

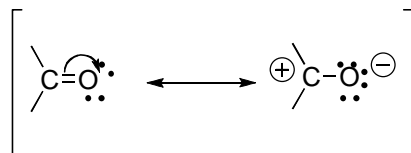
8. Wittig Reaction

M. Jones: Wittig Reaction, 16.17, pp 876-877.

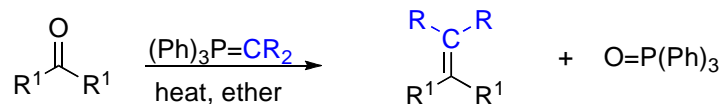
This procedure has been adapted from the microscale procedure described in the third edition of *Macroscale and Microscale Organic Experiments* by Kenneth L. Williamson (Houghton Mifflin, Boston, 1999) and *Chem 333 Lab Experiment 9 The Wittig Reaction With Chemiluminescence!* found at <http://www.udel.edu/chem/koh/lab9.pdf> by John T. Koh at the University Of Delaware.

Background

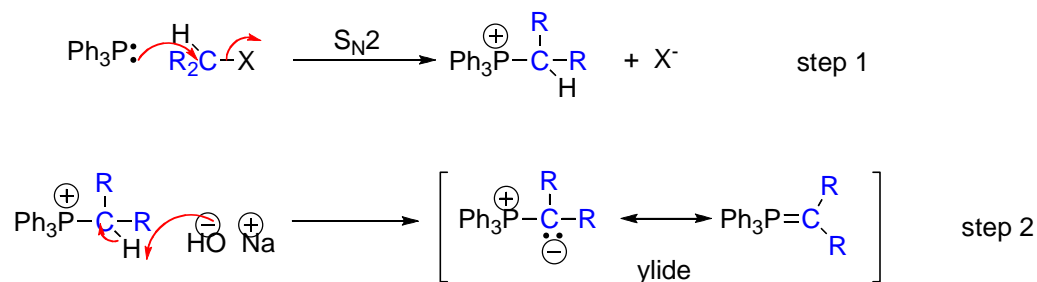
The Wittig reaction belongs to a set of reactions, which add irreversibly to the carbon of the carbonyl-containing compounds such as aldehydes and ketones. The addition is to the carbon of the carbonyl group because there is a partial positive charge on that carbon as shown in the resonance structures below:



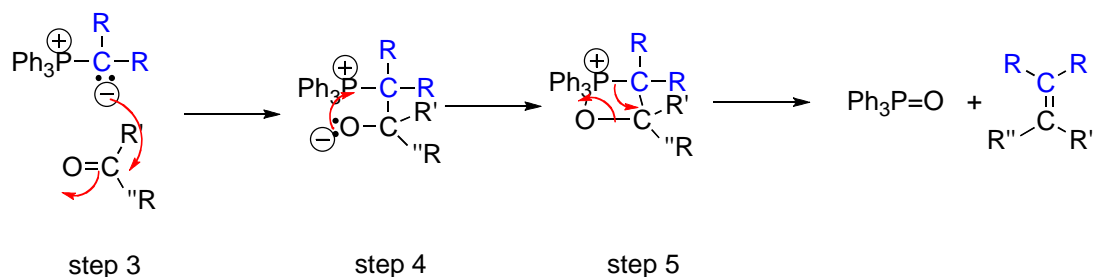
The Wittig reaction is named after Georg Wittig (1897-1987) and was so useful as a C-C bond formation reaction that he won the Nobel Prize in 1979. A general Wittig reaction is depicted below:



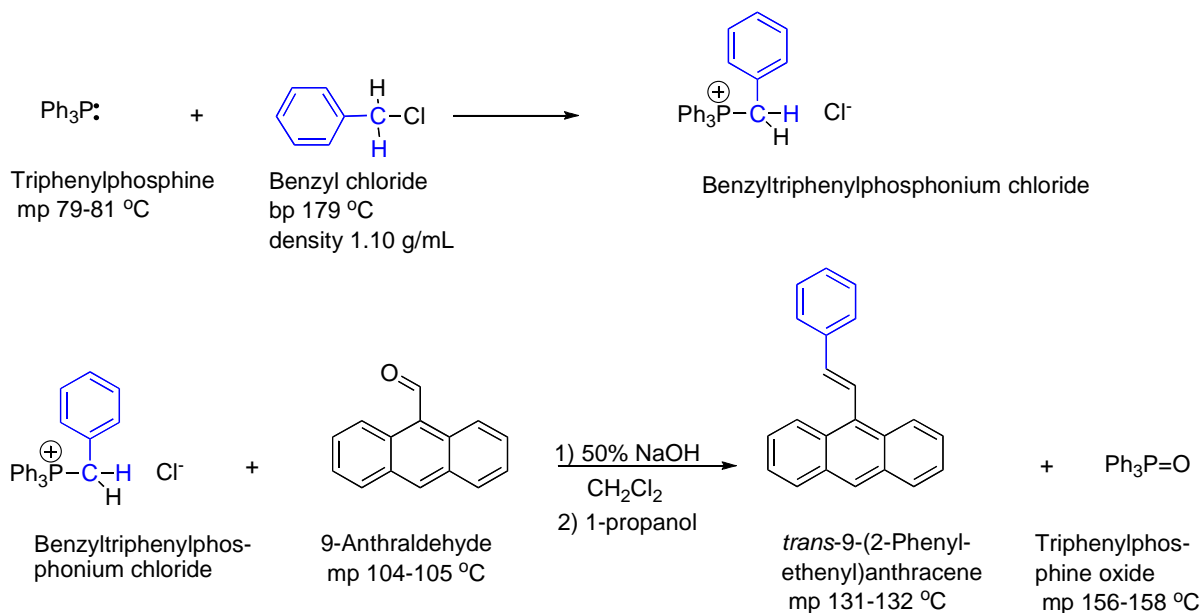
There are seven steps in this reaction. The first step is to form a phosphonium ion. Phosphorus is a good nucleophile. In this reaction, the nucleophile is triphenylphosphine [(C₆H₅)₃P or Ph₃P], which adds to the C of the RX forming phosphonium ion. In the second step, a base, such as sodium hydroxide (NaOH) or butyl lithium (BuLi), is used to deprotonate and forms the ylide (Wittig reagent).



The ylide is used in the Wittig reaction. The ylide then acts as a nucleophile and adds to the carbonyl carbon. The resulting alkoxide oxygen (-OR) adds to the phosphorus in an intramolecular closure reaction to form a four-membered ring, an oxaphosphetane. This ring fragments to form triphenylphosphine oxide and the alkene.



You will be performing a Wittig reaction using benzyltriphenylphosphonium chloride and 9-anthraldehyde as reagents and sodium hydroxide as the base. You are not starting with triphenylphosphine and benzyl chloride so you will be doing the first step. The overall reaction is given below.



Now for something different!

Chemiluminescence is the result of a chemical reaction involving direct emission of light (luminescence) without first going through an intermediate stage involving heat. The light sticks that children carry when trick-or-treating at Halloween are one such example of a chemiluminescent reaction. The design of a light stick is simple, a plastic tube with a glass vial inside of it. The plastic tube contains an oxalate, like the product synthesized in this experiment, and the glass vial contains an activator, typically hydrogen peroxide. The light stick is activated by bending the plastic tube, and thus rupturing the glass vial. This allows the chemicals to mix and then react. The reaction releases light, causing the stick to glow!

Cautions and tips:

- Use caution when weighing the ylide.
- Make sure to label and keep track of the two test tubes
- Remember to identify the organic layer. If in doubt, add a drop of water to help tell the different layers apart.
- Make sure to use a clean spatula, filter flask, and reaction tube. The reaction tubes should be cleaned with soap, water and a brush first, rinsed thoroughly, and dried (if needed rinse with acetone).
- Make sure to return the top to the bottles.
- Wear gloves to protect your hands from staining.

Experiment

There are two parts to this experiment.

Part A. Wittig Reaction

To a small reaction tube, add 200 mg of benzyltriphenylphosphonium chloride, 115 mg of 9-anthraldehyde, and 1.0 mL of dichloromethane. With a syringe, add 0.26 mL of a 50% NaOH solution dropwise to the reaction tube. Flick the tube every few drops to mix the reagents thoroughly. After the addition is complete, cap the reaction tube and shake vigorously for 30 minutes. Add 1.5 mL of water and 1.5 mL of dichloromethane to the tube. Shake the tube to mix the two layers, and then extract the organic layer, placing it into a clean reaction tube. Wash the aqueous layer twice more with dichloromethane (2 x 1 mL) and combine the organic washes with the other organic layer. Dry the dichloromethane with sodium sulfate and then remove the solvent with a pipette. Wash the pellets with a small amount of dichloromethane. Combine all of the dichloromethane washes. Evaporate off the solvent in the hood. To the solid that remains, add 4 mL of propanol and recrystallize the product. Determine the melting point and % yield.

Part B. Chemiluminescence Procedure

Transfer the remainder of your product and 2 mL of dichloromethane into a small test tube. Take this product to the hood in the IR spectroscopy room. Inside the hood, add 2 mL of a 10% oxalyl chloride/dichloromethane solution and 2 mL of 30% hydrogen peroxide. Use a pipette to thoroughly mix the solution. Turn off the light and observe the chemical reaction. Record your observations.