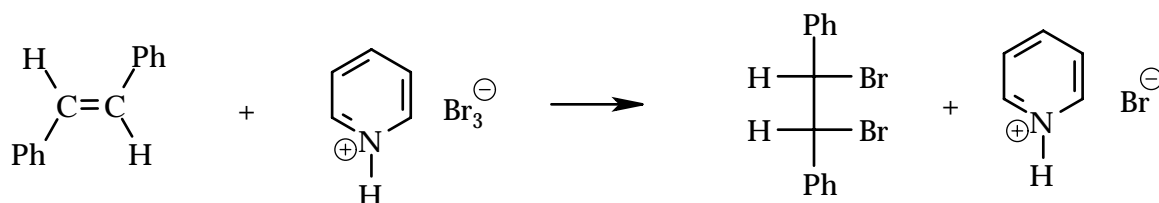


EXPERIMENT 6 PART II. *meso*-STILBENE DIBROMIDE

Introduction

The bromination of an alkene is illustrated in this experiment. In this particular reaction, bromination of *trans*-stilbene generates a compound with two chiral centers, leading to the possibility that the product could be either the *meso* or the *d,l* diastereomer. The exclusive formation of the *meso* diastereomer shows that the reaction is stereospecific and occurs with anti stereochemistry (mechanism below).

The bromination reagent in this experiment is the pyridinium salt of the tribromide ion, Br_3^- , which can be used as a source of Br_2 in some reactions. This solid salt is easier and safer to handle than molecular bromine. It is commonly known as pyridinium bromide perbromide.

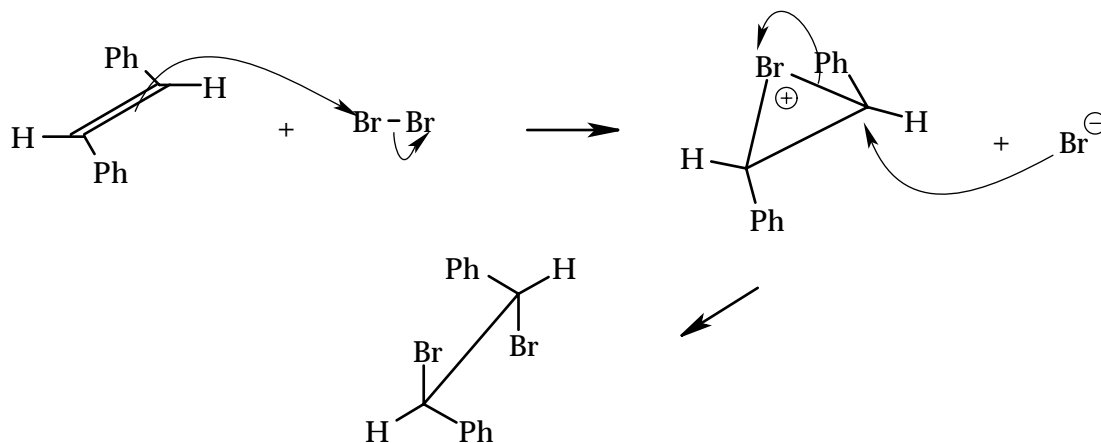


Discussion

Bromination of an alkene (cyclic or acyclic) is an example of an electrophilic addition reaction. The reaction proceeds in two stages. The first stage involves the formation of a cyclic bromonium ion intermediate. In special circumstances, this intermediate can be isolated or observed using NMR. The second stage is a nucleophilic attack by a bromide ion on the intermediate, with inversion occurring at the carbon atom attacked, to yield a vicinal dibromide. This second stage is like an $\text{S}_{\text{N}}2$ process. Cyclic alkenes such as cyclohexene provide evidence that the reaction is an anti addition, the bromine atoms being introduced trans to one another.

It is important to realize that if two different groups are present on one or both of the sp^2 carbon atoms of the alkene linkage, chiral carbon centers are generated on bromination of these carbon atoms. In the case with *trans*-stilbene, two chiral centers are generated, yielding the *meso* dibromide. The absence of the *d,l* diastereomer confirms that the reaction is stereospecifically anti. (Syn addition would have given *d,l*.)

The mechanism of the bromination reaction is outlined below.



Bromination of alkenes using a Br_2/CCl_4 solution (a red-brown color) is frequently used as a qualitative test for the presence of unsaturation in a compound. Rapid loss of color from the reagent is a positive test.

Experimental Procedures

Estimated time to complete the reaction: 1 hour.

Physical Properties of Reactants, Product, and Solvent

Compound	MW	Wt./Vol.	mp (°C)	bp (°C)	Density (g/mL)
<i>trans</i> -Stilbene	180.25	100 mg	124-125		
Glacial acetic acid				118	1.05
Pyridinium bromide perbromide	319.8	200 mg	205		
<i>meso</i> -Stilbene dibromide	340.07		238		

Reaction Conditions

In a 4" test tube, 100 mg of *trans*-stilbene is dissolved in 2 mL of glacial acetic acid by heating in a bath of boiling water, and then 200 mg of pyridinium bromide perbromide is added. The mixture is stirred constantly with continued heating at 100 °C for 7 minutes. The reaction mixture is cooled to room temperature, and the product collected by suction filtration and washed with methanol.

When the crystals are dry, they are weighed and the melting point determined. No further purification is necessary.

