ISSN 1070-4280, Russian Journal of Organic Chemistry, 2020, Vol. 56, No. 3, pp. 521–523. © Pleiades Publishing, Ltd., 2020.

A Simple and Effective Method for Catalytic Oxidation of Alcohols Using the Oxone/Bu_4NHSO_4 Oxidation System

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Received November 25, 2019; revised December 16, 2019; accepted December 18, 2019

Abstract—A simple and efficient procedure is reported for the oxidation of alcohols to carbonyl compounds with Oxone (potassium peroxymonosulfate) in the presence of tetrabutylammonium hydrogen sulfate as catalyst with excellent conversion and high selectivity using chloroform as solvent at room temperature. The efficiency of several phase-transfer catalysts in the oxidation of benzyl alcohols and benzydrol was studied. The proposed catalytic system was also evaluated in the oxidation of alcohols in water at room temperature.

Keywords: alcohols, oxidation, aldehydes, ketones, tetrabutylammonium hydrogen sulfate

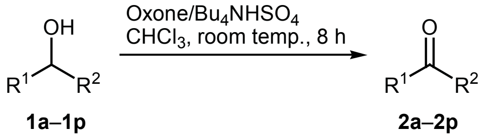
DOI: 10.1134/S1070428020030240

Oxone is a white crystalline solid containing potassium peroxymonosulfate ($KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) as oxidizing species. It is a commercially available oxidant that easily oxidizes many functional groups. Oxone is easy to handle, nontoxic, soluble in water, and relatively inexpensive, and it generates nonpolluting by-products; therefore, it is an attractive green reagent [1]. Oxone as a stable oxidant has been widely studied in synthetic organic chemistry, e.g., in epoxidation of olefins [2], esterification of alcohols [3], oxidation and halogenation of C–H bond [4], oxidation of sulfides [5], organotrifluoroborates [6], and alcohols [7, 8], as well as in other oxidation processes [9]. Furthermore, it was also used in the manufacturing industry [10].

The oxidation of alcohols to aldehydes and ketones is one of the most common classes of oxidation reactions in organic chemistry [11, 12]. Aldehydes and ketones represent important intermediates for the preparation of various other chemicals. Many excellent catalytic systems have been already reported for the oxidation of alcohols. To provide a more convenient procedure and environmentally benign process for the oxidation of alcohols, herein we report the use of Oxone as an oxidant and tetrabutylammonium hydrogen sulfate as a phase transfer catalyst (PTC) in the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds. Six other phase transfer catalysts (TBAHS, TPAHS, TEAHS, TMAHS, TBAC, and TBAB) were also examined to evaluate their performance in this oxidation reaction. Furthermore, the catalytic oxidation procedure was investigated using water as solvent.

A series of alcohols, including substituted benzyl alcohols, benzhydrols, and long-chain aliphatic alcohols were oxidized with Oxone in chloroform at room temperature in the presence of 1.5 equiv of tetrabutylammonium hydrogen sulfate (Scheme 1). The results are summarized in Table 1. It is seen that benzyl alcohols were oxidized to the corresponding benzaldehydes with excellent conversion (Table 1, entry nos. 1–3, 6–9). The conversion of benzhydrol to benzophenone was 88%. Long-chain aliphatic alcohols could also be oxidized to the corresponding aldehydes, but the conversion was low. Furthermore, no over-oxidation of aldehydes to carboxylic acids was observed under the given conditions. A probable catalytic cycle for the oxidation of benzyl alcohols with Oxone was proposed in [13].

Scheme 1.



For R^1, R^2, see Table 1.

Table 1. Oxidation of alcohols with Oxone/Bu_4NHSO_4 using chloroform[a] and water[b] as solvents

Entry no.	Alcohol no.	R^1	R^2	Conversion,[c] %		Product no.
				chloroform	water	
1	**1a**	Ph	H	100	14	**2a**
2	**1b**	4-ClC_6H_4	H	100	74	**2b**
3	**1c**	3-MeC_6H_4	H	100	13	**2c**
4	**1d**	2-MeC_6H_4	H	23	34	**2d**
5	**1e**	Ph	Ph	88	–[d]	**2e**
6	**1f**	4-ClC_6H_4	Ph	100	84	**2f**
7	**1g**	4-$MeOC_6H_4$	H	100	31	**2g**
8	**1h**	3-$PhOC_6H_4$	H	100	36	**2h**
9	**1i**	4-$O_2NC_6H_4$	H	100	39	**2i**
10	**1j**	$PhCH_2$	H	25	–[d]	**2j**
11	**1k**	$Me(CH_2)_{10}$	H	21	7	**2k**
12	**1l**	$Me(CH_2)_{14}$	H	36	5	**2l**
13	**1m**	$Me(CH_2)_{16}$	H	62	4	**2m**
14	**1n**	4-MeC_6H_4	Ph	–[d]	12	**2n**
15	**1o**	4-$MeOC_6H_4$	4-$MeOC_6H_4$	–[d]	90	**2o**
16	**1p**	$(CH_2)_5$		–[d]	9	**2p**

