Iodination of Alkyl Aryl Ethers by Mercury(II) Oxide–Iodine Reagent in Dichloromethane

Kazuhiko Orito,* Takahiro Hatakeyama, Mitsuhiro Takeo, Hiroshi Suginome
Organic Synthesis Divison, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan
Fax +81(11)7066598
Received 13 March 1995

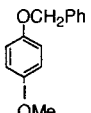
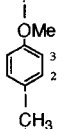
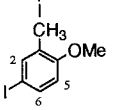
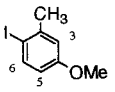
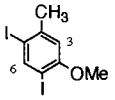
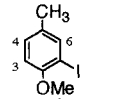
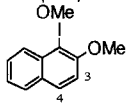
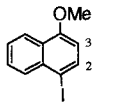
A convenient method for selective mono- and diiodination of alkyl aryl ethers by mercury(II) oxide–iodine reagent in dichloromethane is reported.

In connection with our study on lignan synthesis, based on the β-scission of alkoxyl radicals which are generated by photolysis of the hypoiodites prepared by treating the corresponding alcohols with mercury(II) oxide–iodine reagent,[1] it became necessary to investigate the reactivities of the reagent toward aromatic compounds. According to a survey of the literature, in 1908 Kauffmann and Fritz reported iodination of hydroquinone dimethyl ether by mercury(II) oxide–iodine reagent.[2] Similar aromatic iodinations have since been carried out by Kauffmann[3] and others[4–12] using EtOH or benzene as solvent. However, the relative reactivities of alkyl aryl ethers to the reagent are still unclear. This prompted us to examine the reactions of alkoxy-substituted benzenes and naphthalenes with the reagent, and we now wish to report a convenient method for the selective iodination of alkyl aryl ethers using mercury(II) oxide–iodine reagent in dichloromethane.

The preliminary experiments revealed that the present method induced a highly selective aromatic iodination in an electrophilic manner. For instance, when 1,3,5-trimethoxybenzene, the most reactive alkyl aryl ether used in the present study, was treated with mercury(II) oxide and iodine (each one mol equiv) in dichloromethane (0.25 M), iodine was consumed at room temperature within 6 min to produce a monoiodo derivative quantitatively. 1,3-Dimethoxybenzene required 20 min to produce 1-iodo-2,4-dimethoxybenzene. Anisole provided 4-iodoanisole after 7 h. Increasing the ratio of the reagents to 3:3, diiodination of 1,3,5-trimethoxybenzene was completed after 15 min. 1,3-Dimethoxybenzene required 30 min to be iodinated completely into 1,5-diiodo-2,4-dimethoxybenzene. In contrast, anisole gave no diiodide.

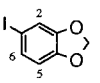
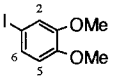
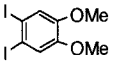
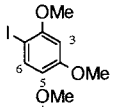
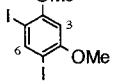
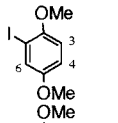
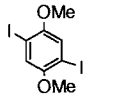
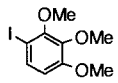
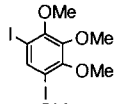
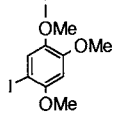
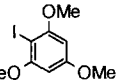
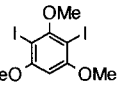
On the basis of the above results, a variety of alkyl aryl ethers were further examined for the selective iodination using mainly 1:1, 3:3 and 5:5 molar ratios of mercury(II) oxide and iodine. The results are shown in Tables 1–3. Alkylbenzenes, such as toluene, xylene and tetralin, were recovered unchanged. Iodination of benzyl phenyl

Table 1. Iodination of Monoalkoxybenzenes and -naphthalenes with HgO–I_2 in CH_2Cl_2

