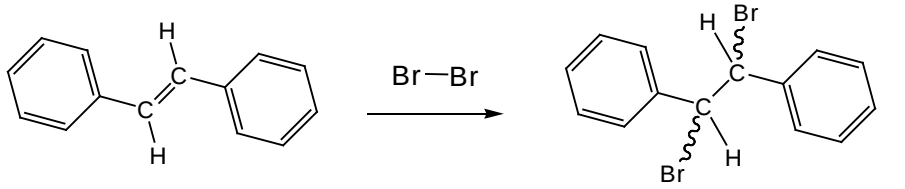
1. X_2 Addition to Alkenes: Bromination of *trans*-Stilbene

Reference: **Organic Chemistry, 4th ed., M. Jones:**
Section 10.2b, Addition of X_2 to Alkenes, pp. 414-421, esp. Figs. 10.7 – 10.14.
Section 4.8, Diastereomers… *meso* compounds…, pp. 164-169.

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_2 to *trans*-stilbene (Figure 1).

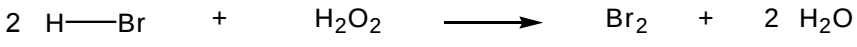


trans-Stilbene
MW 180.25
mp 122-124 °C

1,2-Dibromo-1,2-diphenylethane
mp 238 °C for the *meso* compound
mp 113 °C for a racemic mixture

Figure 1. The general reaction for the addition of Br_2 to *trans*-stilbene.

Molecular bromine (Br_2) is a brown, highly corrosive, fuming liquid. Rather than use it directly, Br_2 will be generated *in situ* in this reaction from the reaction of hydrobromic acid and hydrogen peroxide (Figure 2).



47% hydrobromic acid (by weight) d = 1.49

30% hydrogen peroxide (by weight) d = 1.11

Bromine d = 3.12 MW = 159.808

Figure 2. The generation of Br_2 *in situ*.

In another lab use, Br_2 is used as an indicator for the presence of excess alkenyl and alkynyl π bonds by the observation of a color change from brown to clear in. Bromine reacts with these bonds, but not aromatic rings, making it possible to distinguish between unsaturated molecules containing aromatic rings and those containing carbon-carbon π bonds.

Product Considerations of the Br_2 Addition

Theoretically, Br_2 could add either *anti* (opposite sides) or *syn* (same side) in this reaction. An example of the different addition products of Br_2 to cyclohexene is given in Figure 3. Note that for the time being, we have left the stereochemistry ambiguous in the reaction in Figure 1, above; that is left for you to discover (but note lecture and textbook).

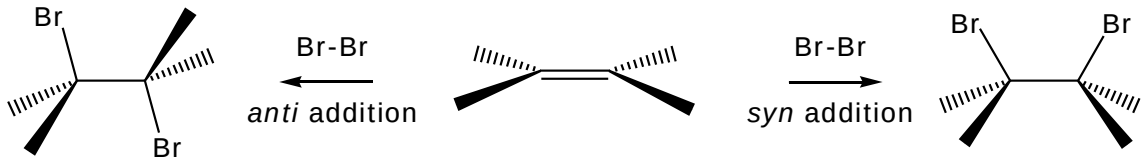


Figure 3. Possible products from the *syn* or *anti* addition of Br_2 to an alkene.

However, the <u>*mechanism*</u> of the reaction and the <u>*starting alkene*</u> will influence the outcome of the reaction, *especially* the stereochemical outcome. For instance, specifically starting with a symmetrical ring compound or "*Z*" alkene, the *anti*- or *syn*-additions would give rise to two different results (See Figure 4):

anti addition gives a *racemic* mixture (for the symmetric "*Z*-" or cycloalkane)
syn addition gives a *meso* compound (for the symmetric "*Z*-" or cycloalkane)

