
EXPERIMENT 2

BROMINATION OF AN ALKENE:

PREPARATION OF STILBENE DIBROMIDE

Chemical Concepts

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

Green Lessons

Safer solvents; safer reagents.

Estimated Lab Time

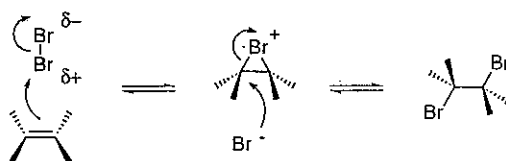
2–2.5 hours

Introduction

Simple hydrocarbons are relatively unreactive. In order to enhance their reactivity, thereby allowing their elaboration into more complex molecules, it is often necessary to introduce more reactive functional groups. Alkenes (olefins) – hydrocarbons containing the carbon-carbon double bond functional group – may be “halogenated” to form alkyl halides, which are then capable of undergoing a variety of further chemical transformations.

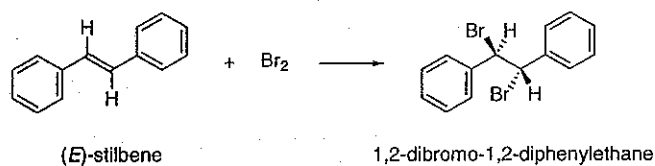
The bromination of an alkene, in which bromine adds across the double bond to yield a “vicinal” (1,2-) dibromide, is an example of an addition reaction. The generally accepted pathway for this reaction involves an ionic mechanism in which the electron-rich alkene acts as a nucleophile (a species that attacks electron-deficient centers) and the bromine acts as an electrophile (a species that reacts with centers of greater electron density). As bromine and the alkene approach one another, the Br–Br bond becomes polarized ($\text{Br}^{\delta+}\text{--Br}^{\delta-}$). The more positively charged Br atom is transferred to the alkene, yielding a cyclic bromonium ion and a bromide ion. In a second step, a bimolecular nucleophilic

substitution reaction (S_N2), the bromide ion attacks one of the carbon atoms of the cyclic bromonium ion, opening the three-membered ring and leading to the vicinal dibromide.



Mechanism for bromination of an alkene

In this experiment, you will carry out the bromination of (*E*)-stilbene (*trans*-stilbene), affording 1,2-dibromo-1,2-diphenylethane (stilbene dibromide). Typically, bromination of an alkene is accomplished using bromine in a chlorinated solvent such as tetrachloromethane (carbon tetrachloride) or dichloromethane (methylene chloride). Both of these solvents are suspected to be carcinogenic. Some brominations may also be carried out in glacial acetic acid, a volatile and corrosive liquid. We will use an alcohol, ethanol, as a safer alternative solvent.

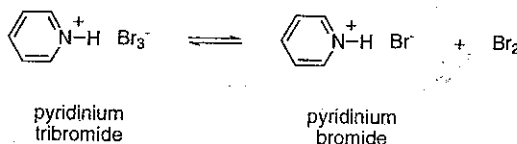


*Bromination of (*E*)-stilbene*

Elemental bromine is volatile and highly corrosive, causing severe burns upon contact with the skin and extremely irritating upon inhalation. An alternative reagent, popularized by Djerassi and Scholz, is pyridinium tribromide [42]. This reagent exists in rapid equilibrium with pyridinium hydrobromide and bromine (reaction below) and thus provides for the “slow release” of bromine into the reaction

42. C. Djerassi and C. R. Scholz, *J. Am. Chem. Soc.* **1948**, *70*, 417.

medium. (When a reagent is generated in the reaction medium rather than added to it, it is said that the reagent is prepared *in situ*.) An additional advantage of pyridinium tribromide is that it is an easily weighed solid. In contrast, liquid bromine is more difficult to measure out, by either weight or volume, due to its volatility, density, and hazardous and irritating vapors.



In situ generation of bromine from pyridinium tribromide

Pre-Lab Preparation

- Study the technique sections in your lab manual regarding gravity and 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: Pyridinium tribromide is corrosive and a lachrymator. Avoid contact and clean up any spills immediately, particularly on the balance, the metal parts of which will quickly be corroded. Ethanol is volatile and flammable; avoid open flames.

Reaction

1. Place a magnetic stir bar, 2.0 g of (*E*)-stilbene, and 40 mL of ethanol in a 125 mL Erlenmeyer flask. (Be sure to record the exact mass of the stilbene you use.) Clamp the flask in place on a magnetic stirrer/hot plate. (The clamp will allow you to remove the flask from the hot plate without burning yourself in the event that the solution starts to boil too vigorously.)
2. With heating and stirring, dissolve the stilbene. (Be careful not to turn the heat up too far – the hot plate may be slow to heat at first, but then heat up very quickly. Once hot, it will take a long time to cool down again!)
2. Wearing disposable gloves, add 4.0 g of pyridinium tribromide. If solid material adheres to the interior walls of the flask, use a little ethanol to rinse it down.
3. Heat with stirring for 5 minutes after the addition of reagents is complete, then remove from the flask from the hot plate, using caution to avoid contact with the hot flask. The product dibromide should quickly begin to precipitate or crystallize.

Workup and Isolation

4. Let the reaction mixture cool to room temperature, then chill the mixture in an ice bath. Collect the product by vacuum filtration. Set aside a small amount of this “crude” product so that you can measure its melting point later.
5. Wash the isolated solid with a small amount of ice-cold methanol to remove any adsorbed pyridinium salts. Continue to draw air through your product until it is dry.

Characterization

6. Determine the mass of your purified product and measure its melting point. Also measure the melting point of the crude product. If time allows, record the melting point of (*E*)-stilbene in order to check the calibration of your melting point apparatus.
7. If time permits, confirm the identity of your compound by performing a mixture melting points determination with an authentic sample of stilbene dibromide [mp 241 °C (decomposition)]. You might also try a mixture melting point determination for a mixture of your product and (*E*)-stilbene.

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 and for the crude product. If you carried out any mixture melting point determinations, report the results.
3. Did the methanol rinse result in a more pure product?
4. Explain your evidence for your product's identity and purity.
5. In your words, explain the difference between melting and dissolving.
6. Bromide is a better nucleophile toward the intermediate bromonium ion than ethanol. What product would be obtained if ethanol did carry out this nucleophilic attack?
7. Calculate the atom economy for the reaction. How does it compare with the alternative bromination procedure described in Experiment 3?
8. Perform an economic analysis for the preparation of dibromostilbene via this route.

Experiment Development Notes

This experiment was developed based upon initial leads from Wilcox and Wilcox (*Experimental Organic Chemistry*, Prentice Hall, 1995) and the original report of the tribromide reagent by Djerassi and Scholz [42]. The reaction has been made greener by substituting ethanol for acetic acid as the reaction solvent in addition to substituting pyridinium hydrobromide perbromide for liquid bromine.