JOC The Journal of Organic Chemistry

Article

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Preparation and X-ray Structural Study of 1-Arylbenziodoxolones

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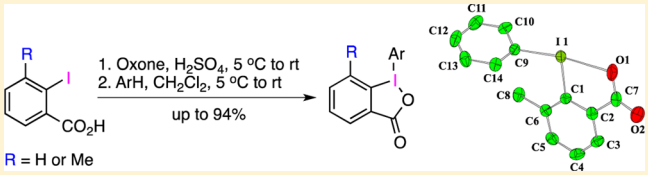
Supporting Information

ABSTRACT: Various 1-arylbenziodoxolones can be conveniently prepared from 2-iodobenzoic acid and arenes by a one-pot procedure using Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) as an inexpensive and environmentally safe oxidant. This procedure is also applicable for the synthesis of the 7-methylbenziodoxolone ring system using 2-iodo-3-methylbenzoic acid as starting compound. Structures of four 1-arylbenziodoxolone derivatives were established by single-crystal X-ray diffraction analysis. An enhanced reactivity of 1-aryl-7-methylbenziodoxolones toward nucleophiles compared to unsubstituted 1-arylbenziodoxolones has been found.



1. INTRODUCTION

Hypervalent iodine reagents have emerged as versatile and environmentally benign reagents for various synthetically useful oxidative transformations.[1] Particularly useful are hypervalent iodine five-membered heterocycles, known under collective name "benziodoxoles".[2] The most important representatives of this class of compounds are 2-iodoxybenzoic acid (IBX)[1k,l] and 2-iodosylbenzoic acid (IBA),[2] which have found broad synthetic application as common oxidants. Recently, numerous new iodine-substituted derivatives of benziodoxoles have been prepared, and their utility as "atom transfer" reagents has been demonstrated.[2a] Especially important are the benziodoxole derivatives bearing a C-substituent on iodine, such as 1-trifluoromethylbenziodoxoles, which are useful reagents for electrophilic trifluoromethylation of nucleophilic substrates,[3] and alkynylbenziodoxoles, excellent acetylene-transfer reagents.[2a]

Despite a significant recent interest in the carbon-substituted benziodoxoles, the chemistry and structural features of the most stable compounds of this structural class, 1-arylbenziodoxoles remain almost uninvestigated. 1-Phenyl-1,2-benziodoxole-3(1*H*)-one **2a**, commonly known under the names of 1-phenylbenziodoxolone or diphenyliodonium-2-carboxylate, is the most important representative of arylbenziodoxoles. 1-Phenylbenziodoxolone **2a** is a classical reagent that is commonly used for the generation of benzyne under heating or UV irradiation.[4,5] It has also found synthetic application for the preparation of *o*-substituted benzoic acids, which serve as important intermediate products in the synthesis of various biologically active compounds.[6] Phenylbenziodoxolone **2a** is commercially available or can be prepared by the oxidation of 2-iodobenzoic acid **1** with potassium persulfate followed by addition of benzene according to the procedure published in *Organic Syntheses* (Scheme 1).[4] The original procedure was first reported in 1960 by Beringer and Lillien,[7] and it has also been used for the synthesis of substituted phenylbenziodoxoles **3**–**6**.[5d,e,8]

More recently, Merritt and Olofsson reported a modified procedure for the synthesis of phenylbenziodoxole in 66% yield by a one-pot reaction of 2-iodobenzoic acid with *m*-chloroperoxybenzoic acid, trifluoromethanesulfonic acid, and benzene in CH_2Cl_2 at 80 °C followed by addition of aqueous ammonia.[9] This procedure has a limited practical value due to the use of expensive reagents and harsh reaction conditions under elevated pressure in a sealed flask.

In this paper, we describe an optimized general procedure for a convenient one-pot preparation of 1-arylbenziodoxolones from 2-iodobenzoic acid and various arenes using Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) as an inexpensive and environmentally safe oxidant. This procedure is also applicable for the synthesis of the 7-methylbenziodoxolone ring system using 2-iodo-3-methylbenzoic acid **7** as starting compound. Structures of key products have been established by single crystal X-ray diffraction. We also report an enhanced reactivity of 1-aryl-7-methylbenziodoxolones toward nucleophiles compared to nonsubstituted 1-arylbenziodoxolones.

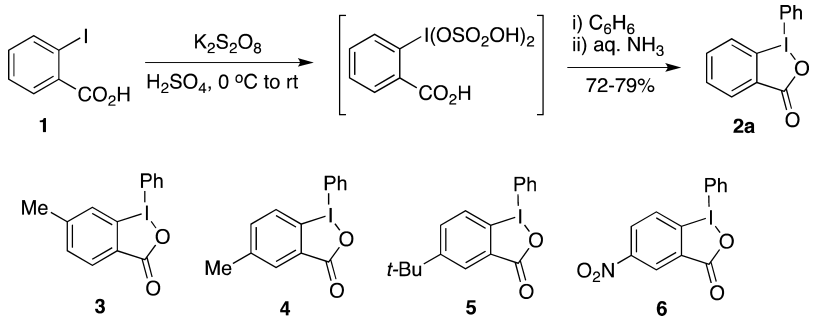
2. RESULTS AND DISCUSSION

We have developed an optimized general procedure for one-pot preparation of 1-arylbenziodoxolones on the basis of a modified procedure for preparation of product **1a** published in *Organic Syntheses*.[4] The key differences consist of the use of Oxone instead of potassium persulfate at the first step and a modified product isolation procedure using $NaHCO_3$ as a base. These modifications result in an increased yield of product **1a** (up to 92% of crude product or 88% after additional recrystallization from water) and allow facile preparation of various new 1-arylbenziodoxolones (Table 1).

