Purpose

The purpose of this experiment is to synthesize 1,4-diphenyl-1,3-butadiene from cinnamaldehyde. The product will be analyzed with IR spectroscopy, NMR spectroscopy, and melting point determination.

Learning Objectives

Synthesize an alkene using a Wittig reaction.

Use TLC to analyze the reaction mixture.

Purify the product using recrystallization.

Determine if the product Wittig reaction is an E- or Z-alkene.

Identify a product of a reaction using IR spectroscopy.

Identify a product of a reaction using ^{13}C NMR spectroscopy.

Identify the product of a reaction from ^{1}H NMR spectroscopy.

Laboratory Skills

Set up a reaction

Perform a vacuum filtration

Perform a melting point determination

Perform a TLC analysis

Perform a recrystallization

Calculate percent yield of a reaction

Analyze an IR spectrum of the product of the reaction.

Analyze a ^{13}C NMR spectrum of the product.

Analyze a ^{1}H NMR spectrum of the product.

Equipment

- 10 or 25 mL round bottom flask
- Separatory funnel
- TLC plates and capillary tubes
- Boiling chips
- Sand bath
- Ice bath
- Vacuum filtration set-up
- Melting point apparatus
- FTIR instrument
- NMR instrument
- NMR tube

Chemicals

- *trans*-Cinnamaldehyde
- Benzyltriphenylphosphonium chloride
- Dichloromethane, CH_2Cl_2
- 10 M NaOH
- $CDCl_3$

Introduction

The Wittig Reaction

The Wittig reaction has been used as a good general method for preparing alkenes from aldehydes or ketones.

The Wittig reaction is one of the most widely used methods for forming carbon-carbon double bonds, because it is easy to carry out and often gives high yields of pure product. It is named after its discoverer, German chemist Georg Wittig.

The reaction involves the addition of a phosphorus ylide to an aldehyde or ketone to form double bond with the elimination of phosphine oxide (see Figure WT.1)

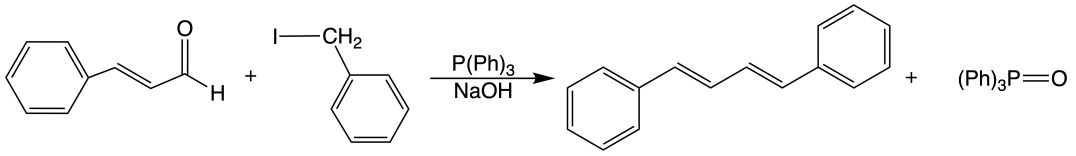


Figure WT.1: General scheme for a Wittig reaction.

This reaction proceeds through two steps. First, the phosphorus ylides are usually prepared by treatment of a phosphonium salt with a base, and phosphonium salts are usually prepared from the phosphine and an alkyl halide as shown in Figure WT.2.

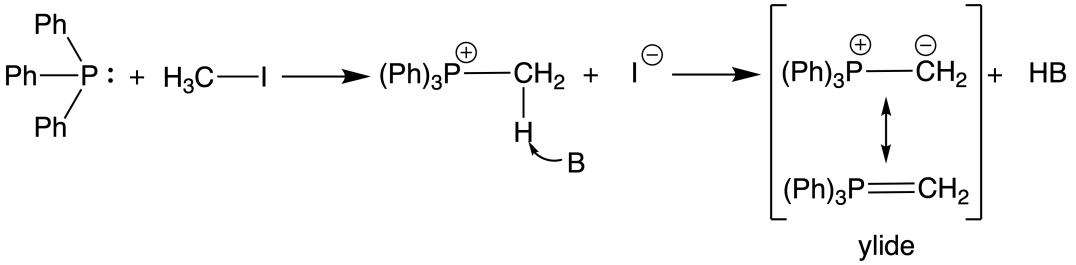


Figure WT.2: General mechanism for the formation of a phosphorus ylide.

In the second step, phosphorous ylide (also called a phosphorane) reacts with a carbonyl compound with to form a 4-membered ring intermediate, oxaphosphetane. This intermediate then undergoes a bond rearrangement which leads directly to the alkene and the triphenylphosphine oxide as shown in Figure WT.3.

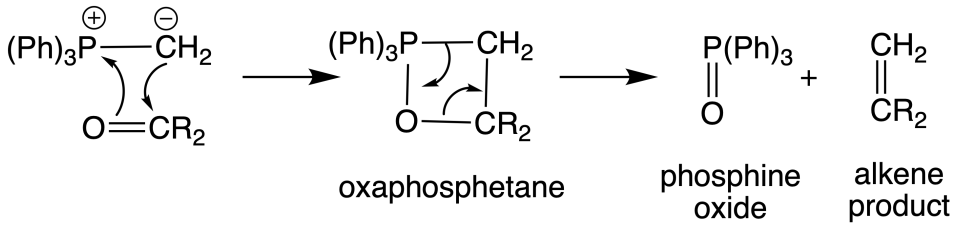


Figure WT.3: General mechanism for the reaction of a phosphorus ylide with a ketone.

