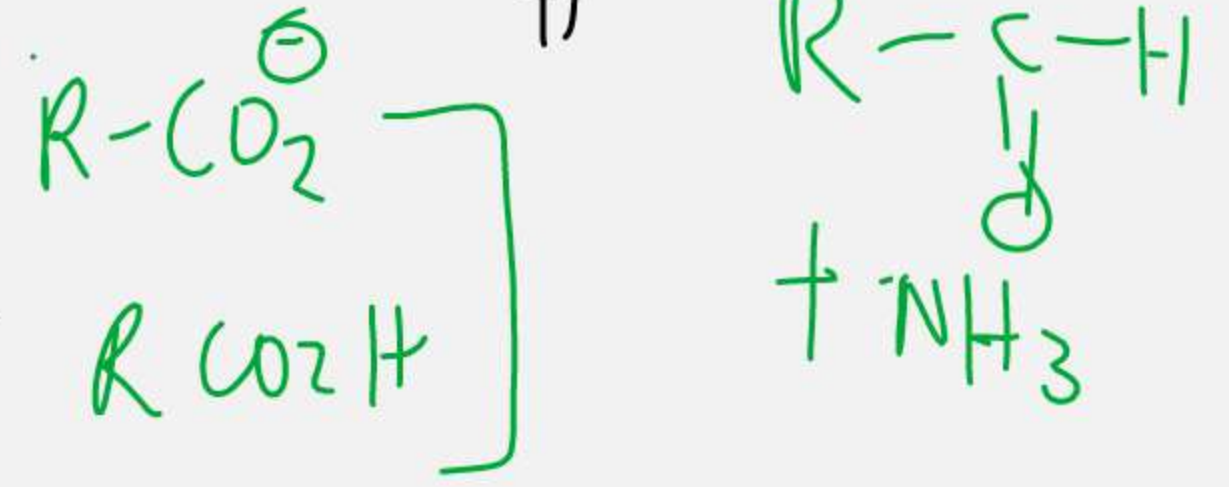
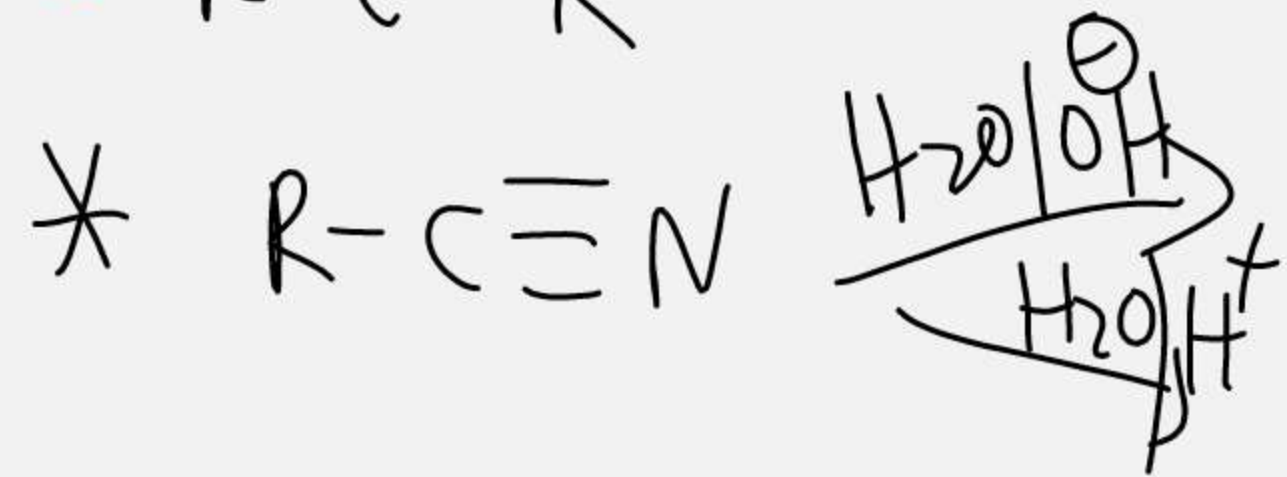
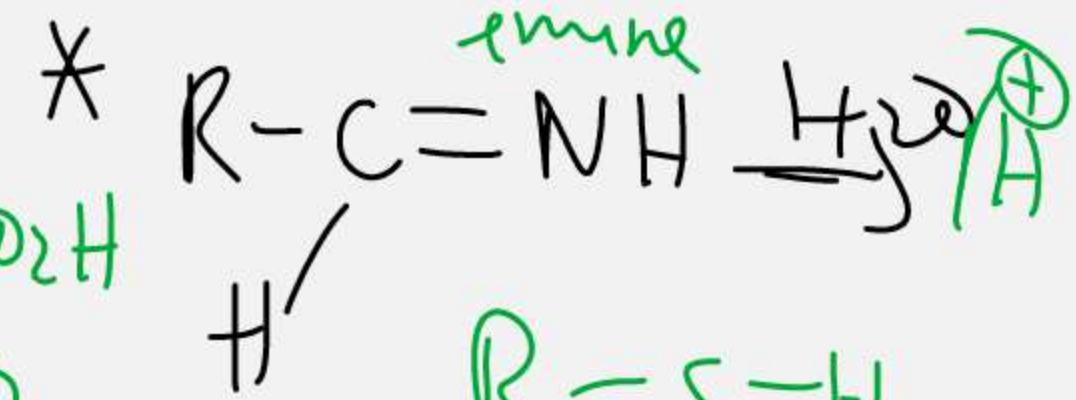
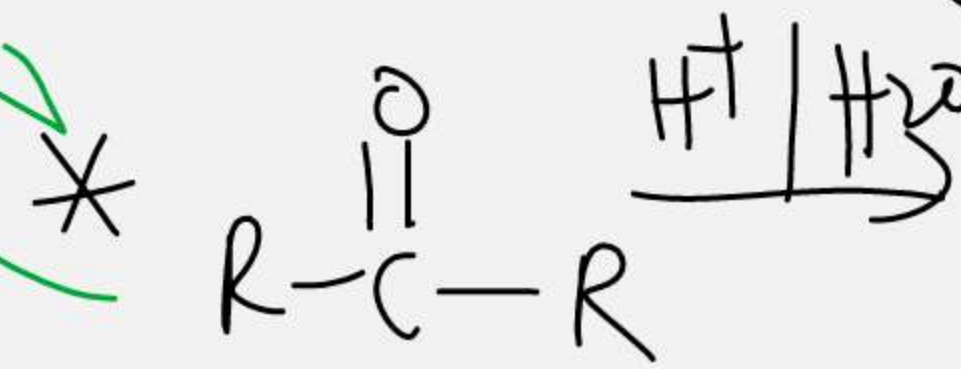
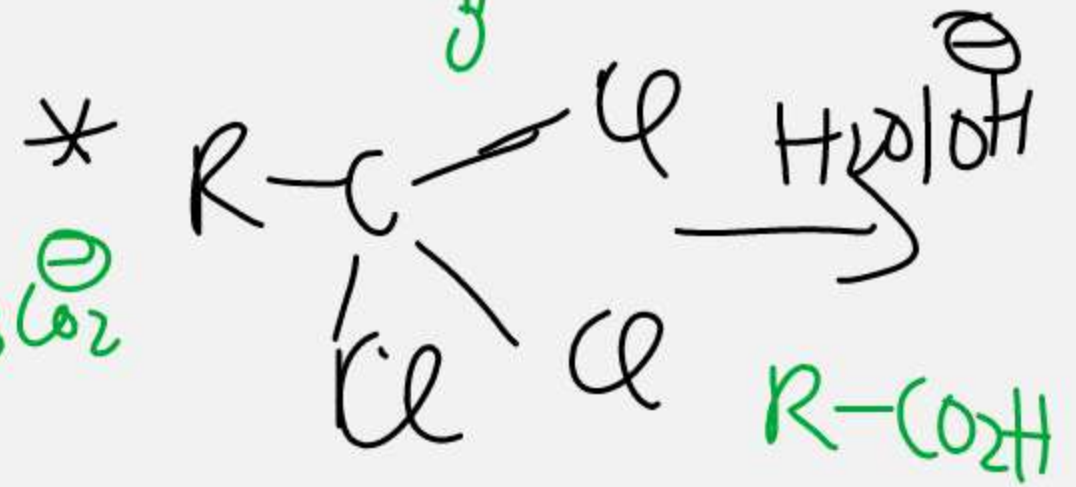
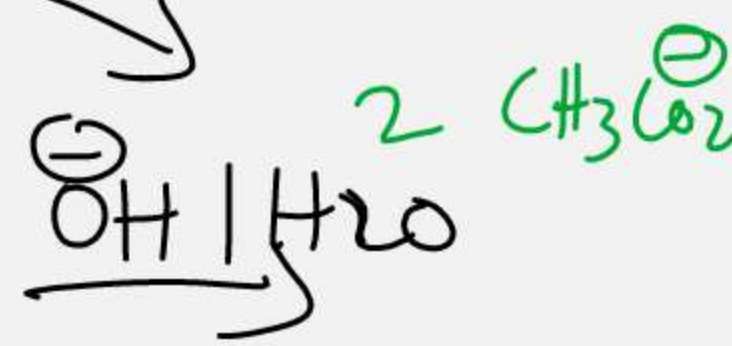
