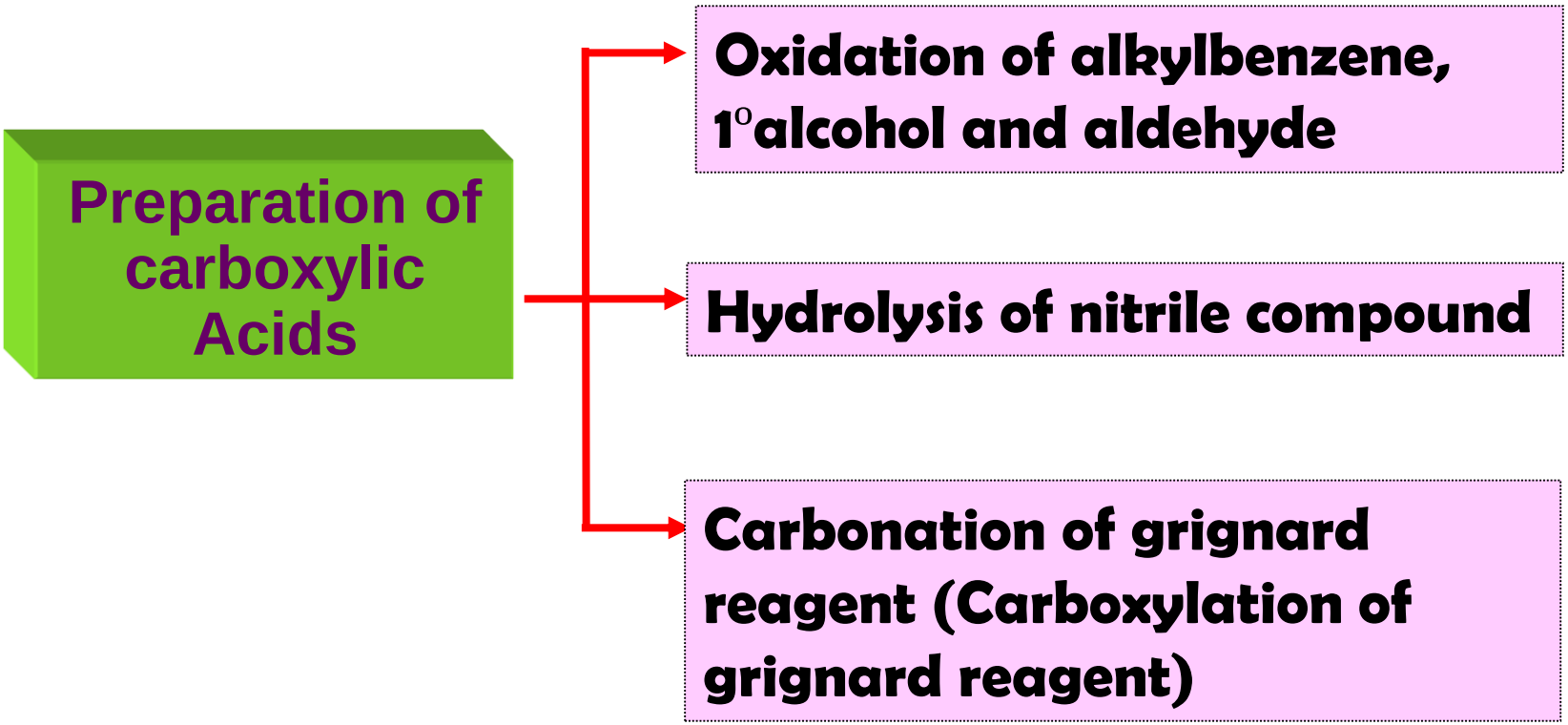
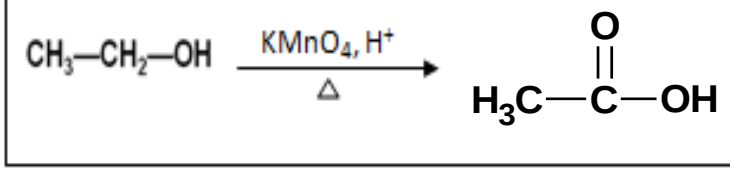
TOPIC 10.4 Carboxylic acids and its derivatives



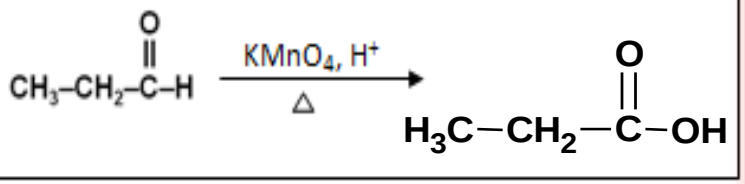
PREPARATION OF CARBOXYLIC ACIDS

1) Oxidation

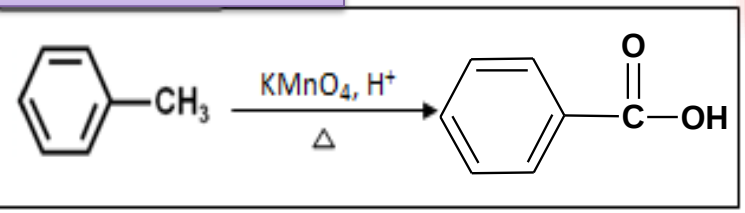
1° Alcohol



Aldehyde



Alkyl benzene



3) Hydrolysis of nitrile compound

CH_3CH_2Cl

↓ NaCN

CH_3CH_2CN

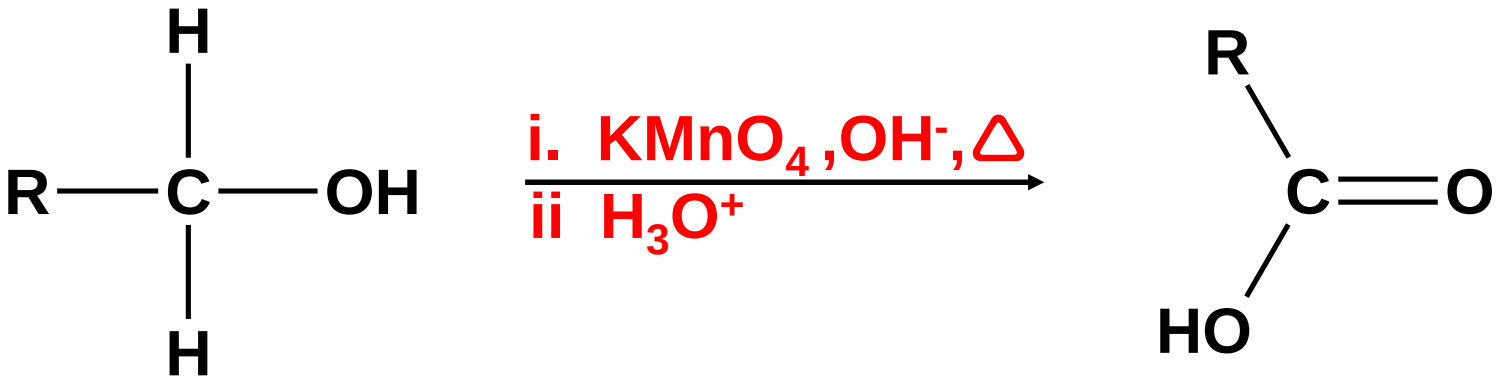
↓ H_2O, H^+

CH_3CH_2COOH

2) Carbonation of grignard reagent

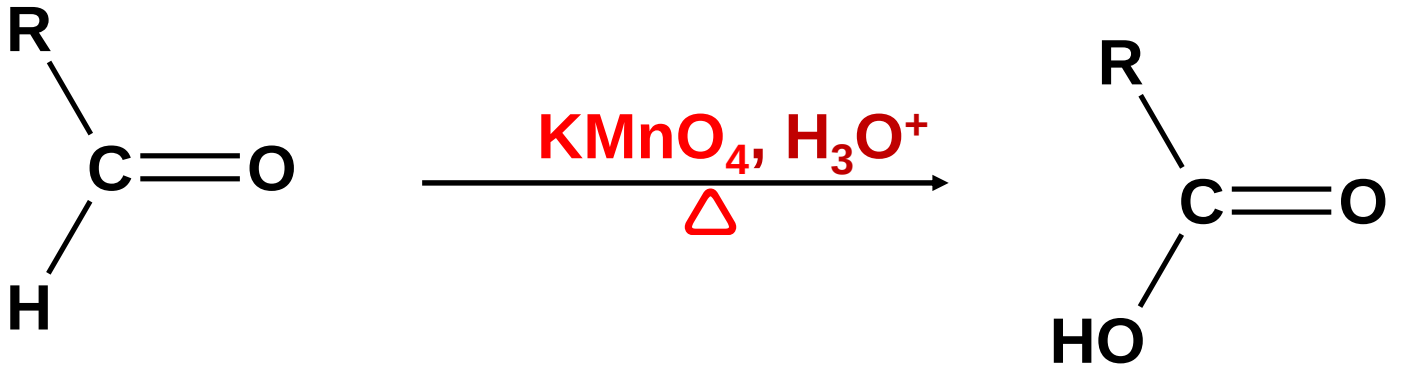
$$CH_3CH_2Br \xrightarrow[\text{dry ether}]{Mg} CH_3CH_2MgBr \xrightarrow[[2]\,H_3O^+]{[1]\,CO_2} CH_3CH_2COOH$$

