

7/1/24

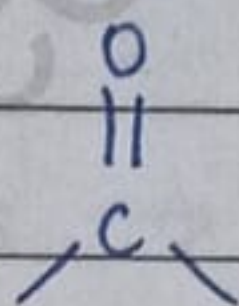
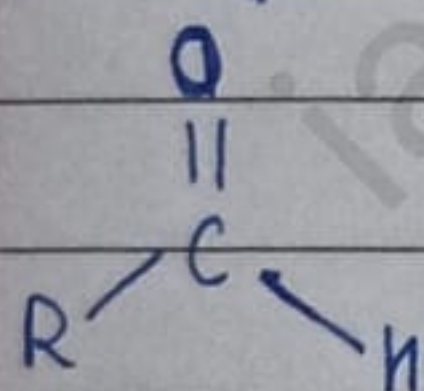
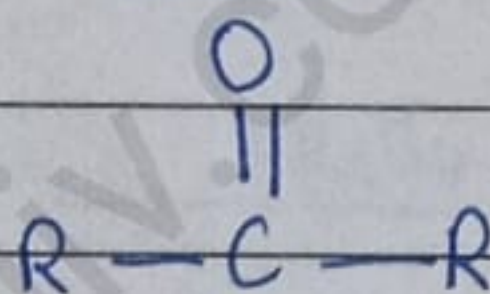
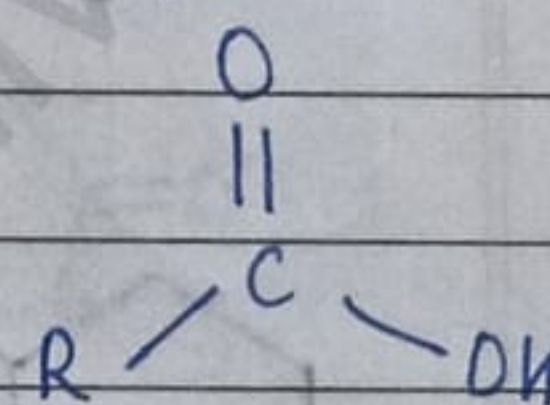
CHAPTER-8

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

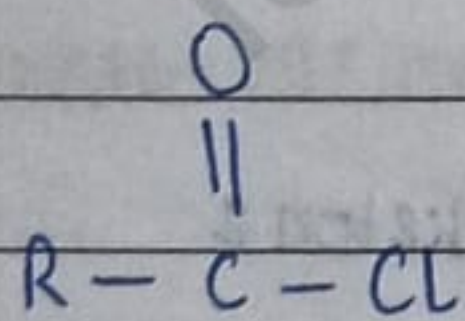
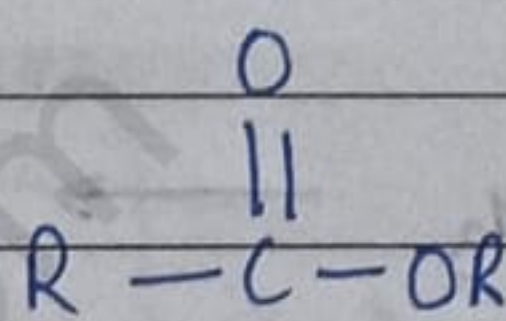
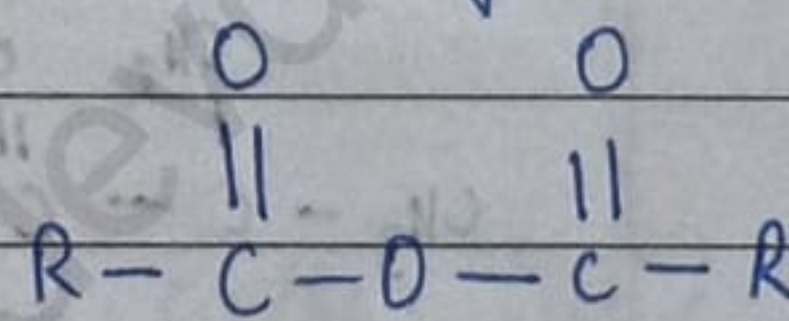
★ INTRODUCTION

• CARBONYL GROUP

Compounds in which carbon and oxygen hold double bond between them are referred as carbonyl compounds.

AldehydesKetonesCarboxylic Acids

• DERIVATIVES OF CARBOXYLIC ACID

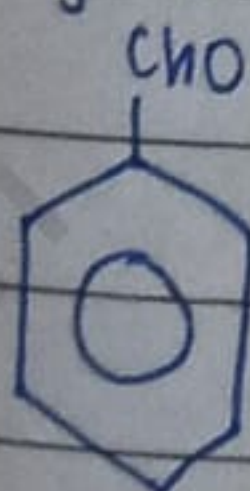
Acid halideEsterAcid anhydride

• COMMON NAMES

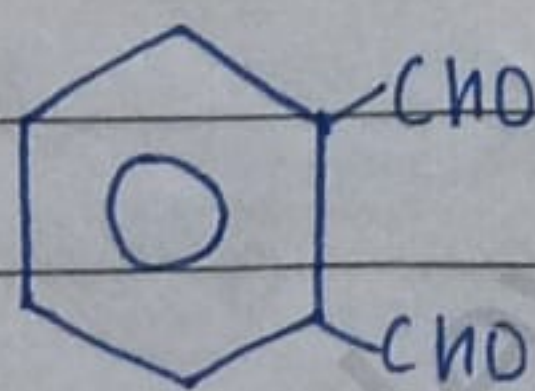
* ALDEHYDE

$\text{HCHO} \rightarrow$ Formaldehyde

$\text{CH}_3\text{CHO} \rightarrow$ Acetaldehyde



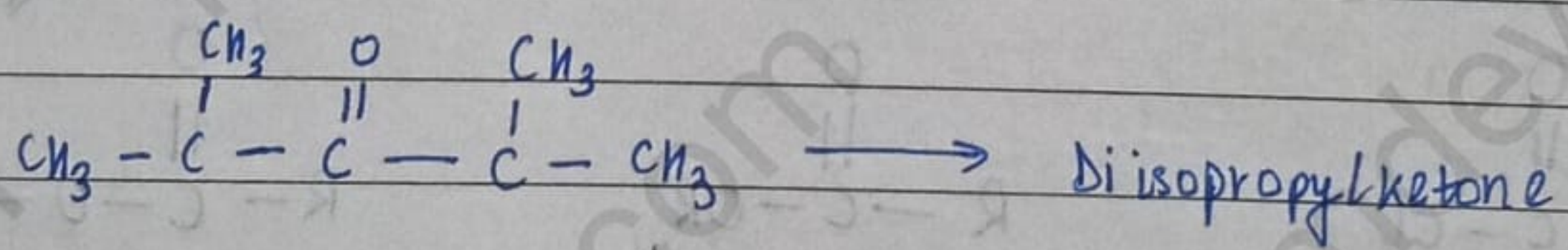
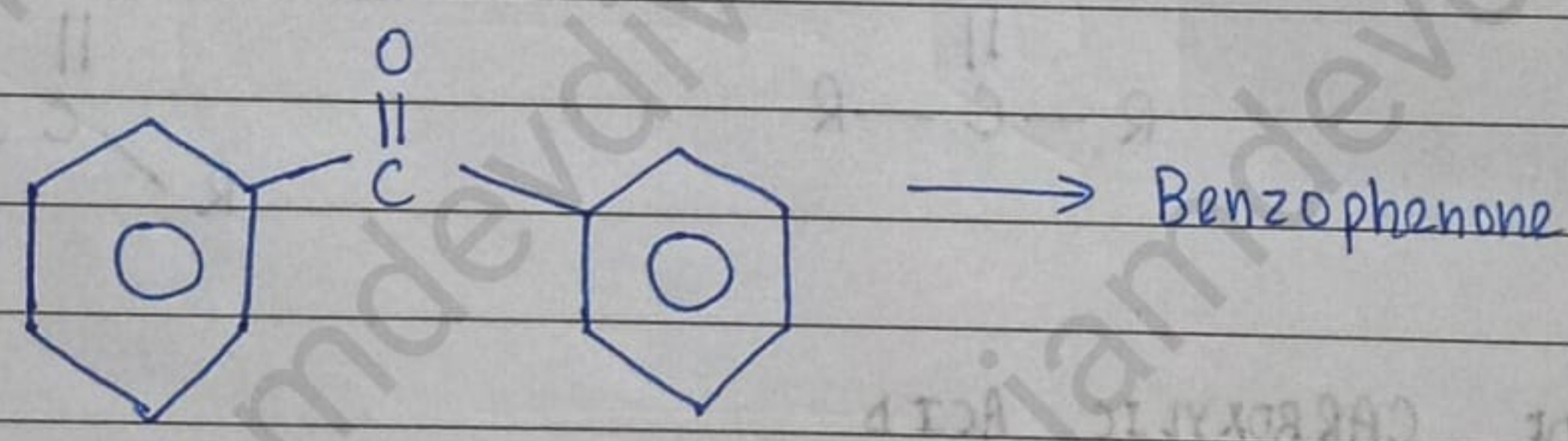
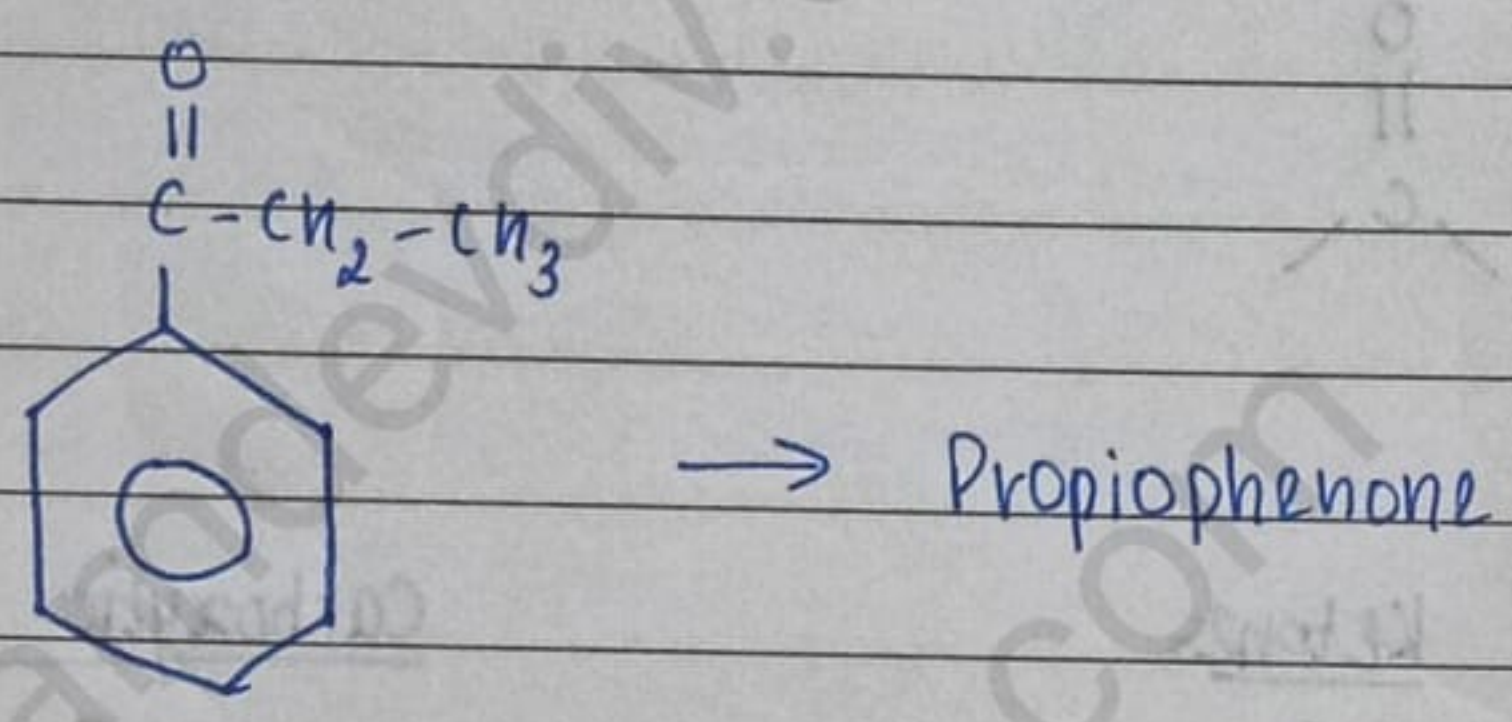
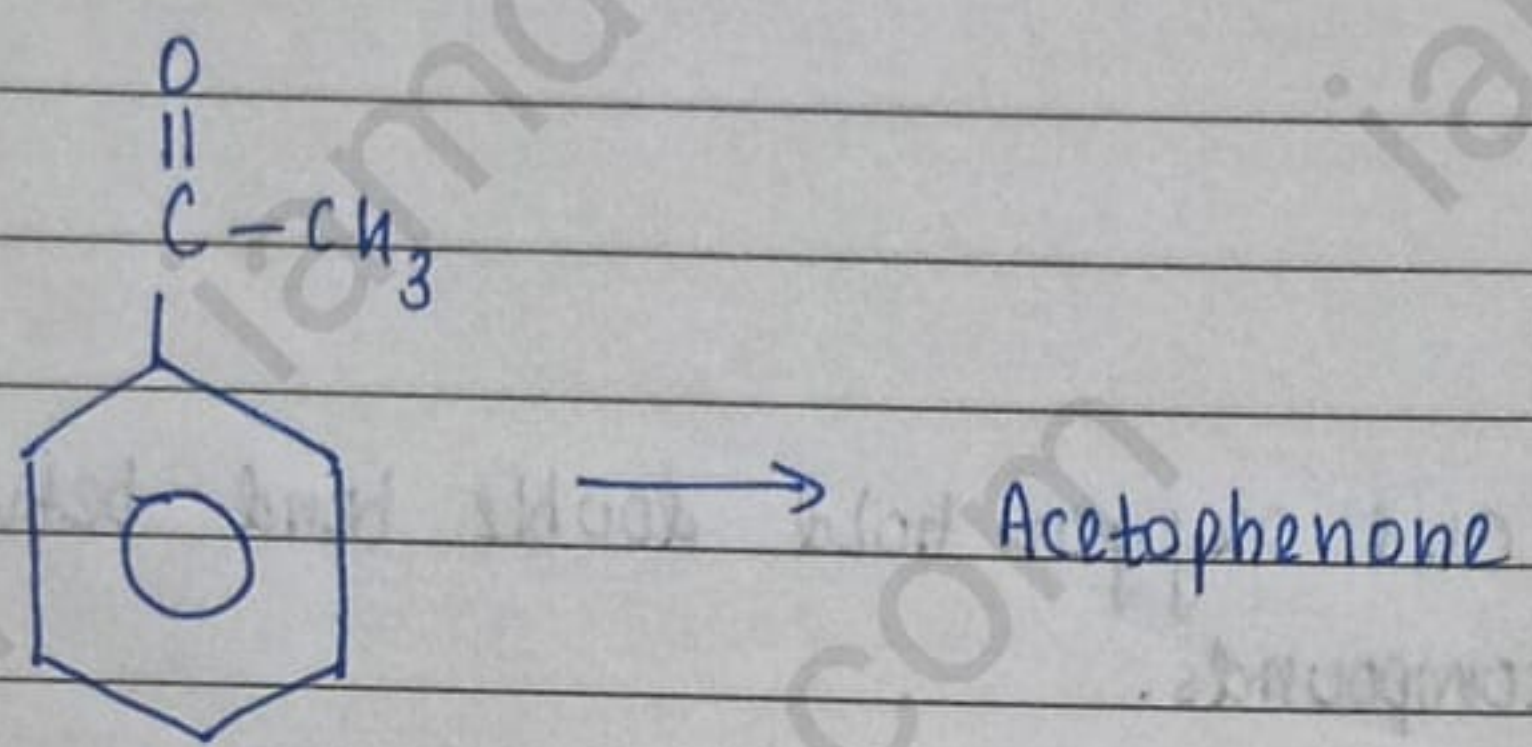
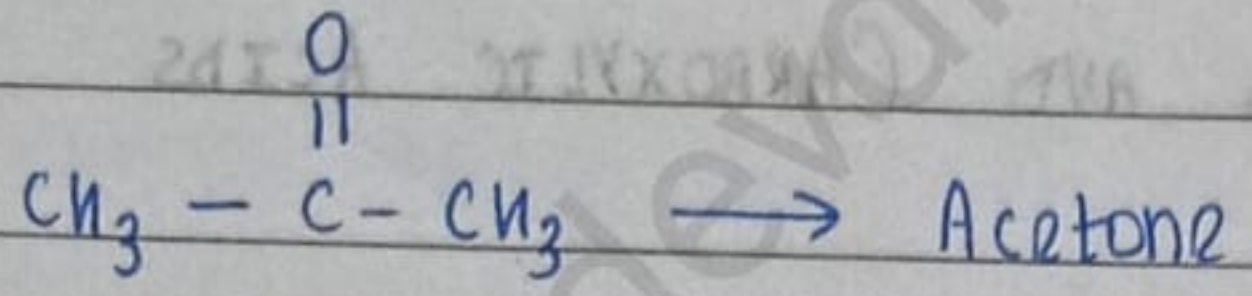
\rightarrow Benzaldehyde



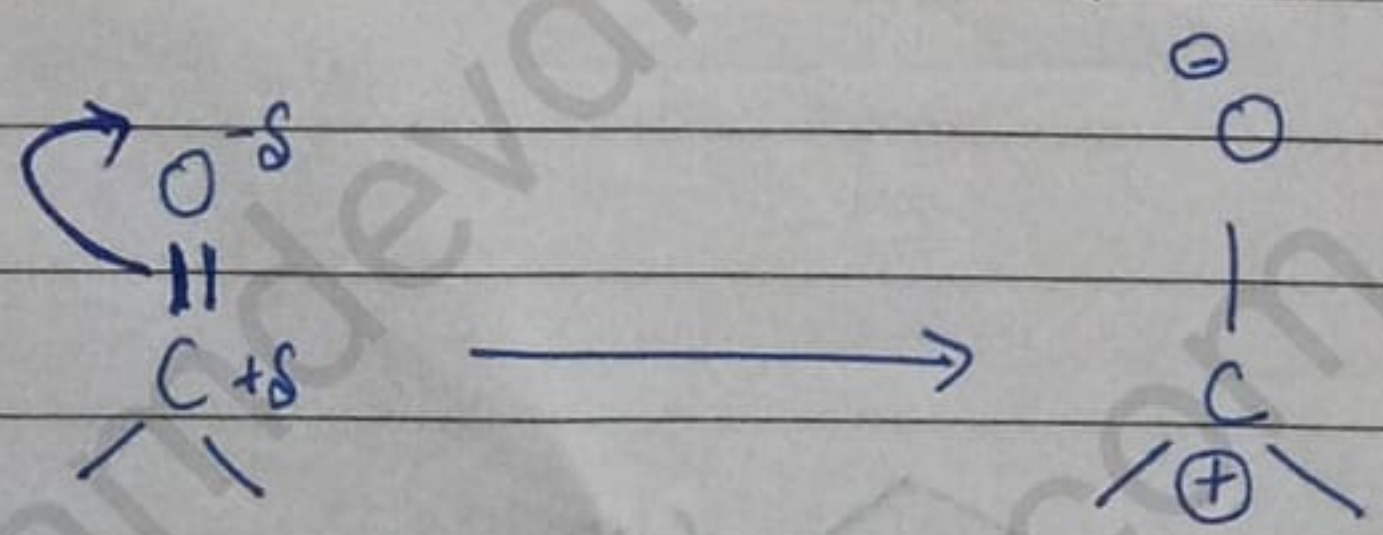
\rightarrow Phthalaldehyde

$\text{CH}_2=\text{CH}-\text{CHO} \rightarrow$ Acrolein

* KETONE



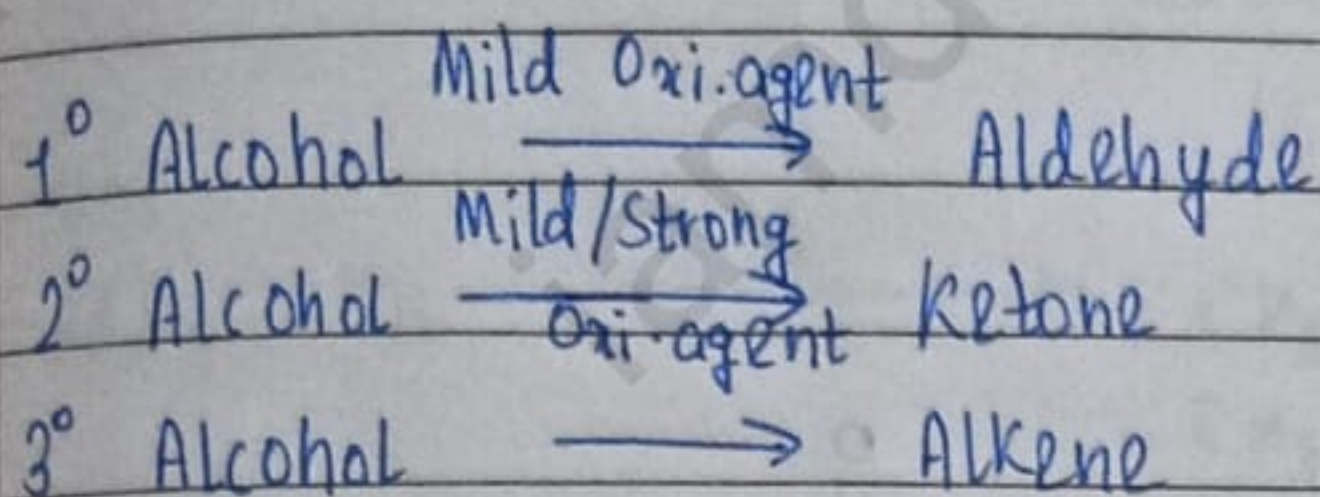
• STRUCTURE OF CARBONYL COMPOUND



sp^2
trigonal planar
Bond angle = 120°

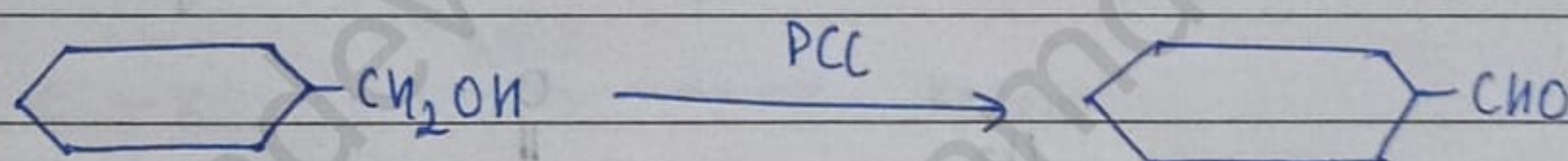
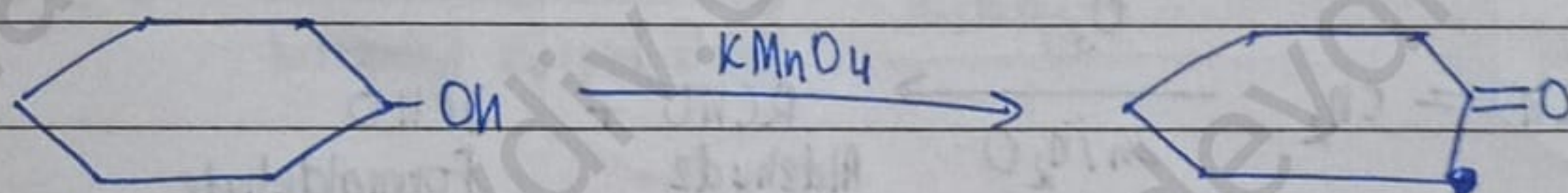
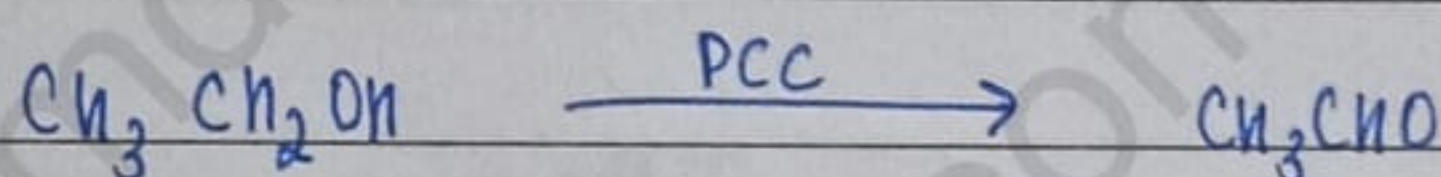
★ PREPARATION OF ALDEHYDES AND KETONES

• BY OXIDATION OF ALCOHOL

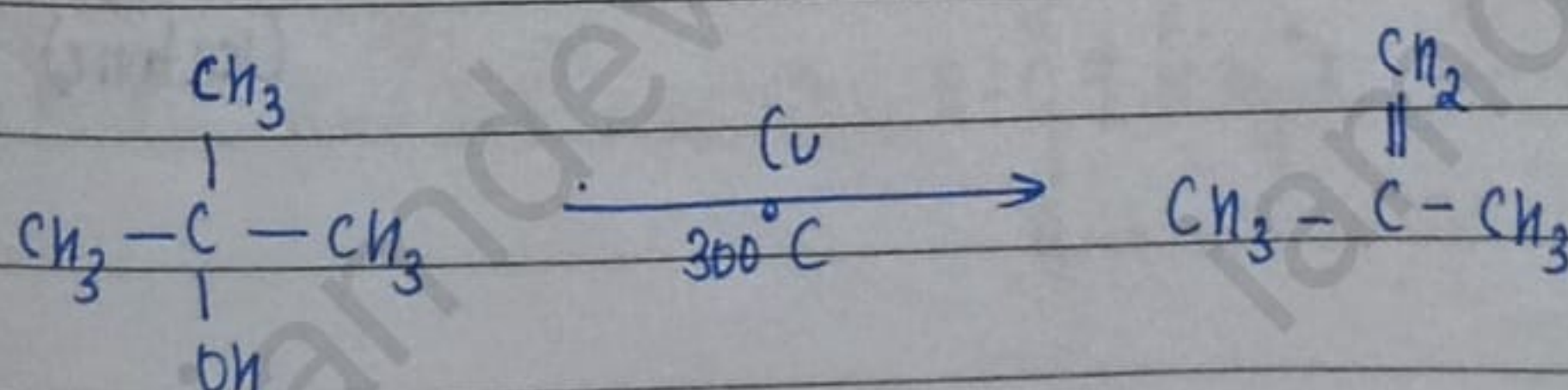
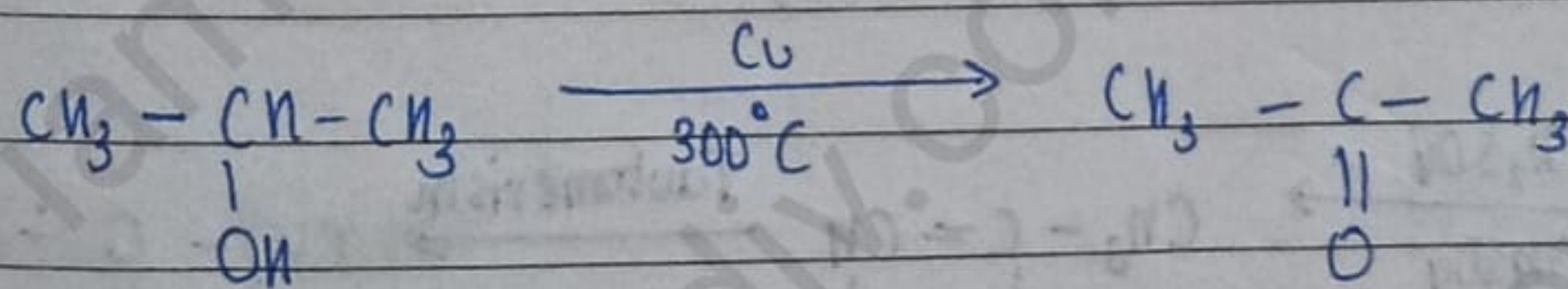
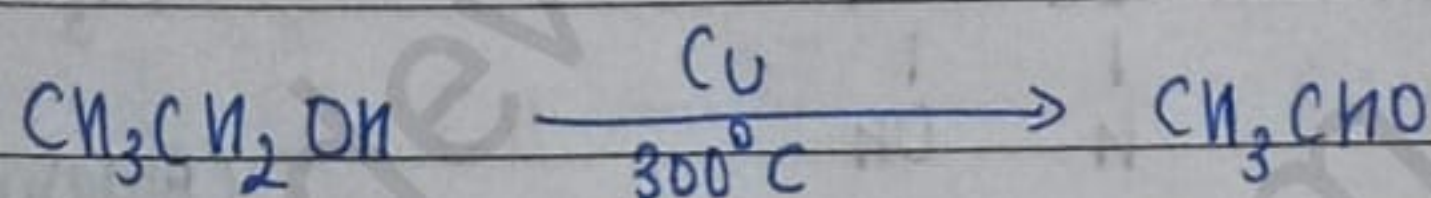
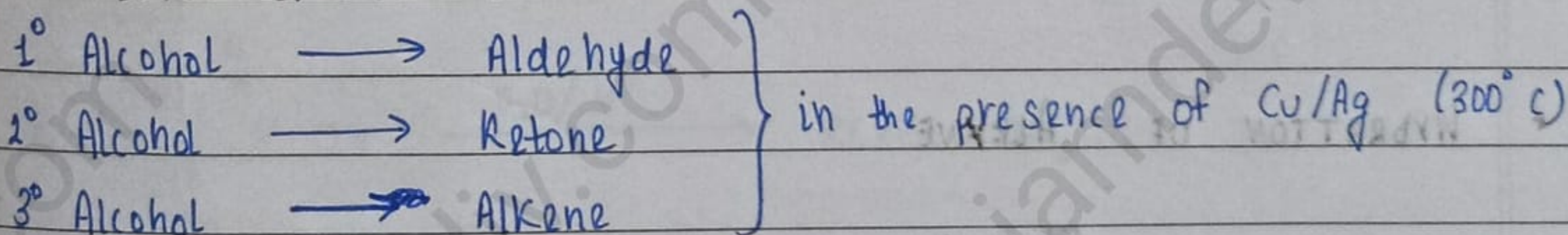


