

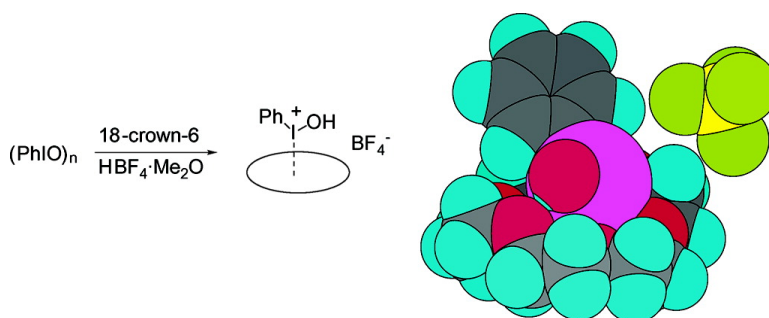
Communication

Isolation, Characterization, and Reaction of Activated Iodosylbenzene Monomer Hydroxy(phenyl)iodonium Ion with Hypervalent Bonding: Supramolecular Complex PhIOH·18-Crown-6 with Secondary I...O Interactions

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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

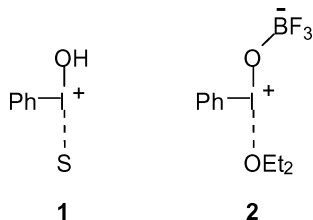
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Iodosylbenzene (ISB), a versatile oxygen-atom transfer agent in organic and biomimetic syntheses,¹ is a polymer bridged by secondary I···O hypervalent interactions² and hence is essentially insoluble in all nonreactive organic solvents.³ In most of the oxidations with ISB, addition of Brønsted or Lewis acids is required to increase the activity through its depolymerization or their coordination to its oxygen atom.¹ For instance, HBF₄- or TfOH-catalyzed reactions using ISB are believed to involve as a reactive species the generation of the protonated hydroxy(phenyl)iodonium ion PhI⁺OH that undergoes a variety of oxidative transformations under mild conditions,^{4,5} while intermediacy of the zwitterionic species **2** is proposed for the BF₃-Et₂O-catalyzed oxidations.⁶ Extensive spectroscopic studies by Richter, Koser, and co-workers suggested that in an acidic aqueous solution ISB mostly exists as hydroxy(phenyl)iodonium ion **1** (S = H₂O), ligated with at least one water molecule at an apical site of the iodine(III) atom.^{7,8}

Detailed structures of these reactive species in the solid state as well as in solution, however, are virtually unknown, because their isolation appears to be very difficult because of the lack of thermal stability. In fact, the electrophilic hydroxy-λ³-iodane **1** (S = BF₄⁻), generated from ISB by the reaction with HBF₄-Me₂O at -50 to 0 °C in dichloromethane, decomposes at room temperature within a few minutes to give a black tar.⁵ Herein, we report the isolation and characterization of the protonated ISB monomer **1** [S = 18-crown-6 (18C6)], stabilized by the coordination of 18C6 through secondary I···O bonding.⁹ The crystalline crown ether complex is stable at ambient temperature, but reactive enough to effect oxidations of a variety of functional groups under mild conditions.



When the reaction of ISB with HBF₄-Me₂O was carried out in the presence of equimolar 18C6 in dichloromethane at -78 to 0 °C, the complex **1**·BF₄⁻ (S = 18C6) was obtained quantitatively as a yellow powder after repeated decantation with hexane and diethyl ether at -60 to -40 °C. The complex is soluble in MeCN, MeOH, water, DMSO, and dichloromethane, but not in less polar solvents (chloroform, benzene, diethyl ether, and ethyl acetate).

Most importantly, the complexation with 18C6 dramatically increased the stability of **1**: thus, no decomposition of **1**·BF₄⁻ (S = 18C6) was detected when it was left standing under ambient conditions over 10 days. In solution, however, it gradually decomposes at room temperature with half-life times (*t*_{1/2}) of 6 h in CD₂Cl₂ and 25 h in CD₃CN. It should be noted that the complex is more stable in water (*t*_{1/2} = 5 days).

