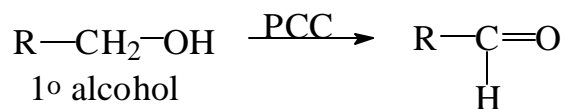


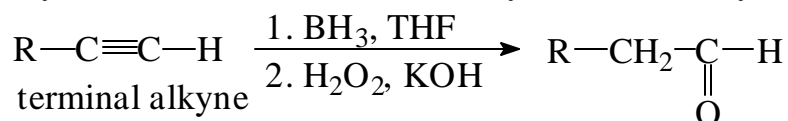
Aldehydes and Ketones

Preparation of Aldehydes —

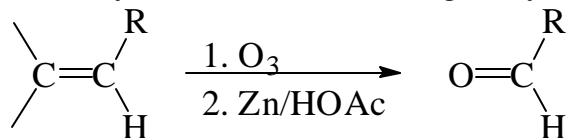
☞ Oxidation of Primary Alcohols ---



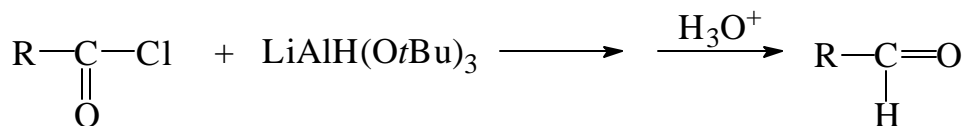
☞ Hydroboration of a Terminal Alkyne, followed by Tautomerization ---



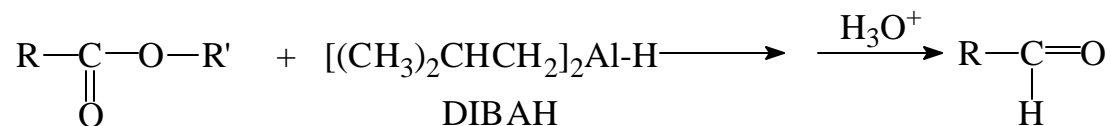
☞ Ozonolysis of Alkenes Having Vinylic Hydrogen ---



☞ Reduction of Acid Chlorides ---

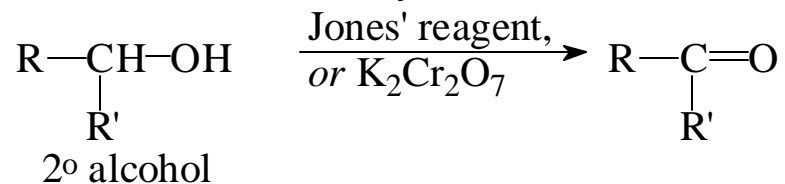


☞ Reduction of Esters ---

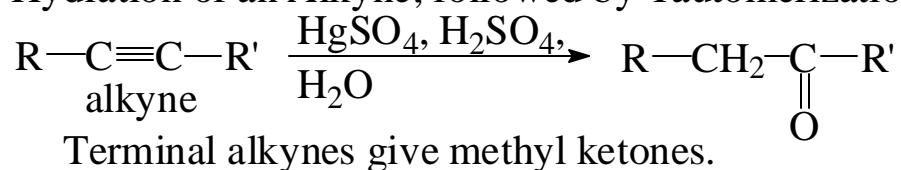


Preparation of Ketones —

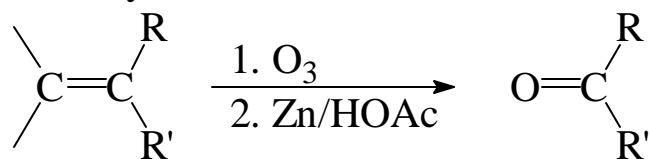
☞ Oxidation of Secondary Alcohols ---



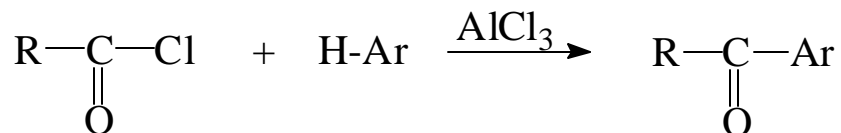
☞ Hydration of an Alkyne, followed by Tautomerization ---



☞ Ozonolysis ---

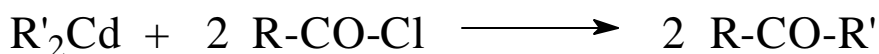
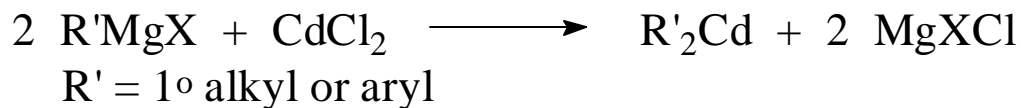


☞ Friedel-Crafts Acylation ---



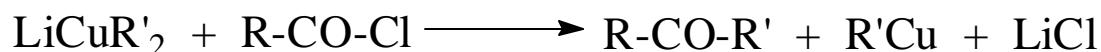
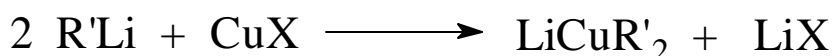
Substituents on ring cannot be meta directors or amino

☞ Reaction of Organocadmium or Organocuprate Compounds with Acid Chlorides ---



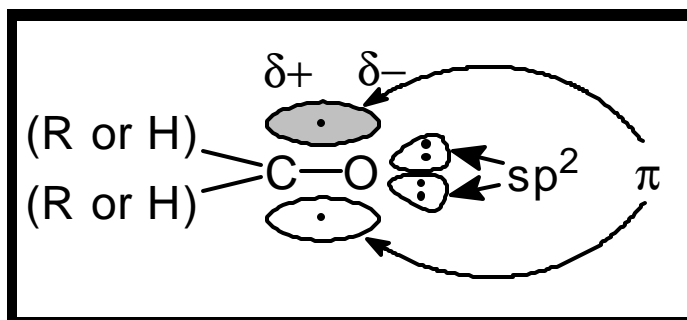
R, but not R', may have $-\text{NO}_2$, $-\text{CN}$, $-\text{CO-}$ and $-\text{COOR}$.

