cially ethanethiol, is necessary for this debromination (run 4 in Table IV). The rate of the reaction may depend on the concentration of aluminum chloride (compare run 1 and 5 in Table IV). These facts may suggest the intervension of a cationic species such as **23** or **24** in the mechanism. Resuls of runs 1 and 2 in Table IV indicate that in a push–pull mechanism the function of aluminum chloride as a Lewis acid is comparable between those two reaction conditions because considerable amount of demethylated products were obtained in both cases. A simple push–pull mechanism for this debromination can hardly explain the remarkable retardation of the rate without dichloromethane as a cosolvent. Although there is no direct evidence to distinguish between a simple cationic species **23** and a radical cationic species **24**, we prefer the latter to explain all the findings obtained.

Almost all of the existing methods for dehalogenation of aromatic compounds involve one- or two-electron transfer from the reagent to the substrate.[8] Hence, the substitution of electron-withdrawing group(s) on the aromatic ring facilitates the reductive removal of halogen atoms in the reported methods. On the other hand, electron-donating group(s) accelerate the dehalogenation with the present method, since the mechanism involves a cationic species as an intermediate.

Experimental Section

IR spectra were recorded with a JASCO A-202 diffraction grating infrared spectrophotometer, and ^1H NMR spectra were obtained with a JEOL JNM-FX 100 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. GLC analyses were performed with a Shimazu Model GC-4CM instrument.

Materials. Compounds **1**, **2**, **7–15**, and **17–19** and those used in runs 1, 2, and 5 in Table I and in all runs in Table II are commercially available. The starting halophenol derivatives **3**,[9] **5**,[10] and **16**,[11] those listed in runs 3,[12] 4,[13] and 6[14] in Table I, ethyl *p*-hydroxyphenylacetate[15] (the product from run 4 in Table I), 5-bromo-2-hydroxybenzoic acid (**4**),[16] and naphthyl sulfides **20**[17] and **21**[17] are known.

Dithioacetal 6. To a stirred solution of aluminum chloride (6.10 g, 46 mmol) and ethanethiol (5 mL) in dichloromethane (20 mL) was added 3-iodonanisaldehyde (**5**) (2.62 g, 10 mmol) in nitrogen under ice-cooling. After being stirred for 3 h at the same temperature, the reaction mixture was poured into water and extracted with dichloromethane. The organic layer was dried (Na_2SO_4), filtered, and evaporated to afford a residue, which was purified by column chromatography over silica gel with elution of dichloromethane–hexane (1:2), giving **6** as a colorless crystal (0.64 g, 18%). Analytically pure sample was obtained by recrystalization from ether–hexane: mp 67–68 °C; IR (KBr) 3100–3400, 2970, 1590, 1495, 1405, 1260, 1205 cm^{-1}; NMR ($CDCl_3$) δ 1.22 (t, J = 7.5 Hz, 6 H), 2.55 (q, J = 7 Hz, 2 H), 2.57 (q, J = 7.5 Hz, 2 H), 4.83 (s, 1 H), 5.39 (s, 1 H), 6.92 (AB d, J = 9 Hz, 1 H), 7.35 (AB dd, J = 2, 9 Hz, 1 H), 7.74 (d, J = 2 HZ, 1 H). Anal. Calcd for $C_{11}H_{15}OIS_2$: C, 37.29; H, 4.27. Found: C, 37.25; H, 4.17.

General Procedure for Dehalogenation. A mixture of substrate (1 mmol), ethanethiol (0.4 mL), methanol-free dichloromethane (2 mL), and aluminum chloride was stirred in nitrogen under the conditions described in Tables I and II. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and evaporated to afford a residue which was purified by column chromatography over silica gel or analyzed by GLC. GLC analyses were performed with a 20% SF-96 (3 m × 3 mm) column. Column temperature and internal standards are as follows, respectively, for phenol, anisole, and diethyl disulfide at 100 °C, *n*-decane; for phenetole at 80 °C, *n*-nonane; for *p*-bromophenol, *p*-bromoanisole, and *m*-bromoanisole at 150 °C, *n*-tridecane.

