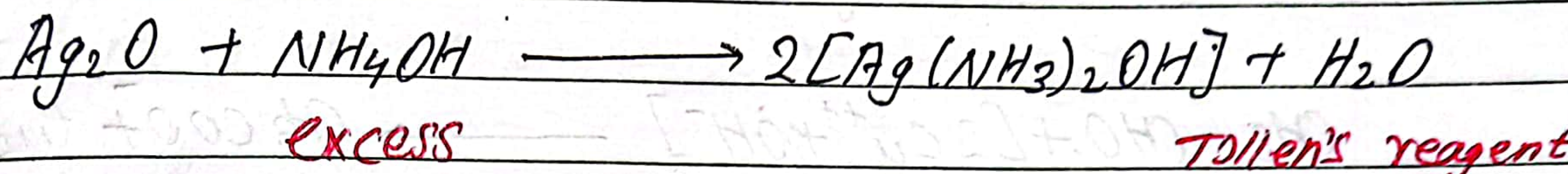
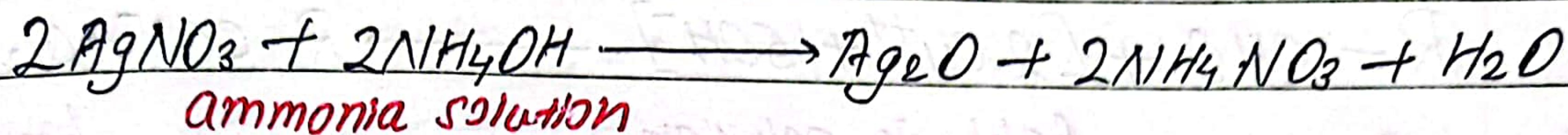


tertiary alcohol.

17 Tollen's test

→ The ammoniacal solution of silver nitrate, containing Ag⁺ ion complex in the form of diamine silver hydroxide [Ag(NH₃)₂OH] is called Tollen's reagent.

When an aldehyde is warmed with Tollen's reagent in a dry and clean test tube the ammoniacal silver ion is reduced to metallic silver which deposits on the inner wall of the test tube shining like a mirror. So, the shining of silver wall of the test-tube is called silver mirror and this reaction is also known as mirror test.



* Ketone do not give the test.

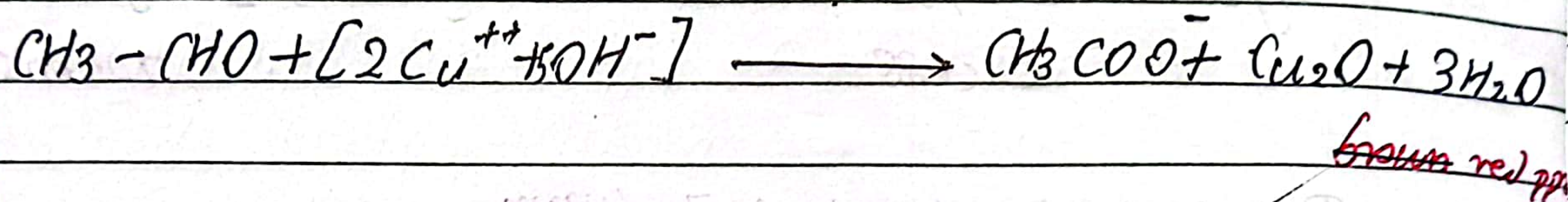
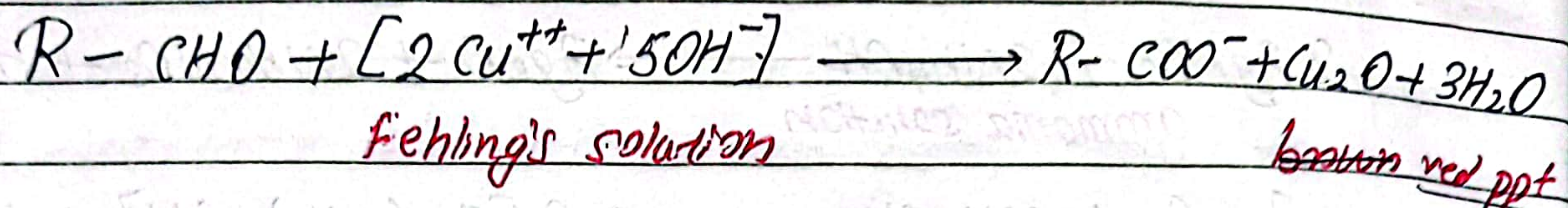
18 Fehling's test, Benedict test

* Fehling's test

→ The equivalent mixture of copper sulphate solution (CuSO_4) and sodium hydroxide solution containing some sodium potassium tartrate (i.e. Rochelle's salt) in the form of copper tartrate complex (copper ion complex) is called Fehling's Fe^- solution.

When an aliphatic aldehyde is heated with Fehling's solution the Cu^{++} ions is reduced to red oxide of Copper (Cu_2O) giving a brown red ppt.

Signature

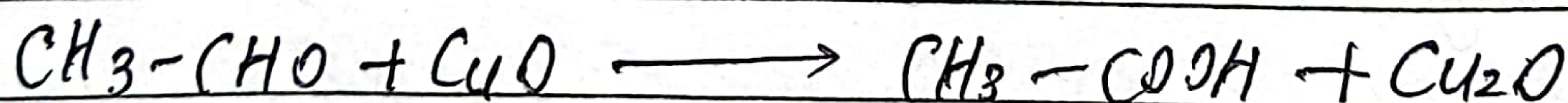
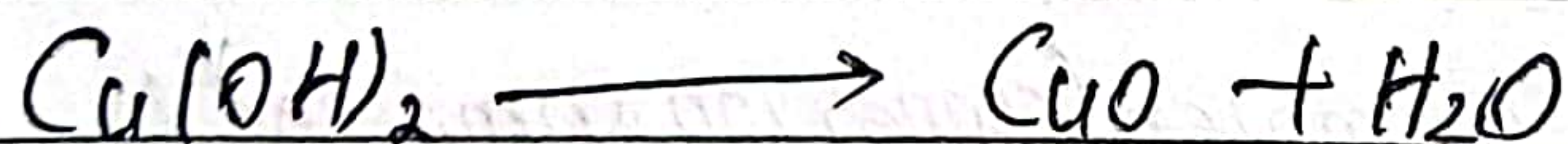
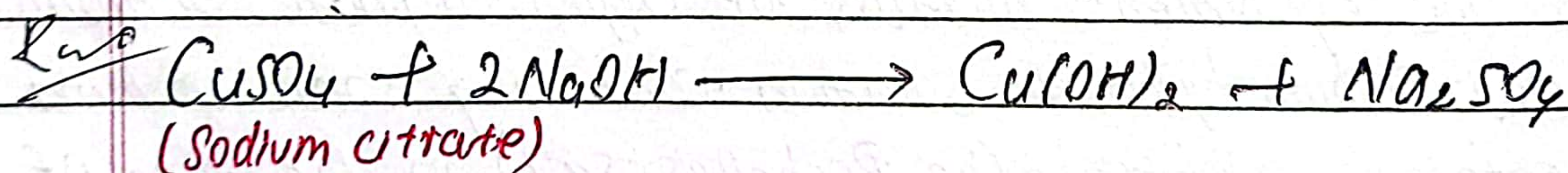


* Ketones and aromatic aldehydes do not give the test.

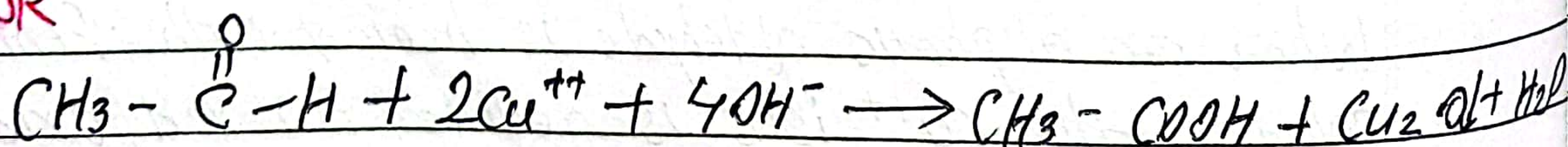
* Benedict's test

→ Benedict's solution is also the alkaline solution of copper ion complex with citrate ions. The reaction of Benedict's solution is similar to Fehling solution.

Among the above mentioned reactions, Tollen's test, Fehling test and Benedict's test are used to differentiate aldehydes from ketones.