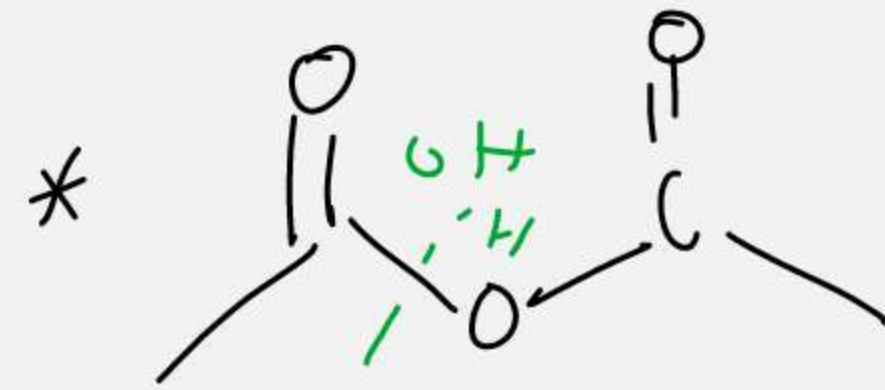
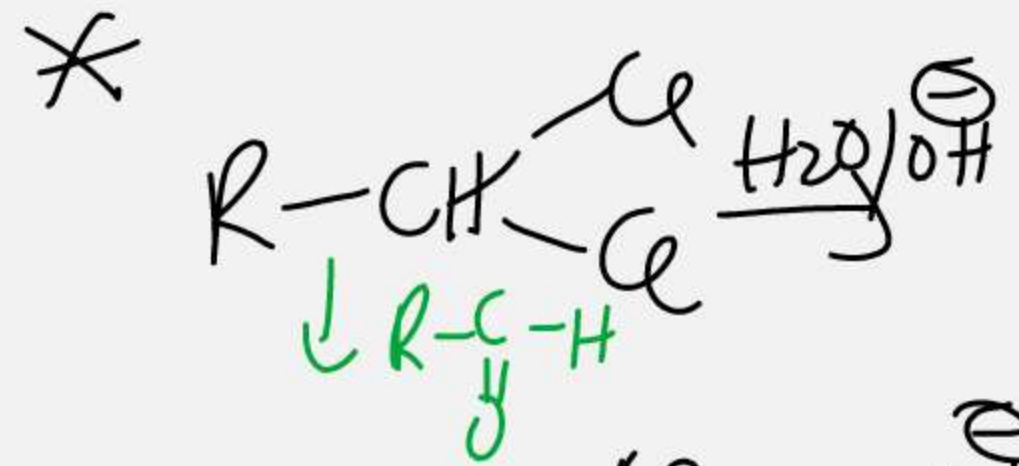
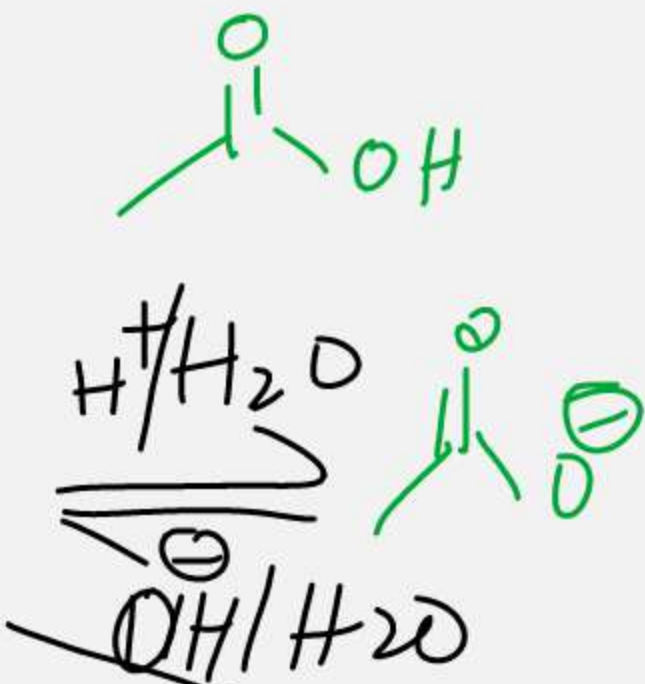
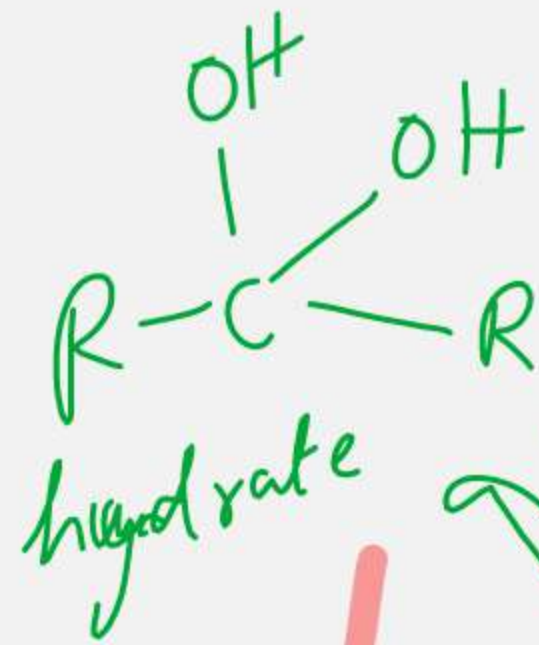
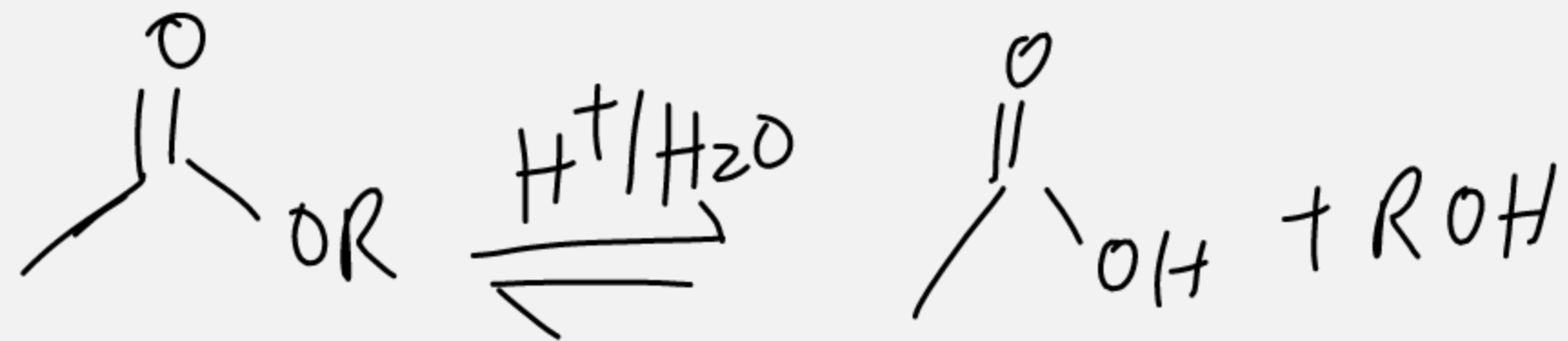


