جامعة الانبار

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قسم : الكيمياء الصيدلانية

اسم المادة باللغة العربية: الكيمياء العضوية

اسم المادة باللغة الإنكليزية: **Organic Chemistry**

المرحلة: الثانية

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عنوان المحاضرة باللغة العربية: الكيمياء العضوية العملي التجربة الخامسة

عنوان المحاضرة باللغة الإنكليزية: **Practical Organic Chemistry (5)**

Exp. 5

Identification of Aldehydes and Ketones

Aldehydes are compounds of the general formula **RCHO,** ketones are compounds of the general formula **RR'CO.** The groups R and R' may be aliphatic or aromatic. (In one aldehyde, HCHO, R is H).

Aldehydes **Ketone**

Both aldehydes and ketones contain the carbonyl group C=O, and are often referred to collectively as carbonyl compounds. It is the carbonyl (the functional group) that largely determines the chemistry of aldehydes and ketones.

It is not surprising to find that aldehydes and ketones resemble each other closely in most of their properties. However, there is a hydrogen atom attached to the carbonyl group of aldehyde, and there are two organic groups attached to the carbonyl group of ketones. This difference in structure affects their properties in two ways: (a) aldehydes are quite easily oxidized, whereas ketones are oxidized only with difficulty; (b) aldehydes are usually more reactive than ketones toward nucleophilic addition, the characteristic reaction of carbonyl compounds.

The polar carbonyl group makes aldehydes and ketones polar compounds, and hence they have higher boiling points than non-polar compounds of comparable molecular weight. By themselves, they are not capable of intermolecular hydrogen bonding since they contain hydrogen bonded only to carbon, as a result they have lower boiling points than comparable alcohols or carboxylic acids.

The lower aldehydes and ketones are appreciably soluble in water, presumably because of hydrogen bonding between solute and solvent molecules; borderline solubility is reached at about five carbons. Aldehydes and ketones are soluble in the usual organic solvents.

In a carbon-carbon double bond C=C, both the σ- and π-electron clouds are symmetrically distributed between the two carbon atoms. In the carbon-oxygen double bond (i.e. carbonyl group) C=O, both the σ- and π-bonds are polarized, the electrons being distributed unequally between the two atoms. Owing to the greater electronegativity of the oxygen atom, this atom has the greater share of the bonding electrons and the distortion of the π-electron density can be represented in several ways. As a result of the permanent polarization of the bond, the carbon atom is electrophilic in character and is therefore susceptible to nucleophilic attack, i. e. attack by reagents which are able to donate an electron-pair to the carbon atom and form new bond. Conversely, the oxygen atom is susceptible to electrophilic attack, i. e. attack by an electron-pair acceptor, but this usually involves the comparatively simple step of protonation (i. e. reaction with H^+).

1- (2,4-Dinitrophenylhydrazine) test (general test)

Both aldehydes and ketones give yellow or orange precipitate with 2,4-Dinitrophenylhydrazine reagent.

Procedure

To 2 drops of the compound add 3 drops of the reagent, a yellow or orange precipitate will be formed. If the compound is insoluble in water, dissolve it in 1 cm^3 of methanol and then add the reagent.

2- Tollen's test

All aldehydes reduce ammonium silver oxide (Tollens reagent), and oxidize to carboxylic acids, while ketones cannot be oxidize, they need stronger oxidizing agents. Tollen's reagent is the combination of silver nitrate solution with ammonium hydroxide in the presence of sodium hydroxide solution. Silver ions reduced from this reagent to silver element in the form of silver mirror on the inner side of the test tube.

Procedure

To prepare Tollen's reagent add 2-3 drops of 10% sodium hydroxide solution to 3 cm^3 of 5% silver nitrate solution, and then add drop wise 10% ammonia solution with continuous shaking until all the brown precipitate of silver oxide is dissolved. This reagent should be freshly prepared.

In a test-tubes put 2 cm^3 of Tollen's reagent, then add few drops of the compound. Silver mirror will be formed on the walls of the test-tubes. (If silver does not precipitate, heat for a while on a water bath. The excessive heating will cause of appearance of a false positive test by decomposition of the reagent.

The formed silver mirror can be washed using dilute nitric acid. If the test tube is not very clean, silver metal forms merely as a granular gray or black precipitate. False negative tests are common with water insoluble aldehydes. A negative result indicates that the compound is a ketone.

3- Fehling's test

This test, like Tollen's test, is used to distinguish aldehydes from ketones. Only aldehydes can reduce Fehling's reagent (blue solution) and give red precipitate, due to the reduction of Cu^{2+} to Cu^{1+}. The red product is cuprous oxide Cu_2O.

Aromatic aldehydes do not give this test because of their sensitivity toward basic media.

Procedure

Fehling's A solution is an aqueous solution of copper sulfate ($CuSO_4.5H_2O$) with few drops of conc. H_2SO_4, whereas Fehling's B solution is an aqueous solution of potassium sodium tartrate ($C_4H_4KNaO_6.4H_2O$) and sodium hydroxide.

In a test-tube put 3 cm^3 of the compound, then add 1 ml Fehling A and 1 ml Fehling B, then heat the test-tube for 5 minutes. The blue color of the mixture changes to red. Ketones don't change the color of this reagent.

4- Iodoform test

This test special for aldehydes and ketones containing a terminal methyl group:

These compounds include acetaldehyde, acetone, acetophenone, and benzyl methyl ketone. All of them have a methyl group attached to the carbonyl group.

Procedure

To 0.2 cm^3 of compound add 2 cm^3 distilled water (or 2 cm^3 dioxane for water insoluble compounds), add about 1cm^3 of 10% sodium hydroxide solution, then add iodine solution drop wise with shaking until either a yellow iodoform precipitate is produced (or add 2 cm^3 of 0.5 M potassium iodide solution and 4 cm^3 sodium hypochlorite solution). Warm the mixture to 50°C for 2 minutes in a water bath, and then cool it. A yellow crystals of iodoform (Triiodomethane) are produced.

5- Sodium nitroprusside $Na_2[Fe(CN)_5NO]$ test

This test is also special for aldehydes and ketones containing a terminal methyl group.

Procedure

In a test-tube put 1 cm^3 of the compound, then add 1 cm^3 of 5% sodium nitroprosside $Na_2[Fe(CN)_5NO].2H_2O$ solution, then add a drops of 30% NaOH solution. The result is red color.

6- Cannizzaro reaction

Benzaldehyde, salicylaldehyde, and formaldehyde can undergo Cannizzaro reaction because they do not have alpha hydrogen atom.

In this type of reactions the aldehyde undergoes a self oxidation-reduction in the presence of a strong basic medium to yield a mixture of the corresponding alcohol and the salt of the corresponding carboxylic acid (or the acid itself). Therefore, one molecule of the aldehyde serves as the oxidizing agent while the other serves as the reducing agent.

Procedure

Put in a test-tube 1 ml Benzaldehyde, and then add few drops 30% NaOH, and heat gently on a water bath with shaking for few minutes. A precipitate of sodium benzoate is produced. Dissolve this precipitate by adding few drops of distilled water, and then add drops of concentrated hydrochloric acid to liberate benzoic acid as a white precipitate.

Put in a test-tube 1 cm^3 acetaldehyde, then add few drops 30% NaOH solution. Yellow plastic material will be formed its color change to brown with time, and does not dissolve in water.

Formaldehyde can undergo this reaction, however, this reaction can't be relied on for testing formaldehyde since the acid produced, formic acid, is liquid that can't be observed separately as compared to the solid benzoic acid resulted from benzaldehyde.