Coordination Chemistry

Synthesis, Characterization, and Reaction of Crown Ether Complexes of Aqua(hydroxy)(aryl)iodonium Ions

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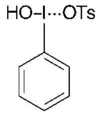
The Koser reagent, [hydroxy(tosyloxy)iodo]benzene (**1**; Ts = *p*-toluenesulfonyl), is a useful oxidizing agent for a range of organic substrates.[1] It has been reported that upon dissolution in water the λ^3-iodane undergoes complete ionization to give the hydroxy(phenyl)iodonium cation (PhI^+OH).[2] The hydroxy(phenyl)iodonium ion does not form an ion pair with a tosylate ion and is presumed to be ligated with at least one water molecule at an apical site of the iodine(III) center. This aqua(hydroxy)(phenyl)iodonium ion **2** ($L = H_2O$) is highly soluble in water with a pK_a value of 4.30 at 20 °C.



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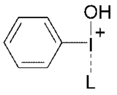

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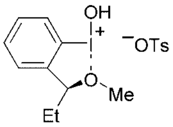

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Iodosylbenzene is a polymer bridged by secondary I···O hypervalent interactions,[3] and hence is essentially insoluble in both nonreactive organic solvents and water at near neutral pH conditions;[4] however, at $pH < 2.3$ iodosylbenzene is highly soluble in water, in which **2** ($L = H_2O$) was also assumed to be a primary monomeric species.[2]

Aqua complexes of λ^3-iodanes with a water molecule coordinated to an iodine(III) center are unique, and there are no well-established precedents. Therefore, direct evidence supporting the proposed structure of **2** ($L = H_2O$) is highly desirable. Recently, Wirth and co-workers synthesized an interesting chiral hydroxyiodonium ion **3**, in which the oxygen atom of the *ortho* methoxymethyl group replaces the tosylate ligand of the Koser reagent with a near-linear O–I···O triad.[5] We have reported the isolation and characterization of the crown ether complex **2**·BF_4^- (L = [18]crown-6) of hydroxy(phenyl)iodonium ion. In this complex, an oxygen atom of the crown ether is tightly bound to the iodine(III) center at the apical site and forms a T-shaped structure with linear O–I···O hypervalent bonding.[6] Herein, we report the first synthesis

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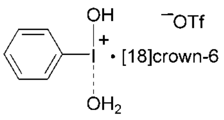
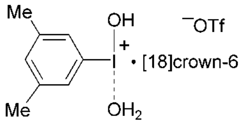
and characterization of the aqua complexes **4** (Tf = trifluoromethanesulfonyl) of (hydroxy)(aryl)iodonium ions, which are stabilized by the coordination of [18]crown-6 through secondary I···O bonding. The crystalline crown ether complex **4a** is stable at ambient temperature and oxidizes a variety of functional groups under mild conditions, especially in water.



4a



4b

The exposure of (diacetoxyiodo)benzene to trimethylsilyl trifluoromethanesulfonate (1.1 equiv) in the presence of [18]crown-6 (1 equiv) in dichloromethane at −50 to 0 °C under nitrogen resulted in ligand exchange at the iodine(III) -center. The aqua crown ether complex **4a** was obtained in 91 % yield as a white powder after repeated decantation with hexane and diethyl ether at −40 °C. Complex **4b** was prepared in a similar way from 3,5-dimethyl(diacetoxyiodo)-benzene[7] in 92 % yield. The aqua complex **4a** is soluble in dichloromethane, chloroform, acetonitrile, acetone, and methanol, but not in the less polar solvents diethyl ether and hexane. Interestingly, complex **4a** is stable in the solid state as well as in solution: No decomposition was detected when it was left standing in air at room temperature for 10 days. As a solution in $CDCl_3$, the half-life ($t_{1/2}$) of **4a** at room temperature was found to be approximately 2 weeks, whereas that of the crown ether complex $\mathbf{2}\cdot BF_4^-$ (L = [18]crown-6) is only 6 hours as a solution in dichloromethane.[6]

In the ^{1}H NMR spectrum of **4a** in CD_3CN, the signals for the aromatic hydrogen atoms are comparable to those reported for hydroxy(phenyl)(triflato)-λ^3-iodane.[8] The observed downfield shift (0.05 ppm) of a methylene singlet for **4a** relative to that for [18]crown-6 suggests the formation of a crown ether complex in solution. The ^{13}C NMR signal for [18]crown-6 ($\delta = 71.2$ ppm in CD_3CN) is shifted to higher field ($\delta = 70.8$ ppm) in the complex.

