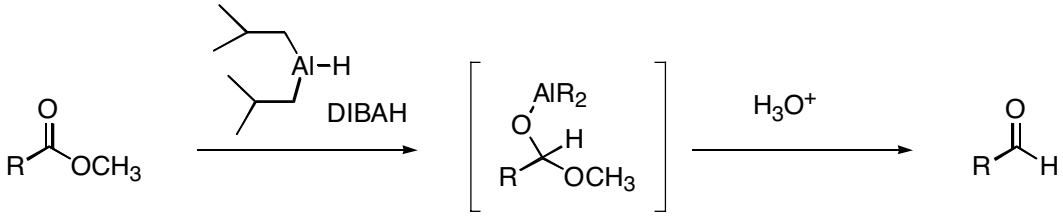
These notes can be obtained at: http://www.ndsu.nodak.edu/instruct/grcook/chem342/notes.shtml

Chapter 19: Aldehydes and Ketones: Nucleophilic Addition Reactions

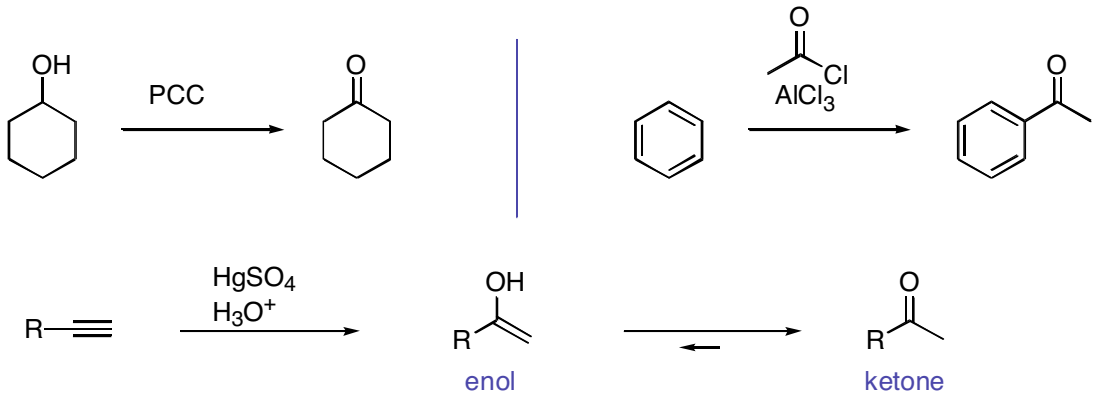
Preparation of Aldehydes and Ketones

Aldehydes can be prepared from carboxylic esters by a partial reduction using diisobutylaluminum hydride (DIBAH). The hydride does not add twice because at the temperature of the reaction, the aldehyde is not formed. It is only formed when the reation is quenched by the addition of acid. Thus, the aldehyde can be obtained without reduction all the way to the alcohol.



stable at -78 °C

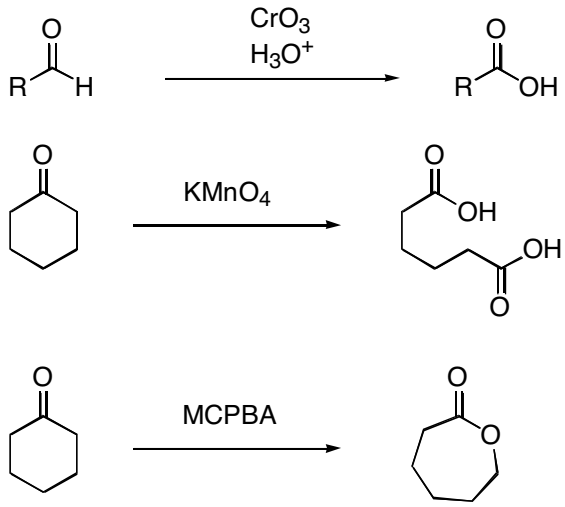
Ketones can be prepared by oxidation of secondary alcohols, Freidel-Crafts acylation of benzyene rings, oxymercuration of alkynes or by coupling with Gilman Reagents.



