
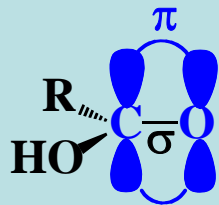


Chapter 18

Carboxylic Acids and Their Derivatives: Nucleophilic Addition-Elimination at the Acyl Carbon

Carboxylic acids are a family of organic compounds with the functional group  which is also written as $-\text{CO}_2\text{H}$ or COOH .

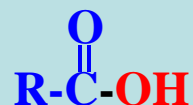
The carbon-oxygen double bond is made up of a σ -bond and a π -bond. The carbon atom is sp^2 hybridized, which explains the trigonal planar geometry at this center.



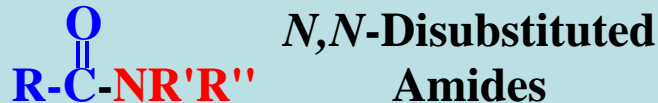
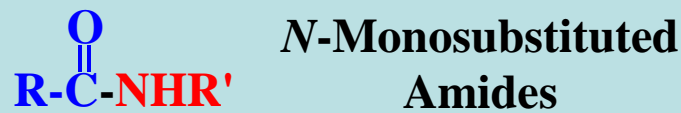
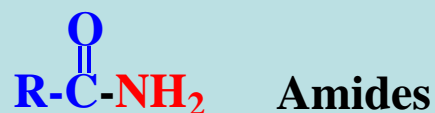
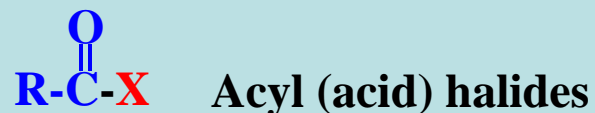
R may be alkyl, aryl or simply H

Carboxylic Acid Derivatives

The carboxyl group consists of two parts, the **acyl group** and the attached **hydroxyl group**:



The acid derivatives are compounds in which the hydroxyl group is replaced with another group or a halogen atom. The principal examples are:



Another class of carboxylic acid derivatives are the nitriles, which qualify because on hydrolysis, like all of the other derivatives above, they yield carboxylic acids.



Nomenclature of Carboxylic Acids

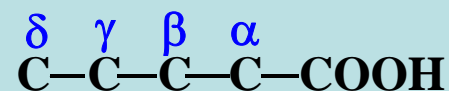
Common names are frequently used for the simpler carboxylic acids that have been known for hundreds of years.

HCOOH
Formic acid
(from Latin
formica, ant)

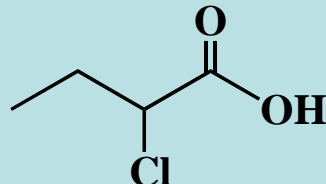
CH₃COOH
Acetic acid
(from Latin
acetum, vinegar)

CH₃CH₂CH₂COOH
Butyric acid
(from Latin
butyrum, butter)

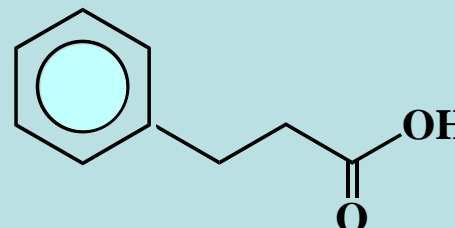
In common names, the positions of substituents are often given by α , β , γ ...



Examples



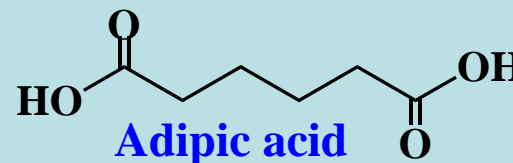
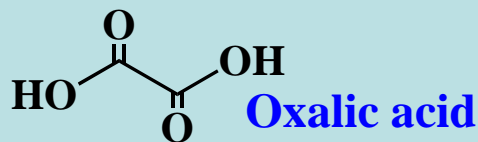
α -Chlorobutyric acid



β -Phenylpropionic acid

The simple dicarboxylic acids have common names, they are the ones usually used, and it is advisable to learn them at least through the six-carbon one. These are oxalic, malonic, succinic, glutaric, and adipic acid.