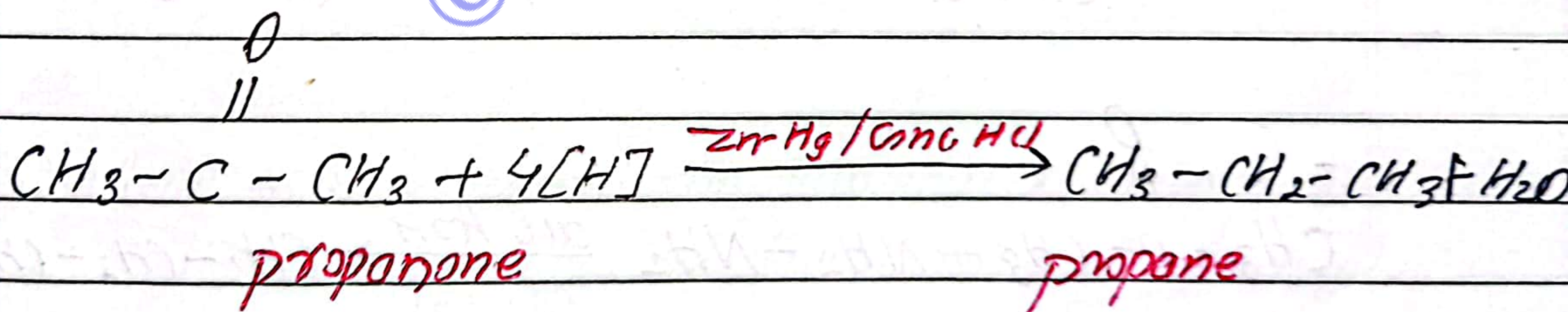
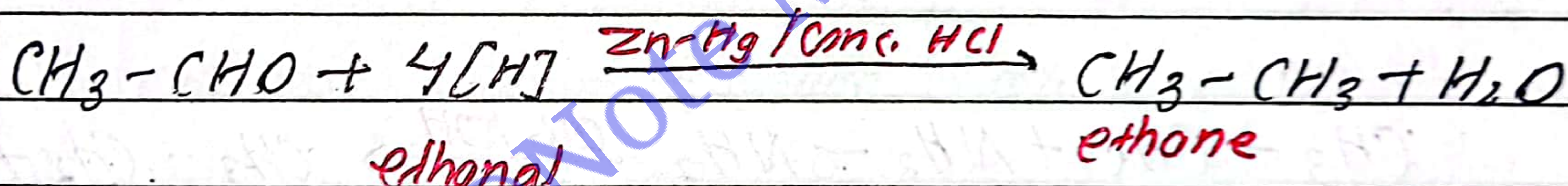
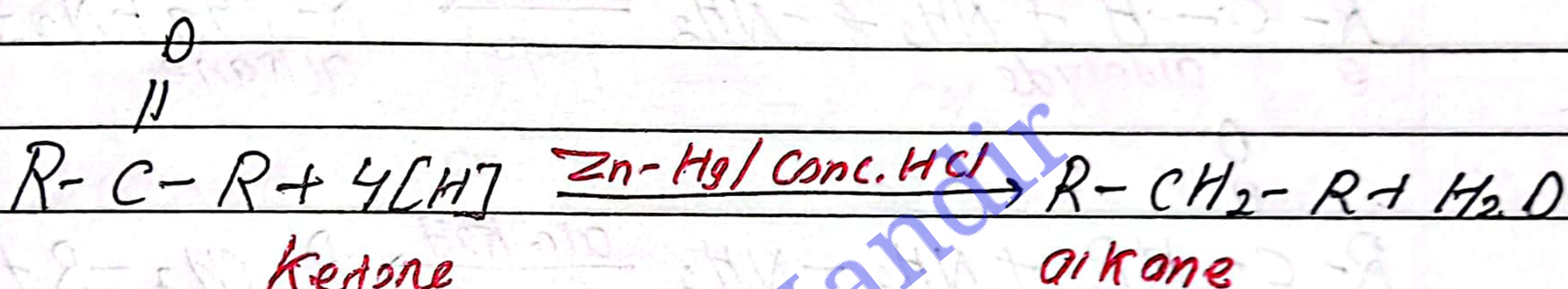
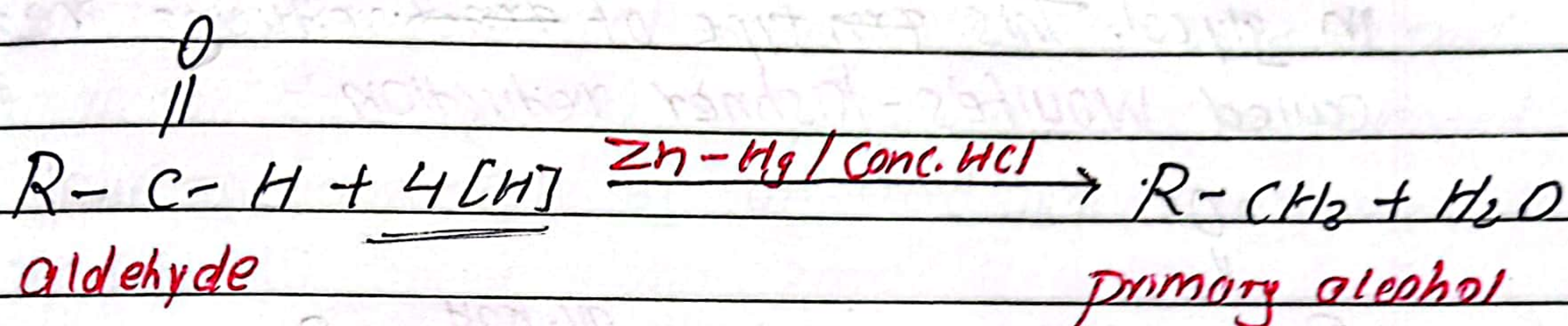


OR



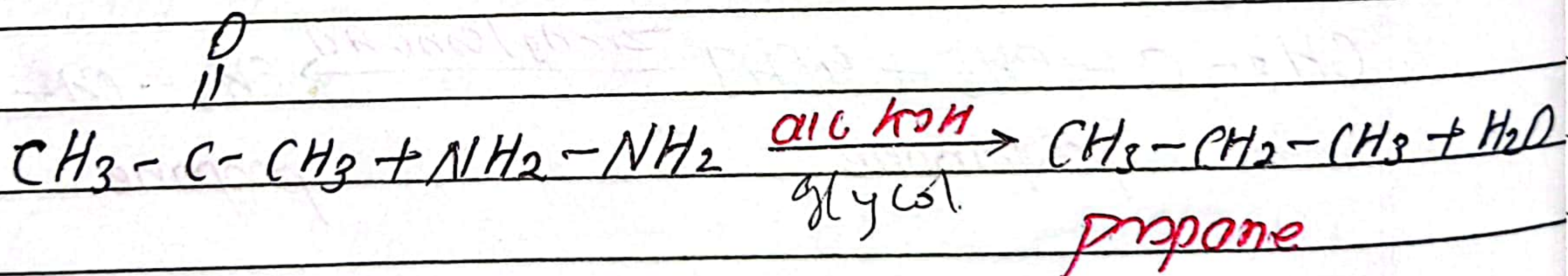
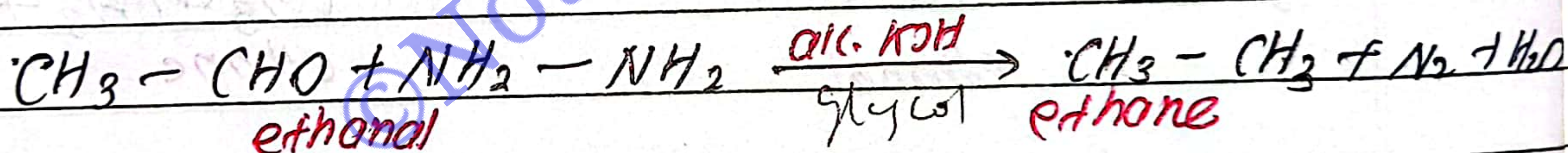
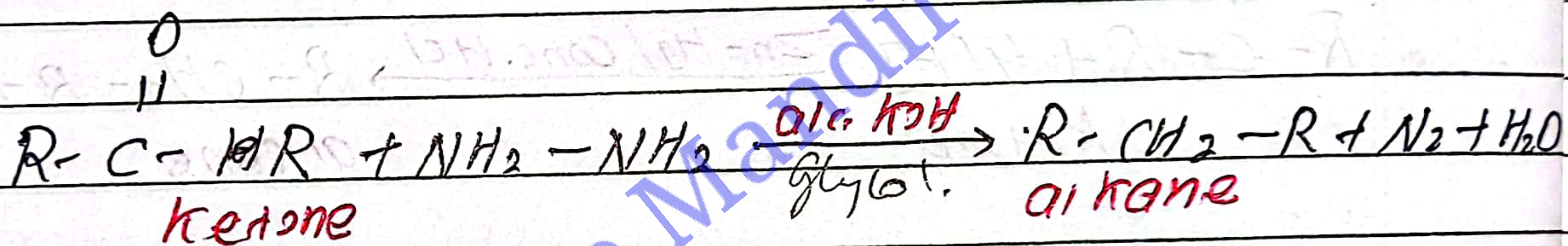
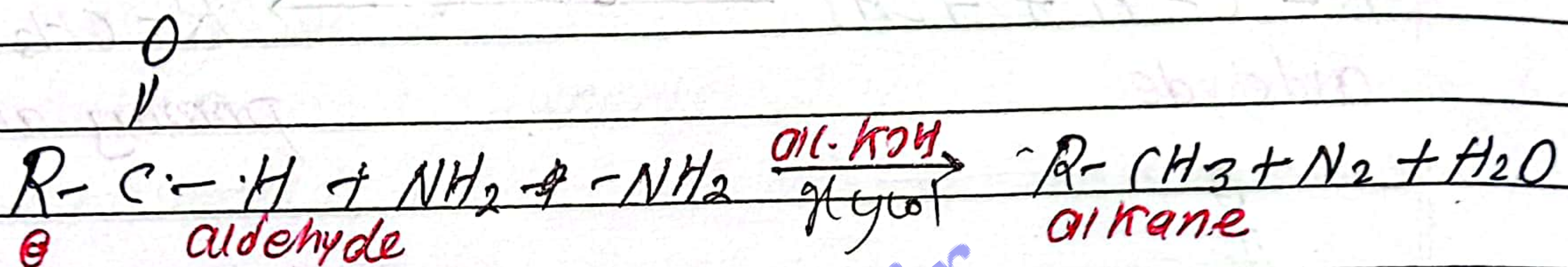
19 Clemmensen's reduction