This procedure affords analytically pure products **2** in generally high yields in the form of thermally stable, white, microcrystalline solids. Lower yields (40–62%) are observed in the case of sterically hindered substrates (entries 8, 14, and 15). In the reactions of 2-iodo-3-methylbenzoic acid **7**, a significant darkening at the end of reaction was observed that required

Received: February 4, 2013
Published: March 12, 2013

Scheme 1. Known 1-Arylbenziodoxolones



additional treatment of the reaction mixture with activated carbon. All new products were analyzed by ^{1}H and ^{13}C NMR, elemental analysis, and structures of products **2b**, **2g**, **2n**, and **2o** were established by single-crystal X-ray crystallography (Figure 1).

X-ray data of products **2b**, **2g**, **2n**, and **2o** demonstrate the presence of complex intra- and/or intermolecular interactions typical for hypervalent iodine compounds. All products were crystallized using water (water/methanol in the case of **2o**) as a solvent. In compounds **2g** and **2n**, solvent molecules were not observed in the unit cells, while water or water and methanol molecules were observed in the unit cells of products **2b** and **2o**. The following similarities were observed in the crystal structures of compounds **2b**, **2g**, **2n**, and **2o**: (i) iodine(III) centers have classic distorted (O–I–C angles varies between 162.57° and 169.19°) T-shape conformation; (ii) iodine–carbon bond length in the iodine–arylcarboxylate fragment (2.130–2.152 Å) is always longer compared to the corresponding iodine–carbon bond length in the iodine–aryl fragment (2.096–2.126 Å); (iii) iodine centers are involved in the formation of the five–membered C–I–O–C–C benziodoxole ring (iodine–oxygen bond length varies between 2.482 and 2.559 Å); (iv) iodine centers form secondary intermolecular contacts with oxygen atoms of either solvent molecules or oxygen atoms of carboxylic group in neighboring molecules; (v) C–I–C angles in compounds with less sterically demanding arylcarboxylate substituents (compounds **2b**, 92.4° and **2g**, 93.4°) are close to that observed earlier in parent 1-phenylbenziodoxole **1a** (95.2°),[10] while the same angle in more sterically crowded compounds **2n** and **2o** are significantly larger (99.38° and 100.74°, respectively); (vi) degree of coplanarity of the C–I–O–C–C fragment and the parent benzene ring depends on the steric properties of the arylcarboxylate part of the molecule. Indeed, in compounds **2b** and **2g**, which are derived from unsubstituted iodosylbenzoic acid, the C–C–C(O)–O torsion angles are close to zero (6.11° and 2.12°, respectively) resulting in a nearly coplanar arrangement of the iodine–containing five–membered and parent six–membered fragments. Introduction of methyl group in the position 3 of iodosylbenzoic acid fragment, on the other hand, results in significant distortion of C–C–C(O)–O torsion angle (11.81° for **2n** and 18.51° for **2o**) and thus deviation of the C–I–O–C–C fragment from plane of the six-membered benzene ring.

It was previously established that the reactions of 1-phenylbenziodoxolone **2a** with nucleophiles (e.g., amines) proceed exclusively in the benziodoxolone ring with substitution of PhI and formation of the respective *o*-substituted benzoic acids.[6] This reactivity pattern is in agreement with general regioselectivity of the reactions of nonsymmetrical iodonium salts with nucleophiles, in which substitution occurs predominantly in the more electron-deficient aromatic ring.[11] It is also known from the literature that the reactions of 1-phenylbenziodoxolone **2a** with nucleophiles proceed only at temperatures above 80 °C and require the presence of copper catalysts.[6c] The low reactivity of arylbenziodoxolones compared to the noncyclic diaryliodonium salts[1h] can be explained by a significant stabilization of the cyclic halonium ions due to the strong intramolecular hypervalent halogen–oxygen interaction[12] in the benziodoxole ring. It would be interesting to compare the reactivity of 1-phenylbenziodoxolone **2a** with 1-phenyl-7-methylbenziodoxolone **2n**, which has a methyl group in the *ortho* position to the phenyliodonium group. It has been previously observed that the *o*-methyl-substituted aromatic ring in a nonsymmetrical diaryliodonium salt shows enhanced reactivity toward nucleophiles (the so-called "*ortho*-effect"), which is explained by the effect of steric factors on configuration of the reaction intermediate.[13]

We have investigated the reactions of benziodoxolones **2a** and **2n** with sodium azide in aqueous acetonitrile under reflux conditions (Scheme 2). While compound **2a** was inert under these conditions after 1.5 h, the *ortho*-substituted 1-phenyl-7-methylbenziodoxolone **2n** was completely converted to the azide **8** and iodobenzene just in 30 min. The product of substitution **8** was isolated as an off-white microcrystalline precipitate from the aqueous solution after removal of PhI and addition of HCl. Furthermore, 1-phenyl-7-methylbenziodoxolone **2n** demonstrated high reactivity even toward such a poor nucleophile as water. Refluxing the solution of compound **2n** in aqueous acetonitrile for 1 h resulted in complete conversion to 3-methylsalicylic acid **9** and iodobenzene after 1 h (Scheme 2).

