



Dicarboxylic acids

Prepared by

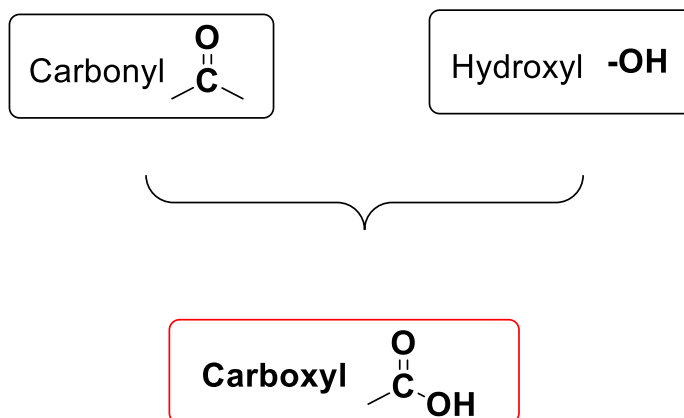
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Chemistry Department – Faculty of Science

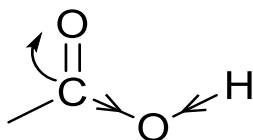
Organic Chemistry
2nd physics and chemistry department
Second semester - 2022

Carboxylic acids

A carboxylic acid is an organic compound whose functional group is the carboxyl group. What is a carboxyl group? A carboxyl group is a carbonyl group (C=O) with a hydroxyl group (—OH) bonded to the carbonyl carbon atom. A general structural representation of a carboxyl group is RCOOH.



Carboxylic group has 3 polar bonds as shown here

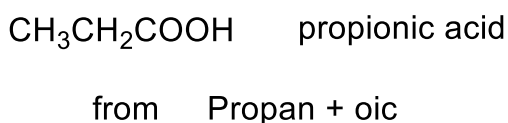


IUPAC Nomenclature for Carboxylic Acids

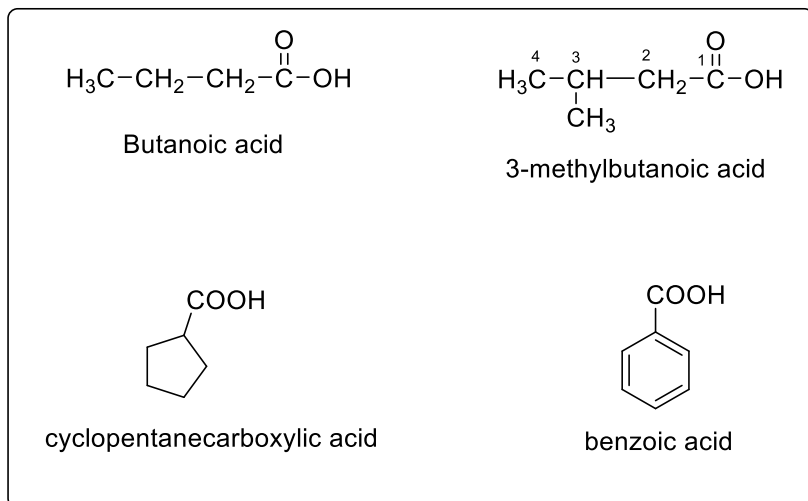
The naming of carboxylic acids is simple. You simply find the longest carbon chain which includes the carboxylic group. Use that

as the stem for the name, cross off the -e on the ending of the alkane name and replace it with **-oic acid**.

I think you can see how that works, if you look at this example (which is also shown in Example 1-a in your workbook). It gives you, in this case (with a three-carbon-atom chain), the name propanoic acid.



As with aldehydes, it is not necessary to indicate where the acid functional group is because it has to be at the end of the molecule, on the #1 carbon. There is no way that this functional group can be anywhere else. Therefore, if there is any numbering to be done, it will be to show where additional alkyl groups or other groups are attached to the carbon chain. The numbering starts from the carboxylic group.



Common Names for Carboxylic Acids

Carboxylic acids are another example of a situation where the compounds were known and named long before anyone thought of the IUPAC method of naming compounds. Consequently, many carboxylic acids have their own common name which is distinct from the IUPAC name. The two most important of these (and the only two you will be held responsible for in this course) are shown below. They are **formic acid** and **acetic acid**.

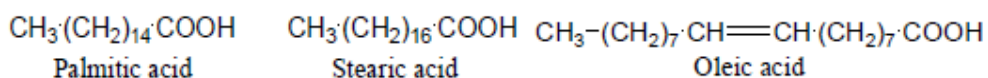
Here is the structural formula for **formic acid** (H-COOH) Its IUPAC name is **methanoic acid**, using the **meth** stem because it has **one** carbon atom and so on.

Structural Formula	Latin or Greek Root	Common Name*
H—COOH	form-	formic acid
CH ₃ —COOH	acet-	acetic acid
CH ₃ —CH ₂ —COOH	propion-	propionic acid
CH ₃ —(CH ₂) ₂ —COOH	butyr-	butyric acid
CH ₃ —(CH ₂) ₃ —COOH	valer-	valeric acid
CH ₃ —(CH ₂) ₄ —COOH	capro-	caproic acid

For more details, you can see this table with translation.

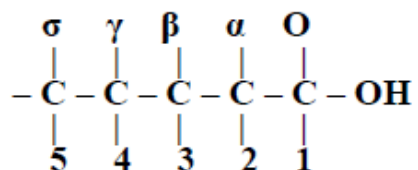
Latin root	Common Names	Compound
Formica تعني النمل	Formic acid	HCO ₂ H
Acetum تعني الخل	Acetic acid	CH ₃ COOH
Proto تعني الدهن	Propionic acid	CH ₃ CH ₂ COOH
Butyrum تعني الزبدة	Butyric acid	CH ₃ (CH ₂) ₂ COOH
تعني زهرة الناردين Valere	Valeric acid	CH ₃ (CH ₂) ₃ COOH
Caper تعني الماعز	Caproic acid	CH ₃ (CH ₂) ₄ COOH

Carboxylic acid with long chain is called fatty acid for example:



Naming using Greek letters α , β , γ , δ etc.

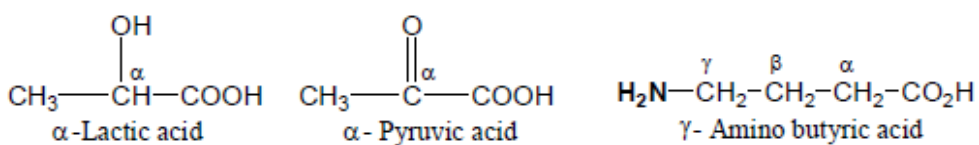
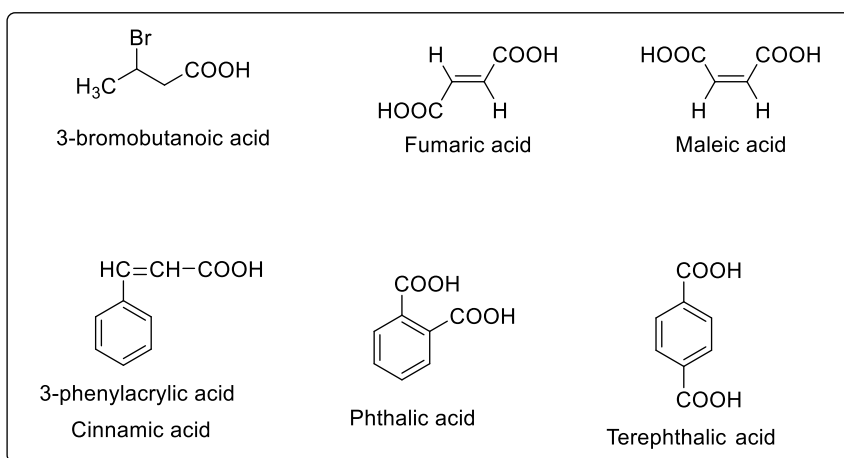
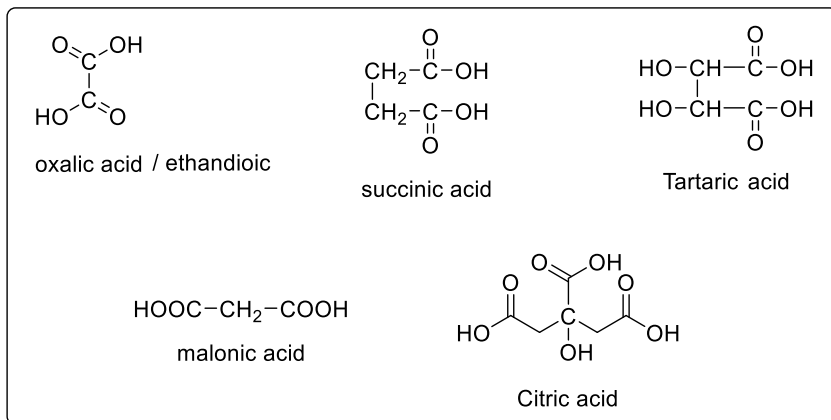
There are two ways to identify substituent carbons in carboxylic acid: numbers or Greek letters. Using numbers, the carboxyl group carbon is given the number one.



