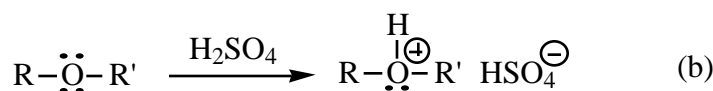
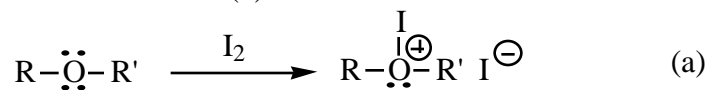


Chem 4563 Organic Qualitative Analysis

Ethers and Sulfides-Functional Group Tests

1. Introduction

Ethers (R-O-R') as a class of compounds are relatively unreactive and only slightly polar. The ether oxygen is slightly nucleophilic and will form a complex on treatment with iodine (a), and can be protonated by concentrated sulfuric acid (b):



Because of their solubility in conc. sulfuric acid most ethers are in solubility class N₂. However, diaryl ethers are often insoluble in conc. sulfuric acid, due to the extensive conjugative delocalization of the lone-pair electrons into the aryl rings, and are in class I. Some dialkyl ethers are also soluble in concentrated HCl.

The unreactivity of aliphatic ethers makes the problem of classifying them a difficult one. Aromatic ethers (R-O-Ar) on the other hand, are somewhat easier to classify.

Sulfides (R-S-R') can be expected when the compound contains sulfur and does not show an active hydrogen of the thio (R-SH) when treated with sodium metal. Aliphatic and most aromatic sulfides have unpleasant odors somewhat resembling that of hydrogen sulfide (rotten egg smell). Most sulfides belong to the MN solubility classification. Most aliphatic sulfides are liquids, aromatic sulfides are liquids or low-melting solids.

2. Tests for Ethers

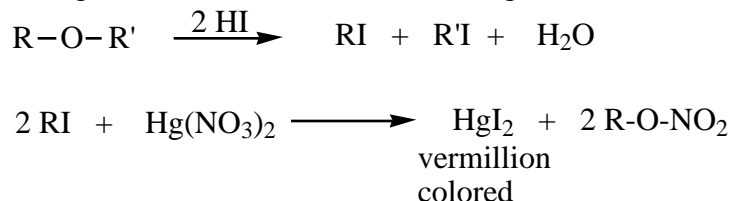
Both aromatic and aliphatic ethers will react with I₂ to form a complex, and hydroiodic acid to form alkyl iodide cleavage products. However only aryl ethers will react with bromine water to give bromine substitution products.

a. Iodine Charge-Transfer Test

When iodine is dissolved in compounds containing π -electrons or nonbonded electron pairs, a brown colored solution results. The brown color is due to the formation of a complex between the iodine and the π or nonbonded electrons. This test should only be employed with liquid unknowns. Saturated hydrocarbons and their fluorinated or chlorinated derivatives, and aromatic hydrocarbons give violet solutions. Alkenes, alkynes and ethers give brown solutions.

b. Hydroiodic Acid Test (Zeisels Alkoxy Test)

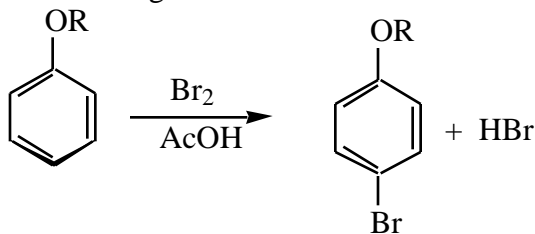
The relatively unreactive C-O bonds in an ether can be cleaved by treatment with conc. HI to give two alkyl iodides and water. The alkyl iodides produced can react with mercuric nitrate, Hg(NO₃)₂, to give the orange-red colored mercuric iodide (HgI₂).



Because the test depends on the volatility of the alkyl iodide produced, this class reaction is most useful for ethers that contain a methyl, ethyl, n-propyl or isopropyl group; although higher alkyl groups such as n-butyl or isoamyl will also give a positive test. Other functional groups that will give alkyl iodides under the conditions of this test are alcohols, esters and acetals.

c. Bromine/Acetic Acid Test

The oxygen of an aromatic ether activates the ring to bromine substitution reactions. This reaction is similar to that undergone by phenols and anilines, but requires stronger conditions. Glacial acetic acid is used to activate the bromine and make it a very potent electrophile. A positive result is indicated by a rapid discharge of the orange red color of bromine.

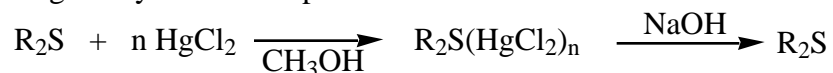


This reaction can also be used as a means of preparing a solid derivative for characterization.

3. Tests for Sulfides

a. Mercuric Chloride Complexes

Most sulfides give crystalline complexes when treated with mercuric chloride (HgCl₂).



The sulfide, neat or in alcohol solution, is added drop wise to a saturated solution of mercuric chloride in alcohol. The complex, which usually precipitates immediately, varies in ratio of mercuric chloride to sulfide, depending on the structure of the sulfide. The sulfides may be regenerated from the complex by addition of dilute aqueous hydroxide. This procedure may be used as both a classification test and/or as a method for obtaining a solid derivative.