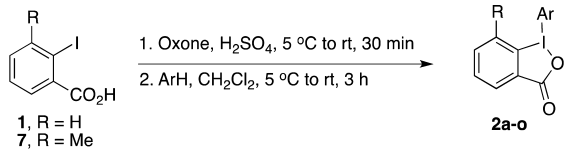
We assume that the dramatic enhancement of reactivity observed in the reactions of 1-phenyl-7-methylbenziodoxolone **2n** with nucleophiles is explained by the increased bulkiness of the aromatic ligand, forcing it to stay predominantly in the equatorial position of the trigonal bipyramidal intermediate (Scheme 3).[13] In the trigonal bipyramidal intermediate **A** formed by the initial addition of nucleophile X:$^{-}$ to the iodonium center, the most electron-deficient ligands, X and the benzoate group, occupy the axial positions. Ligand coupling, which proceeds as the S_NAr substitution reaction between the axial ligand X and the aryl group in equatorial position,[13] is unlikely to occur in the intermediate **A** because of the electron-rich character of the equatorial phenyl ligand. However, since the equatorial positions are roomier than the axial positions, it is reasonable that a bulkier *ortho*-substituted group would be forced to occupy the equatorial position, switching the equilibrium toward the intermediate **B**. Ligand coupling in the intermediate **B** leads to a reductive elimination of PhI and transfer of the nucleophile to the *ortho*-substituted electron-deficient aryl group situated in the equatorial position (Scheme 3).

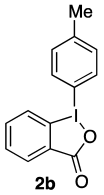
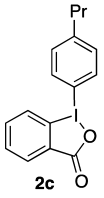
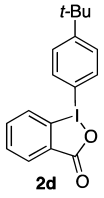
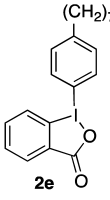
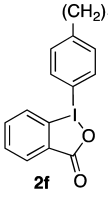
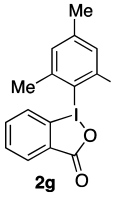
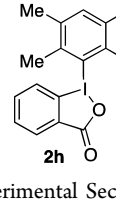
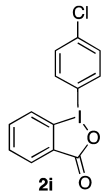
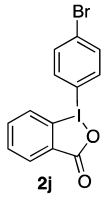
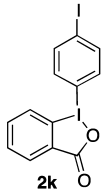
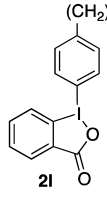
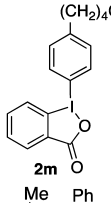
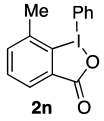
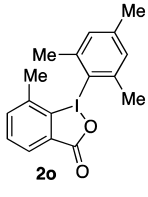
3. CONCLUSIONS

In summary, we have developed a convenient procedure for the preparation of various 1-arylbenziodoxolones from 2-iodobenzoic

dx.doi.org/10.1021/jo400212u | J. Org. Chem. 2013, 78, 3767–3773

Table 1. Preparation of 1-Arylbenziodoxolones 1a–o[a]



Entry	2-Iodo-benzoic acid	ArH	Product **2**	Yield (%)[b]
1	**1**	PhH	**2a**	88
2	**1**	$PhCH_3$	 **2b**	81
3	**1**	PhC_3H_7	 **2c**	94
4	**1**	$PhC(CH_3)_3$	 **2d**	82
5	**1**	$Ph(CH_2)_7Me$	 **2e**	89
6	**1**	$Ph(CH_2)_{12}Me$	 **2f**	86
7	**1**	$1,3,5\text{-}Me_3C_6H_3$	 **2g**	78
8	**1**	$1,2,4,6\text{-}Me_4C_6H_2$	 **2h**	40
9	**1**	PhCl	 **2i**	57
10	**1**	PhBr	 **2j**	83
11	**1**	PhI	 **2k**	91
12	**1**	$Ph(CH_2)_4CO_2H$	 **2l**	83
13[c]	**1**	$Ph(CH_2)_4CO_2Me$	 **2m**	89
14	**7**	PhH	 **2n**	52
15	**7**	$1,3,5\text{-}Me_3C_6H_3$	 **2o**	62

[a]For detailed procedures, see the Experimental Section [b]Yields of recrystallized, analytically pure products.

acid and arenes by a one-pot procedure using Oxone as an inexpensive and environmentally safe oxidant. This procedure is also applicable for the synthesis of the 7-methylbenziodoxolone ring system starting from 2-iodo-3-methylbenzoic acid **7**. Structures of four 1-arylbenziodoxole derivatives were established by single-crystal X-ray diffraction analysis. An enhanced reactivity of 1-aryl-7-methylbenziodoxolones toward nucleophiles has been found and rationalized similarly to the "*ortho*-effect" previously

dx.doi.org/10.1021/jo400212u | *J. Org. Chem.* 2013, 78, 3767–3773

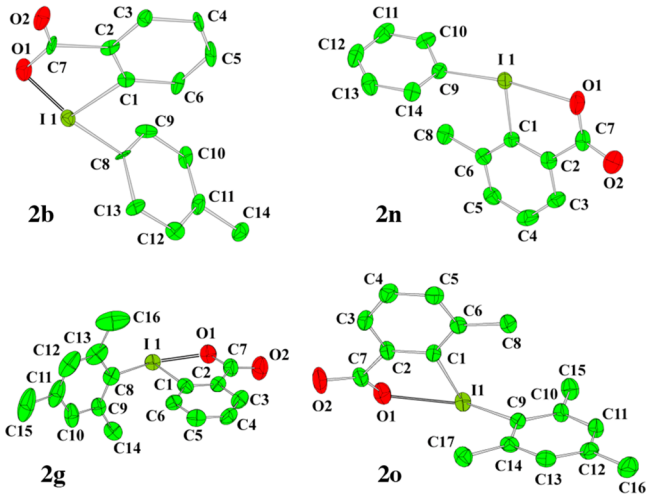
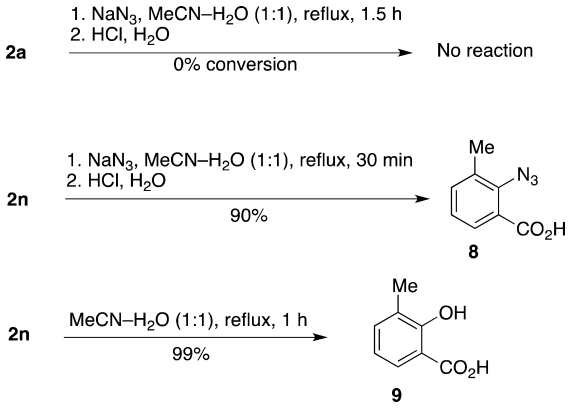


