TEMPO-Mediated Oxidation of Alcohols with Ion-Supported (Diacetoxyiodo)benzenes

Yusuke Suzuki, Masataka Iinuma, Katsuhiko Moriyama, Hideo Togo*

Graduate School of Science, Chiba University, Yayoi-cho 1-33, Inage-ku, Chiba 263-8522, Japan

Received: 31.01.2012; Accepted after revision: 15.02.2012

Abstract: The oxidation of secondary alcohols and primary alcohols with novel ion-supported (diacetoxyiodo)benzenes (IS-DIB) in the presence of a catalytic amount of 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO) in dichloromethane at room temperature proceeded efficiently to provide the corresponding ketones and aldehydes, respectively, in good yields with high purity. Isolation of the product was easily accomplished by simple diethyl ether extraction of the reaction mixture and subsequent removal of the solvent from the extract. Moreover, ion-supported iodobenzenes, which were co-products derived from IS-DIB in the present oxidation, were recovered in good yields and could be re-oxidized to IS-DIB for reuse in the same oxidation.

Key words: oxidation, ion-supported (diacetoxyiodo)benzene, alcohol, TEMPO, aldehyde, ketone, reuse

Organic synthesis that features high efficiency, low toxicity, little odor, and atom economy, and produces a minimal amount of reaction waste is very important for green chemistry. Therefore, efficient organic synthesis with less toxic reagents has been pursued actively.[1] The oxidation of alcohols to ketones or aldehydes is one of the most fundamental, widespread, and important reactions in both research laboratories and production plants.[2] Among the various methods for the oxidation of alcohols to ketones or aldehydes, the Swern oxidation[3] with dimethyl sulfoxide (DMSO) and oxalyl chloride or trifluoroacetic anhydride and the Dess–Martin oxidation[4] with 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-2-one (Dess–Martin periodinane) are the most popular, efficient, and selective methods for the preparation of ketones or aldehydes from alcohols in organic synthesis, because both reactions do not require any toxic metals, that is, they are metal-free oxidation reactions and proceed under mild and nearly neutral conditions. However, each reaction still has a major drawback. Dimethyl sulfide, a co-product of the Swern oxidation, is a highly malodorous volatile compound that makes handling of the reaction extremely difficult, and Dess–Martin pentavalent periodinane is explosive. In 1997, the 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO)-mediated oxidation of alcohols to ketones or aldehydes with (diacetoxyiodo)benzene (DIB) in dichloromethane (CH_2Cl_2) at room temperature was reported[5a] and has become a very popular method for the efficient and selective oxidation of alcohols to ketones or aldehydes, due to simple experimental operation, the use of nonexplosive trivalent iodine, and the lack of unpleasant odor.[5] However, the reaction produces a stoichiometric amount of iodobenzene as a co-product, which must be purified by troublesome column chromatography on silica gel. To solve this problem and simplify the isolation of the desired product, the polymer-supported DIB, poly[4-(diacetoxyiodo)styrene], was developed.[5b] However, there are still drawbacks, such as the low purity of carbonyl compounds after filtration of the reaction mixture due to the presence of low-molecular weight polymer-supported iodobenzenes. Moreover, the elemental analysis of polymer-supported DIB must be carried out in each preparation of polymer-supported DIB to evaluate the loading rate of (diacetoxy)iodo groups in the polymer-supported DIB. Recently, the oxidation of alcohols with a 1-(4′-diacetoxyiodobenzene)-3-methylimidazolium tetrafluoroborate/KBr/[emim]BF_4 system[6a] and a 1-(4′-diacetoxyiodobenzene)-3-methylimidazolium tetrafluoroborate/3-methylimidazolium-supported TEMPO/water system[6b] was reported. However, there are still certain drawbacks, such as addition to carbon–carbon double bond of substrates by bromonium ion species and solubility of substrates in water. Here, as part of our ongoing studies of trivalent iodines for organic synthesis,[7] we would like to report the TEMPO-mediated oxidation of alcohols to ketones or aldehydes with ion-supported (diacetoxyiodo)benzenes (IS-DIB).

