

## Synthesis of *Trans,Trans*-1,4-Diphenyl-1,3-Butadiene Via Wittig Reaction with Phosphonium Ylide

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**Abstract :** The reaction of stabilized phosphonium ylide from benzyltriphenylphosphonium chloride with cinnamaldehyde was induced to yield *trans,trans* form of 1,4-diphenyl-1,3-butadiene with high stereoselectivity by the Wittig reaction. The Wittig salt (benzyl triphenyl phosphonium chloride) was synthesized by nucleophilic substitution reaction of triphenyl phosphine using benzylchloride with good yield (60.3%). The final product, *trans,trans*-1,4-diphenyl-1,3-butadiene, was obtained as a solid form 58.6% yield (overall yield = 35.3%) and determined by TLC (Thin Layer Chromatography) and <sup>1</sup>H-NMR spectroscopy.

**Key words :** phosphonium ylide, stereoselectivity, wittig reaction, NMR

### 1. Introduction

The formation reactions of a new alkene are important in organic synthesis [1-4]. The aldol condensation with dehydration has been used to form a new alkene from carbonyl compounds. This reaction has a limitation that one of the carbonyl compounds must have no -hydrogen and the other compound must be a ketone or an aldehyde with an acidic proton [2]. The Wittig reaction, discovered by George Wittig in 1954, overcame the above limitation of aldol condensation and is applicable to a various kinds of carbonyl compounds. Also, the Wittig reaction gives a great advantage over most other alkene synthesis because the exact location of an alkene can be predicted in the product. The Wittig reaction is used to create a new alkene from a carbonyl compound via phosphonium ylide as a nucleophile. The stability of phosphorus ylide is ascribed to resonance between the two structures (Figure 1). The double-bonded resonance structure (ylide form) requires ten electrons in the valence shell of phosphorus, using a 3d orbital. The bond between carbon and phosphorus is weak and the ylide form (charged structure) is the major contributor. (phosphorus-stabilized carbanion) [2].

The ratio of *cis*- and *trans*-alkene products of Wittig reaction is dependent upon the nature of the ylide and the kinds of ylide-prepared solutions such as salt-free solution of the ylide or an ylide-wittig salt complex [2]. Generally, the formations of *cis*-alkene (*Z*-alkene) and *trans*-alkene (*E*-alkene) are preferred from nonstabilized ylides and stabilized ylides, respectively [2]. The benzyltriphenylphosphonium chloride as a Wittig salt occupies a borderline position between stabilized and nonstabilized ylides [4]. Wittig, G *et al* reported that the reaction of benzyltriphenylphosphonium

chloride with benzaldehyde was produced the mixture of *cis*- (30 %) and *trans*-stilbene (70 %) with 82 % yield [4,5].

In this study, a phosphonium ylide is reacted with cinnamaldehyde to synthesize the *trans, trans*-1,4-diphenyl-1,3-butadiene by Wittig reaction. The purpose of this study is to see if only *trans,trans* isomer of product can be obtained preferentially as a solid form after removing of *cis, trans* isomer as an oil form.

### 2. Experimental section

#### 2.1. Preparation of Benzyltriphenylphosphonium Chloride (Wittig Salt)

2.2 g of triphenylphosphine (MW = 262.3), 1.44 mL of benzylchloride (MW = 126.6, d = 1.10 g/mL), and 8.0 mL of xylenes, and a magnetic stir bar were added to a 100-mL round-bottom flask. The mixture was heated under reflux for 1.5 hours. After cooling in an ice bath for 5 minutes, the Wittig salt was collected by vacuum filtration and washed with cold petroleum ether [1,2].