Figure 1. Perspective view of 1-arylbenziodoxolones **2b**, **2g**, **2n**, and **2o** with 50% ellipsoid probability. Selected distances (Å) and angles (deg) for **2b** (two independent molecules in the unit cell): I(1)−C(1) 2.126(7), 2.135(6); I(1)−O(1) 2.518(5), 2.509(5); I(1)−C(8) 2.115(5), 2.113(6); C(8)−I(1)−O(1) 164.01(19), 165.2(2); C(1)−I(1)−C(8) 91.3(2), 93.5(3). **2g**: I(1)−C(1) 2.130(10); I(1)−O(1) 2.491(7); I(1)−C(8) 2.096(10); C(8)−I(1)−O(1) 166.8(3); C(1)−I(1)−C(8) 93.4(4). **2n** (three independent molecules in the unit cell): I(1)−C(1) 2.151(4), 2.151(4), 2.154(4); I(1)−O(1) 2.494(3), 2.482(3), 2.471(3); I(1)−C(9) 2.123(4), 2.127(4), 2.129(4); C(9)−I(1)−O(1) 169.60(16), 167.52(15), 170.46(17); C(1)−I(1)−C(9) 99.90(17), 98.10(17), 100.13(17). **2o** (four independent molecules in the unit cell): I(1)−C(1) 2.136(5), 2.126(4), 2.141(5), 2.142(4); I(1)−O(1) 2.566(3), 2.595(4), 2.503(4), 2.571(3); I(1)−C(9) 2.117(4), 2.118(5), 2.122(5),2.120(4); C(9)−I(1)−O(1) 160.24(14), 162.98(15), 164.87(16), 162.19(4); C(1)−I(1)−C(9) 100.05(16), 99.76(18), 101.74(18), 101.40(16).

Scheme 2. Reactions of 1-Phenylbenziodoxolones with Nucleophiles



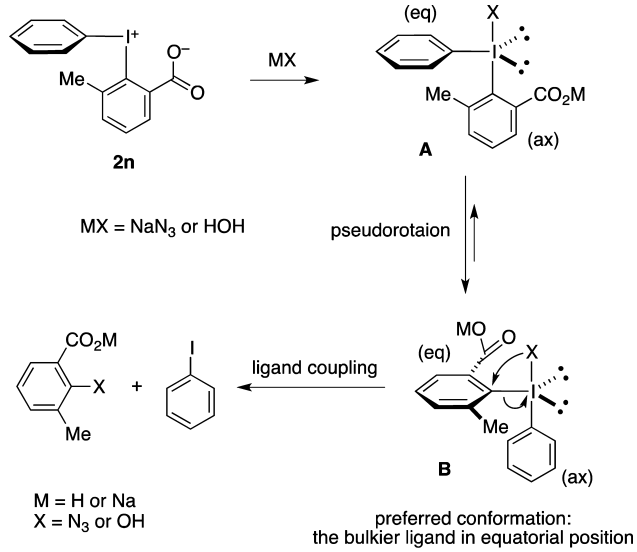
observed in the reactions of nonsymmetrical diaryliodonium salts with nucleophiles.

4. EXPERIMENTAL SECTION

2-Iodobenzoic acid, all aromatic precursors, and other reagents and solvents were from commercial sources and used without further purification from freshly opened containers. NMR spectra were recorded at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). Chemical shifts (δ) are reported in parts per million.

General Procedure for Preparation of 1-Arylbenziodoxolones (2a−o). The finely crushed, solid 2-iodobenzoic acid **1** or **7** (4.033 mmol) was mixed with powdered Oxone (1.5−1.6 g, 2.4−2.6 mmol)

Scheme 3. Explanation of Enhanced Reactivity of *Ortho*-Substituted Benziodoxolone 2n



in a 100 mL round-bottom flask and stirred without solvent for 5 min using a magnetic stirrer until a homogeneous reaction mass was formed. Then the reaction mixture was cooled with ice to 5 °C and, under magnetic stirring, precooled to 5 °C. H_2SO_4 (total 3.2 mL) was added via syringe by 0.2 mL portions to the center of the reaction mixture. After addition of each portion of H_2SO_4, the reaction mass was mechanically shaken to achieve better mixing; the color of the resulting mass can vary from pale yellow to brown depending on the intensity of mixing. After all H_2SO_4 was added, the magnetic stirring was continued for 30 min at room temperature, the mixture was cooled to 5 °C, and CH_2Cl_2 (4 mL) and ArH (4.0−11.0 mmol) were added. The magnetic stirring of the resulting mixture was continued at 5 °C for 1 h and then at room temperature for 2 h. The reaction mixture was recooled to 5 °C and CH_2Cl_2 (10 mL), and then a saturated aqueous solution of $NaHCO_3$ was added in small portions until pH 8.0. The organic layer was separated, and the aqueous layer was additionally extracted with CH_2Cl_2 (10 mL). The organic extracts were combined and dried with Na_2SO_4, the solvent was evaporated, and the crystalline product was dried in vacuum. Additional purification of products **2** can be performed by crystallization from water.