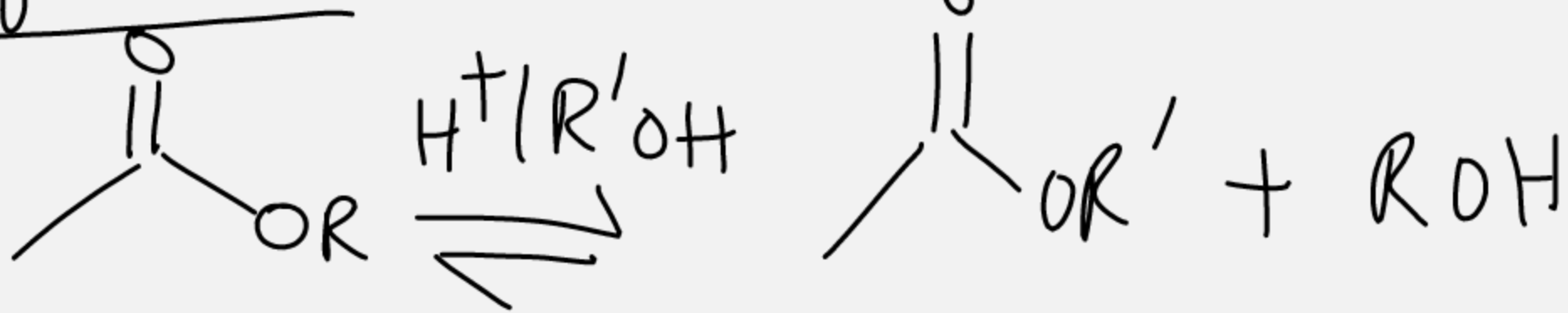
Hydrolysis



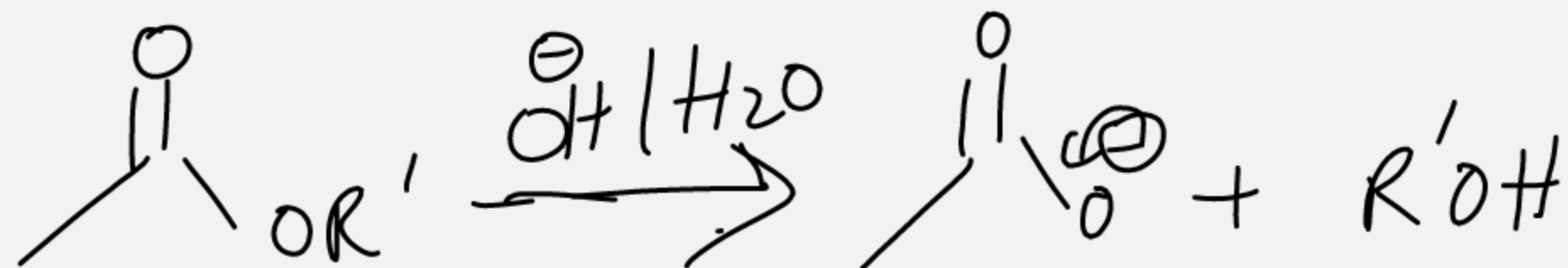
* Acid catalysed ester Hydrolysis



* Transesterification Rxn

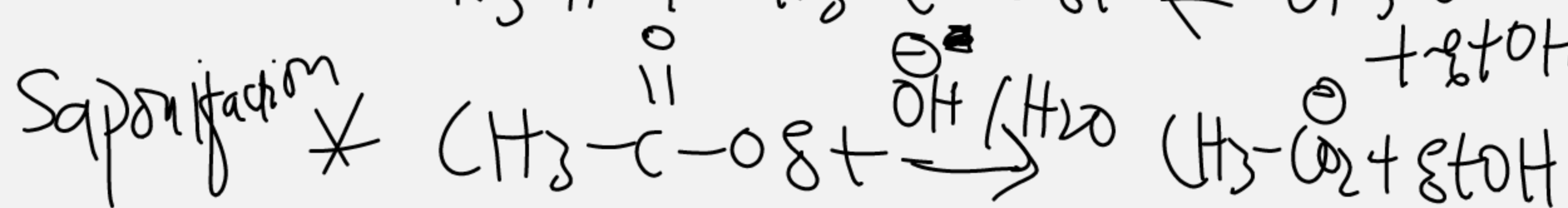
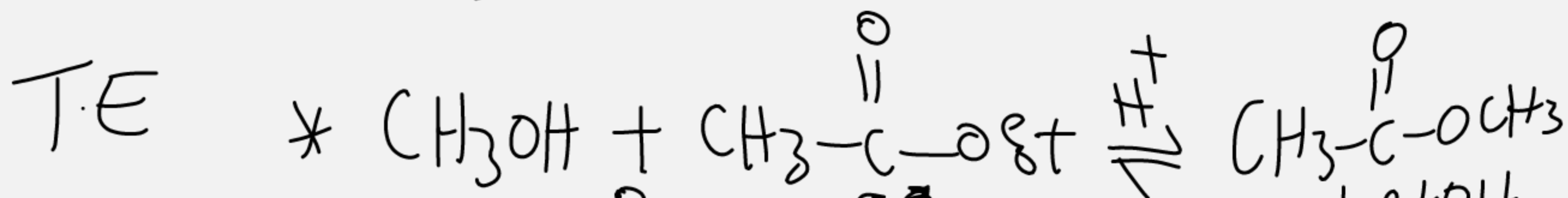
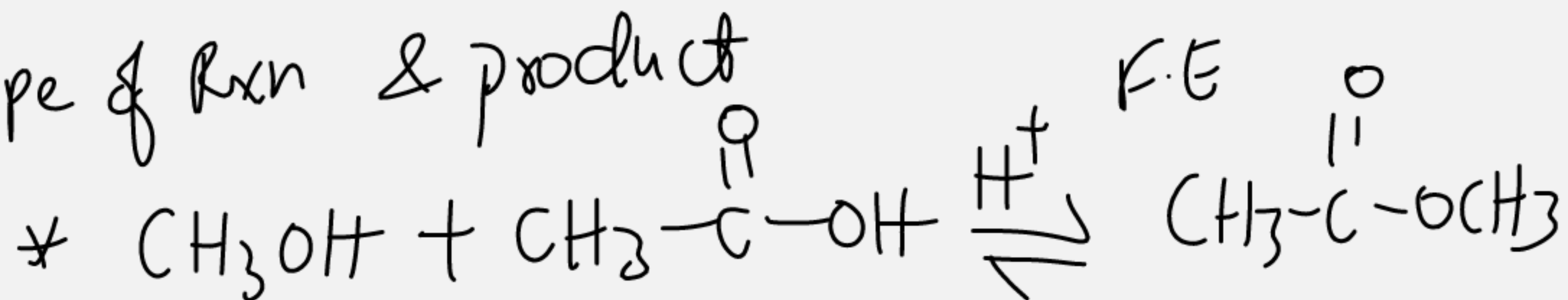


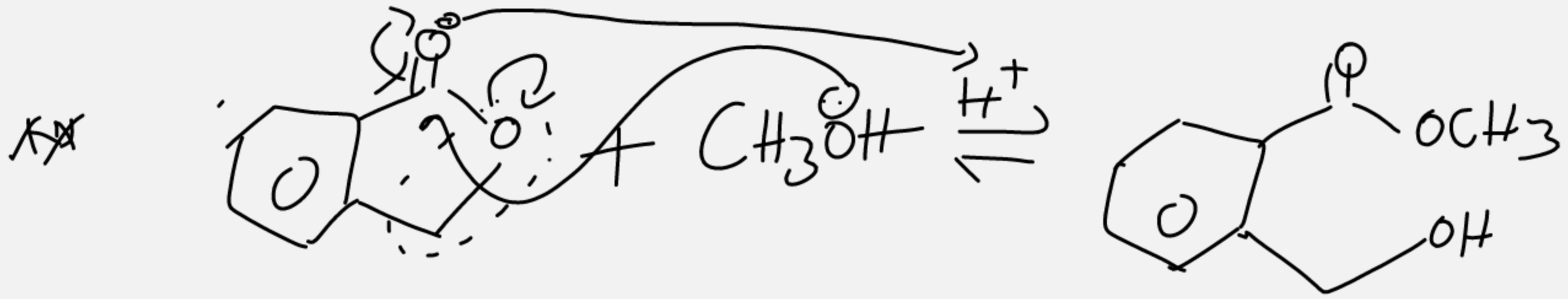
* Base Catalysed Hydrolysis of Ester (Saponification)



