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A Solvent-Free Oxidation of Alcohols in an Organic Laboratory

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Chemical oxidations of alcohols are widely utilized in organic synthesis (1) and are routinely covered in organic chemistry textbooks. Unfortunately, few experiments have been developed for the undergraduate laboratory involving the chemical oxidation of alcohols (2). Among the published procedures for the undergraduate laboratory, most involve the use of hypochlorite solutions (2a–c) as the oxidizer or Cr(VI)-based supported oxidizing reagents (2d–f). This lack of experiments is most likely due to the inherent toxicity and disposal costs of most of the oxidizing reagents used to accomplish these transformations.

Recently, Shaabani and Lee (3) have reported a procedure for the solvent-free oxidation of thiols, sulfides, diols, and alcohols using a mixture of KMnO_4 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The relatively low toxicity and availability of the oxidizing reagent (4) coupled with the simplicity of their procedure led us to investigate the possibility of converting their oxidation process into a form applicable to the teaching laboratory. The oxidation of alcohols to ketones under solvent-free conditions (5) has not yet been utilized in the undergraduate teaching laboratory. However, there has been one laboratory exercise reported in this *Journal* (2g) detailing the oxidation of benzoin to benzil using alumina-supported active MnO_2 . Though this reaction involves a solvent-free, supported oxidant, the reaction takes place in CH_2Cl_2 over a 2-hour period. The laboratory we have developed offers several advantages over many of the existing exercises involving chemical oxidations including lower toxicity of the reagents (relative to Cr(VI) species), environmental friendliness, the ability to reduce the amount of waste generated and hazardous materials used, and the overall cost effectiveness of the reactions. All of these advantages are important considerations in the development and implementation of a new teaching laboratory.

In this experiment, a ground mixture of KMnO_4 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was used to oxidize a series of secondary alcohols to their corresponding ketones under solvent-free conditions (Scheme I). Cyclohexanol (1a), 2-octanol (2a), and benzhydrol (3a) were selected as suitable alcohols owing to their low cost, low toxicity, and for their ability to be completely oxidized in a one-hour time period. Thin-layer chromatography (TLC) was used to monitor the reaction's progress. Furthermore, since the reaction yields were near quantitative, the students obtained enough material to characterize their product by NMR, GC–MS, or IR.

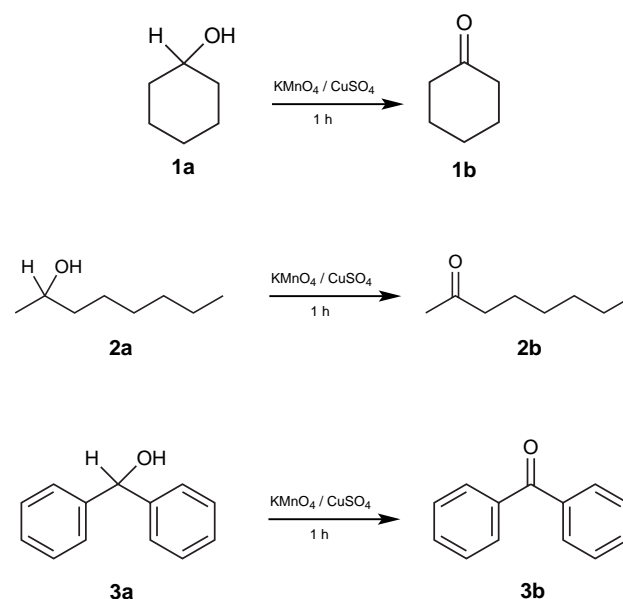
Experimental Procedure

A powdered mixture of the oxidant was prepared by grinding 1.58 g (10.0 mmol) of KMnO_4 with 2.50 g (10.0 mmol) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with a mortar and pestle until the mixture was visually homogeneous. The alcohol (1a, 2a, or 3a) (4.82 mmol) was added to a 25-mL round bottom flask, followed by the addition of ca. 4 g (10 mmol) of the oxidant

mixture. The resulting reaction mixture was stirred vigorously with a spatula until the flask began to become warm indicating initiation of the exothermic reaction. A reflux condenser was immediately attached and the flask was placed in a preheated hot water or steam bath at ca. 100 °C. After 1 h, the reaction was complete. The mixture was cooled to room temperature and desorbed from the solid reaction byproduct with two 10-mL portions of hexane. The hexane solution was suction filtered. Drying of the filtrate with MgSO_4 , gravity filtration, and evaporation of the solvent produced the desired ketone (1b, 2b, or 3b) in near quantitative yield. TLC analysis using 5:1 hexane:ethyl acetate as the elution solvent confirmed that the alcohol had been consumed.¹ Comparison was also made between the infrared spectra of the starting material and the product.²

Hazards

Potassium permanganate is a potent oxidizing agent.³ Care should be taken when used in conjunction with organic materials and strong acids. Thermal decomposition may yield toxic fumes of manganese oxides. Keep reaction temperature at 100 °C or below to help to avoid thermal decomposition. Hexane is a flammable solvent. Further health and safety notes may be found in the Supplemental Material.^W Safety glasses should be worn at all times.



Scheme I. Oxidation of secondary alcohols to their corresponding ketones under solvent-free conditions.

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^WSupplemental Material

Instructions for the students and notes for the instructor are available in this issue of *JCE Online*.

Notes

1. It may be necessary to develop the TLC plates in an iodine chamber.
2. Incorporation of infrared spectroscopy into this laboratory works well as students can clearly see the change from the spectra of the starting alcohol to the resulting ketone.
3. It may be necessary to decompose excess permanganate by gently heating the reaction byproduct with 10 mL of ethyl alcohol.

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