Mild oxidising agents \rightarrow PCC, $\text{CrO}_3 + \text{pyridine}$
 Strong oxidising agents \rightarrow Jones reagent, $\text{CrO}_3 + \text{H}_2\text{O}$, KMnO_4 , PDC

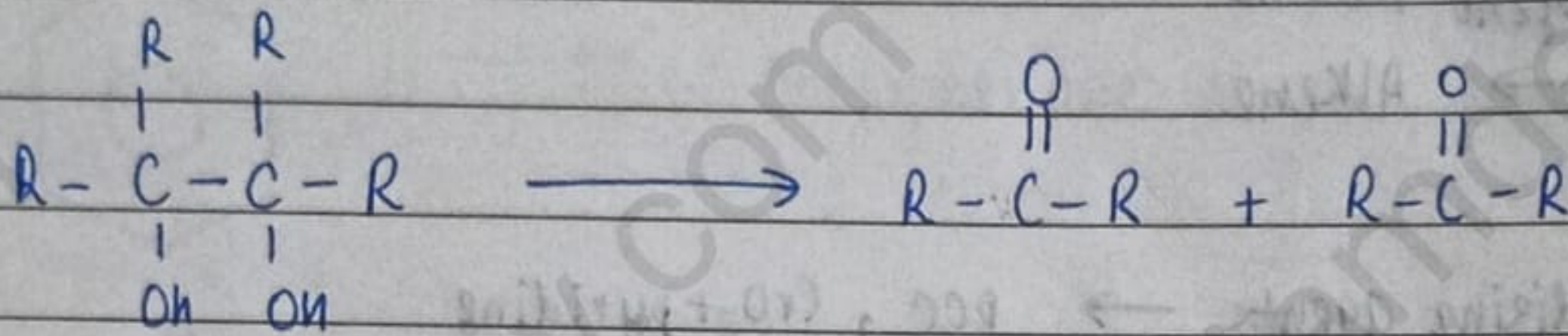
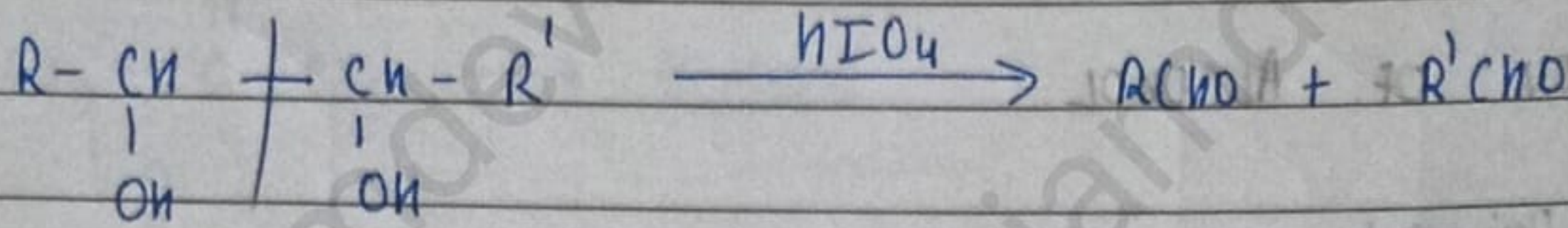
Examples:



• BY DEHYDROGENATION OF ALCOHOL

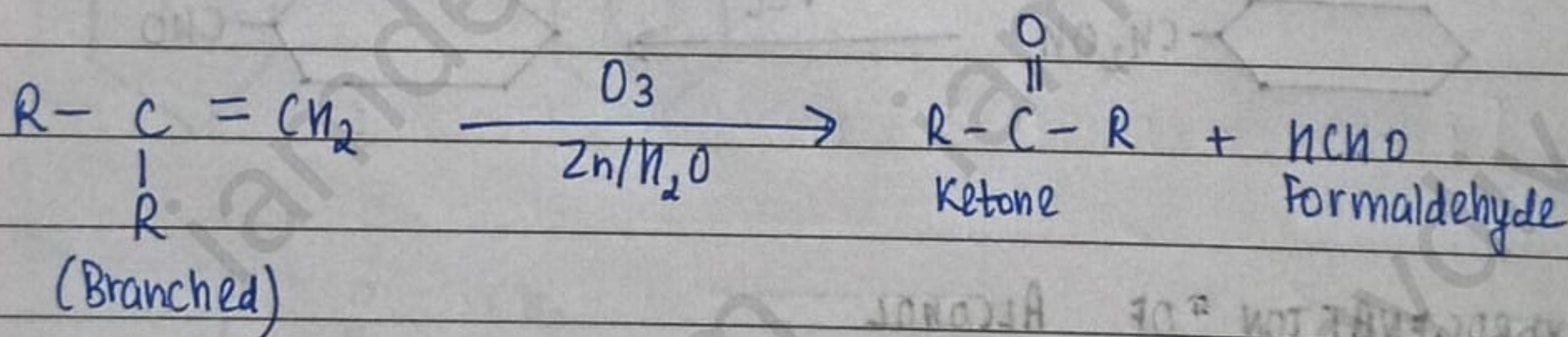
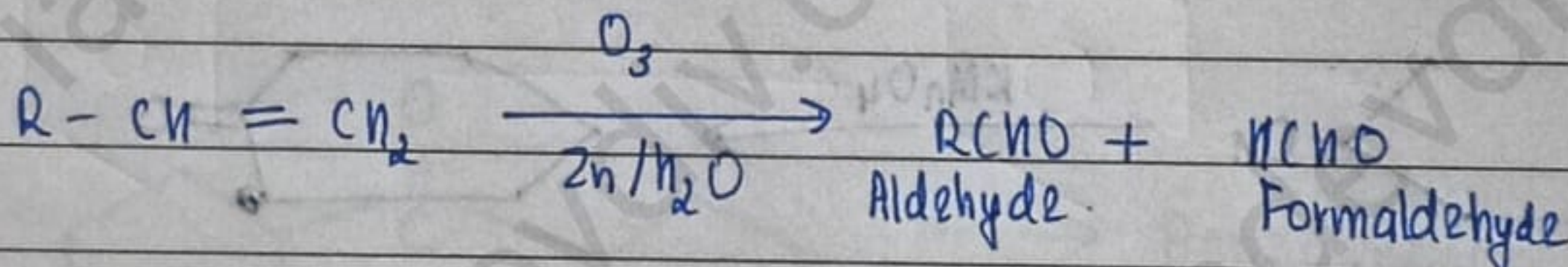


- BY OXIDATION OF ALCOHOL [BY KIO_4 / $\text{Pb}(\text{CH}_3\text{COO})_4$]

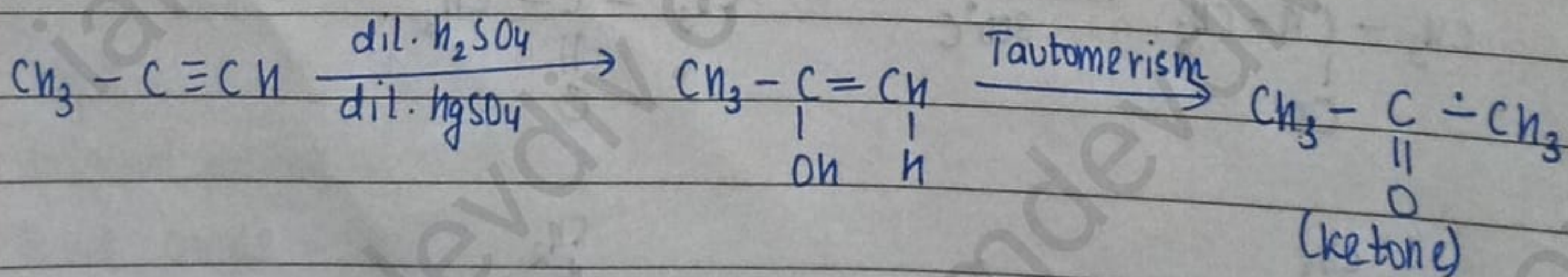
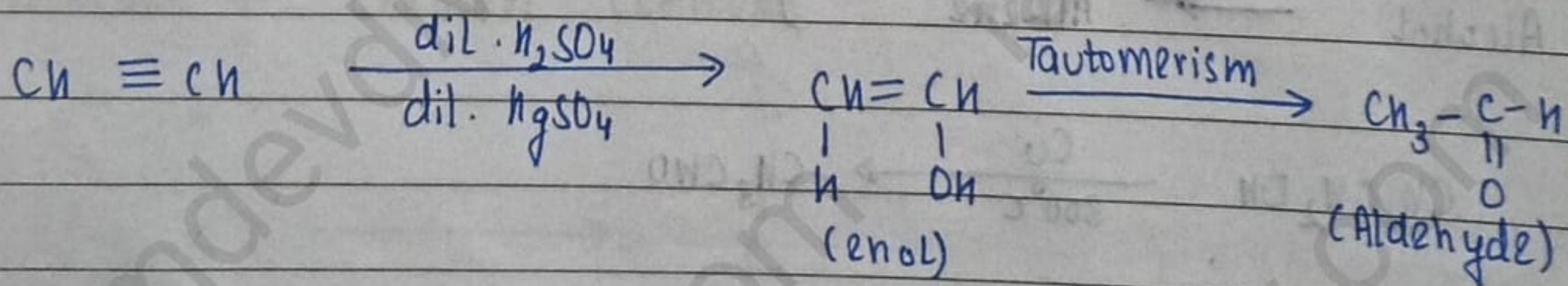


- BY HYDROCARBONS

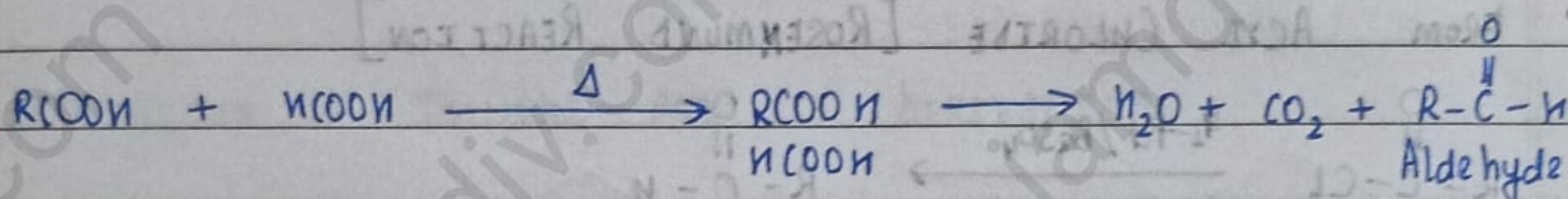
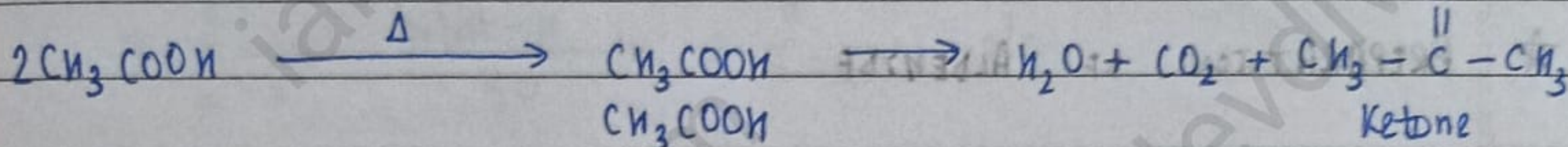
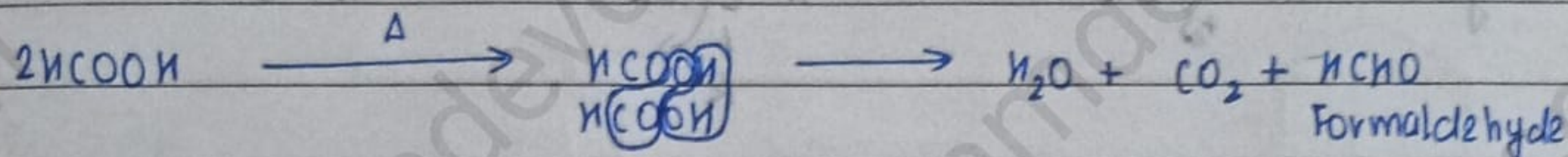
* OZONOLYSIS



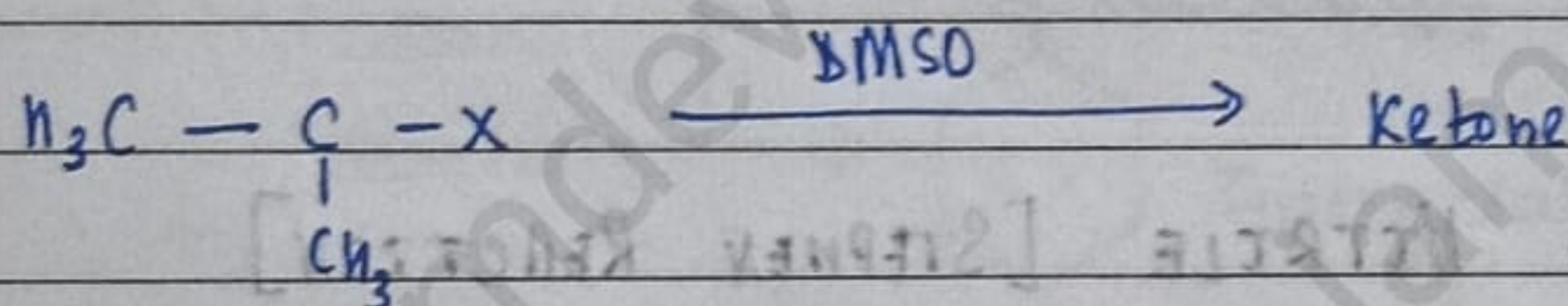
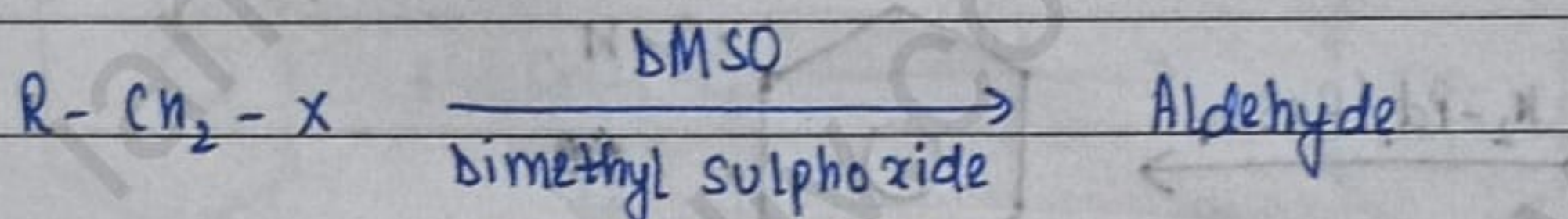
* HYDRATION OF ALKYNE



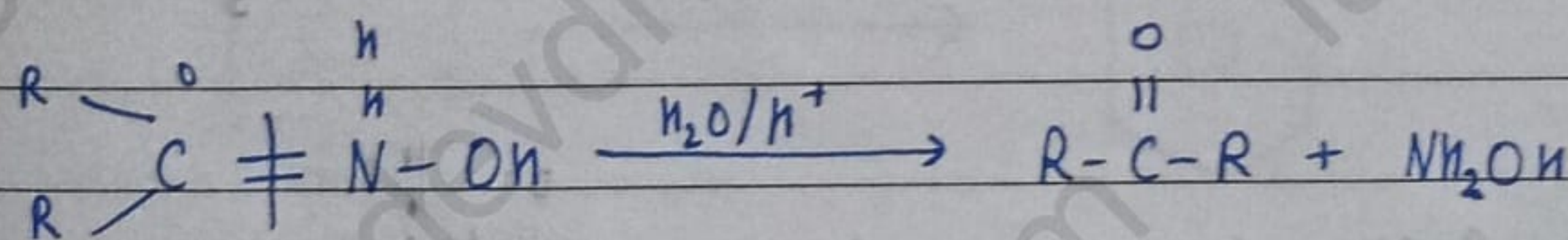
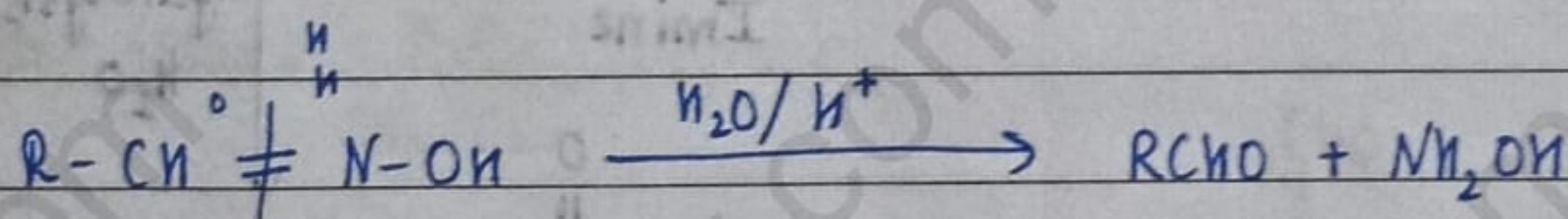
• THERMAL DECOMPOSITION OF MONOCARBOXYLIC ACID



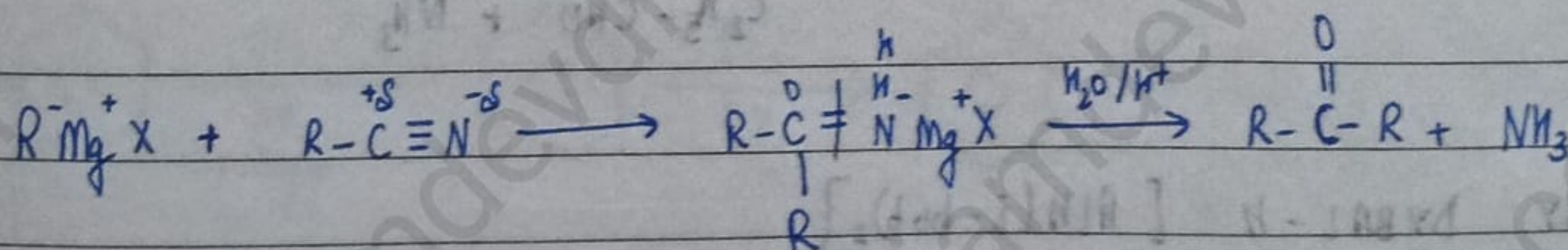
• FROM ALKYL HALIDE

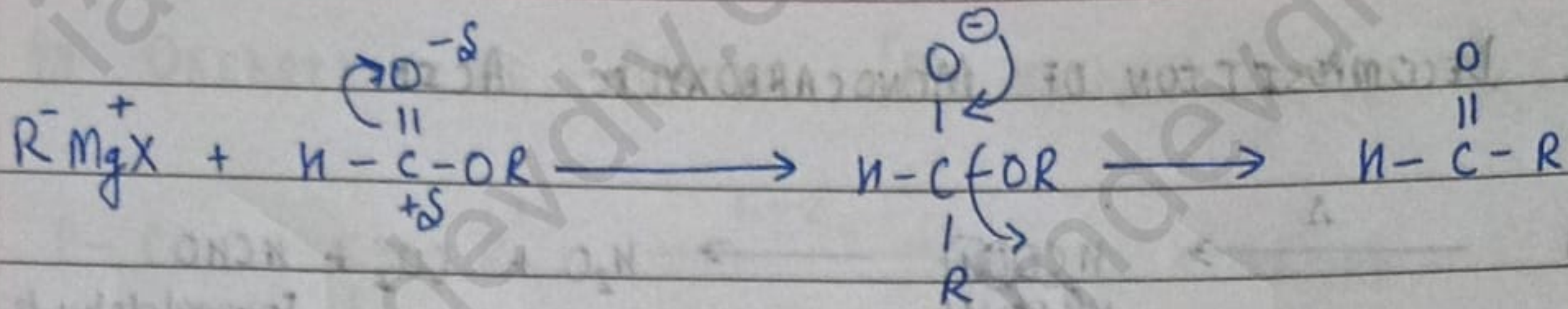


• HYDROLYSIS OF CARBONYL DERIVATIVE



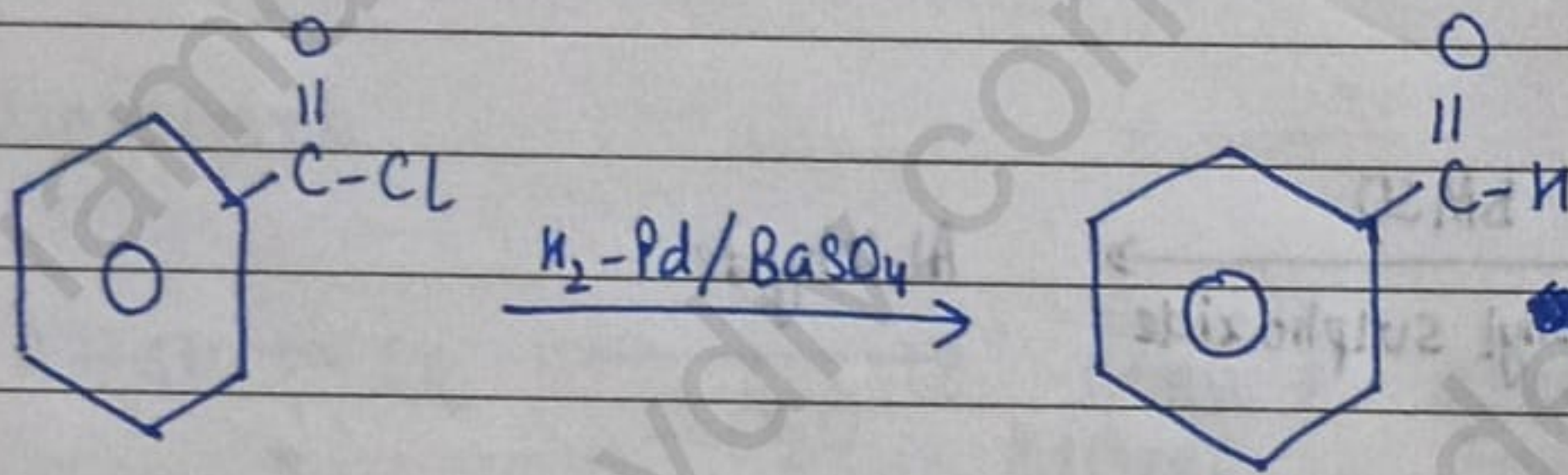
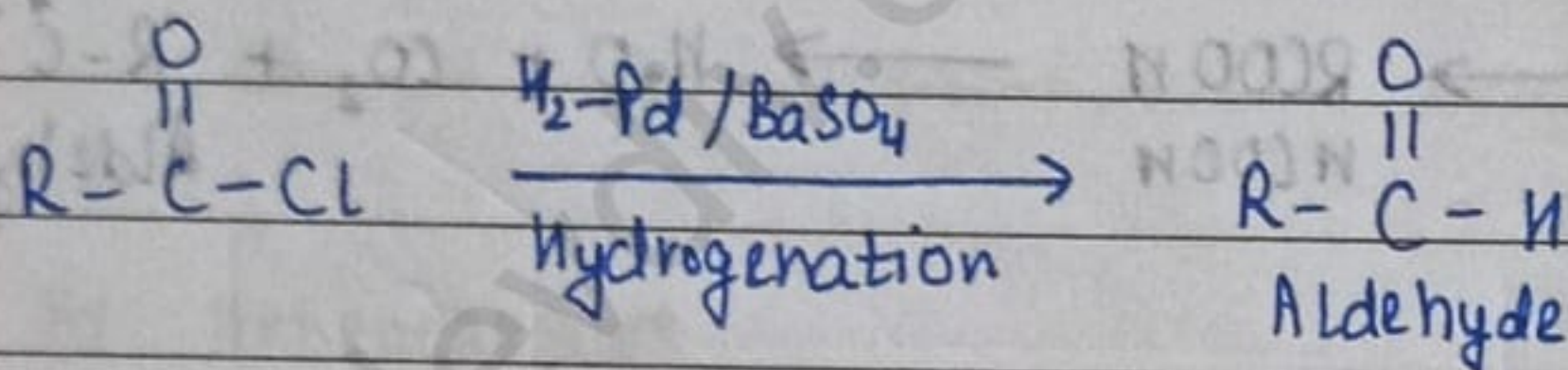
• GRIENARD REAGENT



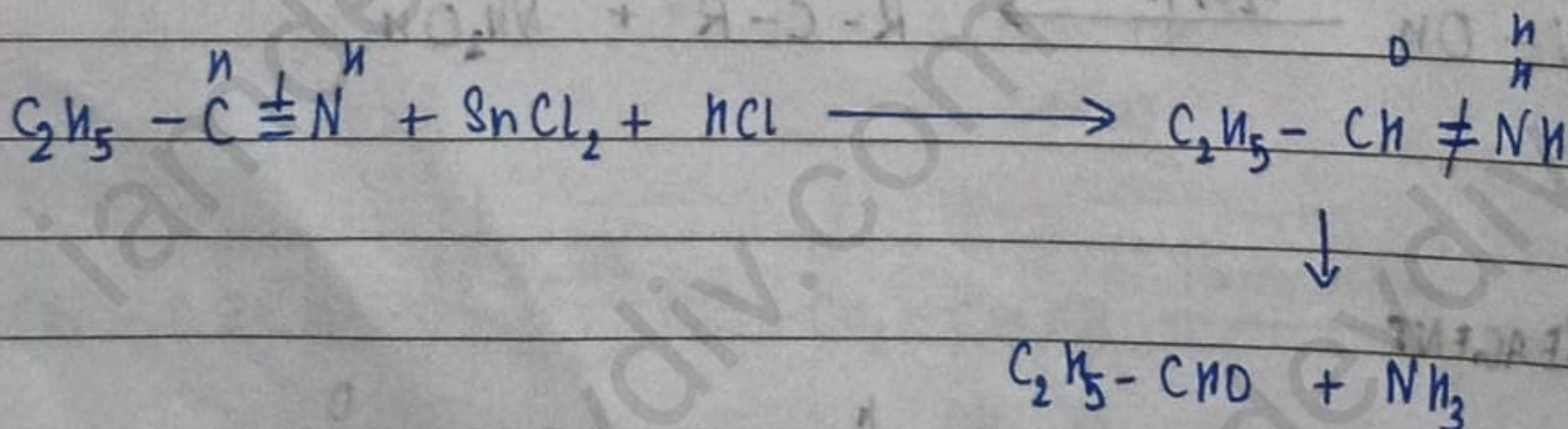
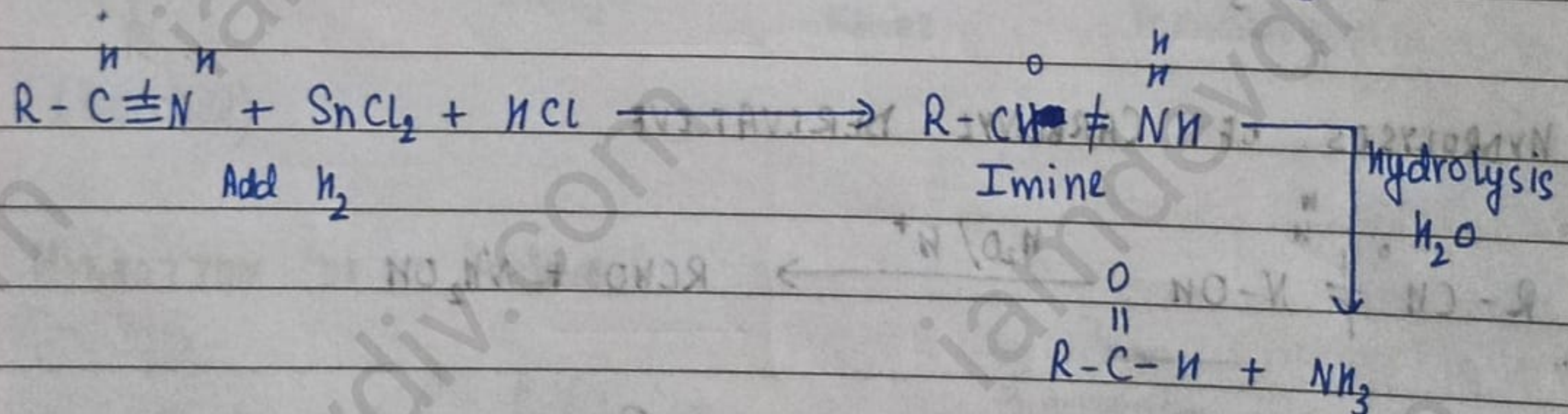


★ PREPARATION OF ALDEHYDE

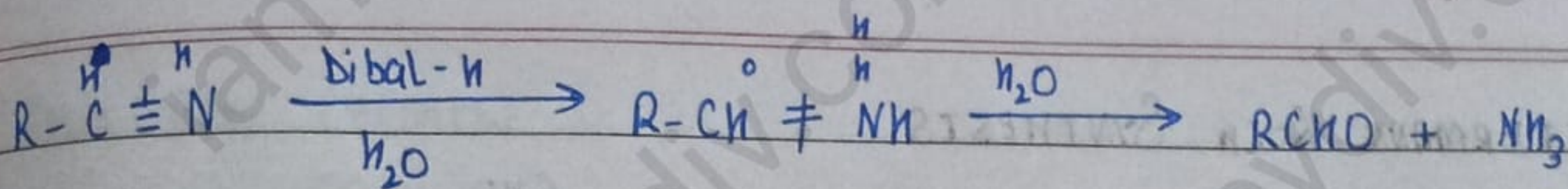
• FROM ACYL CHLORIDE [ROSEMMUND REACTION]



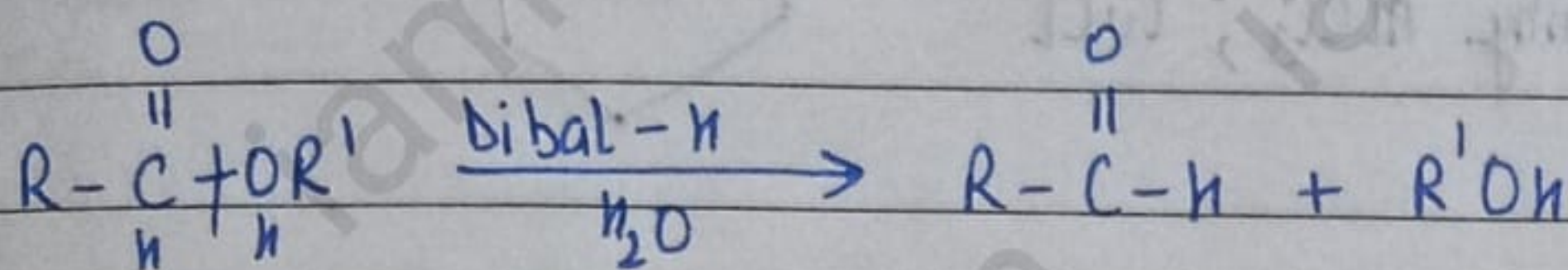
• BY REDUCTION OF NITRILE [STEPHEN REACTION]



• BY DYBAL-H [ALN(i-but)₂]

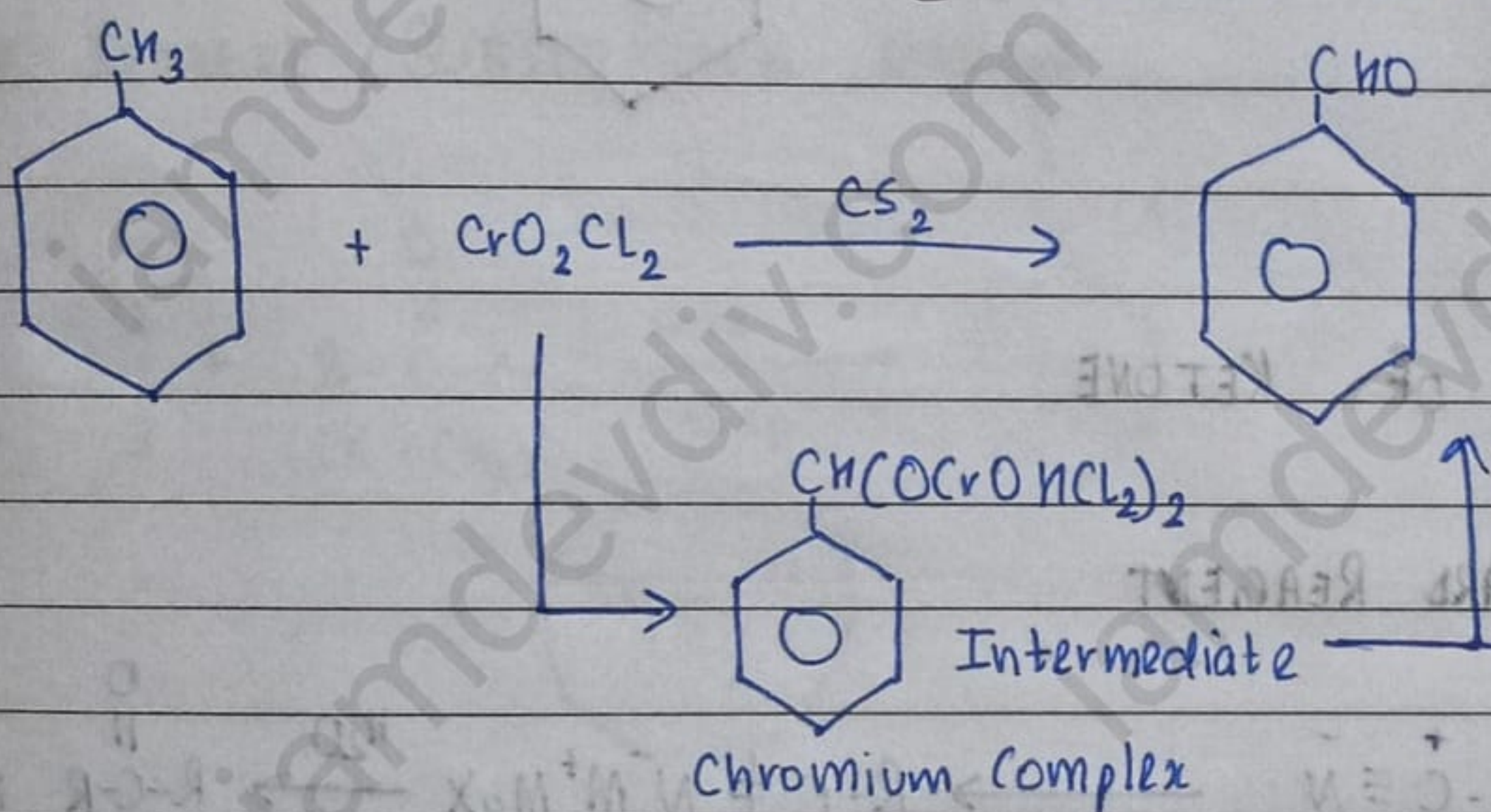


By ester

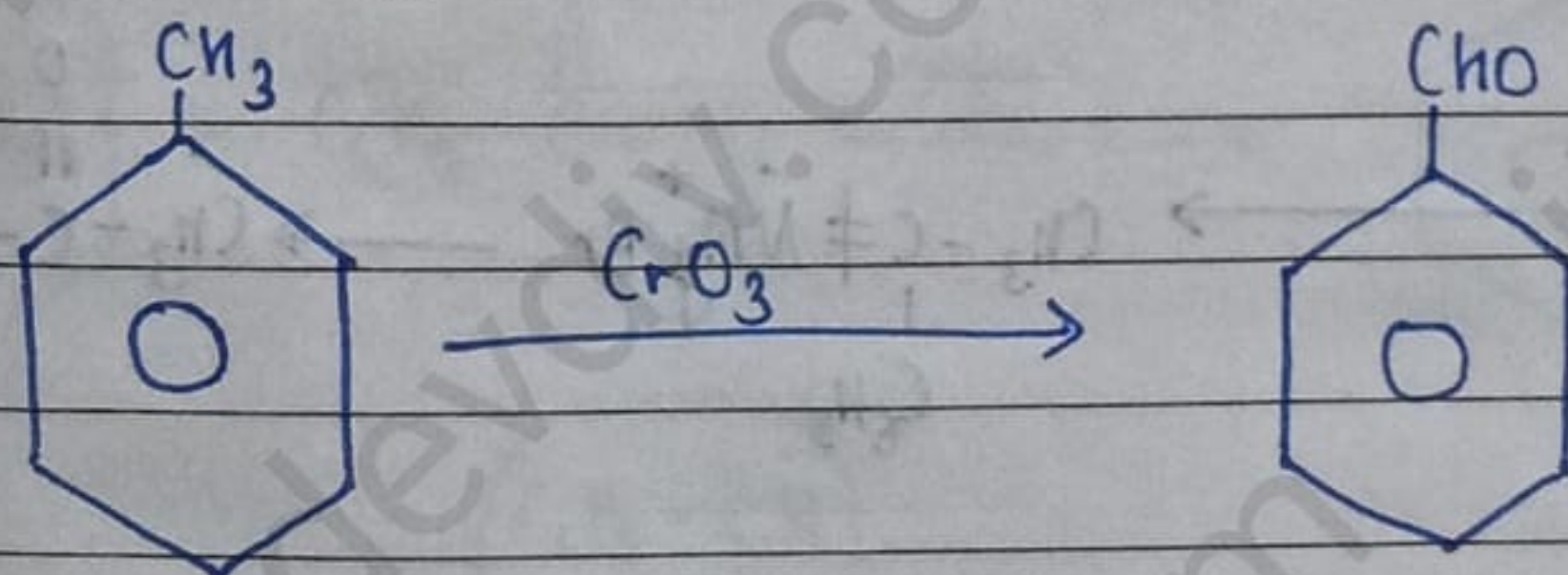


OXIDATION OF TOLUENE AND ITS DERIVATIVES

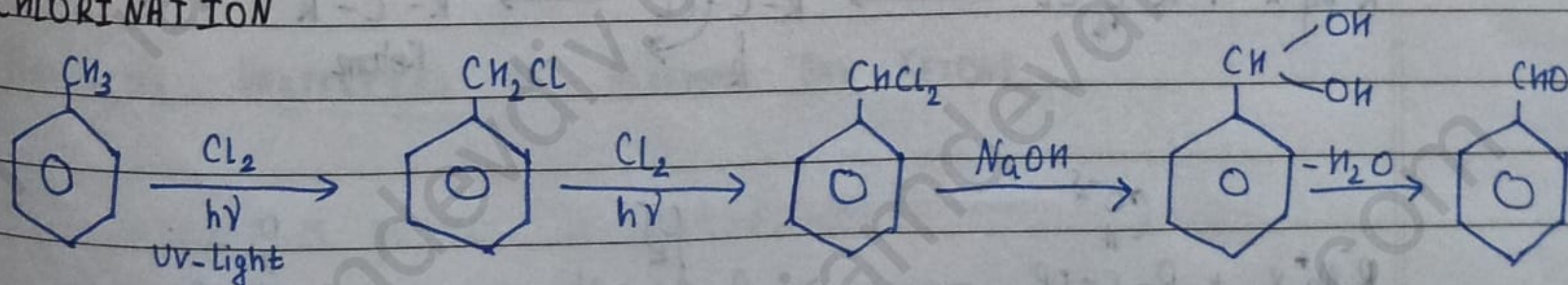
* BY CHROMYLCHLORIDE $[\text{CrO}_2\text{Cl}_2]$ (ETARD REACTION)



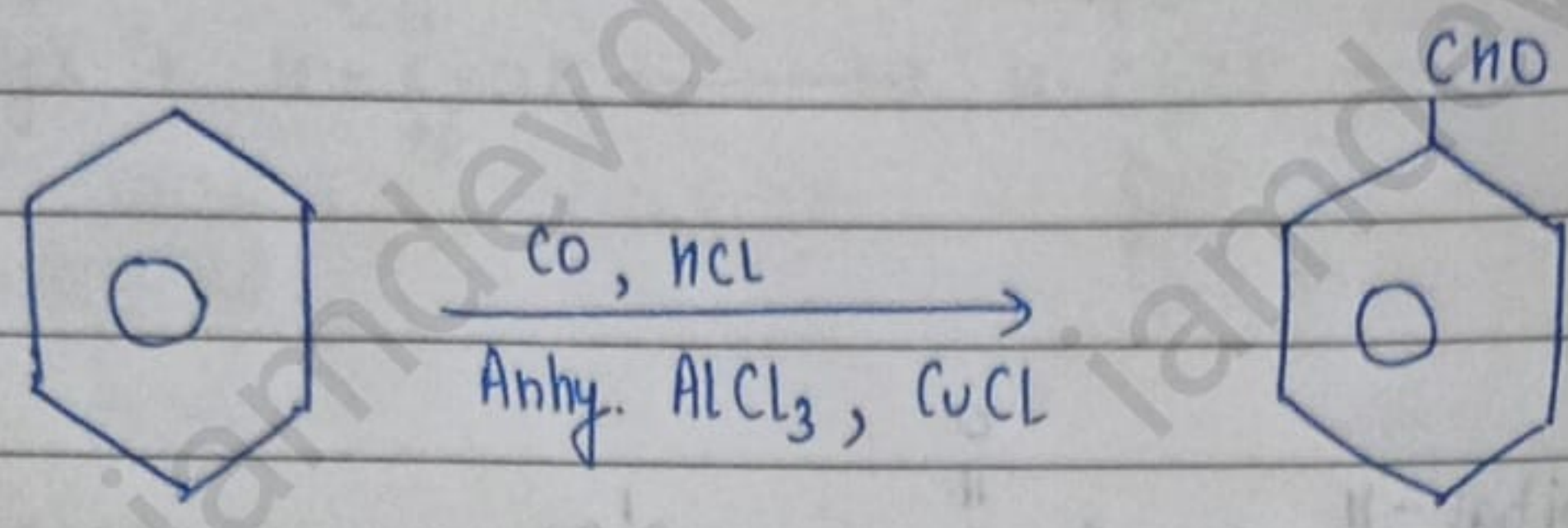
* BY USING CrO_3



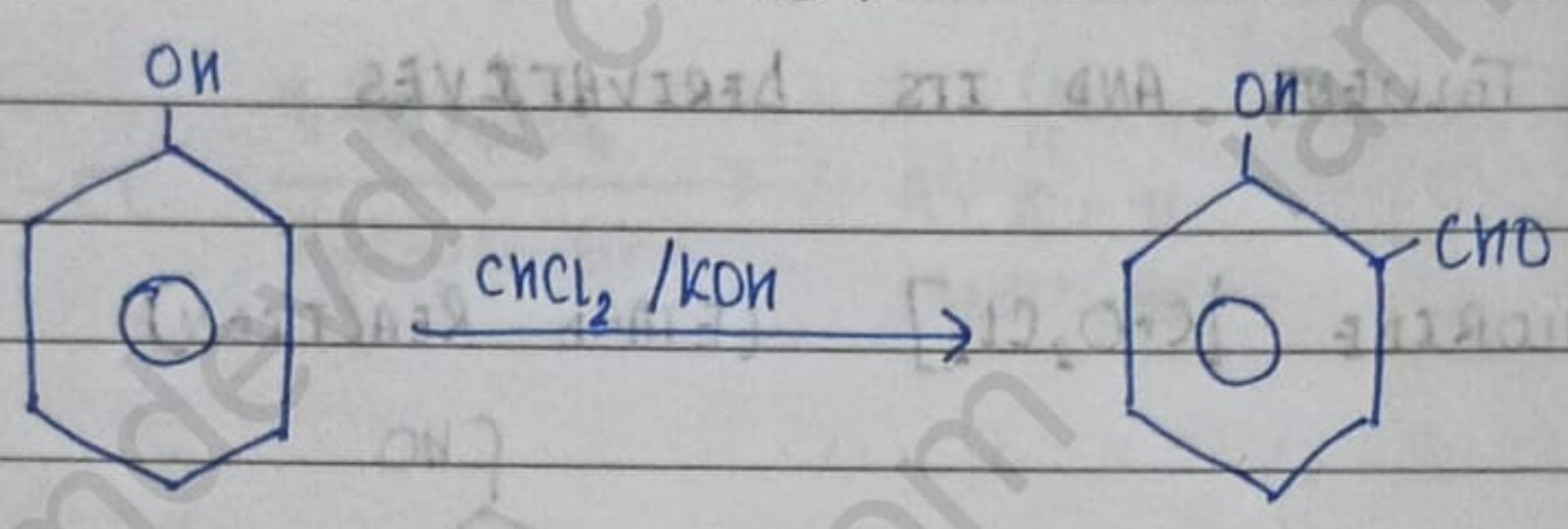
* CHLORINATION



* GATTERMANN KOCH SYNTHESIS

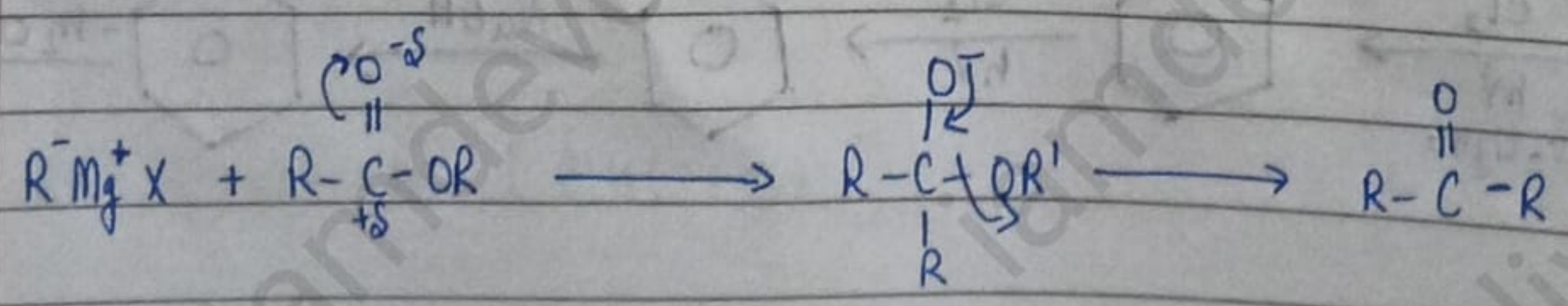
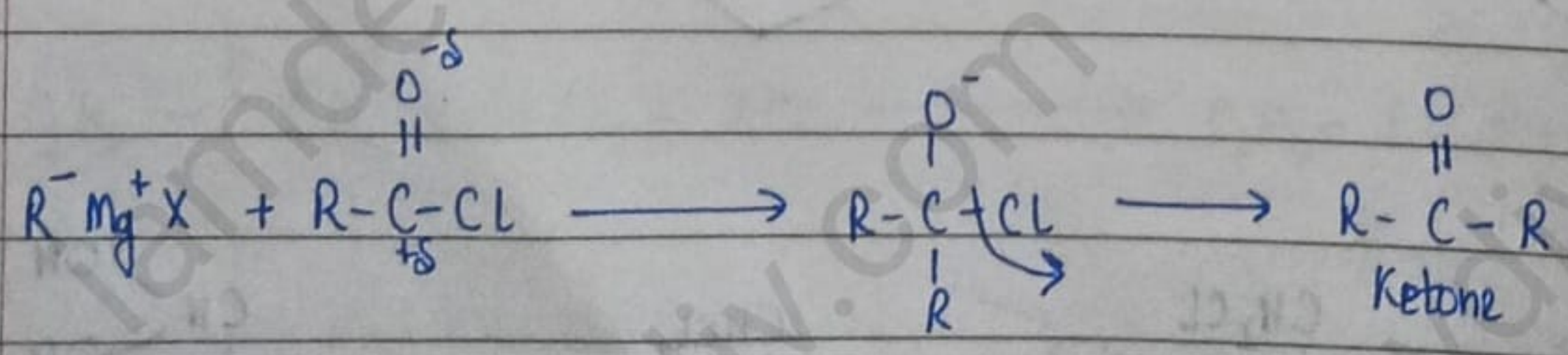
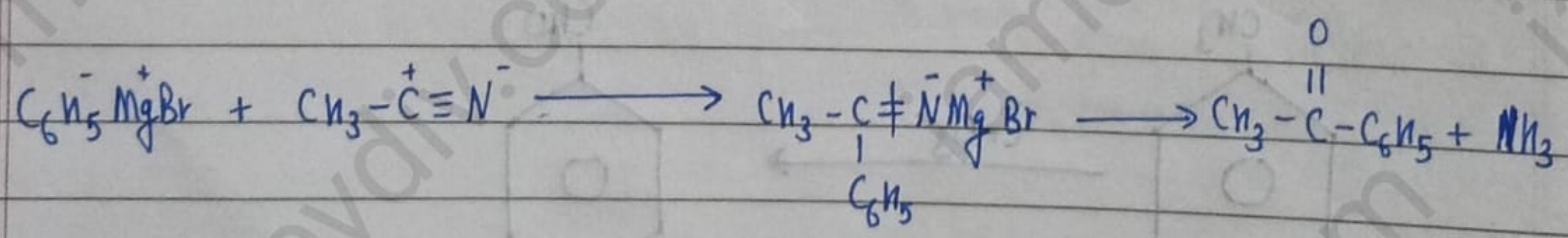
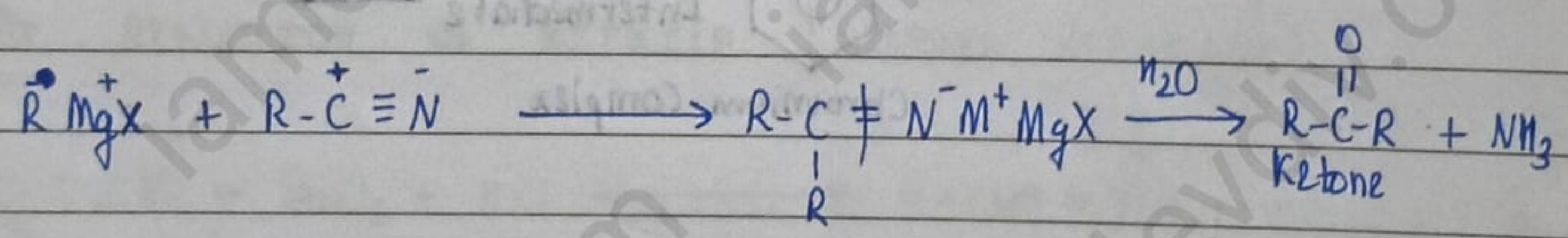


