SHORT PAPER

J. Chem. Research (S), 2001, 476–477

$ZrCl_4$/wet SiO_2 promoted oxidation of alcohols by $(NH_4)_2[Cr_2O_7]$ in solution and solvent free condition†

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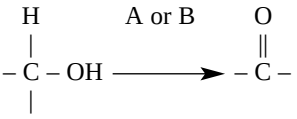
Ammonium dichromate in the presence of $ZrCl_4$ and wet SiO_2 was used as an effective oxidising agent for the oxidation of benzylic and secondary aliphatic alcohols in solution and solvent free condition.

Keywords: ammonium dichromate, oxidation of benzylic and secondary aliphatic alcohols

Although many useful procedures for the oxidation of alcohols to the corresponding carbonyl compounds by Cr(VI) based oxidants, have been reported,[1–9] the general problem cannot be considered definitely settled. The chief disadvantages against most of these reagents and their use in organic chemistry in spite of their power, are lack of selectivity, long reaction time, strong protic and aqueous conditions and tedious work up.

In this paper we wish to report a convenient and simple method for the oxidation of benzylic and secondary aliphatic alcohols to their corresponding aldehydes or ketones in solution and solvent free conditions. Oxidation of different types of benzylic and secondary aliphatic alcohols was investigated in the absence of solvent by ammonium dichromate in the presence of $ZrCl_4$ and wet SiO_2 (Scheme 1, Table 1). In a simple procedure, a mixture of reactants was stirred at room temperature for the appropriate time (Table 1). Both types of the above-mentioned compounds reacted efficiently and the corresponding carbonyl compounds were isolated in high yields.

In order to compare the obtained results with those obtained in solution, we studied the oxidation reaction in *n*-hexane. As shown in the Table 1, there are appreciable difference between the results obtained in solution and those in solvent free conditions. (For example, Scheme 2 shows that the oxidation of 1-phenyl ethanol in *n*-hexane proceeded in 45% yield after 0.17 h, whereas the reaction in solvent free condition proceeded in 89% yield during the same time). In conclusion, by omiting the solvent, in addition to ease of the work up procedure, the reaction time was reduced and the need for solvent is avoided.



A: $(NH_4)_2[Cr_2O_7]/ZrCl_4$/wet SiO_2, Solvent Free, r.t.
B: $(NH_4)_2[Cr_2O_7]/ZrCl_4$/ wet SiO_2, *n*-Hexane, r.t. or reflux

Scheme 1

Primary aliphatic alcohols do not undergo oxidation by this method (Table 1, entries 12, 13). Therefore, this methodology shows selectivity and is suitable for oxidative selection between benzylic or secondary aliphatic alcohols and primary alcohols. This is shown by the competitive reaction between benzyl alcohol and *n*-butanol in *n*-hexane in which, after 9 minutes all of the benzyl alcohol was converted to the benzaldehyde, whereas the *n*-butanol was unchanged.

It should be noted that the oxidation reaction did not proceed using $ZrCl_4$, ammonium dichromate or wet SiO_2 alone, even after prolonged heating. These results could be attributed to the

Table 1 Oxidation of alcohols by ammonium dichromate in the presence of $ZrCl_4$ and wet SiO_2 in *n*-hexane or solvent free condition at room temperature

Ent.	Substrate	Product	Solvent free oxidation		Oxidation in solvent	
			Time/h	Yield/%	Time/h	Yield/%
1	Benzyl alcohol	Benzaldehyde	0.05	92	0.15	95
2	4-Bromobenzyl alcohol	4-Bromo-benzaldehyde	0.26	90	0.58	87
3	4-Chlorobenzyl alcohol	4-Chloro-benzaldehyde	0.17	85	0.42	88
4	2-Chlorobenzyl alcohol	2-Chloro-benzaldehyde	0.28	90	1	90
5	4-Methoxybenzyl alcohol	4-Methoxy-benzaldehyde	1.5	87	1.7	85
6	4-Benzyloxybenzyl alcohol	4-Benzyloxy-benzaldehyde	0.83	90	3.2	85
7	4-Methylbenzyl alcohol	4-Methyl-benzaldehyde	0.12	95	0.3	90
8	1-Phenyl ethanol	Acetophenone	0.17	89	1.25	87
9	Diphenylcarbinol	Benzophenone	0.33	96	4	90
10	Cyclohexanol	Cyclohexanone	2	90	1.5	85[a]
11	1-Phenyl-2-propanol	Phenyl-2-propanone	1.8	91	1.7	93[a]
12	1-Butanol	Butanal	3	0	3	0[a]
13	1-Octanol	Octanal	3	0	4	0[a]