Oxidation of primary alcohol & aldehyde



1º alcohol

carboxylic acid



aldehyde

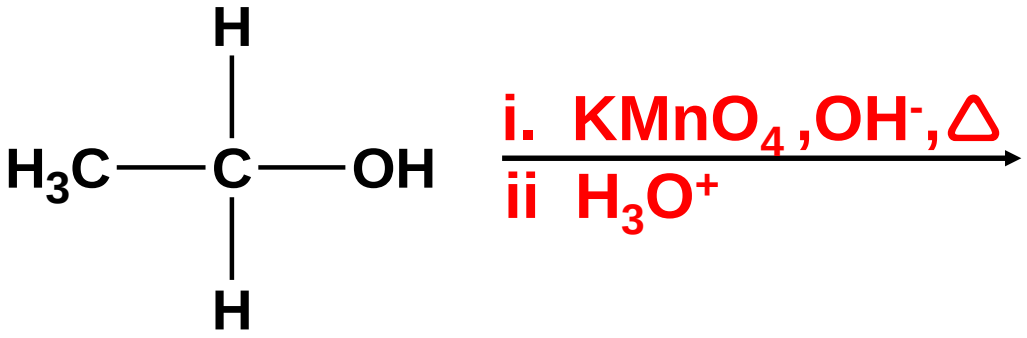
carboxylic acid

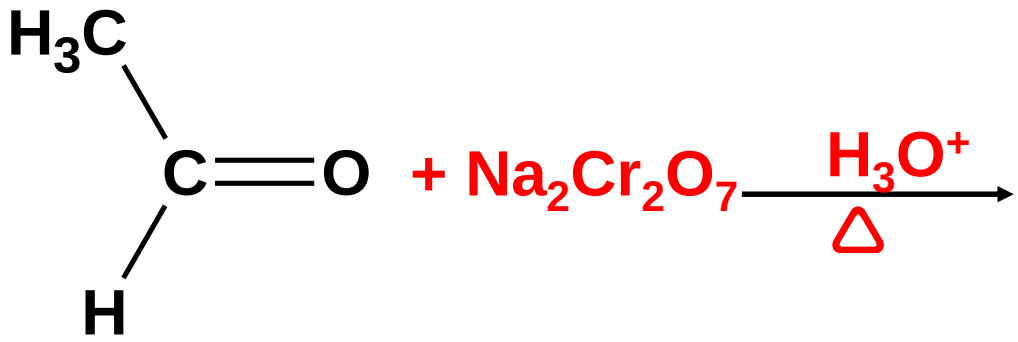
Other Common oxidizing agents are :

- **Hot, acidified $Na_2Cr_2O_7$ solution**
- **Hot, acidified $K_2Cr_2O_7$ solution**
- **Hot, acidified CrO_3 solution**

EXERCISE 4

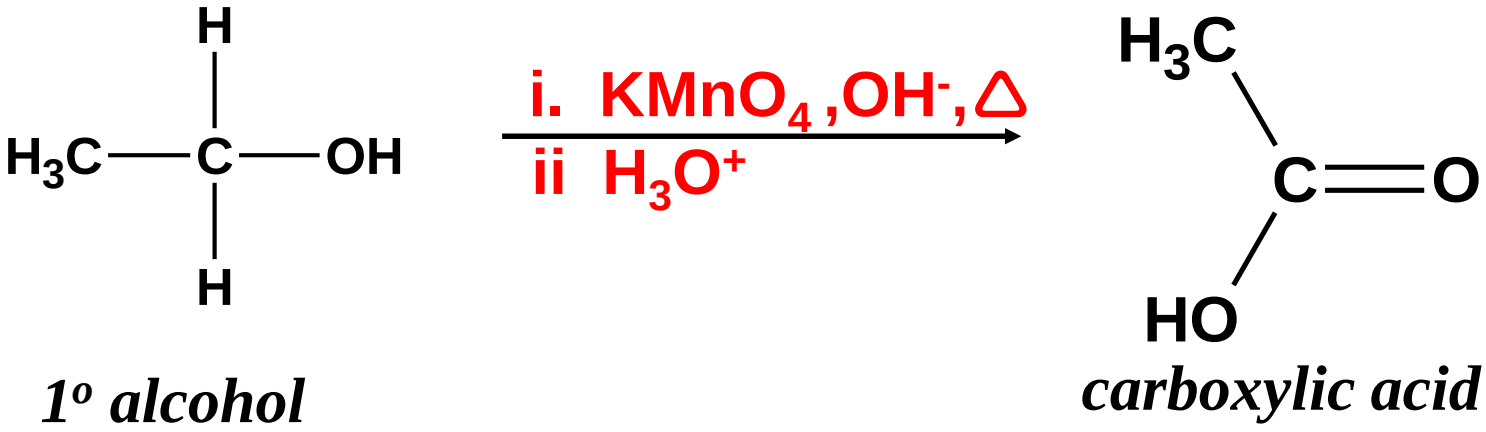
Show the relevant carboxylic acid in the following reaction





