

# Ionic TEMPO in Ionic Liquids: Specific Promotion of the Aerobic Oxidation of Alcohols

Tsunehisa Hirashita,<sup>\*,[a]</sup> Makoto Nakanishi,<sup>[a]</sup> Tomoya Uchida,<sup>[a]</sup> Masakazu Yamamoto,<sup>[a]</sup> Shuki Araki,<sup>[a]</sup> Isabel W. C. E. Arends<sup>[b]</sup> and Roger A. Sheldon<sup>\*,[b], [c]</sup>

**Abstract:** The main objective of this study was to design a recyclable TEMPO derivative which could be used as a catalyst, in an ionic liquid solvent, for the aerobic oxidation of alcohols using NaNO<sub>2</sub> and HCl as co-catalysts. To this end, a TEMPO derivative bearing a quaternary ammonium group, [4-Bu<sub>2</sub>MeN-TEMPO] [PF<sub>6</sub>] (1), was prepared. It was subsequently shown that this ionic TEMPO is an efficient catalyst for the aerobic oxidation of a variety of primary and secondary alcohols, exhibiting a synergistic effect with ionic liquid solvents and readily outperforming analogous oxidations in methylene chloride. Moreover, the ionic TEMPO could be recycled five times with no loss of activity.

## Introduction

The selective oxidation of alcohols is one of the most important reactions in organic synthesis.<sup>[1]</sup> There is a growing concern to develop greener oxidation processes that obviate the need for a stoichiometric amount of toxic heavy metals. The 2,2,6,6-tetramethylpiperidiny-*N*-oxyl<sup>[2]</sup> (TEMPO)-catalysed oxidation of alcohols has emerged as a clean and economical oxidation process using bleach or dioxygen as terminal oxidizing agents.<sup>[3]</sup> In general, TEMPO-catalysed oxidations proceed with high chemoselectivity; the over-oxidation of aldehydes to carboxylic acids is very slow, because TEMPO prevents auto-oxidation under aerobic conditions.<sup>[4]</sup>

Because of its high atom efficiency, oxygen (air) is usually the oxidant of choice and aerobic oxidations are considered one of the greenest oxidation processes; however, they are usually performed with the aid of a catalytic amount of transition-metal compounds. Metal contamination of products causes serious issues in the field of fine chemicals and pharmaceuticals manufacture. The best way to avoid this contamination is to obviate the need for metal catalysts for oxidative processes. Recently, an appealing aerobic oxidation of alcohols catalysed

by TEMPO and nitrite or its precursor has been introduced in this field.<sup>[5]</sup> However, these reactions are normally performed in aqueous biphasic systems using methylene dichloride as organic phase<sup>[4e]</sup>. Hence, from the point of view of green chemistry, the design of a greener protocol for this oxidation is necessary.

Ionic liquids have been used as alternative organic solvents with low vapour pressure; safety issues associated with the flammability of mixtures of oxygen and volatile organic solvents in the gas phase can thus be circumvented. Moreover, ionic liquids have the potential to immobilise catalysts and recycle them for further reaction.<sup>[6]</sup> Metal-free aerobic oxidation of alcohols with recyclable catalysts immobilised in ionic liquids is a desirable method for the preparation of aldehydes and ketones. The TEMPO-catalysed oxidation in ionic liquids and the recyclability of the ionic liquids in the process have been successfully examined in the literature.<sup>[7]</sup> Because TEMPO is a rather expensive material, a technique that facilitates its separation from the products and its reuse should be considered. However, extraction of the reaction products from the ionic liquid with an organic solvent results in leaching of TEMPO, which prevents its recycling. In order to overcome this difficulty, TEMPO derivatives containing polar functionalities have been tested.<sup>[8]</sup> Besides their recyclability, the use of ionic liquids as media for the aerobic oxidation of alcohols catalysed by a stable *N*-oxy radical, has not been systematically investigated.<sup>[7e, 8a, 9]</sup> Herein we report an expeditious aerobic oxidation of alcohols catalysed by NaNO<sub>2</sub>/HCl using a suitable ionic liquid and a TEMPO derivative bearing an ammonium moiety. The recyclability of the ionic liquid and catalyst is also discussed.

