

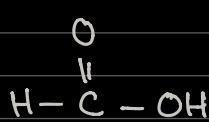
CARBOXYLIC ACIDS : ORGANIC CHEMISTRY

General Formula : $C_nH_{2n+1}COOH$

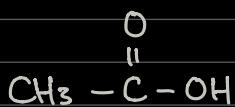
: $R - C - OH$

Physical Properties :

1st Acid Methanoic Acid



2nd Acid Ethanoic Acid



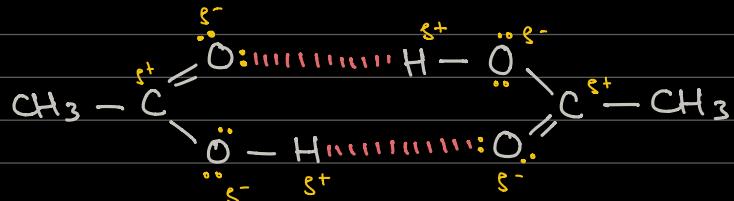
States at RTP :

1 carbon – 9 carbon acids → liquids

> 9 carbon acids → white crystalline solids

↳ They show strong intermolecular H bonds

- Ethanoic Acid exists as a dimer due to H-bonding between 2 ethanoic acid molecules:



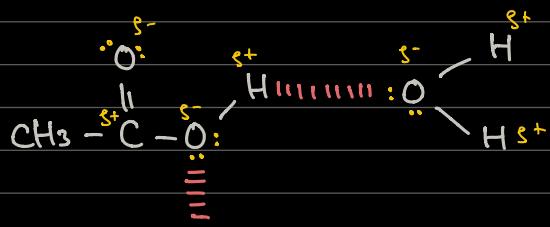
Ethanoic Acid Dimer, $M_r = 120$

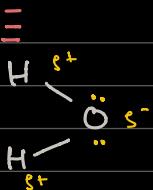
aka. Glacial Acetic Acid

↳ fine, ice like crystals

Solubility:

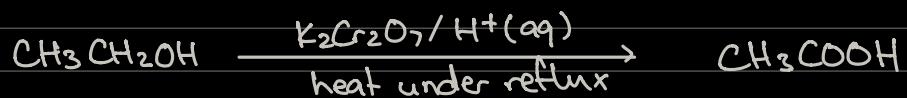
- lower acids are very soluble in water as they can form H-bonds with water
- Solubility decreases as number of carbons increases (vdw forces start to dominate)





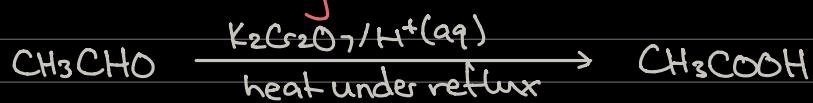
Preparation of Carboxylic Acids:

1. Oxidation of 1° alcohols

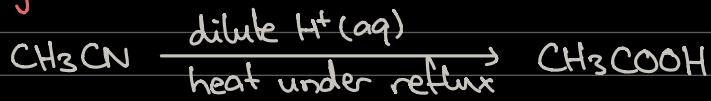


Note: $\text{KMnO}_4 / \text{H}^+(\text{aq})$ could also be used as the OA instead of $\text{K}_2\text{Cr}_2\text{O}_7$

