



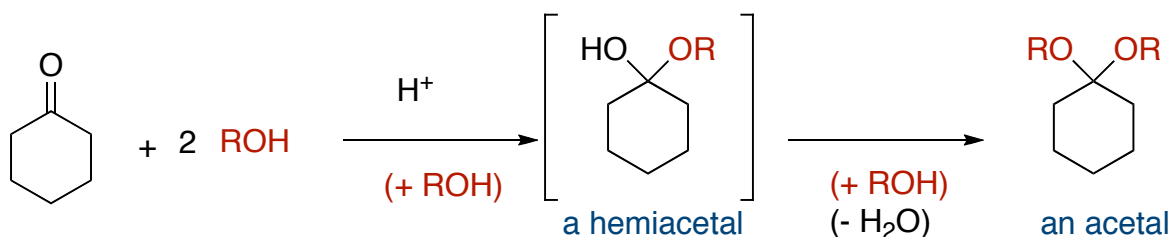
# Chem 342 • Organic Chemistry II

Lecture Summary 22 - 23 Mar 2009

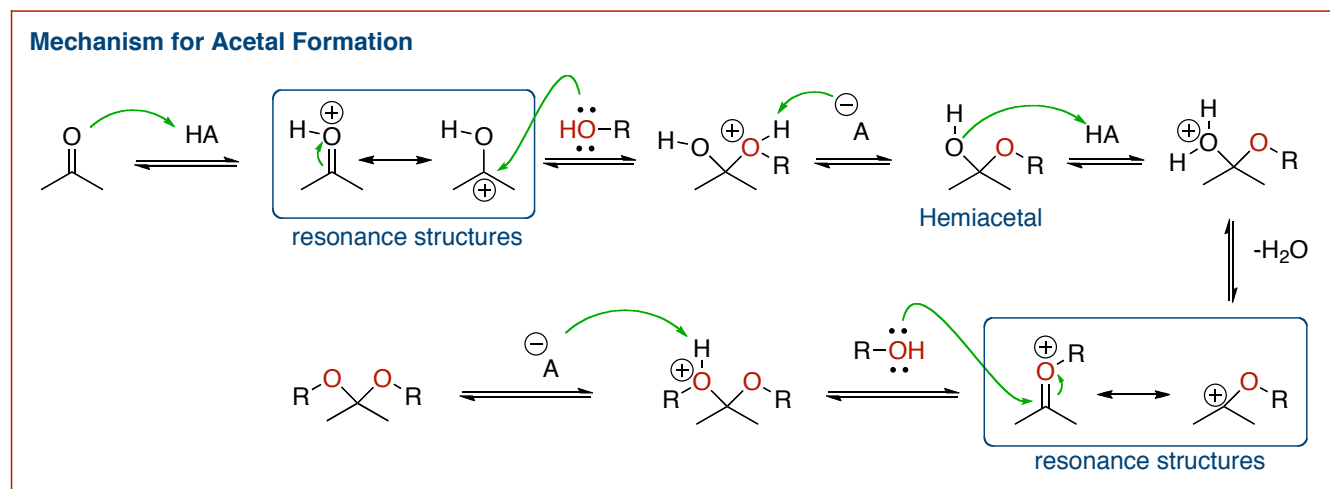
## Chapter 19 - Aldehydes and Ketones: Nucleophilic Addition Reactions

### Acetals

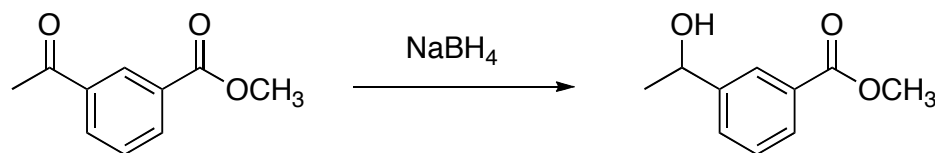
An acetal is similar to a hydrated carbonyl except instead of water adding, an alcohol is added. Acetals are relatively stable and can be used as protecting groups for aldehydes and ketones. Two equivalents of alcohol add to form a stable acetal.



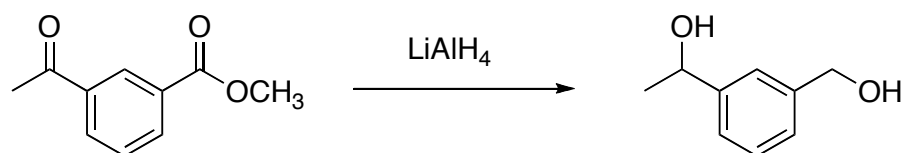
### NEED TO KNOW MECHANISM



Acetals are commonly used as protecting groups as they are quite stable. Reactive aldehydes and ketones can be converted to an acetal in the presence of an ester to keep it from reacting with reducing agents or Grignard reagents. The acetal is convenient as it can be made easily and removed easily. Since the acid catalyzed acetal formation is readily reversible it can be manipulated easily to favor one side or the other. To make an acetal an excess of the alcohol is used and water is removed. To remove the acetal it is hydrolyzed by an excess of water. This is also acid catalyzed and the mechanism is exactly the same except in reverse.