## Results and Discussion

### Synthesis of [4-Bu<sub>2</sub>MeN-TEMPO] [PF<sub>6</sub>] (1).

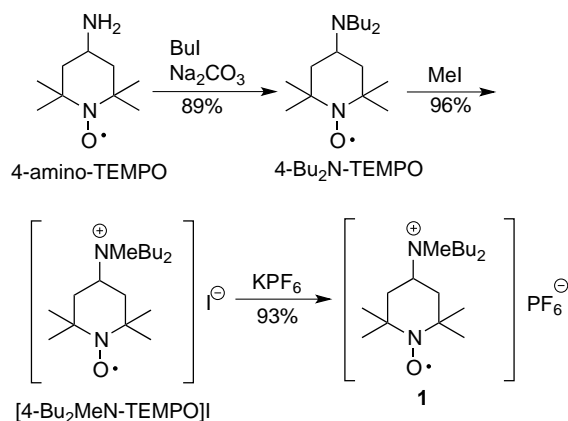
In order to recycle the catalyst in the ionic liquid, an ammonium tag was introduced into TEMPO (Scheme 1). The ionic TEMPO 1 was prepared by alkylation of 4-amino-TEMPO with *n*-butyl iodide, followed by quaternisation with MeI. Ion exchange with KPF<sub>6</sub> gave [Bu<sub>2</sub>MeN-TEMPO][PF<sub>6</sub>] as a pale orange solid in good yield.<sup>[10]</sup>

[a] Dr. T. Hirashita, M. Nakanishi, T. Uchida, M. Yamamoto, Prof. S. Araki, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555 (Japan)  
E-mail: hirasita@nitech.ac.jp

[b] Prof. I. W. C. E. Arends, Prof. R. A. Sheldon, Biocatalysis and Organic Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft (The Netherlands)

[c] Prof. R. A. Sheldon, School of Chemistry, University of the Witwatersrand, Johannesburg 2050 (Republic of South Africa)

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**Scheme 1.** Synthesis of [4-Bu<sub>2</sub>MeN-TEMPO] [PF<sub>6</sub>] (**1**).

### Catalytic activity of **1** in aerobic oxidation

We first examined the oxidation of benzyl alcohol (**2a**) using 3 mol% of ionic TEMPO **1**, 5 mol% of NaNO<sub>2</sub>, and 10 mol% of HCl in [bmim][PF<sub>6</sub>]. Benzaldehyde was obtained in 99% yield in 1 h (Table 1, entry 1).

**Table 1.** Oxidation of **2a** with **1**<sup>[a]</sup>

Entry	Solvent <sup>[b]</sup>	Time (h)	Yield (%) of Aldehyde <sup>[b]</sup>	Recovery (%) of <b>2a</b> <sup>[c]</sup>
1	[bmim][PF <sub>6</sub> ]	1	99	0
2	[bmim][NTf <sub>2</sub> ]	1	53	43
3	[bmim][NTf <sub>2</sub> ]	16	99	0
4	[bmpy][PF <sub>6</sub> ]	1	52	40
5	[bmpy][PF <sub>6</sub> ]	16	99	0
6 <sup>d</sup>	[bmim][PF <sub>6</sub> ]	1	0 <sup>e</sup>	83

[a] Reaction conditions: **2a** (0.50 mmol), **1** (0.015 mmol), NaNO<sub>2</sub> (0.025 mmol), HCl (0.050 mmol) in ionic liquid (0.5 mL), air, RT. [b] bmim (1-butyl-3-methylimidazolium); bmpy (1-butyl-4-methylpyridinium). [c] GC yield. [d] Without **1**. [e] Benzoic acid was obtained in 4% yield.

In [bmim][NTf<sub>2</sub>] a slower oxidation rate was observed than in [bmim][PF<sub>6</sub>] (entry 2), and a high yield can be obtained by simply prolonging the reaction time (entry 3). The reaction in [bmpy][PF<sub>6</sub>] showed a lower oxidation rate, with a trend similar to that of the reaction performed in [bmim][NTf<sub>2</sub>] (entries 4 and 5). In a blank experiment in [bmim][PF<sub>6</sub>], benzaldehyde was not

detected, benzoic acid was formed in 4% yield, and **2a** was recovered almost quantitatively. These results demonstrate the importance of a proper choice of the ionic liquid in promoting the oxidation reaction.

