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Preparation and Reductive Decomposition of 2-Iodoxybenzenesulfonic Acid. X-ray Crystal Structure of 1-Hydroxy-1*H*-1,2,3-benziodoxathiole 3,3-Dioxide

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2-Iodoxybenzenesulfonic acid (in a cyclic tautomeric form of 1-hydroxy-1*H*-1,2,3-benziodoxathiole 1,3,3-trioxide), a thia-analog of 2-iodoxybenzoic acid (IBX) and a potentially important oxidizing reagent, was prepared by two different pathways: direct oxidation of 2-iodobenzenesulfonic acid and hydrolysis of the methyl ester of 2-iodylbenzenesulfonic acid. The resulting l-hydroxy-1*H*-1,2,3-benziodoxathiole 1,3,3-trioxide was found to be thermally unstable and highly reactive towards organic solvents. The structure of its reductive decomposition product, l-hydroxy-1*H*-1,2,3-benziodoxathiole 3,3-dioxide (the cyclic tautomeric form of 2-iodosylbenzenesulfonic acid), was established by single-crystal X-ray diffraction.

Introduction

During the past decade, the chemistry of pentavalent iodine oxidizing reagents has attracted significant research interest.[1] Various types of hypervalent iodine(V) compounds (λ^5-iodanes) have been reported and some of them have emerged as reagents of choice for synthetically useful oxidative transformations because of their high chemoselectivity, mild reaction conditions, and environmentally benign nature. Cyclic and pseudocyclic hypervalent iodine reagents that are designed on the basis of the benziodoxole system represent an especially important class of iodanes with rich and synthetically useful chemistry.[1–3] In particular, heterocyclic λ^5-iodane 1-hydroxy-1*H*-1λ^5-benzo[*d*][1,2]iodoxol-1,3-dione (**1a**), known under the name of its tautomeric form of 2-iodoxybenzoic acid (IBX) (**1b**), has received widespread application in organic synthesis as a highly efficient and mild oxidant that can be used for the selective oxidation of primary and secondary alcohols and for a variety of other important oxidations.[2,3] However, the explosive character and low solubility of IBX in common organic solvents except DMSO restrict practical application of this reagent.

Several IBX derivatives and analogs have been reported in the literature by different research groups.[4–6] In particular, investigations from our group have resulted in a series of stable and soluble IBX derivatives: IBX-amides **2**,[5a] IBX-esters **3**,[5b] as well as their sulfur-containing analogs 2-iodylsulfonamides **4**,[5c] and 2-iodylsulfonate esters **5** (Figure 1).[5d] The synthesis of polymer-supported IBX derivatives has been reported as well.[6,7] All of these reagents have demonstrated promising oxidizing abilities toward alcohols and sulfides. It should also be noted that the oxidizing properties of the sulfur-containing analogs of IBX-esters and amides (structures **4** and **5**) were noticeably stronger in

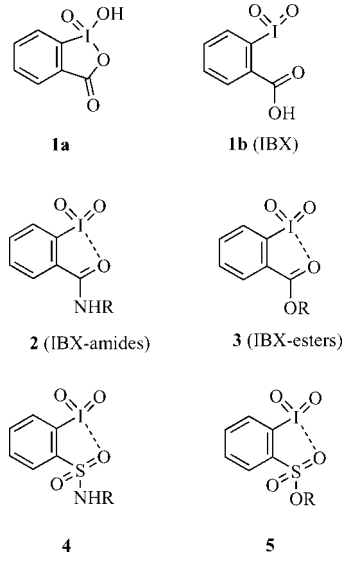

Figure 1. 2-Iodoxybenzoic acid (IBX) and its derivatives and analogs.

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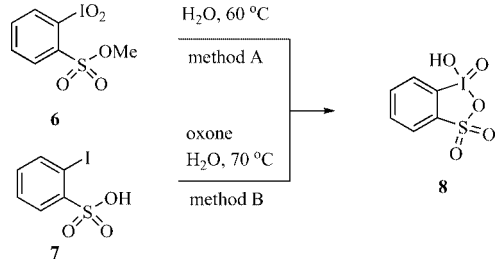
comparison with those of the original IBX-esters and amides, which is probably due to the greater electron-withdrawing nature of the sulfonyl group.[5c,5d]

With the importance of the pentavalent iodine reagents taken into consideration, and IBX especially, we have attempted to prepare the analog of IBX bearing the sulfonyl group in the five-membered ring with a goal to further investigate the influence of the *ortho*-substituent on the stability and the reactivity of cyclic iodine reagents. Herein, we report the preparation of 2-iodoxybenzenesulfonic acid (**8**) as well as the structure of the product of its reductive decomposition, 1-hydroxy-1*H*-1,2,3-benziodoxathiole 3,3-dioxide (**9**).

Results and Discussion

We have developed two different synthetic approaches to compound **8** (Scheme 1). The first approach (method A) involves the hydrolysis of known ester **6**;[5c] the second procedure (method B) involves the direct oxidation of 2-iodobenzenesulfonic acid (**7**) by a procedure similar to that used for the preparation of IBX.[8] The first approach affords analytically pure product **8** whereas the direct oxidation of iodobenzenesulfonic acid (**7**) by oxone gives the final product that is, according to elemental analysis, contaminated with approximately 10% of inorganic impurities. Because of the very high solubility of product **8** in water, it is almost impossible to separate all inorganic impurities left from the oxidation when method B is used, and therefore, method A provides a better synthetic approach to 2-iodylbenzenesulfonic acid. Product **8** is an unstable compound that decomposes to form iodine(III) heterocycle **9**[9] after several days of storage or upon contact with organic solvents, such as acetonitrile, DMSO, and methanol. It is insoluble in chloroform, dichloromethane, and other nonpolar solvents.



Scheme 1.

Despite the low stability and high reactivity of **8** towards organic solvents, we were able to obtain reliable identification data including ^{1}H- and ^{13}C NMR, IR, HRMS, and elemental analysis. In particular, the high resolution ES mass spectrum of compound **8** displays the appropriate molecular ion, and the elemental analysis is in agreement with the monohydrate formula **8·H$_2$O**. The ^{13}C NMR spectrum of a freshly prepared sample of compound **8** in D_2O shows the signal of the *ipso*-carbon, C–I(V), at about 143 ppm, which is characteristic of iodylarenes;[5] this signal disappears when the sample is stored for several days at which point the signal of C–I(III) in reductive decomposition product **9**[9,10] emerges at about 140 ppm. The contact of compound **8** with methanol or DMSO leads to almost instantaneous reduction to benziodoxathiole **9** as indicated by ^{13}C NMR spectroscopy. Because of the low stability of compound **8**, we were not able to investigate its oxidative reactivity towards organic substrates; however, its high reactivity toward methanol and DMSO is indicative of the stronger oxidizing properties compared with those of IBX.

Several attempts were performed to grow single-crystals of compound **8** suitable for X-ray analysis with the use of methanol, methanol/acetonitrile, or acetonitrile as solvents. In each case, however, only benziodoxathiole **9**, which results from the reductive decomposition of compound **8**, was identified by X-ray analysis as the final crystalline material. Depending on the solvent used for crystallization, three different crystal structures of product **9** were determined: (1) space group $P\bar{1}$, for crystals of a hydrate obtained from methanol (structure **9a**), (2) space group $P2_1/n$ for crystals obtained from methanol/acetonitrile (structure **9b**), and (3) space group $P2_12_12_1$ for crystals obtained from acetonitrile (structure **9c**). Molecular structure of benziodoxathiole **9** crystallized in the $P2_12_12_1$ space group (crystal structure **9c**) is shown in Figure 2. Selected bond lengths for structure **9c** in comparison to the similar known structure of 1-hydroxy-5-methyl-1*H*-1,2,3-benziodoxathiole 3,3-dioxide (**10**)[10] are listed in the Table 1.

