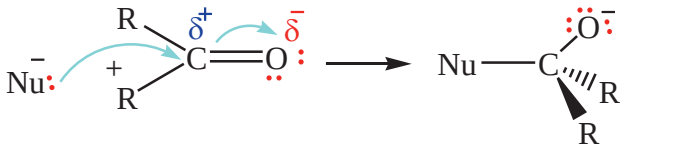
Reactions of aldehydes and ketones

The partially positive charge on the carbonyl carbon is the cause of the most common reaction theme of the carbonyl group, the addition of a nucleophile (Nu:) to form a tetrahedral carbonyl addition intermediate.

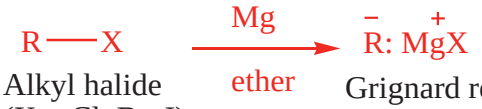


Tetrahedral carbonyl addition intermediate

a. Addition

i. Addition of Grignard Reagents to Aldehydes and Ketones

The addition of carbon nucleophiles is the most important type of nucleophilic addition to a carbonyl group because these reactions form new carbon–carbon bonds. The Grignard reagent is an alkylmagnesium halide.

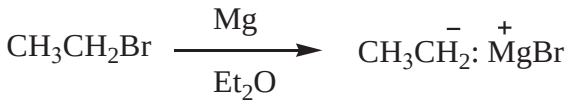


Alkyl halide (X = Cl, Br, I)

Grignard reagent

R = alkyl or aryl

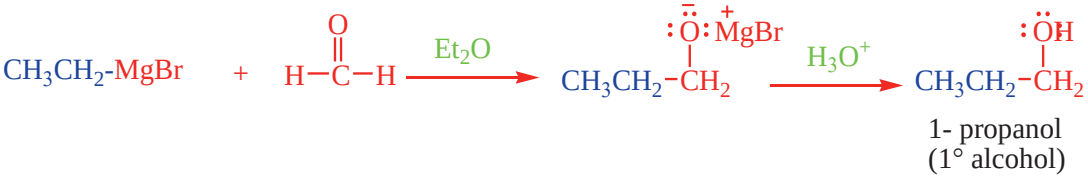
Example:



1. Addition to Formaldehyde Gives a 1°Alcohol

Treatment of a Grignard reagent with formaldehyde, followed by hydrolysis in aqueous acid, gives a primary alcohol:

Example:

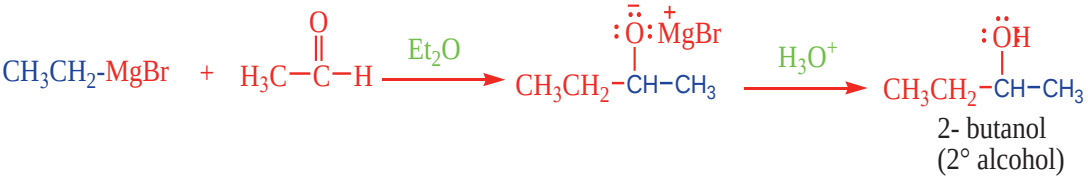


1- propanol
(1° alcohol)

2. Addition to an Aldehyde (Except Formaldehyde) Gives a 2°Alcohol

Treatment of a Grignard reagent with any aldehyde other than formaldehyde, followed by hydrolysis in aqueous acid, gives a secondary alcohol:

Example:

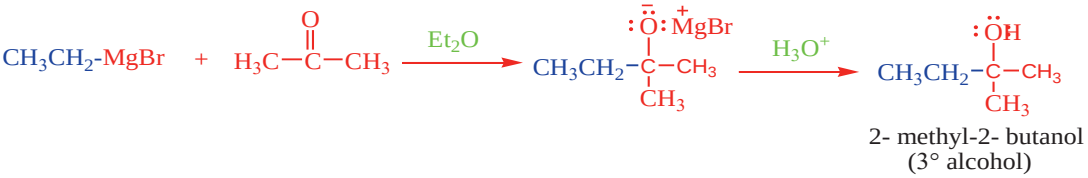


2- butanol
(2° alcohol)

3. Addition to a Ketone Gives a 3°Alcohol

Treatment of a Grignard reagent with a ketone, followed by hydrolysis in aqueous acid, gives a tertiary alcohol.

Example:

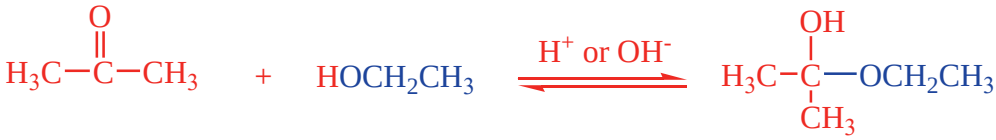


2- methyl-2- butanol
(3° alcohol)

ii. Addition of Alcohol: formation of Acetals

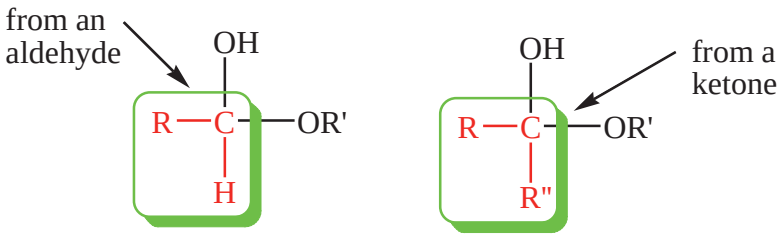
The addition of a molecule of alcohol to the carbonyl group of an aldehyde or a ketone forms a hemiacetal (a half-acetal). This reaction is catalyzed by both acid and base: Oxygen adds to the carbonyl carbon and hydrogen adds to the carbonyl oxygen.

Example:



A hemiacetal

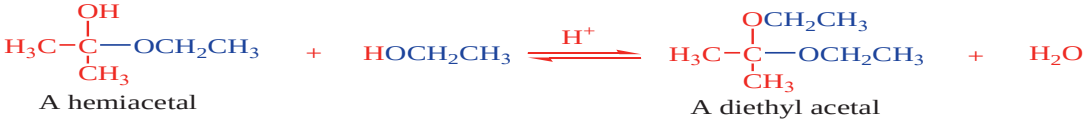
The functional group of a hemiacetal is a carbon bonded to an −OH group and an −OR or −OAr group:



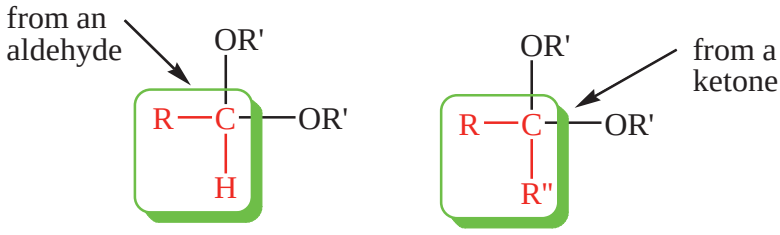
Hemiacetals

Hemiacetals can react further with alcohols to form acetals plus a molecule of water. This reaction is acid catalyzed.

Example:



The functional group of an acetal is a carbon bonded to two −OR or −OAr groups:



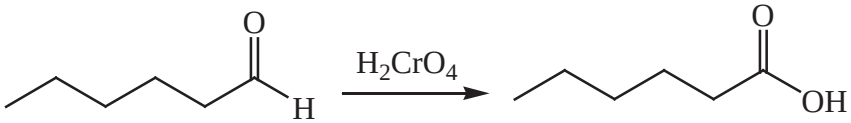
Acetals

a. Oxidation

i. Oxidation of Aldehydes to Carboxylic Acids

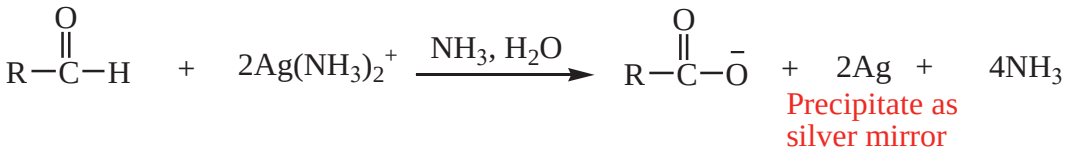
Aldehydes are oxidized to carboxylic acids by a variety of common oxidizing agents, including chromic acid and molecular oxygen. In fact, aldehydes are one of the most easily oxidized of all functional groups.

Example:



Hexanal — Hexanoic acid

When Tollens' reagent ($Ag(NH_3)_2^+$) is added to an aldehyde, the aldehyde is oxidized to a carboxylic anion, and Ag^+ is reduced to metallic silver. If this reaction is carried out properly, silver precipitates as a smooth, mirror like deposit—**hence the name silver-mirror test**:



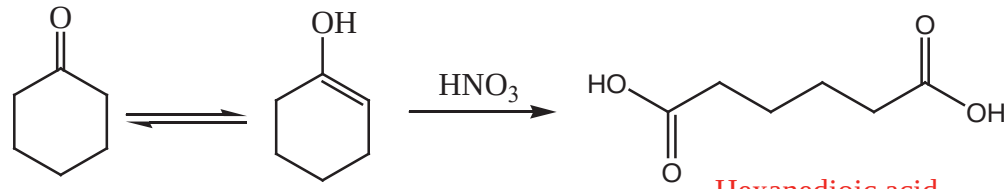
Precipitate as silver mirror

Tollens' reagent does not react with Aldehydes, which can be used to distinguish aldehydes from ketones. Nowadays, Ag^+ is rarely used for the oxidation of aldehydes, what do you think the reason?

ii. Oxidation of Ketones to Carboxylic Acids

Ketones are much more resistant to oxidation than are aldehydes. For example, ketones are not normally oxidized by chromic acid or potassium permanganate. Ketones undergo oxidative cleavage, via their enol form, by potassium dichromate and potassium permanganate at higher temperatures and by higher concentrations of nitric acid, HNO_3.

Example:



Cyclohexanone (keto form) | Cyclohexanone (enol form) | Hexanedioic acid (adipic acid)

c. Reduction

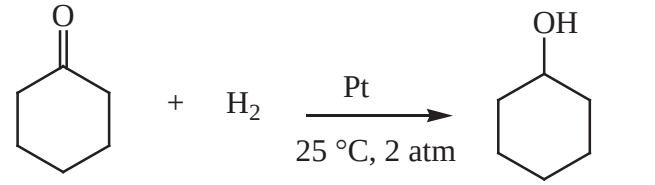
Aldehydes are reduced to primary alcohols and ketones to secondary alcohols:

An aldehyde | A primary alcohol | A ketone | A secondary alcohol

i. Catalytic Reduction

The carbonyl group of an aldehyde or a ketone is reduced to a hydroxyl group by hydrogen in the presence of a transition metal catalyst, most commonly finely divided palladium, platinum, nickel, or rhodium.

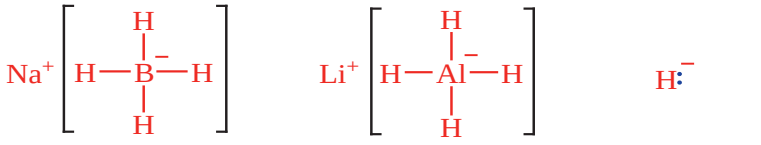
Example:



Cyclohexanone | Cyclohexanol

ii. Metal Hydride Reductions

By far the most common laboratory reagents used to reduce the carbonyl group of an aldehyde or a ketone to a hydroxyl group are sodium borohydride and lithium aluminum hydride. Each of these compounds behaves as a source of hydride ion, a very strong nucleophile.



Sodium borohydride | Lithium aluminum hydride | Hydride ion

Lithium aluminum hydride is a very powerful reducing agent; it rapidly reduces not only the carbonyl groups of aldehydes and ketones, but also those of carboxylic acids and their functional derivatives. Sodium borohydride is a much more selective reagent, reducing only aldehydes and ketones rapidly.

Example: