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Potassium 4-Iodylbenzenesulfonate: Preparation, Structure, and Application as a Reagent for Oxidative Iodination of Arenes

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A new hypervalent iodine(V) compound, potassium 4-iodylbenzenesulfonate, was prepared by the oxidation of 4-iodobenzensulfonic acid with Oxone in water. This potassium salt can be further converted into 4-iodylbenzenesulfonic acid by treatment with the acidic form of Amberlyst 15 in water. A single-crystal X-ray structure of potassium 4-iodylbenzenesulfonate revealed the presence of polymeric chains in the solid state due to a combination of numerous intra- and intermolecular interactions. Potassium 4-iodylbenzenesulfonate will likely find many practical applications as a thermally stable and water-soluble hypervalent iodine-based oxidant, particularly useful as a reagent for oxidative iodination of aromatic substrates. This reagent can be effectively recovered from the reaction mixture (92 % recovery) by treatment of the aqueous layer with Oxone at 60 °C for 2 h, followed by filtration of the precipitate.

Introduction

Compounds containing polyvalent iodine have recently emerged as versatile and environmentally benign reagents for various synthetically important oxidative transformations.[1,2] Particularly useful are hypervalent iodine(V) compounds (λ^5-iodanes), such as 2-iodoxybenzoic acid (IBX) and its derivatives, which are selective oxidants commonly used in the synthesis of natural products.[2] However, despite its importance, IBX is not a perfect reagent and has some serious drawbacks, such as potentially explosive properties.[3] In addition, IBX and its derivatives (e.g., Dess–Martin periodinane) have a serious disadvantage with respect to the principles of Green Chemistry since they are normally used as non-recyclable, stoichiometric reagents.[4]

In 2006 we reported the preparation and reactivity of 2-iodoxybenzenesulfonic acid (IBS), a thia analog of IBX and a powerful oxidant.[5] More recently, Ishihara and coworkers have demonstrated that IBS can be used as an extremely active catalyst for the selective oxidation of alcohols using Oxone as stoichiometric oxidant.[6] Unfortunately, 2-iodoxybenzenesulfonic acid is highly hygroscopic and thermally unstable, and therefore cannot be considered a potentially useful, common hypervalent iodine reagent.

In search of a powerful and stable hypervalent iodine(V) oxidant, an alternative to IBX and IBS, we have investigated 4-iodobenzenesulfonic acid as a possible precursor to potentially useful iodyl derivatives. In this paper, we present the synthesis, structural characterization, and reactivity of potassium 4-iodylbenzenesulfonate, which can be prepared by the oxidation of 4-iodobenzensulfonic acid with Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) in water. This potassium salt can be further converted into 4-iodylbenzenesulfonic acid by treatment with the acidic form of Amberlyst 15 in water. Potassium 4-iodylbenzenesulfonate may find practical applications as a thermally stable and water-soluble hypervalent iodine oxidant, particularly useful as a reagent for oxidative iodination of aromatic substrates. This reagent can be effectively recovered from the reaction mixture (92% recovery) by treatment of the aqueous layer with Oxone at 60 °C for 2 h, followed by filtration of the precipitate.

Results and Discussion

Starting compound, 4-iodobenzenesulfonic acid (**1**), was prepared in excellent yield by a modified procedure of Christensen[7] by treatment of iodobenzene with concentrated sulfuric acid at 50 °C (Scheme 1). Compared to the original procedure,[7] we used concentrated H_2SO_4 instead

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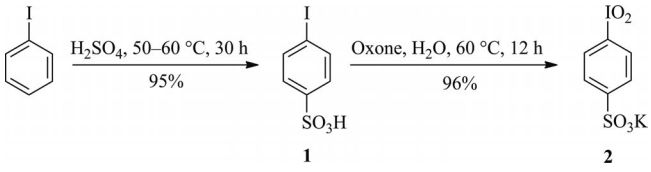
of oleum and higher reaction temperature; these changes resulted in an improved yield and better regioselectivity (exclusive formation of the *para* isomer). 4-Iodobenzenesulfonic acid (**1**) can be recrystallized from chloroform/hexane and was found to be a very hygroscopic product that should be stored in a dessicator with anhydrous $CaCl_2$. The oxidation of iodide **1** with 2.5 equiv. of Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) in water at 60 °C afforded potassium 4-iodylbenzenesulfonate (**2**) in the form of a white, microcrystalline precipitate, which can be conveniently separated from the solution by simple filtration.



Scheme 1. Preparation of 4-iodobenzenesulfonic acid (**1**) and potassium 4-iodylbenzenesulfonate (**2**).

In contrast to many other organoiodine(V) derivatives, compound **2** has an exceptionally high thermal stability. Crude samples of **2** slowly decompose without melting at about 400 °C. However, samples additionally recrystallized from water, melt with explosion at 278–280 °C and should be handled with appropriate caution (for comparison, IBX melts with explosion at 233 °C). We did not see any changes in physical or chemical properties of the sample of **2** after one year of storage at room temperature.

Compound **2** was analyzed by NMR spectroscopy, elemental analysis and single-crystal X-ray crystallography. In particular, ^{13}C NMR spectra of product **2** in D_2O showed a characteristic signal of the C–IO_2 *ipso*-carbon atom at δ = 152.0 ppm, which is typical of iodylarenes.[8] X-ray data of **2** demonstrated the presence of complex intra- and intermolecular interactions typical for iodine(V) compounds (Figure 1). The iodine center forms three covalent bonds with two terminal oxygen atoms and one aryl carbon atom. The I=O (ca. 1.8 Å) and I–C(Aryl) (ca. 2.1 Å) bond lengths are typical for previously described iodine(V) centers.[8a,8d–8f,8i–8l] Both terminal oxygen atoms lie out of the phenyl ring plane with O1–I1–C-1–C6 and O2–I1–C1–C2 torsion angles of 43.18° and 33.06°, respectively. The SO_3^- group has close to a tetrahedral geometry with all three S=O bond lengths observed close to ca. 1.45 Å, which is in the range typical of organic sulfoacids.

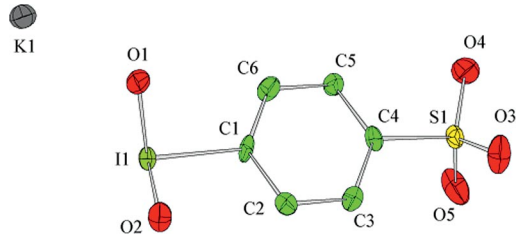


Figure 1. View of potassium 4-iodylbenzenesulfonate (**2**) with 50% ellipsoid probability. Selected distances [Å] and angles [°]: I1–O1 1.799(7), I1–O2 1.793(7), I1–C1 2.104(9), C4–S1 1.774(9), S1–O4 1.448(8), S1–O3 1.447(8), S1–O5 1.443(8); O1–I1–O2 102.8(3).

The crystal packing diagram for compound **2** is presented in Figure 2. Similar to numerous iodine(V)[8a,8d–8f,8i–8l] and especially iodine(III) compounds,[9] compound **2** forms polymeric chains in the solid state. Specifically, individual molecules of compound **2** form polymeric chains along the crystallographic *a*-axis in head (IO_2 group) to tail (SO_3^- group) fashion. These polymeric chains are closely spaced between each other and form short contacts within a chain (between IO_2 and SO_3^- groups). In addition, polymeric chains are reinforced by short interchain contacts, which involve intermolecular interactions between (i) neighboring IO_2 and SO_3^- fragments and (ii) IO_2 or SO_3^- contacts with the potassium cation. The first type of such intermolecular contacts is shown in Figure 3. Each iodine atom is involved in the coordination with oxygen atoms from the neighboring SO_3^- groups along the crystallographic *a*-axis [I–O3(A) distance 2.982 Å], SO_3^- groups of neighboring polymeric chains [I–O5(C) distance 2.769 Å] and IO_2 groups of another neighboring molecule [I–O1(B) distance 2.931 Å]. Each of these distances is significantly shorter than the sum of van der Waals radii of iodine and oxygen. Thus, each molecule of compound **2** is involved in close intermolecular contacts with three neighboring molecules. Similarly, the potassium cations in the

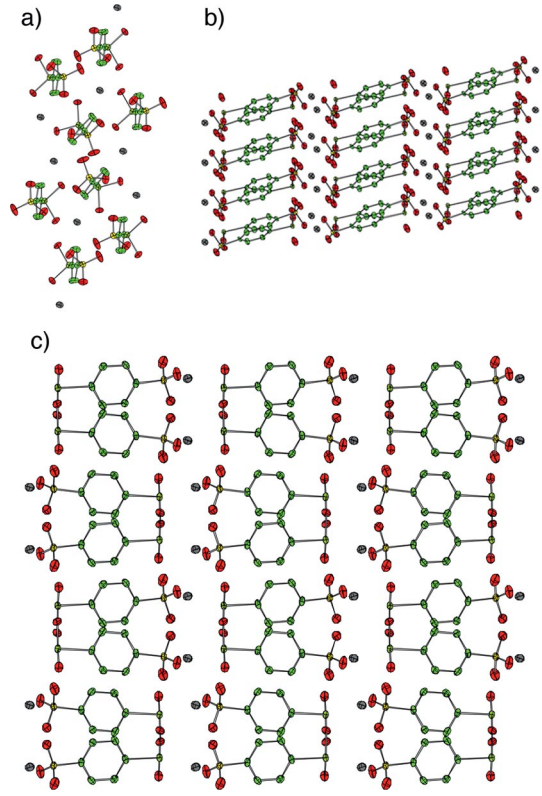


Figure 2. Crystal-packing diagram for potassium 4-iodylbenzenesulfonate (**2**): (a) along the *a*-axis, (b) along the *b*-axis, (c) along the *c*-axis.

crystal structure of compound **2** are aligned along the crystallographic *a*-axis and form eight short intermolecular contacts with seven neighboring molecules (Figure 4). These consist of three η^1 interactions with the O1 and O2 atoms of IO_2 groups, three η^1 interactions with the O3 and O4 atoms of the SO_3^- group, and one η^2 coordination with the O4 and O5 atoms of the SO_3^- group. All K^+–IO_2 distances were observed in the 2.817–2.944 Å range and K^+–SO_3^- η^1 interactions in the 2.737–2.798 Å range. The K^+–η^2 coordination is highly asymmetric with the K^+–O5 distance much shorter (2.883 Å) than the K^+–O4 distance (3.133 Å).

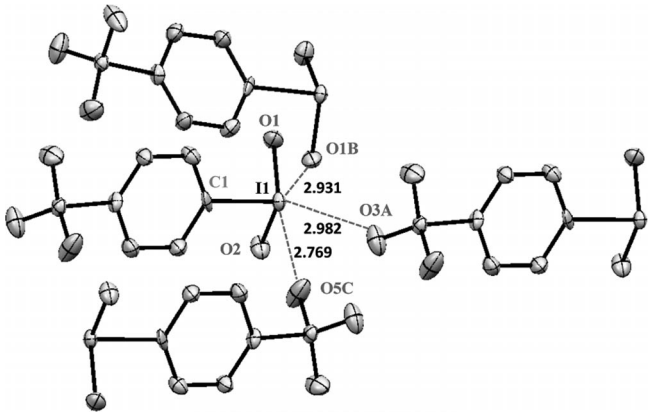


Figure 3. Intra- and intermolecular contacts at the iodine(V) center.

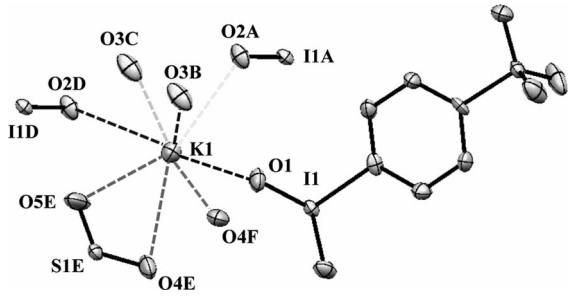
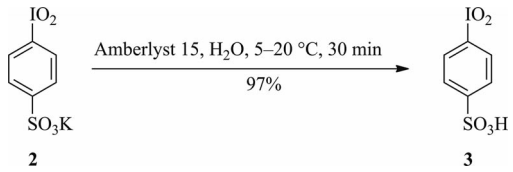


Figure 4. Close contacts of the potassium cation [Å]: K1–O1 2.817, K1–O2A 2.944, K1–O3B 2.766, K1–O3C 2.798, K1–O2D 2.918, K1–O5E 2.883, K1–O4E 3.133, K1–O4F 2.737.

Potassium salt **2** can be further converted into 4-iodylbenzenesulfonic acid (**3**) by treatment with the acidic form of Amberlyst 15 in water (Scheme 2). Acid **3** is highly hygroscopic and has a lower thermal stability than **2** (m.p. 142 °C with explosion).



Scheme 2. Preparation of 4-iodylbenzenesulfonic acid (**3**).

Since potassium 4-iodylbenzenesulfonate (**2**) has high thermal stability and is more convenient to handle relative to the highly hygroscopic acid **3**, it has greater potential for practical use as an oxidant in organic synthesis, especially, in aqueous solution. We have investigated the use of compound **2** as a reagent for oxidative iodination of aromatic substrates. This is a particularly important area of application of hypervalent iodine oxidants, because iodoarenes are widely used as building blocks in organic synthesis. Iodoarenes serve as indispensable substrates for numerous methods of C–C, C–N, and C–O bond formation, for the preparation of heterocyclic and organometallic compounds, and for many other important synthetic procedures.[10]

The results of oxidative iodination of arenes **4** by using reagent **2** as an oxidant are summarized in Table 1. In general, reagent **2** served as an efficient oxidant in the iodination of various aromatic compounds **4** bearing electron-withdrawing or electron-donating substituents in different ring positions. The most efficient procedure (Method A), useful for deactivated or weakly activated aromatic rings, consists of arene treatment with iodine and reagent **2** in the presence of sulfuric acid (Table 1, Entries 1–16 and 20). A convenient modification of this procedure (Method B) involves the use of Amberlyst 15 instead of sulfuric acid (Table 1, Entries 9–12 and 14). In the case of the strongly activated aromatic substrates, such as dimethoxybenzenes (Table 1, Entries 17–19), a milder procedure in the presence of acetic acid has been used (Method C).

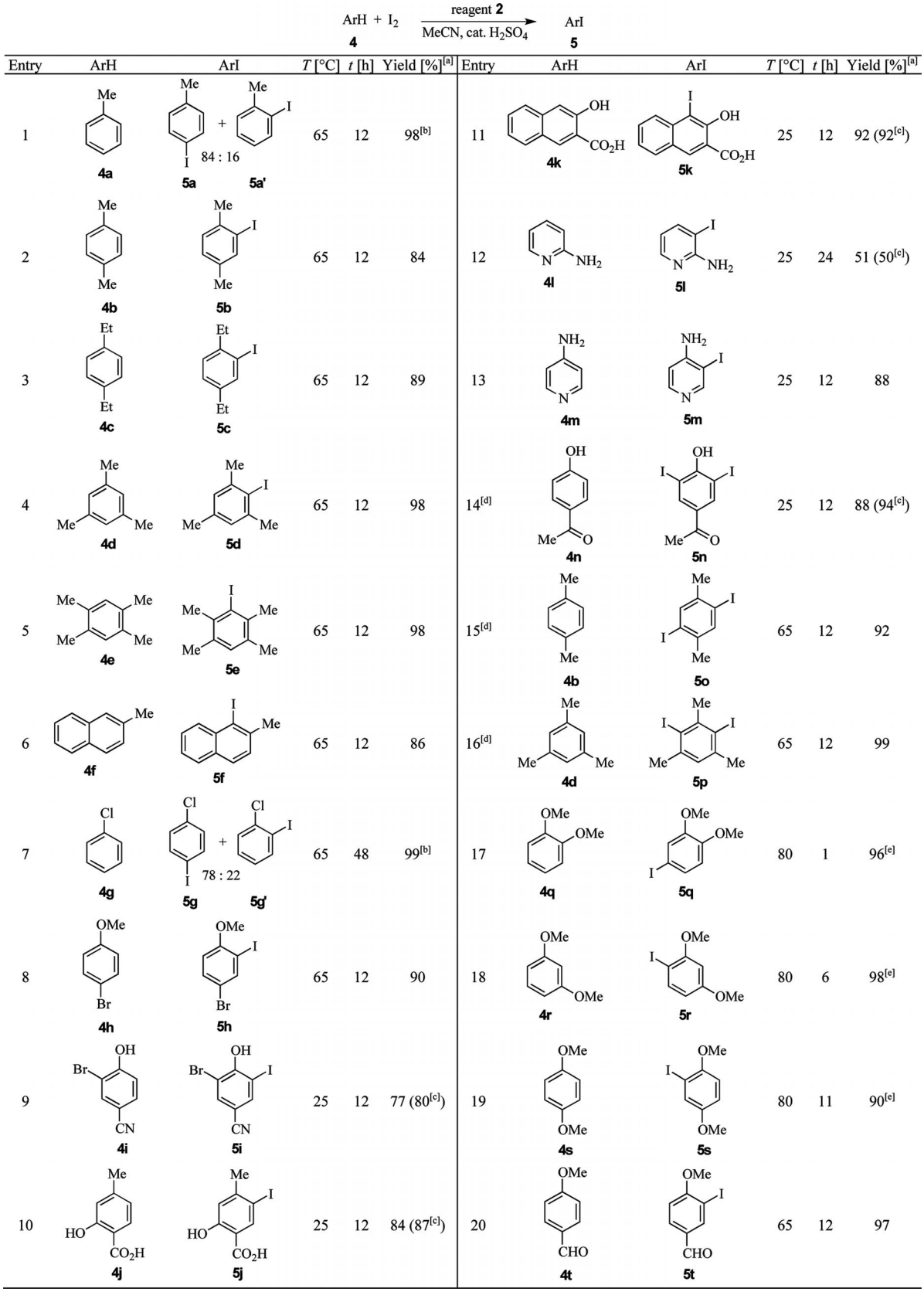
Methods A and B are applicable for the preparation of diiodoarenes (Table 1, Entries 14–16) and for the iodination of deactivated aromatic compounds, such as chlorobenzene (Table 1, Entry 7). The reactivity of reagent **2** in the oxidative iodination of chlorobenzene is comparable to the reactivity of $PhI(OAc)_2$ under similar conditions. However, the reaction of reagent **2** is much cleaner, affording regioisomers **5g** and **5g′** in 99% yield. For comparison purposes, oxidative iodination of chlorobenzene **4g** with $PhI(OAc)_2$/I_2 under the same conditions affords only 60% of **5g** and **5g′** (3:1 ratio) and about 40% of *o*- and *p*-diiodobenzenes due to the tangential iodination of PhI formed from $PhI(OAc)_2$ during the course of reaction.

Finally, we have demonstrated that reagent **2** can be effectively recovered from the reaction mixture (92% recovery) after removal of organic products by treatment of the aqueous layer with Oxone at 60 °C for 2 h, followed by filtration of the precipitate of compound **2**.

Conclusions

We have prepared a new hypervalent iodine(V) compound, potassium 4-iodylbenzenesulfonate (**2**), by the oxidation of 4-iodobenzensulfonic acid with Oxone in water. This potassium salt can be further converted into 4-iodylbenzenesulfonic acid by treatment with the acidic form of Amberlyst 15 in water. Elucidation of the single-crystal X-ray structure of **2** revealed the presence of polymeric chains in the solid state due to a complex combination of intra-

Table 1. Use of potassium 4-iodylbenzenesulfonate (**2**) as a reagent for oxidative iodination of aromatic compounds.



Entry	ArH	ArI	T [°C]	t [h]	Yield [%][a]	Entry	ArH	ArI	T [°C]	t [h]	Yield [%][a]
1	**4a**	**5a** + **5a'** (84 : 16)	65	12	98[b]	11	**4k**	**5k**	25	12	92 (92[c])
2	**4b**	**5b**	65	12	84	12	**4l**	**5l**	25	24	51 (50[c])
3	**4c**	**5c**	65	12	89	13	**4m**	**5m**	25	12	88
4	**4d**	**5d**	65	12	98	14[d]	**4n**	**5n**	25	12	88 (94[c])
5	**4e**	**5e**	65	12	98	15[d]	**4b**	**5o**	65	12	92
6	**4f**	**5f**	65	12	86	16[d]	**4d**	**5p**	65	12	99
7	**4g**	**5g** + **5g'** (78 : 22)	65	48	99[b]	17	**4q**	**5q**	80	1	96[e]
8	**4h**	**5h**	65	12	90	18	**4r**	**5r**	80	6	98[e]
9	**4i**	**5i**	25	12	77 (80[c])	19	**4s**	**5s**	80	11	90[e]
10	**4j**	**5j**	25	12	84 (87[c])	20	**4t**	**5t**	65	12	97

[a] Yields of isolated products **5** prepared by Method A (see Exp. Sect.) unless otherwise noted. [b] Determined by GC using standard authentic samples. [c] In parentheses, yield of isolated product **5** prepared by Method B (see Exp. Sect.) is given. [d] 2 equiv. of iodine were used. [e] Yield of isolated product **5** prepared by Method C (see Exp. Sect.).

and intermolecular interactions. Compound **2** will likely find many practical applications as a thermally stable and water-soluble hypervalent iodine oxidant, particularly useful as a reagent for oxidative iodination of aromatic substrates. This oxidant can be effectively recovered from reaction mixtures by treatment of the aqueous layers with Oxone at 60 °C for 2 h, followed by filtration of **2**, a readily isolated precipitate.