When Greek letters are used, Greek letters are used to designate the position of substituent relative to the carbon of the carboxyl group. The carbon of the carboxyl group is NOT given a Greek letter. 6) A special group of carboxylic acids are those that also have a keto group. They are called alpha-keto carboxylic acid

Polyfunctional Carboxylic Acids

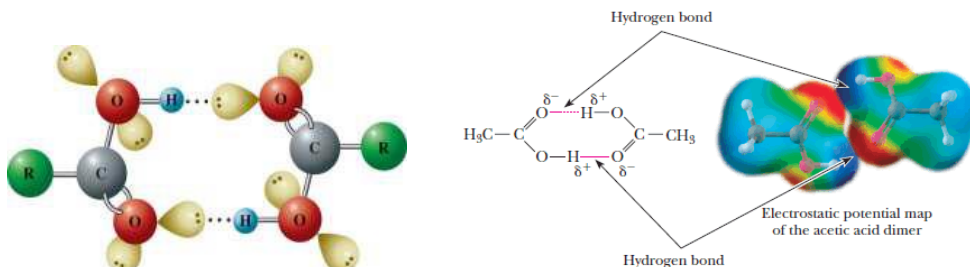
Dicarboxylic acids are organic compounds that are substituted with two carboxylic acid functional groups. They are important metabolic products of fatty acids when they undergo oxidation.



Physical Properties of Carboxylic Acids

Carboxyl groups exhibit very strong hydrogen bonding. A given carboxylic acid molecule form two hydrogen bonds to another carboxylic acid molecule, producing a “dimer”, a complex with a mass twice that of a single molecule. Compounds with carboxyl

groups have higher boiling points than alcohols. This is because the carboxyl groups hydrogen bond more strongly than alcohols.



Carboxyl groups make molecules very soluble in water because the group can strongly hydrogen bond with water.

Physical Properties of carboxylic acids derivatives

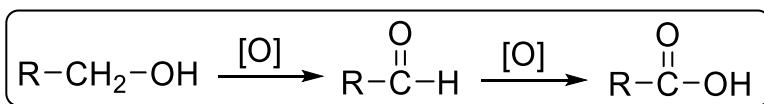
Depending upon the substituent replacing -OH of the carboxylic functional group the physical properties could change. However, they have lower boiling and melting points than parent acid.

Preparation of Carboxylic Acids

1- By Oxidation:

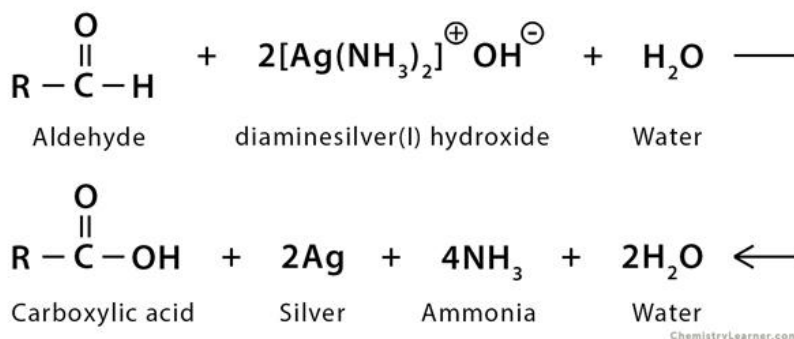
A) Oxidation of Primary alcohols or aldehydes:

Carboxylic acids are easily by oxidation of primary alcohols and aldehydes. When the oxidation process begins with an alcohol it is difficult to stop at the aldehyde stage of oxidation.



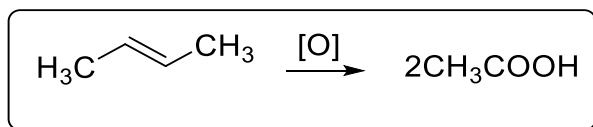
Oxidation using basic $[\text{Ag}(\text{NH}_3)_2]^+$: A basic $[\text{Ag}(\text{NH}_3)_2]^+$ in aqueous ammonia reduces to metallic silver (mirror) with aldehyde oxidized to carboxylic acid.

Tollens' Test



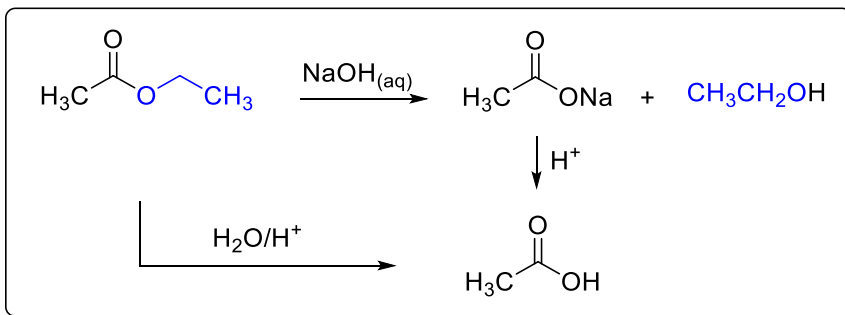
The commercial manufacture of silver mirrors uses a similar process.

B) Oxidation of Alkenes: using $\text{K}_2\text{Cr}_2\text{O}_7$ or O_3



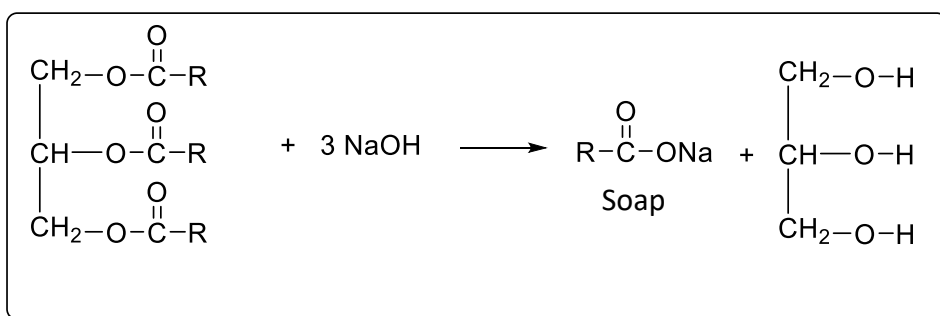
2- By Hydrolysis:

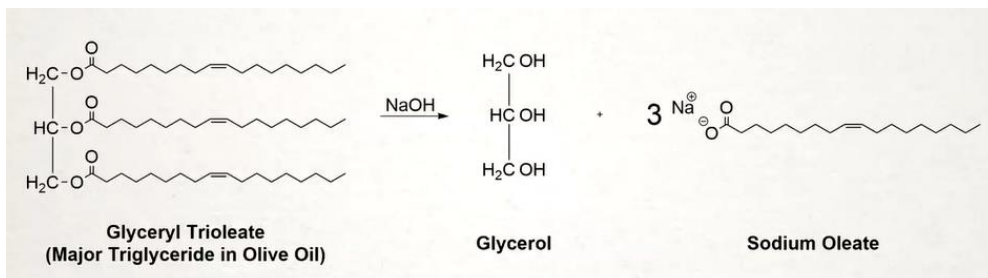
A) Hydrolysis of esters -COO-: In acidic or basic catalyst



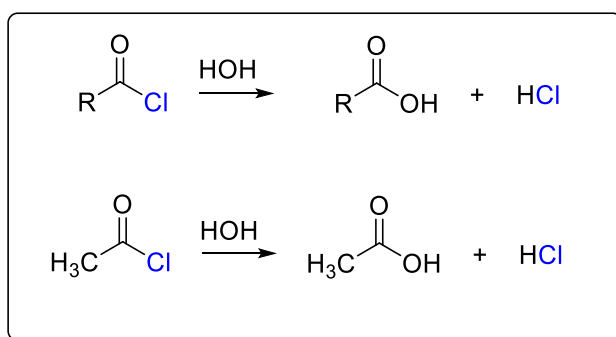
This is very important reaction because it can prepare fatty acids from fats or oils.

Base-catalysed hydrolysis is often called saponification (**soap-making**) saponification is irreversible because a carboxylate salt is formed. Saponification of triglycerides and action of soap in the emulsification of grease and oils. Soap has been around for hundreds of years. In its simplest form, soap is made by heating fat in boiling water that also has sodium hydroxide (NaOH) or potassium hydroxide (KOH) ions in it. Each fat molecule breaks down into three molecules of fatty acids. The molecules of fatty acids then react with the sodium or potassium ions to form soap molecules and glycerine.

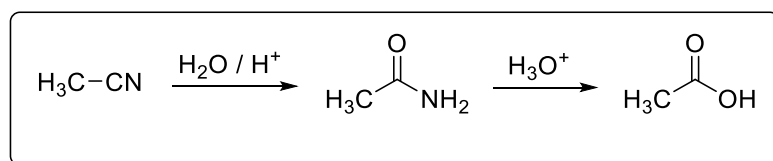




B) Hydrolysis of **Acid halide** RCOX:



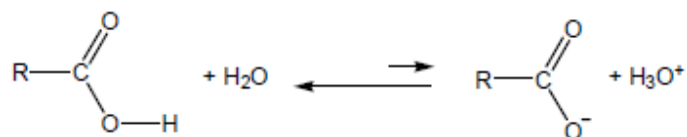
C) Hydrolysis of **Nitriles** RCN:

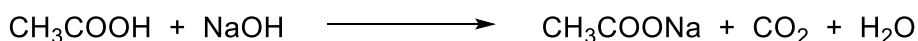
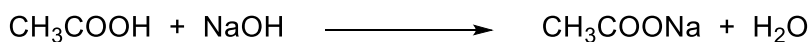


Reactions of Carboxylic Acid

1- Reaction with bases to form acid salts (Acidity).

Carboxylic acids are weak acids



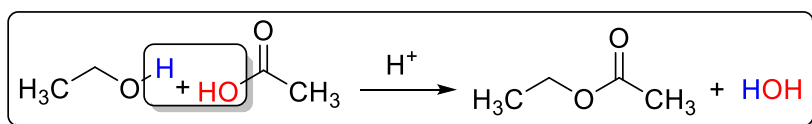


Naming carboxylic acid follows certain pattern for example the structural formula for the compound. Since this sodium salt of propanoic acid ($\text{CH}_3\text{CH}_2\text{COONa}$) so start from propanoic acid is a three-carbon acid with no carbon-carbon double bonds and this negative ion without the H^+ atom is called **propanoate**. There this salt is named: **sodium propanoate**.

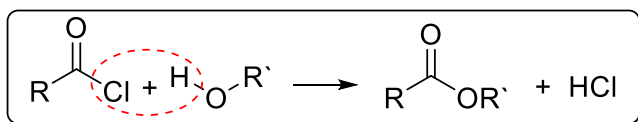
When the carboxylic acids form salts, the hydrogen in the $-\text{COOH}$ group is replaced by a metal. Sodium alkan oate (propan- oate).

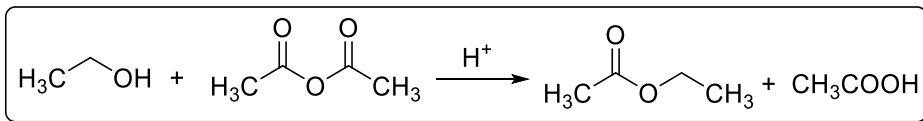
2- Ester formation:

Ester can be formed from reaction of carboxylic acids with alcohols in the presence of acidic catalyst as follow:



Also, Ester can be formed from reaction of acid halide or acid anhydride with alcohols in the presence of acidic catalyst as follow:



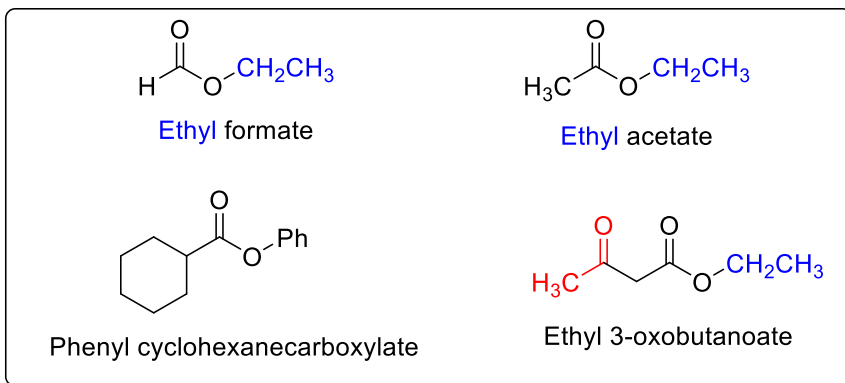


Note: the acid loses an -OH units and the alcohol loses a -H in this reaction.









Naming Esters:

1. Identify the alkyl group that is attached to the oxygen atom
2. Number according to the end closest to the -CO- group regardless of where alkyl substituents are.
3. Determine the alkane that links the carbon atoms together. If there is a separation of a continuous link of carbon atoms due to the oxygen atom, individually name the two alkanes before and after the oxygen atom. The longer structural alkane is the one that should contain the carbonyl atom.
4. The format is as follows: (alkane further from carbonyl) (alkane closest to carbonyl)(parent chain)
5. Change the parent chain -e ending and replace it with an **-oate**.