.....



Structural Features of Aldehydes and Ketones

Both contain the carbonyl group and only carbons or hydrogens bonded to this group. In aldehydes at least one hydrogen is joined to the carbonyl carbon (formaldehyde has two). In ketones, only carbons are bonded to the carbonyl carbon. Since ordinary carbanions and hydride ions are very poor leaving groups, substitution does not usually occur at the carbonyl carbon of aldehydes or ketones.

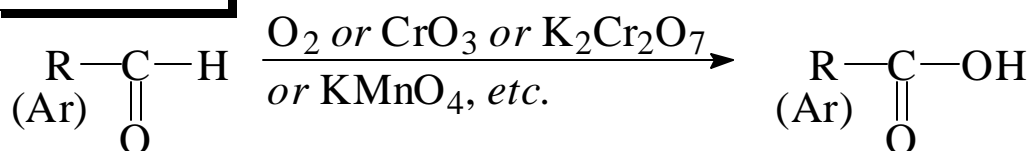


Reactions of Aldehydes and Ketones —

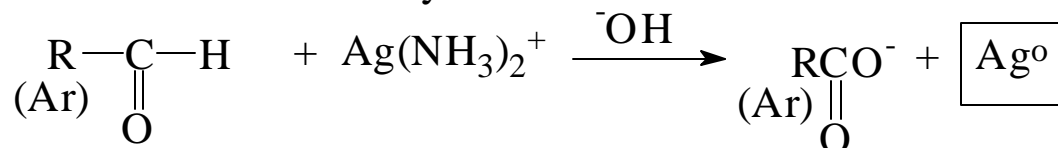
Oxidation —

Aldehydes are easily oxidized to carboxylic acids, ketones are not.

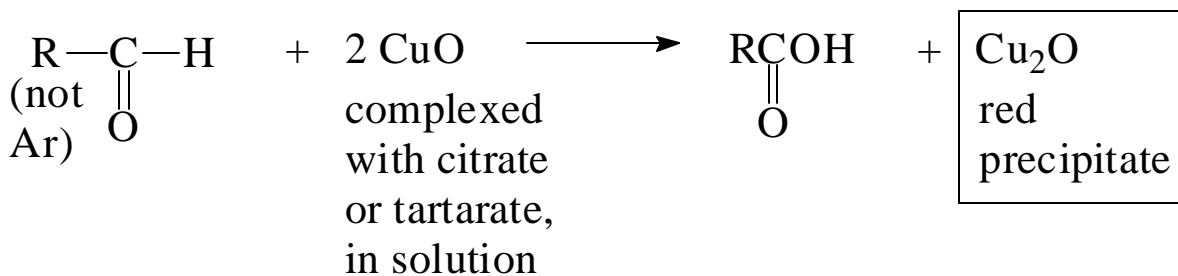
Aldehydes



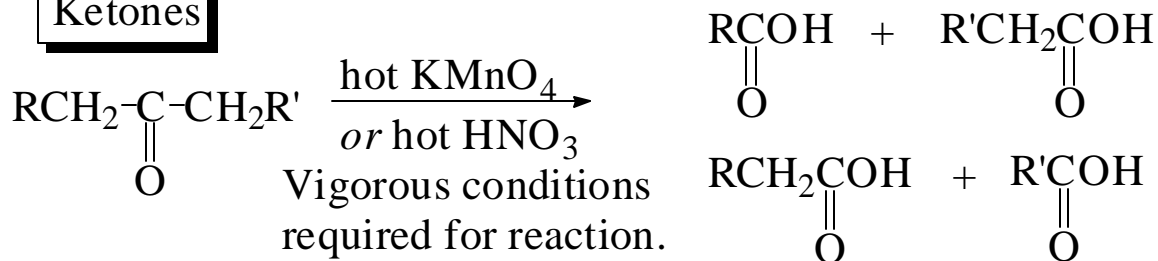
Tollen's test for aldehydes:



Fehling's test, Benedict's test:

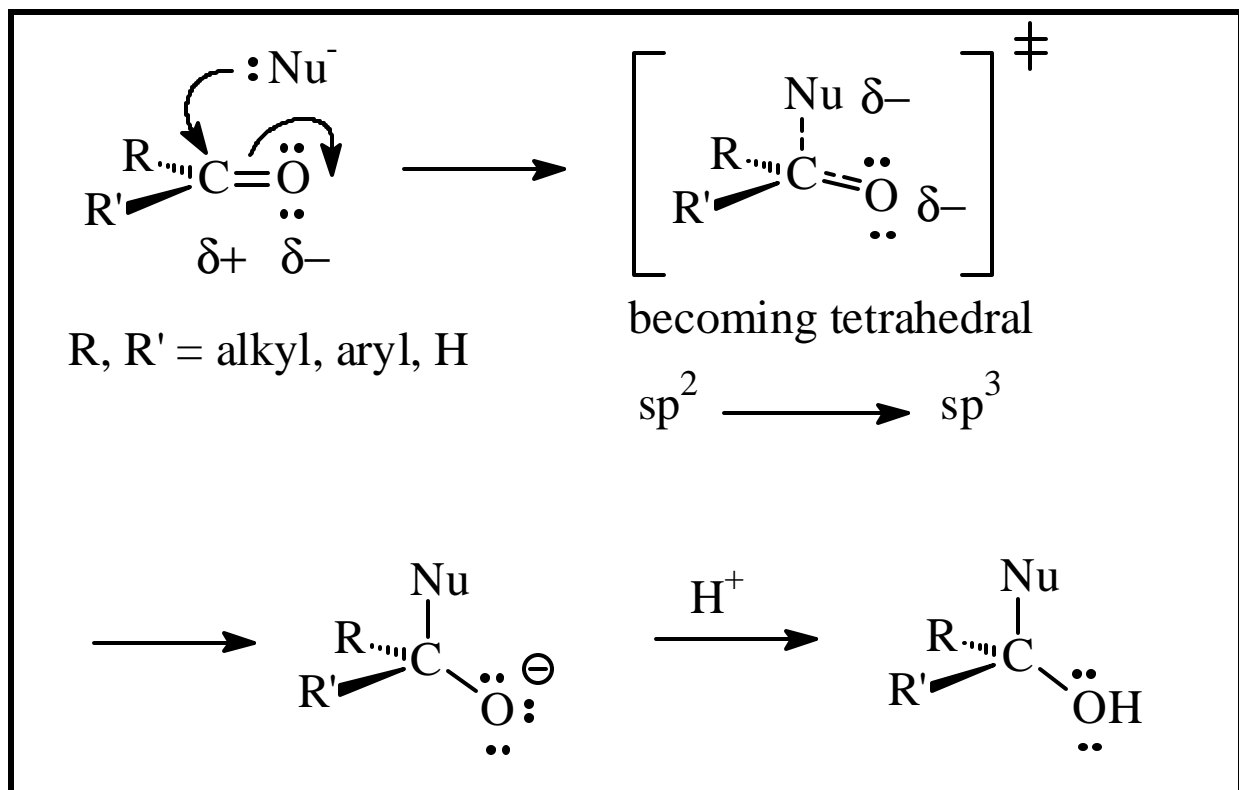


Ketones



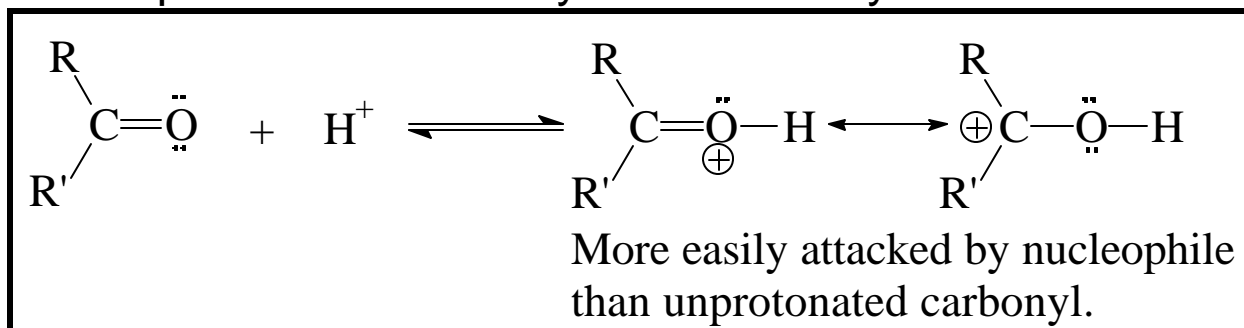
Nucleophilic Additions —

:Nu or :Nu⁻ is a generic nucleophile.



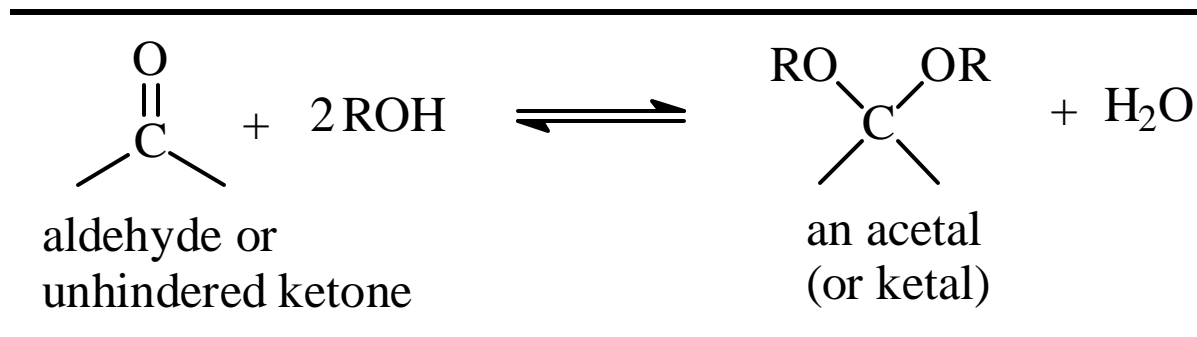
Since there is an increase in crowding on going from reactant to transition state ($\sim 120^\circ$ to $\sim 109^\circ$), some steric effects might be expected. This is one reason aldehydes (less crowded) are more reactive than ketones.

