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Mild and selective oxidation of alcohols to aldehydes and ketones using $NaIO_4$/TEMPO/NaBr system under acidic conditions

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Abstract—A TEMPO-catalyzed selective oxidation of alcohols to the corresponding aldehydes and ketones using $NaIO_4$ as the terminal oxidant is reported. The $NaIO_4$/TEMPO/NaBr system provides a mild and efficient method for the oxidation of alcohols that are sensitive to basic conditions. Furthermore, the recoverable ionic liquid immobilized TEMPO-catalyzed oxidation of benzyl alcohol in ionic liquid–H_2O medium is also developed.

1. Introduction

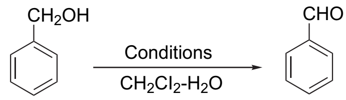
Oxidation of alcohols to carbonyl compounds is among the most important functional group transformations available to the synthetic chemists.[1] In recent years, nitroxyl radical TEMPO (2,2,6,6-tetramethylpiperdine-1-oxyl) has been extensively used as a catalyst for the catalytic oxidation of alcohols to corresponding carbonyl compounds. Typically, such oxidations are carried out in the presence of a catalytic amount of TEMPO and a stoichiometric amount of a terminal oxidant such as bleach (NaClO),[2] sodium chlorite,[3] sodium bromite,[4] sodium or calcium hypochlorite,[5] *N*-chlorosuccinimide (NCS),[6] *m*-chloroperbenzoic acid (*m*-CPBA),[7] trichloroisocyanuric acid,[8] *tert*-butyl hypochlorite,[9] [bis(acetoxy)iodo] benzene (BAIB),[10] Oxone,[11] iodine,[12] oxygen or air.[13] To the best of our knowledge, sodium periodide ($NaIO_4$), a stable and conventional inorganic nonmetal oxidant, has not been used for these transformations. Herein, we describe a TEMPO-mediated oxidation method using $NaIO_4$ as the terminal oxidant and NaBr as co-catalyst. Compared with the systems that performed under basic conditions, especially the extensively used NaClO/TEMPO/NaBr system that works at 0 °C and pH 8.6–9.5,[2a] the present $NaIO_4$/TEMPO/NaBr system could work at room temperature without generation of over-oxidized product. Also this buffer-free system provides an alternative method for the oxidation of alcohols that are sensitive to basic conditions.

2. Results and discussion

2.1. $NaIO_4$/TEMPO/NaBr system for the selective oxidation of alcohols to aldehydes and ketones under two-phase conditions (CH_2Cl_2–H_2O)

Initially, we attempted the $NaIO_4$/TEMPO/CH_2Cl_2–H_2O (1:1) system for the oxidation of benzyl alcohol, and the results are summarized in Table 1. We found that benzyl

Table 1. Oxidation of benzyl alcohol under different conditions



Entry	Conditions	Time (h)	Yield[d] (%)
1	1.2 equiv $NaIO_4$, 1 mol % TEMPO[a]	28	90
2	1.2 equiv $NaIO_4$, 1 mol % TEMPO, 10 mol % NaBr[a]	10	96
3	1.2 equiv $NaIO_4$, 1 mol % TEMPO, 10 mol % NaCl	16	96
4	1.2 equiv $NaIO_4$, 1 mol % TEMPO, 10 mol % NaBr, pH 2.0[b]	10	95
5	3 equiv $NaIO_4$, 1 mol % TEMPO, 10 mol % NaBr	10	96
6	1.2 equiv $NaIO_4$, 1 mol % TEMPO, 10 mol % (n-Bu)$_4$NBr, 10 mol % NaBr	10	96
7	1.2 equiv $NaIO_4$, 1 mol % TEMPO, 10 mol % NaBr, reflux	8	96
8	1 equiv $NaIO_4$	48	10
9	1.2 equiv $NaIO_4$, 1 mol % TEMPO, 10 mol % NaBr, pH 8.6[c]	24	5

[a] Aqueous layer pH 4.0.
[b] Aqueous layer pH was adjusted with 0.5 M H_2SO_4.
[c] Aqueous layer pH was adjusted with $NaHCO_3$.
[d] Isolated yield.

Keywords: Oxidation; Alcohols; Aldehydes; Ketones; Sodium periodide; TEMPO; Ionic liquids.