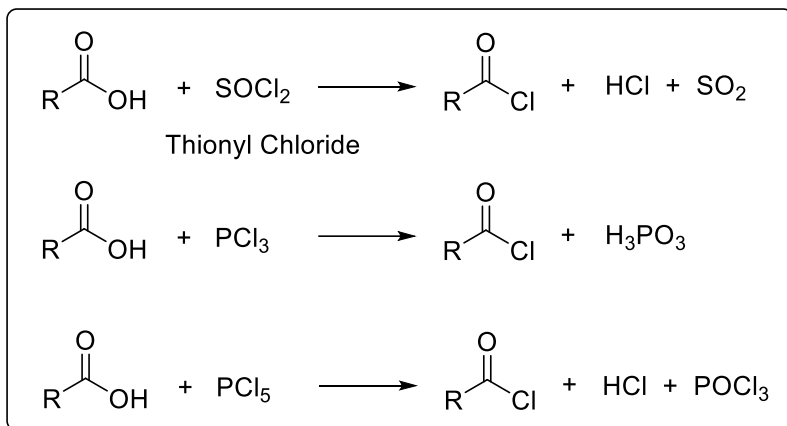
Example: $\text{CH}_3\text{COOC}_2\text{H}_5$ ---→ Ethyl ethano**ate** or Ethyl acetate



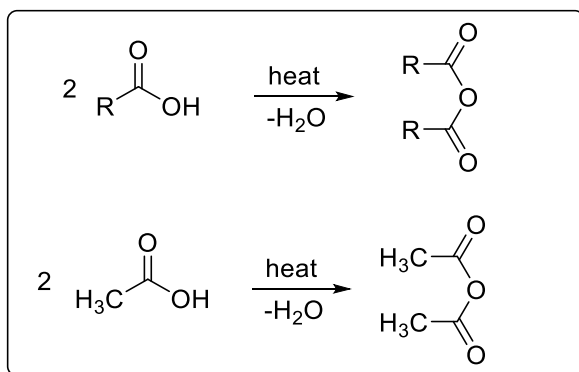
Esters as Perfumes

<chem>CCOC(=O)C</chem> أسيتات الينثايل (رائحة اللافندر)			<chem>CCOC(=O)CC</chem> أسيتات الإيثيل (رائحة الغراء)
<chem>CCOC(=O)C</chem> بيوتيرات الينثايل (رائحة الدراق)			<chem>CCOC(=O)C</chem> فورمات الأيثيل (رائحة الليمون)
<chem>CCOC(=O)C</chem> أسيتات الميثيل (رائحة طلاء الأظافر)			<chem>CCOC(=O)C</chem> أيزوفاليرات الأيثيل (رائحة التفاح)
<chem>CCOC(=O)C</chem> أنثرائيت الميثيل (رائحة العنب/الباسمين)			<chem>CCOC(=O)C</chem> لاكتات الأيثيل (رائحة الكريمة)

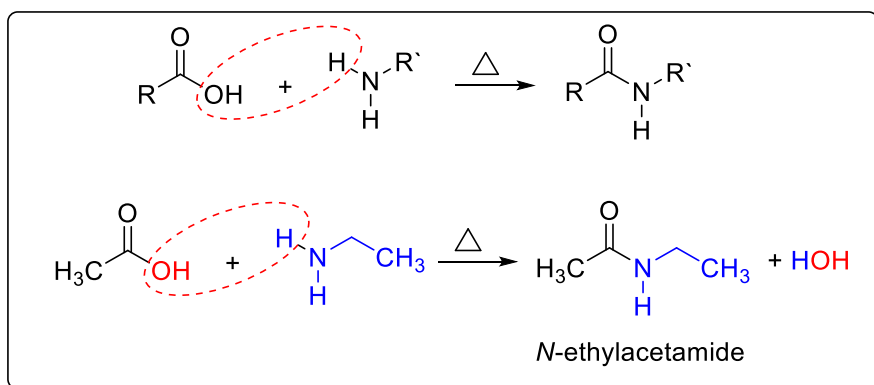
3- Acid halide formation:



4- Acid anhydride formation:

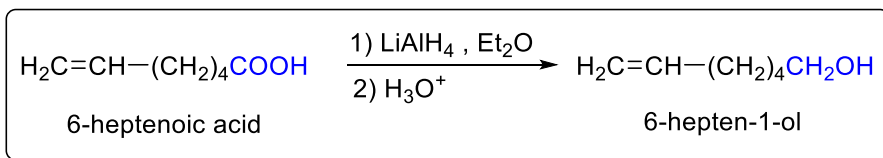


5- Amide formation:



6- Reduction of carboxylic acids:

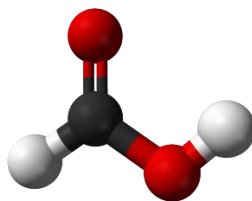
By using reducing agents like LiAlH_4 .



Monocarboxylic acids

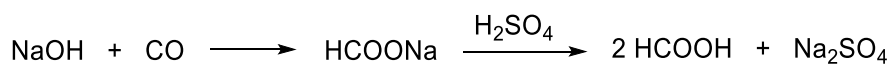
In this part we will focus on monocarboxylic acids.

HCOOH Methanoic

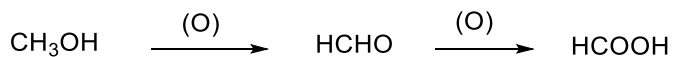


Synthesis:

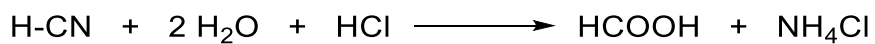
1- In industry:



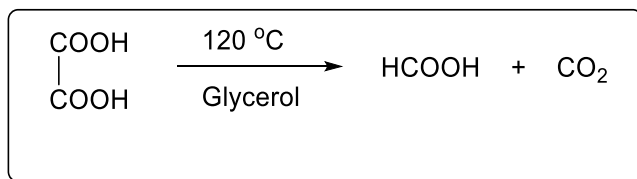
2- Oxidation of methyl alcohol or formaldehyde:



3- Hydrolysis of hydrogen cyanide:

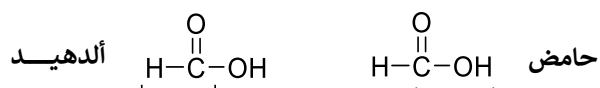


4- Heating of oxalic acid in the presence of glycerol:

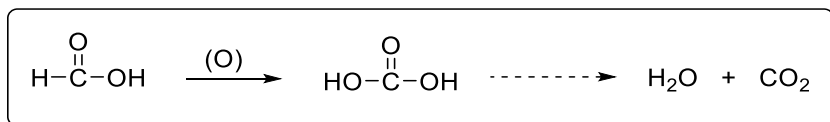


Reactions:

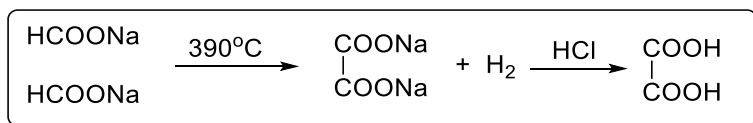
Formic acid has free hydrogen atom with COOH group, that's mean it react some time as acid or an aldehyde.



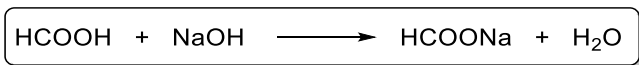
1- Oxidation:



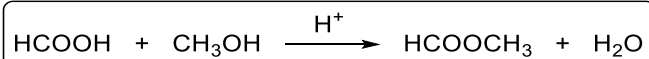
2- Conversion to oxalic acid:



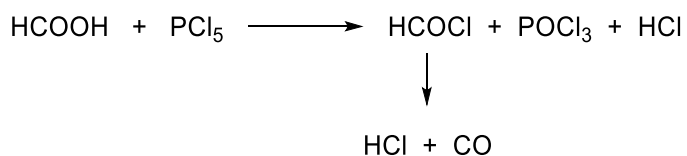
3- Salt formation:



5- Ester formation:



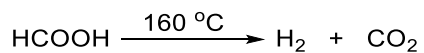
6- Reaction with PCl_5 :



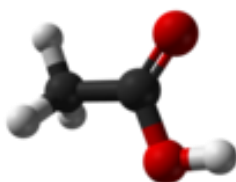
7- Reaction with ammonia:



8- Elimination of COOH :