The ¹H NMR spectrum of the complex in CD₃CN showed simply a sharp methylene singlet (δ 3.64 ppm) and a set of signals assigned to the monosubstituted phenyl group [δ 8.26 (*o*), 7.81 (*p*), and 7.67 (*m*) ppm]. A broad exchangeable singlet with D₂O at δ 8.01 ppm indicates the presence of a hydroxy group, which was further supported by the characteristic IR absorptions at 3533 and 2471 cm⁻¹.¹⁰ The observed downfield shift (0.13 ppm) of a methylene singlet in **1**·BF₄⁻ (S = 18C6) as compared to that of 18C6 suggests the complex formation between **1** (S = BF₄⁻) and 18C6 in solution. The ¹³C resonance of 18C6 at δ 71.2 ppm is shifted to higher field (δ 70.7 ppm) in the complex.

Firm evidence for the association in solution is obtained by mass spectroscopy.⁹ Cold-spray ionization (CSI) MS for **1**·BF₄⁻ (S = 18C6) taken in positive mode in MeCN at -20 °C revealed the most prominent peak of the molecular ion [PhIOH·18C6]⁺ at *m/z* 485. Interestingly, in MeOH, a base peak corresponding to [PhIOMe·18C6]⁺ at *m/z* 499 was observed in addition to the remarkable molecular ion peak, indicating the intervention of a facile ligand exchange of the hydroxy group on the iodine(III) by the solvent MeOH.¹¹

Single crystals for X-ray analysis were obtained by recrystallization from acetone-hexane at -30 °C.¹² Figure 1 reveals a protonated iodosylbenzene structure with a single I(1)-O(1) bond, which is slightly shorter than that predicted (1.99 Å) for covalent radii but comparable to the reported values for [hydroxy(tosyloxy)-iodo]benzene¹³ and cyclic hydroxy-λ³-iodanes.^{3b} Including a close contact between I(1) and a crown ether oxygen O(2) through secondary bonding, the geometry around the iodine in **1**·BF₄⁻ (S = 18C6) is T-shaped with a near-linear O(1)-I(1)···O(2) triad (171.7°). The close contact, in addition to the other weak I(1)···O(3) and I(1)···O(4) bonding, will be responsible for increasing the stability of the complex.

Strong intramolecular hydrogen bonding H(10)···O(5) (1.92 Å) of the hydroxy ligand on the iodine(III) will also lead to the enhanced thermal stability. The presumed highly acidic nature of H(10) will be responsible for the pronounced hydrogen bonding.¹⁴

The versatility of the supramolecular complex as an oxidizing agent is noteworthy, and the reactions shown in Scheme 1 illustrate the broad range of the utility. All of the reactions proceed smoothly without further activation of the complex by adding an external

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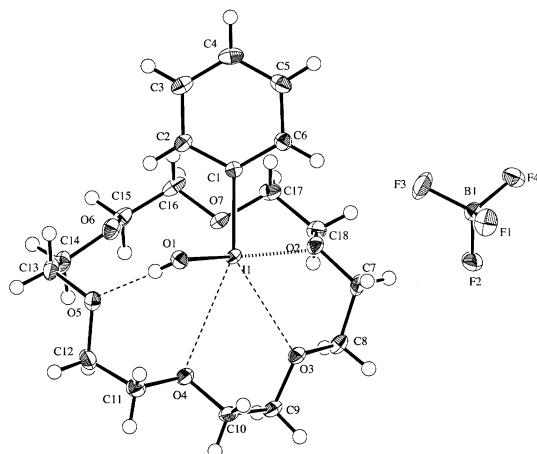
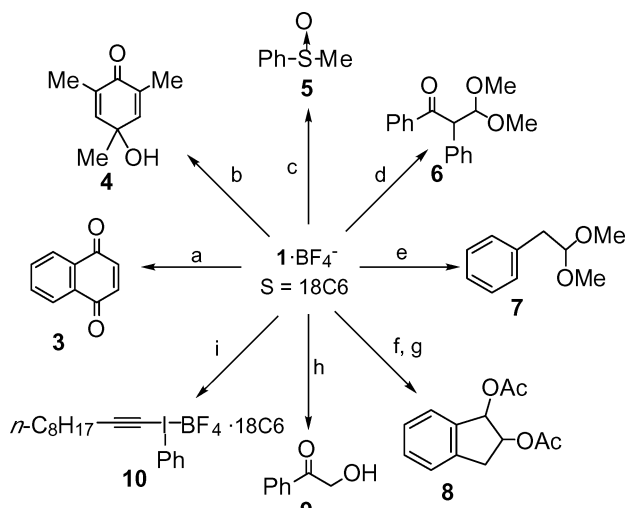