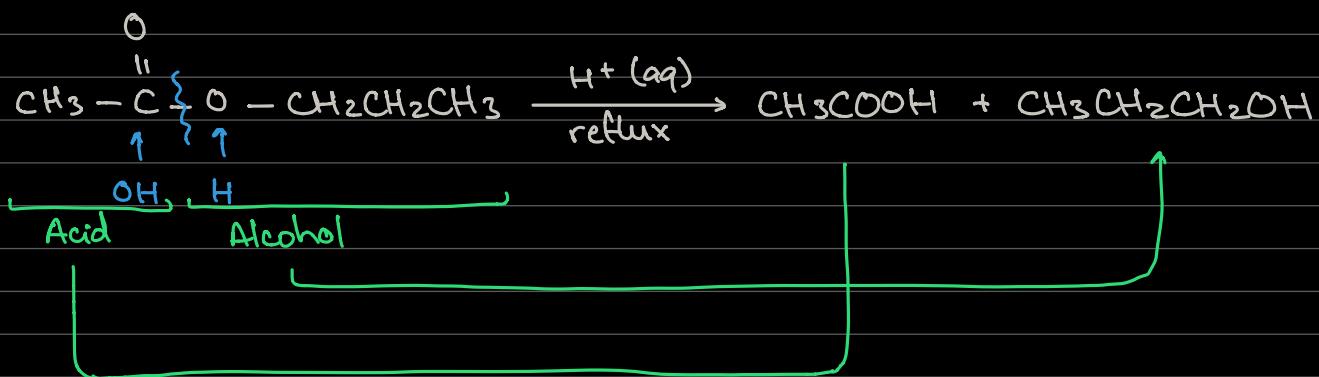
2. Oxidation of Aldehydes



3. Hydrolysis of Nitriles



4. Hydrolysis of Esters (Acid Hydrolysis)



ACID DERIVATIVES

↳ substances prepared from carboxylic acids

AS Esters $\underline{\text{R}-\text{C}(=\text{O})-\text{O}-\text{R}'}$



A2 Amides $\underline{\text{R}-\text{C}(=\text{O})-\text{N}-\text{H}}$

Mostly Acyl Chlorides $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{Cl}$
A2

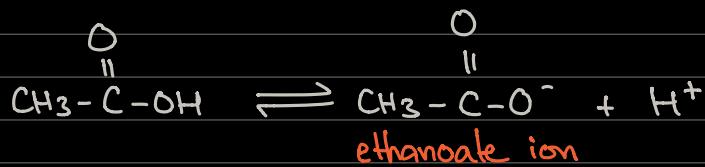
Note in Syllabus Acid Anhydrides $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{C}-\text{R}' \rightarrow$ two acids joined together by eliminating a water molecule.

ACIDITY OF CARBOXYLIC COMPOUNDS

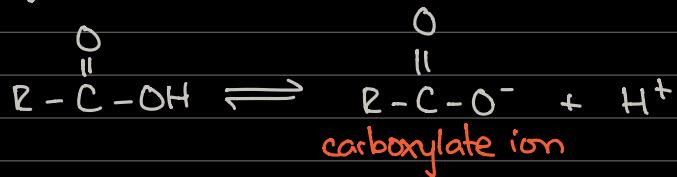
- Are weak acids
- A weak acid dissociates partially in water

Note: mineral acids i.e.
HCl, HNO₃, etc. are
strong acids

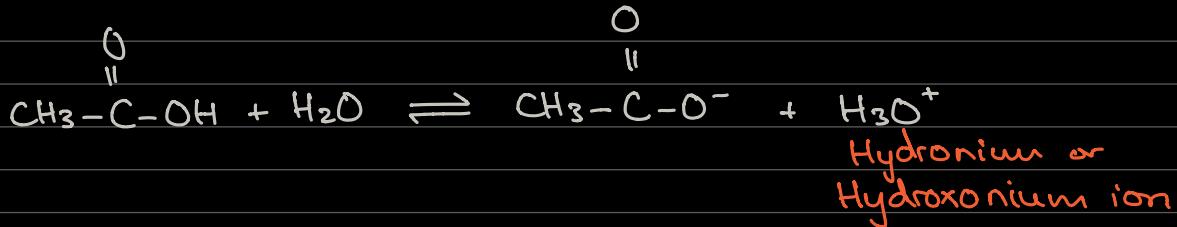
Example:



More generally:



with water:



ACIDITY OF CARBOXYLIC ACIDS vs. Alcohols

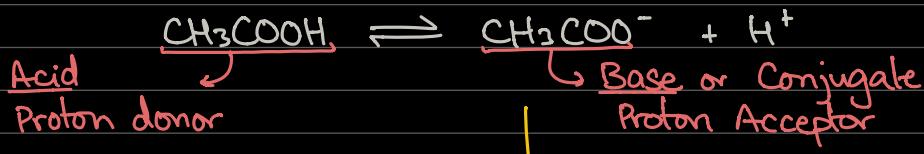
Alcohols

- Alcohol + Na → Rxn.
- Alcohol + NaOH → No Rxn.
- Alcohol + Na₂CO₃ → No Rxn.

Carboxylic Acids

- Acid + Na → Rxn.
- Acid + NaOH → Rxn.
- Acid + Na₂CO₃ → Rxn.