Recrystallization from acetone/diethyl ether/hexane at −30 °C afforded single crystals of **4a** suitable for X-ray crystallographic analysis.[9] Figure 1 illustrates a T-shaped structure, ligated with one water molecule at the apical site of the iodine(III) center of hydroxy(phenyl)iodonium ion with a near-linear O1-I1-O2 triad (173.96°). Including the close contact between one of the crown ether oxygen atoms, O7, and the iodine center, the complex adopts a distorted square-planar geometry around the iodine atom. A rms deviation of 0.082 Å was observed for I1, O1, O2, O7, and C1 from their least-squares plane, and the sum of the iodine-centered bond angles is Σ°I = 360.1°.

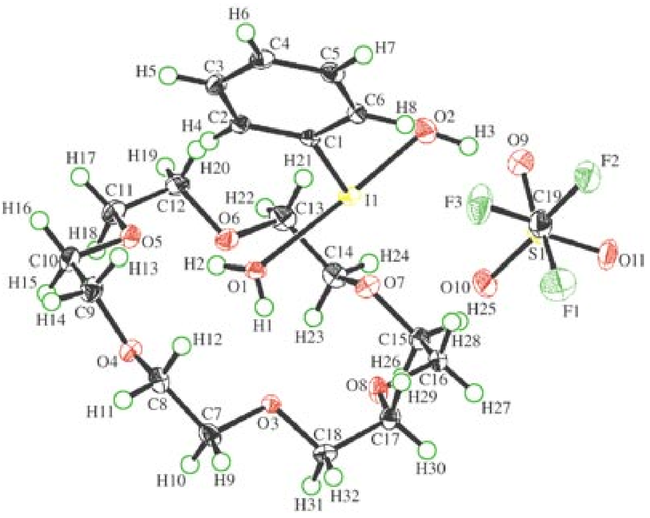
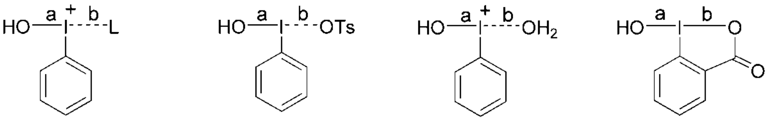


Figure 1. ORTEP drawing of **4a**. Selected bond lengths [Å] and angles [°]: I1–C1 2.117(2), I1–O2 1.967(2), I1–O1 2.392(2), I1···O7 2.942(2), O3···H1 2.04(4), O5···H2 1.91(4), O9···H3 1.9582, C1-I1-O2 92.32(3), C1-I1-O1 81.80(8), O2-I1-O1 173.96(7).

The linear O1-I1-O2 hypervalent bonding[10] is highly unsymmetrical, as observed in polymeric iodosylbenzene (2.04 and 2.38 Å).[3] The hydroxy ligand in **4a** is tightly bound to the iodine(III) center with an O2–I1 distance of 1.967 Å, which is slightly shorter than that predicted for covalent radii (1.99 Å), whereas the water ligand is loosely bound (O1–I1, 2.392 Å). Scheme 1 depicts the varying degrees of the unsymmetrical nature of the hypervalent bonding in the known hydroxy-λ^3-iodanes, in which HO–I bond distances (a) increase in the order shown from left to right. Interestingly, the other I–O distances (b) decrease in this order. It is noteworthy that the hypervalent bonding of a neutral water molecule to the iodine(III) center in **4a** is much stronger than that of the tosylate anion in the Koser reagent (**1**).



