

Addition Reactions: Preparation of Dibromostilbene

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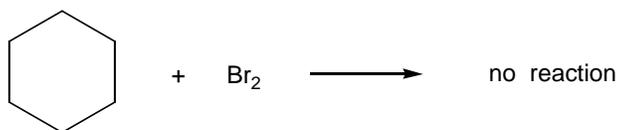
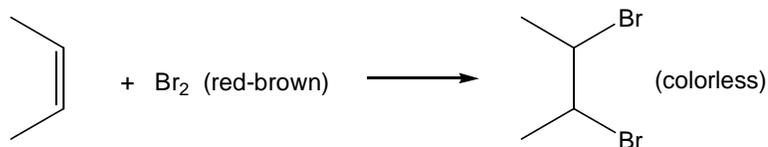
Green Chemistry

Green chemistry is a relatively new area of chemistry whose goal is to develop environmentally friendly synthetic reactions and industrial processes. Ways to accomplish that goal are to introduce reactions and industrial processes that avoid use of reagents (reactions should be catalytic and the catalyst reusable), avoid use of solvents if possible, and minimize formation of byproducts. Unless reaction is a rearrangement or an addition, it will always involve formation of byproducts. Even in case of an addition reaction, which does not involve formation of byproducts, we want to avoid use of hazardous reagents such as bromine. If our goal is green chemistry, when synthesizing a particular compound we should choose the reaction that produces environmentally friendly byproducts (for example water, lower alcohols, nitrogen, etc.).

In this laboratory exercise, you will examine environmentally friendly addition reactions of bromine.

Addition of Bromine to an Alkene

Bromine test for unsaturation involves addition of bromine to an alkene. A positive test is a color change from red-brown color of bromine to colorless solution (the reaction product bromoalkane is colorless). The test is positive only with double and triple carbon-carbon bonds. Thus, it can be used to distinguish between multiple bonds and rings as unsaturations.



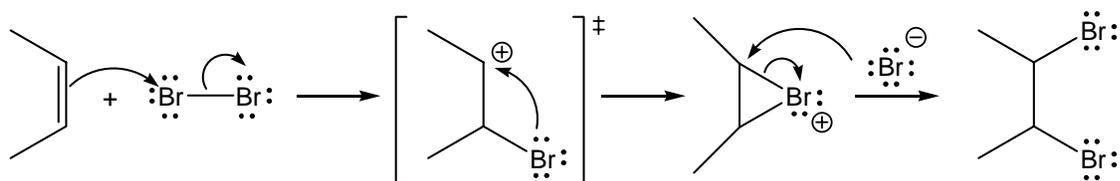
A direct addition of bromine to an alkene without presence of a solvent is a highly exothermic reaction and is not a useful preparative procedure. Usually, we use a chlorinated solvent, such as dichloromethane, as a reaction medium. Alternatives are to generate bromine in situ (in the reaction mixture) and use an environmentally friendly solvent, such as ethanol, or to do a “vanishing-phase reaction.”

Experimental Techniques:

- Reaction under reflux
- Vacuum filtration
- Filtration through fluted filter paper
- Recrystallization
- Determination of melting point
- Hot filtration

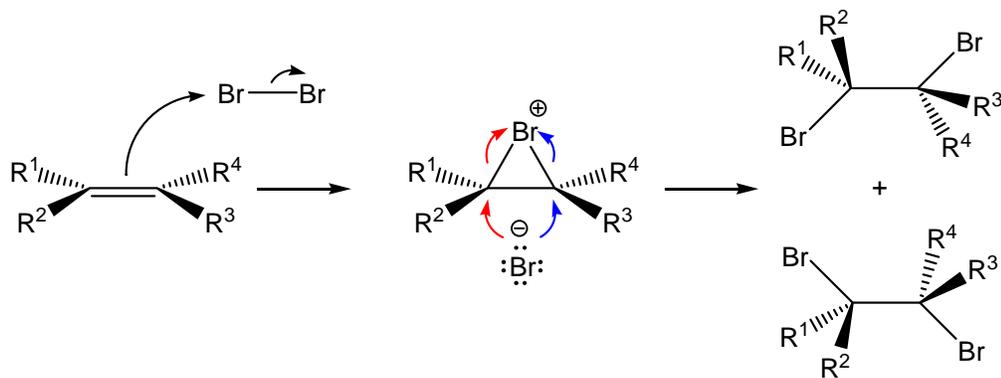
A vanishing-phase reaction is procedure in which solvent does not dissolve any of the reactants and is instead used to separate them. Therefore, one reactant must have density higher than the solvent (so that it is at the bottom of the reaction vessel) while the other reactant has density lower than the solvent so that it is on top. The solvent is in a layer between the two. As the reagent in the lower layer evaporates and passes through the solvent, it reaches the top layer and reacts with it. Since the rate of evaporation is low the reaction proceeds at a moderate rate, instead of a vigorous (and often violent) reaction if the two reagents were mixed without the solvent. Since the solvent does not dissolve the reactants and products, it can be recovered and reused.

Reaction mechanism involves interaction of a bromine molecule with π orbital of the alkene. The first step involves a charge separation. Note that the carbocation is formed in the transition state and is not an intermediate. The intermediate is a cyclic bromonium ion. The bromonium ion reacts with a bromide ion to give the product – dibromoalkane.

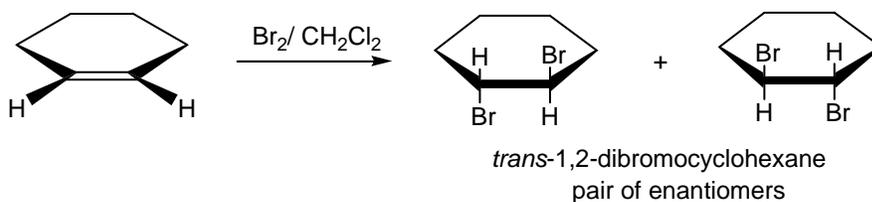
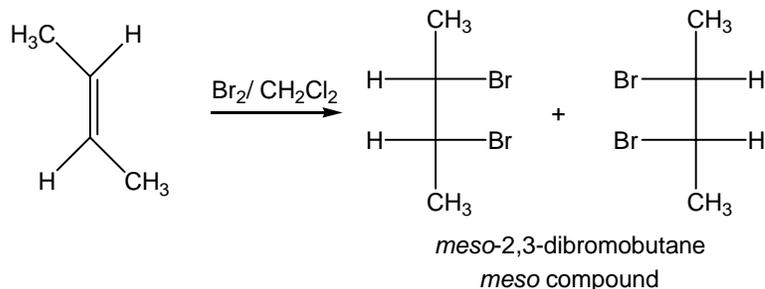


The reaction product is a vicinal dibromide (bromine atoms are on the neighboring carbon atoms).

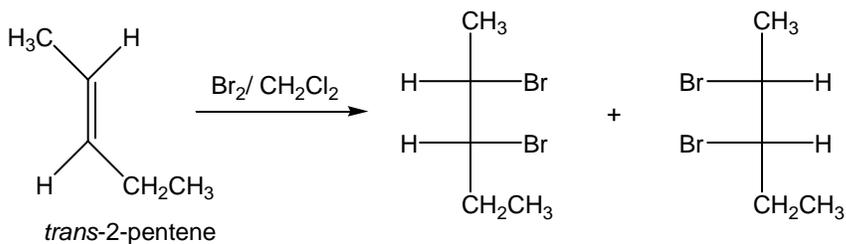
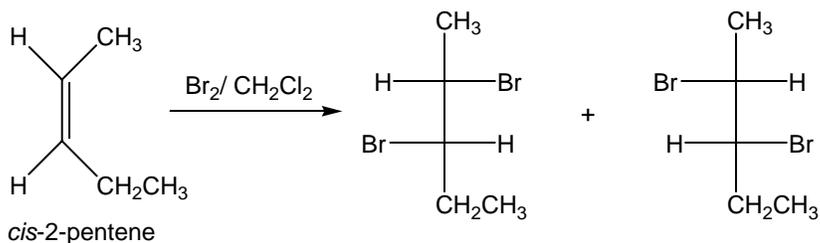
Addition of bromine across the double bond proceeds with *anti* stereochemistry. It means that two bromine atoms add to the opposite sides of the double bond.



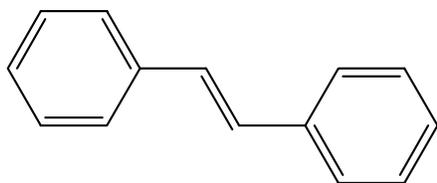
Since only two out of the possible four diastereomers are formed, the reaction is stereoselective. The reaction products are either a pair of enantiomers, or a meso compound if the substituents on the double bond are identical.