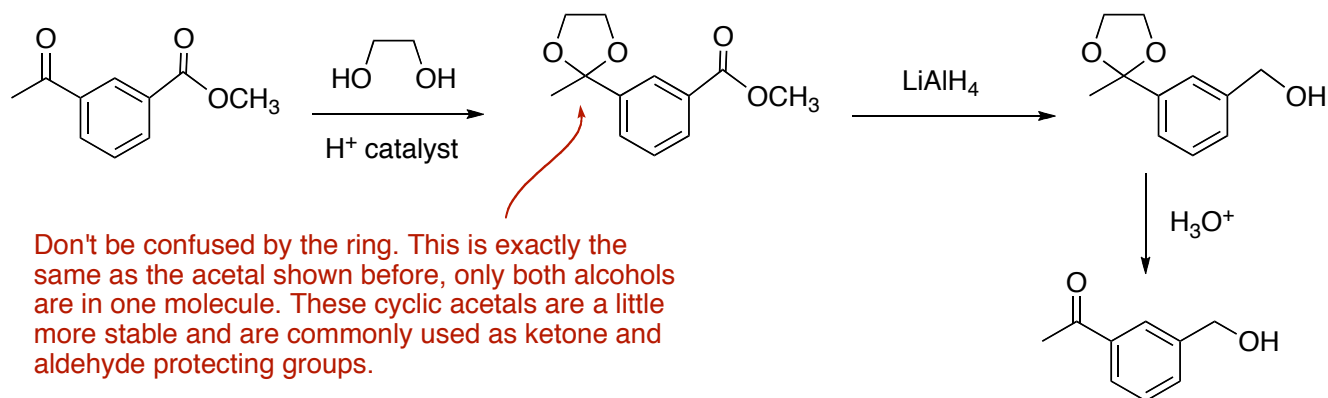


sodium borohydride reduces the ketone



lithium aluminum reduces the ketone and the ester

How do we reduce the ester but not the ketone? Protect the ketone as an acetal first!!

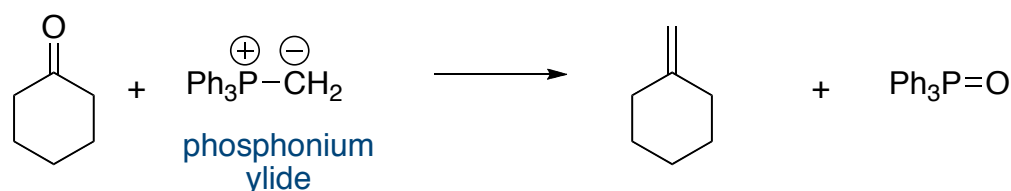


Don't be confused by the ring. This is exactly the same as the acetal shown before, only both alcohols are in one molecule. These cyclic acetals are a little more stable and are commonly used as ketone and aldehyde protecting groups.

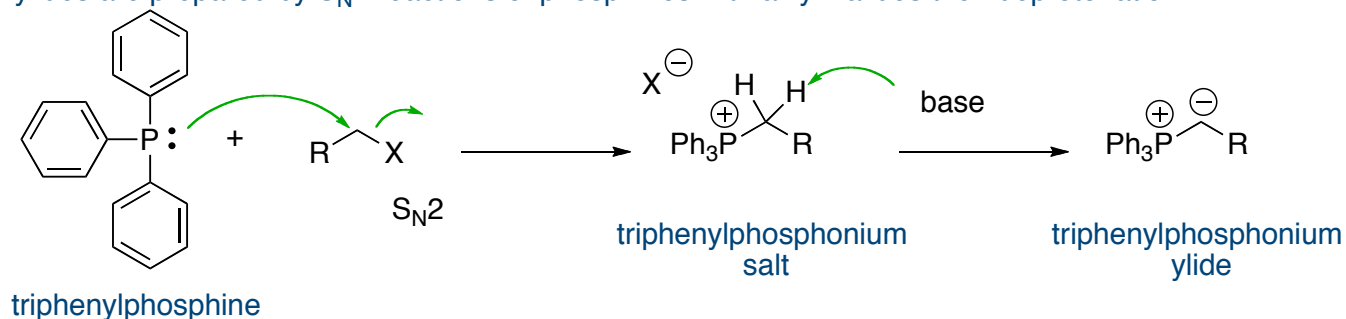
## The Wittig Reaction

Essentially the reverse of an ozonolysis, the Wittig reaction takes a ketone or aldehyde and makes alkenes from them by adding carbons. A phosphonium ylide is the reagent necessary for this transformation. Phosphonium ylides are prepared by the  $\text{S}_{\text{N}}2$  reaction of phosphines with alkyl halides. The resulting salt can be deprotonated with a base such as butyl lithium. The mechanism involves the attack of the nucleophilic ylide onto the carbonyl followed by loss of a phosphine oxide.