→ Aldehydes or Ketones if treated with zinc amalgam in presence of conc. HCl produce alkanes. This reaction is known as **Clemmensen's reduction**



20 Woulfe's - kishner reduction (Reduction with hydrazine and alcoholic alkali)

→ Aldehydes ^{or} ketones can be reduced to alkane when heated with hydrazine and ethylene glycol in glycol. This ~~rxn~~ type of ~~rxn~~ reducing reaction is called Woulfe's - kishner reduction

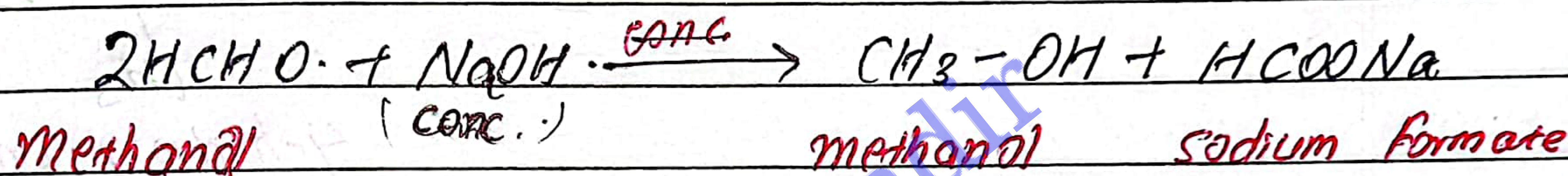


21. Cannizzaro's reaction, aldol condensation

320

* Cannizzaro's reaction

→ Aldehydes of lacking α -hydrogen atoms (like HCHO , $\text{C}_6\text{H}_5\text{CHO}$, $\text{R}_3\text{C} \cdot \text{CHO}$, etc) undergo self oxidation and reduction (self redox) in presence of concentrated alkali to form salt of an acid and a primary alcohol is called **Cannizzaro's reaction**.

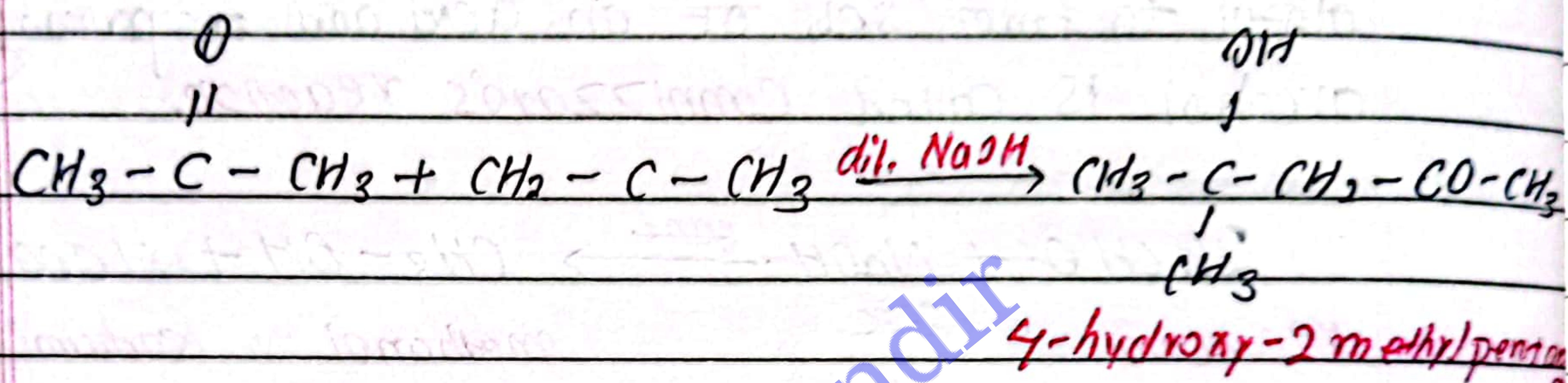
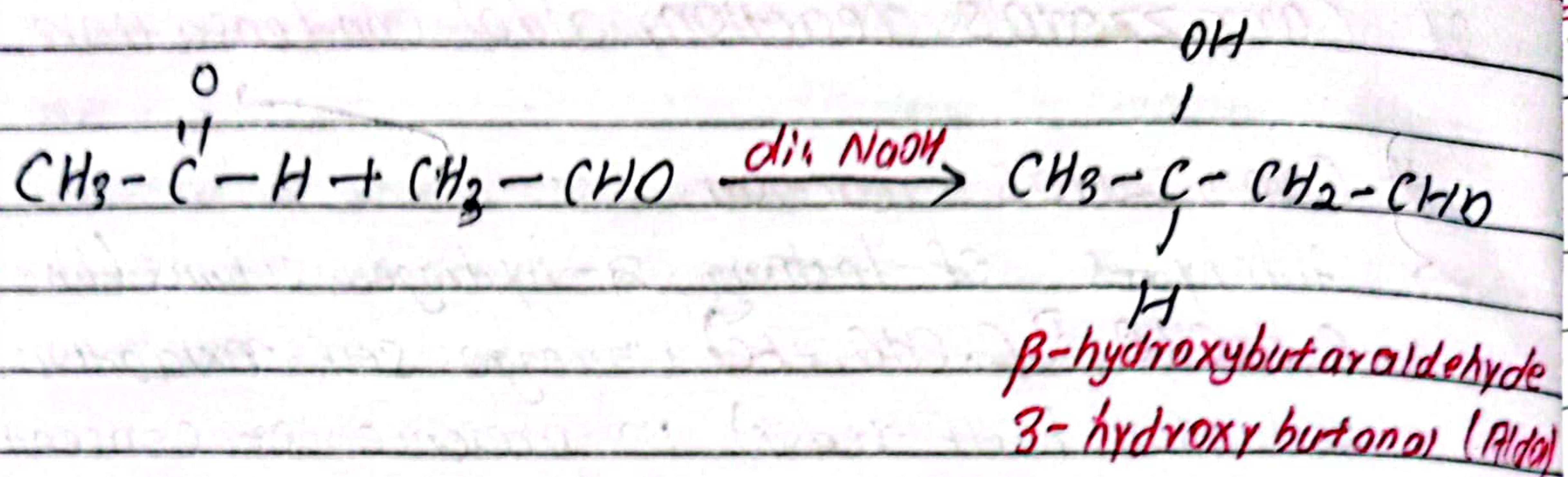


In the above reaction one molecule of methanol is oxidised to Sodium formate simultaneously the other molecule is reduced to corresponding alcohol.

* Aldol condensation

→ Condensation between two molecules of an aldehydes or a ketone having at least one α -hydrogen in presence of dilute alkali to form β -hydroxy α -hydroxy aldehyde or β -hydroxy ketone is known as aldol condensation.