Examples

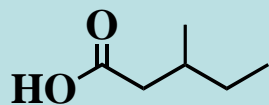


Systematic Names of Carboxylic Acids

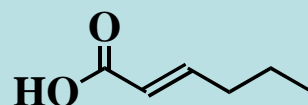
IUPAC systematic names are derived from the name of the longest-chain alkane present (the parent compound), dropping the final *-e*, and adding *-oic acid*.

Note: Count carboxyl carbon as part of the parent chain.

Examples

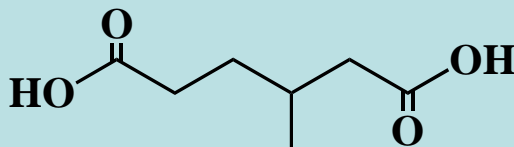


3-Methylpentanoic acid

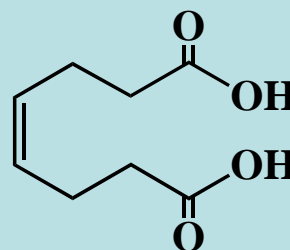


(E)-2-Hexenoic acid

Dicarboxylic acids can be named similarly although most have common names that are the ones usually used.



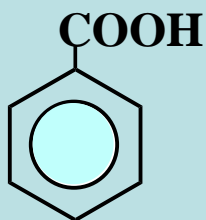
3-Methylhexanedioic acid



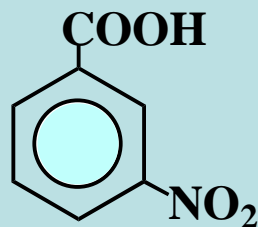
(Z)-4-Octenedioic acid

Aromatic Acids: Benzoic Acids

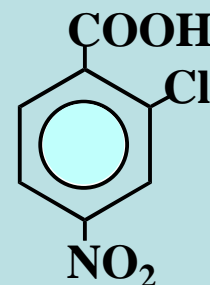
The carboxylic acids derived from benzene are named as derivatives of **benzoic acid**, using the standard notations to indicate positions of substituent groups.



Benzoic acid



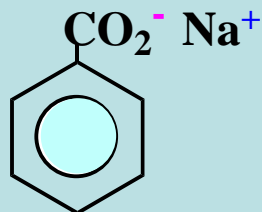
***m*-Nitrobenzoic acid**



2-Chloro-4-nitrobenzoic acid

Salts of Carboxylic Acids

To name a salt, use the name of the **cation** (sodium, ammonium, etc.) followed by the name of the acid with "**ic acid**" changed to "**ate**."



