**WITTIG SYNTHESIS OF *TRANS*-STILBENE**

**Required Pre-Lab Readings:** McMurry, 7th Ed. Sect. 19.11, pp 720 - 723.

**Techniques you must be prepared to perform:** reflux; extraction; rotary evaporation; recrystallization.

**Introduction**

The Wittig Reaction, named after 1979 Noble Laureate Georg Wittig, allows the preparation of an alkene by the reaction of an aldehyde or ketone with the ylide generated from a phosphonium salt (Scheme 1). The geometry of the resulting alkene depends on the reactivity of the ylide. If the ylide is resonance stabilized (R is conjugated to the double bond of the ylide; *e.g.* phenyl, NO2, a ketone, etc.) it is not as reactive as when R is an alkyl group and results in (*E*)-alkenes. Non-stabilized ylides lead to (*Z*)-alkenes.



Scheme 1. The general Wittig reaction

The ylides themselves are generated from the corresponding phosphonium salt (Scheme 2). Phosphonium salts are relatively stable and have reasonable shelf lives. However, the ylides are highly reactive and decompose upon standing. Thus, ylides are generally prepared *in situ* (as in this experiment) or immediately prior to use.



Scheme 2. Preparation of ylides

Both experimental and theoretical evidence supports a mechanism for the Wittig reaction that proceeds through a four-membered cyclic intermediate, an oxaphosphetane (Scheme 3). The formation of the oxaphosphatane is concerted, but asynchronous. That means that both new sigma bonds do form at the same time, but one lags behind the other. In the transition state the carbon-carbon bond of the oxaphosphatane is much more formed that the oxygen-phosphorous bond. It can best be described as a double nucleophilic addition, where the ylide carbon donates electron density to the carbonyl carbon, starting carbon-carbon bond formation. As electron density builds on the carbonyl oxygen, it is able to bond to the ylide phosphorous. It is a combination of steric repulsion and dipole-dipole interactions between the ylide and carbonyl compound that results in the formation of either an E or Z oxaphosphatane. Once formed the oxaphosphatane decomposes to form the alkene of the same stereochemistry and the phosphineoxide. When the ylide anion can be stabilized by resonance the oxaphosphetane and product have the E configuration and when the anion cannot be stabilized they are Z.



Scheme 3. The Wittig Reaction Mechanism

**Procedure**



Place benzaldehyde (10 mmol, \_\_\_\_ g, \_\_\_\_ mL), benzyltriphenylphosphonium chloride (10 mmol, \_\_\_\_ g), methylene chloride (10 mL) and a magnetic stir bar into a 50 mL round bottomed flask. Add a reflux condenser and stir the mixture as vigorously as possible while maintaining a vortex. Carefully add 7.5 mL of 10 M aqueous sodium hydroxide through the top of the condenser. The solution should spontaneously warm and turn yellow. Gently heat the reaction and reflux for 30 min. After the reflux, cool the solution in an ice-bath, and pour the mixture into a separatory funnel. Add water to help separate the layers (Why do you need to do this?).

Remove the aqueous layer and dry the organic phase over anhyd. Na2SO4. Decant or filter the solution and remove the methylene chloride by rotary evaporation under reduced pressure. The residue is a mixture of *cis*- and *trans*-stilbene and triphenylphoshpine oxide. Add 8 mL of absolute ethanol, stir thoroughly, and warm if necessary to dissolve, then cool the solution in an ice bath for 10 min. Suction filter the crude *trans*-stilbene and recrystallize it from absolute ethanol (6 – 10 mL). During the recrystallization add a few drops of water (one at a time) to the boiling solution until the solution just becomes cloudy (the cloud point – Why do you do this?) and then cool. Collect the pure product by suction filtration and wash it with a little cold ethanol. Allow the sample to air-dry. Record the weight and melting point of your product in your notebook and have the instructor (or lab assistant) initial it.

Turn in your product along with your lab report. The vial must have a label on it with the following information: 1) name, 2) lab day, 3) name or structure of compound 4) weight.

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| Name: |  |  | Date: |  |

Overall Reaction (chemical drawing software):

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| --- | --- | --- | --- | --- |
| Measured benzaldehyde: |  |  | Theo mmol *cis/trans*-stilbene: |  |
|  |  |  |  |  |
| mmol benzaldehyde: |  |  | Theo mass *cis/trans*-stilbene: |  |
|  |  |  |  |  |
| Mass phosphonium salt: |  |  | Mass recovered *trans*-stilbene: |  |
|  |  |  |  |  |
| mmol phosphonium salt: |  |  | mmol recovered *trans*-stilbene: |  |
|  |  |  |  |  |
|  |  |  | % yield *trans*-stilbene: |  |

Observed melting point of recovered *trans*-stilbene:

Literature melting point:

Literature source:

Show complete calculations: (use a separate sheet if necessary)

What is the name of the type of molecule which possess adjacent positive and negative charges?

Which is the more stable isomer in your product mixture and why?

Why is triphenylphosphine oxide a major drawback to the Wittig reaction?

Write out the complete mechanism for Wittig reaction performed in this experiment to produce *trans*-stilbene, giving the names for the different intermediates produced.

Provide the **major** products or starting materials for the following Wittig-related reactions.

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