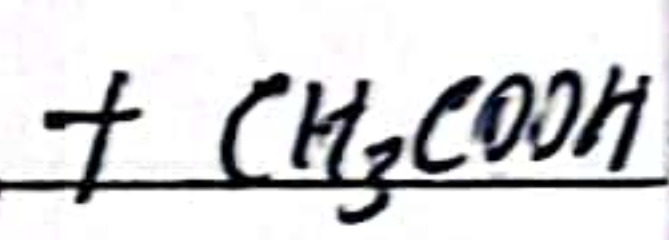
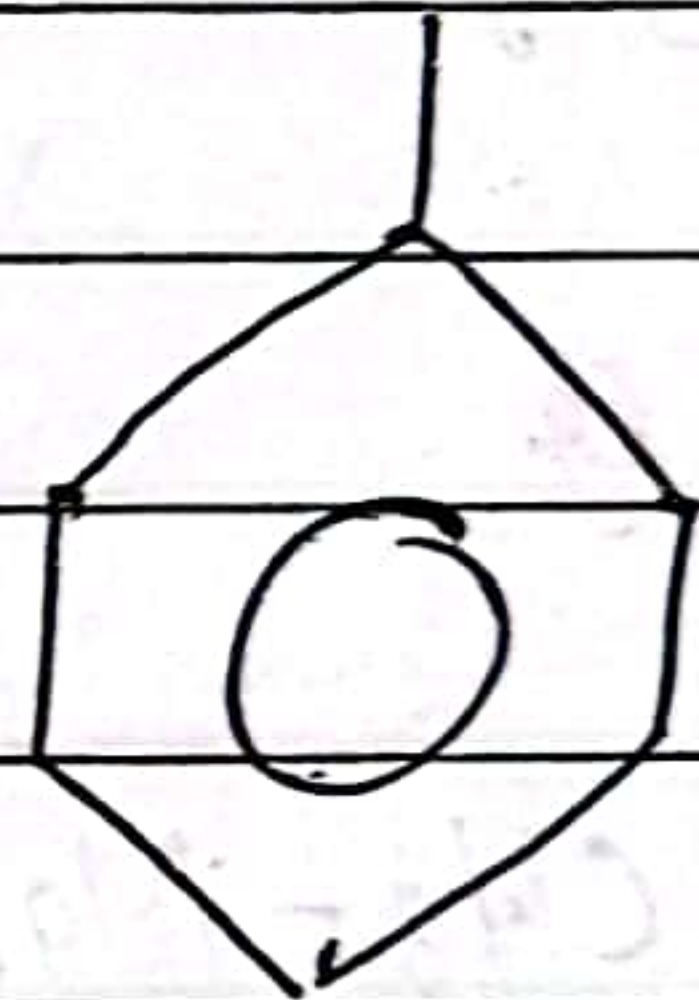
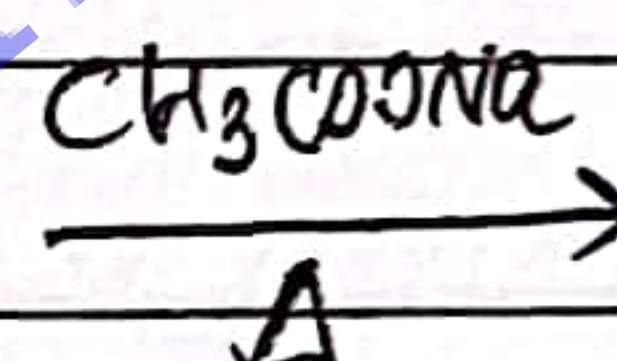
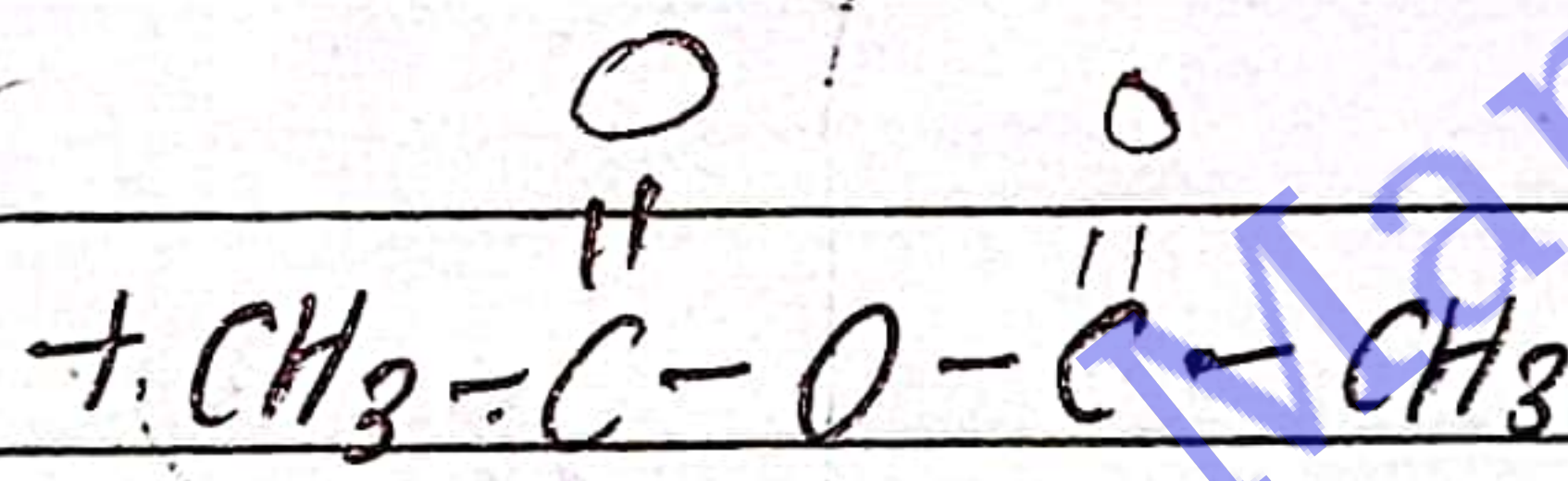
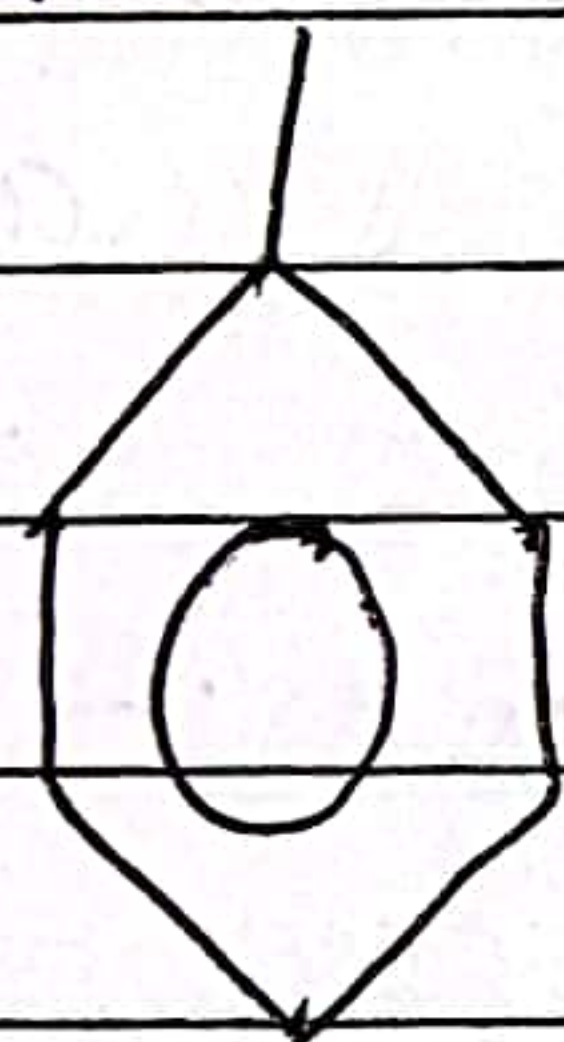
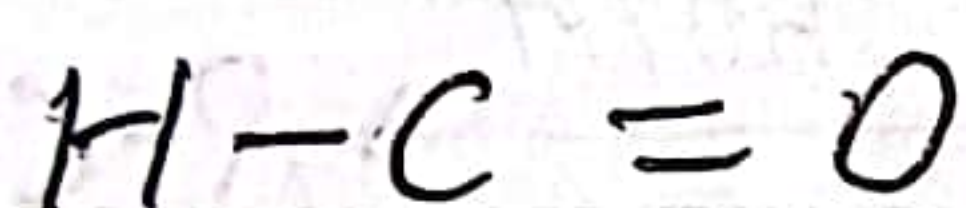
Some important examples of aldol condensation reaction are given as below:-



- Aldehydes or ketone, having lack of α-hydrogen do not undergo aldol condensation reaction.