1-(Ethylthio)-4-chloronaphthalene (22). To a stirred solution 4-chloro-1-naphthol (**18**) (180 mg, 1 mmol) in dichloromethane (2 mL) was added ethanethiol (0.4 mL) and aluminum chloride (187 mg, 1.4 mmol). The mixture was stirred for 1 h at 0 °C under nitrogen, poured into ice–water, and extracted with dichloromethane. The organic layer was washed with brine, dried, and chromatographed over silica gel with 5% dichloromethane–hexane to afford naphthalene (16 mg, 9%), 1-(ethylthio)-4-chloronaphthalene as an oil [(65 mg, 29%); IR ($CHCl_3$) 3060, 1580, 1505, 1365, 990 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (t, J = 7 Hz, 3 H), 2.95 (q, J = 7 Hz, 2 H), 7.2–7.8 (m, 4 H), 8.1–8.6 (m, 2 H); high-resolution mass spectrum, calcd for $C_{12}H_{11}ClS$ (M^+) m/e 222.0269, obsd 222.0261] and 1-(ethylthio)naphthalene (**21**, 111 mg, 59%).

Registry No. **3**, 7120-41-4; **4**, 4068-76-2; **5**, 2314-37-6; **6**, 91238-73-2; **7**, 106-48-9; **8**, 87-64-9; **9**, 367-12-4; **10**, 615-58-7; **11**, 2432-14-6; **12**, 695-96-5; **13**, 3964-56-5; **14**, 118-79-6; **15**, 573-97-7; **16**, 91238-72-1; **17**, 2050-49-9; **18**, 604-44-4; **19**, 2050-76-2; **20**, 32551-87-4; **21**, 17539-31-0; **22**, 91238-74-3; β-naphthol, 135-19-3; naphthalene, 91-20-3; 1-bromo-2-methoxybenzene, 578-57-4; 2-bromo-4-methylphenol, 6627-55-0; 2-bromo-4-methylphenyl acetate, 86614-21-3; ethyl 3-bromo-4-hydroxybenzeneacetate, 29121-25-3; 2-iodophenol, 533-58-4; methyl 3-iodo-4-methoxybenzoate, 35387-93-0; phenol, 108-95-2; 4-methylphenol, 106-44-5; ethyl 4-hydroxybenzeneacetate, 17138-28-2; methyl 4-hydroxybenzoate, 99-76-3; 4-bromophenol, 106-41-2; 1-bromo-4-methoxybenzene, 104-92-7; 1-bromo-4-ethoxybenzene, 588-96-5; 1-bromo-4-phenoxybenzene, 101-55-3; 4-iodophenol, 540-38-5; 1-iodo-4-methoxybenzene, 696-62-8; 2-chlorophenol, 95-57-8; methoxybenzene, 100-66-3; ethanethiol, 75-08-1; diethyl sulfide, 352-93-2; aluminum chloride, 7446-70-0.

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Direct Condensation of [Hydroxy(tosyloxy)iodo]arenes with Thiophenes. A Convenient, Mild Synthesis of Aryl(2-thienyl)iodonium Tosylates

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Aryl(2-thienyl)iodonium salts are active microbicides and, for that reason, have been the object of considerable attention in the patent literature.[1] The most common synthetic approach to such iodonium salts entails the condensation of bis(acyloxy)iodoarenes with thiophenes in the presence of a strong acid (e.g., H_2SO_4, Cl_3CCO_2H, CF_3CO_2H), a method which may preclude the incorpora-

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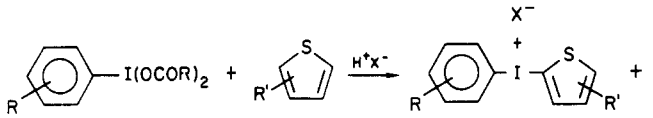
Table I. Aryl(2-thienyl)iodonium Tosylates from Reactions of [Hydroxy(tosyloxy)iodo]arenes with Thiophenes (1 + 2 → 3; eq 2)

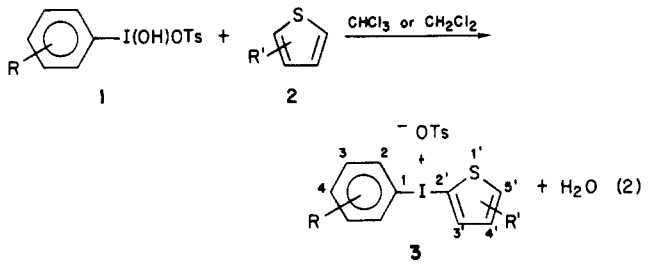
1	2	2/1[a]	conditions,[b] time in h	3, % yield
R	R′			
H	H	3.0	4	77
H	2-Me	2.0	4	89
H	2-Et	2.0	2	88
H	3-Me	2.0	2	78
H	2-Br	1.0	66	31
H	2-CH_2OH	1.0	~2	80
H	2-CHO	2.0	34	33
2-Me	H	1.0	4 days[c]	48
2-Me	2-Me	2.0	3.5	88
2-Me	2-Et	2.0	3.5	84
2-Me	3-Me	2.0	3.5	73
3-Me	H	2.6	3	68
4-Me	H	1.0	10 days[c]	57
2-F	H	4.0	5	65
2-F	2-Me	3.0	3.5	86
4-Cl	H	5.0	6.5	68
4-Cl	2-Me	1.5	2.5	89
4-Cl	2-Et	4.3	24	56
4-Cl	3-Me	5.0	48	19
4-Br	2-Me	4.6	24	67
4-I	2-Me	3.0	30	32

