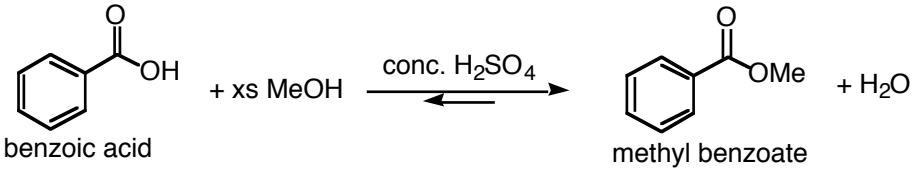
Lab5: Preparation of Methyl Benzoate



Reaction: Place 6.1 g of benzoic acid and 20 mL of methanol in a 100-mL round-bottomed flask, and carefully pour 2 mL of concentrated sulfuric acid down the side of the flask. Swirl the flask to mix the reagents, attach a reflux condenser, and gently heat the mixture at reflux for 45 min. (Power controller setting ~ 6. Boiling chips can be used for the reaction.)

Work-up/Extraction: Cool the solution and transfer it to a separatory funnel containing 50 mL of water. Rinse the flask with 40 mL of dichloromethane, and add the rinsing to the separatory funnel. Shake the funnel to extract methyl benzoate and benzoic acid into the dichloromethane layer (bottom); **vent the funnel often**. Remove the organic and aqueous layers and wash the organic layer with a 25-mL portion of water. Remove the organic-layer (bottom) and wash with 25 mL of 0.6 M aqueous sodium bicarbonate. **CAUTION: foaming may occur.** Swirl the open funnel for a few seconds to assure that no vigorous reaction occurs; then shake the stoppered funnel **with frequent venting**. Separate the organic (bottom) layer. Test the remaining (top) aqueous layer to see that it is basic to litmus paper (pH 7-8, dark green). If not, repeat the washing of the organic layer with an additional 25-mL portion of aqueous sodium bicarbonate. Combine this with the first bicarbonate washing and **SAVE THE SOLUTION**. Wash the dichloromethane layer with a 25-mL portion of saturated sodium chloride, then dry the dichloromethane solution with anhydrous magnesium sulfate.

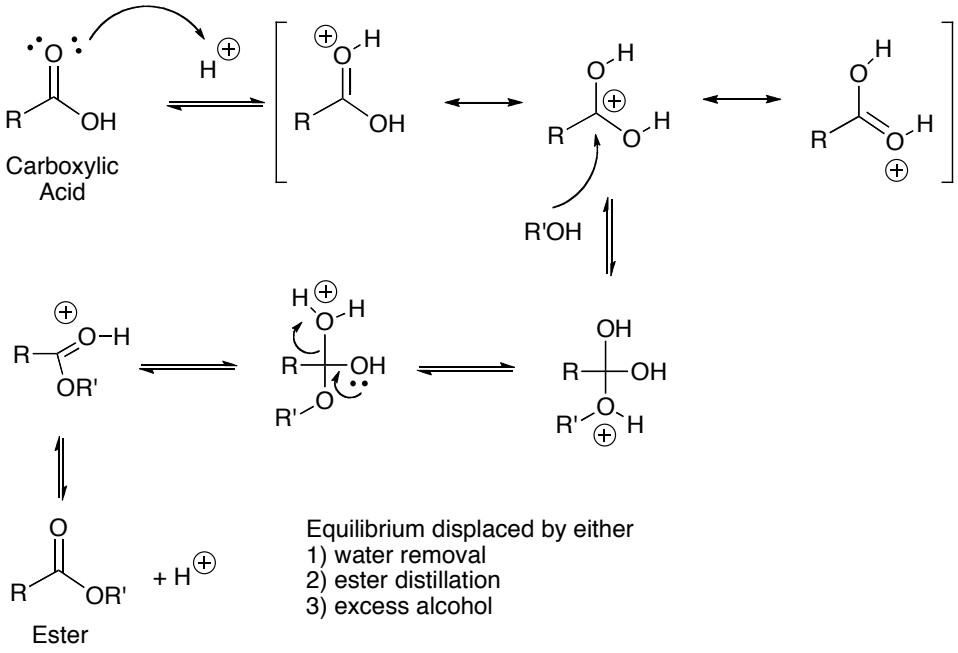
Purification/Solvent removal: Remove the drying agent by gravity filtration into a 100-mL round-bottomed flask. Set up a simple distillation apparatus using the 100-mL flask, as the pot. (Since dichloromethane is very volatile, cool the receiving flask, and a power controller setting at, or below 3). Remove the dichloromethane by distillation and place the distillate (the dichloromethane in the receiver) in the waste dichloromethane recovery bottle.
Purification of the product (PhCOOMe) by distillation: Transfer the crude methyl benzoate into a 50-mL round-bottomed flask, and setup an apparatus for simple distillation. Distill the ester using *an air-cooled condenser* (this means NO WATER goes through, disconnect the tubing) rather than a water-cooled condenser (which can crack because of the high boiling point of the ester). [Power controller setting at 10. You can/should use aluminum foil and glass wool to insulate the still head.] Collect the material boiling above 190° C in a weighed receiver, and calculate the yield. Methyl benzoate should be disposed into the non-halogenated (acetone) waste container.

Recovery of unreacted benzoic acid: [Note: this is very similar to the extraction lab] This step should be conducted during the simple distillation removing CH_2Cl_2. Recover the unchanged benzoic acid from the aqueous sodium bicarbonate washing by carefully acidifying the basic solution with concentrated HCl. Cool the solution in ice and add the HCl dropwise since the reaction is exothermic and foaming occurs (CO_2 evolution). Collect the precipitate of benzoic acid by vacuum filtration. Determine the weight of the dry benzoic acid and calculate the theoretical yield of methyl benzoate based on the weight of benzoic acid with which you started (6.1 g) less the weight of benzoic acid recovered. Turn in the product into the labeled container.

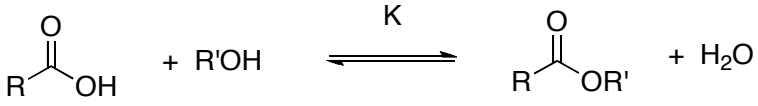
TIPS: - During the extractions, make sure you know which layer you want. In doubt?? SAVE EVERYTHING!!
- Don't forget to answer the problem assignment in your notebook. It will be graded.

- As always, drawing a purification chart may help you understand the procedure, and avoid throwing away something you need later.

MECHANISM (Fischer esterification)



The overall process of esterification is one involving an equilibrium among a variety of compounds, and for the reaction to give a high yield; the equilibrium must be shifted toward the products: the desired ester, and water. This can be accomplished either by removing one or more of the products from the reaction mixture as they are formed or by using a large excess of one of the starting reagents.
The effect of the latter approach is obvious from consideration of the mass law relating starting materials and products (equation). Increasing the amount of either the alcohol or the carboxylic acid will result in an increase in the amount of products formed since the equilibrium constant. K, for the reaction-must remain constant at a given temperature, no matter what quantity of either reagent is used.



$$K = \frac{[RCOOR'][H_2O]}{[RCOOH][R'OH]}$$

Problem Assignment

THIS PROBLEM MUST BE ANSWERED IN YOUR NOTEBOOK AND WILL BE GRADED.

Assuming the equilibrium constant for the esterification of benzoic with methanol is K = 3, calculate the theoretical yield of methyl benzoate expected using the molar amounts used in the experiment (Lab 11, above).
Concentrated sulfuric acid is added as a catalyst in the esterification procedure, even though another acid (benzoic acid) is one of the organic reagents used. Why is the sulfuric acid necessary?