Three IS-DIB, *N*-methyl-*N*-[3-(4′-diacetoxyiodo)phenyl-1-propyl]pyrrolidium 4″-methylbenzenesulfonate **A**, *N*-methyl-*N*-[3-(4′-diacetoxyiodo)phenoxy-1-propyl]-pyrrolidium 4″-methylbenzenesulfonate **B**, and *N*-[3-(4′-diacetoxyiodo)phenoxy-1-propyl]-*N*,*N*,*N*-trimethylammonium 4″-methylbenzenesulfonate **C** (Figure 1), were pre-

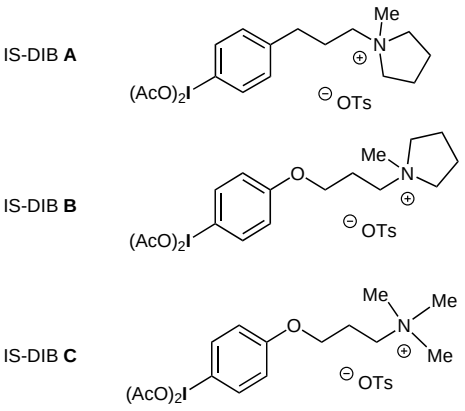
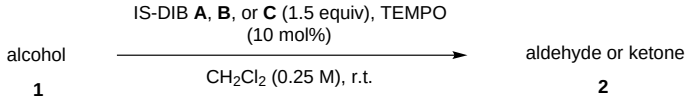


Figure 1

SYNLETT 2012, 23, 1250–1256
Advanced online publication: 20.04.2012
DOI: 10.1055/s-0031-1290766; Art ID: ST-2012-U0093-L

pared by the oxidation of *N*-methyl-*N*-[3-(4′-iodophenyl)-1-propyl]pyrrolidinium 4″-methylbenzene-sulfonate (pre-**A**), *N*-methyl-*N*-[3-(4′-iodophenoxy)-1-propyl]pyrrolidinium 4″-methylbenzenesulfonate (pre-**B**), and *N*-[3-(4′-iodophenoxy)-1-propyl]-*N*,*N*,*N*-trimethylammonium 4″-methylbenzenesulfonate (pre-**C**),[8] respectively, with sodium perborate in acetic acid at 45 °C.[9] Precursors pre-**A**, pre-**B**, and pre-**C** were easily prepared from commercially available 3-phenylpropanoic acid in four steps and *p*-iodophenol in three steps, respectively.

Table 1 Oxidation of Alcohols with IS-DIB **A**–**C**



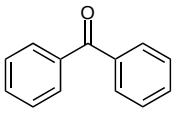
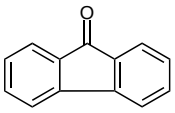
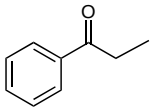
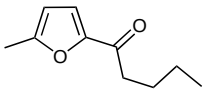
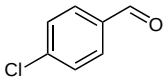
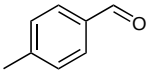
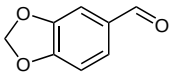
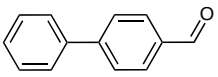
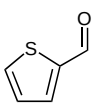
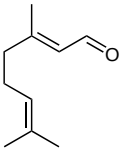
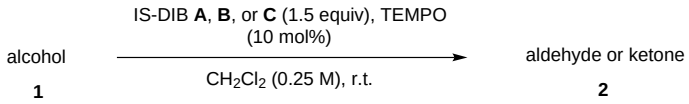
IS-DIB or DIB	Ketone or aldehyde (**2**) time (h), yield (%) [purity (%)]	
		
	2a	**2b**
IS-DIB **A**	12 , 99 [99]	15, 99 [99]
IS-DIB **B**	10, 99 [99]	12, 99 [99]
IS-DIB **C**	9, 97 [98]	18, 99 [97]
DIB	5, 99 [48]	
		
	2c	**2d**
IS-DIB **A**	4, 94 [99]	9, 97 [99]
IS-DIB **B**	4.5, 99 [99]	10.5, 93 [98]
IS-DIB **C**	8, 97 [97]	9, 99 [99]
		
	2e	**2f**
IS-DIB **A**	6, 96 [99]	2, 95 [99]
IS-DIB **B**	2, 98 [99]	1.5, 98 [99]
IS-DIB **C**	6, 98 [99]	8, 98 [99]
		