### Effect of ammonium tag and solvent

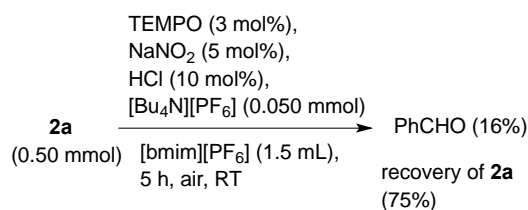
In order to clarify the conditions for a faster oxidation, a set of reactions was performed in [bmim][PF<sub>6</sub>] and CH<sub>2</sub>Cl<sub>2</sub> (Table 2). Compared with the reaction using TEMPO **1** in [bmim][PF<sub>6</sub>] oxidation in CH<sub>2</sub>Cl<sub>2</sub> was found to be sluggish, affording benzaldehyde in only 49% yield in 10h (entry 2). In contrast, when TEMPO was used better results were obtained in CH<sub>2</sub>Cl<sub>2</sub> (entry 3). Under the conditions reported in the literature<sup>[5e]</sup>, the corresponding aldehyde was obtained in 77% yield, although a longer reaction time (13h) was needed (entry 4).

**Table 2.** Solvent and catalyst effect on the oxidation of **2a**<sup>[a]</sup>

Entry	Catalyst	Solvent	Time (h)	Yield (%) <sup>[b]</sup>	TOF (h <sup>-1</sup> )
1	<b>1</b>	[bmim][PF <sub>6</sub> ]	1	99	33
2	<b>1</b>	CH <sub>2</sub> Cl <sub>2</sub>	10	49 (51)	1.6
3	TEMPO	[bmim][PF <sub>6</sub> ]	10	27 (64)	0.9
4	TEMPO	CH <sub>2</sub> Cl <sub>2</sub>	13	77 (23)	2.0

[a] Reaction conditions: **2a** (0.50 mmol), TEMPO or **1** (0.015 mmol), NaNO<sub>2</sub> (0.025 mmol), 1 M HCl (0.050 mmol), solvent (ionic liquid: 1.5 mL or CH<sub>2</sub>Cl<sub>2</sub>: 5 mL), air, RT. [b] GC yield. Values in parentheses show the recovery of **2a**.

In order to confirm the importance of the ammonium group bound to TEMPO, the reaction was carried out in the presence of the individual components: the oxidation of **2a** in the presence of TEMPO and tetrabutylammonium hexafluorophosphate gave benzaldehyde in a lower yield as compared with that obtained using catalyst **1** (Scheme 2).



**Scheme 2.** Oxidation of **2a** with TEMPO in the presence of [Bu<sub>4</sub>N][PF<sub>6</sub>].

These results clearly indicate that the use of ionic TEMPO **1** in the ionic liquid is crucial for increasing the oxidation rate.

### Aerobic oxidation of alcohols with **1**

Having established the optimum conditions, the scope and limitations were examined using a series of alcohols (Fig. 1). The results are summarised in Table 3. Benzylic alcohols **2a**, **2b**, and **3a** were easily oxidised to the corresponding aldehydes in high yields (entries 1–3), whereas benzylic alcohol **3b** with an electron-withdrawing group was significantly less reactive (entry 4). Allylic alcohol **4** was converted to cinnamaldehyde in good yield (entry 5). Normally, cyclic secondary alcohol **5** resists oxidation because of steric factors: for instance, the TEMPO-

catalysed reaction in  $\text{CH}_2\text{Cl}_2$  generates cyclohexanone only in 37% conversion and with 91% selectivity after 24 h.<sup>[5e]</sup> In contrast, the present method afforded cyclohexanone in high yields, although a longer reaction time was required (entries 6 and 7). In  $[\text{bmim}][\text{PF}_6]$ , aliphatic alcohol **6** was mainly converted into acetal **11** originating from the reaction of the formed aldehyde with **6** (entry 8). The formation of acetal in a protic ionic liquid has been previously reported;<sup>[11]</sup> however, this side reaction can be suppressed by switching the ionic liquid to  $[\text{bmim}][\text{NTf}_2]$ , which affords the corresponding aldehyde in moderate yield (entry 9). Secondary aliphatic alcohols **7** and **8** were converted into the corresponding ketones in excellent yields (entries 10 and 11). Moreover, the oxidation of unsaturated aliphatic alcohol **9** afforded the corresponding aldehyde in moderate yield (entry 12).  $\beta$ -Phenethyl alcohol (**10**) gave predominantly the corresponding acetal **12** (entry 13). Using oxygen instead of air in  $[\text{bmim}][\text{NTf}_2]$  under heating was found to accelerate the reaction: phenylacetaldehyde was obtained in moderate yield and formation of acetal **12** was suppressed, presumably by the faster oxidative process (entry 14).