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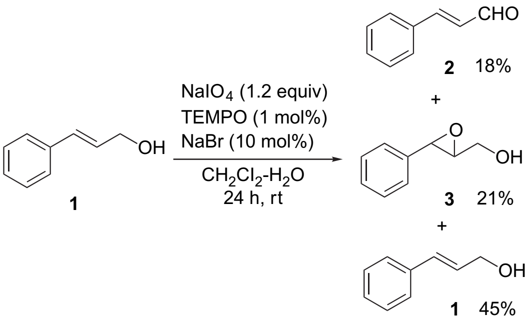
alcohol was completely oxidized to benzaldehyde by $NaIO_4$ (1.2 equiv) and TEMPO (0.01 equiv) in CH_2Cl_2–H_2O (1:1) two-phase system at room temperature (Table 1, entry 1). Furthermore, NaBr and NaCl (10 mol %) could significantly promote the transformation (Table 1, entries 2 and 3) without generation of overoxidized product. In the $NaIO_4$/TEMPO/NaBr system, the aqueous layer was maintained at pH 4.0 during the reaction. When the aqueous layer was adjusted at pH 2.0 with 0.5 M H_2SO_4 (Table 1, entry 4), the reaction gave a similar yield (Table 1, entry 2). Increasing the amount of $NaIO_4$ (Table 1, entry 5) or adding phase transfer catalyst (Table 1, entry 6) did not improve the yield, but refluxing could accelerate the reaction somewhat (Table 1, entry 7). In all cases, TEMPO was necessary. Otherwise, the reaction proceeded very slowly and gave poor yield (Table 1, entry 8). It is noteworthy that when the aqueous layer was buffered at pH 8.6 (Table 1, entry 9), only 5% yield was obtained.

As the next step, we used the $NaIO_4$/TEMPO/NaBr system to oxidize various alcohols under the optimized reaction conditions (Table 2). It was found that primary benzylic alcohols could be oxidized to the corresponding aldehydes in excellent yields. The electron-withdrawing group substituted benzylic alcohols (Table 2, entry 2) reacted faster than the electron-donating group substituted benzylic alcohols (Table 2, entries 3–5). The chloro-substituted benzylic alcohols (Table 2, entries 6 and 7) exhibited a similar reactivity with benzylic alcohol (Table 2, entry 1). Refluxing could promote the reactions (Table 2, entries 2′ and 7′). Primary aliphatic alcohols (Table 2, entries 8 and 9) as well as secondary aliphatic and benzylic alcohols (Table 2, entries 10 and 11) could also be oxidized to the corresponding aldehydes and ketones in excellent yields after a prolonged reaction time (20–28 h).

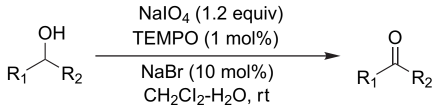
We also examined the unsaturated alcohol, cinnamic alcohol (**1**) (Scheme 1). It was found that besides cinnamaldehyde (**2**, 18%) and unreacted cinnamic alcohol (**1**, 45%), an epoxide 3-phenyl oxiranemethanol (**3**) was also obtained in 21% yield (determined by GC–MS). Taking into account the $NaIO_4$-mediated selective halogenation of alkenes and aromatics using alkali metal halides,[14] we attributed the formation of the epoxide to the electrophilic addition of hypohalogenous acid to the double bond of cinnamic alcohol, which was followed by an intramolecular nucleophilic substitution in one-pot procedure.

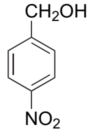
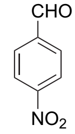
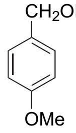
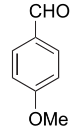
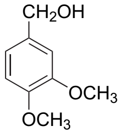
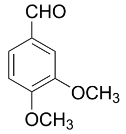
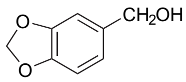
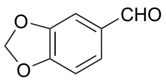
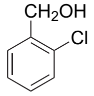
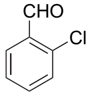
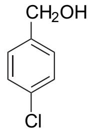
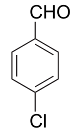
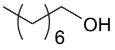
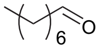
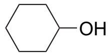
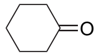
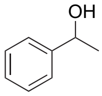
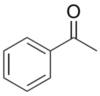


Scheme 1. Oxidation of cinnamic alcohol.