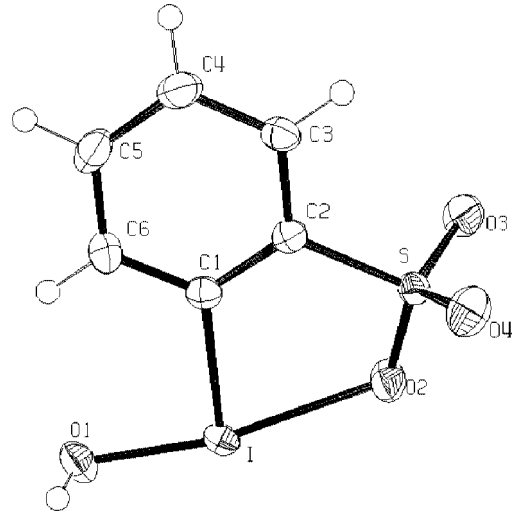
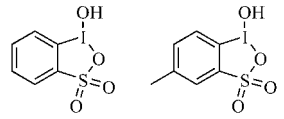


Figure 2. Perspective view of the molecular structure of benziodoxathiole **9** crystallized in the $P2_12_12_1$ space group (crystal structure **9c**). Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

For structures **9a**–**c**, the intramolecular bond lengths are approximately the same; however, the secondary bonding motifs are different (Figure 3). In all three structures the hypervalent iodine center has square-planar geometry, which is typical for iodine(III) compounds. In the case of the $P\bar{1}$ space group (structure **9a**), two molecules related by an inversion center are found in the unit cell. These two molecules are strongly connected by hydrogen bonds [1.904(6)–1.938(7) Å] that are formed by the hydrogen

Table 1. Selected bond lengths for structure **9** in comparison to the known structure of 1-hydroxy-5-methyl-1*H*-1,2,3-benziodoxathiole 3,3-dioxide (**10**).[10]



9 **10**

Bond[a]	Structure **9c**	Benziodoxathiole **10**
I–O1	1.9334(18)	1.933(5)
I–O2	2.3809(19)	2.372(5)
I–C1	2.116(3)	2.125(6)
S–O2	1.473(2)	1.440(5)
S–O3	1.438(2)	1.406(6)
S–O4	1.438(2)	1.415(9)
S–C2	1.775(3)	1.759(6)

[a] The numbering scheme refers to the thermal ellipsoid projection shown in Figure 2.

atoms of the cocrystallized water and the oxygen atoms of the sulfonyl groups, as shown in Figure 3a. Another short contact that is found in this structure is the secondary bonding between the oxygen atom of the water molecule and the hypervalent iodine from the neighboring unit cell [3.005(2) Å]. This additional interaction provides the connection between the two dimers and builds a three-dimensional polymeric network. In the second space group, $P2_1/n$ (structure **9b**), two crystallographically independent molecules are found in the unit cell. Weak secondary bonding [3.004(3) Å] interactions between an iodine atom from one of the molecules and a sulfonyl oxygen from the cycle of a neighboring molecule link the two molecules. The second type of secondary bonding in this structure is due to the intermolecular interaction between the hypervalent iodine and a sulfonyl oxygen from a second molecule [2.807(3) Å]. In the last space group, $P2_12_12_1$ (structure **9c**), one molecule is found in the asymmetric unit. In this case, secondary bonding also plays a significant role in the arrangement of