[a] Initial concentration of 1 ~0.1–0.3 M; molar ratios rounded off to 2 significant figures. [b] $CHCl_3$ at reflux except where specified otherwise. [c] CH_2Cl_2 at room temperature.

tion of acid-sensitive functional groups in the iodonium ion nucleus; eq 1.[1a,c-f,2-5] In this paper, we describe a



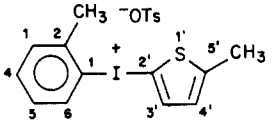
particularly convenient synthesis of this important class of compounds via the direct condensation of various [hydroxy(tosyloxy)iodo]arenes 1[6] with thiophenes 2 in either chloroform or dichloromethane, a procedure which obviates the necessity of an added catalyst; eq 2.[7,8] The aryl(2-



thienyl)iodonium tosylates 3, thus prepared, were typically isolated by their precipitation from the reaction solution with added Et_2O (sometimes after partial concentration) or by evaporation of the reaction solvent and subsequent trituration of the residual material with Et_2O. For example, after a mixture of 13.6 mmol of *o*-[hydroxy(tosyloxy)iodo]toluene (1, R = 2-Me) and 27.1 mmol of 2-methylthiophene in $CHCl_3$ (50 mL) had been heated under reflux for 3.5 h, the resulting solution was treated with Et_2O until clouding occurred whereupon *o*-tolyl(5-methyl-2-thienyl)iodonium tosylate separated. More Et_2O was subsequently added to ensure complete precipitation, and the product was isolated (5.84 g, 88%) and characterized by elemental (C, H, I) and ^1H NMR analyses. Table I contains a listing of 21 aryl(2-thienyl)iodonium tosylates which have been obtained by this method, including a summary of reaction conditions and yields. Among these, some bear substituents in both rings while others are substituted only in the thiophene ring or the arene ring. The CH_2OH and CHO substituents are unusual for aryl(2-thienyl)iodonium salts.

The substituent pattern in the iodonium ions is regulated by two factors. Obviously, the position of groups in the arene ring will correspond to that of the starting [hydroxy(tosyloxy)iodo]arene. The location of thienyl substituents, however, conforms to expectations of an electrophilic substitution resaction; i.e., for 2-substituted thiophenes, aryliodination is directed to C-5, but, for 3-methylthiophene, aryliodination is directed to C-2.

The structures of the iodonium salts were deduced from their elemental compositions (C, H, I) and ^1H NMR spectra. For example, the ^1H NMR spectrum (in CD_3OD) of *o*-tolyl(5-methyl-2-thienyl)iodonium tosylate (see below)



exhibits a 3 H singlet at δ 2.32 (Me of TsO^-), a 3 H singlet at δ 2.51 (Me attached to thiophene ring), a 3 H singlet at δ 2.66 (Me of *o*-tolyl group), and a 10 H "multiplet" from ca. δ 6.65 to 8.35 (aromatic hydrogens). Among the multiplets in the aromatic region, there is an obvious low-field 1 H "doublet" at δ 8.20 (*o*-hydrogen of tolyl group) and an obvious high-field 1 H doublet (with fine structure) at δ 6.74 (4′-hydrogen).

Several trends in the ^1H NMR spectra (CD_3OD) of the aryl(2-thienyl)iodonium tosylates are evident. The methyl resonance of the tosylate ion generally appears at δ ~2.3 and is coincident with the methyl resonances of the *m*-tolyl and *p*-tolyl ligands (at least for the two examples studied). However, the methyl peak of the *o*-tolyl ligand generally appears at lower field (δ ~2.65) while the absorptions of methyl groups attached to the thiophene ring are typically located somewhere in between. The aromatic region is complex and comprised of a series of closely spaced and overlapping multiplets. However, when the aryl ligand is phenyl, the ortho hydrogens often appear as a 2 H "doublet of multiplets" at lower field than the remaining aromatic resonances. Similarly, when the aryl ligand is *o*-tolyl, the ortho hydrogen is evident as a low-field doublet. In the case of *o*-fluorophenyl group, the ortho hydrogen is manifest as a broad, low-field apparent triplet. Finally, in some spectra, the 4′-H of the thiophene ring can be seen as a high-field doublet (in the aromatic region) with superimposed fine structure.