Entry	Substrate	HgO–I_2O (mol ratio)/ Reaction Time (h)	Product	Yield (%) Crude/Purified	mp (solvent) or bp/pressure (Torr) (Lit. mp or bp) (°C)
1	$PhOCH_2Ph$	1:1/12		94/87	60–61 (MeOH) (61–62[28])
2	PhOMe	1:1/7		92/84	51–52 (aq MeOH) (52,[29] 53–55[28])
3	*o*-MeC_6H_4OMe	1:1/2.5		100/92	75–76 (MeOH) (75–76,[30] 77–78,[28] 79–80[36])
4	*m*-MeC_6H_4OMe	1:1/0.5		94/76	44 (MeOH) (42–44,[28] 43–45[31])
5	*m*-MeC_6H_4OMe	7:7/20		97/80	100–102 (CH_2Cl_2–MeOH) (102–103[31])
6	*p*-MeC_6H_4OMe	1:1/10		99/77	57–58/0.2 (30.5–31,[28] 30–31[32])
7	2-$MeOC_{10}H_7$	1:1/40 min		100/87	89 (pet. ether)[a] (88,[29] 88–89[23])
8	1-$MeOC_{10}H_7$	1:1/1		100/72	52–54 (MeOH) (52–55,[33] 54–56[34])

[a] Petroleum ether bp 30–60 °C.

Table 2. Iodination of Di- and Trialkoxybenzenes with $HgO-I_2$ in CH_2Cl_2

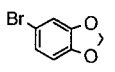
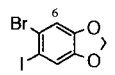
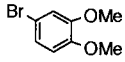
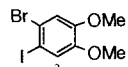
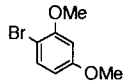
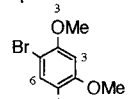
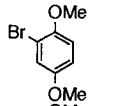
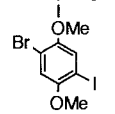
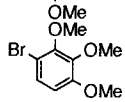
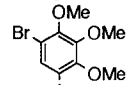
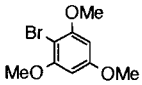
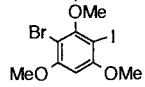
Entry	Substrate	$HgO-I_2O$ (mol ratio)/ Reaction Time (h)	Product	Yield (%) Crude/Purified	mp (solvent) or bp/pressure (Torr) (Lit. mp or bp) (°C)
9	1,2-methylenedioxybenzene	1 : 1/9		79/50	78.5–79/0.7 (98/1,[10] 116–125/10[35])
10	1,2-methylenedioxybenzene	5 : 5/23		75/52	93–95 (MeOH–Et_2O) (82–83[35])
11	1,2-dimethoxybenzene	1 : 1/3		98/86	68–74/0.2 (33–34[28])[a]
12	1,2-dimethoxybenzene	5 : 5/16		91/81	133–134 (MeOH) (132,[36] 134,[29] 132–133.5[28])
13	1,3-dimethoxybenzene	1 : 1/20 min		99/84	77/0.2 (40,[3] 40–41,[7] 163/14[3])
14	1,3-dimethoxybenzene	3 : 3/0.5		88/86	199–200 (CH_2Cl_2–MeOH) (198–199[28,29], 200–202[37])
15	1,4-dimethoxybenzene	1 : 1/7		88/72	70–75/0.2 (118–120/3–4,[9] 157/10[2])
16	1,4-dimethoxybenzene	5 : 5/36		85/72	170–170.5 (CH_2Cl_2–Et_2O) (167–168,[38] 171,[2,29,36] 171–172[28])
17	1,2,3-trimethoxybenzene	1 : 1/35 min		98/82	90/0.4 (41–42,[4] 40–42[5])[a]
18	1,2,3-trimethoxybenzene	5 : 5/10		86/76	54 (MeOH)
19	1,2,4-trimethoxybenzene	1 : 1/7		99/72	67.5–68.5 (CH_2Cl_2–MeOH) (70–71,[6,39] 70,[37] 70–72[35])
20	1,3,5-trimethoxybenzene	1 : 1/0.1		99/87	122–123 (CH_2Cl_2–MeOH) (119–121,[40] 122–123[11])
21	1,3,5-trimethoxybenzene	3 : 3/0.25		99/92	134–135 (CH_2Cl_2–MeOH) (133.5[28])

[a] Lit. value given as mp.

ether thus took place regioselectively only at the 4 position of its phenoxy group (entry 1). Kihara and colleagues reported that iodination of *N*-acetyl-3,4-dimethoxy-β-phenethylamine at its 5 position was achieved by using DMSO as solvent, but not in EtOH.[12] We found that this iodination proceeded smoothly by our method in spite of a heterogeneous state using CH_2Cl_2 as solvent. Monoalkoxy-substituted benzenes selectively afforded the monoiodides in good yields (entry 1–8). *m*-Methoxytoluene could be converted into the diiodide in good yield by treatment with HgO and I_2 (each 7 equiv) for 20 h (entry 5 in Table 1). Most of the di- and trimethoxybenzenes afforded the diiodides in excellent yields (Table 2). Selective diiodination of 1,2,4-trimethoxybenzene failed.