	2g	**2h**
IS-DIB **A**	3.5, 98 [99]	8, 99 [99]
IS-DIB **B**	3.5, 97 [99]	6, 99 [99]
IS-DIB **C**	8, 95 [92]	6, 98 [98]
		
	2i	**2j**

Table 1 Oxidation of Alcohols with IS-DIB **A**–**C** (continued)



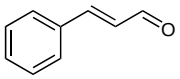
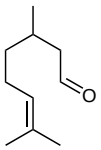
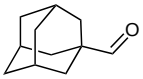
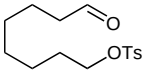
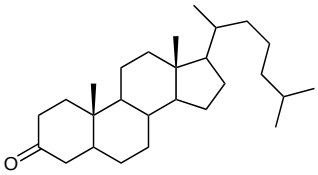
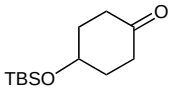
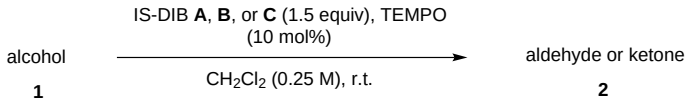
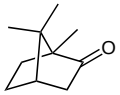
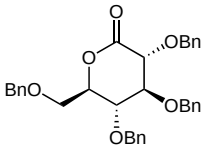
IS-DIB or DIB	Ketone or aldehyde (**2**) time (h), yield (%) [purity (%)]	
IS-DIB **A**	2, 99 [99]	1.5, 97 [99]
IS-DIB **B**	3, 99 [99]	1.5, 94 [99]
IS-DIB **C**	6, 99 [99]	2, 99 [98]
DIB	1.5, 99 [48]	
	 **2k**	 **2l**
IS-DIB **A**	2, 99 [99]	2, 97 [99]
IS-DIB **B**	2, 98 [99]	1.5, 92 [99]
IS-DIB **C**	4, 98 [99]	2, 99 [99]
IS-DIB **A**[a]	1.5, 95 [99]	1.5, 96 [99]
IS-DIB **B**[a]	2, 99 [99]	2, 98 [98]
IS-DIB **C**[a]	4, 99 [98]	2, 98 [99]
	 **2m**	 **2n**
IS-DIB **A**	10, 95 [97]	7, 80 [80]
IS-DIB **B**	12, 84 [83]	6, 79 [79]
IS-DIB **C**	18, 91 [88]	8, 81 [81]
DIB	4, 91 [50]	2, 99 [48]
	 **2o**	 **2p**
IS-DIB **A**	8, 96 [99]	16, 92 [95]
IS-DIB **B**	7, 95 [99]	16, 97 [97]
IS-DIB **C**	8, 97 [97]	8, 86 [85]
DIB	6, 97 [49]	7, 97 [49]

Table 1 Oxidation of Alcohols with IS-DIB **A**–**C** (continued)



IS-DIB or DIB	Ketone or aldehyde (**2**) time (h), yield (%) [purity (%)]	
		
	2q	**2r**
IS-DIB **A**	9, 96 [99]	4, 98 [99]
IS-DIB **B**	6, 95 [99]	5, 99 [99]
IS-DIB **C**	12, 99 [99]	6, 94 [94]
DIB	4.5, 99 [48]	1.5, 97 [48]

[a] Recovered and regenerated IS-DIB was used.

