Oxidation of Alcohols Using $(NH_4)_2Cr_2O_7$ in the Presence of Silica Chloride/Wet SiO_2 in Solution and under Solvent Free Conditions

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Since the appearance of Collins reagent in 1968,[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 a great deal of continued interest in organic synthesis. In recent years, several efficient Cr(VI) reagents such as pyridinium chlorochromate,[2] pyridinium dichromate,[3] 1,1,3,3-tetramethylguadinium dichromate[4] and Dowex 1-X8 (on which Cl^- is replaced by dichromate and bisulfate ions)[5] have been interested to improve the selectivity, the mildness and the effectiveness of the oxidant species, especially in the oxidation of complex and highly sensitive compounds. Although many Cr(VI) reagents are available for the oxidation of organic substrates,[6-11] they have certain limitations such as instability of the reagents, the need of an excess amount of the reagent, low selectivity, long reaction time, tedius work-up and occurring of undesirable side reactions. Therefore, there still exists a need for highly efficient and mild oxidizing agents.

In continuation of our studies on the application of silica chloride[12-14] we were interested in using this reagent in combination of $(NH_4)_2Cr_2O_7$ and wet SiO_2 for the oxidation of alcohols to their corresponding carbonyl compounds.

In this manuscript we wish to report a convenient, effective and simple method for the oxidation of alcohols to their corresponding carbonyl compounds in solution and under solvent free conditions. Oxidation of different types of alcohols was investigated in the absence of solvent by ammonium dichromate in the presence of silica chloride and wet SiO_2 (Scheme 1, Table 1). In a simple procedure, a mixture of reactants was stirred on an oil bath (80 °C) for the appropriate time (Table 1). Different alcohols were oxidized efficiently and the corresponding carbonyl compounds were isolated in good to high yields. Over-oxidation of the products, using this method, was not obsereved.

$$R_1R_2CHOH \xrightarrow{\text{(I) or (II)}} R_1R_2CO$$

I: $(NH_4)_2Cr_2O_7$/ silica chloride/ wet SiO_2, solvent free, 80 °C
II: $(NH_4)_2Cr_2O_7$/ silica chloride/ wet SiO_2, n-hexane, reflux

Scheme 1

In order to compare the obtained results with those obtained in solution, we studied the oxidation reaction in *n*-hexane. As shown in Table, by omiting the solvent in addition to the ease of the work-up procedure, the reaction time was reduced and the need for solvent is avoided.

It should be noted that oxidation did not proceed using ammonium dichromate, silica chloride or wet SiO_2 alone.

Table 1. Oxidation of alcohols to their corresponding carbonyl compounds in *n*-hexane or under solvent free conditions

Entry	Substrate	Product[a]	Solvent free oxidation		Oxidation in solution	
			Time (min)	Yield (%)[b]	Time (min)	Yield (%)[b]
1	Benzyl alcohol	Benzaldehyde	3	90	7	95
2	2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	30	92	80	90
3	2-Bromobenzyl alcohol	2-Bromobenzaldehyde	15	82	70	80
4	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	5	85	25	82
5	1-Phenyl ethanol	Acetophenone	15	92	80	90
6	1-Phenyl-propan-2-ol	Phenylpropan-2-one	15	86	65	90
7	3-Phenyl-propan-1-ol	3-Phenylpropanal	10	87	80	90
8	1-Octanol	Octanal	10	90	15	85
9	Cyclohexanol	Cyclohexanone	10	85	35	80
10	Benzoin	Benzil	15	80	130	75
11	Cinnamylalcohol	Cinnamaldehyde	10	87	130	–[c]
12	Phenylethylene glycol	Phenylglyoxal	22	90	50	–[c]

[a]all products were characterized by IR and ^{1}H-NMR spectra and by comparison with authentic samples. [b]Isolated yield. [c]Mixture of products.

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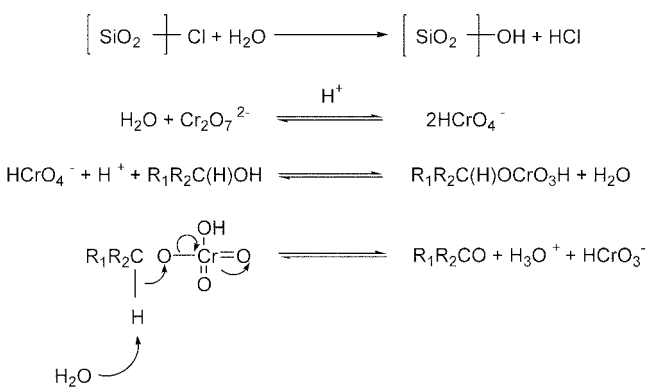
Table 2. Comparison of some of the results obtained by the oxidation with $(NH_4)_2Cr_2O_7$ in the presence of silica chloride/ wet SiO_2 (1), with some of those reported by chromic acid on amberlyst A-26 (2), crosslinked polyvinyl-pyridine-supported ferric dichromate (3) and pyrazinium dichromate (4)

Entry	Substrate	(Oxidant/Substrate) (h) (Yield %)			
		(1)	(2)	(3)	(4)
1	Benzyl alcohol	(1)(0.05)(90)	(13)(1)(98)	(1)(1.5)(35)	(1)(3.5)(73)
2	1-Phenyl ethanol	(1)(0.25)(92)	-	(1)(1)(35)	(1)(3.5)(91)



Scheme 2

These results could be attributed to the probable *in situ* generation of H_2CrO_4 in low concentration at the surface of wet SiO_2 by silica chloride and ammonium dichromate. The following plausible mechanisem can be considered for the oxidation reaction (Scheme 2).[15,16]

In order to show the oxidizing ability of this system, we have compared some of the results with some of those reported in the literature (Table 2).[2,17,18]

In summary ammonium dichromate in the presence of silica chloride/wet SiO_2 can serve as an efficient reagent for the oxidation of alcohols to their corresponding carbonyl compounds.

The yields are almost quantitative and the procedure is simple and convenient.

Experimental Section

Oxidation of benzyl alcohol to the benzaldehyde in *n*-hexane. A typical procedure: Benzyl alcohol (0.108 g, 1 mmol) was added to a suspension of silica chloride (0.3 g), wet SiO_2 (50% *ww*, 0.2 g) and $(NH_4)_2Cr_2O_7$ (0.252 g, 1 mmol) in *n*-hexane (5 mL). The mixture was refluxed for 7 min. (The progress of the reaction was monitored by TLC) and filtered. The residue was washed with CH_2Cl_2 (10 mL). Then anhydrous $MgSO_4$ was added to the filtrate and filtered after 10 min. Evaporation of the solvent followed by column chromatography gave the benzaldehyde in 95% yield.

Oxidation of 2-chlorobenzyl alcohol to the 2-chlorobenzaldehyde under solvent free condition. A typical procedure: 2-Chlorobenzyl alcohol (0.127 g, 1 mmol) was added to a mixture of silica chloride (0.3 g), wet SiO_2 (50% *ww*, 0.2 g) and $(NH_4)_2Cr_2O_7$ (0.252 g, 1 mmol) and the mixture was heated on an oil bath (80 ^oC) with stirring for 30 min. (The progress of the reaction was monitored by TLC). The mixture was treated with 10 mL of CH_2Cl_2 and filtered. The filtrate was treated with $MgSO_4$ and the drying agent was fitered off after 10 min. The solvent was removed from the filtrate, and the residue was subjected to column chromatography on silica gel to obtain 92% of 2-chlorobenzaldehyde.

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