

Experiment 11: Reactions of the common functional groups Part II: Alcohols and alkyl halides

Objectives

The purpose of this experiment is to illustrate to the student a selection of those reactions that are typical of two important classes of organic compounds: **alcohols and alkyl halides**. In this experiment, a variety of tests will be performed on a selection of known compounds. In a later experiment, the student will be expected to use the same tests plus Infrared and NMR analysis to identify assigned unknown compounds.

Theory

As we have previously stated in the introduction to *Chemistry 350's* Experiment 6, spectroscopic techniques have replaced many of the "wet" techniques that were formerly used by organic chemists to determine the identity of an unknown compound. However, many of the older techniques do illustrate the chemical differences between the various chemical families, thus there is much to be said for studying these techniques in an introductory organic chemistry course.

In this experiment you will study two reactions that enable organic chemists to distinguish between primary, secondary and tertiary alcohols. You will also examine the behaviour of several alkyl halides and some related compounds under both S_N1 and S_N2 conditions.

Reactions of Alcohols

Primary and secondary alcohols can be oxidized by a variety of reagents, whereas tertiary alcohols are not oxidized under normal conditions (see Figure 11.1). Depending on the conditions and the reagents used, primary alcohols can be oxidized to aldehydes or carboxylic acids. Secondary alcohols are oxidized to ketones:

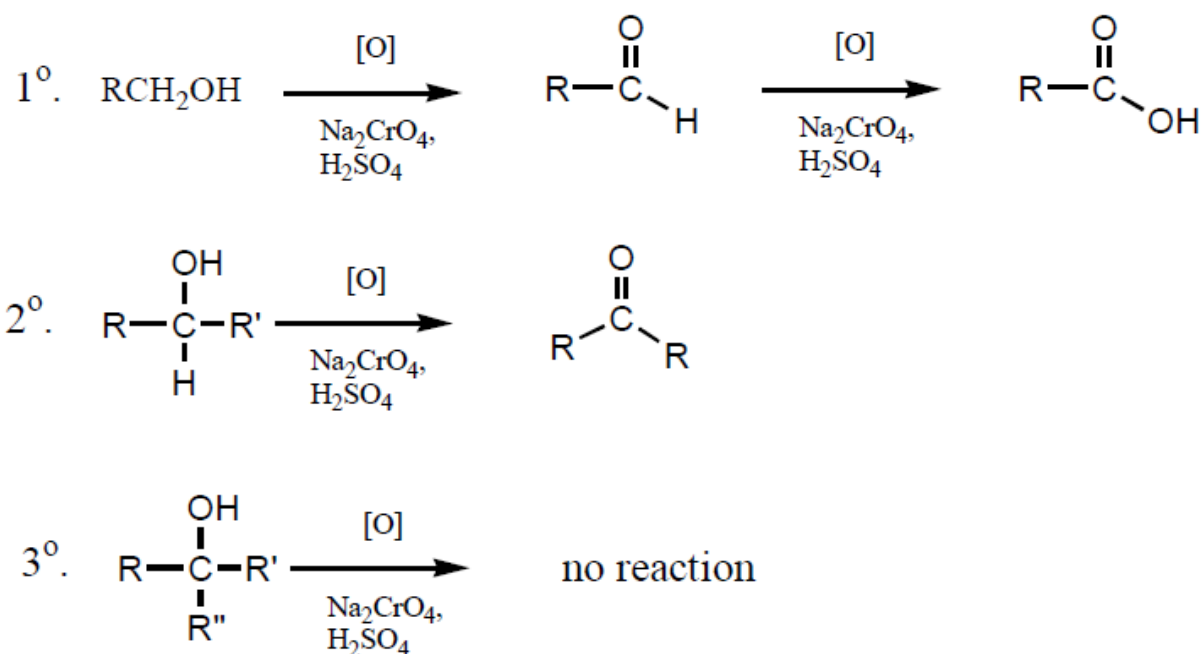


Figure 11.1 Oxidation reactions of primary, secondary and tertiary alcohols.

The oxidizing agent used in this experiment is a mixture of sodium dichromate and sulfuric acid. If a reaction occurs, the yellow-orange colour of the oxidizing agent changes to green, due to the formation of chromium(III) ions.

When the reaction can proceed via the formation of a stable carbocation, an alcohol will react with a mixture of hydrochloric acid and zinc chloride (known as Lucas reagent) to form an alkyl halide (see Fig. 11.2). The alkyl halide that forms is insoluble in the aqueous reaction mixture and thus the solution becomes cloudy if a reaction occurs. In general, tertiary alcohols react immediately, secondary alcohols produce 'cloudiness' within a few minutes, and primary alcohols do not react even after being allowed to stand for an hour or more:

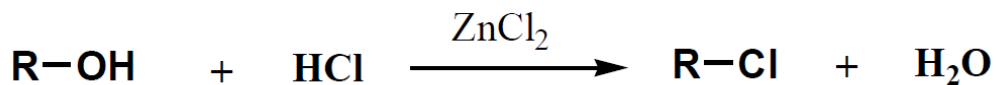


Figure 11.2 Lucas reagent reactions of alcohols.

Reactions of Alkyl Halides

Alkyl halides can react with nucleophiles by either an S_N1 or S_N2 mechanism. By studying the behaviour of an unknown alkyl halide under conditions that are known to favour either one of these two mechanisms, it may be possible to make certain deductions regarding the structure of the unknown compound. In this experiment, you will use known compounds to observe how structural variations influence the rate at which a compound reacts in an S_N1 or S_N2 reaction.