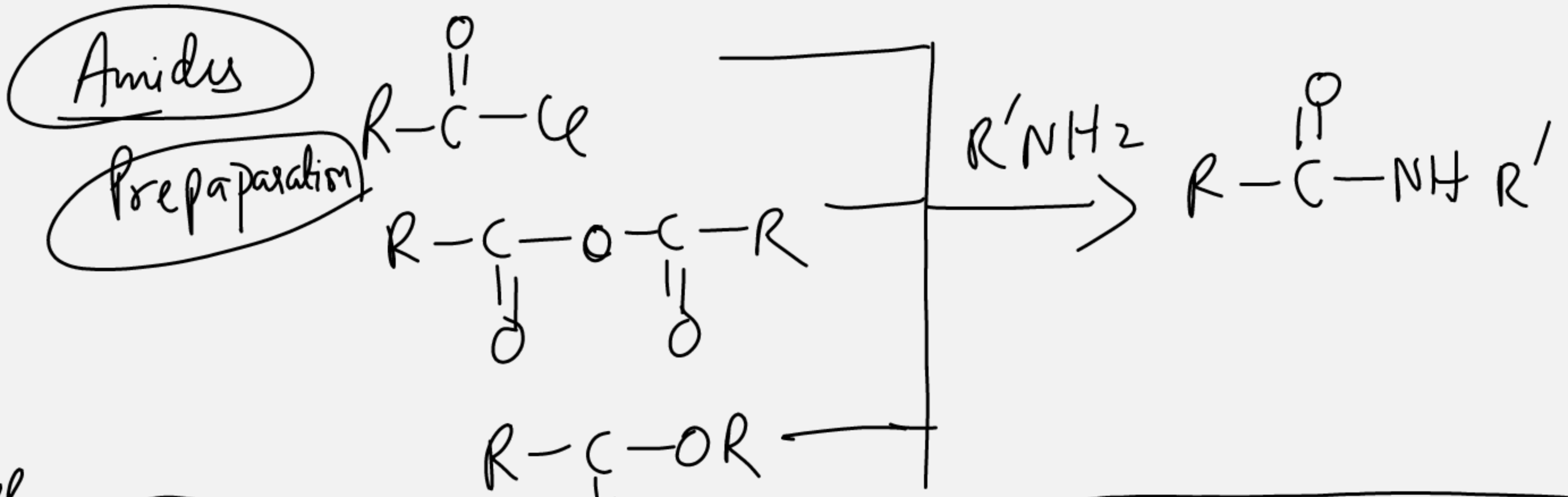
Irreversible process

Q write type of Rxn & product

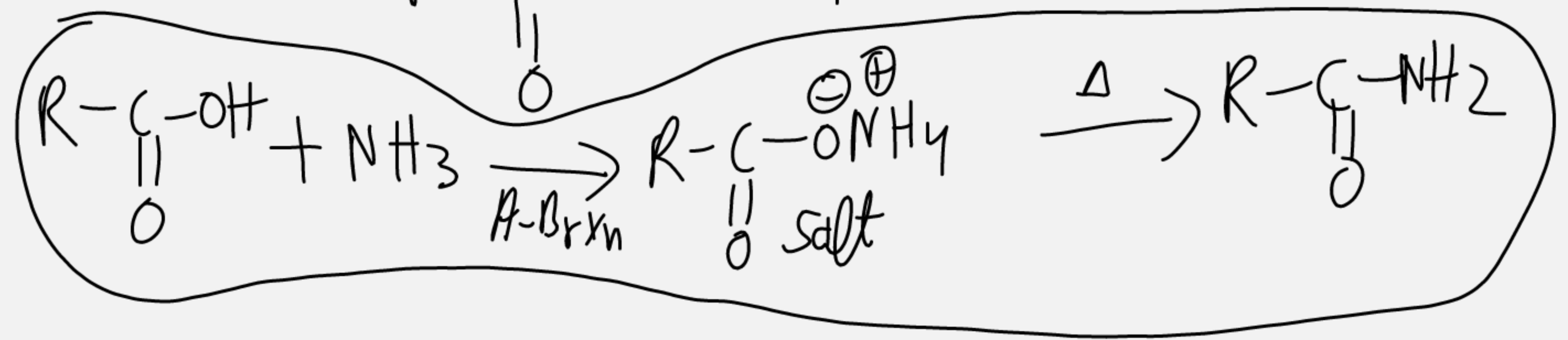




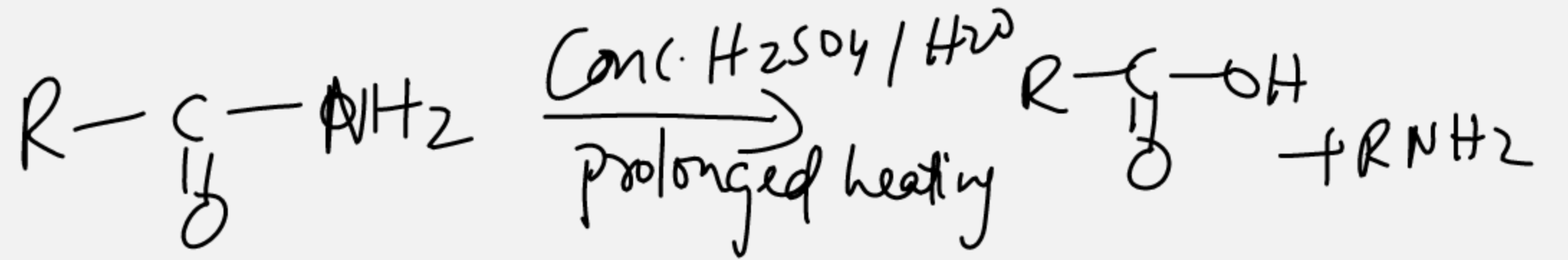
①



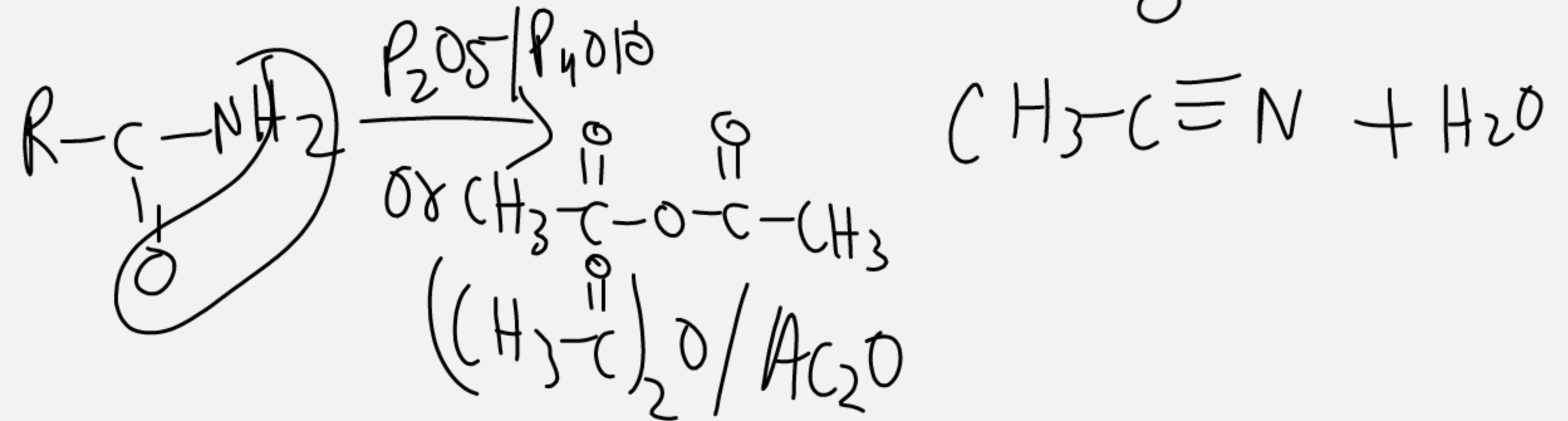
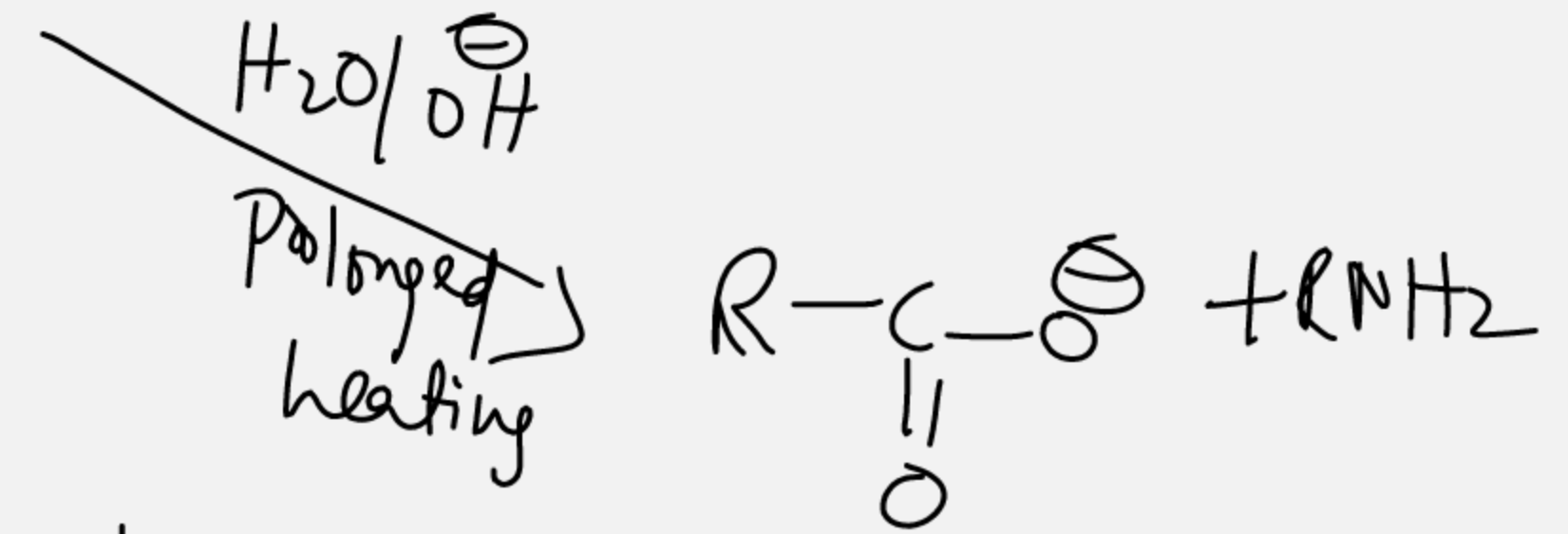
Prep

