

Fig. 36-1



## Experiment 36

# A GREEN WITTIG REACTION

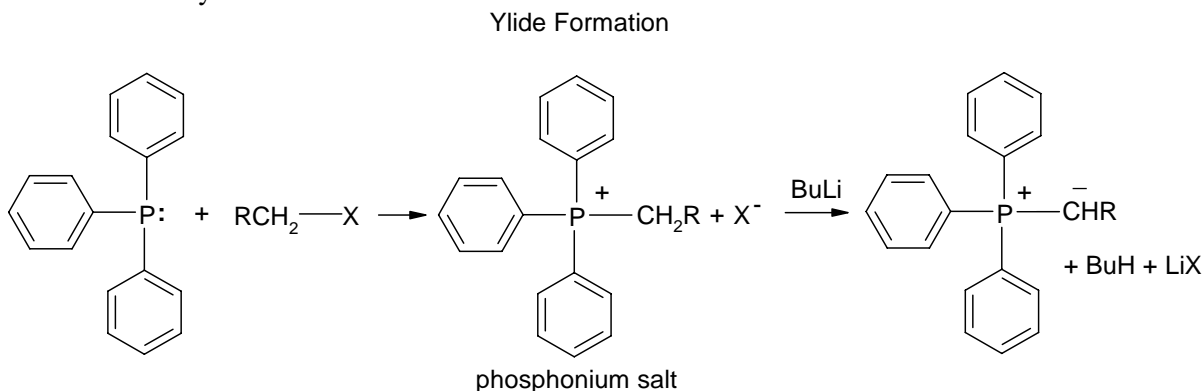
### Text Topics

Wittig reaction.

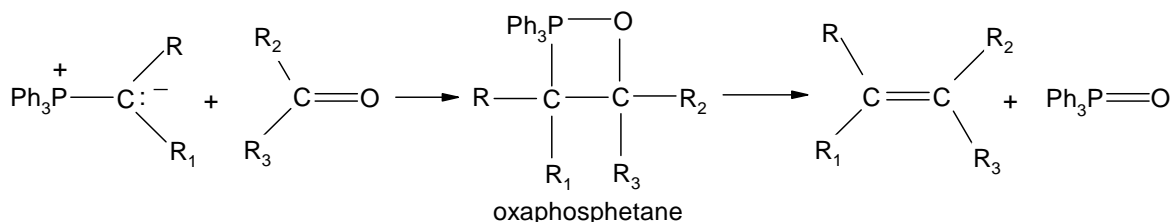
Georg Wittig (1897- 1987)  
 received Nobel prize in 1979 for discovery of Wittig reaction  
[http://nobelprize.org/nobel\\_prizes/chemistry/laureates/1979/wittig-cv.html](http://nobelprize.org/nobel_prizes/chemistry/laureates/1979/wittig-cv.html)

### Discussion

Like the Grignard, Diels-Alder and aldol reactions, the Wittig reaction is extremely useful in synthetic organic chemistry because of its ability to form carbon-carbon bonds. The Wittig is especially valuable because it forms carbon-carbon double bonds. The first step in a Wittig synthesis is the reaction of triphenylphosphine with an alkyl halide. The product is then reacted with a very strong base such as butyl lithium to form an ylide.

