

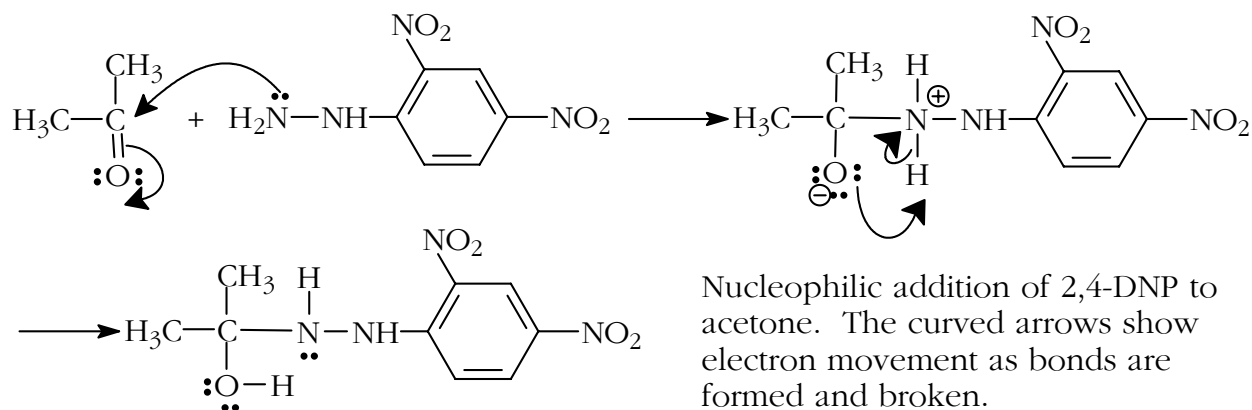
EXPERIMENT #9 – IDENTIFICATION OF ALDEHYDES AND KETONES

Introduction

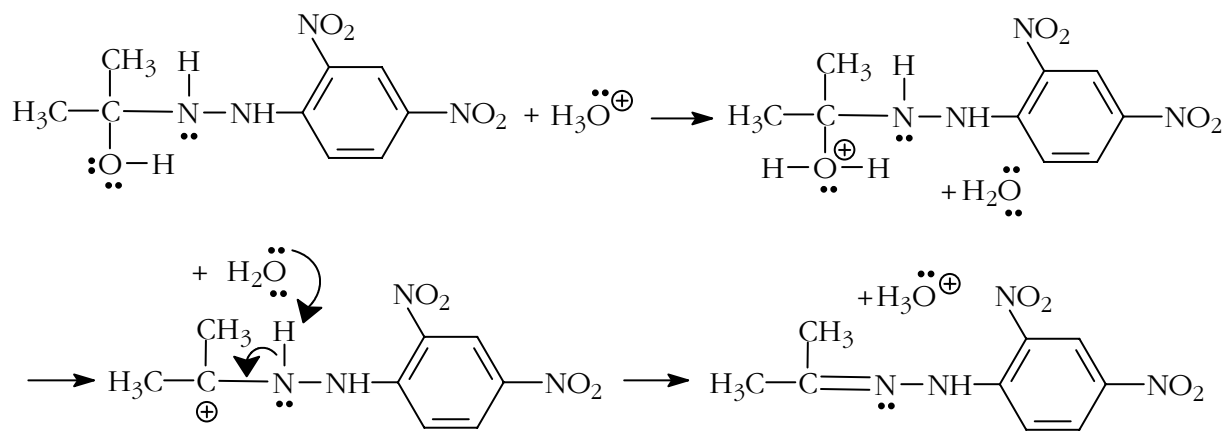
Aldehydes and ketones share the carbonyl functional group which features carbon doubly bonded to oxygen. In the case of ketones there are two carbon atoms bonded to the carbonyl carbon and no hydrogens. In the case of aldehydes there is at least one hydrogen bonded to the carbonyl carbon; the other attachment may be to a carbon or a hydrogen. In all cases the carbon(s) that are attached to the carbonyl group may be aliphatic (not part of an aromatic ring) or aromatic (part of an aromatic ring). Since they share the carbonyl group, aldehydes and ketones share much of their chemistry, but they are different enough to be considered different classes of compounds. This situation is similar to that of alcohols and phenols which both share the -OH group.

Aldehydes and ketones both undergo a reaction type known as *nucleophilic addition*. Under less acidic conditions, in this type of reaction a *nucleophile* (a species that can donate a pair of electrons, in other words a Lewis base) donates a pair of electrons toward the carbonyl carbon forming a single bond to it. At the same time the double bond between the carbonyl carbon and oxygen becomes a single bond as one bonding pair of electrons in the double bond moves to become an unshared pair on the oxygen. The oxygen now has one bond to it and it holds three pairs of unshared electrons, so it has a negative charge. Consequently, the oxygen picks up a proton from somewhere (possibly one that was attached to the nucleophilic atom that attacked the carbonyl carbon) and becomes an -OH group. Under more acidic conditions the results are pretty much the same, but the sequence in which they happen is more or less reversed. In this case, a proton (from an acid) attaches itself to one of the unshared pairs of electrons on the oxygen. The carbonyl group now has a +1 charge and is very inviting to even a weak nucleophile. [You can't have a strong nucleophile in an appreciably acidic solution because strong nucleophiles are moderate to strong bases and moderate to strong bases don't hang out in acidic solutions.] So, a nucleophile attacks the carbonyl carbon forming a bond and the doubly bonded oxygen of the carbonyl becomes an -OH, as before. Both of these scenarios are sketched out below, using specific examples.

First case – less acidic solution: reaction of 2,4-dinitrophenylhydrazine with acetone.

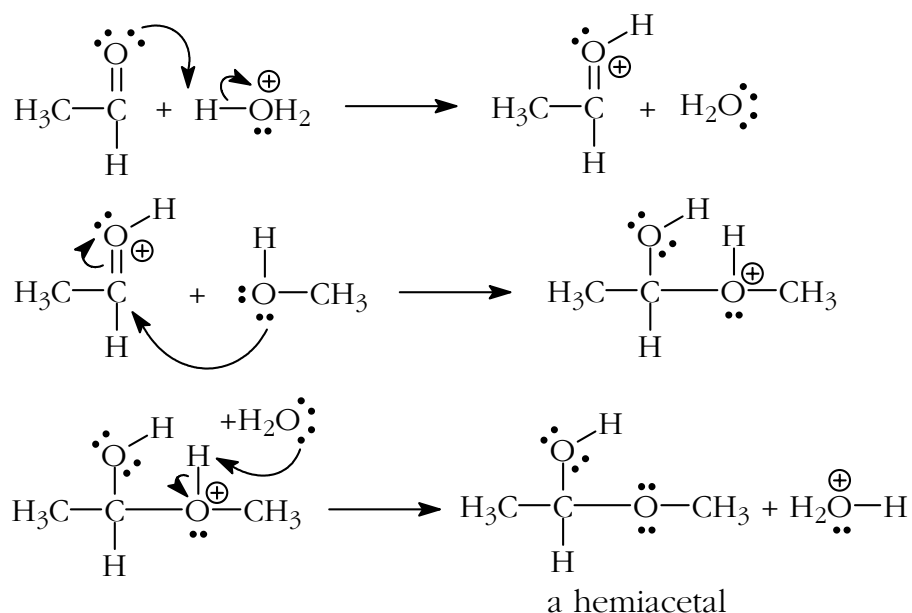


As we shall see just below, this product is not usually the one that is isolated. Rather this product undergoes an elimination reaction in which the $-OH$ is removed from the carbon to which it is attached and the hydrogen is removed from the nitrogen immediately to the right, resulting in a double bond between the nitrogen and carbon and a molecule of water. The final product is known as a 2,4-dinitrophenylhydrazone. You'll be reacting aldehydes and ketones with 2,4-dinitrophenylhydrazine to make 2,4-dinitrophenylhydrazones in this experiment.



Note that an acid, H_3O^+ , is needed as a catalyst in the first reaction above; it forms a molecule of water as one of the products in the first step. In the second step a second molecule of water is produced, but this water molecule is shown getting protonated in the third step to produce H_3O^+ , so it is used up. Consequently only one molecule of water is produced overall. Also note that the H_3O^+ that is used in the first step is reformed in the third step; this is the nature of a catalyst – it speeds up a reaction, but is not consumed in the reaction.

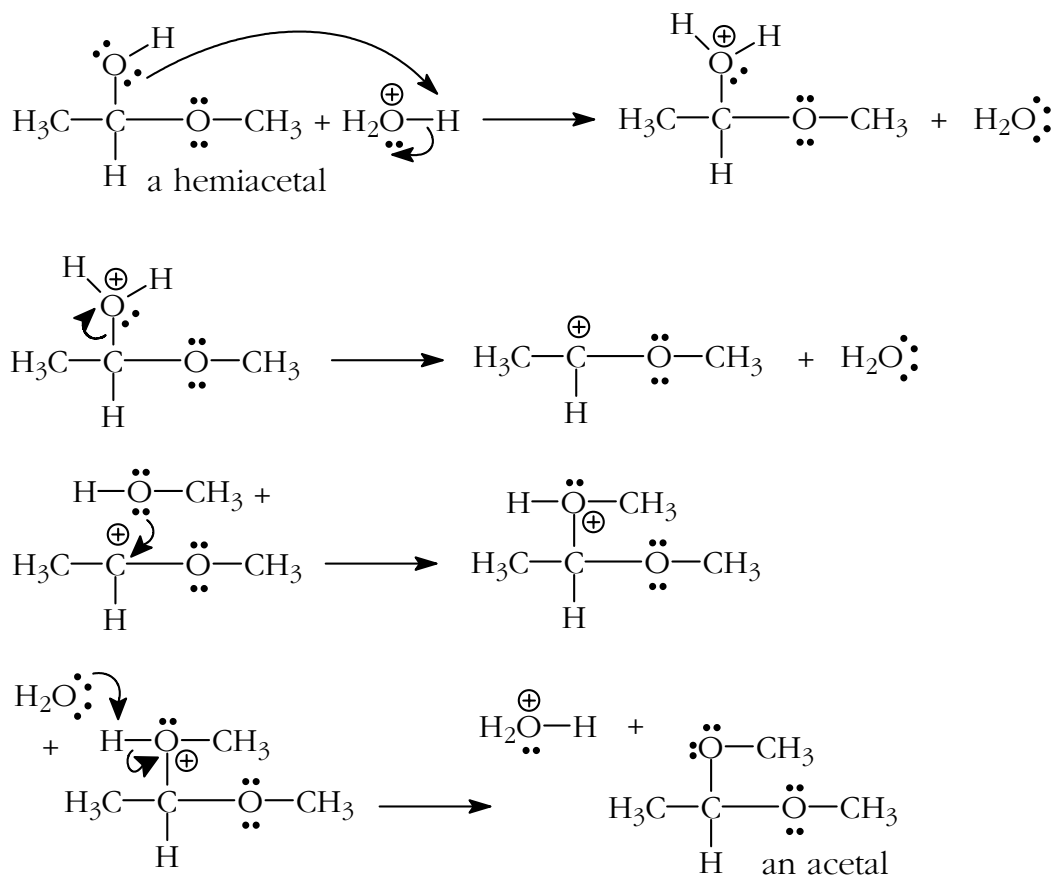
Second case – more acidic solution: reaction of methanol with acetaldehyde.



In the first step of this mechanism the acid catalyst, H_3O^+ , protonates the oxygen of the carbonyl group giving it a +1 charge. In the second step, the weakly nucleophilic oxygen of methanol donates a pair of electrons toward the carbon of the carbonyl group to form a new bond. In the third step the protonated hemiacetal transfers a proton to the water molecule formed in the first step to give the hemiacetal and a hydronium ion. Note that the hydronium ion that was used in the first step is regenerated in the third step; it is not consumed. This reaction is acid catalyzed. If the acetaldehyde were not protonated by the acid in the first step, its reaction with methanol would be extremely slow because methanol is a weak nucleophile.

Hemiacetals, the products of reactions between alcohols and either aldehydes or ketones, are important in carbohydrate chemistry. Sugars are, for the most part, polyhydroxy aldehydes and ketones. So, a sugar has both of the functional groups that react together to form a hemiacetal.

It turns out that hemiacetals can react with alcohols to give compounds known as *acetals*. Acetals have a tetrahedral carbon that has two oxygens bonded to it with the oxygens, in turn, being bonded to other carbon atoms. This reaction is also important in carbohydrate chemistry and an example is shown below. We will again use methanol as the alcohol and the hemiacetal that was formed above.



Regardless of which mechanism actually operates, these reactions are usually referred to as nucleophilic additions.

Procedure

Note: Acetone, often used to clean and dry laboratory glassware, is a methyl ketone and must be removed from the glassware before use.

Using a ring stand, ring, wire gauze, microburner, and a beaker that will conveniently hold 5 test tubes, set up a water bath that you can maintain at 60°C.

Label five test tubes as follows: (1) 3-methylbutanal (aliphatic aldehyde), (2) benzaldehyde (aromatic aldehyde), (3) cyclohexanone (ketone), (4) propanone *aka* acetone (methyl ketone), (5) unknown. **In each of the following tests start with 5 drops of the corresponding compound in the test tube.**

1. Chromic Acid Test –

Caution!

Chromic acid is toxic and corrosive. If you get any on yourself, wash it off with lots of water. As usual, wear goggles to protect your eyes.

Add 4 drops of chromic acid solution, agitating the tube after each addition. Let stand for 10 minutes. Note any color change and approximately how long it takes to occur. Record your results.

2. Tollens' Test –

Caution!

Dispose of the Tollens' reagent by washing it down the drain with lots of water as soon as you're done using it. Likewise, wash the contents of the test tubes down the drain as soon as you're done with the tests. Upon standing Tollens' reagent can form an explosive compound. As usual, wear goggles.

Prepare the Tollens' reagent in a 25 ml Erlenmeyer flask by mixing 5 ml of 9% aqueous silver nitrate with 5 ml of 10% aqueous sodium hydroxide. To the resulting mixture add 10% aqueous ammonia, dropwise with shaking, until the brown precipitate of silver oxide *just dissolves; do not add excess ammonia*.

For the Tollens' test to work well the test tubes in which it is conducted must be very clean – water must form a sheet on the glass, not drops. They do not have to be dry.

Dissolve the 5 drops of compound you added to each of the test tubes in *bis*(2-ethoxyethyl)ether by adding this solvent dropwise, with agitation, until a homogeneous solution is obtained. Then add 2 ml of Tollens' reagent and agitate. Place the tubes into a 60°C water bath for 5 minutes. A positive test for an aldehyde will be a silver mirror formed on the test tube if the test tube was clean; if the test tube was not clean, a black precipitate will form. Record your results on the report sheet. Clean the test tubes with 1 M nitric acid.

3. Iodoform Test –

To each of the test tubes containing the compounds to be tested, add 2 ml of water and agitate. If the compound is not soluble, add dioxane dropwise with agitation until the mixture is homogeneous. Add 2 ml of 6 M aqueous sodium hydroxide. Agitate. Place the tubes into a 60°C water bath for 3 or 4 minutes and, leaving the tubes in the bath, add the iodine-potassium iodide solution dropwise with occasional agitation (to agitate, remove the tube from the bath momentarily) until the brown color persists for 2 minutes in the tube. Add 6 M aqueous sodium hydroxide, dropwise with agitation, until the brown color dissipates. Keep the tubes in the water bath for 5 minutes. Remove the tubes from the bath and observe the contents. You are looking for a yellow precipitate of iodoform, indicative of acetaldehyde or a methyl ketone. Record your results. Clean the test tubes.

4. 2,4-Dinitrophenylhydrazine Test –

Add 20 drops of the 2,4-dinitrophenylhydrazine to each of the tubes containing the compounds to be tested. If no precipitate forms immediately, heat for 5 minutes in the 60°C water bath. Record your observations.

Identify your unknown as completely as you can based on your data. Your unknown will be either an aldehyde or ketone.