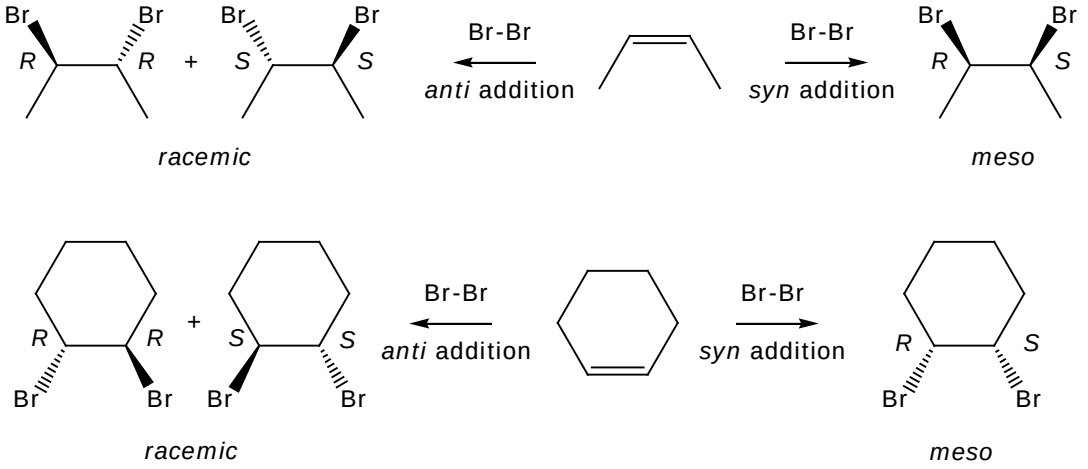
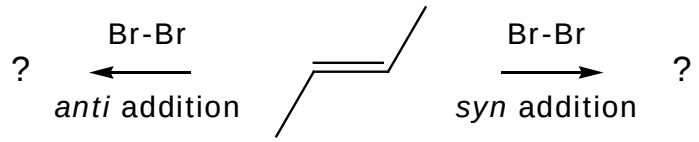


Figure 4. The different stereochemical outcomes for *anti* or *syn* addition of Br_2 to two alkene examples.

In the case of the cycloalkane, the racemic mixture from the *anti* addition consists of the *trans*-dibromocycloalkane products. In the *syn* addition, the product has a *cis*-dibromo configuration on the cycloalkane ring. Remember, the terms *cis*, *trans*, *anti*, and *syn* refer to the <u>*geometrical relationship*</u> between substituents or groups on a molecule in a specified molecule or reaction scheme. For example, here on the ring alkene, the *anti* addition gave the '*trans* product', but for the linear alkene, we refer to the '*anti* product'. ***<u>Only</u>*** the assignment of *R* or *S* in the products gives an *unambiguous* assignment of the geometrical arrangement and relationship of the resulting molecules. More complex alkenes could give diastereomers, etc.

Now, be careful… What is the result of *anti* or *syn* addition to a symmetrical "*E*-" alkene? Complete the reaction below, giving the stereochemical products and check for their relationship: is one result *meso*, is one *racemic? Both/and?* You must determine *R* and *S* at each chiral center and/or rotational conformations before correctly answering.



Mechanistic Considerations of the Br_2 Addition

The mechanism of addition of bromine to an alkene is a classic case in organic chemistry. Because of electronic and steric considerations, in the typical case, the mechanism proceeds through a "bromonium ion" intermediate (Figure 5), with the second bromine adding as bromide in an *anti* fashion (not that we're against nice clothes…). The first step is the addition of Br to form a bromonium ion intermediate, which can be formed above or below the plane of the ring. The bromide must add on the opposite side, at either carbon, and opens the bromonium ion ring resulting in the two enantiomers. Note that in this mechanistic pathway, ***only*** the products from *anti* addition can form (Figure 5).