Sodium benzoate



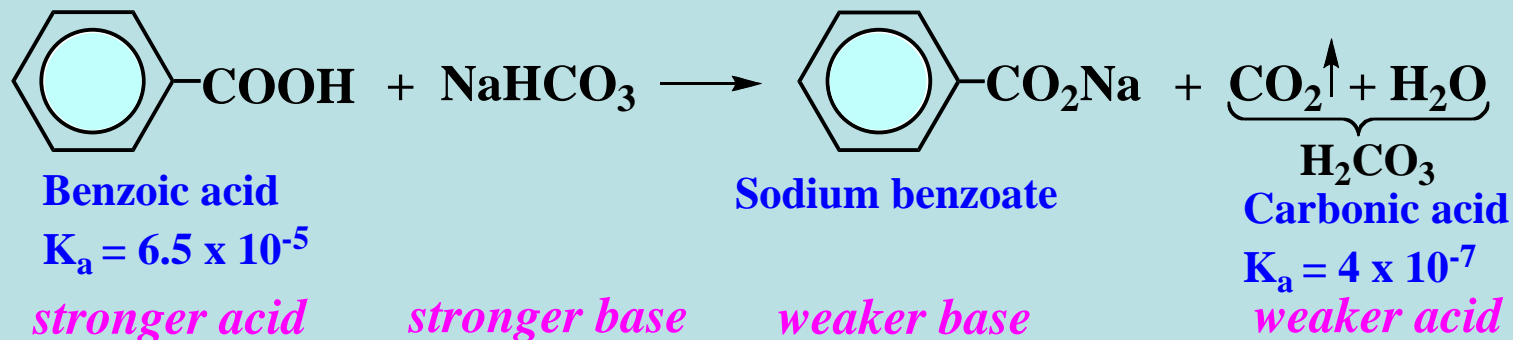
Magnesium propanoate

or

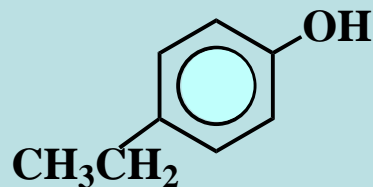
Magnesium propionate

Carboxylic Acids: Comparison with Phenols

Carboxylic acids are sufficiently acidic to react with an aqueous solution of sodium bicarbonate to produce their carboxylate salts:



Phenols are the hydroxyl derivatives of aromatic hydrocarbons, an example being:



A classic way to distinguish between carboxylic acids ($pK_a \sim 4-5$) and phenols ($pK_a \sim 10$) is by their solubility in an aqueous solution of sodium bicarbonate: Carboxylic acids will dissolve while (water insoluble) phenols will not. Both will dissolve in an aqueous solution of a strong base like NaOH.

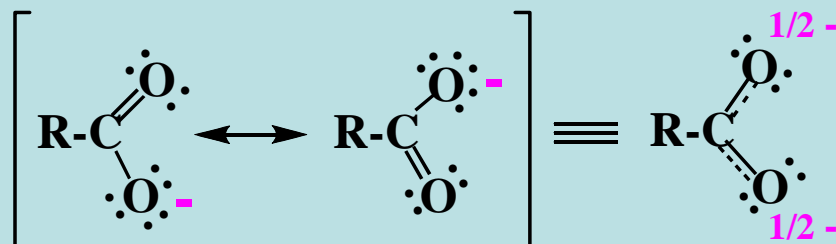
A Comparison of the Acid Strength of Carboxylic Acids and Alcohols

Carboxylic acids are considerably more acidic than alcohols in the absence of special electronic influences.



The enhanced acidity of carboxylic acids is attributed to the greater stability of the carboxylate anion compared with the alkoxide anion, which shifts the equilibrium more to the product side.

Resonance theory explains this stability through two equivalent resonance structures that contribute to the hybrid.



X-ray analysis of sodium formate shows equivalent C-O bond lengths of 1.27 Å, consistent with this picture of a resonance hybrid.

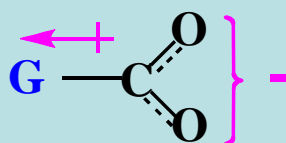
Effect of Substituents on Acidity

Any factor that stabilizes the anion more than it stabilizes the acid should **increase acidity** (decrease the magnitude of pK_a). Any factor that destabilizes the anion relative to the acid should **decrease acidity**.

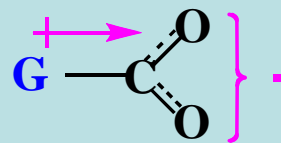


Electronic Influences

The electronic effect of a substituent **G** operates more strongly on the anion (charged species) than on the carboxylic acid (neutral species).



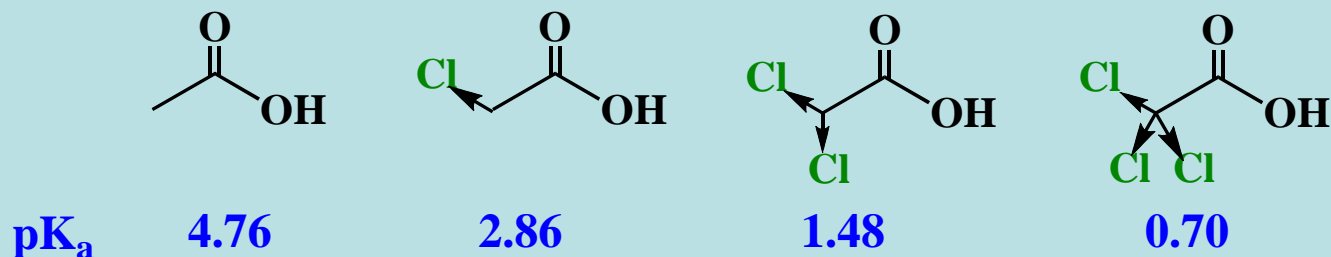
Electron withdrawal
Stabilizes the anion and
increases acidity



