

Experiment 7 - Preparation of 1,4-diphenyl-1,3-butadiene

OBJECTIVE

To provide experience with the “Wittig Reaction”, one of the most versatile reactions available for the synthesis of an alkene.

INTRODUCTION

The carbon-carbon double bond, the “Functional Group” of all alkenes, is a very common functionality. It can be prepared in a variety of ways, many of which involve an “Elimination” reaction. For example, alcohols may be dehydrated under the influence of strong acid, or alkyl halides may be dehydrohalogenated in the presence of strong base. Both of these reactions have the disadvantage of employing harsh reaction conditions. In addition, the former reaction frequently results in skeletal rearrangement.

A very general procedure for connecting two molecular fragments to make a new and larger molecule was announced in 1954 by the German Chemist Georg Wittig. For this discovery, Wittig was awarded the Nobel Prize in Chemistry in 1979.

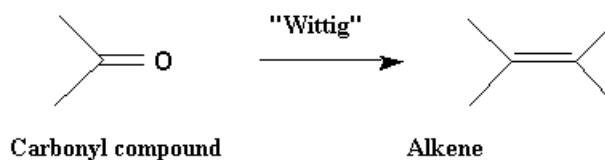


Figure 1

In a typical Wittig reaction, an alkyl halide is reacted with triphenyl phosphine to form a phosphonium salt.

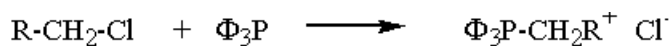


Figure 2

The phosphonium salt is then reacted with the carbonyl compound in the presence of a strong base to produce the alkene and triphenylphosphine oxide.



Figure 3

Consult your lecture text for the mechanism and other details of this very useful reaction.

Equation

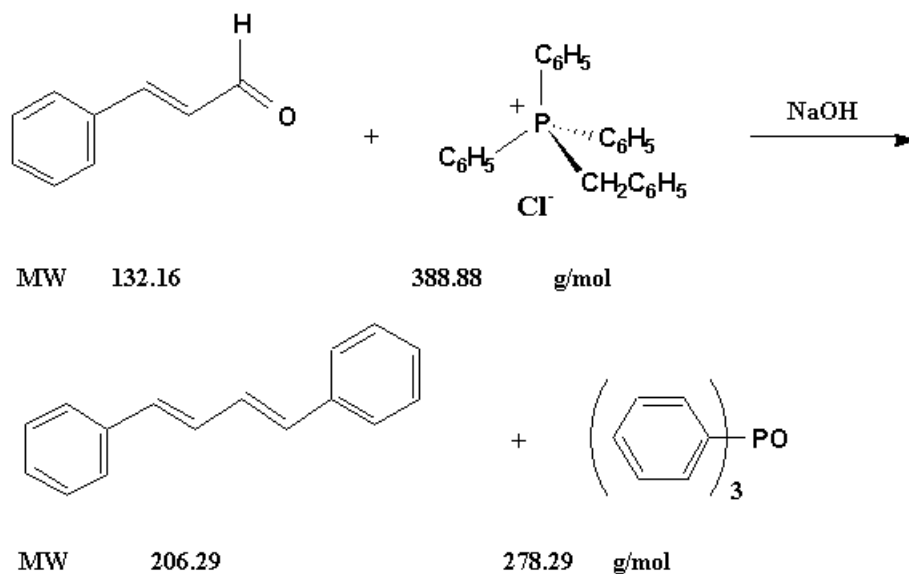


Figure 4

PRE-LAB

Complete the pre-lab assignment in WebAssign.

CAUTION: Sodium hydroxide is highly corrosive. Rinse any spills with large amounts of cold water. Methylene chloride, or dichloromethane (CH_2Cl_2), a common component of paint and varnish remover, is a very volatile, toxic compound. Avoid breathing the vapors. Immediately seek fresh air if you should breathe a large amount of the vapor and feel light headed.

PROCEDURE

[adapted from: S. W. Breuer, *J. Chem. Educ.* **1991**, 68, A58-A60.]

Use only clean and DRY glassware!

Quickly weigh approximately 0.38 g of benzyltriphenylphosphonium chloride into a clean and DRY 5 mL conical vial. [Keep the supply bottle capped except for the few seconds needed to remove a sample for weighing.] Record the exact weight and cap the vial immediately to minimize contact with humid air.

Carefully add three (3) drops of pure cinnamaldehyde (d. = 1.05 g/mL) to the vial and weigh again. If there is not at least 120 mg of the aldehyde, add an additional drop and weigh again.

Add 1 mL of methylene chloride and the magnetic stir vane to the reaction vial, cap the vial and begin to stir on the magnetic stir plate. DO NOT HEAT!

Carefully add 0.5 mL of a concentrated NaOH solution [Already prepared; 8 g/10 mL water] to the reaction vial and stir for about 20 minutes after the addition.

CAUTION: Concentrated sodium hydroxide (NaOH) is very corrosive. It will burn the skin. Wash any area that contacts the solution with copious amounts of cold water.

Pour the contents of the reaction vial into a 6" test tube. Rinse the reaction vial successively with one mL of methylene chloride and then 3 mL of water. Add the washings to the test tube and vigorously mix by drawing the contents of the tube up into a Pasteur pipet and expelling the liquid back into the test tube several times. Allow the test tube to stand and then carefully transfer the lower layer (CH_2Cl_2) into a second *clean* 6" test tube. Extract the remaining aqueous layer in the first tube with two successive 2 mL portions of CH_2Cl_2 . Dry the combined CH_2Cl_2 washings in the second test tube with anhydrous magnesium sulfate for about 5-10 min. with occasional swirling.

Filter by gravity through a pipet filter, into a third clean *and tared* 6" test tube. Carefully evaporate the CH_2Cl_2 **IN THE HOOD** using a slow stream of nitrogen. Place the test tube in a warm sand bath to accelerate the evaporation. Weigh the tube after the liquid disappears.

From the tare weight, calculate and record this "Crude Yield".

IN THE HOOD, carefully dissolve the solid in about 4 mL of *boiling* 95% ethanol.

Allow the clear solution to cool slowly for about 5-10 min. while you clean up some of the equipment you have been using. Place the tube in an ice bath to complete crystallization. Isolate the crystals by the normal centrifugation process. Record the weight and melting point of this "Purified Product". Calculate a Percent Yield of the recrystallized product. Submit a sample of your dry product in a melting point capillary along with the pages from your Notebook for this day.

Waste Disposal

Alcohol from the recrystallization may be washed down the drain with tap water. The aqueous solution in the first 6" test tube should be poured into the waste bottle labeled "AQUEOUS WIT-TIG WASTE". Any solid product should be added to the jar marked "STUDENT PREPARATION - 1,4-DIPHENYL-1,3-BUTADIENE".

IN-LAB QUESTIONS

Download and print the worksheet. You will use this worksheet to record your answers to the In-Lab questions.

Questions

Record the following data.

Question 1: Amount of cinnamaldehyde ----- g, ----- mol

Question 2: Amount of Wittig reagent ----- g, ----- mol

Question 3: Theoretical Yield of product ----- mol, ----- g

Question 4: Actual Yield -----

Question 5: Percentage Yield -----

Question 6: Melting Point ----- (observed), ----- (reported)

Question 7: Record your calculations.