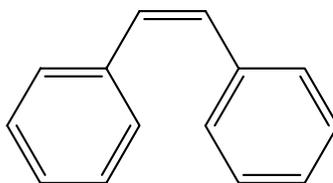
The reaction is also stereospecific since the *cis* isomer (for example, *cis*-2-pentene) gives one pair of enantiomers and the *trans* isomer (for example, *trans*-2-pentene) gives the other pair of enantiomers.



In this laboratory exercise, your task will be to prepare, isolate, purify and characterize dibromostilbene. Your starting material will be either *cis*- or *trans*-2-stilbene.



trans-stilbene



cis-stilbene

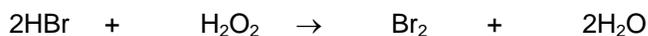
Atom Economy

From the point of view of atom economy, addition reactions are among the most efficient. There are no byproducts, since all of the atoms of the reagent add to the substrate to give the product.

Safe Reagents

While atom economy of an addition reaction is excellent, it is not the only consideration when designing a green chemistry process. In an addition of bromine to an alkene, we have to use elemental bromine. Elemental bromine is a highly corrosive and toxic liquid, which at room temperature releases dangerous fumes. It has to be handled in fumehood. A process that requires use of elemental bromine cannot be considered to be a green chemistry process.

In this experiment, you will prepare bromine in the reaction mixture (*in situ*) in a reaction between hydrobromic acid and hydrogen peroxide. The only byproduct of the reaction is water.



Both 47% hydrobromic acid and 30% hydrogen peroxide have to be handled with care (wear gloves). However, they are considerably less hazardous compared to bromine. Therefore, we made a minor sacrifice with respect to atom economy so that we can use safer reagents.

Beilstein Test for Alkyl Halides

Copper salts produce an intense blue-green color when placed in a flame. A red-hot copper wire reacts with an alkyl halide to form the corresponding copper halide. When placed in a flame, a blue-green color indicates that the organic compound contains a halogen (Cl, Br or I).

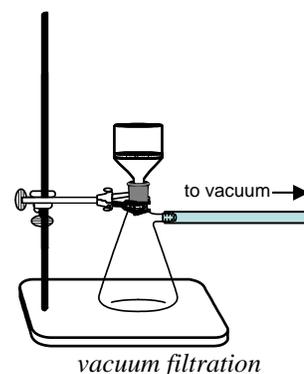
Procedures

Part I: Bromination of *trans*-Stilbene*

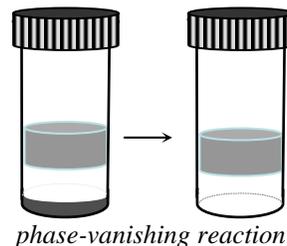
Hydrobromic acid is corrosive. Wear gloves when working with it. Hydrogen peroxide is a strong oxidizing agent and may damage clothing and skin. Ethanol is flammable.

1. Place a stirring bar, 0.5 g of *trans*-stilbene and 10 mL of ethanol in a 25 mL round bottom flask.
2. Set up a micro-scale reflux apparatus (Figure 1).
3. Heat the reaction mixture with stirring until ethanol begins to reflux.
4. With a pipette, through the condenser, add 1.2 mL of 47% hydrobromic acid dropwise. Some solid may precipitate.
5. With a different pipette, through the condenser, add 0.8 mL of 30% hydrogen peroxide dropwise. Color of the reaction mixture will change. Record the color change.
6. Continue stirring under reflux until the reaction mixture becomes white.
7. Remove the flask from the heating mantle and allow it to cool to room temperature.
8. Add concentrated solution of sodium bicarbonate to the flask until pH of the reaction mixture is between 5 and 7.
9. Cool the reaction mixture in an ice bath.
10. Collect the product by vacuum filtration. Rinse the product with cold water.
11. If necessary, recrystallize the product from ethanol.
12. Allow the product to dry, determine its mass and melting point.
13. Do the Beilstein test on the product.

This procedure does not work on cis-stilbene due to poor solubility of it in ethanol.



FC-72 is a trade name for perfluorohexane (C₆F₁₄).



The solvent (FC-72) can be reused and should be returned to the original container.

*Melting points reported in the literature are:
meso-dibromostilbene 241°C
(±)-dibromostilbene 113-114 °C*

Part II: Bromination of *cis*-Stilbene

Bromine is corrosive. One should wear gloves when working with it and use it in a fumehood only. **Do not handle bromine yourself!** Your professor or TA will deliver bromine into the reaction vessel.