As a confirmation of the structural assignments, selected examples of the aryl(2-thienyl)iodonium tosylates were converted by metathesis to the corresponding iodide salts. Pyrolysis of the iodide salts, in the solid state, gave rea-

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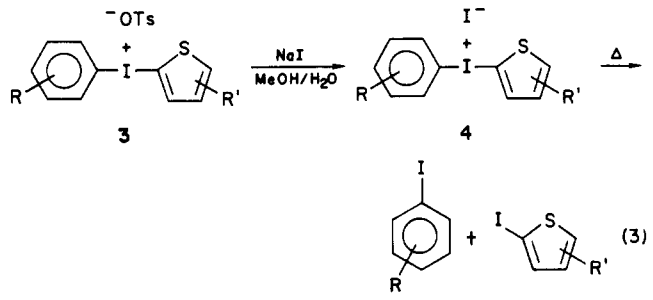
Table II. Thermolysis of Aryl(2-thienyl)iodonium Iodides (eq 3)

4[a]		% yield of	ArI	ThI[b]
R	R′	4 from 3	R	R′
H	3′-Me	92	H	3-Me[c]
2-Me	3′-Me	89	2-Me	3-Me[c]
H	5′-Me	93	H	5-Me[c]
H	5′-Br	89	H	5-Br[c]
3-Me	H	83	3-Me	H
2-Me	5′-Me	90	2-Me	5-Me
2-Me	H	79	2-Me	H

[a] For numbering of iodonium skeleton, see eq 2. [b] n-R′-2-iodothiophene. [c] The ArI:ThI mole ratios (by H^1 NMR) were 1.11, 1.09 (or 1.02), 1.02 (or 1.07), and 1.11, respectively, for the indicated reactions.

sonably clean mixtures of an iodoarene and an iodothiophene, these being identified by ^1H NMR comparisons with authentic mixtures; eq 3. In some cases, it was



possible to estimate the molar ratio of the components in the pyrolysis mixtures by integration of appropriate ^1H NMR resonances. For example, treatment of the iodonium tosylate from the reaction of o-[hydroxy(tosyloxy)iodo]-toluene (1, R = 2-Me) with 3-methylthiophene with sodium iodide gave the corresponding iodide salt in 89% yield. Pyrolysis of a portion of the iodide salt at 135 °C gave a 1.08:1.00 mole mixture of o-iodotoluene and 2-iodo-3-methylthiophene, thus confirming the structure of the tosylate salt as o-tolyl(3-methyl-2-thienyl)iodonium tosylate. Similar experiments are summarized in Table II.

Experimental Section

General Methods. The ^1H NMR spectra reported herein were recorded on a Varian EM-360 NMR spectrometer. Chemical shifts are given relative to internal tetramethylsilane, and integrations are rounded off to the nearest whole number. The number of "protons" reported for a given multiplet is based on the combined integration of all resonances in the spectrum (except for those of minor impurities) divided by the total number of "protons" in the molecule under consideration. Elemental compositions were determined at Galbraith Labs in Knoxville, TN. Decomposition points of aryl(2-thienyl)iodonium tosylates are uncorrected.

The [hydroxy(tosyloxy)iodo]arenes utilized in this study were prepared by procedures similar to those already described in the literature.[6,7] The reaction conditions and workups for the preparation of the aryl(2-thienyl)iodonium tosylates reported herein were similar (albiet, not identical) to the two example procedures given below. For the remaining compounds, the elemental compositions, melting points, and ^1H NMR spectra are given.

Phenyl(3-methyl-2-thienyl)iodonium Tosylate. A stirred mixture of [hydroxy(tosyloxy)iodo]benzene (1, R = H) (5.03 g, 12.8 mmol), 3-methylthiophene (2.51 g, 25.6 mmol), and $CHCl_3$ (50 mL) was heated under reflux for 2 h. The resulting golden-brown solution was allowed to cool to room temperature, and Et_2O was added, with stirring, to the cloud-point whereupon a solid began to separate from solution. After 25 min, an excess of Et_2O was added to ensure complete precipitation, and the product was isolated, washed with Et_2O, dried in air, and identified as phenyl(3-methyl-2-thienyl)iodonium tosylate: yield 4.71 g (78.1%); mp 147–150 °C dec; ^1H NMR (CD_3OD) δ 2.33 (s, 3 H, Me of $^-$OTs), 2.48 (s, 3 H, Me of thienyl group), 6.85–8.25 (m, 11 H, Ar H, includes an obvious 2 H "d of m" at δ 8.02). Anal. Calcd for $C_{18}H_{17}IS_2O_3$: C, 45.77; H, 3.63; I. 26.86. Found: C, 45.73; H, 3.66; I. 26.92.

o-Tolyl(2-thienyl)iodonium Tosylate. A mixture of o-[hydroxy(tosyloxy)iodo]toluene (5.01 g, 12.3 mmol), thiophene (1.03 g, 12.3 mmol), and CH_2Cl_2 (25mL) was stirred for 4 days at room temperature. The resulting light brown solution was then allowed to evaporate to dryness in a hood, and the residual material was triturated overnight with Et_2O. The crude product, a solid (3.76 g), was then dissolved in a minimum quantity of MeOH, reprecipitated with Et_2O, isolated, washed with Et_2O, dried in air, and identified as o-tolyl(2-thienyl)iodonium tosylate: white, crystalline solid; yield 2.75 g (47.8%); mp 144–148 °C; ^1H NMR (CD_3OD) δ 2.33 (s, 3 H, Me of $^-$OTs), 2.67 (s, 3 H, Me of o-tolyl group), 6.85–8.4 (m, 11 H, Ar H, includes an obvious 1 H d at δ 8.26). Anal. Calcd for $C_{18}H_{17}ISO_3$: C, 46.92; H, 3.94; I, 26.09. Found: C, 46.96; H, 3.99; I. 26.25.

Phenyl(2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 157–160 °C dec; ^1H NMR (CD_3OD) δ 2.33 (s, 3 H), 6.9–8.3 (m, 12 H). Anal. Calcd for $C_{17}H_{15}IS_2O_3$: C, 44.55; H, 3.30; I, 27.69. Found: C, 44.53; H, 3.30; I, 27.36.

Phenyl(5-methyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O; white crystals; mp 135–137 °C dec; ^1H NMR (CD_3OD) δ 2.32 (s, 3 H), 2.53 (s, 3 H), ~6.6–8.25 (m, 11 H, includes 2 H "d of m" at 8.05 and 1 H d (fine structure) at 6.75). Anal. Calcd for $C_{18}H_{17}IS_2O_3$: C, 45.77; H, 3.63; I. 26.87. Found: C, 45.52; H, 3.69; I, 26.93.

Phenyl(5-ethyl-2-thienyl)iodonium tosylate: precipitated from reaction solution, after volume reduction to 20 mL, with Et_2O; white crystals; mp 114–117 °C dec; ^1H NMR (CD_3OD) δ 1.23 (t, 3 H, Me of Et group), 2.32 (s, 3 H), 2.89 (q, 2 H), 6.65–8.3 (m, 11 H, includes 2 H "d of m" at δ 8.07). Anal. Calcd for $C_{19}H_{19}IS_2O_3$: C, 46.92; H, 3.94; I, 26.09. Found: C, 46.93; H, 3.99, I, 26.09.

Phenyl(5-bromo-2-thienyl)iodonium tosylate: isolated after evaporation of the reaction solvent, trituration of the dark crystalline "residue" with Et_2O, and reprecipitation of the crude solid from MeOH with Et_2O; light brown crystals, mp 157–160 °C dec; ^1H NMR (CD_3OD) δ 2.33 (s, 3 H), 6.95–8.25 (m, 11 H, includes 2 H "d of m" at 8.14). Anal. Calcd for $C_{17}H_{14}IBrS_2O_3$: C, 38.00; H, 2.63; I, 23.62. Found: C, 38.08; H, 2.61; I, 23.90.

Phenyl(5-(hydroxymethyl)-2-thienyl)iodonium tosylate: product crystallized directly from the reaction solvent; white crystals; mp 133–136 °C dec; ^1H NMR (Me_2SO-d_6) δ 2.27 (s, 3 H), 4.70 (s, 3 H), 6.75–8.4 (m, 11 H). Anal. Calcd for $C_{18}H_{17}IS_2O_4$: C, 44.26; H, 3.52; I. 25.98. Found: C, 43.86; H, 3.94; I. 25.94.