Iodination of methylenedioxybenzene proceeded slower than that of 1,2-dimethoxybenzene to give the corresponding mono- and diiodides (entry 9, 10, 22). This can be accounted for by a lower electron-releasing effect of the methylenedioxy group, compared with that of the 1,2-dimethoxy group.[13] No triiodide was formed in any cases, even at the boiling temperature of CH_2Cl_2. Iodinations of alkoxy-substituted bromobenzenes (entry 22–27) proceeded slower than those of the corresponding iodobenzenes, but gave the monoiodides in good yields (Table 3).

Table 3. Iodination of Di- and Trialkoxylbromobenzenes with $HgO–I_2$ in CH_2Cl_2

Entry	Substrate	$HgO–I_2O$ (mol ratio)/ Reaction Time (h)	Product	Yield (%) Crude/Purified	mp (solvent) or bp/pressure (Torr) (Lit. mp or bp) (°C)
22		2 : 2/29		52/45	70–71 (pet. ether)[a]
23		2 : 2/24		100/64	90–92 (pet. ether)[a]
24		2 : 2/15		100/94	169–171 (CH_2Cl_2–MeOH)
25		6 : 6/72		91/72	142–143 (MeOH)
26		4 : 4/72		96/87	92–97/0.2
27		2 : 2/8		94/89	116–117 (CH_2Cl_2–MeOH)

[a] Petroleum ether bp 30–60 °C.

When 1,3,5-trimethoxybenzene was treated with mercury(II) oxide (0.25 mol equiv) and iodine (0.5 mol equiv), the color of iodine disappeared after 10 min and 0.5 mol of the monoiodide was obtained. This result suggests that the iodination proceeds via a similar pathway to the reaction of alcohols with $HgO–I_2$ to generate hypoiodites.[14–16] The reaction between one mole of mercury(II) oxide and two moles of iodine generates iodine oxide, which act as an electrophile to iodinate two moles of the substrates, probably through hypoiodous acid, as shown in Figure 1. Most other current methods,[17] as well as the recently reported systems (I_2–HgO–HBF_4–SiO_2,[18] I_2–$AgNO_2$,[19] I_2–Ag_2SO_4,[20,21] BTMA–ICl_2,[22] PSVP–ICl_2,[23] ICl–Pyridine[24])[25] for the direct iodination of aromatic compunds require acidic or basic reagents or solvents, and liberate acidic substances such as HI, HCl, H_2SO_4, HNO_3, HIO_3, $HClO_4$, AcOH, CF_3CO_2H. The present iodination provides neutral conditions, and the reagent is so mild that alkylbenzenes are not iodinated, as described above. Carbonyl compounds, such as acetophenone, α-tetralone and cyclohexanone, were also unaffected under these conditions, although the $HgCl_2$–I_2 system is known to give α-iodocarbonyl compounds.[26]

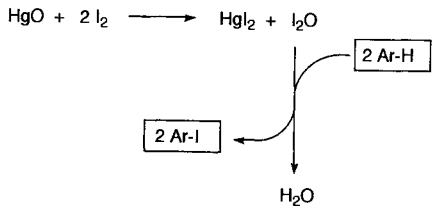


Figure 1

Thus, mercury(II) oxide–iodine in CH_2Cl_2 offers a practical system for the selective iodination of alkyl aryl ethers.[27]

Mps were measured with a Yanagimoto micro melting point apparatus, and are uncorrected. Bps are uncorrected. IR spectra were taken on a JASCO IR-810 infrared spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-JX270 FT high resolution spectrometer. NMR samples were prepared using $CDCl_3$ (99.8 atom % D, containing 0.03 % v/v TMS, Aldrich). Mass spectra were taken on a JEOL JMS-DX300 spectrometer at 70 eV. Mercury(II) oxide (red) was purchased from Kanto Chem. Co. The substrates used in this study are commercially available except 1-bromo-2,3,4-trimethoxybenzene[41] and 2-bromo-1,3,5-trimethoxybenzene.[42]

Iodination of Alkyl Aryl Ethers; General Procedure:

A suspension of the appropriate alkyl aryl ether (5 mmol), HgO (red, 5 mmol) and iodine (5 mmol) in CH_2Cl_2 (20 mL) was stirred at r.t. for the time noted in Tables, monitoring the reaction by TLC (silica gel; benzene), and the precipitates were removed by suction filtration. The filtrate was washed with 5% aq $Na_2S_2O_3$ (20 mL) and water (30 mL), dried ($MgSO_4$), and evaporated to dryness. The residue was crystallized from the appropriate solvent, or distilled under reduced pressure. The ^1H NMR spectra data of the products from entries 1–17, 19–21 are listed below.

