

Silica chromate as an oxidising agent for the chemoselective oxidation of alcohols and the oxidative deprotection of trimethylsilyl ethers

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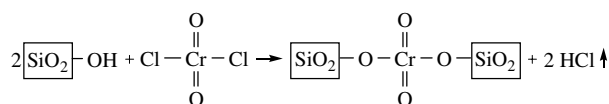
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Silica chromate easily converts primary and secondary alcohols to corresponding carbonyl compounds in the presence of wet SiO₂ both in dichloromethane and under solvent-free conditions at room temperature with good to excellent yields. Primary and secondary trimethylsilyl ethers were converted into the corresponding carbonyl compounds or alcohols by using silica chromate and wet SiO₂ in dichloromethane at room temperature with good to excellent yields.

The oxidation of alcohols to carbonyl compounds is one of the most important reactions in synthetic organic chemistry.^{1–18} It is of interest to use heterogeneous systems for performing oxidation in industry and technologies.^{19,20}

The aim of this work was to overcome the limitations and drawbacks of the reported methods such as tedious work-up, acidic media, and safety problems. Solvent-free organic synthesis seems a highly useful technique, especially, for industry, and it has many advantages.^{21–23} Moreover, we attempted to develop a high-yielding conversion of alcohols into aldehydes and ketones using a synthetic silica-based oxidant.

In continuation of our previous studies,²⁴ we found that silica gel reacts with dichloro chromium oxide to give silica chromate. Note that the reaction is easy and clean without any work-up procedure because HCl gas is evolved from the reaction vessel immediately (Scheme 1).[†] Here we report a simple, cheap, mild and chemoselective method for the effective oxidation of alcohols to corresponding carbonyl compounds using silica



Scheme 1

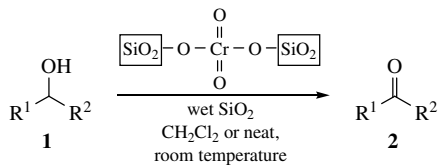
chromate in the presence of wet SiO₂ both in solution and under solvent-free conditions.[‡]

[†] Chemicals were purchased from Fluka, Merck and Aldrich. The oxidation products were characterised by comparison of their spectral (IR, ¹H NMR), TLC and physical data with those for authentic samples.

[‡] *Preparation of silica chromate.* A 500 ml suction flask was equipped with a constant-pressure dropping funnel containing dichloro chromium oxide (23.2 g, 0.15 mol) and a gas inlet tube for conducting HCl gas over an adsorbing solution (water). Silica gel (100 g) was placed in the flask and dichloro chromium oxide was added dropwise for 20 min at room temperature. After the addition, the mixture was shaken for 90 min. A brown solid (silica chromate) was obtained quantitatively.

Different primary and secondary alcohols **1** were subjected to oxidation in the presence of silica chromate and wet SiO₂ in dichloromethane or under solvent-free conditions at room temperature (Scheme 2, Table 1).

An allylic alcohol was converted to the corresponding carbonyl compound in high yields and carbon-carbon double bonds were intact in the course of reaction (Table 1, entry 18).



We observed that the secondary hydroxyl group in 1-phenyl-1,2-ethanediol was selectively oxidised into the corresponding ketone both in solution and under solvent-free conditions (Scheme 3, Table 1, entry 14).

Although oxidation reactions were performed in the absence of wet SiO₂ (50/50, w/w) only by using silica chromate, the reaction time increased (Scheme 4 and Table 1, entries 2 and 17). The oxidation did not occur in the absence of silica

Table 1 Oxidation of alcohols **1** to carbonyl compounds **2** with a combination of silica chromate and wet SiO₂ (50%) in dichloromethane (A) and under solvent-free conditions (B) at room temperature.^a