The oxidation of secondary and primary alcohols with IS-DIB **A**, **B**, **C**, or DIB in the presence of TEMPO in CH_2Cl_2 at room temperature was carried out by means of the same experimental procedure as that described in the literature.[5a] Thus, to a solution of IS-DIB **A**, **B**, or **C** (1.5 equiv) in CH_2Cl_2 were added alcohol (1.0 equiv) and TEMPO (0.1 equiv). Then, the mixture was stirred at room temperature. After the disappearance of alcohol, the solvent was removed. Water was added to the residue, and the mixture was extracted with diethyl ether three times. After drying the solution with Na_2SO_4, filtration, and removal of the solvent, ketone or aldehyde was obtained in good yield with high purity.[10] Thus, when diphenylmethanol (**1a**) was used as the substrate in the oxidation with IS-DIB **A**, **B**, and **C**, benzophenone (**2a**) was obtained in 99%, 99%, and 97% yields with 99%, 99%, and 98% purity, respectively, as shown in Table 1. Here, use of an excess amount of IS-DIB suppressed the contamination of TEMPO into the diethyl ether extracts from the reaction mixture. On the other hand, when DIB was used as the oxidant for the oxidation of diphenylmethanol (**1a**) under the same conditions and procedure, benzophenone (**2a**) was obtained in 99% yield, but its purity was 48% due to the presence of iodobenzene. Therefore, the purification of benzophenone by column chromatography on silica gel was required. When IS-DIB **A**, **B**, or **C** was used as the oxidant, the oxidation product was obtained in good yield with high purity by simple diethyl ether extraction of the reaction mixture and subsequent removal of the solvent from the extract. The same oxidation reactions of 9-fluorenol (**1b**), 1-phenyl-1-propanol (**1c**), and 1-(5′-methylfuran-2′-yl)-1-pentanol (**1d**) were carried out under the same conditions and procedure to give the corresponding ketones **2b**, **2c**, and **2d** in good yields with high purity, respectively. Moreover, the same treatment of benzylic and allylic alcohols, such as *p*-chlorobenzyl alcohol (**1e**), *p*-methylbenzyl alcohol (**1f**), piperonyl alcohol (**1g**), 4-phenylbenzyl alcohol (**1h**), 2-thiophenemethanol (**1i**), geraniol (**1j**), and *trans*-cinnamyl alcohol (**1k**), with IS-DIB **A**, **B**, and **C** under the same conditions and procedure provided the corresponding aromatic aldehydes **2e–i** and α,β-unsaturated aldehydes **2j** and **2k** in good yields with high purity, respectively. The oxidations of primary alcohols, such as β-citronellol (**1l**), 1-adamantanemethanol (**1m**), and 8-(*p*-methylbenzenesulfonyloxy)-1-octanol (**1n**), with IS-DIB **A**, **B**, and **C** in the presence of TEMPO at room temperature provided the corresponding aldehydes **2l–n** in good yields with high purity, respectively, although the yield and purity were slightly decreased in the oxidation of 8-(*p*-methylbenzenesulfonyloxy)-1-octanol (**1n**). When DIB was used as the oxidant in the same oxidation of 1-adamantanemethanol (**1m**) and 8-(*p*-methylbenzenesulfonyloxy)-1-octanol (**1n**) under the same conditions and procedure, the corresponding aldehydes **2m** and **2n** were obtained in good yields, respectively. However, the purity was 50% and 48%, respectively, again due to the presence of iodobenzene. The same TEMPO-mediated oxidation of ketones, such as β-cholestanol (**1o**), 4-(*tert*-butyldimethylsilyloxy)-1-cyclohexanol (**1p**), borneol (**1q**), and 2,3,4,6-*tetra*-*O*-benzyl-D-glucose (**1r**), with IS-DIB A, B, and C gave the corresponding ketones **2o–r** in good yields with high purity, respectively.

On the other hand, the purity of ketones **2o–r** obtained with DIB was 49%, 49%, 48%, and 48%, respectively, although the yields were quite good.

Then, the reuse of IS-DIB **A**, **B**, and **C** in the oxidation of alcohols in the presence of TEMPO was carried out. After the extraction of the oxidation product from the reaction mixture with diethyl ether, the aqueous solution was extracted with chloroform to recover ion-supported iodobenzenes in good yields.[10] The recovered ion-supported

iodobenzenes were re-oxidized with sodium peroxoborate in acetic acid at 45 °C to regenerate IS-DIB **A**, **B**, and **C**, respectively, in good yields. Reuse of the recovered and regenerated IS-DIB **A**, **B**, and **C** for the oxidation of *trans*-cinnamyl alcohol (**1k**) and β-citronellol (**1l**) in the presence of TEMPO under the same conditions as those of the first reactions provided the corresponding aldehydes **2k** and **2l** in good yields with high purity again, as shown in Table 1. Thus, IS-DIB **A**, **B**, and **C** can be regenerated and reused for the same oxidation.

In conclusion, the TEMPO-mediated oxidation of secondary and primary alcohols with IS-DIB **A**, **B**, and **C** provided the corresponding ketones and aldehydes in good yields with high purity by simple diethyl ether extraction of the reaction mixture and subsequent removal of the solvent from the extract. Moreover, ion-supported iodobenzenes, which were the co-products of the present reactions and derived from IS-DIB **A**, **B**, and **C**, could be recovered in good yields and regenerated and reused for the same oxidation of alcohols, maintaining high yields and high purity of the products. Thus, the present IS-DIB **A**, **B**, and **C** are simplified reagents for the isolation of ketones or aldehydes, and are user-friendly and environmentally benign reagents for the TEMPO-mediated oxidation of alcohols.