- When compared with alcohols, carboxylic acids are stronger acids



Organic Acids are weak acids because their respective ions are strong bases and readily accept the dissociated protons, resulting in a simultaneous backwards reaction (unstable ion)

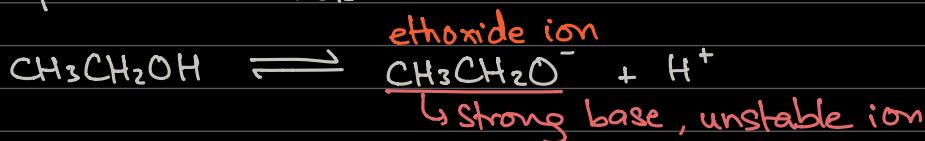
As compared to strong acids:



Weak Base or a stable base

- Does not cause a significant backwards reaction

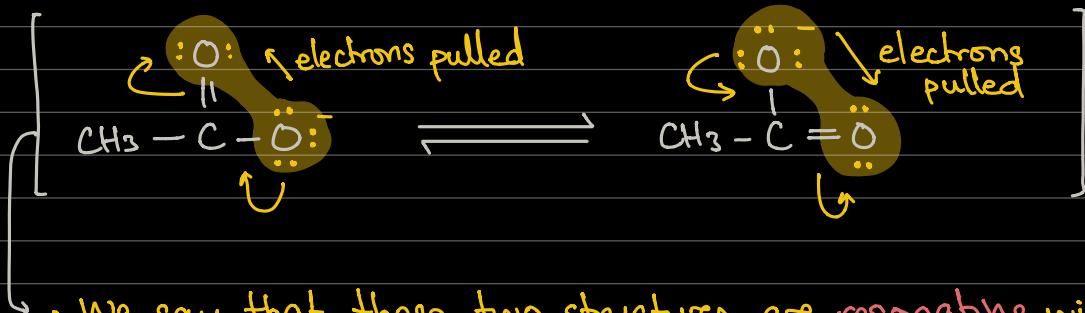
As compared to alcohols:



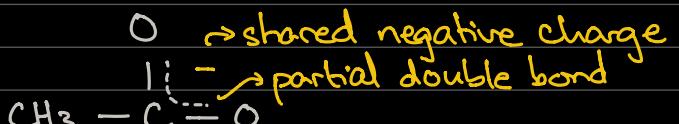
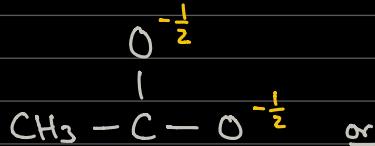
Note: $\text{R}-\text{O}^-$

alcooxide ion

- An acid is stronger if its anion is more stable



- We say that these two structures are resonating with each other
- Hence, they're called resonance hybrids
- Due to the negative charge flipping between the two Os, the negative charge is spread out / delocalised over two EN oxygen atoms
- whenever charge is spread out → it leads to stability

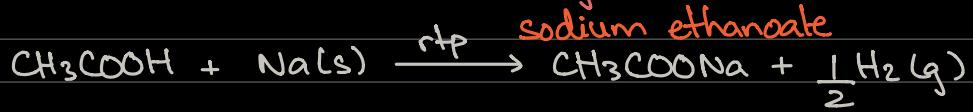


- The ethanoate ion is therefore more stable than the ethoxide ion
- So it is more dissociated
- The acid is a stronger acid.

TYPICAL ACID-LIKE REACTIONS OF CARBOXYLIC ACIDS

1. Reaction with Metals \rightarrow Salt + H₂(g)

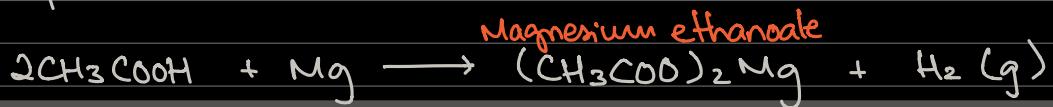
Example:



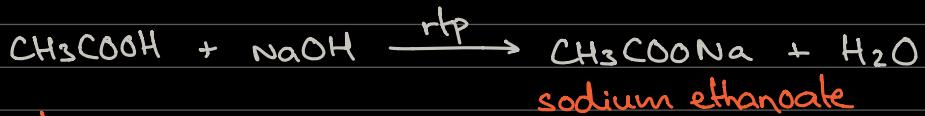
Observation:

Colorless gas evolved that extinguished a burning splint with a pop sound

Example:



