

ORGANIC CHEMISTRY I (CHGN 223)

GREENER BROMINATION OF STILBENE

Spring 2026

Chemical Concepts

Halogenation of alkenes; reactions at elevated temperature; reflux; vacuum filtration; melting point determination

Green lessons

Safer solvents and reagents; Relative nature of green chemistry

Estimated Lab Time

Approximately 2.5 hours

Chemicals Needed

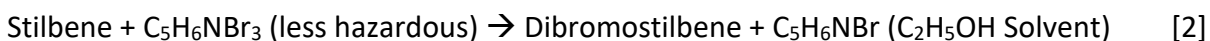
(E)-stilbene (*trans*-stilbene), 30% Hydrogen peroxide (H_2O_2), concentrated Hydrobromic acid ($\text{HBr}_{(\text{aq})}$), Ethanol, and saturated Sodium bicarbonate ($\text{NaHCO}_{3(\text{aq})}$) solution

Apparatus Needed

Hotplate/Stirrer, Variac, Heating Mantle, 50 mL Boiling flask, West condenser, and Buchner funnel

Introduction

Last week's experiment, Brominating Alkenes (SYNT 719), provided an introduction to the halogenation of alkenes. This is considered to be a green chemistry experiment because it replaces the traditional reaction [1], which uses a hazardous solvent (dichloromethane) with a relatively innocuous solvent (ethanol), and replaces hazardous Bromine (Br_2) with a safer and easier to handle reagent, pyridinium tribromide ($\text{C}_5\text{H}_6\text{NBr}_3$) [2]. Pyridinium tribromide releases Br_2 *in situ* and thus, the chemist can avoid direct contact with this hazardous reagent. Consequently, it represents a greener chemistry experiment.



However, Experiment 719 is not without its own limitations. It is not a particularly atom economical reaction. Atom economy is defined as the percent of atomic weight of all the starting materials that appear in the desired product. For example, the atom economy of Reaction [1] is calculated as:

$$\text{Atom Economy (AE)} = [(\text{MW}_{\text{product}})/(\text{MW}_{\text{reactant 1}} + \text{MW}_{\text{reactant 2}} + \text{etc.})]*100$$

$$\text{AE} = [(\text{MW}_{\text{dibromostilbene}})/(\text{MW}_{\text{stilbene}} + \text{MW}_{\text{bromine}})]*100$$

$$\text{AE} = [(340 \text{ g/mol})/(180 \text{ g/mol} + 160 \text{ g/mol})]*100 = 100\%$$

If the atom economy is improved, then less waste that is generated. As a pre-lab assignment you are asked to calculate the atom economy for reaction [2]. The student is not exposed to the hazardous Br₂ liquid, but more waste (C₅H₆NBr) has been generated, and it will require disposal. One of the goals of Green Chemistry is to avoid the generation of hazardous waste. In addition, the preparation of the reagent, pyridinium tribromide, requires the use of Br₂ in its manufacture. Thus, we have simply shifted the use of the hazardous Br₂ reagent from the chemist's laboratory to the company that manufactures the pyridinium tribromide reagent, rather than doing away with it entirely.

As advances in organic reaction chemistry continue to be made, further green improvements are made possible. In this experiment, we again take advantage of the *in situ* generation of bromine, through the oxidation of hydrobromic acid (HBr) with hydrogen peroxide (H₂O₂), to effect the bromination of the (E)-stilbene to 1,2-dibromo-1,2-diphenylethane (dibromostilbene) as shown in equation [3]¹⁻⁴. Although the requisite reagents (HBr + H₂O₂) must be handled with care, they appear to represent an improvement over pyridinium tribromide, as your post lab analysis will indicate. In addition, the ethanol solvent is replaced with water.



In situ formation of bromine by oxidation of Hydrobromic acid with Hydrogen peroxide

Pre-Lab Preparation

1. Review the technique sections in your lab manual regarding heating a reaction at reflux, vacuum filtration and melting point determination.
2. Answer the pre-lab questions prior to coming to lab.

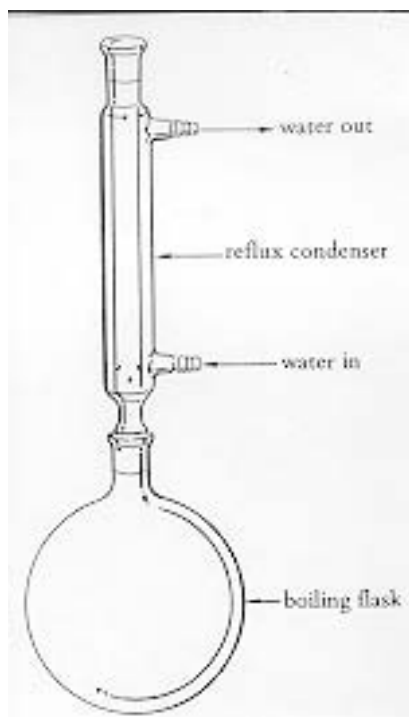
Experimental Procedure:

The experimental conditions represent adaptations from references 1 and 2.

CAUTION: *Hydrobromic acid is corrosive. Avoid contact and inhalation of vapors, and clean up any spills immediately. Hydrogen peroxide (30%) is a strong oxidizer and will readily damage clothing and body tissues, including skin. Ethanol is flammable; avoid open flames.*

Reaction

1. Place a magnetic stir bar, 0.25 g of (E)-stilbene, and 5 mL of ethanol into a 50 mL round-bottom flask. Fit the flask with a water-cooled reflux condenser as shown below. Make certain the ground-glass joint is lubricated with a very thin film of grease to prevent it from ceasing and check before heating the mixture that the joint seal is tight.



2. Clamp the flask so that it may be heated and stirred with the magnetic stir bar while heating with the heating mantle. Continually stir the mixture while heating it to the reflux temperature (i.e. the boiling temperature of the solvent) until the majority of the solid has dissolved.
3. Slowly add 0.6 mL of concentrated aqueous hydrobromic acid ($\text{HBr}_{(\text{aq})}$). This will probably cause some of the stilbene to precipitate, but continued heating and stirring should cause the majority of the solid to redissolve. (Go on with the next step even if some remains undissolved.)

4. Measure out 0.4 mL of 30% hydrogen peroxide (H_2O_2) and add it drop wise to the reaction mixture. The initial colorless mixture will change in color to a dark golden-yellow or orange color. Since bromine (Br_2) is orange in color, this indicates that bromine is being generated *in situ*.
5. Continue to stir and heat the reaction mixture at reflux until the yellow-orange color fades and the mixture becomes a cloudy white. This color change indicates that the bromine has been consumed in the reaction. This typically takes roughly 20 minutes at reflux.

Workup and Isolation

1. Raise the entire apparatus from the heating mantle and allow it to cool to room temperature. Checking with pH paper, carefully adjust the pH of the solution to a pH between 5 and 7 through the addition of saturated $\text{NaHCO}_{3(\text{aq})}$. NaHCO_3 is a weak base and is used to neutralize any unreacted hydrobromic acid. In some cases, very little NaHCO_3 is required.
2. Cool the reaction mixture in an ice bath to bring more of the product out of solution. Shake the flask to suspend as much of the solid as possible and pour the suspended solid into a Buchner funnel for vacuum filtration. Remove any remaining solid from the flask by rinsing the flask with small volumes of cold water and pouring into the funnel. A wash of the solid, while still in the funnel, with a couple of mL of very cold Ethanol (cooled in an ice bath) can help to remove additional impurities, but care must be used to avoid dissolving inordinate amounts of the product. Continue to draw air through your product until it appears dry. Transfer the solid to a dry filter paper on a watch glass and place it in the oven to assure that it dries completely.

Characterization

1. Determine the mass of your product and measure its melting point [literature value: mp 241 °C (decomposition)].

References

1. T. -L. Ho, B. G. B. Gupta, and G. A. Olah, "Phase Transfer Catalyst Promoted Halogenation of Alkenes with Hydrohalic Acid/Hydrogen Peroxide," *Synthesis*, **1977**, 10, 676-677.
2. L.C. McKenzie, L.M. Huffman, and J.E. Hutchison, "Evolution of a Green Chemistry Laboratory Experiment: Greener Brominations of Stilbene", *J. Chem. Ed.*, **2005**, 82(2), 306.
3. Rothenberg and Clark, "On Oxyhalogenation, Acids, and Non-mimics of Bromoperoxidase Enzymes," *Green Chemistry*, **2000**, (2), 248.
4. K.M. Doxee and J.E. Hutchison, "Green Organic Chemistry", **2004**, Brooks & Cole, USA.



NOTE: A graduate student was working with approximately 500 mL of liquid bromine under a hood. She was wearing a lab coat over her shorts. She dropped the container and it fell out of the hood, spilling onto her lower leg. Because she was unable to irrigate the affected area right away, she suffered a partial-thickness burn to her lower leg. She underwent several episodes of debriding (removal of dead skin) and related treatments, which were quite painful, but her injuries healed. The photo shows the injured area eight days after the injury. The Green Chemistry approach eliminates the possibility of exposure to such a hazardous chemical.

Additional Notes

“Americans Robert H. Grubbs and Richard R. Schrock and France's Yves Chauvin have won the 2005 Nobel Prize in Chemistry for their work on developing the metathesis reaction. The process is used daily in "Green Chemistry", as it allows smarter, more efficient production reducing potentially hazardous waste. It is used often in pharmaceutical and plastics development.”¹ Green chemistry promotes the reduction of chemical risks by addressing the hazards of compounds as well as their exposure, and “involves inventing new methods of reducing the chemical hazards while producing superior products in a more efficient and more economical fashion.”² Risk to People or Environment = f (exposure, hazard)

¹ CBC Health and Science News, 05 October, **2005**, 6:30:41 EDT

² K.M. Doxee and J.E. Hutchison, “Green Organic Chemistry”, **2004**, Brooks & Cole, USA.

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