

1,4-Diphenyl-1,3-Butadiene

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Introduction

The Wittig reaction is an organic chemistry synthesis technique that allows the creation of a new carbon-carbon bond. The process involves the conversion of aldehydes and ketones into alkenes via a nucleophilic addition pathway. Discovered by Georg F. K. Wittig, a German chemist who received the Nobel Prize in chemistry in 1979 for his work on phosphorous-containing compounds, the reaction involves the formation of an ylide—a negatively charged carbon atom that is balanced by a positively charged phosphorous atom—which reacts with a carbonyl containing species by replacing the oxygen atom (McMurry 721).

In this experiment I synthesized *trans,trans*-1,4-diphenyl-1,3-butadiene by using the Wittig reaction method. This was accomplished in three major steps: 1) formation of the phosphonium salt benzyltriphenylphosphonium chloride by the reaction of triphenylphosphine with benzyl chloride; 2) abstraction of a benzylic hydrogen by treatment of sodium ethoxide base to form an ylide; and 3) reaction of the ylide with cinnamaldehyde to form the desired product, including its cis-trans isomer and triphenylphosphine oxide (see Figures 1-3).

There are no common uses or commercial applications for the product *trans,trans*-1,4-Diphenyl-1,3-butadiene. It is a somewhat unique hydrocarbon in that it contains two benzene rings joined together by a carbon chain containing two C=C double bonds. The usefulness of this compound seems to be limited to the sphere of academia where its synthesis procedure serves as an effective way to practice the steps of the Wittig reaction.

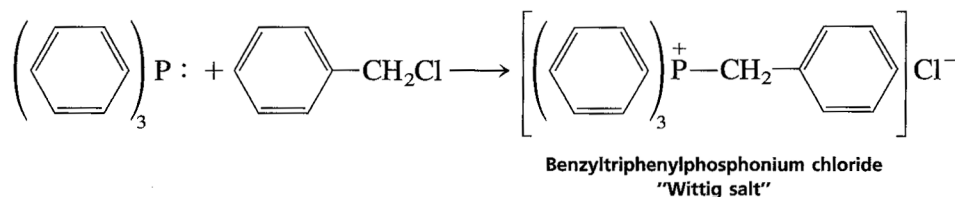


Figure 1. Preparation of benzyltriphenylphosphonium chloride (Pavia 342).

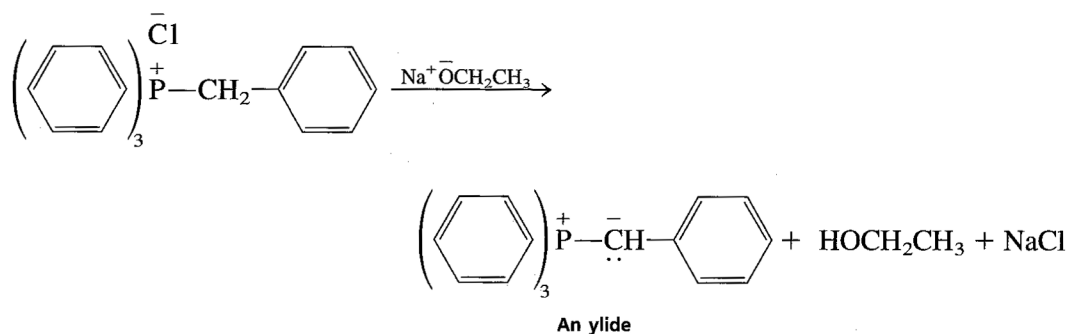


Figure 2. Formation of the ylide, a negatively charged carbon atom (Pavia 342).