22 Perkins reaction, Benzoin Condensation

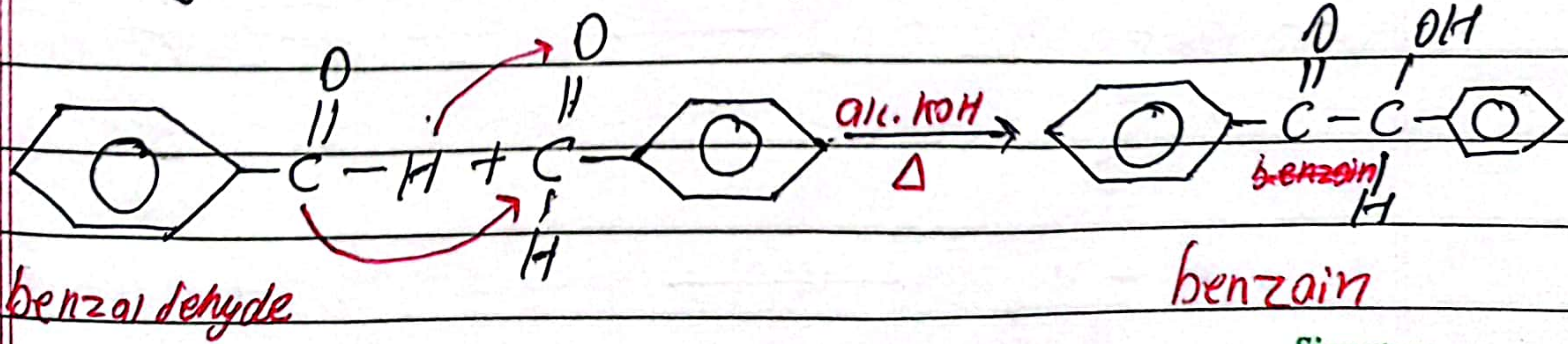
→ When aromatic aldehyde like benzaldehyde is condensed with aliphatic acid anhydride having at least two α -hydrogens like acetic anhydride in presence of salt of corresponding acid such as sodium acetate α - β -unsaturated acid is formed. This reaction is known as Perkins condensation reaction. The α - β unsaturated acid is called cinnamic acid.



α - β -unsaturated acid
(cinnamic acid)

* Benzoin Condensation.

→ Benzaldehyde if heated with alcoholic solution of potassium cyanide, yields α -hydroxy ketone known as benzoin. In the reaction two molecules of benzaldehyde undergo condensation to give a molecule of benzoin.

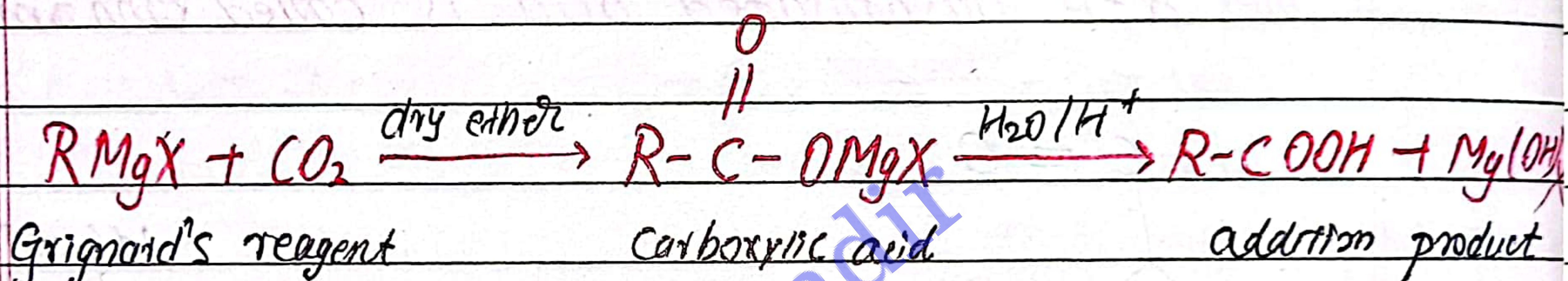


Signature

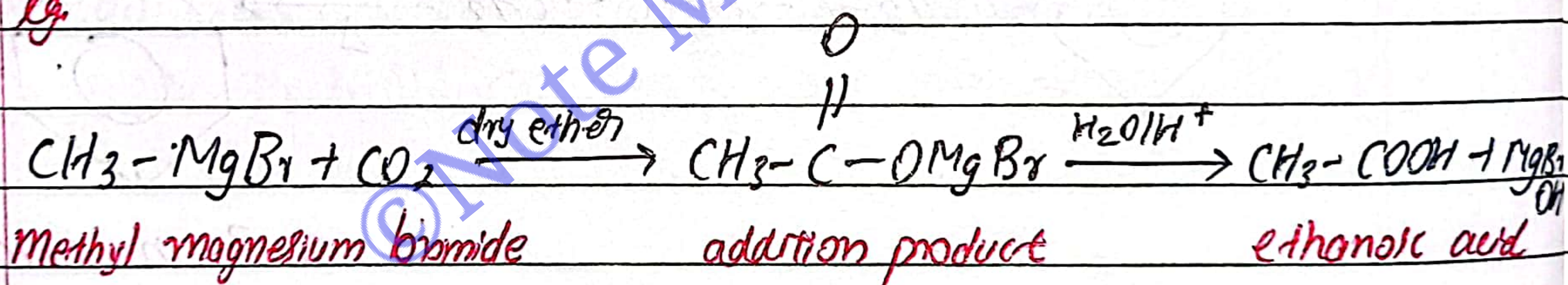
Carboxylic Acid

23. Grignard Carboxylic reaction

→ Carboxylic carbondioxide gas if passed through dry ether solution of Grignard's reagent produces an addition product. The addition product undergoes hydrolysis with mineral acid giving Carboxylic acid.



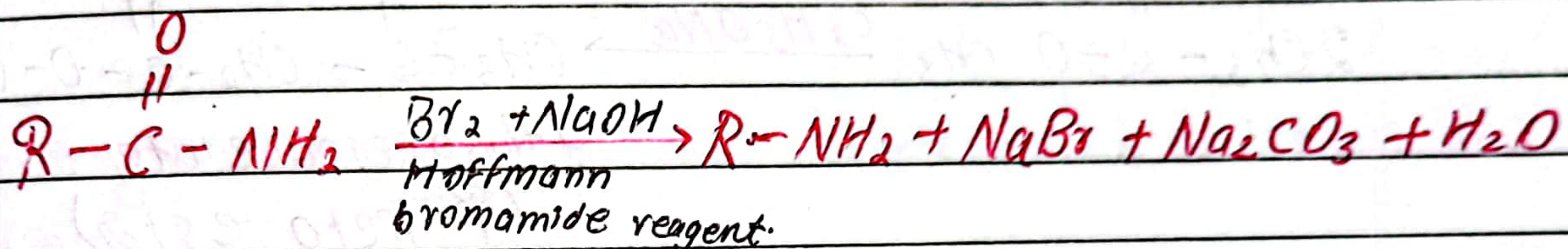
eg.



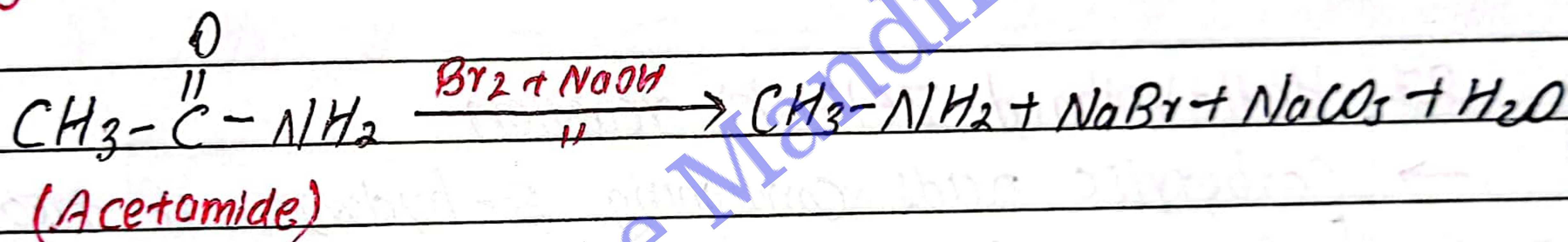
* Methanoic acid can not be prepared by this method.

24 Hoffmann bromamide reaction

→ When an amide is treated with bromine in an aqueous or ethanolic solution of sodium hydroxide, degradation of amide takes place leading to the formation of primary amine.