#### 2.2. Preparation of *trans,trans*-1,4-Diphenyl-1,3-Butadiene

1.92 g of benzyltriphenylphosphonium chloride (MW = 388.9), 8.0 mL of absolute ethanol, and a magnetic stir bar were added to a 50 mL round-bottom flask and stirred until the salt is dissolved into ethanol. 0.66 g of potassium tert-butoxide (MW = 112.21) was added into the mixture and stirred for another 15 minutes. The mixture was changed into yellow while it was stirred. At the same time, 0.60 mL of pure cinnamaldehyde (MW = 132.2, d = 1.11 g/mL) and 2.0 mL of absolute ethanol was prepared in a test tube. This solution was added to the round-bottom flask containing ylide and stirred for 10 minutes. After cooling in an ice bath for another 10 minutes, the crystals was collected by vacuum filtration and then

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washed with cold absolute ethanol. The filtrate at this point was saved for TLC experiment. The yellow color of the crystals was removed after they were dissolved into 12 mL of deionized water and collected by vacuum filtration. The final product was obtained after the recrystallization process using hot 95% ethanol. The percentage yield of the final product, *trans,trans*-1,4-diphenyl-1,3-butadiene, was calculated [1,2].

### 2.3. TLC Analysis

The products from the filtrate without dilution and the final solid product diluted with acetone were spotted on a silica gel TLC plate (4 × 4 cm) and developed in petroleum ether. Lastly, the spots were observed under a short wavelength UV light and in an iodine chamber. The  $R_f$  values of the spots were calculated.

### 2.4. $^1\text{H-NMR}$ Spectroscopy

$^1\text{H-NMR}$  spectrum (400 MHz,  $\text{CDCl}_3$ ) was obtained on a Bruker model AV-400 spectrophotometer and was used to determine a predominance of *trans,trans*-1,4-diphenyl-1,3-butadiene.

## 3. Results and Discussion

The reaction of a phosphonium ylide with cinnamaldehyde gave 58.6 % yield of *trans,trans*-1,4-diphenyl-1,3-butadiene by Wittig reaction. The overall percentage yield of the experiment was 35.3 %, and this value was smaller than G. Wittig's result [3]. His group used benzaldehyde as a carbonyl compound and obtained a 70% *trans*-stilbene with 82% yield from the Wittig reaction, using benzyltriphenylphosphonium chloride. In this experiment, cinnamaldehyde, a bulkier aldehyde than benzaldehyde, was used, and the Wittig salt was under reflux for 1.5 hours, which could be a short time for reflux. These might be reasons for obtaining smaller product yield than the Wittig's result.

Comparing to the melting point from literature (152°C), the melting point range of final product was 148-150°C after recrystallization with hot 95% ethanol. This result confirmed that the final solid product was pure *trans,trans*-1,4-diphenyl-1,3-butadiene.

### 3.1. TLC (Thin Layer Chromatography) and $R_f$ value Study

The  $R_f$  values of spots on TLC plate were shown in Table 1. The product spots were observed under a short wavelength UV light and then in an iodine chamber. Although it was hard to find any

differences in colors of spots under a UV light (all white) and in an iodine chamber (all brownish yellow), the positions of spots could be recognized by their  $R_f$  values.

The  $R_f$  value of the lower spot of Lane 1 (filtrate) was 0.17, and that of the upper spot of filtrate was 0.30. The only one spot on Lane 2 (*trans,trans*-isomer) had 0.30 of the  $R_f$  value. Based on these values, the lower spot on Lane 1 might be triphenylphosphine oxide or the *cis,trans*-1,4-diphenyl-1,3-butadiene. The upper spot on Lane 1 and the spot on Lane 2 had same  $R_f$  values, therefore they were *trans,trans*-1,4-diphenyl-1,3-butadiene.

### 3.2. $^1\text{H-NMR}$ Spectroscopy Study

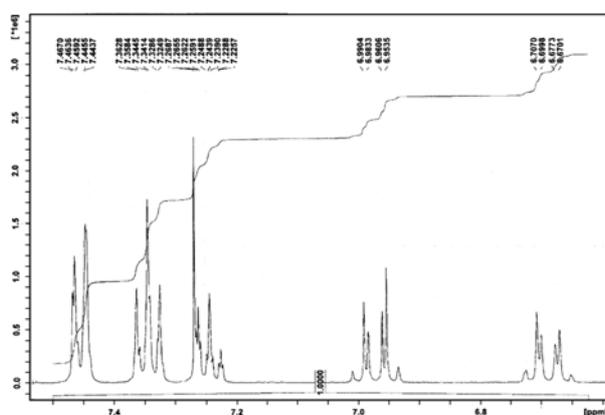
From the  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) spectrum of the final product, it turned out to be *trans,trans*-1,4-diphenyl-1,3-butadiene rather than *cis,trans*-1,4-diphenyl-1,3-butadiene (Scheme 4).