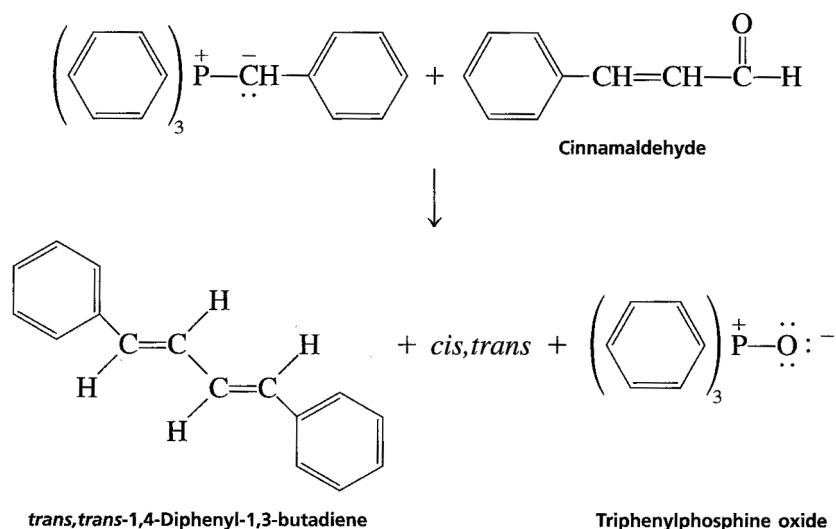


Figure 3. Reaction with cinnamaldehyde to form *trans,trans*-1,4-diphenyl-1,3-butadiene (Pavia 344).

Experimental Procedure

Formation of the the Wittig salt benzyltriphenylphosphonium chloride

A simple apparatus was assembled from a condenser and 100mL round bottom flask, both of which were secured to a ring stand with clamps. A heating mantle and a magnetic stir plate were then positioned directly underneath, with the mantle carefully arranged so that it enveloped the bottom portion of the flask.

The 100mL round bottom flask was then removed and 2.126g of triphenylphosphine was added, followed by 1.44mL of liquid benzyl chloride. Next, an amount of 8mL of xylenes (a mixture of ortho, meta and para isomers) was added which, upon mixing, caused about half of the solid to dissolve. A magnetic stir bar was inserted before reattaching the flask to the apparatus. Both the heating mantle and magnetic

stir plate were turned on high, resulting in the complete dissolution of the solid. Once slight boiling began the heating mantle was adjusted to a lower setting.

The reaction was left alone to continue for a total of 75 minutes. After about 10 minutes the mixture began to take on a cloudy white appearance, a change which became more pronounced as time passed. At the end of the duration the heating mantle was removed and the round bottom flask was left to cool to room temperature before being submerged in an ice bath for approximately five minutes. A very finely grained solid was observed at this point, fully white in color. The solid was separated by using vacuum filtration and a Büchner funnel, and was washed with three 4mL portions of ice cold petroleum ether. After drying for about 15 minutes the benzyltriphenylphosphonium product was weighed and the amount retrieved was found to be 1.243g.

Preparation of the ylide

The Wittig salt was next transferred to a dry 50mL round bottom flask, with 0.677g added from an secondary source to ensure completeness of coming reactions. A second apparatus was configured for stirring, which consisted only of a ring stand, clamp and magnetic stir plate. Absolute anhydrous ethanol was added to the 50mL flask in an amount of 8.0mL, which was followed by 3.0mL of sodium ethoxide. The mixture was stirred for 15 minutes and changed to an opaque yellow-orange appearance.

Reaction of the ylide with cinnamaldehyde

In a small test tube 0.60mL of pure cinnamaldehyde was added along with 2.0mL of absolute ethanol. The two were mixed with a Pasteur pipet and then transferred to the 50mL round bottom flask. This caused an immediate color change to a strong orange and the formation of a precipitate became visible after less than five seconds. The contents were left to react for 10 minutes before being transferred to an ice bath, where it was left for another 10 minutes. The solid was then separated by vacuum filtration with a Büchner funnel and washed with ice cold absolute ethanol. The filtered liquid, a clear red mixture, was quickly wrapped in paper towels to shield it from light and then set aside to be used for thin layer chromatography analysis (exposing the *cis,trans* isomer to light causes it to be photochemically converted to the *trans,trans* compound).

Separation of impurities

The crude product was added to a 50mL beaker along with 12.0mL of deionized water. After thorough stirring the solid was separated by using vacuum filtration with a Büchner funnel. The pure product was then transferred to a clean 100mL round bottom flask and applied to the high vacuum evaporator for about 20 minutes.