Experimental Section

General: All commercial reagents were ACS reagent grade and used without further purification. All other reagents and solvents were of commercial quality from freshly opened containers. All melting points were determined in an open capillary tube with a Mel-temp II® melting point apparatus, an SRS OptiMelt apparatus or an Electrothermal IA 9200 instrument. NMR spectra were recorded with a Bruker AM-200 NMR spectrometer at 200 MHz (^{1}H NMR) and a Varian Unity Inova 500 MHz NMR spectrometer at 500 MHz (^{1}H NMR), 125 MHz (^{13}C NMR); chemical shifts are reported in parts per million (ppm). GC–MS analysis was carried out with an HP 5890A gas chromatograph by using a 5970 series mass-selective detector. High-resolution mass spectra (HRMS) were obtained by using a Waters LCT Premier spectrometer with micromass MS software by using electrospray ionization (ESI). Analytical thin-layer chromatography was performed with precoated silica gel 60 F254 plates (Merck, Darmstadt), and the spots were visualized with UV light at 254 nm.

Preparation of 4-Iodobenzensulfonic Acid (1): Concentrated sulfuric acid (50 mL, 80 g, 0.82 mol) was added to iodobenzene (20 mL, 36.4 g, 0.178 mol) whilst stirring, and the reaction mixture was heated to 50 °C. The stirring was continued at 50–60 °C for 30 h; the color of the reaction mixture became pink after about 3 h. Then the reaction mixture was stirred with hexane (20 mL) for 5 min in order to remove unreacted iodobenzene; the hexane layer was separated and discarded. The sulfuric acid layer was extracted with small portions of boiling chloroform (total 100 mL) by removing the upper layer (solution of product in $CHCl_3$) with a pipette. The chloroform solution was concentrated to a small volume, and crystals of product **1** were filtered, washed with hexane, and dried in vacuo. Yield of **1**: 48.0 g (95%), m.p. 66–68 °C (ref.[7] m.p. 70 °C). ^{1}H NMR (500 MHz, D_2O): δ = 7.90 (dd, J = 8.5, 2.0 Hz, 2 H, Ar), 7.52 (dd, J = 8.5, 1.5 Hz, 2 H, Ar) ppm. ^{13}C NMR (125 MHz, D_2O): δ = 142.0, 138.0, 127.0, 97.7 ppm.

Preparation of Potassium 4-Iodylbenzenesulfonate (2): 4-Iodobenzenesulfonic acid (**1**) (2.840 g, 10 mmol) was added to a solution of Oxone (15.35 g, 25 mmol) in water (10 mL) with stirring at 60 °C. The reaction mixture was left overnight, then cooled to room temp. After 1 h at room temp., the precipitate was filtered and washed two times with water (2 × 5 mL). The solid was dried in vacuo to give 3.400 g (96%) of white powder as final product; m.p. 278–280 °C (recrystallized from water; explodes at m.p.). $C_6H_4IKO_5S$ (354.16): calcd. C 20.35, H 1.14, I 35.83, S 9.05; found C 20.26, H 1.10, I 36.07, S 8.86. ^{1}H NMR (500 MHz, D_2O): δ = 8.14 (m, C_6H_4) ppm. ^{13}C NMR (125 MHz, D_2O): δ = 152.0, 147.1, 127.6, 127.3 ppm.

Single-Crystal X-ray Diffraction Analysis: Single crystals of product **2** suitable for X-ray crystallographic analysis were obtained from a solution of **2** in acetic acid. X-ray diffraction data were collected with a Rigaku Rapid II diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 298 K. Multi-scan absorption correction was applied to the data by using the CrystalClear 2.0 program (Rigaku Inc., 2010). The structure was solved by Patterson methods (PATTY) using the CrystalStructure 4.0 program and refined by full-matrix least-squares refinement on F^2 by using the Crystals for Windows program. Crystal data for **2**: $C_6H_4IKO_5S$ (354.16), monoclinic, space group $P2_1/c$, a = 10.0311(7), b = 13.0707(5), c = 7.0632(3) Å, β = 96.682(7), V = 919.79(8) Å^3, Z = 4, μ = 4.151 mm^{-1}, 6226 reflections measured, unique 2193; final R_1 = 0.0554, R_w = 0.1576. CCDC-894690 contains the supplementary crystallographic data for compound **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of 4-Iodylbenzenesulfonic Acid (3): A suspension of potassium 4-iodylbenzenesulfonate (**2**) (1.073 g, 3.03 mmol) in H_2O (30 mL) was cooled to 5 °C, and Amberlyst 15 (10.0 g) was added and the mixture stirred at room temp. for 30 min. The reaction mixture was then filtered, the solid Amberlyst residue was washed on the filter with water (10 mL), and the combined aqueous filtrates were concentrated and dried under vacuum. Yield of **3**: 0.930 g (97%), m.p. 142–142.5 °C (explodes). HRMS (ESI, negative ionization): calcd. for $C_6H_5IO_5S$ [M – H]$^-$ 314.8824, found 314.8815 [M – H]$^-$. ^{1}H NMR (200 MHz, D_2O): δ = 8.11 (m, C_6H_4) ppm. ^{13}C NMR (125 MHz, D_2O): δ = 151.7, 146.9, 127.4, 127.1 ppm.

