Discovery Experiment

Solvent Effects on the Stereochemistry of Bromination

According to the literature (Buckles, R. E.; Bader, J. M.; Thurmaier, R. J., *J. Org. Chem.* **1962**, *27*, 4523–4527), the stereochemical outcome of the bromination of (Z)-stilbene is dependent upon the polarity of the solvent used in the reaction. Develop a protocol for confirming this report, using NMR spectroscopy (see Hartshorn, M. P.; Opie, M. C. A.; Vaughan, J., *Aust. J. Chem.* **1973**, *26*, 917–920) as the analytical tool for analyzing the stereochemistry of the reaction as a function of solvents of differing polarities. Consult with your instructor before undertaking any experimental procedures for evaluating the reported solvent effect.

Discovery Experiment

Substituent Effects on the Stereochemistry of Bromination

Apply the Microscale Procedure given for bromination of (*E*)-stilbene to study this reaction with one or more substituted (*E*)-stilbenes bearing electron-withdrawing or electron-donating substituents. Develop a protocol whereby you could demonstrate the stereochemical outcome of the dibromide(s) produced. Guidance for determining the stereochemical result is available in the following references: Buckles, R. E.; Bader, J. M.; Thurmaier, R. J., *J. Org. Chem.* **1962**, *27*, 4523–4527; Hartshorn, M. P.; Opie, M. C. A.; Vaughan, J., *Aust. J. Chem.* **1973**, *26*, 917–920. Compare your result(s) with those of others who have explored the reaction with substituted stilbenes different from yours. Consult with your instructor before undertaking any experimental procedures.

WRAPPING IT UP

Decolorize any *solutions* in which the color of bromine is visible by the dropwise addition of cyclohexene; then discard the resulting solutions together with *all other non-aqueous solutions* in a container for halogenated organic liquids. Pour all aqueous solutions down the drain.

B. Bromination of (E)-Cinnamic Acid

Discovery Experiment

Purpose To demonstrate the stereochemistry of bromination of an alkene.

SAFETY ALERT

1. **Wear safety glasses or goggles and suitable protective gloves while performing the experiment.**
2. **Pyridinium tribromide releases molecular bromine, so it should be considered a hazardous chemical. Do not let it come into contact with your skin because it may cause severe burns. If it does get on your skin, wash the area immediately with soap and warm water, then soak the affected area in a 0.6 *M aqueous* solution of sodium thiosulfate.**
3. **Bromine reacts with acetone to produce a powerful lachrymator, α-bromoacetone, $BrCH_2COCH_3$. Therefore, do *not* rinse residual pyridium tribromide out of glassware with acetone!**

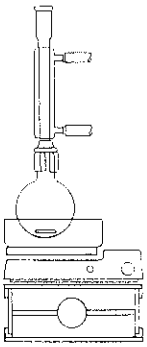
4. ***Glacial* acetic acid is caustic and can cause severe chemical burns. If it comes in contact with your skin, rinse the area immediately with cool water, followed by 5% *aqueous* solution of sodium bicarbonate.**

MINISCALE PROCEDURE

Preparation Refer to the online resources to read the MSDS for the chemicals used in this experiment. Answer the Pre-Lab Exercises. Review Sections 2.7, 2.10, 2.11, 2.17, 2.22, and 3.2.

Apparatus A 50-mL round-bottom flask, ice-water bath, apparatus for heating under reflux, magnetic stirring, and vacuum filtration.

Setting Up Equip the flask with a stirbar and add 0.8 g of (*E*)-cinnamic acid and 10 mL of *glacial* acetic acid to it. Stir the mixture to effect dissolution.



Bromination and Isolation Add 1.76 g of pyridinium tribromide to the flask and stir the mixture; the pyridinium tribromide may not completely dissolve. Equip the flask with a reflux condenser and heat the reaction mixture under reflux for about 45 min. Allow the reaction mixture to cool to room temperature and slowly add 20 mL of water to the mixture with continued stirring. Cool the reaction mixture in an ice-water bath and then isolate the product by vacuum filtration. Wash the filter cake with 5 mL of cold 10% *aqueous* sodium bisulfite solution to remove color, followed by 5 mL of cold water. Recrystallize the crude product from a 1:1 mixture of 95% ethanol and water.

Analysis Weigh the product and determine the yield. Measure the melting point to determine the stereochemistry of bromination. *Caution*: Do *not* use mineral oil as the heating fluid for this determination! Obtain IR and ^{1}H NMR spectra of your starting material and product and compare them with those of authentic samples (Figs. 10.38–10.41)[1].

MICROSCALE PROCEDURE

Preparation Refer to the online resources to read the MSDS for the chemicals used in this experiment. Answer the Pre-Lab Exercises. Review Sections 2.7, 2.10, 2.11, 2.17, 2.22, and 3.2.

Apparatus A 5-mL conical vial, apparatus for heating under reflux, magnetic stirring, vacuum filtration, and Craig tube filtration.

Setting Up Equip the vial with a spinvane and add 150 mg of (*E*)-cinnamic acid and 1.5 mL of *glacial* acetic acid to it. Stir the mixture to effect dissolution.

Bromination and Isolation Add 330 mg of pyridinium tribromide to the vial and stir the contents of the flask; the pyridinium tribromide may not completely dissolve. Set up the apparatus for reflux and heat the reaction mixture under reflux for about