

CITRUS COLLEGE

ORGANIC CHEMISTRY 211L

SUPPLEMENT

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Melting Point Determination

Procedure:

Grind 0.1 – 0.2 g of the unknown sample with mortar and pestle. Introduce enough sample into a capillary tube to give a column of about 2-3 mm in height. Pack the sample in the capillary tube. Heat the sample so the temperature increases at a rate of 10°C/min. Determine the approximate melting point of your unknown. After allowing the instrument to cool 10°C below this point, repeat this melting point with a second sample of your unknown in a new capillary tube heating at a rate of 1°C/min near the approximate melting point. This time you must determine a **range** for the melting point (e.g. 100°-101°C). Your recorded range must indicate the temperature at which the sample begins to melt and the temperature at which the sample finishes melting (clear liquid). Your sample is one of the compounds in **Table I**.

From the list in **Table I** select two or three compounds which have melting points nearest to the melting point of your unknown. Determine mixture melting points (50:50) for each of these selected compounds with your unknown. This is done by taking equal amount of your unknown and one of the selected compounds, then mixing them thoroughly and grinding them. Prepare a capillary tube with this mixed sample. Determine the melting point **range**. If you observe a depression and lowering of this reading, repeat with a fresh mixture of your unknown and the second selected choice from **Table I**. Identify your unknown.

Cleaning Up: All solid samples must be placed into the unknown test tube and returned to the instructor. Melting point capillaries must be disposed in the waste box.

Table I

<u>Compound</u>	<u>Melting Point (°C)</u>
Resorcinol	110.5 - 111
Acetanilide	113.5 - 114
Benzoic Acid	121.5 - 122
Succinimide	123 - 125
Benzamide	128 - 129
<i>Trans</i> -Cinnamic Acid	132 - 133
Benzoin	136 - 137
Salicylamide	140 - 141
Diphenylacetic Acid	147 - 149
Benzilic Acid	150 - 153
Adipic Acid	151 - 153
Salicylic Acid	158.5 - 159
Bezanilide	164 - 165

Crystallization

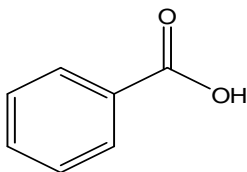
Procedure:

Place approximately 1.0 g of impure benzoic acid and 30-35 mL of water in a 125-mL Erlenmeyer flask. Heat to dissolve most of the sample. Separate the insoluble impurity by gravity filtration using a fluted filter paper, and stemless funnel. In order to decrease the loss of material at this stage: **1)** keep the whole apparatus hot, **2)** add small quantities of the solution to the funnel at a time, **3)** keep the solution to be filtered hot, and **4)** add **small** quantities of hot water to dissolve any crystals forming on the filter paper.

Cover the Erlenmeyer flask with a watch glass and allow the filtrate to cool to room temperature without disturbance. When the flask is at room temperature, cool it further in ice-bath. Collect the crystals by vacuum filtration. Remove filter paper from the funnel and air-dry overnight.

Determine the melting point of the impure and the dried pure benzoic acid. Weigh the recovered benzoic acid, and calculate the percent recovery. Turn-in your sample of purified benzoic acid to the instructor.

Cleaning Up: Impure benzoic acid must be placed in the waste jar.



Benzoic Acid

Extraction

Procedure:

Weigh 0.30 g of adipic acid into a 125 mL Erlenmeyer flask. Add 25.0 mL of distilled water and heat the flask on a hot plate with occasional swirling until the acid dissolves. Cool the flask to room temperature in an ice bath.

Transfer the acid solution into a clean, separatory funnel and extract with 25.0 mL diethyl ether. To ensure that equilibrium has achieved, gently shake the stoppered funnel, venting frequently by inverting the funnel and opening the stopcock, pointing up, away from you, and in the hood!

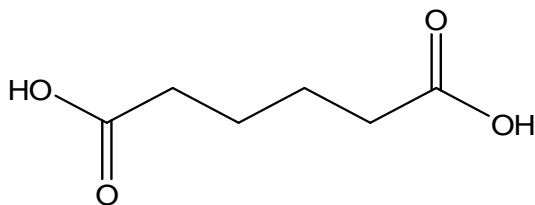
Let the layers to separate. Drain the aqueous layer and discard properly. Add 10.0 mL saturated sodium chloride solution (brine) to the separatory funnel. "Dry" the ether layer by mixing it with the brine solution with frequent venting. Drain the aqueous layer and discard properly. Drain the ether layer into a clean dry Erlenmeyer flask. Rinse the funnel with 5.0 mL ether and add to the ether solution. Add anhydrous CaCl_2 to the ether solution for final drying. The wet CaCl_2 will clump together. Continue adding CaCl_2 until it is freely floating. Decant the ether solution in to 125 mL dry, tarred Erlenmeyer flask. Evaporate the ether in the hood in a 50°C water bath.

Determine the mass of the adipic acid recovered. Calculate the percent recovery.

Cleaning up: Place all waste into the proper waste jars.

