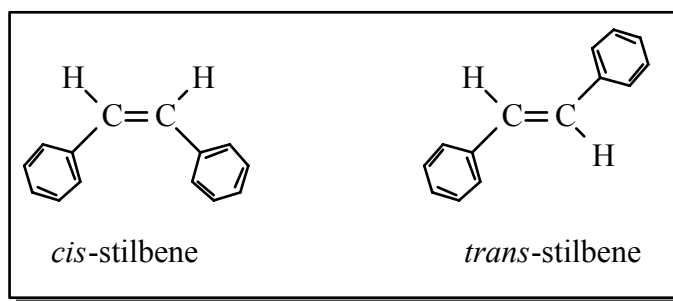


In the first part of this unit you will investigate the synthesis of stilbene by reacting benzyltriphenylphosphonium bromide with benzaldehyde. The experience you gain in this experiment will be very useful to you when you are ready to prepare your target stilbene.

Figure 2
Geometric Isomers: *cis*-Stilbene and *trans*-Stilbene



Preparation of Stilbene

Note 1- It is critical that the equipment and the chemicals you use in this reaction be dry. You should wash your glassware, rinse it with acetone, and place it in an oven for at least 15 minutes before assembling your apparatus. Drying your glassware during the pre-lab recitation period is an efficient way to use your time. In order to minimize the exposure of your reactants to moisture, you should perform the reaction under an atmosphere of dry nitrogen gas.

Note 2- One person from each team should distill enough benzaldehyde for the entire team. Plan to perform the distillation during the time when the phosphonium salt is reacting with the *n*-butyl lithium.

Note 3- This experiment requires you to perform several operations simultaneously if you are going to complete the required work in the allotted time. Read the entire experimental procedure. Then develop a list of things you will do and a sequence in which you propose to do them. Have a plan in your head before you come into lab. It may be helpful for you to create a flow diagram showing the sequence in which you plan to perform the required operations.

Note 4- Before you attempt the synthesis of stilbene, you should have solutions of the following compounds available for TLC comparison: benzyltriphenylphosphonium bromide in 95% ethanol, benzaldehyde in hexanes, triphenylphosphine oxide in 95% ethanol, *trans*-stilbene in THF. Review the procedure described in Unit 1M for the preparation of TLC reference samples. Team members should share the responsibility for preparing the various solutions. Store each solution in a screw-capped 4 mL vial. Label the vials and save them for future reference.

Generation of the ylide

Add 1.00 ± 0.05 mmol of benzyltriphenylphosphonium bromide and 5 ± 0.5 mL of toluene to a 25 mL round bottom flask containing a magnetic spin bar. Attach a Claisen adapter to the flask. Attach a condenser to the side-arm of the adapter and seal the other

arm with a teflon-coated septum. (The teflon-coated side should face the reaction mixture.) Flush the flask with a gentle stream of nitrogen. Add 1.0 equivalents of 1.6M n-butyl lithium solution to the stirred suspension of the phosphonium salt. Continue to stir for approximately 15 minutes.

Reaction of the ylide with benzaldehyde

Using a 5 mL syringe, inject a volume of 0.25M solution of benzaldehyde in toluene that contains 1.0 equivalents of benzaldehyde. Mix thoroughly. Continue mixing until TLC analysis indicates that all the limiting reagent has reacted. Filter the solid (presumably $(C_6H_5)_3P=O$) from the liquid. After the solid has dried, determine its mass. Save this material for IR analysis.

Remove the solvent from the filtrate using a rotary evaporator. Transfer the residue from the flask to a piece of filter paper. Blot the solid on the filter paper until any traces of solvent have been absorbed. Weigh the dry product. Set aside approximately 5 mg of this material for IR analysis and mp determination.

Recrystallization of the crude product

Dissolve the remainder of the crude product in the minimum volume of boiling 95% EtOH. Add an additional 0.2 mL of boiling solvent and filter the resulting solution through a filter pipet that you have pre-heated into a Craig tube that in a sand bath at $90 \pm 10^\circ C$. Carefully add boiling water drop-by-drop to the filtered solution until it becomes cloudy and crystals begin to form. Remove the tube from the heat and after a few minutes immerse it into an ice-water bath.

Put the top half of the Craig apparatus into the Craig tube and invert the apparatus into a centrifuge tube. Place the assembly into a centrifuge and spin for 1-2 minutes to drain the solvent. (Each assembly must be counterbalanced so that the centrifuge works properly.)

Remove the Craig assembly from the centrifuge tube and transfer the solid onto a tared piece of filter paper. Allow the solvent to evaporate before weighing the product.

Product Analysis

You will record four physical properties of the sample of stilbene that you prepare in this experiment: 1. mp 2. IR spectrum 3. 1H -NMR spectrum 4. GC-MS. In addition, you will also record the ^{13}C -NMR spectrum of a sample of *trans*-stilbene that has been prepared for you.

mp Determination

Determine the mp range of the crude and recrystallized samples of stilbene that you prepared. You should measure the mp of an authentic sample at the same time. The melting point of *cis*-stilbene is approximately $-5^\circ C$. The melting point range of *trans*-stilbene is $122-124^\circ C$. Reduce the heating rate to $2^\circ C/minute$ during the last stage of your determination.

IR Spectra

Prepare a $5 \pm 3\%$ mixture of your presumed $Ph_3P=O$ and KBr. Record the IR spectrum of this mixture. Save the spectrum in your folder. Compare your spectrum to the spectra of authentic triphenylphosphine oxide in the ReferenceSpectra folder.

Prepare a 5±3% mixture of your sample of stilbene and KBr. Record the IR spectrum of this mixture. Save the spectrum in your folder. Compare your spectrum to the spectra of authentic *cis*-stilbene and *trans*-stilbene in the ReferenceSpectra folder.

NMR Spectrum

Dissolve 5-10 mg of your sample of stilbene in 600±50 µL of CDCl₃. Filter this sample into an NMR tube and record its ¹H-NMR spectrum. Save the spectrum in your folder. Compare your spectrum to the spectrum of authentic *trans*-stilbene in the ReferenceSpectra folder.

Record the ¹³C-NMR spectrum of the authentic sample of *trans*-stilbene that has been prepared for you. Save this spectrum in your folder.

GC-MS

Operating instructions for the GC-MS are available on the computer that controls the instrument. There is a hard copy of these instructions on the bench next to the instrument.

A handout entitled "**Instructions for Preparing Samples for MS and GC-MS Analysis**" is also available on the GC-MS bench. Follow these instructions carefully. It is essential that the concentration of the solution you prepare be in the range of 10 pg/µL. A sample with a concentration of 100 pg/µL will overload the mass spectrometer and disable the instrument for other students.