Organic Chemistry II Drill (CHEM2220D) Module 7. Carboxylic Acids and Derivatives

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CARBOXYLIC ACIDS AND THEIR DERIVATIVES

A STUDENT SHOULD BE ABLE TO:

1. Give the IUPAC name given the structure, and draw the structure given the name, of carboxylic acids and their metal salts, acyl chlorides, esters, and amides. Give the common name of simple nitriles. Also, draw the structure given any of the following common names: phthalic, oxalic, malonic, succinic and glutaric acids; formic and acetic acids and their salts, chlorides, esters, and amides; and acetic and phthalic anhydrides.

2. Predict the solubility of carboxylic acids and their derivatives in water and in various acidic and basic solutions. Compounds containing previously studied functional groups may also be included.

3. Predict the relative acidity and basicity of compounds and ions. Important criteria include:

The normal order of acidity of functional groups is:

$$\text{RSO}_3\text{H} > \text{HX} > \text{RCO}_2\text{H} > \text{ArOH} > \text{RSH} > \text{H}_2\text{O} > \text{ROH} > \text{RC} = \text{CH} > \text{H}_2 > \text{RNH}_2 > \text{R} = \text{CH}_2 > \text{RH}$$

Within a functional group family, conjugate acids are stronger acids than conjugate bases. That is: $\text{H}_3\text{X}^+ > \text{H}_2\text{X} > \text{HX}^-$

Within a functional group family, electron-donating (activating) groups give stronger bases, and electron-withdrawing (deactivating) groups give stronger acids. The effect of an electron-withdrawing group depends on its proximity to the carboxylic acid moiety.

The stronger the acid, the weaker its conjugate base (and vice versa).

4. Predict the product of reactions giving rise to carboxylic acids (many of these are review), and the reactions of carboxylic acids and their derivatives, when given starting materials and reaction conditions. Important reactions include:

- Acid-base reactions. Stronger acid + stronger base $\rightarrow$ weaker acid + weaker base.
- Oxidation of $1^\circ$ alcohols, aldehydes, alkylbenzenes, and alkynes.
- Hydrolysis of nitriles.
- Reductions with lithium aluminum hydride (LAH).
- Carboxylation (carbonation) of Grignard reagents.
- Nucleophilic acyl substitution (interconversion of carboxylic acids and their derivatives).
- Reactions of acyl halides and esters with $\text{R}_2\text{CuLi}$ and $\text{LiAl(OR)}_3\text{H}$

5. Predict and explain experimental results from your knowledge and understanding of nucleophilic acyl substitution mechanisms.

6. Use the reactions of #4 above, plus others learned earlier, to propose syntheses of carboxylic acids and related compounds.

7. Predict and interpret spectra and solubility test results to identify unknown carboxylic acids and their derivatives.
Solubility Tests for Monofunctional Compounds

This section tells you how to predict results for known compounds and use results to classify unknowns. Some are useful as stand-alone tests, but compounds that dissolve in water are soluble in all of the other reagents listed here; follow the whole scheme to get the best possible information. For these tests, “soluble” means “one drop of unknown will dissolve in one mL of solvent”. Compounds that are “insoluble” may still dissolve in a large volume of water.

Solubility in water

If a compound is soluble in water, the compound has about four carbons or less and contains N, O, or more than one polar functional group. If the compound contains five or six carbons, it may be soluble (slightly soluble). If the compound contains six carbons or more, it will be insoluble if there is only one functional group, but may be soluble with multiple groups. If the compound is soluble, the solution is then tested with litmus paper.

- If the solution turns blue litmus red, the unknown is a carboxylic acid.
- If the solution turns red litmus blue, the unknown is an amine.
- If the solution is neutral to litmus, the unknown includes a neutral O- or N-containing functional group such as an alcohol, ether, aldehyde, ketone, ester, or amide.

If the compound is insoluble in water, go on to the next solubility test.