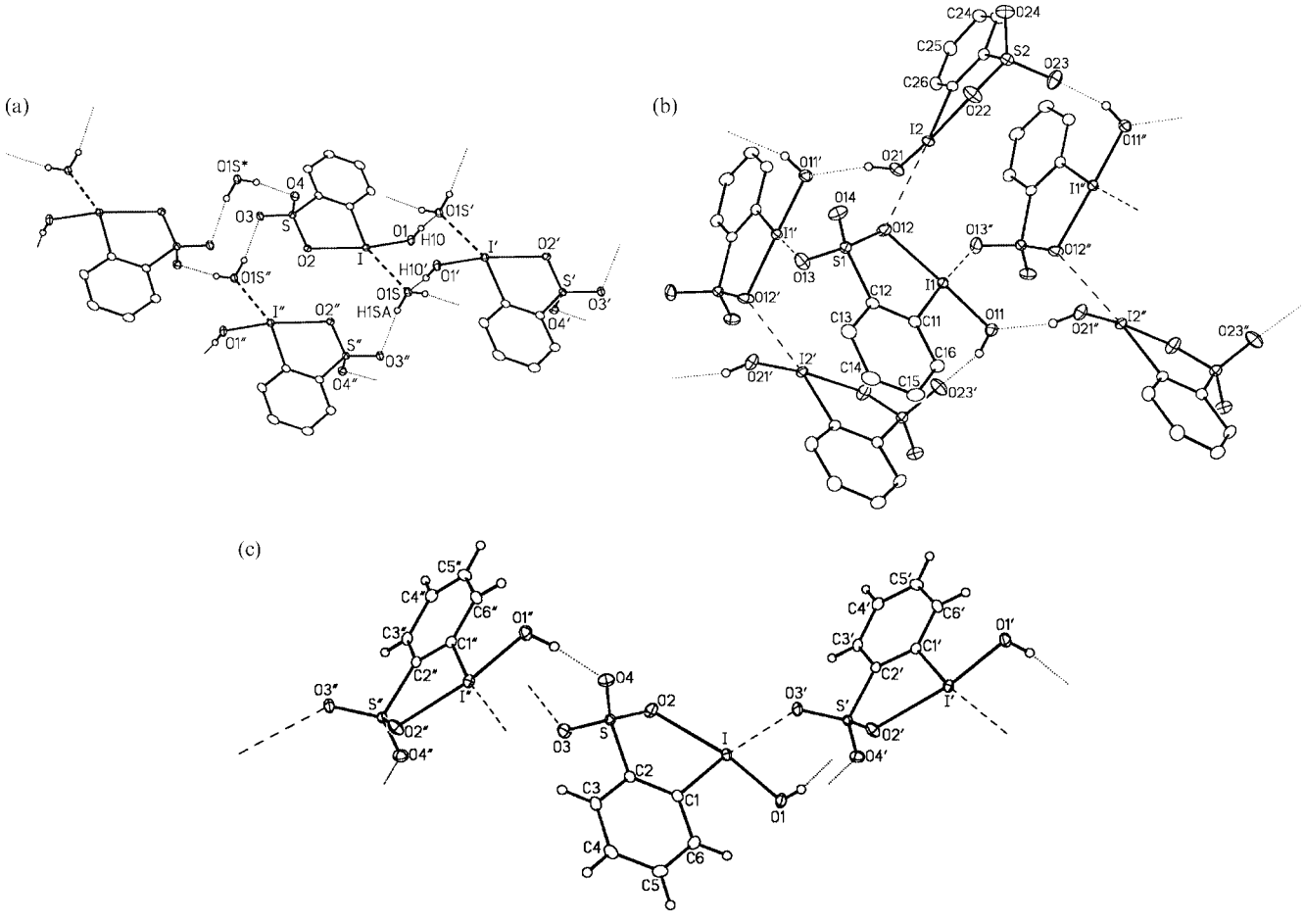


Figure 3. a) Perspective view of the crystal packing of benziodoxathiole **9a** in space group $P\bar{1}$. Selected distances [Å]: O3"···H1SB* 1.94; O4···H1SB* 1.90; O1S···I 3.005(2); H1O···O1S 1.86. b) Perspective view of the crystal packing of benziodoxathiole **9b** in space group $P2_1/n$. Selected distances [Å]: O12···I2 3.004(3); O13"···I1 2.807(3); H11O···O23′ 1.87; H21O···O11′ 1.93. c) Perspective view of the crystal packing of benziodoxathiole **9c** in space group $P2_12_12_1$. Selected distances [Å]: I···O3′ 2.847(2); H1O"···O4 1.90. In all cases, hydrogen atoms are omitted for clarity, and non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

the molecules in the solid state; the strong interaction between a sulfonyl oxygen and the iodine center [2.847(2) Å] is the main motif in this crystal structure. It is worth noting that in all three cases (**9a**–**c**), hydrogen bonding between the hydroxylic hydrogens and the oxygen atoms of different types are present, which makes the three-dimensional polymeric network even stronger.