Phenyl(5-formyl-2-thienyl)iodonium tosylate: precipitated from reaction solution (cooled at −10 °C) with Et_2O; mp 132–135 °C dec; ^1H NMR (CD_3OD) δ 2.33 (s, 3 H), 5.63 (s, 1 H), 6.9–8.35 (m, 11 H, includes 2 H "d of m" at δ 8.12). Anal. Calcd for $C_{18}H_{15}IS_2O_4$: C, 44.44; H, 3.11; I. 26.09. Found: C, 44.05; H, 3.28; I, 25.86.

o-Tolyl(5-methyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 132–133 °C dec; ^1H NMR (CD_3OD) δ 2.32 (s, 3 H), 2.51 (s, 3 H), 2.66 (s, 3 H), 6.65–8.35 (m, 10 H, includes 1 H d at δ 8.20 and 1 H d (with fine structure) at δ 6.74). Anal. Calcd for $C_{19}H_{19}IS_2O_3$: C, 46.92; H, 3.94; I, 26.09. Found: C, 46.96; H, 3.99; I, 26.25.

o-Tolyl(5-ethyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 130–132 °C dec; ^1H NMR (CD_3OD) δ 1.22 (t, 3 H), 2.32 (s, 3 H), 2.67 and 2.84 (s and q, multiplets overlap, 4.6 H), 6.65–8.35 (m, 10.4 H, includes 1 H d at 8.21 and 1 H d at 6.78). Anal. Calcd for $C_{20}H_{21}IS_2O_3$: 48.00; H, 4.24; I, 25.36. Found: C, 47.88; H, 4.28; I, 25.36.

o-Tolyl(3-methyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 138–141 °C dec; ^1H NMR (CD_3OD) δ 2.31 (s, 3 H), 2.48 (s, 3 H), 2.64 (s, 3 H), ~6.35–8.35 (m, 10 H, includes 1 H d at δ 8.15). Anal. Calcd for $C_{19}H_{19}IS_2O_3$: C, 46.92; H. 3.94; I. 26.09. Found: C, 46.90; H, 3.94; I, 26.18.

m-Tolyl(2-thienyl)iodonium tosylate: precipitated from reaction solution with Et_2O, after volume reduction to 5 mL, white crystals; mp 151–154 °C dec; ^1H NMR (CD_3OD) δ 2.33 (s, 6 H),

6.85–8.05 (m, 11 H). Anal. Calcd for $C_{18}H_{17}IS_2O_3$: C, 45.76; H, 3.63; I, 26.86. Found: C, 45.93; H, 3.79; I, 27.08.

p-Tolyl(2-thienyl)iodonium tosylate: isolated by evaporation of the reaction solvent and trituration of the residual brown crystals with Et_2O; white crystals; mp 110–113 °C dec; ^1H NMR (CD_3OD) δ 2.33 (s, 5.5 H), 6.85–8.35 (m, 11.5 H), peaks of minor impurities apparent. Anal. Calcd for $C_{18}H_{17}IS_2O_3$: C, 45.76; H, 3.63; I, 26.86. Found: C, 45.94; H, 3.68; I, 26.60.

(o-Fluorophenyl)(2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 137–139 °C dec; ^1H NMR (CD_3OD) δ 2.34 (s, 3 H), 6.9–8.5 (m, 11 H, includes 1 H br "t" at δ 8.30). Anal. Calcd for $C_{17}H_{14}IFS_2O_3$: C, 42.86; H, 2.97; I, 26.64. Found: C, 42.68; H, 3.07; I, 26.44.

(o-Fluorophenyl)(5-methyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 135–137 °C dec; ^1H NMR (CD_3OD) δ 2.30 (s, 3 H), 2.51 (s, 3 H), 6.6–8.4 (m, 10 H, includes 1 H br "t" at δ 8.18 and 1 H d at 6.72). Anal. Calcd for $C_{18}H_{16}IFS_2O_3$: C, 44.08; H, 3.29; I, 25.88. Found: C, 44.10; H, 3.29; I, 25.83.

(p-Chlorophenyl)(2-thienyl)iodonium tosylate: product crystallized from reaction solvent, white crystals; mp 146–147 °C dec; ^1H NMR (Me_2SO-d_6) δ 2.29 (s, 3 H), 6.9–8.5 (m, 11 H); peaks of minor impurities apparent. Anal. Calcd for $C_{17}H_{14}IClS_2O_3$: C, 41.43; H, 2.87; I. 25.75. Found: C, 41.60; H, 2.99; I. 25.59.

