LAB 18: CARBOXYLIC ACIDS AND ESTERS:
ESTERIFICATION & SAPONIFICATION

PURPOSE: To observe the properties of carboxylic acids and their salts.
To investigate the properties of the acid salt of quinine.
To synthesize esters from carboxylic acids and alcohols.

SAFETY CONCERNS:
Always wear safety goggles.
Sodium Hydroxide, sulfuric Acid, Hydrochloric Acid, and Glacial Acetic Acids are dangerous to
skin eyes, mucus membranes and clothes. Use these with caution. If contacted, wash with soap
and copious amounts of water.

CARBOXYLIC ACIDS:
The tart and sour tastes of fruits and other foods are due to the presence of carboxylic acids.
Small carboxylic acids are often volatile with sharp or pungent odors. The tart taste and strong
smell of vinegar is due to acetic acid (ethanoic acid). Butyric acid (butanoic acid) contributes to
the stench of rancid butter and of body odor.

Carboxylic acids, RCOOH, have a polar carboxyl group on the end of a nonpolar hydrocarbon
chain. The carboxyl group (-COOH) is more polar than the hydroxyl (-OH) of an alcohol so
carboxylic acids are usually more soluble in water than are alcohols of equal carbon length.

Carboxylic acids react readily with bases to form salts. Carboxylic acid salts, (or carboxylate
salts) being ionic, are usually water soluble even if the original carboxylic acid (such as those
with five or more carbons) is not water soluble. The name of a carboxylic acid salt derives from
the acid that formed it. The first word in the name comes from the cation of the base used, and
the second word is the name of the acid with its –ic ending changed to –ate.

<table>
<thead>
<tr>
<th>Carboxylic Acid (water soluble)</th>
<th>Base</th>
<th>Carboxylic Acid Salt (water soluble)</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{propanoic acid} ]</td>
<td>(\text{NaOH})</td>
<td>[\text{sodium propanoate}]</td>
<td>(\text{water})</td>
</tr>
</tbody>
</table>

Long chain carboxylic acids are called fatty acids. The carboxylic acid salts of fatty acids are
called soaps.

<table>
<thead>
<tr>
<th>Carboxylic Acid (not water soluble)</th>
<th>Base</th>
<th>Carboxylic Acid Salt (water soluble)</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{dodecanoic acid} ] (\text{(lauric acid; a fatty acid)})</td>
<td>(\text{NaOH})</td>
<td>[\text{sodium dodecanoate}] (\text{(sodium laurate; a soap)})</td>
<td>(\text{water})</td>
</tr>
</tbody>
</table>
Neutralization of Amine Bases with Acids:
Because amines are basic they react readily with acids to form salts. Amine salts are much more soluble in water than the corresponding amines.

\[
\begin{align*}
\text{Amine Base} & \quad \text{Acid} & \quad \text{Amine Salt} \\
\text{CH}_3-N-H & + \text{HCl} & \rightarrow \text{CH}_3-N^\circ-H \quad \text{Cl}^\circ \\
\text{H} & & \text{H} \\
\text{Amine Salt} & \quad \text{Amine Base}
\end{align*}
\]

Amines (free bases) may be regenerated from the salt by treatment with a base such as sodium hydroxide.

\[
\begin{align*}
\text{Amine Salt} & \quad \text{Base} & \quad \text{Amine Base} \\
\text{CH}_3-N^\circ-H \quad \text{Cl}^\circ & + \text{NaOH} & \rightarrow \text{CH}_3-N-H + \text{H}_2O + \text{NaCl} \\
\text{H} & & \text{H}
\end{align*}
\]

**ALKALOIDS:**
Alkaloids are naturally occurring nitrogen compounds with basic properties. These complex molecules come from plants and many have medical uses. They are generally insoluble in water, and are often found in commercial products in the form of their water-soluble acid salts.

<table>
<thead>
<tr>
<th>Alkaloid + Acid (water insoluble)</th>
<th>Alkaloid Acid Salt (water soluble)</th>
<th>Alkaloid Acid Salt + Base (water soluble)</th>
<th>Alkaloid (water insoluble)</th>
</tr>
</thead>
</table>

The pure alkaloid (in its “free base” or conjugate base form) can be obtained as a precipitate from its acid salt by treatment with a base such as sodium hydroxide.