As shown in Figure 2, the Ha (Ha') and Ph (Ph') group is related with *cis* position, and Hb (Hb') and Ph (Ph') group is related with germinal-position in the *trans,trans* isomer of 1,4-diphenyl-1,3-butadiene. In *cis,trans* isomer, Ha and Ph group is related with *cis* position, and Hb (Hb') and Ph (Ph') group is related with germinal position. However, Ha' and Ph' group of *cis-trans* isomer is related with *trans* position (Table 2).

Using  $^1\text{H-NMR}$  (400 MHz) spectroscopy, J. B. Lambert *et al* [4] reported that the chemical shifts of  $^3J_{\text{trans}}$

**Table 2. The relationships between hydrogens and Ph (phenol) Groups of *trans-trans*- and *cis,trans*-1,4-diphenyl-1,3-butadiene**

| Compound                   | Bond    | Relationship     |
|----------------------------|---------|------------------|
| <i>Trans,trans</i> -isomer | Ph-Ha   | $^3J_{cis}$      |
|                            | Ph-Hb   | $^3J_{germinal}$ |
|                            | Ph'-Ha' | $^3J_{cis}$      |
|                            | Ph'-Hb' | $^3J_{germinal}$ |
| <i>Cis,trans</i> -isomer   | Ph-Ha   | $^3J_{cis}$      |
|                            | Ph-Hb   | $^3J_{germinal}$ |
|                            | Ph'-Ha' | $^3J_{trans}$    |
|                            | Ph'-Hb' | $^3J_{germinal}$ |

**Figure 3.  $^1\text{H-NMR}$  spectrum of *trans, trans*-1,4-diphenyl-1,3-butadiene.**

In the  $^1\text{H-NMR}$  spectrum of solid product obtained from this experiment, two d.d.d. (doublet of doublet of doublet) peaks appeared at  $\delta 6.6-6.7$  ppm (Ha, Ha') and  $\delta 6.9-7.0$  ppm (Hb, Hb') as the fingerprint of *trans,trans* structure of 1,4-diphenyl-1,3-butadiene (Figure 3).

Because the *trans*-cinnamaldehyde has one *trans* form of  $\text{Ph-CH=CH-Ph}$  structure, the one big d.d.d.(doublet of doublet of doublet) peak would appear around  $\delta 6.8$  ppm in the spectrum. However the product, *trans,trans*-1,4-diphenyl-1,3-butadiene, has two *trans* forms of  $\text{Ph-CH=CH-}$  structures. The two d.d.d peaks, which were divided from the big d.d.d. peak around  $\delta 6.8$  ppm,

appeared at  $\delta 6.6-6.7$  ppm (Ha, Ha') and  $\delta 6.9-7.0$  ppm (Hb, Hb').

There was no d.d.d. (doublet of doublet of doublet) peak in more upfield than  $\delta 6.6-6.7$  ppm which would be the region for  $^3J_{trans}$  (Ph-H) relation in the structure of product. This indicated that there was no *cis,trans* isomer but the *trans,trans* isomer of 1,4-diphenyl-1,3-butadiene in the product.

## 4. Conclusion

The *trans,trans*-1,4-diphenyl-1,3-butadiene was synthesized by wittig reaction with phosphonium ylide and cinnamaldehyde as a carbonyl compound. The overall yield of the final product was 35.3%. The contents and the purity of the product were determined by the melting point ( $148-150^\circ\text{C}$ ) and the results of thin layer chromatography and  $^1\text{H-NMR}$  spectrum. These results indicated that the wittig reaction with phosphonium ylide was a successful reaction to prepare the formation of alkene from carbonyl compounds.

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