Supporting Information

Isolation, Characterization, and Reaction of Activated Iodosylbenzene Monomer Hydroxy(phenyl)iodonium Ion with Hypervalent Bonding: Supramolecular Complex $PhI^{+}OH$·18-Crown-6 with Secondary I···O Interactions

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Preparation of $PhI(OH)BF_4$·18-Crown-6 Complex. To a stirred suspension of iodosylbenzene (165 mg, 0.75 mmol) and 18-crown-6 (199 mg, 0.75 mmol) in dichloromethane (4.2 mL) was added dropwise tetrafluoroboric acid-dimethyl ether complex (111 mg, 0.83 mmol) at -78 °C under nitrogen and the mixture was warmed to 0 °C over 3.5 h. After filtration, dichloromethane was evaporated under an aspirator vacuum at 0 °C to give an oil, which was washed several times with hexane and then with diethyl ether by decantation at -60 to -40 °C to give a pure $PhI(OH)BF_4$·18-crown-6 complex (435 mg, 100%) as a yellow powder. Recrystallization of the complex (200 mg) from acetone-hexane at -30 °C gave bright yellow prisms (35 mg): some decomposition of the complex was observed during the recrystallization at -30 °C. Mp 88-93 °C (decomposition); IR (Nujol) 3533, 2471, 1567, 1353, 1300, 1245, 1150-1000, 955, 836, 750, 611 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 8.26 (d, J = 8.1 Hz, 2H), 8.01 (br s, 1H), 7.81 (t, J = 7.3 Hz, 1H), 7.67 (dd, J = 8.1, 7.3 Hz, 2H), 3.64 (s, 24H); ^{13}C NMR (75 MHz, CD_3CN) δ 136.4, 134.5, 132.4, 123.1, 70.7. Anal. Calcd for $C_{18}H_{30}BF_4IO_7$: C, 37.85; H, 5.12. Found: C, 37.52; H, 5.11.

Oxidation of 1-Naphthol. To a stirred solution of $PhI(OH)BF_4$·18-crown-6 (67 mg, 0.12 mmol) in water (4 mL) was added 1-naphthol (8.1 mg, 0.056 mmol) at 0 °C under nitrogen and the mixture was gradually warmed to room temperature over 3 h. The mixture was diluted with water and extracted with dichloromethane. The extract was dried over Na_2SO_4 and concentrated under aspirator vacuum to give an oil, which was purified by preparative TLC (SiO_2, hexane-ethyl acetate 7:3) to give naphthoquinone (**3**) (6 mg, 67%):[1] ^1H NMR (400 MHz, $CDCl_3$) δ8.10 (dd, J = 5.9, 3.3 Hz, 2H), 7.77 (dd, J = 5.9, 3.3 Hz, 2H), 6.99 (s, 2H).

Oxidation of 2,4,6-Trimethylphenol. To a stirred solution of $PhI(OH)BF_4$·18-crown-6 (51 mg, 0.089 mmol) in water (3 mL) was added 2,4,6-trimethylphenol (10 mg, 0.074 mmol) at 0 °C under nitrogen and the mixture was gradually warmed to room temperature over 3 h. The mixture was diluted with water and extracted with dichloromethane. The extract was dried over Na_2SO_4 and concentrated under aspirator vacuum to give an oil, which was purified by preparative TLC (SiO_2, hexane-ethyl acetate 7:3) to give 4-hydroxy-2,4,6-trimethylcyclohexa-2,5-dienone (**4**) (10.4 mg, 92%):[2] ^1H NMR (400 MHz, $CDCl_3$) δ6.62 (s, 2H), 1.88 (s, 6H), 1.85 (s, 1H). 1.45 (s, 3H).

Oxidation of Thioanisole. To a stirred solution of $PhI(OH)BF_4$·18-crown-6 (48 mg, 0.084 mmol) in water (3 mL) was added thioanisole (8.5 mg, 0.068 mmol) at room temperature under nitrogen and the mixture was stirred for 3 h.. After addition of NaCl, the mixture was extracted with dichloromethane. The extract was dried over Na_2SO_4 and concentrated under aspirator vacuum to give an oil, which was purified by preparative TLC (SiO_2, ethyl acetate) to give methyl phenyl sulfoxide (**5**) (9.4 mg, 98%) as

a colorless oil:[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ7.66 (br d, *J* = 7.2 Hz, 2H), 7.57-7.48 (m, 3H), 2.74 (s, 3H).