Clean-up and Waste Disposal

All waste materials should be placed in the waste container labeled "Stilbene Bromination Wastes".

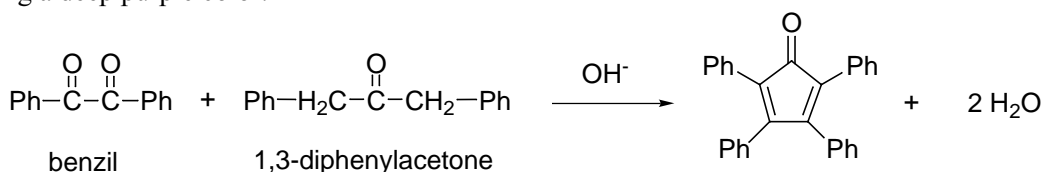
Questions

1. Solid salts containing the tribromide ion (Br_3^-) are sometimes used as a source of Br_2 in bromination reactions. Write the Lewis structure for Br_3^- , showing formal charge.
2. Give the mechanism, showing stereochemistry clearly, for the bromination of *cis*-stilbene. Explain why the product is called *d,l*-stilbene dibromide.
3. What by-product could potentially be formed in this reaction as a consequence of using acetic acid as the solvent? Give the mechanism for its formation.

EXPERIMENT 6 PART III. TETRAPHENYLCYCLOPENTADIENONE

Introduction

This experiment is an example of the aldol condensation in which two ketones, one of which has no α -hydrogen atoms, are the reactants. It is unique because the selected reagents lead to the formation of a carbocyclic ring system. The aldol product initially formed undergoes elimination of water to yield a material that has a highly conjugated system of double bonds. In general, the more conjugation in a molecule, the less energy required to promote the π electrons to a higher energy level. In this case, energy in the visible region of the spectrum is absorbed, resulting in a compound having a deep purple color.



The mechanism involves a sequence of two aldol condensations. The first is intermolecular, the second intramolecular. The aldol product undergoes a facile base-catalyzed elimination of water.

The hydroxide catalyst is furnished as a quaternary ammonium hydroxide in methanol. This is much more easily handled on a small scale than the very hygroscopic sodium or potassium hydroxides.

Experimental Procedures

Estimated time to complete the experiment: 1.5 hours.

Physical Properties of Reactants, Product, and Solvents

Compound	MW	Wt./Vol.	mp (°C)	bp (°C)
1,3-Diphenylacetone	210.28	50 mg	35	
benzil	210.23	50 mg	95	
Triethylene glycol*	150.18	0.25 mL		285
Benzyltrimethylammonium hydroxide (40 wt% solution in methanol; d = 0.92 g/mL)	167.25	50 L		
Tetraphenylcyclopentadienone	384.48		220-221	

* The reaction solvent is triethylene glycol (HO-CH₂-CH₂-O-CH₂-CH₂-O-CH₂-CH₂-OH), a trimer of ethylene glycol (HO-CH₂-CH₂-OH). It is a relatively polar solvent whose high boiling point allows a reaction to be carried out at a high temperature, hence a shorter reaction time.

Reagents and Equipment

The reaction is to be carried out in a 2.0-mL conical vial equipped with a magnetic spin vane and air condenser. Triethylene glycol (0.25 mL) is placed in the vial first, using the vial markings to measure, followed by 50 mg of 1,3-diphenylacetone and 50 mg of benzil. The spin vane is then placed in the vial, which is attached to the air condenser.

Note: The benzil used in this reaction must be free of benzoin impurity.

Reaction Conditions

The mixture is now heated with stirring for ten minutes in an aluminum block maintained at 155-165 °C. The benzil dissolves during this time.

The reaction solution is removed from the heat source and immediately 50 mL of a 40 wt. % benzyltrimethylammonium hydroxide-methanol solution is added through the air condenser to the hot reactants with gentle shaking (use the delivery pipet provided). The vial and contents are again heated for 2-3 minutes at 150-160 °C and then allowed to cool. As the cooling occurs, the appearance of dark purple crystals of tetraphenylcyclopentadienone is evident. Cooling may be accelerated by placing the vial under a stream of cold water.

Isolation of Product

With stirring, 0.7 mL of ice-cold methanol is added and the mixture cooled in an ice bath for 5-10 minutes. The dark crystals are collected by suction filtration using a Hirsch funnel. The reaction vial and crystals are rinsed with several drops of cold methanol. The dropwise addition of ice-cold methanol to the crystals is continued until the filtrate is colorless or nearly so. The crystalline product is dried.

Purification and Characterization

No recrystallization is to be done. The product is of sufficient purity for use in the preparation of hexaphenylbenzene.

Weigh the product and calculate the percentage yield. Determine the melting point and compare it with the literature value. Obtain an IR spectrum of the material.

Clean-Up and Waste Disposal

The filtrate from the suction filtration is to be placed in the container labeled "Tetraphenylcyclopentadienone Waste".

Questions

1. Write the mechanism for this reaction, showing all steps clearly. Use correct electron pushing. (Omit repetitive steps.)
2. What feature of this molecule is responsible for the fact that it is colored? Explain.
3. A possible by-product in this reaction would result from the condensation/elimination of diphenylacetone with itself. Give the structure of this compound.
4. How many moles of the base catalyst were used in this experiment?