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Oxidation of alcohols using $(NH_4)_2Cr_2O_4$ in the presence of $Al(HSO_4)_3$ and wet SiO_2

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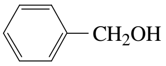
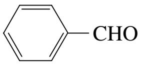
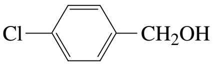
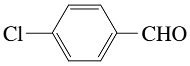
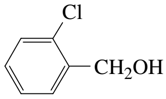
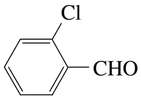
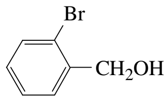
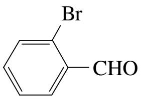
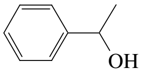
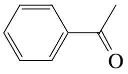
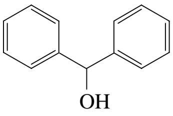
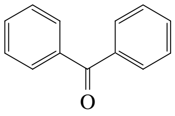
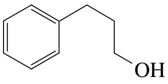
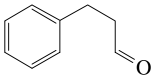
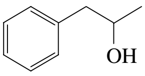
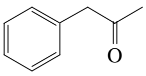
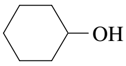
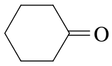
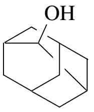
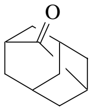
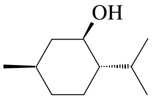
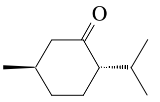
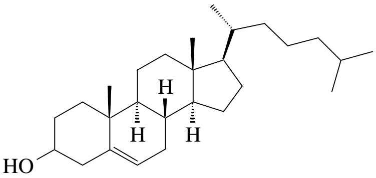
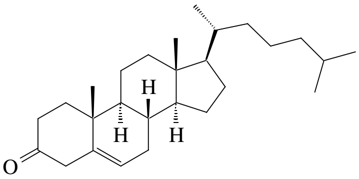
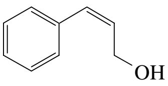
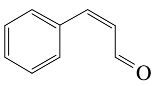
A mild and efficient method for the oxidation of alcohols by ammonium dichromate in the presence of $Al(HSO_4)_3$ and wet SiO_2 in solution or under solvent-free conditions is reported.

Since the appearance of Collins reagent,[1] the development of new Cr^{VI}-based oxidants for the effective and selective oxidation of organic substrates, in particular, alcohols, under mild conditions has attracted attention in organic synthesis. Efficient

Table 1 Oxidation of alcohols by ammonium dichromate in the presence of $Al(HSO_4)_3$ and wet SiO_2.[a]

Entry	Substrate	Product	Oxidation in the absence of solvent		Oxidation in solution	
			Time/h	Yield (%)	Time/h	Yield (%)
1			0.5	92	1	85
2			0.17	95	0.1	90
3			0.75	90	0.08	87
4			0.67	83	0.25	90
5			0.1	90	0.17	89
6			0.3	95	0.3	93
7			1	90	0.5	85
8			1.2	86	0.83	82
9			0.75	90	0.7	90
10			3	90	2.5	82
11			1.5	85	2.2	85
12			2	85	0.5	86
13			1.5	—[b]	1	—[b]

[a]Isolated yield. [b]Mixture of products.

chromium(VI) reagents have been reported, such as *n*-butylphosphonium dichromate,[2] pyridinium chlorochromate,[3,4] pyrazinium dichromate,[5] ferric dichromate,[6] Dowex 1-X8 (on which Cl^- is replaced by dichromate and bisulfate ions),[7] 1,1,3,3-tetramethylguadinium dichromate,[8] γ-picolinium chlorochromate[9] and CrO_3/NBu_4HSO_4.[10]

However, the utility of Cr^{VI} reagents in the oxidative transformation is compromised due to their power, instability, low selectivity, long reaction time, strong protic and aqueous conditions and tedious work-up. Thus, a milder, more selective and inexpensive reagent is still desirable.

Here we report a mild, simple, efficient and convenient method for the oxidation of alcohols into carbonyl compounds in solution and under solvent-free conditions.[†]

The oxidation of alcohols in *n*-hexane as a solvent, using ammonium dichromate in the presence of $Al(HSO_4)_3$ and wet SiO_2 (Scheme 1) at room temperature was studied. Yields and reaction times are given in Table 1. Over-oxidation of the products, using this method, was not observed.

In order to compare the results with those obtained in the absence of a solvent, we studied the oxidation reaction under solvent free conditions (Table 1).

$$R^1R^2CHOH \xrightarrow{\text{i or ii}} R^1R^2CO$$

Scheme 1 *Reagents and conditions*: i, $(NH_4)_2Cr_2O_7/Al(HSO_4)_3$/wet SiO_2, solvent free, room temperature; ii, $(NH_4)_2Cr_2O_7/Al(HSO_4)_3$/wet SiO_2, *n*-hexane, room temperature.

