Organic chemistry laboratory

IDENTIFICATION OF ALCOHOLS

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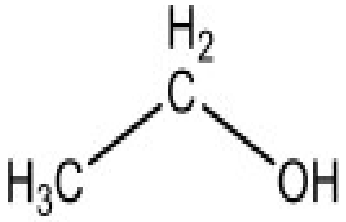
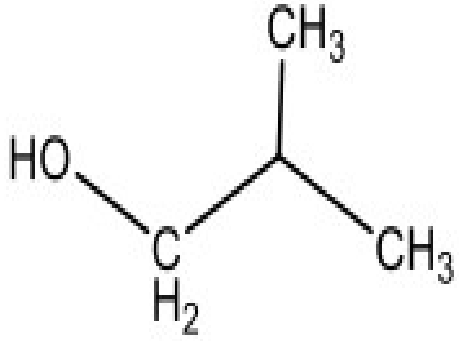
- **Alcohols are organic compounds that may be considered as derivatives of water in which one of the hydrogen atoms of water molecule (H-O-H) has been replaced by an alkyl or substituted alkyl group. Therefore, properties of alcohols may be related to properties of both water and hydrocarbons. The alkyl group could be primary, secondary, or tertiary, and may be open chain or cyclic. Accordingly, alcohols may be defined as organic compounds that contain hydroxyl groups attached to alkyl, substituted alkyl, or cyclic alkyl group.**

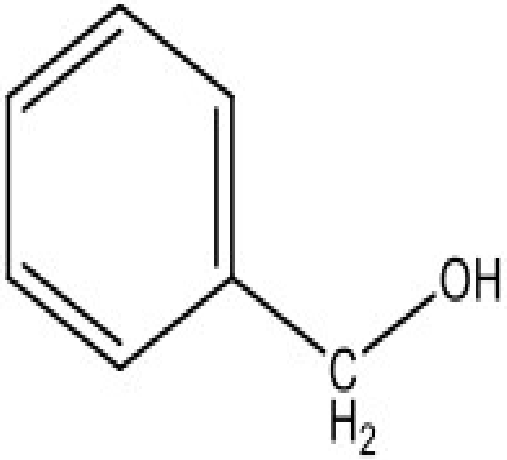
Methanol



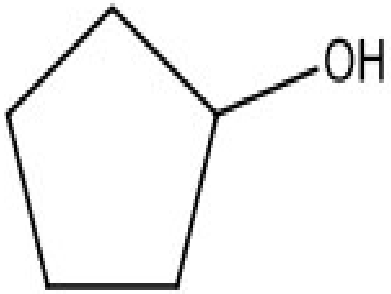
Ethanol



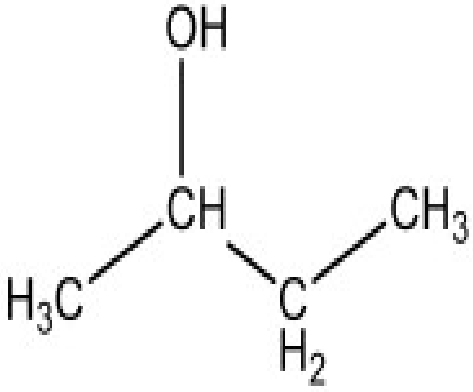
Isobutanol



benzyl alcohol



cyclopentanol



sec-butanol

Physical properties

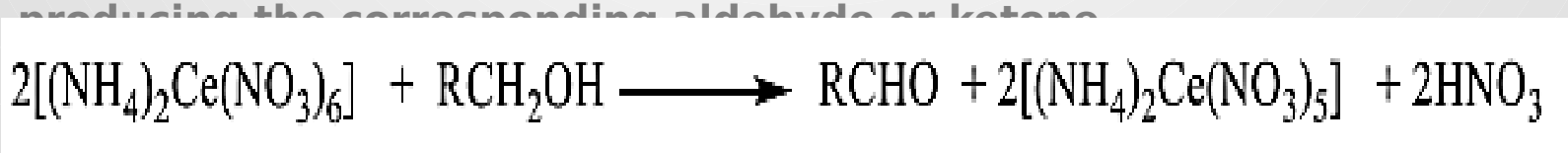
- **- Alcohols are colourless liquids with a special faint odour. Benzyl alcohol and cyclohexanol have characteristic odours.**
- **- Aliphatic alcohols burn with blue flame (without smoke) while aromatic alcohols burn with yellow smoky flame.**
- **- Boiling points of alcohols are considerably high (being associated liquids); they increase as the molecular weight (number of carbons) increases.**
- **- Alcohols are miscible with water except benzyl alcohol, cyclohexanol, and sec-butanol (which is very slightly soluble in water.**

