DOI: 10.1002/adsc.200505356

Catalyst-Free Oxidation of Alcohols at Room Temperature Using Water as Solvent

Ziqiang Lei,* Yaoxia Yang, Xiangzhen Bai

Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering,
Northwest Normal University, Lanzhou 730070, People's Republic of China
Fax: (+86)-931-797-0359, e-mail: leizq@nwnu.edu.cn

Received: September 12, 2005; Revised: March 17, 2006; Accepted: March 24, 2006

Abstract: An effective, cheap, environmentally benign and catalyst-free oxidation of alcohols was carried out at room temperature using tetra-*n*-butylammonium Oxone® (TBA-OX) as oxidant with moderate to high selectivity for most of the alcohols using water as the solvent.

Keywords: alcohols; catalyst-free oxidation; oxidation; tetra-*n*-butylammonium Oxone®; water as solvent

Alcohol oxidations have traditionally been performed with stoichiometric amounts of high-valent transition metal salts or oxidants that generate relatively large amounts of metal-bearing hazardous waste and are usually run in chlorinated solvents.[1–3] In an attempt to provide a more environmentally benign process for alcohol oxidations, a variety of catalytic oxidation procedures using water as the only solvent has been investigated.[4–9] Liang and co-workers[10] reported a transition metal-free catalyst system for aerobic alcohol oxidations in dichloromethane at high reaction temperature. Although molecular oxygen was used as a terminal oxidant, other additives such as Br_2, $NaNO_2$ and nitroxyl radicals TEMPO (2,2,6,6-tetramethyl-piperidyl-1-oxy) were used to achieve the reactions. Surendra and co-workers[11,12] also reported a transition metal-free catalyst system for the oxidation of alcohols with *o*-iodoxybenzoic acid (IBX) or *N*-bromosuccinimide (NBS) catalyzed by β-cyclodextrin in a water/acetone mixture. On the basis of green principles, Ji[13] reported a facile, transition metal-free and substrate-selective oxidation of alcohols with NaOCl catalyzed by β-cyclodextrin using water as the solvent.

We have developed an effective, facile and catalyst-free oxidation of alcohols using water as solvent. Benzyl alcohol, substituted benzyl alcohols, benzhydrol, substituted benzhydrols, cyclic and aliphatic alcohols were oxidized to their corresponding aldehydes and ketones at room temperature in moderate to high selectivity by the mild and cheap oxidant tetra-*n*-butylammonium Oxone® (TBA-OX). At first we developed a procedure in which alcohols were oxidized with tetra-*n*-butylammonium Oxone® in dichloromethane (Table 1). Later we found that similar oxidation reactions could occur entirely in water although the conversion and product selectivity were somewhat lower (Table 2). The procedure is very simple, cheap and offers other distinct advantages over the existing methods.

TBA-OX was first used for the oxidation of sulfides and sulfur-containing amino acid derivatives[14] but has never before been used for the oxidation of alcohols.

On the basis of the smooth oxidation of benzyl alcohol with tetra-*n*-butylammonium Oxone®, different reaction conditions including the amount of tetra-*n*-butylammonium Oxone® used and the ratio of alcohol to tetra-*n*-butylammonium Oxone® were investigated. In water the optimum ration of alcohol to the oxidant is 1:2.

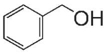
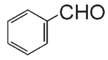
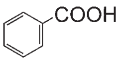
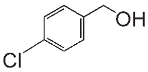
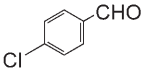
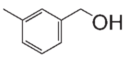
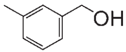
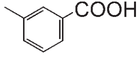
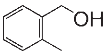
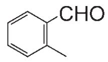
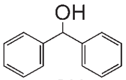
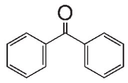
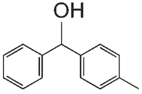
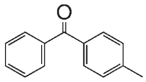
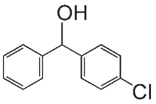
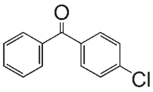
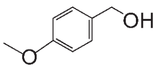
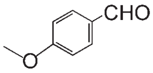
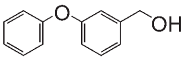
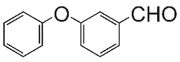
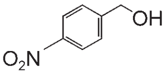
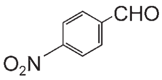
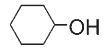
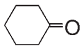
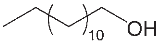
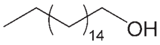
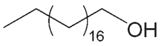
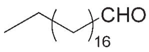
In conclusion, a series of alcohols includes benzylic and primary aliphatic alcohols were oxidized to the corresponding aldehydes and ketones at room temperature using tetra-*n*-butylammonium Oxone® as oxidant and water as solvent in good to moderate conversion and with similar selectivity. The oxidation procedure is mild, cheap and metal-free.

