1. Wittig reactions are very convenient to generate an alkene starting with a ketone or aldehyde. Draw the mechanism for cyclohexanone reacting with a phosphorous ylide. Indicate product and all intermediate structures for this reaction.

Other types of ylides can also react with ketones and aldehydes, but alkenes are not the favored product in these reactions. Draw the mechanism for the following ketones reacting with either a sulfur ylide or diazomethane. Realize that the first step is identical with a nucleophile reacting at the electrophilic carbonyl carbon in all of these ylide reactions.

What is the energetic driving force for alkene products in a Wittig reaction?

Formation of strong phosphorous-oxygen bonds drives the Wittig reaction. Phosphorous is extremely oxophilic, meaning that it forms strong bonds with oxygen. With sulfur ylides, the sulfur does not form as strong of bonds with oxygen and thus the sulfur would rather leave as a good dimethylthioether leaving group to form an epoxide. With diazomethane, cannot form five bonds to nitrogen so the same mechanism with phosphorous ylides is not possible. With small rings the favored process is a ring expansion to form the ketone with a gaseous nitrogen-leaving group.
2. The formation of acetals is an equilibrium driven process. Draw a mechanism for the formation of acetal from cyclohexanone with methanol.

![Mechanism for the formation of acetal from cyclohexanone with methanol.](image)

How will the equilibrium change for the following ketones and aldehydes? Which has the greatest equilibrium constant for the acetal? Why?

The equilibrium will favor the acetal more going from left to right for the carbonyls shown. The trifluoroacetalddehyde shown on the far right has the greatest equilibrium for the acetal. As the electrophilicity of the carbonyl carbon increases (i.e. more partial positive charge on the carbonyl carbon) the reactivity of the carbonyl reacting with methanol increases and the equilibrium becomes shifted to the acetal form.

Knowing that the reaction is under equilibrium control, what experimental conditions concerning the methanol used can be undertaken to affect acetal formation?

Increasing the concentration of methanol. As methanol concentration increases, the equilibrium becomes shifted to the acetal. Typically these reactions are run with methanol as the solvent.

If the acetal formation is still not favored by equilibrium, what other conditions can be undertaken to affect the equilibrium?

Remove water azeotropically. Because water is a leaving group in this equilibrium, if the water is removed then the equilibrium will be shifted to the acetal.