Solubility in 5% NaOH

If the compound is soluble in 5% NaOH but insoluble in water, it is acidic, either a phenol (ArOH) or a carboxylic acid (RCO₂H). This is reaction solubility, not “like-dissolves-like” solubility; the alkaline test solution reacts with acidic compounds to give ionic, water-soluble products. You must run the water solubility test first for this test to be useful; 5% NaOH is 95% water, and compounds that dissolve in water also dissolve in 5% NaOH.

To distinguish between phenols and carboxylic acids, you can use the NaHCO₃ solubility test (next). If the compound is insoluble in 5% NaOH, use the 5% HCl solubility test.

Solubility in 5% NaHCO₃

Sodium bicarbonate is a weaker base than NaOH. This is another reaction-solubility test; bicarbonate ion reacts with carboxylic acids but not with phenols to produce water-soluble salts. The reaction also generates carbon dioxide, and the visible bubbles make this a useful stand-alone test for carboxylic acids.

Solubility in 5% HCl

This is yet another reaction-solubility test. Basic organic compounds (amines) react with the acid to give water-soluble ionic products. As with the 5% NaOH test, it is necessary to test with water first, for the same reason.

If the compound is insoluble in 5% HCl, use the next (and last) solubility test.

Solubility in concentrated H₂SO₄

Alkenes, alkynes, and compounds that contain N and O are protonated by this extremely powerful acid, and the ionic products of these reactions dissolve. Concentrated sulfuric acid is approximately 94% acid. Compounds that contain only alkyl groups, halogen atoms, and benzene rings (RH, RX, ArH, ArX) will fail to dissolve.
To best prepare for this module, please work appropriate Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES FOR THIS UNIT SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

1.1 Draw the structure of each of the following compounds.
   a) malonic acid  
   b) acetic anhydride  
   c) sodium formate
   d) acetonitrile  
   e) phthalic anhydride  
   f) dimethyl succinate

1.2 Name each of the following compounds.
   a) (CH₃)₃CCH₂COOH  
   b) 
   c) 
   d)  
   e)  
   f) 

2.1 Which of the following compounds is most soluble in water?
   a) CH₃CH₂COOCH₃  
   b) CH₃COOCH₂CH₃  
   c) CH₃CH₂COOH  
   d) CH₃(CH₂)₃CHO

2.2 Which of these compounds (a) does not dissolve in H₂O but does dissolve in 5% NaOH(aq)? (b) does not dissolve in H₂O but does dissolve in 5% HCl(aq)?
   a) CH₃CH₂CH₂CO₂CH₂CH₃  
   b) CH₃CH₂CO₂H  
   c) CH₃CH₂NHCH₃  
   d) C₆H₅CH₂CO₂H  
   e) C₆H₅CH₂NH₂  
   f) C₆H₅CH₂OH

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3.1 Which of the following compounds is the strongest acid?

a) COOH  b) SO₃H  c) OH  d) CH₂OH

3.2 Which of the following compounds is the weakest acid?

a) COOH  b) COOH  c) COOH  d) COOH

3.3 Which of the following compounds is the weakest base?

a) CO₂⁻  b) CO₂⁻  c) O⁻  d) O⁻

3.4 Which of the following compounds is the strongest acid?

a)  b)  c)  d)

4. Predict the product(s) of each of the following reactions.

a) \( \text{CH}_3\text{NH}_2 \quad \text{room temp.} \quad \text{CO}_2\text{H} \)
4. continued

b) \[ \text{Br} \quad \text{Mg ether} \rightarrow \text{CO}_2 \rightarrow \text{H}_3\text{O}^+ \]

c) \[ \begin{align*} \text{H}_3\text{C} & \quad \text{1. KMnO}_4, \cdot \text{OH}, \\
\text{Cl} & \quad \text{H}_2\text{O, heat} \\
\text{CH}_2\text{CH}_3 & \quad \text{2. H}_3\text{O}^+ \end{align*} \]