Oxidation of Chalcone. To a stirred solution of PhI(OH)BF_4·18-crown-6 (31 mg, 0.054 mmol) in MeOH (1.5 mL) was added chalcone (10 mg, 0.049 mmol) at room temperature under nitrogen and the mixture was stirred for 18 h. The mixture was diluted with water and extracted with dichloromethane. The extract was dried over Na_2SO_4 and concentrated under aspirator vacuum to give an oil, which was purified by preparative TLC (SiO_2, hexane-ethyl acetate 7:3) to give 3,3-dimethoxy-1,2-diphenylpropan-1-one (**6**) (9.5 mg, 72%):[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ7.98 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.3 Hz 1H), 7.46-7.38 (m, 4H), 7.31 (dd, *J* = 7.7, 7.3 Hz, 2H), 7.28-7.21 (1H), 5.14 (d, *J* = 8.8 Hz, 1H), 4.92 (d, *J* = 8.8 Hz, 1H), 3.45 (s, 3H), 3.22 (s, 3H).

Oxidation of Styrene. To a stirred solution of PhI(OH)BF_4·18-crown-6 (33 mg, 0.058 mmol) in MeOH (1 mL) was added styrene (5.4 mg, 0.052 mmol) at 0°C under nitrogen, and the mixture was stirred for 1.5 h at the temperature and then for 11 h at room temperature. The mixture was quenched with a saturated aqueous $NaHCO_3$ solution at 0°C and extracted with dichloromethane. The extract was dried over Na_2SO_4 and concentrated under aspirator vacuum to give an oil, which was purified by preparative TLC (SiO_2, hexane-ethyl acetate 8:2) to give (2,2-dimethoxyethyl)benzene (**7**) (6.4 mg, 73%) as a colorless oil:[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ7.33-7.19 (m, 5H), 4.56 (t, *J* = 5.5 Hz 1H), 3.34 (s, 6H), 2.92 (d, *J* = 5.5 Hz, 2H).

Oxidation of Indene. (a) Synthesis of *trans*-1,2-Diacetoxyindan (*trans*-8). To a stirred solution of PhI(OH)BF_4·18-crown-6 (47 mg, 0.082 mmol) in acetic acid (1.5 mL) was added acetic anhydride (35 mg, 0.34 mmol) at room temperature under nitrogen and the mixture was stirred for 2 h. To this mixture was added indene (8.0 mg, 0.068 mmol) at 16 °C and the mixture was stirred for 1 h at the temperature. After addition of water and extraction with dichloromethane, the extract was dried over Na_2SO_4 and concentrated under aspirator vacuum to give an oil, which was purified by preparative TLC (SiO_2, hexane-ethyl acetate 7:3) to give *trans*-**8** (14.4 mg, 89%):[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.22 (4H), 6.25 (d, *J* = 3.7 Hz 1H), 5.45 (ddd, *J* = 7.1, 4.5, 3.7 Hz, 1H), 3.54 (dd, *J* = 16.4, 7.1 Hz, 1H), 2.90 (dd, *J* = 16.4, 4.5 Hz, 1H), 2.12 (s, 3H), 2.08 (s, 3H). The *trans*-**8** was contaminated with a small amount of *cis* isomer (10%).

