

**SILICA SULFURIC ACID/ $\text{KBrO}_3$ /WET  $\text{SiO}_2$  AS AN EFFICIENT  
HETEROGENEOUS SYSTEM FOR THE OXIDATION OF ALCOHOLS  
UNDER MILD CONDITIONS**

**BiBi Fatemeh Mirjalili,<sup>a</sup> Mohammad Ali Zolfigol,<sup>\*b</sup> Abdolhamid Bamoniri,<sup>c</sup> Zahra Zaghaghi,<sup>a</sup> and Azizeh Hazar<sup>a</sup>**

<sup>a</sup> Department of Chemistry, College of Science, Yazd University, Yazd. P.O. Box. 89195-741, Iran.

<sup>b</sup> Department of Chemistry, College of Science, Bu-Ali Sina University, Hamadan. Zip Code 65174, P.O. Box 4135, Iran, E-mail: Zolfi@basu.ac.ir.

<sup>c</sup> Department of Chemistry, College of Science, Kashan University, Kashan, Zip Code 51167, Iran.

Received 07-11-2002

**Abstract**

A combination of silica sulfuric acid and potassium bromate in the presence of wet  $\text{SiO}_2$  were used as an effective oxidizing agent for the oxidation of alcohols to their corresponding aldehyde or ketone derivatives in dichloromethane, acetonitrile or toluene with good yields.

**Introduction**

For oxidation of organic functionalities, one turns often to high-valent metal oxides or their mineral salts.<sup>1</sup> Classical reagents of this type are manganese dioxide ( $\text{MnO}_2$ ), potassium permanganate ( $\text{KMnO}_4$ ), chromium trioxide ( $\text{CrO}_3$ ), potassium chromate ( $\text{K}_2\text{CrO}_4$ ), and potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ).<sup>2</sup> These are all frequently-used reagents, either in the laboratory or in industry, and yet they are beset with multiple liability. For satisfactory and reproducible results, these oxidants demand rigorous 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.

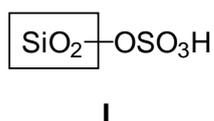
Furthermore, the elevated reflux temperatures required by some oxidation procedures will favor inopportune secondary reactions. Likewise, the presence of strong acids or bases, which are required adjuncts as catalysts for some reactions, often leads to detrimental side reactions. As an example, the oxidation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

aldehydes by a chromium(VI) salt in sulfuric acid is often accompanied by the formation of an 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. 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 and silica chloride,<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 to replace sulfuric acid in organic reactions without any limitations such as sulfonation of activated aromatic rings and destruction of acid sensitive functional groups.<sup>9-13</sup> Since the heterogeneous reagent systems have many advantages such as simple experimental procedures, mild reaction conditions and minimization of chemical wastes as compared to their liquid phase counterparts.<sup>8-10</sup> Our goal, in undertaking this line of work, was two-fold: (a) to overcome the limitations and drawbacks of the reported methods such as: tedious work-up, strongly acidic media ( $H_0 \sim -8$ ), and safety problems (storage, handling, using and also presence of toxic transition metal cations such as  $Cr^{+3}$ ,  $Hg^{+2}$ ,  $Cu^{+2}$  within molecular structure of the reagents), (b) moreover, high-yielding production of carbonyl compounds using a novel combination of reagents are our main interest. The above facts, encouraged us to seek a completely heterogeneous system for the oxidation of various alcohols, and we have investigated a number of different reaction conditions based upon the *in situ* generation of  $HBrO_3$  at the surface of  $SiO_2$  in low concentration by inorganic acidic resin i.e. silica sulfuric acid and potassium bromate.

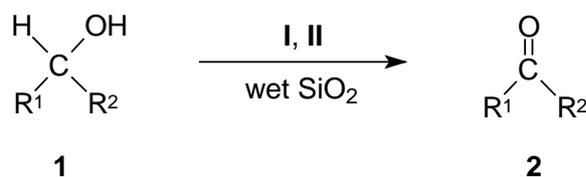
## Results and discussion

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 heterogeneous conditions (Scheme 1).



