Experiment 22: Addition and Elimination Reactions:

**Synthesis of Diphenylacetylene from trans-Stilbene**

Certain acetylenes are synthesized readily by an addition-elimination sequence starting with the corresponding alkene. You will employ this method to prepare diphenylacetylene from trans-stilbene.

\[
\begin{align*}
\text{trans-stilbene} & \xrightarrow{B_2} \text{stilbene dibromide} & \xrightarrow{2\text{KOH}} \triangle & \text{diphenylacetylene} \\
\end{align*}
\]

On mechanistic grounds, which stereoisomeric dibromide do you expect to obtain from the addition reaction, the meso isomer or the racemic mixture of enantiomeric R, R and S, S isomers? (The experiment will provide the opportunity to test whether your expectation is correct, since the meso dibromide melts at 238°C while the racemic mixture of dibromides melts at 114°C.)

You will use pyridinium bromide perbromide (right) as the brominating agent; it serves as an in situ source of bromine through the following equilibrium:

\[
B_3^- \xrightarrow{} Br_2 + Br^- + \text{pyridinium bromide perbromide}
\]

This stable, crystalline salt is more convenient to handle than bromine, and has been found to possess far greater stereoselectivity than bromine itself in the bromination of alkenes such as cis- and trans-stilbenes. Note that each mole of the reagent (MW 320) releases one mole of Br₂.

The second step requires a very high temperature in order to complete the reaction in a reasonable time. This is accomplished by carrying out this
step in a solvent of very high boiling point and heating in an oil bath at 160°C. Caution is necessary when working around such a hot bath.

Procedure

1. Place 0.0055 mole of trans-stilbene in 20 mL of acetic acid in a 50 mL Erlenmeyer flask. Heat the mixture on a steam bath until all of the stilbene dissolves. Then add 0.0063 mole of pyridinium bromide perbromide (Caution: corrosive; wear gloves) and mix the reactants by swirling. If necessary, use an additional small amount of acetic acid to rinse into solution any crystals of the reagent that have adhered to the walls of the flask. Continue heating on the steam bath for another 1-2 minutes until the separation of the small plates of the crystalline dibromide appears complete.

2. Cool the reaction mixture in cold water (do not use an ice bath or the acetic acid will freeze). Collect the product by vacuum filtration and wash it with a small amount of cold methanol to remove all or most of the yellowish color. Save a small amount of this stilbene dibromide to take a melting point after it is dry. Weigh the remainder of your product now and continue with the next step. If you have less than 0.5 g, consult your TA.

3. In a large test tube which you obtain from your TA place the remainder of your stilbene dibromide (at least 0.5 gram) along with 3 pellets of potassium hydroxide. (These consist of about 85% KOH and 15% water. Three pellets weigh about 0.5 g; it is not necessary to weight them since you are using an excess.) If you have more than 1.5 g stilbene dibromide, use 4 KOH pellets. Caution: Potassium hydroxide is very hygroscopic and very caustic; pour it out quickly and recap the bottle immediately. Clean up any spills with a damp paper towel.

Add 4 mL of triethylene glycol.

4. As a heat source for the dehydrobromination reaction, use a sand bath that has been regulated to 160-170°C. To prepare your sand bath, fill your heating mantle with sand. Set the step control at 60 Volts early in the lab and work on getting it regulated. It is helpful to stir the bath with a glass rod (not the thermometer). Do not over-heat it or leave it unattended. If the sand gets too hot, the thermometer can explode.
When the temperature is regulated, use a clamp to mount the test tube containing your reaction mixture in the sand bath, occasionally mixing the contents of the test tube with a glass stirring rod while maintaining the sand bath at 160-170°C. Caution: Hot sand can cause painful burns!! After the potassium bromide begins to separate out, continue heating for five minutes more. Remove the test tube from the sand bath (Reminder: the test tube is hot!) and cool it to room temperature in room temperature water.

5. Add 20 mL of water to the cooled reaction mixture, and collect the resulting nearly colorless diphenylacetylene by vacuum filtration. The crude product need not be dried, but can be recrystallized directly from 95% ethanol in the hood. Review the procedure for recrystallization. Essentially, you dissolve your product in the minimum necessary volume of hot ethanol, carry out a hot gravity filtration, and let the hot ethanol solution stand undisturbed while it cools slowly; this should lead to the formation of large colorless crystals. After the first crop of crystals has been collected by vacuum filtration, concentrate the mother liquor by boiling it to obtain a second crop of pure material, which is also collected by vacuum filtration. Combine the two crops of crystals, and after allowing the product to dry determine the yield and melting point, and submit the sample to your TA. The reported melting point of diphenylacetylene is 61°C.

6. Your Lab Report should include answers to the following questions:

A. What results would have been obtained in this experiment if cis-stilbene had been used instead of trans-stilbene as the starting material? That is, would the intermediate or final products have been different, and if so, how?

B. How could you determine whether the elimination step occurs by the E₁ or the E₂ mechanism?

C. In this synthesis why do we first add two bromine atoms to trans-stilbene if we are just going to take them off again?