Solubility classification

- **Alcohols are polar compounds because of the presence of the hydroxyl group which is also responsible for their ability to form hydrogen bonding. The degree of the polarity depends on the size of the alkyl side chain; the polarity decreases as the size of the alkyl side chain increases, or in another word, as the hydroxyl group hydrocarbon ratio of alcohols increases, their water solubility increases and vice versa. Besides, low molecular weight alcohols are soluble in water due to hydrogen bonding ability with water molecules. Therefore, alcohols that are soluble in water and ether are classified under class S1 such as ethanol and methanol. Alcohols that are insoluble in water are related to class N such as benzyl alcohol, sec-butanol, and cyclohexanol.**

Chemical properties

- - Alcohols are neutral compounds that don't change the colour of litmus paper.
- - All reactions of alcohols are related to its active hydroxyl group and are of two types:
- a) removal of the hydroxyl itself as in the reaction with hydrogen halides to form alkyl halides or in the dehydration reaction to form a double bond.
- b) removal of the proton only from the active hydroxyl as in the formation of esters or in the reaction with active metals such as sodium.
- **1. General test (Ceric ammonium nitrate reagent)**
- 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 coloured complex is an intermediate for the oxidation of alcohols by the Ce (IV) solution. This red colour disappears after a reasonable time due to completing the oxidation of this intermediate and the reduction to the colourless Ce (III) solution producing the corresponding aldehyde or ketone

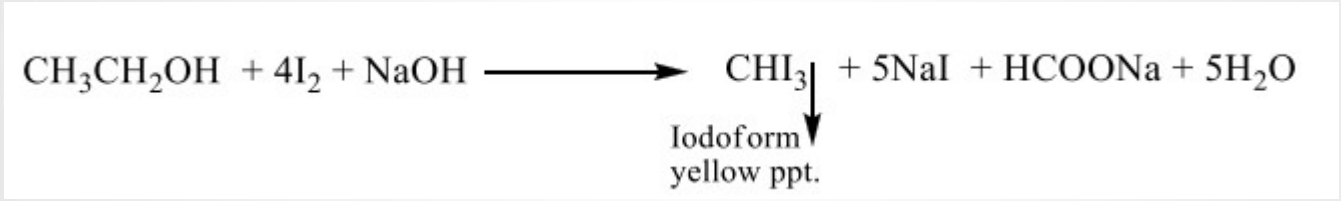


Procedure

- **Water soluble (miscible) alcohols; mix two drops of the alcohol with one drop of ceric ammonium nitrate solution. A red complex indicates a positive test**
- **Water insoluble (immiscible) alcohols; mix two drops of the alcohol with 0.5 ml dioxane, shake well, and add one drop of the reagent to get a positive red complex.**
- **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.**

Specific tests .2

- **a) Iodoform (Haloform) 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 produced oxidizing agent 'sodium hypoiodite', which also causes the aldehyde or ketone to be tri-iodinated on the terminal methyl group producing iodoform as a yellow precipitate.**

Lucas test

- This test often provides classification informations on alcohols and is used to distinguish between the different types of alcohols (primary, secondary, or tertiary). It depends on the formation of alkyl chloride as a second liquid phase**. Lucas reagent** is prepared from anhydrous zinc chloride and concentrate dhydrochloric acid. Zinc chloride is added to increase the ionization of hydrochloric acid.
- Benzyl alcohol shows the fastest positive result. Tertiary alcohols are faster in the formation of conjugated halides than secondary alcohols. Primary alcohols and methanol don’t react and don’t form two layers.

Procedure

- Mix 2-4 drops of the alcohol with few drops of Lucas reagent and observe the results:
- 1. benzyl alcohol gives immediate result as shown by the appearance of two phases.
- 2. tertiary alcohols give two phases that separate within 2-3 minutes.
- 3. secondary alcohols give two phases that separate after 15-20 minutes (giving a cloudy solution).
- 4. In primary alcohols one layer appears

Oxidation reaction

- **(with potassium permanganate)**
- Primary alcohols oxidase to cross ponding carboxylic acid, Secondary alcohols oxidase to a cross ponding ketones, and tertiary alcohols don’t oxidase the result from oxidation of primary alcohols rapidly oxidase to form carboxylic acids with manganese di oxide(brown ppt.) , Secondary alcohols oxidase after 3-5 min., and tertiary alcohols don’t oxidase (the color of solution is purple).

Procedure

- To 0.5ml of alcohol add 5-8 drops from potassium permanganate and then observed the result