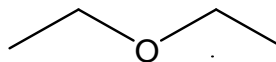
Safety Note: *Diethyl ether is extremely flammable. Do not use it in the presence of open flame or in the presence of hot plate left on high.*

$\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ Adipic Acid



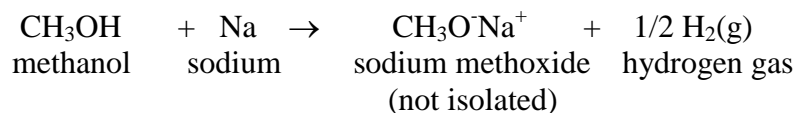
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$

Diethyl Ether (Ether)

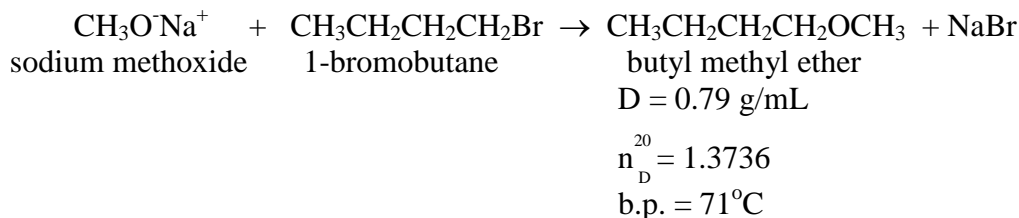


Synthesis of Butyl Methyl Ether

Step 1 – Preparation of Sodium Methoxide:



Step 2 – Reaction of Sodium Methoxide and 1-Bromobutane:



Discussion:

A Williamson ether synthesis consists of two separate reactions: 1) preparation of an alkoxide, 2) the reaction of this alkoxide with an alkyl halide.

Sodium methoxide is prepared by the addition of sodium metal to methanol. A large excess of methanol is used to act as solvent for the sodium methoxide. The exothermic nature of the reaction causes methanol to boil. To prevent methanol from boiling away, a **reflux condenser** is attached to the reaction flask. Methanol vapors condense in the condenser and the liquid runs back into the flask. Because of the vigor of the reaction, sodium must be added slowly; otherwise methanol will boil violently, overwhelming the capacity of the reflux condenser, and spew out of the condenser. An uncontrolled reaction of this type is called a runaway reaction, may throw flammable solvent and corrosive chemicals over laboratory students and the work area.

In this experiment, small pieces of sodium are added to the flask through the reflux condenser tube. Should the sodium stick to the sides of the condenser, a long L-shaped rod can be used to push it down into the methanol solution. After all sodium has reacted, excess methanol is removed by distillation. Decreasing the volume of the solvent – increases the rate of the reaction. Sodium methoxide is extremely basic and absorbs water from the air and is converted to methanol and sodium hydroxide, so step 2 must be carried out at this point.

After excess methanol has been distilled, the flask containing sodium methoxide is refitted with reflux condenser, and 1-bromobutane is added in small portions through condenser. As the reaction proceeds, sodium bromide precipitates. After all the 1-bromobutane has been added, the reaction mixture is heated at reflux to complete the reaction.

After the reaction has been carried out, the product must be isolated from the reaction mixture and purified. The general procedure is termed a **work-up**. The first step in work-up in this experiment is the addition of water to dissolve the sodium bromide. Two phases result: an aqueous-methanol phase and an organic phase. *n*-Butyl methyl ether and

methanol form an **azeotrope** that boils at 56°C, and can easily be separated by distillation. The distillate contains *n*-butyl methyl ether and methanol, while the residue contains water, sodium bromide, and the bulk of the methanol.

The next step is to remove methanol from the product ether. Methanol is water-soluble, but the ether is not. An aqueous extraction of the methanol can be used at this point. An aqueous solution of calcium chloride is used to extract methanol from the ether. The presence of the salt in the aqueous layer **“salts out”** the ether so that it is not carried into the water solution by methanol. After extraction, the ether is dried with calcium chloride. Finally, the product is purified by distillation (b.p. = 65-68°C).

Safety Note 1: Methanol is toxic and flammable. Ingestion or excessive inhalation of the vapors can cause blindness or death. Wash any splashes with water.

Safety Note 2: The sodium metal must not come into contact with water. Do not throw sodium scraps down the sink or wash the work area with wet towel or sponge. The reason is twofold: 1) the reaction of sodium with water is very exothermic and the hydrogen gas formed usually ignites and explodes, 2) the other product of the reaction, sodium hydroxide, is corrosive to both clothing and skin.

Safety Note 3: Hydrogen gas is given off in this experiment. Flames cannot be used in the lab.

Safety Note 4: Sodium methoxide is strong base and very caustic. Wash any spills with copious amount of water.

Procedure:

Week 1:

Step 1 – Preparation of Sodium Methoxide. Place 135 mL of methanol in 250-mL round-bottom flask and fit the flask with a reflux condenser. Add 4.67 g of diced sodium metal through the condenser, 1-2 pieces at a time, allowing the reaction to subside before adding the next piece. If the sodium sticks to the inside of the condenser tube, push it into the reaction flask with the L-shape rod.