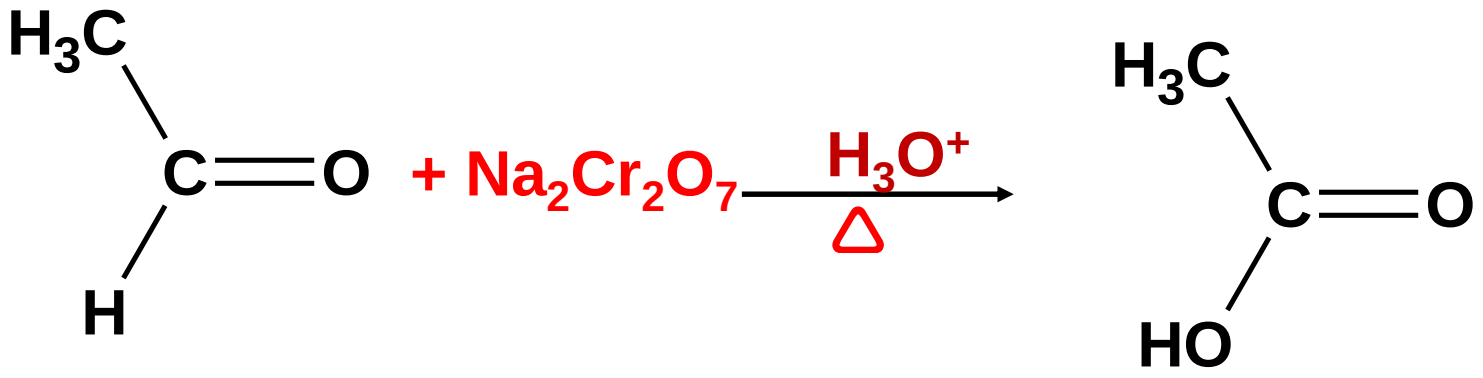
ANSWER

Show the relevant carboxylic acid in the following reaction



1º alcohol

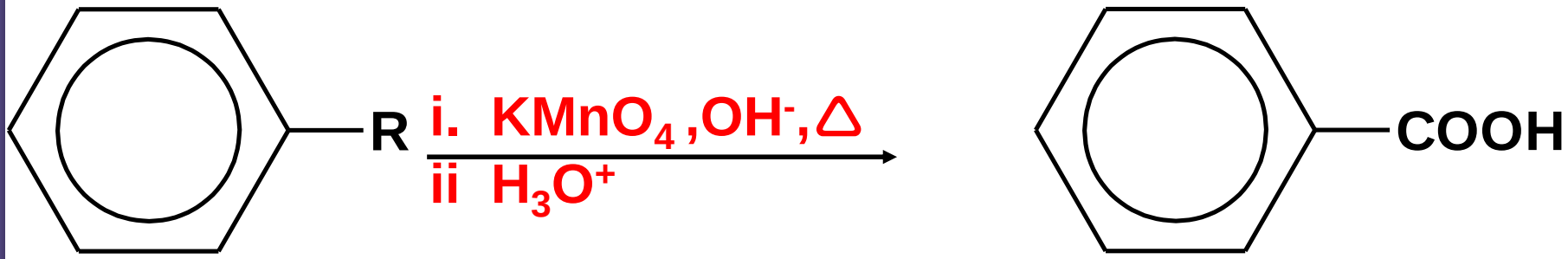
carboxylic acid



aldehyde

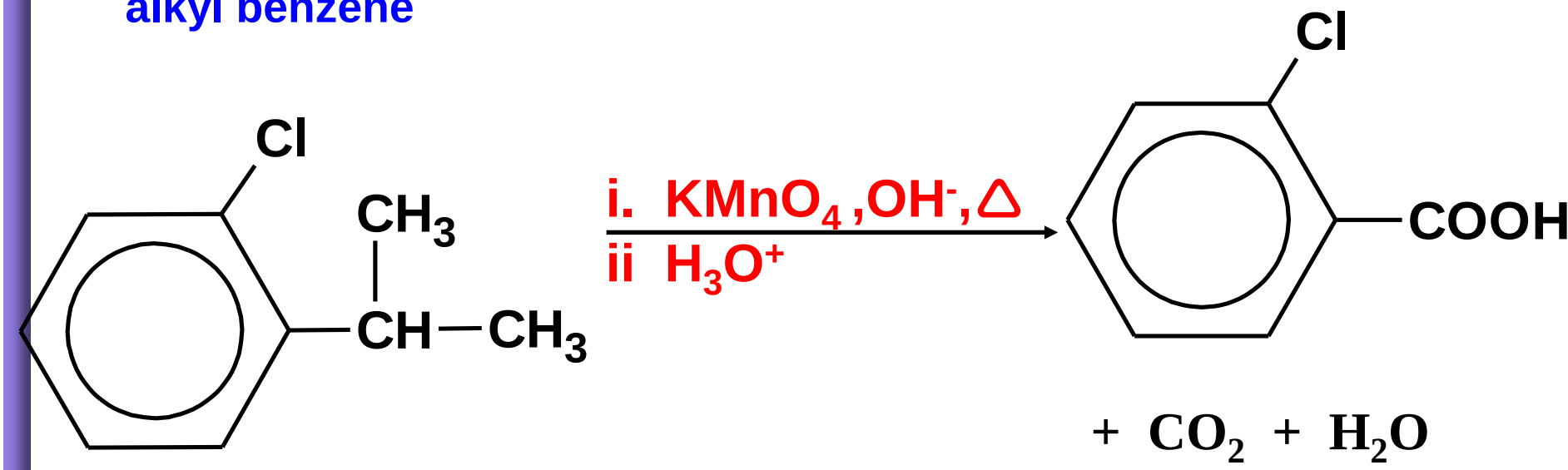
carboxylic acid

Oxidation of Alkyl Benzene



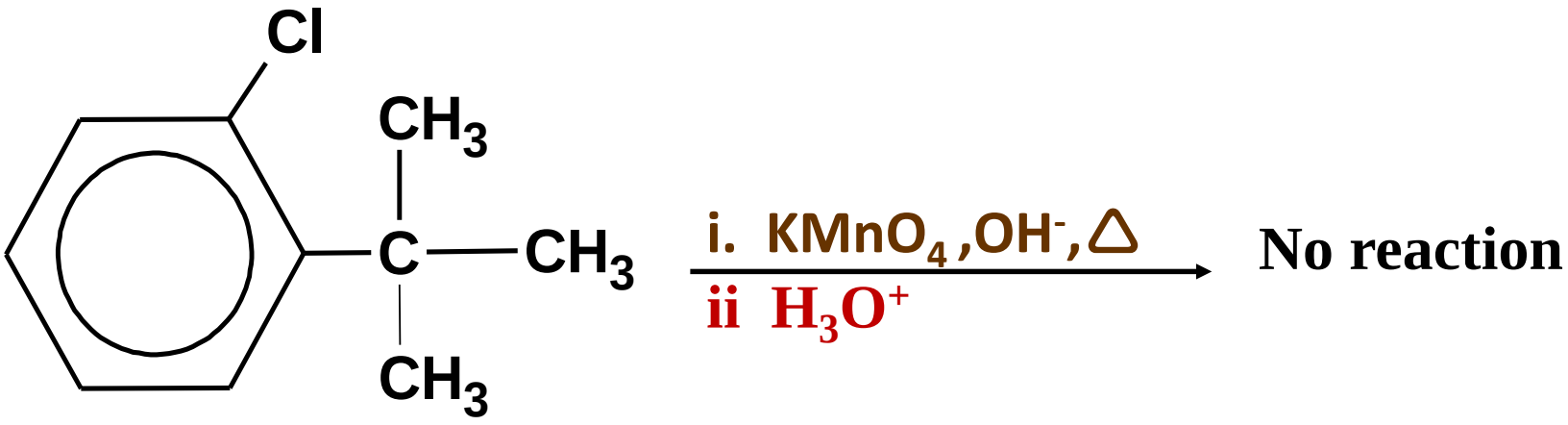
alkyl benzene

carboxylic acid

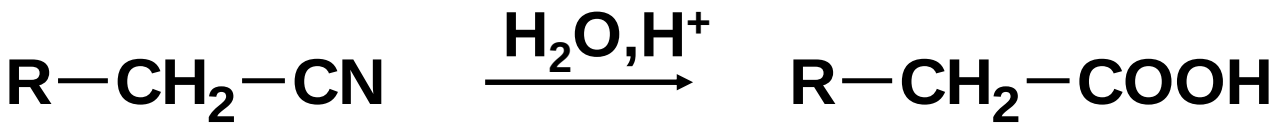


+ CO_2 + H_2O

If the alkyl group attached to the benzene ring does not contain benzylic hydrogen, therefore the alkyl benzene cannot be oxidized