4-Benzyloxy-1-iodobenzene (Entry 1):

^1H NMR: δ = 5.03 (s, 2H, CH_2), 6.75 (AB type, J = 9.0 Hz, 2H, 3- and 5-H), 7.37 (br s, 5H, PhH), 7.55 (AB type, J = 9.0 Hz, 2H, 2- and 6-H).

1-Iodo-4-methoxybenzene (Entry 2):

^1H NMR: δ = 3.77 (s, 3H, OCH_3), 6.67, 7.55 (AB type, J = 8.8 Hz, 2H, 3,5- and 2,6-H).

1-Iodo-4-methoxy-3-methylbenzene (Entry 3):

^1H NMR: δ = 2.16 (s, 2H, CH_3), 3.79 (s, 3H, OCH_3), 6.58 (d, J = 8.6 Hz, 1H, 5-H), 7.42 (d, J = 2.0 Hz, 1H, 2-H), 7.44 (dd, J = 8.6, 2.0 Hz, 1H, 6-H).

1-Iodo-4-methoxy-2-methylbenzene (Entry 4):

^{1}H NMR: δ = 2.39 (s, 2H, CH_3), 3.77 (s, 3H, OCH_3), 6.47 (dd, J = 8.6, 2.9 Hz, 1H, 5-H), 6.81 (1H, d, J = 2.9 Hz, 3-H), 7.65 (1H, d, J = 8.6 Hz, 6-H).

1,5-Diiodo-2-methoxy-4-methylbenzene (Entry 5):

^{1}H NMR: δ = 2.40 (s, 2H, CH_3), 3.84 (s, 3H, OCH_3), 6.71 (s, 1H, 6-H), 8.10 (s, 1H, 3-H).

1-Iodo-2-methoxy-5-methylbenzene (Entry 6):

^{1}H NMR: δ = 2.26 (s, 2H, CH_3), 3.85 (s, 3H, OCH_3), 6.72 (d, J = 8.3 Hz, 1H, 3-H), 7.09 (dd, J = 8.3, 2.0 Hz, 4-H), 7.60 (1H, d, J = 2.0 Hz, 6-H).

1-Iodo-2-methoxynaphthalene (Entry 7):

^{1}H NMR: δ = 4.03 (s, 3H, OCH_3), 7.22 (d, J = 8.9 Hz, 1H, 3-H), 7.38 (ddd, J = 7.9, 6.9, 1.3 Hz, 1H, 6-H), 7.54 (ddd, J = 8.6, 6.9, 1.3 Hz, 1H, 7-H), 7.74 (br d, J = 7.9 Hz, 1H, 5-H), 5.83 (br d, J = 8.9 Hz, 1H, 4-H), 8.14 (br d, J = 8.6 Hz, 1H, 8-H).

1-Iodo-4-methoxynaphthalene (Entry 8):

^{1}H NMR: δ = 3.99 (s, 3H, OCH_3), 6.59 (d, J = 7.9 Hz, 1H, 3-H), 7.50 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H, 6-H), 7.58 (ddd, J = 7.9, 6.9, 1.3 Hz, 1H, 7-H), 7.95 (d, J = 7.9 Hz, 1H, 2-H), 8.02 (dd, J = 8.3, 1.3 Hz, 1H, 5-H), 8.23 (dd, J = 7.9, 1.3 Hz, 1H, 8-H).

1-Iodo-3,4-methylenedioxybenzene (Entry 9):

^{1}H NMR: δ = 5.94 (s, 2H, OCH_2O), 6.58 (d, J = 8.6 Hz, 1H, 5-H), 7.11 (d, J = 1.5 Hz, 1H, 2-H), 7.15 (dd, J = 8.3, 1.5 Hz, 1H, 6-H).

1,2-Diiodo-4,5-methylenedioxybenzene (Entry 10):

^{1}H NMR: δ = 5.97 (s, 2H, OCH_2O), 7.30 (s, 2H, 3- and 6-H).