[a] Reaction conditions: solvent $CHCl_3$ (3 mL), alcohol (1 equiv), Oxone (0.88 equiv), Bu_4NHSO_4 (1.5 equiv), 8 h, 25°C.
[b] Reaction conditions: solvent H_2O (2 mL), alcohol (1 equiv), Oxone (2 equiv), Bu_4NHSO_4 (1.5 equiv), 10 h, room temperature.
[c] According to the GLC data.
[d] No data.

Table 2. Oxidation of alcohols **1b**, **1f**, **1g**, and **1h** with Oxone in the presence of different phase-transfer catalysts[a]

Alcohol no.	Phase-transfer catalyst	Conversion,[b] %	Selectivity,[b] %	Product
1b	TBAHS	>99	100	**2b**
	TPAHS	51	100	
	TEAHS	11	100	
	TMAHS	–	–	
	TBAC	31	100	
	TBAB	23	100	
1f	TBAHS	>99	100	**2f**
	TPAHS	>99	100	
	TEAHS	97	100	
	TMAHS	3	100	
	TBAC	44	100	
	TBAB	51	100	
1g	TBAHS	>99	100	**2g**
	TPAHS	64	100	
	TEAHS	24	100	
	TMAHS	4	100	
	TBAC	64	100	
	TBAB	42	100	
1h	TBAHS	>99	100	**2h**
	TPAHS	73	100	
	TEAHS	72	100	
	TMAHS	13	100	
	TBAC	36	100	
	TBAB	35	100	

[a] Reaction conditions: solvent: CH_2Cl_2 (3 mL), alcohol (1 equiv), Oxone (1 equiv), PTC (1.5 equiv), 10 h, room temperature.
[b] According to the GLC data.

We also examined the efficiency of other phase-transfer catalysts in the oxidation of 4-chlorobenzyl alcohol (**1b**), 4-chlorobenzhydrol (**1f**), 4-methloxybenzyl alcohol (**1g**), and 3-phenoxybenzyl alcohol (**1h**). The catalysts used were tetrabutylammonium hydrogen sulfate (TBAHS), tetrapropylammonium hydrogen sulfate (TPAHS), tetraethylammonium hydrogen sulfate (TEAHS), tetramethylammonium hydrogen sulfate (TMAHS), tetrabutylammonium chloride (TBAC), and tetrabutylammonium bromide (TBAB). The results are summarized in Table 2. Most of the selected PTCs showed catalytic activity in the oxidation of alcohols with different conversions. The best results were obtained with TBAHS (>99% conversion). Relatively good catalytic was also observed for TPAHS under the same conditions. However, TMAHS had basically no catalytic activity in the oxidation of these alcohols. Thus, the longer alkyl radical in tetraalkylammonium salt favors better catalytic activity in this oxidation process.

Considering the environmental impact, the oxidation of alcohols in water as a solvent was investigated (Table 1). The system Oxone/TBAHS showed a good activity for the oxidation of some benzyl alcohols and benzhydrols in water at room temperature, but the conversion was generally lower than in chloroform. 4-Chlorobenzyl alcohol (**1b**), 4-chlorobenzhydrol (**1f**), and 4,4′-dimethoxybenzhydrol (**1o**) were oxidized to the corresponding carbonyl compounds with a conversion of up to 90%. However, the conversions of cyclohexanol (**1p**) and long-chain aliphatic alcohols **1k**–**1m** did not exceed 9%.

In conclusion, we have proposed a simple, efficient, inexpensive, metal-free, and environmentally friendly catalytic procedure for the oxidation of benzyl alcohols and benzhydrols to the corresponding aldehydes and ketones using Oxone as an oxidant and tetrabutylammonium hydrogen sulfate as a catalyst in chloroform at room temperature. However, it remains desirable to find milder conditions and achieve higher conversions and greater selectivities in water solution.

EXPERIMENTAL

A typical reaction was carried out as follows: benzyl alcohol (1 equiv), Oxone (0.88 equiv), and PTC (1.5 equiv) were dissolved in 3 mL of chloroform in a 10-mL glass reactor. The mixture was stirred for 8 h, and the substrate conversion and product formation were monitored by GLC. The products were identified by comparing with authentic samples using GC or GC/MS analysis.

FUNDING

This work was supported by the Nature Science Foundation of China (project nos. 21563026, 21764012) and by the Scientific Research Ability Promotion Program of Young Teachers of Northwest Normal University (project no. NWNU-LKQN-18-18).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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