

## Silica Sulfuric Acid/Potassium Permanganate/Wet SiO<sub>2</sub> as an Efficient Heterogeneous Method for the Oxidation of Alcohols under Mild Conditions

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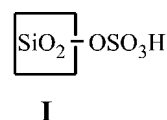
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For oxidation of organic functionalities, one turns often to high-valent metal oxides or their mineral salts.<sup>1</sup> Classic reagents of this type are manganese dioxide (MnO<sub>2</sub>), potassium permanganate (KMnO<sub>4</sub>), chromium trioxide (CrO<sub>3</sub>), potassium chromate (K<sub>2</sub>CrO<sub>4</sub>), and potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>).<sup>2</sup> 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.<sup>3</sup> For instance, overoxidation of aldehydes to carboxylic acids is often unavoidable side reaction.

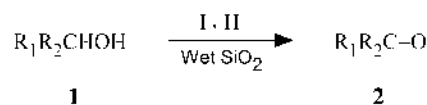
Furthermore, the elevated reflux temperatures required by some oxidation procedures will favor inopportune secondary reactions. Likewise, the presence of strong acids or bases, which are required adjuncts as catalysts for some reactions, often leads to detrimental side reactions. As an example, the oxidation 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.<sup>4</sup>

Along this line, we have introduced potentially useful oxidants for selective oxidation and oxidative deprotection of different functional groups.<sup>5</sup> 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.<sup>6</sup> 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.<sup>7</sup> In continuation of our studies on the application of inorganic acidic salts<sup>8</sup> 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.<sup>9</sup> 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.<sup>8,9</sup> 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), KMnO<sub>4</sub> (II), and wet SiO<sub>2</sub> 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), KMnO<sub>4</sub> (II), and wet SiO<sub>2</sub> 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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**Table 1.** Oxidation of various alcohols to aldehyde and ketones by silica sulfuric acid (I),  $\text{KMnO}_4$  (II), and wet  $\text{SiO}_2$  60% w/w in organic solvent under heterogeneous condition

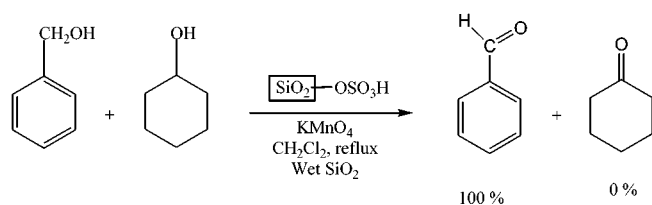
Entry	Substrate	Product	Substrate (mmole)	$\text{KMnO}_4$ (mmole)	Wet $\text{SiO}_2$ (g)	Silica Sulfuric Acid (g)	Solvent	Condition	Time (min)	Yield <sup>a</sup> (%)
1	Benzyl alcohol	Benzaldehyde	2	1	0.16 0.25	0.16 0.25	$\text{CH}_2\text{Cl}_2$	Reflux	30	95 100
2	Cyclohexanol	Cyclohexanone	2	1	0.24	0.24	$\text{CH}_2\text{Cl}_2$	Reflux	30	80
3	<i>m</i> -Methoxy benzylalcohol	<i>m</i> -Methoxy benzaldehyde	2	1	0.24	0.24	Toluene	Reflux	30	98
4	Hydroquinone	<i>p</i> -Benzoquinone	2	1	0.24	0.24	$\text{CH}_2\text{Cl}_2$	Reflux	30	99
5	Benzhydrol	Benzophenone	2	1	0.24	0.24	Toluene	Reflux	30	95
6	1-Hexanol	Hexanal	2	1	0.24	0.24	$\text{CH}_2\text{Cl}_2$	Reflux	30	80
7	Benzoin	Benzil	2	1	0.24	0.24	$\text{CH}_2\text{Cl}_2$	Reflux	60	65
8	<i>P</i> -Chloro benzylalcohol	<i>P</i> -Chloro benzaldehyde	2	1	0.24	0.24	$\text{CH}_2\text{Cl}_2$	Reflux	30	98
9	2-Pentanol	2-Pentanone	2	1	0.24	0.24	$\text{CH}_2\text{Cl}_2$	Reflux	30	85
10	1-Butanol	Butanal	2	1	0.24	0.24	$\text{CH}_2\text{Cl}_2$	Reflux	30	95
11	Benzopinacol	Benzophenone	1	0.5	0.12	0.12	Toluene	Reflux	30	99
12	Mandelic Acid	Benzaldehyde	1	0.5	0.14	0.14	Toluene	Reflux	30	60
13	Benzylalcohol + Cyclohexanol	Benzaldehyde	2 + 2	1	0.24	0.24	$\text{CH}_2\text{Cl}_2$	Reflux	30	98 0

<sup>a</sup>Isolated yields.

of the solvent. The results and reaction conditions are tabulated in the Table 1.

Since transition metal cations are highly toxic and carcinogenic species, its application with any dispersion is very interesting for organic and biochemists. In this article, a new procedure with clean work-up and easy removal of chemical waste (due to the heterogeneous nature) was described. In contrast to the reported procedure for the oxidation of alcohols by using pyridinium chlorochromate (PCC) both in solution<sup>10</sup> and solvent free conditions,<sup>11</sup> we observed a good chemoselectivity between aliphatic and benzylic alcohols. In order to show the chemoselectivity of the method we have carried out the successful oxidation of benzyl alcohol in the presence of cyclohexanol (Scheme 2 and Entry 13).

In conclusion, the cheapness and the availability of the reagents, easy and clean work-up, and high yields make this method attractive for the large-scale operations. This procedure is very simple and contamination by over oxidation side-products is avoided. Moreover, the new element here is that the reaction is heterogeneous. This could be worthwhile for overcoming of the limitations of chromium based oxidant. We believe that the present methodology would be an important addition to existing methodologies.

**Scheme 2**

## Experimental Section

**General.** Chemicals such as alcohols, potassium permanganate, toluene, dichloromethane and silica gel were purchased from Fluka, Merck and Aldrich chemicals companies. Silica sulfuric acid was synthesized according to the our previously reported procedure.<sup>9</sup> The oxidation products were characterized by comparison of their spectral (IR, <sup>1</sup>H-NMR), TLC and physical data with the authentic samples.

**Oxidation of hydroquinone to *p*-benzoquinone, a typical procedure.** A mixture of hydroquinone (0.22 g, 2 mmole), potassium permanganate (0.158 g, 1 mmole), silica sulfuric acid (0.24 g) and wet  $\text{SiO}_2$  (60% w/w, 0.24 g) in 3 mL dichloromethane was stirred under reflux condition for 30 minutes. The heterogeneous mixture was filtered and the solvent was removed under reduced pressure. The solid was crystallized by *n*-hexane. The *p*-benzoquinone was obtained in quantitative yield.

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