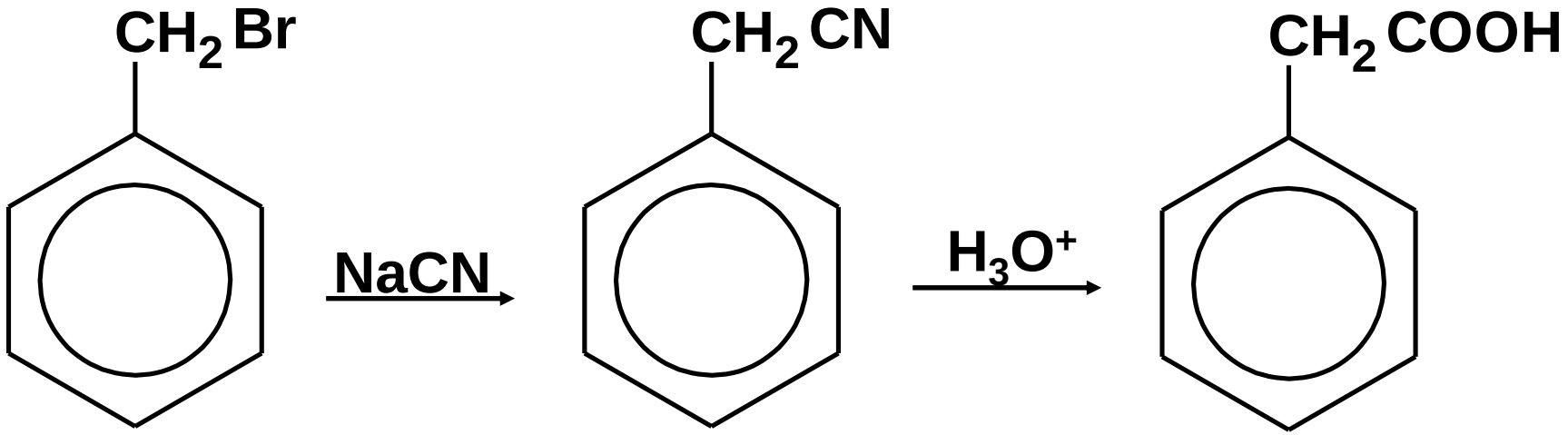


Hydrolysis of Nitrile Compound



nitrile compound

carboxylic acid

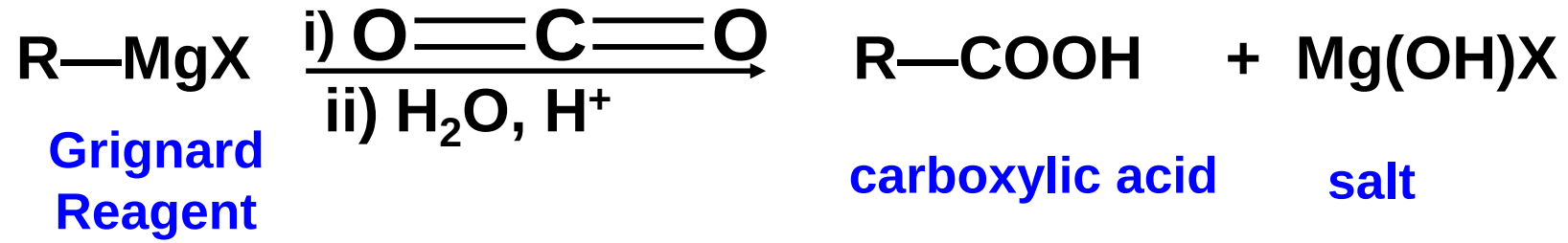


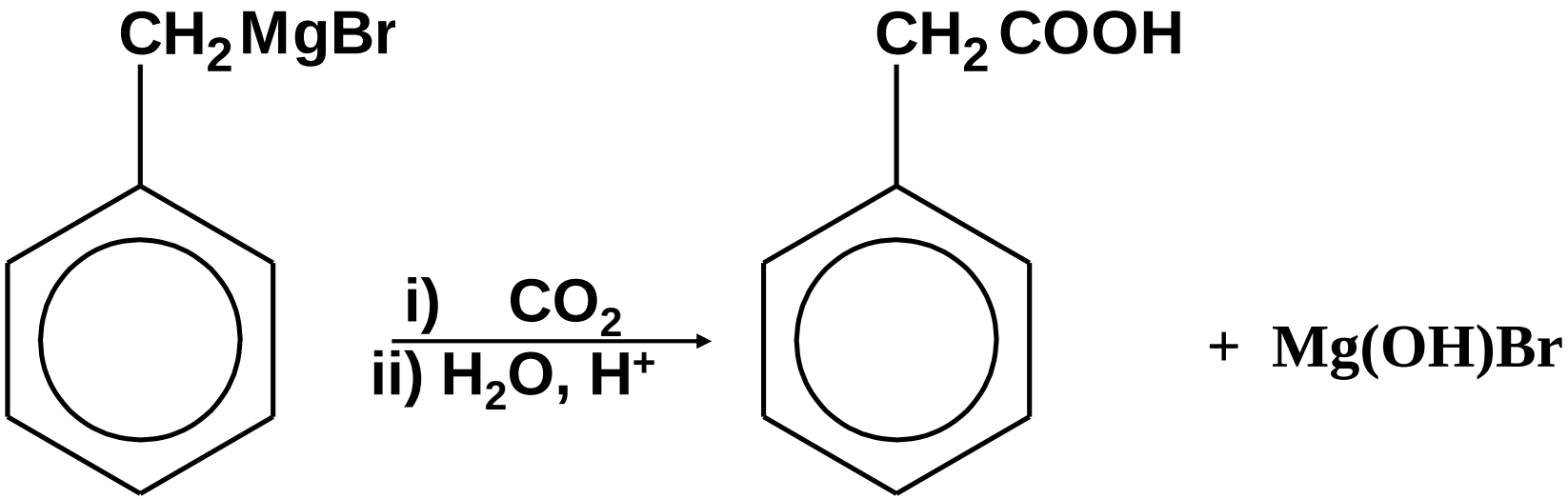
alkyl halide

nitrile compound

carboxylic acid

Carbonation of Grignard Reagents



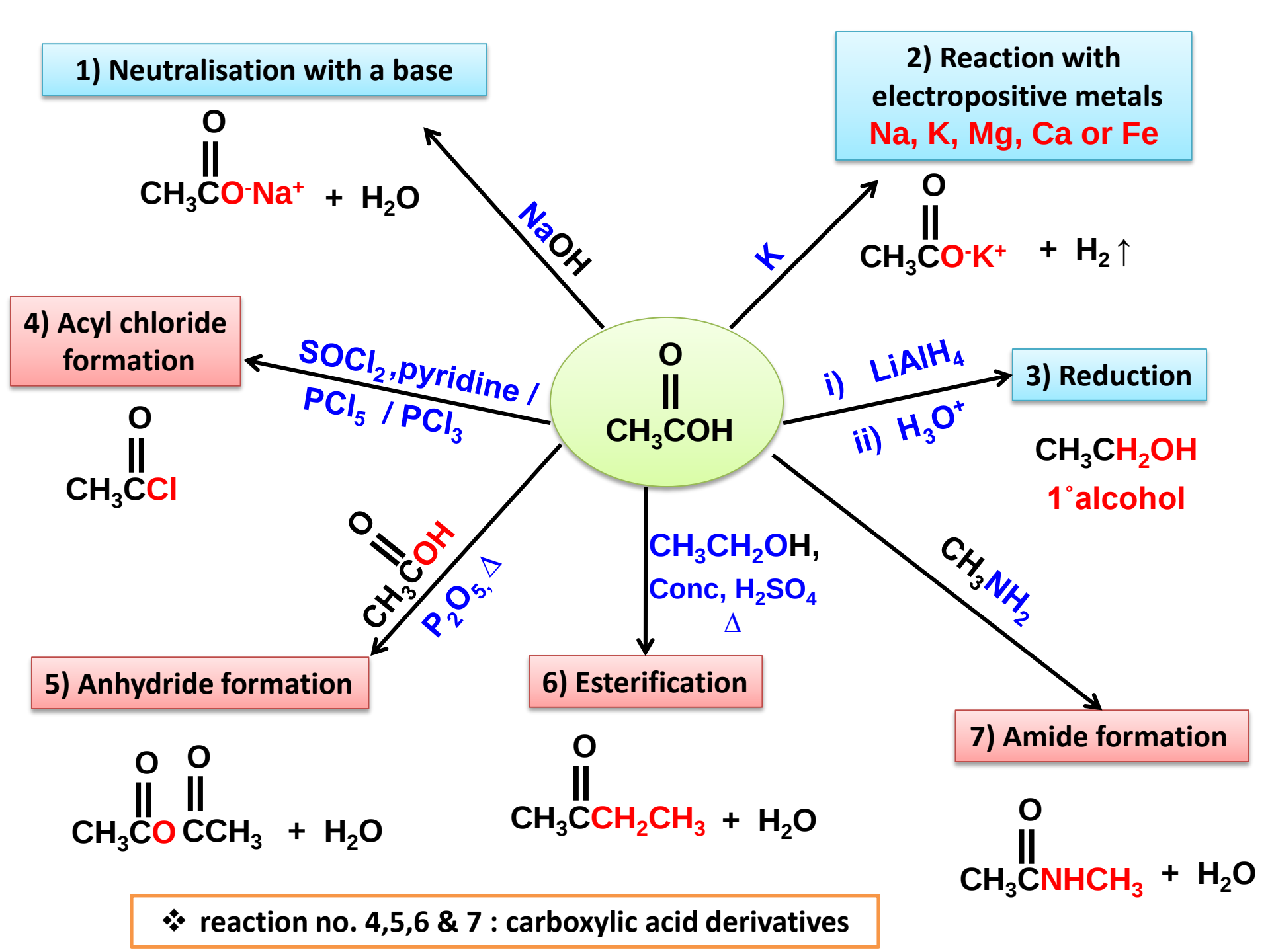


THE END

TOPIC 10.5 Carboxylic acids and its derivatives

Chemical properties of carboxylic Acids

- **Chemical properties**
  - Neutralisation with a base
  - Reaction with electropositive metals
  - Reduction with $LiAlH_4$ followed by H_3O^+
  - Acyl chloride formation
  - Anhydride formation
  - Esterification
  - Amide formation
- **Reducing property of methanoic acid**
  - Using acidified solution $KMnO_4$
  - Tollens' Reagent


1) Neutralisation with a base
$CH_3CO^-Na^+ + H_2O$
NaOH
2) Reaction with electropositive metals
Na, K, Mg, Ca or Fe
K
$CH_3CO^-K^+ + H_2\uparrow$
4) Acyl chloride formation
CH_3COCl
$SOCl_2$, pyridine / PCl_5 / PCl_3
CH_3COH
i) $LiAlH_4$
ii) H_3O^+
3) Reduction
CH_3CH_2OH
1˚alcohol
CH_3COOH
P_2O_5, Δ
CH_3CH_2OH, Conc, H_2SO_4 Δ
CH_3NH_2
5) Anhydride formation
$(CH_3CO)_2O + H_2O$
6) Esterification
$CH_3CCH_2CH_3 + H_2O$
7) Amide formation
$CH_3CNHCH_3 + H_2O$
❖ reaction no. 4,5,6 & 7 : carboxylic acid derivatives

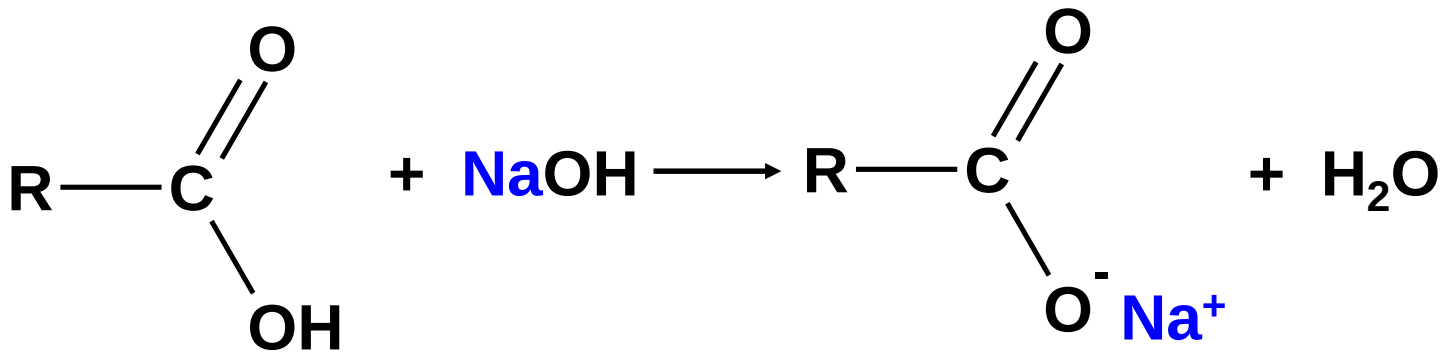
Main reactions of carboxylic acids :

- **The reaction that involves the donation of H^+ from –OH group.**
- **The reaction that involves the substitution of —OH group.**
- **The reaction that involves the reduction with $LiAlH_4$ followed by hydrolysis to form primary alcohol.**

