Chem 342

Lecture Summary 21
March 08, 2004

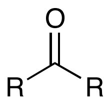
Be An Electron

All chemical reactions are simply a rearrangement of electrons (bonds). Many generalities can be found if you can identify what functionality is the electron rich group (nucleophile) and which is electron poor (electrophile). If you have some knowledge of the polarity of functional groups and keep in mind that if you make a bond, generally you need to break a bond to maintain proper valency (eg only 4 bonds to C) you should be able to predict many types of reactions. Some functional groups can react as either an electrophile or a nucleophile depending on what it is reacting with. Carbonyls are an example of this type of species.

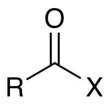
Chapter 19 - Aldehydes and Ketones: Nucleophilic Addition Reactions

Carbonyl Compounds

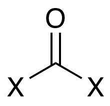
Carbonyl compounds exist in three different oxidation states.



aldehydes
ketones

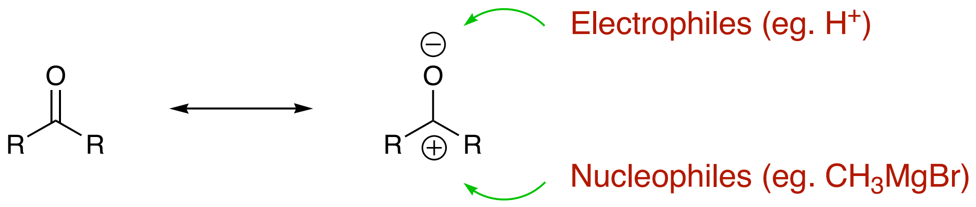


carboxylic acid
and derivatives

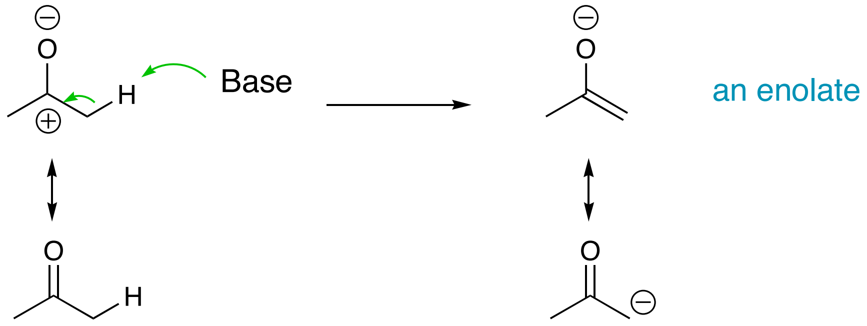


carbonic acid
and derivatives

Carbonyls are polarized toward the oxygen. Thus, nucleophiles will react at the carbon and electrophiles at the oxygen.

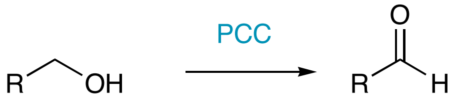


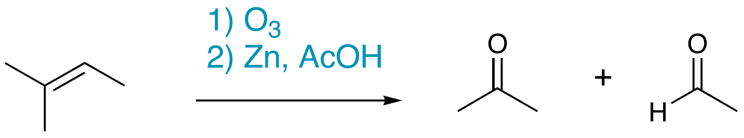
The α-position of carbonyls is more acidic than typical alkanes due to the electron withdrawing affect of the carbonyl carbon. Thus, enolates can be readily prepared with suitable bases. These represent another class of carbon nucleophiles.



