

Solvent-free Oxidation of Alcohols by Silica Sulfuric Acid/Sodium Dichromate Dihydrate or Potassium Permanganate/Wet SiO₂ System

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A combination of silica sulfuric acid and sodium dichromate dihydrate or potassium permanganate in the presence of wet SiO₂ was used as an effective oxidizing agent for oxidation of alcohols to their corresponding aldehydes or ketones in solvent free conditions.

Keywords: Silicasulfuric acid; Oxidation; Alcohols; Solvent free.

INTRODUCTION

Recently, some chemists found that many reactions proceed efficiently in the solid state. In deed, in many cases, solid state organic reaction occurs more efficiently and more selectively than does its solution counterpart. The solvent free reaction has many advantages such as reduced pollution, low costs, simplicity in process, and easier work-up. These factors are especially important in industry.¹

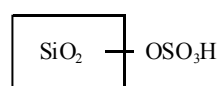
For oxidation of organic functionalities, one turns often to transition metal catalysts,² high-valent metal oxides or their mineral salts.³ Classic reagents of this type are manganese dioxide (MnO₂), potassium permanganate (KMnO₄), chromium trioxide (CrO₃), potassium chromate (K₂CrO₄), and potassium dichromate (K₂Cr₂O₇),⁴ and pyridinium chlorochromate.⁵ These are all frequently-used reagents, whether in the laboratory or in industry, and yet they are beset with multiple liabilities. 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 or 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. For instance, overoxidation 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, 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, followed by the ready oxidation of this intermediate to an ester.⁶

RESULTS AND DISCUSSION

We have introduced potentially useful oxidants for selective oxidation and oxidative deprotection of different functional groups.⁷ Therefore, we decided to choose a new reagent or reagent systems to overcome the above limitations. In addition, for our purpose 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 advantages, and environmental protection.⁸ In addition, there is current research and general interest in solvent free systems because of the importance such systems have in industry and in developing technologies.⁹ In continuation of our studies on the application of inorganic acidic salts we found that silica sulfuric acid (**I**) is an excellent candidate for acid sulfuric replacement in organic reactions without any limitations such as destruction of acid sensitive functional



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Table 1. Oxidation of Various Alcohols to Aldehyde and Ketones by Silica Sulfuric Acid (I), Na₂Cr₂O₇·2H₂O (II), and Wet SiO₂ 60% w/w in Solvent Free Conditions

Entry	Substrate	Product	Substrate (mmole)	Na ₂ Cr ₂ O ₇ ·2H ₂ O (mmole)	Wet SiO ₂ (g)	Silica Sulfuric Acid (g)	Condition	Time (min)	Yield ^a (%)
1	Benzyl alcohol	Benzaldehyde	2.9	1	0.35	0.15	r.t	30	95
2	Cyclohexanol	Cyclohexanone	4.38	1.85	0.45	0.45	r.t	30	65
3	m-Methoxy benzylalcohol	m-Methoxy benzaldehyde	1.85	0.64	0.35	0.1	r.t	30	90
4	Hydroquinone	p-Benzoquinone	1	0.33	0.3	0.05	r.t	30	95
5	Benzhydrol	Benzophenone	3	1	1	0.15	r.t with grinding	30	90
6	1-Hexanol	Hexanal	3	1	0.25	0.15	r.t	30	70
7	Benzoin	Benzil	3	1.3	2	0.2	r.t with grinding	60	30
8	P-Chloro benzylalcohol	P-Chloro benzaldehyde	3	1	0.35	0.15	r.t	30	90
9	2-Pentanol	2-Pentanone	3	1	0.25	0.15	r.t	30	70
10	1-Butanol	Butanal	3	1	0.25	0.15	r.t	30	95
11	Mandelic Acid	Benzaldehyde	0.75	0.25	0.9	0.037	r.t with grinding	60	40
12	Bezylalcohol + Cyclohexanol	Benzaldehyde	0.3 + 0.3	1	0.35	0.15	r.t	30	95 ^b
									0

