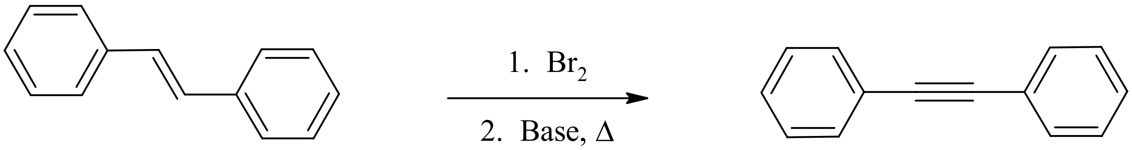
Synthesis of Diphenylacetylene

Introduction

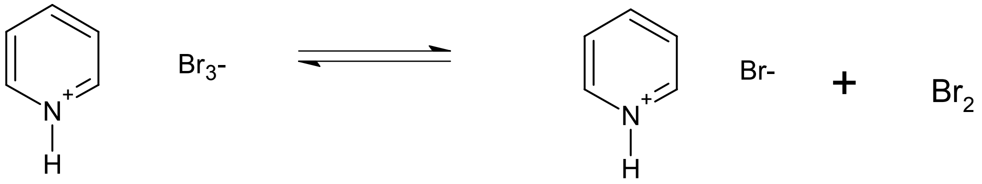
In this experiment you will generate the carbon-carbon triple bond of an alkyne, by the standard method of brominating the double bond of an alkene followed by heating the vicinal dibromide product with strong base to eliminate two equivalents of hydrogen bromide. This is a two step synthesis in which the first step proceeds very rapidly and essentially quantitatively (almost 100% yield of product). In this synthesis your starting alkene is trans-stilbene, and the alkyne product is diphenylacetylene.



trans-stilbene

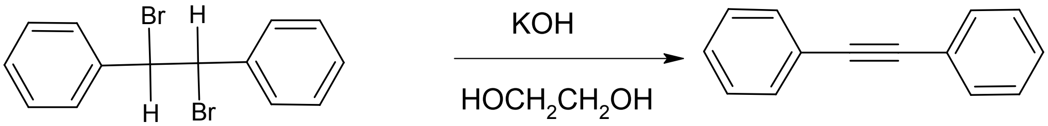
diphenylacetylene

Although the first step could be accomplished by using elemental bromine which is a red liquid that is highly corrosive and is a lachrymator, you are going to generate your bromine *in situ* (in the reaction mixture) using a solid reagent, pyridinium hydrobromide perbromide. This reagent generates the bromine for the reaction via the following equilibrium:



pyridinium hydrobromide perbromide

When the vicinal dihalide formed from the addition reaction is heated with a strong base in a high-boiling solvent, two equivalents of HBr are eliminated generating the alkyne functional group.



Diphenylacetylene

Safety Notes:

Although pyridinium hydrobromide perbromide is much easier to handle than liquid bromine, it is a caustic reagent which can cause burns and should be handled with care. Wearing gloves is a wise precaution. Wash any contact areas with copious amounts of water.

Potassium hydroxide is a caustic base which is corrosive to skin and clothing. Wearing gloves is a wise precaution. Wash any contact areas with copious amounts of water.

Experimental Procedure

Preparation of Stilbene Dibromide

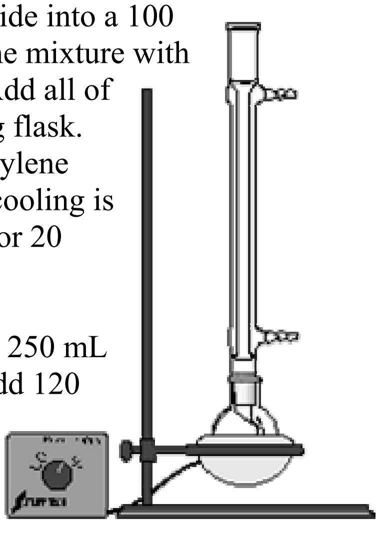
In a 125L Erlenmeyer flask, dissolve 2.0 g of trans-stilbene in 40 mL of glacial acetic acid by waming on a hot plate. Carefully add 4.0 g of pyridinium hydrobromide perbromide and mix the reagents by swirling. Using a small pipet and a small amount of acetic acid, rinse any crystals from the sides of the flask and heat the mixture for an additional 2-3 minutes. Small plate-like crystals of stilbene dibromide should precipitate almost immediately.

Cool the flask in cold running water, collect the solid by suction filtration in a Büchner funnel, and wash the collected solid with 10-15 mL of cold methanol to remove any yellow color. Dry the product by drawing air through the funnel for several minutes while beginning the next part of the procedure. You will need to treat the filtrate before discarding it in the sink. Dilute the liquid in the filter flask with water and add enough sodium bisulfate to remove the orange color. The resulting solution can be poured down the drain.

Preparation of Diphenylacetylene

Place approximately 1.5 g (~20 pellets) of potassium hydroxide into a 100 mL boiling flask and add 20 mL of ethylene glycol. Swirl the mixture with warming until most of the potassium hydroxide dissolves. Add all of your stilbene dibromide and two boiling stones to the boiling flask. Attach an air-cooled reflux condenser to the flask. Since ethylene glycol is such a high boiling solvent (bp 196-198°C), water cooling is unnecessary. Heat the mixture to boiling and gently reflux for 20 minutes.

At the end of the reflux period, decant the hot solution into a 250 mL Erlenmeyer flask and cool it to room temperature. Slowly add 120 mL of water while swirling the flask. Allow the mixture to stand at room temperature for 15 minutes. The diphenylacetylene should begin to separate as a yellow



solid. After cooling the mixture in an ice bath, collect it by suction filtration in a Büchner funnel. Rinse the Erlenmeyer with some cold water and pour it over the solid in the funnel. Discard the aqueous filtrate down the drain.

Purify your impure diphenylacetylene by recrystallization from a mixture of ethanol and water. Dissolve the solid in 10-15 mL of warm ethanol by heating the solution on a hot plate. Do not overheat the solution. You should keep the temperature of the flask no hotter than your hand can stand. While swirling the flask, add water dropwise until the solution just becomes cloudy. You should need no more than 1 mL of water. Allow the mixture to cool to room temperature. When crystallization is complete, collect the crystals by suction filtration and allow them to air dry by continuing to draw air through them via the suctioning process.

Determine the actual yield and calculate the overall percentage yield (clearly showing your calculations) from trans-stilbene. Characterize your product by determining its melting point and performing a bromine test to detect the presence of unsaturation in the product.

Questions To Be Answered in Your Notebook

1. Draw the mechanism for the addition of bromine to the double bond of stilbene dibromide.
2. Draw a Newman projection for the stilbene dibromide product. Is this isomer of stilbene dibromide chiral?
3. Would you obtain the same final product by this experimental procedure if you used cis-stilbene instead of trans-stilbene? If your answer is no, explain why not, and show what the product would be.
4. If you do this bromination-debromination process on cyclohexene, the final product obtained is not an alkyne. Why not? What is the most likely structure of the final product?