* REIMEN-TEIMANN REACTION

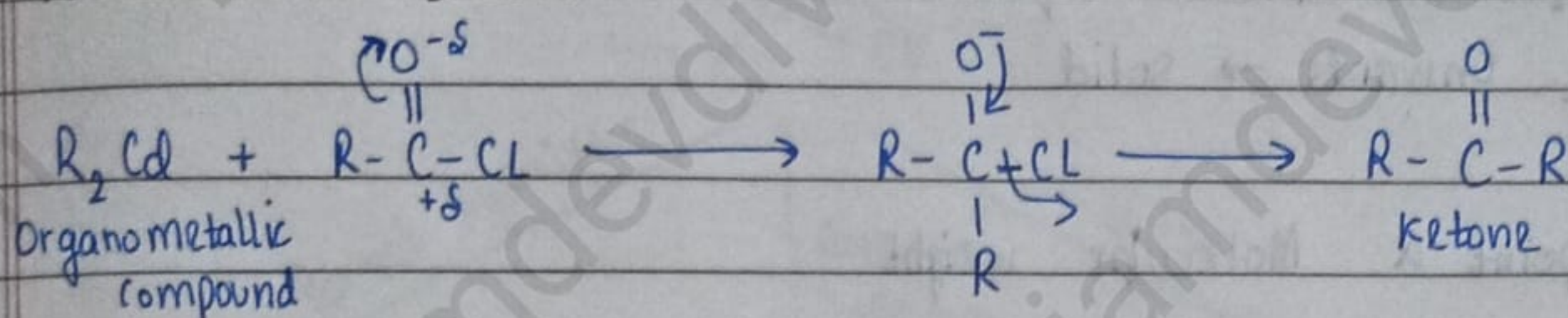


★ PREPARATION OF KETONE

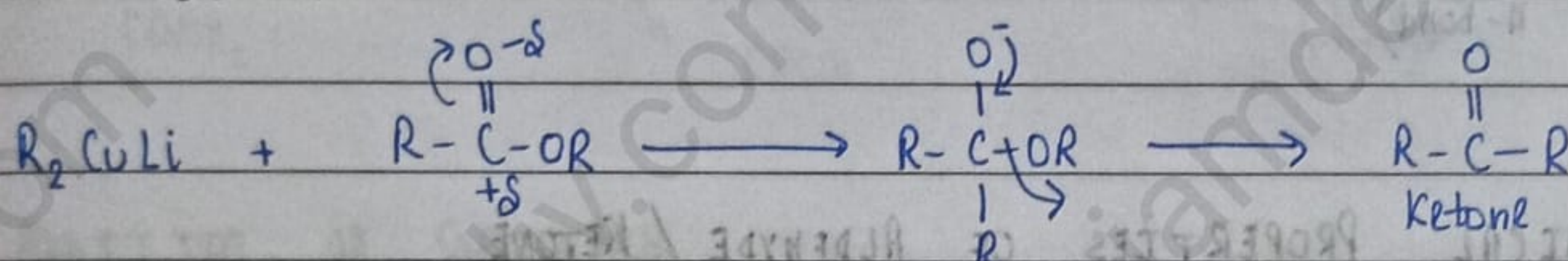
• FROM GRIGNARD REAGENT



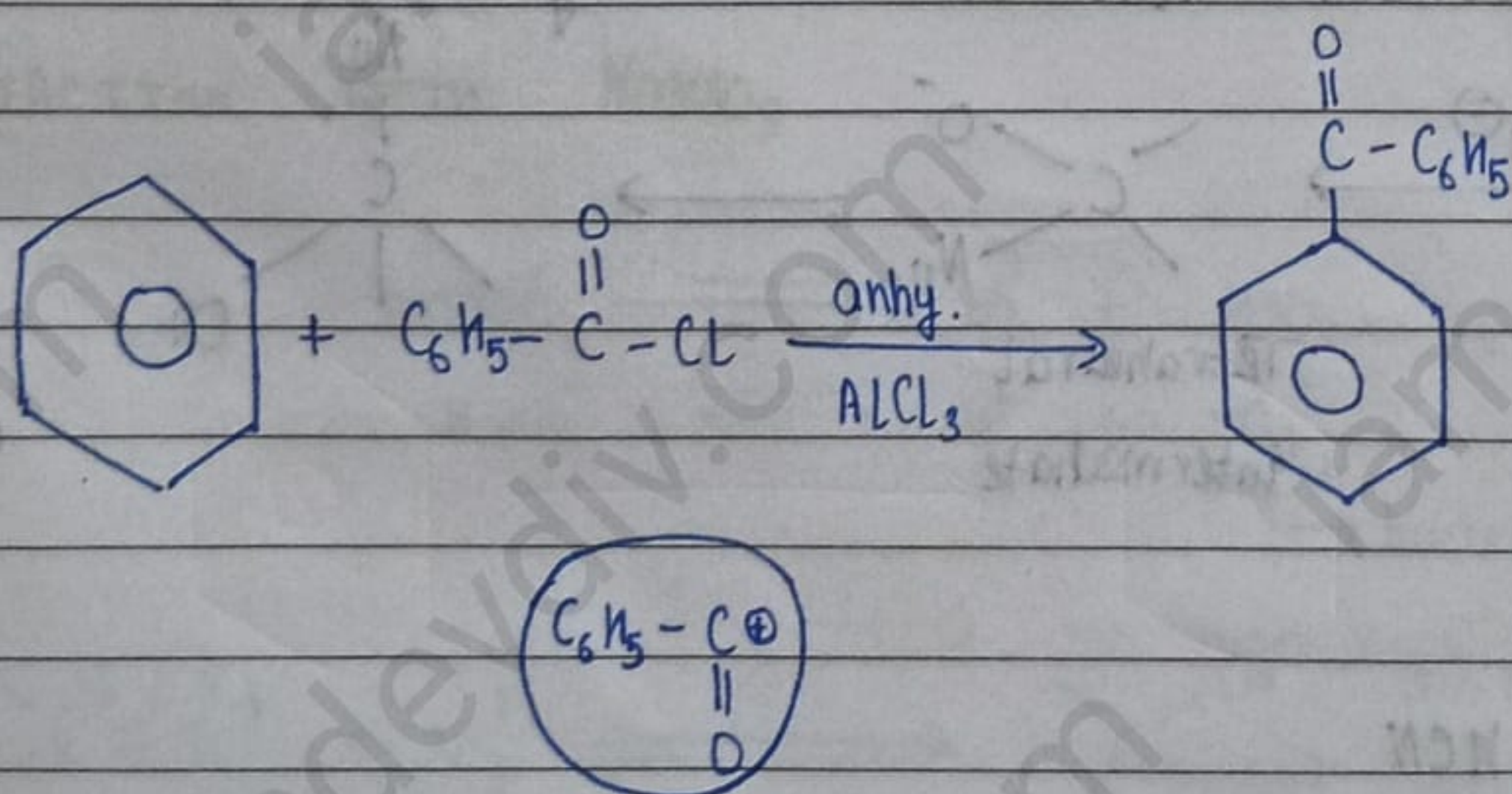
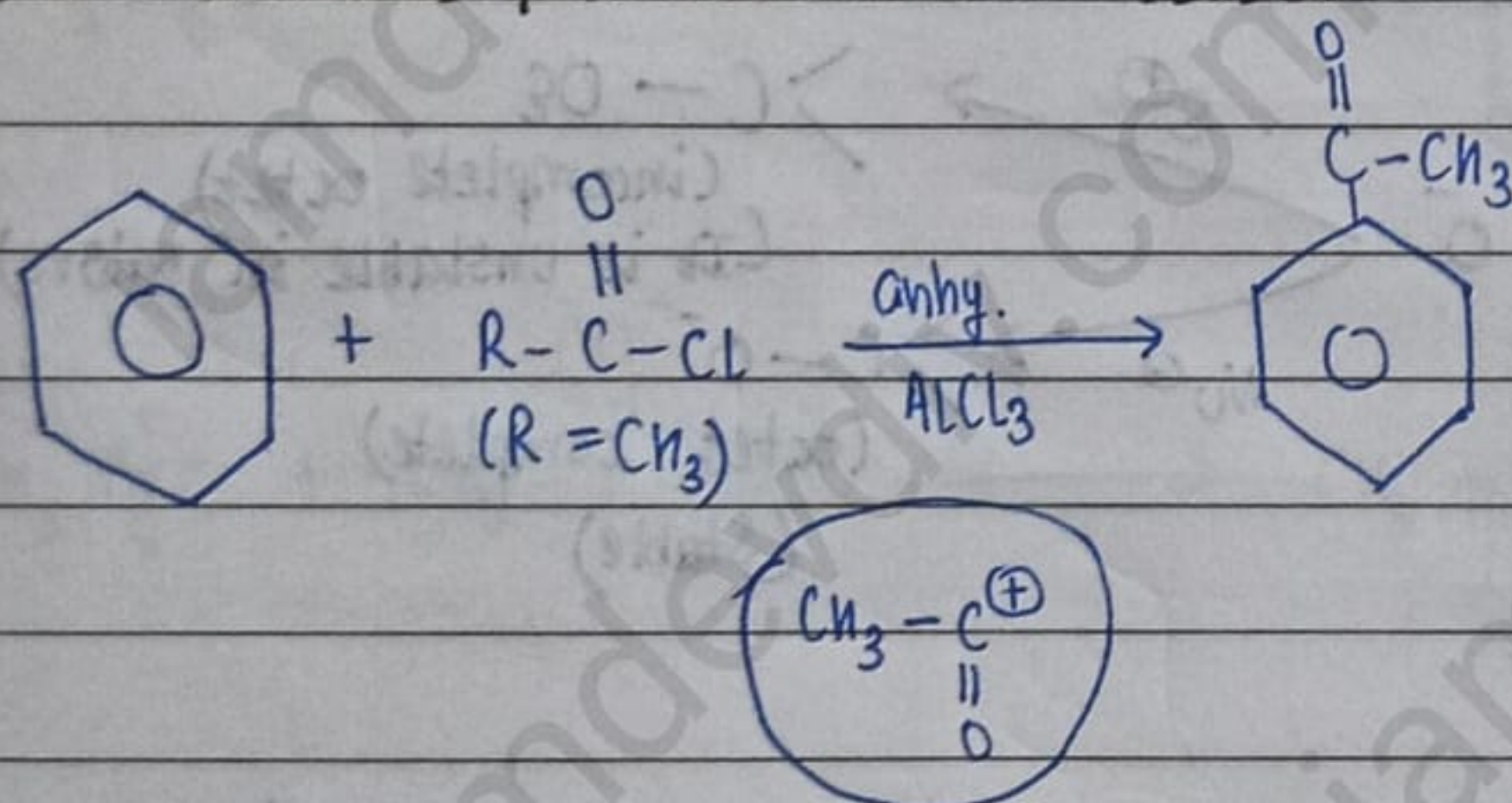
- FROM ACYL CHLORIDE



- FROM GILLMANN'S REAGENT



- FROM BENZENE / SUBSTITUTED BENZENE



★ PHYSICAL PROPERTIES OF ALDEHYDE AND KETONE

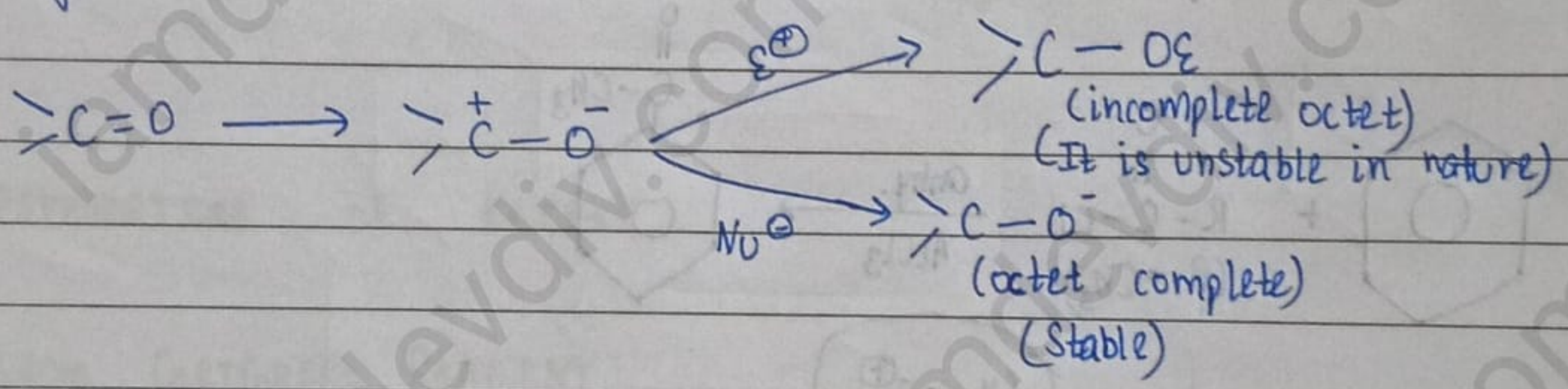
Formaldehyde is gaseous in nature.
(HCHO)

- From C_2 to C_{11} \rightarrow liquid
- From C_{12} onwards \rightarrow solid
- Boiling point \propto Molecular weight

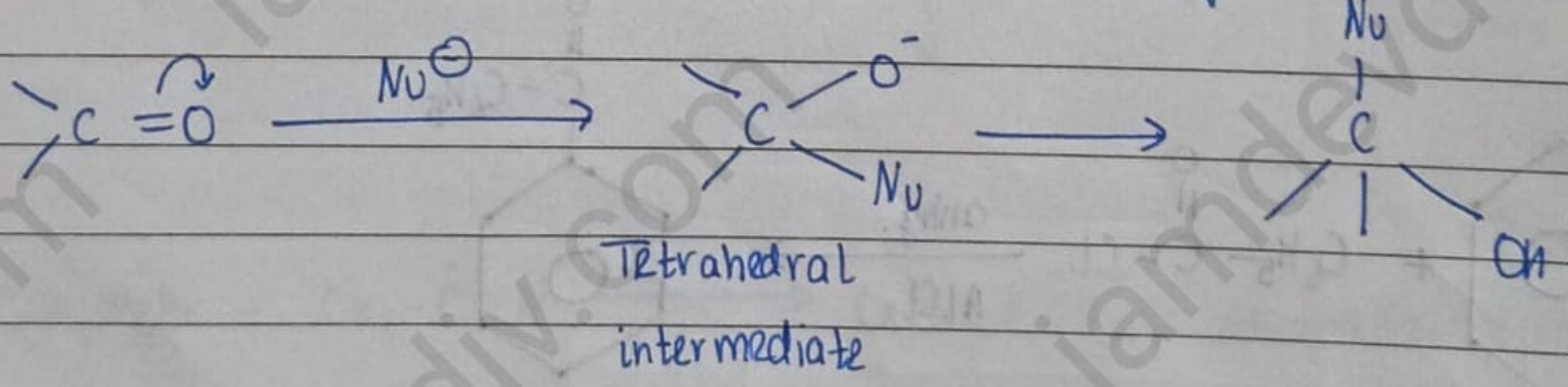
Alcohol > Aldehyde / ketone > Alkane
 (Intermolecular H-bond) ; (Poles \rightarrow dipole)

★ CHEMICAL PROPERTIES OF ALDEHYDE / KETONE

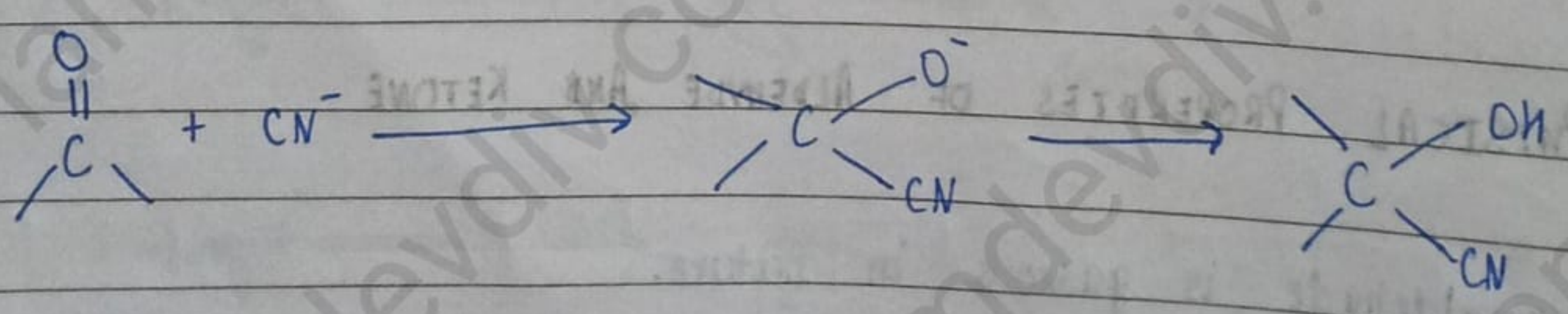
They show nucleophilic addition reaction

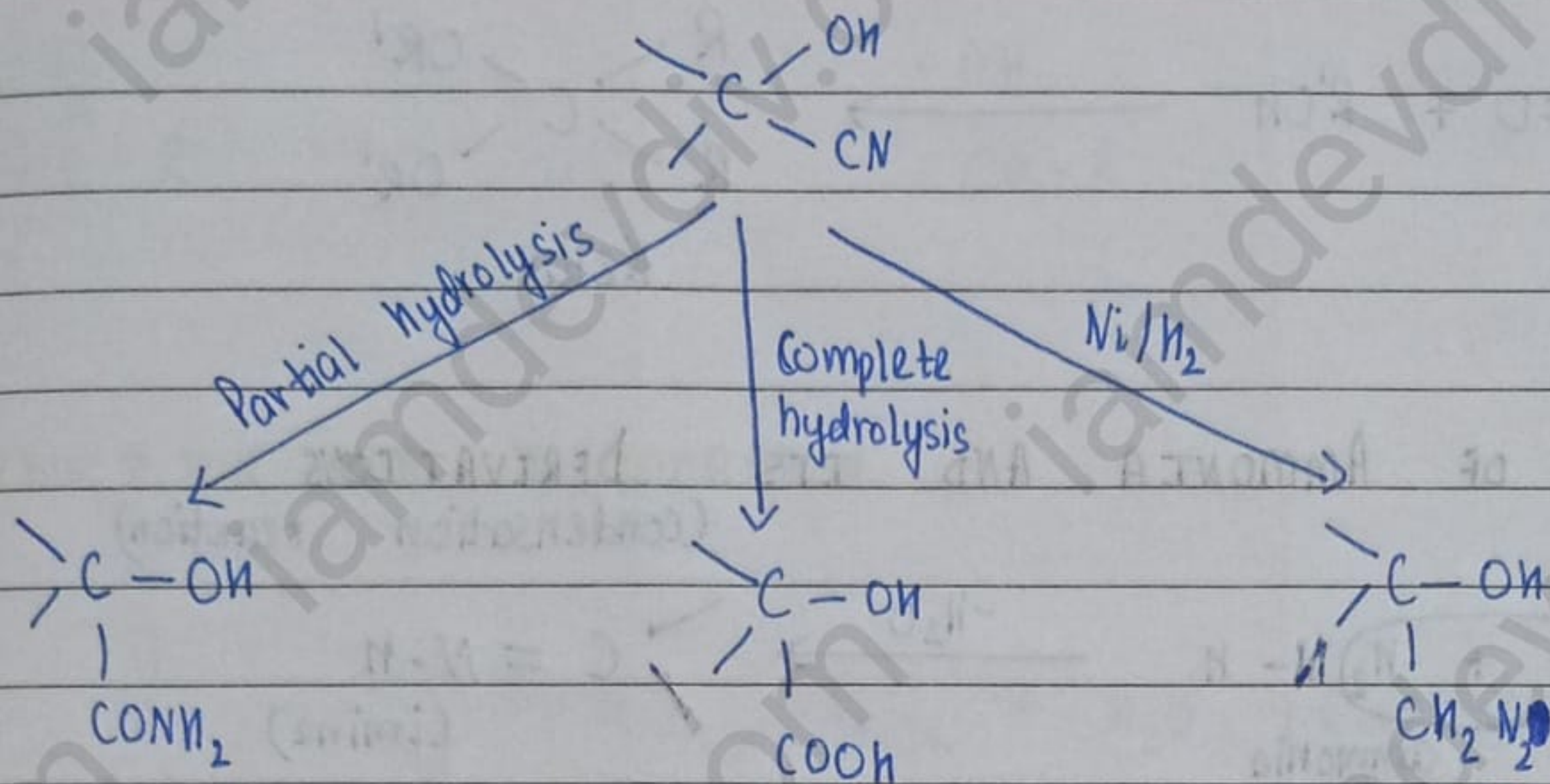


• NUCLEOPHILIC ADDITION REACTION (Reactivity \propto -Mx -I)

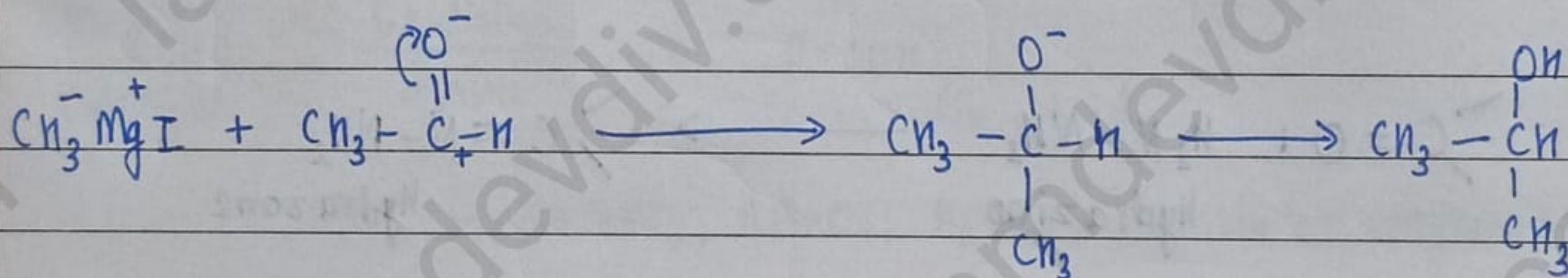
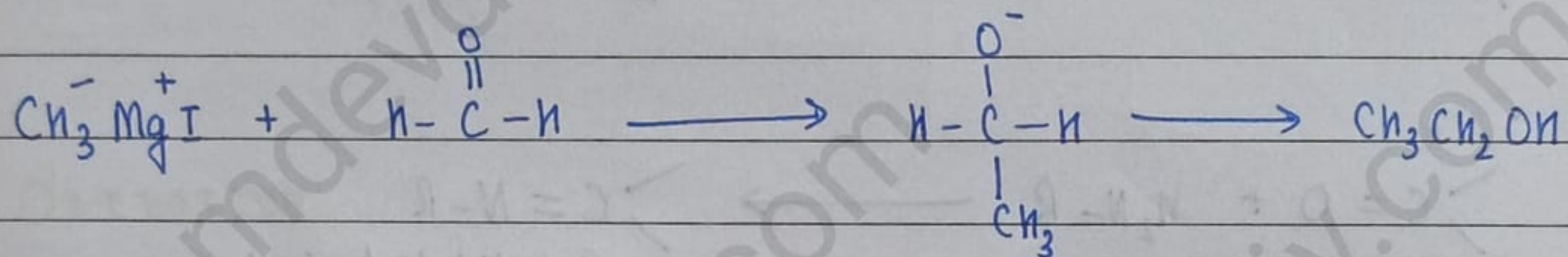


• ADDITION OF HCN

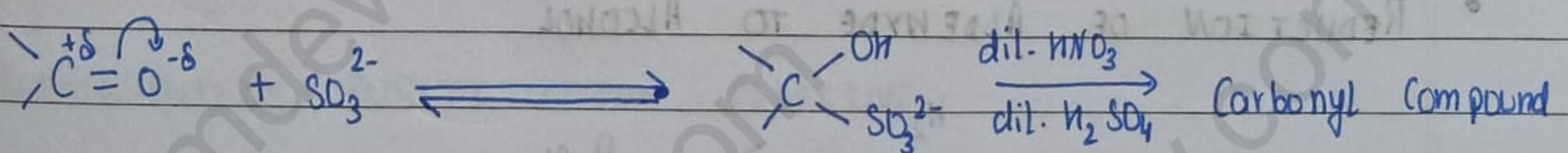
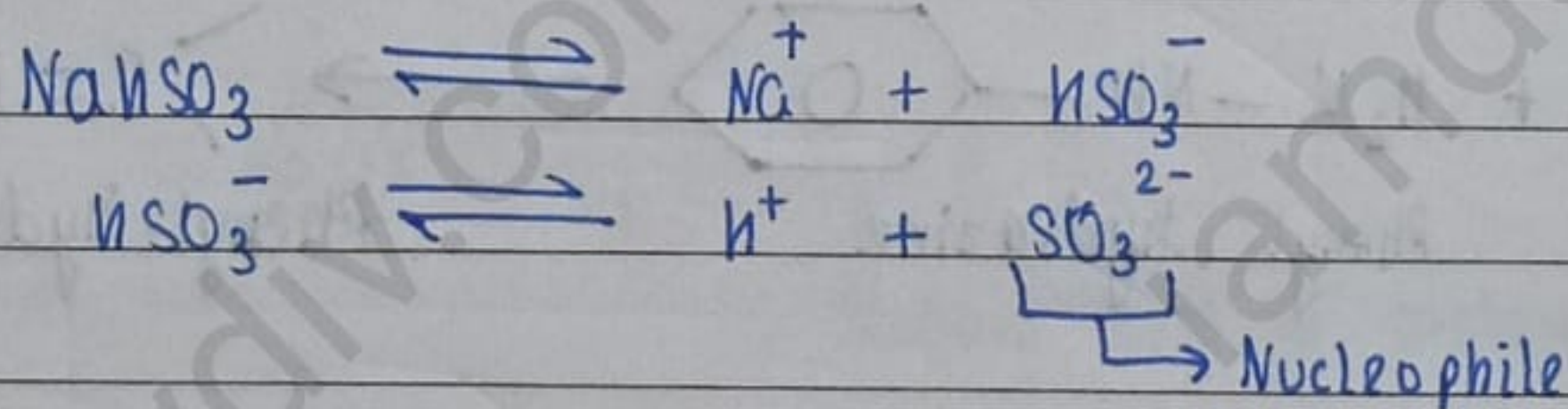




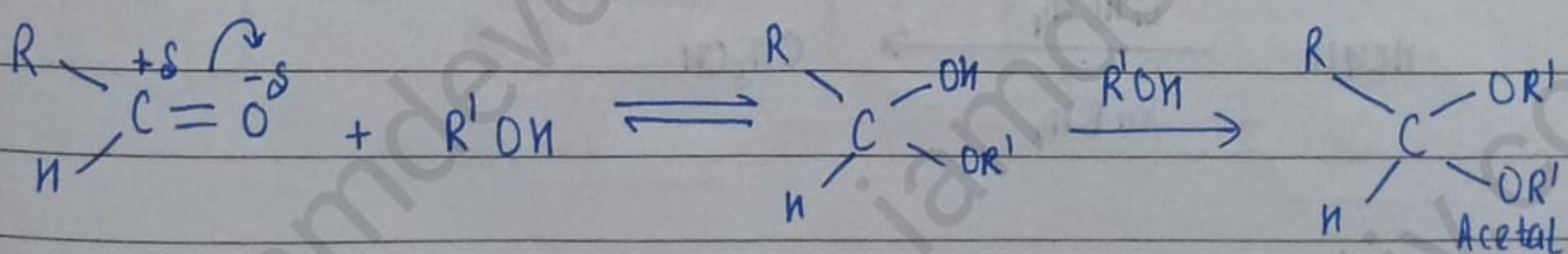
• ADDITION OF GRIGNARD

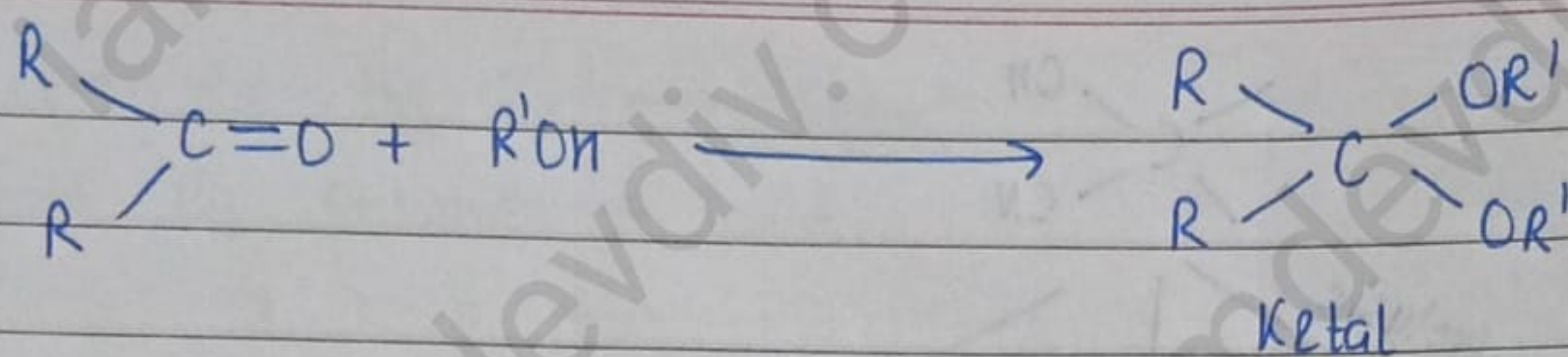


• REACTION WITH NaHSO_3

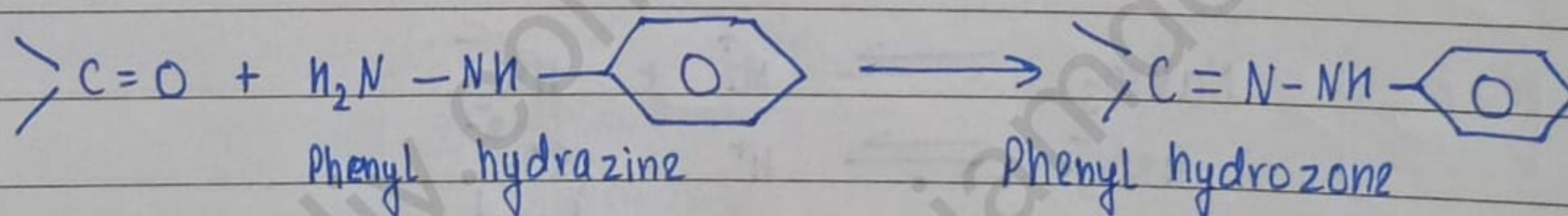
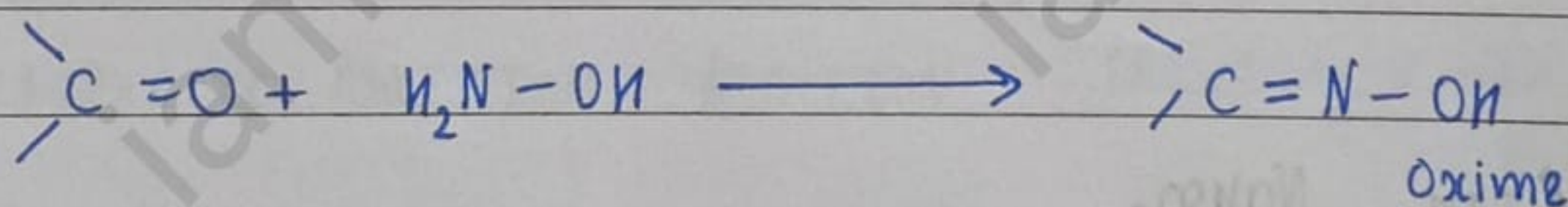
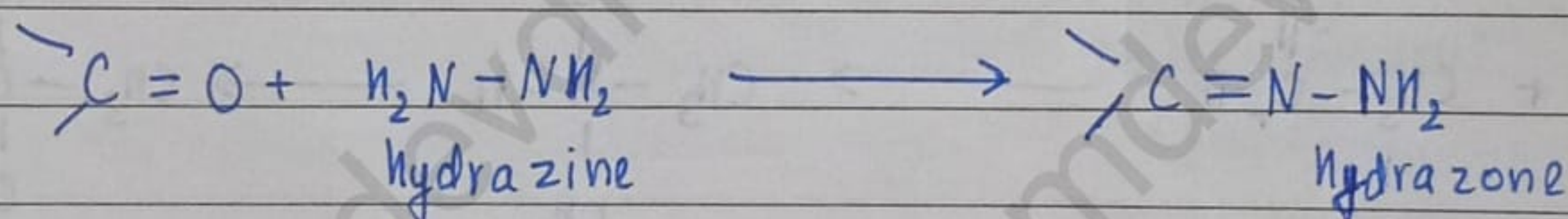
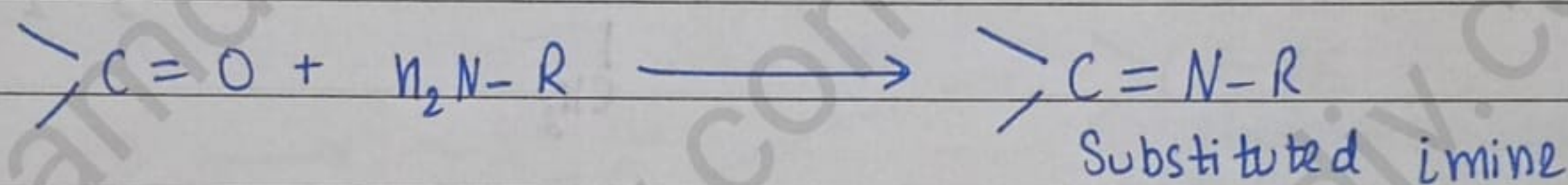
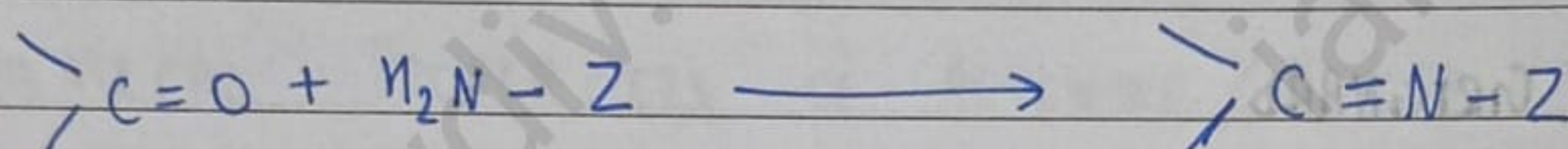
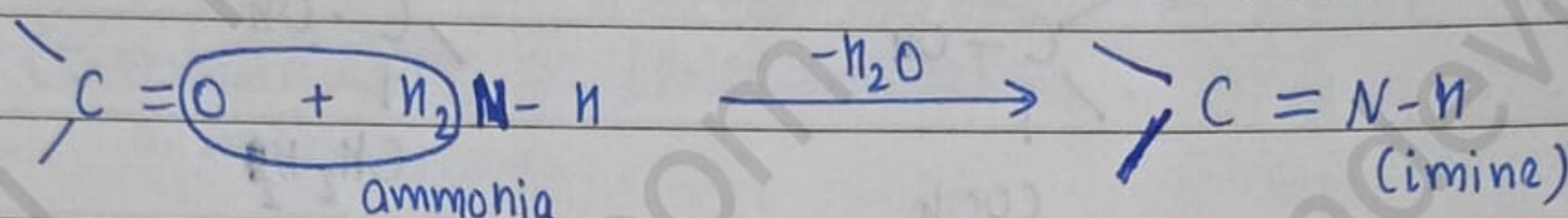