1-Iodo-3,4-dimethoxybenzene (Entry 11):

^{1}H NMR: δ = 3.85 (s, 6H, $2OCH_3$), 6.61 (d, J = 8.5 Hz, 1H, 5-H), 7.14 (d, J = 2.0 Hz, 1H, 2-H), 7.19 (dd, J = 8.5, 2.0 Hz, 1H, 6-H).

1,2-Diiodo-4,5-dimethoxybenzene (Entry 12):

^{1}H NMR: δ = 3.82 (s, 6H, OCH_3), 7.35 (s, 2H, 3- and 6-H).

1-Iodo-2,4-dimethoxybenzene (Entry 13):

^{1}H NMR: δ = 3.79, 3.85 (each s, 3H, $2OCH_3$), 6.37 (dd, J = 8.6, 2.6 Hz, 1H, 5-H), 6.43 (d, J = 2.6 Hz, 1H, 3-H), 7.64 (1H, d, J = 8.6 Hz, 6-H).

1,5-Diiodo-2,4-dimethoxybenzene (Entry 14):

^{1}H NMR: δ = 3.88 (6H, s, OCH_3), 6.37, 8.03 (each s, each 1H, 3- and 6-H).

2-Iodo-1,4-dimethoxybenzene (Entry 15):

^{1}H NMR: δ = 3.75, 3.82 (each s, each 3H, $2OCH_3$), 6.75 (d, J = 9.2 Hz, 1H, 3-H), 6.86 (d, J = 9.2, 2.6 Hz, 1H, 4-H), 7.34 (d, J = 2.6 Hz, 1H, 6-H).

1,4-Diiodo-2,5-dimethoxybenzene (Entry 16):

^{1}H NMR: δ = 3.82 (s, 6H, OCH_3), 7.19 (s, 2H, 3- and 6-H).

1-Iodo-2,3,4-trimethoxybenzene (Entry 17):

^{1}H NMR: δ = 3.84, 3.87, 3.88 (each s, each 3H, $3OCH_3$), 6.49, 7.41 (AB type, J = 9.2 Hz, each 1H, 5- and 6-H).

1,5-Diodo-2,3,4-trimethoxybenzene (Entry 18):

^{1}H NMR: δ = 3.87, 3.88, 3.89 (each s, 3H, $3OCH_3$), 7.89 (s, 1H, 6-H).

EI MS: m/z = 420 (M^+, 100), 405 [$(M - CH_3)^+$, 23.6].

Anal. Calc. for $C_9H_{10}I_2O_3$: C, 25.34; H, 2.40; I, 60.43. Found: C, 25.61; H, 2.41; I, 60.33.

1-Iodo-2,4,5-trimethoxybenzene (Entry 19):

^{1}H NMR: δ = 3.83, 3.87, 3.89 (each s, each 3H, $3OCH_3$), 6.57 (s, 1H, 3-H), 7.04 (s, 1H, 6-H).

2-Iodo-1,3,5-trimethoxybenzene (Entry 20):

^{1}H NMR: δ = 3.82 (s, 3H, OCH_3), 3.86 (s, 3H, $2OCH_3$), 6.17 (s, 2H, 3- and 5-H).

1,3-Diiodo-2,4,6-trimethoxybenzene (Entry 21):

^{1}H NMR: δ = 3.90 (s, 9H, $3OCH_3$), 6.25 (s, 1H, 5-H).

1-Bromo-2-iodo-4,5-methylenedioxybenzene (Entry 22):

^{1}H NMR: δ = 5.99 (s, 2H, OCH_2O), 7.10 (each s, 1H, 6- and 3-H).

EI MS: m/z = 327 (M^+, 99.1), 326 (M^+, 100), 201 [$(M - I)^+$, 13.8], 199 [$(M - I)^+$, 13.7].

Anal. calc. for $C_7H_4BrIO_2$: C, 25.72; H, 1.23; Br + I, 63.26. Found: C, 25.44; H, 1.21; Br + I, 63.16.

1-Bromo-2-iodo-4,5-dimethoxybenzene (Entry 23):

^{1}H NMR: δ = 3.84 (s, 6H, $2OCH_3$), 7.08, 7.23 (each s, each 1H, 6- and 3-H).