1-Phenyl-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2a). The reaction of 2-iodobenzoic acid **1** (1.00 g, 4.033 mmol), Oxone (1.6 g, 2.6 mmol), H_2SO_4 (total 3.2 mL), and benzene (0.8 mL) according to the general procedure afforded 1.27 g (92%) of crude product **2a**, isolated as an off-white crystalline solid, which was further purified by crystallization from water to give 1.21 g (88%) of 1-phenyl-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one monohydrate: mp 221−222 °C (from water) (lit.[5a] mp 220 °C of monohydrate); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.36 (dd, J = 1.5, 7.5 Hz, 1 H), 7.99 (dd, J = 1.0, 7.5 Hz, 2 H), 7.73 (m, 1 H), 7.57 (m, 2 H), 7.52 (m, 1 H), 7.35 (ddd, J = 1.5, 7.0, 8.5 Hz, 1 H), 6.72 (d, J = 8.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.8, 137.2, 133.5, 133.4, 132.5, 132.4, 131.7, 130.4, 126.4, 115.7, 115.4.

1-(4-Methylphenyl)-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2b). The reaction of 2-iodobenzoic acid **1** (248 mg, 1.0 mmol), Oxone (400 mg, 0.65 mmol), H_2SO_4 (total 0.8 mL), and toluene (0.2 mL) according to the general procedure afforded 288 mg (81%) of product **2b** monohydrate, isolated as off-white crystals: mp 217−219 °C (from water); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.36 (dd, J = 1.5, 7.5 Hz, 1 H), 7.88 (d, J = 8.0 Hz, 2 H), 7.53 (m, 1 H), 7.38 (m, 3 H), 6.76 (d, J = 8.5 Hz, 1 H), 2.50 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.7, 143.6, 137.2, 133.5, 133.4, 132.7, 132.6, 130.6, 126.1, 115.6, 111.1, 21.8. Anal. Calcd for $C_{14}H_{13}IO_3$: C, 47.21; H, 3.68; I, 35.63. Found: C, 47.23; H, 3.59; I, 35.66. Single crystals of product **2b** suitable for X-ray crystallographic analysis were obtained by slow crystallization from water. For details on crystal structure of compound **2b** see the CIF file in Supporting Information.

dx.doi.org/10.1021/jo400212u | J. Org. Chem. 2013, 78, 3767−3773

1-(4-Propylphenyl)-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2c). The reaction of 2-iodobenzoic acid **1** (248 mg, 1.0 mmol), Oxone (400 mg, 0.65 mmol), H_2SO_4 (total 0.8 mL), and propylbenzene (0.2 mL) according to the general procedure afforded 353 mg (94%) of product **2c**·$^1/_2H_2O$, isolated as off-white crystals: mp 180−182 °C (from water); ^{1}H NMR (CD_3OD, 500 MHz) δ 8.24 (dd, J = 1.5, 7.5 Hz, 1 H), 8.03 (d, J = 8.0 Hz, 2 H), 7.60 (m, 1 H), 7.47 (m, 3 H), 6.84 (dd, J = 1.0, 8.5 Hz, 1 H), 2.75 (t, J = 7.5 Hz, 2 H), 1.72 (sep, J = 7.5 Hz, 2 H), 1.00 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (CD_3OD, 125 MHz) δ 170.1, 149.8, 138.8, 135.3, 134.6, 133.9, 133.4, 131.9, 128.8, 116.3, 112.1, 39.0, 25.6, 14.2. Anal. Calcd for $C_{16}H_{15}IO_2$·$^1/_2H_2O$: C, 51.22; H, 4.53; I, 33.82. Found: C, 51.07; H, 4.24; I, 33.90.

1-(4-*tert*-Butylphenyl)-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2d). The reaction of 2-iodobenzoic acid **1** (248 mg, 1.0 mmol), Oxone (400 mg, 0.65 mmol), H_2SO_4 (total 0.8 mL), and *tert*-butylbenzene (0.2 mL) according to the general procedure afforded 312 mg (82%) of product **2d**, isolated as off-white crystals: mp 233.5−234 °C (from water) (lit.[5d] mp 248 °C); ^{1}H NMR (CD_3OD, 500 MHz) δ 8.27 (dd, J = 1.5, 7.5 Hz, 1 H), 8.05 (d, J = 8.5 Hz, 2 H), 7.71 (d, J = 8.5 Hz, 2 H), 7.63 (ddd, J = 1.0, 7.5 Hz, 1 H), 7.50 (m, 1 H), 6.87 (dd, J = 1.0, 8.5 Hz, 1 H), 1.41 (s, 9 H); ^{13}C NMR (CD_3OD, 125 MHz) δ 170.0, 158.3, 138.6, 134.8, 133,5, 131.91, 131.90, 131.89, 130.4, 128.8, 116.3, 112.1, 36.4, 31.6. Anal. Calcd for $C_{17}H_{17}IO_2$: C, 53.70; H, 4.51; I, 33.38. Found: C, 53.85; H, 4.46; I, 33.43.

1-(4-Octylphenyl)-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2e). The reaction of 2-iodobenzoic acid **1** (248 mg, 1.0 mmol), Oxone (400 mg, 0.65 mmol), H_2SO_4 (total 0.8 mL), and octylbenzene (0.25 mL, 1.13 mmol) according to the general procedure afforded 396 mg (89%) of product **2e**·$^1/_2H_2O$, isolated as off-white crystals: mp 123−124 °C (from water); ^{1}H NMR (CD_3OD, 500 MHz) δ 8.27 (d, J = 7.5 Hz, 1 H), 8.03 (d, J = 6.5 Hz, 2 H), 7.64 (m,1 H), 7.49 (m, 3 H), 6.86 (d, J = 8.5 Hz, 1 H), 2.78 (t, J = 7.5 Hz, 2 H), 1.70 (m, 2 H),1.34 (m, 10H), 0.91 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (CD_3OD, 125 MHz) δ 170.2, 150.2, 138.8, 135.4, 134.6, 133.4, 133.3, 131.9, 128.9, 116.3, 112.0, 37.0, 33.2, 32.5, 30.7, 30.54, 30.49, 23.9, 14.6. Anal. Calcd for $C_{21}H_{25}IO_2$·1/2H_2O: C, 56.63; H, 5.90; I, 28.49. Found: C, 56.30; H, 6.11; I, 27.85.