^a Isolated yields.^b Competitive reaction.Table 2. Oxidation of Various Alcohols to Aldehyde and Ketones by Silica Sulfuric Acid (I), KMnO₄ (II), and Wet SiO₂ 60% w/w under Solvent Free Conditions

Entry	Substrate	Product	Substrate (mmole)	KMnO ₄ (mmole)	Wet SiO ₂ (g)	Silica Sulfuric Acid (g)	Condition	Time (min)	Yield ^a (%)
1	Benzyl alcohol	Benzaldehyde	2	1	0.35	0.35	r.t	30	90
2	Cyclohexanol	Cyclohexanone	2	1	0.24	0.4	r.t	30	70
3	m-Methoxy benzylalcohol	m-Methoxy benzaldehyde	2	1	0.24	0.35	r.t	30	90
4	Hydroquinone	p-Benzoquinone	2	1	0.24	0.5	r.t	30	95
5	Benzhydrol	Benzophenone	2	1	0.24	1	r.t with grinding	30	90
6	1-Hexanol	Hexanal	2	1	0.24	0.4	r.t	30	70
7	Benzoin	Benzil	2	1	0.24	1	r.t with grinding	30	30
8	p-Chloro benzylalcohol	p-Chloro benzaldehyde	2	1	0.24	0.35	r.t	30	95
9	2-Pentanol	2-Pentanone	2	1	0.24	0.4	r.t	30	80
10	1-Butanol	Butanal	2	1	0.24	0.4	r.t	30	90
11	Mandelic Acid	Benzaldehyde	1	0.5	0.14	0.5	r.t with grinding	30	35
12	Bezylalcohol + Cyclohexanol	Benzaldehyde	2 + 2	1	0.35	0.35	r.t	30	90 ^b
									0

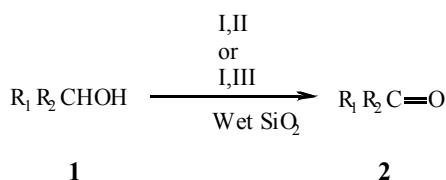
^a Isolated yields.^b Competitive reaction.

groups.¹⁰ 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.¹⁰⁻¹³ The above facts en-

couraged 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 aldehydes

or ketones (**2**) under mild and solvent free conditions (Scheme I).

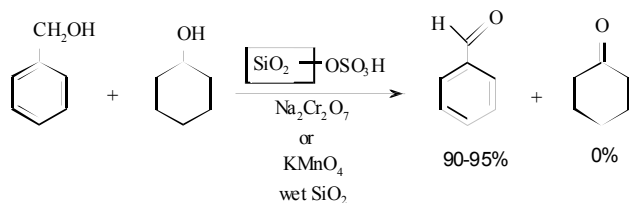
Scheme I



In this work, different types of alcohols (**1**) were subjected to oxidation reaction in the presence of silica sulfuric acid (**I**), $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (**II**) or KMnO_4 (**III**), and wet SiO_2 (60% w/w) without any solvent. The oxidation reactions were performed under mild and solvent free conditions with excellent yields (Tables 1 and 2). It was also observed that the oxidation of primary alcohols (**1**) gives only aldehyde.

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 II and Entry 13 in both tables).

Scheme II



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

EXPERIMENTAL SECTION

General

Chemicals such as alcohols, sodium dichromate dihydrate, potassium permanganate, dichloro methane and silica gel 60 (0.040-0.063 mm, cat. No = 109385, Merck) were pur-

chased from Fluka, Merck and Aldrich chemical companies. Silica sulfuric acid was synthesized according to the previously reported procedure.^{10,11} The oxidation products were characterized by comparison of their spectra (IR, ¹H NMR), TLC and physical data with the authentic samples.

Oxidation of hydroquinone to *p*-benzoquinone, a typical procedure

A mixture of hydroquinone (0.12 g, 1 mmole), potassium permanganate (0.1 g, 0.33 mmole), silica sulfuric acid (0.05 g) and wet SiO_2 (60% w/w, 0.3 g) in a vessel was shaken for 30 minutes. Then 10 mL of CH_2Cl_2 as solvent was added to the vessel, and the heterogeneous mixture was filtered. 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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