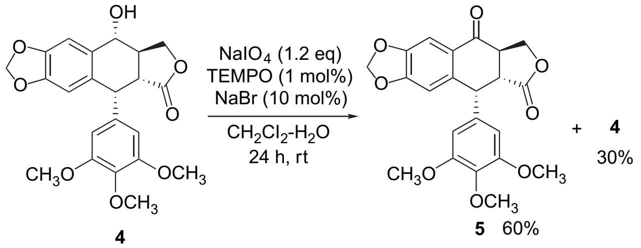
Compared with the extensively used and more active NaOCl/TEMPO/KBr system,[2a,15] which must be buffered at pH 8.6–9.5 and requires 0 °C reaction temperature, our $NaIO_4$/TEMPO/NaBr system works efficiently under slightly acidic conditions (pH~4.0). Therefore, our procedure provides an alternative methodology for the oxidation of alcohols that are sensitive to basic conditions. Using the $NaIO_4$/TEMPO/NaBr system, natural product podophyllotoxin (**4**), which is unstable under basic conditions, was oxidized to ketone **5** in 60% isolated yield (not optimized) with a 30% recovery of substrate **4** (Scheme 2). Under the reaction conditions, both the lactone ring opened and C-2 isomerized products were not observed.

Table 2. Oxidation of various primary and secondary alcohols



Entry	Alcohols[a]	Products	Time (h)	Yield (%)[c]
1	$C_6H_5CH_2OH$	C_6H_5CHO	10	96
2			8	96
2′			6[b]	95
3			15	95
4			15	96
5			15	95
6			12	95
7			12	95
7′			10[b]	96
8	$C_6H_5CH_2CH_2OH$	$C_6H_5CH_2CHO$	20	95
9			28	96[d]
10			28	95[d]
11			18	95

[a] Reaction conditions: alcohol (50 mmol), TEMPO (0.5 mmol), $NaIO_4$ (60 mmol), NaBr (5 mmol), DCM (100 ml), water (120 ml), rt.
[b] Under reflux conditions.
[c] Isolated yield.
[d] Determined by GC.



Scheme 2. Oxidation of podophyllotoxin (**4**) to ketone **5**.

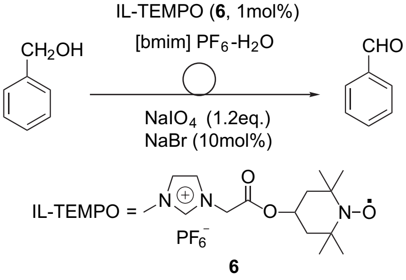
2.2. Recoverable ionic liquid immobilized TEMPO-catalyzed oxidation of benzyl alcohol using $NaIO_4$ in ionic liquid–H_2O two-phase condition

Although low catalyst concentrations are required for an efficient transformation, product separation and TEMPO recovery remain key issues in TEMPO-catalyzed oxidation. Consequently, several solid-supported TEMPO moieties have been developed, which include silica-supported TEMPO,[16] sol–gel entrapped TEMPO[17] and polyamine immobilized piperidinyl oxyl (PIPO).[18] These catalysts are heterogeneous in nature and are readily recovered by simple filtration from the reaction medium. Recently, it was reported that soluble polymer poly(ethylene glycol)-supported TEMPO catalysts (PEG-TEMPOs) exhibited high activity for the chemoselective oxidation of alcohols.[19] This class of catalysts could be readily recovered via precipitation with diethyl ether.

In the last decade, room temperature ionic liquids (RTILs) have become promising candidates to replace traditional solvents used in organic chemistry for their interesting properties such as high thermal stability, nonvolatility, high loading capacity, easy recyclability and tunable polarity. A number of chemical reactions can be performed in ionic liquids.[20] Recently, the so-called 'task-specific ionic liquids' immobilized catalysts have been demonstrated to be an effective strategy for facilitating product separation and catalyst recovery.[21] More recently, a TEMPO-derived task-specific ionic liquid (IL-TEMPO) (**6**) for oxidation of alcohols by the Anelli protocol has been reported.[22]

In order to develop a recoverable TEMPO-catalyzed and environmentally friendly oxidation process, we investigated IL-TEMPO-catalyzed $NaIO_4$ oxidation of benzyl alcohol in [bmim]PF_6–H_2O medium (Table 3). Compared with the CH_2Cl_2–H_2O medium version, the IL-TEMPO-catalyzed oxidation in water–IL two-phase conditions showed similar activity and selectivity. The crude product could easily be separated from the IL medium by simple extraction with diethyl ether. The IL solution containing the catalyst **6** could be reused up to six times without significant decrease of catalytic activity and selectivity.

