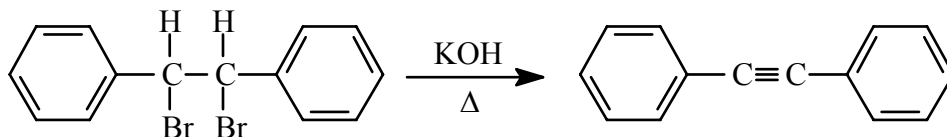


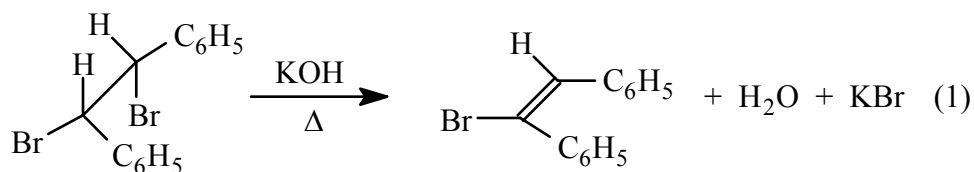
Unit 4M: Introduction to Organic Synthesis IV

Preparation of diphenylacetylene (Last updated 8/17/04)



The formation of diphenylacetylene from 1,2-dibromo-1,2-diphenylethane (*meso*-stilbene dibromide) involves a type of elimination reaction known as a dehydrobromination. In fact, the overall transformation requires two sequential dehydrobrominations. The first reaction is outlined in Equation 1. There are three points about this reaction that are noteworthy:

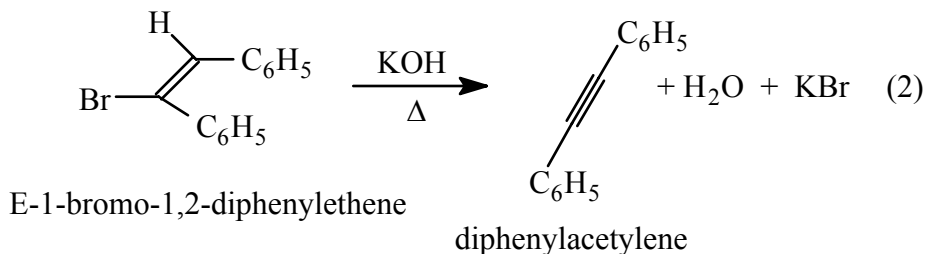
1. Kinetic studies have shown that the rate of the reaction depends upon the concentration of the *meso*-stilbenedibromide and the concentration of KOH. Consequently this reaction is described as an E2 reaction, where E2 is an abbreviation for a bimolecular elimination.
2. Only E-1-bromo-1,2-diphenylethene is produced from *meso*-stilbenedibromide. None of the Z-stereoisomer is formed.
3. The activation energy for this reaction (and for E2 reactions in general) is lowest when the dihedral angle between the H-C and the Br-C bonds that are broken in the process is 180° , i.e. the H and the Br are anti to each other. This stereochemical alignment is shown in Equation 1.



meso-stilbenedibromide

E-1-bromo-1,2-diphenylethene

Formation of diphenylacetylene from E-1-bromo-1,2-diphenylethene, Equation 2, requires a second dehydrobromination. Since the dihedral angle between the H-C and Br-C bonds in this alkene is not 180° , the activation energy for reaction 2 is higher than that for reaction 1. This means either that you have to use a stronger base than KOH, or that you have to increase the temperature of the reaction. One way to increase the temperature of the reaction is to use a high boiling solvent.



Preparation of diphenylacetylene

Preliminary Planning

Complete the Pre-Laboratory Exercises that accompany this handout.

Experimental Procedure

Mix approximately 10 mg of each of the following samples in 100 μL of methylene chloride: *meso*-stilbene dibromide (Not all of the *meso*-stilbene dibromide may dissolve.), authentic diphenylacetylene. **Label each sample. Save them for future work.**

In a 13x100 mm test tube, mix 1.0 ± 0.1 mmol of *meso*-stilbene dibromide with 2.2 ± 0.1 mmol of KOH and 500 μL of triethylene glycol. Heat the mixture in a sand bath until the internal temperature is $170 \pm 10^\circ\text{C}$. Maintain the reaction in this temperature range for 10 minutes or until the reaction mixture ceases to boil. Mix periodically during this interval and check the reaction progress *via* TLC. Cool the mixture to 0°C and add 2 mL of ice cold water. Mix thoroughly and cool the mixture on ice if no solid is apparent. Isolate the solid by vacuum filtration. Remove the last traces of water by blotting the material on a piece of filter paper. Determine your crude yield. Recrystallize the crude solid from 95% ethanol. Weigh the recrystallized solid.

Product Analysis

Record the melting point, IR spectrum, GC-MS spectrum, and the $^1\text{H-NMR}$ spectrum of your product.

mp Determination

Record the mp range of both the crude product and a recrystallized sample. It is good practice to record the mp of a sample of authentic material at the same time. Remember that the heating rate should be approximately $2^\circ\text{C}/\text{minute}$ during the final stages of each determination.

IR Spectrum

Prepare a $5 \pm 3\%$ mixture of your diphenylacetylene in KBr. Record the IR spectrum of this mixture. Save the spectrum in your folder. Print a copy to submit with your Post-Lab report. Compare your spectrum to the three spectra of authentic diphenylacetylene in the ReferenceSpectra folder.

GC-MS

Prepare a solution of your product with a concentration of approximately 1×10^{-8} g/ μL . Methylene chloride is an appropriate solvent. Follow the directions on the desktop of the computer that controls the instrument. From the Sequence Setup the method you should use is Xcalibur/CHY252meth/StilbeneSequence.

¹H-NMR

Prepare a solution of your product in CDCl₃ and record the ¹H-NMR of your recrystallized sample. Integrate the peaks and include a peak table on your NMR spectrum.

Summary

Completion of Unit 4M requires that you receive an S for each of the following:

1. Pre-Laboratory Exercises
2. Post-Laboratory Exercises
3. Final Report