Acknowledgement

Financial support in the form of a Grant-in-Aid for Scientific Research (No. 23655142) from the Ministry of Education, Culture, Sports, Science, and Technology in Japan, Iodine Research Project in Chiba University, and Futaba Electronics Memorial Foundation is gratefully acknowledged.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(8) **Typical Procedure for the Preparation of *N*-Methyl-*N*-[3-(4′-iodophenyl)-1-propyl]pyrrolidinium 4′′-Methylbenzenesulfonate (pre-A):** To a solution of 3-(4′-iodophenyl)-1-propyl tosylate (5 mmol, 2.08 g) in MeCN (20 mL) was added 1-methylpyrrolidine (1.10 equiv, 5.50 mmol, 0.585 mL). The mixture was stirred for 16 h at 60 °C. After the reaction, the reaction mixture was concentrated in vacuo. H_2O (20 mL) was added to the residue, the aqueous layer was washed with Et_2O (30 mL) once and then extracted with $CHCl_3$ (3 × 30 mL). The organic layer was dried over Na_2SO_4. Then, removal of the solvent under reduced pressure afforded *N*-methyl-*N*-[3-(4′-iodophenyl)-1-propyl]pyrrolidinium 4′′-methylbenzenesulfonate (pre-A) in 99% yield. If necessary, the residue was washed with EtOAc to afford the product in >99% purity. *N*-Methyl-*N*-[3-(4′-iodophenoxy)-1-propyl]pyrrolidinium 4′′-methylbenzenesulfonate (pre-**B**) and *N*-[3-(4′-iodophenoxy)-1-propyl]-*N*,*N*,*N*-trimethylammonium 4′′-methylbenzenesulfonate (pre-**C**) were prepared in 99% yield and 99% yield, respectively, by the same procedure.
***N*-Methyl-*N*-[3-(4′-iodophenyl)-1-propyl]pyrrolidinium 4′′-Methylbenzenesulfonate:** mp 127–129 °C. IR (Nujol): 1185, 798 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.93–2.03 (m, 2 H), 2.05–2.10 (m, 4 H), 2.31 (s, 3 H), 2.57 (t, *J* = 7.5 Hz, 2 H), 3.09 (s, 3 H), 3.50 (t, *J* = 6.7 Hz, 2 H), 3.53–3.65 (m, 4 H), 6.90 (d, *J* = 8.2 Hz, 2 H), 7.11 (d, *J* = 8.2 Hz, 2 H), 7.54 (d, *J* = 8.2 Hz, 2 H), 7.73 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.27, 21.54, 25.44, 31.57, 48.26, 63.20, 64.20, 91.63, 125.79, 128.67, 130.53, 137.65, 139.25, 139.48, 144.02. ESI-HMRS: *m/z* calcd for $C_{14}H_{21}NI$ [M^+]: 330.0713; found: 330.0705.
***N*-Methyl-*N*-[3-(4′-iodophenoxy)-1-propyl]pyrrolidinium 4′′-Methylbenzenesulfonate:** mp 114–116 °C. IR (Nujol): 1195, 1010, 818 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.08–2.23 (m, 6 H), 2.30 (s, 3 H), 3.15 (s, 3 H), 3.54–3.72 (m, 6 H), 3.92 (t, *J* = 5.8 Hz, 2 H), 6.60 (d, *J* = 9.1 Hz, 2 H), 7.09 (d, *J* = 8.2 Hz, 2 H), 7.50 (d, *J* = 9.1 Hz, 2 H), 7.71 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.23, 21.55, 23.99, 48.27, 61.16, 64.27, 64.38, 83.24, 116.90, 125.70, 128.63, 138.22, 139.22, 144.02, 158.04. ESI-HMRS: *m/z* calcd for $C_{14}H_{21}ONI$ [M^+]: 346.0662; found: 346.0655.