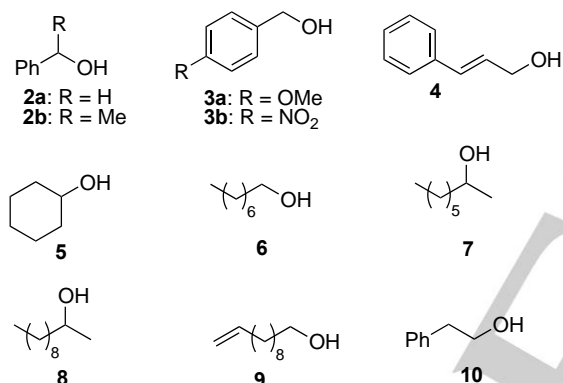


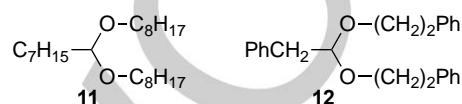
Figure 1. Selected alcohol substrates.

Table 3. Oxidation of various alcohols<sup>[a]</sup>

Entry	Alcohol	Conditions <sup>[b]</sup>	Time (h)	Yield (%) <sup>[c]</sup>
1 <sup>d</sup>	<b>2a</b>	3/5/10	1	99
2	<b>2b</b>	3/5/10	1	99
3	<b>3a</b>	5/10/10	1	98
4	<b>3b</b>	5/10/10	16	90 (2)
5	<b>4</b>	5/10/20	2	99
6	<b>5</b>	5/10/20	5	79 (12)
7	<b>5</b>	5/10/20	16	92
8	<b>6</b>	5/8/16	5	36 (13), <b>11</b> : 51
9 <sup>e</sup>	<b>6</b>	5/8/16	5	68 (22)
10	<b>7</b>	5/8/16	5	91

11	<b>8</b>	5/10/20	3	99
12	<b>9</b>	5/8/16	5	50 (19)
13	<b>10</b>	5/8/16	5	18 (21), <b>12</b> : 56
14 <sup>e,f</sup>	<b>10</b>	5/8/16	5	59 (13)

[a] Reaction conditions: alcohol (0.50 mmol) in  $[\text{bmim}][\text{PF}_6]$  (1.5 mL) under air at RT. [b]  $1/\text{NaNO}_2/\text{HCl}$  (mol%). [c] Determined by GC. Values in parentheses show the recovery of the starting alcohol. [d] Entry 1 in Table 1. [e] In  $[\text{bmim}][\text{NTf}_2]$ . [f] Performed under  $\text{O}_2$  (balloon pressure) at 60 °C.



Thus, the optimum ionic liquid for this reaction depends on the alcohol employed. Whereas  $[\text{bmim}][\text{PF}_6]$  was preferable for the oxidation of **2a** as shown in Table 1, the use of  $[\text{bmim}][\text{NTf}_2]$  resulted in the selective oxidation of a primary aliphatic alcohol (Table 3, entry 9).

#### Aerobic oxidation of octan-2-ol with **1**

We next tested the oxidation of **7**, as a representative aliphatic secondary alcohol, in a series of ionic liquids with different anionic counterparts (Table 4). In contrast to the case of primary alcohols,  $[\text{bmim}][\text{PF}_6]$  was superior to  $[\text{bmim}][\text{NTf}_2]$  (entries 1 and 2) and to  $[\text{bmim}][\text{BF}_4]$ , which resulted in slow oxidation (entry 3). Ionic liquid  $[\text{bmim}][\text{OTf}]$  was also suitable for the oxidation of **7** (entry 4).

Table 4. Oxidation of **7** with **1** in ionic liquids<sup>[a]</sup>

Entry	Solvent	Yield of 2-octanone (%) <sup>[b]</sup>	Recovery of <b>7</b> <sup>[b]</sup>
1	$[\text{bmim}][\text{PF}_6]$	91	0
2	$[\text{bmim}][\text{NTf}_2]$	78	0
3	$[\text{bmim}][\text{BF}_4]$	69	24
4	$[\text{bmim}][\text{OTf}]$	91	0

[a] Reaction conditions: **7** (0.50 mmol), **1** (0.015 mmol),  $\text{NaNO}_2$  (0.025 mmol),  $\text{HCl}$  (0.050 mmol), ionic liquid (1.5 mL) under air atmosphere at RT for 5 h. [b] GC yield.