Nucleophilic additions may be acid catalyzed —

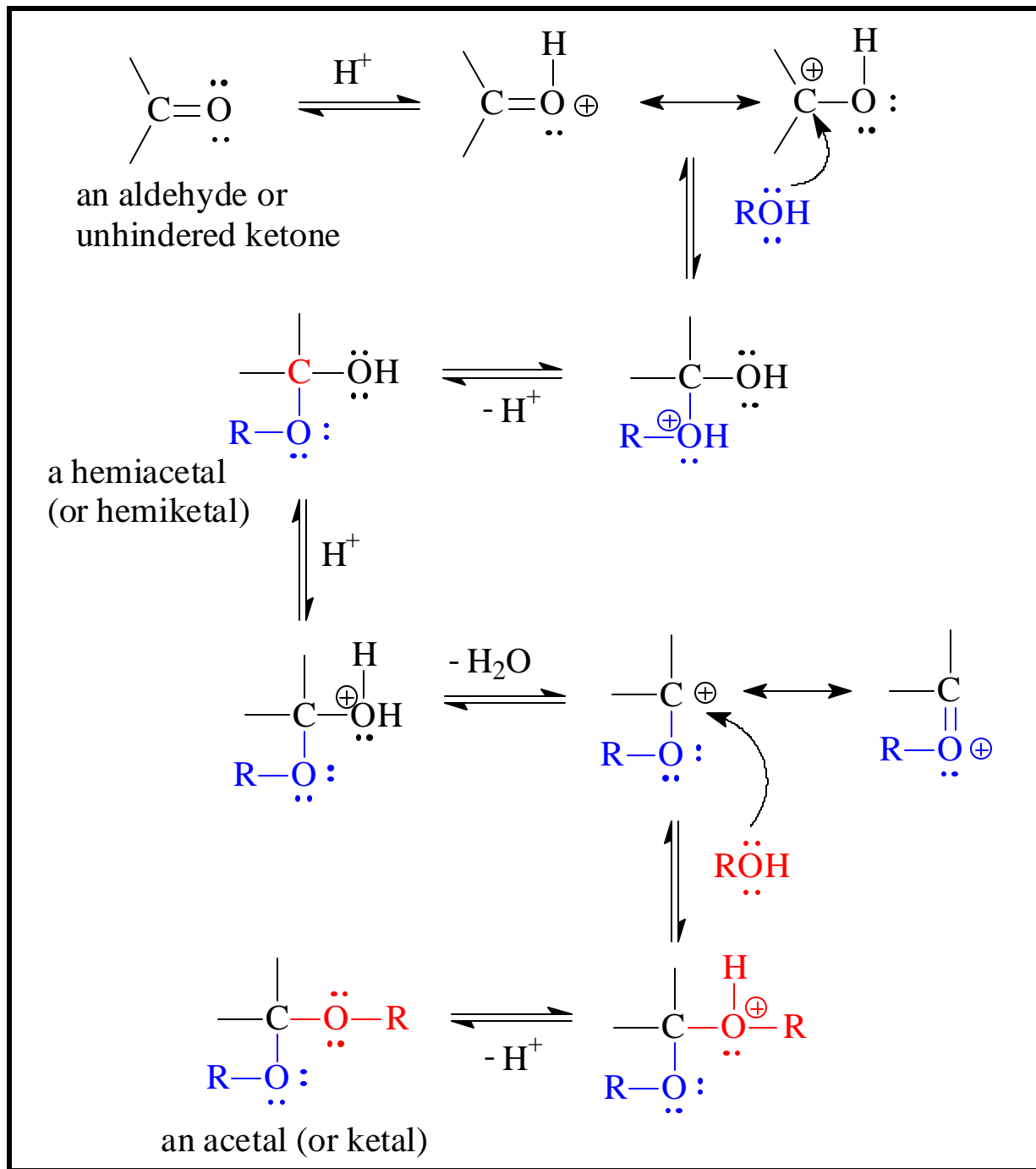


However, when acid catalysis is employed one should usually be careful to avoid completely converting the *nucleophile* to its conjugate acid (which would be much less nucleophilic).