EI MS: m/z = 344 (M^+, 96.7), 342 (M^+, 100), 329 [$(M - CH_3)^+$, 29.0], 327 [$(M - I)^+$, 60.6].

Anal. calc. for $C_8H_8BrIO_2$: C, 28.02; H, 2.35; Br + I, 60.30. Found: C, 28.10; H, 2.40; Br + I, 60.07.

1-Bromo-5-iodo-2,4-dimethoxybenzene (Entry 24):

^{1}H NMR: δ = 3.88, 3.90 (each s, each 3H, $2OCH_3$), 6.43, 7.84 (each s, each 1H, 3- and 6-H).

EI MS: m/z = 343 (M^+, 99.2), 341 (M^+, 100), 328 [$(M - OCH_3)^+$, 12.6], 326 [$(M - OCH_3)^+$, 13.2].

Anal. calc. for $C_8H_8BrIO_2$: C, 28.02; H, 2.35; Br + I, 60.30. Found: C, 27.90; , 2.33; Br + I, 60.05.

1-Bromo-4-iodo-2,5-dimethoxybenzene (Entry 25):

^{1}H NMR: δ = 3.83, 3.84 (each s, each 3H, $2OCH_3$), 7.14, 7.29 (each s, each 1H, 6- and 3-H).

EI MS: m/z = 344 (M^+, 97.9), 342 (M^+, 100), 329 [$(M - CH_3)^+$, 58.6], 327 [$(M - I)^+$, 27.7].

Anal. calc. for $C_8H_8BrIO_2$: C, 28.02; H, 2.35; Br + I, 60.30. Found: C, 28.09; H, 2.38; I, 60.19.

1-Bromo-5-iodo-2,3,4-trimethoxybenzene (Entry 26):

^{1}H NMR: δ = 3.89 (s, 3H, OCH_3), 3.90 (s, 6H, $2OCH_3$), 7.68 (s, 1H, 6-H).

EI MS: m/z = 373 [$(M - H)^+$, 99.0], 371 [$(M - H)^+$, 100], 358 $(M - CH_4)^+$, 29.7], 356 [$(M - CH_4)^+$, 30.4].

Anal. calc. for $C_9H_{10}BrIO_3$: C, 28.98; H, 2.70; Br + I, 55.45. Found: C, 29.04; H, 2.85; Br + I, 55.48.

2-Bromo-4-iodo-1,3,5-trimethoxybenzene (Entry 27):

^{1}H NMR: δ = 3.86, 3.90, 3.91 (each s, each 3H, $3OCH_3$), 6.31 (s, 1H, 5-H).

EI MS: m/z = 374 (M^+, 96.1), 372 (M^+, 100).

Anal. calc. for $C_9H_{10}BrIO_3$: C, 28.98; H, 2.70; Br + I, 55.45. Found: C, 29.19; H, 2.76; Br + I, 55.65.

N-Acetyl-2-iodo-4,5-dimethoxy-β-phenethylamine:

This iodide was obtained by treatment of *N*-acetyl-3,4-dimethoxy-β-phenethylamine with HgO–I_2 (3:3) for 4 h, in the same manner as noted above, in 88% yield, mp 109–110 °C (benzene) (Lit.[12] mp 110–111 °C).

(1) Orito, K.; Yorita, K.; Suginome, H. *Tetrahedron Lett.* **1991**, *32*, 5999.
(2) Kauffmann, H.; Fritz, I. *Ber.* **1908**, *41*, 4413.
(3) Kauffmann, H.; Kieser, F. *Ber.* **1912**, *39*, 2333.
(4) Baker, W.; Kirby, A.W.W.; Montgomery, L.V. *J. Chem. Soc.* **1932**, 2876.
(5) Erdtman, H.G.H. *Proc. Soc. London* **1934**, *A143*, 191.
(6) Hughes, G.K.; Neil, K.G.; Ritchie, E. *Aust. J. Sci. Res.* **1950**, *3A*, 497.
(7) Stjernström, N.S. *Acta Chem. Scand.* **1960**, *14*, 1274.
(8) Kallianpur, C.S.; Merchant, J.R. *Indian Chem. Soc.* **1961**, 27.
(9) Brockmann, H., Vorbrüggen, H. *Chem. Ber.* **1962**, *95*, 810.
(10) El'tsov, A.V. *Zh. Obshch. Khim.* **1964**, *34*, 2739; *Chem. Abstr.* **1964**, *61*, 14666a.

