Chapter 19 - Aldehydes and Ketones: Nucleophilic Addition Reactions

Carbonyl Compounds

Carbonyls are polarized toward the oxygen. Thus, nucleophiles will react at the carbon and electrophiles at the oxygen. Depending on the type of carbonyl compound, the initial intermediate will be protonated eventually or if it is a good leaving group, a carbonyl can be formed by elimination. The new carbonyl compound could react again with strong nucleophiles such as hydride reagents and Grignard reagents.
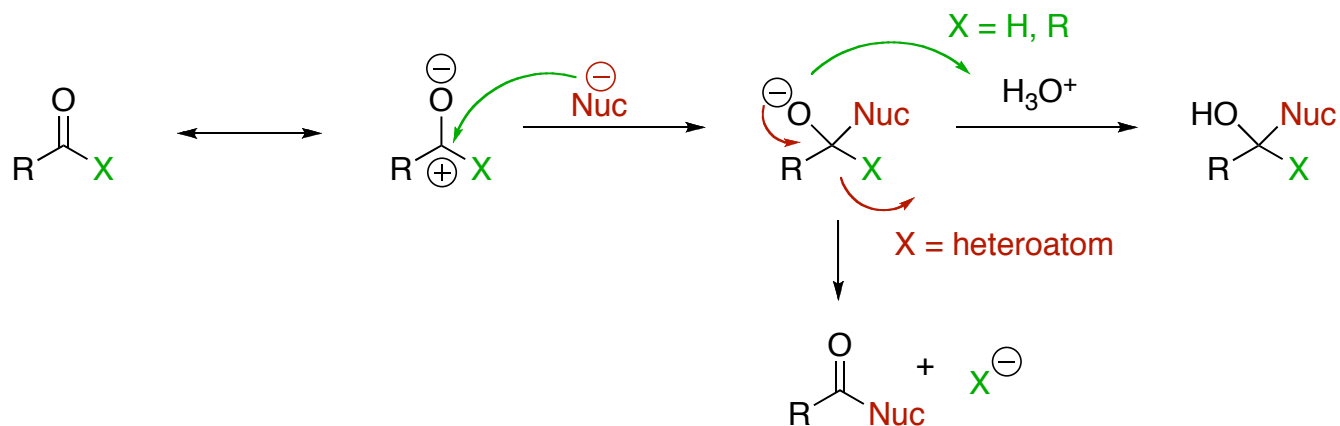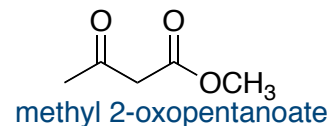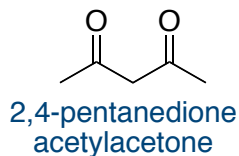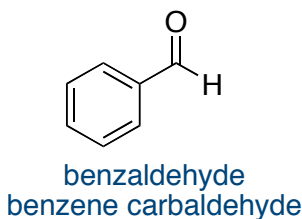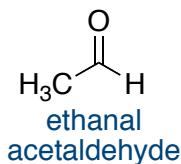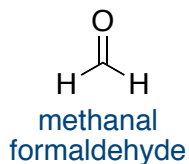
The α-position of carbonyls is more acidic than typical alkanes due to the electron withdrawing affect of the carbonyl carbon. Thus, enolates can be readily prepared with suitable bases. These represent another class of carbon nucleophiles.
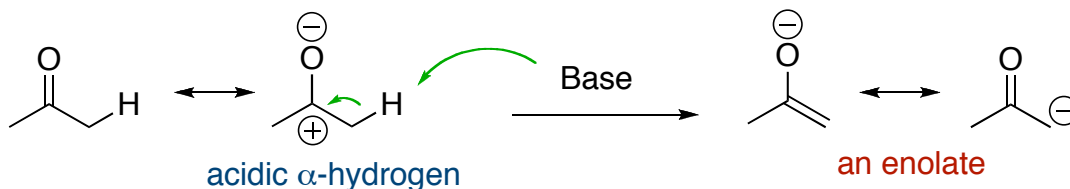
Nomenclature Examples for Aldehydes and Ketones

Aldehydes and ketones follow systematic naming but there are many common names. IUPAC names for aldehydes end in -al, and for ketones in -one.

| methanal | ethanal | benzaldehyde | 2,4-pentanedione | methyl 2-oxopentanoate |
| formaldehyde | acetaldehyde | benzene carbaldehyde | acetylacetone | |