(p-Chlorophenyl)(5-methyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 131–134 °C dec; ^1H NMR (CD_3OD) δ 2.28 (s, 3 H), 2.50 (s, 3 H), 6.57–8.20 (m, 10 H). Anal. Calcd for $C_{18}H_{16}IClS_2O_3$: C, 42.66; H, 3.19; I, 25.04. Found: C, 42.77; H, 3.24; I, 25.14.

(p-Chlorophenyl)(5-ethyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp (after reprecipitation from MeOH with Et_2O) 124–131 °C dec; ^1H NMR (Me_2SO-d_6) δ 1.21 (t, 3 H), 2.30 (s, 3 H), 2.92 (q, 2 H), 6.75–8.45 (m, 10 H, includes 1 H d at δ 7.93); weak s of an impurity at δ 3.36. Anal. Calcd for $C_{19}H_{18}IClS_2O_3$: C, 43.81; H, 3.49; I, 24.36. Found: C, 43.89; H, 3.65; I, 24.57.

(p-Chlorophenyl)(3-methyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 139–142 °C dec; ^1H NMR (CD_3OD) δ 2.33 (s, 3 H), 2.50 (s, 3 H), 6.85–8.2 (m, 10 H). Anal. Calcd for $C_{18}H_{16}IClS_2O_3$: C, 42.66; H, 3.19; I, 25.04. Found: C, 42.43; H, 3.32; I, 24.86.

(p-Bromophenyl)(5-methyl-2-thienyl)iodonium tosylate: precipitated from reaction solvent with Et_2O, white crystals; mp 133–135 °C dec; ^1H NMR (Me_2SO-d_6) δ 2.29 (s, 3 H), 2.53 (s, 3 H), 6.7–8.35 (m, 10 H, includes 1 H d (hint of fine structure) at δ 6.87. Anal. Calcd for $C_{18}H_{16}IBrS_2O_3$: C, 39.21; H, 2.93; I, 23.02. Found: C, 39.53; H, 3.04; I, 23.35.

(p-Iodophenyl)(5-methyl-2-thienyl)iodonium tosylate: product precipitated from reaction solution with Et_2O after unreacted p-$IC_6H_4I(OH)OTs$ removed (0.39 g) and after volume reduction to 5 mL, yellow crystals; mp 125–128 °C dec; ^1H NMR (CD_3OD) δ 2.35 (s, 3 H), 2.57 (s, 3 H), 6.65–8.0 (m, 10 H, includes intense s at δ 7.79 and 1 H d (with fine structure) at δ 6.81). Anal. Calcd for $C_{18}H_{16}I_2S_2O_3$: C, 36.13; H, 2.70; I, 42.42. Found: C, 36.30; H, 2.96; I, 42.09.

Registry No. 1 (R = H), 27126-76-7; 1 (R = 2-Me), 73177-97-6; 1 (R = 3-Me), 84383-97-1; 1 (R = 4-Me), 73177-96-5; 1 (R = 2-F), 84383-95-9; 1 (R = 4-Cl), 73178-07-1; 1 (R = 4-Br), 73178-08-2; 1 (R = 4-I), 73178-09-3; 2 (R′ = H), 110-02-1; 2 (R′ = 2-Me), 554-14-3; 2 (R′ = 2-Et), 872-55-9; 2 (R′ = 3-Me), 616-44-4; 2 (R′ = 2-Br), 1003-09-4; 2 (R′ = 2-CH_2OH), 636-72-6; 2 (R′ = 2-CHO), 98-03-3; 3 (R = H, R′ = 3′-Me), 91228-41-0; 3 (R = 2-Me, R′ = H), 91228-43-2; 3 (R = H, R′ = H), 91228-44-3; 3 (R = H, R′ = 5′-Me), 91228-46-5; 3 (R = H, R′ = 5′-Et), 91228-48-7; 3 (R = H, R′ = 5′-Br), 91228-50-1; 3 (R = H, R′ = 5′-CH_2OH), 91228-52-3; 3 (R = H, R′ = 5′-CHO), 91228-54-5; 3 (R = 2-Me, R′ = 5′-Me), 91228-56-7; 3 (R = 2-Me, R′ = 5′-Et), 91228-58-9; 3 (R = 2-Me, R′ = 3′-Me), 91228-60-3; 3 (R = 3-Me, R′ = H), 91228-61-4; 3 (R = 4-Me, R′ = H), 91228-62-5; 3 (R = 2-F, R′ = H), 91228-64-7; 3 (R = 2-F, R′ = 5′-Me), 91228-66-9; 3 (R = 4-Cl, R′ = H), 58506-46-0; 3 (R = 4-Cl, R′ = 5′-Me), 91228-68-1; 3 (R = 4-Cl, R′ = 5′-Et), 91228-70-5; 3 (R = 4-Cl, R′ = 3′-Me), 91228-72-7; 3 (R = 4-Br, R′ = 5′-Me), 91228-74-9; 3 (R = 4-I, R′ = 5′-Me), 91228-76-1; 4 (R = H, R′ = 3′-Me), 91228-77-2; 4 (R = 2-Me, R′ = 3′-Me), 91228-78-3; 4 (R = H, R′ = 5′-Me), 91228-79-4; 4 (R = H, R′ = 5′-Br), 91228-80-7; 4 (R = 3-Me, R′ = H), 38070-40-5; 4 (R = 2-Me, R′ = 5′-Me), 91228-81-8; 4 (R = 2-Me, R′ = H), 91228-82-9; ArI (R = H), 591-50-4; ArI (R = 2-Me), 615-37-2; ArI (R = 3-Me), 625-95-6; ThI (R′ = 3-Me), 16494-40-9; ThI (R′ = 5-Me), 16494-36-3; ThI (R′ = 5-Br), 29504-81-2; ThI (R′ = H), 3437-95-4.