***N*-[3-(4′-Iodophenoxy)-1-propyl]-*N*,*N*,*N*-trimethylammonium 4′′-Methylbenzenesulfonate:** mp 222–226 °C. IR (KBr) 1285, 1010, 816 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.12–2.19 (m, 2 H), 2.29 (s, 3 H), 3.08 (s, 9 H), 3.46 (t, *J* = 8.3 Hz, 2 H), 4.02 (t, *J* = 6.0 Hz, 2 H), 6.80 (d, *J* = 9.0 Hz, 2 H), 7.12 (d, *J* = 7.9 Hz, 2 H), 7.47 (d, *J* = 7.9 Hz, 2 H), 7.61 (d, *J* = 9.0 Hz, 2 H). ^{13}C NMR (100 MHz, DMSO): δ = 20.74, 22.42, 52.25, 62.84, 64.84, 83.53, 117.29, 125.44, 128.00, 137.51, 138.01, 145.80, 158.04. HRMS (APPI): *m/z* calcd for $C_{12}H_{19}ONI$ [M^+]: 320.0506; found: 320.0499.

Typical Procedure for the Preparation of *N*-Methyl-*N*-[3-(4′-diacetoxyiodo)phenyl-1-propyl]pyrrolidinium 4′′-Methylbenzenesulfonate (IS-DIB A): To a solution of *N*-methyl-*N*-[3-(4′-iodophenyl)-1-propyl]pyrrolidium 4′′-methylbenzenesulfonate (5 mmol, 2.50 g) in AcOH (50 mL) was added portionwise $NaBO_3·4H_2O$ (10 equiv, 50 mmol, 7.69 g). The mixture was stirred for 15 h at 45 °C. After the reaction, the reaction mixture was concentrated in vacuo, then the residue was dissolved in H_2O (50 mL), and the obtained mixture was washed with Et_2O (50 mL) once. Then, the aqueous layer was extracted with $CHCl_3$ (5 × 30 mL). The organic layer was dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded *N*-methyl-*N*-[3-(4′-diacetoxyiodo)-phenyl-1-propyl]pyrrolidium 4′′-methylbenzenesulfonate in the range of 60–70% yields (counteranion; TsO^-/AcO^- = 1:1; IS-DIB **A**). The counteranion was completely converted into the tosylate anion by the stirring treatment of the obtained IS-DIB **A** with $PTSA·H_2O$ (1.0 equiv) in MeCN (20 mL) at r.t. overnight. Then the solvent was removed, and H_2O (20 mL) was added to the residue. The aqueous layer was washed with Et_2O and then extracted with $CHCl_3$ (3 × 30 mL). Finally, removal of the solvent gave IS-DIB **A**. IS-DIB **B** and **C** were prepared from pre-**B** and pre-**C** in the range of 60–70% yields, respectively, by the same procedure. The purity of IS-DIB **A**, **B**, and **C** was estimated to be nearly 90% by ^1H NMR spectroscopy, due to containing a trace amount of pre-A, pre-B, and pre-C, respectively.

***N*-Methyl-*N*-[3-(4′-diacetoxyiodo)phenyl-1-propyl]-pyrrolidinium 4′′-Methylbenzenesulfonate (IS-DIB A): viscous oil. IR (neat):** 1646, 1556, 1272, 799 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ (cation) = 2.00 (s, 6 H), 2.06–2.29 (m, 6 H), 2.78 (t, *J* = 7.8 Hz, 2 H), 3.14 (s, 3 H), 3.54–3.73 (m, 6 H), 7.36 (d, *J* = 8.6 Hz, 2 H), 7.99 (d, *J* = 8.6 Hz, 2 H); δ (anion TsO^-) = 2.35 (s, 3 H), 7.17 (d, *J* = 8.2 Hz, 2 H), 7.77 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.28, 21.50, 21.80, 25.27, 31.83, 48.34, 63.47, 64.33, 118.75, 125.68, 128.66, 131.08, 135.11, 139.61, 143.31, 144.49, 176.46. ESI-HMRS: *m/z* calcd for $C_{18}H_{27}O_4NI$ [M^+]: 448.0979; found: 448.0967.

