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Recyclable 2nd generation ionic liquids as green solvents for the oxidation of alcohols with hypervalent iodine reagents

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Abstract—Alcohols undergo smooth oxidation with iodoxybenzoic acid (IBX) or with Dess–Martin-Periodinane (DMP) in hydrophilic [bmim]BF_4 and hydrophobic [bmim]PF_6 ionic liquids at room temperature under mild conditions to afford the corresponding carbonyl compounds in excellent yields with high selectivity. IBX and DMP promoted oxidations are faster in ionic liquids when compared to conventional solvents such as DMSO, DMF, EtOAc and H_2O. The recovery of the byproduct iodosobenzoic acid (IBA) is especially simple in ionic liquids. The recovered ionic liquids can be recycled in subsequent reactions with consistent activity.

1. Introduction

Hypervalent iodine reagents have attracted increasing interest as oxidants in organic synthesis due to their mild, selective and environmentally benign oxidizing properties.[1] Among various hypervalent iodine reagents, IBX is a versatile oxidizing agent because of its high efficiency, easy availability, mild reaction conditions, and its stability against moisture and air.[2] The wide functional group tolerance and high-yielding reactions without over oxidation have made IBX very familiar for the oxidation of primary alcohols.[3] IBX also oxidizes *vic*-diols to α-diketones without cleaving the glycol C–C bond[4] and allows the selective oxidation of 1,4-diols to γ-lactols.[5] Recently, IBX has been employed as an efficient oxidizing agent in DMSO for the clean oxidation of alcohols to carbonyl compounds even in the presence of thioethers and amino compounds.[6] Subsequently, polymer-supported IBX reagents have also been developed to promote oxidation reactions.[7] In recent reports, the use of IBX as a mild oxidant has been extended to many other elegant oxidative transformations.[8] More recently, practical IBX oxidations have been reported in organic solvents such as acetone, ethyl acetate, chloroform, benzene and acetonitrile.[9] However, IBX oxidations in organic solvents typically require longer reaction times at high temperature to accomplish the reaction. The high temperature reaction conditions are not only detrimental to certain functional groups, but also to the control of chemoselectivity. Owing to the volatile nature of organic solvents, no attempt has been made to recycle them, thereby making the process more convenient, economic and eco-friendly. Recent demand for eco-friendly chemical processes has led to the development of several clean and practical oxidations and still awaits further improvements towards high-yielding, clean, safe and efficient methods for the oxidation of alcohols.

In recent times, ionic liquids have gained recognition as possible environmentally benign alternatives to the more volatile organic solvents.[10] Ionic liquids possess many attractive properties, such as wide liquid range, negligible vapor pressure, high thermal stability and good solvating ability for a wide range of substrates and catalysts, which alleviate some of the environmental issues. Their non-volatile nature can reduce the emission of toxic organic compounds and facilitate the separation of products and/or catalysts from the reaction solvents. Furthermore, ionic liquids are found to be an efficient reaction media for the immobilization of transition metal based catalysts, Lewis acids and enzymes.[11] The hallmark of such ionic liquids is the ability to alter their properties as desired by manipulating their structure with respect to the choice of organic cation or anion and side chain attached to the organic cation (Fig. 1).

These structural variations offer flexibility to the chemist to

n = 1 = [bmim]PF_6 n = 5 = [octmim]PF_6

n = 3 = [hmim]PF_6

Figure 1.

Keywords: Dess–Martin-Periodinane; Iodoxybenzoic acid; Iodosobenzoic acid.

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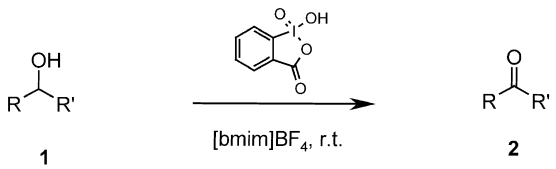
devise the most idealized solvent, catering for the needs of any particular process. Their unprecedented ability to solvate a broad spectrum of substrates of organic and inorganic nature has widened the horizon of their applicability.[12]

2. Results and discussions

With an ever increasing quest for the exploration of newer reactions in ionic liquids, herein we wish to report, for the first time, the use of ionic liquids as novel and recyclable polar reaction media for hypervalent iodine reagent promoted oxidation reactions of alcohols (Scheme 1).

