A Greener Bromination of Cyclohexene: An Organic Experiment for Non-Majors

Margaret E. Kerr, Ph.D., Aaron Stairs, Khanh Vo, Worcester State College, 486 Chandler Street, Worcester, MA 01602. email: mkerr@worcester.edu

Modified from ***Green Organic Chemistry: Strategies, Tools, and Laboratory Experiments.*** Doxsee, K.M.; Hutchison, J.E. Thompson Learning: Mason, OH, 2002.

Introduction

The reaction of alkenes is an important topic in organic chemistry. Bromination of alkenes is typically taught using elemental Br_2 in a solvent such as carbon tetrachloride or methylene chloride. While this is a useful way to teach the reaction in a lecture setting, in practice it is highly toxic and not appropriate for use in a teaching laboratory. Bromination of alkenes can be accomplished in a greener manner by generating Br_2 *in situ* using HBr and H_2O_2 according to the following reaction:

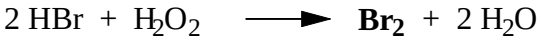
$$2\ HBr + H_2O_2 \rightarrow Br_2 + 2\ H_2O$$

This method avoids the handling of Br_2 by anyone in the laboratory. While care must be taken to avoid contact with HBr and peroxide, overall the chemicals used are far less toxic. Due to the small scale of this reaction and the lack of solid reagents, no solvent is required. For larger scale reactions, ethanol is used as the solvent in place of carbon tetrachloride or methylene chloride. Once Br_2 is formed, an alkene can be added to the flask to be brominated.

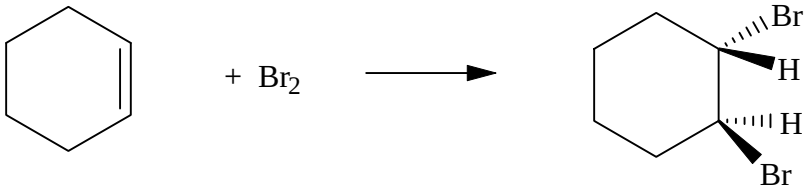
This particular reaction using cyclohexene as the alkene was developed to provide a quick bromination that utilizes minimal amounts of specialty glassware. The reaction can be used as a demonstration or in courses designed for high school students or undergraduate non majors.

The reaction sequence is shown below.

Reaction 1



Reaction 2



Materials

200 mL round bottom flask
Ring stand with utility clamp
Stir/hot plate
Reflux condenser
Cyclohexene
30% hydrogen peroxide
HBr

Safety

Avoid skin exposure to HBr and H_2O_2 and avoid breathing any HBr fumes. Cyclohexene has an unpleasant smell, although it is relatively non toxic. Wear safety goggles at all times. Due to the small scale of this reaction, a solvent is not required. If the reaction is scaled up, ethanol should be used as a solvent.

Procedure

To begin the reaction, place 2.4 mL of 30% H_2O_2 and a magnetic stir bar in a clean 200 mL round bottom flask. The flask will then be clamped to a ring stand and placed over a stir plate. Place a reflux condenser on top of the flask. Water doesn't need to be running through the condenser. Once the condenser is in place and the peroxide is stirring, slowly add 40 drops of HBr (approximately 1.6 mL) through the opening in the top of the condenser. Try to drop the acid down the center of the condenser without hitting the side walls. As soon as the HBr is added, the solution should turn from clear to "blood red" with some yellow/brown fumes. Once the solution begins to bubble, add 40 drops of cyclohexene (approximately 1.4 mL) through the top of the condenser, again taking care to minimize the amount dropped onto the sidewalls of the condenser. The color of the solution should slowly fade over the course of several minutes until the solution becomes colorless or faintly yellow. At this point, the reaction is complete.