

## Preparation of Aspirin, Methyl Salicylate and Nylon

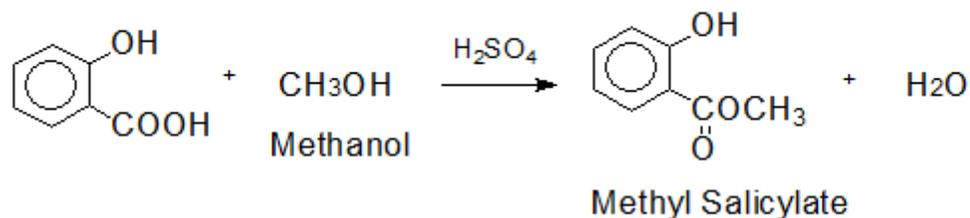
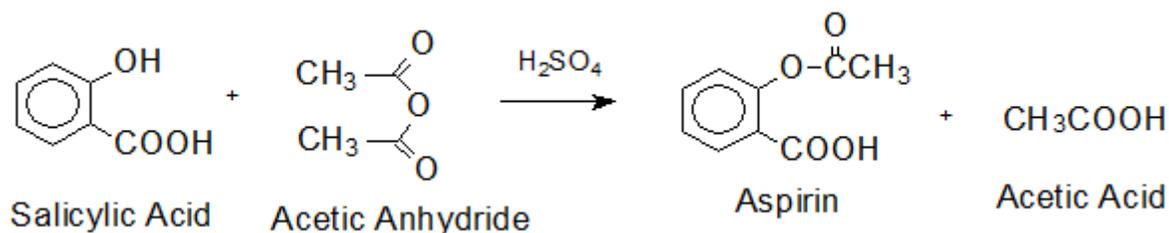
### Experiment #9

**Objective:** To observe the contrasts in appearance and odor of two different esters of salicylic acid, namely aspirin and methyl salicylate. The preparation of nylon will be demonstrated.

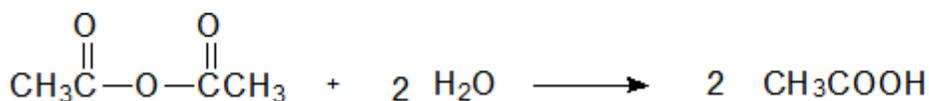
#### Introduction

Salicylic acid is a phenolic acid, indicating it has two functional groups on the benzene ring, an -OH group and a -COOH group. Aspirin and oil of wintergreen are esters of salicylic acid. Aspirin is the ester of salicylic acid and acetic acid (acetyl salicylic acid), whereas oil of wintergreen is the ester of salicylic acid and methanol (methyl salicylate). The chemical name for aspirin, acetyl salicylic acid, is not easily recognized as the name of an ester. However, the chemical name for oil of wintergreen, methyl salicylate, should readily be recognized as the name of an ester.

In the preparation of aspirin the -OH group of salicylic acid reacts with the acetyl group of acetic acid or acetic anhydride to form acetyl salicylic acid. The formation of aspirin will proceed faster if acetic anhydride is used in place of acetic acid. However, acetic anhydride will hydrolyze in the presence of water to form acetic acid, slowing down the reaction. Hence, the reaction vessel must be very DRY to ensure a complete reaction. Sulfuric acid,  $H_2SO_4$ , is used as a dehydrating agent. The aspirin will be isolated by filtration and washed several times with ice cold deionized water to remove the water soluble impurities (acetic acid and sulfuric acid). Aspirin is quite insoluble in ice cold water, but is relatively soluble in warm water (1 g dissolves in 100 mL water at  $37^\circ C$ ).