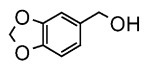
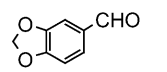
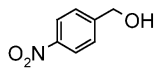
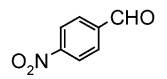
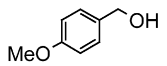
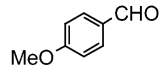
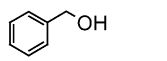
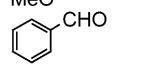
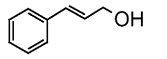
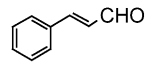
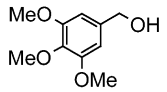
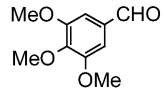
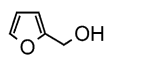
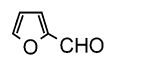
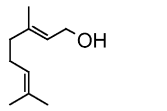
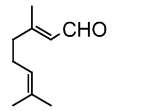
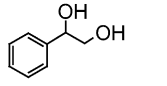
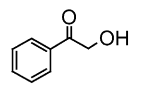
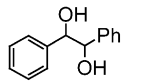
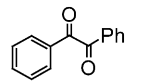
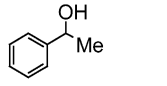
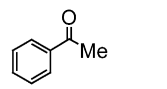
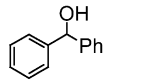
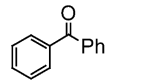
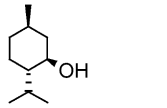
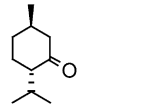
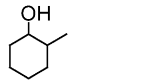
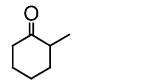
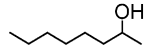
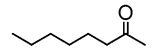
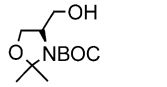
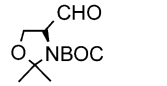


Scheme 1.

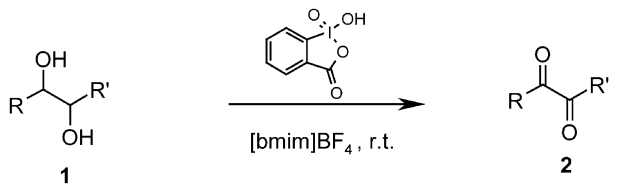
For instance treatment of benzyl alcohol with IBX in hydrophilic [bmim]BF_4 ionic liquid afforded benzaldehyde in 91% yield. The oxidation is very clean and complete within 4.0 h at room temperature. In a similar manner, various primary and secondary alcohols underwent smooth oxidation with IBX to give the corresponding aldehydes and ketones in high yields. In all cases, the reactions proceeded readily at room temperature with high efficiency. The oxidation of chiral primary alcohols proceeds without epimerization (entry p Table 1). α,β-Unsaturated alcohols also oxidized to the corresponding carbonyls in high yields (entries e, h, Table 1). Tertiary alcohols did not undergo oxidation under these conditions. No over oxidation of aldehydes to acids was observed in the case of the oxidation of primary alcohols. The results obtained with alcohols prompted us to extend this process to the oxidation of *vic*-diols. 1,2-Diols such as styrene diol and 1,2-diphenyl ethane-1,2-diol (pinacol) underwent smooth oxidation with IBX to the corresponding 1,2-diketones without the cleavage of the glycol C–C bond (Scheme 2).