[a]Under reflux conditions

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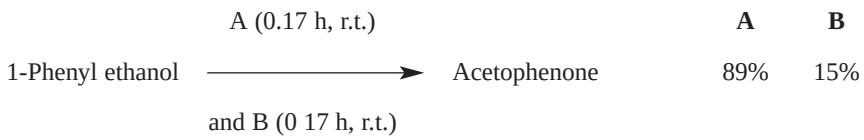
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.



Scheme 2

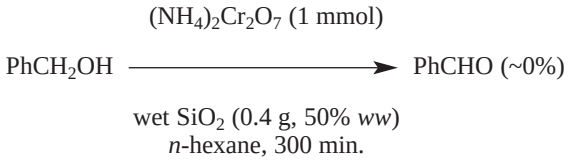
Table 2 Comparison of some of the results obtained by the oxidation with ammonium dichromate in the presence of $ZrCl_4$ and wet SiO_2 (1), with some of those reported by crosslinked polyvinyl-pyridine-supported ferric dichromate (2),[6] 1,1,3,3-tetramethylguanidium dichromate (3),[8] and chromic acid on Amberlist A-26 (4)[9]

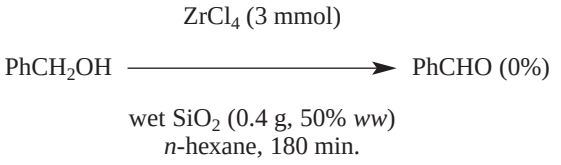
Entry	Substrate	(h) (Yield/%)			
		(1)	(2)	(3)	(4)
1	Benzyl alcohol	(0.05) (92)	(1.5) (75)	(4) (93)	(1) (98)
2	Cyclohexanol	(2) (90)	(8) (70)	(16) (88)	(3) (77)

probable *in situ* generation of H_2CrO_4 at the surface of SiO_2 in low concentration by $ZrCl_4$ and ammonium dichromate.

In order to show the oxidising ability of this method we have compared some of the results with some of those reported in the literature (Table 2).[6,8,9]

In conclusion, the present procedure of oxidation of alcohols with ammonium dichromate in the presence of $ZrCl_4$ and wet SiO_2 provides a very convenient and efficient method for conversion of alcohols to their corresponding carbonyl compounds.





Scheme 3

Experimental

Oxidation of benzyl alcohol to the benzaldehyde under solvent free condition. A typical procedure: To a mixture of $ZrCl_4$ (0.699 g, 3 mmol), wet SiO_2 [(SiO_2/H_2O: 20% *ww*), 0.4 g)] and $(NH_4)_2[Cr_2O_7]$ (0.252 g, 1 mmol), was added benzyl alcohol (0.108 g, 1 mmol). The resultant mixture was shaken at room temperature for 3 minutes (the progress of the reaction was monitored by TLC).

The reaction mixture was triturated with CH_2Cl_2 (10 ml) and then filtered. Anhydrous $MgSO_4$ was added to the filtrate and filtered after 10 min. Evaporation of the solvent followed by column chromatography on silica gel gave the benzaldehyde in 92% yield.

Oxidation of 4-methylbenzyl alcohol to 4-methylbenzaldehyde in n-hexane. A typical procedure: To a suspension of $ZrCl_4$ (0.699 g, 3 mmol), wet SiO_2 (50% *ww*, 0.4 g) and $(NH_4)_2[Cr_2O_7]$ (0.252 g, 1 mmol) in n-hexane (5 ml), 4-methylbenzyl alcohol (0.122 g, 1 mmol) was added and stirred at room temperature for 18 minutes (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 on silica gel gave 4-methylbenzaldehyde in 90% yield.

We are thankful to Guilan University Council for the partial support of this work.

Received 13 March 2001; accepted 6 July 2001
Paper 00/813

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