Experiment 5: Electrophilic Addition
Bromination of trans-Stilbene

Introduction
As discussed in Experiment 2, bromine reacts readily with alkenes by electrophilic addition to yield the corresponding vicinal dibromide products. This reaction is not only a simple test for the presence of double bonds, but also a useful reaction in its own right. Halogens are some of the most synthetically useful functional groups in organic chemistry. The purpose of this experiment is to carry out the addition of bromine to trans-stilbene and gain insight into the stereochemistry and possible mechanism of the reaction.

The source of bromine will be the reaction of potassium bromate (a Br\(^+\) source) with hydrobromic acid (a Br\(^-\) source). This avoids the need to directly dispense and transfer bromine solutions which are highly toxic and corrosive. The reaction equations for the generation of bromine and its reaction with trans-stilbene are as follow:

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\begin{align*}
KBrO_3 & \quad + \quad 6 \text{HBr} \quad \rightarrow \quad 3 \text{H}_2\text{O} & \quad + \quad \text{KBr} & \quad + \quad 3 \text{Br}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{Br} & \quad \text{Br} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{Br} & \quad \text{Br} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

Pre-Lab Questions:

1. Draw all of the possible stereoisomers of the expected product, 1,2-dibromo-1,2-diphenylethane. Label each stereocenter as R or S. Are any of the possibilities meso compounds?

2. Consider the two possibilities of syn versus anti addition of Br\(_2\) to the double bond of trans-stilbene. Syn addition occurs when the two bromine atoms add from the same side of the double bond. Anti addition occurs when the two bromine atoms add from opposite sides of the double bond.

Which of the stereoisomers would be formed from syn addition? Which would be formed from anti addition? It may help to use your molecular models here.
**Procedure**

Note: Bromine is a highly toxic and corrosive to skin and mucous membranes. Inhalation of bromine vapors is very harmful. In this experiment, the hazard potential of bromine is minimized by generating the bromine in small amounts in situ and generation of bromine (adding the HBr) should only occur after your apparatus has been hooked up to a working aspirator.

Dissolve 0.30g of trans-stilbene in 5mL of hexanes a 10 mL round-bottomed flask with a magnetic stir bar (note, the stilbene may not fully dissolve). While stirring, add 0.20g of potassium bromate. Fit the flask with an air condenser and vacuum adapter as shown in the diagram below. Check to make sure that your aspirator is producing a good vacuum and connect the hose to the vacuum adapter.

Leaving the aspirator running, take the vacuum adaptor off for a moment and quickly pipette 0.8 mL of 48% hydrobromic acid (HBr) into the stirring reaction mixture. Replace the adaptor immediately so that excess bromine is removed and doesn’t get into the air of the laboratory.

Stir the reaction for 30 minutes at room temperature. After the reaction is complete, quench it by adding 1-hexene dropwise until all of the remaining bromine has been consumed.

Filter off the solid from the reaction mixture by suction filtration using a Hirsh funnel. Rinse any residual solid from the reaction flask into the funnel using cold hexanes. Wash the solid with a small amount of cold hexanes and dry it by pulling air through it for a few minutes.

Transfer the product to a 50 mL Erlenmeyer flask and recrystallize it from xylene. Start by adding a stir bar and about 5 mL of xylene to the flask and bringing it to a boil in a sand bath (bp ~ 140°C). **Caution: Boiling Xylenes is very hot.** Do not use a boiling stick in this solution, use boiling chips or a stir bar to promote boiling. Add solvent slowly while maintaining boiling until all of the solid dissolves. Cool the solution slowly to room temperature and collect the resulting crystals by suction filtration. The melting point of the recrystallized product is determined, and a sample is submitted for 1H NMR. If necessary, review these techniques in experiments 4 and 1, respectively.

If your NMR sample does not fully dissolve, filter the sample before putting it in the NMR tube by passing it through a plug of glass wool in a Pasteur pipette. Take a small piece of glass wool and roll it into a pea-sized ball between your fingers. Push the glass wool into the tapered end of the pipette using the tip of another pipette to make a filter. Use the pipette as a funnel to filter your solution into a vial.
Figure: Apparatus to remove noxious gases formed during reaction.

In your lab report:

The melting point of meso-1,2-dibromo-1,2-diphenylethane is 238 °C. The melting point of a racemic mixture of (R,R) and (S,S) enantiomers is 111 °C. Reference 1H NMR spectra of the meso isomer and racemic mixture are available from your TA.

Compare your melting point and NMR data with the reference data. Did the bromination reaction produce the meso isomer, a racemic mixture of R,R and S,S enantiomers, or a mixture of all of the isomers? What can you deduce about the mechanism of the reaction from the product you obtained?

Propose a mechanism for this reaction that is consistent with your results.

As always report crude and recrystalized yields, melting points and discuss sources of error.