d) \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \quad \text{NaCN} \rightarrow \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ \]

e) \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H} \quad \begin{align*} & \text{1. SOCl}_2 \\
& \text{2. ex. CH}_3\text{CH}_2\text{MgBr} \\
& \text{3. H}_2\text{O} \end{align*} \]

f) \[ \text{Cl} \quad \text{(CH}_3\text{)}_2\text{CuLi} \]

g) \[ \text{NH}_2 \quad \text{H}_3\text{O}^+, \text{H}_2\text{O, heat} \]

h) \[ \text{1. LiAlH}_4 \\
\text{2. H}_3\text{O}^+ \]

i) \[ \text{CH}_3\text{CH}_2\text{C\equivCCH}_3 \quad \text{O}_3 \rightarrow \text{Zn, H}_2\text{O} \]

j) \[ \text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2 \quad \begin{align*} & \text{1. O}_3 \\
& \text{2. DMS} \end{align*} \]
5. Propose a mechanism for each of the following reactions. Include lone pairs, intermediates and curved arrows.

a) \[ \text{Cl}_2 + 2 \text{OH}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} \]  

b) \[ \text{Cl}_2 + \text{CH}_3\text{O}^- \rightarrow \text{Cl}^- + \text{CH}_3\text{O} \]  

c) \[ \text{OH}_2 + \text{CH}_3\text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{O} \]  

d) \[ \text{OH}_2 + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{OH} + \text{CH}_3\text{O} \]
6. Propose a synthesis of each of the indicated compounds from the given starting material and any other needed reagents.

   a) methyl benzoate from toluene

   b) \[
   \text{from}
   \]

   c) \[
   \text{from}
   \]

   d) benzamide from styrene

   e) \[
   \text{from}
   \]

   f) ethyl benzoate from bromobenzene

   g) \[
   \text{from}
   \]
7.1 For these questions, choose the answer from the list of possible compounds.

a) Which of the following compounds has a broad peak in its IR spectrum in the 2500-3500 cm\(^{-1}\) region, and gives an aqueous solution that turns blue litmus red?

b) Which one gives a broad, strong absorption peak in its IR spectrum near 3400 cm\(^{-1}\), is insoluble in water and 5\% NaOH\(_{\text{(aq)}}\), but is soluble in conc. H\(_2\)SO\(_4\)?

c) Which one is insoluble in water, and soluble in both 5\% NaOH\(_{\text{(aq)}}\) and 5\% NaHCO\(_3\)\(_{\text{(aq)}}\)?

d) Which one has only one peak in its proton NMR spectrum?

The possible answers are:

\[
\begin{array}{cccc}
\text{A} & \text{B} & \text{C} & \text{D} & \text{E} \\
\text{CH}_3\text{CO}_2\text{H} & \text{H}_3\text{C} & \text{C} & \text{CH}_3 & \text{COOH} \\
& & \text{C} & \text{OH} & \text{C} \\
& & & \text{CH}_2\text{OH} & \text{CH}_2\text{OH} \\
\end{array}
\]

7.2 Of the following compounds: a) which one turns blue litmus red when dissolved in water? b) Which is neutral to litmus when dissolved in water? c) Which is insoluble in water but soluble in 5\% NaOH\(_{\text{(aq)}}\) and 5\% NaHCO\(_3\)\(_{\text{(aq)}}\)? d) Which is insoluble in both water and 5\% NaOH\(_{\text{(aq)}}\)?

\[
\begin{array}{cccc}
\text{A} & \text{B} & \text{C} & \text{D} & \text{E} \\
& \text{CO}_{2}\text{H} & \text{OH} & \text{CH}_2\text{OH} & \text{CH}_3\text{CO}_2\text{H} \\
\text{C}_6\text{H}_5 & \text{C}_6\text{H}_5 & \text{C}_6\text{H}_{11} & \text{CH}_3\text{CH}_2 & \text{CH}_3 \\
\end{array}
\]