Table 3. Oxidation of benzyl alcohol to benzaldehyde using $NaIO_4$ in the recovered IL immobilized TEMPO-IL solution[a]



Run	1	2	3	4	5	6
Time (h)	15	15	16	16	16	16
Isolated yield (%)	98	95	95	94	93	93

[a] In 20 mmol scale.

3. Conclusion

In summary, we have developed a novel and efficient TEMPO-catalyzed oxidation of alcohols to the corresponding aldehydes and ketones using $NaIO_4$ as the terminal oxidant. The reaction could be performed at room temperature under two-phase conditions. The procedure provides an alternative method for the oxidation of alcohols that are sensitive to basic conditions. Furthermore, the $NaIO_4$/IL immobilized TEMPO/RTIL system was also developed and could be recycled up to six times without remarkable deactivation.

4. Experimental

4.1. General

All chemicals were of reagent grade and used as purchased. ^1H NMR spectra were recorded in deuterated solvent on Bruker Avance-500 spectrometer operating at 500 MHz or on Bruker Avance-300 spectrometer operating at 300 MHz. ^{13}C NMR spectra were recorded in deuterated solvent on Bruker Avance-500 spectrometer operating at 125 MHz. Infrared spectra were recorded on a Nicolet Nexus 470 FT-IR spectrometer and measured as thin film or in KBr. Melting points were measured on WRS-1B digital melting point apparatus. Capillary gas chromatography was performed on a Hewlett–Packard HP 6890 gas chromatograph/mass spectra instrument (GC–MS). Mass spectra (EI, 70 eV) were recorded on an HP5989B mass spectrometer. ESI-MS spectra were recorded on a Bruker Daltonics Esquire 3000 plus instrument. HRMS data were obtained on a Bruker FT-ICR-MS Apex III apparatus.

4.2. Typical experimental procedure for oxidation of alcohols using $NaIO_4$/NaBr/TEMPO system

4-Nitrobenzyl alcohol (7.65 g, 50 mmol) and TEMPO (78 mg, 0.5 mmol) were dissolved in DCM (100 ml). Then the aqueous $NaIO_4$ (12.84 g, 60 mmol) and NaBr (0.51 g, 5 mmol) solution (120 ml) were added. The reaction mixture was vigorously stirred at room temperature and monitored by TLC. For 10 h, after completion, the organic layer was washed by NaS_2O_3 aqueous solution and then dried over anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by silica gel chromatography eluting with EtOAc–hexane (1:3) to give 4-nitrobenzyl aldehyde (7.25 g, 96% yield).

4.2.1. Benzaldehyde. Colourless liquid; IR (neat): ν= 1700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, ppm): δ=7.48–7.52 (m, 2H), 7.60–7.65 (m, 1H), 7.85–7.90 (m, 2H), 9.95 (s, 1H); MS (EI): *m*/*z* 106 (M^+).

4.2.2. 4-Nitrobenzaldehyde. Light yellow solid; mp 104–106 °C; IR (KBr): ν=1710 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ=8.10 (d, J=8.6 Hz, 2H), 8.40 (d, J=8.6 Hz, 2H), 9.90 (s, 1H); MS (EI): *m/z* 151 (M$^+$).

4.2.3. 4-Methoxybenzaldehyde. Colourless liquid; IR (neat): ν=1688 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ=3.85 (s, 3H), 7.00 (d, J=8.2 Hz, 2H), 7.85 (d, J=8.2 Hz, 2H), 9.80 (s, 1H); MS (EI): *m/z* 136 (M$^+$).

4.2.4. 3,4-Dimethoxybenzaldehyde. Colourless liquid; IR (neat): ν=1690 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ=3.80 (s, 3H), 3.85 (s, 3H), 7.20–7.30 (m, 3H), 9.85 (s, 1H); MS (EI): *m/z* 166 (M$^+$).