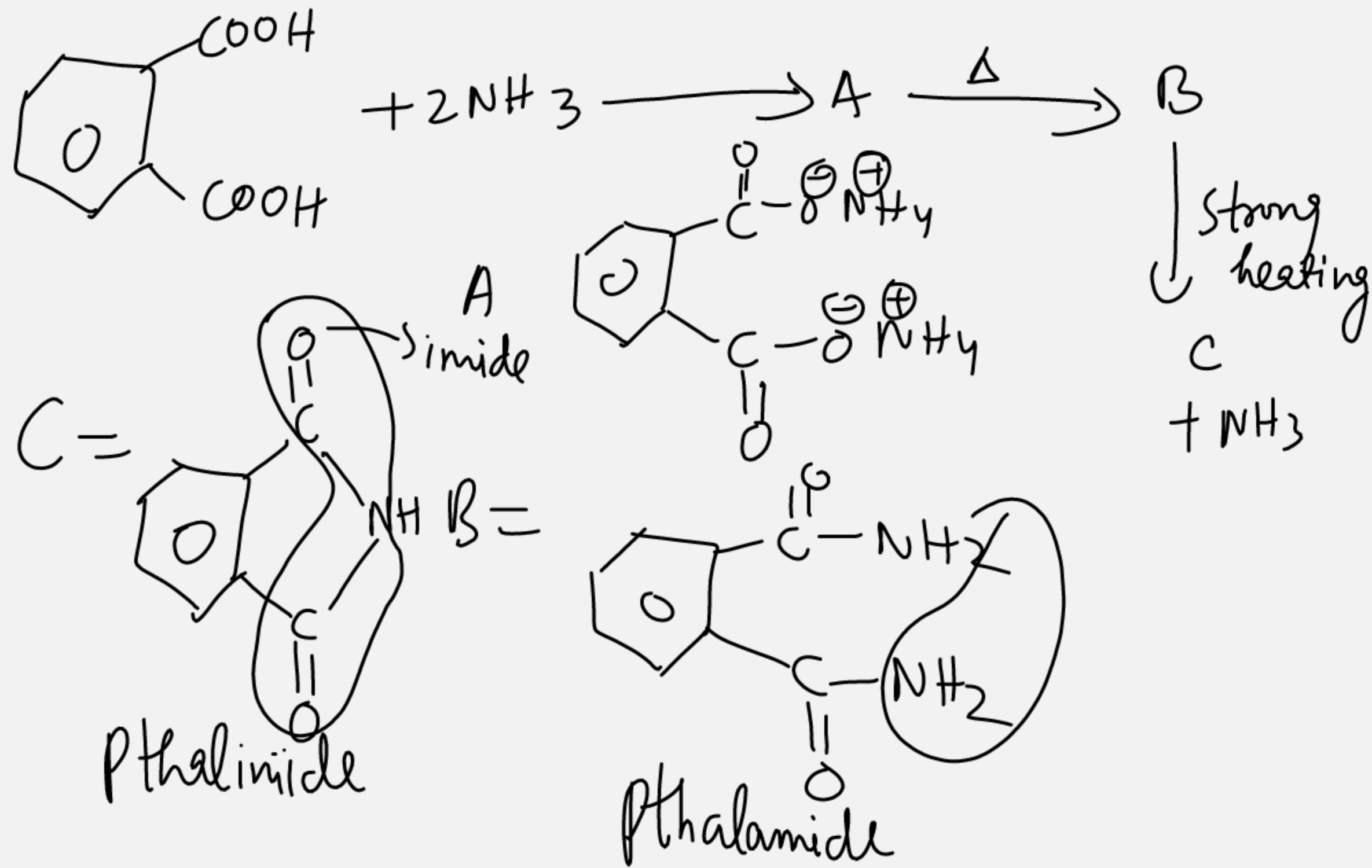


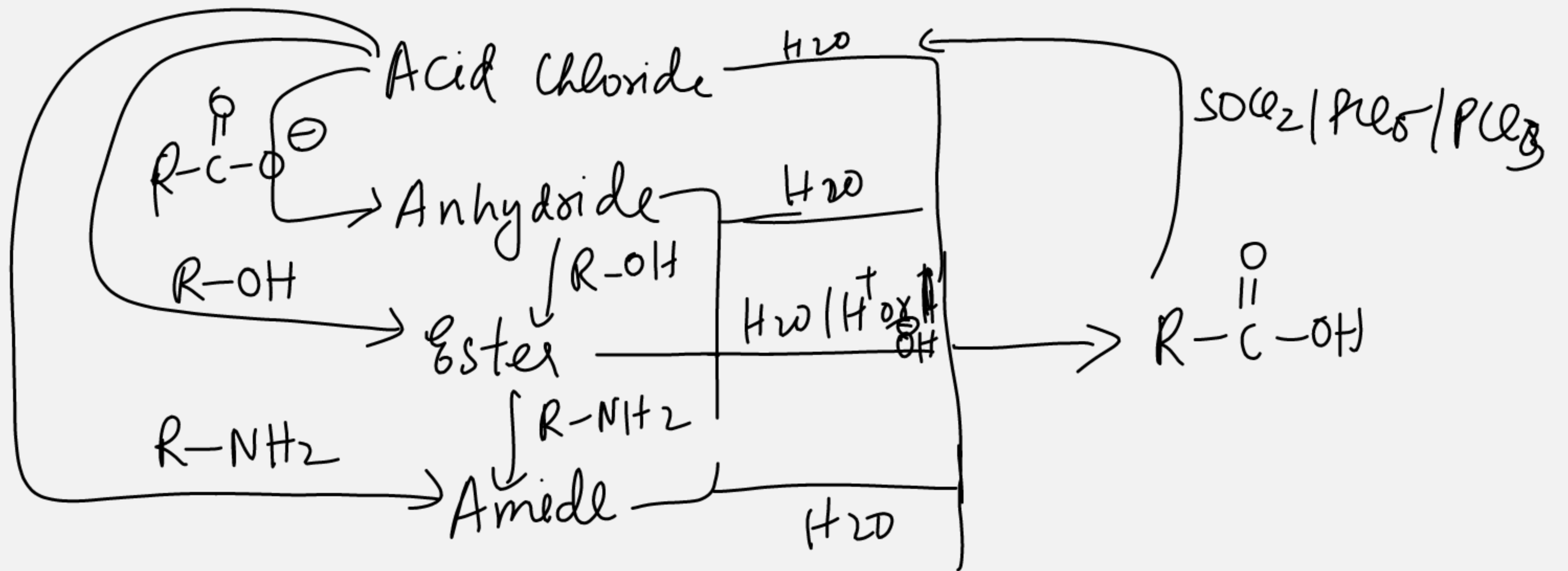
Amide Hydrolysis



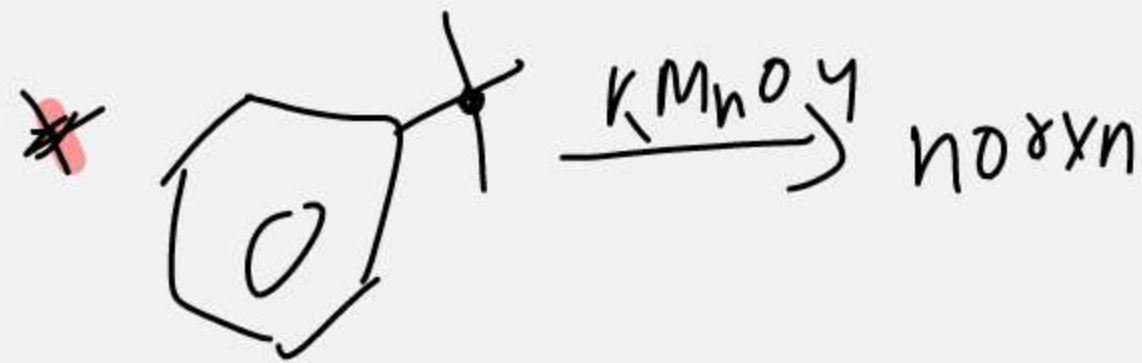
Dehydration of Amide



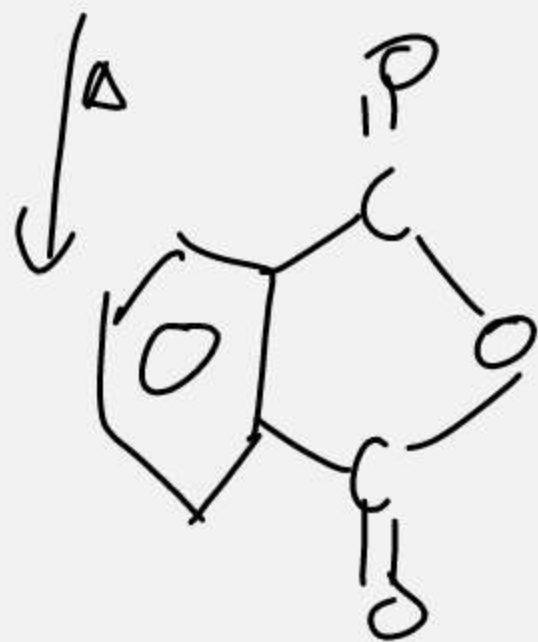
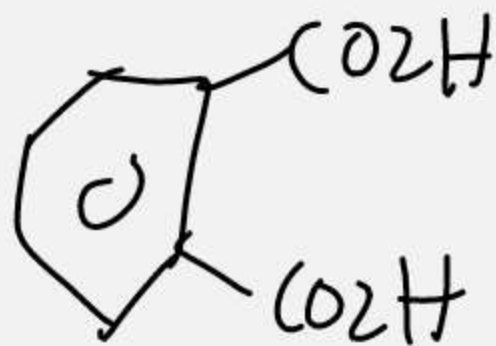
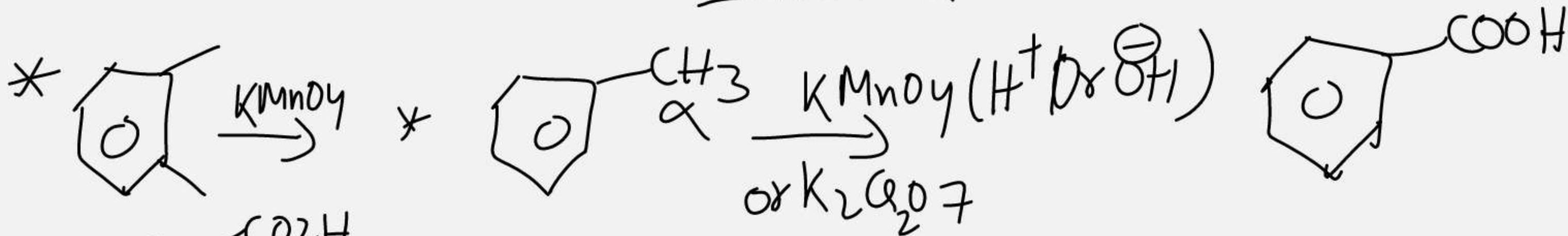




Carboxylic acid preparation



Preparation

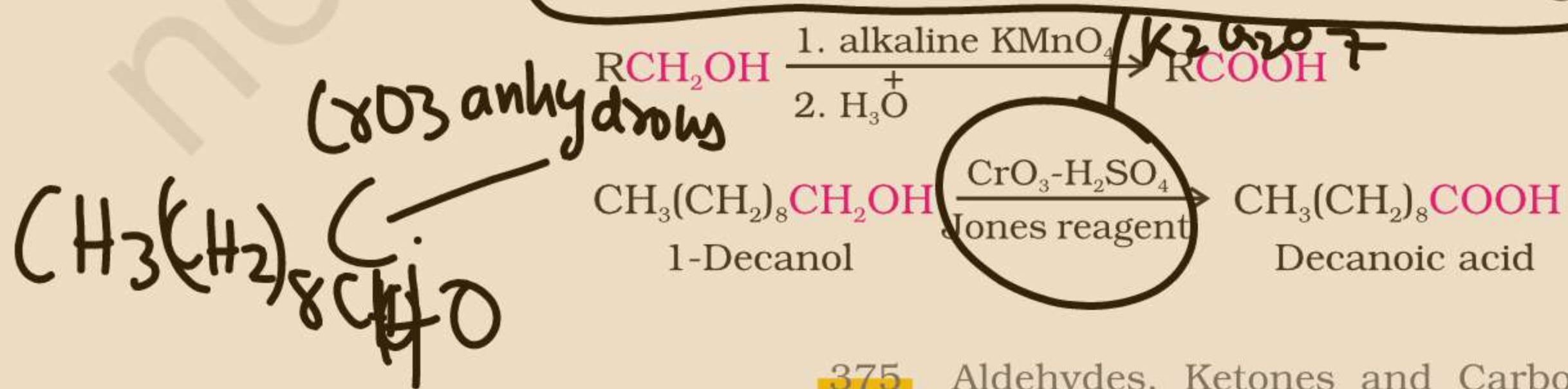


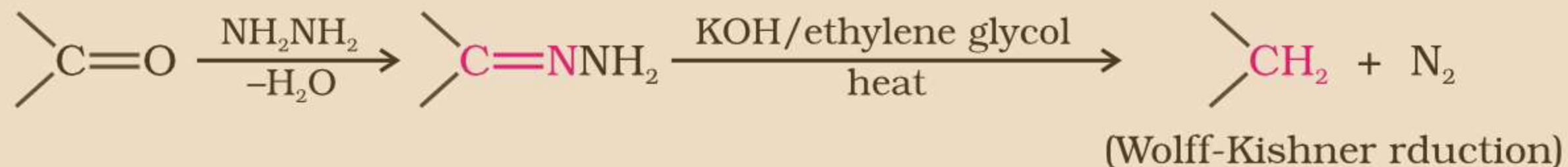
12.7 Methods of Preparation of Carboxylic Acids

Some important methods of preparation of carboxylic acids are as follows.

