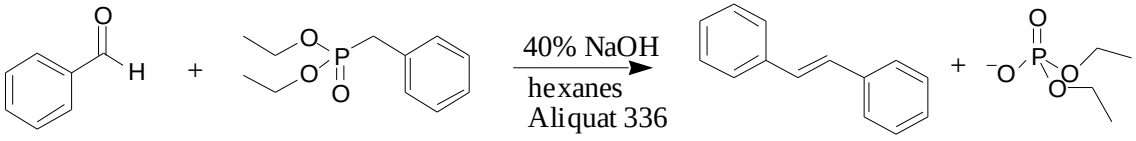
Wittig reaction

Introduction

In this lab, we will be performing a Wittig reaction, reacting an aldehyde with an ylid to make an alkene.

Instead of using a regular Wittig, however, we will be using a variation called the Horner-Emmons Wittig reaction. This variation has several advantages: it gives only the *trans* product, it uses a much milder base that is easier to handle, it gives a water soluble byproduct which is easy to separate from the product, and it gives only the trans product. The reason that all of these advantages occur is a change in the structure of the ylid – instead of a triphenylphosphine ylid, we will use a diethylphosphonate ylid. Its H's are much more acidic, and its byproduct is negatively charged.

The 40% NaOH that will serve as a base introduces water as a solvent, but neither of the other two starting materials are soluble in water, so hexane is added as a second solvent. Aliquat 336 is a phase transfer catalyst which carries the hydroxide ion into the hexane so that it can act as the base.



Reagents	volume	density	mass	MW	mmoles	eq
benzaldehyde	0.220 ml					1.00
diethylbenzylphosphonate						1.00
aliquat 336	5 drops	x	x	x	x	x
40% NaOH (aq)	3 mL	1.4 g/ml	soln: NaOH:			
hexanes	3 mL	x	x	x	x	x
stilbene	x	x				1.00

melting point of stilbene _____

Procedure

Before coming to lab:

- Review what you learned about the Wittig reaction from Chem 2320.
- Read the entire lab to make sure you understand what you will be doing.
- Read the explanation of "Purifying a Solid by Recrystallization," which we will be using for the first time in this experiment. Then review the following techniques:
  - Refluxing a Reaction
  - Extraction and washing
  - Drying an Organic Solution
  - Filtering a Solid from Solution
  - Analyzing Mixtures by TLC
  - Measuring a Melting Point

- Do all of the calculations needed to fill out the reagent table.
- Write an introduction in your lab manual, making sure to include the reaction and the table.
- Answer the pre-lab questions on-line.

Set up and run the reaction:

- Add a spin bar and all reagents to a 10 ml round bottom flask. Use a needle and syringe to dispense the benzaldehyde. Avoid getting the base or the reaction mixture on the ground glass joint as base can cause the joint to "freeze" after heating. See me if yours gets frozen.
- Stir vigorously at reflux for 1 hour.

Isolate the product:

- Allow the reaction to cool to room temperature.
- Remove the spin bar. Transfer the reaction to a separatory funnel, rinsing the flask with several ml of hexane and adding it to the sep funnel.
- Remove the water layer. Wash the organic layer once with water to get rid of the base and the diphosphonate ester. If an emulsion forms, add some saturated aqueous NaCl to the mixture, which should help the layers to separate.
- Dry the organic layer over sodium sulfate.
- Prepare a TLC plate with spots of the two starting materials, your crude product, and the authentic product (check spots by UV light). Develop the plate in 10% ethyl acetate in hexanes (prepare this solution in your graduated cylinder and mix well before using). Analyze the results: Do you see a product spot? Is the product contaminated with starting materials? The product should be a bright blue color under UV light.
- Pour your solution into a round bottom flask, then rinse the sodium sulfate with hexane and add that too. Rotovap the solution to obtain the crude product (remember, the crude product is not an intermediate, but rather product that has been isolated but not yet purified). Since the product is solid but the starting materials are liquid, how solid your crude product is at this point is additional evidence of the proportion of product to starting materials that you have obtained.

Purify the product:

- Prepare the recrystallization solvent by boiling about 50 ml of ethanol in a beaker on your hot plate, adding a spin bar to keep it from bumping.
- Add enough boiling solvent to the round bottom flask to dissolve all of the materials (solid and liquid) in your round bottom flask. Transfer this solution to a beaker, rinsing the flask with a little more boiling ethanol.

- Heat the beaker on your hot plate until the solvent is boiling. Make sure that all of the solid has dissolved (if not, add more solvent). Make sure not to boil off too much of the solvent, or you won't have any liquid to filter off.

- Take the beaker off the heat and let it cool. Product crystals should slowly form, even as you watch. If little or no product crystallizes, boil a little bit of solvent off on your hot plate, then let it cool again.

- When you are satisfied with the amount of crystals you have, cool it to room temperature, then in ice, and then filter the crystals off.

Characterize the product:

- Observe the appearance of your final product. Authentic stilbene is a white crystalline solid.

- Obtain the mass of the purified product and calculate the % yield. The average student yield on this reaction is 21%.

- Prepare a TLC solution of the purified product by adding a small amount to your TLC vial, then adding a low or medium polarity solvent to dissolve it. Prepare a TLC plate with the staring materials, your product, your filtrate, and the authentic product. Develop the plate using 10% ethyl acetate in hexanes as the eluting solvent. What do you observe?

- Obtain the melting point and compare it to the correct value.

- Your conclusion should discuss appearance of your product compared to the authentic product, your mass and % yield, a discussion of what your TLC's told you, and a discussion of your melting point (including a comparison to the correct mp and what the range tells you about purity).

After lab:

- Finish writing up your procedure, observations, and conclusions.

- Print out the questions on the next page and fill them out. Turn in this sheet with the carbon copies of your lab (in 2 separate piles).

Questions for Wittig Reaction

Name: _____

1) List all of the ways in which the Horner-Emmons variation is more useful or easier to perform than the standard Wittig reaction. (3 pts)

2) Propose a mechanism for this reaction by comparing it to a standard Wittig reaction. (2 pts)

3) It is important not to contaminate this reaction with acetone. What product would result if acetone were present? (1 pt)

4) Aliquat 336, the phase transfer catalyst in this reaction, is a common name for trioctylmethylammonium chloride. (3 pts)

a) Using this name, draw the structure of this compound.

b) Why is it soluble in both hexane and water?

c) What ion does it likely transport?

5) Benzaldehyde is slowly oxidized to benzoic acid by contact with air. (2 pts)

a) If there is benzoic acid contamination in the benzaldehyde, what will it do in this reaction?

b) Will this be a problem? Why or why not?

6) When purifying a solid by recrystallization, where do the impurities go? (1 pt)

7) What would happen if you added too much solvent during recrystallization? What could you do to fix this problem? (2 pts)