Arylcarbinols gave comparatively better yields than aliphatic alcohols. This method is highly selective to oxidize secondary alcohols in the presence of primary alcohols especially in case of styrene diol (entry i, Table 1). The method is very mild and compatible with a wide range of functional groups such as methoxy, methylenedioxy, phenoxy ethers, carbamates and acetonides present in the substrate. IBX shows enhanced reactivity and selectivity in ionic liquids compared to organic solvents. For instance, treatment of 1-phenyl ethanol with IBX in [bmim]BF_4 at room temperature for 4.5 h afforded acetophenone in 93% yield whereas the same reaction in refluxing chloroform or in refluxing ethyl acetate after 8.0 h gave the desired ketone in 75 and 79% yields, respectively. In these organic solvents, high temperature reaction conditions and longer reaction times are typical to achieve comparable yields to those obtained in ionic liquids at room temperature. Lowering the reaction temperature was detrimental to the efficiency of this procedure. Although, IBX promoted oxidations proceed smoothly at room temperature in DMSO, the reactions typically require long reaction times (12–15 h) to obtain the products in good yields. Since the products are fairly soluble in hydrophilic [bmim]BF_4 ionic liquid, they can be easily separated by simple extraction

Table 1. IBX- and DMP-promoted oxidation of alcohols in ionic liquids

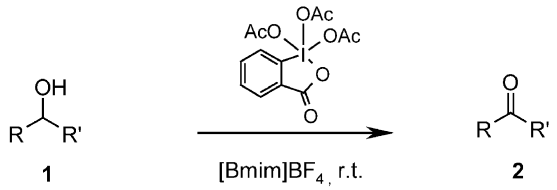
Entry	Alcohol	Aldehyde[a]	IBX		DMP	
	1	**2**	Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]
a			3.5	97	2.5	95
b			6.5	90	4.0	93
c			3.0	95	2.0	97
d			4.0	91	3.0	82[c]
e			3.5	93	2.5	91
f			5.0	92	3.0	96
g			3.5	95	2.5	89
h			4.5	94	3.0	90
i			5.5	92	3.5	87
j			6.0	95	4.0	85
k			4.5	93	3.5	96
l			4.0	91	3.5	95
m			6.0	86	4.5	89
n			6.5	87	5.0	91
o			7.5	89	5.0	93
p			5.5	87	4.0	90

[a] All products were charaterized by ^{1}H NMR, IR and mass spectroscopy.
[b] Yield refers to pure products after chromatography.
[c] Fifteen percent of benzoic acid was isolated.



Scheme 2.

with diethyl ether. Then the rest of the ionic liquid was diluted with water and filtered to recover the byproduct iodosobenzoic acid (IBA). The recovered IBA was reoxidized to IBX and could be reused in subsequent reactions. The regenerated IBX is indistinguishable from the freshly prepared one from *o*-iodobenzoic acid. The aqueous phase was lyophilized to recover the ionic liquid. The recovered ionic liquid was recycled in subsequent reactions with consistent activity. The products were obtained of the same purity as in the first run, and no decrease in yield was obtained in runs carried out using recycled ionic liquid. For instance, treatment of cinnamyl alcohol with IBX in hydrophilic [bmim]BF_4 ionic liquid gave 93, 92 and 93% yields over three cycles. Although, similar results were also obtained in hydrophobic [bmim]PF_6, the recovery of IBA is especially simple in [bmim]BF_4 due to its hydrophilic nature. The scope and generality of this process is illustrated with respect to various alcohols and IBX and the results are presented in the Table 1. Furthermore, Dess–Martin-Periodinane (DMP) was also immobilized in ionic liquids to perform oxidation reactions under mild conditions (Scheme 3).



Scheme 3.

In contrast to IBX, the oxidation reactions are faster with DMP in ionic liquids and results are summarized in Table 1. Ionic liquids used in this study were obtained from Fluka. The purity of [bmim]PF_6 is ≥97.0 (NMR).