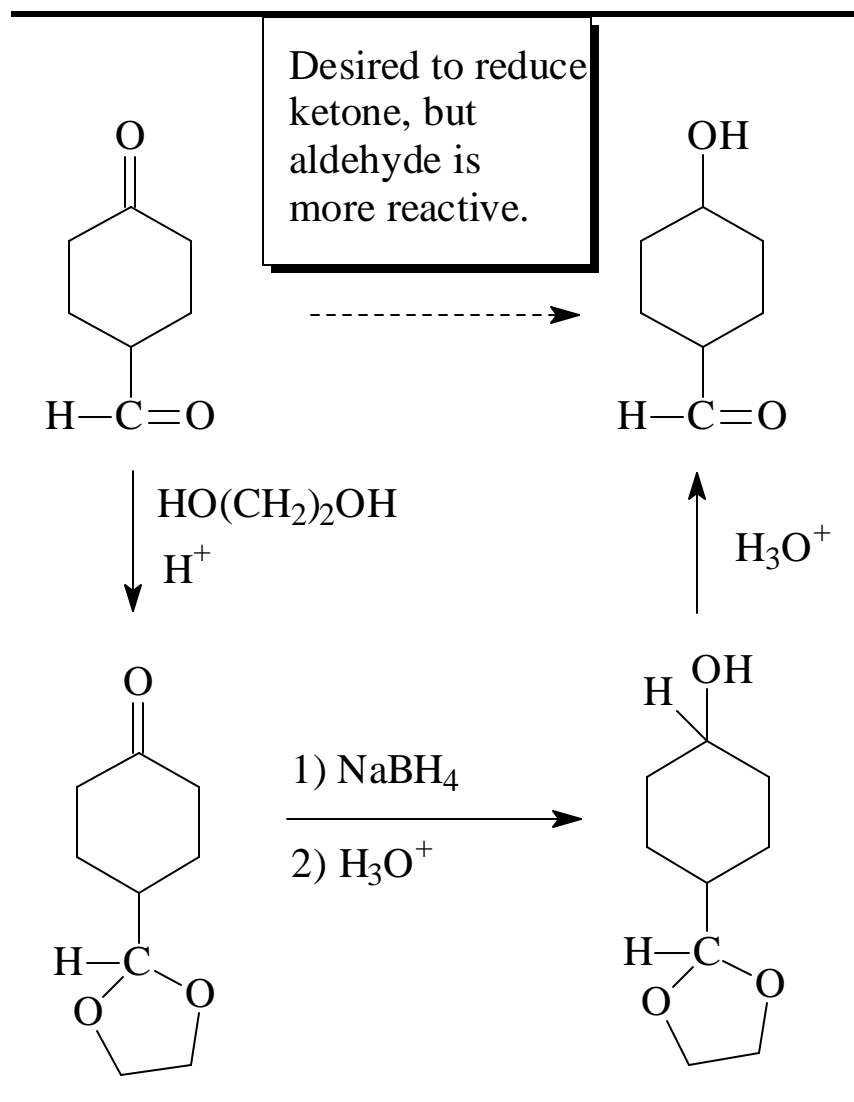
Acetal (ketal) Formation —



Mechanism —

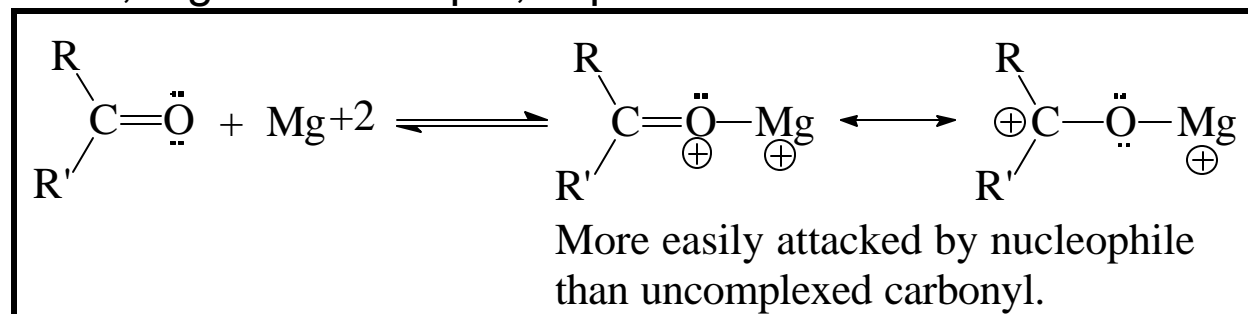


Acetals (ketals) undergo acid hydrolysis to regenerate the carbonyl compound, but are inert to many other reaction conditions (they are a type of ether); therefore they are employed as protecting groups. For example —

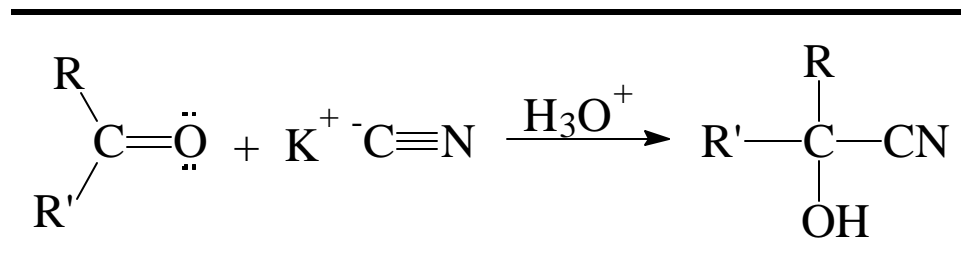


Addition of Grignard Reagents —

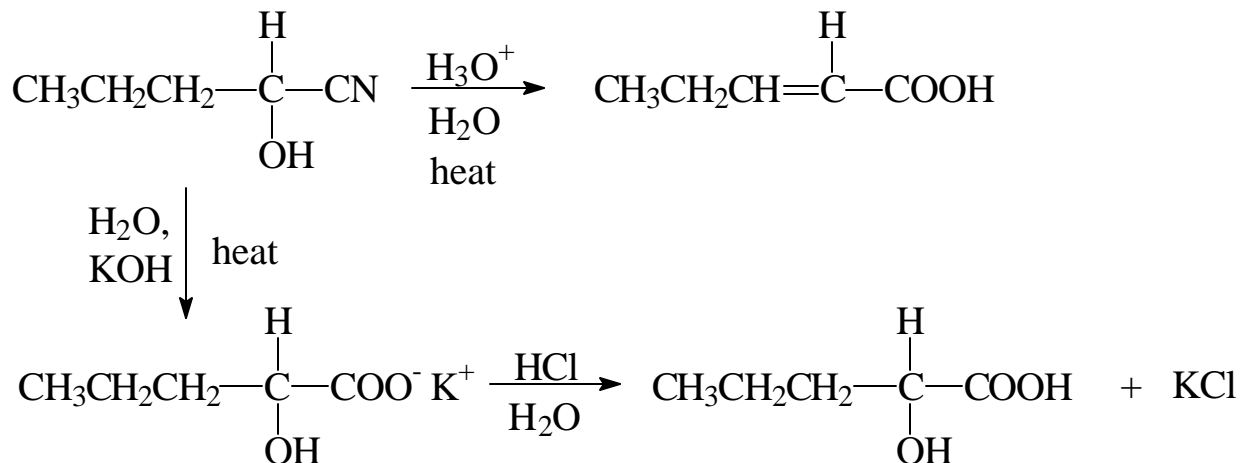
Already extensively discussed: a powerful method for synthesis of alcohols. Catalysis by a Bronsted-Lowry acid is not an option. However, catalysis by certain Lewis acids, Mg^{+2} for example, is possible.