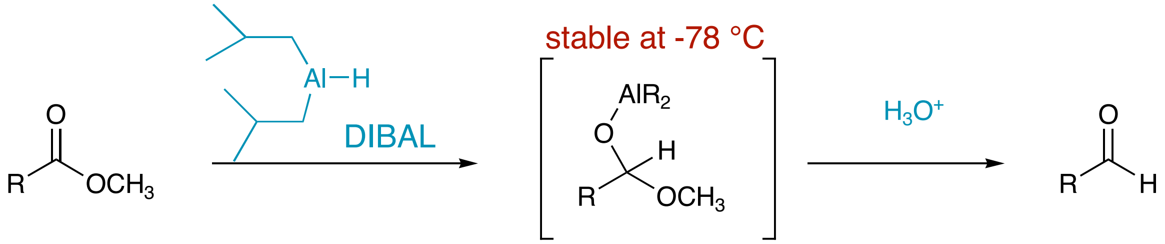
Preparation of Aldehydes and Ketones

Aldehydes and ketones can be prepared by the oxidation of alcohols. For aldehydes, only PCC will stop at the aldehyde oxidation state. Other oxidants will oxidize all the way to the carboxylic acid. Ozonolysis of alkenes is also a good way to prepare carbonyl compounds.

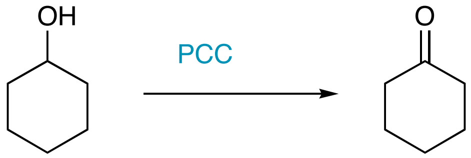


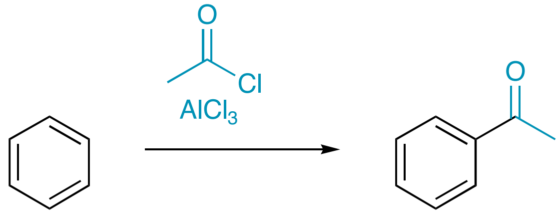


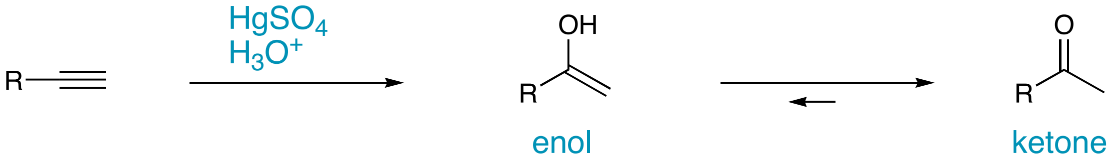
Aldehydes can be prepared from carboxylic esters by a partial reduction using diisobutylaluminum hydride (DIBAL sometimes called DIBAH). The hydride does not add twice because at the temperature of the reaction, the aldehyde is not formed. It is only formed when the reation is quenched by the addition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

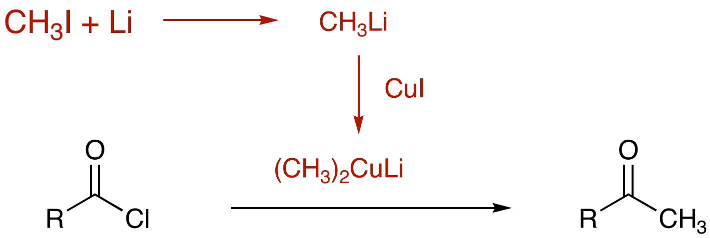


Ketones can be prepared by oxidation of secondary alcohols, Freidel-Crafts acylation of benzyene rings, oxymercuration of alkynes or by coupling with Gilman Reagents.



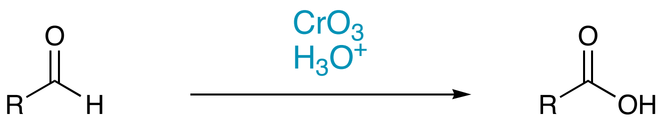






Gilman Reagents can be made from nearly any organic iodide or bromide

Aldehydes can be oxidized to carboxylic acids using Jones Reagent (CrO_3/H^+). Ketones are relatively inert to oxidation. Potassium permanganate will oxidize the C-C bond next to a ketone. Chromium reagents are inert toward ketones.



Jones Oxidation