**Quinine:**
The alkaloid base, Quinine, an antipyretic (fever-reducer), was for a long time the only known remedy for malaria. Quinine binds to the DNA of malaria-infected cells and inhibits their replication. Only infected cells are affected because they absorb quinine in higher concentrations than unaffected cells. The alkaloid is found in the bark of the cinchona tree; these trees were extensively cultivated in Indonesia in the late 19th century. When the Japanese invasion of Indonesia in World War II cut off the supply of quinine needed by Allied troops, American chemist Robert Burns Woodward succeeded in synthesizing quinine from coal tar. Woodward was renowned for his ability to synthesize complex organic substances and was awarded the 1956 Nobel Prize in chemistry.
**ESTERS:**  
When *carboxylic acids* are combined with *alcohols* in the presence of an acid catalyst an *esterification* reaction occurs to form *esters* and *water*. The reverse reaction, *hydrolysis*, decomposes an ester into a carboxylic acid and an alcohol. Esterification and hydrolysis are in equilibrium. Thus, the ester product is favored when an excess of acid or alcohol is used or when water or the ester is removed as soon as it forms. Hydrolysis is made possible by addition of water.

![Esterification](image)

The name of an ester indicates the acid and the alcohol that combined to form it. The first word in the name comes from the alkyl group of the alcohol, and the second word is the name of the acid with its –ic ending changed to –ate.

Many esters are colorless liquids with pleasant, fruity aromas. The aroma of various flowers and fruits, and the flavor of many foods are due to the presence of esters. Octyl acetate gives oranges their characteristic odor and flavor; pentyl acetate gives the flavor of pears or bananas. The flavor and odor of raspberries come from isobutyl formate. An ester of salicylic acid is methyl salicylate, which give the flavor and odor of oil of wintergreen used in candies and ointments for sore muscles.

When an ester is hydrolyzed in the presence of a base, the reaction is called *saponification*. The products are the salt of the carboxylic acid and the alcohol. Although esters are usually insoluble in water, the ionic salts and short chained alcohols formed are soluble.

![Basic Hydrolysis](image)
PROCEDURES:

ACTIONS:

I. CARBOXYLIC ACIDS AND THEIR SALTS:
1. Obtain 4 clean dry test tubes (any size) and label them A, B, C, and D. Into each tube place about 2 mL of deionized water.¹

A. ODOR & SOLUBILITY, & pH OF ACIDS:
2. Into the tubes add the following acids and mix each well²:
   - Tube 1A; add 10 drops of glacial Acetic acid³.
   - Tube 1B; add 10 drops of Butyric acid⁴.
   - Tube 1C; add about 0.1g⁵ of solid Benzoic acid.⁶
3. Note the odor⁷ of each acid solution on your report sheet.
4. In the non-shaded boxes of the report sheet, record the solubility of each acid in water at room temperature. (S = soluble, I = insoluble, PS = partially soluble).
5. Determine and record the pH of each soluble or partially soluble acid solution.⁸

B. ODOR, SOLUBILITY, & pH OF SALTS:
6. To each carboxylic acid solution add 3 mL of 3M NaOH. Stopper each tube and shake vigorously to mix. Determine the pH of each solution as before. If a solution is not basic, continue to mix in more NaOH dropwise until the solution is basic. Record the final pH.
7. Note the solubility⁹ and the odor¹⁰ of the now basic salt solutions and compare each to the solubility and odor of the solutions before the addition of base.

C. REACIDIFICATION
8. To each basic salt solution add 3 mL of 3M HCl and stopper & shake to mix. Determine the pH of each. If a solution is not acidic, continue to mix in more HCl dropwise until the solution is acidic. Record the final pH.
9. Record your observations. (Does the original odor return? Original solubility?)

D. EQUATIONS
10. Using condensed structural formulas write the equations for the reactions of each acid with NaOH and then equations for the reactions of each salt formed with acid. Include names of the sodium salts formed.