7.3 Identify the following unknown from the given spectroscopic information.

\[\text{C}_4\text{H}_8\text{O}_3\]

IR: broad peak in 2500-3500 cm\(^{-1}\) region, and a peak at 1715 cm\(^{-1}\)

\(^1\text{H}\) NMR:
- triplet, \(\delta\) 1.27, 3H
- quartet, \(\delta\) 3.66, 2H
- singlet, \(\delta\) 4.13, 2H
- singlet, \(\delta\) 10.95, 1H

7.4 Which of the compounds below fits these data?

\(^1\text{H}\) NMR:
- doublet, \(\delta\) 1.4, 6H
- multiplet, \(\delta\) 2.2, 1H
- doublet, \(\delta\) 4.1, 2H
- multiplet, \(\delta\) 7.1, 5H

\[
\begin{array}{cccc}
a) & b) & c) & d) \\
\text{C}_6\text{H}_5 & \text{CO}_2\text{H} & \text{CO}_2\text{H} & \text{CO}_2\text{H} \\
& \text{CH}_3 & \text{C}_6\text{H}_5 & \text{CH}_3\text{CH}_2 \\
& \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\end{array}
\]

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SOLUTIONS TO SAMPLE PROBLEMS:

1.1

a) malonic acid
\[ \begin{array}{c}
\text{HO} \\
\text{C} \\
\text{C} \\
\text{O} \\
\text{OH}
\end{array} \]

b) acetic anhydride
\[ \begin{array}{c}
\text{C} \\
\text{O} \\
\text{C} \\
\text{O}
\end{array} \]

c) sodium formate
\[ \begin{array}{c}
\text{H} \\
\text{O} \\
\text{Na}
\end{array} \]

d) acetonitrile
\[ \text{N} \equiv \text{C} \text{CH}_3 \]

e) phthalic anhydride
\[ \begin{array}{c}
\text{O} \\
\text{C} \\
\text{O}
\end{array} \]

f) dimethyl succinate
\[ \begin{array}{c}
\text{O} \\
\text{C} \\
\text{O}
\end{array} \]

1.2

a) 3,3-dimethylbutanoic acid
b) ethyl propanoate
c) 2-phenylpropanamide
d) benzoyl chloride
e) N-ethyl-N-methylbutanamide
f) cyclobutane carboxylic acid

2.1

2.2

a) d
b) e

3.1

3.2

a

3.3

b

3.4

3.5

4.

Predicting the products of reactions.

a) \[
\text{C}_6\text{H}_5\text{CO}_2\text{H} + \text{CH}_3\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{C}_2\text{O}^- + \text{H}_3\text{C}^-\text{NH}_3
\]

b) \[
\text{C}_6\text{H}_5\text{Br} + \text{Mg} \text{ether} \rightarrow \text{C}_6\text{H}_5\text{CO}_2\text{H}
\]

c) \[
\text{H}_3\text{C} - \text{C}_6\text{H}_5 - \text{CH}_2\text{CH}_3
\text{C}_6\text{H}_5\text{CO}_2\text{H}
\]

1. \text{KMnO}_4, ^{-}\text{OH}, \text{H}_2\text{O, heat}
2. \text{H}_3\text{O}^+

4. \[
\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{NaCN} \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}
\]
4. continued

e) CH₃CH₂CH₂CH₂CO₂H  \xrightarrow{1. \text{SOCl}_2} \xrightarrow{2. \text{ex. CH}_3\text{CH}_2\text{MgBr}} \xrightarrow{3. \text{H}_2\text{O}} \text{OH}

f) \text{Cl} \xrightarrow{(\text{CH}_3)_2\text{CuLi}} \text{CH}_3

g) \text{OH} \xrightarrow{\text{H}_3\text{O}^+, \text{H}_2\text{O}} \text{heat} \xrightarrow{\text{heat}} \text{OH}

h) \xrightarrow{1. \text{LiAlH}_4} \xrightarrow{2. \text{H}_3\text{O}^+} \text{OH}

i) CH₃CH₂C≡CCH₃  \xrightarrow{\text{O}_3} \xrightarrow{\text{Zn, H}_2\text{O}} \text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{COOH}

j) CH₃CH₂CH₂CH=CH(CH₃)₂  \xrightarrow{1. \text{O}_3} \xrightarrow{2. \text{DMS}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{COOH}

