Pavia, et al. "Introduction to Organic Laboratory Techniques – a small-scale approach" Harcourt, 1998 p 104-105

Required Reading

Review:	Techniques 1, 2	
	Experiment 8	
	Technique 6	Physical Constants Part B, Boiling Points
New:	Essay	Esters—Flavors and Fragrances
	Techniques 7, 8, 9	

Procedure for Synthesis of Methyl Salicylate

Special Instructions

Be careful when dispensing sulfuric acid; it is very corrosive and will attack your skin if you make contact with it. If you get sulfuric acid on your skin, wash the affected area with copious quantities of running water for 10–15 minutes.

It is recommended that two students combine their crude ester and work as a pair to perform the vacuum distillation. The distillation will work better with a larger quantity of material.

The experiment should be started at the very beginning of the period, since a long reflux time is needed to esterify salicylic acid and obtain a respectable yield. Enough time should remain at the end of the period to perform the extractions and to place the product over the drying agent. Since vacuum distillation is sometimes a bit tricky, the distillation should be performed during a second period if possible.

Waste Disposal

Any aqueous solutions should be placed in the appropriate container for dilute aqueous waste. Place any excess ester in the nonhalogenated organic waste container.

Procedure

Apparatus. Assemble a reflux apparatus using a 100-mL round-bottom flask and a water-cooled condenser (refer to Technique 3, Fig. 3.8, p. 619). Assemble the entire apparatus on a single ring stand so that the reaction mixture can be swirled if necessary. Use a heating mantle to heat the reaction.

Reaction Mixture. Place 9.7 g of salicylic acid (0.07 mole) and 25 mL of methanol (density 0.8 g/mL) in the flask. Swirl the flask and heat the contents slightly to help dissolve the salicylic acid. *Carefully* add 10 mL of concentrated sulfuric acid *in small portions* to the mixture in the flask. After each addition, immediately swirl the flask. A white precipitate may form, but it will dissolve after the mixture is heated. Add a

corrundum boiling stone and reconnect the flask. Do not use a calcium carbonate (marble) boiling stone because it will dissolve in the acidic medium.

Reflux. Heat the mixture under gentle reflux for 1 hour. Occasionally swirl the mixture to assure that the reactants are well mixed. During the heating period, the mixture will turn cloudy, and a layer of product will form on top of the mixture. When the reflux period is finished, disconnect or remove the heating source and allow the reaction to cool to room temperature.

Extractions. Disassemble the apparatus and transfer the reaction mixture to a separatory funnel (125-mL) placed in a ring attached to a ring stand. Be sure that the stopcock is closed and, using a funnel, pour the mixture into the top of the separatory funnel. Also be careful to avoid transferring the boiling stone, or you will need to remove it after the transfer. Rinse the reaction flask with 25 mL of methylene chloride and add it to the separatory funnel. Stopper the funnel, mix the phases by careful shaking and venting (Technique 7, Section 7.4 and Fig. 7.6, pp. 690 and 693). Allow the phases to separate and then unstopper the funnel and drain the lower methylene chloride layer through the stopcock into a beaker or other suitable container. Next, extract the contents with a second 25-mL portion of methylene chloride and combine it in the beaker with the first extraction. Discard the remaining contents of the separatory funnel into the halogenated organic waste since they may contain methylene chloride. Return the saved methylene chloride layers (in the beaker) to the separatory funnel. Extract the combined methylene chloride layers with 25 mL of water. Drain the lower organic layer, discard the top aqueous layer into the aqueous waste container, and return the organic layer to the separatory funnel. Now extract the organic layer with 25 mL of 5% aqueous sodium bicarbonate just as you did previously with water. When finished, repeat the extraction once again with another 25 mL of 5% sodium bicarbonate.

Drying. Transfer the crude ester to a clean, dry 125-mL Erlenmeyer flask and add approximately 2.0 g of anhydrous sodium sulfate. Cork the mixture, swirl it, and allow it to stand for 10–15 minutes. If the mixture does not appear dry (the drying agent clumps and does not "flow," the solution is cloudy, or drops of water are obvious), transfer the ester to a new clean, dry 125-mL Erlenmeyer flask and add a new 1.0-g portion of anhydrous sodium sulfate to complete the drying. If you are going to wait until the next period to distill your product, you may stopper it here (over the sodium sulfate) with a cork (do not use a rubber stopper) and leave it in your locker.

Distillation. Assemble an apparatus for distillation under reduced pressure using your smallest round-bottom flask to distill from (Technique 9, Fig. 9.1, p. 718). Use a heating mantle to heat and install a monometer in the system if one is available (Technique 9, Fig. 9.9, p. 729). Fit the distilling flask with a capillary ebulliator tube that reaches to the bottom of the flask (Technique 9, Fig. 9.1, p. 718). The bleeder tube supplied with most organic kits will serve as an ebulliator if it is equipped with a piece of rubber tubing. The tubing is closed by a screw clamp until a gentle stream of bubbles is passed into the solution when the vacuum is applied to the system. A trap must be used between the aspirator (or vacuum line) and the distillation