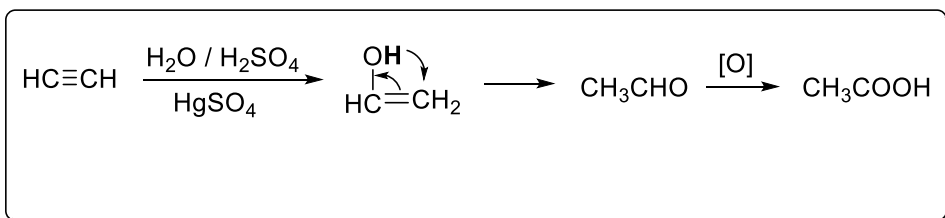


CH₃COOH Acetic acid

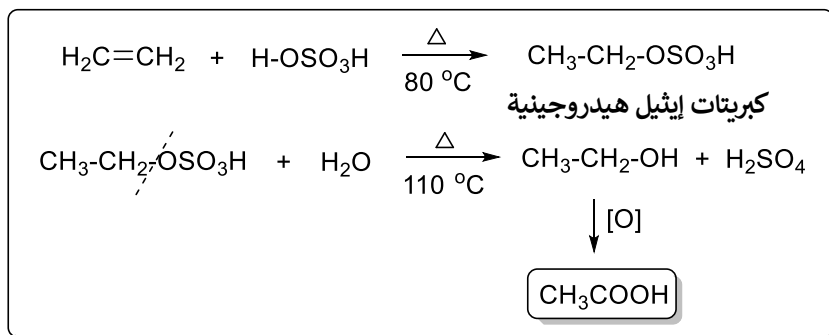


Synthesis:

1- In industry: from acetylene



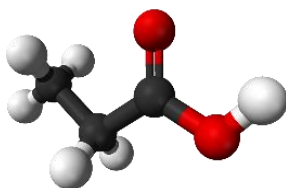
2- From ethene:



Reactions:

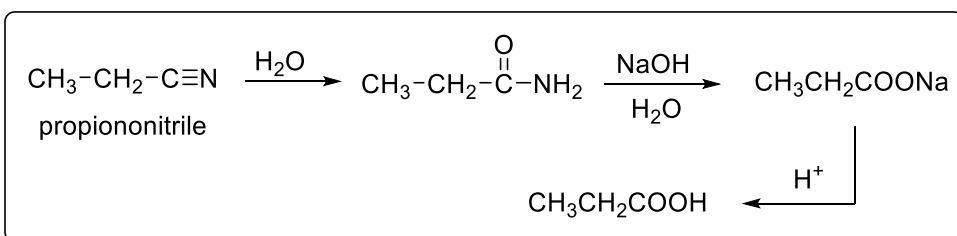
It reacts like we discussed in reactions of carboxylic acids previous lecture.

CH₃CH₂COOH Propionic or propanoic acid

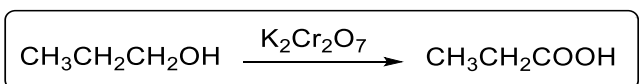


Synthesis:

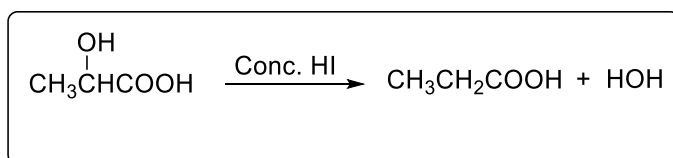
1- Hydrolysis of ethyl cyanide (propionitrile):



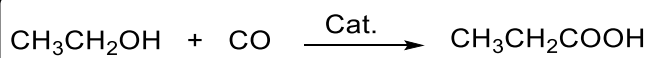
2- Oxidation of propanol:



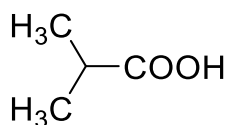
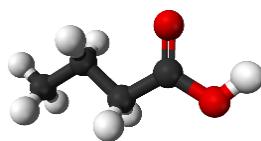
3- Reduction of lactic acid:



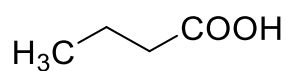
4- Reaction of ethanol with CO:



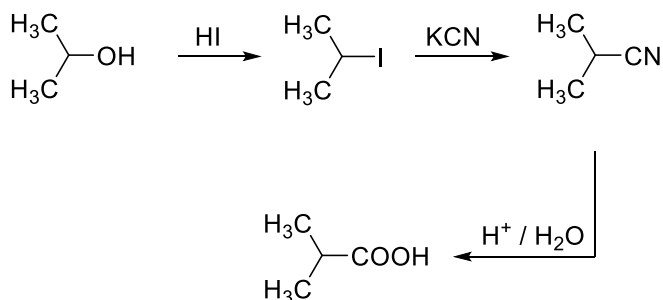
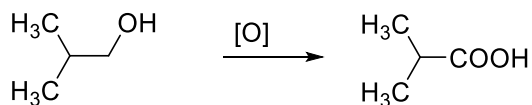
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ Butanoic acid



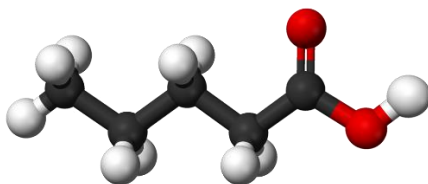
isobutyric acid



butyric acid



Pentanoic acid / Valeric acid

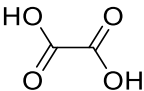
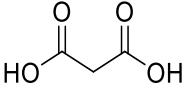
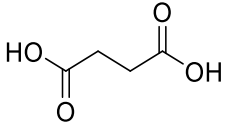
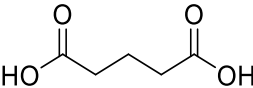
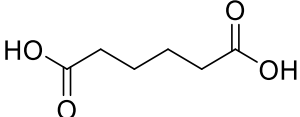


H. W

Dicarboxylic acids

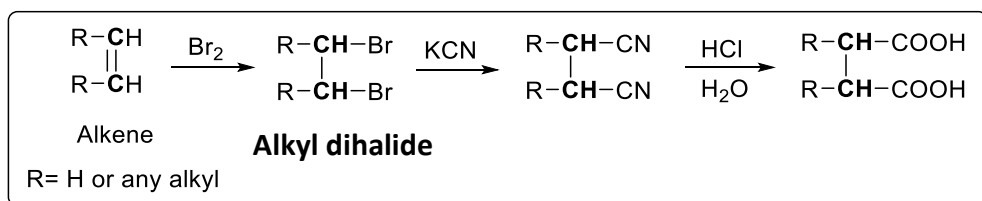
Nomenclature:

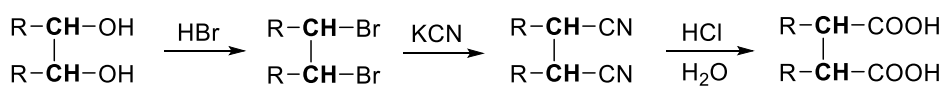
The corresponding alkane + dioic

Structure formula	IUPAC	Common name	n
	ethanedioic	Oxalic acid	0
	propanedioic	Malonic acid	1
	butanedioic	Succinic acid	2
	pentanedioic	Glutaric acid	3
	hexanedioic	Adipic acid	4

Synthesis:

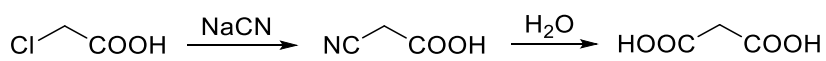
1) From alkenes and glycols:





R=H Ethylene glycol

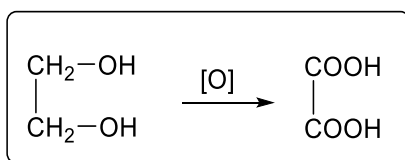
R= H or any alkyl



Chloroacetic acid

Malonic acid

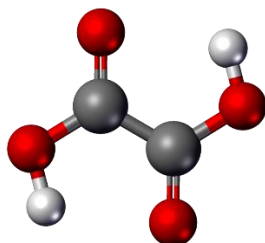
2) Oxidation of dihydroxy alcohols:



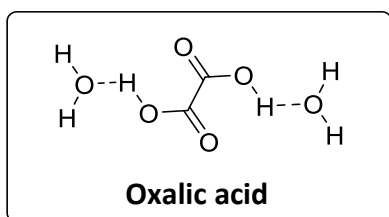
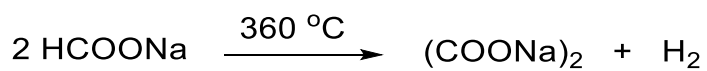
Properties:

Solid – soluble in water – acidic effect on litmus paper.

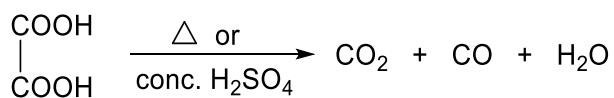
Oxalic acid



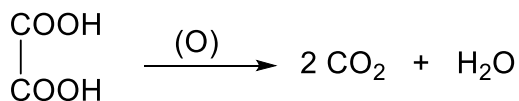
1) In industry:



1- Cracking with heating

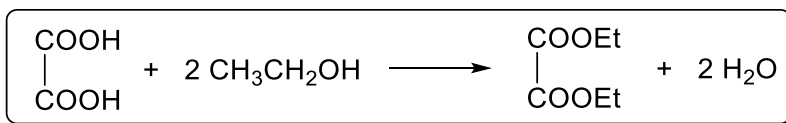


2- Oxidation:

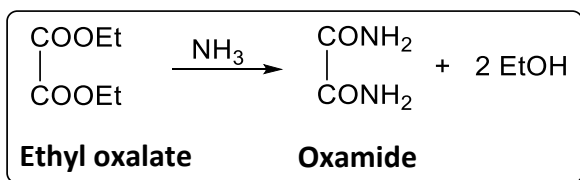


3- It cannot form anhydrides

4- Ester formation:



5- Ethyl oxalate reacts with ammonia to form oxamide.

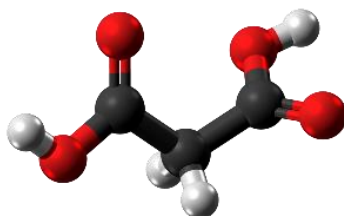


The main uses in industry

- Cleaning or bleaching, especially to remove rust.
- Oxalic acid is also an important reagent in chemistry - the lanthanides.
- Oxalic acid is used to restore old wood.
- Oxalic acid is rubbed on marble statues to increase luster

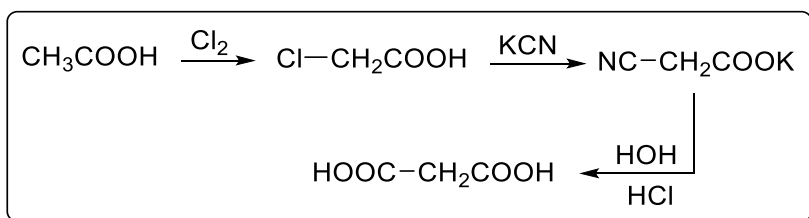
Oxalic is also used in the manufacture of ink and salts with antimony used in dyeing and printing.

Malonic acid

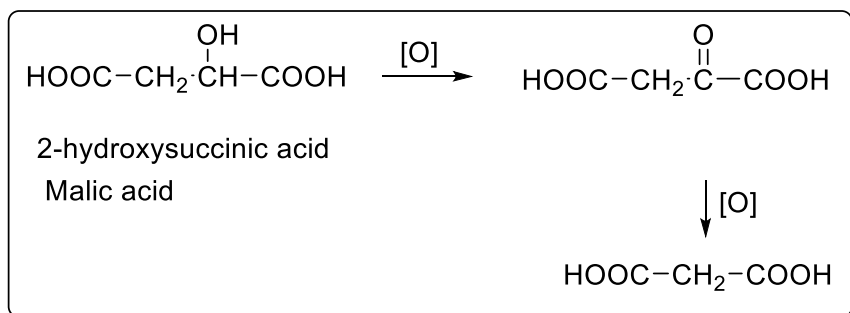


Synthesis:

1) From chloroacetic acid:



2) Oxidation of malic acid:



Physical properties:

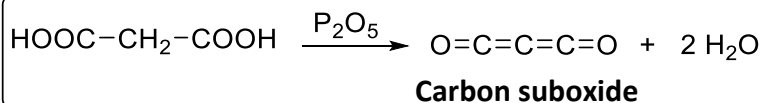
Solid – m.p 135.5 °C – Soluble in water and alcohol.

Chemical properties:

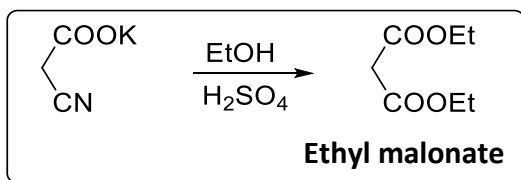
- 1- By heating at 130-150 °C in H₂SO₄: to give acetic acid and CO₂



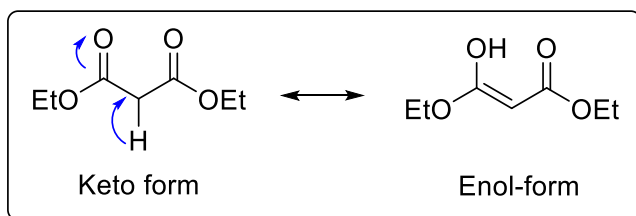
- 2- Heating in P₂O₅



- 3- Ester malonate formation:

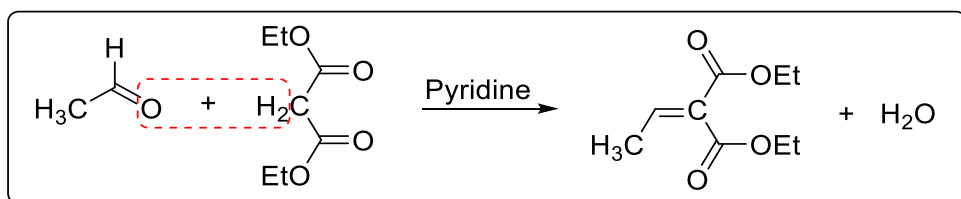


There are two forms for ethyl malonate (keto and enol form).