General Procedures for the Oxidative Iodination of Arenes

Method A (Monoiodination or Diiodination): To a mixture of an appropriate arene (0.2 mmol), iodine (0.11–0.22 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (0.06–0.12 mmol) in MeCN (0.5 mL) was added aqueous H_2SO_4 (5%, 0.5 mL), and the reaction mixture was stirred at the appropriate temperature as indicated in Table 1; the reactions were monitored by TLC and GC–MS. Then, 5% aqueous Na_2SO_3 (0.5 mL) and water (5 mL) were added, and the mixture was shaken for 5 min. After this, in most cases the precipitation of crystalline products of iodination directly from the reaction mixture was observed. The precipitate was filtered, washed with water, and dried to afford analytically pure crystalline products. In some cases [2-iodo-1,4-dimethylbenzene (**5b**), 1,4-diethyl-2-iodobenzene (**5c**), 1-iodo-2-methylnaphthalene (**5f**), 4-bromo-2-iodoanisole (**5h**), 1-iodo-4-methylbenzene (**5a**) and 1-iodo-2-methylbenzene (**5a′**), 1-chloro-4-iodobenzene (**5g**) and 1-chloro-2-iodobenzene (**5g′**)], when precipitation of crystalline products was not observed, the reaction mixture was extracted with ethyl acetate (5 mL), and the extract was washed with water and dried with Na_2SO_4. The pure iodoarenes were characterized by NMR spectroscopy after evaporation of the solvent.

Method B: To a mixture of an appropriate arene (0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (19.5 mg, 0.055 mmol) in MeCN (0.5 mL) werer added Amberlyst 15 (100 mg) and water (0.5 mL). The reaction mixture was stirred at room temp. as indicated in Table 1; the reactions were monitored by TLC. Then, 5% aqueous Na_2SO_3 (0.5 mL) and water (5 mL) were added, and the mixture was shaken for 5 min, then extracted with ethyl acetate (5 mL), and the extract was washed with water and dried with Na_2SO_4. The pure iodoarenes were characterized by NMR spectroscopy after evaporation of the solvent. The yields of products prepared according to Method B are given in Table 1.

Method C: To a solution of dimethoxybenzene (138 mg, 1.0 mmol) in acetic acid (5 mL), iodine (127 mg, 0.5 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (106 mg, 0.3 mmol) were added with stirring at 80 °C. After additional stirring for the time indicated in

Table 1, the mixture was cooled to room temp., and ice-cold water was added. The product was extracted with dichloromethane (20 mL) and the extract washed with $NaHCO_3$ (10% in water) and dried with Na_2SO_4. Evaporation of dichloromethane gave the pure product.

4-Iodotoluene (5a) and 2-Iodotoluene (5a′): Reaction of toluene (**4a**) (18.4 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (21 mg, 0.06 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (monoiodination Method A at 65 °C), afforded a mixture (98%) of 1-iodo-4-methylbenzene (**5a**)/1-iodo-2-methylbenzene (**5a′**) (84:16) according to GC–MS analysis by using available standards.

2-Iodo-1,4-dimethylbenzene (5b): Reaction of 1,4-dimethylbenzene (**4b**) (21.2 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (19.5 mg, 0.055 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (monoiodination Method A at 65 °C), afforded 39 mg (84%) of product **5b** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (s,1 H), 7.10 (d, J = 7.5 Hz, 1 H), 7.06 (d, J = 7.5 Hz, 1 H), 2.42 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3) ppm.[11]

1,4-Diethyl-2-iodobenzene (5c): Reaction of 1,4-diethylbenzene (**4c**) (26.8 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (21 mg, 0.06 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (monoiodination Method A at 65 °C), afforded 46.3 mg (89%) of product **5c** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (s, 1 H), 7.25 (s, 1 H), 7.12 (s, 1 H), 2.69 (q, J = 7.5 Hz, 2 H, CH_2), 2.56 (q, J = 7.5 Hz, 2 H, CH_2), 1.22–1.17 (m, 6 H, CH_3) ppm.

2-Iodo-1,3,5-trimethylbenzene (5d): Reaction of 1,3,5-trimethylbenzene (**4d**) (24 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (21 mg, 0.06 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (monoiodination Method A at 65 °C), afforded 48.2 mg (98%) of product, isolated as a microcrystalline white solid, m.p. 28–29.5 °C (ref.[12] m.p. 30–31 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.90 (s, 2 H_{arom}) 2.44 (s, 6 H, CH_3), 2.25 (s, 3 H, CH_3) ppm.

3-Iodo-1,2,4,5-tetramethylbenzene (5e): Reaction of 1,2,4,5-tetramethylbenzene (**4e**) (26.8 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (21 mg, 0.06 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (monoiodination Method A at 65 °C), afforded 51 mg (98%) of product **5e**, isolated as a microcrystalline white solid, m.p. 77–79 °C (ref.[13] m.p. 78.5–79 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.89 (s, 1 H_{arom}), 2.44 (s, 6 H, CH_3), 2.31 (s, 6 H, CH_3) ppm.

1-Iodo-2-methylnaphthalene (5f): Reaction of 2-methylnaphthalene (**4f**) (28.4 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (21 mg, 0.06 mmol) in MeCN (0.5 mL) according to the general procedure (monoiodination Method A at 65 °C), afforded 46 mg (86%) of product **5f** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.23 (d, J = 8.5 Hz, 1 H), 7.74 (d, J = 8.5 Hz, 1 H), 7.72 (d, J = 8.0 Hz, 1 H), 7.53–7.57 (m, 1 H), 7.44–7.47 (m, 1 H), 7.37 (d, J = 8.0 Hz, 1 H), 2.71 (s, 3 H, CH_3) ppm.[12]

1-Chloro-4-iodobenzene (5g) and 1-Chloro-2-iodobenzene (5 g′): Reaction of chlorobenzene (**4g**) (22.5 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (21 mg, 0.06 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (monoiodination Method A at 65 °C), afforded a mixture (99%) of 1-chloro-4-iodobenzene (**5g**)/1-chloro-2-iodobenzene (**5g′**) (78:22) according to GC–MS analysis by using available standards.