• ADDITION OF ALCOHOL

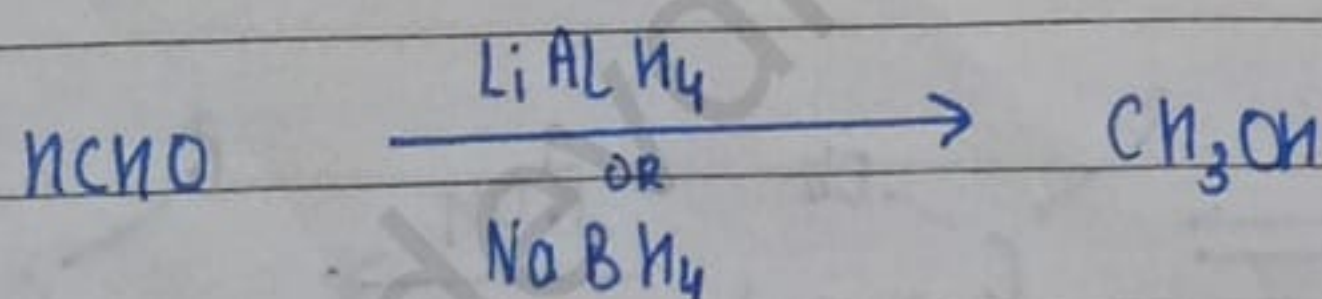
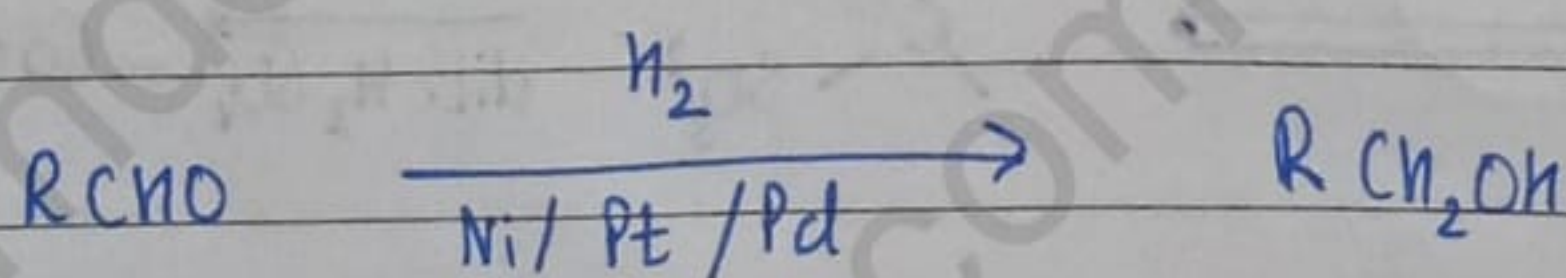


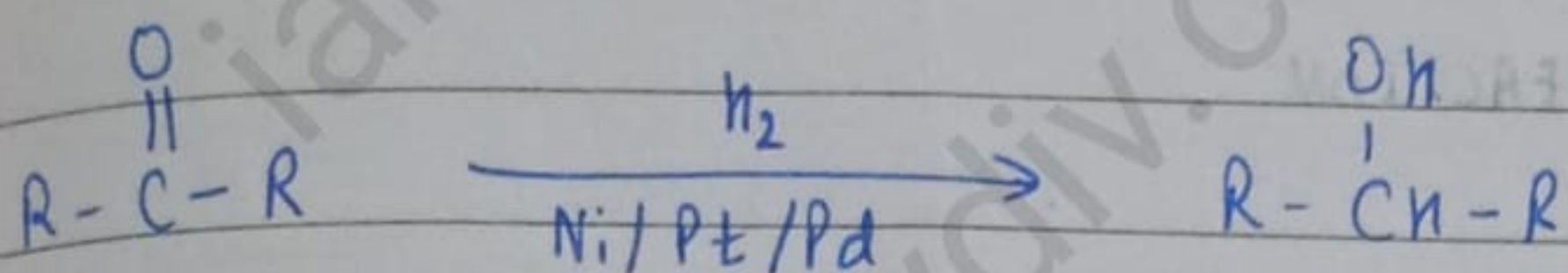


• ADDITION OF AMMONIA AND ITS DERIVATIVES
(condensation reaction)

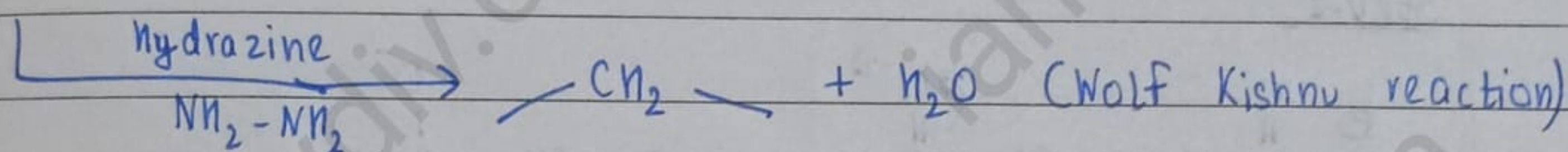
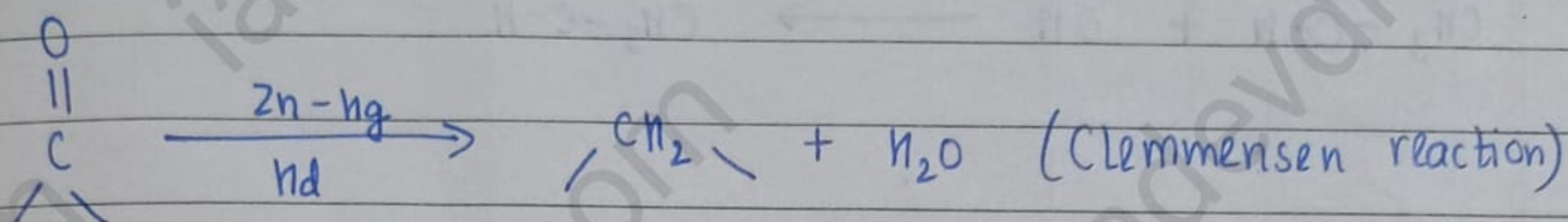


• REDUCTION OF ALDEHYDE TO ALCOHOL

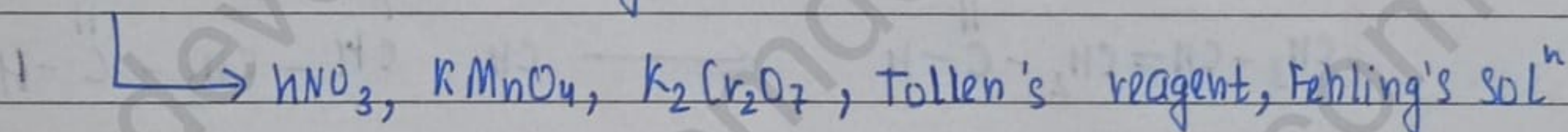
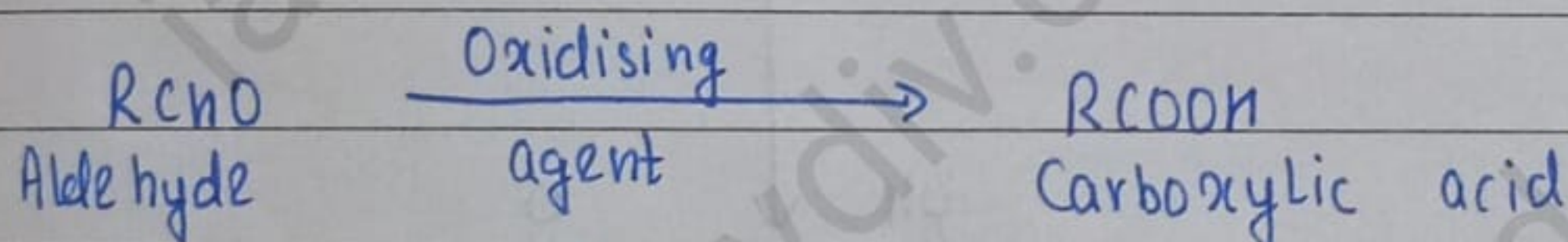




• REDUCTION TO HYDROCARBON

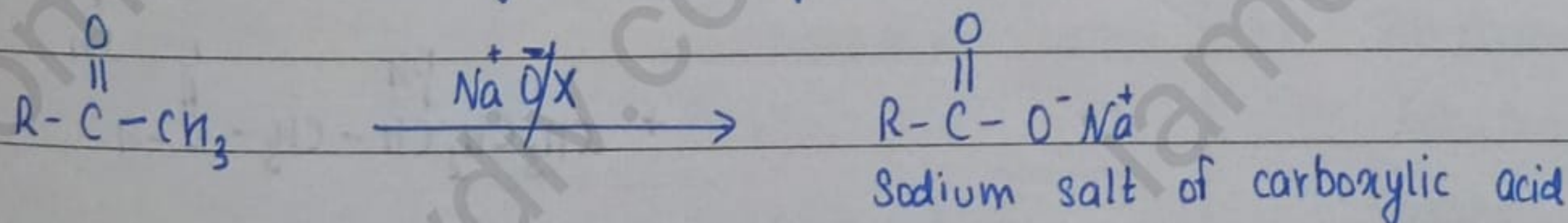


• OXIDATION

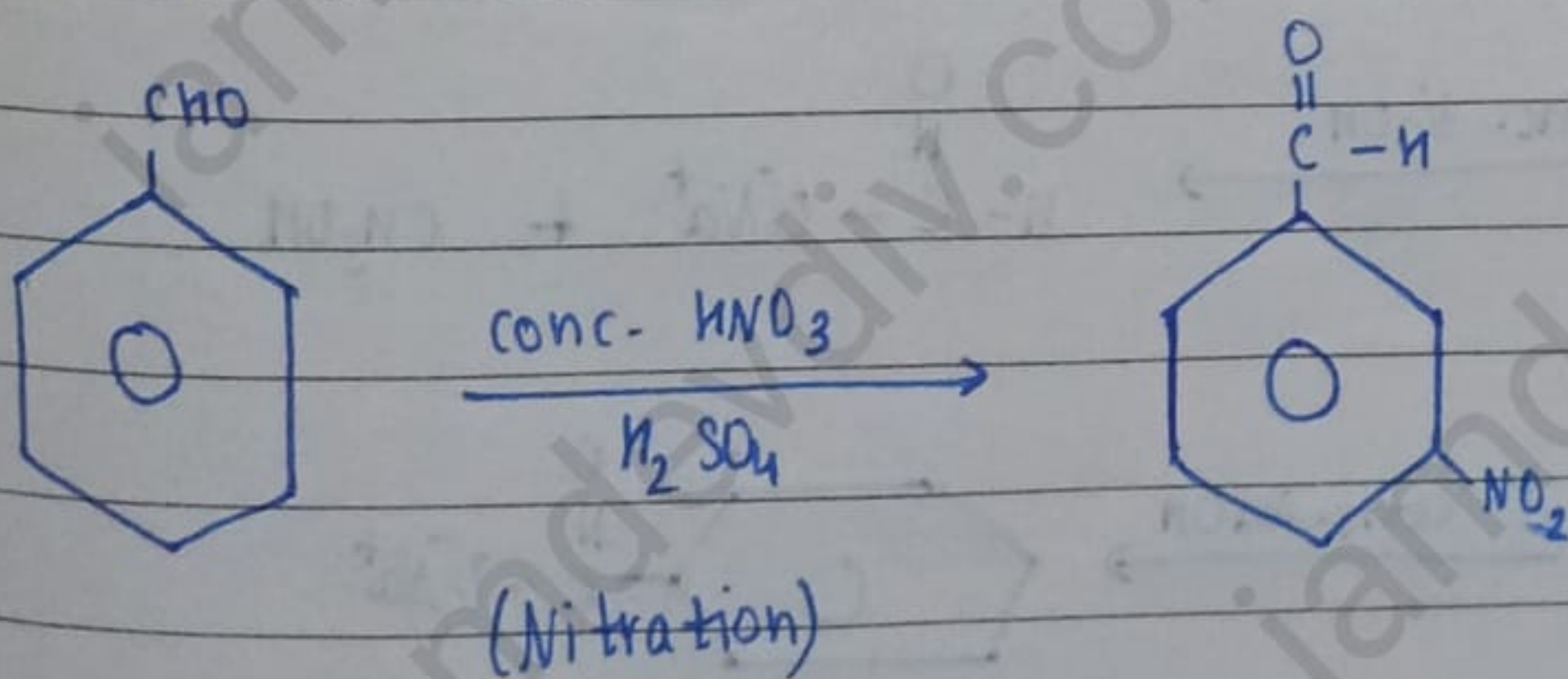


• BY HALOFORM

Oxidation of methyl ketone by haloform

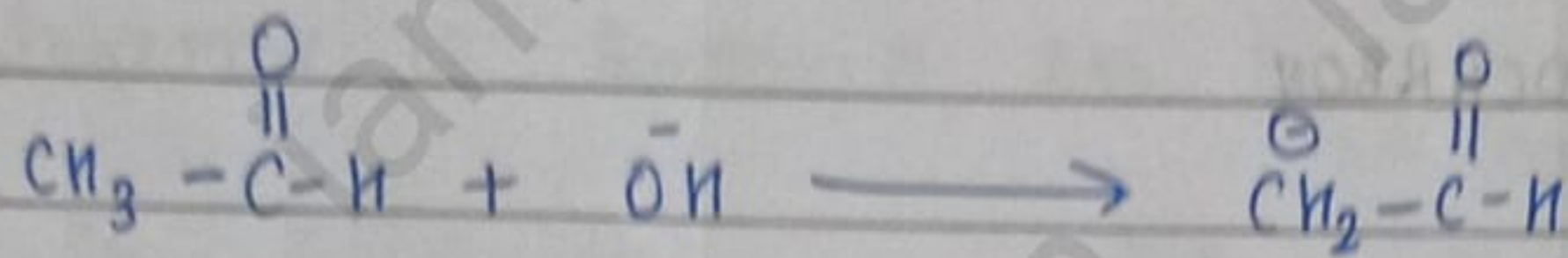


• ELECTROPHILIC SUBSTITUTION REACTION

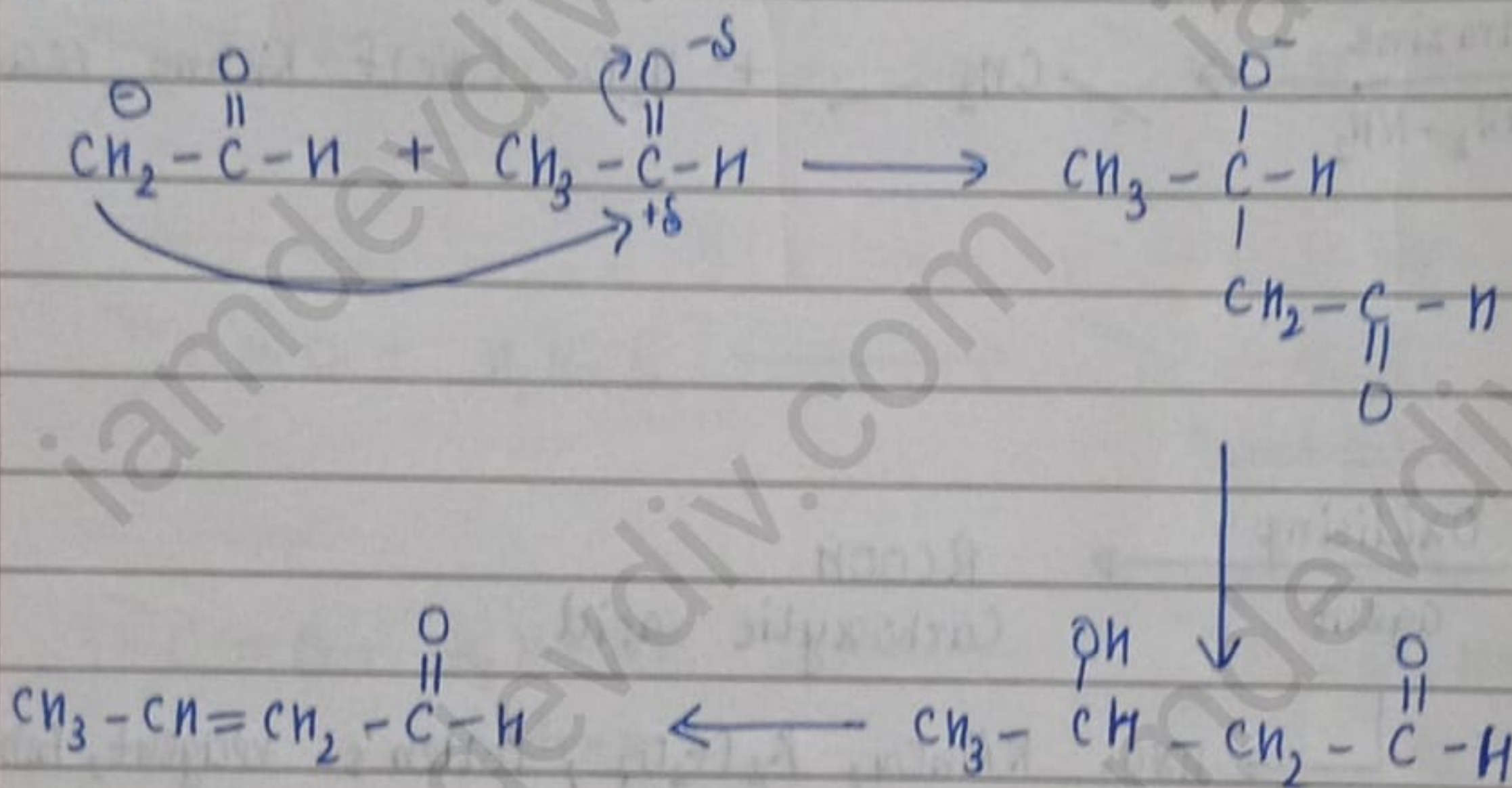


• ALDOL CONDENSATION REACTION

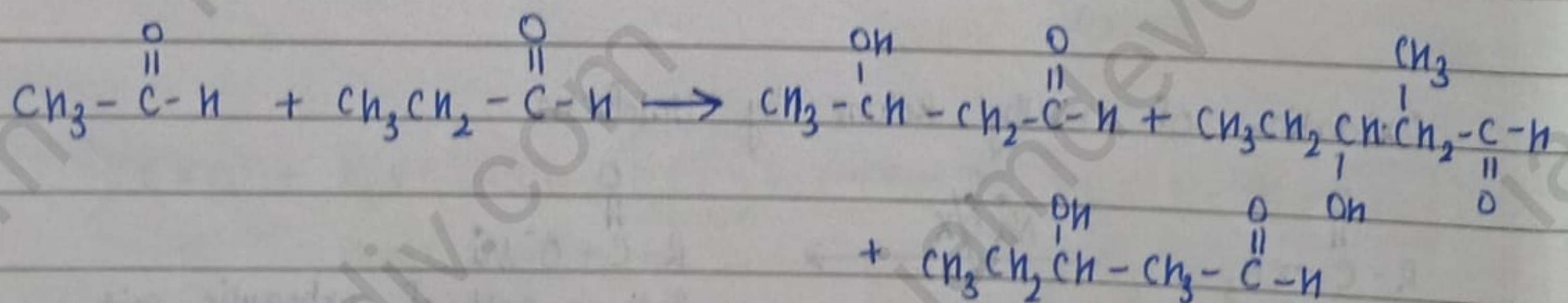
Step 1 → Formation of Carbanion



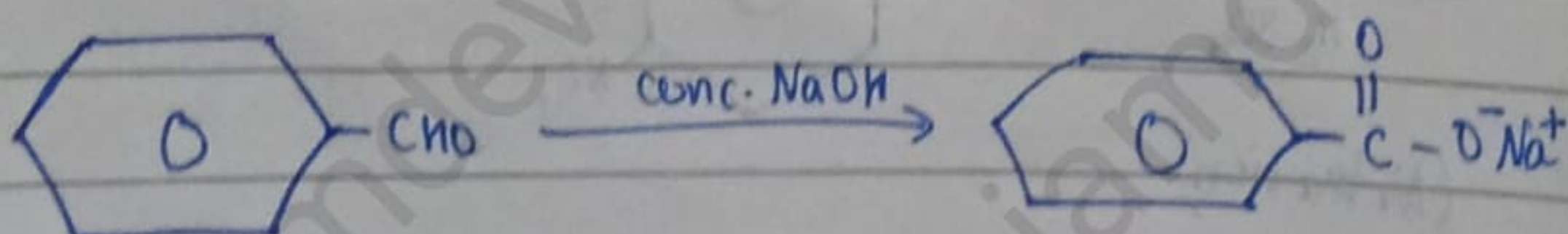
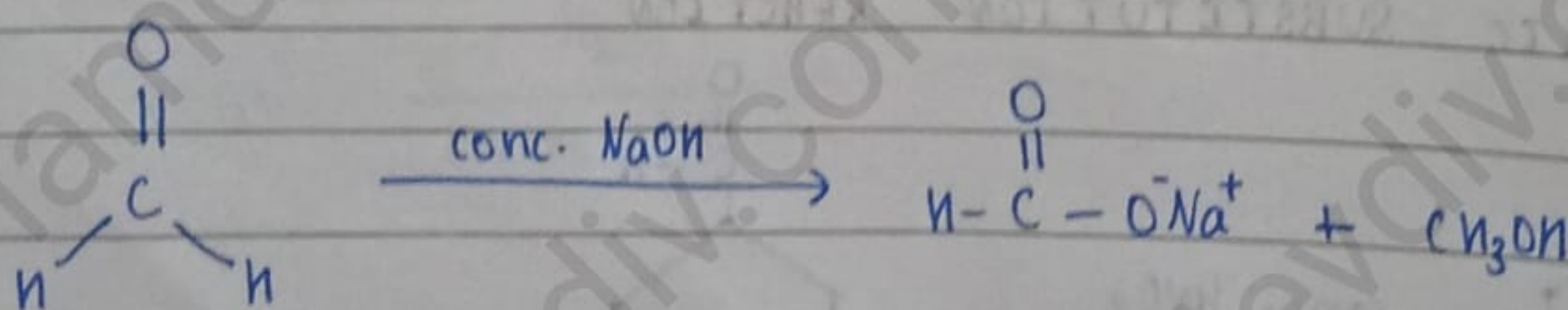
Step-2



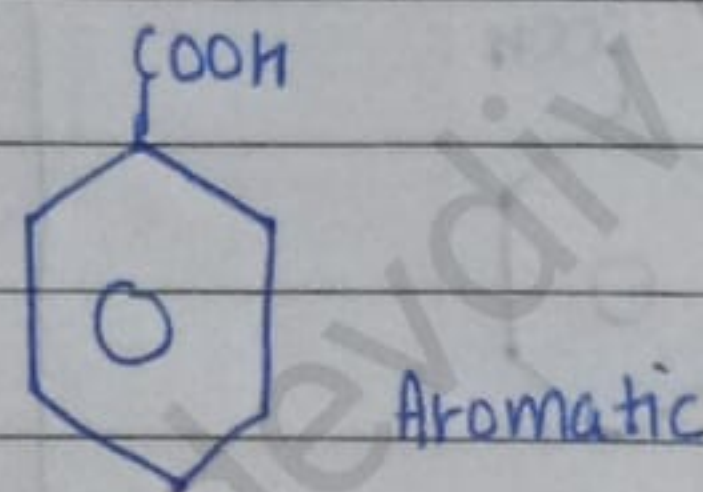
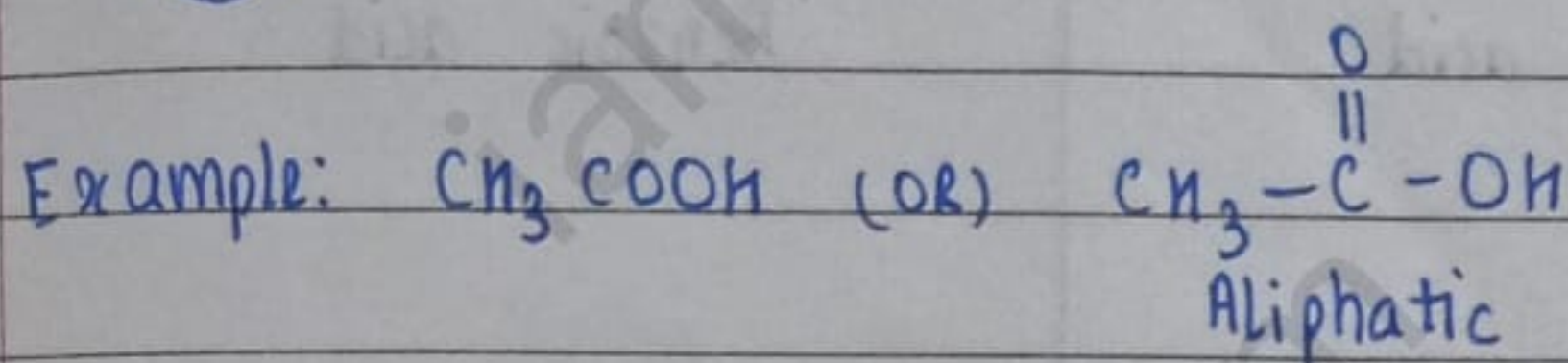
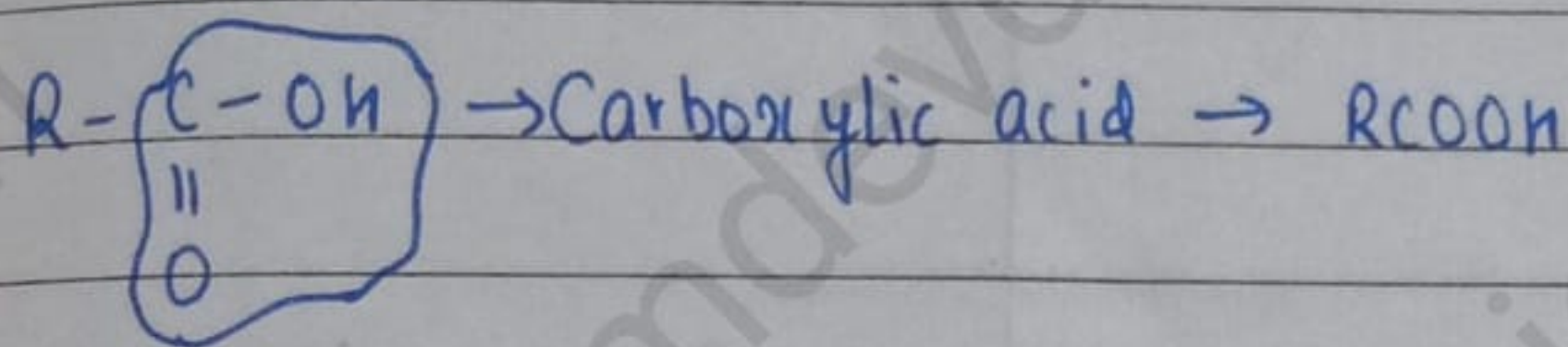
• CROSS ALDOL CONDENSATION