NOTES:
¹The measurement does not need to be exact. You can determine 2 mls for the first tube with a graduated cylinder and then eyeball the height of water in the second tube to match.
²Mixing can be done by tapping the sides of the test tubes, by stirring with a glass rod, or by stoppering and shaking.
³The IUPAC name of Acetic acid is Ethanoic Acid. Glacial acetic acids refers to the concentrated form.
⁴The IUPAC name of Butyric acid is Butanoic Acid.
⁵The amount does not need to be exact. About 0.1g could be anywhere between 0.08 and 0.12g.
⁶Other names for Benzoic Acid are: Benzene Carboxylic Acid; Phenylmethanoic Acid, and Phenylformic Acid.
⁷Note odor by wafting (cautiously moving your hand quickly over the open end of the test tube) the vapors toward your nose.
⁸If using pH paper then determine the pH by dipping a stirring rod into the solution, then touching it to a piece of universal indicator paper. Compare the color of the wet paper with the color chart on the pH paper container and report the pH.
⁹Carboxylic acid salts are ionic. Most ions easily hydrate with water so are usually water soluble even if the original carboxylic acid is not water soluble.
¹⁰The identity of the odor is not as important as if or how the odor changed from what it was before base was added.
II. PROPERTIES OF QUININE:
1. Pour two 25-mL portions of tonic water into two beakers and label them A and B.

2. Test the pH of tonic water and note whether the solution is acidic (A) or basic (B).

3. Place the beakers A and B under black light (UV light) and observe if the samples are fluorescent.

4. Keep solution A as a reference. To solution B add, while stirring, 3M sodium hydroxide (NaOH) solution drop-by-drop until the fluorescence completely disappears. Test the pH and record whether the solution is acidic (A) or basic (B).

5. Remove the black light and to solution B (now containing both tonic water and NaOH) with stirring add vinegar (a 5% solution of acetic acid; CH₃COOH) until the solution again fluoresces. Test the pH and record whether the solution is acidic (A) or basic (B).

III. PREPARATION OF ESTERS:
1. Set up a hot water bath by filling your largest beaker 1/3 full of water and heating it on a hot plate only until it reaches near 80°C.¹¹

2. Obtain 9 stoppered dry¹² test tubes and label them A, B, C, etc to I with a pencil¹³ or grease marker.

3. Into tube #A put
   20 drops glacial acetic acid (CH₃COOH),
   20 drops ethanol (CH₃CH₂OH), and
   5 drops concentrated sulfuric acid (H₂SO₄)¹⁴

   Into tube #B put
   About 0.2g¹⁵ of Salicylic acid,
   20 drops methanol (CH₃OH), and
   5 drops concentrated sulfuric acid (H₂SO₄)

¹¹Use a thermometer to monitor the temperature. Do not overheat. You may remove some of the heated water and add tap water to maintain temperature if needed. If the temperature gets too high some of the esters formed will evaporate and be lost.

¹²Any water present in the test tube will serve to shift the equilibrium back toward reactants and away from the desired product esters.

¹³Some test tubes have a white patch on which you can write with pencil.

¹⁴Concentrated Sulfuric Acid (H₂SO₄) is dangerous to your skin, eyes, and clothes. Do not breathe the vapors. Wash hands with soap and water immediately if contacted.

¹⁵The amount does not need to be exact. Between 0.18 and 0.22g is sufficient.
Into tube #C put
20 drops glacial acetic acid (CH$_3$COOH),
20 drops pentanol $^{16}$ (CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$OH), and
5 drops concentrated sulfuric acid (H$_2$SO$_4$)

Into tube #D put
About 0.2g $^{15}$ of Benzoic acid,
20 drops ethanol (CH$_3$CH$_2$OH), and
10 drops concentrated sulfuric acid (H$_2$SO$_4$)

Into tube #E put
20 drops formic acid $^{17}$ (HCOOH),
20 drops octanol [CH$_3$(CH$_2$)$_6$CH$_2$OH], and
5 drops concentrated sulfuric acid (H$_2$SO$_4$)

Into tube #F put
20 drops glacial acetic acid (CH$_3$COOH)
20 drops benzyl alcohol PhCH$_2$OH, and
5 drops concentrated sulfuric acid (H$_2$SO$_4$)

Into tube #G put
About 0.2g $^{15}$ of trans-Cinnamic acid
20 drops 3-methylbutanol $^{18}$ (CH$_3$)$_2$CHCH$_2$CH$_2$OH
5 drops concentrated sulfuric acid (H$_2$SO$_4$)

Into tube #H and #I put your own different combinations:
A carboxylic acid of your choice $^{19}$ (about 0.2g if solid; 20 drops if liquid)
20 drops of an alcohol of your choice $^{20}$
5 drops concentrated sulfuric acid (H$_2$SO$_4$)

4. Stopper and shake each tube to mix well.

5. With the stoppers on loosely, place all 9 tubes into the 60-80°C water bath. $^{21}$ Continue working on other parts of the lab and come back later to check the tubes.

