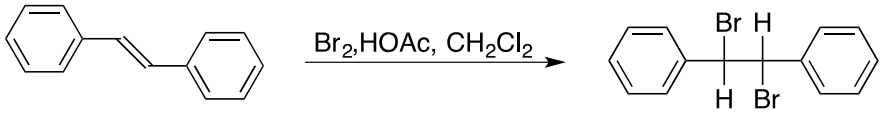
Reference: Clemson University, CH 2270

Addition of A Halogen To An Alkene – Synthesis of Stilbene Dibromide

Materials

From the Chemicals Hood:	Nothing from the Stockroom
Glacial acetic acid *trans*-stilbene 1 M Br_2 in dichloromethane solution Methanol Saturated sodium bisulfite aqueous solution	

In this experiment you will synthesize stilbene dibromide by reacting the alkene *trans*-stilbene with elemental bromine (Br_2).



trans-stilbene stilbene dibromide

The mechanism of the reaction proceeds through a cyclic bromonium ion intermediate and this can get a little complicated, as you could imagine four different yet similar mechanisms for the formation of stilbene dibromide. Because *trans*-stilbene is a symmetrical compound the first addition of a bromine atom can occur from either the "top" or the "bottom" of the alkene. There is no chemical (or geometrical) difference. Notice that the bromine molecule, though formally non-polar, has a weak Br-Br bond and is polarizable, especially when approached by a nucleophilic alkene (**Figures 1** and **4**).

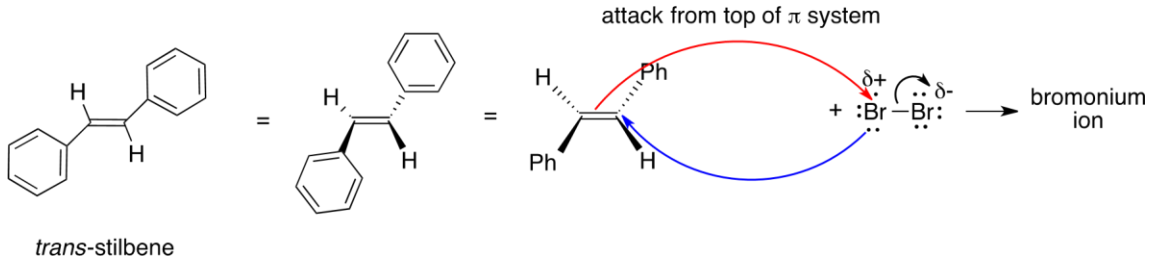
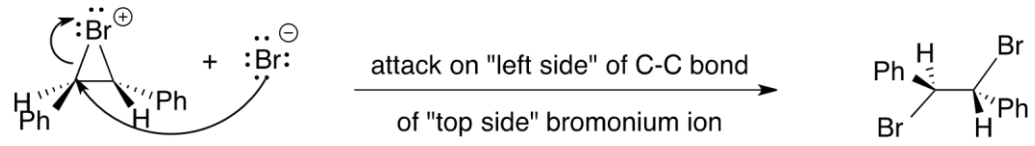


Figure 1. Addition of Bromine to the "top" of the Alkene of *trans*-Stilbene

Subsequent addition of the bromide anion to the still-symmetrical bromonium ion can occur from the left- or right-side of the carbon-carbon bond (**Figures 2**, **3**, **5**, and **6**).