Although, in most cases, by omitting the solvent, the reaction time increased, but the work-up procedure became easier and the need for solvent was avoided. This method is unsuitable for the oxidation of allylic alcohols (Table 1, entry 13).

Table 2 Comparison of the results obtained by oxidation with ammonium dichromate in the presence of $Al(HSO_4)_3$ and wet SiO_2 (1), with published data for 1,1,3,3-tetramethylguanidium dichromate (2)[8] and γ-picolinium chlorochromate (3).[9]

Entry	Substrate	Oxidant/substrate, time/h, yield (%)		
		(1)	(2)	(3)
1	Benzyl alcohol	0.3, 0.5, 92	2, 4, 93	1, 0.3, 75
2	Diphenylcarbinol	0.3, 0.25, 95	2, 8, 98	1, 0.3, 92

Note that oxidation did not proceed with ammonium dichromate, $Al(HSO_4)_3$ or wet SiO_2 alone, even after prolonged heating. These results can be explained by the probable *in situ* generation of H_2CrO_4 in a low concentration at the surface of wet SiO_2 by $Al(HSO_4)_3$ and ammonium dichromate.

To illustrate the efficiency of the proposed method, Table 2 compares our results with relevant published data.[8,9]

In conclusion, the ready availability and low cost of the reagents, the simple and clean work-up, the high product yields and the mild reaction conditions all make this method a useful addition to the present methodologies for the oxidation of alcohols. In addition, these properties render this method attractive for use in large-scale operations.

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[†] Commercial chemicals (Fluka, Merck and Aldrich) and silica gel 60 (0.063–0.2 mm, 70–230 mesh) from Merck were used. Products were separated and purified by chromatography and identified by comparison of melting points, IR and NMR spectra and refractive indices with those reported for authentic samples. All the yields refer to isolated products. The purity determination and reaction monitoring were performed by TLC on silica gel Polygram SILG/UV 254 plates. Column chromatography was carried out on Merck Kisselgel 60H.

Preparation of $Al(HSO_4)_3$. A 500 ml suction flask was equipped with a constant-pressure dropping funnel. A gas outlet was connected to a vacuum system through an absorbing solution (water) and an alkali trap. Anhydrous aluminium chloride (66.7 g, 0.5 mol) was charged into the flask, and concentrated sulfuric acid (147.1 g, 1.5 mol) was added dropwise for 40 min at room temperature. HCl gas was evolved immediately. After completion of the addition of H_2SO_4, the mixture was shaken for 30 min, meanwhile, the residual HCl was exhausted by suction. A white solid material was thus obtained (158.5 g). $Al(HSO_4)_3$ was characterised by the determination of its H^+ content by titration with NaOH (calc. 0.95%, found 0.96%), and SO_4^{2-} was determined by precipitation with Ba^{2+} (calc. 90.57%, found 90.48%). Al^{3+} was determined by conversion to Al_2O_3 (calc. 8.48%, found 8.31%) and spectrophotometry using complex formation with aluminon (calc. 8.48%, found 8.38%).[11]

Oxidation of 2-bromobenzyl alcohol to 2-bromobenzaldehyde in n*-hexane. A typical procedure.* 2-Bromobenzyl alcohol (0.187 g, 1 mmol) was added to a mixture of $Al(HSO_4)_3$ (0.316 g, 1 mmol), wet SiO_2 (50 wt%, 0.1 g) and $(NH_4)_2Cr_2O_7$ (0.076 g, 0.3 mmol) in *n*-hexane (5 ml). The resulting mixture was stirred at room temperature for 14 min. The progress of the reaction was monitored by TLC and the mixture was filtered upon completion. The residue was washed with CH_2Cl_2 (10 ml). For the removal of trace water, which may be transfered from wet SiO_2 to the filtrate, anhydrous $MgSO_4$ was added to the filtrate and the mixture was filtered after 10 min. Evaporation of the solvent followed by column chromatography gave 2-bromobenzaldehyde in 90% yield.

Oxidation of 4-chlorobenzyl alcohol to 4-chlorobenzaldehyde under solvent-free conditions. A typical procedure. 4-Chlorobenzyl alcohol (0.142 g, 1 mmol) was added to a mixture of $Al(HSO_4)_3$ (0.316, 1 mmol), wet SiO_2 (50 wt%, 0.1 g) and $(NH_4)_2Cr_2O_7$ (0.076 g, 0.3 mmol). The resulting mixture was shaken at room temperature for 10 min. The progress of the reaction was monitored by TLC. The reaction mixture was treated with 10 ml of CH_2Cl_2 and then filtered. For the removal of trace water, which may be transfered from wet SiO_2 to the filtrate, anhydrous $MgSO_4$ was added to the filtrate and the mixture was filtered after 10 min. Evaporation of the solvent followed by column chromatography gave 4-chlorobenzaldehyde in 95% yield.

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