(11) Bacon, R.G.R.; Wright, J.R. *J. Chem. Soc. (C)* **1969**, 1978.
(12) Kihara, M.; Kobayashi, S. *Chem. Pharm. Bull.* **1978**, *26*, 155.
(13) Isono, N.; Mori, M. *J. Org. Chem.* **1995**, *60*, 115.
(14) Akhtar, M.A.; March, S. *J. Chem. Soc. (C)* **1966**, 937.
(15) Forbes, C.P.; Googen, A.; Lane, H.A.H. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2346.
(16) Cambie, R.C.; Hayward, R.C.; Lindsay, B.G.; Phan, A.T.; Rutledge, P.S.; Woodgate, P.D. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1961.
(17) Merkushev, E.B. *Synthesis* **1988**, 923.
(18) Barluenga, J.; Campos, P.J.; Gonzáles, J.M.; Asensio, G. *J. Chem. Soc. Perkin Trans. 1* **1984**, 2623.
(19) Sy, W.-W.; Lodge, B.A. *Tetrahedron Lett.* **1989**, *30*, 3769.
(20) Sy, W.-W.; Lodge, B.A.; By, A.W. *Synth. Commun.* **1990**, *20*, 877.
(21) Sy, W.-W. *Synth. Commun.* **1992**, *22*, 3215.
(22) Kajigaeshi, S.; Kakinami, T.; Yamasaki, H.; Fujisaki, S.; Okamoto, T. *Chem. Lett.* **1987**, 2109.
Idem *Chem. Lett.* **1988**, 795.
Idem *Bull. Chem. Soc. Jpn*, **1988**, *61*, 600.
(23) Sket, B.; Zupet, P.; Zupan, M. *J. Chem. Soc. Perkin Trans. 1* **1989**, 2279.
(24) Muathen, H.A. *J. Chem. Research (S)* **1994**, 405; *J. Chem. Research (M)*, **1994**, 2201.
(25) Similar iodinations occurred also with Pb $OAc)_4$–I_2 and Ag_2O–I_2. A detailed study on these reagents is under way.
(26) Barluenga, J.; Martinez-Gallo, J.M.; Najera, C.; Yus, M. *Synthesis* **1986**, 678.
(27) We have also found that this reagent is a good system for the similar iodination of aniline derivatives and the selective oxidation of sulfides to sulfoxides, and these studies are under way.
(28) Kajigaeshi, S. Kakinami, T.; Moriwaki, M.; Watanabe, M.; Fujisaki, S.; Okamoto, T. *Chem. Lett.* **1988**, 795.
(29) Jones, B.J.; Richardson, E. *J. Chem. Soc.* **1953**, 713.
(30) Suter, C.M.; Schuetz, R.D. *J. Org. Chem.* **1951**, *16*, 117.
(31) Sletzingger, M.; Dawson, C.R. *J. Org. Chem.* **1949**, *14*, 670.
(32) Beaven, G.H.; Hall, D.M.; Lesslie, M.S.; Turner, E.E.; Bird, G.R. *J. Chem. Soc.* **1954**, 131.
(33) Stubbs, H.W.; Tucker, S.H. *J. Chem. Soc.* **1954**, 227.
(34) Edwards, J.D.; Cashaw, J.L. *J. Am. Chem. Soc.* **1954**, *76*, 6141.
(35) Dallacker, F.; Adolphen, G. *Liebigs Ann. Chem.* **1966**, *691*, 134.
(36) Robinson, G.M. *J. Chem. Soc.* **1916**. *109*, 1078.
(37) Meerwein, H.; Hofmann, P.; Schill, F. *J. Prakt. Chem.* **1940**, *154*, 266.
(38) Sargent, T.III.; Shulgin, A.T.; Mathis, C.A. *J. Med. Chem.* **1984**, *27*, 1071.
(39) Blatchly, J.M.; McOmie, J.F.; Searle, J.B. *J. Chem. Soc. (C)* **1969**, 1350.
(40) Riedl, W. *Liebigs Ann. Chem.* **1955**, *597*, 148.
(41) Friedman, D.; Ginsburg, D. *J. Org. Chem.* **1958**, *23*, 16.
(42) Mayer, W.; Fikentscher, R.; Schmidt, J.; Schmidt, O.T. *Chem. Ber.* **1960**, *93*, 2761.