bromonium ion

Figure 2. Attack of Bromide Anion to the "Left Side" Carbon of a Bromonium Ion

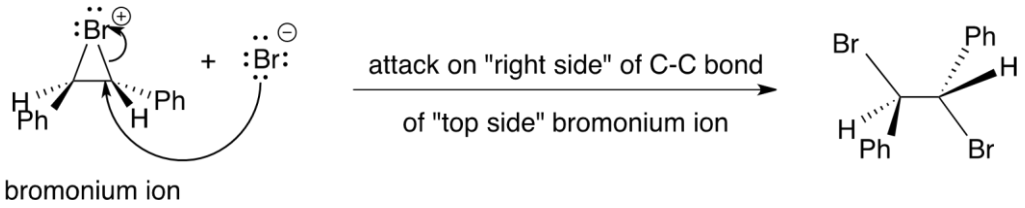


Figure 3. Attack of Bromide Anion to the "Right Side" Carbon of a Bromonium Ion

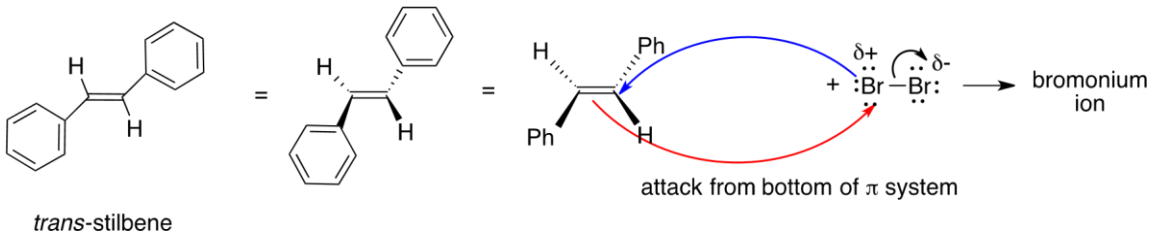


Figure 4. Addition of Bromine to the "bottom" of the Alkene of *trans*-Stilbene

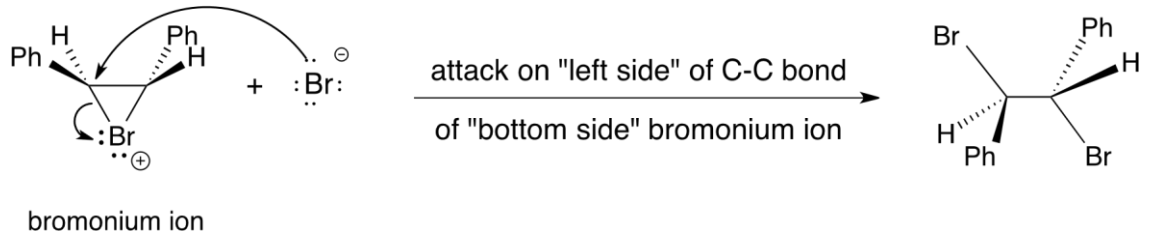


Figure 5. Attack of Bromide Anion to the "Left Side" Carbon of a Bromonium Ion

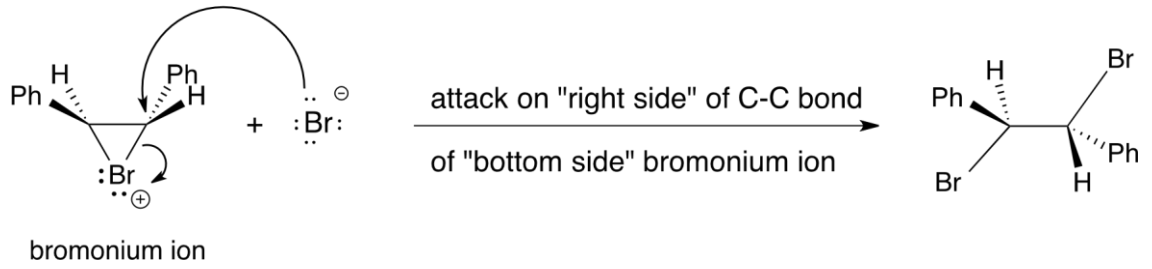


Figure 6. Attack of Bromide Anion to the "Right Side" Carbon of a Bromonium Ion The product of this reaction has two stereogenic centers, and since all three substituents on each stereogenic center are the same (bromine, phenyl, hydrogen), one of the isomers of stilbene dibromide is a meso compound (mp 241-243 □C). The other two isomers of stilbene dibromide are the (+) and (-) enantiomers. If these are formed it will be as the racemic mixture (mp 114-115 □C).