***N*-Methyl-*N*-[3-(4′-diacetoxyiodo)phenoxy-1-propyl]-pyrrolidinium 4′′-Methylbenzenesulfonate (IS-DIB B): viscous oil. IR (neat):** 1650, 1583, 1275, 1010, 823 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ (cation) = 1.98 (s, 6 H), 2.18–2.29 (m, 6 H), 3.17 (s, 3 H), 3.59–3.74 (m, 6 H), 4.13 (t, *J* = 5.6 Hz, 2 H), 6.93 (d, *J* = 9.1 Hz, 2 H), 7.97 (d, *J* = 9.1 Hz, 2 H); δ (anion TsO^-) = 2.31 (s, 3 H), 7.12 (d, *J* = 8.2 Hz, 2 H), 7.73 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.28, 21.58, 22.03, 23.85, 48.46, 61.51, 64.51, 64.85, 111.67, 117.03, 125.66, 128.66, 137.02, 138.20, 143.32, 160.77, 176.43. ESI-HMRS: *m/z* calcd for $C_{18}H_{27}O_5NI$ [M^+]: 464.0928; found: 464.0919.

3-[4′-(Diacetoxyiodo)phenoxy]-1-propyl-*N*,*N*,*N*-trimethylammonium 4′′-Methylbenzenesulfonate (IS-DIB C): viscous oil. IR (neat): 1650, 1243, 1040, 812 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.98 (s 6 H), 2.30–2.35 (m 2 H), 3.28 (s, 9 H), 3.67 (t, *J* = 8.4 Hz, 2 H), 4.13 (t, *J* = 5.5 Hz, 2 H), 6.96 (d, *J* = 9.1 Hz, 2 H), 8.00 (d, *J* = 9.1 Hz, 2 H); δ (anion TsO^-) = 2.31 (s, 3 H), 7.12 (d, *J* = 8.2 Hz, 2 H), 7.71 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.24, 21.43, 23.03, 53.44, 64.12, 64.68, 111.79, 116.98, 126.35, 129.23, 137.09, 138.19, 142.44, 160.76, 176.63. ESI-HMRS: *m/z* calcd for $C_{16}H_{25}NI$ [M^+]:438.0772; found: 438.0760.

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(10) **General Procedure for the Oxidation of Alcohols with IS-DIB A, B, and C in the Presence of TEMPO:** To a solution of IS-DIB **A**, **B,** or **C** (1.5 equiv, 0.75 mmol) in CH_2Cl_2 (2 mL) were added alcohol (0.5 mmol) and TEMPO (10 mol%, 0.05 mmol). Then, the reaction mixture was stirred for 2 h at r.t. Then, the reaction mixture was concentrated in vacuo, H_2O (20 mL) was added to the residue, and the aqueous layer was extracted with Et_2O (3 × 20 mL). The organic layer was dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the product (ketone or aldehyde), and purity of the product was estimated by ^1H NMR spectroscopy. On the other hand, the aqueous layer was extracted with $CHCl_3$ three times (3 × 20 mL). Then, the organic layer was washed with aq Na_2SO_3 and brine. The organic layer was dried over Na_2SO_4, and removal of the solvent under reduced pressure afforded ion-supported iodobenzene (recovery rate: 75–90%).

Typical Procedure for the Regeneration of *N*-methyl-*N*-[3-(4′-diacetoxyiodo)phenyl-1-propyl]pyrrolidinium 4′′-Methylbenzenesulfonate (IS-DIB A): To a solution of *N*-methyl-*N*-[3-(4′-iodophenyl)-1-propyl]pyrrolidinium 4′′-methylbenzenesulfonate (5 mmol, 2.50 g) in AcOH (50 mL) was added portionwise $NaBO_3·4H_2O$ (10 equiv, 50 mmol, 7.69 g). The mixture was stirred for 15 h at 45 °C. After the reaction, the reaction mixture was concentrated, and H_2O (20 mL) was added to the residue. Then the aqueous solution was washed with H_2O once, and then extracted with $CHCl_3$ five times (3 × 30 mL). The organic layer was dried over Na_2SO_4. Then, removal of the solvent at 45 °C under reduced pressure afforded *N*-methyl-*N*-[3-(4′-diacetoxyiodo)phenyl-1-propyl]pyrrolidinium 4′′-methylbenzenesulfonate (TsO^-/AcO^- = 1:1). The counteranion was completely converted into the tosylate anion by the stirring treatment of the obtained IS-DIB **A** with $PTSA·H_2O$ (1.0 equiv) in MeCN (20 mL) at r.t. overnight. Then the solvent was removed and, and H_2O (20 mL) was added to the residue. The aqueous layer was washed with Et_2O and then extracted with $CHCl_3$ (3 × 30mL). Finally, removal of the solvent gave the regenerated IS-DIB **A**.

