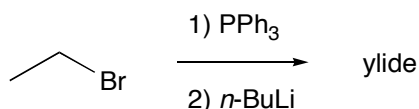
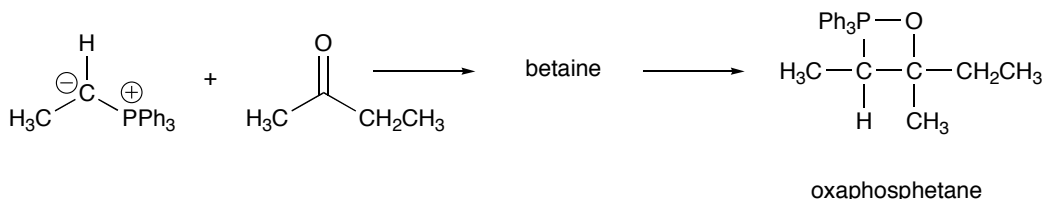


Chem 2062 Spring 2006
Ch 18 Group Work

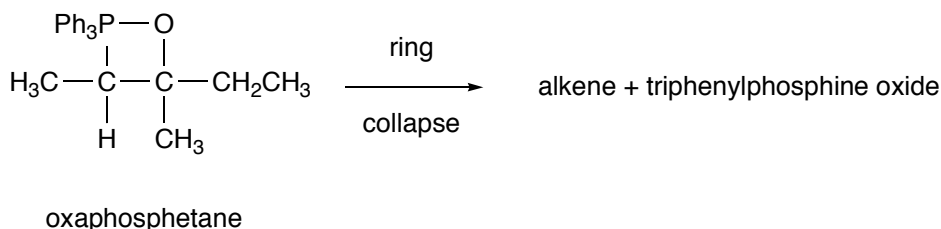
- Yesterday we learned that a phosphorus ylide is produced by reaction of triphenylphosphine with a primary alkyl halide, followed by deprotonation with *n*-BuLi. Why must the alkyl halide be primary? What is the formal charge on phosphorus in the ylide? The resulting ylide is resonance-stabilized. Without using your book (notes are ok), draw the full mechanism for the following reaction, showing both resonance structures of the resulting ylide. Make sure each of your reactions is balanced (*i.e.* show all side products).



- Draw the mechanism of a reaction of the phosphorus ylide below with 2-butanone. (Hint, the ylide is the nucleophile). Your initial product should have both a + charge and a – charge in the molecule. This is called a betaine. The betaine forms one bond to become an oxaphosphetane (4-membered ring containing oxygen and phosphorus.) Without using your book, draw the mechanism for the reactions below.

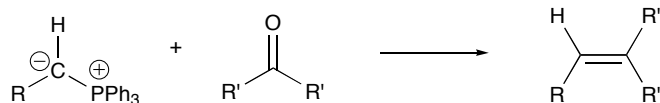


- The oxaphosphetane formed in the above reaction is an important intermediate in the Wittig reaction. Without using your book, show, using two simultaneous curved arrows, how the P–C and O–C bonds can be broken, while at the same time P=O and C=C double bonds are formed. This process is known as ring collapse. You should end up with an alkene and triphenylphosphine oxide. What is the driving force for this reaction? (Hint, is there anything particularly unstable about the oxaphosphetane?)

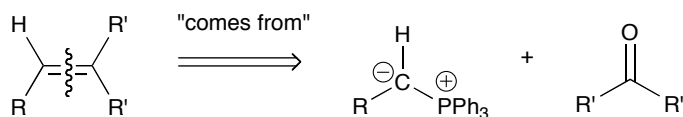


- Unfortunately the Wittig reaction has very little *E/Z* selectivity. Remembering that the product is an alkene and *E* and *Z* are stereochemical indicators for double bonds, what does this mean? Draw both the *E* and the *Z* product of the reaction above.

5. The general formula for the Wittig reaction is shown below. Note which fragment the H on the double bond came from.



When planning a Wittig synthesis, it's best to work backwards. In the compound you want to synthesize, first identify the bond that was formed by drawing a squiggly line through it, then identify the compounds that were used to synthesize it. We use a retrosynthetic arrow (double-lined arrow) which means "comes from" to show this, as below:



All of the following compounds could be synthesized by a Wittig reaction. Identify the bond that's formed, and use a retrosynthetic arrow to show the compounds that it comes from. Finally, draw the reactions in the forward, synthetic, direction, to show the actual reaction that would take place.