Asymmetric Reduction of Representative Ketones with *tert*-Butoxyisopinocampheylborane, a New Chiral Reducing Agent

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Monoisopinocampheylborane ($IpcBH_2$), a less hindered, optically active borane reagent, is highly effective for the asymmetric hydroboration of hindered olefins.[1,2]

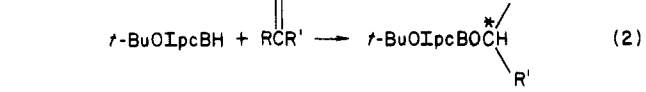
However, in the reduction of prochiral ketones, it achieves only moderate asymmetric induction.[3] As part of a recent investigation of the reaction of representative monoalkylboranes with alcohols,[4] we observed that $IpcBH_2$ reacts at 0 °C with only 1 mol of *tert*-butyl alcohol (eq 1).

$$IpcBH_2 + t\text{-BuOH} \rightarrow \underset{\mathbf{1}}{t\text{-BuOIpcBH}} \qquad (1)$$

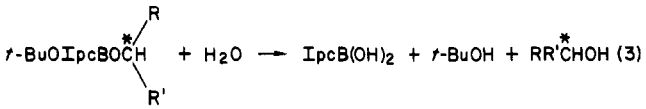
There is no significant reaction with a second mole of *tert*-butyl alcohol at 0 °C. (2,6-Dimethylphenol also reacts with $IpcBH_2$ similarly at 25 °C.)

The IR spectrum of $IpcBH_2$ in THF exhibits a strong absorption at 1549 cm^{-1}, characteristic of typical boron–hydrogen bridges. However, this bridge absorption disappears completely in 1. Consequently, the product must be the monomeric species. Many years ago, Burg established that dimethoxyborane, $(CH_3O)_2BH$ is monomeric.[5] Apparently, the present derivative also shows the same decreased tendency to dimerize.

The ready synthesis of this new derivative 1 encouraged us to explore its utility for the asymmetric reduction of representative ketones.[6] Accordingly, several such ketones were treated with the reagent in THF at 0 °C. The reductions proceeded readily (eq 2). Hydrolysis produced



(2)



(3)

the desired alcohol (eq 3). Distillation provided the product. It was purified by GC and the rotation measured. The results are summarized in Table I.

(1) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1977**, *99*, 5514.
(2) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *J. Org. Chem.* **1982**, *47*, 5074.
(3) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *Tetrahedron* **1981**, *37*, 3547.
(4) Research in progress with Kim, G. P.; Kim, K. W.
(5) Burg, A. B.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1933**, *55*, 4020.
(6) Hydroboration with 1 proceeds relatively slowly with 1-octene requiring 3 h for completion at 0 °C. The reaction with more hindered olefins, such as 2-methyl-2-butene, is much slower. Consequently, asymmetric reduction of ketones in the presence of many types of double bonds is practical. The utility of chiral hydroboration of representative alkenes by this new reagent is under exploration.

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