2 (L = [18]crown-6) — a: 1.937(2), b: 2.598(2)

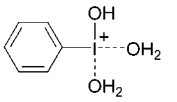
1 — a: 1.940(4), b: 2.473(3)

4a — a: 1.967(2), b: 2.392(2)

5 — a: 2.00, b: 2.30

Scheme 1. Distances of hypervalent O–I–O bonding interactions in hydroxy-λ^3-iodanes.

The ligated water molecule is in firm contact with [18]crown-6 through two hydrogen-bonding interactions, O3···H1 and O5···H2. Furthermore, the highly acidic nature of the hydroxy ligand (pK_a 4.3)[2] results in another hydrogen-bonding interaction with the triflate anion (O9···H3, 1.9582 Å). All of these close contacts are responsible for the enhanced thermal stability of complex **4a**. Based on the structure of **4a**, a monomeric iodosylbenzene species in an aqueous acidic medium is proposed to be a tetracoordinate square-planar iodonium ion **6**, in which two water molecules



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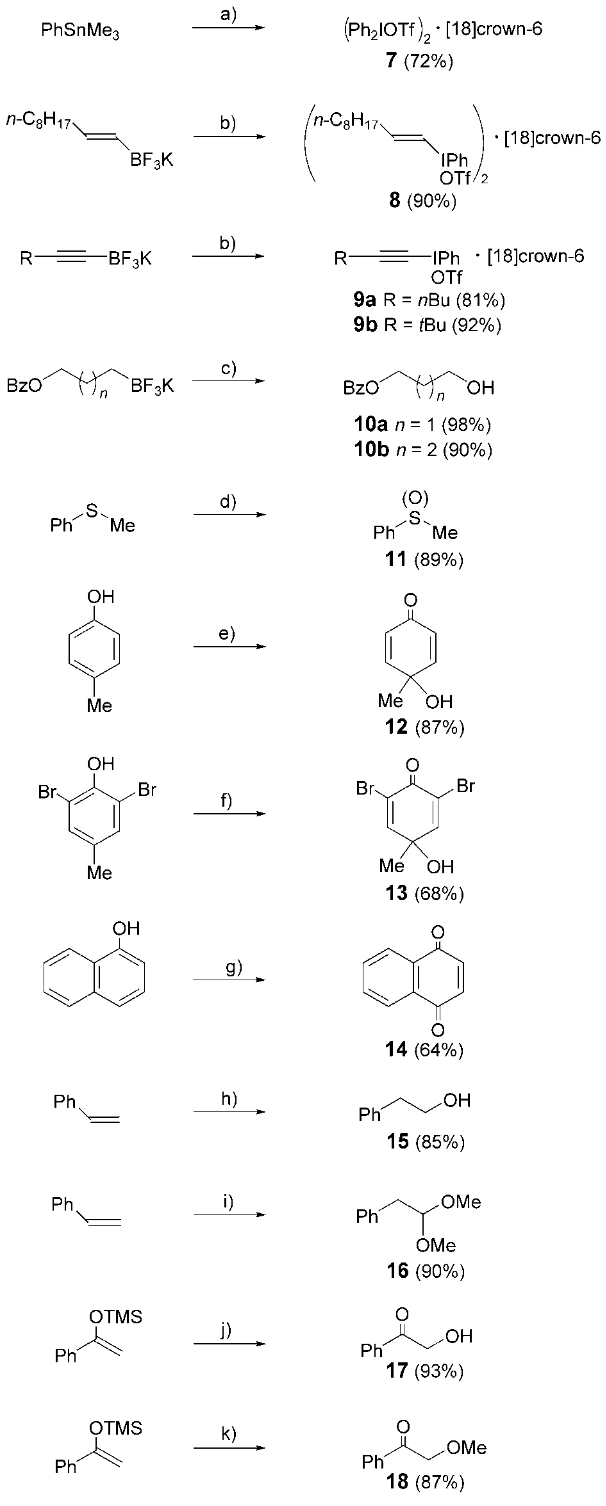
coordinate to the iodine center through hypervalent interactions.