Test for impurities

The melting point was measured and compared to the literature value. Also, the HNMR spectrum was analyzed by preparing a sample of product dissolved in deuteriochloroform. IR spectroscopy was used to make additional observations about the products using a KBr pellet. Comparisons between the *trans,trans* and *cis,trans* isomers were made by obtaining R_f values through thin layer chromatography procedures.

Results

Yield, melting point and appearance

Table 1. Data for the synthesis of *trans,trans*-1,4-diphenyl-1,3-butadiene using the Wittig reaction.

Product	Yield (g)	Yield (%)	Experimental Melting Point	Literature Melting Point	Appearance
<i>trans,trans</i> -1,4-diphenyl-1,3-butadiene (Pure)	0.256g	25.1%	152.7°C – 153.3°C	152°C [†]	White solid with orange hue

[†] (Pavia 346)

HNMR, IR and TLC Data Summary

IR results produced two areas of interest: the C—H signal for an alkene at 3014.4cm^{-1} , and the two aromatic ring signals at 1442.3cm^{-1} and 1490.3cm^{-1} (see Figure 4). HNMR results are entirely consistent with the expected results: a pair of slightly overlapping signals appears from the 6.5ppm to 7.5ppm range, one representing the 4 vinylic hydrogens attached to the pi bonded carbons and another representing the 10 aryl hydrogens attached to the benzene rings (see Figure 5).

Thin layer chromatography results were incomplete due to complications during the development process, a shortage of required materials, and the light sensitive *cis,trans* isomer, which imposed a time limit. The obtained R_f values—0.21 for *cis,trans* and 0.22 for *trans,trans*—are nearly identical, which is certainly inaccurate: variance is expected due to their slightly different chemical properties.

Discussion and Conclusion

The Wittig reaction was performed successfully and a pure product was retrieved, which is supported by the data obtained from HNMR, IR and melting point measurements. The yield was somewhat low at only 25.1%, but this is attributable to the number of filtrations and the amount of glassware that was required to be used throughout the procedure. It is expected that better handling techniques would increase the amount of the final product. Another area where the yield could be increased is during the formation of the Wittig salt benzyltriphenylphosphonium chloride. The insufficient amount after this first step indicates that a longer reaction period is required to avoid having to supplement the reactant from another source.