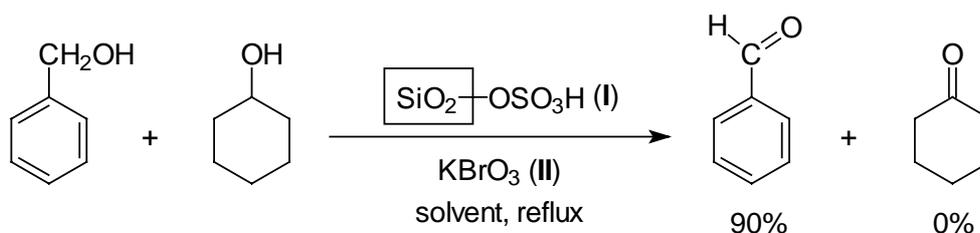
Different types of alcohols (**1**) were subjected to oxidation reaction in the presence of silica sulfuric acid (**I**),  $\text{KBrO}_3$  (**II**), and wet  $\text{SiO}_2$  in dichloromethane, acetonitrile or toluene. The oxidation reactions were performed under completely heterogeneous conditions with good to excellent yields (Table). It was also observed that the oxidation of primary alcohols (**1**) gives only aldehydes.

The present oxidation reaction can be readily carried out only by placing silica sulfuric acid (**I**),  $\text{KBrO}_3$  (**II**), and wet  $\text{SiO}_2$  in dichloromethane, acetonitrile or toluene in a reaction vessel with efficiently stirring the resulting heterogeneous mixture under reflux conditions. The results and reaction conditions are shown in the Table.



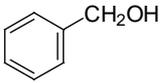
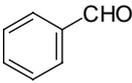
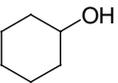
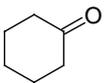
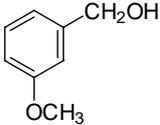
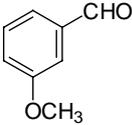
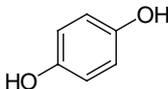
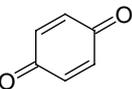
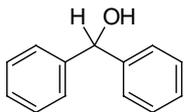
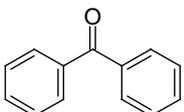
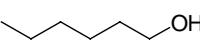
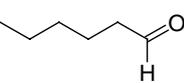
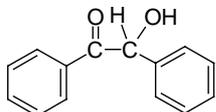
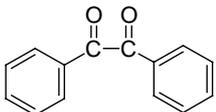
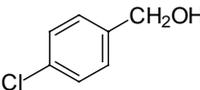
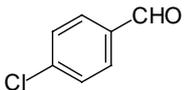
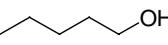
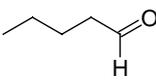
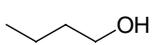
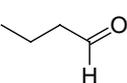
**Scheme 1**

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 11).



**Scheme 2**

**Table.** Oxidation of various alcohols (2.5 mmol) to aldehyde and ketons by silica sulfuric acid (**I**) (0.2 g),  $\text{KBrO}_3$  (**II**) (1 mmol, 0.16 g), and wet  $\text{SiO}_2$  (60% w/w, 0.2 g) in organic solvent under heterogeneous condition.

Entry	Substrate	Product	Solvent	Conditions	Time (min)	Yield (%)
1			$\text{CH}_3\text{CN}$	Reflux	45	90
2			$\text{CH}_2\text{Cl}_2$	R.T.	30	95
3			$\text{PhCH}_3$	Reflux	60	60
4			$\text{CH}_2\text{Cl}_2$	R.T.	30	97
5			$\text{CH}_2\text{Cl}_2$	Reflux	90	70
6			$\text{CH}_3\text{CN}$	Reflux	45	85
7			$\text{PhCH}_3$	Reflux	60	70
8			$\text{CH}_2\text{Cl}_2$	Reflux	30	95
9			$\text{CH}_3\text{CN}$	Reflux	45	85
10			$\text{CH}_3\text{CN}$	Reflux	45	88
11	Benzyl alcohol + Cyclohexanol	Benzaldehyde + Cyclohexanone	$\text{CH}_3\text{CN}$	Reflux	45	90 0

### Conclusions

The cheapness and the availability of the reagents, and excellent 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 oxidation reaction occurred under heterogeneous conditions. We believe that the present method would be an important addition to existing methodologies.