1-(4-Tridecylphenyl)-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2f). The reaction of 2-iodobenzoic acid **1** (248 mg, 1.0 mmol), Oxone (400 mg, 0.65 mmol), H_2SO_4 (total 0.8 mL) and 1-phenyltridecane (0.30 mL, 1.01 mmol) according to the general procedure afforded 443 mg (86%) of product **2f**·$^1/_2H_2O$, isolated as off-white crystals: mp 126−127 °C (from water); ^{1}H NMR (CD_3OD, 500 MHz) δ 8.28 (dd, J = 1.5, 7.5 Hz, 1 H), 8.03 (d, J = 8.0 Hz, 2 H), 7.64 (ddd, J = 1.0, 7.5, 8.0 Hz,1 H), 7.49 (m, 3 H), 6.87 (d, J = 8.0 Hz, 1 H), 2.78 (t, J = 7.5 Hz, 2 H), 1.71 (m, 2 H), 1.34 (m, 20 H), 0.90 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (CD_3OD + $CDCl_3$, 125 MHz) δ 169.9, 149.94, 149.93, 138.5, 133.19, 133.18, 131.75, 131.74, 128.6, 116.1, 111.4, 36.9, 33.0, 32.2, 30.69, 30.67, 30.63, 30.6, 30.44, 30.38, 30.37, 30.2, 23.7, 14.6. Anal. Calcd for $C_{26}H_{35}IO_2$·$^1/_2H_2O$: C, 60.58; H, 7.04; I, 24.62. Found: C, 60.92; H, 6.94; I, 24.52.

1-(2,4,6-Trimethylphenyl)-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2g). The reaction of 2-iodobenzoic acid **1** (248 mg, 1.0 mmol), Oxone (400 mg, 0.65 mmol), H_2SO_4 (total 0.8 mL), and 1,3,5-trimethylbenzene (0.15 mL, 1.1 mmol) according to the general procedure afforded 300 mg (78%) of product **2g** monohydrate, isolated as off-white crystals: mp 223−223.5 °C (from water) (lit.[5a] mp 213−214 °C); ^{1}H NMR (CD_3OD, 500 MHz) δ 8.31 (dd, J = 1.5, 7.5 Hz, 1 H), 7.66 (m, 1H), 7.49 (ddd, J = 1.5, 7.0, 9.0 Hz), 1H), 7.29 (s, 2H), 6.79 (d, J = 8.5 Hz, 1 H), 2.53 (s, 6H), 2.43 (s, 3 H); ^{13}CNMR (CD_3OD, 125 MHz) δ 170.2, 145.7, 145.0, 135.7, 135.4, 133.9, 132.2, 131.0, 127.5, 120.4, 114.3, 26.6, 21.4. Single crystals of product **2g** suitable for X-ray crystallographic analysis were obtained by slow crystallization from water. For details on crystal structure of compound **2g** see the CIF in the Supporting Information.

1-(2,3,5,6-Tetramethylphenyl)-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2h). The reaction of 2-iodobenzoic acid **1** (248 mg, 1.0 mmol), Oxone (400 mg, 0.65 mmol), and H_2SO_4 (total 0.8 mL) was performed according to the general procedure. Then a solution of 1,2,4,5-tetramethylbenzene (140 mg, 1.05 mmol) in 2.0 mL of CH_2Cl_2 was added by 0.1 mL portions and stirred at 5 °C for 30 min; a change of the color to dark cherry was observed. After that, 5.0 mL of CH_2Cl_2 was added, and the organic layer was separated from aqueous acidic solution. The treatment of organic layer according to general procedure afforded 156 mg (40%) of product **2h**·$^1/_2H_2O$, isolated as off-white crystals: mp 221.5−222.5 °C (from water); ^{1}H NMR (CD_3OD, 500 MHz) δ 8.31 (dd, J = 1.5, 7.5 Hz, 1 H), 7.66 (ddd, J = 0.5, 1.0, 7.5 Hz, 1 H), 7.48 (ddd, J = 1.0, 1.5, 6.5 Hz 1 H), 7.37 (s, 1H), 6.80 (dd, J = 1.0, 8.5 Hz, 1 H), 2.51 (s, 6 H), 2.41 (s, 6 H); ^{13}C NMR (CD_3OD, 125 MHz) δ 170.2, 140.4, 138.0, 137.7, 135.7, 135.4, 133.8, 132.1, 128.0, 126.6, 114.4, 24.1, 21.6. Anal. Calcd for $C_{17}H_{17}IO_2$•1/2H_2O: C, 52.46; H, 4.66; I, 32.60. Found: C, 52.43; H, 4.68; I, 32.85.

1-(4-Chlorophenyl)-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2i). The reaction of 2-iodobenzoic acid **1** (248 mg, 1.0 mmol), Oxone (400 mg, 0.65 mmol), H_2SO_4 (total 0.8 mL) and chlorobenzene (0.20 mL, 1.97 mmol) according to the general procedure afforded 215 mg (57%) of product **2i** monohydrate, isolated as off-white crystals: mp 226−226.5 °C (from water); ^{1}H NMR (CD_3OD, 500 MHz) δ 8.26 (dd, J = 1.5, 8.0 Hz, 1 H), 8.13 (d, J = 8.5 Hz, 2 H), 7.65 (m, 3 H), 7.53 (m, 1 H), 6.89 (d, J = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 167.3, 139.1, 138.8, 133.5, 132.4, 132.0, 130.4, 126.7, 116.2, 113.8. Anal. Calcd for $C_{13}H_{10}ClIO_3$: C, 41.46; H, 2.68; I, 33.70. Found: C, 41.56; H, 2.54; I, 33.82.