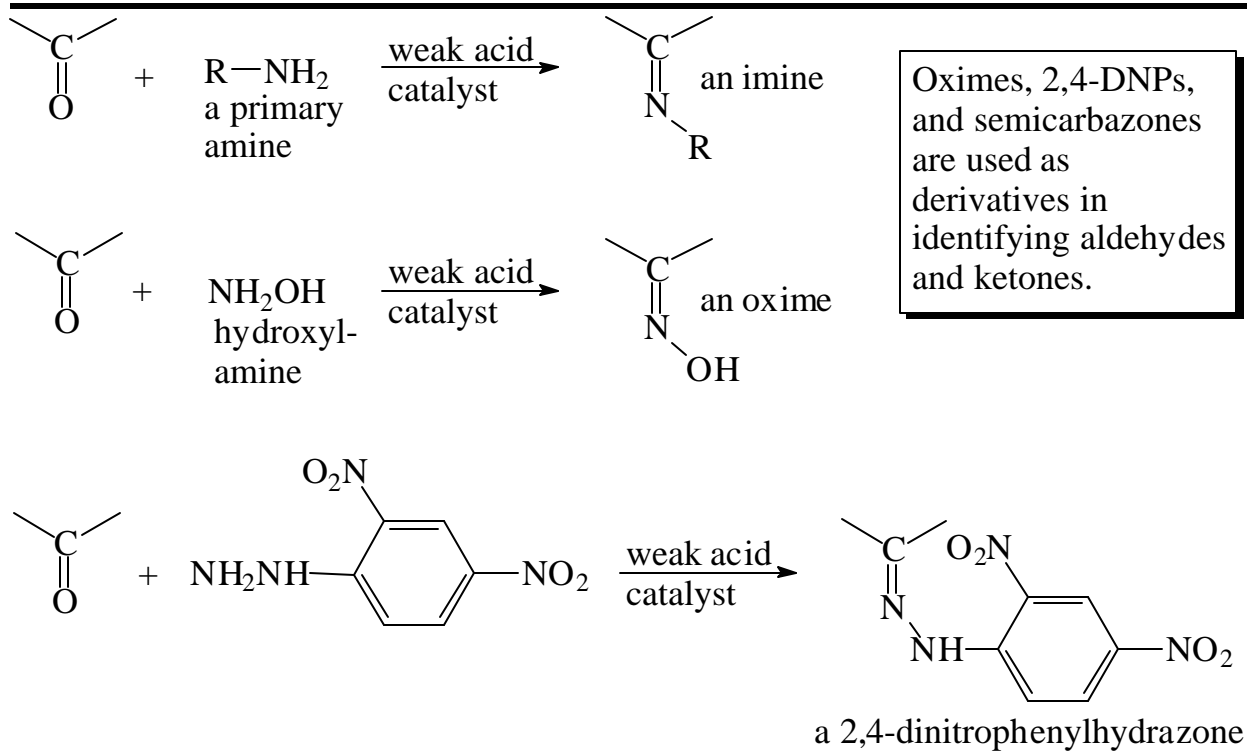
Formation of Cyanohydrins —



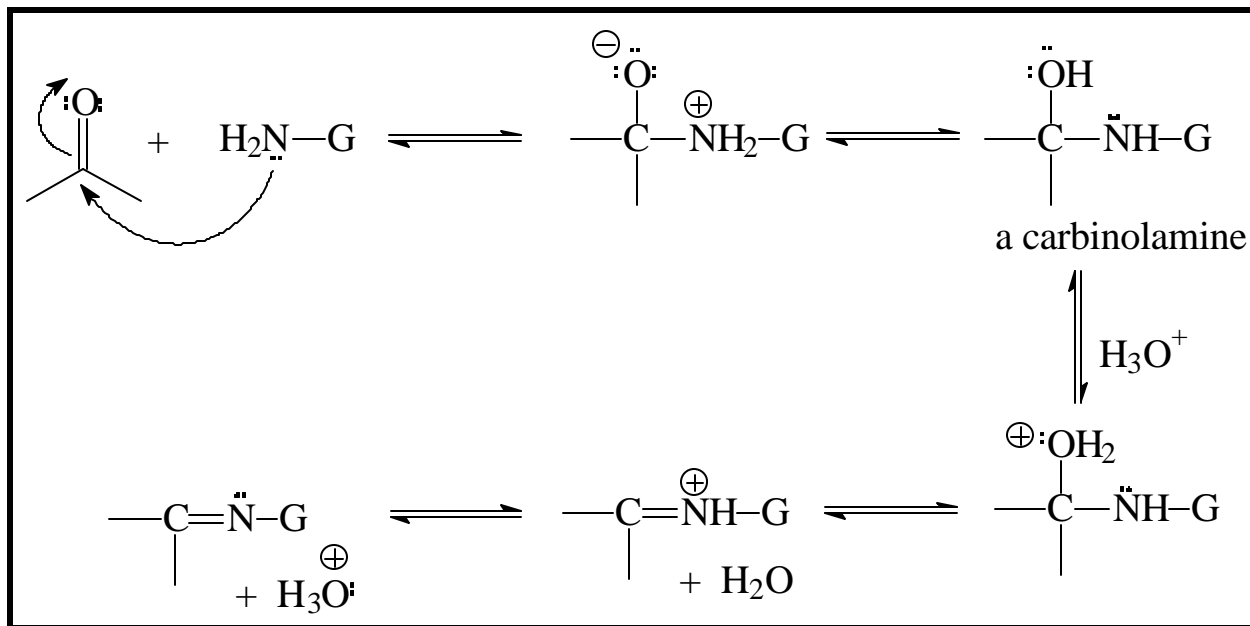
These compounds can be hydrolyzed by base or acid to give α -hydroxyacids or α,β -unsaturated acids, respectively.