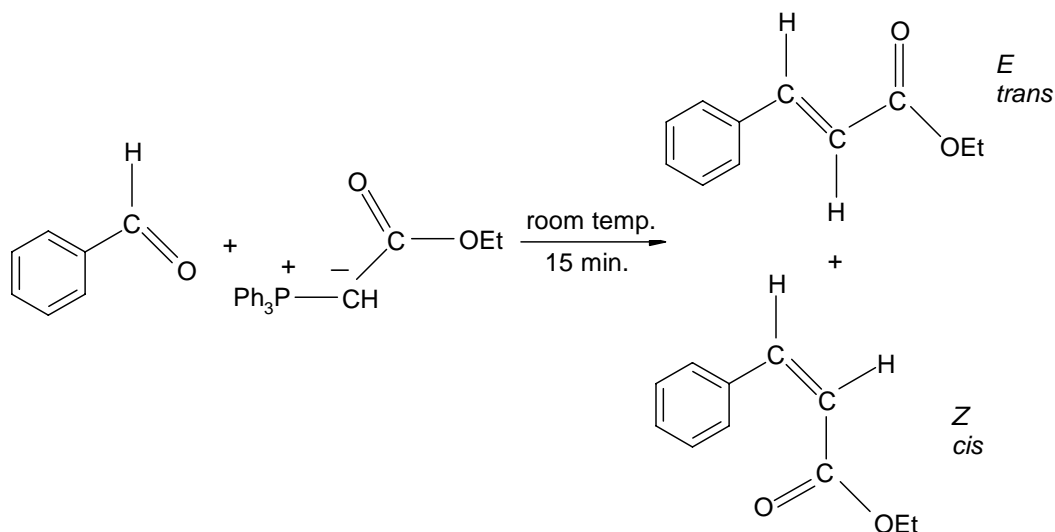


The ylide is then reacted with a carbonyl compound to yield an alkene.



If, as illustrated in the example above, geometric isomerism of the alkene is possible, determination of the stereoselectivity might be required followed by separation of the stereoisomers.

To decrease the time required for the Wittig reaction and to eliminate the hazardous use of butyl lithium, a commercially available ylide will be used in today's experiment. The procedure will therefore require only mixing of the ylide with the carbonyl followed by a simple work-up procedure.



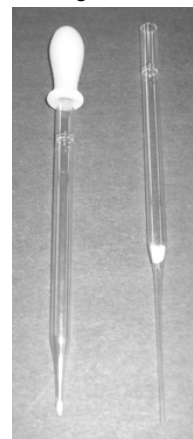
Because a pair of geometric isomers are possible products, after isolation of the product, nmr will be used to determine the stereoselectivity of the reaction.

## Procedure

Add 0.20 g of the ylide [(carbethoxymethylene)triphenylphosphorane] and 0.050 g of benzaldehyde to a 3 mL conical vial equipped with a magnetic spin vane. Stir the mixture for about 15 minutes, add 3 mL of hexanes and stir the suspension for another 5 minutes. Use a filtering pipet to remove and transfer the solvent to a clean vial. Repeat the hexane extraction of the solid with an additional 3 mL of hexane and combine the two hexane layers. Evaporate the hexanes and analyze the mixture using nmr.

The ratio of the cis to trans isomers formed involves an integration of two olefinic hydrogen signals in the  $^1\text{H}$ nmr spectrum. The hydrogen  $\alpha$  to the carboxyl in the *E* isomer gives a doublet (coupling constant of 15.9 Hz) centered at 6.44  $\delta$  in  $\text{CDCl}_3$ . The  $\alpha$  hydrogen for the *Z* isomer give a doublet (coupling constant of 12.3 Hz) centered at 5.95  $\delta$ . The ratio of the integration of the latter to the former should give the cis to trans ratio.

Fig. 36-2



Left - filter tip pipet with cotton in tip  
Right - filtering pipet

## References

Leung, S. H.; Angel, S. A. *J. Chem. Ed.*, **2004**, *81*, 1492-1493.

Nguyen, K. C.; Weizman, H. *J. Chem. Ed.*, **2007**, *84*, 119-121.

very recent suggestions for Wittig reactions: Morsch, I. A.; Deak, L.; Tiburzi, D.; Schuster, H.; Meyer, B. *J. Chem. Ed.*, **2014**, *91*, 611-614, MacKay, J. A.; Wetzel, N. R. *J. Chem. Ed.*, **2014**, *91*, 722-725.

## Prelaboratory Preparation - *Experiment 36*

First, be sure to list all the goals of the experiment. Prepare a table for insertion of useful and observed data such as molecular mass, mass, moles, melting points and percent yields and recoveries. Locate the Wittig reaction in the *Reaction Map of Organic Chemistry* in **Appendix C** and include the reaction number with your report.

## Observations

Report all relevant observations including, masses, melting ranges and nmr spectra.

## Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. What was the identity of your product and did it agree with your prediction? Explain your answer.
3. What was the *Z* to *E* ratio and how did you determine it? If one geometric isomer predominated, suggest explanations for this result.
4. How could the percent yield and recoveries have been improved?
5. Write a mechanism for the reaction of a carbonyl with an ylide.