4.2.5. 4-Chlorobenzaldehyde. White solid; mp 45–46 °C; IR (KBr): ν=1703 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ=7.55 (d, J=7.8 Hz, 2H), 7.85 (d, J=7.8 Hz, 2H), 9.95 (s, 1H); MS (EI): *m/z* 141 (M$^+$).

4.2.6. 2-Chlorobenzaldehyde. Colourless liquid; IR (neat): ν=1705 cm^{-1} (C═O); ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ=7.33–7.48 (m, 3H), 7.75 (d, J=8.0 Hz, 1H), 10.25 (s, 1H); MS (EI): *m/z* 141 (M$^+$).

4.2.7. 3,4-Methylenedioxybenzaldehyde. White solid; mp 83–84 °C; IR (KBr): ν=1682 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.00 (s, 2H), 6.95–7.35 (m, 3H), 9.82 (s, 1H); MS (EI): *m/z* 150 (M$^+$).

4.2.8. Phenylacetaldehyde. Colourless liquid; IR (neat): ν=1710 cm^{-1} (C═O); ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ=3.25 (d, J=2 Hz, 2H), 7.05–7.10 (m, 2H), 7.25–7.30 (m, 3H), 9.75 (t, J=2 Hz, 1H); MS (EI): *m/z* 120 (M$^+$).

4.2.9. Acetophenone. Colourless liquid; IR (neat): ν=1680 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ 2.58 (s, 3H), 7.45–7.48 (m, 2H), 7.53–7.55 (m, 1H), 7.90 (d, J=8.5 Hz, 2H); MS (EI): *m/z* 120 (M$^+$).

4.2.10. Cyclohexanone. Colourless liquid; IR (neat): ν=1700 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ=1.70–1.78 (m, 2H), 1.85–1.92 (m, 4H), 2.40 (t, J=6.8 Hz, 4H); MS (EI): *m/z* 98 (M$^+$).

4.2.11. Octanal. Colourless liquid; IR (neat): ν=1720 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ=0.96 (t, J=7.2 Hz, 3H), 1.20–1.35 (m, 8H), 1.60–1.70 (m, 2H), 2.43 (t, J=7.2 Hz, 2H), 9.75 (s, 1H); MS (EI): *m/z* 128 (M$^+$).

4.3. Oxidation of podophyllotoxin (4) to picropodophyllone (5)

The procedure was similar to the oxidation of 4-nitrobenzyl alcohol above. White solid; mp 155–160 °C; IR (KBr): ν=2920, 1778, 1668, 1475, 1245, 1126, 938 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ=3.25 (d, J=1.55 Hz, 1H), 3.51 (s, 1H), 3.75 (s, 6H), 3.82 (s, 3H), 4.37 (ddd, J=9.0, 4.5, 1.5 Hz, 1H), 4.55 (s, 1H), 4.85 (d, J=9.2 Hz, 1H), 6.00 (s, 1H), 6.06 (s, 1H), 6.39 (s, 2H), 6.70 (s, 1H), 7.55 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$, ppm): δ=43.5, 43.8, 46.6, 56.5, 60.8, 70.5, 102.5, 104.7, 107.1, 109.5, 127.5, 137.8, 138.6, 139.9, 149.2, 154.7, 155.2, 175.8, 193.5; ESI-MS: *m/z* 435 ([M+Na]$^+$).

4.4. Synthesis of IL immobilized TEMPO (6)

Compound **6** was synthesized according to the literature procedures.[22] Red solid; mp 53–54 °C; IR (KBr): ν=3055, 2977, 2933, 1736, 1567, 1266, 1173 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{25}N_3O_3$ (M−PF$_6$): 295.1890, found: 295.1898.

4.5. Experimental procedure for oxidation of benzyl alcohol to benzaldehyde using NaIO$_4$ in the recoverable IL immobilized TEMPO-IL solution

To a solution of benzyl alcohol (2.16 g, 20 mmol) and IL-TEMPO (90 mg, 0.2 mmol) in [bmim]PF$_6$ (20 ml) was added the solution of NaIO$_4$ (5.14 g, 24 mmol) and NaBr (0.21 g, 2 mmol) in water (20 ml). The mixture was vigorously stirred at room temperature. After the oxidation (TLC monitoring) was completed, the product was separated from the IL medium by extraction with ether (3×30 ml). The organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum. The product was purified by flash silica gel chromatography eluting with EtOAc–hexane (1:5). The recovered IL containing the IL-TEMPO could be reused for consecutive recycling experiments.