• CANNIZARO REACTION

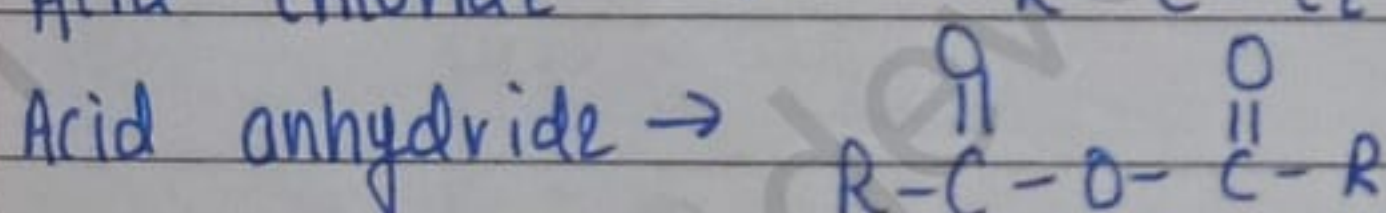
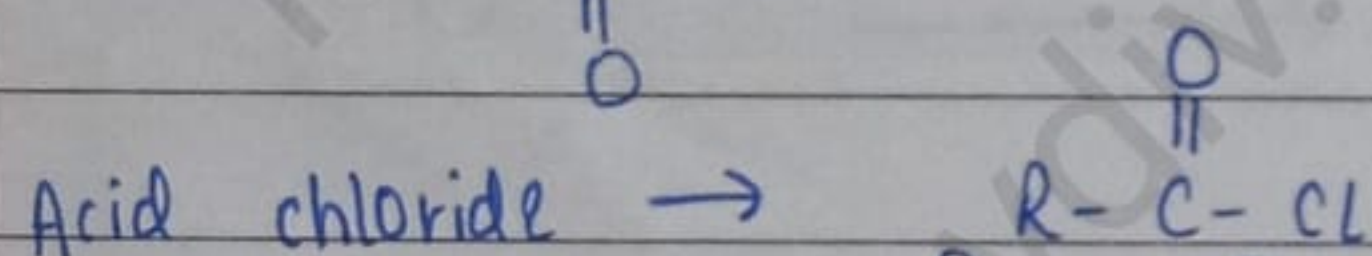
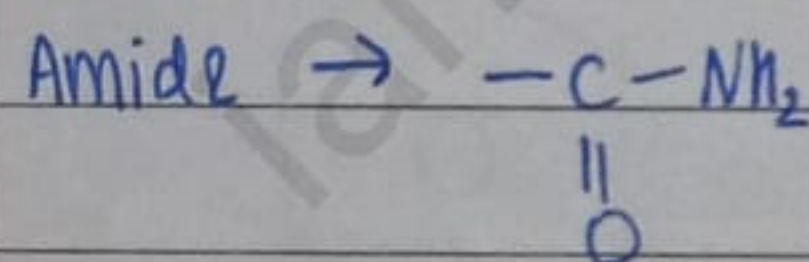
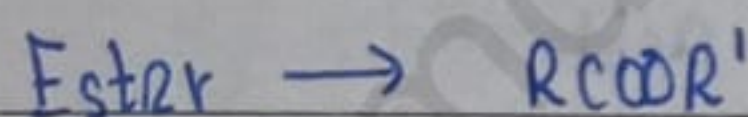


★ CARBOXYLIC ACID



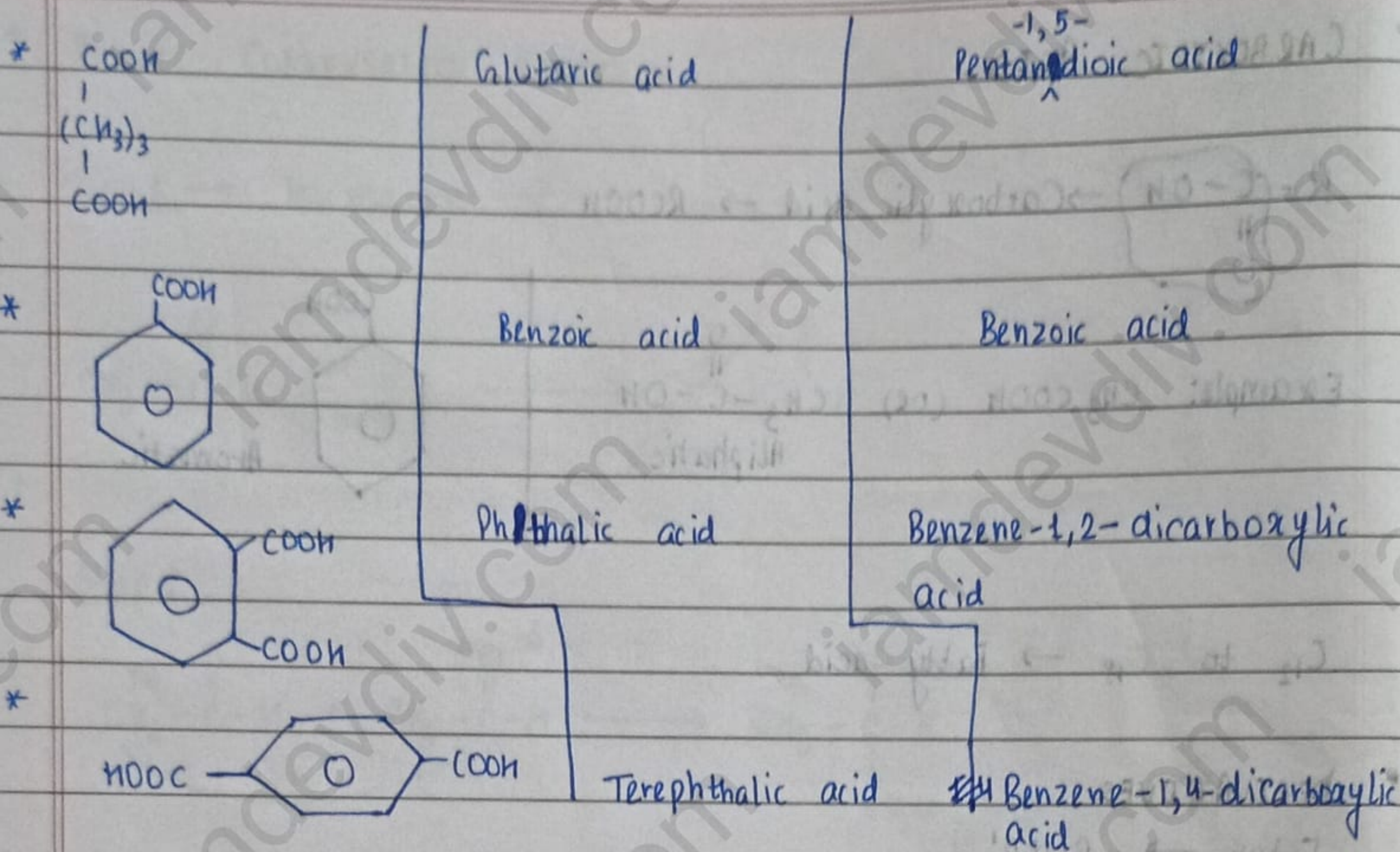
C_{12} to $\text{C}_{18} \rightarrow$ Fatty acid

• DERIVATIVES



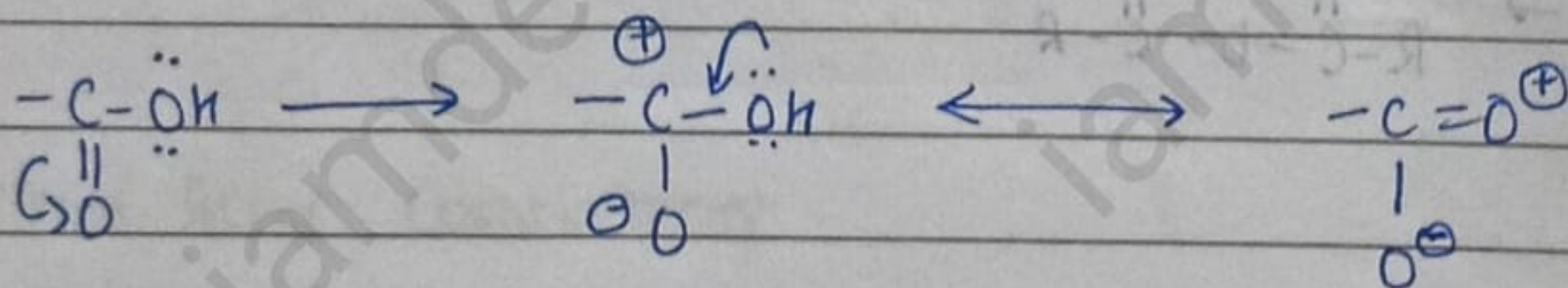
• NOMENCLATURE

| COMPOUND | COMMON NAME | IUPAC |
|--|----------------|---------------------------|
| * HCOOH | Formic acid | Methanoic acid |
| * CH_3COOH | Acetic acid | Ethanoic acid |
| * $\text{CH}_3\text{CH}_2\text{COOH}$ | Propanoic acid | Propanoic acid |
| * $\begin{array}{c} \text{COOH} \\ \\ \text{COOH} \end{array}$ | Oxalic acid | Ethanedioic acid |
| * $\begin{array}{c} \text{COOH} \\ \\ \text{CH}_2 \\ \\ \text{COOH} \end{array}$ | Malonic acid | Propane-1,3-dioic acid |
| * $\begin{array}{c} \text{COOH} \\ \\ (\text{CH}_2)_2 \\ \\ \text{COOH} \end{array}$ | Succinic acid | -1,4- Butanedioic acid |



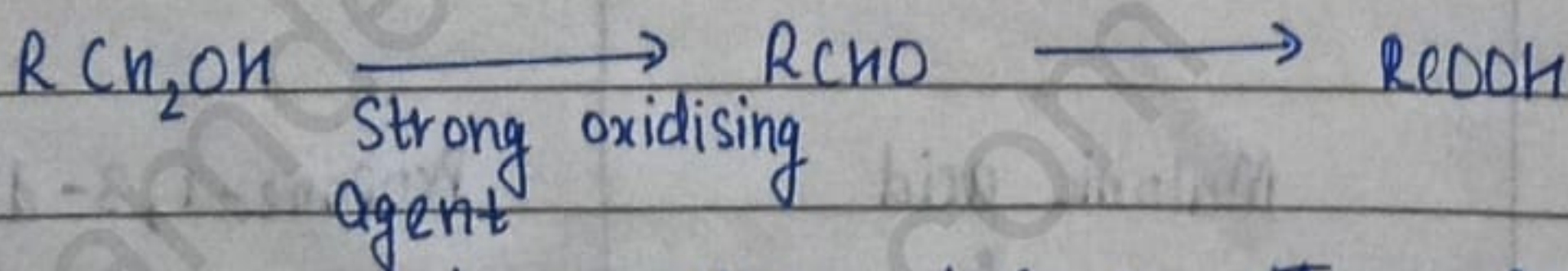
• STRUCTURE

"Resonance stabilized"



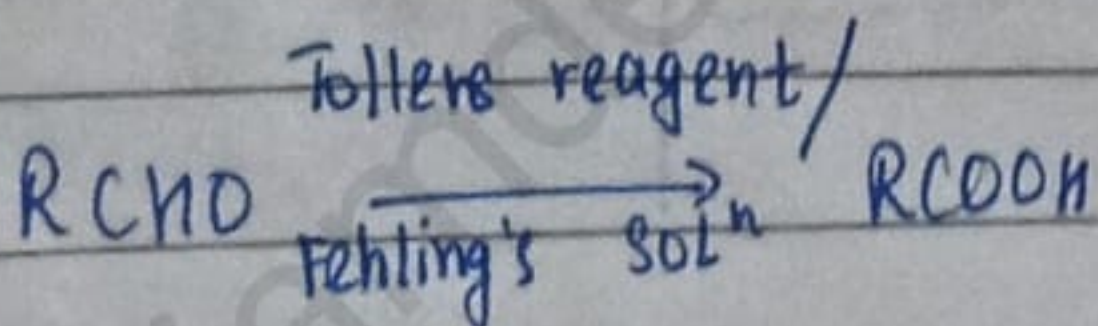
★ METHODS OF PREPARATION OF CARBOXYLIC ACID

• FROM PRIMARY ALCOHOL

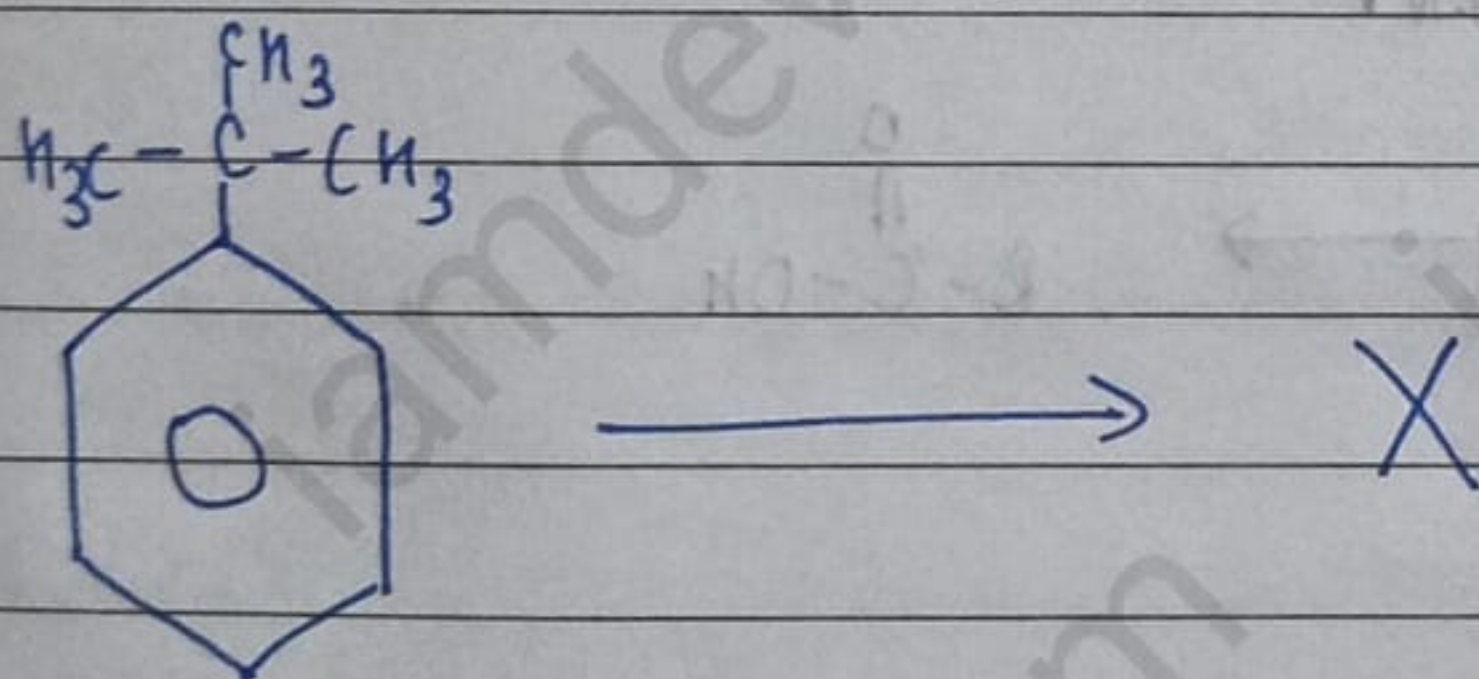
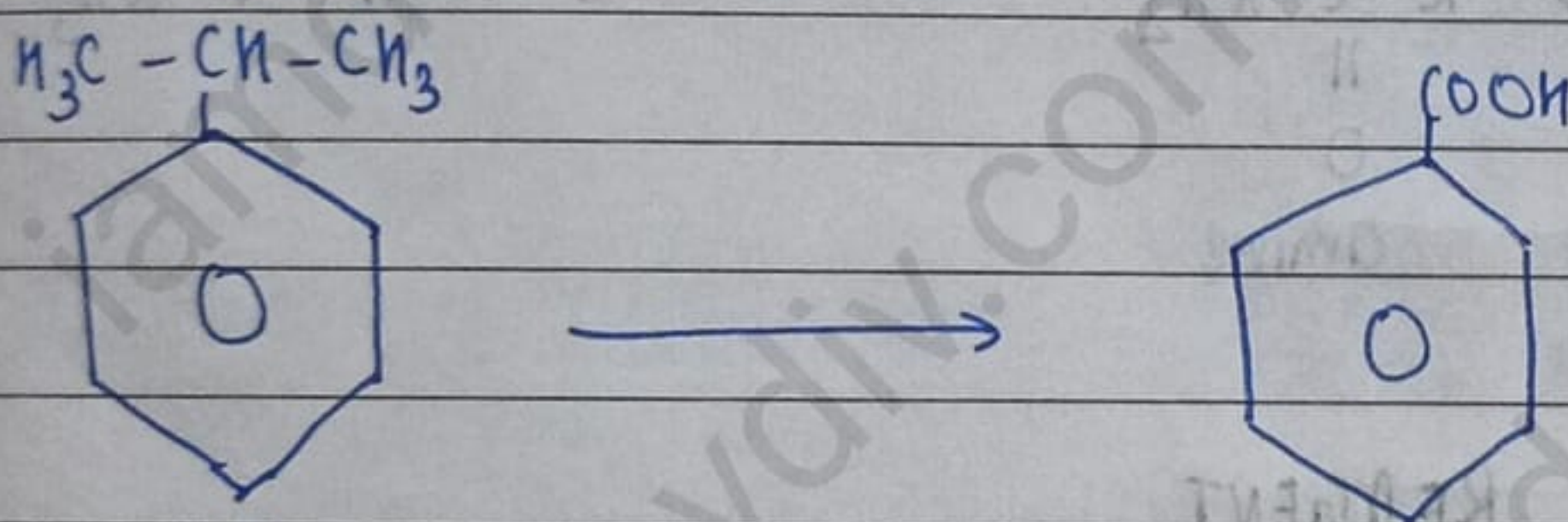
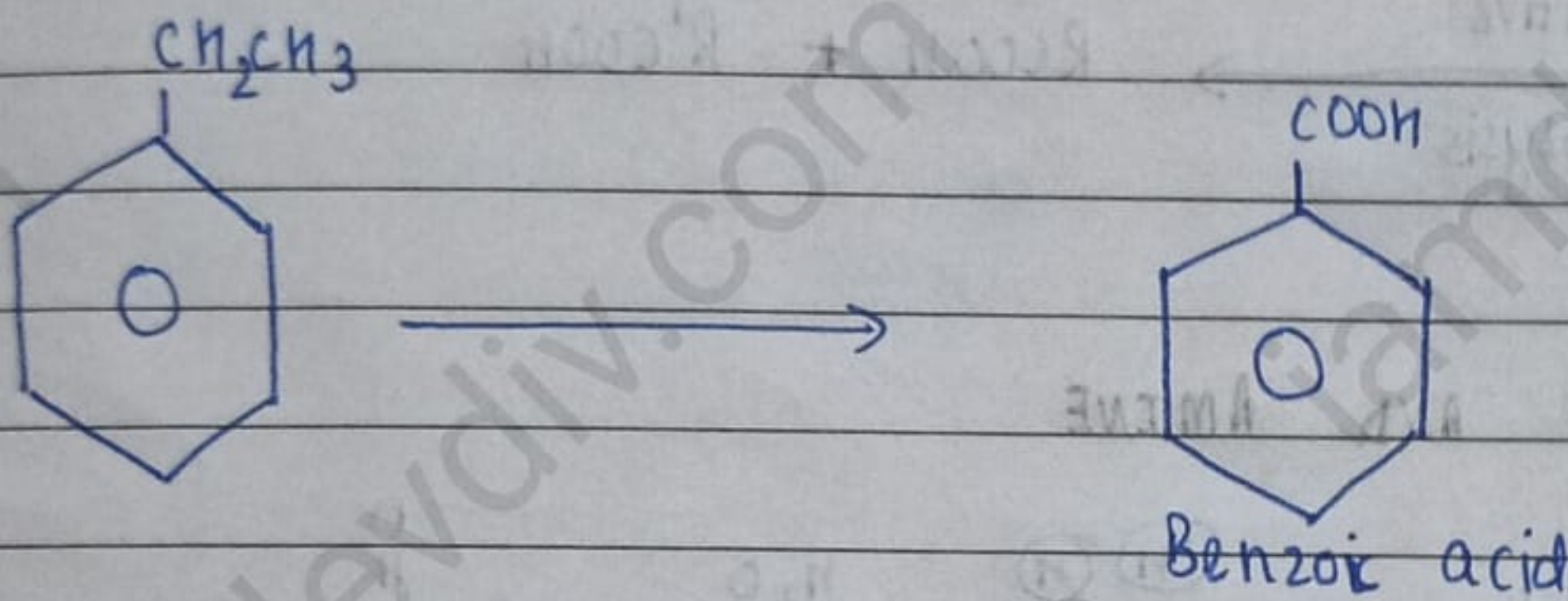
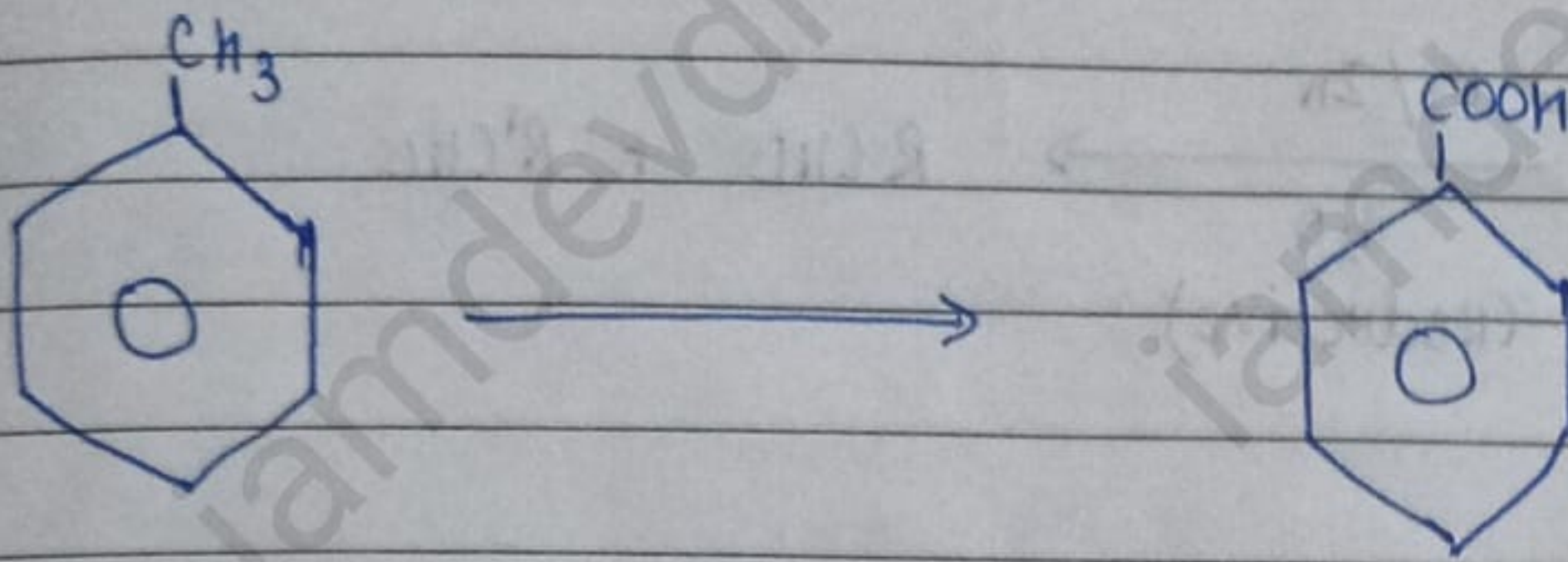


↳ KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, Jones Reagent ($\text{CrO}_3 + \text{H}_2\text{SO}_4$)

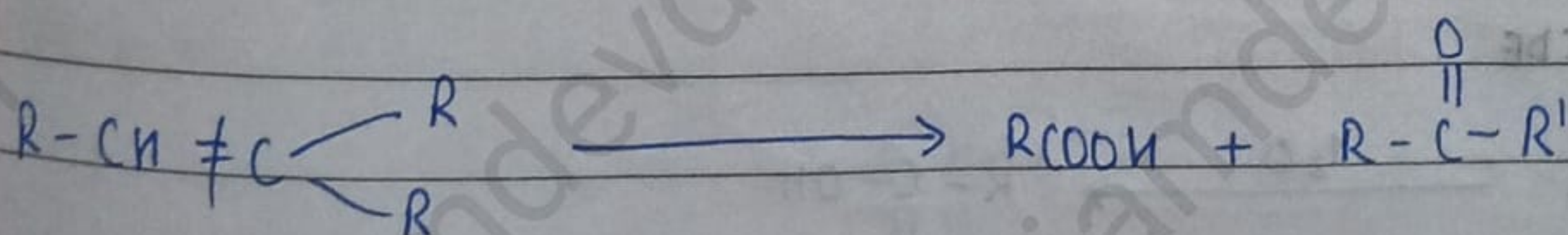
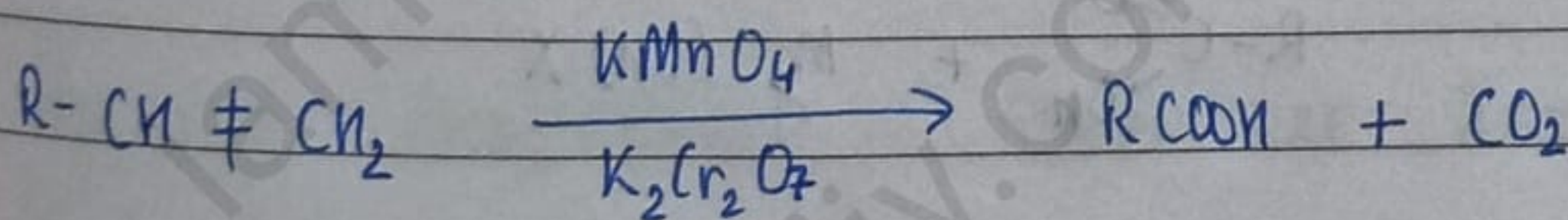
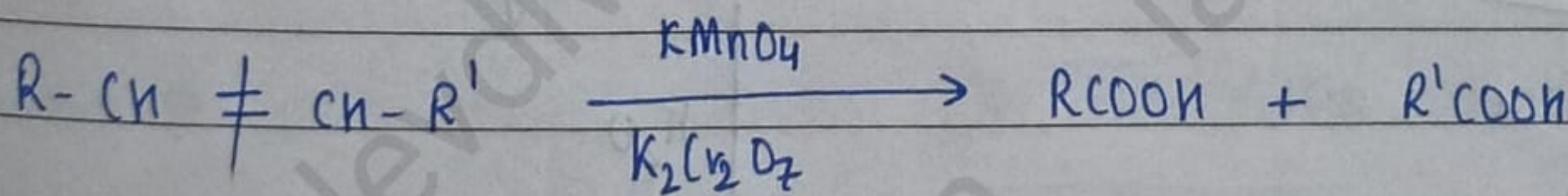
• FROM ALDEHYDE