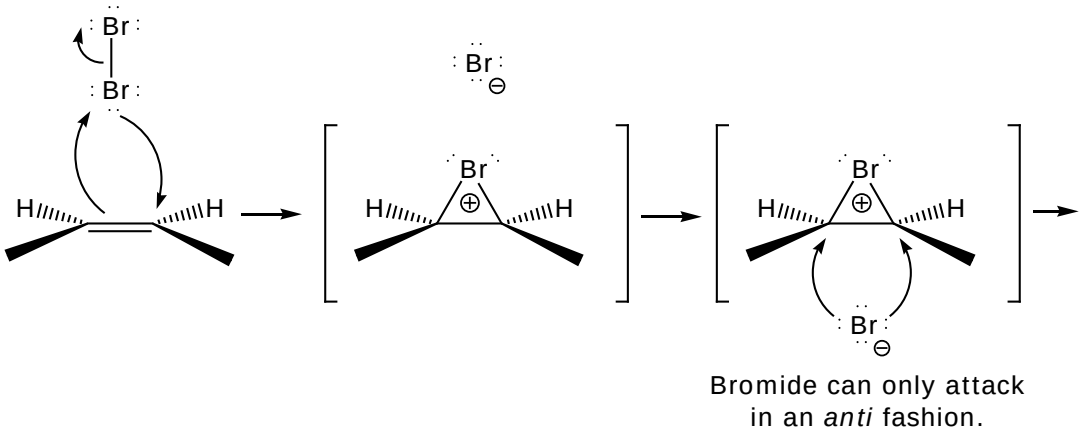
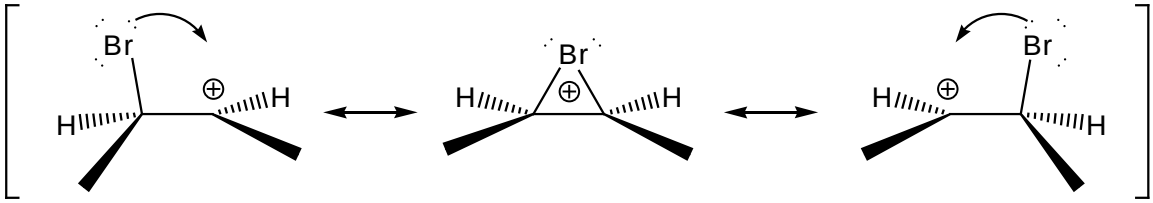


Figure 5. The mechanism for the *anti* addition of Br_2 to *Z*-butene; this results in the *racemic* product in Figure 4.

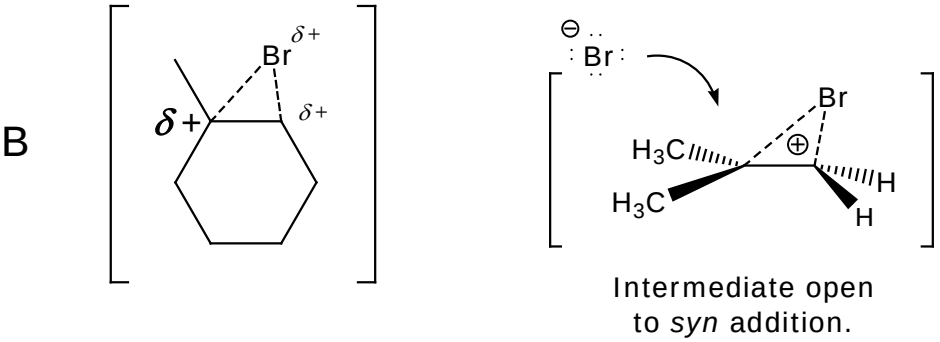
So how can we get a 'cis' addition product in this reaction? Note that if unexpected products form in a reaction, chemists need to explain how the product arose within the known mechanism, or be able to propose an alternate mechanism for the resulting products.

So far, we have just considered symmetrical starting materials and their stereochemical products. Depending on the alkene undergoing the addition reaction, there may be electronic, steric, or strain effects that modify the bromonium ion intermediate or the mechanistic pathway. For instance, one can consider the bromonium ion as the middle of

two extreme 'resonance structures' (Scheme A, below), and further consider *asymmetric* bromonium ion formation when there is the possibility of a 3° versus 2° carbon (or 3° *vs*. 1°; or 2° *vs*. 1°) (Scheme B). A group that preferentially stabilizes the partial (+) charge on a carbon, or blocks *anti* attack, could allow for a *syn* addition pathway. Also note Fig. 10.19 in the Jones reference. Other products could arise from other reagents in the reaction, or from reactions after the addition reaction is complete.



A



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 thermometer apparatus and don't go over it.

Experiment

Experimental procedure. Add 0.200 g of *trans*-stilbene, a boiling chip, and 8 mL of ethanol into a dry, clean 25 mL Erlenmeyer 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 water) dropwise through the top of the reflux condenser to the solution with swirling. Next, 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). After H_2O_2 addition, allow rxn to continue aminimum of 15 minutes.

Note: In the actual lab, the % compositions of HBr, acetic acid, and hydrogen peroxide may differ slightly from that listed above. Consult instructor if you have a question.

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. **CAUTION!** Please make sure that you do not exceed the temperature limit of your Mel-Temp thermometer!