3. Conclusion

In this paper, we have demonstrated that hydrophilic [bmim]BF_4 ionic liquid is an efficient and polar alternative to conventional solvents for the IBX and DMP promoted oxidations. This method avoids the use of polar organic solvents such as DMSO or DMF and high temperature reaction conditions for IBX oxidations. Enhanced reaction rates, high conversions and greater selectivities are the notable features observed in ionic liquids. The use of an easily accessible and recyclable ionic liquid makes this procedure quite simple, more convenient and environmentally benign.

4. Experimental

4.1. General methods

Melting points were recorded on Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer FT-IR 240-c spectrophotometer using KBr optics. ^{1}H and ^{13}C NMR spectra were recorded on Gemini-200 spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. IBX and DMP were prepared according to the reported procedure in the literature.[13]

4.2. General procedure for the oxidation of alcohols

To a stirred solution of alcohol (1 mmol) in 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4, Fluka, 2 mL) ionic liquid was added IBX (1.2 mmol) or DMP (1.0 mmol) at room temperature and stirring was continued for the appropriate time (Table 1). After completion of the reaction, as indicated by TLC, the product was extracted with diethyl ether (3×10 mL). The combined ether extracts were concentrated in vacuo and the resulting product was directly charged on a small silica gel column and eluted with a mixture of ethyl acetate–*n*-hexane (2:8) to afford the pure carbonyl compound. The rest of the ionic liquid was diluted with water and filtered to remove the IBA. The aqueous phase was lyophilized to recover the ionic liquid. The products were characterized by comparison of their NMR, IR, Mass, TLC, mixed TLC analysis and physical data with authentic samples. The spectral data of all the products were identical with those of authentic samples.[14] Spectroscopic data for selected products is as follows.

4.2.1. 2a: 3,4-(Methylenedioxy)-benzaldehyde. Low melting solid, mp 35–37 °C, (lit.[14e] 36–37 °C), IR (KBr): ν 3074, 2849, 1704, 1600, 1548, 1436, 1229, 1116, 1083, 912, 860, 781 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.01 (s, 2H), 6.82–7.50 (m, 3H), 9.81 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, proton decoupled): δ 102.3, 105.2, 108.0, 128.2, 131.7, 148.5, 153.6, 190.2. EIMS: *m*/*z* (%): 150 (M^+, 11), 136 (32), 107 (100), 79 (43), 51 (61).

4.2.2. 2b: 4-Nitro-benzaldehyde. Light yellow solid, mp 104–105 °C (lit.[15a] 106–107 °C), IR (KBr): ν 3093, 2978, 2864, 1713, 1605, 1540, 1343, 1294, 1197, 853, 820, 740 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.07 (d, J=8.5 Hz, 2H), 8.36 (d, J=8.5 Hz, 2H), 10.25 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 123.6, 129.9, 139.4, 150.4, 189.8. EIMS: *m*/*z* (%): 151 (M^+, 45), 150 (100), 77 (16), 51 (24).

4.2.3. 2c: 4-Methoxy-benzaldehyde. Colourless liquid (lit.[15a]), IR (neat): ν 1701, 1607, 1386, 1308, 1207, 1169, 847, 808 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.95 (s, 3H), 7.33 (d, J=7.9 Hz, 2H), 7.78 (d, J=7.9 Hz, 2H), 9.97 (s, 1H). EIMS: *m*/*z* (%): 136 (M^+, 60), 135 (100), 107 (26), 92 (18), 77 (45), 63 (21).

4.2.4. 2d: Benzaldehyde. Colourless liquid (lit.[15d]), IR (neat): ν 3064, 3031, 2852, 2820, 2732, 1702, 1654, 1597, 1584, 1455, 1391, 1311, 1204, 1167, 1023, 828, 746, 688,

650 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.45–7.67 (m, 3H), 7.87–7.90 (m, 2H), 9.90 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 129.0, 129.6, 134.4, 136.4, 192.3. EIMS: *m/z* (%): 106 (M^+, 34), 105 (74), 77 (100), 51 (22).