(b) Synthesis of *cis*-1,2-Diacetoxyindan (*cis*-8). To a stirred suspension of PhI(OH)BF_4·18-crown-6 (48 mg, 0.084 mmol) in dichloromethane (1 mL) and acetic acid (1 mL) was added a solution of indene (8.0 mg, 0.068 mmol) in dichloromethane (1.5 mL) at -20 °C under nitrogen and the mixture was stirred for 1.5 h at the temperature. The mixture was diluted with water and extracted with dichloromethane. The extract was dried over Na_2SO_4 and concentrated under aspirator vacuum to give an oil, which was purified by preparative TLC (SiO_2, hexane-ethyl acetate 7:3) to give a 1:1 mixture of regioisomeric *cis*-indan-1,2-diol monoacetates (9.8 mg, 74%).[6] The monoacetates (3.6 mg, 0.019 mmol) were dissolved in acetic anhydride (0.8 mL) and pyridine (0.5 mL) at room temperature and the mixture was stirred for 2 days. Concentration under aspirator vacuum gave pure *cis*-**8** (4.1 mg, 92%):[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ7.43-7.21 (4H), 6.22 (d, *J* = 5.5 Hz 1H), 5.54 (dt, *J* = 6.5, 5.5 Hz, 1H), 3.25 (dd, *J* = 15.9, 6.5 Hz, 1H), 3.13 (dd, *J* = 15.9, 5.5 Hz, 1H), 2.09 (s, 3H), 2.07 (s, 3H).

Oxidation of Silyl Enol Ether (11). (a) In Acetonitrile-Water. To a stirred solution of PhI(OH)BF_4·18-crown-6 (25 mg, 0.043 mmol) in acetonitrile (0.5 mL) and water (0.5 mL) was added a solution of 1-phenyl-1-(trimethylsilyloxy)ethylene (**11**) (7.5 mg, 0.039 mmol) in acetonitrile (1 mL) at 0 °C under nitrogen and the mixture was stirred for 1 h. The mixture was diluted with water and extracted with dichloromethane. The extract was dried over Na_2SO_4 and concentrated under aspirator vacuum to give an oil, which was purified by preparative TLC (SiO_2, hexane-ethyl acetate 7:3) to give the α-hydroxy ketone **9** (3.9 mg, 73%):[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ7.93 (d, *J* = 8.1 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.52 (dd, *J* = 8.1, 7.3 Hz, 2H), 4.90 (d, *J* = 4.0 Hz, 2H), 3.51 (t, *J* = 4.0 Hz, 1H).

(a) Under Solvent-Free Conditions. To the finely powdered PhI(OH)BF_4·18-crown-6 (34 mg, 0.06 mmol) was added silyl enol ether **11** (35 mg, 0.18 mmol) at -78 °C under argon and the mixture was gradually warmed to room temperature over 3.5 h. After addition of water, the mixture was extracted

with dichloromethane. The extract was dried over Na_2SO_4 and concentrated under aspirator vacuum to give an oil, which was purified by preparative TLC (SiO_2, hexane-ethyl acetate 7:3) to give the 1,4-diphenylbutane-1,4-dione (10.3 mg, 74%) and the α-hydroxy ketone **9** (1.2 mg, 15%).[8] 1,4-Diphenylbutane-1,4-dione: ^{1}H NMR (400 MHz, $CDCl_3$) δ8.05 (br d, *J* = 7.7 Hz, 4H), 7.59 (br t, *J* = 7.2 Hz, 2H), 7.49 (dd, *J* = 7.7, 7.2 Hz, 4H), 3.48 (s, 4H).

Synthesis of Alkynyl-λ^3-iodane·18-crown-6 Complex (10). To a stirred solution of PhI(OH)BF_4·18-crown-6 (52 mg, 0.091 mmol) and HgO (0.7 mg, 0.003 mmol) in dichloromethane (1.5 mL) was added 1-decyne (10 mg, 0.072 mmol) at room temperature under nitrogen and the mixture was stirred for 3 h. The mixture was quenched with a saturated aqueous $NaBF_4$ solution and extracted with dichloromethane. The extract was filtrated and concentrated under aspirator vacuum to give an oil, which was washed several times with hexane and then with diethyl ether by decantation at -78 °C to give 1:1.5 1-decynyl(phenyl)tetrafluoroborato-λ^3-iodane·18-crown-6 complex (32.9 mg, 56%). Recrystallization from dichloromethane-diethyl ether-hexane gave the 1:1 complex **10** as colorless needles: mp 91-92 °C; IR (KBr) 3083, 2921, 2181, 1562, 1468, 1354, 1250, 1150-1000, 957, 838, 747, 680 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.70 (t, *J* = 7.3 Hz, 1H), 7.58 (dd, *J* = 8.4, 7.3 Hz, 2H), 3.66 (s, 24H), 2.64 (t, *J* = 7.3 Hz, 2H), 1.62-1.54 (quint, *J* = 7.3 Hz, 2H), 1.39-1.21 (m, 10H), 0.88 (t, *J* = 7.3 Hz, 3H). Anal. Calcd for $C_{28}H_{46}BF_4IO_6$: C, 48.57; H, 6.70. Found: C, 48.17; H, 6.56.