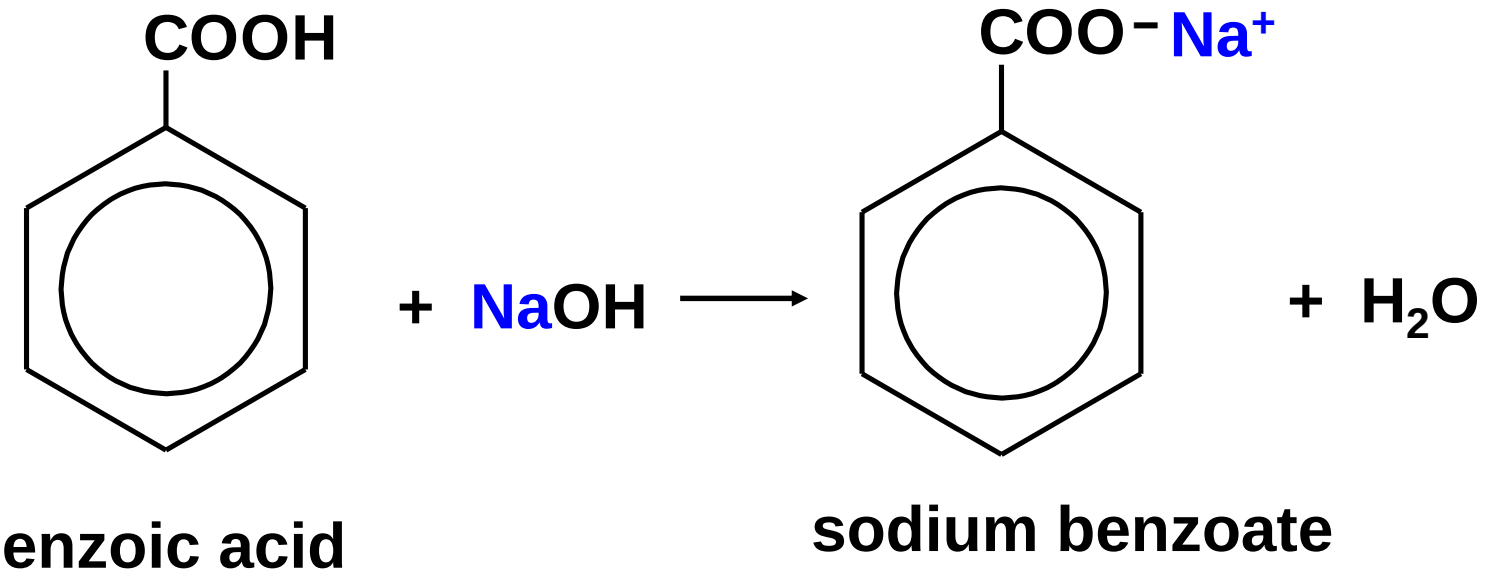
The reaction that involves the donation of H^+ from OH group

❑ Neutralisation

- **Carboxylic acids are acidic, it can react with base such as NaOH (aq) to give metal carboxylate salts,**

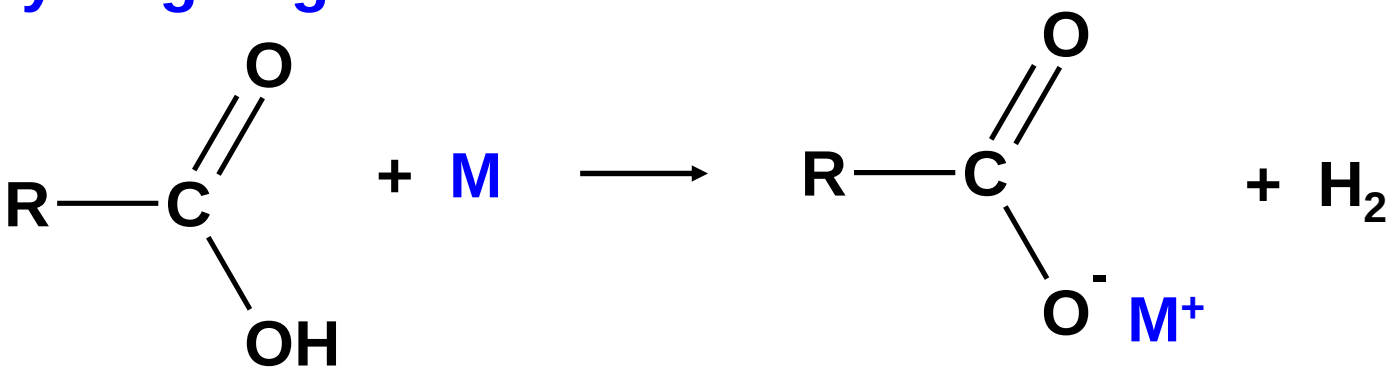


Example :



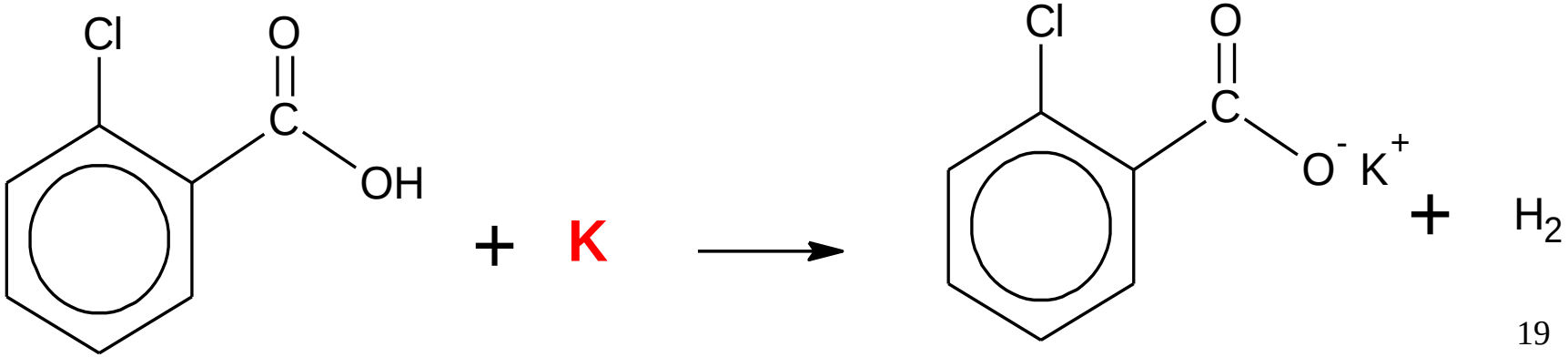
benzoic acid **sodium benzoate**

- **Reaction with electropositive metals such as Na, K, Mg, Ca or Fe produces carboxylate salt and hydrogen gas**



M = Metal

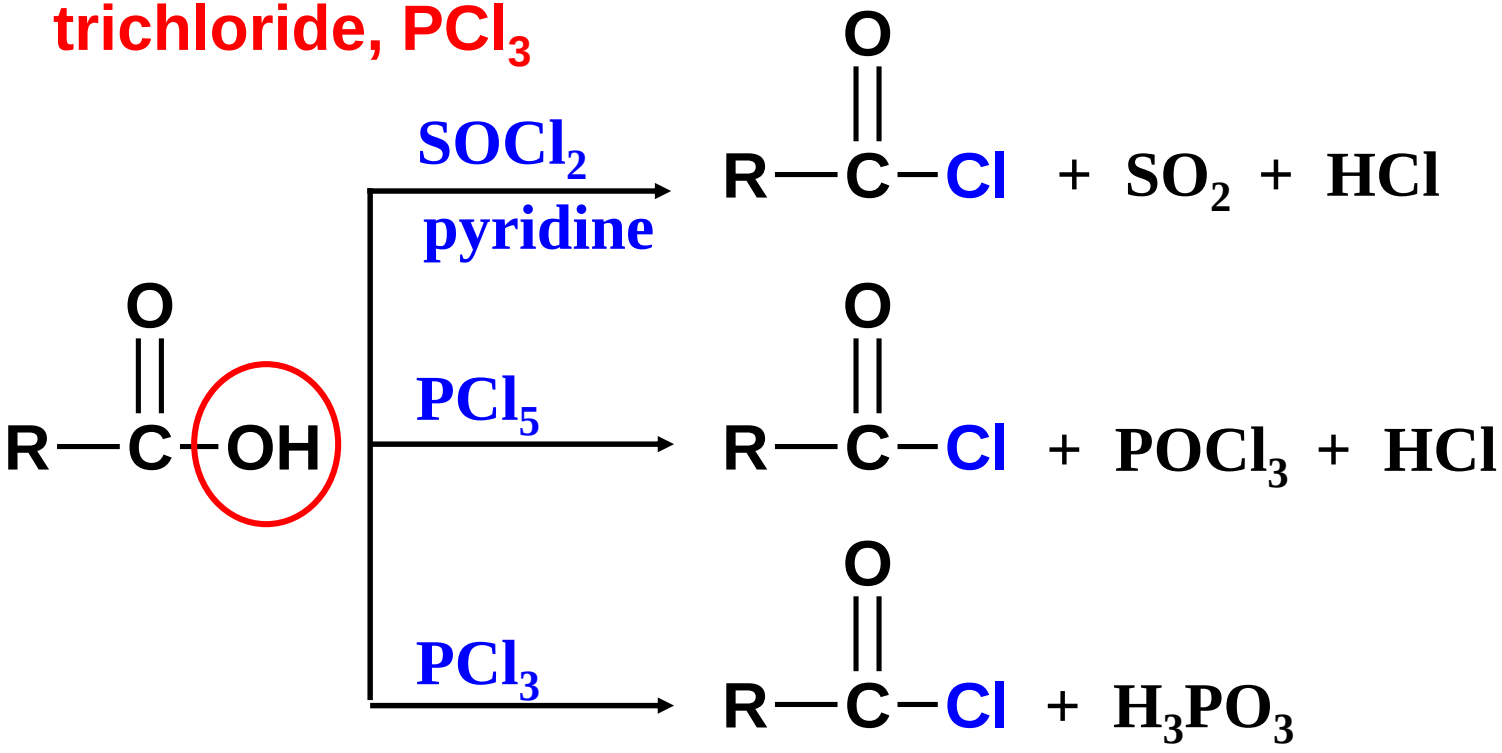
Example :