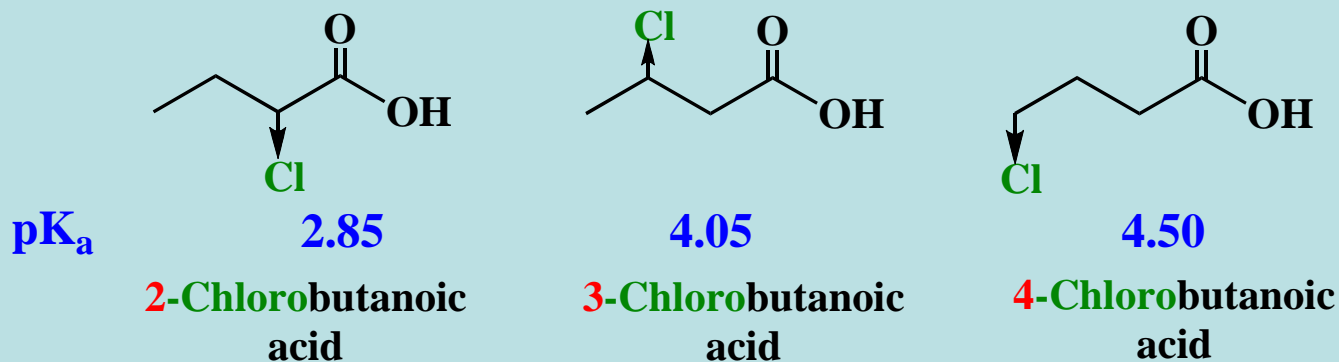
Electron release
Destabilizes the anion
and decreases acidity

Some Examples of Substituent Effects

Electron-withdrawing α -substituents increase acidity:

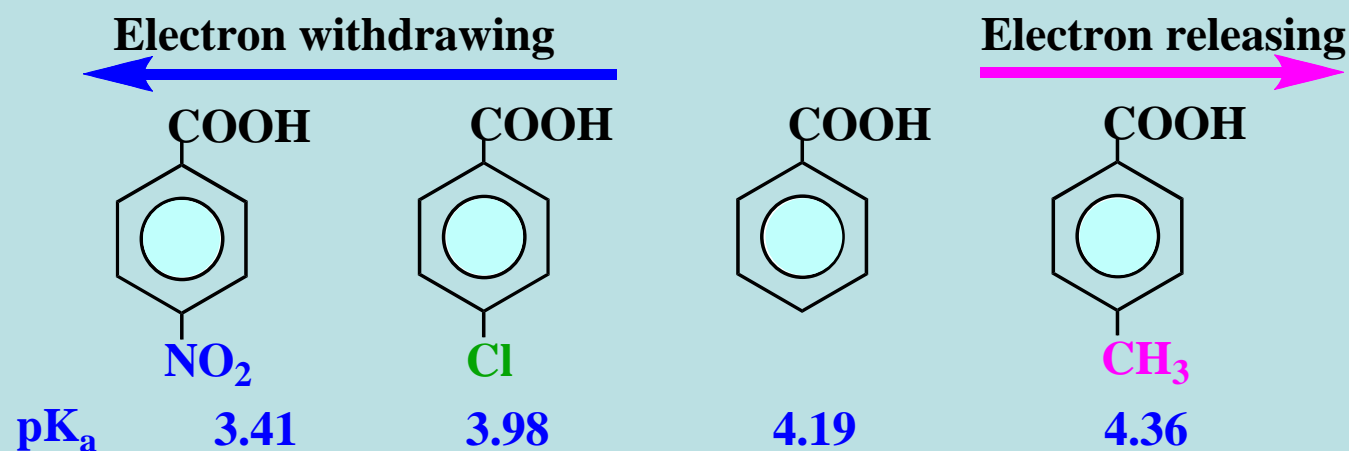


The more remote an electron-withdrawing substituent is from the carbonyl group, the less its effect:



Substituent Effects in Benzoic Acids

Substituents introduced into the *para* position of a benzoic acid affect the acidity as expected for the electronic influence on the stability of the benzoate anion.