4-Bromo-2-iodoanisole (5h): Reaction of 4-bromoanisole (**4h**) (37.4 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (21 mg, 0.06 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (monoiodination Method A at 65 °C), afforded 56.3 mg (90%) of product **5h** as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 (d, J = 2.5 Hz, 1 H), 7.41 (dd, J = 9.0, 2.5 Hz, 1 H), 6.69 (d, J = 9.0 Hz, 1 H), 3.86 (s, 3 H, CH_3) ppm.[14]

3-Bromo-4-hydroxy-5-iodobenzonitrile (5i): Reaction of 3-bromo-4-hydroxybenzonitrile (**4i**) (39.6 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (21 mg, 0.06 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (monoiodination Method A at room temp.), afforded 49.9 mg (77%) of product **5i**, isolated as microcrystalline solid, m.p. 188–190 °C (from benzene/hexane, 5:1) (ref.[15] m.p. 190–191 °C). HRMS (ESI): calcd. for C_7H_2BrINO $[M - H]^-$ 321.8365, found 321.8379. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.11 (d, J = 1.9 Hz, 1 H), 7.94 (d, J = 1.9 Hz, 1 H) ppm.

2-Hydroxy-5-iodo-4-methylbenzoicAcid (5j): Reaction of 2-hydroxy-4-methylbenzoic acid (**4j**) (30.4 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (19.5 mg, 0.055 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (monoiodination Method A at room temp.), afforded 46.7 mg (84%) of product **5j** as white crystals, m.p. 217–219 °C (from hexane/EtOAc, 6:1). HRMS (ESI): calcd. for $C_8H_6IO_3$ $[M - H]^-$ 276.9362, found 276.9364. ^{1}H NMR (200 MHz, CD_3OD): δ = 7.82 (d, J = 1.3 Hz, 1 H), 7.71 (d, J = 1.3 Hz, 1 H), 2.29 (s, 3 H) ppm.

3-Hydroxy-4-iodo-2-naphthoic Acid (5k): Reaction of 3-hydroxy-2-naphthoic acid (**4k**) (37.6 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (19.5 mg, 0.055 mmol) in MeCN (0.5 mL) according to the general procedure (monoiodination Method A at room temp.), afforded 57.8 mg (92%) of product **5k**, isolated as a yellow crystalline solid, m.p. 208–210 °C (dec.) [ref.[16] m.p. 210 °C (dec.)]. HRMS (ESI): calcd. for $C_{11}H_6IO_3$ $[M - H]^-$ 312.9362, found 312.9377. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.62 (s, 1 H), 8.10 (d, J = 8.0 Hz, 1 H), 7.43 (td, J = 8.0, 1.0 Hz, 1 H), 7.90 (d, J = 8.0 Hz, 1 H), 7.66 (td, J = 7.0, 1.3 Hz, 1 H) ppm.

2-Amino-3-iodopyridine (5l): Reaction of 2-aminopyridine (**4l**) (18.8 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (19.5 mg, 0.055 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (monoiodination Method A at room temp.), afforded 22.4 mg (51%) of product, isolated as a white crystalline solid, m.p. 83–85 °C (from hexane/EtOAc, 3:1) (ref.[17] m.p. 86 °C). HRMS (ESI): calcd. for $C_5H_6IN_2$ $[M + H]^+$ 220.9576, found 220.9583. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.07 (d, J = 1.7 Hz, 1 H), 7.67 (dd, J = 8.8, 2.3 Hz, 1 H), 6.47 (dd, J = 8.8, 0.6 Hz, 1 H) ppm.

4-Amino-3-iodopyridine (5m): Reaction of 4-aminopyridine (**4m**) (18.8 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (19.5 mg, 0.055 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (monoiodination Method A at room temp.), afforded 38.7 mg (88%) of product **5m**, isolated as white needle-shaped crystals, m.p. 74–76 °C (ref.[18] m.p. 76–77 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 8.12 (d, J = 5.5 Hz, 1 H), 6.60 (d, J = 5.5 Hz, 1 H), 4.62 (br. s, 2 H, NH_2) ppm.

4-Hydroxy-3,5-diiodoacetophenone (5n): Reaction of 4-hydroxyacetophenone (**4n**) (27.2 mg, 0.2 mmol), iodine (55.9 mg, 0.22 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (42.5 mg, 0.12 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (diiodination Method A at room temp.), afforded 68.3 mg (88%) of product, isolated as a white crystalline solid, m.p. 159–160 °C (from MeOH/H_2O, 1:1) (ref.[12] m.p. 158–160 °C). HRMS (ESI): calcd. for $C_8H_5I_2O_2$ [M – H]$^-$ 386.8379, found 386.8378. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.35 (s, 2 H), 2.54 (s, 3 H, CH_3) ppm.

2,5-Diiodo-1,4-dimethylbenzene (5o): Reaction of 1,4-dimethylbenzene (**4o**) (21.2 mg, 0.2 mmol), iodine (55.9 mg, 0.22 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (42.5 mg, 0.12 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (diiodination Method A at 65 °C), afforded 65.8 mg (92%) of product **5o**, isolated as white needle-shaped crystals, m.p. 102.5–103.5 °C (ref.[19] m.p. 103–104 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (s, 2 H), 2.34 (s, 6 H, CH_3) ppm.