4.2.5. 2e: *trans*-Cinnamaldehyde. Pale yellow liquid (lit.[15a]), IR (neat): ν 3078, 2986, 2834, 1706, 1605, 1534, 1455, 1263, 1075, 876, 687 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.65 (d, J=16.7 Hz, 1H), 6.69 (dd, J=6.5, 16.7 Hz, 1H), 7.43–7.37 (m, 3H), 7.54–7.50 (m, 2H), 9.65 (d, J=6.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 128.5, 128.6, 129.2, 131.4, 134.1, 152.8, 193.7. EIMS: *m/z* (%): 132 (M^+, 31), 90 (59), 77 (100), 51 (39).

4.2.6. 2f: 3,4,5-Trimethoxy benzaldehyde. Light yellow solid, mp 73–74 °C (lit.[15b] 73–75 °C), IR (KBr): ν 3069, 2987, 2842, 1705, 1600, 1567, 1459, 1384, 1226, 892, 764 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 3.80 (s, 3H), 3.90 (s, 6H), 7.10 (s, 2H), 9.86 (s, 1H). EIMS: *m/z* (%): 196 (M^+, 40), 165 (68), 103 (100), 74 (27), 49 (32).

4.2.7. 2g: 2-Furfuraldehyde. Pale yellow liquid (lit.[14c]), IR (neat): ν 2985, 1698, 1605, 1519, 1168, 1032, 826, 785 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.60 (d, J=5.0 Hz, 1H), 7.25 (d, J=5.0 Hz, 1H), 7.70 (s, 1H), 9.70 (s, 1H). EIMS: *m/z* (%): 96 (M^+, 17), 67 (11), 84 (38), 43 (30), 41 (100), 26 (26).

4.2.8. 2h: 3,7-Dimethyl-2,6-octadienal (citral). Colorless liquid (lit.[15e]), IR (neat): ν 2850, 1720, 1609, 1533, 1470, 1414, 1370, 1060, 895, 723 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.60 (s, 3H), 1.90 (s, 3H), 2.20 (s, 3H), 2.60 (m, 4H), 5.10 (s, 1H), 5.85 (d, 1H, J=7.0 Hz), 9.80 (d, 1H, J=7.0 Hz). EIMS: *m/z* (%): 152 (M^+, 21), 123 (9), 110 (72), 68 (100), 41 (38).

4.2.9. 2i: α-Hydroxy-acetophenone. Pale yellow solid, mp 85–87 °C (lit.[15c] 89–90 °C), IR (KBr): ν 3421, 1689, 1600, 1456, 1409, 1301, 1231, 1106, 970, 761, 683 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.50 (brs, 1H, OH), 4.89 (s, 2H), 7.49–7.67 (m, 3H), 7.92–7.95 (m, 2H). EIMS: *m/z*(%): 136 (M+1), 105 (77), 77 (100), 51 (17).

4.2.10. 2j: Benzil. Yellowish solid, mp. 94–95 °C (lit.[15a] 93–95 °C), IR (neat): ν 2930, 2863, 1721, 1695, 1450, 1428, 1375, 1314, 1156, 1053, 995, 866, 734, 650 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.53 (t, 4H, J=8.2 Hz), 7.62 (t, 2H, J=8.2 Hz), 8.0 (d, 4H, J=8.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 128.8, 130.2, 132.8, 134.9, 194.5. EIMS: *m/z* (%): 210 (M^+, 11), 133 (27), 105 (100), 77 (60), 51 (40).

4.2.11. 2k: Acetophenone. Colourless liquid (lit.[15c]), IR (neat): ν 3060, 3005, 2924, 1686, 1599, 1582 1359, 1266, 1182, 1078, 1024, 955, 760, 690 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.55 (s, 3H), 7.38–7.46 (m, 2H), 7.48–7.55 (m, 1H), 7.90–7.95 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): 28.2, 128.0, 128.7, 133.0, 137.0, 198.0. EIMS: *m/z* (%): 120 (M^+, 16), 105 (100), 77 (24), 51 (18).

