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Clean and Selective Oxidation of Alcohols with Oxone and Phase-Transfer Catalysts in Water

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Abstract—A new, simple, metal-free, and eco-friendly procedure has been proposed for the oxidation of alcohols with Oxone (potassium peroxymonosulfate) in water in the presence of six phase-transfer catalysts (PTC). Phase-transfer catalysts were found to display high catalytic activity in water solution. Furthermore, the oxidation of alcohols was also carried out with relatively good conversion and selectivity in water without any catalyst.

Keywords: alcohols, oxidation, phase-transfer catalyst, aldehydes, ketones

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INTRODUCTION

The oxidation of alcohols to the corresponding carbonyl compounds is a fundamental transformation in organic synthesis and is of major importance in both laboratory and industrial synthetic chemistry [1–3]. The oxidation of alcohols was traditionally carried out with the use of large amounts of noxious transition metal compounds such as chromates and permanganates [4, 5] or organic solvent [6, 7] or complicated reaction conditions were required [8–10]. In an attempt to provide a more environmentally benign process for alcohol oxidation, a variety of catalytic oxidation procedures using water as the only solvent have been investigated [11–15]. Bolm et al. [16] presented a metal-free oxidation system for the oxidation of alcohols using TEMPO/Oxone® in the presence of a catalytic amount of Bu_4NBr. Surendra et al. [17, 18] reported a transition metal-free catalytic system for the oxidation of alcohols with *o*-iodoxybenzoic acid (IBX) or *N*-bromosuccinimide (NBS) catalyzed by β-cyclodextrin in aqueous acetone. Thottumkara et al. [19] reported a highly efficient oxidation of alcohols using IBX/Oxone® oxidation system in aqueous acetonitrile. Wu et al. [20] reported $AlCl_3$/Oxone oxidation of alcohols in aqueous medium to attain excellent conversion and selectivity. Moriyama et al. [21] described a halide-catalyzed selective oxidation of alcohols with KBr/Oxone in aqueous acetone. Some of these processes also generated equivalent amounts of metal waste, which are environmentally undesirable. Therefore, development of green, selective, and efficient catalysts for the oxidation of alcohols is important for both economic and environmental reasons.

Oxone is a white crystalline solid which is easy to handle, nontoxic, soluble in water, cheap, and stable. Therefore, it has received much attention in the field of oxidation of alcohols [22–24]. Phase-transfer catalysts (PTC) facilitate reactant transport from one phase into another phase where the reaction occurs. It is a special form of heterogeneous catalysis, which is one of the most useful methods in synthetic organic chemistry [25, 26]. In an effort to provide a more convenient procedure and environmentally benign process for the oxidation of alcohols with commercially available Oxone as oxidant we used a series of phase-transfer catalysts and water as solvent.

Herein we report a green, simple, and efficient method for the oxidation of alcohols to the corresponding carbonyl compounds using Oxone as an oxidant and six phase-transfer catalysts in aqueous solution.

RESULTS AND DISSUSSION

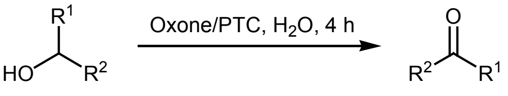
A number of substituted benzyl alcohols, benzhydrol, and its derivatives were oxidized with Oxone in water at certain temperature in the presence of

0.5 equiv of phase-transfer catalysts (Scheme 1). 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 1.

It was found that all PTCs were active catalysts for the oxidation of alcohols. Benzyl alcohol, benzhydrol, and their derivatives were easily oxidized to the corresponding carbonyl compounds in aqueous solution with excellent conversion (Table 1, entry nos. 1, 6, 10). In most cases, the oxidation selectivity was 100%, except for benzyl alcohol (**1a**), 3-methylbenzyl alcohol (**1b**), and 2-methylbenzyl alcohol (**1c**), and no other oxidation products were detected.

Considering the environmental impact, the oxidation of alcohols in water without any catalyst was also investigated. A series of alcohols, including substituted benzyl alcohols, benzhydrols, and long-chain aliphatic alcohols were oxidized with Oxone in water at certain temperature. The results were summarized in Table 2. Benzyl alcohols were oxidized to the corresponding benzaldehydes and benzoic acids with a good conversion (Table 2, entry nos. 1, 2). Most of the oxidation reactions showed 100% selectivity, except for benzyl alcohol (**1a**), 4-nitrobenzyl alcohol (**1d**), and 4-chlorobenzyl alcohol (**1e**) (Table 2, entry nos. 1, 4, 5). The oxidation of 4-chlorobenzhydrol (**1g**) and 4,4′-dimethoxybenzhydrol (**1i**) to the corresponding ketones in water solution was characterized by excellent conversion and selectivity. Cyclic alcohols could not be easily oxidized to the corresponding cyclic ketones in this oxidation system. Long-chain aliphatic alcohols were also difficult to oxidize under the given conditions. This may be due to the molecular structure of these alcohols.

Scheme 1.



