جامعة الانبار

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قسم : الكيمياء الصيدلانية

اسم المادة باللغة العربية: الكيمياء العضوية

اسم المادة باللغة الإنكليزية: **Organic Chemistry**

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عنوان المحاضرة باللغة العربية: الكيمياء العضوية العملي التحربة الرابعة

عنوان المحاضرة باللغة الإنكليزية: **Practical Organic Chemistry(4)**

Exp. 4

Identification of Alcohols

All alcohols contain the hydroxyl group (-OH) attached to a saturated carbon. These have the general formula R-OH, where R is an alkyl or substituted alkyl group. The group may be primary, secondary, or tertiary; it may be open chain or cyclic; it may contain a double bond, a halogen atom, an aromatic ring, or additional hydroxyl group. The -OH group is the functional group, determines the properties characteristic of this family. Variations in structure of the R group may affect the rate at which the alcohol undergoes certain reactions, and even, in a few cases, may affect the kind of reaction.

Alcohol molecules are polar, because the –OH group is highly polar. Force of attraction between alcohol molecules obviously must be greater than between molecules of alkanes. Hydrogen bonding account for this.

The presence of an alcohol group sharply increases the tendency to dissolve in water. Methane, for example, is insoluble in water, but methyl alcohol is completely soluble, because of the hydrogen bonding with water. Low molecular weight alcohols are soluble in water and ether are classified under class $\boldsymbol{S_1}$ such as methanol and ethanol. Alcohols that are insoluble in water are related to class ***N*** such as benzyl alcohol, *sec*-butanol, and cyclohexanol.

Alcohols are saturated compounds containing the functional group –OH. They can undergo nucleophilic substitution reactions, in which the hydroxyl group is displaced by other groups, or they can undergo elimination reactions, involving the loss of the elements of water when reacted with a dehydrating agent. Primary and secondary alcohols also undergo oxidation and the hydroxyl group shows acidic properties when treated with reactive metals.

1- Ceric ammonium nitrate test (general test)

Ceric ammonium nitrate (yellow solution) is an oxidizing agent that reacts with alcohols to give a red complex and with phenols to give a brown to greenish brown precipitate.

Each mole of the alcohol requires two moles of the reagent. The red complex is an intermediate for the oxidation of alcohols by the Ce(IV) solution. This red color disappears after a reasonable time due to completing the oxidation of this intermediate and the reduction to the colorless Ce(IV) solution producing the corresponding aldehyde or ketone.

This test gives positive results with primary, secondary, and tertiary alcohols (up to 10 carbons), poly hydroxylated compounds such as carbohydrates, and hydroxylated carboxylic acids, aldehydes and ketones.

Procedure

Mix 2 drops of the alcohol with 1 drop of ceric ammonium nitrate solution. A red complex indicates a positive test. If the alcohol is insoluble with water dissolve the two drops of alcohol with 0.5 cm^3 dioxane, shake well, and add one 1 drop of the reagent.

2- Iodoform test

This test is specific for alcohols which have a free methyl group and a hydrogen attached to the carbon bearing the hydroxyl group such as ethanol and *sec*-butanol.

The overall reaction is:

The alcohol is oxidized to the corresponding aldehyde or ketone by the action of the oxidizing agent 'sodium hypoiodite' which also cause the aldehyde or ketone to be tri-iodinated on the terminal methyl group producing iodoform as a yellow precipitate.

Procedure

To 0.2 cm^3 of alcohol 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. If the alcohol is ethanol or *sec*-butanol, fine yellow crystals of iodoform (Triiodomethane) are produced.

3- Salicylic acid test

When salicylic acid reacts with methanol, methyl salicylate is formed, and the smell of it is very distinguishable.

Procedure

Heat 1 cm^3 of (methanol) with spatula load of salicylic acid and a few drops of conc. H_2SO_4 for 1 minute. Cool and pour the mixture into about 10 cm^3 of distilled water in a small beaker and note the smell of methyl salicylate.

4- Acetic acid test

Ethanol can be confirmed by reaction with glacial acetic acid. Ethyl acetate (ethanoate) is formed, and the smell of it is distinguishable.

$$\mathbf{C_2H_5OH + CH_3COOH \quad CH_3COOC_2H_5 + H_2O}$$

Procedure

put 1 cm^3 of the substance into a test-tube then adding 1 cm^3 of glacial acetic acid and a few drops of conc. H_2SO_4. Heat the tube for one minute and then pour the mixture into about 10 cm^3 of water in a small beaker. The fruity odour of ethyl acetate (ethanoate) should be apparent.

5- Potassium dichromate test

When ethanol is reacted with potassium dichromate in the presence of conc. H_2SO_4, acetaldehyde (ethanol) is formed and it is replaced acetic acid.

$$\underset{\text{orange}}{\mathbf{2Cr_2O_7^{2-} + 16H^+ + 3CH_3CH_2OH}} \quad \underset{\text{green}}{\mathbf{4Cr^{3+} + 3CH_3COOH + 11H_2O}}$$

Procedure

Make up 4 cm^3 of a concentrated solution of potassium dichromate and add 1 cm^3 of conc. H_2SO_4. Warm the mixture gently and then add 0.5 cm^3 of ethanol: the sweet smell of acetaldehyde should become apparent and it is replaced by the sharp smell of acetic acid.

5- The Lucas test

This is done to distinguish between primary, secondary and tertiary alcohols. It depends on the formation of alkyl chloride as a second liquid phase. Lucas reagent is zinc chloride dissolved in conc. HCl. Zinc chloride is added to increase the ionization of hydrochloric acid.

$$ZnCl_2 + HCl \qquad ZnCl_3^- + H^+$$

Benzyl alcohol gives the fastest positive result. Tertiary alcohols are faster in the formation of conjugated halides than secondary alcohols. Primary alcohols don't form two layers.

Procedure

Put 1 cm^3 of the alcohol into a test-tube. Add 6 cm^3 of Lucas reagent, cork the test-tube and shake it. Allow it to stand for five minutes.

With primary alcohol of low relative mass, the aqueous layer remains clear, with secondary alcohols, chlorides separate on standing for 15-20 minutes, with tertiary alcohols separation takes place immediately.