Carboxilic acid and derivatives **Assist proff: idries Muhson al mashkor**

Introduction

The combination of a carbonyl group and a hydroxyl on the same carbon atom is called a carboxyl group. Compounds containing the carboxyl group are distinctly acidic and are called carboxylic acids. The carboxyl group is one of the most widely occurring functional groups in chemistry and biochemistry. Not only are carboxylic acids themselves important, but the carboxyl group is the parent group of a large family of related compounds called carboxylic acid derivatives.

Classification and Nomenclature of carboxylic acids.

1. Classification of carboxylic acids.

Carboxylic acids are classified according to the substituent bonded to the carboxyl group. **An aliphatic** acid has an alkyl group bonded to the carboxyl group, while **an aromatic** acid has an aryl group. The simplest acid is formic acid, with a proton bonded to the carboxyl group. Fatty acids are long-chain aliphatic acids derived from the hydrolysis of fats and oils.

2. Nomenclature of carboxylic acids.

A. Common Names

Several aliphatic carboxylic acids have been known for hundreds of years, and their common names reflect their historical sources. **Formic acid** was extracted from ants: formica in Latin. **Acetic acid** was isolated from vinegar, called acetum ("sour") in Latin. **Propionic acid** was considered to be the first fatty acid, and the name is derived from the Greek protos pion ("first fat"). **Butyric acid** results from the oxidation of butyl aldehyde, which is found in butter: butyrum in Latin. **Caproic**($CH_3(CH_2)_4COOH$), **caprylic**($CH_3(CH_2)_6COOH$), and **capric acids** ($CH_3(CH_2)_8COOH$) are found in the skin secretions of goats: caper in Latin.

In common names, the positions of substituents are named using Greek letters. Notice that the lettering begins with the carbon atom adjacent to the carboxyl carbon, the α-carbon. With common names, the prefix iso- is sometimes used for acids ending in the $-CH(CH_3)_2$ grouping.

2. IUPAC Names:

The IUPAC nomenclature for carboxylic acids are obtained by dropping the final –e of the name of the alkane corresponding to the longest chain in the acid and by adding –oic acid uses the name of the alkane that corresponds to the longest continuous chain of carbon atoms. The carboxyl carbon atom is assigned number 1. The examples as follows:

	$HCOOH$	CH_3COOH	$CH_3(CH_2)_{10}COOH$
IUPAC name:	**methanoic acid**	**ethanoic acid**	**dodecanoic acid**
Common name:	**formic acid**	**acetic acid**	**lauric acid**

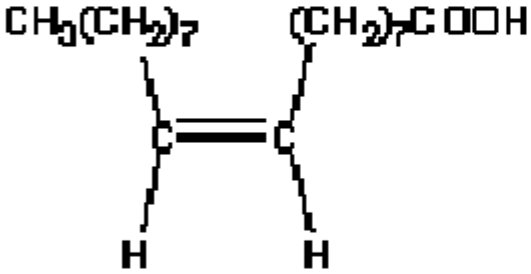
	$CH_3(CH_2)_{14}COOH$	$CH_3(CH_2)_{16}COOH$
IUPAC name:	**hexadecanoic acid**	**octadecanoic acid**
Common name:	**palmitic acid**	

stearic acid

Unsaturated acids

cis-$HO_2C—CH=CH—CO_2H$ Maleic acid

trans-$HO_2C—CH=CH—CO_2H$ Fumaric acid



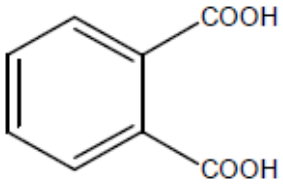
Oleic acid = cis-9-octadecenoic acid

75% of olive oil is oleic acid

DAA

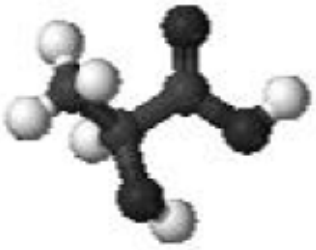
Some other acids with common names

- Diacids
  - Oxalic HOOC-COOH
  - Malonic $HOOC-CH_2-COOH$
  - Succinic $HOOC-CH_2CH_2-COOH$
  - Phthalic



- Hydroxyacid
  - Lactic acid

(S)-2-hydroxypropanoic acid



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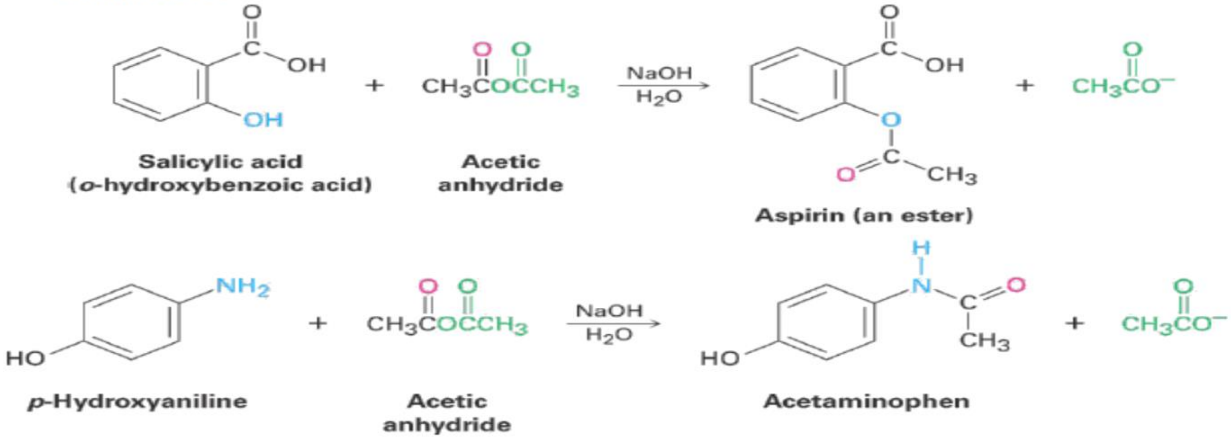
Acetylation

- Acetic anhydride forms acetate esters from alcohols and *N*-substituted acetamides from amines

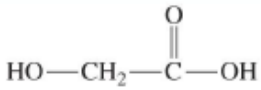
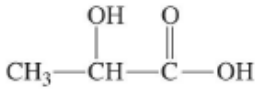
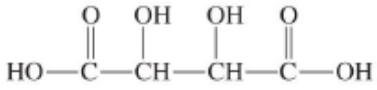
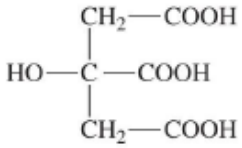
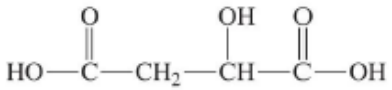


Alpha Hydroxy Acids (AHAs)

Alpha hydroxy acids (AHAs) are naturally occurring carboxylic acids with a hydroxyl group (–OH) on the carbon adjacent to the carboxyl group.

Alpha hydroxy acids (AHAs)

- are used to remove acne scars and age spots
- were used by Cleopatra, Queen of Egypt, who bathed in sour milk, which contains lactic acid, an AHA

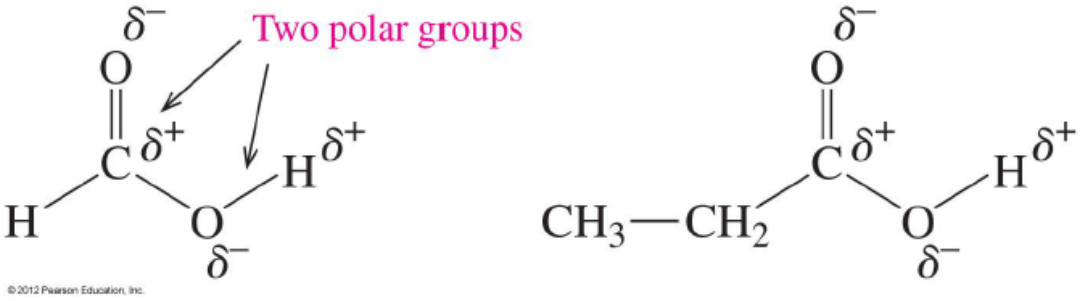
Alpha Hydroxy Acid (Source)	Condensed Structural Formula
Glycolic acid (sugar cane, sugar beet)	
Lactic acid (sour milk)	
Tartaric acid (grapes)	
Citric acid (lemons, oranges, grapefruit)	
Malic acid (apples, grapes)	

Polarity of Carboxylic Acids

Carboxylic acids are strongly polar because they have two polar groups

hydroxyl (–OH) and

carbonyl (C=O)



Solubility in Water

Carboxylic acids

- form hydrogen bonds with many water molecules
- with one to four carbon atoms are very soluble in water
- as the number of carbons increases, the solubility of the carboxylic acid in water is reduced

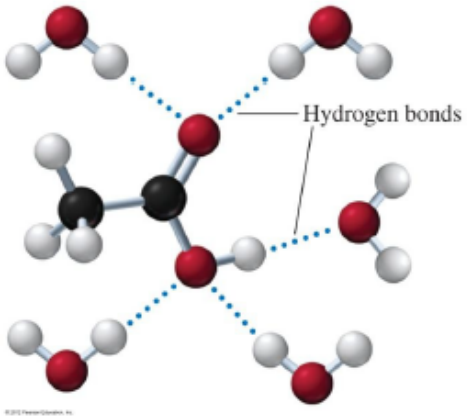


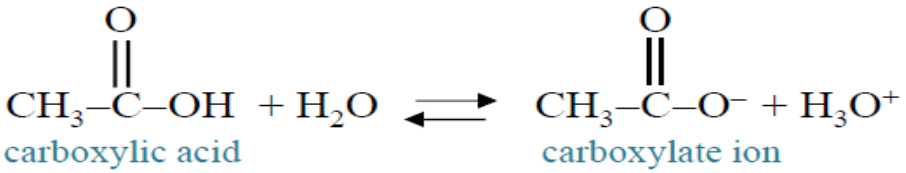
TABLE 14.2 Properties of Selected Carboxylic Acids

IUPAC Name	Condensed Structural Formula	Solubility in Water
Methanoic acid	HCOOH	Soluble
Ethanoic acid	$CH_3—COOH$	Soluble
Propanoic acid	$CH_3—CH_2—COOH$	Soluble
Butanoic acid	$CH_3—CH_2—CH_2—COOH$	Soluble
Pentanoic acid	$CH_3—CH_2—CH_2—CH_2—COOH$	Slightly soluble
Hexanoic acid	$CH_3—CH_2—CH_2—CH_2—CH_2—COOH$	Slightly soluble

Acidity of Carboxylic Acids

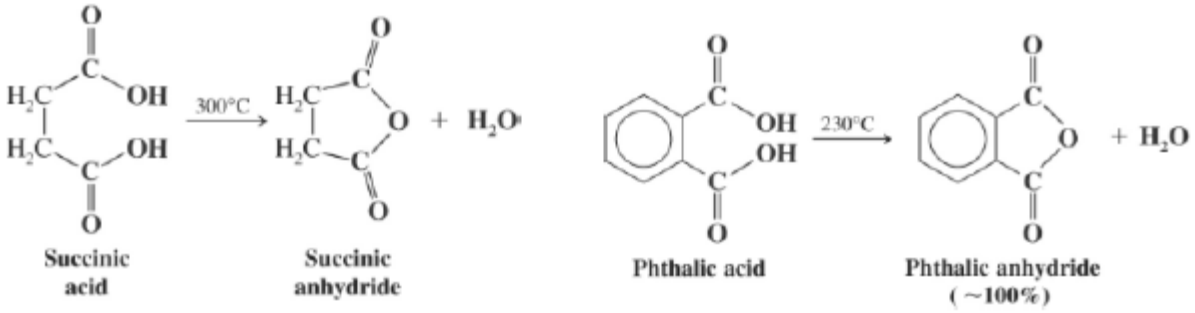
Carboxylic acids

- are weak acids
- ionize in water to produce carboxylate ions and hydronium ions
- can lose a proton because two oxygen atoms in carboxylate ion stabilize negative charge



carboxylic acid carboxylate ion

- **Cyclic anhydrides with 5- and 6-membered rings can be synthesized by heating the appropriate diacid**



- **Reactions of Carboxylic Acid Anhydrides**
  - **Carboxylic acid anhydrides are very reactive and can be used to synthesize esters and amides**
    - ➡ **Hydrolysis of an anhydride yields the corresponding carboxylic acids**

♦ Esters

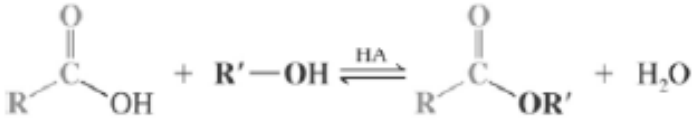
● Synthesis of Esters: Esterification

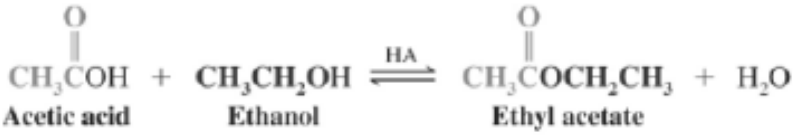
➡ Acid catalyzed reaction of alcohols and carboxylic acids to form esters is called Fischer esterification