#### Recyclability of **1**

Next, the recyclability of the catalytic system was examined in the oxidation of **2a**. After the first run, the product was separated from the ionic liquid layer by extraction with diethyl ether. The ionic liquid containing ionic TEMPO **1** was directly reused for the next oxidation. Although addition of new  $\text{NaNO}_2$  and  $\text{HCl}$  was required, no decrease in yield was observed up to five recycles (Table 5).

Table 5. Recycling of ionic TEMPO **1** and  $[\text{bmim}][\text{PF}_6]$  for the oxidation of **2a**<sup>[a]</sup>

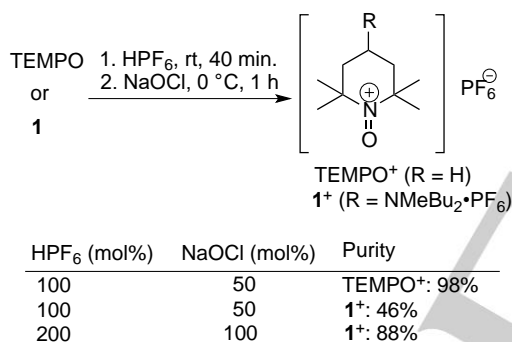
Run	Yield (%) <sup>[b]</sup>	Recovery of <b>2a</b> (%) <sup>[b]</sup>
1	99	0

2	99	0
3	99	0
4	98	0
5	95	0
6	92	0

[a] Reaction conditions: **2a** (0.50 mmol), **1** (0.015 mmol), NaNO<sub>2</sub> (0.025 mmol), HCl (0.050 mmol), [bmim][PF<sub>6</sub>] (1.5 mL), air, RT for 1 h. The ionic phase recovered from the previous reaction was used. NaNO<sub>2</sub> (0.025 mmol) and HCl (0.050 mmol) were added. [b] GC yield.

### Stoichiometric oxidation

In order to gain insight into the catalytic role of **1**, oxidation of **2a** using stoichiometric amount of oxoammonium **1**<sup>+</sup> was tested. Oxoammonium **1**<sup>+</sup> was prepared according to the literature procedure described for [TEMPO<sup>+</sup>][BF<sub>4</sub>].<sup>[12]</sup> After exposure of **1** to HPF<sub>6</sub>,<sup>[13]</sup> the reaction mixture was treated with NaOCl. The purity of the resulting oxoammonium salt was estimated by oxidation of an excess amount of benzyl alcohol. TEMPO<sup>+</sup> obtained by this procedure showed a good purity (98%), whereas the oxoammonium derived from **1** was only 46% pure (Scheme 3). However, a satisfactory result was obtained using a double amount of reagents (88% purity of **1**<sup>+</sup>).



**Scheme 3.** Preparation of oxoammonium salts.

Stoichiometric oxidation of **2a** with TEMPO<sup>+</sup> or **1**<sup>+</sup> was carried out in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, and [bmim][PF<sub>6</sub>], and the results are summarised in Table 6.

**Table 6.** Stoichiometric oxidation of **2a** with TEMPO<sup>+</sup> or **1**<sup>+</sup>[a]

Entry	Oxidant	Solvent	Time (h)	Yield of aldehyde (%) <sup>[b]</sup>	Recovery of <b>2a</b> (%) <sup>[b]</sup>
1	<b>1</b> <sup>+</sup>	[bmim][PF <sub>6</sub> ]	0.25	96	0
2	<b>1</b> <sup>+</sup>	CH <sub>3</sub> CN	0.25	100	0
3	<b>1</b> <sup>+</sup>	CH <sub>2</sub> Cl <sub>2</sub>	1.5	64	36
4	TEMPO <sup>+</sup>	[bmim][PF <sub>6</sub> ]	1.5	23	66
5	TEMPO <sup>+</sup>	CH <sub>3</sub> CN	1.5	70	24
6	TEMPO <sup>+</sup>	CH <sub>2</sub> Cl <sub>2</sub>	1.5	92	6

[a] Reaction conditions: **2a** (0.09 mmol), TEMPO<sup>+</sup> or **1**<sup>+</sup> (0.10 mmol) in solvent (1.0 mL) at RT. [b] Determined by GC.

Comparison of the results in Tables 2 and 6 reveals a similar tendency in the stoichiometric and catalytic oxidations. The reaction with **1**<sup>+</sup> in CH<sub>3</sub>CN and [bmim][PF<sub>6</sub>] proceeded faster than that in CH<sub>2</sub>Cl<sub>2</sub> (entries 1–3), whereas TEMPO<sup>+</sup> was most efficient in CH<sub>2</sub>Cl<sub>2</sub> (entries 4–6). It should be noted that **1**<sup>+</sup> was not completely dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and therefore the above results may not accurately reflect the reaction rate of **1**<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub>.