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References and notes

1. (a) Larock, R. C. *Comprehensive Organic Transformation. A Guide to Functional Group Preparation*; VCH: New York, NY, 1989; (b) Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, *7*, 639–666; (c) Kim, S. S.; Jung, H. C. *Synthesis* **2003**, 2135–2137; (d) Sheldon, R. A.; Arends, I. W. C. E.; ten Brink, G.-J.; Dijksman, A. *Acc. Chem. Res.* **2002**, *35*, 774–781.
2. (a) Anelli, P. L.; Biffi, C.; Montanari, F.; Quici, S. *J. Org. Chem.* **1987**, *52*, 2559–2562; (b) Anelli, P. L.; Banfi, S.; Montanari, F.; Quici, S. *J. Org. Chem.* **1989**, *54*, 2970–2972; (c) Anelli, P. L.; Montanari, F.; Quici, S. *Org. React.* **1990**, *61*, 212–219; (d) Bolm, C.; Fey, T. *Chem. Commun.* **1999**, 1795–1796; (e) Leanna, M. R.; Sowin, T. J.; Morton, H. E. *Tetrahedron Lett.* **1992**, *33*, 5029–5032.
3. Zhao, M.; Li, J.; Mano, E.; Song, Z.; Tschaen, D. M.; Grabowski, E. J. J.; Reider, P. J. *J. Org. Chem.* **1999**, *64*, 2564–2566.
4. Inokuchi, T.; Matsumoto, S.; Nishiyama, T.; Torri, S. *J. Org. Chem.* **1990**, *55*, 462–466.
5. Nwauka, S. D.; Keehn, P. M. *Tetrahedron Lett.* **1982**, *23*, 3131–3134.
6. Einborn, J.; Einborn, C.; Ratajczak, F.; Pierre, J.-L. *J. Org. Chem.* **1996**, *61*, 7452–7454.