1-(4-Bromophenyl)-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2j). The reaction of 2-iodobenzoic acid **1** (248 mg, 1.0 mmol), Oxone (400 mg, 0.65 mmol), H_2SO_4 (total 0.8 mL), and bromobenzene (0. Twenty mL, 1.91 mmol) according to the general procedure afforded 350 mg (83%) of product **2j** monohydrate, isolated as off-white crystals: mp 222−222.5 °C (from water); ^{1}H NMR (CD_3OD, 500 MHz) δ 8.25 (dd, J = 1.5, 7.5 Hz, 1 H), 8.03 (d, J = 8.5 Hz, 2 H), 7.80 (d, J = 8.5 Hz, 2 H), 7.62 (m, 1 H), 7.51 (m, 1 H), 6.88 (d, J = 8.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 170.0, 140.4, 136.3, 135.5, 134.6, 133.4, 132.0, 129.0, 128.8, 116.3, 114.7. Anal. Calcd for $C_{13}H_{10}BrIO_3$: C, 37.09; H, 2.39; I, 30.14. Found: C, 37.02; H, 2.24; I, 29.92.

1-(4-Iodophenyl)-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2k). The reaction of 2-iodobenzoic acid **1** (248 mg, 1.0 mmol), Oxone (400 mg, 0.65 mmol), H_2SO_4 (total 0.8 mL), and iodobenzene (0. Fifteen mL, 1.35 mmol) according to the general procedure afforded 428 mg (91%) of product **2k**, isolated as off-white crystals: mp 224−225.5 °C (from water); ^{1}H NMR (CD_3OD, 500 MHz) δ 8.27 (dd, J = 1.5, 7.5 Hz, 1 H), 8.02 (d, J = 8.5 Hz, 2 H), 7.88 (d, J = 8.5 Hz, 2 H), 7.65 (m, 1 H), 7.54 (ddd, J = 1.5, 6.0, 8.5 Hz, 1 H), 6.90 (d, J = 8.5 Hz, 1 H); ^{13}C NMR (CD_3OD, 125 MHz) 170.2, 142.4, 140.2, 135.6, 134.4, 133.4, 132.0, 129.1, 116.3, 115.4, 101.2. Anal. Calcd for $C_{13}H_8I_2O_2$: C, 34.70; H, 1.79; I, 56.40. Found: C, 34.76; H, 1.59; I, 56.67.

1-(4-(4-Carboxybutyl)phenyl)-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2l). The reaction of 2-iodobenzoic acid **1** (248 mg, 1.0 mmol), Oxone (400 mg, 0.65 mmol), H_2SO_4 (total 0.8 mL), and 5-phenylpentanoic acid (178 mg, 1.0 mmol) in 1.0 mL CH_2Cl_2 was carried out according to the general procedure. The isolation of the product was performed by the following workup: the reaction mixture was neutralized by $NaHCO_3$ to pH 6.0, the precipitate was filtered, washed with water, and dried to afford 352 mg (83%) of product **2l**, isolated as off-white crystals: mp 234.5−235.5 °C (from water); ^{1}H NMR (CD_3OD, 500 MHz) δ 8.28 (dd, J = 2.0, 8.5 Hz, 1 H), 8.02 (m, 2 H), 7.63 (m, 1 H), 7.49 (m, 3 H), 6.87 (d, J = 7.55 Hz, 1 H), 2.81 (t, J = 7.5 Hz, 2 H), 2.35 (t, J = 7.5 Hz, 2 H), 1.76 (m, 2 H), 1.68 (m, 2 H); ^{13}C NMR (CD_3OD, 125 MHz) 177.3, 170.1, 149.7, 138.9, 135.3, 134.8, 133.4, 133.3, 131.9, 128.8, 116.3, 112.3, 36.6, 34.8, 31.7, 25.7. Anal. Calcd for $C_{18}H_{17}IO_4$: C, 50.96; H, 4.04; I, 29.91. Found: C, 50.92; H, 4.02; I, 29.91.

1-(4-(4-(Methoxycarbonyl)butyl)phenyl)-1*H*-1λ^3-benzo[*b*]-iodo-3(2*H*)-one (2m). The reaction of 2-iodobenzoic acid **1** (248 mg, 1.0 mmol), Oxone (400 mg, 0.65 mmol), H_2SO_4 (total 0.8 mL), and methyl-5-phenylpentanoate (215 mg, 1.12 mmol) in 1.0 mL CH_2Cl_2 according to the general afforded 406 mg (89%) of product **2m**·$^1/_2H_2O$, isolated as off-white crystals: mp 132.5−134 °C (from water); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.43 (dd, J = 1.5, 7.5 Hz, 1 H), 7.91 (d, J = 8.0 Hz, 2 H), 7.59 (m, 1 H), 7.43 (m, 3 H), 6.80 (d, J = 8.5 Hz, 1 H), 3.69 (s, 3 H), 2.76 (t, J = 7.0 Hz, 2 H), 2.38 (t, J = 6.5 Hz, 2 H), 1.73 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 173.8, 167.7, 148.1, 137.4, 134.3, 133.0, 132.2, 130.8, 126.6, 115.4, 110.2, 51.6, 35.6, 33.7, 30.4, 24.5. Anal. Calcd

dx.doi.org/10.1021/jo400212u | J. Org. Chem. 2013, 78, 3767−3773

for $C_{19}H_{21}IO_4 \cdot {}^1/_2H_2O$: C, 51.02; H, 4.51; I, 28.37. Found: C, 50.87; H, 4.43; I, 28.45.