### Comparison of TEMPO and ionic TEMPO (**1**) in ionic liquids

For the catalytic and stoichiometric oxidations, CH<sub>2</sub>Cl<sub>2</sub>, which is typically used for TEMPO-catalysed reactions, was a superior solvent to [bmim][PF<sub>6</sub>]. The oxidation in acetonitrile also yielded better results than those obtained in [bmim][PF<sub>6</sub>]. This is in good agreement with the literature reports,<sup>[9a]</sup> which ascribe this tendency to the different viscosities of molecular solvents and ionic liquids. In contrast, TEMPO<sup>+</sup>-mediated oxidations in an alternative ionic liquid, *N*-butyl-*N*-methyl pyrrolidinium bis(trifluoromethylsulfonyl)imide, proceeded faster than those in acetonitrile,<sup>[9b]</sup> suggesting that the reaction rate of the TEMPO<sup>+</sup>-mediated oxidation is strongly dependent on the ionic liquid employed. On the other hand, the results related to the use of **1** were found to be quite different. The reactions in [bmim][PF<sub>6</sub>] proceeded at a clearly faster rate than those performed in CH<sub>2</sub>Cl<sub>2</sub>, and approximately the same results were obtained in acetonitrile. This trend can be rationalized by assuming that more polar solvents preferably promote the formation and reaction of the highly active oxoammonium **1**<sup>+</sup> containing both oxoammonium and ammonium groups,<sup>[14]</sup> thus compensating for the high viscosity of the ionic liquid. As compared with the ionic liquid, acetonitrile served as a good solvent giving the same level of conversion. However, [bmim][PF<sub>6</sub>] is superior to acetonitrile in separating the products from the reaction mixture while keeping the catalyst in the solvent to be reused in the next reaction.

## Conclusions

TEMPO derivative **1** proved to be an effective mediator for the aerobic oxidation of alcohols in ionic liquids. This study clearly demonstrates the importance of careful screening of ionic liquids with respect to the selectivity as well as the acceleration. In addition, a strong synergistic effect between ionic-TEMPO **1** and ionic liquids became apparent. The use of **1** and an ionic liquid plays a key role in increasing the oxidation rate. The ammonium tag on **1** is responsible not only for recycling the *N*-oxy radical in the ionic liquid phase but also for enhancing the oxidation rate.



## Experimental Section

### General Methods

IR spectra were recorded on a JASCO IRA-102 spectrophotometer. <sup>1</sup>H NMR spectra were obtained in CDCl<sub>3</sub> or CD<sub>3</sub>CN using a Varian Mercury 300 spectrometer (300 MHz) with Me<sub>4</sub>Si as internal standard; *J*-values are given in Hz. GC analyses were performed on a SHIMADZU GC-14B and GC-2014 fitted with a capillary column and a flame ionization detector. Elemental analyses were carried out with a Perkin Elmer 2400II analyzer. Melting points were measured on a Yanaco MP 50533 and are uncorrected. Ionic liquids were purchased from Kanto Chemical and were used as received. All alcohols were commercially available and distilled before use.

### Experimental Procedures

**Preparation of 4-Bu<sub>2</sub>N-TEMPO:** A mixture of 4-amino-TEMPO (1.62 g, 9.45 mmol), *n*-butyl iodide (4.5 mL, 39.6 mmol), and K<sub>2</sub>CO<sub>3</sub> (8.23 g, 59.5 mmol) in acetonitrile (50 mL) was refluxed for 23 h. The product was diluted with diethyl ether (150 mL), washed with water (40 mL × 3) and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure to give 4-Bu<sub>2</sub>N-TEMPO (2.38 g, 89%).

**4-Bu<sub>2</sub>N-TEMPO:** *R*<sub>f</sub> = 0.82 (SiO<sub>2</sub>/EtOH); <sup>1</sup>H NMR was recorded after addition of phenylhydrazine (one drop) to the NMR sample tube. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.94 (t, *J* = 7.1 Hz, 6H), 1.16 (s, 6H), 1.22 (s, 6H), 1.30–1.42 (m, 4H), 1.46–1.71 (br s, 6H), 1.79–1.83 (m, 2H), 2.65 (br s, 4H), 3.17–3.22 ppm (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ ppm): 14.144, 19.925, 20.694, 31.234, 32.796, 41.227, 50.323, 50.371, 59.253. IR (neat): ν = 3448, 2955, 2871, 2809, 1639, 1464, 1376, 1362, 1328, 1287, 1243, 1217, 1195, 1089, 1074, 1035, 937, 903, 867, 735, 680 cm<sup>-1</sup>.