Silver nitrate dissolved in ethanol is a useful reagent for assessing the reactivity of an alkyl halide in an S_N1 reaction (see Fig. 11.3). The nitrate ion is a poor nucleophile, thus reaction by an S_N2 mechanism is unlikely to occur. In addition, ethanol is a moderately powerful ionizing solvent and will favour reaction by the S_N1 route. The formation of an insoluble silver halide also serves to enhance the forward reaction. (**Note:** products other than ROEt are formed, e.g., alkene addition products).

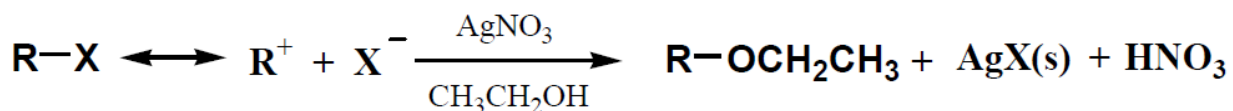


Figure 11.3 Silver nitrate S_N1 reactions of alkyl halides.

Acetone is a solvent of low polarity, which makes it a useful solvent for S_N2 reactions. Iodide ion is an excellent nucleophile, thus if a chemist wishes to study the S_N2 reactions of an alkyl halide, the reaction of the alkyl halide with potassium (or sodium) iodide dissolved in acetone is a good choice, a.k.a. Finkelstein reaction.

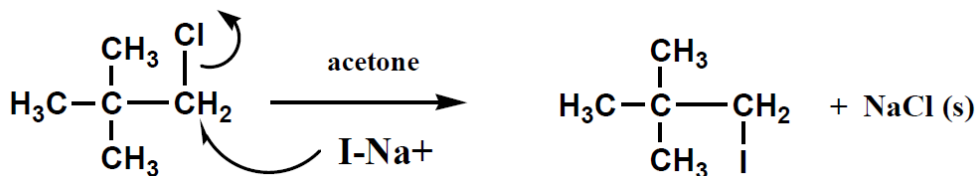


Figure 11.4 Sodium iodide S_N2 reactions of alkyl halides.

Although potassium and sodium iodide are soluble in acetone, the corresponding chlorides and bromides are insoluble, and the formation of a precipitate increases the tendency of the reaction to proceed to the right. Remember that an S_N2 mechanism goes through a bimolecular transition state.

Summary Table of Chemical Diagnostic Functional Group Tests:

Chemical Family	Solubility Class	Function Group Tests	Comment
Alkane	Neutral	Bromine Test, Sulfuric acid Test	Slow reaction, unreactive to Baeyer and sulfuric acid tests
Alkene	Neutral	Baeyer Test Bromine Test	Fast reaction. Color of reagent fades. No HBr formed in Bromine Test.
Alkyne	Neutral	Ammoniacal Silver Test	Terminal triple bond detected. Pptte formed
Alcohol	Neutral	1. Acetyl chloride treatment to form ester, then Ferric Hydroxamate Test 2. Chromate Oxidation 3. Lucas's test (ZnCl₂ in HCl) Derivative Formation 1. 3-5-dinitrobenzoates 2. α -naphthylurethanes	-Forms the hydroxamate ester, then a Fe ³⁺ colored complex -Test for 1° and 2° alcohols. 3° alcohols do not react -Test for 2° or 3° alcohols. Solution turns cloudy. -must be performed in a fumehood. -alcohol and glassware must be absolutely dry.
Alkyl Halides	Neutral (Acid/Base Insoluble)	1. Silver Nitrate/Ethanol 2. Sodium iodide/Acetone 3. Beilstein Test Derivative Formation 1. S-alkylthiuronium picarates 2. Nitro compounds	-Ag nitrate test negative for vinyl and aryl halides. -both tests classify as 1°, 2° or 3° halogenated hydrocarbons -green to blue green flame indicates halogen compd.-test unreliable -Tertiary alkyl halides do not form this derivative. -may form mono-, di- or tri-nitro compounds
Ester	Neutral	1. Hydrolysis to carboxylic acid 2. Ferric hydroxamate Test	-Saponification with 30% NaOH then acidification. -Deep red-purple complexes formed with Fe ³⁺
Aldehyde	Neutral	1. 2,4-dinitrophenylhydrazine (2,4-DNP) 2. Tollen's Test	-Forms the 2,4-DNP derivative, a highly coloured precipitate. -Silver mirror formed in Tollen's Test
Ketone	Neutral	1. 2,4-dinitrophenylhydrazine (2,4-DNP) 2. Tollen's Test 3. Iodoform Test	-Forms the 2,4-DNP derivative, a highly coloured precipitate. -No silver mirror formed in Tollen's Test -detects methyl ketones. Yellow pptte & medicinal odor
Amide	Neutral	1. Amide Hydrolysis, 2. Ferric hydroxamate Test	-Saponification with 30% NaOH and detection of NH ₃ in vapors. -See esters. Required more drastic reaction (>150° C)
Carbohydrate	Neutral	1. Benedict's Reagent 2. Tollen's Test	-Detects reducing sugars. Brick red pptte of Cu ₂ O formed. -silver mirror formed by reducing sugars (aldehydes and α -hydroxy ketones)
Phenol	Weak Acid	1. Ferric Chloride Test, 2. Pauly Test	-Blue or purple complex for simple phenols. Red or green complexes with polysubstituted phenols -Red, orange, yellow-green or blue azo compounds formed when treated with diazonium salt of sulfanilic acid
Carboxylic acid	'Strong' Acid	Solubility	Soluble in 5% NaOH and sat. KHCO ₃
Amine	'Strong' Base	1. Hinsberg Test, 2. Pauly Test for aromatic amines	-Forms the sulfonamide of 1° and 2° amines -Red, orange, yellow-green or blue azo compounds formed when treated with diazonium salt of sulfanilic acid