

Silica Sulfuric Acid/Potassium Permanganate/Wet SiO₂ as an Efficient Heterogeneous Method for the Oxidation of Alcohols under Mild Conditions

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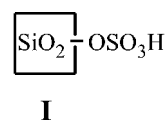
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For oxidation of organic functionalities, one turns often to high-valent metal oxides or their mineral salts.¹ Classic reagents of this type are manganese dioxide (MnO₂), potassium permanganate (KMnO₄), chromium trioxide (CrO₃), potassium chromate (K₂CrO₄), and potassium dichromate (K₂Cr₂O₇).² These are all frequently-used reagents, whether in the laboratory or in industry, and yet they are beset with multiple liability. For satisfactory and reproducible results, these oxidants demand vigorous control of the experimental conditions. The other drawbacks against such oxidants and their use in multistage organic synthesis, in spite of their power, are also their lack of selectivity, strong protic and aqueous conditions, low yields of the products, and tedious work-up.³ For instance, overoxidation of aldehydes to carboxylic acids is often unavoidable side reaction.

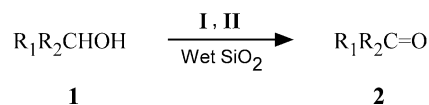
Furthermore, the elevated reflux temperatures required by some oxidation procedures will favor inopportune secondary reactions. Likewise, the presence of strong acids or bases, which are required adjuncts as catalysts for some reactions, often leads to detrimental side reactions. As an example, the oxidation of primary alcohols to aldehydes by a chromium (VI) salt in sulfuric acid is often accompanied by formation of a hemiacetal between the resulting aldehyde and the alcohol substrate, following by the ready oxidation of this intermediate to an ester.⁴

Along this line, we have introduced potentially useful oxidants for selective oxidation and oxidative deprotection of different functional groups.⁵ Therefore, we decided to choose a new reagent or reagent systems to overcome the above limitations. In addition, for our propose both clean and easy work-up were also important. On the other hand, any reduction in the amount of sulfuric acid needed and/or any simplification in handling procedures is required for risk reduction, economic advantage and environment protection.⁶ In addition, there is current research and general interest in heterogeneous systems because of the importance such systems have in industry and in developing technologies.⁷ In continuation of our studies on the application of inorganic acidic salts⁸ we found that silica gel reacts with chlorosulfonic acid to give silica sulfuric acid (I). It is interesting to

note that the reaction is easy and clean without any work-up procedure because HCl gas is evolved from the reaction vessel immediately. Therefore, we also find that silica sulfuric acid (I) is an excellent candidate for acid sulfuric replacement in organic reactions without any limitations such as sulfonation of activated aromatic rings and destruction of acid sensitive functional groups.⁹ Since the heterogeneous reagent systems have many advantages such as simple experimental procedures, mild reaction conditions and to minimization of chemical wastes as compared to their liquid phase counterparts.^{8,9} The above facts, encouraged us to seek a completely heterogeneous system for the oxidation of various alcohols. In this article we would like to report a simple and convenient method for the effective conversion of alcohols (1) to their corresponding aldehyde or ketone derivatives (2) under mild and heterogeneous conditions (Scheme 1).



Different types of alcohols (1) were subjected to oxidation reaction in the presence of silica sulfuric acid (I), KMnO₄ (II), and wet SiO₂ in dichloromethane or toluene. The oxidation reactions were performed under mild and completely heterogeneous conditions with excellent yields (Table 1). It was also observed that the oxidation of primary alcohols (1) gives only aldehyde.



Scheme 1

The present oxidation reaction can be readily carried out only by placing silica sulfuric acid (I), KMnO₄ (II), and wet SiO₂ in dichloromethane or toluene in a reaction vessel and efficiently stirring the resulting heterogeneous mixture under reflux conditions. The highly pure aldehyde or ketone derivative (2) can be obtained by simple filtration and evaporation

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