**Preparation of [4-Bu<sub>2</sub>MeN-TEMPO]:** 4-Bu<sub>2</sub>N-TEMPO (2.24 g, 7.92 mmol) was treated with MeI (2.5 mL, 40 mmol) in acetonitrile (40 mL) and heated at reflux for 3 h. After the complete consumption of 4-Bu<sub>2</sub>N-TEMPO, as monitored by TLC, the solvent was removed under reduced pressure affording [4-Bu<sub>2</sub>MeN-TEMPO] (3.23 g, 96%).

**[4-Bu<sub>2</sub>MeN-TEMPO]:** *R*<sub>f</sub> = 0.78 (Al<sub>2</sub>O<sub>3</sub>/EtOH). <sup>1</sup>H NMR was recorded after addition of phenylhydrazine (one drop) to the NMR sample tube. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.03 (t, *J* = 7.4 Hz, 6H), 1.23 (s, 6H), 1.32 (s, 6H), 1.44–1.60 (m, 4H), 1.68–1.84 (m, 4H), 1.88 (d, *J* = 12 Hz, 2H), 2.02 (d, *J* = 9.6 Hz, 2H), 3.22 (s, 3H), 3.30–3.62 ppm (m, 5H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ ppm): 13.714, 19.678, 24.419, 32.479, 37.916, 46.840, 59.186, 59.597, 64.477. IR (KBr): ν = 3434, 2962, 2867, 1633, 1463, 1362, 1245, 1195 cm<sup>-1</sup>.

**Preparation of ionic TEMPO 1:** [4-Bu<sub>2</sub>MeN-TEMPO] (2.15 g, 5.06 mmol) and KPF<sub>6</sub> (1.06 g, 5.74 mmol) were mixed in distilled water (40 mL) and acetone (40 mL) at room temperature for 3 h. The product was extracted with methylene chloride, washed with water and brine, and dried over Na<sub>2</sub>SO<sub>4</sub> to give [4-Bu<sub>2</sub>MeN-TEMPO][PF<sub>6</sub>] (1, 2.08 g, 93%).

**[4-Bu<sub>2</sub>MeN-TEMPO][PF<sub>6</sub>] (1):** *R*<sub>f</sub> = 0.80 (Al<sub>2</sub>O<sub>3</sub>/EtOH); m.p. 167–169 °C; <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded after addition of phenylhydrazine (one drop) to the NMR sample tube. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN): δ = 0.97 (t, 6H, *J* = 7.2 Hz), 1.14 (s, 6H), 1.18 (s, 6H), 1.32–1.40 (m, 4H), 1.64–1.72 (m, 6H), 1.92–1.95 (m, 2H), 2.83 (s, 3H), 3.13–3.19 (m, 4H), 3.43–3.51 ppm (m, 1H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN): δ = 13.80 19.56, 20.29, 24.77, 32.87, 38.31, 46.09, 59.69, 60.02, 65.18 ppm; IR (KBr): ν = 2970, 2879, 1637, 1469, 1384, 1368, 1243, 1198, 1105, 843, 741, 679 cm<sup>-1</sup>; HRMS (ESI<sup>+</sup>): *m/z*. Calc. for C<sub>18</sub>H<sub>38</sub>N<sub>2</sub>O (cation): 298.2984; found:

298.3002; HRMS (ESI<sup>-</sup>): *m/z*: calcd for PF<sub>6</sub> (anion): 144.9642; found: 144.9636; elemental analysis: calcd (%) for C<sub>18</sub>H<sub>38</sub>F<sub>6</sub>N<sub>2</sub>OP (443.47): C 48.75, H 8.64, N, 6.3; found: C 49.08, H 8.82, N 6.23.

### NaNO<sub>2</sub>/HCl-mediated oxidation of alcohols catalysed by ammonium TEMPO 1 (Table 1, entry 1).

A mixture of benzyl alcohol (52 μL, 0.50 mmol), NaNO<sub>2</sub> (1.7 mg, 25 μmol), 1 M HCl (50 μL), and ionic TEMPO 1 (6.7 mg, 3 mol%) in [bmim][PF<sub>6</sub>] (1.5 mL) was stirred at room temperature for 1 h. The product was extracted with ether (5 mL × 5). The yield was determined by GC using hexadecane as an internal standard.