5. Mechanisms:

a)

\xrightarrow{\text{Cl}^\ominus + 2 \text{HO}^\ominus} \text{Cl}^\ominus \xrightarrow{\text{OH}} \text{OH} \xrightarrow{-\text{Cl}^\ominus} \text{H}_2\text{O}^\ominus + \text{CH}_3\text{COO}^\ominus

b)

\xrightarrow{\text{Cl}^\ominus + \text{CH}_3^\ominus} \text{Cl}^\ominus \xrightarrow{\text{O}^\ominus} \text{O}^\ominus \rightarrow \text{O}^\ominus \text{O}^\ominus \rightarrow \text{CH}_3\text{O}^\ominus + \text{CO}^\ominus
5. continued

c) 

\[
\begin{align*}
\text{Acetone} & \xrightarrow{\text{H}^+} \text{Formaldehyde} \\
\text{CH}_3 & \xrightarrow{\text{H}_2\text{O}} \text{Formic acid} \\
\text{H}_2\text{O} & \xrightarrow{\text{H}_2\text{O}} \text{Acetic acid}
\end{align*}
\]

\text{weak nucleophile}

\[
\begin{align*}
\text{CH}_3 & \xrightarrow{\text{H}^+} \text{Formaldehyde} \\
\text{H}_2\text{O} & \xrightarrow{\text{H}_2\text{O}} \text{Acetic acid}
\end{align*}
\]

d) 

\[
\begin{align*}
\text{Acetone} & \xrightarrow{\text{H}^+} \text{Formaldehyde} \\
\text{HOCH}_2\text{CH}_3 & \xrightarrow{\text{H}_2\text{O}} \text{Acetone} \\
\text{H}_2\text{O} & \xrightarrow{\text{H}_2\text{O}} \text{Acetone}
\end{align*}
\]

\[\text{B} = \text{CH}_3\text{OH} \text{ or } \text{H}_2\text{O}\]

\[+ \text{CH}_3\text{OH} \rightarrow \text{Acetone} \]

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6. Propose a synthesis.

a) \[
\begin{align*}
&\text{1. KMnO}_4, \cdot \text{OH,} \\
&\text{H}_2\text{O, heat} \\
&\text{2. H}_3\text{O}^+ \\
\rightarrow &\text{phenylacetic acid} \\
&\text{acetic acid, heat} \\
&\text{CH}_3\text{OH} \\
&\text{phenylacetate} \\
\end{align*}
\]

b) \[
\begin{align*}
&\text{phenylacetate} \\
&\text{H}_2\text{O} \\
&\text{H}_3\text{O}^+ \text{, heat} \\
&\text{1. SOCl}_2 \\
&\text{2. ex. NH}_3 \\
\rightarrow &\text{phenylacetic acid} \\
\end{align*}
\]

c) \[
\begin{align*}
&\text{phenylacetic acid} \\
&\text{Br}_2 \text{, light} \\
&\text{1. Mg, ether} \\
&\text{2. CO}_2 \\
&\text{3. H}_3\text{O}^+ \\
\rightarrow &\text{phenylacetic acid} \\
\end{align*}
\]

d) \[
\begin{align*}
&\text{phenylacetic acid} \\
&\text{1. KMnO}_4, \cdot \text{OH,} \\
&\text{H}_2\text{O, heat} \\
&\text{2. H}_3\text{O}^+ \\
&\text{1. SOCl}_2 \\
&\text{2. ex. NH}_3 \\
\rightarrow &\text{phenylacetic acid} \\
\end{align*}
\]