Gilman Reagents can be made from nearly any organic iodide or bromide

Oxidation of Aldehydes and Ketones

Aldehydes can be oxidized to carboxylic acids using Jones Reagent (CrO_3/H^+). Ketones are relatively inert to oxidation. There are only a couple of reagents which cleave the carbon-carbon bond next to a ketone - permanganate and mcpba.

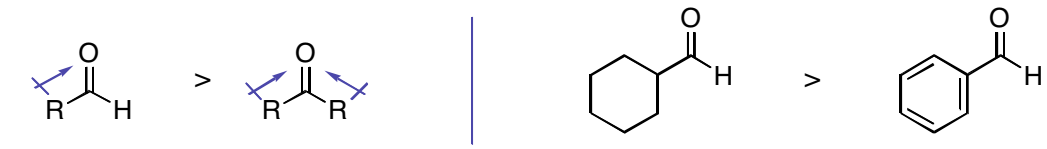


Jones Oxidation

Baeyer-VIllager Oxidation

Reactivity of Aldehydes and Ketones

Aldehydes are more reactive than Ketones toward nucleophilic attack because they are less hindered and the plus charge on the carbonyl carbon is more stabilized with more alkyl groups. Conjugation also stabilizes carbonyls and makes them less reactive.

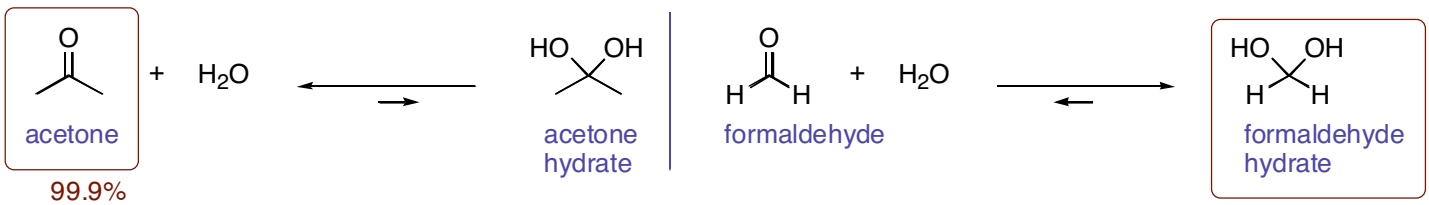


more reactive

more reactive

Hydration of Aldehydes and Ketones

In water, aldehydes and ketones are in equilibrium with the hydrated form. Most carbonyls largely favor the ketone form. A couple of examples, eg. formaldehyde, favors the hydrated form - but this is rare.



acetone

99.9%

acetone hydrate

formaldehyde

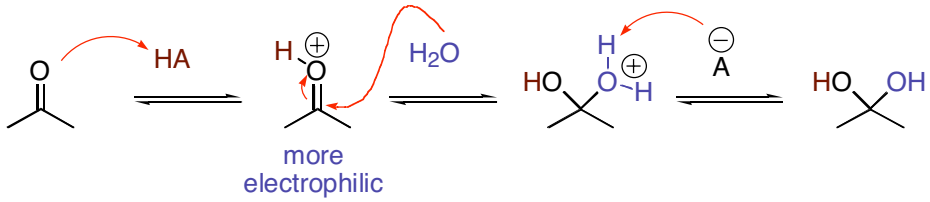
formaldehyde hydrate

99.9%

Mechanism for the Hydration of Aldehydes and Ketones

The reaction of a carbonyl with water is very slow. It can be catalyzed by either acid or base. It is useful to understand the mechanism for this process because it relates to many reactions of carbonyl compounds.

Acid Catalyzed Hydration acid activates the carbonyl making it more reactive (more electrophilic) so water can add



Base Catalyzed Hydration hydroxide is a more reactive nucleophile than water and can add more readily to the carbonyl