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.
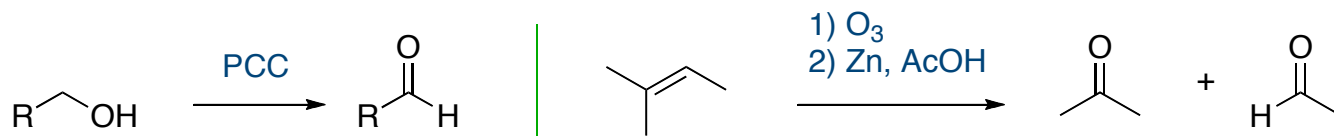
Aldehydes can be prepared from carboxylic esters by a partial reduction using diisobutylaluminum hydride (DIBAL sometimes called DIBAH or DIBAL-H). The hydride does not add twice because at the temperature of the reaction, the aldehyde is not formed. It is only formed when the reaction is quenched by the addition of acid. Acid also destroys any remaining DIBAL reagents. Thus, the aldehyde can be obtained without reduction all the way to the alcohol.
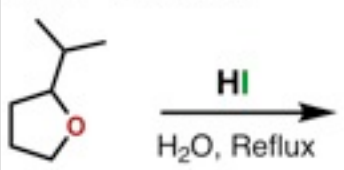
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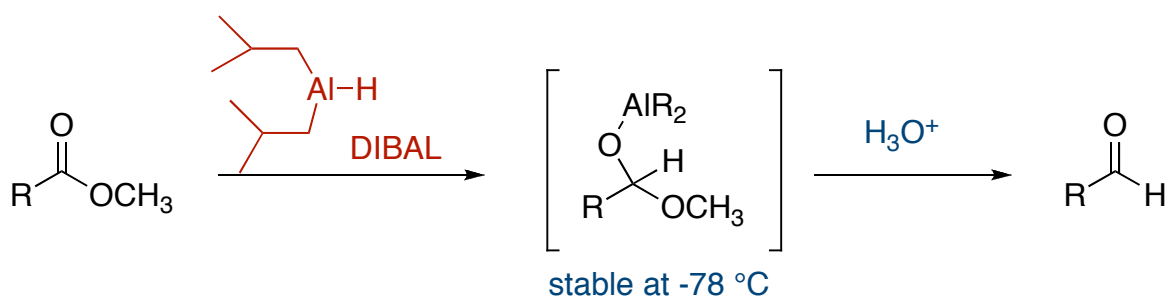
Ketones can be prepared by oxidation of secondary alcohols, Freidel-Crafts acylation of benzene rings, oxymercuration of alkynes or by coupling of acyl halides with Gilman Reagents.

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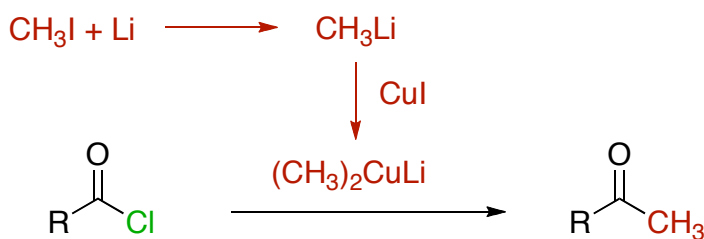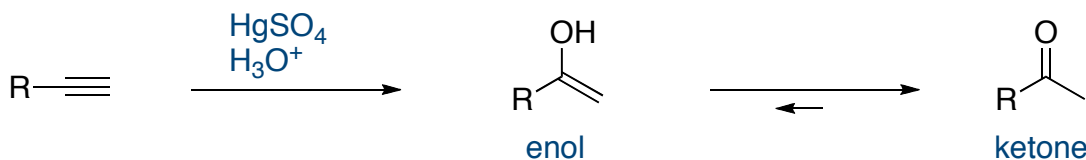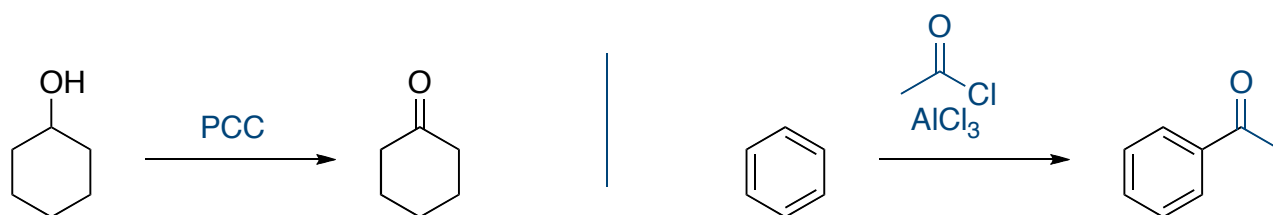
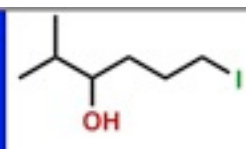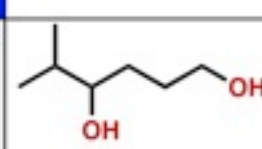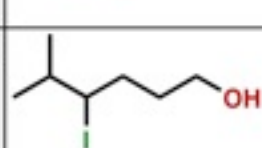Gilman Reagents can be made from nearly any organic iodide or bromide

Q: What is the product of the reaction of the following cyclic ether with HI?

HI
————→
H_2O, Reflux

☑ 1:

☐ 2:

☐ 3:

☐ 4: