

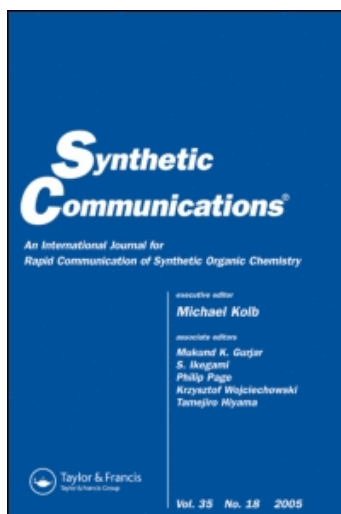
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Chenjie Zhu^a; Yunyang Wei^a; Lei Ji^a

^a School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, China

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CATALYTIC OXIDATION OF ALCOHOLS TO CORRESPONDING ALDEHYDES OR KETONES WITH TEMPO-MEDIATED IODOSOBENZENE IN WATER IN THE PRESENCE OF A SURFACTANT

Chenjie Zhu, Yunyang Wei, and Lei Ji

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, China

An efficient, facile, and rapid oxidation of alcohols to the corresponding aldehydes or ketones with a stoichiometric amount of iodosobenzene (PhIO) in the presence of catalytic amounts of 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO), KBr, and a surfactant, such as SDS (sodium dodecylsulfate), was reported. The oxidation proceeded in water at room temperature to afford aldehydes or ketones in excellent yields and high selectivity without overoxidation to carboxylic acids. Selective oxidation of primary alcohols in the presence of secondary alcohols was also achieved with the catalytic system of PhIO/TEMPO/KBr/SDS. A possible mechanism for the oxidation was supposed.

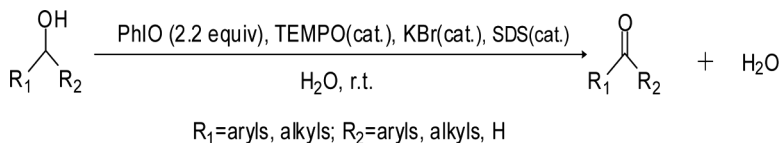
Keywords: Alcohols; iodosobenzene; oxidation; TEMPO; water as solvent

INTRODUCTION

The selective oxidation of alcohols to the corresponding aldehydes or ketones is a fundamental transformation both in laboratory synthesis and industrial production.^[1] Numerous oxidizing reagents^[2] (for example, CrO₃, KMnO₄, and MnO₂) in stoichiometric amounts have been traditionally employed to accomplish this transformation but with considerable drawbacks such as the use of expensive reagents and volatile organic solvents and discharge of environmentally pernicious wastes. The demands for environmentally benign and ecoconscious chemical processes in recent years are encouraging chemists to search for clean, high-yielding, highly selective, and economical oxidation methods. In the past decade, hypervalent iodine reagents have become increasingly appreciated by organic chemists for their mild and highly chemoselective oxidizing properties.^[3–6] For example, the widely utilized pentavalent iodine reagents such as Dess–Martin periodinane (DMP)^[7–9] and its precursor 2-iodoxybenzoic acid (IBX)^[10–12] oxidize alcohols mildly and efficiently to carbonyl compounds in excellent yields in organic solvents such as CH₂Cl₂, dimethylsulfoxide (DMSO), and acetone. However, these iodine(V) reagents are potentially explosive because of the organopentavalent iodine structure. Thus, the

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Address correspondence to Yunyang Wei, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China. E-mail: ywei@mail.njust.edu.cn



Scheme 1. Oxidation of alcohols catalyzed by PhIO/TEMPO/KBr/SDS in water.

readily available and stable iodine(III) oxidants such as iodosobenzene (PhIO) and bis(acetoxy)iodobenzene [PhI(OAc)₂] attract much attention.

On the other hand, it is well known that nitroxyl radicals, such as 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO), promote oxidation of various alcohols to the corresponding carbonyl compounds effectively under mild reaction conditions.^[13–18] Recently, De Mico and coworkers reported a mild and selective method for the oxidation of primary and secondary alcohols using a catalytic amount of TEMPO and bis(acetoxy)iodobenzene [PhI(OAc)₂] as a reoxidant.^[19] In contrast to iodine(V)-based reagents and PhI(OAc)₂, there are few reports concerning the use of PhIO as a reoxidant for TEMPO.^[20,21] Very recently, PhIO was demonstrated by Tohma et al. to be an effective reagent for the oxidation of alcohols in aqueous media in the presence of a catalytic amount of potassium bromide. Although secondary alcohols led to ketones in good yields, primary alcohols were converted to carboxylic acids, not aldehydes.^[22]

In continuation of our interest in exploring systems on the oxidation of organic compounds,^[23] especially alcohols,^[24,25] here we report a facile procedure for the oxidation of alcohols to the corresponding carbonyl compounds with a stoichiometric amount of PhIO in the presence of catalytic amounts of TEMPO, KBr, and a surfactant, such as SDS. The oxidation proceeded in water at room temperature to afford aldehydes or ketones in excellent yields and high selectivity without overoxidation to carboxylic acids (Scheme 1).

RESULTS AND DISCUSSION

Oxidation of 4-Nitrobenzyl Alcohol with PhIO/TEMPO/KBr/Surfactants

Because of the polymeric structure of PhIO_n, which makes it insoluble in most organic solvents, the majority of its reactions require in the presence of a catalytic amount of Lewis acids,^[26–28] such as Ru,^[29] Yb,^[20,30] Bi,^[21] and Re^[21] compounds to generate activated monomeric species. Recently, Tohma et al. had found that the activation of the iodosobenzene polymer ([PhIO]_n) with inorganic bromide salts in water is a powerful method for the effective oxidation of alcohols.^[22] Secondary alcohols were oxidized to ketones in excellent yields with the PhIO/KBr system. Under the same conditions, primary alcohols and diols were oxidized to the corresponding carboxylic acid or lactones, respectively. To develop a method to selectively oxidize alcohols to aldehydes or ketones, we studied the oxidation of 4-nitrobenzyl alcohol with the PhIO/TEMPO/KBr system in water. Development of aqueous-phase reactions is one of the active fields in organic synthesis because

of demands for green chemical processes,^[31,32] such as the oxidation of alcohols.^[33,34] When 4-nitrobenzyl alcohol was stirred in water with PhIO/TEMPO/KBr at room temperature for 2 h, 94% conversion of the alcohol was observed. However, the selectivity to aldehyde was low (48%), and only 43% of 4-nitrobenzaldehyde was isolated (Table 1, entry 1). About one half of the alcohol was overoxidized to the corresponding acid.

It is well known that in aqueous-phase reactions, addition of surfactants can improve the reactions by solubilization^[35,36] or micelle formation effects.^[37–39] To improve the selectivity of the oxidation of alcohols with the PhIO/TEMPO/KBr system in water, we examined the effects using a variety of surfactants, including anionic, cationic, and nonionic surfactants. Among those surfactants examined, SDS, an anionic surfactant, and cetyltrimethyl ammonium bromide (CTAB), a cationic surfactant, were found to be the most effective. In the presence of 20 mol% of SDS, the oxidation of 4-nitrobenzyl alcohol in water completed in 2 h at room temperature with 99% conversion of the reactant and about 95% isolated yield of the corresponding 4-nitrobenzaldehyde (Table 1, entry 6). Tween-80 had only a slightly beneficial effect on the oxidation (Table 1, entry 4). Tetrabutylammonium bromide (TBAB) and triethylbenzylammonium chloride (TEBAC) had no beneficial effect on the reaction, as most of the alcohol was overoxidized to the corresponding acid (Table 1, entries 2 and 3). These results show a clear correlation between the reaction selectivity and the hydrophile–lipophile balance (HLB) value of the surfactants used.^[40] The greater the HLB value of the surfactant used was, the greater reaction selectivity was observed. To reach a reasonable selectivity, the HLB value of the surfactant used should be greater than 15. For surfactants with similar HLB values, ionic surfactants gave better results than nonionic surfactants. A surfactant with an HLB value greater than 15 was often used as an emulsifier for the formation of oil in water (O/W) emulsions or as a solubilization agent. During the experiment, we observed that in the cases of CTAB, SDS, or Tween-80 as surfactant, the reaction mixture was an emulsion all the time, but when TBAB or TEBAC was used as a surfactant, the reaction proceeded in two stages. At the initial stage of the reaction, the reaction mixture was an emulsion, and at the later stage, the reaction mixture

Table 1. Effect of surfactants on the oxidation of p-nitrobenzyl alcohol^a

Entry	Surfactant/HLB ^b	Conversion/selectivity ^c (%)	Yield ^d (%)
1	—	94/48	43
2	TBAB/8.8	99/37	30
3	TEBAC/11.4	91/31	28
4 ^e	Tween-80/15	80/79	65
5	CTAB/15.8	99/90	87
6	SDS/40	99/95	95

^aReaction conditions: p-nitrobenzyl alcohol (1 mmol), PhIO (2.2 mmol), TEMPO (0.1 mmol), KBr (0.2 mmol), surfactant (0.2 mmol), water (5 mL) at room temperature for 2 h.

^bCalculated according to Davis law.

^cGC conversion and selectivity.

^dIsolated yield.

^e0.1 g Tween-80 was added.

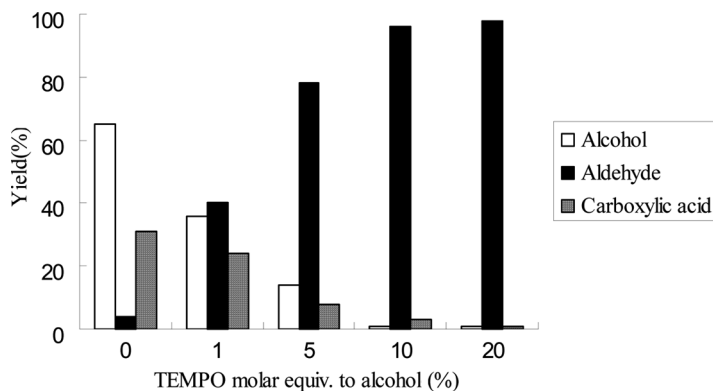


Figure 1. Effects of the amounts of TEMPO on the oxidation of 4-nitrobenzyl alcohol. Reaction conditions: 4-nitrobenzyl alcohol (1 mmol), PhIO (2.2 mmol), KBr (0.2 mmol), surfactant (0.2 mmol), TEMPO, and water (5 mL) at room temperature for 1 h.

gradually turned clean and solid was precipitated. It is believed that the selectivity of the reaction decreases significantly at the later stage; that is, when the reactants, especially TEMPO, could not disperse efficiently in the reaction mixture, the system would actually become a PhIO/KBr system and lead to the formation of 4-nitrobenzoic acid.

To optimize the conditions of the oxidation, the dosages of TEMPO and PhIO were studied using 1 mmol of 4-nitrobenzyl alcohol as substrate. The reaction proceeded without any problem, even with 1 mol% TEMPO, except it took a longer reaction time. Addition of 10 mol% of TEMPO was enough to guarantee high conversion and selectivity (Fig. 1).

Figure 2 shows that to guarantee high conversion and good aldehyde to acid selectivity, less than 2.2 equivalents of PhIO should be used. Remarkable overoxidation of aldehyde to acid occurred when 2.5 equivalents of PhIO was used.

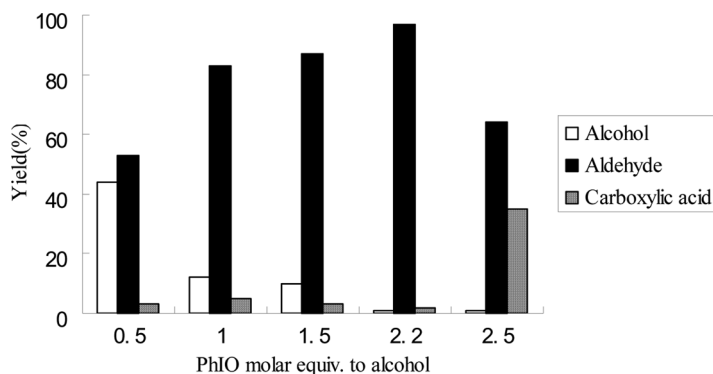
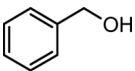
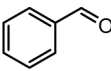
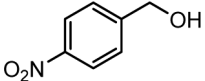
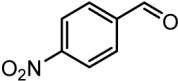
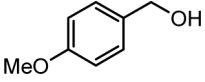
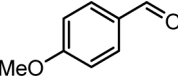
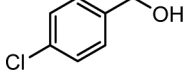
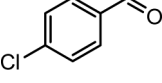
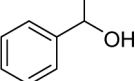
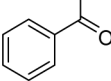
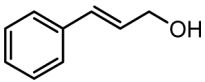
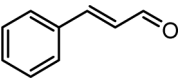
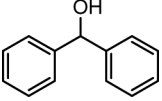
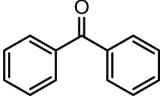
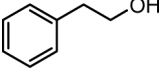
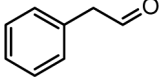
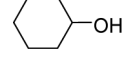
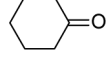
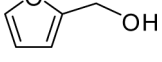
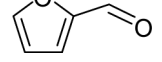
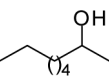
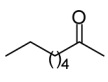


Figure 2. Effects of the amounts of PhIO on the oxidation of 4-nitrobenzyl alcohol. Reaction conditions: 4-nitrobenzyl alcohol (1 mmol), PhIO, KBr (0.2 mmol), surfactant (0.2 mmol), TEMPO (0.1 mmol), and water (5 mL) at room temperature for 0.5 h.

Oxidation of a Variety of Alcohols with PhIO/TEMPO/KBr/SDS System

The scope of the present four-component oxidizing system PhIO/TEMPO/KBr/SDS toward various kinds of alcohols, including benzylic, allylic, heterocyclic, and aliphatic alcohols, was examined. Results are summarized in Table 2.

Table 2. PhIO/TEMPO/KBr/SDS-catalyzed oxidation of alcohols to aldehydes or ketones^a

Entry	Alcohols	Products	Time (h)	Conversion ^b (%)	Yield ^c (%)
1			0.5	99	93
2			1	99	92
3			0.25	99	98
4			0.5	95	94
5 ^d			2	91	85
6			1	95	90
7			7	90	84
8			4	80	72
9 ^d			6	79	64
10 ^d			8	65	48
11	$n\text{-C}_{11}\text{H}_{23}\text{-CH}_2\text{OH}$	$n\text{-C}_{11}\text{H}_{23}\text{-CHO}$	6	94	78
12			8	90	75

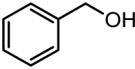
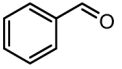
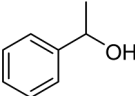
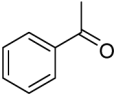
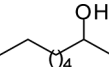
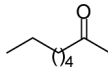
^aReaction conditions: alcohol (1 mmol), PhIO (2.2 mmol), TEMPO (0.1 mmol), KBr (0.2 mmol), surfactant (0.2 mmol), and water (5 mL) at room temperature.

^bGC conversion.

^cYields of isolated products unless otherwise noted.

^dYields were determined by GC.

Table 3. Competitive oxidation of primary and secondary alcohols^a

Entry	Substrate	Product	Time (h)	Yield ^b (%)
1			0.5	95
	+ 	+ 		<10
2	$n\text{-C}_{11}\text{H}_{23}\text{-CH}_2\text{OH}$	$n\text{-C}_{11}\text{H}_{23}\text{-CHO}$	4	88
	+ 	+ 		27

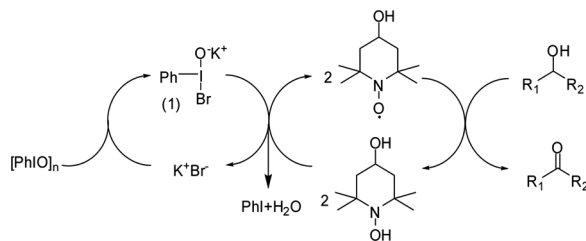
^aThe reactions were carried out on a 1:1 mixture of primary and secondary alcohols, on a 1-mmol scale.^bIsolated yield.