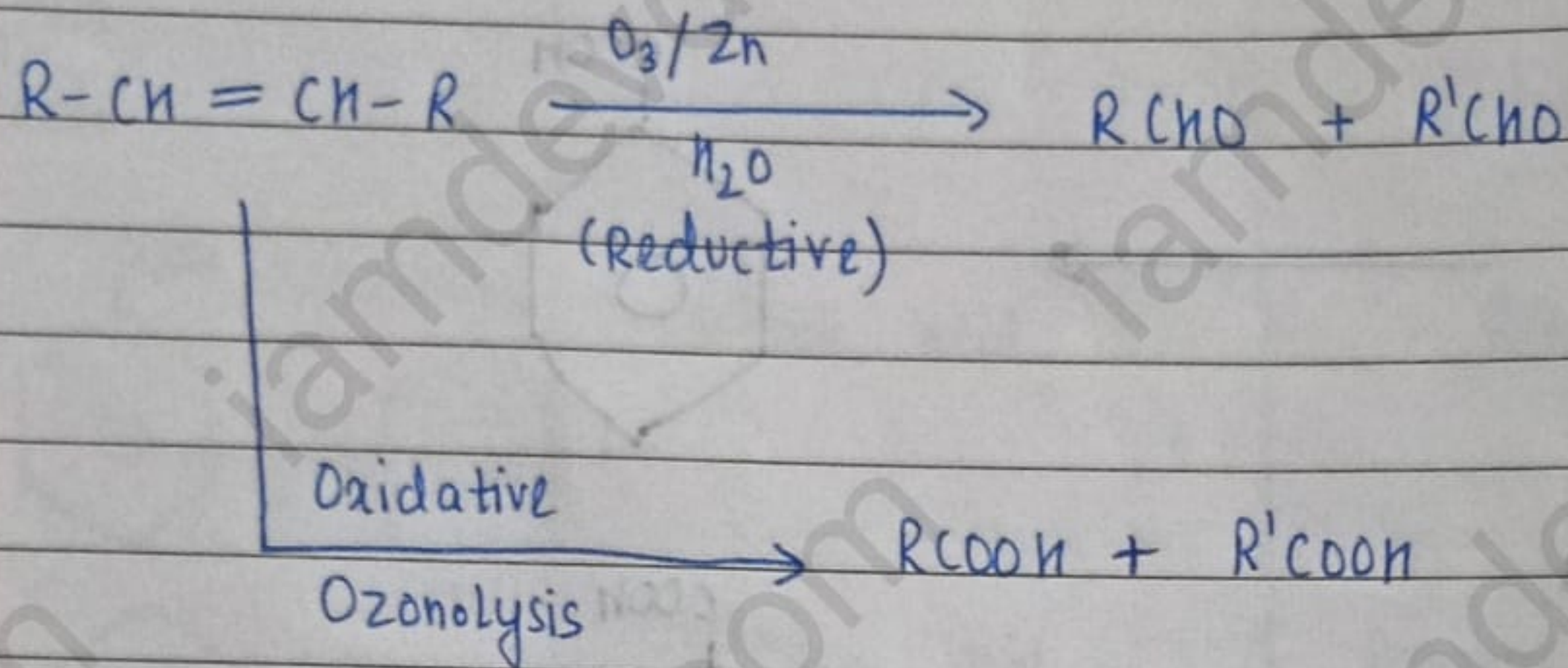
• FROM ALKYL BENZENE



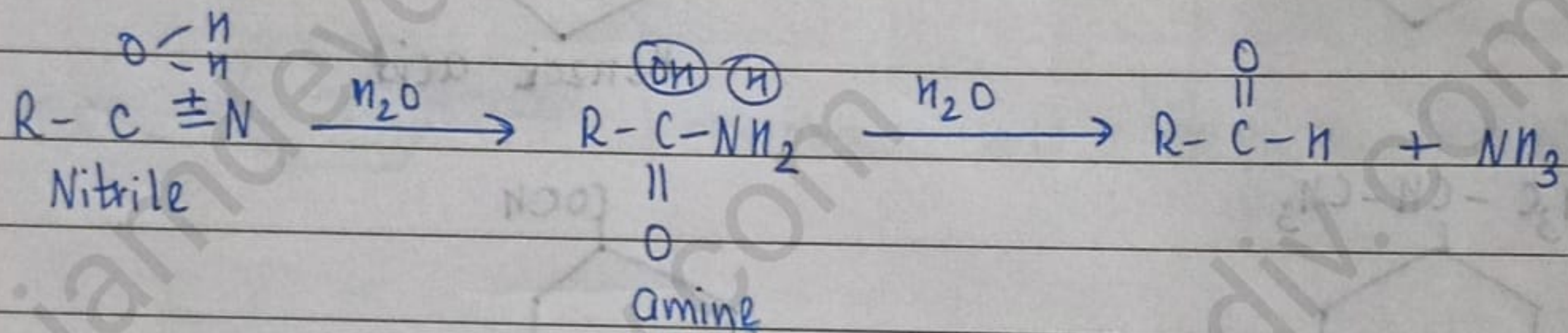
• FROM ALKENE



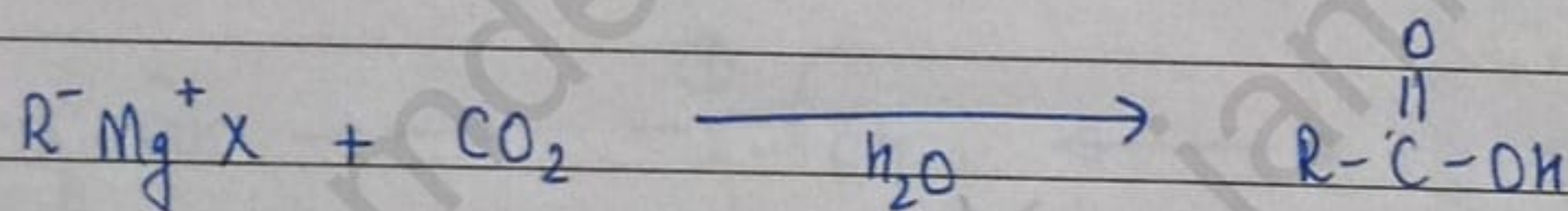
- OZONOLYSIS



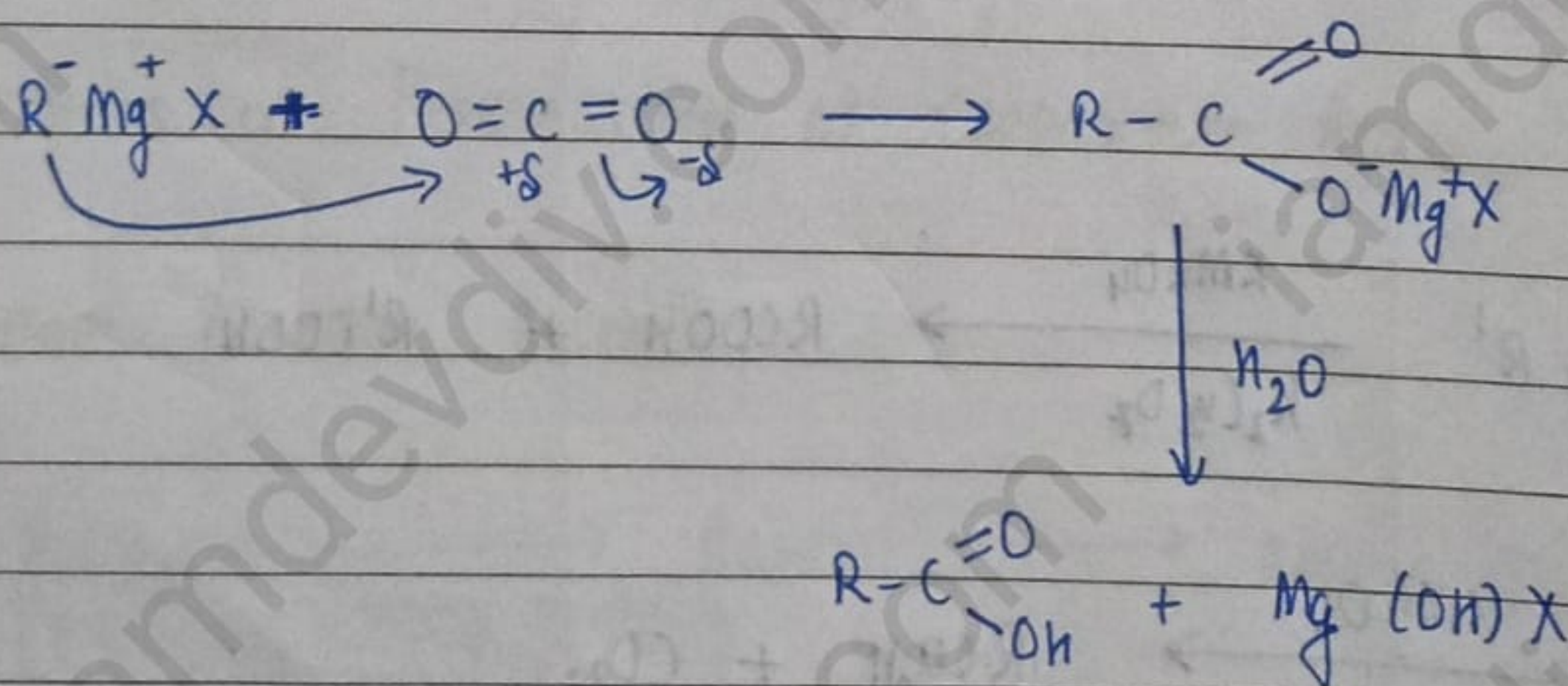
- FROM NITRILE AND AMINE



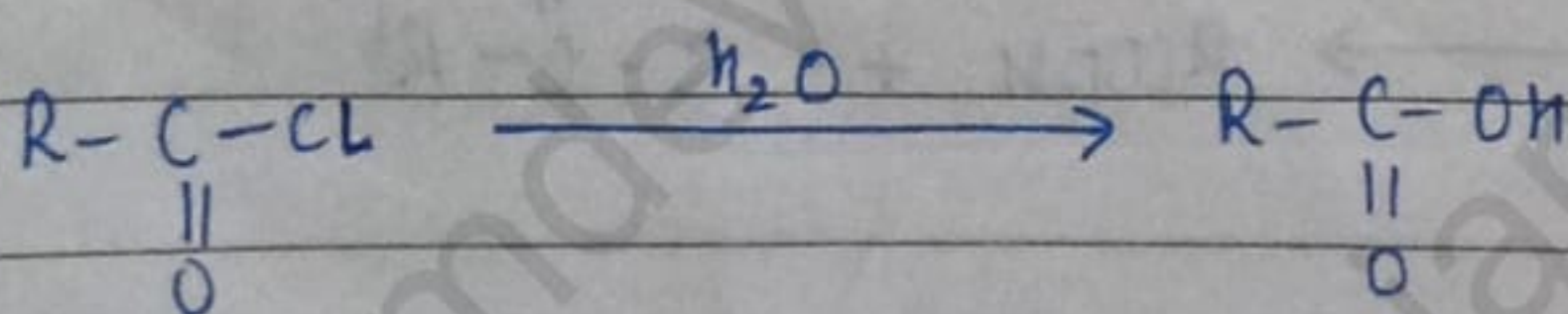
- FROM GRIGNARD REAGENT



Mechanism

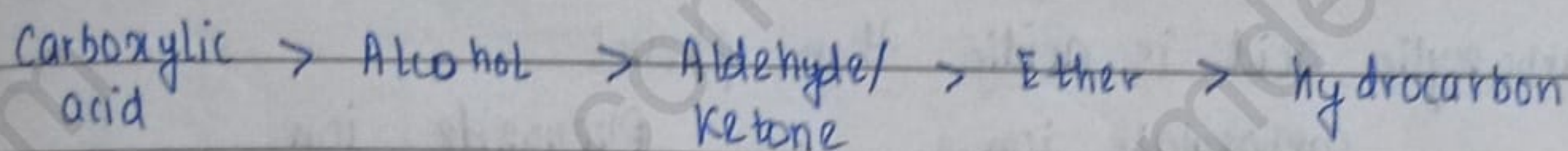


- ACYL HALIDE

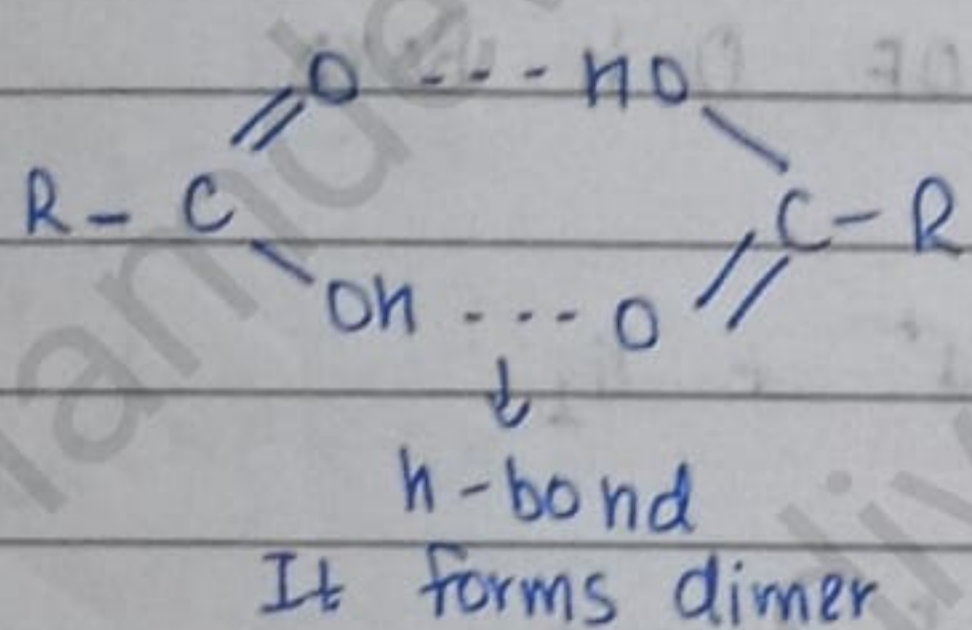


★ PHYSICAL PROPERTIES OF CARBOXYLIC ACID

- Aliphatic carboxylic compounds upto 9 carbon atoms are colourless liquid and higher ones are waxy solid in nature.
- BOILING POINT \propto MOLECULAR WEIGHT



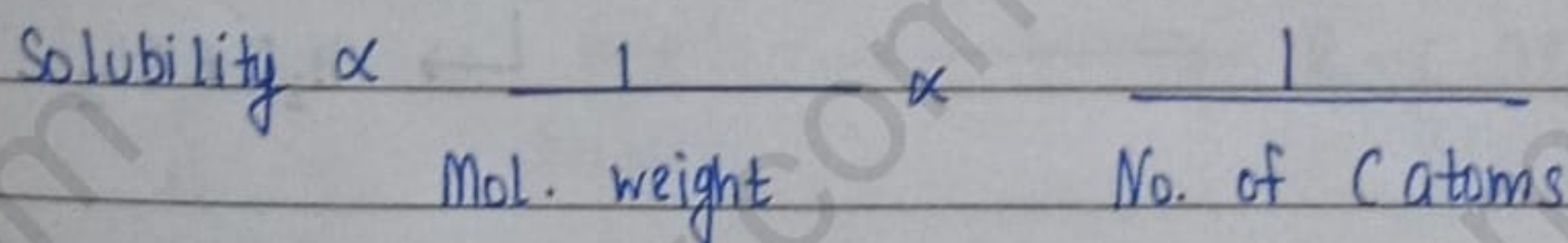
Reason



Due to the strong intermolecular H-bonding and formation of dimer they have more boiling point in comparison to Alcohol, Aldehyde and ketones.

It forms dimer in vapour phase.
It forms monomer in aqueous phase.

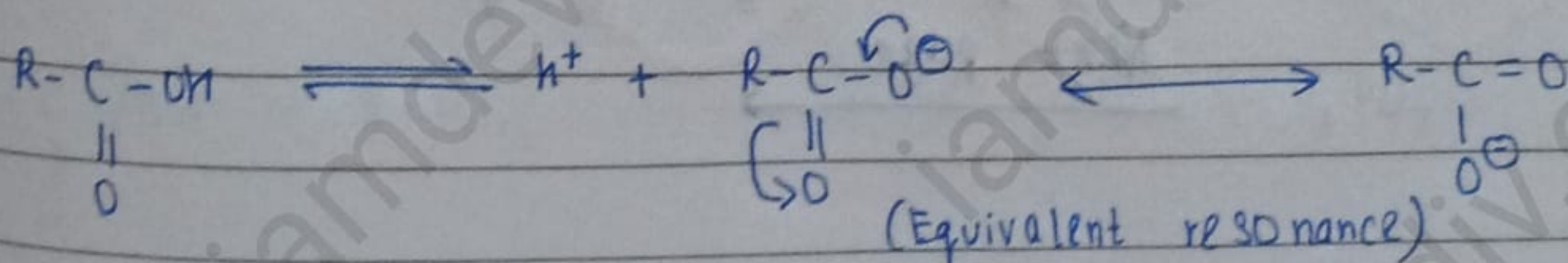
• SOLUBILITY

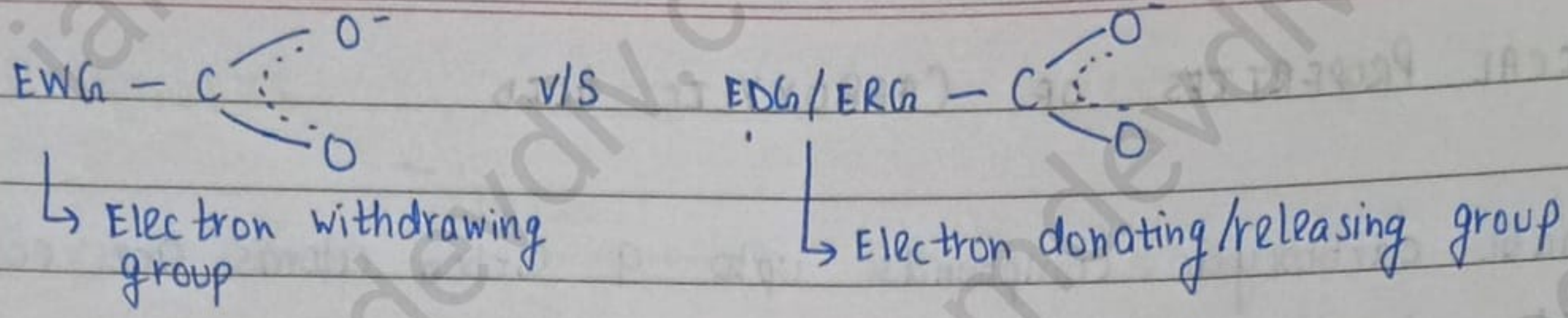


Aliphatic carboxylic compounds upto four carbon atoms are miscible in water due to H-bond.

★ CHEMICAL PROPERTIES OF CARBOXYLIC ACID

• ACIDITY

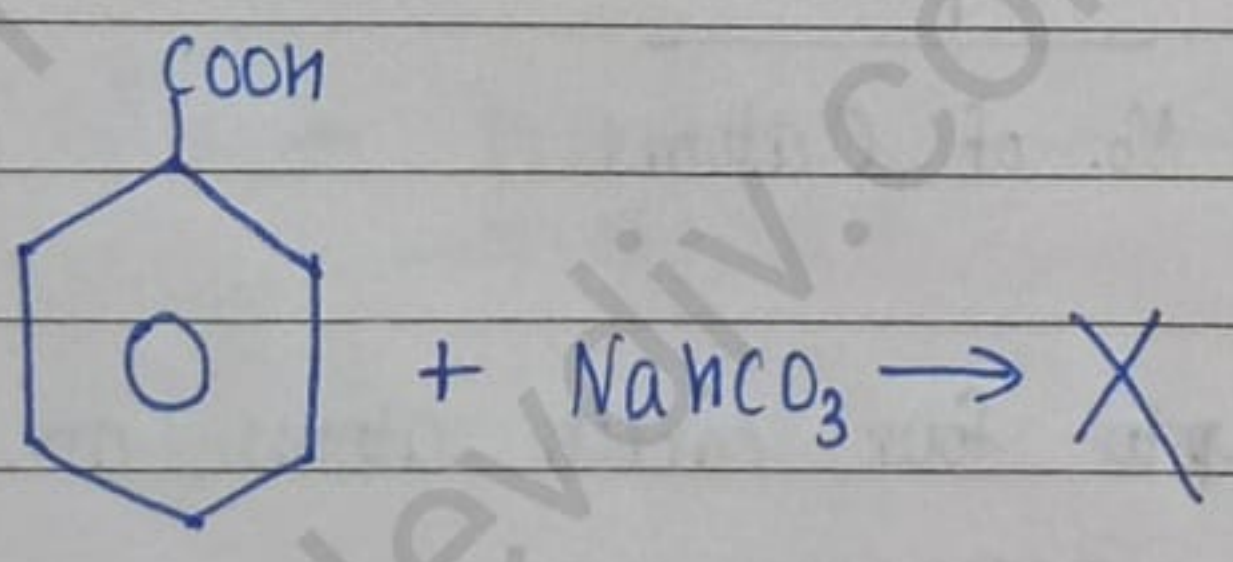
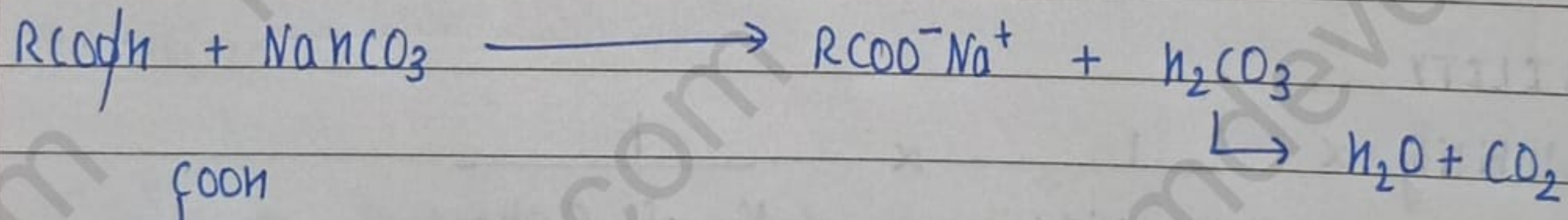
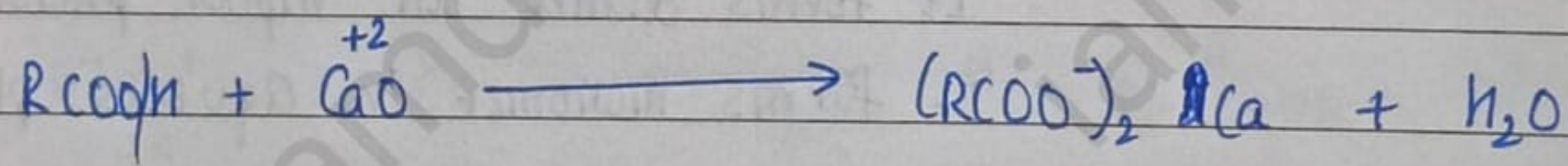
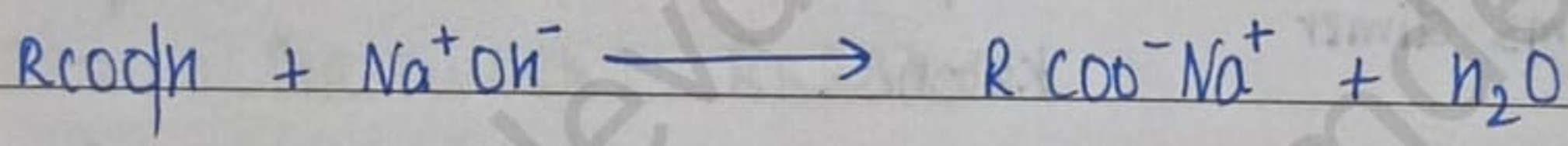
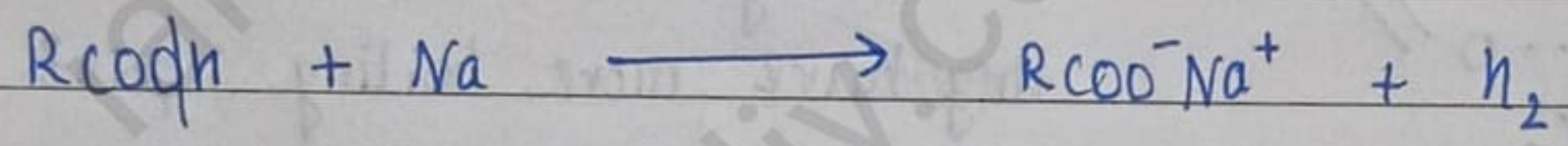




Acidic strength $\propto \frac{EWG}{EDG} \propto \frac{-M \alpha - I}{+M \alpha + I} \propto \frac{1}{pK_a}$

→ Carboxylic acid is acidic than phenol
 Carboxylate ion > Phenoxide ion
 (Equivalent Resonance) (Resonance)

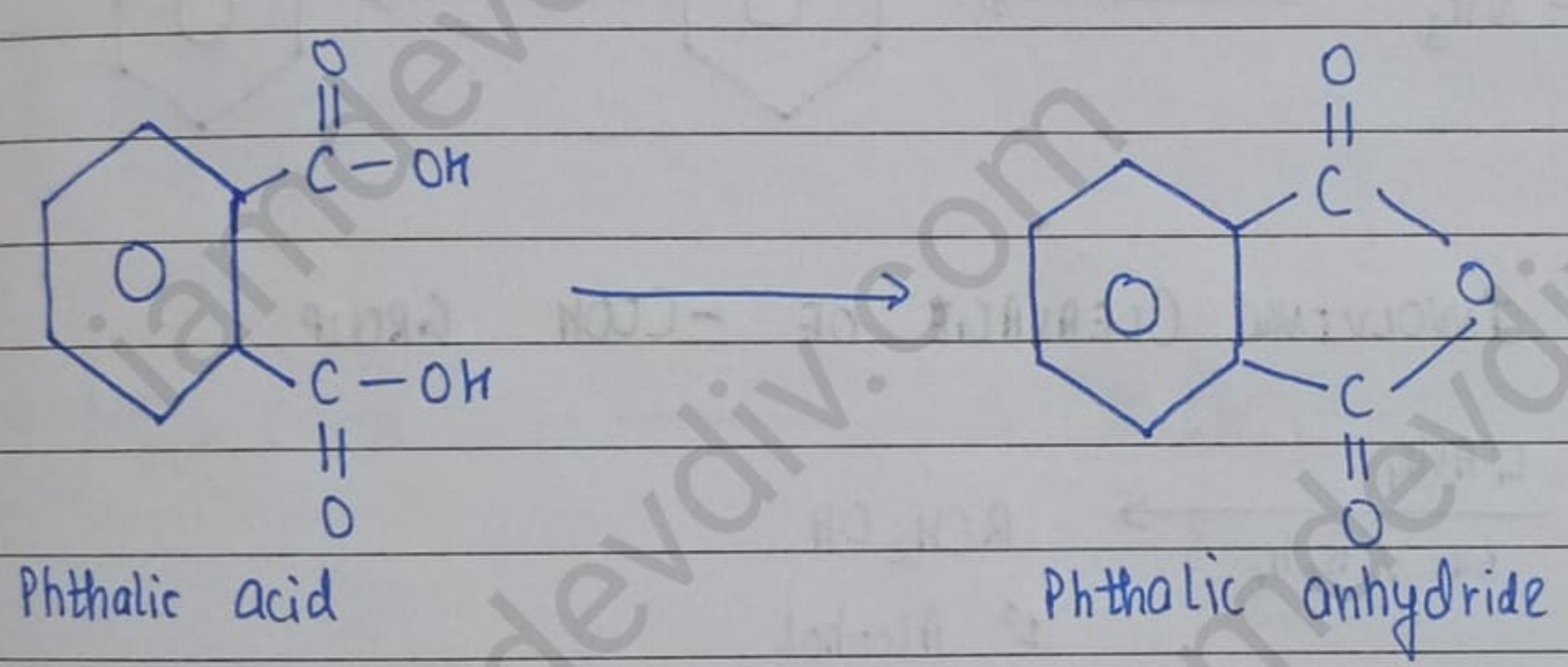
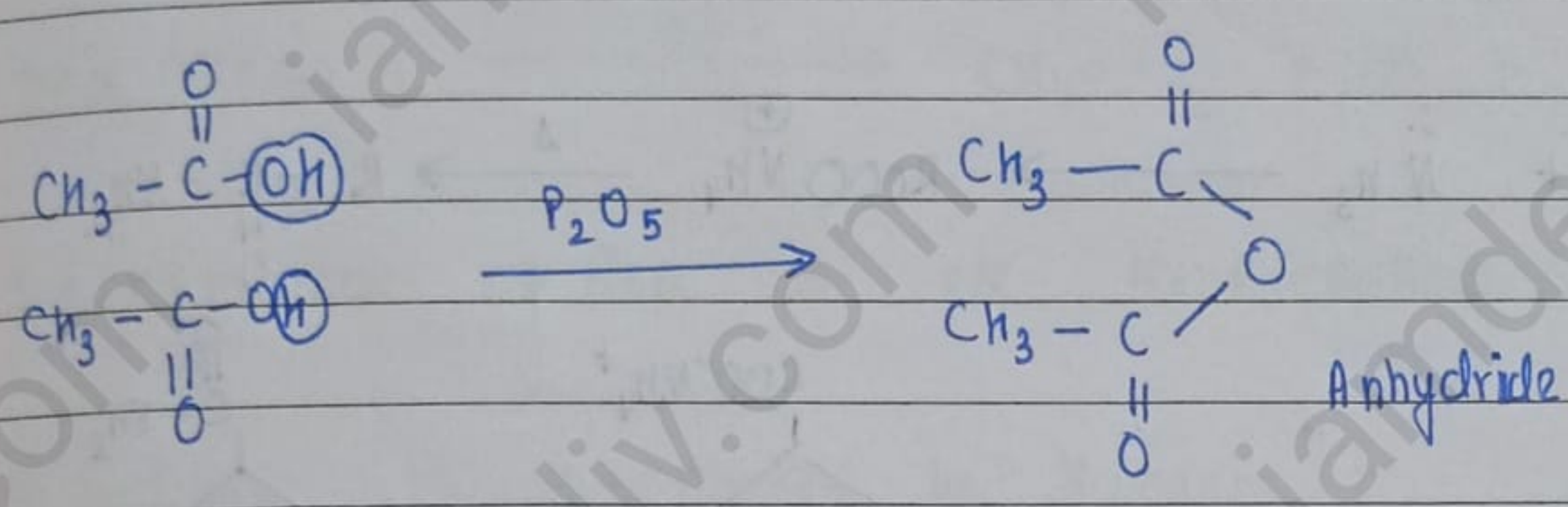
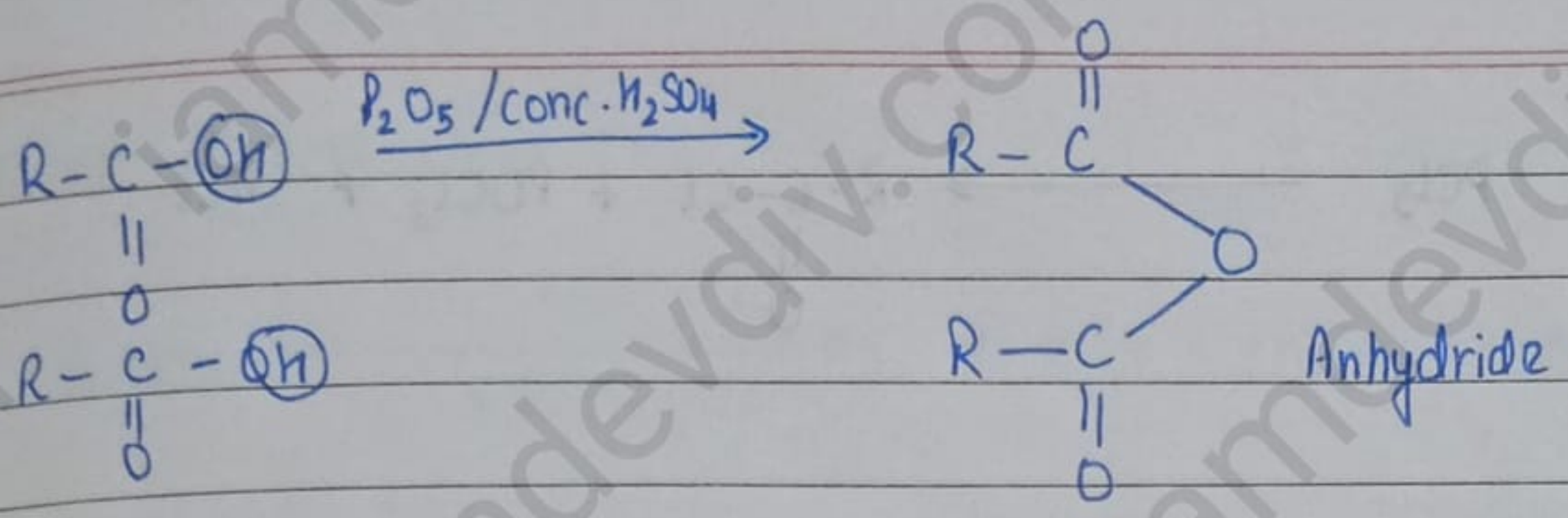
• REACTIONS INVOLVING CLEAVAGE OF O-H BOND