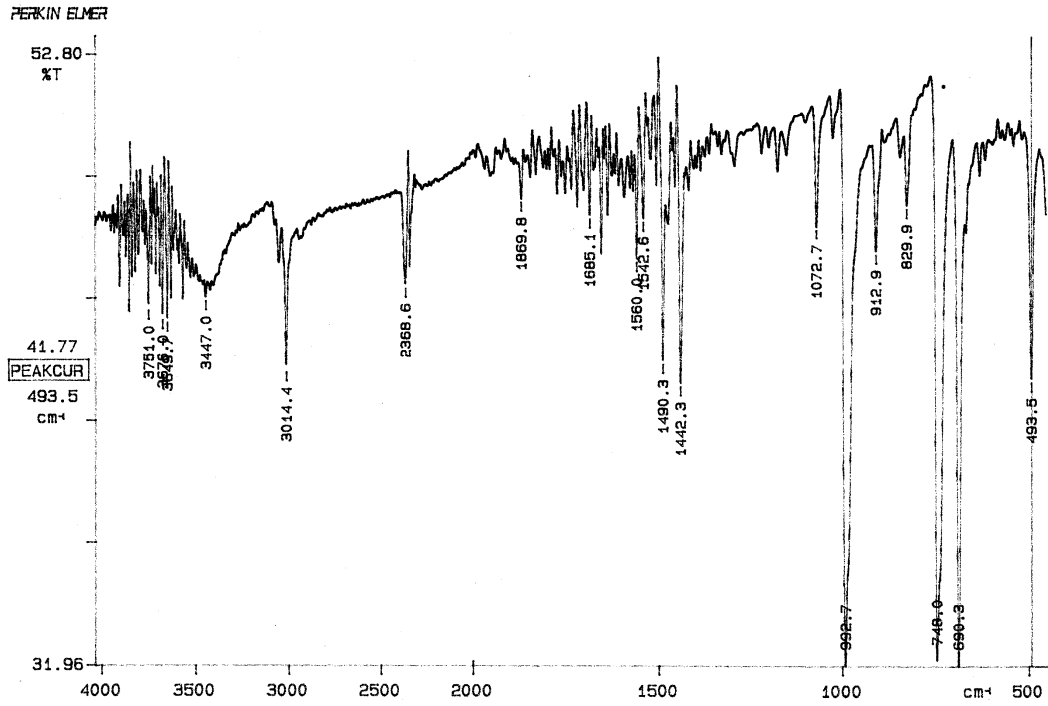


Figure 4. IR spectrum for *trans,trans*-1,4-diphenyl-1,3-butadiene.

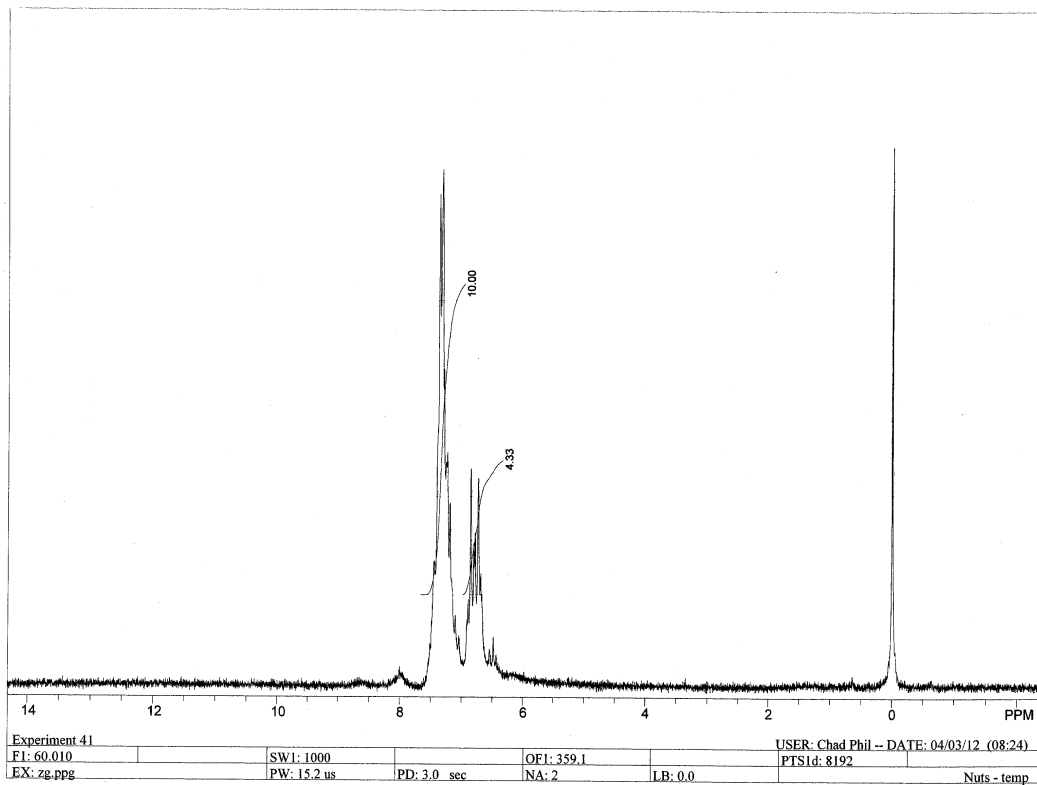


Figure 5. HNMR spectrum for *trans,trans*-1,4-diphenyl-1,3-butadiene.

References

McMurry, J. *Organic Chemistry*. 7th ed. Belmont, CA: Brookes/Cole, 2008.

Pavia, D.L., Lampman, et al. *Introduction to Organic Laboratory Techniques, A Small Scale Approach*. 2nd ed. Belmont, CA: Brookes/Cole, 2005.