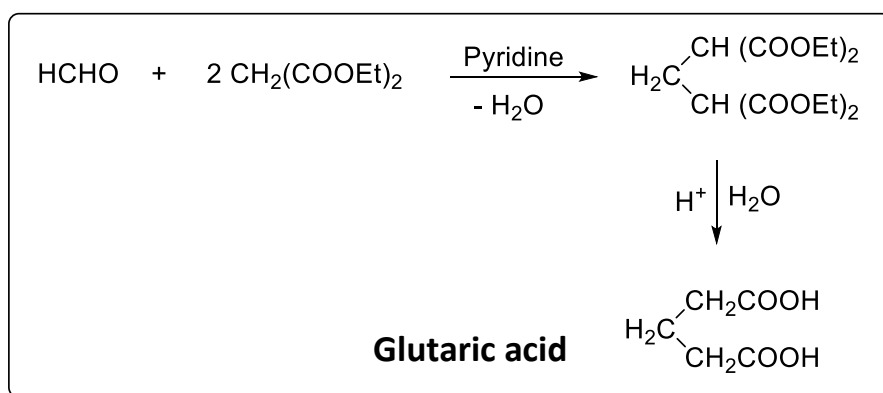


1) **تفاعل كيوفيناجل: knoevenagel reaction**

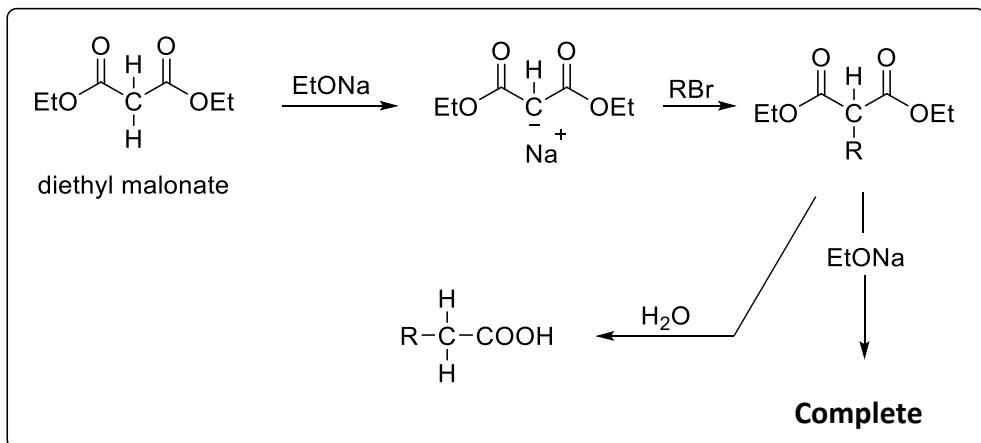
It is condensation reaction between the aldehyde and active compounds containing active methylene like ethyl malonate in weak basic catalyst like pyridine.



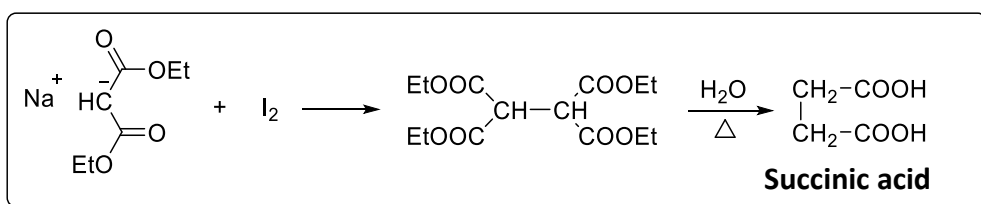
Also, glutaric acid can be formed by reaction of formaldehyde with diethyl malonate.



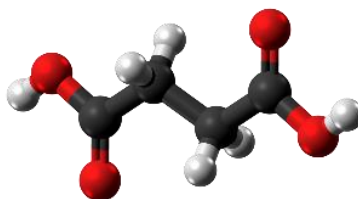
2) Addition of alkyl group in ester compound:



Succinic acid can be formed by reaction of ethyl malonate with I_2 .

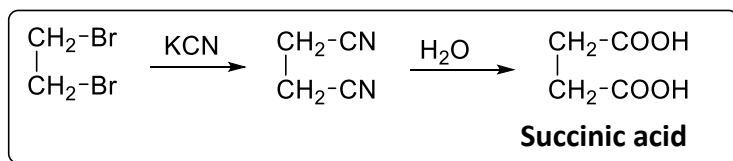


Succinic acid / Butanedioic



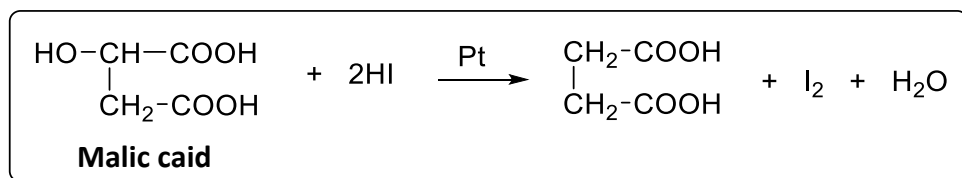
Synthesis:

1) From ethyl bromide:

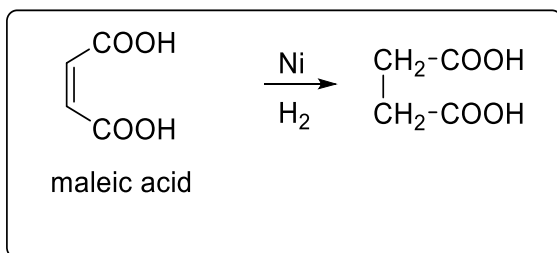


2) From ester malonate with I_2 as discussed previously.

3) By reduction of malic acid:



4) Or by reduction of maleic acid

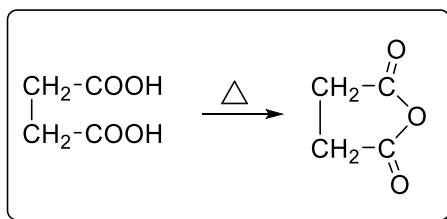


Physical properties:

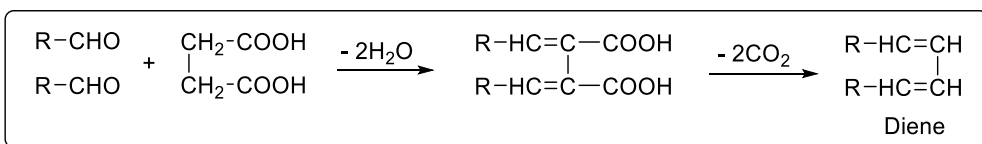
Whit crystals – m.p 185 °C – soluble in water and alcohol.

Chemical properties:

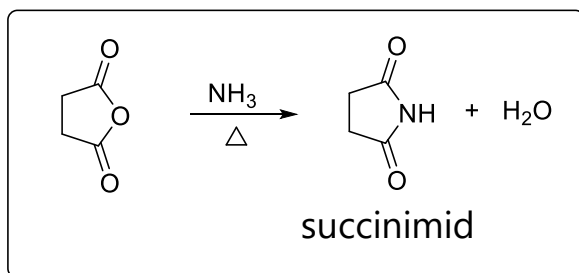
1) Anhydride formation by heating:



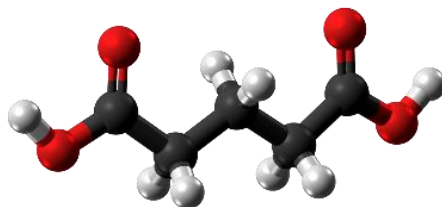
2) Condensation with aldehydes:



3) Succinic anhydride reacts with ammonia to form succinimide.

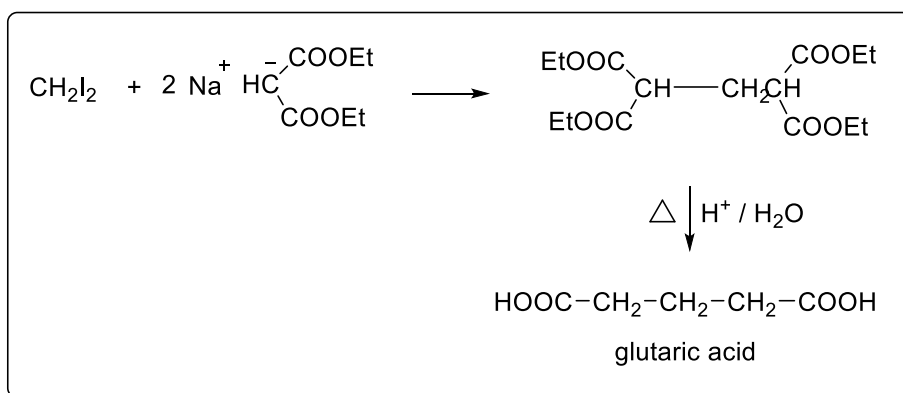


Pentanedioic acid / Glutaric acid



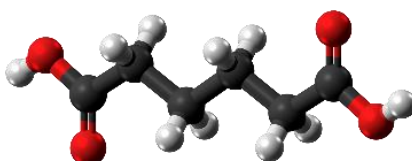
Synthesis:

- 1- From hydrolysis of related cyanide.
- 2- From condensation of formaldehyde with ester malonate.
- 3- From ethyl malonate with methylene iodide



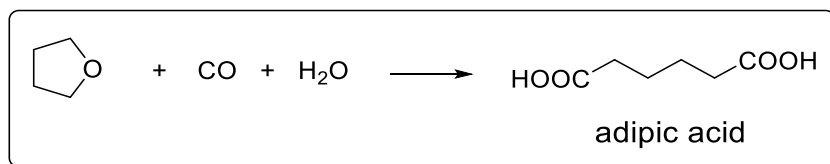
Glutaric acid has all acid properties, it can form anhydride, esters, and amides ,,,,,, ect.