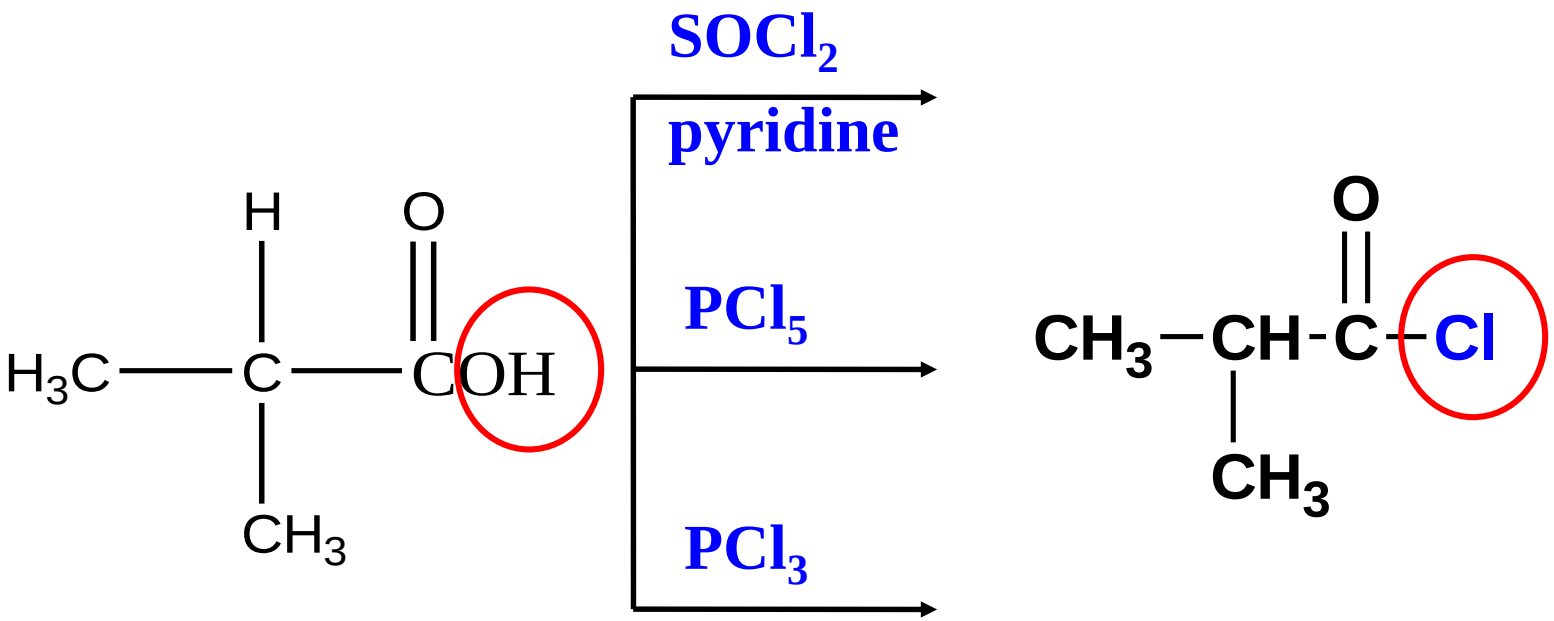
The reaction that involves the substitution of –OH group (to form its derivatives)

i. Acid chloride formation

Acid chloride can be prepared from the reaction of carboxylic acids with thionyl chloride, $SOCl_2$; phosphorous pentachloride, PCl_5 ; phosphorous trichloride, PCl_3

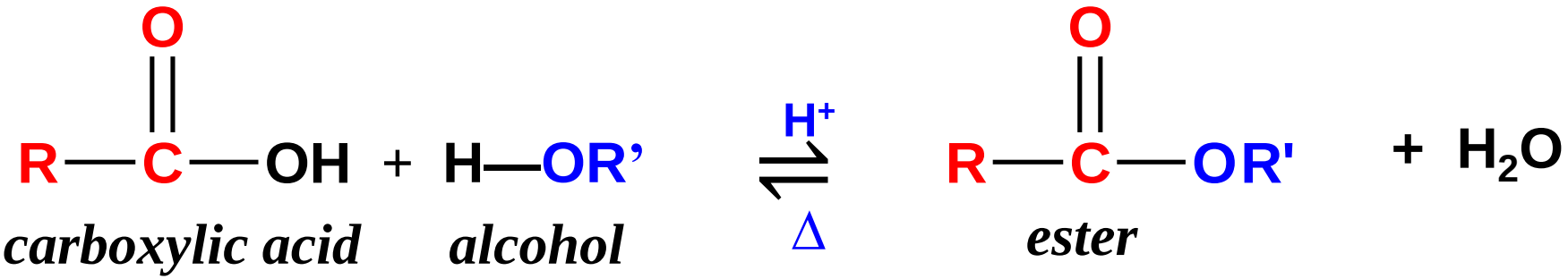


Example :



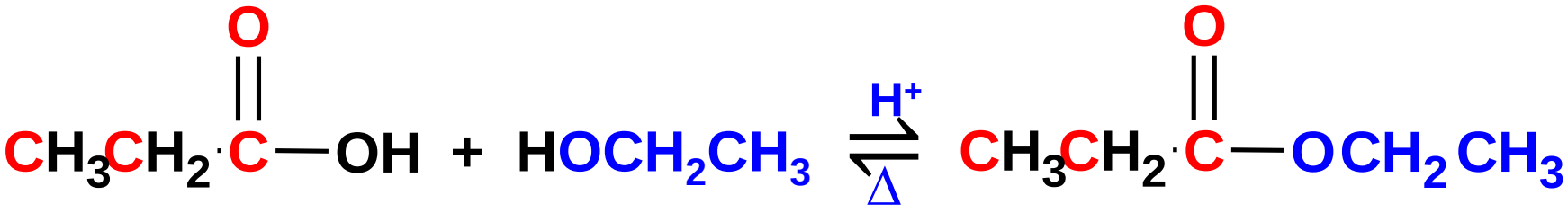
ii. Esterification

Carboxylic acids react with alcohols in the presence of mineral acid catalyst to produce esters.



carboxylic acid *alcohol* *ester*

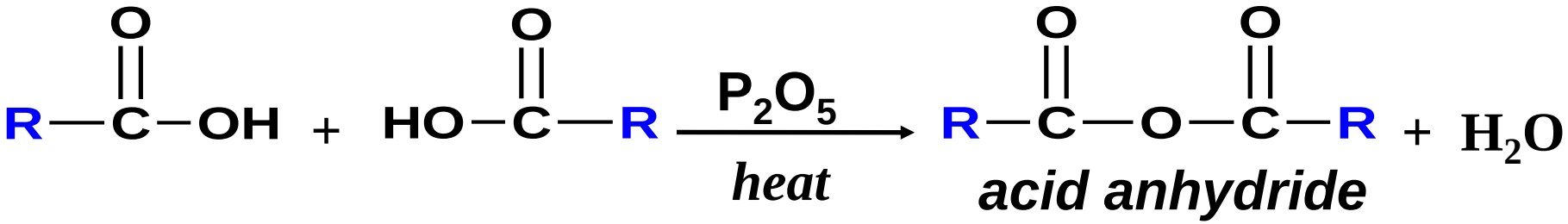
Example :



propanoic acid *ethanol* *ethyl propanoate*

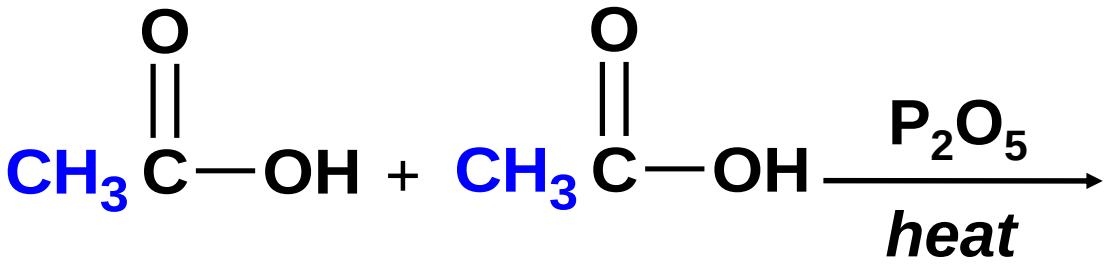
iii. Acid anhydride formation

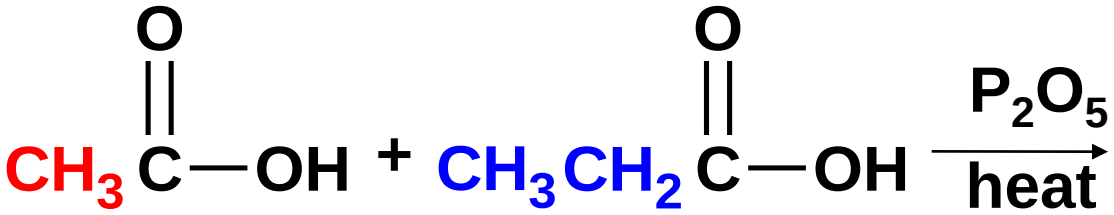
Acid anhydrides can be prepared from carboxylic acids in the presence of by phosphorous pentoxide, P_2O_5.



