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Volume 54, 2001

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Aust. J. Chem. **2001**, *54*, 405–406

Oxidation of Alcohols by $(NH_4)_2Cr_2O_7$ in Solution and Under Solvent-Free Conditions

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Ammonium dichromate in the presence of $Mg(HSO_4)_2$ and wet SiO_2 was used as an effective oxidizing agent for the oxidation of alcohols in solution and under solvent-free conditions.

Manuscript received: 16 August 2001.
Final Version: 2 October 2001.

Introduction

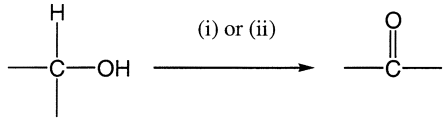
The oxidation of alcohols to carbonyl compounds is one of the fundamental reactions in synthetic organic chemistry. There are many useful Cr^{VI} based oxidants for this purpose,[1] of which Jones' reagent,[2] CrO_3/NBu_4HSO_4,[3] n-butylphenylphosphonium dichromate,[4] pyridinium chlorochromate,[5,6] pyrazinium dichromate,[7] ferric dichromate,[8] polyvinylpyridine-supported ferric dichromate,[9] polyethyleneimine-supported silver dichromate[10] and Dowex 1X8 (on which Cl^- is replaced by dichromate and bisulfate ions[11]) are examples.

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 workup. Thus, a milder, more selective and inexpensive reagent is still desirable.

In this paper we report a convenient and simple method for the conversion of alcohols into their corresponding aldehydes or ketones in solution and under solvent-free conditions.

Results and Discussion

The oxidation of various alcohols was investigated using $(NH_4)_2Cr_2O_7$ in the presence of $Mg(HSO_4)_2$ and wet SiO_2 (Scheme 1), at room temperature. Yields and reaction times are given in Table 1. Over-oxidation of the products, using this method, was not observed.



Scheme 1. (i) $(NH_4)_2Cr_2O_7/Mg(HSO_4)_2$/wet SiO_2, solvent-free, room temperature; (ii) $(NH_4)_2Cr_2O_7/Mg(HSO_4)_2$/wet SiO_2, n-hexane, room temperature.

The omission of the solvent not only eases the workup, but reduces the reaction time. This method is not suitable for the oxidation of allylic alcohols (Table 1, entry 13).

It should be noted that oxidation did not proceed using any of $Mg(HSO_4)_2$, ammonium dichromate or wet SiO_2 alone (Table 1, entries 14–16). These results could be attributed to the in situ generation of H_2CrO_4 in low concentration at the surface of wet SiO_2 by the solid inorganic acidic salts ($Mg(HSO_4)_2$ and $(NH_4)_2Cr_2O_7$).

Conclusions

The ready availability and low cost of the reagents, the simple and clean workup, 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.

Experimental

Oxidation of Benzyl Alcohol to Benzaldehyde Under Solvent-Free Conditions: a Typical Procedure

To a mixture of $Mg(HSO_4)_2$ (0.654 g, 3 mmol), wet SiO_2 (50% w/w, 0.1 g) and $(NH_4)_2Cr_2O_7$ (0.126 g, 0.5 mmol), was added benzyl alcohol (0.108 g, 1 mmol). The resultant mixture was shaken at room temperature for 3 min. The progress of the reaction was monitored by thin-layer chromatography (TLC). The reaction mixture was triturated with CH_2Cl_2 (10 mL) and then filtered. Anhydrous $MgSO_4$ was added to the filtrate and the mixture filtered after 10 min. Evaporation of the solvent followed by column chromatography on silica gel gave the benzaldehyde in 92% yield.

Oxidation of 2-Bromobenzyl Alcohol to 2-Bromobenzaldehyde in n-Hexane: a Typical Procedure

To a suspension of $Mg(HSO_4)_2$ (0.654 g, 3 mmol), wet SiO_2 (50% w/w, 0.1 g) and $(NH_4)_2Cr_2O_7$ (0.126 g, 0.5 mmol) in n-hexane (5 mL) was added 2-bromobenzyl alcohol (0.187 g, 1 mmol) and the resultant

 10.1071/CH01104 0004-9425/01/060405

Table 1. Oxidation of alcohols by ammonium dichromate in the presence of $Mg(HSO_4)_2$ and wet SiO_2 in n-hexane or under solvent-free conditions at room temperature

Entry	Substrate	Product[A]	Solvent-free oxidation		Oxidation in solvent	
			Time (min)	Yield[B] (%)	Time (min)	Yield[B] (%)
1	Benzyl alcohol	Benzaldehyde	5	92	5	95
2	4-Bromobenzyl alcohol	4-Bromobenzaldehyde	5	90	5	92
3	2-Bromobenzyl alcohol	2-Bromobenzaldehyde	5	90	10	85
4	2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	5	89	5	85
5	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	5	90	15	85
6	4-Benzyloxybenzyl alcohol	4-Benzyloxybenzaldehyde	15	90	15	80
7	2-Nitrobenzyl alcohol	2-Nitrobenzaldehyde	5	95	15	92
8	1-Phenyl ethanol	Acetophenone	5	90	30	88
9	Diphenylcarbinol	Benzophenone	5	92	75	90
10	Cyclohexanol	Cyclohexanone	30	85	240	—[C]
11	1-Phenylpropan-2-ol	Phenylpropan-2-one	10	90	300	—[C]
12	3-Phenylpropan-1-ol	3-Phenylpropanal	10	87	60	—[C]
13	Cinnamyl alcohol	Cinnamaldehyde	5	—[C]	5	—[C]
14	Benzyl alcohol	Benzaldehyde	100	5[D]	300	7[D]
15	Benzyl alcohol	Benzaldehyde	100	0[E]	180	0[E]
16	Benzyl alcohol	Benzaldehyde	110	0[F]	180	0[F]

[A] All products were characterized by infrared (IR) and ^1H nuclear magnetic resonance (NMR) spectroscopy and by comparison with authentic samples. [B] Isolated yield. [C] Mixture of products. [D] In the absence of $Mg(HSO_4)_2$. [E] In the absence of $(NH_4)_2Cr_2O_7$. [F] In the absence of wet SiO_2.

mixture was stirred at room temperature for 10 min. The progress of the reaction was monitored by TLC and the mixture filtered upon completion. The residue was washed with CH_2Cl_2 (10 mL). Anhydrous $MgSO_4$ was added to the filtrate and the mixture filtered after 10 min. Evaporation of the solvent followed by column chromatography on silica gel gave 2-bromobenzaldehyde in 85% yield.

Acknowledgments

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

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