The aqua complexes **4** serve as versatile oxidizing agents, especially in water, which is, of course, a safe, cheap, and environmentally benign solvent. The reactions shown in Scheme 2 illustrate the broad range of their applications. The exposure of phenyltrimethylstannane to **4a** in water at room temperature resulted in facile ligand exchange at the iodine center and afforded the diphenyl-λ^3-iodane·[18]crown-6 complex **7**.[11] Similarly, borate–λ^3-iodane exchange of 1-alkenyl and 1-alkynyl trifluoroborates produced the corresponding 1-alkenyl λ^3-iodane and 1-alkynyl λ^3-iodane complexes with [18]crown-6 (e.g. **8** and **9**) in high yields.[12,13] On the other hand, the reaction with alkyl trifluoroborates resulted in the introduction of a hydroxy group to yield primary alcohols **10**. All of these reactions proceed smoothly without further activation of **4a** by adding an external acid catalyst.

The oxidation of sulfides and *p*-substituted phenols in water produced sulfoxides and *p*-quinols, respectively. The yield of 2,6-dibromo-*p*-quinol **13** increased to 68 % when the aqua complex **4b** was used instead of **4a** (55 %). 1-Naphthol gave naphthoquinone (**14**) in good yield. The oxidation of styrene in water produced phenylacetaldehyde, and after reduction with $NaBH_4$ 2-phenylethanol was obtained in 85 % yield. The use of methanol as a solvent afforded the dimethyl acetal **16**.[14] The α-hydroxy ketone **17** was obtained by the oxidation of a silyl enol ether in the presence of water, whereas in methanol a methoxy group was introduced at the α position to give **18**.

We have presented the synthesis and characterization of a crown ether complex of aqua(hydroxy)(phenyl)iodonium ion, which is assumed to be a primary monomeric iodosylbenzene species in an acidic aqueous medium. The complex is stable in the solid state as well as in solution and serves as a versatile oxidant in water.



Scheme 2. Reaction of the aqua complexes **4** with nucleophiles under nitrogen. a) **4a** (1.5 equiv), H_2O, room temperature, 6 h; b) **4a** (1.5 equiv), H_2O, RT, 3 h; c) **4a** (1.2 equiv), H_2O, room temperature, 3 h; d) **4a** (1 equiv), H_2O, 0 °C, 3 h; e) **4a** (1.2 equiv), H_2O, 0 °C→RT, 3 h; f) **4b** (1.5 equiv), H_2O, room temperature, 6 h; g) **4a** (2.1 equiv), H_2O, 0 °C→RT, 3 h; h) 1. **4a** (1.1 equiv), H_2O, room temperature, 3 h; 2. $NaBH_4$ (2.2 equiv), MeOH, room temperature, 0.5 h; i) **4a** (1.1 equiv), MeOH, room temperature, 26 h; j) **4a** (1.1 equiv), H_2O/MeCN 2:5, 0 °C, 1 h; k) **4a** (1.1 equiv), MeOH, −78 °C→RT, 7 h. Bz = benzoyl, TMS = trimethylsilyl.

Experimental Section

4a: Trimethylsilyl trifluoromethanesulfonate (152 mg, 0.69 mmol) was added dropwise at −50 °C under nitrogen to a solution of (diacetoxyiodo)benzene (200 mg, 0.62 mmol) and [18]crown-6 (164 mg, 0.62 mmol) in CH_2Cl_2 (6.7 mL). The mixture was gradually warmed to 0 °C over 4 h. The solvent was evaporated under an aspirator vacuum at 0 °C to give a yellow oil, which was washed several times with hexane and diethyl ether by decantation at −40 °C to give **4a** (368 mg, 0.56 mmol, 91 %) as a white powder. Recrystallization of **4a** (100 mg) from acetone/diethyl ether/hexane at −30 °C gave colorless prisms (35 mg): m.p. 61–63 °C; ^{1}H NMR (400 MHz, CD_3CN): $\delta = 8.24$ (d, $J = 8.0$ Hz, 2H), 7.78 (t, $J = 7.3$ Hz, 1H), 7.64 (dd, $J = 8.0$, 7.3 Hz, 2H), 3.56 ppm (s, 24H); ^{13}C NMR (75 MHz, CD_3CN): $\delta = 136.3, 134.4, 132.4, 123.3, 70.8$ ppm; IR (nujol): $\tilde{\nu} = 3564$, 3485, 1354, 1285, 1109, 1038, 965, 842, 638 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{32}F_3IO_{11}S$ (652.42): C 34.98, H 4.94; found: C 35.22, H 4.88.