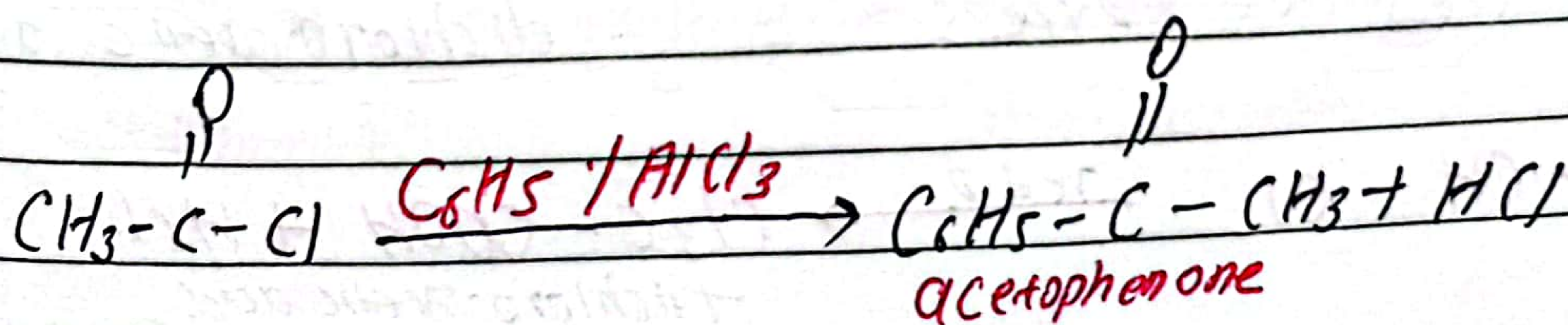
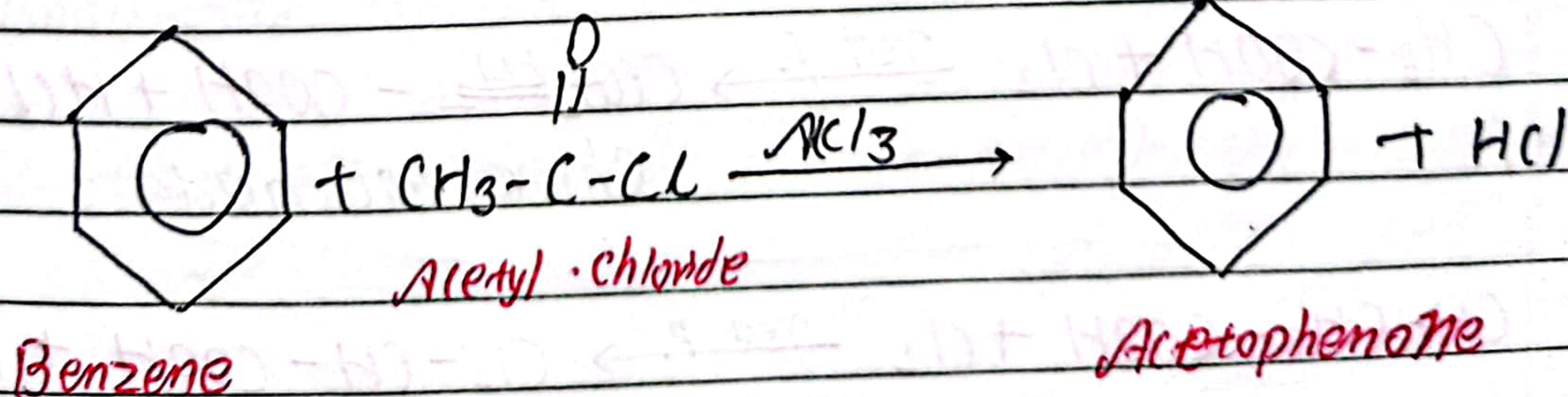


eg.



25 Friedel Craft acylation

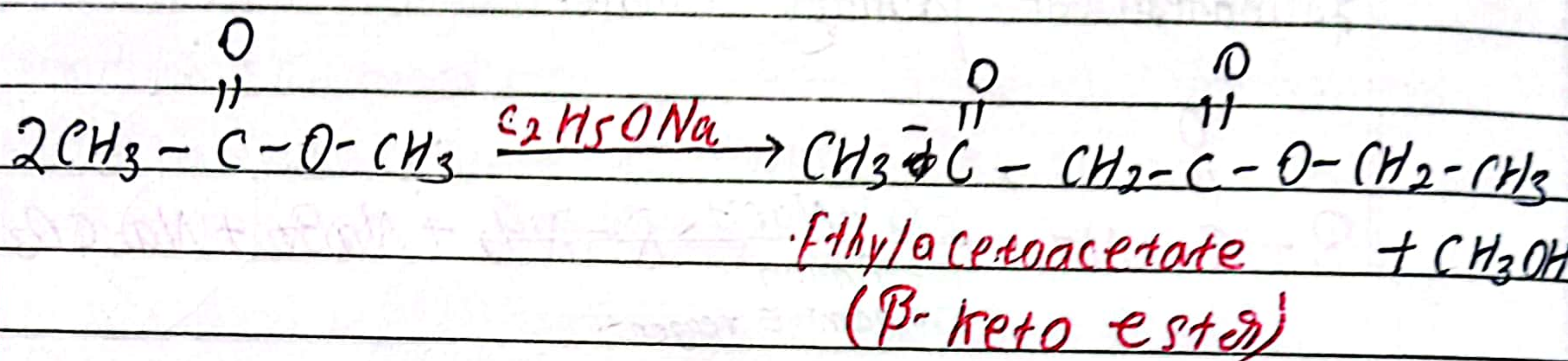
→ The reaction of benzene with an acyl halide or acid anhydride in the presence of Aluminium chloride yields acyl benzene.



Signature

26 Claisen condensation

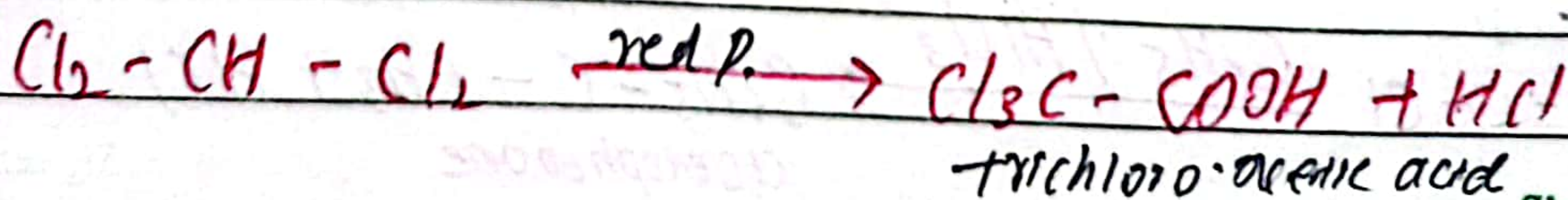
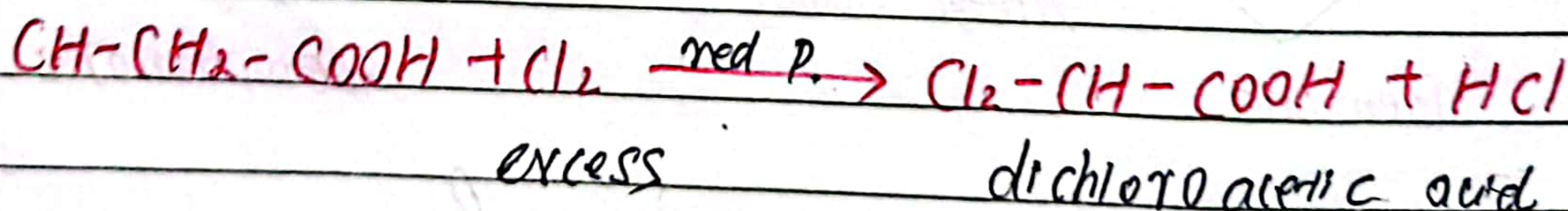
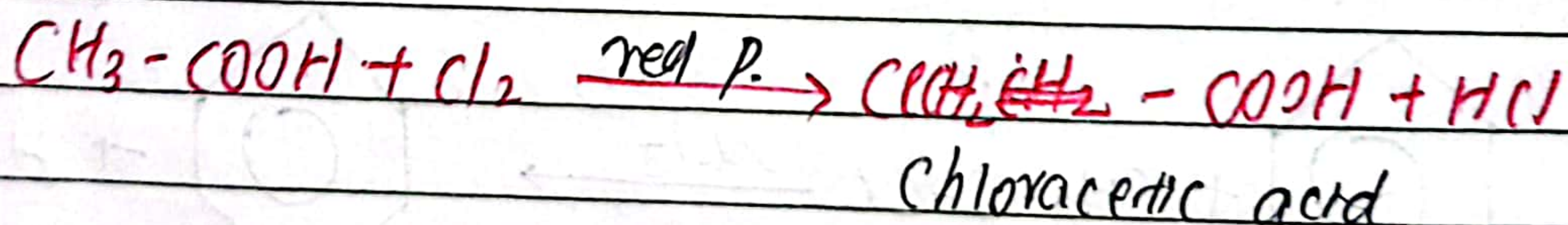
→ Esters with α -hydrogen atom on treat with a strong base eg ($\text{C}_2\text{H}_5\text{ONa}$) undergo self condensation to produce β -keto esters



27 Hell-Volhard-Zelinski reaction

→ Carboxylic acids containing α -hydrogen if treated with bromine or chlorine in presence of red phosphorus gives α -halo carboxylic acids

The chemical reaction undergoes halogenation unless all α -hydrogen are replaced. If excess bromine or chlorine will be used.