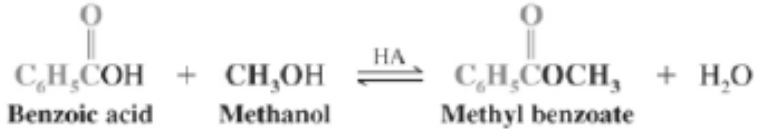
➡ Fischer esterification is an equilibrium process

★ Ester formation is favored by use of a large excess of either the alcohol or carboxylic acid

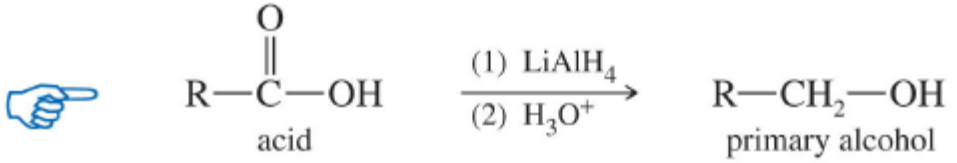
★ Ester formation is also favored by removal of water



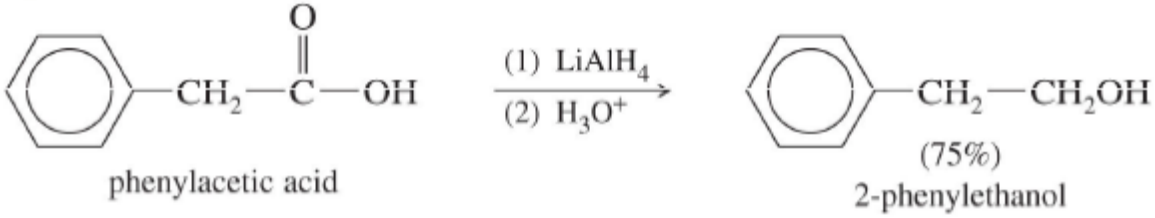




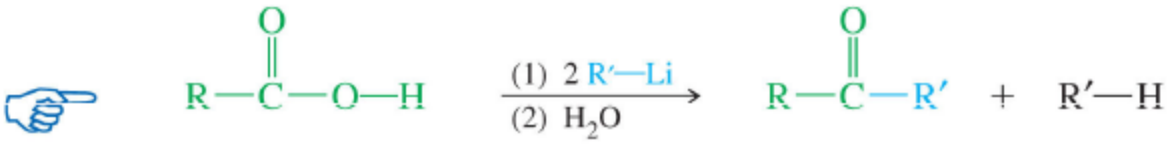
• Reduction of Acids to Primary Alcohols (20-13)



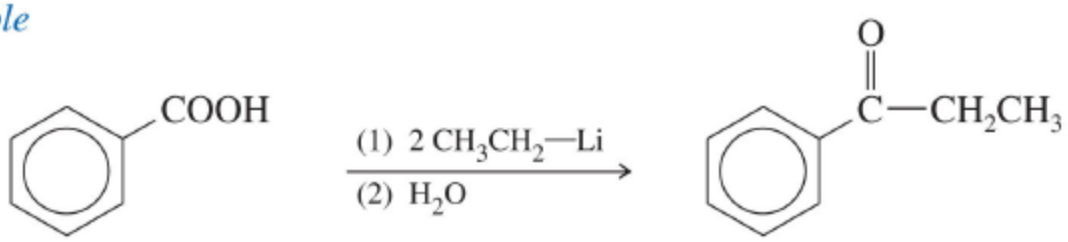
Example



- **Alkylation of Acids to form Ketones** (20-14)