4.2.12. 2l: Benzophenone. White solid, mp. 49–50 °C (lit.[15a] 49–51 °C), IR (neat): ν 3060, 1658, 1598, 1577, 1447, 1317, 1276, 1176, 1150, 1074, 1028, 999, 941. 919, 810, 763, 697, 638 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.44 (m, 4H), 7.51–7.57 (m, 2H), 7.87 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 127.7, 129.9, 132.8, 136.5, 196.5. EIMS: *m/z* (%): 182 (M^+, 19), 105 (68), 77 (100), 51 (27).

4.2.13. 2m: Menthone. Colorless liquid (lit.[15e]), IR (neat): ν 2956, 2928, 2871, 1711, 1457, 1711, 1367, 1286, 1246, 1155, 1117, 1093, 1044, 994, 866, 747, 608 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.86 (d, J=6.7 Hz, 3H), 0.91 (d, J=6.7 Hz, 3H), 1.01 (d, J=6.2 Hz, 3H), 1.34–1.40 (m, 2H), 1.80–2.20 (m, 6H), 2.18–2.37 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.7, 21.2, 22.3, 25.9, 27.9, 33.9, 35.5, 50.8, 55.8, 212.0. EIMS: *m/z* (%): 154 (M^+, 18), 111 (35), 83 (100), 55 (43).

4.2.14. 2n: 2-Methyl cyclohexanone. Colourless liquid (lit.[7a]), IR (neat): ν 2930, 2863, 1721, 1450, 1428, 1375, 1314, 1156, 1053, 995, 866, 734, 650 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.00 (d, 3H, J=6.5 Hz), 1.34–1.37 (m, 1H), 1.64–1.82 (m, 3H), 2.10–2.42 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.6, 25.3, 28.1, 36.1, 41.7, 45.4, 213.7. EIMS: *m/z* (%): 112 (M^+, 11), 97 (21), 84 (38), 69 (43) 56 (100).

4.2.15. 2o: 2-Octanone. Colourless liquid (lit.[15d]), IR (neat): ν 2959, 2932, 2856, 1716, 1593, 1467, 1413, 1363, 1278, 1227., 1167, 1115, 1034, 945, 720 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 0.90 (t, 3H, J=7.0 Hz), 1.30 (m, 6H), 1.56 (m, 2H), 2.16 (s, 3H), 2.44 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.3, 22.5, 24.0, 29.1, 29.9, 31.8, 43.8, 209.2. EIMS: *m/z* (%): 128 (M^+, 39), 85 (100), 57 (72), 29 (21).

4.2.16. 2p: *N*-Boc-D-serinal acetonide (Garner aldehyde). Colourless oil (lit.[14d]), IR (neat): ν 2948, 2835, 1712, 1604, 1546, 1438, 1222, 1064, 932, 878, 764 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 1.37 (s, 3H), 1.41 (s, 3H), 1.43 (s, 9H), 3.52 (dd, J=8.3, 8.7 Hz, 1H), 3.73 (dd, J=2.9, 8.7 Hz, 1H), 3.90 (m, 1H), 9.34 (brs, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 23.8, 24.7, 25.8, 26.7, 28.3, 63.5, 64.7, 81.1, 81.4, 94.4, 95.1, 151.3, 152.6, 199.5. EIMS: *m/z* (%): 229 (M^+, 16), 156 (21), 128 (47), 86 (100), 72 (41), 54 (29).