Green Variation

In the original Wittig reaction, a triphenylphosphonium halide was added to a solution of *n*-butyllithium in diethyl ether. Once the ylide had formed, the carbonyl compound was added and heated to reflux overnight.

In this lab, we will carry out a Wittig reaction to synthesize 1,4-diphenyl-1,3-butadiene from cinnamaldehyde (see Figure WT.4).

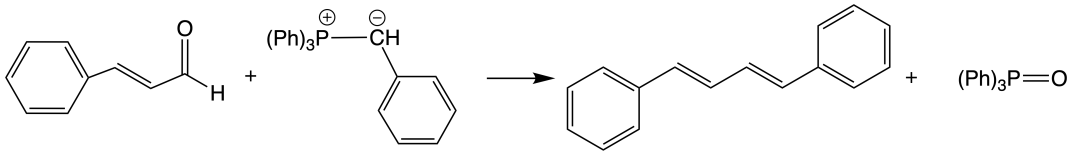


Figure WT.4: Wittig reaction for the formation of 1,4-diphenyl-1,3-butadiene.

In this particular Wittig, the alpha protons of the phosphonium salt are sufficiently acidic to be deprotonated by aqueous NaOH, allowing the reaction to be carried out in aqueous solution. This makes this method much greener than the normal Wittig conditions of using *n*-butyllithium in ether or DMF.

It should be noted, however, that the traditional Wittig reaction has very poor atom economy, generating an 18-carbon side product ($Ph_3P=O$). Thus, to make this a greener reaction, we would also need to recycle this side product through a reduction process.

Procedure

Safety Precautions

Safety goggles are required.

All work should be performed in the fume hood.

trans-Cinnamaldehyde is a skin irritant.

Benzyltriphenylphosphonium chloride is toxic and corrosive.

Dichloromethane is a suspected carcinogen.

NaOH is toxic and corrosive.

Ethanol is flammable and an irritant. Wash thoroughly with soap and water if skin contact is made.

$CDCl_3$ is toxic.

Wittig Synthesis

1. Add 3.00 mmol of *trans*-cinnamaldehyde, 3.30 mmol of benzyltriphenylphosphonium chloride (BTPC), and a magnetic stir bar to a 50 mL Erlenmeyer or round-bottom flask.

2. Carefully add 15.0 mL 10M NaOH and stir the suspension for 30 min at room temperature.

3. Collect the crude solid product by vacuum filtration washing with water until the filtrate is no longer basic to litmus.

4. Allow the solid to dry on the Büchner funnel for 10 min.

5. Save a sample of the crude for melting point determination and TLC analysis.

6. Recrystallize the crude product from the minimum volume of boiling ethanol.

7. Determine the final yield after drying on a Büchner funnel for at least 10 min.

8. Allow the product to dry.

9. Weigh the mass of your product and record on your data sheet.

10. Measure the melting point of both your crude product and your recrystallized product. Record these values on the data sheet.

TLC Analysis of Wittig Reaction

1. Prepare spotting solutions of (1) cinnamaldehyde, (2) benzyltriphenylphosphonium chloride (BTPC), (3) the crude product, and (4) the final product by dissolving 10 mg of each compound in 1.0 mL CH_2Cl_2.

2. Obtain a TLC plate (silica gel with fluorescein indicator) and use a straight edge to lightly make a pencil line 1 cm from one end.

3. Spot each solution at even intervals along the pencil line on the plate. Make sure to record in your notebook the order in which you make these spots.

4. Develop the TLC plate in a TLC jar using 1:9 ethyl acetate/hexane as the elution solvent.

5. Visualize the plate under UV light and outline all spots lightly with a pencil.

6. Measure distances of all spots, calculate R_f values and carefully sketch the developed plate in your lab notebook.

7. Obtain an IR spectrum of the product.

8. Dissolve a small amount (~10 mg) of the product in 700 µL of $CDCl_3$, place the solution in an NMR tube, and obtain a proton NMR spectrum.

9. Dissolve a small amount (~10 mg) of the product in 700 µL of $CDCl_3$ (see note below), place the solution in an NMR tube, and obtain a carbon NMR spectrum.

> Check with your instructor. You may be able to use the same sample for both proton and carbon NMR. However, the NMR instrument at your school may require a more concentrated sample for carbon NMR.