Experiment Section

General Remarks

All of the alcohols used in the reactions were obtained from ABCR GmbH & Co. KG and used as received without further purification. TBA-OX was prepared from commercially available Oxone® by a procedure described in the literature[14]. Simply extracting an aqueous solution of oxone® and tetra-*n*-butylammonium bisulfate with dichloromethane, drying, and evaporating gave the product. TBA-OX is readily soluble in dichloromethane, chloroform, acetone, acetonitrile, and water.

Table 1. Oxidation of alcohols by oxidant n-Bu_4NHSO_5 using dichloromethane as solvent.

Entry	Alcohol	Product	Molar ratio of oxidant to alcohol	Time [h]	Conversion [%]	Selectivity [%]	Yield [%][a]
1		 	1:1	0.5	70	40 60	
2			1:1	0.5	97	100	63
3		 	1:1	0.5	80	79 21	
4			1:1	0.5	70	100	
5			1:1	8	100	100	
6			1:1	8	100	100	
7			1:1	0.5	100	100	72
8			1:1	0.5	100	100	
9			1:1	0.5	100	100	
10			1:1	0.5	100	100	
11			1:1	8	79	100	
12			1:1	8	64	100	
13			1:1	8	52	100	
14			1:1	8	63	100	

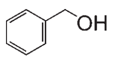
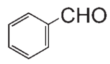
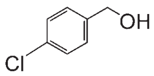
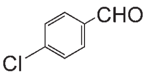
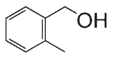
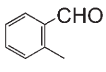
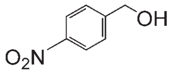
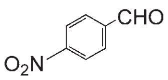
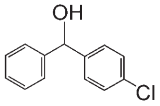
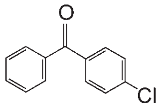
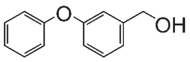
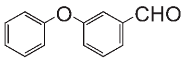
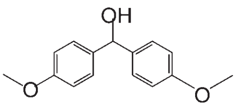
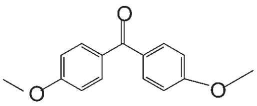
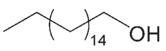
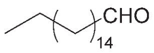
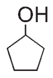
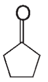
Reaction conditions: 3 mL of dichloromethane at room temperature. Percentage conversion and selectivity were determined by GC.

[a] Yield of isolated product.

Alcohol Oxidation

A typical reaction was carried out as follows: tetra-n-butylammonium Oxone (TBA-OX) 275.5 mg (0.291 mmol) and benzyl alcohol (0.146 mmol) were dissolved in 2 mL of water (or 3 mL of dichloromethane). The mixture was stirred for 0.5–8 h at room temperature. Formation of products and consumption of substrates were monitored by GC. The identity of products was determined either by comparison with authentic samples using gas chromatography or by GC/MS analysis. The conversion and product selectivity were determined using GC analysis. The results are shown in Table 1 (in dichloromethane) and Table 2 (in water).

Table 2. Oxidation of alcohols by oxidant n-Bu_4NHSO_5 using water as solvent.

Entry	Alcohol	Product	Conversion [%]	Selectivity [%]	Yield [%][a]
1			40	100	
2			74	100	35
3			61	86	
4			76	100	
5			63	100	48
6			74	100	
7			100	100	68
8			42	65	
9			30	51	

Reaction conditions: Solvent: H_2O (2 mL); Bu_4NHSO_5:alcohol = 2:1(mmol/mmol); 10 h at room temperature. Percentage of conversion and selectivity were determined by GC.

