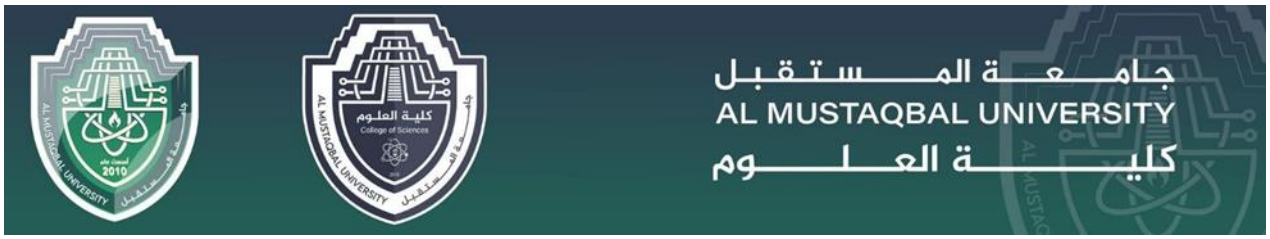

Lab of Organic Chemistry

2nd stage

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Lecture 3&4: Qualitative tests for alcohols

Department of Bio Chemistry

1. 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 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; the tri-iodinated methyl group will then leave by the action of excess sodium hydroxide as a yellow precipitate, iodoform.

Procedure

a. Dissolve the compound (**2-3 drops or 100mg**) in water (**2-3ml**) in a test tube and add **1ml of 10% sodium hydroxide**.

b. To this add a saturated solution of iodine-potassium iodide in water with stirring until the dark colour of iodine persists.

c. Heat the solution in a **boiling water bath** for **1-2 minutes** or **hot water bath for 5 minutes**; shaking the test tube occasionally. It is likely that some or all of the dark color of the iodine reagent will be discharged.

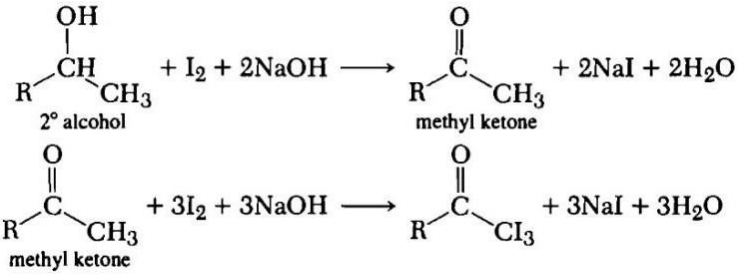
d. If the dark color of the iodine reagent is still apparent following heating, add **dropwise 10% sodium hydroxide** solution until the dark color of the iodine reagent has been discharged. Shake the mixture in the test tube (corked) during the addition of sodium hydroxide. Care need not be taken to avoid adding excess sodium hydroxide.

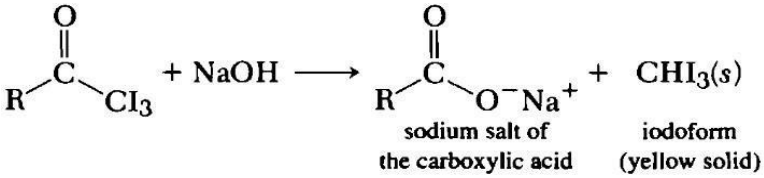
e. After the dark iodine color of the solution has been discharged, fill the test tube with water to within **2cm** of the top. Cork the test tube and shake it vigorously.

Allow the tube to stand for at least **15minutes** at room temperature. The appearance of a pale yellow precipitate of iodoform constitutes a positive test.

f. The yellow precipitate usually settles out slowly onto the bottom of the test tube. Sometimes, the yellow color of iodoform is masked by a dark substance.

Both ethanol and sec-butanol give positive iodoform test and they can be differentiated only by testing their solubility in water; sec-butanol is less soluble in water than ethanol.



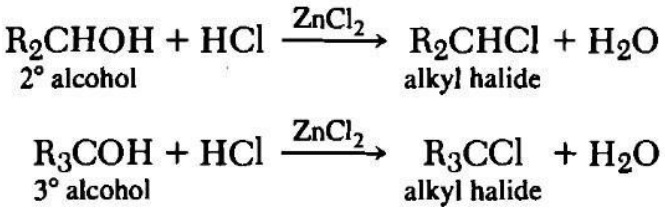


2. Lucas Test

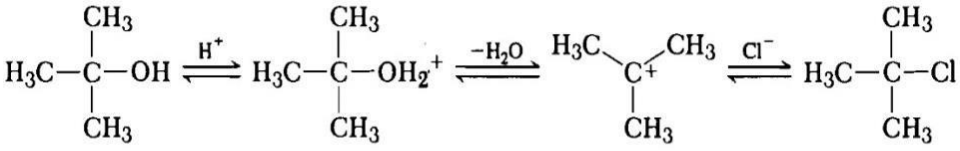
This test often provides classification information on alcohols and is used to distinguish between the different types of alcohols (primary, secondary, or tertiary). It depends on the formation of alkyl chloride as a second liquid phase.

Lucas reagent is prepared from anhydrous zine chloride and concentrated hydrochloric acid. Zinc chloride is added to increase the ionization of hydrochloric acid.

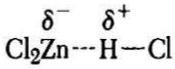
Benzyl alcohol shows the fastest positive result. Tertiary alcohols are faster in the formation of conjugated halides than secondary alcohols. Primary alcohols and methanol don't react and don't form two layers.



The mechanism of the Lucas test is an S_N1-type process as follows:



The role of the $ZnCl_2$ is to enhance the reactivity of the HCl by polar coordination:



Procedure

Mix **2-4** drops of the alcohol with ***few*** drops of Lucas reagent and observe the results:

i. Benzyl alcohol gives immediate result as shown by the appearance of two phases.

ii. Tertiary alcohols give two phases that separate within **2-3** minutes.

iii. Secondary alcohols give two phases that separate after **15-20** minutes (giving a cloudy solution).

iv. In primary alcohols one layer appears.