2. Reaction with Alkalies \rightarrow Salt + Water



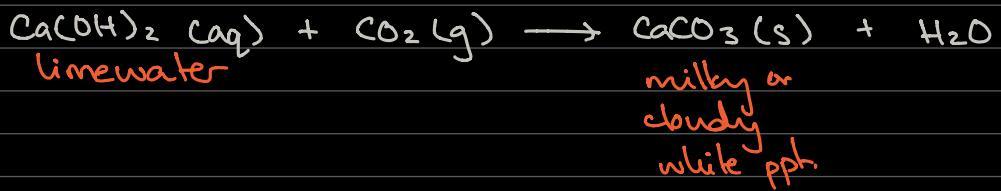
Observation:

3. Reaction with carbonates \rightarrow salt + water + CO₂



Observation:

Effervescence of a colorless gas which turns lime water milky or cloudy



4. Reaction with NaHCO₃ \rightarrow salt + H₂O + CO₂



Distinguishing between alcohols, phenols, and carboxylic acids



Unknown X

↓ add Na

Fizzing

Could be R-OH, RCOOH,
or $\text{C}_6\text{H}_5\text{-OH}$

No fizzing

no OH groups present

↓ add NaOH (aq)

Reaction

No Reaction

It's R-OH

Could be RCOOH
or $\text{C}_6\text{H}_5\text{-OH}$

↓ add Na_2CO_3 (aq)

Fizzing

It's RCOOH

No Fizzing

It's $\text{C}_6\text{H}_5\text{-OH}$

Note: The best identification for a carboxylic acid is the reaction with sodium carbonates

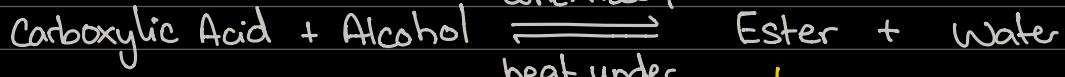
	Na	NaOH	Na_2CO_3
--	----	------	--------------------------

Acid	CH_3COOH	✓	✓
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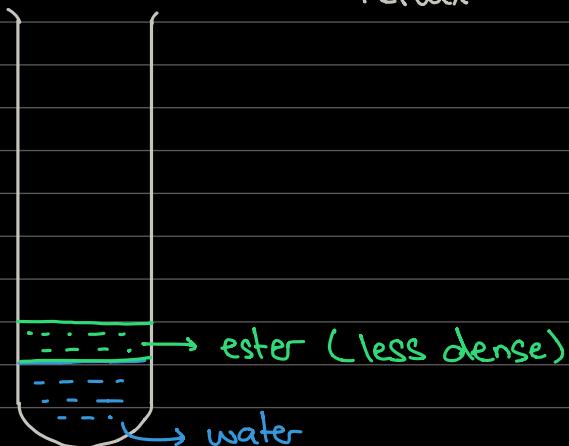
Alcohol	CH_3OH	✓	✗
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Phenol	$\text{C}_6\text{H}_5\text{-OH}$	✓	✓
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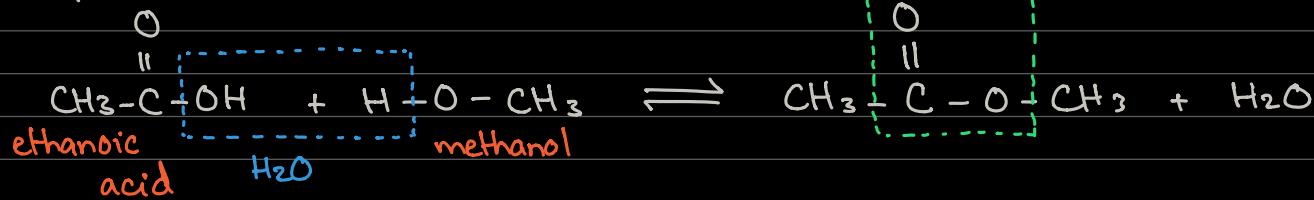
ESTERIFICATION : ALCOHOLS + ACIDS



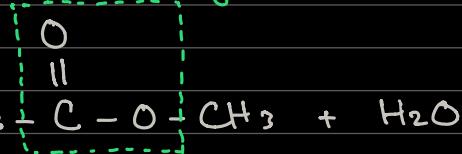
↳ Sweet smelling liquid which forms a separate layer on top of the water



Example :



ester linkage

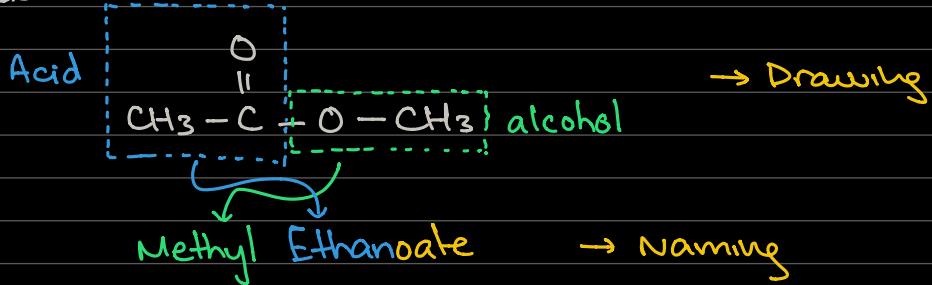


Naming vs. Drawing of esters :

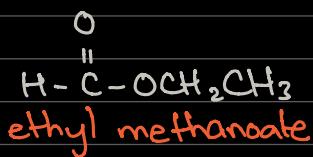
1. Drawing : Draw the acid part first, ie. $\text{R}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-$

2. Naming : Name the alcohol part first, followed by the acid part and the name ends in the suffix -oate.

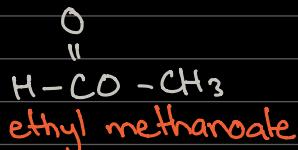
Example :



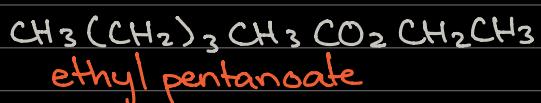
Example :



Example :

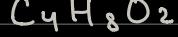


Example :



ISOMERIC ESTERS

Q. How many isomeric esters can be made from the following molecular formula?



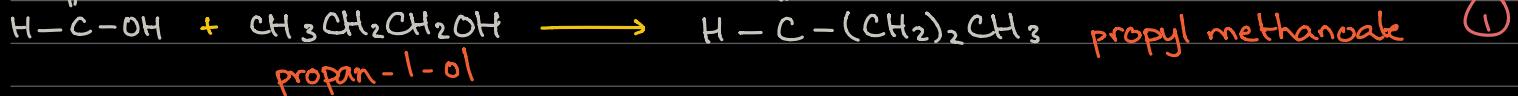
Acid Alcohol

1C

3C

O

||



2C 2C

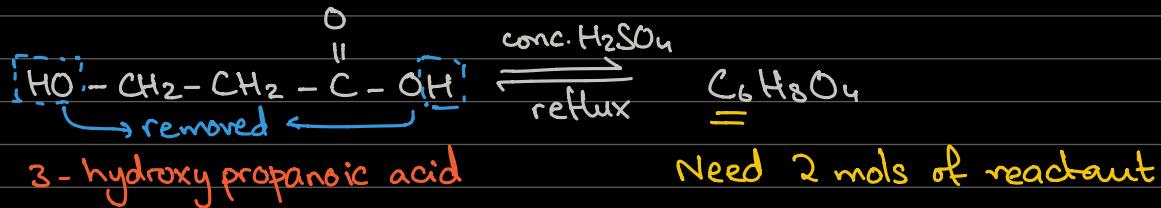


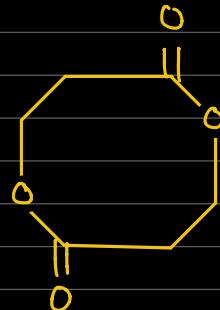
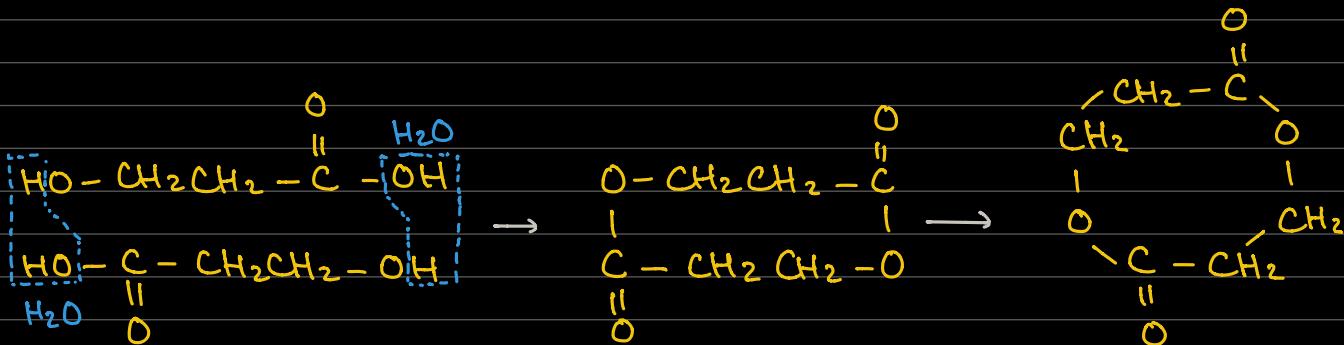
3C 1C



Ans: 4 isomeric esters.