[a] Yield of isolated products.

Procedure for Isolating Products

To a solution of the alcohol substrate (0.291 mmol) in water or in dichloromethane (10 mL) was added the required amount of the oxidant (TBA-OX).The mixture was then stirred at room temperature for 10 h (0.5 h in dichloromethane). The reaction was monitored by TLC until all starting alcohol was converted. After completion of the reaction in water, the mixture was extracted with dichloromethane (3 × 10 mL). The solvent of the combined organic layers was removed under reduced pressure to give the desired crude product. Analytically pure products were obtained after column chromatography (silica gel) using petroleum ether and ethyl acetate (10:1, v/v) as eluent.

***p*-Chlorobenzaldehyde** (Table 1 and Table 2, entry 2): ^{1}H NMR (C_6D_6, 400 MHz): δ = 6.62–6.60 (2H, Ar–H), 6.89–6.87 (2H, Ar–H), 9.1 (1H, CHO); ^{13}C NMR (400 MHz): δ = 189.83, 140.24, 135.08, 130.72, 129.22, 128.22, 128.00.

4-Chlorodiphenyl ketone (Table 1, entry 7 and Table 2, entry 5): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.26 (2H, Ar–H), 7.80–7.44 (2H, Ar–H), 7.77–7.72 (4H, Ar–H), 7.63–7.59 (1H, Ar–H); ^{13}C NMR (400 MHz): δ = 195.49, 138.88, 137.21, 135.84, 132.63, 131.44, 129.91, 128.62, 128.39.

4,4′-Dimethoxydiphenyl ketone (Table 1, entry 7): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.80–7.78 (4H, Ar–H), 6.97–6.95 (4H, Ar–H), 3.88 (6H, CH_3); ^{13}C NMR (400 MHz): δ = 194.44, 162.804, 134.75, 132.21, 113.66, 55.44.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (No. 20174031 and 20474052) and Key Laboratory of Eco-Environment-Related Polymer Materials (Northwest Normal University), Ministry of Education.

References

[1] R. A. Sheldon, J. K. Kochi, *Metal Catalyzed Oxidation of Organic Compounds*, Academic Press, New York, **1981**.

[2] G. Cainelli, G. Cardillo, *Chromium oxidants in organic chemistry*, Springer, Berlin, **1984**.

[3] S. V. Ley, A. Madin, *Comprehensive organic synthesis*, (Eds.: B. M. Trost, I. Fleming, S. V. Ley), Pergamon, Oxford, **1991**, Vol. 7, pp 251–289.

[4] G. J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636–1639.

[5] H. Tohma, S. Takizawa, T. Maegawa, Y. Kita, *Angew. Chem. Int. Ed.* **2000**, *39*, 1306–1307.

[6] H. Tohma, T. Maegawa, S. Takizawa, Y. Kita, *Adv. Synth. Catal.* **2002**, *344*, 328–337.

[7] Y. Uozumi, R. Nakao, *Angew. Chem. Int. Ed.* **2003**, *42*, 194–197.

[8] D. Sloboda-Rozner, P. L. Alsters, R. Neumann, *J. Am. Chem. Soc.* **2003**, *125*, 5280–5281.

[9] B. P. Buffin, J. P. Clarkson, N. L. Belitz, A. Kundu, *J. Mol. Catal.: Chem.* **2005**, *225*, 111–116.

[10] R. H. Liu, X. M. Liang, C. Y. Dong, X. Q. Hu, *J. Am. Chem. Soc.* **2004**, *126*, 4112–4113.

[11] K. Surendra, N. S. Krishnaveni, M. A. Reddy, Y. V. D. Nageswar, K. R. Rao, *J. Org. Chem.* **2003**, *68*, 2058–2059.

[12] N. S. Krishnaveni, K. Surendra, K. R. Rao, *Adv. Synth. Catal.* **2004**, 346, 346–350.

[13] H. B. Ji, D. P. Shi, M. Shao, Z. Li, L. F. Wang, *Tetrahedron Lett.* **2005**, *46*, 2517–2520.

[14] B. M. Trost, R. Braslau, *J. Org. Chem.* **1988**, *53*, 532–537.