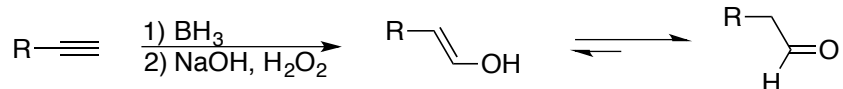


Chapter 19 - Reaction Summary

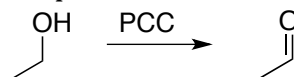
Reactions of Aldehydes and Ketones

Preparation of Aldehydes (Review)

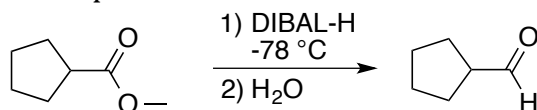
- Aldehydes can be prepared by the hydroboration of terminal alkynes, which follows anti-Markovnikov addition of water across the triple bond.



- PCC Oxidation of 1° alcohols will provide aldehydes. Most other oxidation reagents are too powerful and will go directly to the carboxylic acid.

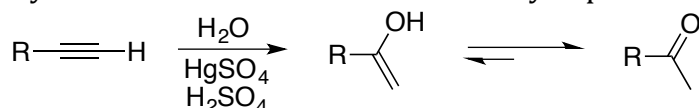


- DIBAL-H reduction of esters and acid chlorides provides aldehydes following an aqueous workup.

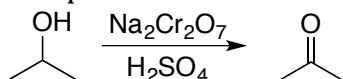


Preparation of Ketones (Review)

- Hydration of a terminal or internal alkyne provides the ketone product.

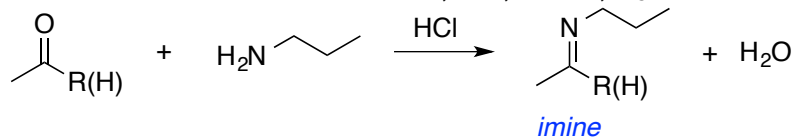


- Oxidation of secondary alcohols using $\text{M}_2\text{Cr}_2\text{O}_7$ or CrO_3 in the presence of aqueous sulfuric acid provides ketones.

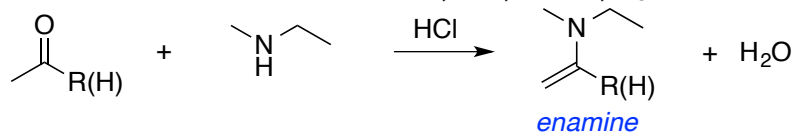


Addition of Nitrogen Nucleophiles

- Addition of 1° amines to aldehydes and ketones provides imine products.
 - The reaction is usually carried in the presence of a trace acid.
 - Common acids include TsOH , HCl , H_2SO_4 , H_3PO_4

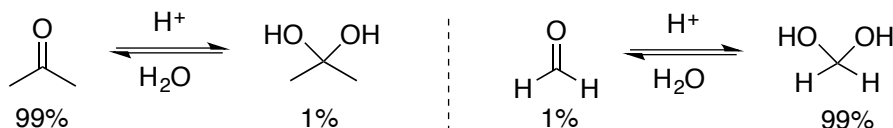


- Addition of 2° amines provides an enamine product.
 - The reaction is usually carried in the presence of a trace acid.
 - Common acids include TsOH , HCl , H_2SO_4 , H_3PO_4



Addition of H₂O – Hydration of Aldehydes and Ketones

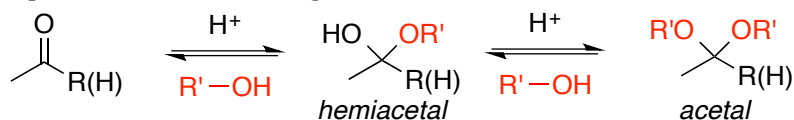
- Addition of water to aldehydes and ketones is catalyzed by either acid or base.
- The reaction is an equilibrium process. Less stable carbonyl compounds, such as aldehydes favor the hydration product while more stable carbonyl compounds, such as ketones favor the carbonyl compound.



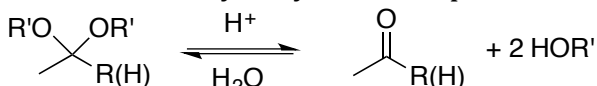
- Electron withdrawing groups on the carbonyl carbon will destabilize the carbonyl and result in a higher percentage of hydrate.

Addition of Alcohols to Aldehydes and Ketones

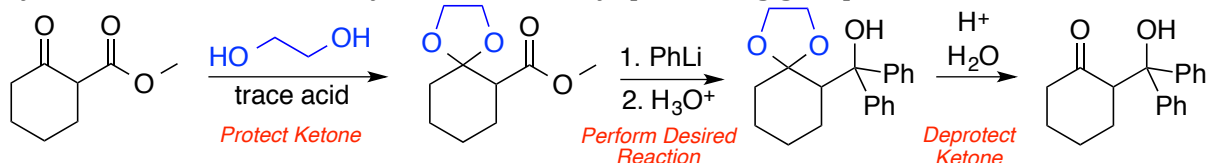
- The reaction is an equilibrium process.
- The reaction is catalyzed with acid.
- Removal of water during the course of the reaction or an excess of one of the reagents drives the reaction to favor products.
- Addition of the first equivalent of alcohol provides a hemiacetal. Addition of the second equivalent of alcohols gives the acetal.



- Acetals can be hydrolyzed in the presence of acid and an excess of water.

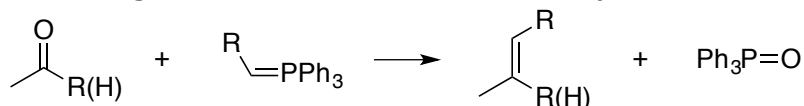


- Cyclic acetals are commonly used as carbonyl protecting groups.

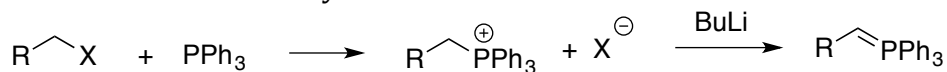


The Wittig Reaction

- The Wittig reaction is used to convert aldehydes and ketones to alkenes.



- The driving force of the Wittig reaction is formation of the Ph₃P=O byproduct which has a strong phosphorus oxygen double bond.
- While there are ways to get selectivity in Wittig reactions, for this class we will just assume you get a mixture of *E* and *Z* double bonds.
- The Wittig reagent “ylide” is prepared from an alkyl halide and PPh₃ followed by treating with a base such as butyllithium.



- Methyl and primary alkyl halides work best. Secondary alkyl halides also work, but tertiary do not.