Q. Draw a cyclic ester with the molecular formula $\text{C}_6\text{H}_8\text{O}_4$ from the following reactant using conc. H_2SO_4



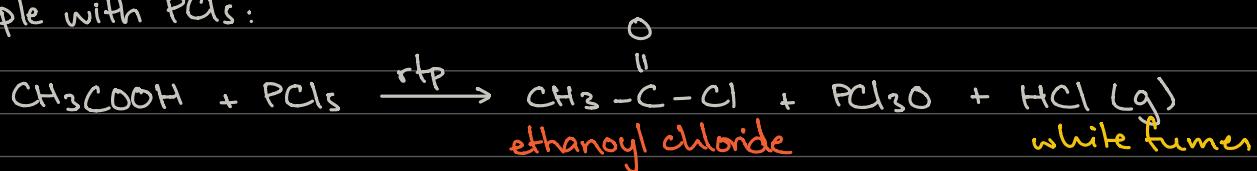


REACTIONS OF THE -OH GROUP

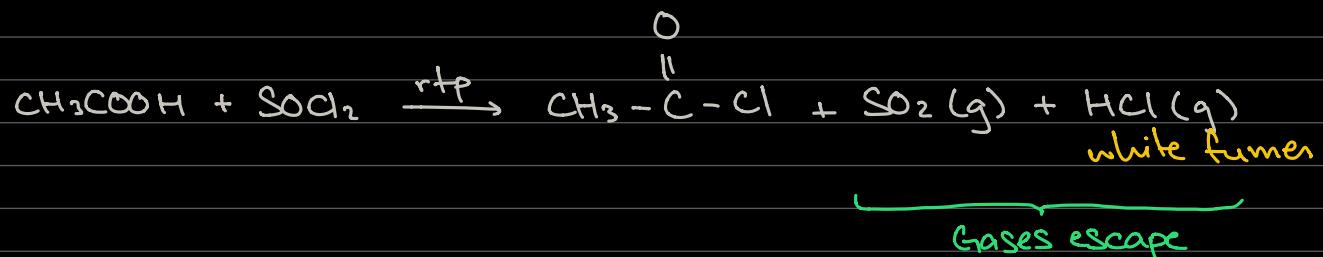
O → Derivative
 \parallel
 $\text{R}-\text{C}-\text{Cl}$

Rxn. with PCl_5 or SOCl_2 (thionyl chloride) → Acyl Chloride

Example with PCl_5 :



Example with SOCl_2 :

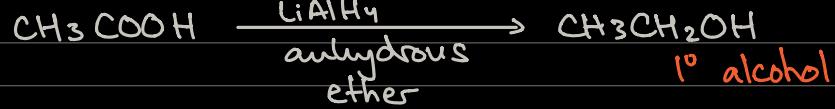


REDUCTION OF CARBOXYLIC ACIDS gives 1° alcohols

1° alcohol $\xrightarrow{\text{oxidation}}$ Carboxylic Acids

Carboxylic Acids $\xrightarrow[\text{as Solvent}]{\text{LiAlH}_4, \text{dry ether}}$ 1° alcohol

Example:



Example CH_3



HYDROLYSIS OF ESTERS

• Ester linkage is broken and a water molecule adds across each ester linkage

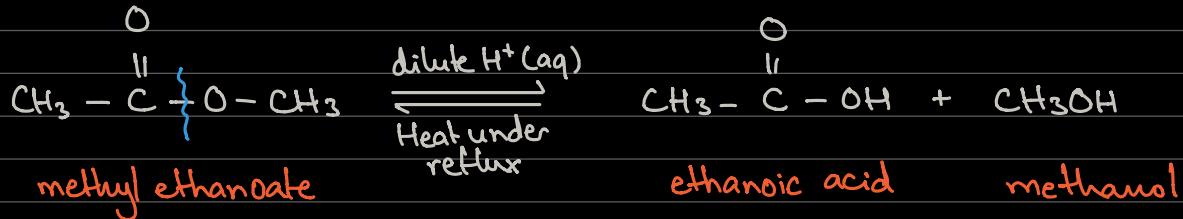
OH goes to acid
 H goes to alcohol

1. Acid Hydrolysis (Slow Rxn)

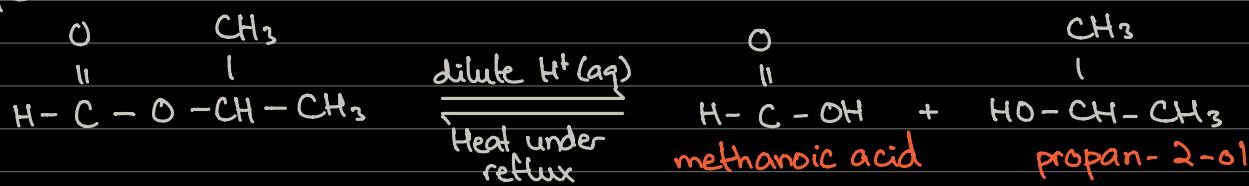
Reagent: Dilute HCl

Condition: Heat under reflux for several hours

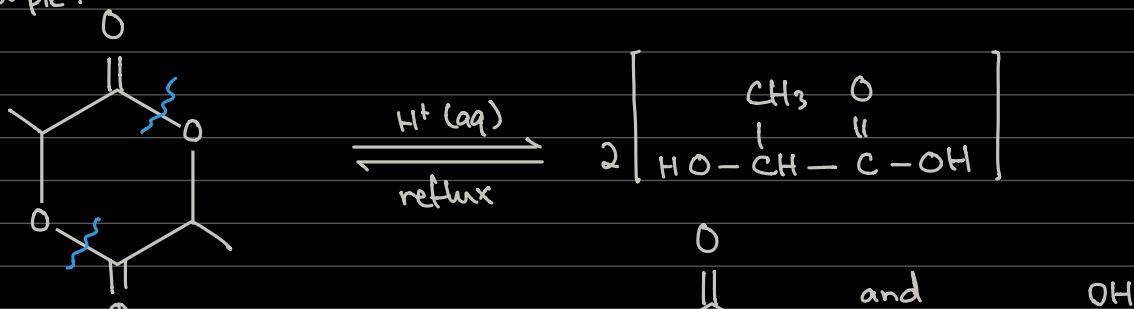
Example:

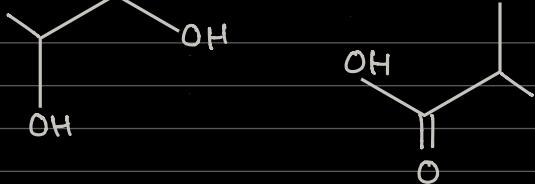


Example:



Example:



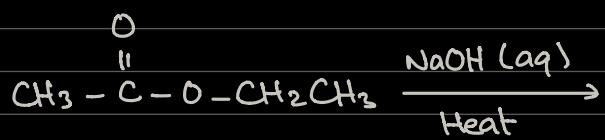


Acid + Alcohol $\xrightleftharpoons[\text{Dilute HCl}]{\text{conc. H}_2\text{SO}_4}$ favours the forward esterification rxn.
Ester + H₂O favours the backward hydrolysis rxn.

2. Alkaline Hydrolysis (Fast Rxn) → Note: This rxn is not reversible because a salt is formed

Reagent: NaOH (aq)

Condition: Heat



COMMERCIAL IMPORTANCE OF ALKALINE HYDROLYSIS

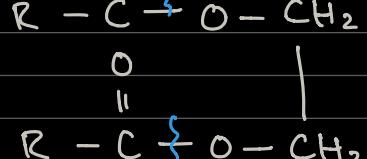
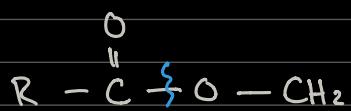
- Manufacture of soap (saponification)

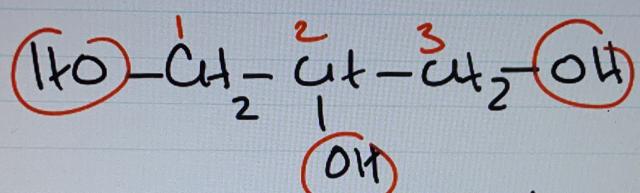
- Soap is made from fat

↳ Fats are glycerol triesters of long chain carboxylic acids
↳ from glycerol

- Heat fat with NaOH, which causes ester linkages to hydrolyse and the sodium salt of the long chain of carboxylic acid is obtained as soap.