1a–1m **2a–2m**

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

In summary, we have proposed a green, efficient, inexpensive, metal-free, and environmentally friendly procedure for the oxidation of benzylic primary and secondary alcohols to the corresponding aldehydes and ketones in water using Oxone as oxidant and phase-transfer catalyst with excellent conversion and selectivity. Furthermore, the oxidation of alcohols was also

Table 1. Oxidation of alcohols with Oxone in the presence of different phase-transfer catalysts in water[a]

Entry no.	Alcohol no.	R^1	R^2	Phase-transfer catalyst	Conversion, ^{b} %	Selectivity,^{b} %	Product no.
1	**1a**	Ph	H	TBAHS	100	56	**2a**
				TPAHS	100	60	
				TEAHS	96	67	
				TMAHS	100	34	
				TBAC	100	61	
				TBAB	100	74	
2	**1b**	3-MeC$_6$H$_4$	H	TBAHS	68	91	**2b**
				TPAHS	67	95	
				TEAHS	75	100	
				TMAHS	61	100	
				TBAC	82	94	
				TBAB	84	78	
3	**1c**	2-MeC$_6$H$_4$	H	TBAHS	69	84	**2c**
				TPAHS	78	83	
				TEAHS	83	100	
				TMAHS	59	100	
				TBAC	74	91	
				TBAB	96	55	

Table 1. (Contd.).

Entry no.	Alcohol no.	R^1	R^2	Phase-transfer catalyst	Conversion,[b] %	Selectivity,[b] %	Product no.
4	**1d**	4-$O_2NC_6H_4$	H	TBAHS	73	100	**2d**
				TPAHS	60	100	
				TEAHS	73	100	
				TMAHS	65	100	
				TBAC	46	100	
				TBAB	99	100	
5	**1e**	4-ClC_6H_4	H	TBAHS	>99	100	**2e**
				TPAHS	100	100	
				TEAHS	>99	100	
				TMAHS	>99	100	
				TBAC	74	100	
				TBAB	>99	100	
6	**1f**	4-$MeOC_6H_4$	H	TBAHS	50	100	**2f**
				TPAHS	69	100	
				TEAHS	69	100	
				TMAHS	46	100	
				TBAC	65	100	
				TBAB	57	100	
7	**1g**	4-ClC_6H_4	Ph	TBAHS	77	100	**2g**
				TPAHS	84	100	
				TEAHS	71	100	
				TMAHS	80	100	
				TBAC	52	100	
				TBAB	67	100	
8	**1i**	4-$MeOC_6H_4$	4-$MeOC_6H_4$	TBAHS	69	100	**2i**
				TPAHS	100	100	
				TEAHS	69	100	
				TMAHS	76	100	
				TBAC	82	100	
				TBAB	88	100	
9	**1j**	3-$PhOC_6H_4$	H	TBAHS	70	100	**2j**
				TPAHS	33	100	
				TEAHS	62	100	
				TMAHS	80	100	
				TBAC	46	100	
				TBAB	90	100	
10	**1m**	Ph	Ph	TBAHS	100	100	**2m**
				TPAHS	100	100	
				TEAHS	100	100	
				TMAHS	100	100	
				TBAC	100	100	
				TBAB	100	100	

[a] Reaction conditions: solvent: H_2O (3 mL), alcohol (1.5 equiv), Oxone (1 equiv), PTC (0.071 equiv), 4 h, 70°C.
[b] According to the GC data.

Table 2. Oxidation of alcohols with Oxone in water in the absence of a catalyst[a]

Entry no.	Alcohol no.	R^1	R^2	Conversion,[b] %	Selectivity,[b] %	Product no.
1	**1a**	Ph	H	98	57	**2a**
2	**1b**	3-MeC_6H_4	H	52	100	**2b**
3	**1c**	2-MeC_6H_4	H	64	100	**2c**
4	**1d**	4-$O_2NC_6H_4$	H	48	83	**2d**
5	**1e**	4-ClC_6H_4	H	96	76	**2e**
6	**1f**	4-$MeOC_6H_4$	H	44	100	**2f**
7	**1g**	4-ClC_6H_4	Ph	84	100	**2g**
8	**1h**	4-MeC_6H_4	Ph	71	100	**2h**
9	**1i**	4-$MeOC_6H_4$	4-$MeOC_6H_4$	91	100	**1i**
10	**1j**	3-$PhOC_6H_4$	H	41	100	**2j**
11	**1k**	$Me(CH_2)_6$	H	7	100	**2k**
12	**1l**	$(CH_2)_5$		9	100	**2l**

[a] Reaction condition: solvent: H_2O (3 mL), alcohol (2.0 equiv), Oxone (1 equiv), 4 h and 65°C.
[b] According to the GC data.

carried out with relatively good to moderate conversion and similar selectivity in aqueous solution without any catalyst.

EXPERIMENTAL

A typical reaction was carried out as follows: alcohol (1.0 equiv), Oxone (1.5 equiv), and PTC (0.5 equiv) were dissolved in 3 mL of water in a 10-mL glass reactor. The mixture was stirred for 4 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.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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