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References and notes

1. (a) Varvoglis, A. *Hypervalent iodine in organic synthesis*; Academic: San Diego, 1997. (b) Wirth, T.; Hirt, U. H. *Synthesis* **1999**, 1271–1287.
2. (a) Hartman, C.; Meyer, V. *Chem. Ber.* **1893**, *26*, 1727–1732. (b) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123–1178. (c) Kitamura, T.; Fujiwara, Y. *Org. Prep. Proc. Int.* **1997**, *29*, 409–458.
3. Wirth, T. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 2812–2814.
4. (a) Frigerio, M.; Santagostino, M. *Tetrahedron Lett.* **1994**, *35*, 8019–8022. (b) De Munari, S.; Frigerio, M.; Santagostino, M. *J. Org. Chem.* **1996**, *61*, 9272–9279.
5. (a) Corey, E. J.; Palani, A. *Tetrahedron Lett.* **1995**, *36*,

7945–7948. (b) Corey, E. J.; Palani, A. *Tetrahedron Lett.* **1995**, *36*, 3484–3488.
6. Frigerio, M.; Santagostino, M.; Sputore, S.; Palmisano, G. *J. Org. Chem.* **1995**, *60*, 7272–7276.
7. (a) Mulbaier, M.; Giannis, A. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 4393–4394. (b) Reed, N. N.; Delgado, M.; Hereford, K.; Clapham, B.; Janda, K. D. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 2047–2049.
8. (a) Nicolaou, K. C.; Montagnon, T.; Baran, P. S. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 993–996. (b) Nicolaou, K. C.; Gray, D. L. F.; Montagnon, T.; Harrison, S. T. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 996–1000. (c) Nicolaou, K. C.; Montagnon, T.; Baran, P. S.; Zhong, Y. L. *J. Am. Chem. Soc.* **2002**, *124*, 2245–2258. (d) Nicolaou, K. C.; Barn, P. S.; Zhong, Y. L.; Barluenga, S.; Hunt, K. W.; Kranich, R.; Vega, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 2233–2244.
9. Magdziak, D.; Rodriguez, A. A.; Van De Water, R. W.; Pettus, T. R. R. *Org. Lett.* **2002**, *4*, 285–288.
10. Recent reviews on ionic liquids: (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083. (b) Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789.
11. (a) Sheldon, R. *Chem. Commun.* **2001**, 2399–2407. (b) Ansari, I. A.; Gree, R. *Org. Lett.* **2002**, *4*, 1507–1509.
12. (a) Le Boulaire, V.; Gree, R. *Chem. Commun.* **2000**, 2195–2196. (b) Yao, Q. *Org. Lett.* **2002**, *4*, 2197–2199. (c) Namboodiri, V. V.; Varma, R. S. *Chem. Commun.* **2002**, 342–343. (d) Kim, D. W.; Song, C. E.; Chi, D. Y. *J. Am. Chem. Soc.* **2002**, *124*, 10278–10279.
13. IBX was prepared according to the Dess–Martin procedure: (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155–4156. (b) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277–7287.
14. (a) Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1999**, *64*, 6750–6755. (b) Cardillo, G.; Orena, M.; Sandri, S. *Synthesis* **1976**, 394–396. (c) Matsuo, J.; Iida, D.; Tatani, K.; Mukaiyama, T. *Bull. Chem. Soc. Jpn* **2002**, *75*, 223–234. (d) Avenoza, A.; Cativiela, C.; Corjana, F.; Peregrina, J. M.; Zurbano, M. M. *Synthesis* **1997**, 1146–1150. (e) Sorg, G.; Mengel, A.; Jung, G.; Rademann, J. *Angew. Chem. Int. Ed. Engl.* **2001**, *39*, 4395–4397. (f) Wei, Z. L.; Li, Z. Y.; Lin, G. Q. *Tetrahedron* **1998**, *54*, 13059–13072.
15. (a) Peterson, K. P.; Larock, C. K. *J. Org. Chem.* **1998**, *63*, 3185–3189. (b) Manchand, P. S.; Belica, P. S.; Wong, H. S. *Synth. Commun.* **1990**, *20*, 2659–2666. (c) Koo, B. S.; Lee, C. K.; Lee, K. J. *Synth. Commun.* **2002**, *32*, 2115–2123. (d) Ali, M. H.; Wiggin, C. J. *Synth. Commun.* **2001**, *31*, 3383–3393. (e) More, J. D.; Finney, N. S. *Org. Lett.* **2002**, *4*, 3001–3003.