Entry	Substrate ^a 1	Product 2	t/min for A (B)	Yield (%) ^b for A (B)
1	Benzyl alcohol	Benzaldehyde	35 (2)	90 (93)
2	Benzyl alcohol	Benzaldehyde	60 (30)	91 (88) ^c
3	2-Phenylethanol	2-Phenylethanal	120 (110)	91 (93)
4	2-Phenylpropan-1-ol	2-Phenylpropan-1-al	115 (115)	92 (93)
5	2,4-Dichlorobenzyl alcohol	2,4-Dichlorobenzaldehyde	30 (25)	91 (90)
6	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	30 (20)	90 (92)
7	Heptan-1-ol	Heptan-1-al	25 (15)	89 (91)
8	Cyclohexanol	Cyclohexanone	25 (20)	90 (90)
9	Pentan-1-ol	Pentan-1-al	25 (15)	88 (91)
10	3-Methylbutan-1-ol	3-Methylbutan-1-al	60 (40)	90 (100) ^d
11	Butan-2-ol	Butan-2-one	15 (15)	89 (100) ^d
12	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	50 (40)	65 (70) ^d
13	Benzhydrol	Benzophenone	60 (25)	70 (79) ^d
14	1-Phenylethan-1,2-diol	1-Phenyl-2-hydroxyethanone	25 (40)	90 (90)
15	Tetraphenylethyleneglycol	Benzophenone	60 (40)	50 (60) ^d
16	Indan-1-ol	Indan-1-one	15 (45)	91 (92)
17	Indan-1-ol	Indan-1-one	45 (90)	90 (87) ^c
18			20 (20)	92 (91)

^aSilica chromate: wet SiO₂:substrate (0.3 g:0.2 g:1 mmol). ^bIsolated yields. ^cReactions were performed in the absence of wet SiO₂. ^dConversion.

[‡] A typical procedure for oxidation of benzyl alcohol to benzaldehyde in CH₂Cl₂. A suspension of benzyl alcohol (0.54 g, 5 mmol), silica chromate (1.5 g) and wet SiO₂ (1 g, 50% w/w) in CH₂Cl₂ (40 ml) was stirred at room temperature for 40 min (the progress of the reaction was monitored by TLC) and then filtered. The residue was washed with CH₂Cl₂ (40 ml). Anhydrous Na₂SO₄ (4 g) was added to the filtrate and filtered off after 20 min. Dichloromethane was removed. The yield was 0.490 g (92%).

A typical procedure for oxidation of benzyl alcohol to benzaldehyde under solvent-free conditions. A mixture of benzyl alcohol (0.108 g, 1 mmol), silica chromate (0.3 g) and wet SiO₂ (0.2 g, 50% w/w) was shaken at room temperature for 20 min (the progress of the reaction was monitored by TLC). Dichloromethane (10 ml) was added to the reaction mixture and stirred. The suspension was filtered, and the residue was washed with CH₂Cl₂ (20 ml). Anhydrous Na₂SO₄ (2 g) was added to the filtrate and filtered off after 20 min. Dichloromethane was removed. Benzaldehyde was obtained, and the yield was 0.098 g (93%).

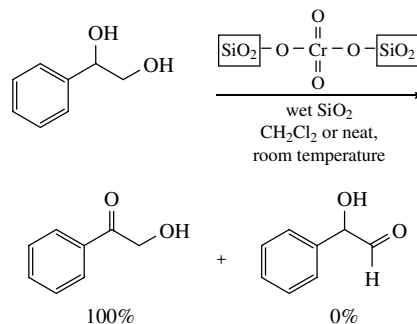
Table 2 Deprotection and oxidative deprotection of trimethylsilyl ethers by silica chromate in the presence of wet SiO₂ in dichloromethane.^a

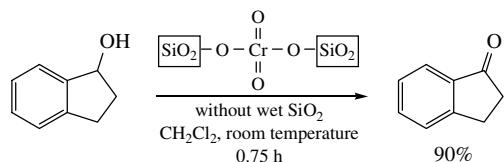
Entry	Substrate	Product	t/min	Yield ^b (%)
1			30	85
2			45	96
3			50	82
4			45	73
5			30	95
6			30	95
7			40	82
8			45	88
9			20	84
10			15	90
11			45	70
12			15	95
13			25	65

^aSubstrate/silica chromate/wet SiO₂ (1 mmol/0.3 g/0.2 g). ^bIsolated yields.

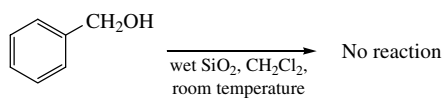
chromate by using wet SiO₂ (50/50, w/w), (Scheme 5). Thus, wet SiO₂ (50/50, w/w) is needed for increasing the reactions rate (Table 1, entries 1, 2, 16 and 17).