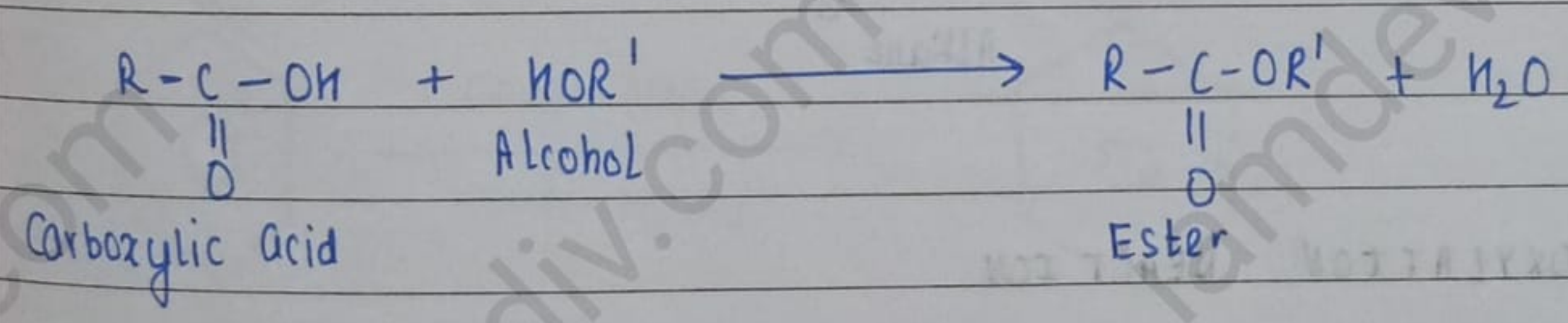
• REACTIONS INVOLVING CLEAVAGE OF C-OH BOND

* FORMATION OF ANHYDRIDE (Dehydrating agent → Remove H₂O)

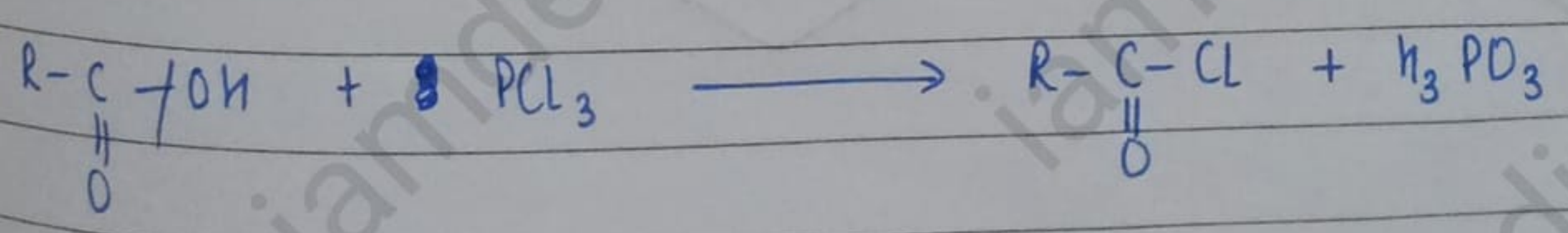
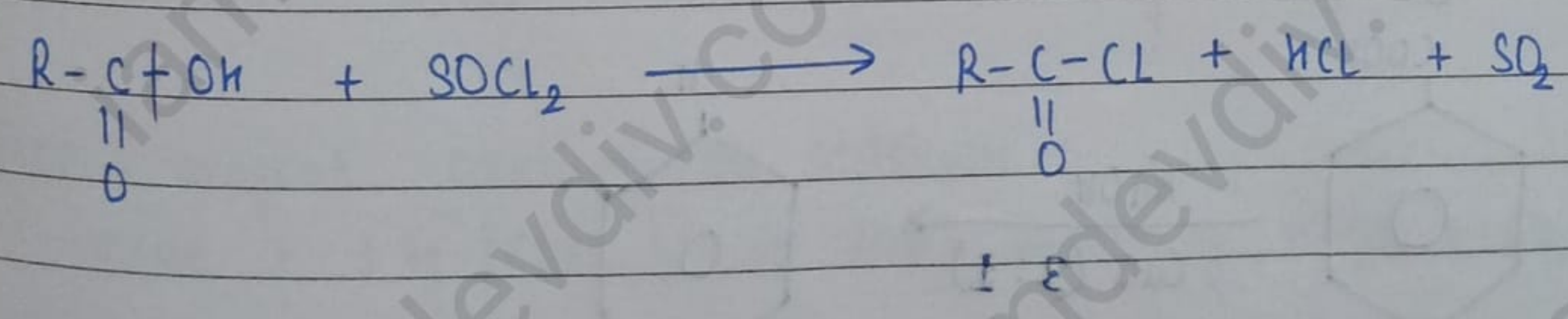
Next page →

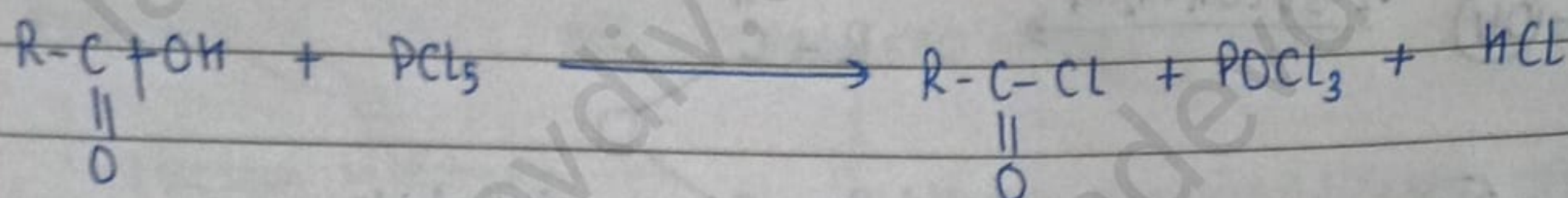


* ESTERIFICATION

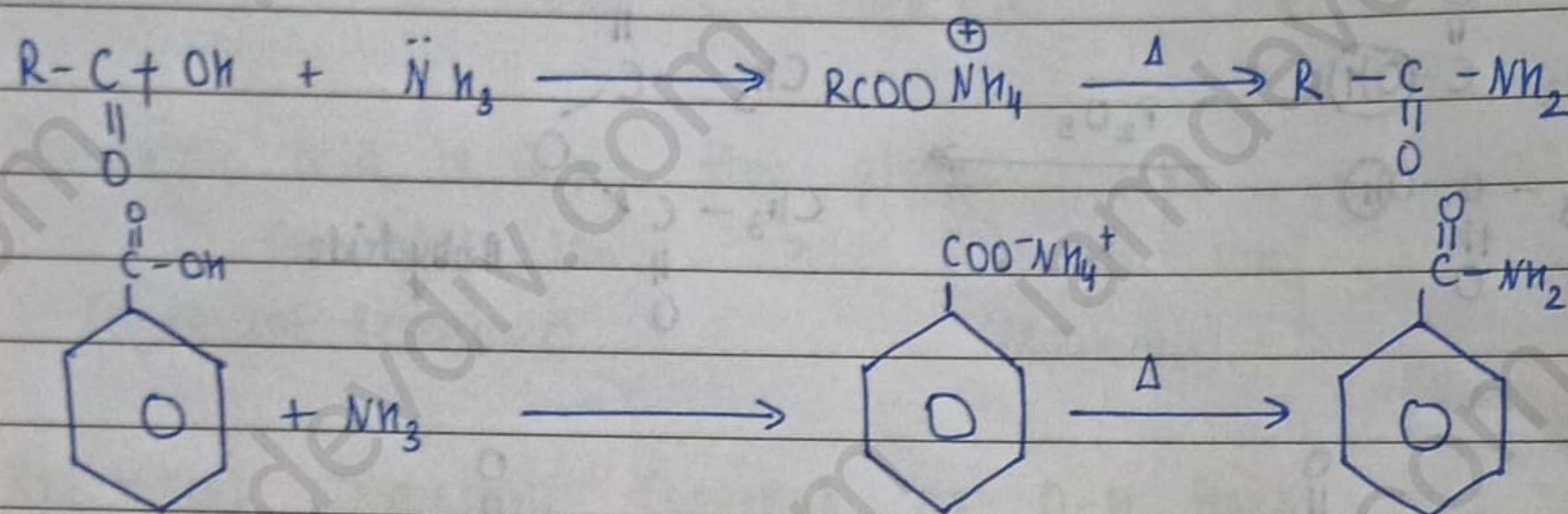


* REACTION WITH PCl₃, PCl₅, SOCl₂

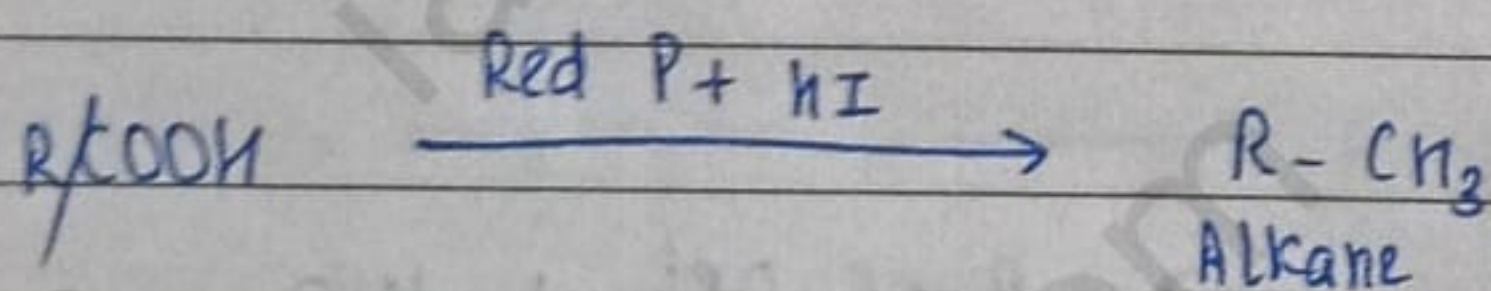
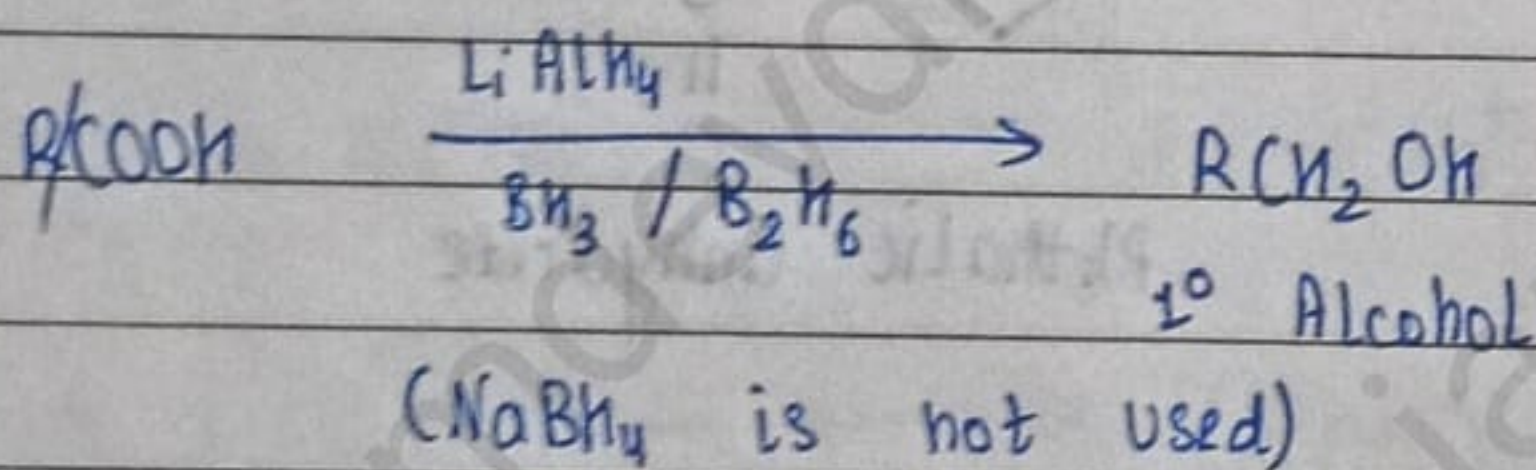




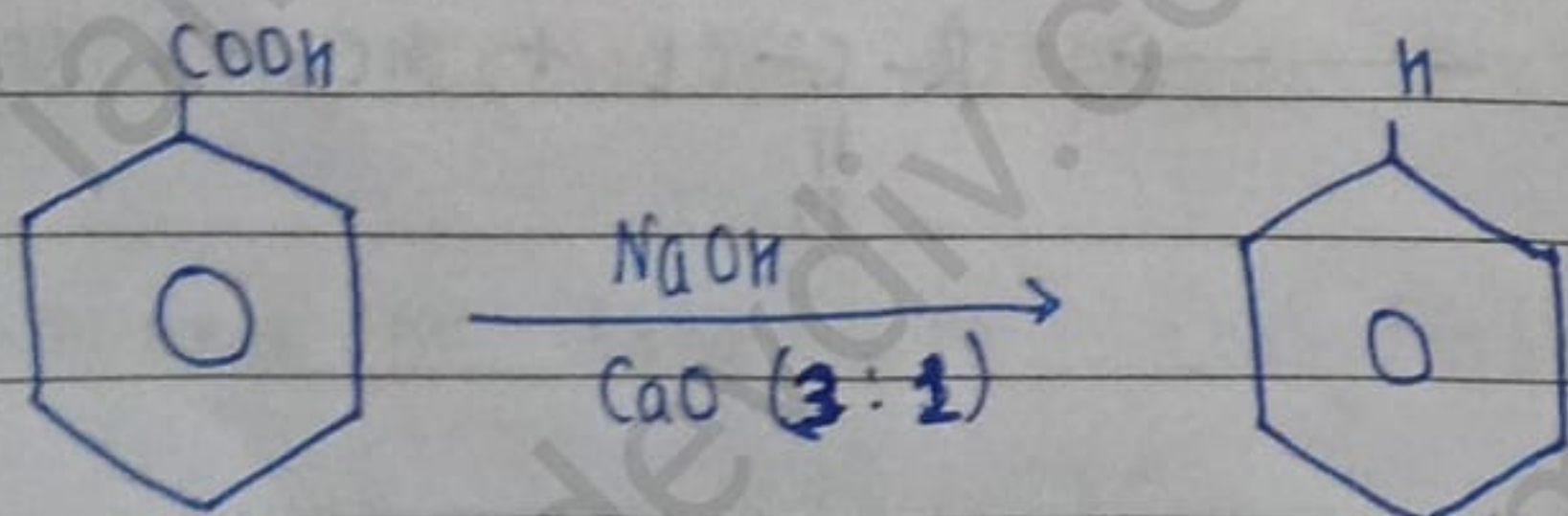
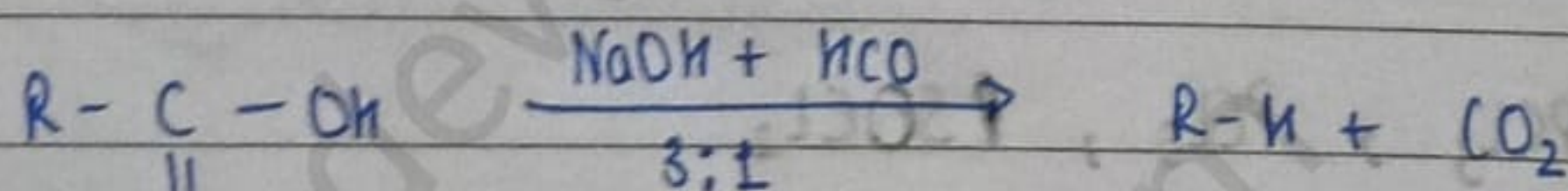
* REACTION WITH AMMONIA



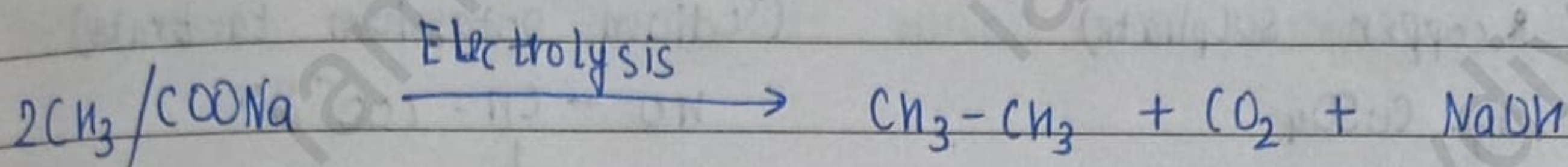
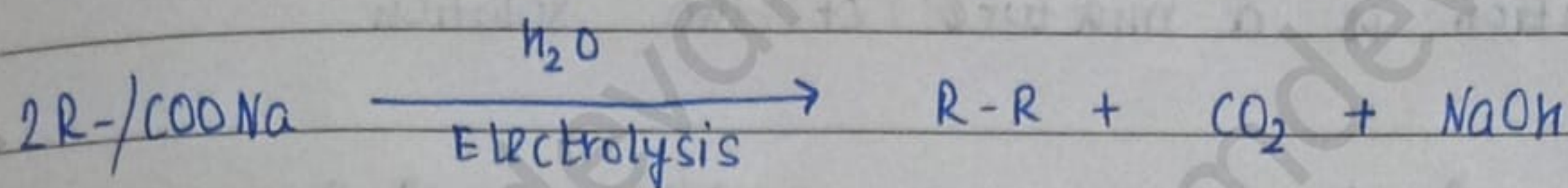
• REACTIONS INVOLVING CLEAVAGE OF -COOH GROUP



* DECARBOXYLATION REACTION

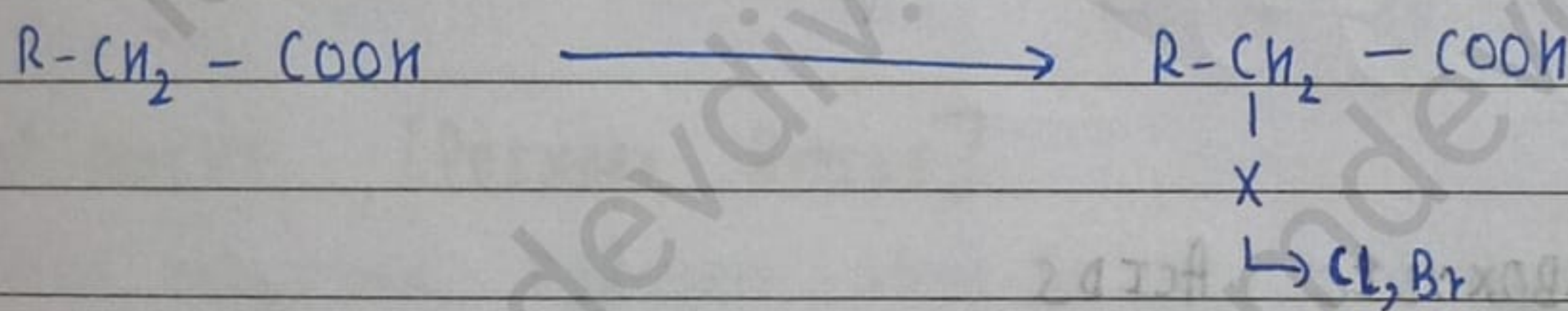
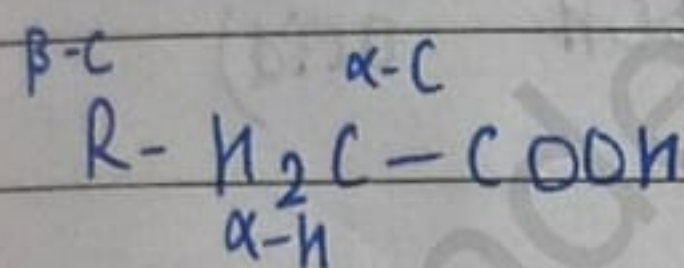


* KOLBE ELECTROLYSTS

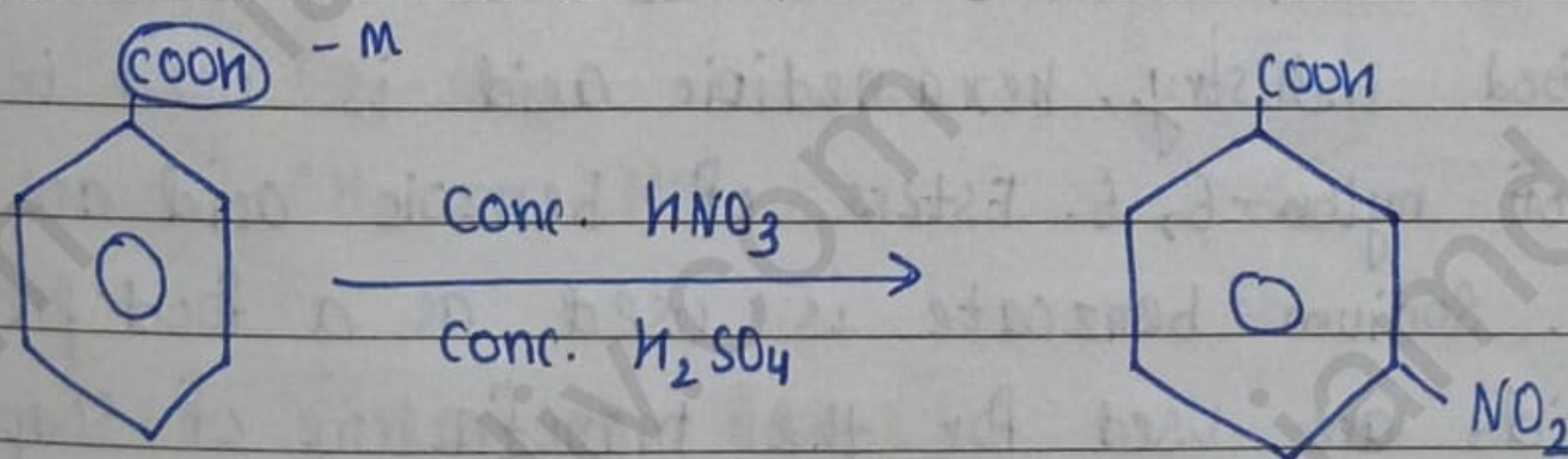


• SUBSTITUTION REACTION IN HYDROCARBONS

" α -hydrogen is substituted by Halogen"



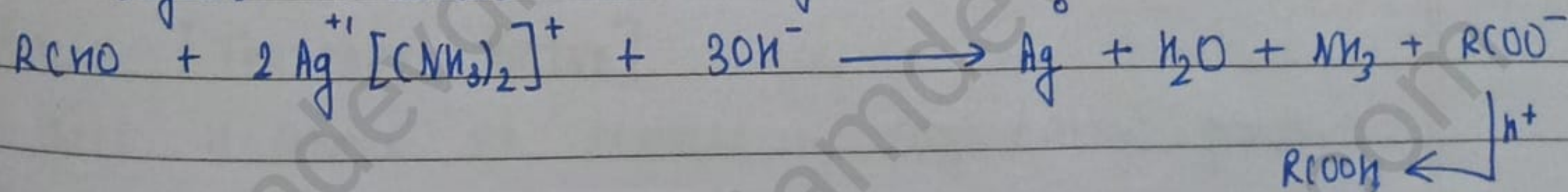
* RING SUBSTITUTION



★ TOLLEN'S REAGENT

~~Ammonical~~ Ammonical Silver Nitrate Solution $[\text{Ag}(\text{NH}_3)_2]^+$

Tollen's reagent oxidises all aldehyde

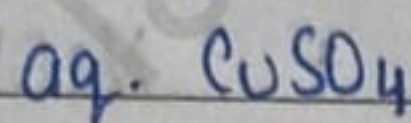


★ FEHLING'S SOLUTION

Fehling solution is a mixture of two solution

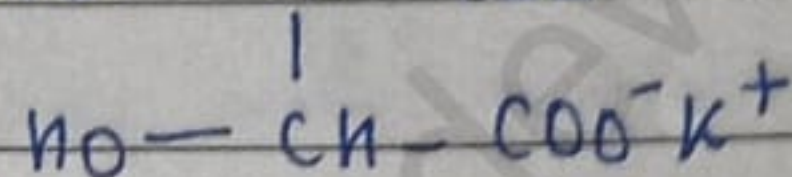
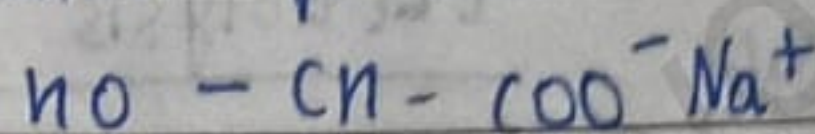
Fehling solⁿ A

(aq. copper sulphate)

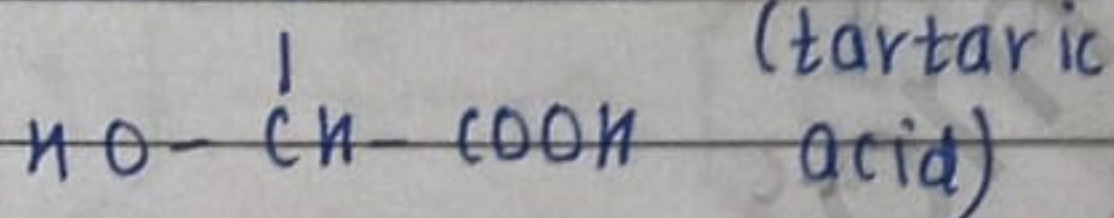
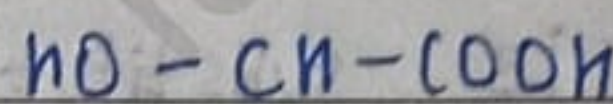


Fehling solⁿ B

(Sodium potassium tartrate)



↓ made from



Fehling's solution is not a distinguishable test for aromatic aldehyde

★ USES OF CARBOXYLIC ACIDS

Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries. Ethanoic acid is used as solvent and as vinegar in food industry. Hexanedioic acid is used in the manufacture of nylon-6,6. Esters of benzoic acid are used in perfumery. Sodium benzoate is used as a food preservative. Higher fatty acids are used for the manufacture of soaps and detergents.