EXERCISE 5

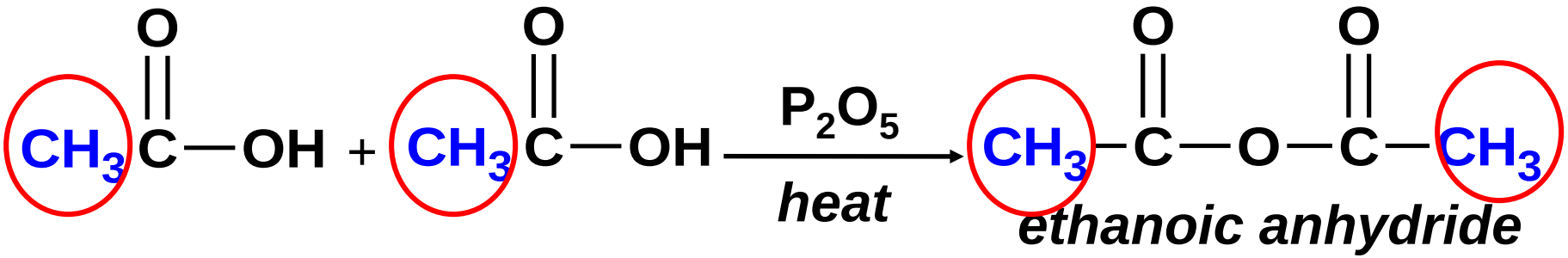
Complete the following reaction:





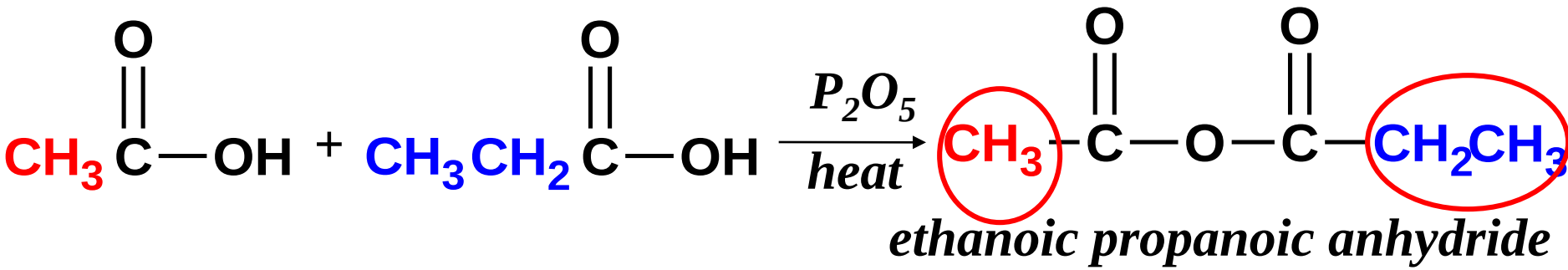
ANSWER

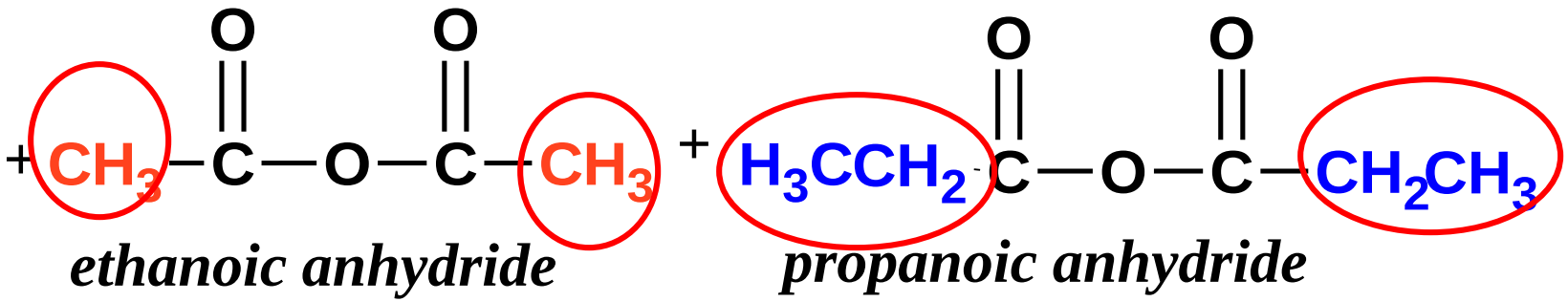
Complete the following reaction:



+ H_2O

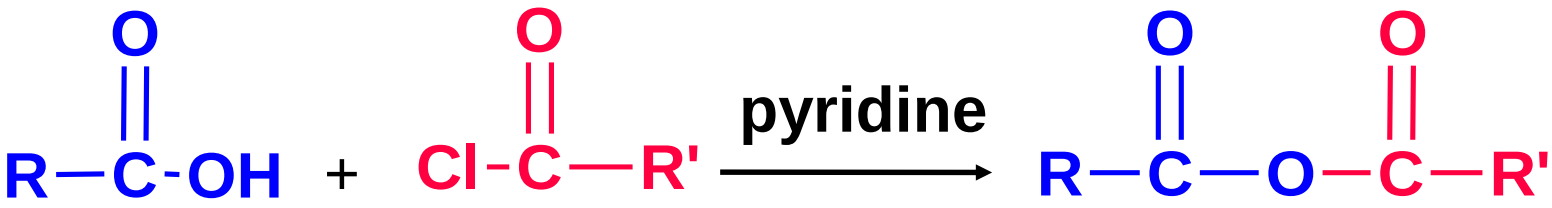
ANSWER


CH3COOH + CH3CH2COOH
P2O5
heat
CH3COOCOCH2CH3
ethanoic propanoic anhydride


+ CH3COOCOCH3
ethanoic anhydride
+ H3CCH2COOCOCH2CH3
propanoic anhydride

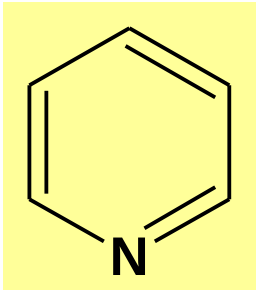
+ H_2O

Acid anhydride also can be prepared by reacting carboxylic acid with acid chloride in pyridine.