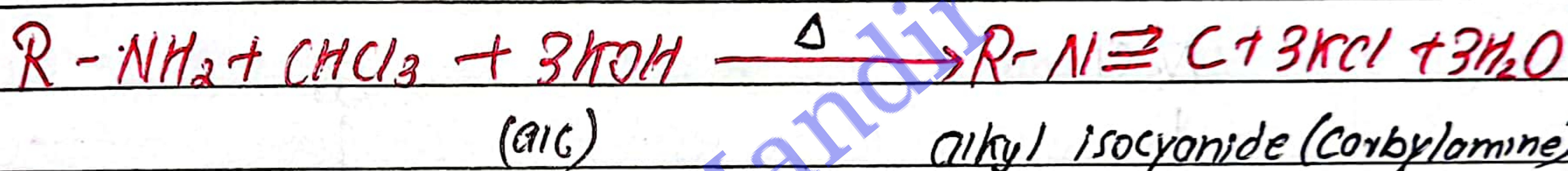
Nitro Compounds

* No name reaction

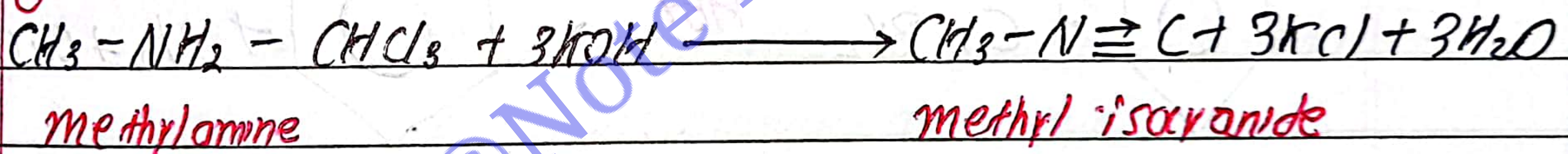
Amines

28 Carbylamine reaction

→ Primary amine if warmed with chloroform and alcoholic ~~isocyanide~~ solution of KOH, yields a compound having very offensive odour known as Carbylamine or isocyanide.

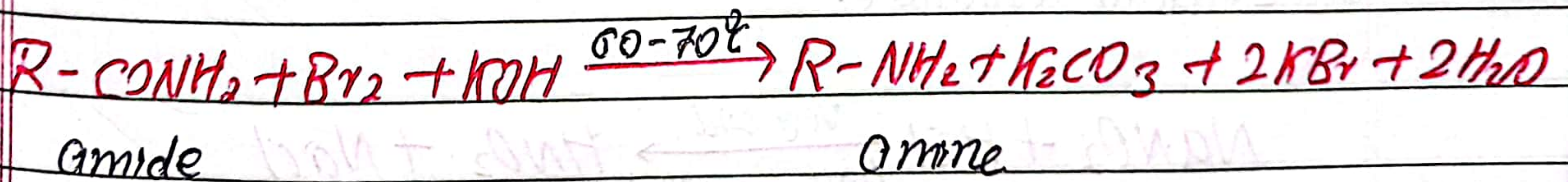


eg.

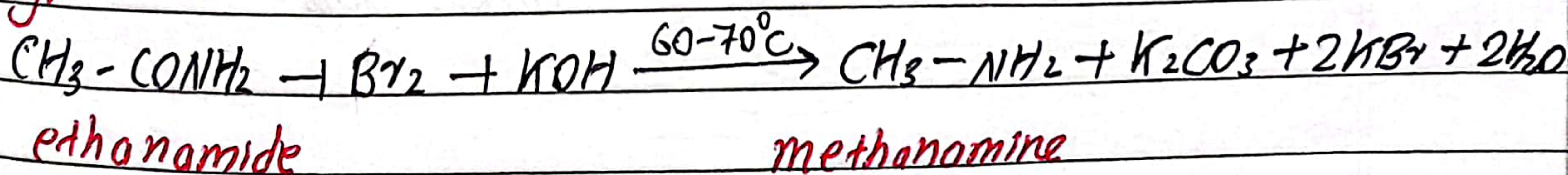


29 Hoffmann hypobromide reaction

→ Primary amide in presence with 10% aq. NaOH or NaOH solution is heated with bromine at $60^\circ - 70^\circ\text{C}$ until the reddish colour of bromine is discharged.

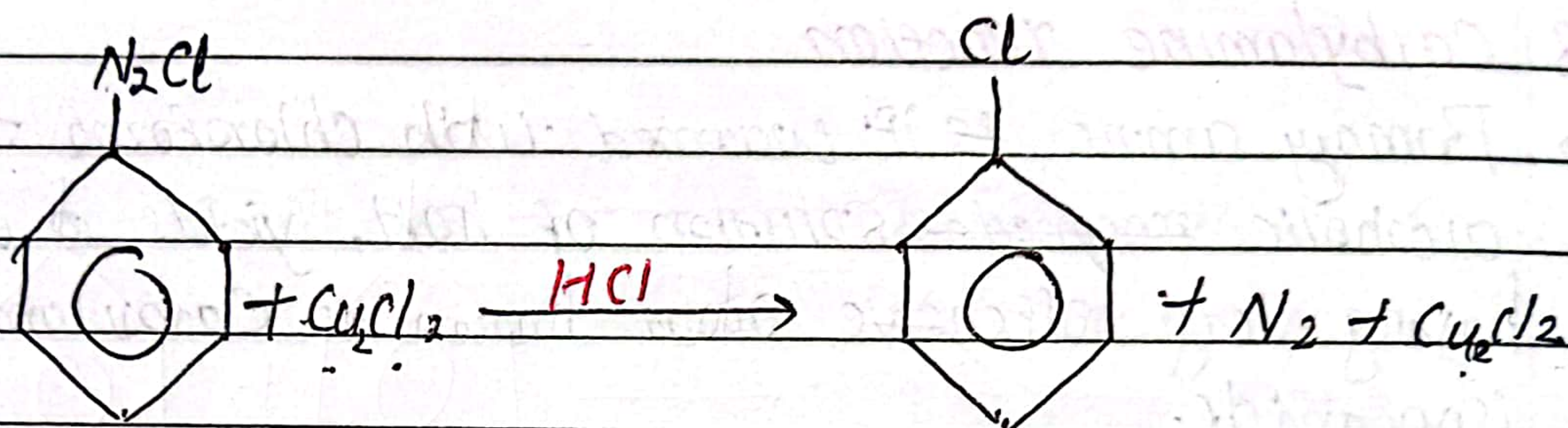


lg.

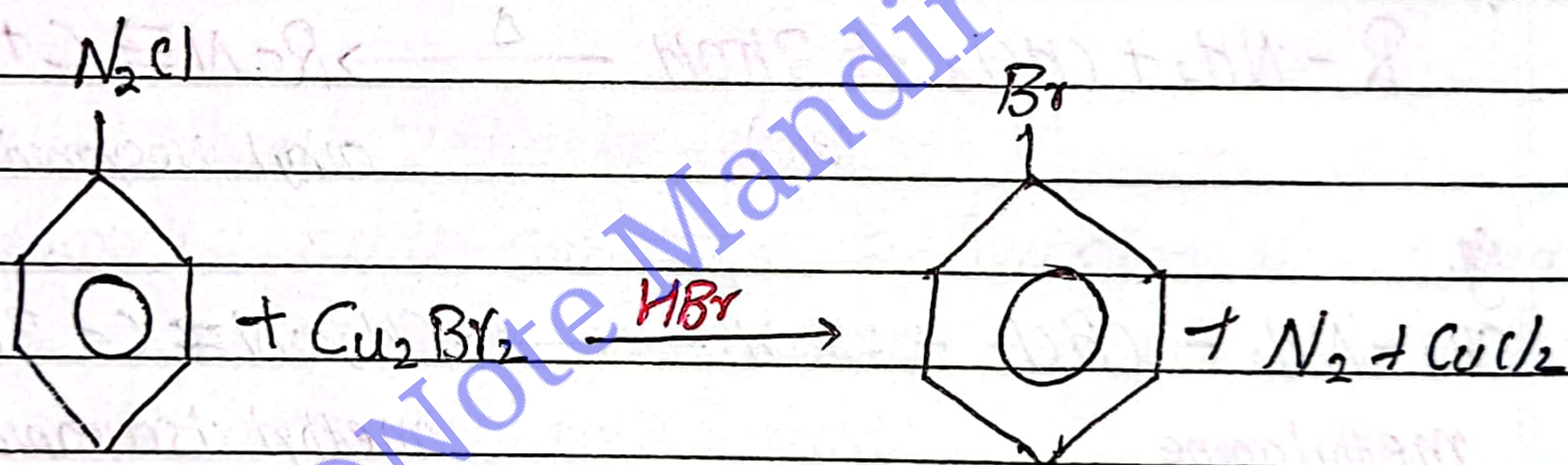


30 Sandmeyer's reactions

→ When diazonium salt is treated with cuprous halide in presence of a halo acid, then haloarene is obtained.