2,4-Diiodo-1,3,5-trimethylbenzene (5p): Reaction of 1,3,5-trimethylbenzene (**4d**) (24 mg, 0.2 mmol), iodine (55.9 mg, 0.22 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (42.5 mg, 0.12 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (diiodination Method A at 65 °C), afforded 73.6 mg (99%) of product **5p**, isolated as white needle-shaped crystals, m.p. 80–81.5 °C (ref.[19] m.p. 82 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.00 (s, 1 H), 2.93 (s, 3 H, CH_3), 2.42 (s, 6 H, CH_3) ppm.

4-Iodo-1,2-dimethoxybenzene (5q): Reaction of 1,2-dimethoxybenzene (**4q**) (138 mg, 1.0 mmol), iodine (127 mg, 0.5 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (106 mg, 0.3 mmol) in acetic acid (5 mL) according to the general procedure (monoiodination Method C at 80 °C), afforded 253 mg (96%) of product, isolated as an oil that can be crystallized in a refrigerator. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22 (dd, J = 8.5 and 2.0 Hz, 1 H), 7.11 (d, J = 2.0 Hz, 1 H), 6.61 (d, J = 8.5 Hz, 1 H), 3.85 (s, 3 H, 2-OCH_3), 3.84 (s, 3 H, 1-OCH_3) ppm.[20]

4-Iodo-1,3-dimethoxybenzene (5r): Reaction of 1,3-dimethoxybenzene (**4r**) (138 mg, 1.0 mmol), iodine (127 mg, 0.5 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (106 mg, 0.3 mmol) in acetic acid (5 mL) according to the general procedure (monoiodination Method C at 80 °C), afforded 258 mg (98%) of product, isolated as an oil that can be crystallized in a refrigerator. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.5 Hz, 1 H), 6.43 (d, J = 2.5 Hz, 1 H), 6.32 (dd, J = 8.5, 2.5 Hz, 1 H), 3.85 (s, 3 H, 3-OCH_3), 3.80 (s, 3 H, 1-OCH_3) ppm.[21]

2-Iodo-1,4-dimethoxybenzene (5s): Reaction of 1,4-dimethoxybenzene (**4s**) (138 mg, 1.0 mmol), iodine (127 mg, 0.5 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (106 mg, 0.3 mmol) in acetic acid (5 mL) according to the general procedure (monoiodination Method C at 80 °C), afforded 237 mg (90%) of product **5s**, isolated as a pink oil that can be crystallized in a refrigerator. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 (d, J = 3.0 Hz, 1 H), 6.86 (dd, J = 9.0, 3.0 Hz, 1 H), 6.75 (d, J = 9.0 Hz, 1 H), 3.82 (s, 3 H, 4-OCH_3), 3.75 (s, 3 H, 1-OCH_3) ppm.[22]

3-Iodo-4-methoxybenzaldehyde (5t): Reaction of 4-methoxybenzaldehyde (**4t**) (27.2 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (21 mg, 0.06 mmol) in MeCN (0.5 mL) and aqueous H_2SO_4 (5%, 0.5 mL) according to the general procedure (monoiodination Method A at 65 °C), afforded 50.8 mg (97%) of product **5t**, isolated as white crystals, m.p. 104–106 °C (ref.[23] m.p. 104.5–106.5 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.83 (s, 1 H), 8.31 (d, J = 2.0 Hz, 1 H), 7.86 (dd, J = 8.5, 2.0 Hz, 1 H), 6.93 (d, J = 8.5 Hz, 1 H), 3.98 (s, 3 H, OCH_3) ppm.

Iodination Procedure with Recovery of Potassium 4-Iodylbenzenesulfonate (2). Preparation of 4-Bromo-2-iodoanisole (5h): To a mixture of 4-bromoanisole (**4h**) (468 mg, 2.5 mmol), iodine (350 mg, 1.38 mmol) and potassium 4-iodylbenzenesulfonate (**2**) (347 mg, 0.98 mmol) in MeCN (3.0 mL) was added aqueous H_2SO_4 (5%, 3.0 mL), and the reaction mixture was stirred at 80 °C for 12 h; the reaction was monitored by TLC and GC–MS. The reaction mixture was then cooled to room temp. and extracted with hexanes (6.0 mL). Concentration of the hexanes layer gave 634 mg (81%) of 4-bromo-2-iodoanisole (**5h**). Oxone (1.2 g) was added to the water layer after extraction. This mixture was stirred at 60 °C for 2 h, then cooled to 5 °C, and the resulting precipitate was filtered, washed with water (3 × 1.0 mL), and dried to afford 320 mg (92% recovery) of potassium 4-iodylbenzenesulfonate (**2**).

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for key products.

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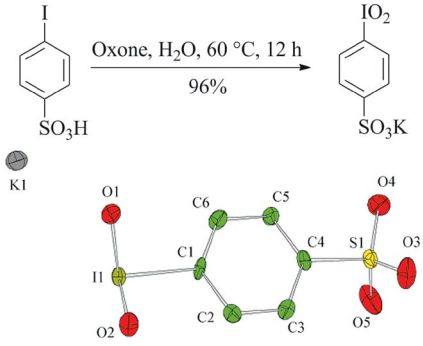
A new hypervalent iodine(V) compound, potassium 4-iodylbenzenesulfonate, was prepared by oxidation of 4-iodobenzenesulfonic acid with Oxone in water. This new reagent promises many practical applications as a thermally stable, water-soluble and recyclable hypervalent iodine oxidant, particularly useful for oxidative iodination of aromatic substrates.



Keywords: Iodine / Hypervalent compounds / Iodination / Oxidation / X-ray diffraction