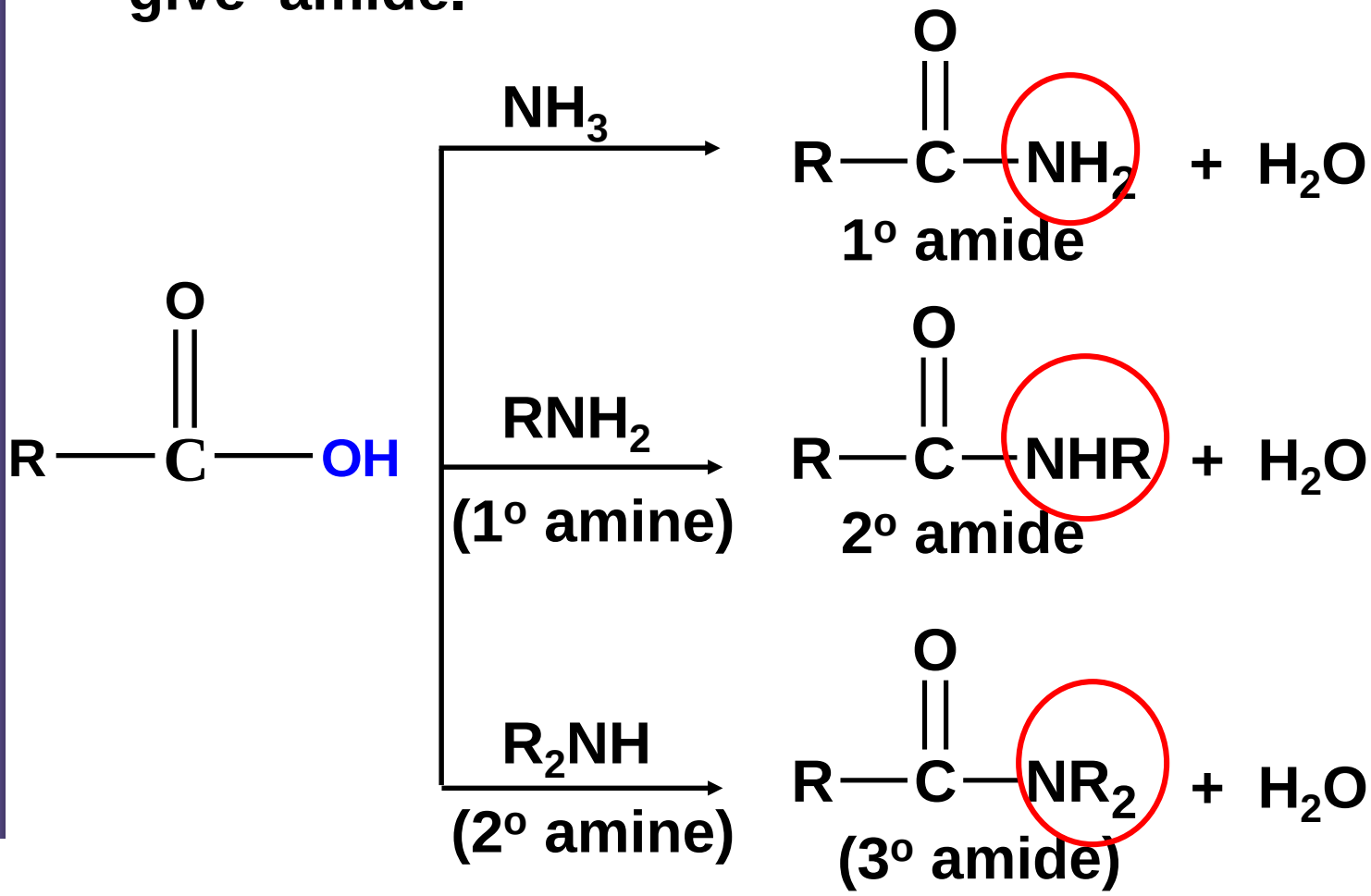
+ HCl

pyridine:-

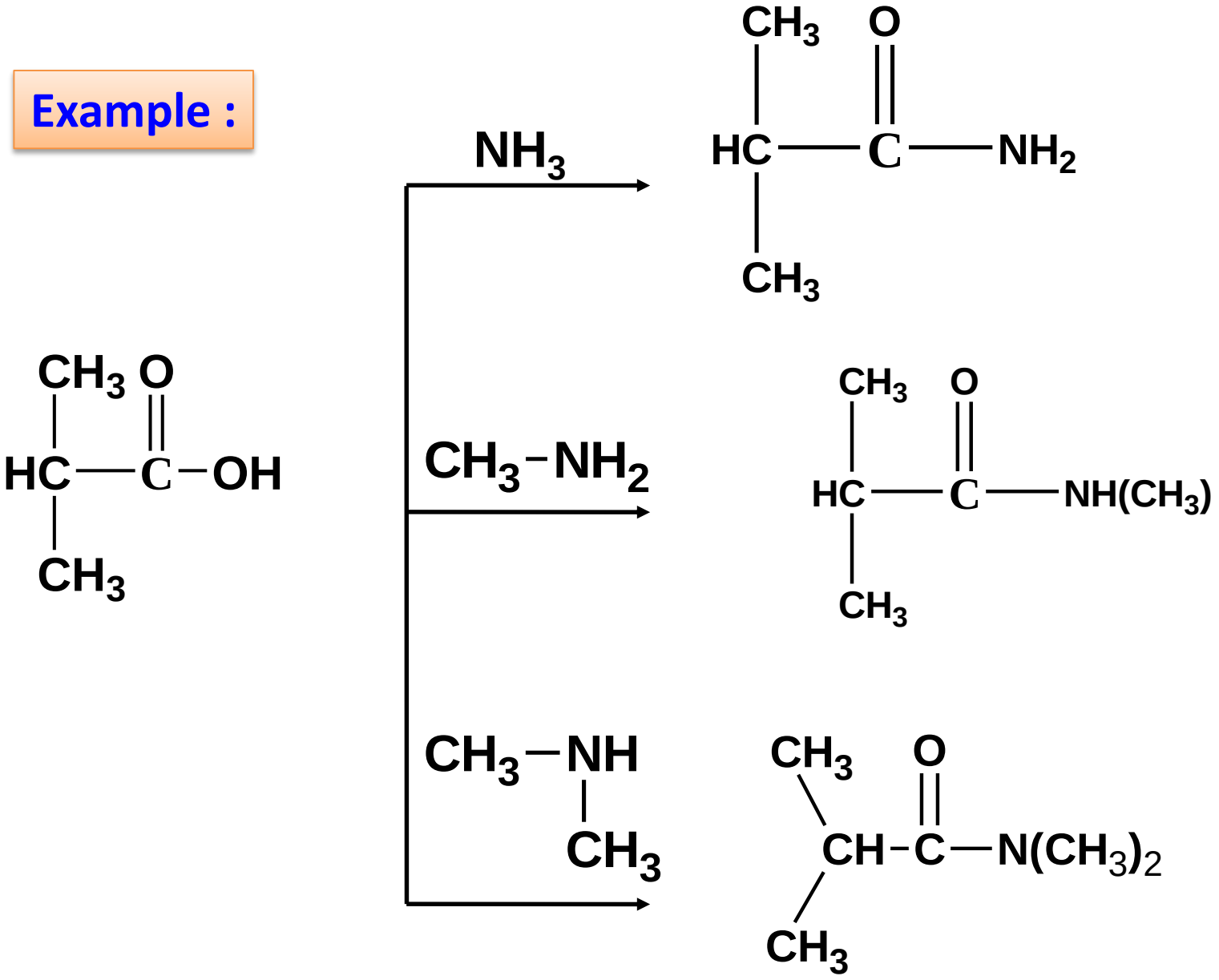


iv. Amides formation

Reaction of carboxylic acids with an ammonia or amine give amide.

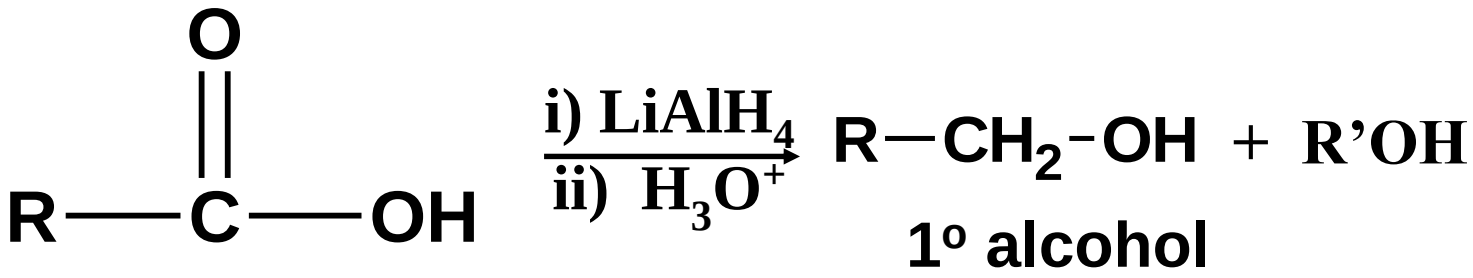


Example :

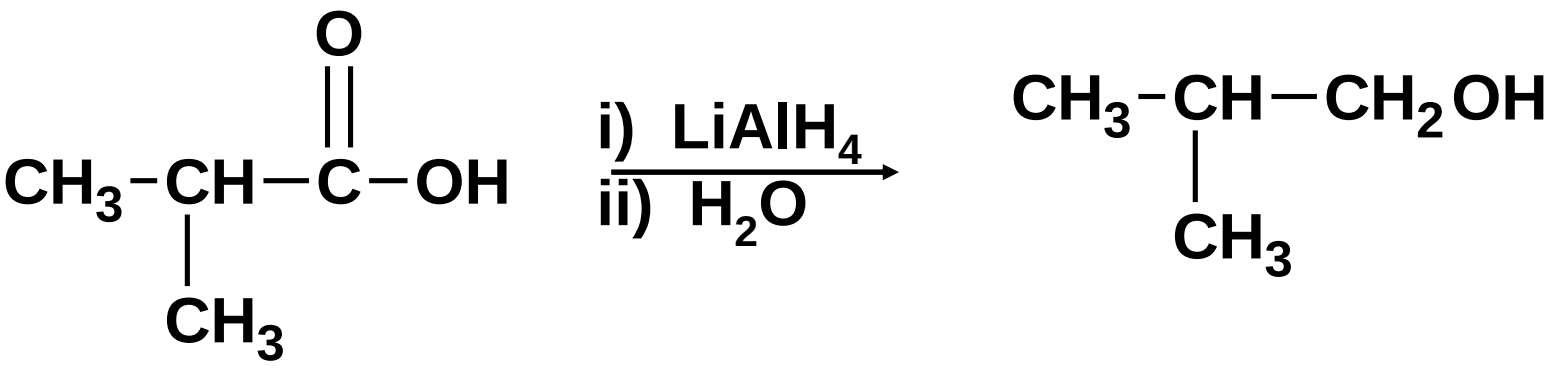

CH3 O
HC C OH
CH3
NH3
CH3 O
HC C NH2
CH3
CH3 – NH2
CH3 O
HC C NH(CH3)
CH3
CH3 – NH
CH3
CH3 O
CH C N(CH3)2
CH3

The reaction that involves the reduction with $LiAlH_4$ followed by hydrolysis to form primary alcohol

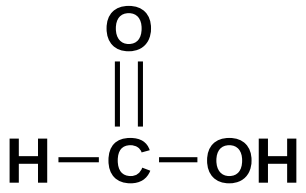
Carboxylic acid are reduced to primary alcohols by reaction with lithium aluminium hydride, $LiAlH_4$ followed by hydrolysis



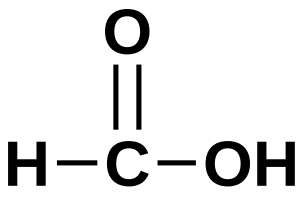
Example :



Methanoic acid, HCOOH as a reducing agent

- Methanoic acid molecule,  is a reducing agent.

- It **shows reducing properties** in reactions with acidified $KMnO_4$ or $K_2Cr_2O_7$ and Tollens' reagent.



$KMnO_4$,H^+ ,heat

$CO_2 + H_2O + Mn^{2+}$

Observation :
purple colour of $KMnO_4$ decolourised

$[Ag(NH_3)_2{}^+OH^-]$

$Ag\downarrow + CO_2 + H_2O$

Observation : silver mirror formed

THE END