6. After 8-10 minutes remove the stoppers from each tube and note the odor produced. $^{22}$

7. Complete or write the equations for the esterification reactions you performed including the structures and names of the products formed.

$^{16}$The common names of Pentanol are amyl alcohol and pentyl alcohol.

$^{17}$The IUPAC name of Formic acid is methanoic acid.

$^{18}$The common name of 3-methylbutanol is isoamyl alcohol.

$^{19}$You have many acids available to you such as:
Methanoic (Formic) Acid
Ethanoic (Acetic) Acid
Propanoic (Propionic) Acid
Butanoic (Butyric) Acid
Benzoic Acid
Salicylic Acid and
Trans-Cinnamic Acid

$^{20}$You have many alcohols available to you such as:
Methanol
Ethanol
Propanol
Pentanol (Amyl Alcohol)
3-methylbutanol (Isoamyl Alcohol)
Octanol and
Benzyl Alcohol

$^{21}$You do not want the water to get too hot or the esters you make will evaporate away.

$^{22}$You should be able to detect the aroma of pear, banana, butter rum, orange, chocolate, fingernail polish remover and the mint scent of wintergreen. Decide which of the tubes belongs to which aroma and record the correct aroma on the report sheet.
LAB 18: CARBOXYLIC ACIDS & ESTERS:  

NAME__________________  
DATE__________________  

PRE LAB EXERCISES:

1. Which of the following would be most soluble in water?
   A. propanol    B. propanoic acid    C. sodium propanoate    D. all are equally soluble

2. Esters have common odors characteristic of
   A. fruits    B. skunk    C. natural gas    D. rancid oils

3. When preparing esters what type of water bath is required?
   A. ice @ 0°C    B. boiling water    C. room temperature    D. 60-80 °C

4. If your skin comes in contact with sodium hydroxide (NaOH) or sulfuric acid (H₂SO₄) what should you do?
   A. scream    B. curse    C. wash immediately with soap and lots of water

5. Draw structures for the following:

<table>
<thead>
<tr>
<th>Acetic Acid</th>
<th>Benzoic Acid</th>
<th>Sodium butanoate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Salicylic acid</th>
<th>Formic Acid</th>
<th>Ethyl Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6. Which acid and alcohol are needed to prepare **Methyl butanoate**? Show the reaction and name the starting materials.

```
Esterification →

Carboxylic Acid + Alcohol → Ester + Water

methyl butanoate

Name ___________________  
Name ___________________
```

CH105 Lab 18: Carboxylic Acids & Esters (P15)  89
Lab 18: Carboxylic Acids & Esters

Name: 

Report: Partner: Date:

I. Carboxylic Acids & Salts:

1A. Acetic Acid

Another name for the Acid = ______________________
Name of the Salt = ______________________

<table>
<thead>
<tr>
<th>Property</th>
<th>A. Water Solution</th>
<th>B. NaOH solution</th>
<th>C. HCl Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acid</td>
<td>Salt</td>
<td></td>
</tr>
<tr>
<td>Draw the structural formulas for the missing organic compounds.</td>
<td>+ NaOH $\rightarrow$</td>
<td>+ NaOH $\rightarrow$ + HCl $\rightarrow$</td>
<td></td>
</tr>
<tr>
<td>Odor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solubility/pH</td>
<td>Solubility</td>
<td>pH</td>
<td>Solubility</td>
</tr>
</tbody>
</table>

1B. Butyric Acid

Another name for the Acid = ______________________
Name of the Salt = ______________________

<table>
<thead>
<tr>
<th>Property</th>
<th>A. Water Solution</th>
<th>B. NaOH solution</th>
<th>C. HCl Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acid</td>
<td>Salt</td>
<td></td>
</tr>
<tr>
<td>Draw the structural formulas for the missing organic compounds.</td>
<td>+ NaOH $\rightarrow$</td>
<td>+ NaOH $\rightarrow$ + HCl $\rightarrow$</td>
<td></td>
</tr>
<tr>
<td>Odor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solubility/pH</td>
<td>Solubility</td>
<td>pH</td>
<td>Solubility</td>
</tr>
</tbody>
</table>