### Experimental

**General:** Chemicals such as alcohols, potassium bromate, dichloromethane, toluene, acetonitrile and silica gel were purchased from Fluka, Merck and Aldrich chemical companies. Silica sulfuric acid was synthesized according to our previously reported procedure.<sup>9-11</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 (0.275 g, 2.5 mmol), potassium bromate (0.167 g, 1 mmol), silica sulfuric acid (0.2 g) and wet SiO<sub>2</sub> (60% w/w, 0.2 g) in dichloromethane (5 mL) was stirred at room temperature for 30 minutes. The heterogeneous mixture was filtered and washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (10%, 2×20 mL). The organic phase was collected. Anhydrous Na<sub>2</sub>SO<sub>4</sub> (2 g) was added to the solution and filtered after 15 minutes. Dichloromethane was removed. The solid was crystallized from *n*-hexane. The *p*-benzoquinone was obtained in good yield (Table).

### Acknowledgements

Financial support for this work by the research affairs, Yazd University, Yazd, Iran and also Bu-Ali Sina University, Hamadan, Iran are gratefully acknowledged.

### References

1. M. Hudlicky, *Oxidation in Organic Chemistry*, ACS Monograph, 1990, pp 186.
2. B. M. Trost, *Comprehensive Organic Synthesis (Oxidation)*, Pergamon press, New York, 1991, Vol. 7.
3. E. W. Warnhoff, D. G. Martin, W. S. Johnson, *Org. Syn.* **1963**, *4*, 162–163.
4. H. O. House, *Modern Synthetic Reactions*, 2nd ed. W. A. Benjamin: Menlo Park, CA, 1972, pp 257-291.
5. (a) H. Firouzabadi, N. Iranpoor, M. A. Zolfigol, *Synth. Commun.* **1998**, *28*, 377–385.  
(b) H. Firouzabadi, N. Iranpoor, M. A. Zolfigol, *Synth. Commun.* **1998**, *28*, 1179–1187.  
(c) N. Iranpoor, H. Firouzabadi, M. A. Zolfigol, *Synth. Commun.* **1998**, *28*, 367–375.  
(d) H. Firouzabadi, N. Iranpoor, M. A. Zolfigol, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2169–2173.  
(e) N. Iranpoor, H. Firouzabadi, M. A. Zolfigol, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 905–909.  
(f) F. Shirini, M. A. Zolfigol, B. Mallakpour, S. E. Mallakpour, A. R. Hajipour, *Aust. J. Chem.* **2001**, *54*, 405–406.

6. J. M. Riego, Z. Sedin, J. M. Zaldivar, N. C. Marziano, C. Tortato, *Tetrahedron lett.* **1996**, *37*, 513-516.
7. N. J. Turro, *Tetrahedron* **1987**, *43*, 7, 1589–1616.
8. (a) F. Shirini, M. A. Zolfigol, B. Mallakpour, S. E. Mallakpour, A. R. Hajipour, I. M. Baltork, *Tetrahedron Lett.* **2002**, *43*, 1555–1556. (b) M. A. Zolfigol, M. Torabi, S. E. Mallakpour, *Tetrahedron* **2001**, *57*, 8381–8384, and references cited therein.
9. M. A. Zolfigol, *Tetrahedron* **2001**, *57*, 9509–9511.
10. B. F. Mirjalili, M. A. Zolfigol, A. Bamoniri, *J. Korean Chem. Soc.* **2001**, *45*, 546–548.
11. Zolfigol, M. A. Bamoniri, A. *Synlett* **2002**, *10*, 1621–1624.
12. B. F. Mirjalili, M. A. Zolfigol, A. Bamoniri, *Molecules* **2002**, *7*, 751–755.
13. B. F. Mirjalili, M. A. Zolfigol, A. Bamoniri, A. Zarei, *Bull. Korean Chem. Soc.* **2003**, *24*, 400–402.

### Povzetek

Za oksidacijo alkoholov v ustrezne aldehide in ketone smo uporabili kombinacijo žveplene kisline na silikagelu, kalijevega bromata in vlažnega SiO<sub>2</sub>. Reakcije so potekle v acetonitrilu, diklorometanu ali toluenu z dobrimi izkoristki.