10. Place the remaining product in the solid waste container as indicated. All solutions should go in the appropriate waste container(s).

11. Wash all glassware and clean up.

Wittig Reaction

Draw a balanced equation for the reaction. Include drawings of the structures of the reactant and both possible isomers of the product (E,Z and E,E).

Calculations and Analysis

Complete the table below by entering the relevant literature values and completing the calculations.

Report Table WT.1: Reactants and Products Table

	Molar Mass (g/mol)	Mass used or produced (g)	Moles used or produced (mol)
Cinnamaldehyde			
BTPC			
1,4-diphenyl-1,3-butadiene			

Product theoretical yield (g) _____

Product percent yield (%) _____

Melting Point Determination

Literature melting point of (E,E)-1,4-diphenyl-1,3-butadiene _____

Melting point of crude product _____

Melting point of recrystallized product _____

Does the melting point obtained for your product indicate that your sample is (E,E)-1,4-diphenyl-1,3-butadiene? Or a mixture of isomers?

Was there a difference in the melting point of the crude and the melting point of the recrystallized product?

TLC Analysis

Draw a picture of your TLC plate after development.

Report Table WT.2: Reactants and Products Table

	Distance Spot Traveled in cm)	**R_f**
Lane 1: *trans*-cinnemaldehyde		
Lane 2: BTPC		
Lane 3: Crude Product		
Lower or only spot		
Upper spot (leave blank if none present)		
Lane 4: Recrystallized Product		
Lower or only spot		
Upper spot (leave blank if none present)		

Do you see a pronounced difference between the TLC of the crude and recrystallized in terms of Z/E products?

IR Analysis

See *(Click here)* for more help on interpreting IR spectroscopy.

Online, in the Labflow report, complete the table with 3 Major IR peaks

Report Table WT.3: IR Analysis

IR Peak, cm^{-1}	Bond Type

If available, compare your spectrum to reference spectra. *(Click here)* to access the SDBS database of spectra, where you may find reference spectra for the starting material(s) and/or product.

^{1}H NMR Analysis

See *(Click here)* for more help on interpreting ^{1}H NMR spectroscopy.

Online, in the Labflow report, complete the following table to analyze the NMR signals in ppm.

Report Table WT.4: Proton NMR Analysis

Chemical shift, ppm	Integration	Multiplicity	Partial structure

If available, compare your spectrum to reference spectra. *(Click here)* to access the SDBS database of spectra, where you may find reference spectra for the starting material(s) and/or product.

^{13}C NMR Analysis

See *(Click here)* for more help on interpreting ^{13}C NMR spectroscopy.

Online, in the Labflow report, complete the following table to analyze the NMR signals in ppm.

Report Table WT.5: Carbon NMR Analysis

Chemical shift, ppm	Bonding environment

If available, compare your spectrum to reference spectra. *(Click here)* to access the SDBS database of spectra, where you may find reference spectra for the starting material(s) and/or product.

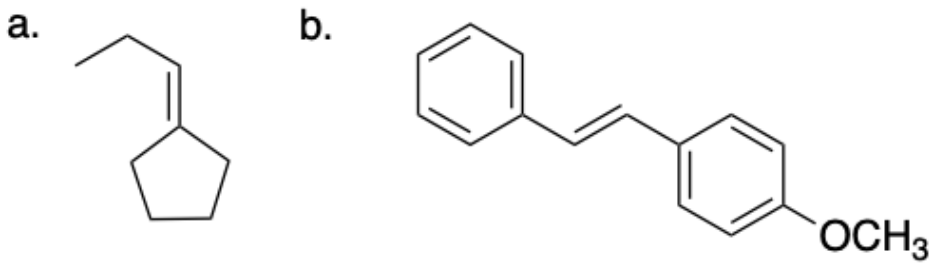
Questions

1. Both the E and Z forms of the alkene will form in this reaction. If you only take into account product stability, which one would you expect to be the major product?

2. Based on the three pieces of data (melting point, TLC, IR, NMR), indicate which product was formed in your experiment.

3. Use 2 pieces of data to comment on whether the ratio of (E,E)-1,4-diphenyl-1,3-butadiene to (E,Z)-1,4-diphenyl-1,3-butadiene changed after recrystallization.

4. Propose a syntheses for the structures shown in Report Figure WT.1 using a Wittig reaction.



Report Figure WT.1: Propose syntheses for these structues using a Wittig reaction.

5. The 12 principles of green chemistry can be found here: ACS Principles of Green Chemistry .

   Identify 3 of the principles that are present in this experiment. Give a short explanation of how they are being applied in this procedure compared to the traditional Wittig reaction.