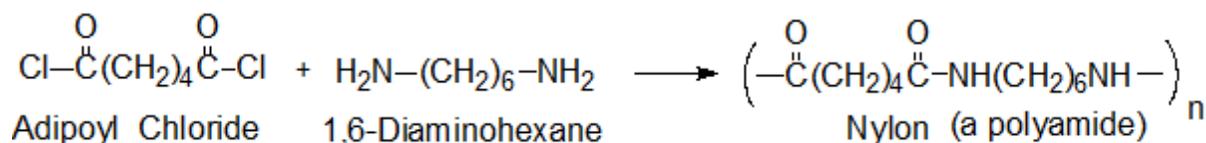
#### Hydrolysis of Acetic Anhydride



Methyl salicylate is a liquid at room temperature (mp =  $-9^\circ C$ ) and is relatively insoluble in water. It is also quite toxic (average lethal dose for adults is 30 mL). However, it is used in

small amounts as a flavoring agent and is used in topical analgesic balms for arthritis and aching muscles. In this experiment you will prepare a very small amount of the methyl salicylate and characterize it by its aroma. It will not be isolated.

Polymers are large molecules (macromolecules) that contain multiple units of smaller molecules, or monomers. Polymers may be natural or synthetic. Natural polymers are found in cotton, silk and wool that are processed to make fibers for textiles. Nylon is a polyamide that is widely used today for fabrics, rope, carpets, gears (in computer printers) and medical devices. Nylon-6,6 is made in the lab by combining 1,6-diaminohexane with adipoyl chloride, an acyl chloride that is more reactive than the corresponding acid (adipic acid). Industrial processes for making nylon use sophisticated machines and chemical additives to give a fine quality polymer.



### Apparatus and Reagents

Balance, buchner funnel, vacuum flask, test tubes, beakers, burner, filter paper, watch glass, acetic anhydride, methanol, ice, salicylic acid, concentrated sulfuric acid, 10% NaOH solution, 5% aqueous solution of 1,6-diaminohexane, and adipoyl chloride solution in hexane.

**WARNING!! Avoid getting these solutions on your skin. Rinse your skin thoroughly if you accidentally spill the solutions on you.**

### Demonstration by the Lab Instructor: Preparation of Nylon.

1. Add about 15 mL of 5% aqueous 1,6-diaminohexane solution to a 50 or 150 mL beaker.
2. Add 10 drops of 10% sodium hydroxide (NaOH) solution and swirl gently to mix.
3. Add about 15 mL of adipoyl chloride solution to a graduated cylinder and carefully pour the adipoyl chloride solution in the beaker containing the diamino-hexane, but avoid mixing the 2 solutions. Tilt the beaker and allow the solution to run down the inside wall of the beaker.
4. Have students notice that there are 2 layers of liquid in the beaker. A white film should form between the two layers. This is the nylon polymer.
5. Take a copper wire with a small hook at one end and gently free the polymer from the walls of the beaker. Hook the polymer near the center of the beaker and slowly raise the wire, twisting it as you raise it to form a continuous rope or thread of nylon. Fresh polymer will form at the interface of the two liquids as you remove some in making the thread. Pull the thread from the center of the beaker, making the fiber as long as you can.
6. Rinse the rope well with water and let it dry on a paper towel. Have students examine the rope and answer questions regarding its properties on the Report Sheet.
7. When finished, completely mix the two reagents and remove any nylon from the beaker. Dispose of the reagent solutions in the waste container in the hood. Put the nylon in a

paper towel and dispose in the trash.

**CAUTION - Use EXTREME CARE with concentrated sulfuric acid and acetic anhydride. Both reagents are highly corrosive.**

## **Procedure**

### **Part A. Preparation of Aspirin**

1. Fill a 250 mL beaker about one-third full with water and heat on a hot plate to 80-90°C, just below boiling. If the water bath begins to boil, turn the temperature down.
2. Place about 50 mL deionized water in a 100 mL beaker and chill it in an ice bath.
3. Accurately weigh about 1 g of salicylic acid on the balance and record the exact weight (to the nearest 0.01 g) on the Report Sheet. The weight should be between 0.90 and 1.10.
4. Transfer the weighed salicylic acid to a large **DRY** test tube and add 2 ml of acetic anhydride.

**CAUTION!! Acetic anhydride is CORROSIVE!**

5. Mix by holding the top of the tube and tapping the bottom with your finger.
6. Add 3 or 4 drops of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$  in the hood) and mix gently as in the previous step.

**CAUTION!! Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is very corrosive! Add this in the hood.**

7. Warm the test tube for ten minutes in the boiling water bath.

Note: You may begin Part B while you are waiting.