↳ Glycerol is also formed

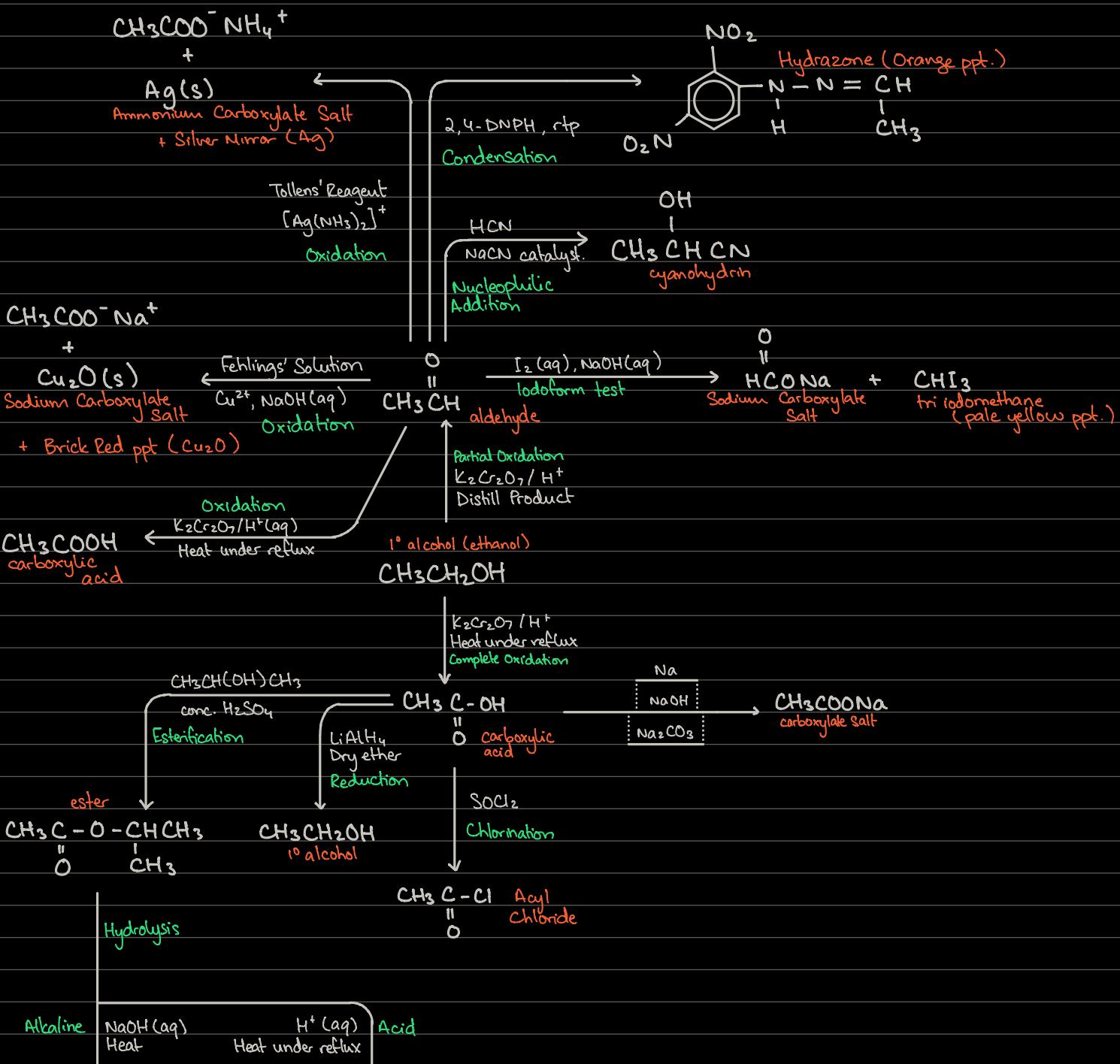


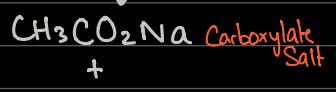


1,2,3-propanetriol

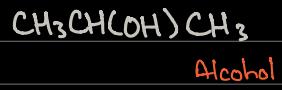
GR

propane-1,2,3-triol

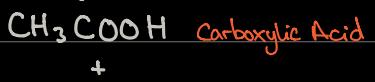




Carboxylate
Salt



Alcohol



+



Alcohol