Conclusions

In conclusion, we have reported the preparation and spectroscopic characterization of 2-iodoxybenzenesulfonic acid [in a cyclic tautomeric form of l-hydroxy-1*H*-1,2,3-benziodoxathiole 1,3,3-trioxide (**8**)], which is a thia-analog of 2-iodoxybenzoic acid (IBX) and a potentially important oxidizing reagent. This compound was prepared by two different pathways: direct oxidation of 2-iodobenzenesulfonic acid or hydrolysis of the methyl ester of 2-iodylbenzenesulfonic acid. The resulting l-hydroxy-1*H*-1,2,3-benziodoxathiole 1,3,3-trioxide was found to be unstable and highly reactive towards organic solvents. The structure of its reductive decomposition product, l-hydroxy-1*H*-1,2,3-benziodoxathiole 3,3-dioxide (**9**) (the cyclic tautomeric form of 2-iodosobenzenesulfonic acid), was established by single-crystal X-ray diffraction analysis.

Experimental Section

Preparation of l-Hydroxy-1*H*-1,2,3-benziodoxathiole 1,3,3-trioxide (8)

Method A (by hydrolysis of methyl sulfonate 6): 1-Iodyl-2-(methoxysulfonyl)benzene **6** (0.103 g, 0.31 mmol) was placed in a round-bottomed flask and distilled water (5 mL) was added. The mixture was heated at 60 °C, stirred for 3 min, and the reaction mixture was then cooled to room temperature and attached to a vacuum system. After complete removal of the water, pure monohydrate **8** was obtained as pale-yellow glass. Yield 0.104 g, 100%. M.p. 97–99 °C (dec). IR (NaCl): 3442, 3070, 1628, 1449, 1425, 1183, 1142, 1104, 1040, 762, 737, 647, 614, 557 cm^{-1}. ^1H NMR (300 MHz, D_2O, $CDCl_3$ external standard): δ = 8.28 (dd, J = 8.3 and 0.9 Hz, 1 H), 8.03 (m, 2 H), 7.91 (td, J = 7.9 and 0.7 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, D_2O, $CDCl_3$ external standard): δ = 143.0, 139.6, 134.3, 133.6, 128.4, 122.5 ppm. $C_6H_5IO_5S{\cdot}H_2O$ (334.09): calcd. C 21.57, H 2.11, I 37.99, S 9.60; found C 21.75, H 2.03, I 37.27, S 9.66. ES-MS: m/z (%) = 338.879 (50) $[M + Na]^+$.

Method B (by direct oxidation of 2-iodobenzenesulfonic acid): To a stirred mixture of 2-iodobenzenesulfonic acid (0.5 g, 1.7 mmol) in distilled water (4.25 mL) heated at 70 °C was added oxone (3.25 g) in small portions over a 15 min period. After the addition was complete, the reaction mixture was stirred for an additional 1 h and cooled to room temperature. Acetonitrile (9 mL) was added to the reaction mixture, and the resulting inorganic precipitate was removed by filtration and extracted with acetonitrile/water (2:1; 3 × 2 mL). The extracts were combined and concentrated in vacuo to afford product **8**.

1-Hydroxy-1*H*-1,2,3-benziodoxathiole 3,3-Dioxide 9 by Reductive Decomposition of 8

Slow evaporation of a methanol solution of compound **8** over a 3–5 d period at room temperature afforded colorless crystals of 1-hydroxy-1*H*-1,2,3-benziodoxathiole 3,3-dioxide in crystal form **9a**. ES-MS: m/z (%) = 300.901 (100) $[M + H]^+$.