1. Place a stirring bar, 0.10 mL of bromine, 1.0-1.5 mL FC-72 and 0.35 mL of *cis*-stilbene in a vial.
2. Place the reaction mixture on a stirrer and stir until the bromine layer disappears.
3. Vacuum filter the reaction mixture.
4. If necessary, recrystallize the product from xylene.
5. Allow the product to dry, determine its mass and melting point.
6. Do the Beilstein test on the product.

* This procedure was adapted from the reference 1.

Part III: Beilstein Test for Alkyl Halides

1. Wrap a copper wire (1 mm diameter or greater) around an end of glass rod leaving 3-4 cm long straight piece. Hold the end of copper wire in a Bunsen burner flame until the flame is colorless.
2. Dip the hot wire in a small amount of compound to be analyzed.
3. Hold the copper wire in the flame and record your observations.

Questions and Exercises

1. Consider the mechanism of a reaction between a stilbene and bromine. What isomer do you expect to be the reaction product? Explain your answer. Does the outcome of the experiment support your analysis?
2. Would you expect that the steric and electronic effects would influence reactivity of bromine towards electrophilic addition to the double bond? How would substituents on the double bond effect the reactivity of it?

Additional Reading

1. Doxsee, K.M.; Hutchison, J.E. *Green Organic Chemistry*, 2004., Brooks/Cole, pp. 120-128.
2. Rothenberg, G.; Clark, J.H. *Green Chemistry* 2000, (2), 248-251.
3. Ho, T.-L.; Gupta, B.G.B.; Olah, G.A. *Synthesis* 1977, 10, 676-7.

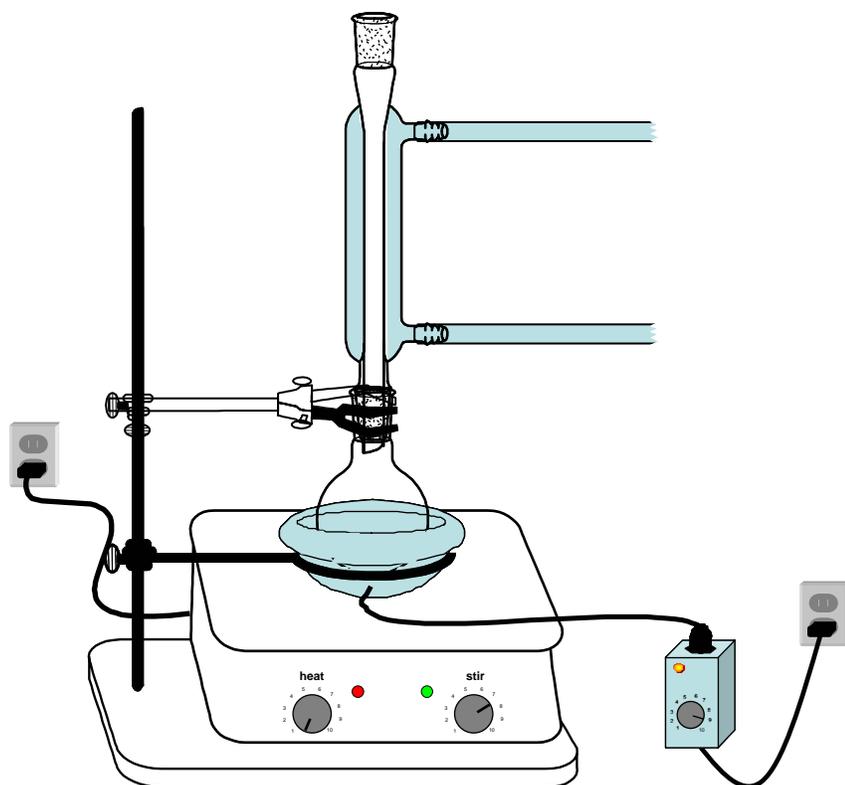


Figure 1. Reaction under reflux.

Pre-Lab Preparation**Preparation of Dibromostilbene***Date:* _____*Name:* _____**Prelab Exercises**

Draw a mechanism and predict what will be the product of bromination of *cis*-stilbene and what will be the product of bromination of *trans*-stilbene.

Signature: _____

Results**Preparation of Dibromostilbene***Date:* _____*Name:* _____*Bromination of trans-Stilbene*

Yield: _____

Appearance: _____

Melting point (°C): _____

Bromination of cis-Stilbene

Yield: _____

Appearance: _____

Melting point (°C): _____

Signature: _____