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EXPERIMENT 3

A GREENER BROMINATION OF STILBENE

Chemical Concepts

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

Green Lessons

Safer solvents; safer reagents; relative nature of green chemistry.

Estimated Lab Time

1 – 2 hours

Introduction

Experiment 2 provided an introduction to and discussion of the halogenation of alkenes. Since this experiment replaces hazardous solvents with a relatively innocuous solvent, ethanol, and replaces bromine with a safer and easier to handle reagent, pyridinium tribromide, it represents a relatively green procedure. However, Experiment 2 is not without its own limitations. As your calculations presumably revealed, it is not a particularly atom economical reaction. In addition, the preparation of the reagent, pyridinium tribromide, requires the use of elemental bromine. Thus, we have simply shifted the use of this hazardous reagent away from the bromination step 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 will take advantage of the *in situ* generation of bromine, through the oxidation of hydrobromic acid with hydrogen peroxide [43], to effect the bromination of (*E*)-stilbene to 1,2-dibromo-1,2-diphenylethane (dibromostilbene). (Refer to Experiment 2 for the chemical details

43. Rothenberg and Clark, "On Oxyhalogenation, Acids, and Non-mimics of Bromoperoxidase Enzymes," *Green Chemistry* **2000**, (2), 248-251.

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of this transformation.) Although the requisite reagents – hydrobromic acid and hydrogen peroxide – must be handled with care, they appear to represent an improvement over pyridinium tribromide, as your post-lab analyses will indicate.

$$2\,HBr + H_2O_2 \longrightarrow Br_2 + 2\,H_2O$$

In situ formation of bromine by oxidation of hydrobromic acid with hydrogen peroxide

Pre-Lab Preparation

- Study the technique sections in your lab manual regarding heating a reaction at reflux, vacuum filtration, and melting point determination.
- Carry out pre-lab preparations as described in Chapter 11, section 11.6A, or as called for by your instructor.

Experimental Procedure

SAFETY PRECAUTIONS: 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. Prepare a hot water bath in a crystallization dish on a stirrer/hot plate.
2. Place a magnetic stir bar, 0.5 g of (*E*)-stilbene, and 10 mL of ethanol in a 100 mL round-bottom flask. Fit the flask with a water-cooled reflux condenser.
3. Clamp the flask so that it may be heated and stirred in the hot water bath. Stir while heating the mixture to reflux, and continue heating and stirring until the majority of the solid has dissolved.

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4. Slowly add 1.2 mL of concentrated aqueous hydrobromic acid. 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.)
5. Measure out 0.8 mL of 30% hydrogen peroxide and add it dropwise to the reaction mixture. The initially colorless mixture will change in color to a dark golden-yellow.
6. Continue to stir and heat the reaction mixture at reflux until the yellow color fades and the mixture becomes a cloudy white. This typically takes roughly 20 minutes at reflux.

Workup and Isolation

7. Remove the flask from the hot water bath and allow it to cool to room temperature. Checking with pH paper, carefully adjust the pH of the solution to pH 5 to 7 through the addition of concentrated aqueous $NaHCO_3$. In some cases, very little $NaHCO_3$ is required.
8. Cool the reaction mixture in an ice bath to bring more product out of solution. Collect the solid that forms by vacuum filtration, rinsing with cold water. A wash with very cold ethanol can help to remove traces of impurities, but care must be used to avoid dissolving inordinate amounts of the product. Continue to draw air through your product until it is dry.

Characterization

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

Post-Lab Questions and Exercises

1. Describe the color and state of your purified product. Report the mass and percent of theoretical yield of the purified product.
2. Report the melting point *range* for your "purified" product.
3. Calculate the atom economy for the reaction. How does it compare with the alternative bromination procedure described in Experiment 2?
4. Perform an economic analysis for the preparation of dibromostilbene via this route.

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Experiment Development Notes

Yields are typically around 90%. Replacement of the 30% hydrogen peroxide with household hydrogen peroxide (3%) is possible, but appears to lead to reduced yields (30-35%). We thank Professor Dieter Lenoir for the initial suggestion for exploring the *in situ* generation of bromine in this way. The experimental conditions represent adaptations from Olah, *et al.* [44] and Rothenberg & Clark [43].

44. 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.