4b: Colorless prisms (recrystallized from acetone/diethyl ether/hexane at −30 °C): m.p. 59–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.75$ (br s, 2H), 7.21 (br s, 1H), 3.69 (s, 24H), 2.36 ppm (s, 6H); ^{13}C NMR (75 MHz, CD_3CN): $\delta = 142.6, 135.9, 133.6, 123.3, 70.8, 21.2$ ppm; IR (nujol): $\tilde{\nu} = 3515$, 1354, 1258, 1107, 1032, 961, 838, 639 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{37}F_3IO_{11.5}S$ (689.50): C 36.58, H 5.41; found: C 36.29, H 5.14.

8: Potassium *trans*-1-decenyl trifluoroborate (9.9 mg, 0.04 mmol) was added at room temperature under nitrogen to a solution of **4a** (39 mg, 0.059 mmol) in H_2O (2.5 mL), and the mixture was stirred for 3 h. The mixture was extracted with CH_2Cl_2 four times. The combined organic phases were filtrated and evaporated under an aspirator vacuum to give an oil, which was washed several times with hexane and then with hexane/diethyl ether by decantation at 0°C to give a 1:1.3 mixture of *trans*-1-decenyl(phenyl)(trifluoromethanesulfonato)-λ^3-iodane and [18]crown-6 (30.6 mg, 0.036 mmol, 90%) as a white powder. Recrystallization from dichloromethane/ethyl acetate/hexane at −30°C gave **8** as colorless needles: m.p. 71.5–72°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.95$ (d, $J = 8.2$ Hz, 4H), 7.70 (t, $J = 7.3$ Hz, 2H), 7.54 (dd, $J = 8.2, 7.3$ Hz, 4H), 6.85–6.72 (m, 4H), 3.69 (s, 24H), 2.34 (q, $J = 7.3$ Hz, 4H), 1.44 (quint, $J = 7.3$ Hz, 4H), 1.32–1.19 (m, 20H) 0.88 ppm (t, $J = 6.8$ Hz, 6H); IR (nujol): $\tilde{\nu} = 3042$, 1563, 1265, 1223, 1152, 1101, 1031, 956, 838, 754, 638 cm^{-1}; elemental analysis calcd (%) for $C_{46}H_{72}F_6I_2O_{12}S_2$ (1249.03): C 44.23, H 5.81; found: C 44.55, H 5.93.

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Keywords: crown compounds · hypervalent compounds · iodine · Koser reagent · oxidation

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[4] We measured the solubility of iodosylbenzene (2.3×10^{-3} M) in water at 25°C by ^{1}H NMR spectroscopy. The ylide-type structure $PhI^+(OH_2)O^-$ was proposed for monomeric iodosylbenzene dissolved in water at near pH 7.[2]

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[9] Crystal data for **4a**: $C_{19}H_{32}F_3IO_{11}S$, colorless block of dimensions $0.20 \times 0.15 \times 0.07$ mm^3, triclinic, $P\bar{1}$ (No. 2), $a = 9.058(5)$, $b = 10.820(7)$, $c = 13.99(1)$ Å, $\beta = 93.95(2)°$, $V = 1307(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.657$ g cm^{-3}. Data collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71075$ Å) at $T = 93$ K, $2\theta_{max} = 59.8°$, 14070 reflections measured, of which 7318 unique ($R_{int} = 0.023$), $\mu = 13.80$ cm^{-1}. The structure was solved by direct methods[15a] and expanded by using Fourier techniques,[15b] $R = 0.042$, $R_w = 0.090$. Some hydrogen atoms were refined isotropically, some were refined by using the riding model, and the rest were included in fixed positions. CCDC-242208 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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