Figure 1. ORTEP drawing of the complex $1 \cdot \text{BF}_4^-$ ($S = 18\text{C}6$). Selected bond lengths (Å) and angles (deg): I(1)–C(1) 2.103(3), I(1)–O(1) 1.937(2), O(1)–H(1O) 0.71(4), I(1)⋯O(2) 2.598(2), I(1)⋯O(3) 2.910(2), I(1)⋯O(4) 3.137(2), O(1)–I(1)–C(1) 91.85(9).

Scheme 1^a



^a Conditions: (a) 1-naphthol, H_2O , 0 °C to room temperature (3 h), 67%; (b) 2,4,6-trimethylphenol, H_2O , 0 °C to room temperature (3 h), 92%; (c) thioanisole, H_2O , room temperature (3 h), 98%; (d) (*E*)-PhC(O)CH=CHPh, MeOH, room temperature (18 h), 72%; (e) styrene, MeOH, 0 °C (1.5 h) then room temperature (11 h), 73%; (f) indene, Ac_2O , AcOH, 16 °C (1 h), 89% (*trans*-**8**); (g) (i) indene, CH_2Cl_2 –AcOH (2.5:1), –20 °C (1.5 h), (ii) Ac_2O , pyridine, room temperature (2 days), 68% (*cis*-**8**); (h) PhC(OTMS)=CH₂ (**11**), MeCN–H₂O (3:1), 0 °C (1 h), 73%; (i) 1-decyne, HgO, CH_2Cl_2 , room temperature (3 h), 56%.

acid catalyst, which indicates that the highly electrophilic nature of Zhdankin's hydroxy- λ^3 -iodane **1** ($S = \text{BF}_4^-$) is maintained in our crown ether complex. It is noted that the complex functions as an efficient oxidizing agent even in water, because of both the moderate solubility and the excellent stability in water. Thus, oxidation of phenols, 1-naphthol and 2,4,6-trimethylphenol, with $1 \cdot \text{BF}_4^-$ ($S = 18\text{C}6$) in water at 0 °C afforded naphthoquinone (**3**) and *p*-quinol **4**, respectively, in good yields.¹ Thioanisole gave a 98% yield of the sulfoxide **5** in water at room temperature with no evidence for formation of methyl phenyl sulfone.

Chalcone and styrene afforded the rearranged acetals **6** and **7** in MeOH, respectively, as reported by Moriarty.⁴ Oxidation of indene in acetic acid in the presence of a small amount of acetic anhydride gave the *trans*-diacetate **8** with 90% stereoselectivity, while the reaction in dichloromethane–acetic acid, followed by acetylation of the resulting vicinal diol monoacetate, produced selectively the *cis*-diacetate **8** in 68% yield.¹⁵ Reaction of the silyl enol ether **11** in MeCN–water afforded the α -hydroxy ketone **9**, while under solvent-free conditions 1,4-diphenylbutane-1,4-dione was produced in 74% yield.¹⁶ Phenyl- λ^3 -iodanation of 1-decyne catalyzed by HgO afforded a 1:1 alkynyl- λ^3 -iodane·18C6 complex **10** directly.¹⁷

In conclusion, we have synthesized the hydroxy- λ^3 -iodane complex, coordinated by a neutral molecule, as stable crystals. The λ^3 -iodane complex serves as a versatile oxidant.

Supporting Information Available: Experimental procedures, compound characterization data for **3**–**10**, CSI-MS (PDF), and X-ray crystallographic data in CIF format for $1 \cdot \text{BF}_4^-$ ($S = 18\text{C}6$). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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