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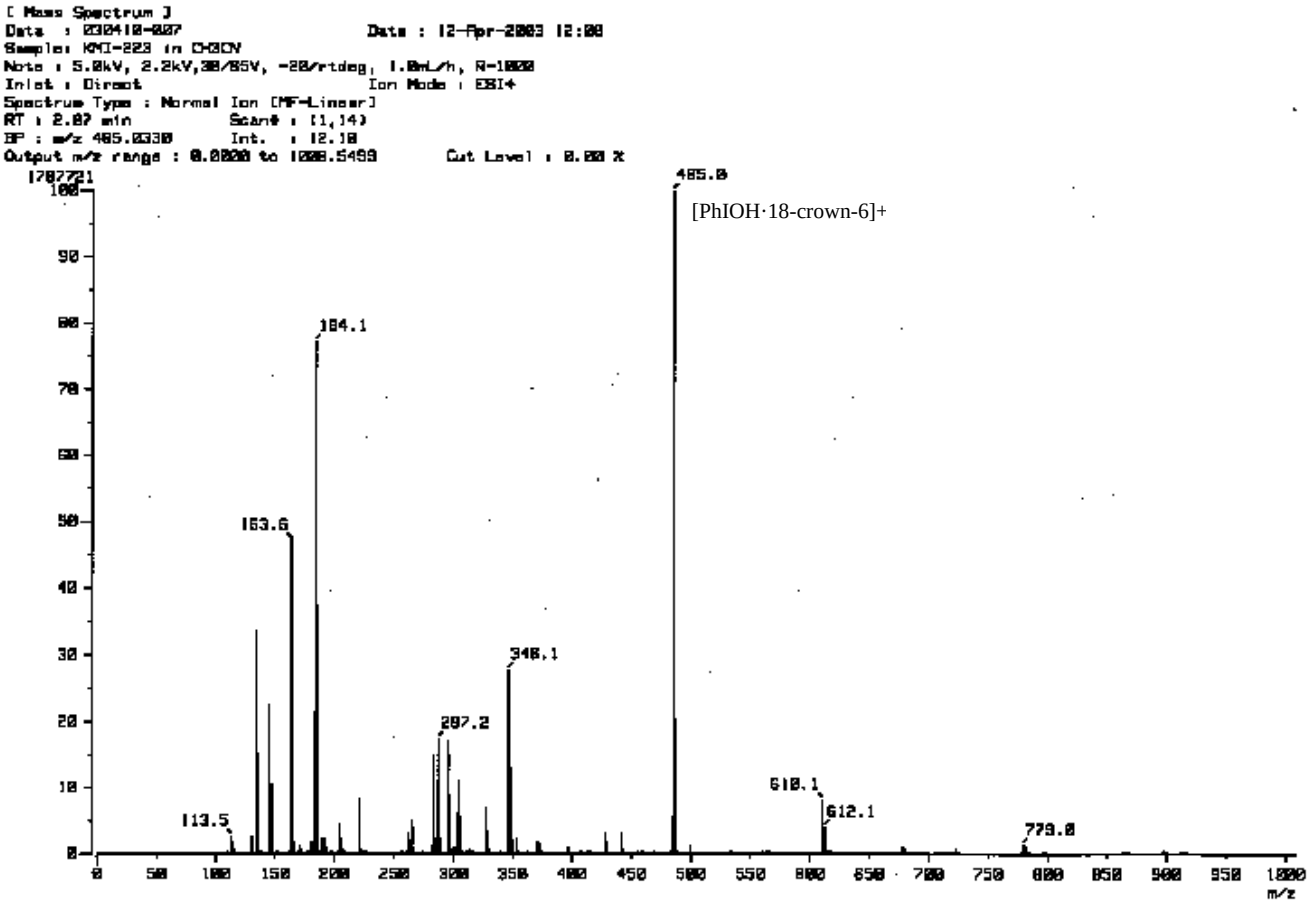
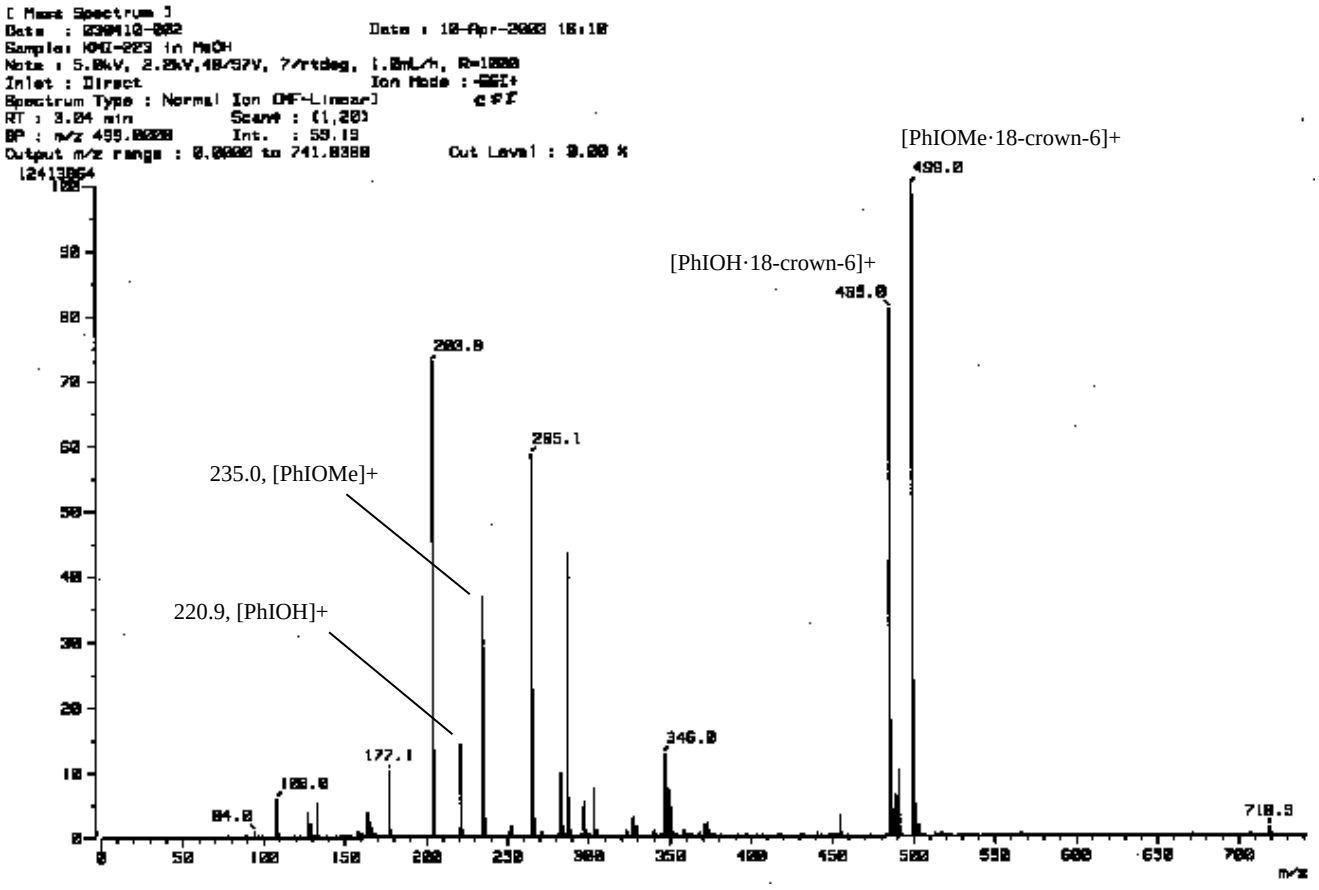


CSI mass spectrum of $PhI(OH)BF_4$·18-crown-6 complex in MeCN



CSI mass spectrum of PhI(OH)BF_4·18-crown-6 complex in MeOH