After the sodium has completely reacted, fit the flask for simple distillation, and distill 80 mL of methanol (b.p. = 64°C) into a graduated cylinder.

Step 2 – Reaction of Sodium Methoxide and 1-Bromobutane. Fit the 250-mL round-bottom flask containing the sodium methoxide with the reflux condenser. Cool the flask to room temperature with an ice bath. Weigh 18.33 g of 1-bromobutane into a 50-mL Erlenmeyer flask. Using a dropper, add the bromobutane to the reaction vessel through the top of the condenser in 1-2 mL aliquots over a 5-minute period. The reaction is exothermic. Do not add all the bromobutane in one portion. Cork the Erlenmeyer flask between additions so that the bromobutane does not evaporate. After the addition has been completed, let the reaction vessel stand at room temperature until the exothermic reaction has been subsided and the methanol ceases to reflux. Then heat the mixture at a

gentle reflux or “simmer” for 15 minutes in an electric flask heater. The mixture will bump because of the precipitated solid; therefore do not attempt a vigorous reflux. Cool to room temperature. Grease the lid and seal the round bottom flask for next week.

Cleaning Up: Discard the distilled methanol and the residue in the round-bottom flask in the waste bottle.

Week 2:

Add 15-20 mL of water to the reaction mixture, if all the NaBr does not dissolve, add a few additional mL of water.

Equip the flask with simple distillation. Distill the two-layered mixture, collecting the material that boils up to 64°C. The volume of the distillate should be 27 mL. Transfer the distillate to a 125-mL separatory funnel and extract with three 10-mL portions of 25% aqueous calcium chloride. Each time drain and discard the aqueous layer (lower layer). Finally drain the product from separatory funnel into a 50-mL Erlenmeyer flask. Add about 2 g of anhydrous calcium chloride, stopper the flask and let it stand for 5 minutes. Decant the dried product into a 25-mL round-bottom flask. Use a dropper to transfer the liquid, being careful not to transfer any solid. Fit the flask with simple distillation; and distill the product, collecting material boiling at 65-68°C (**don't distill to dryness**). A typical yield is about 6.5 g. Calculate percent yield. Measure the refractive index (pages 299-300; Williamson), and run IR spectrum of the product. The product must be turned-in to the instructor.

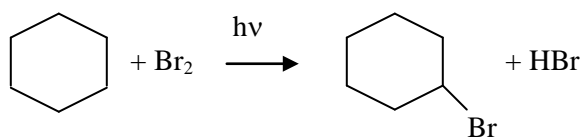
Cleaning Up: The extracted aqueous layer is placed in the waste bottle.

Experimental Notes:

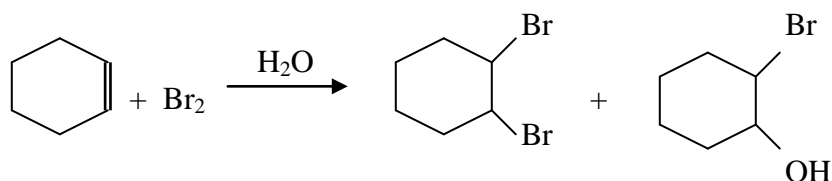
I. The purpose of the reflux condenser is two fold: 1) to maintain the reaction temperature, 2) to avoid solvent loss.

II. Sodium is stored under mineral oil to protect it from air and moisture. Remove the pieces with tweezers, blot off excess mineral oil with tissue, and then add to reaction flask. **Do not allow the Na pieces to sit in the air for any length of time!**

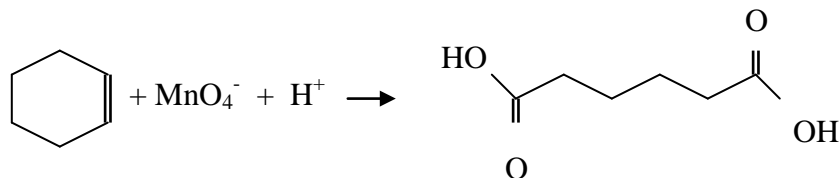
Distinguishing between Alkanes & Alkenes



Bromine in Nonaqueous solution. Treat 0.5-mL sample of ligroin and cyclohexene with 2 to 3 drops of a 3% solution of bromine in dichloromethane.



Bromine Water. Measure 1 mL of a 3% aqueous solution of bromine into each three reaction tubes. Then add 0.3-mL portions of ligroin to two of the tubes and 0.3 mL of cyclohexene to the third. Shake the tubes and record the initial results. Put one of the ligroin containing tube in the desk out of the light and expose the other to a light bulb. When a change is noted, compare the appearance to that of the mixture kept in the dark.



Acid Permanganate Test. Cool 0.3-mL portions of ligroin and cyclohexene add a drop of aqueous solution containing 1% potassium permanganate and 10% sulfuric acid and shake.