1. From primary alcohols and aldehydes

Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate (KMnO_4) in neutral, acidic or alkaline media or by potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and chromium trioxide (CrO_3) in acidic media (Jones reagent)





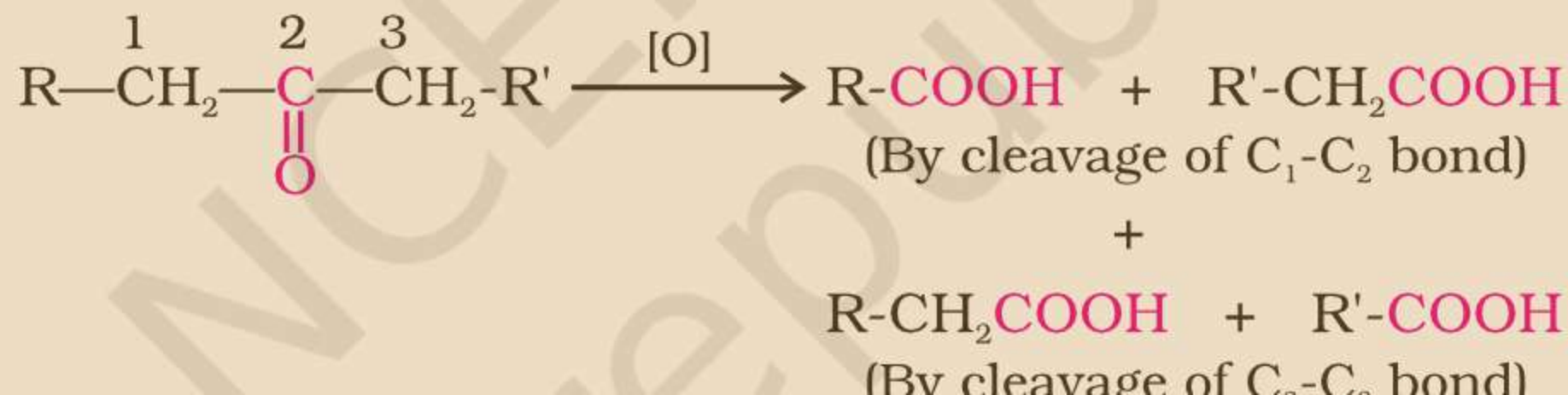
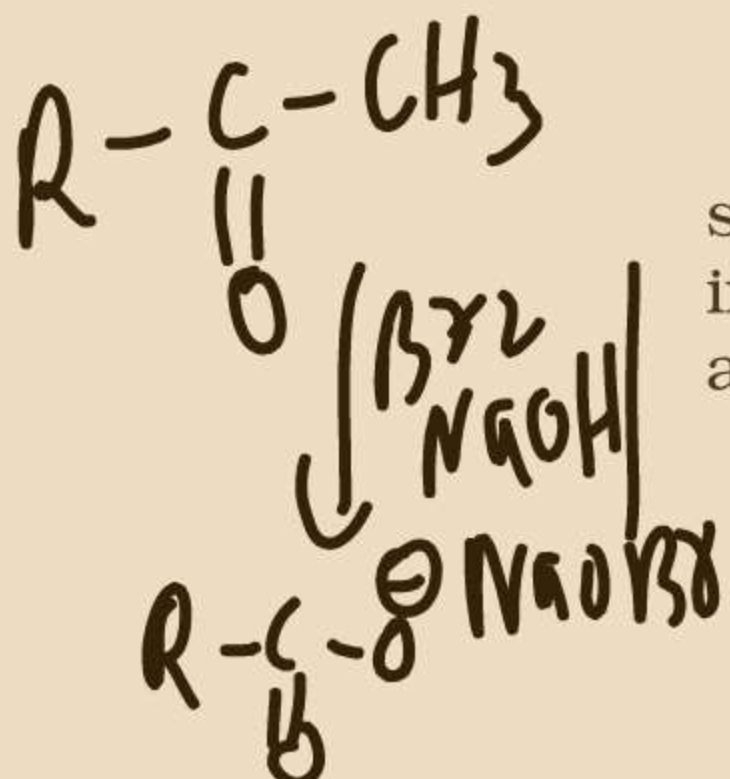
3. Oxidation

Bernhard Tollens (1841-1918) was a Professor of Chemistry at the University of Gottingen, Germany.

Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehlings' reagent also oxidise aldehydes.



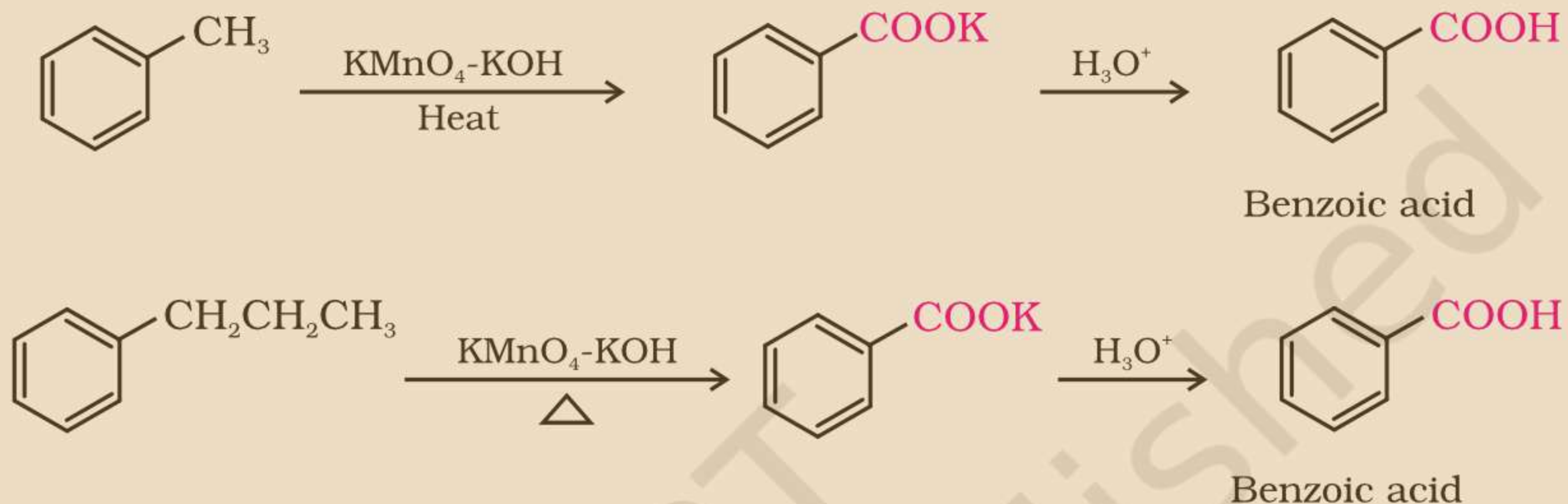
Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.



Carboxylic acids are also prepared from aldehydes by the use of mild oxidising agents (Section 12.4).

2. From alkylbenzenes

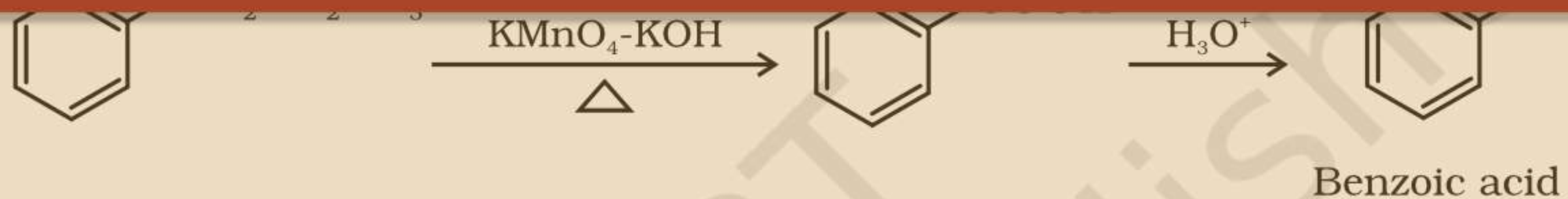
Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected. Suitably substituted alkenes are also oxidised to carboxylic acids with these oxidising reagents (refer Unit 13, Class XI).