Regenerated IS-DIB **B** and **C** were prepared from recovered *N*-methyl-*N*-[3-(4′-iodophenoxy)-1-propyl]pyrrolidinium 4′′-methylbenzenesulfonate (pre-**B**), and *N*-[3-(4′-iodophenoxy)-1-propyl]-*N*,*N*,*N*-trimethylammonium 4′′-methylbenzenesulfonate (pre-**C**), respectively, by the same method and conditions.

Most of ketones and aldehydes in the present study are commercially available, and they are identified with authentic samples, except for the following products.

1-(5′-Methylfuran-2′-yl)-1-pentanone (2d): oil. IR (neat): 3121, 2931, 2827, 1671, 1518, 1452, 876 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.5 Hz, 3 H), 1.39 (sext, *J* = 7.5 Hz, 2 H), 1.69 (quin, *J* = 7.5 Hz, 2 H), 2.39 (s, 3 H), 2.75 (t, *J* = 7.5 Hz, 2 H), 6.14 (d, *J* = 3.4 Hz, 1 H), 7.09 (d, *J* = 3.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.15, 13.33, 21.76, 26.11, 37.17, 108.10, 118.22, 150.84, 156.84, 188.40. ESI-HMRS: *m/z* calcd for $C_{10}H_{15}O_2$ [M + H]: 167.1067; found: 167.1065.

1-Adamantanecarboxaldehyde (2m): mp 140–142 °C (lit.[11] mp 146–148 °C). IR (Nujol): 2815, 2698, 1722 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.68–1.80 (m, 12 H), 2.03–2.09 (m, 3 H), 9.32 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.31, 35.80, 36.52, 44.82, 206.09.

8-(4′-Methylbenzenesulfonyloxy)octanal (2n): oil. IR (neat): 2859, 2723, 1723, 1359, 1176 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21–1.36 (m, 6 H), 1.54–1.58 (m, 4 H), 2.41 (t, *J* = 7.4 Hz, 2 H), 2.45 (s, 3 H), 4.02 (t, *J* = 6.5 Hz, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 7.78 (d, *J* = 8.2 Hz, 2 H), 9.73–9.76 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.43, 21.65, 24.95, 28.45, 28.52, 28.67, 43.58, 70.38, 127.67, 129.66, 132.96, 144.54, 202.50. ESI-HMRS: *m/z* calcd for $C_{15}H_{23}O_4S$ [M + H]: 299.1312; found: 299.1310.

4-[(*tert*-Butyldimethylsilyl)oxy]cyclohexanone (2p): oil (commercial, oil). IR (neat): 1720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.10 (s, 6 H), 0.92 (s, 9 H), 1.83–2.02 (m, 4 H), 2.18–2.28 (m, 2 H), 2.61–2.73 (m, 2 H), 4.10–4.17 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = –5.39, 17.53, 25.24, 33.65, 36.38, 65.39, 211.26. HMRS (APPI): *m/z* calcd for $C_{12}H_{25}O_2Si$ [M + H]: 229.1618; found: 229.1617.

2,3,4,6-Tetra-*O*-benzyl-D-glucono-1,5-lactone (2r): oil. IR (neat): 2919, 2869, 1755, 1454, 1165, 1094, 738, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.64–3.75 (m, 2 H), 3.88–3.98 (m, 2 H), 4.12 (d, *J* = 6.1 Hz, 1 H), 4.43–4.76 (m, 8 H), 4.98 (d, *J* = 11.3 Hz, 1 H), 7.15–7.41 (m, 20 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 68.21, 73.52, 73.69 (2 C), 73.91, 76.01, 78.12, 80.92, 127.79 (3 C), 127.91, 127.96 (3 C), 128.08, 128.37, 128.41 (2 C), 128.45, 136.90, 137.46 (2 C), 137.55, 169.31. ESI-HMRS: *m/z* calcd for $C_{34}H_{35}O_6$ [M + H]: 539.2428; found: 539.2423.

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