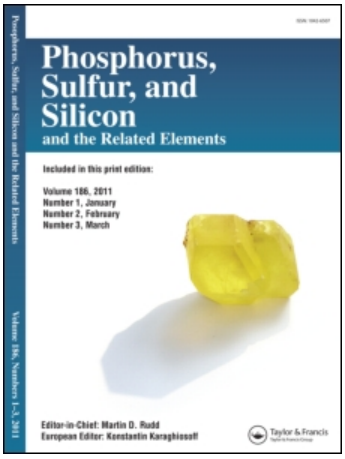

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SILICA SULFURIC ACID/SODIUM DICHROMATE DIHYDRATE AS AN EFFICIENT HETEROGENEOUS METHOD FOR THE OXIDATION OF ALCOHOLS UNDER MILD CONDITIONS

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A combination of silica sulfuric acid and sodium dichromate dihydrate in the presence of wet SiO_2 were used as an effective oxidizing agent for the oxidation of alcohols to their corresponding aldehyde or ketone derivatives in dichloromethane or toluene with excellent yields.

Keywords: Alcohols; aldehydes; oxidation; silica sulfuric acid; sodium dichromate dihydrate

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 (MnO_2), potassium permangenate ($KMnO_4$), chromium trioxide (CrO_3), potassium chromate (K_2CrO_4), and potassium dichromate ($K_2Cr_2O_7$).[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. Other drawbacks against such oxidants and their use in multistage organic synthesis, in spite of their power, are their lack of selectivity, strong protic and aqueous conditions, low yields of the products, and tedious work-up.[3] For instance, over-oxidation of aldehydes to carboxylic acids is often an unavoidable side reaction.

Furthermore, the elevated reflux temperatures required by some oxidation procedures will favor inopportune secondary reactions. Likewise,

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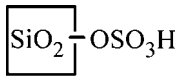
the presence of strong acids or bases, which are required adjuncts as catalysts for some reactions, often leads to detrimental side reactions. As an example, the oxidation of primary alcohols to aldehydes by a chromium (VI) salt in sulfuric acid often is accompanied by formation of an hemiacetal between the resulting aldehyde and the alcohol substrate, followed 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 investigate a new reagent or reagent systems to overcome the above limitations. In addition, for our propose a clean and easy work-up also were important. On the other hand, any reduction in the amount of sulfuric acid needed 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 solid acids[8] 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 condidate for acid sulfuric replacement in organic reactions without any limitations such as sulfonation of activated aromatic rings and destruction of acid sensitive functional groups.[9–12] Furthermore, 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.[8–12] 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 H_2CrO_4 at the surface of SiO_2 in low concentration by inorganic acidic resin, i.e., silica sulfuric acid and sodium dichromate dihydate. In this article we 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).



I

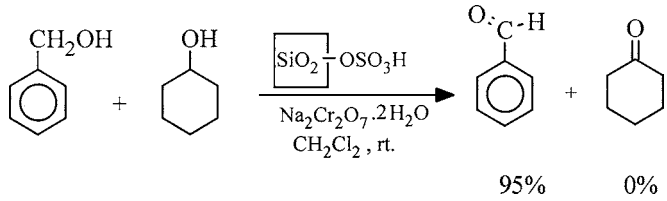
Different types of alcohols (**1**) were subjected to oxidation reaction in the presence of silica sulfuric acid (**I**), $Na_2Cr_2O_7 \cdot 2H_2O$ (**II**), and wet SiO_2 in dichloromethane or toluene. The oxidation reactions were performed under mild and completely heterogeneous conditions with excellent yields (Table I). It was also observed that the oxidation of primary alcohols (**1**) gives only aldehyde.

1 **2**

SCHEME 1

The present oxidation reaction can be readily carried out only by placing silica sulfuric acid (**I**), $Na_2Cr_2O_7 \cdot 2H_2O$ (**II**), and wet SiO_2 in dichloromethane or toluene in a reaction vessel and efficiently stirring the resulting heterogeneous mixture at room temperature or under reflux conditions. The highly pure aldehyde or ketone derivative (**2**) can be obtained by simple filtration and evaporation of the solvent. The results and reaction conditions are tabulated in the Table I.

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 Table I, entry 13).



SCHEME 2

In conclusion, the low cost 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 is an important addition to existing methodologies.

TABLE I Oxidation of Various Alcohols to Aldehyde and Ketons by Silica Sulfuric Acid (**I**), $Na_2Cr_2O_7 \cdot 2H_2O$ (**II**), and Wet SiO_2 60% w/w in Organic Solvent under Heterogeneous Conditions

Entry	Substrate	Product	Substrate (mmol)	$Na_2Cr_2O_7$ (mmol)	Wet SiO_2 (g)	Silica Sulfuric Acid (g)	Solvent	Condition	Time (min)	Yield (%)
1	Benzyl alcohol	Benzaldehyde	2.9	1	0.15	0.15	CH_2Cl_2	R.T.	15	90
					0.3	0.3				95
2	Cyclohexanol	Cyclohexanone	4.3	1.8	0.45	0.45	CH_2Cl_2	Reflux	30	80
					0.27	0.27	Toluene			95
3	m-Methoxy benzylalcohol	m-Methoxy benzaldehyde	1.8	6.4	0.1	0.1	Toluene	Reflux	35	90
4	Hydroquinone	p-Benzoquinone	1	0.33	0.05	0.05	CH_2Cl_2	R.T.	25	99
5	Benzhydrol	Benzophenone	3	1	0.15	0.15	Toluene	Reflux	60	90
6	1-Hexanol	Hexanal	3	1	0.15	0.15	CH_2Cl_2	Reflux	35	80
7	Benzoin	Benzil	3	1.3	0.2	0.2	Toluene	Reflux	60	60
8	P-Chloro benzylalcohol	P-Chloro benzaldehyde	3	1	0.15	0.15	CH_2Cl_2	R.T.	40	90
9	2-Pentanol	2-Pentanone	3	1	0.15	0.15	CH_2Cl_2	R.T.	40	80
					0.3	0.3			30	99
10	1-Butanol	Butanal	3	1	0.15	0.15	CH_2Cl_2	Reflux	30	90
11	Benzopinacol	Benzophenone	0.3	0.1	0.015	0.015	Toluene	Reflux	30	99
12	Mandelic Acid	Benzaldehyde	0.75	0.25	0.037	0.037	Toluene	Reflux	30	65
13	Bezylalcohol + Cyclohexanol	Benzaldehyde	2.9 + 5.8	1	0.15	0.15	CH_2Cl_2	R.T.	30	100 13

EXPERIMENTAL SECTION

General

Chemicals such as alcohols, sodium dichromate dihydrate, 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.[9,10] The oxidation products were characterized by comparison of their spectral (IR, ^{1}H-NMR), TLC, and physical data with the authentic samples.

Oxidation of Hydroquinone to *p*-Benzoquinone. A Typical Procedure

A mixture of hydroquinone (0.1 g, 1 mmol), sodium dichromate dihydrate (0.1 g, 0.33 mm), silica sulfuric acid (0.05 g), and wet SiO_2 (60% w/w, 0.05 g) in 3 mL of dichloromethane was stirred at room temperature for 25 min. 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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