

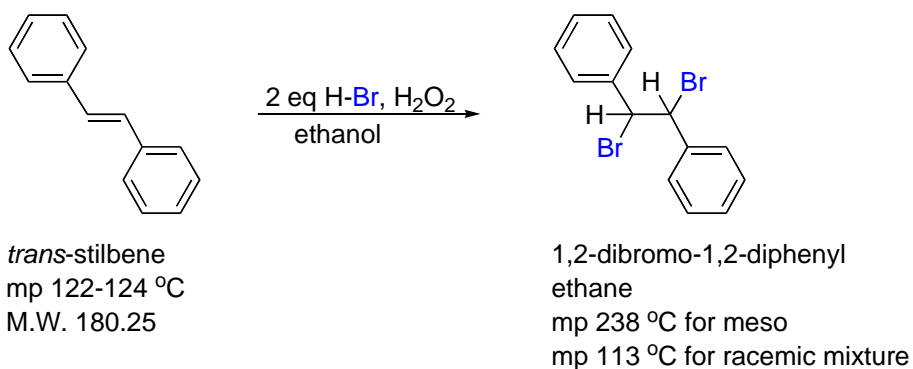
# 10. X<sub>2</sub> Addition to Alkenes: Bromination of *trans*-stilbene

**M. Jones:** Addition of X<sub>2</sub> to Alkenes, 10.2, pgs 438-449  
Addition of Halogens, 10.2b, pgs 442-449, Figures 10.12, 10.13  
Optical Activity, 4.8, pgs 170-176

This procedure has been adapted from the online procedure of Professor Veljka Dragojlovic, at the Oceanographic Center, Nova Southeastern University.

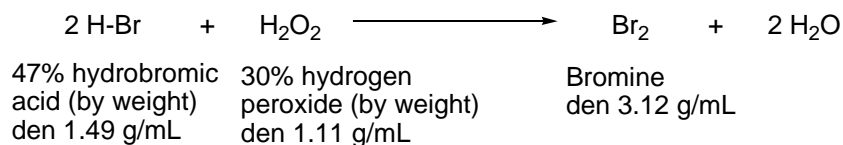
## Background

In this experiment, you will perform the addition of Br<sub>2</sub> to *trans*-stilbene.



**Figure 1.** The general reaction for the addition of Br<sub>2</sub> to *trans*-stilbene.

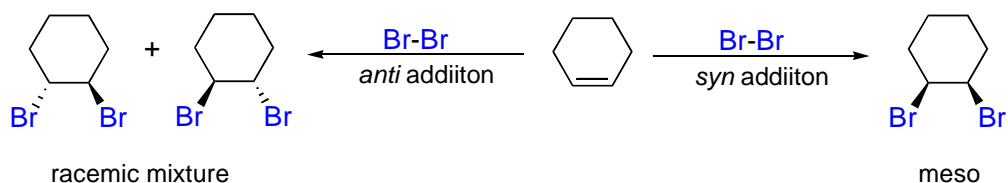
Bromine (Br<sub>2</sub>) is a highly corrosive brown fuming liquid. So rather than use it directly, it will be generated *in situ* for this reaction from hydrobromic acid and hydrogen peroxide.



**Figure 2.** The generation of Br<sub>2</sub> *in situ*.

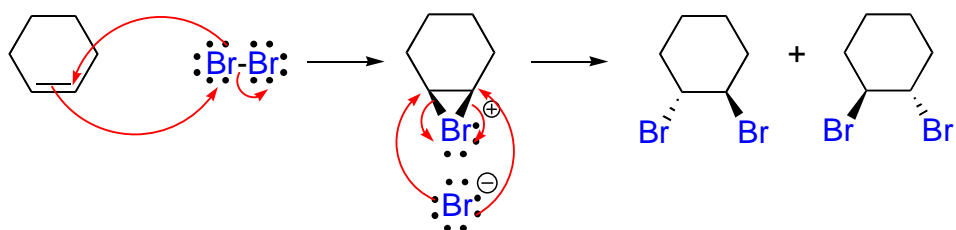
Furthermore, Br<sub>2</sub> is used as an indicator for the presence of  $\pi$  bonds as seen by a color change from brown to clear. It reacts with double and triple bonds but not rings so it is possible to distinguish between unsaturated molecules containing rings and unsaturated molecules containing carbon-carbon  $\pi$  bonds.

So let's look at the mechanism of this reaction. Theoretically,  $\text{Br}_2$  can add either *syn* (same side) or *anti* (opposite sides) in this reaction. An example of the different addition products of  $\text{Br}_2$  to cyclohexene is given in Figure 3.



**Figure 3.** The products from the *syn* and *anti* addition of  $\text{Br}_2$ .

If it adds in the *syn* fashion, then the product would be a meso compound, *cis*-1,2-dibromocyclohexane. On the other hand, the *anti* addition products would be a mixture of two enantiomeric compounds of *trans*-1,2-dibromocyclohexane. There is only one addition type in this reaction, which is the *anti* addition product resulting in the racemic mixture of *trans*-1,2-dibromocyclohexane. The mechanism is shown in Figure 4.



**Figure 4.** The mechanism for the *anti* addition of  $\text{Br}_2$  to cyclohexene.

The first step is the addition of  $\text{Br}$  to form a bromonium ion intermediate, which can be formed above or below the plane of the ring. Then, the bromide anion adds on the opposite side and opens the bromonium ion resulting in the two enantiomers.

**Tips:**

- Record all volumes, weights, and color changes.
- Take care with the handling of hydrobromic acid, and hydrogen peroxide.
- Make sure to check the temperature limit of your Mel Temp apparatus thermometer and don't go over it.

## Experiment

**Experimental procedure.** Add 0.2 g of *trans*-stilbene, a boiling chip, and 8 mL of ethanol into a dry, clean flask. Swirl the mixture to start dissolving the stilbene. Place a reflux condenser on the top of the flask. Heat the mixture to reflux. Use a pipette to slowly add 1.0 mL of 47% hydrobromic acid (in 33% acetic acid) dropwise through the top of the reflux condenser to the solution with swirling. After which, use a syringe to slowly add 0.6 mL of 30% hydrogen peroxide dropwise. Let the reaction mixture reflux and swirl the contents occasionally until the resulting mixture turns white (precipitation of salts). Wait a minimum of 15 minutes.

**Reaction workup and isolation of product.** Cool the flask to room temperature and then carefully neutralize with a saturated solution of sodium bicarbonate. Place the flask in an ice-water bath and filter the resulting solid using vacuum filtration. If necessary, the product can be recrystallized from ethanol. Make sure the resulting product is dry, then weigh. Perform a Beilstein test of the product and record its melting point. Please make sure that you do not exceed the temperature limit of your Mel Temp thermometer!