3. From nitriles and amides

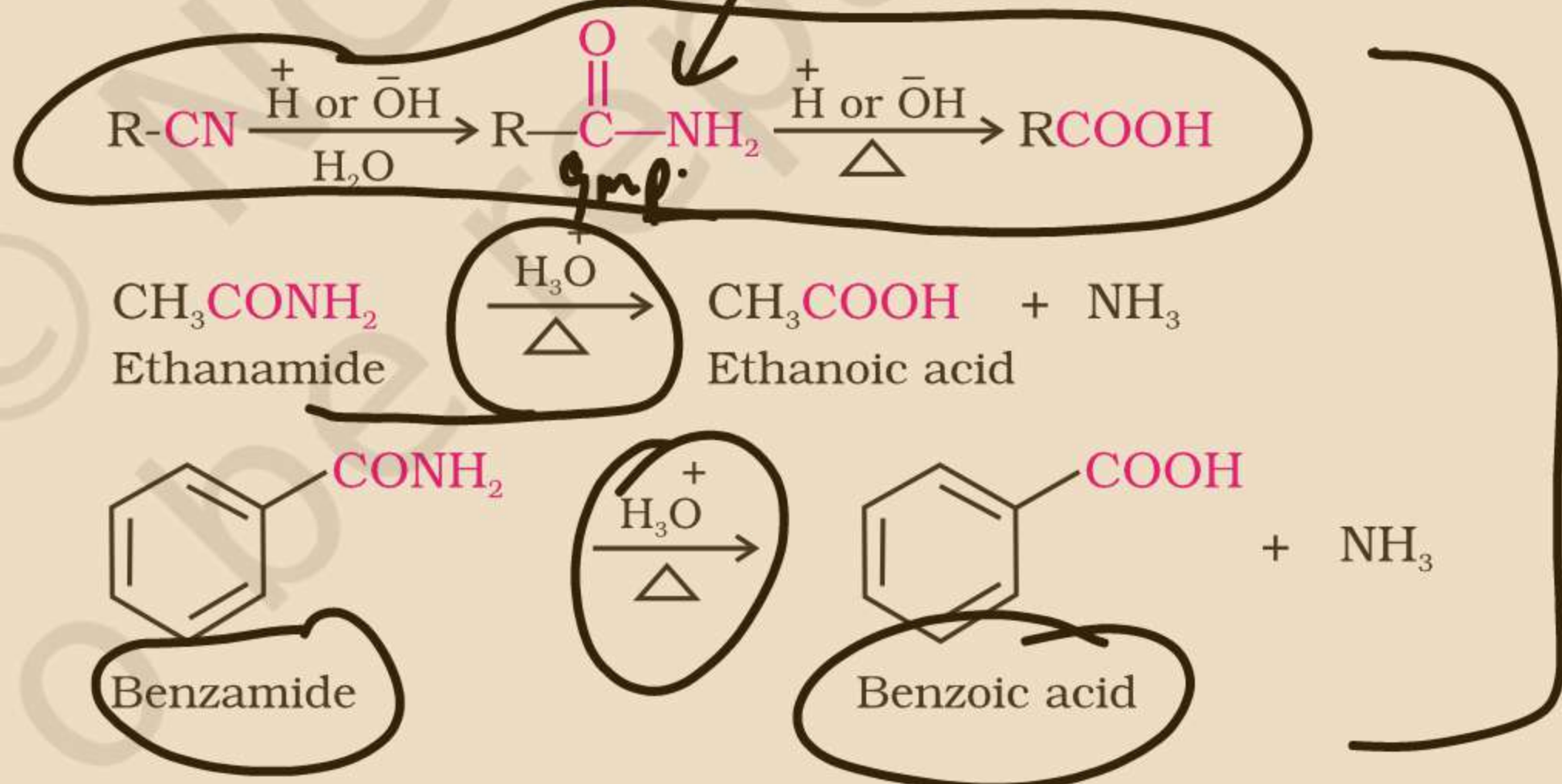
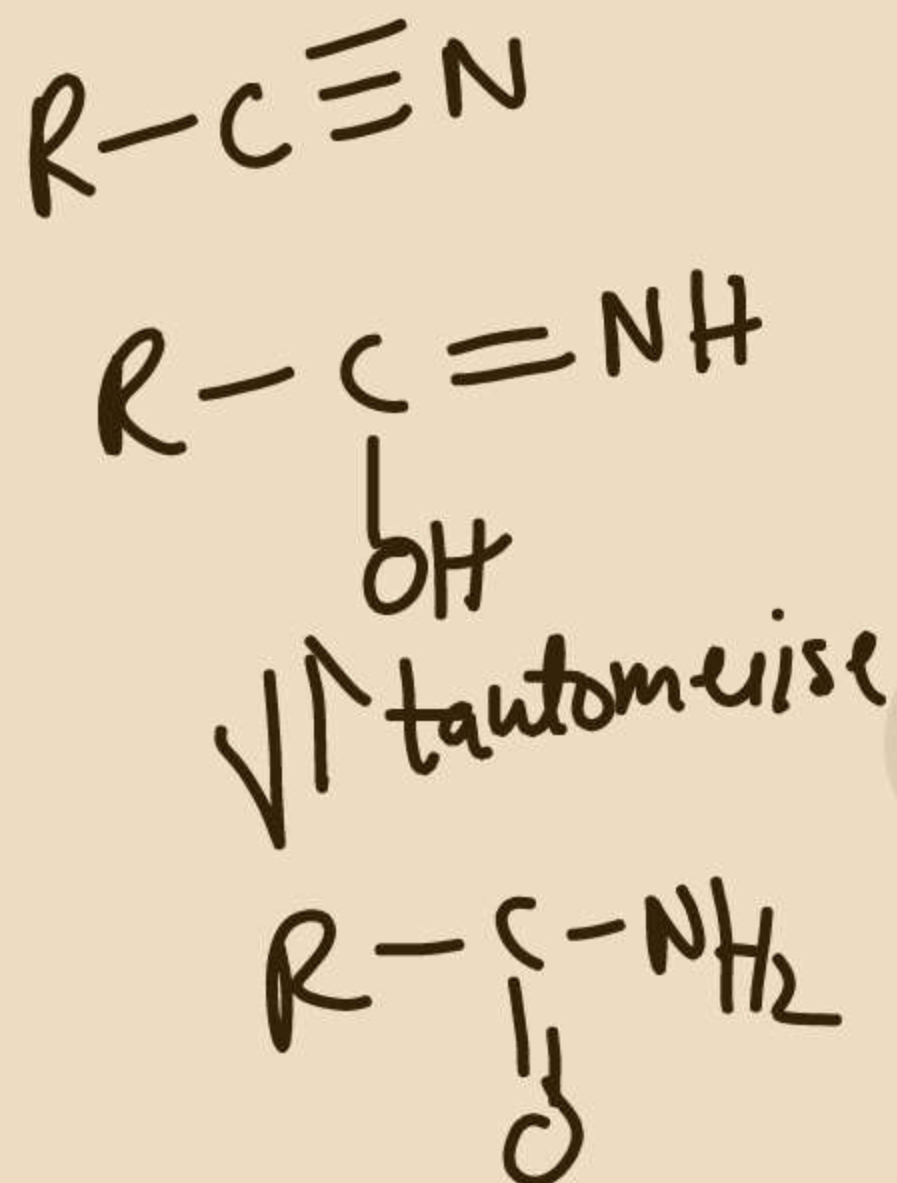
Nitriles and amides can be oxidised to carboxylic acids by the use of mild oxidising agents.





3. From nitriles and amides

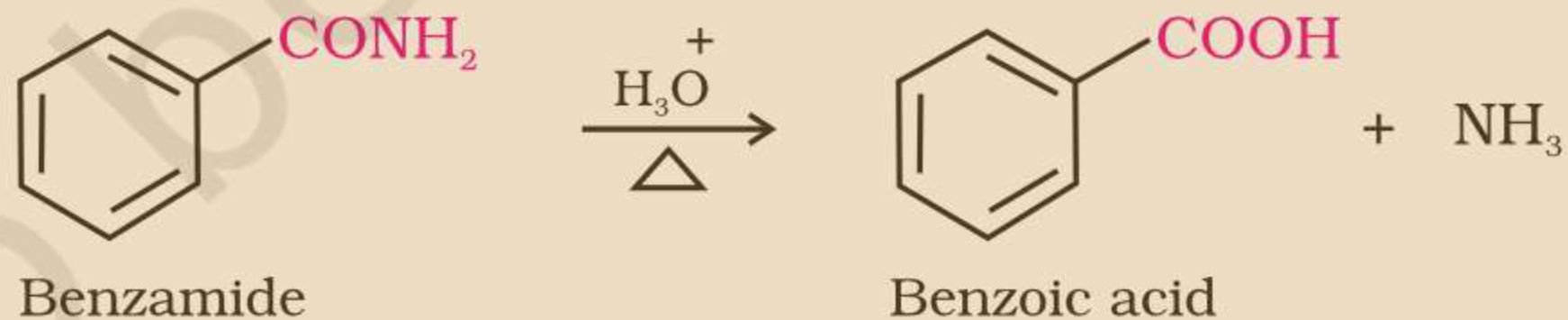
Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or OH^- as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.



4. From Grignard reagents

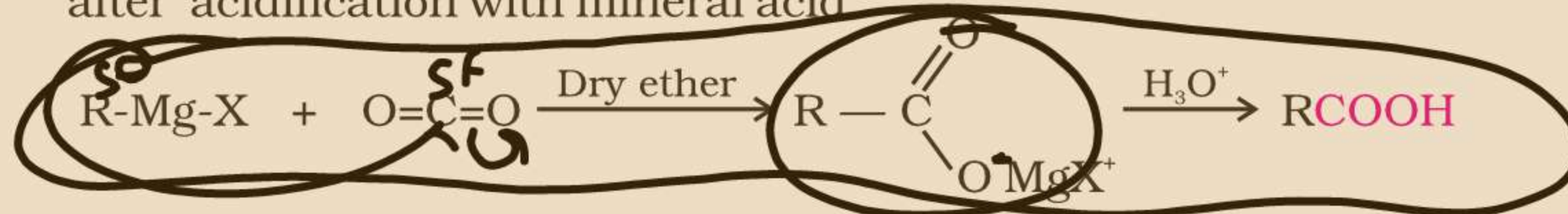
Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids





4. From Grignard reagents

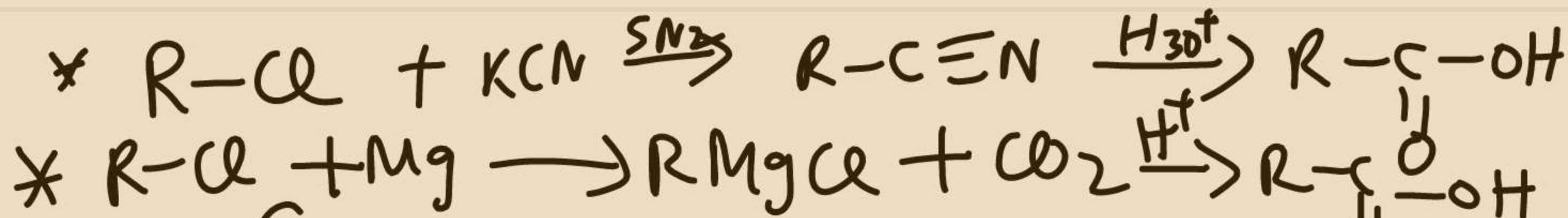
Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid



As we know, the Grignard reagents and nitriles can be prepared from alkyl halides (refer Unit 10, Class XII). The above methods



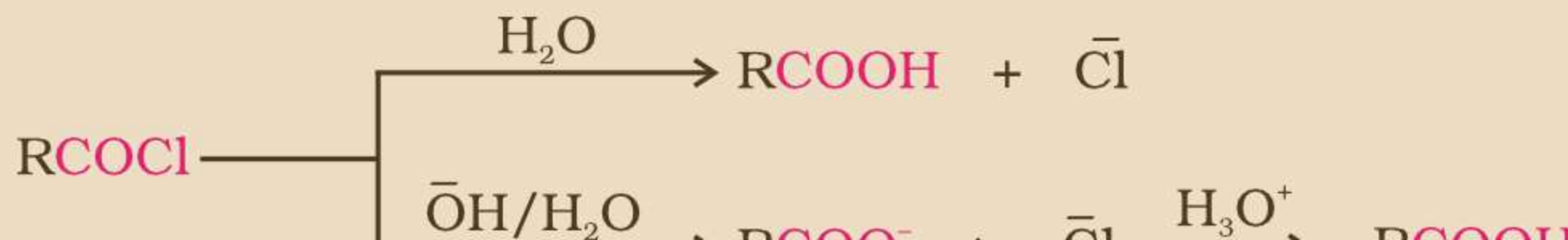
2022-23



(3 and 4) are useful for converting alkyl halides into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides (ascending the series).