Oxidation of alcohol in benzylic and allylic cases provides aldehyde or ketone with high conversion and good yields (Table 2, entries 1–7). Electron-rich and electron-deficient benzylic alcohols show no obvious difference. Even secondary alcohols such as diphenylmethanol were selectively oxidized to ketones effectively (Table 2, entry 7). The double bond of allylic alcohol was not oxidized (Table 2, entry 6). For the oxidation of primary alcohols, no noticeable overoxidation of aldehyde to carboxylic acids was detected. Aliphatic and heterocyclic alcohols were less reactive than benzylic and allylic alcohols toward this system. Aliphatic alcohols were oxidized to the corresponding aldehydes or ketones in reasonable yields in prolonged reaction times (Table 2, entries 8, 11, and 12). For the oxidation of furan-2-yl methanol, a heterocyclic alcohol, less conversion, and less yield were observed even with prolonged reaction time (Table 2, entry 10).

Table 3 shows the results of the competitive oxidation of primary and secondary alcohols. The competing oxidation of an equimolar mixture of benzyl alcohol and 1-phenylethanol resulted in 95% yield of benzaldehyde and less than 10% yield of acetophenone (Table 3, entry 1). Oxidation of an equimolar mixture of dedocan-1-ol and octan-2-ol gave 88% dedocanal and 27% octan-2-one, respectively (Table 3, entry 2). These results suggest that chemoselective oxidation of primary alcoholic functionality in the presence of secondary alcoholic functionality is possible with the present PhIO/TEMPO/KBr/SDS oxidation system in water.

Mechanistic Aspects

The catalytic system of PhIO/KBr for the oxidation of alcohols was first developed by Tohma and coworkers.^[22] Electrospray ionization–mass spectrometric (ESI-MS) studies suggested that a highly reactive iodine species, $\text{C}_6\text{H}_5\text{I}(\text{Br})\text{O}^-\text{K}^+$ (**1**), is first formed in the reaction and then reacts with primary alcohols to yield the corresponding carboxylic acids or with secondary alcohols to give ketones with regeneration of KBr.^[41]



Scheme 2. Tentative mechanism for oxidation of alcohols with PhIO/TEMPO/KBr/SDS.

For the present PhIO/TEMPO/KBr/SDS catalytic oxidation system, both primary and secondary alcohols give carbonyl compounds. TEMPO must play a key role in this selectivity. As a result of these experimental observations and according to Tohma's preceding studies, we propose a possible reaction pathway (Scheme 2). TEMPO would be the active oxidant in this reaction. Polymeric iodosobenzene ($[\text{PhIO}]_n$) is initially depolymerized by KBr to form the highly reactive intermediate **1**, and the role of **1** is to regenerate TEMPO from TEMPOH.

CONCLUSION

In summary, an efficient, facile, and rapid oxidation of alcohols to the corresponding aldehydes or ketones with the PhIO/TEMPO/KBr/SDS system has been developed. $(\text{PhIO})_n$ activated by a catalytic amount of KBr is a new reoxidant of TEMPOH, which allowed the oxidation of primary and secondary alcohols in water at room temperature to afford aldehydes or ketones in excellent yields and high selectivity without overoxidation to carboxylic acids. Selective oxidation of primary alcohols in the presence of secondary alcohols was also achieved. Development of immobilized and recyclable iodine(III) reagents is currently under investigation.

EXPERIMENTAL

All chemicals (analytical reagent grade) were obtained from commercial resources and used without further purification. Gas chromatographic (GC) analysis was performed on an Agilent GC-6820 chromatograph equipped with a $30\text{ m} \times 0.32\text{ mm} \times 0.5\text{ }\mu\text{m}$ HP-Innowax capillary column and a flame ionization detector; ^1H NMR spectra were obtained with tetramethylsilane (TMS) as internal standard using a Bruker DRX 500 (500-MHz) spectrometer. Infrared (IR) spectra were recorded on a Shimadzu spectrometer using KBr discs. Products were all known compounds and were identified by comparing their physical and spectroscopic data with those reported in the literature.

Typical Experimental Procedure for Oxidation of Alcohols

Alcohol (1 mmol), PhIO (2.2 mmol), TEMPO (0.1 mmol), KBr (0.2 mmol), and SDS (0.2 mmol) were mixed with water (5 mL) and stirred at room temperature

for several hours. The reaction progress was checked by gas or thin-layer chromatography (TLC). After completion, the mixture was extracted with n-hexane (5×5 mL) and then filtered. The combined n-hexane phase was concentrated under vacuum, and the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to provide the analytically pure aldehyde or ketone, which was characterized by ^1H NMR and IR analysis.

ACKNOWLEDGMENT

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