Crystal Data for 9a·H_2O: X-ray intensity data were collected at –80 °C with a Bruker PLATFORM/SMART 1000 CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) with the use of a crystal with dimensions of 0.60 × 0.12 × 0.10 mm. $C_6H_7IO_5S$, FW = 318.08 g/mol^3, triclinic space group = $P\bar{1}$ (No. 2), unit cell dimensions: a = 7.8244(6) Å, b = 7.9472(6) Å, c = 8.0000(7) Å, α = 68.0284(11)°, β = 86.6496(11)°, γ = 80.1374(10)°, V = 454.50(6) Å^3, Z = 2, $\rho_{calcd.}$ = 2.324 g/cm^3, μ = 3.739 mm^{-1}, $2\theta_{max}$ = 52.74°, $R_1(F)$ = 0.0189 for 1771 reflections with $F_o^2 \geq 2\sigma(F_o^2)$, $wR_2(F^2)$ = 0.0481 for 1829 independent reflections [$F_o^2 \geq -3\sigma(F_o^2)$] and 126 parameters, $GOF(F^2)$ = 1.058 [$F_o^2 \geq -3\sigma(F_o^2)$].

Slow evaporation of a methanol/acetonitrile (1:1) solution of compound **8** over a 3–5 d period at room temperature afforded colorless crystals of l-hydroxy-1*H*-1,2,3-benziodoxathiole 3,3-dioxide in crystal form **9b**.

Crystal Data for 9b: X-ray intensity data were collected at –80 °C with a Bruker PLATFORM/SMART 1000 CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) with the use of a crystal with dimensions of 0.42 × 0.33 × 0.05 mm. $C_6H_5IO_4S$, FW = 300.06 g/mol^3, monoclinic space group = $P2_1/n$ (No. 14), unit cell dimensions a = 12.7784(13) Å, b = 9.2753(9) Å, c = 14.7718(15) Å, β = 109.456(2)°, V = 1650.8(3) Å^3, Z = 8, $\rho_{calcd.}$ = 2.415 g/cm^3, μ = 4.102 mm^{-1}, $2\theta_{max}$ = 52.70°, $R_1(F)$ = 0.0302 for 2996 reflections with $F_o^2 \geq 2\sigma(F_o^2)$, $wR_2(F^2)$ = 0.0810 for 3356 independent reflections [$F_o^2 \geq -3\sigma(F_o^2)$] and 219 parameters, $GOF(F^2)$ = 1.074 [$F_o^2 \geq -3\sigma(F_o^2)$].

Slow evaporation of an acetonitrile solution of compound **8** over a 3–5 d period at room temperature afforded colorless crystals of l-hydroxy-1*H*-1,2,3-benziodoxathiole 3,3-dioxide in crystal form **9c**.

Crystal Data for 9c: X-ray intensity data were collected at –80 °C with a Bruker PLATFORM/SMART 1000 CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) with the use of a crystal with dimensions of 0.50 × 0.12 × 0.04 mm. $C_6H_5IO_4S$, FW = 300.06 g/mol^3, orthorhombic space group = $P2_12_12_1$ (No. 19), unit cell dimensions a = 5.1895(3) Å, b = 11.7496(6) Å, c = 13.7880(7) Å, V = 840.72(8) Å^3, Z = 4, $\rho_{calcd.}$ = 2.371 g/cm^3, μ = 4.027 mm^{-1}, $2\theta_{max}$ = 52.74°, $R_1(F)$ = 0.0142 for 1701 reflections with $F_o^2 \geq 2\sigma(F_o^2)$, $wR_2(F^2)$ = 0.0360 for 1725 independent reflections [$F_o^2 \geq -3\sigma(F_o^2)$] and 110 parameters, $GOF(F^2)$ = 1.039 [$F_o^2 \geq -3\sigma(F_o^2)$].

CCDC-616821 to -616823 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of the article): Experimental procedures, spectroscopic and other data for the new compounds.

Acknowledgments

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