1-Phenyl-7-methyl-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2n). The reaction of 2-iodo-3-methylbenzoic acid 7 (262 mg, 1.0 mmol), Oxone (400 mg, 0.65 mmol), H_2SO_4 (total 0.8 mL), and benzene (0.4 mL) according to the general procedure afforded 270 mg of product **2n** as dark brown solid. Treatment of this solid with activated carbon in boiling water afforded 185 mg (52%) of product **2n** monohydrate, isolated as off-white crystals: mp 170−172 °C (from water); ^{1}H NMR (CD_3OD, 500 MHz) δ 8.10 (m, 2 H), 7.98 (dd, J = 1.5, 7.5 Hz, 1 H), 7.67 (m, 1 H), 7.51 (m, 3 H), 7.43 (dd, J = 0.5, 7.5 Hz, 1 H), 2.03 (s, 3 H); ^{13}C NMR (CD_3OD, 125 MHz) δ 171.5, 142.4, 140.7, 137.3, 136.9, 133.3, 132.8, 132.5, 131.0, 119.6, 118.0, 25.4. Anal. Calcd for $C_{14}H_{13}IO_3$: C, 47.21; H, 3.68; I, 35.63. Found: C, 47.38; H, 3.65; I, 35.72. Single crystals of product **2n** suitable for X-ray crystallographic analysis were obtained by slow crystallization from water. For details on the crystal structure of compound **2n**, see the CIF in the Supporting Information.

1-(2,4,6-Trimethylphenyl)-7-methyl-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one (2o). The reaction of 2-iodo-3-methylbenzoic acid 7 (314 mg, 1.2 mmol), Oxone (412 mg, 0.67 mmol), H_2SO_4 (total 0.85 mL), and 1,3,5-trimethylbenzene (0.2 mL, 1.44 mmol) according to the general procedure afforded 360 mg of product **2o** as a dark brown solid. Treatment of this solid with activated carbon in boiling water afforded 282 mg (62%) of **1o**, isolated after crystallyzation from water as off-white crystals: mp 148.5−150.5 °C (from water/methanol); ^{1}H NMR (CD_3OD, 500 MHz) δ 8.06 (d, J = 0.5 Hz, 1 H), 7.52 (m, 1 H), 7.41 (d, J = 7.5 Hz, 1 H), 7.18 (s, 2 H), 2.50 (s, 6 H), 2.37 (s, 3 H), 1.86 (s, 3 H); ^{13}C NMR (CD_3OD, 125 MHz) δ 171.2, 145.2, 144.0, 142.1, 140.1, 137.5, 132.1, 131.7, 131.1, 122.6, 118.3, 26.7, 23.5, 21.2. Anal. Calcd for $C_{17}H_{17}IO_2$: C, 53.70; H, 4.51; I, 33.38. Found: C, 53.75; H, 4.48; I, 33.61. Single crystals of product **2o** suitable for X-ray crystallographic analysis were obtained by slow crystallization from water/methanol. For details on the crystal structure of compound **2o**, see the CIF in the Supporting Information.

Reaction of 1-Phenyl-7-methyl-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one 2n with Sodium Azide. Benziodoxolone **2n** (34 mg, 0.1 mmol) and NaN_3 (33 mg, 0.5 mmol) were mixed with acetonitrile (0.4 mL) and water (0.4 mL), and the resulting mixture was refluxed under stirring for 30 min. Then the reaction mixture was cooled, and 2.0 mL of 5% aqueous solution of $NaHCO_3$ was added. Resulting mixture was extracted with hexane (3−4 mL) in order to remove the byproduct PhI. The aqueous solution was acidified by a 5% hydrochloric acid, which resulted in precipitation of 2-azido-3-methylbenzoic acid **8**, which was isolated by filtration as off-white crystals: 16 mg (90%); mp 151.5−153 °C dec (lit.[14] mp 155 °C dec); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.92 (d, J = 8.0 Hz, 1 H), 7.40 (d, J = 7.5 Hz, 1 H), 7.18 (t, J = 7.5 Hz, 1 H), 2.38 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.4, 139.6, 136.1, 134.0, 130.7, 125.5, 123.3, 18.5.

Reaction of 1-Phenyl-7-methyl-1*H*-1λ^3-benzo[*b*]iodo-3(2*H*)-one 2n with Water. Benziodoxole **2n** (34 mg, 0.1 mmol) was mixed with acetonitrile (0.4 mL) and water (0.4 mL), and the resulting mixture was refluxed under stirring for 1 h. Then the reaction mixture was cooled, and 2.0 mL of 5% aqueous solution of $NaHCO_3$ was added. The resulting mixture was extracted with hexane (3−4 mL) in order to remove the byproduct PhI. The aqueous solution was acidified by a 5% hydrochloric acid, which resulted in precipitation of 3-methylsalicylic acid **9**, isolated by filtration as white crystals: 15 mg (99%); mp 161.5−162 °C (lit.[15] mp 161−162 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.62 (s, 1H), 7.78 (dd, J = 1.0 Hz, 8.0 Hz, 1 H), 7.39 (d, J = 7.5 Hz, 1 H), 6.84 (t, J = 7.5 Hz, 1 H), 2.29 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 175.5, 160.9, 138.0, 128.7, 127.1, 119.1, 110.7, 15.8.

■ ASSOCIATED CONTENT

Supporting Information

X-ray data for compounds **2b**, **2g**, **2n**, and **2o** (CIF) and copies of NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by research grants from the National Science Foundation (Nos. CHE-1009038 and 1262479). M.S.Y. and V.V.Z. are also thankful to the Government of Russia for support of their cooperative research program (FCP, GK11.519.11.5010, Zayavka 2011-1.9-519-024-070, Russian Foundation for Basic Research No. 12-03-00978-a, and a Grant from the Government of Russia 2012-220-03-9803).

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