Silyl protecting groups have played increasingly important roles in the synthesis of complicated molecules, especially, in the synthesis of biologically significant products.^{25–29} Although there have been many new reports on the protection and deprotection of silyl groups,^{25–43} the removal of silyl groups under mild conditions with easy work-up procedures is also important.



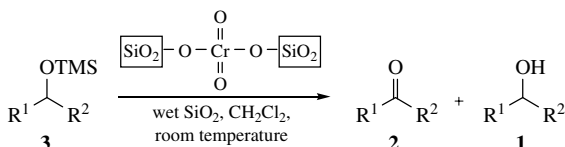


Scheme 4



Scheme 5

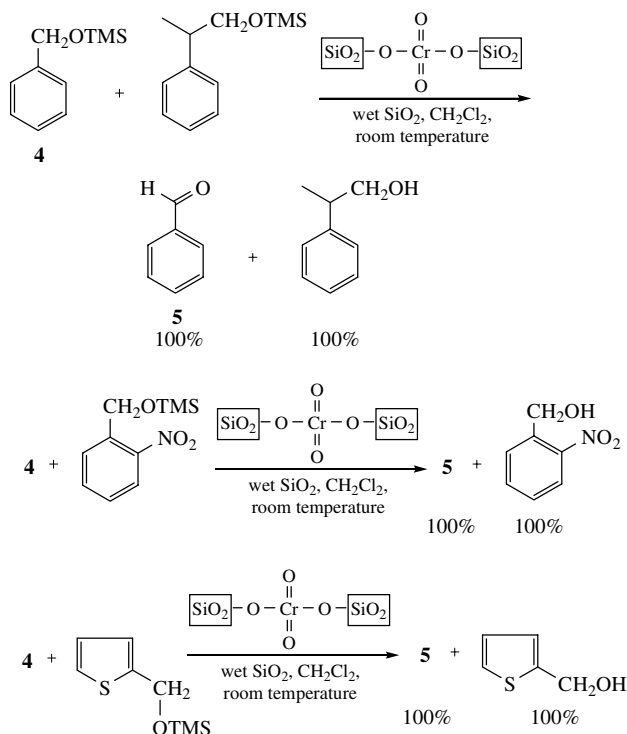
Trimethylsilyl ethers **3** were subjected to the deprotection reaction in the presence of silica chromate and wet SiO₂ in dichloromethane at room temperature with good to excellent yields (Scheme 6 and Table 2).[§]



Scheme 6

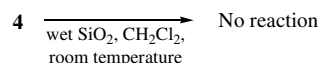
Silica chromate is a very mild and chemoselective oxidant because in the case of aliphatic alcohols (Table 2, entries 8, 9, 11–13) and benzyl alcohols containing electron-withdrawing groups, deprotection did occur. Three competitive reactions (Scheme 7) were carried out.

As shown in Scheme 7 for aliphatic alcohols and electron-deficient aromatic alcohols, only deprotection occurred. Deprotection did not occur when using wet SiO₂ (50/50, w/w) in the absence of silica chromate (Scheme 8).



Scheme 7

[§] *General procedure for the deprotection of trimethylsilyl ethers.* A suspension of trimethylsilyl ether (2 mmol), silica chromate (0.6 g) and wet SiO₂ (0.4 g, 50% w/w) in CH₂Cl₂ (10 ml) was stirred at room temperature for 15–50 min (the progress of the reaction was monitored by TLC) and then filtered. The residue was washed with CH₂Cl₂ (20 ml). Anhydrous Na₂SO₄ (3 g) was added to the filtrate and filtered off after 20 min. Dichloromethane was removed. The pure carbonyl compound or alcohol was obtained.



Scheme 8

To the best of our knowledge, this is the first example of a silica chromium based oxidant with covalent linkages (silica vulcanised with CrO₂ linkages). Thus, we hope that silica chromate would be superior to all of the previously reported chromium-based oxidants^{1–6} because (i) toxic chromium cations could be collected from the reaction mixture easily, (ii) work-up is very simple and pure products obtained solely by filtration and removing of solvent, (iii) no need in chelating agents such as pyridine in pyridinium chlorochromate (PCC).² Moreover, in older procedures, the isolation of oxidation products from the reaction mixture and chelating agents such as pyridine in PCC is difficult.^{2,3}

In conclusion, the cheapness and availability of the reagents, easy and clean work-up and high yields make this method attractive for chemists. We believe that the present methodology could be an important addition to the existing methodologies.

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