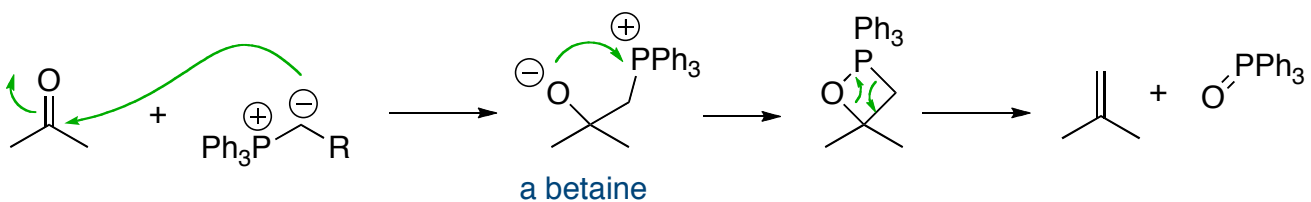
### Wittig Reaction



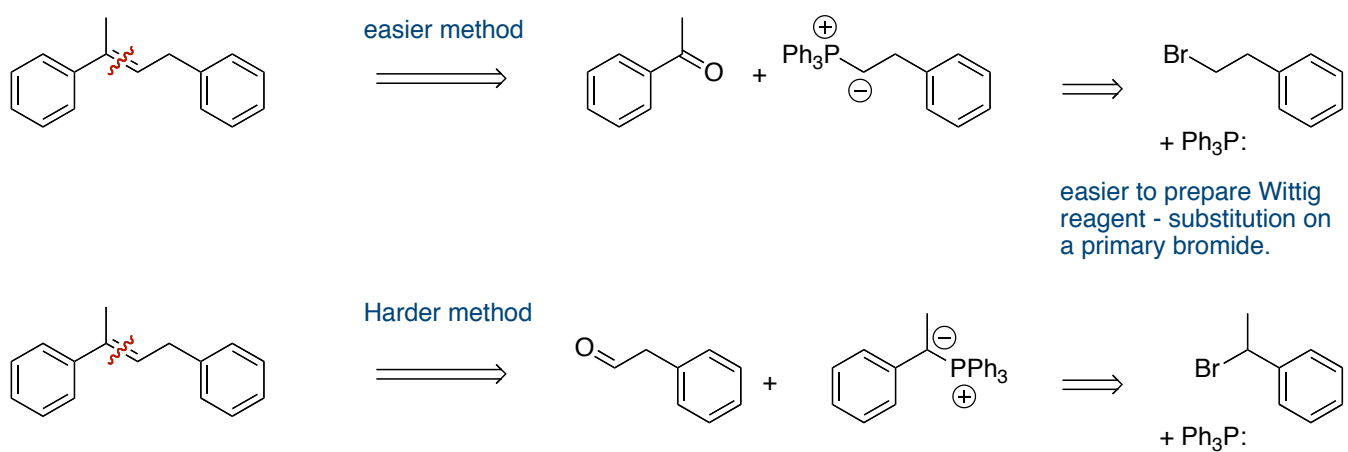
ylides are prepared by  $\text{S}_{\text{N}}2$  reactions of phosphines with alkyl halides then deprotonation



ylides are nucleophilic and will react with carbonyls

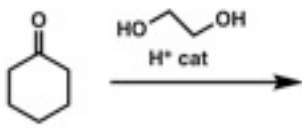


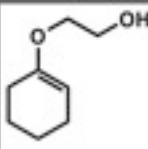
Many alkenes can be prepared by this method. It is easier when thinking about synthetic strategy to use the least substituted end of the desired alkene as the Wittig reagent because it is easier to prepare from an alkyl halide and triphenylphosphine.

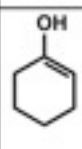


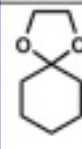
## Daily Quiz

Q: What is the expected product of the reaction of 1,2-ethandiol with cyclohexanone?



1: 

2: 

3: 

4: 