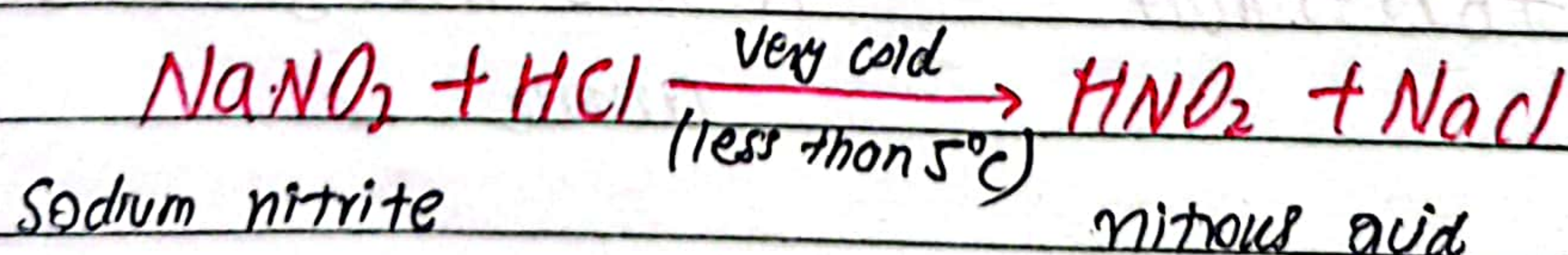
Chlorobenzene

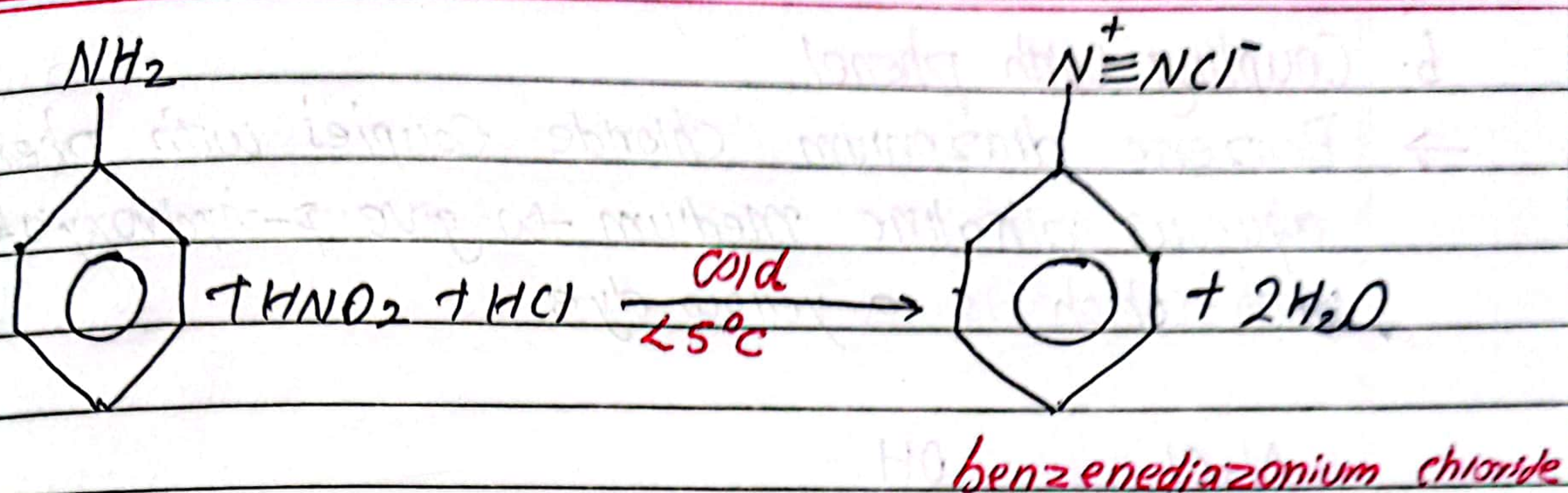


Bromobenzene

31 Diazotization reaction

→ Aniline if treated with ice cold solution of sodium nitrite and hydrochloric acid produces benzene diazonium chloride.



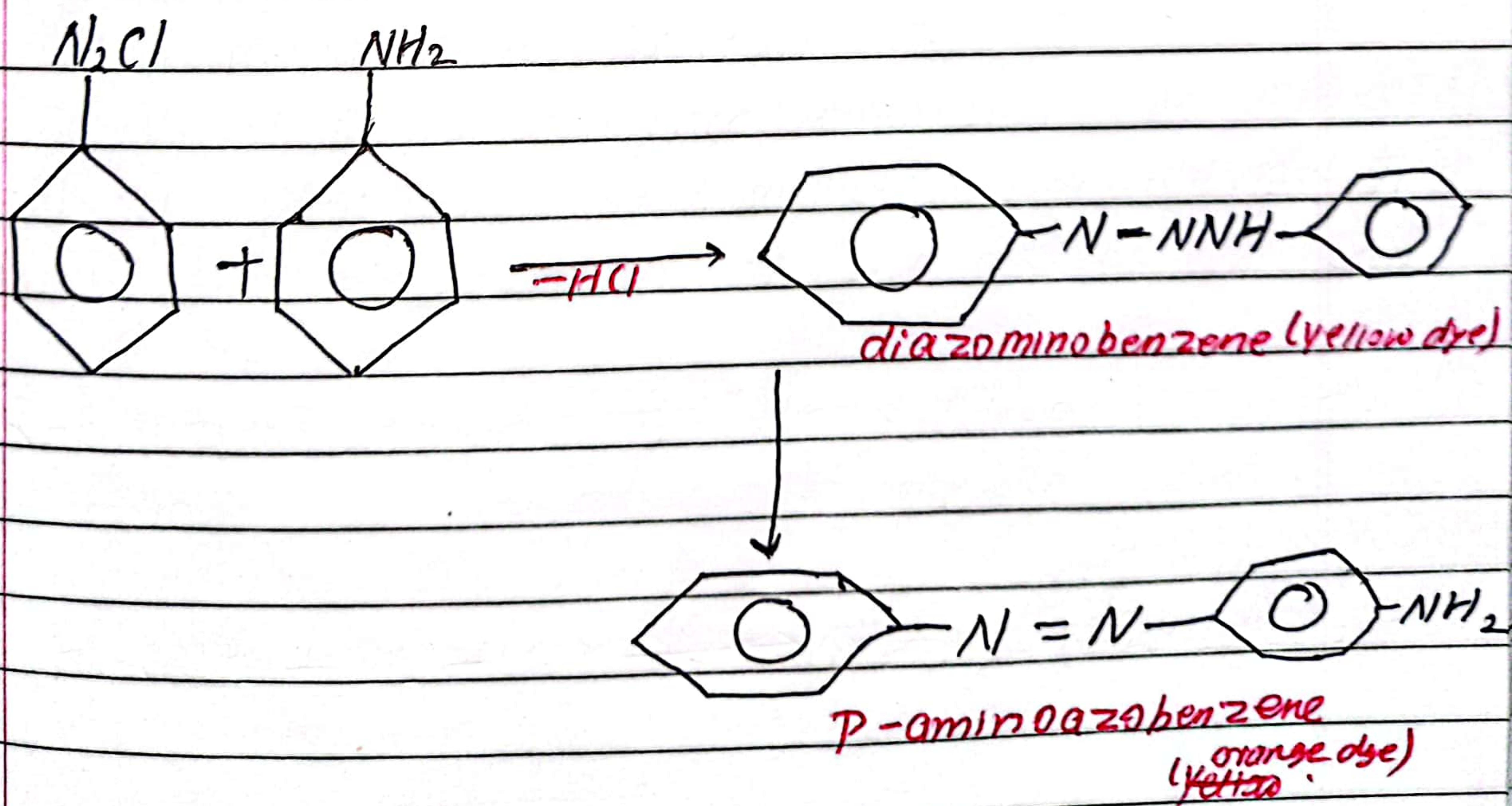


32 Coupling reaction (aniline, phenol)

a) Coupling with aniline

→ Aniline reacts with benzene diazonium chloride to give diazoaminobenzene which is a yellow dye.

The diazoaminobenzene undergoes rearrangement if warmed at 30 to 40°C to produce ~~p~~-aminobenzene **p-aminodiazobenzene**, an orange-red dye.



Signature

b. Coupling with phenol

→ Benzene diazonium chloride couples with phenol under aqueous alkaline medium to give p-hydroxyazobenzene which is a yellow dye