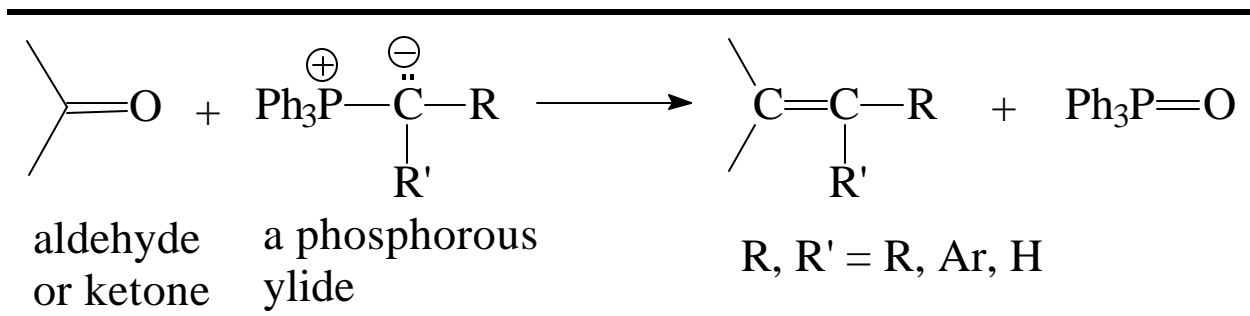
Addition of Derivatives of Ammonia —



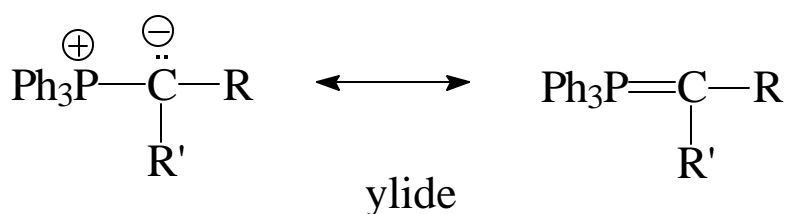
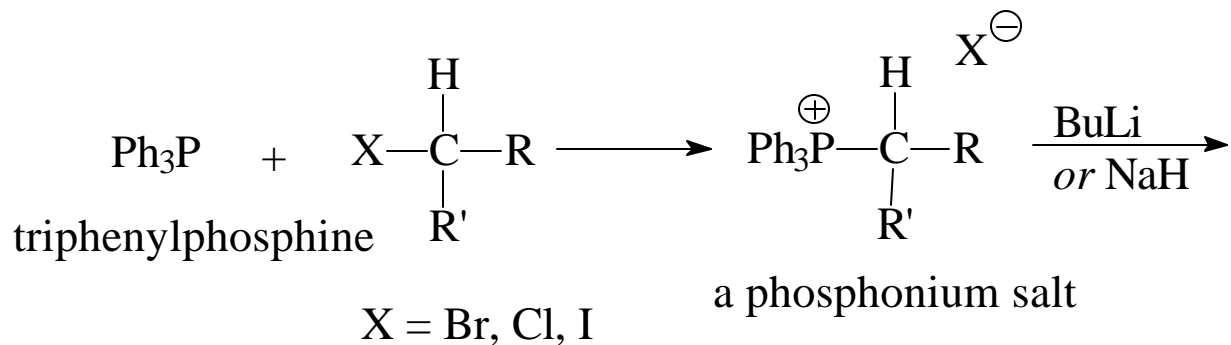
Mechanism —



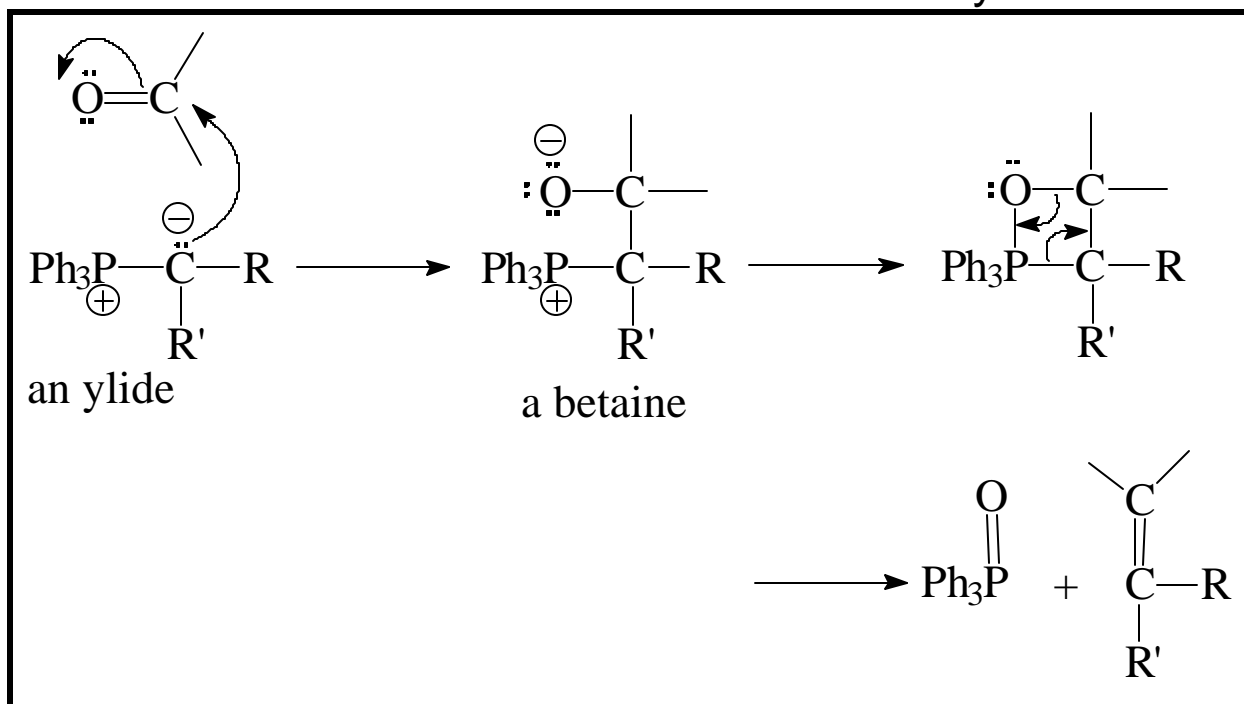
Wittig Reaction —



Preparation of the ylide —

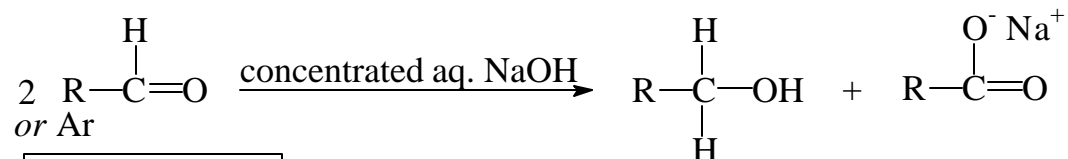
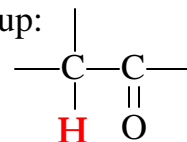


Mechanism for Reaction of Ylide with Carbonyl ---



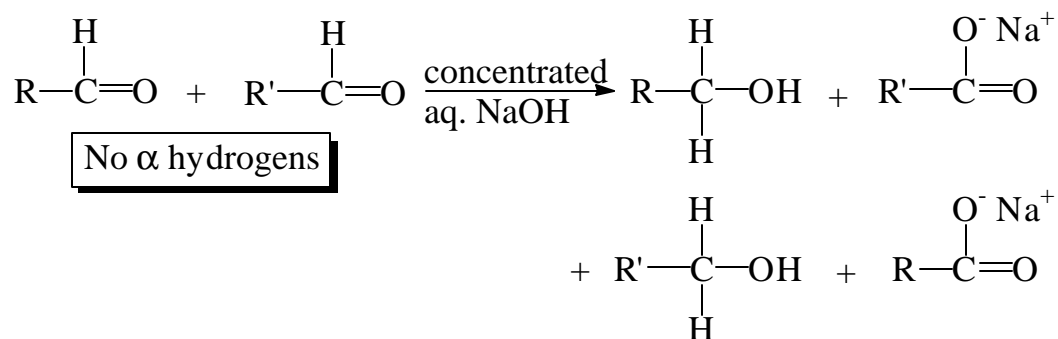
Cannizzaro Reaction —

α hydrogens are hydrogens on an α carbon. An α carbon is one that is attached to the functional group, in this case the C=O group:



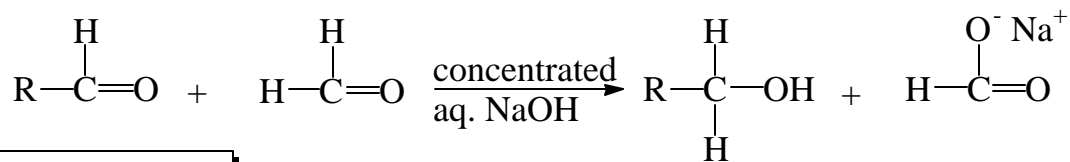
No α hydrogens

Crossed Cannizzaro Reaction ---



No α hydrogens

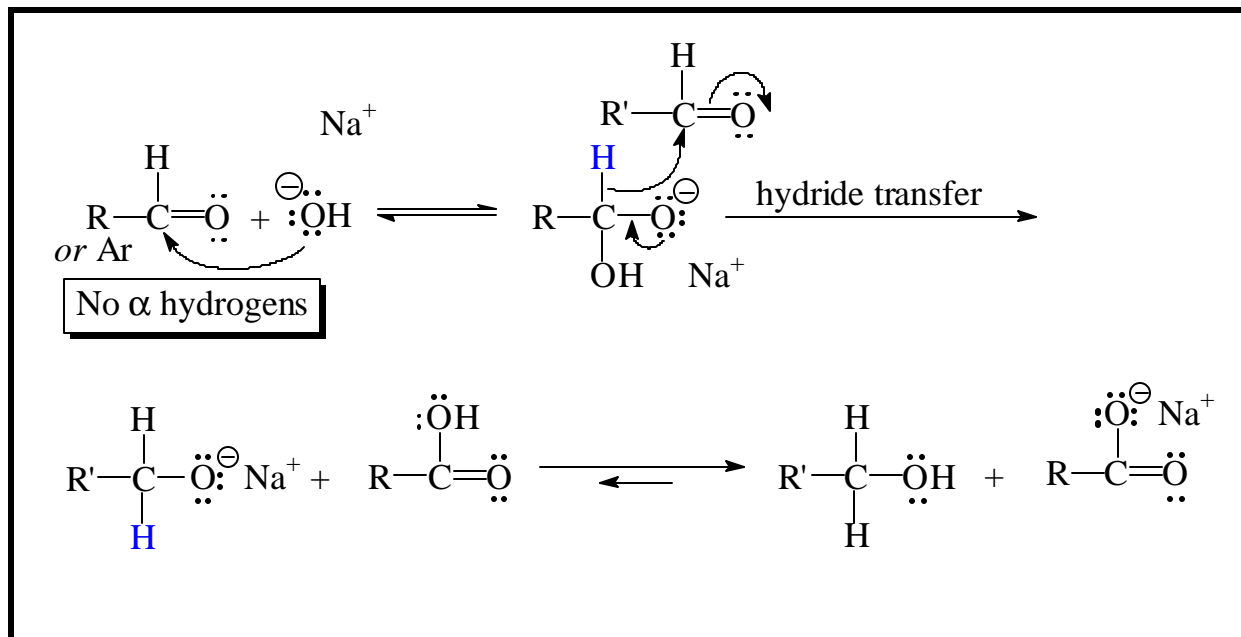
but, if formaldehyde is one of the aldehydes it will be oxidized and not reduced



No α hydrogens formaldehyde

sodium formate

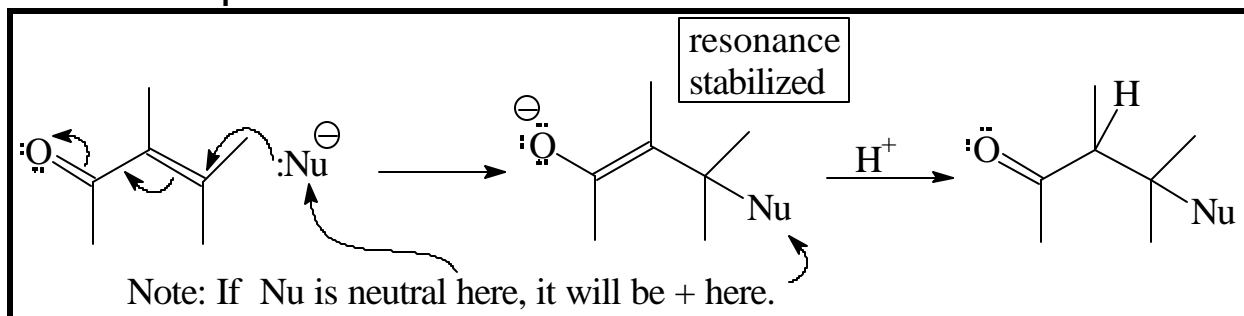
Mechanism —



This reaction is of more interest mechanistically than synthetically owing to the limitation of no α -hydrogens on the aldehyde.

Conjugate Addition of Nucleophiles to α,β -Unsaturated Aldehydes and Ketones ---

The carbonyl group activates the π -bond at the β position for nucleophilic attack.



Common examples of conjugate addition to aldehydes or ketones involve amines, CN^- [especially from $(\text{C}_2\text{H}_5)_2\text{Al-CN}$], and the "R" group from a lithium diorganocopper, $\text{Li}^+ \text{R}_2\text{Cu}^-$, (a Gilman reagent).