1C. Benzoic Acid

Another name for the Acid = ______________________
Name of the Salt = ______________________

<table>
<thead>
<tr>
<th>Property</th>
<th>A. Water Solution</th>
<th>B. NaOH solution</th>
<th>C. HCl Solution</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Acid</td>
<td>Salt</td>
<td></td>
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<td>Odor</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Solubility/pH</td>
<td>Solubility</td>
<td>pH</td>
<td>Solubility</td>
</tr>
</tbody>
</table>

Explanation/Analysis:

**Odor:** Explain why the changes in odor when going from acid to salt form.

**Solubility:** Explain why the changes in solubility when going from acid to salt form.
### II. Properties of Quinine:

<table>
<thead>
<tr>
<th></th>
<th>Acidity? (A) or Base (B)</th>
<th>Observations under Black light</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tonic Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After addition of NaOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After addition of CH₃COOH</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. What is the fluorescent compound present in tonic water?
   - A. Quinine
   - B. The acid salt of Quinine
   - C. NaOH
   - D. CH₃COOH
   - E. Other (state) __________________________

Show the equation for the reaction of quinine acetate with sodium hydroxide: Use structures (not formulas) for organic compounds

**Explanation/Analysis:** Why were the results the way they were? Explain any anomalies
## III. PREPARATION OF ESTERS:

### Complete the Equations:

<table>
<thead>
<tr>
<th>Tube A</th>
<th>Aroma:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanoic Acid + Ethyl Alcohol</td>
<td>Banana/Pear</td>
</tr>
<tr>
<td>Acetic Acid + Ethanol</td>
<td>Butter Rum</td>
</tr>
</tbody>
</table>

Name of Ester: IUPAC =
Common =

### Tube B

| Salicylic Acid + Methyl Alcohol  | Banana/Pear  |
| Acetic Acid + Methanol  | Butter Rum  |

Name of Ester:

### Tube C

| Pentyl Alcohol + Ethanoic Acid  | Banana/Pear  |
| Acetic Acid + Ethanol  | Butter Rum  |

Name of Ester:

### Tube D

| Benzoic Acid + Ethyl Alcohol  | Banana/Pear  |
| Acetic Acid + Ethanol  | Butter Rum  |

Name of Ester:
Complete the Equations:

<table>
<thead>
<tr>
<th>Tube</th>
<th>Substance 1</th>
<th>Substance 2</th>
<th>Reaction</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>Octyl Alcohol</td>
<td>Octanol</td>
<td>+</td>
<td>Methanoic Acid Formic Acid</td>
</tr>
<tr>
<td>F</td>
<td>Benzyl Alcohol</td>
<td>Ethanoic Acid</td>
<td>+</td>
<td>Acetic Acid</td>
</tr>
<tr>
<td>G</td>
<td>Isopentyl Alcohol</td>
<td>Cinnamic Acid</td>
<td>+</td>
<td>3-methylbutanol</td>
</tr>
<tr>
<td>H</td>
<td>Acid</td>
<td>Alcohol</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>Acid</td>
<td>Alcohol</td>
<td>+</td>
<td></td>
</tr>
</tbody>
</table>
**LAB 18: CARBOXYLIC ACIDS & ESTERS:**

**NAME______________**

**RELATED EXERCISES:**

**DATE______________**

1. Which would you predict to have a more pronounced odor?
   A. a carboxylic acid  
   B. a carboxylate salt  
   C. both have similar odors

2. Rank the following in order of decreasing solubility in water. (#1 being most soluble)
   A. Butanoic Acid  
   B. Methyl butanoate  
   C. Sodium butanoate

3. Complete the following esterification:

   ![Esterification Reaction]

   4. Name Product(s):

5. Complete the following acid catalyzed hydrolysis:

   ![Acid Catalyzed Hydrolysis]

   6. Name ester

   7. Name product(s)

8. Complete the following base catalyzed hydrolysis (saponification):

   ![Base Catalyzed Hydrolysis]

   9. Name product(s)

10. Complete the following showing structures and names where indicated:

    ![Reaction with NaOH and HCl]

    **Name** Methyl Salicylate  
    **Name** ________________  
    **Name** ________________
11. **Diphenyl ketone** and **benzoic acid** are both white solids that are insoluble in water. Give a detailed flow chart outlining a method using acid/base chemistry for separating a mixture of these compounds. **Show structures** for each step along the way.