**Octanal diocetyl acetal:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.86–0.90 (m, 9H), 1.2–1.4 (m, 30H), 1.54–1.59 (m, 6H), 3.39–3.44 (m, 2H), 3.53–3.57 (m, 2H), 4.46 ppm (t, *J* = 5.7 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN): δ = 14.23, 22.81, 23.13, 24.95, 26.43, 29.40, 29.44, 29.59, 30.05, 30.46, 31.94, 31.99, 33.56, 65.50, 103.23 ppm.

**Phenylacetaldehyde diphenetyl acetal:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 2.77–2.90 (m, 4H), 2.89 (d, *J* = 5.7 Hz, 2H), 3.49–3.60 (m, 2H), 3.69–3.77 (m, 2H), 4.62 (t, *J* = 5.7 Hz, 1H), 7.10–7.30 ppm (m, 15H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN): δ = 36.44, 40.68, 67.20, 104.10, 126.30, 126.42, 128.36, 128.42, 129.08, 129.70, 137.20, 139.06 ppm.

### Preparation and titration of TEMPO<sup>+</sup> [1<sup>2+</sup>]

To a mixture of TEMPO (78.6 mg, 0.50 mmol) and water (0.2 mL), HPF<sub>6</sub> (65 wt%, 115 μL, 0.50 mmol) was slowly added over a period of 3 minutes at room temperature. After stirring for 40 minutes, NaOCl (1.84 M, 136 μL, 0.25 mmol) was added over 3 minutes at 0 °C, and the mixture was stirred for further 1 hour. The product was filtered and washed with cold aqueous 5% NaHCO<sub>3</sub>, water, and cold diethyl ether. After drying, [TEMPO<sup>+</sup>][PF<sub>6</sub>] was obtained as bright yellow solid (88 mg). A mixture of benzyl alcohol (11.4 μL, 0.11 mmol) and [TEMPO<sup>+</sup>][PF<sub>6</sub>] (15.2 mg, 0.050 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was stirred at room temperature for 17 h. The product was extracted with ether. The yield of benzaldehyde (98%) based on [TEMPO<sup>+</sup>][PF<sub>6</sub>] was determined by GC using hexadecane as an internal standard.

### Preparation and titration of 1<sup>+</sup>

To a mixture of 1 (111 mg, 0.25 mmol) and water (0.4 mL), HPF<sub>6</sub> (65 wt%, 115 μL, 0.50 mmol) was slowly added over a period of 3 minutes at room temperature. After stirring for 40 minutes, NaOCl (1.84 M, 136 μL, 0.25 mmol) was added over 3 minutes at 0 °C, and the mixture was stirred for further 1 hour. The product was filtered and washed with cold aqueous 5% NaHCO<sub>3</sub>, water, and cold diethyl ether. After drying, [1<sup>+</sup>][PF<sub>6</sub>] was obtained as a yellow solid (118 mg). A mixture of benzyl alcohol (10.4 μL, 0.10 mmol) and [1<sup>+</sup>][PF<sub>6</sub>] (29.5 mg, 0.050 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was stirred at room temperature for 17 h. The product was extracted with ether. The yield of benzaldehyde (88%) based on [1<sup>+</sup>][PF<sub>6</sub>] was determined by GC using hexadecane as an internal standard.

### Stoichiometric oxidation of benzyl alcohol by ionic TEMPO 1<sup>+</sup> (Table 6, entry 1)

A mixture of benzyl alcohol (10.2 mg, 0.094 mmol) and ionic TEMPO 1<sup>+</sup> (88% purity, 67 mg, 0.10 mmol) in [bmim][PF<sub>6</sub>] (1.0 mL) was stirred at room temperature for 15 minutes. The product was extracted with diethyl ether (2 mL × 7). The yield was determined by GC analysis using hexadecane as an internal standard.

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**Keywords:** Alcohols • Ionic liquids • Oxidation • Oxygen • Radicals

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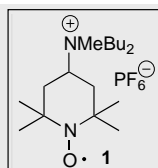
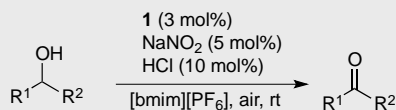
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Text  
Contents

for Table of