7. Rychnovsky, S. D.; Vaidyanathan, R. *J. Org. Chem.* **1999**, *64*, 310–312.
8. (a) de Luca, L.; Giacomelli, G.; Porcheddu, A. *Org. Lett.* **2001**, *3*, 3041–3043; (b) de Luca, L.; Giacomelli, G.; Masala, S.; Porcheddu, A. *J. Org. Chem.* **2003**, *68*, 4999–5001.
9. Melvin, F.; McNeill, A.; Henderson, P. J. F.; Herbert, R. B. *Tetrahedron Lett.* **1999**, *40*, 1201–1202.
10. (a) Mickel, S. J.; Sedelmeier, G. H.; Niederer, D.; Schuerch, F.; Seger, M.; Schreiner, K.; Daeffler, R.; Osmani, A.; Bixel, D.; Loiseleur, O.; Cercus, J.; Stettler, H.; Schaer, K.; Gamboni, R.; Bach, A.; Chen, G.-P.; Chen, W.; Geng, P.; Lee, G. T.; Loeser, E.; McKenna, J.; Kinder, F. R., Jr.; Konigsberger, K.; Prasad, K.; Ramsey, T. M.; Reel, N.; Repic, O.; Rogers, L.; Shieh, W.-C.; Wang, R.-M.; Waykole, L.; Xue, S.; Florence, G.; Paterson, I. *Org. Process Res. Dev.* **2004**, *8*, 113–121; (b) de Mico, A.; Margarita, R.; Parlanti, L.; Vescovi, A.; Piancatelli, G. *J. Org. Chem.* **1997**, *62*, 6974–6977; (c) Paterson, I.; Delgado, O.; Florence, G. J.; Lyothier, I.; Scott, J. P.; Sereinig, N. *Org. Lett.* **2003**, *5*, 35–38.
11. Bolm, C.; Angelika, S.; Magnus, S.; Hildebrand, J. P. *Org. Lett.* **2000**, *2*, 1173–1175.
12. Miller, R. A.; Hoerrner, R. S. *Org. Lett.* **2003**, *5*, 285–287.
13. (a) Mehta, G.; Roy, S. *Org. Lett.* **2004**, *6*, 2389–2392; (b) Mehta, G.; Islam, K. *Org. Lett.* **2004**, *6*, 807–810; (c) Liu, R.; Liang, X.; Dong, C.; Hu, X. *J. Am. Chem. Soc.* **2004**, *124*, 4112–4113; (d) Liu, R.; Dong, C.; Liang, X.; Wang, X.; Hu, X. *J. Org. Chem.* **2005**, *70*, 729–731; (e) Betzemeier, B.; Cavazzini, M.; Quici, S.; Knochel, P. *Tetrahedron Lett.* **2000**, *41*, 4343–4346; (f) Cecchetto, A.; Fontana, F.; Minisci, F.; Recupero, F. *Tetrahedron Lett.* **2001**, *42*, 6651–6653; (g) Dijksman, A.; Mmarino-Gonzalez, A.; Payeras, A. M.; Arends, I. W. C. E.; Sheldon, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 6826–6833; (h) Ben-Daniel, R.; Alsters, P.; Neumann, R. *J. Org. Chem.* **2001**, *66*, 8650–8653; (i) Ansari, I. A.; Gree, R. *Org. Lett.* **2002**, *4*, 1507–1509; (j) Gamez, P.; Arends, I. W. C. E.; Reedijk, J.; Sheldon, R. A. *Chem. Commun.* **2003**, 2414–2415; (k) Minisci, F.; Recupero, F.; Pedulli, G. F.; Lucarini, M. *J. Mol. Catal. A* **2003**, *204–205*, 63–90; (l) Dijiksman, A.; Arends, I. W. C. E.; Sheldon, R. A. *Org. Biomol. Chem.* **2003**, *1*, 3232–3237; (m) Minisci, F.; Recupero, F.; Cecchetto, A.; Gambarotti, C.; Punta, C.; Faletti, R.; Paganelli, R.; Pedulli, G. F. *Eur. J. Org. Chem.* **2004**, 109–119; (n) Semmelhack, M. F.; Schmid, C. R.; Cortes, D. A.; Chou, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 3374–3376; (o) Jiang, N.; Ragauskas, A. J. *Org. Lett.* **2005**, *7*, 3689–3692.
14. Dewkar, G. K.; Narina, S. V.; Sudalai, A. *Org. Lett.* **2003**, *5*, 4501–4504.
15. Montanari, F.; Penso, M.; Quici, S.; Viganò, P. *J. Org. Chem.* **1985**, *50*, 4888–4893; Montanari reported that when buffer is at pH 8.6, hypochlorous acid is distributed between the aqueous and the organic phases. So, under this condition, NaClO/TEMPO system is very active.
16. Fey, T.; Fischer, H.; Bachmann, S.; Albert, K.; Bolm, C. *J. Org. Chem.* **2001**, *66*, 8154–8159.
17. Ciriminna, R.; Blum, J.; Avnir, D.; Pagliaro, M. *Chem. Commun.* **2000**, 1441–1442.
18. Dijksman, A.; Arends, I. *Chem. Commun.* **2000**, 271–272.
19. (a) Pozzi, G.; Cavazzini, M.; Quici, S.; Benaglia, M.; Dell'Anna, G. *Org. Lett.* **2004**, *6*, 441–443; (b) Ferreira, P.; Hayes, W.; Phillips, E.; Rippon, D.; Tsang, S. C. *Green Chem.* **2004**, *6*, 310–312; (c) Ferreira, P.; Phillips, E.; Rippon, D.; Tsang, S. C.; Hayes, W. *J. Org. Chem.* **2004**, *69*, 6851–6859.
20. (a) Hussey, C. L.; Quigley, R.; Seddon, K. R. *Inorg. Chem.* **1995**, *34*, 370–377; (b) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2084; (c) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772–3789; (d) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667–3692.
21. (a) Song, C. E. *Chem. Commun.* **2004**, 1033–1034; (b) Zhao, D.; Fei, Z.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 15876–15882; (c) Geldbach, T. J.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 8114–8115; (d) Audic, N.; Clavier, H.; Mauduit, M.; Guillemin, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 9246–9249; (e) Bmger, R. P. J.; Silva, S. M.; Kamer, P. C.; van Leeuwen, P. W. N. M. *Chem. Commun.* **2004**, 3044–3045.
22. Wu, X. E.; Ma, L.; Ding, M. X.; Gao, L. X. *Synlett* **2005**, 607–610.