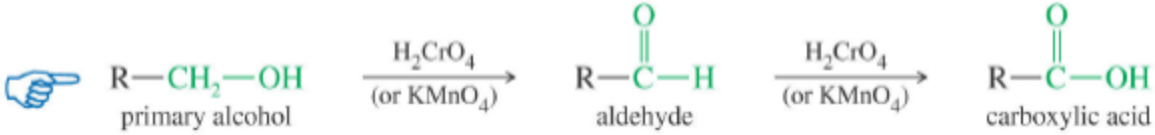
Example



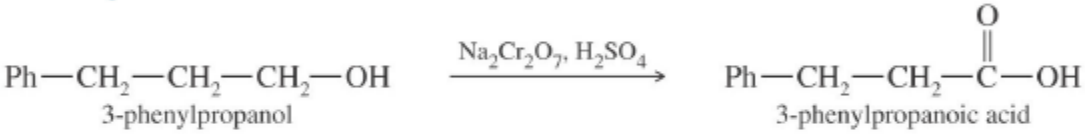
benzoic acid propiophenone

Synthesis of Carboxylic Acids (Review)

- **Oxidation**



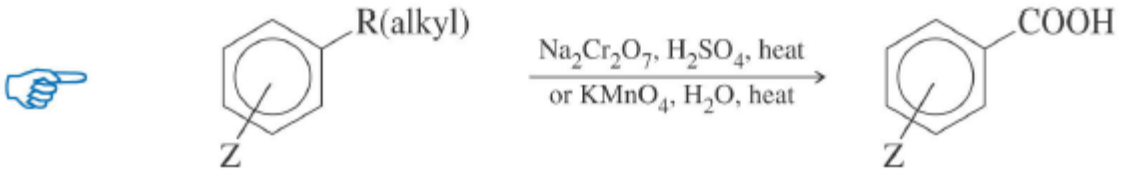
Example



Other reagents such as $KMnO_4$, HNO_3 etc… will also oxidize a 1° alcohol to the corresponding carboxylic acid.

- ## Oxidation of alkyl benzene

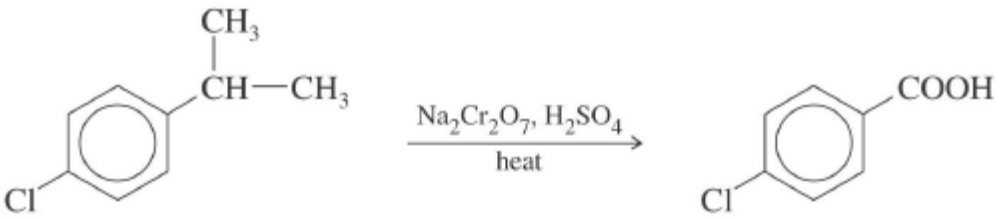
Also provides carboxylic acids as the product. Must have at least one benzylic hydrogen.



an alkylbenzene
(Z must be oxidation-resistant)

a benzoic acid

Example

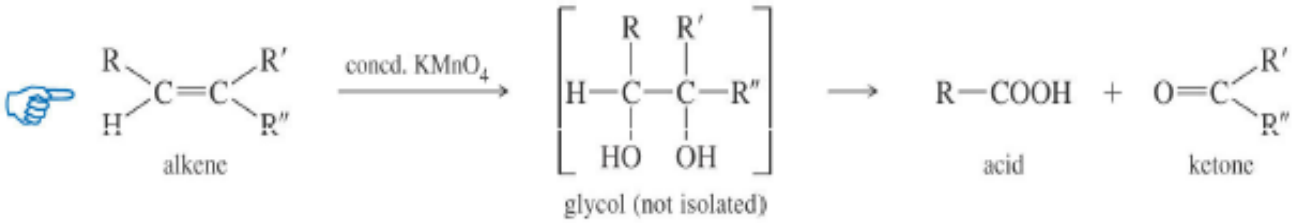


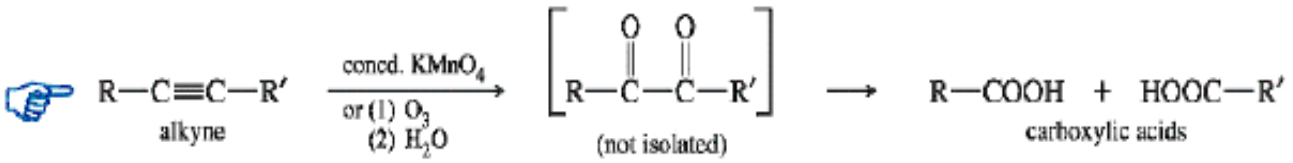
p-chloroisopropylbenzene

p-chlorobenzoic acid

- ## Oxidative cleavage

Alkenes and Alkynes can give carboxylic acid by oxidative cleavage: either with ozone or $KMnO_4$.





Example