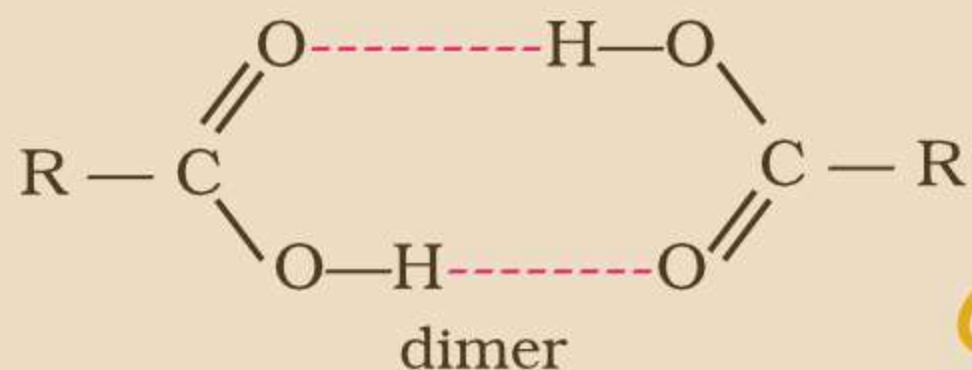
5. From acyl halides and anhydrides

Acid chlorides when hydrolysed with water give carboxylic acids or more readily hydrolysed with aqueous base to give carboxylate ions which on acidification provide corresponding carboxylic acids. Anhydrides on the other hand are hydrolysed to corresponding acid(s) with water.

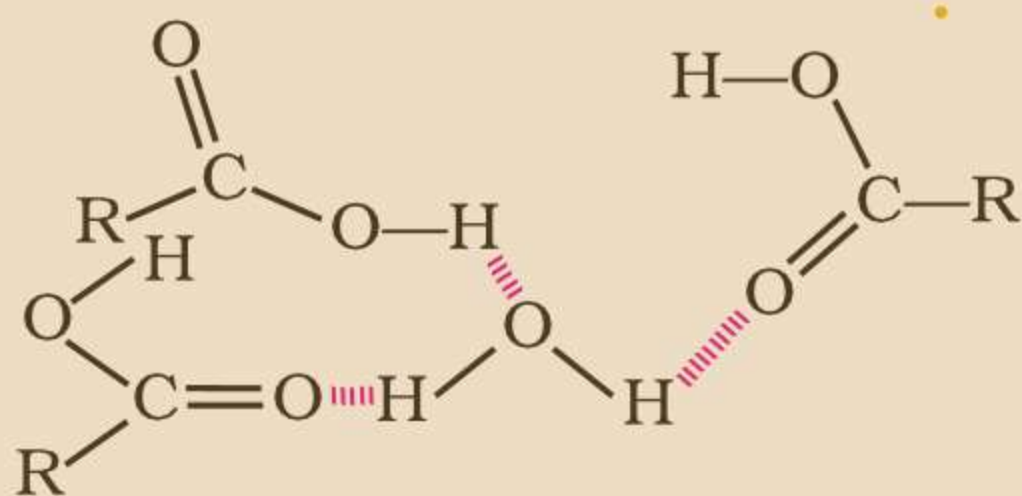


C.A > Alcohol > Carbonyl (compd) > Esters > Alkane
I.M

12.8 Physical Properties



In vapour state or in aprotic solvent



Hydrogen bonding of RCOOH with H₂O

Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility. Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.

Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.



12.9 Chemical Reactions The reaction of carboxylic acids are classified as follows:

12.9.1 Reactions Involving Cleavage of O-H Bond

Acidity

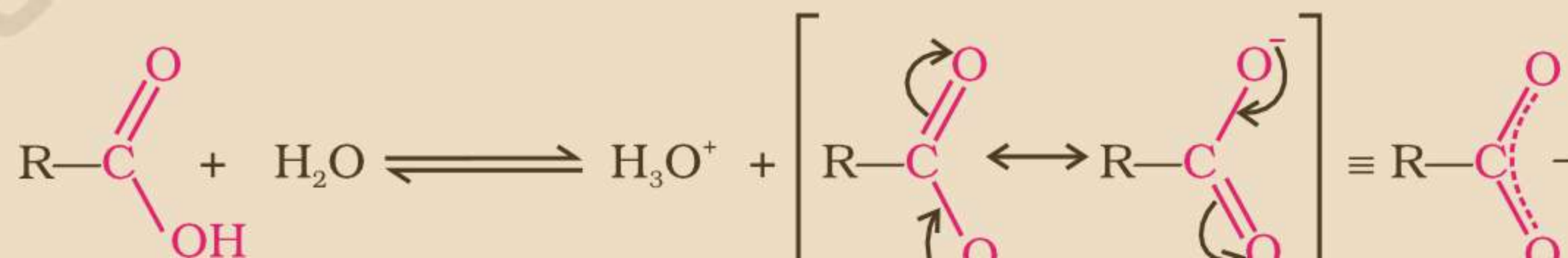
Reactions with metals and alkalis

The carboxylic acids like alcohols evolve hydrogen with electropositive metals and form salts with alkalis similar to phenols. However, unlike phenols they react with weaker bases such as carbonates and hydrogencarbonates to evolve carbon dioxide. This reaction is used to detect the presence of carboxyl group in an organic compound.

Redox
Rxn

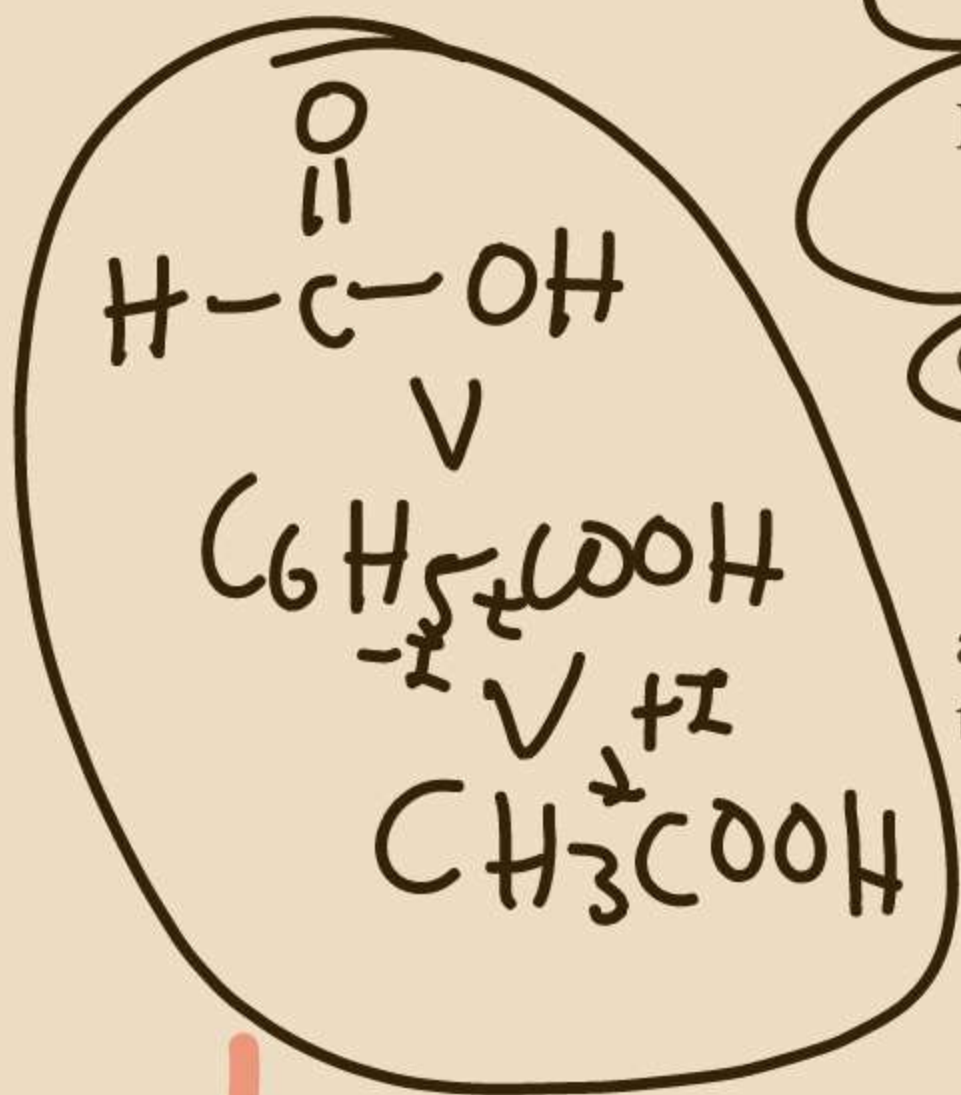


Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.



The effect of the following groups in increasing acidity order is
 $\text{Ph} < \text{I} < \text{Br} < \text{Cl} < \text{F} < \text{CN} < \text{NO}_2 < \text{CF}_3$

Thus, the following acids are arranged in order of increasing acidity (based on pK_a values):



Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below:



This is because of greater electronegativity of sp^2 hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.





Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below:



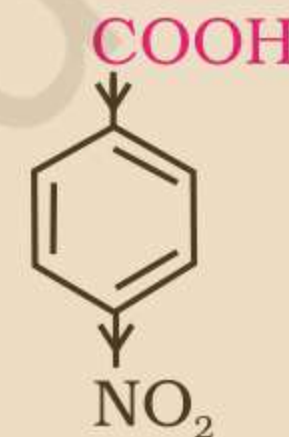
This is because of greater electronegativity of sp^2 hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.



4-Methoxy benzoic acid
($pK_a = 4.46$)



Benzoic acid
($pK_a = 4.19$)



4-Nitrobenzoic acid
($pK_a = 3.41$)