8. After heating for at least 10 minutes in boiling water, transfer 5 mL of ice cold deionized water to a 50 mL beaker and pour the contents of the test tube containing aspirin into it. Alternatively, you may need to pour the 5 mL of cold deionized water into the test tube containing aspirin and use your glass stirring rod to get the solid suspended in the water. Pour this into the 50 mL beaker and place it on the ice bath. Use a small amount of ice cold water to rinse out the test tube and pour it into the beaker. Keep it on ice while you assemble the vacuum filtration apparatus (see Appendix I for diagram of filtration apparatus).
9. Filter the mixture using suction and wash the residue 2 or 3 times with small amounts (about 10 mL) of ice cold deionized water that was placed on ice earlier.

10. Leave the vacuum on for a few minutes to draw air through the filter and dry the product.
11. Transfer the aspirin crystals to a clean weighing paper once they are dry. Place another clean weighing paper on the balance, tare it (zero), and transfer the dried aspirin powder to weigh it. Record the weight on your Report Sheet and calculate your percent yield on the Report Sheet.
12. Show the product to your instructor before discarding it.

### **Part B. Preparation of Methyl Salicylate (Wintergreen Oil)**

1. Weigh about 0.5 g salicylic acid (it need not be accurate, you will not be calculating yield for this part).
2. Transfer the salicylic acid to a clean and **DRY** large test tube and add 1 mL of methanol. Holding the top of the tube, tap the bottom with your finger to stir the mixture. Dissolve the salicylic acid completely in the methanol.
3. Carefully add 3 to 4 drops of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) to the mixture (in the hood) and mix again by tapping the bottom of the tube with your finger.
4. Place the test tube containing this mixture in the hot water bath for 10 min to complete the reaction.
5. After the reaction is complete, remove the test tube from the water bath and allow it to cool. Turn off the hot plate under the water bath.
6. After it has cooled, carefully waft the fumes by passing your hand over the top of the tube toward your nose. Can you smell the minty aroma of wintergreen?
7. If you have difficulty smelling it, you can pour hot water from the water bath into the tube. The aroma of the methyl salicylate should be apparent after it has mixed with warm water.
8. Record your observations and answer the questions on the Report Sheet.





Name \_\_\_\_\_

Section \_\_\_\_\_

**Preparation of Aspirin, Methyl Salicylate and Nylon**

**Experiment #9**

**Data & Report Sheet**

**Part A. Preparation of Aspirin**

1. Weight of salicylic acid used \_\_\_\_\_ g

2. Weight of aspirin recovered \_\_\_\_\_ g

3. Calculate the moles of salicylic acid used:

$$\text{Moles} = \frac{\text{weight (g) [step 1 above]}}{\text{molecular weight (C}_7\text{H}_6\text{O}_3\text{)}} =$$

4. Calculate the moles of aspirin formed:

$$\text{Moles} = \frac{\text{weight (g) [step 2 above]}}{\text{molecular weight (C}_9\text{H}_8\text{O}_4\text{)}} =$$

5. Percentage yield =  $\frac{\text{moles aspirin formed [step 4]}}{\text{moles salicylic acid used [step 3]}} \times 100 =$

**Questions**

1. Write the equation for the preparation of aspirin from salicylic acid and acetic anhydride.

2. Have you prepared pure aspirin? Do you expect any other material to be in your product? What impurities might be in your product after washing and filtering it?

Name \_\_\_\_\_

Section \_\_\_\_\_

3. Are aspirin tablets pure aspirin? If they are not pure aspirin, what else do they contain?
  
4. How would you describe the aroma of methyl salicylate?
  
5. Aspirin and methyl salicylate are both esters of salicylic acid. Do these two different chemical compounds have any similar physiological actions? Describe some of their physiological actions.
  
6. In the preparation of nylon, there are 2 phases, a lower aqueous phase (containing diamino-hexane) and an upper organic phase (with adipoyl chloride). Why is there only a small amount of nylon at the interface of the two phases at any given time, yet it seems you can continue removing it and more appears? What is going on at the interface of the two solutions?
  
7. List several uses for nylon, giving at least one medical use for this polymer. (You may have to check the internet for uses of nylon).