Hexanedioic acid / Adipic acid



Synthesis:

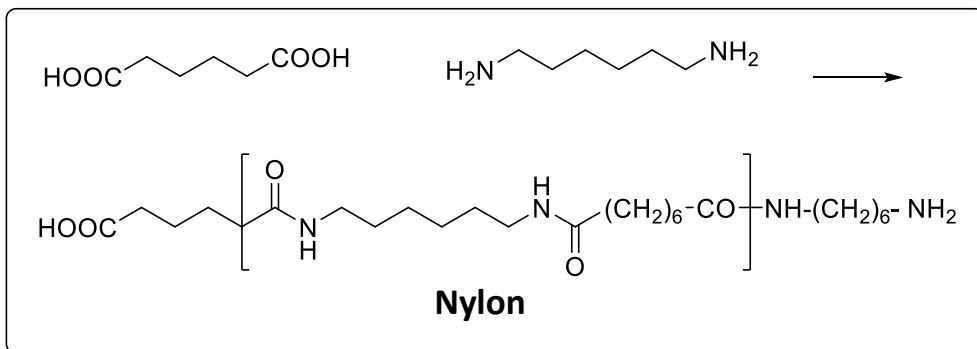
Additional to previous methods, it prepared in industry by reaction of tetrahydrofuran with carbon monoxide and water as shown:



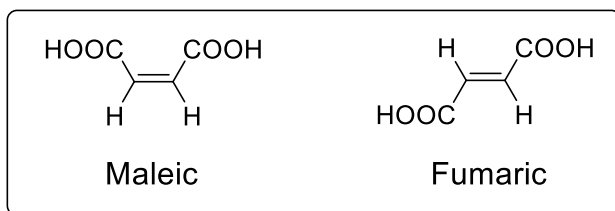
Physical properties: White crystals – mp 150 °C

Chemical properties:

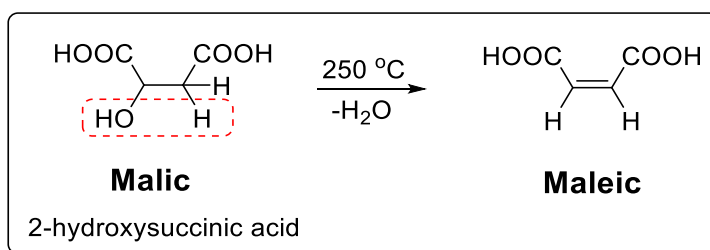
Nylon formation: It is the most important reaction:
Condensation of adipic acid with hexamethylenediamine

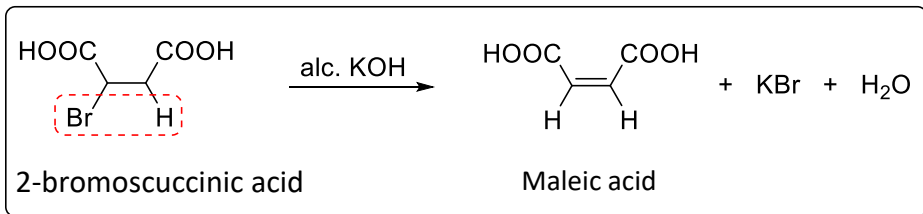


Unsaturated dicarboxylic acids

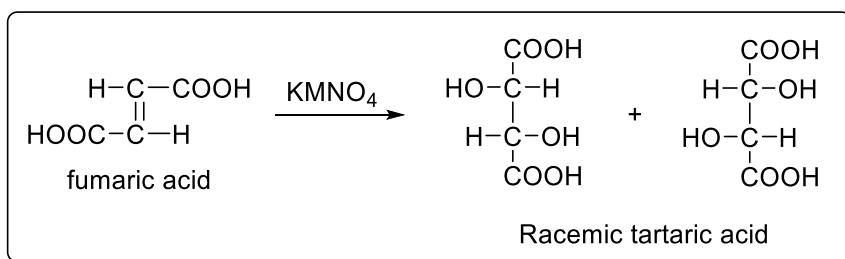
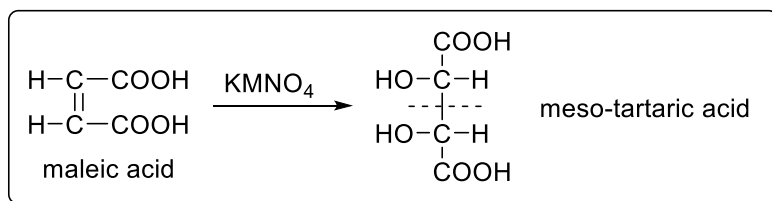
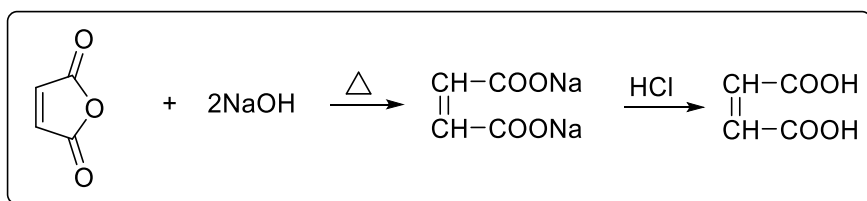
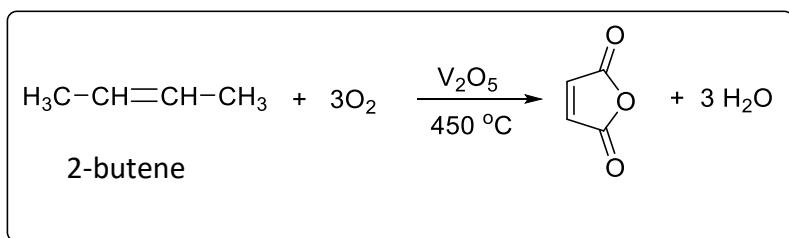


Synthesis of maleic acid:



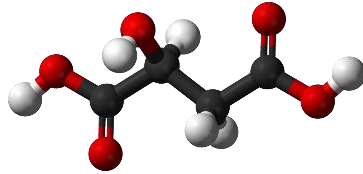


1) Oxidation of 2-butene with vanadium oxide.



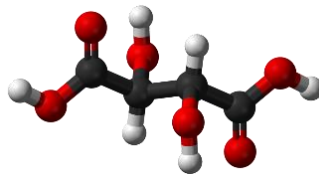
الأحماض الهيدروكسيلية ثنائية وثلاثية القاعدية

2-hydroxysuccinic acid / Malic acid حامض المالك



2,3-Dihydroxybutanedioic acid / حامض الطرطريك

Tartaric acid



Citric acid / حامض الستريك