e) \[
\begin{align*}
&\text{cyclopentane carboxylic acid} \\
&\text{Na}_2\text{Cr}_2\text{O}_7 \\
&\text{H}_2\text{SO}_4, \text{H}_2\text{O} \\
&\text{1. SOCl}_2 \\
&\text{2. ex. NH}_2\text{CH}_3 \\
\rightarrow &\text{cyclopentane carboxylic acid} \\
\end{align*}
\]

f) \[
\begin{align*}
&\text{phenylacetic acid} \\
&\text{Mg, ether} \\
&\text{1. CO}_2 \\
&\text{2. H}_3\text{O}^+ \\
&\text{CH}_3\text{CH}_2\text{OH} \\
&\text{H}_3\text{O}^+ \text{, heat} \\
&\text{phenylacetic acid} \\
\end{align*}
\]

g) \[
\begin{align*}
&\text{phenylacetic acid} \\
&\text{H}_2\text{O} \\
&\text{H}_3\text{O}^+ \text{, heat} \\
&\text{SOCl}_2 \\
&\text{1. 2CH}_3\text{CH}_2\text{MgBr} \\
&\text{2. H}_3\text{O}^+ \\
\rightarrow &\text{phenylacetic acid} \\
\end{align*}
\]

7.1 a) A  b) E  c) C  d) B

7.2 a) E  b) D  c) A  d) C

7.3 \text{CH}_3\text{CH}_2\text{OCH}_2\text{CO}_2\text{H}

7.4 a
1. Which of the following compounds is the strongest acid?
   a) ![Image]
   b) ![Image]
   c) ![Image]
   d) ![Image]

2. **Draw:** benzyl benzoate

3. **Name:**
   ![Image]

4. Predict the major product(s) (if any) of each of the following reactions.
   a) ![Image]
   b) ![Image]
   c) ![Image]

5. Propose a mechanism for the following reaction.
   ![Image]

6. Propose syntheses, from the given starting material and any other needed reagents.
   a) benzamide from benzyl alcohol

   b) CH$_3$CH$_2$CH$_2$CH=O from CH$_3$CH$_2$CH$_2$COCl

   c) ![Image] from ![Image]
1. a) Draw: \(N,N\)-diethylbenzamide  
   b) Draw: benzyl propanoate  
   c) Name:  
   d) Name:  

2. Propose a mechanism for the following reaction.  
   \[
   \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{H}_3\text{O}^+ \text{ heat}} \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O}
   \]

3. Propose a synthesis of the compounds indicated, from the given starting materials and any other needed reagents.  
   a)  
   b)  

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4. Which of the following is the weakest base?
   a) ![Structure](image1.png)  b) ![Structure](image2.png)  c) ![Structure](image3.png)  d) ![Structure](image4.png)

5. Identify the following compound from the given spectroscopic information.
   C₄H₇BrO₂
   IR: broad peak at 2500-3500 cm⁻¹ and a peak at 1715 cm⁻¹
   ¹H NMR spectrum:
   triplet, δ 1.08 (3H)
   multiplet, δ 2.07 (2H)
   triplet, δ 4.23 (1H)
   singlet, δ 10.97 (1H)

6. Predict the product(s) (if any) of each of the following reactions.
   a) ![Reaction](image5.png)
   b) ![Reaction](image6.png)
   c) ![Reaction](image7.png)
   d) ![Reaction](image8.png)

7. For questions (a) and (b), choose the answers from the list of possible compounds shown below.
   a) ![Compound](image9.png) b) ![Compound](image10.png) c) ![Compound](image11.png) d) ![Compound](image12.png) e) ![Compound](image13.png)

   a) Which compound is insoluble in water and 5% NaOH(aq), but is soluble in conc. H₂SO₄?
   b) Which compound is insoluble in water, and soluble in both 5% NaHCO₃(aq) and 5% NaOH?