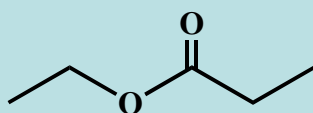
The substituent influence is from a combination of resonance and inductive effects because direct resonance interaction between the benzene ring and the carboxylate anion is not important.

Esters

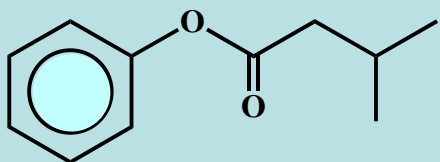
Their two-part names follow the pattern:

[Name of alkyl or aryl group derived from parent alcohol] [Name of carboxylate ion derived from parent acid]

Examples:



Made from ethanol and propanoic acid, so name is **ethyl propanoate**.

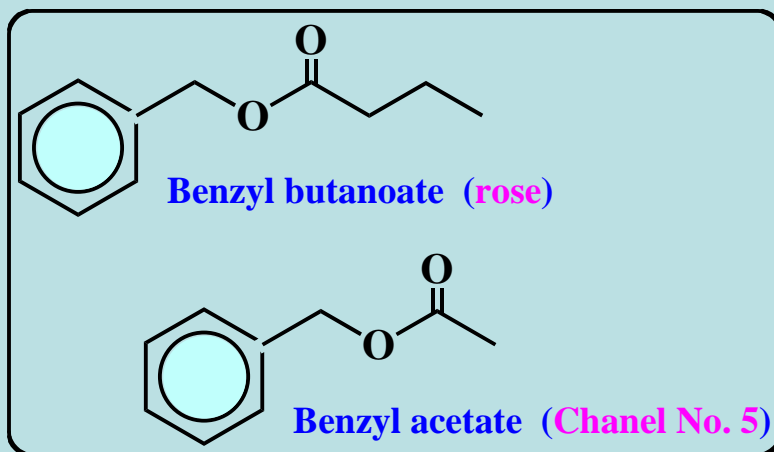
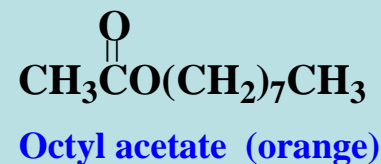
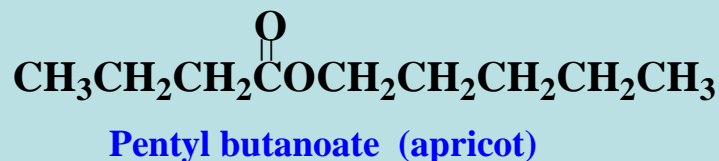
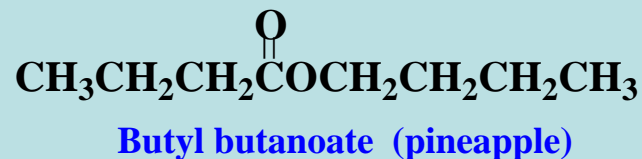
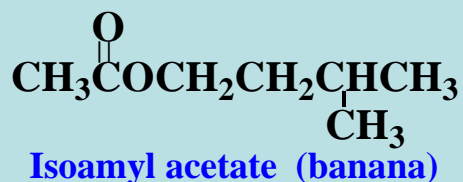


Made from phenol and 3-methylbutanoic acid, so name is **phenyl 3-methylbutanoate**.

Esters are hydrogen-bond acceptors, enhancing their water solubility, but they are not hydrogen-bond donors, lacking a hydrogen on oxygen. Consequently they cannot associate and so have low boiling points and high volatility. Fortunately, they have pleasant, fruit-like odors.

Esters as Perfumes and Flavoring Agents

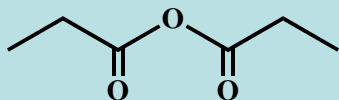
Many esters have pleasant odors and tastes and are used in perfumes and as flavoring agents. A number of these compounds occur in nature where they are responsible for the characteristic odor of fruits.



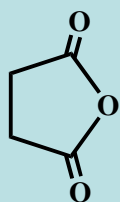
Carboxylic Anhydrides

As the term implies, they are prepared by removing a molecule of water from between two carboxyl groups. They are usually named from the parent acid, simply by replacing the word "acid" with "anhydride."

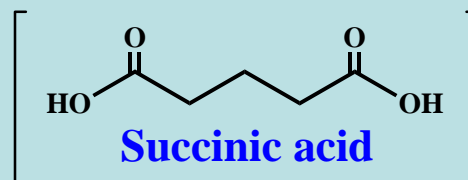
Examples:



Parent acid is propionic acid, so this is **propionic anhydride**.



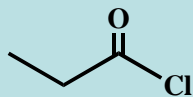
Parent acid is succinic acid, so this is **succinic anhydride**.



Acyl Chlorides (Acid Chlorides)

These are named from the parent acid by dropping "-ic acid" from its name and replacing it with "-yl chloride."

Example:



Propionyl chloride

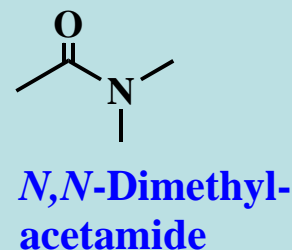
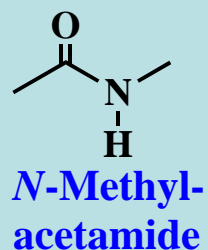
NOTE: Both of the above types of derivatives have intermolecular attractions similar to those of esters, and so they have boiling points in the same range as esters of comparable size.

Both of these types of derivatives are important, powerful donors of their acyl groups and find much use in synthesis.

Amides

The amides considered here need to be distinguished from the metal amide bases like NaNH_2 and $\text{LiN}(\text{i-Pr})_2$ studied earlier. The present ones are of general structure RC(=O)NR'R'' where the different R's may be H's, alkyl groups, or aryl groups. They are named by dropping "-ic acid" from the name of the parent acid and adding "amide."

Examples:



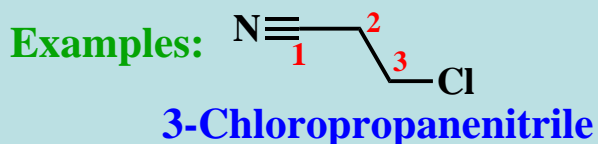
MP (°C)	82	28	-20
BP (°C)	221	205	166

Note how both MP and BP decrease with decreasing opportunity for intramolecular hydrogen bonding.

Nitriles

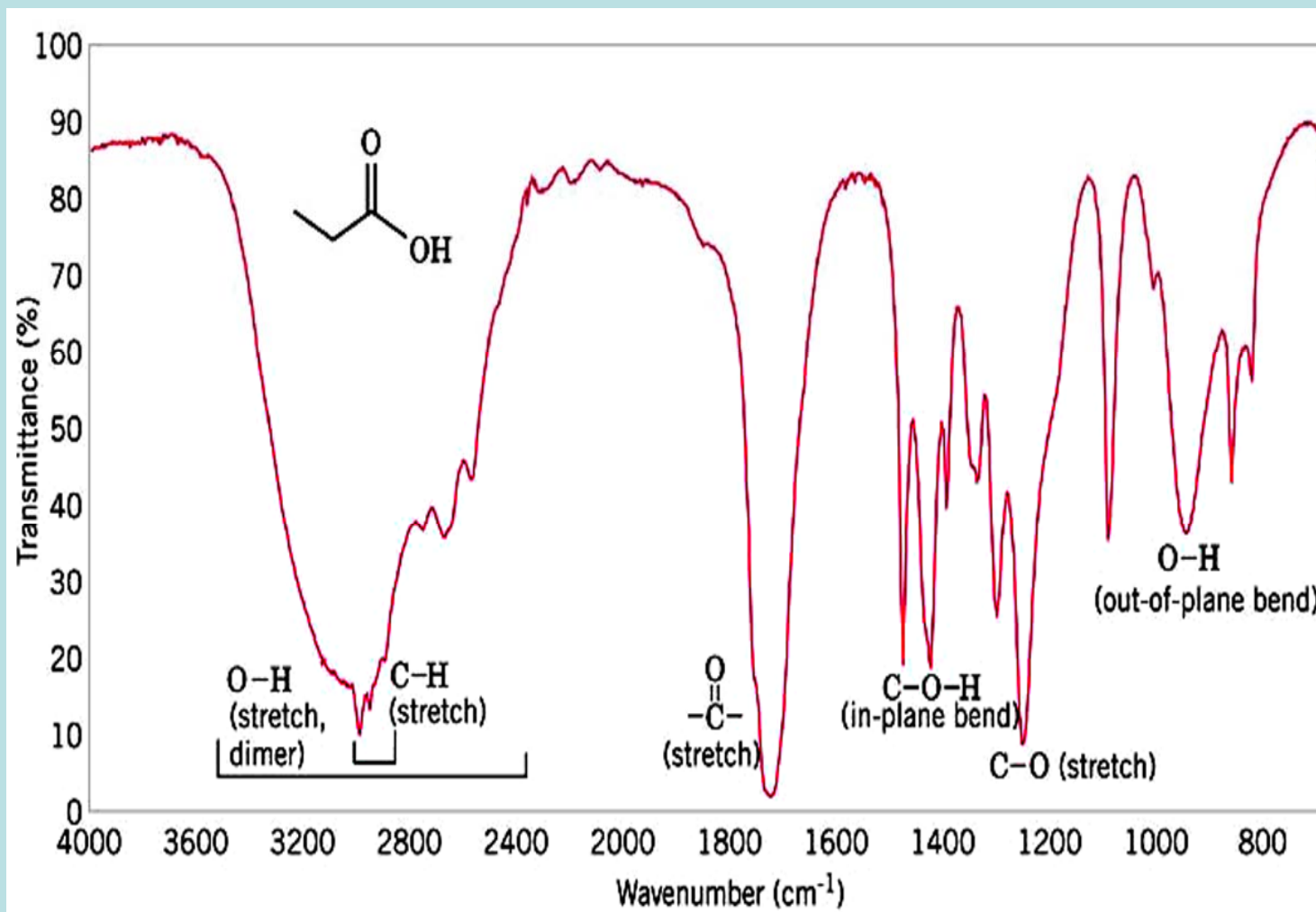
These derivatives are named by adding the suffix "-nitrile" to the name of the parent hydrocarbon, with the C of the CN group counting as part of the parent. Note: chain numbering begins with the nitrile C.

When the CN is attached to a cyclic parent, add "carbonitrile" to the parent name.



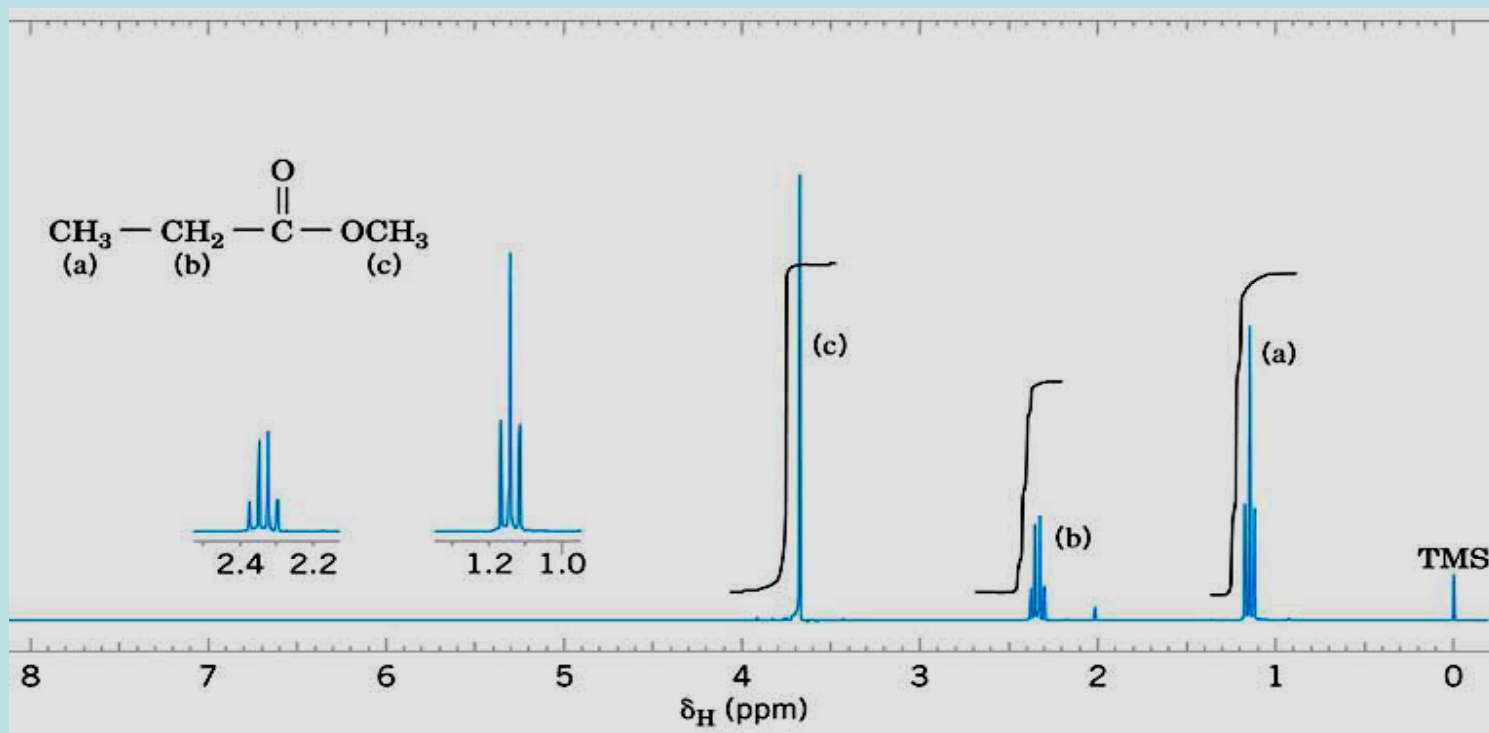
IR Spectrum of Propanoic Acid ("neat", i.e., without dilution)

The C=O stretch frequency is at 1715 cm^{-1} ; in the absence of hydrogen bonding (which enhances carbonyl single-bond character) it would be at about 1760 cm^{-1} .



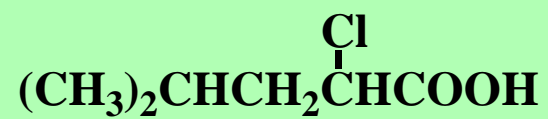
^1H NMR Spectroscopy

The acidic proton of a carboxylic acid is highly deshielded and appears far downfield in the range δ 10-12. Protons on a carbon α to a carbonyl appear in the δ 2.0-2.5 region. The chemical shifts, splitting patterns, and relative intensities of the H resonances of a typical ester are depicted in this methyl propionate spectrum.

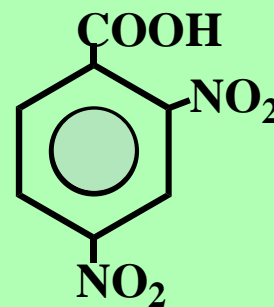


Quiz 18.01

Provide IUPAC (systematic) names for the following carboxylic acids.



2-Chloro-4-methylpentanoic acid



2,4-Dinitrobenzoic acid

Quiz 18.02

In each pair of compounds below, circle the stronger carboxylic acid.

