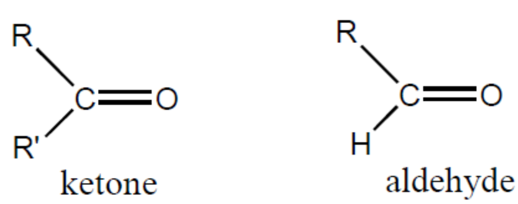
Experiment 15:
Reactions of the common functional groups Part III: Aldehydes and ketones

Objectives

The purpose of this experiment is to illustrate a selection of reactions that are typical of two important classes of organic compounds: aldehydes and ketones. The reactions that have been chosen are intended to demonstrate similarities and differences between these two classes of compounds. Several tests will be performed on a selection of known compounds. In a later experiment, the student will be expected to use the same tests to identify an assigned unknown compound.

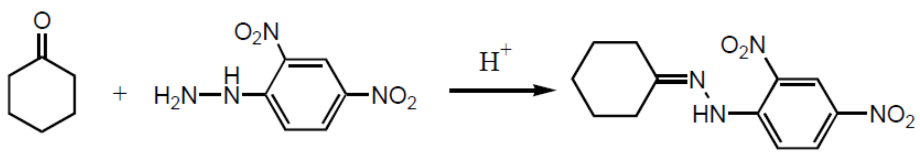
Theory

As you should know, aldehydes and ketones both contain a carbonyl group (C=O). The difference between these two classes of compounds is that ketones have two alkyl (or aryl) groups bonded to the carbonyl-carbon atom, whereas aldehydes have one alkyl (or aryl) group, and one hydrogen atom bonded to the carbonyl-carbon atom.



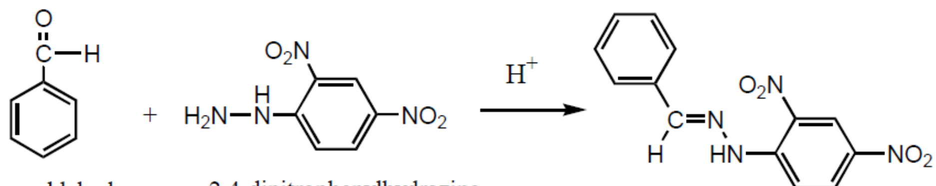
Brady's Reagent

The chemistry of these two classes of compounds is primarily that of the carbonyl group, thus there are several reactions that are common to both aldehydes and ketones. An example of a reaction that is common to both aldehydes and ketones is the reaction with 2,4- dinitrophenylhydrazine (**Brady's reagent**), a reaction that can be used to detect the presence of a carbonyl group.



cyclohexanone 2,4-dinitrophenylhydrazine

2,4-DNP derivative of cyclohexanone



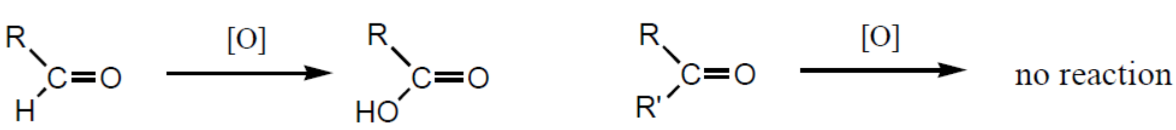
benzaldehyde 2,4-dinitrophenylhydrazine

2,4-DNP derivative of benzaldehyde

The 2,4-dinitrophenylhydrazones that are produced in this reaction are usually brightly coloured: unconjugated ketones give yellow precipitates, conjugated ketones give orange or red precipitates. This reagent is used to prepare derivatives of aldehydes and ketones (derivatives are used to help identify an unknown compound).

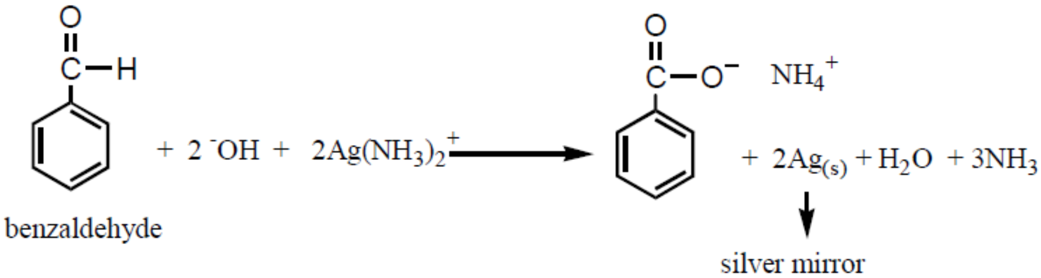
Tollens' Reagent

An important difference between aldehydes and ketones is the ease with which the latter can be oxidized.



aldehyde ketone

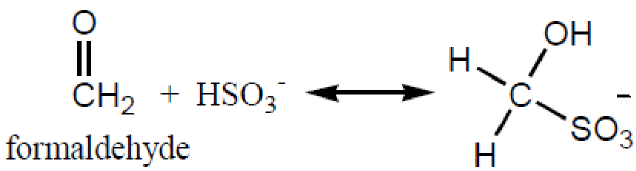
In the so-called "silver mirror test", an ammoniacal solution of silver nitrate **(Tollens' reagent)** is added to the carbonyl compound being investigated. If the latter is an aldehyde, the silver ions are reduced to metallic silver, which is then deposited as a mirror on the side of the test tube. Ketones do not react.



(NOTE: This equation has been balanced correctly)

Schiff's Reagent

A second method for distinguishing between aldehydes and ketones involves the use of **Schiff's reagent**. The usefulness of this test hinges on the ability of aldehydes to form addition compounds with solutions containing bisulfite ions:



Schiff's reagent is a complex of fuchsin (rosaniline hydrochloride) and sulfur dioxide. Fuchsin itself is dark red, but the fuchsin-sulfur dioxide complex is colourless.

Equation 1

fuchsin + SO_2 ⇌ fuchsin-sulfur dioxide complex

(red) → (colourless)

In an aqueous solution of Schiff's reagent, the sulfur dioxide that is present is also in equilibrium with sulfurous acid:

Equation 2

SO_2 (aq) + H_2O (l) ⇌ H_2SO_4 (aq) ⇌ H^+(aq) + HSO_3^-(aq)

↓ aldehyde

aldehyde reacts with bisulfate ions present → $SO_{2\ (aq)}$ gets removed from system → This changes Fuchsin -Sulfur dioxide (colourless) to coloured (red)

Thus, when an aldehyde is added to Schiff's reagent and reacts with the bisulfite ion present, equilibrium (2) shifts to the right and removes $SO_{2\ (aq)}$ from the system. This, in turn, causes equilibrium (1) to shift to the left, with the result that the solution changes from colourless to red. Most ketones do not cause this colour change, although there are exceptions. The test is very sensitive, and traces of aldehyde impurities can give misleading results.

Iodoform Test

The final reaction that will be studied in this experiment enables us to determine whether a given ketone contains a CH_3-(C=O)-group, i.e., allows us to identify methyl ketones. However, care must be taken in using this test, as compounds containing a CH_3-CH(OH)- group also give positive results due to the case of oxidation of the latter to CH_3-(C=O)-.

When treated with a solution of iodine in sodium hydroxide (essentially sodium hypoiodite), methyl ketones react to form iodoform (CHI_3). Thus, this test is often called the iodoform test.