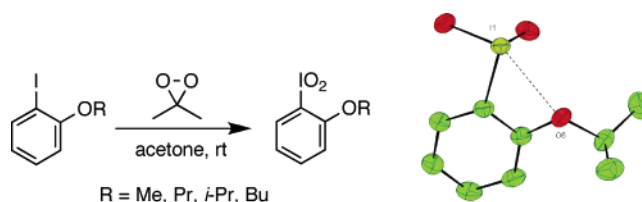# JOC Article

# 2-Iodylphenol Ethers: Preparation, X-ray Crystal Structure, and Reactivity of New Hypervalent Iodine(V) Oxidizing Reagents

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2-Iodylphenol ethers were prepared by the dimethyldioxirane oxidation of the corresponding 2-iodophenol ethers and isolated as chemically stable, microcrystalline products. Single-crystal X-ray diffraction analysis of 1-iodyl-2-isopropoxybenzene **8c** and 1-iodyl-2-butoxybenzene **8d** revealed pseudopolymeric arrangements in the solid state formed by intermolecular interactions between $IO_2$ groups of different molecules. 2-Iodylphenol ethers can selectively oxidize sulfides to sulfoxides and alcohols to the respective aldehydes or ketones.

## Introduction

Oxidizing reagents are essential components of the modern organic synthetic methodology. The selective oxidation of alcohols to the corresponding carbonyl compounds, as well as selective oxidation of sulfides to sulfoxides and other oxidative transformations, often represents the essential steps in the total synthesis of complex natural products. During the past decade, hypervalent iodine compounds have attracted significant interest as mild, selective, and environmentally benign oxidizing reagents in organic chemistry.[1] Particularly usefuls oxidizers are the pentavalent iodine compounds, namely, 1-hydroxy-(1*H*)-benzo-1,2-iodoxol-3-one 1-oxide (2-iodoxybenzoic acid, IBX, **1**) and its acetylation product, Dess—Martin periodinane (DMP, **2**), which are now employed extensively in organic synthesis

as mild and highly selective reagents for the oxidation of alcohols to carbonyl compounds as well as for a variety of other synthetically useful oxidative transformations.[2a,b] However, the explosive character and low solubility of IBX in common organic solvents except DMSO, combined with the susceptibility of DMP to moisture and prolonged storage,[2c] restrict practical application of these reagents.

The low solubility of IBX **1** arises from strong intermolecular secondary I···O contacts, hydrogen bonding, and $\pi$-stacking observed for IBX in solid state.[3] Several research groups have tried to overcome this preparative limitation by performing oxidation at elevated temperatures,[4a] using an ionic liquid and water as a reaction medium,[4b] or functionalizing IBX aromatic core.[4c] Also, several solid-supported reagents in which the IBX scaffold is linked to a polymer have been reported.[5] Another

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fruitful approach initially proposed by Protasiewicz[6] consists of incorporation of an ortho substituent into iodylarene (e.g., sulfone), thus resulting in intramolecular secondary bonding. This ortho stabilization leads to a partial disruption of the polymeric network and consequently enhances solubility. More recently, investigations from our group have resulted in a series of stable and soluble IBX analogues: IBX-amides **3**,[7a] IBX-esters **4**,[7b] as well as 2-iodylsulfonamides[7c] and 2-iodylsulfonate esters.[7d] According to X-ray data, a planar pseudobenziodoxole moiety due to the intramolecular nonbonding iodine−oxygen interaction is a key structural feature present in this series of compounds.[7] Readily available hypervalent iodine reagents **3** and **4** possess reactivity similar to IBX and DMP and proved to be useful oxidizing reagents toward alcohols[7] and sulfides.[8] The synthesis of polymer supported IBX esters and amides has been reported as well.[9] Recently, we have reported on the preparation and oxidative properties of *N*-(2-iodylphenyl)-acylamides (NIPA, **5**), which are soluble and stable IBX analogues having a pseudobenziodoxazine structure.[10]

**1 (IBX)**  **2 (DMP)**

**3 (IBX-amides)**  **4 (IBX-esters)**  **5 (NIPA)**
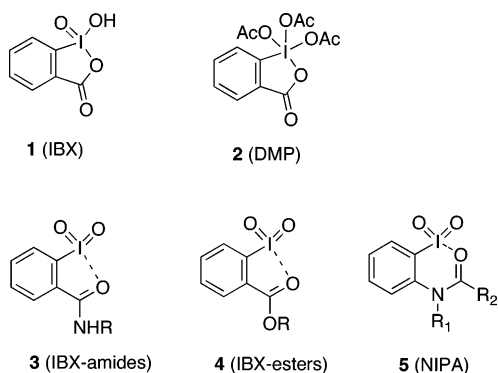
To further explore the effects of ortho substituents, we considered the development and investigation of iodylarenes based on the readily available ethers of 2-iodophenol. Two examples of these compounds, the methyl and ethyl ethers of 2-iodylphenol, were previously reported more than 40 years ago.[11] In these old publications,[11] however, the structure and chemical reactivity of these compounds were not described. Here, we present the synthesis and X-ray structural study of a series of new 2-iodylphenol ethers (**8**, see Scheme 2) and demonstrate that these compounds are potent oxidizing reagents toward alcohols and organic sulfides.

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**SCHEME 1**

**SCHEME 2**

**a**: R = Me (75%)
**b**: R = Pr (89%)
**c**: R = *i*-Pr (76%)
**d**: R = Bu (90%)
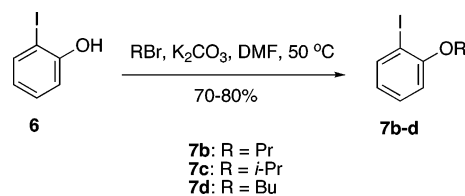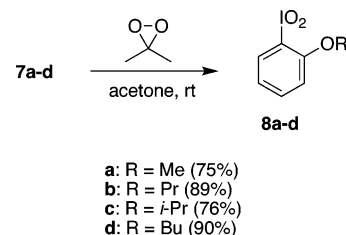
## Results and Discussion

The starting 2-iodophenol ethers **7b**−**d** were prepared by a known procedure[12] from 2-iodophenol **6** and the respective alkyl bromides (Scheme 1), while the methyl ether of 2-iodophenol (**7a**) was purchased from commercial sources.

Phenol ethers **7a**−**d** were then oxidized with dimethyldioxirane to afford 2-iodylphenol ethers **8** in good yields (Scheme 2). Our attempts to use oxidants other than dimethyldioxirane oxidizers (e.g., sodium hypochlorite or Oxone) for this oxidation were unsuccessful.

Products **8** were isolated by filtration of the reaction mixture as white, stable, microcrystalline compounds and were analyzed by NMR spectroscopy, elemental analysis, high-resolution mass spectrometry, and for compounds **8c** and **8d**, by X-ray crystallography. In particular, ^{13}C NMR spectra of products **8** showed the signals of the ipso carbon, C−I, at about 138 ppm, as well as signals corresponding to the carbon in the ortho position, C−O, at about 156 ppm. Compounds **8b** and **8d** were found to be soluble in various solvents, while products **8a** and **8c** appeared to be almost insoluble in any nonpolar organic solvents. It should be noted that compared to IBX all compounds **8** are nonexplosive at the temperatures close to their melting point.

Molecular structures of compounds **8c** and **8d** have been determined by single-crystal X-ray crystallography. The CAM-ERON diagrams of **8c** and **8d** are presented in Figures 1 and 2, while selected metric parameters are listed in Table 1. Both structures revealed a pseudo-cyclic four-membered ring motif formed by close contact (2.881−2.930 Å) between the hyper-valent iodine center and the phenolic oxygen atom, which is smaller than sum of van der Waals radii of iodine and oxygen atoms (Figures 1 and 2).

The crystal packing in compounds **8c** and **8d** is shown in Figures 3 and 4. Examination of these data provides, in particular, a possible explanation of the observed significant difference in solubilities of these two compounds (product **8d** is soluble in various solvents, while **8c** is almost insoluble in any nonpolar organic solvents).

The crystal structure in both cases reveals polymeric-chain arrangements in the solid state formed by the strong intermolecular interactions between $IO_2$ groups of neighboring mol-

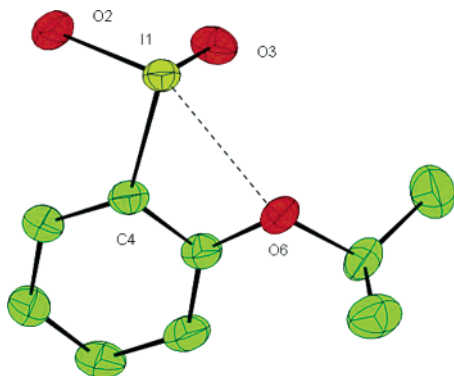(12) Furstner, A.; Davies, P. W.; Lehman, C. W. *Organometallics* **2005**, *24*, 4065.

**FIGURE 1.** CAMERON drawing of the molecule **8c** at the 50% probability level (all hydrogen atoms are omitted for clarity). Close contact within the molecule is shown with a dashed line.
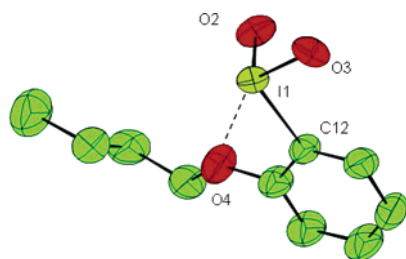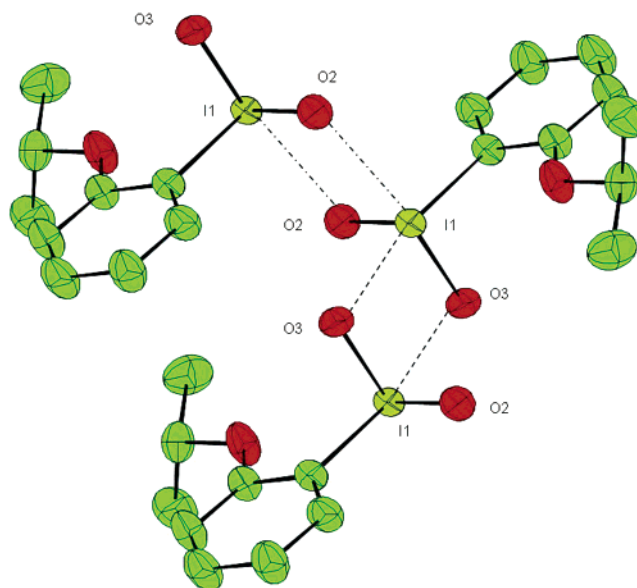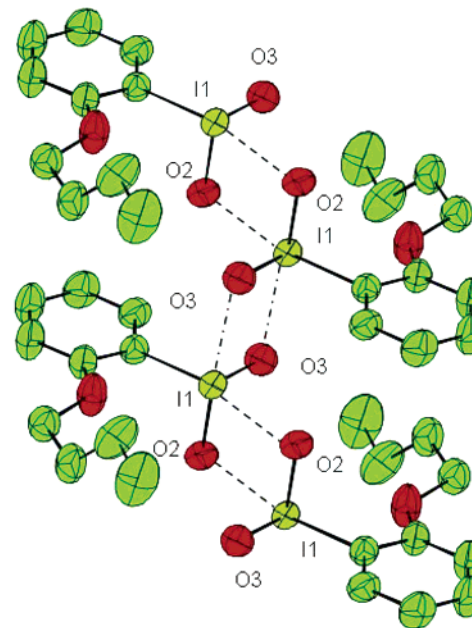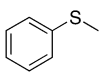


**FIGURE 2.** CAMERON drawing of the molecule **8d** at the 50% probability level (all hydrogen atoms are omitted for clarity). Close contact within the molecule is shown with a dashed line.
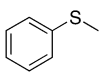
**TABLE 1. Selected Interatomic Distances and Bond Angles in Structures 8c and 8d**

| compound **8c** | | compound **8d** | |
|---|---|---|---|
| bond or bond angle | distance (Å) or angle (deg) | bond or bond angle | distance (Å) or angle (deg) |
| I1−C4 | 2.096 | I1−C12 | 2.108 |
| I1−O2 | 1.803 | I1−O2 | 1.793 |
| I1−O3 | 1.806 | I1−O3 | 1.792 |
| I1···O6 | 2.882 | I1···O4 | 2.931 |
| O2···I1 | 2.740 | O2···I1 | 2.759 |
| O3···I1 | 2.681 | O3···I1 | 2.899 |
| O2−I−O3 | 101.36 | O2−I−O3 | 103.00 |



**FIGURE 3.** CAMERON drawing of the polymeric chain formed by the molecules of **8c** at the 50% probability level (all hydrogen atoms are omitted for clarity). Close contacts between the molecules are shown with a dashed line.
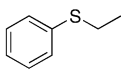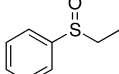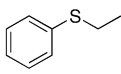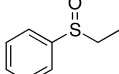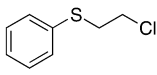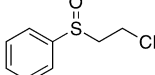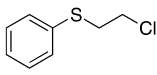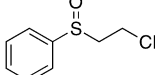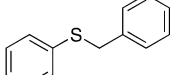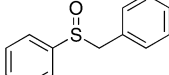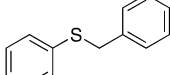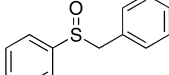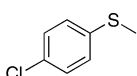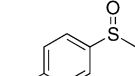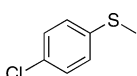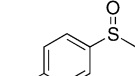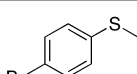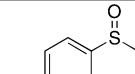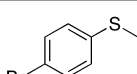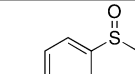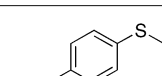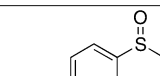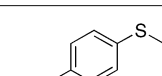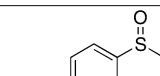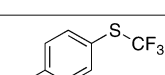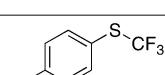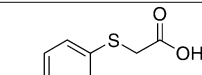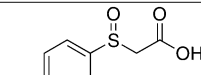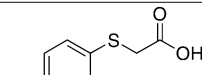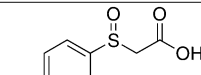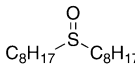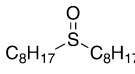


**FIGURE 4.** CAMERON drawing of polymeric chain formed by the molecules of **8d** at the 50% probability level (all hydrogen atoms are omitted for clarity). Close contacts between the molecules are shown with a dashed line.

ecules. According to HRMS experiments, these oligomeric chains also exist in the solution of compounds **8**, as indicated by the presence of $2M^+$ and $3M^+$ peaks in the mass spectra. The average intermolecular I···O distances in the crystal structure of the butyl ether **8d** are about 0.1 Å longer then those in the isopropyl ether of 2-iodylphenol **8c** (Table 1). The relatively weaker intermolecular interactions in the case of the butyl ether of 2-iodylphenol **8d** can be explained by the presence of the more flexible butyl group. The presence of the stronger intermolecular interactions in 2-iodylphenol ether **8c** compared to **8d** provides explanation for the better solubility of compound **8d**.

**Oxidations with 2-Iodylphenol Ethers.** To determine the scope of the reactivity of 2-iodylphenol ethers **8**, we have performed a set of oxidation reactions with organic sulfides and alcohols. To compare the influence of the crystal packing and solublility on the reactivity, the reagents **8c** and **8d** with known X-ray crystal structure were selected.

The oxidation of sulfides was carried out with 0.6 equiv of reagent **8** under conditions previously used in the similar

reactions of IBX-esters.[8] The oxidation proceeds smoothly under reflux in acetonitrile within several hours. To determine the scope and limitations of this procedure, we have oxidized a variety of sulfides using reagents **8c** and **8d** (Table 2). The reaction was found to be compatible with the presence of different substituted phenyl rings as well as benzylic carbons. The oxidation is limited to the sterically nonhindered sulfides, and thus, no reaction occurred with *tert*-butyl sulfide even after 48 h (entry 11). Likewise, the oxidation does not occur when

**TABLE 2. Oxidation of Sulfides to Sulfoxides with Reagents 8c and 8d[a]**

| Entry | Substrate | Product | Reagent | Yield (%) [b,c] | Time (h) |
|---|---|---|---|---|---|
| 1a | | | **8d** | 89 | 2 |
| 1b | | | **8c** | 95 | 5 |
| 2a | | | **8d** | 95 | 2 |
| 2b | | | **8c** | 85 | 7 |
| 3a | | | **8d** | 92 | 4 |
| 3b | | | **8c** | 89 | 7 |
| 4a | | | **8d** | 95 | 3 |
| 4b | | | **8c** | 80 | 5 |
| 5a | | | **8d** | 90 | 4 |
| 5b | | | **8c** | 86 | 6 |
| 6a | | | **8d** | 95 | 4 |
| 6b | | | **8c** | 98 | 8 |
| 7a | | | **8d** | 90 | 3.5 |
| 7b | | | **8c** | 90 | 3 |
| 8a | | No reaction[d] | **8d** | 0 | 48 |
| 8b | | | **8c** | 0 | 48 |
| 9a | | | **8d** | 70 | 3 |
| 9b | | | **8c** | 65 | 4 |
| 10a | | | **8d** | 80 | 5 |
| 10b | | | **8c** | 80 | 6 |
| 11a | | No reaction[d] | **8d** | 0 | 48 |
| 11b | | | **8c** | 0 | 48 |
| 12a | | | **8d** | 87 | 4 |
| 12b | | | **8c** | 82 | 6 |
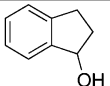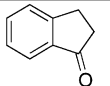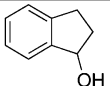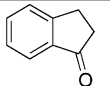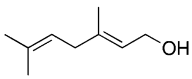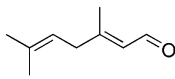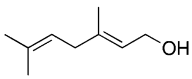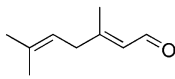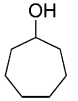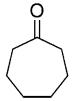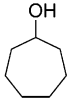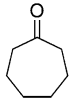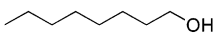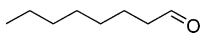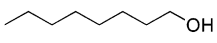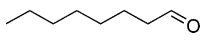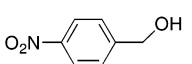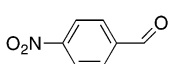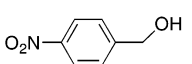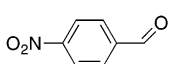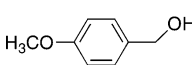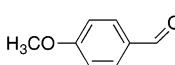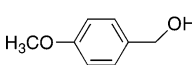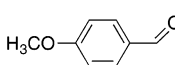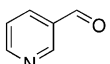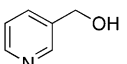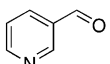
[a] All reactions were carried out under reflux conditions in acetonitrile using 0.6 equiv of reagent **8**. [b] All yields listed in the table are the yields of products isolated after column chromatography. [c] All products were identified by comparison of their NMR data with those reported in the literature. [d] No oxidation product was observed.

the strong electron-withdrawing moieties (e.g., CF$_3$ group) are present in the molecule (entry 8). No significant difference in reactivity between reagents **8c** and **8d** was observed in the oxidation of sulfides.

The reaction conditions for the oxidation of alcohols were optimized using indanol as substrate. Chloroform under reflux conditions was found to be the best solvent for this reaction. We have found, however, that this oxidation is very sensitive to the presence of traces of hydrochloric acid as an impurity in chloroform. The use of unpurified chloroform leads to the formation of indene due to the dehydration of indanol under reaction conditions. To avoid this side reaction, chloroform

**TABLE 3. Oxidation of Alcohols to Carbonyl Compounds with Reagents 8c and 8d[a]**

| Entry | Substrate | Product[b] | Reagent | Time (h) |
|---|---|---|---|---|
| 1a | | | 8d | 7 |
| 1b | | | 8c | 10 |
| 2a | | | 8d | 5.5 |
| 2b | | | 8c | 6 |
| 3a | | | 8d | 4.5 |
| 3b | | | 8c | 11 |
| 4a | | | 8d | 4 |
| 4b | | | 8c | 8 |
| 5a | | | 8d | 2.5 |
| 5b | | | 8c | 2.5 |
| 6a | | | 8d | 2.5 |
| 6b | | | 8c | 2.5 |
| 7a | | | 8d | 3 |
| 7b | | | 8c | 3 |

[a] All reactions were carried out under reflux conditions in chloroform using 1 equiv of reagent **8**. [b] Reaction mixtures were analyzed by GC−MS; only the indicated carbonyl compound was observed in each oxidation with conversion over 99%.

should be distilled and additionally purified by treatment with basic aluminum oxide. In other solvents, such as ethyl acetate, methylene chloride, and acetonitrile, the oxidation of indanol was extremely slow. A wide range of alcohols can be oxidized to the respective carbonyl compounds using reagents **8c** and **8d** in chloroform under reflux. It should be noted that the oxidation of benzylic and allylic alcohols proceeds fast and does not depend on the solubility of the hypervalent iodine reagent.

In contrast, the oxidation of saturated alcohols (e.g., cyclo-heptanol and *n*-octanol) proceeds noticeably slower, and the difference in solubilities between **8c** and **8d** starts to play a significant role, as indicated by the longer reaction time of the less soluble reagent **8c** (Table 3, entries 3 and 4). It should be also noted that this oxidation requires 1 equiv of the reagent **8**, and the trivalent iodine species **9** are formed as side products as confirmed by the NMR experiment (Scheme 3). In particular, the $^1H$ and $^{13}C$ NMR spectra of the reaction mixture from the oxidation of ethanol with reagent **8d** in CDCl$_3$ clearly show the disappearance of the *C*-IO$_2$ signal at 135.6 ppm corresponding to the reagent **8d** and the emergence of the signal at 133.3 ppm of the *C*-IO carbon in trivalent iodine derivative **9** (Ar = 2-BuOC$_6$H$_4$). Further heating of the reaction mixture leads to the extremely slow disproportionation of the trivalent iodine species **9** (around 1% conversion over 24 h) with the formation of compounds **8** and **7**.

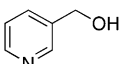To estimate the selectivity of oxidations with reagents **8**, we investigated the reactions of substrates containing both sulfide and hydroxyl functional groups. Two alcohols were tested in
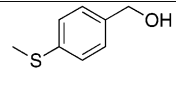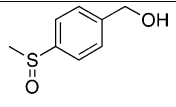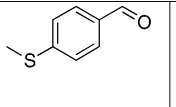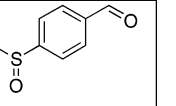
**SCHEME 3**
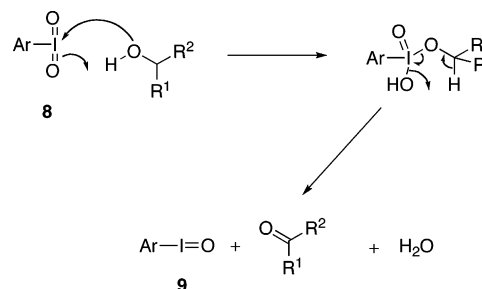
these experiments: 4-(methylthio)benzyl alcohol and 2-(phen-ylthio)ethanol. The reactions were carried out in both chloroform and acetonitrile, and the product ratio was determined by $^1H$ NMR spectroscopy or preparative TLC. In the case of 4-(meth-ylthio)benzyl alcohol, all three possible products of oxidation were detected in the reaction mixture, as well as a small amount of the starting material (Table 4). It should be noted that the results obtained for both solvents are qualitatively similar; however, in acetonitrile the sulfoxide was a major product of the reaction while in chloroform both aldehyde and sulfoxide were detected in approximately equal amounts.

Similar results were obtained from the oxidation of 2-(phen-ylthio)ethanol (Table 5). The reactions in both acetonitrile and chloroform afforded sulfoxide as a major product and aldehyde as a minor product.

**TABLE 4. Oxidation of 4-(Methylthio)benzyl Alcohol with Reagent 8d**

| Solvent/ product (%)[a] | | | | |
|---|---|---|---|---|
| Acetonitrile[b] | 6 | 46 | 32 | 16 |
| Chloroform[c] | 2 | 39 | 34 | 25 |

[a] The ratio of the products was determined by ^{1}H NMR spectroscopy based on the integral intensity of signals corresponding to the methyl groups. [b] The reaction was stopped after refluxing the solution of substrate and reagent **8d** (1 equiv) in MeCN for 15 h. [c] The reaction was stopped after refluxing the solution of substrate and reagent **8d** (1 equiv) in chloroform for 3 h.

**TABLE 5. Oxidation of 2-(Phenylthio)ethanol with the Reagent 8d**

| Solvent/ product (%)[a] | | | | |
|---|---|---|---|---|
| Acetonitrile[b] | 14 | 57 | 29 | 0 |
| Chloroform[c] | 24 | 49 | 25 | 2 |

[a] The ratio of the products was determined by ^{1}H NMR spectroscopy based on the integral intensity of signals corresponding to the methyl groups. [b] The reaction was stopped after refluxing the solution of substrate and reagent **8d** (1 equiv) in MeCN for 15 h. [c] The reaction was stopped after refluxing the solution of substrate and reagent **8d** (1 equiv) in chloroform for 3 h.

## Conclusion

In conclusion, we have reported the preparation, structural characterization, and chemistry of ethers of 2-iodylphenol ethers, the new soluble and nonexplosive pentavalent iodine reagents. 2-Iodylphenol ethers **8** can be conveniently prepared by the dimethyldioxirane oxidation of the corresponding 2-iodophenol ethers **7** and isolated as chemically stable, microcrystalline products. Single-crystal X-ray diffraction analysis of 1-iodyl-2-isopropoxybenzene **8c** and 1-iodyl-2-butoxybenzene **8d** revealed pseudopolymeric arrangements in the solid state formed by intermolecular interactions between $IO_2$ groups of different molecules. The weaker intermolecular interactions in 1-iodyl-2-butoxybenzene **8d** explain better solubility of this product compared to 1-iodyl-2-isopropoxybenzene **8c**. 2-Iodylphenol ethers **8c** and **8d** can selectively oxidize sulfides to sulfoxides and alcohols to the respective aldehydes or ketones.

## Experimental Section

For general experimental methods and synthesis of starting materials **7b**−**d**, see the Supporting Information.

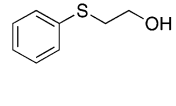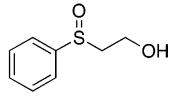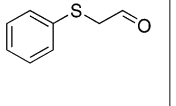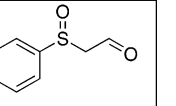**General Procedure for Oxidation of 2-Iodophenol Ethers 7.** Freshly prepared 0.1 M solution of dimethyldioxirane in acetone (30 mL, 3.0 mmol) was added to a stirred mixture of the appropriate 2-iodophenol derivative **7** (1.0 mmol) in 5 mL of dry $CH_2Cl_2$ at 0 °C. The color of the solution immediately changed from colorless to light yellow. The reaction mixture was stirred at room temperature for 8 h, and the resulting white microcrystalline precipitate was separated by filtration; then diethyl ether was added to the filtered solution, and the additional precipitate was filtered. Both precipitates were collected, washed with ether, and dried in a vacuum to afford analytically pure products **8**.

**1-Iodyl-2-methoxybenzene (8a).** Oxidation of 1-iodo-2-methoxybenzene **7a** (0.234 g, 1.0 mmol) according to the general procedure afforded 0.20 g (75%) of product **8a**, isolated as white crystals: mp 181−182 °C (with decomposition); ^{1}H NMR (DMSO-$d_6$) $\delta$ 7.76 (dd, $J$ = 7.8, 1.5 Hz, 1H), 7.60 (td, $J$ = 7.8, 1.5 Hz, 1H), 7.27 (t, $J$ = 7.4 Hz, 1H), 7.24 (d, $J$ = 8.3 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (DMSO-$d_6$) $\delta$ 157.4, 137.6, 134.6, 124.5, 122.3, 113.1, 57.4; ESI HRMS $m/z$ 288.9334 (100) [M + Na]$^+$. Anal. Calcd for $C_7H_7IO_3$: C, 31.60; H, 2.65; I, 47.70. Found: C, 31.79; H, 2.62; I, 47.63.

**1-Iodyl-2-propoxybenzene (8b).** Oxidation of 1-iodo-2-propoxybenzene **7b** (0.261 g, 1.0 mmol) according to the general procedure afforded 0.262 g (89%) of product **8b**, isolated as white crystals: mp 199−201 °C dec; ^{1}H NMR (CDCl$_3$) $\delta$ 7.85 (dd, $J$ = 7.8, 1.5 Hz, 1H), 7.47 (td, $J$ = 7.8, 1.7 Hz, 1H), 7.13 (td, $J$ = 7.7, 1.0 Hz, 1H), 6.95 (dd, $J$ = 8.0, 0.7 Hz, 1H), 4.04 (t, $J$ = 6.6 Hz, 2H), 1.82 (m, 2H), 1.01 (t, $J$ = 7.5 Hz, 3H); ^{13}C NMR (CDCl$_3$) $\delta$ 156.9, 135.5, 134.9, 126.1, 133.6, 122.7, 71.6, 22.3, 10.6; ESI HRMS $m/z$ 316.9685 (100) [M + Na]$^+$. Anal. Calcd for $C_9H_{11}IO_3$: C, 36.76; H, 3.77. Found: C, 36.47; H, 3.95.

**1-Iodyl-2-isopropoxybenzene (8c).** Oxidation of 1-iodo-2-isopropoxybenzene **7c** (0.261 g, 1.0 mmol) according to the general procedure afforded 0.223 g (76%) of product **8c**, isolated as white crystals: mp 200−202 °C dec; ^{1}H NMR (DMSO-$d_6$) $\delta$ 7.74 (dd, $J$ = 7.6, 1.5 Hz, 1H), 7.55 (td, $J$ = 7.7, 1.5 Hz, 1H), 7.24 (m, 2H), 4.78 (m, 1H), 1.31 (d, $J$ = 5.9 Hz, 6H); ^{13}C NMR (DMSO-$d_6$) $\delta$ 155.9, 138.7, 134.4, 124.7, 122.1, 115.0, 72.8, 22.5; ESI HRMS $m/z$ 316.9646 (30) [M + Na]$^+$, 610.9834 (100) [2M + Na]$^+$, 904.9814 (30) [3M + Na]$^+$. Anal. Calcd for $C_9H_{11}IO_3$: C, 36.76; H, 3.77; I, 43.15. Found: C, 36.89; H, 3.59; I, 43.26.

A single crystal of product **8c** suitable for X-ray crystallographic analysis was obtained by slow evaporation of saturated methylene chloride solution of this compound. A crystal (approximate dimensions 0.30 × 0.30 × 0.80 mm$^3$) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted for a data collection at 293(2) K. A unit cell dimensions were determined using 25 reflections in the $\theta$ = 15−18° range ($a$ = 6.2665(15) Å, $b$ = 13.0901(15) Å, $c$ = 12.7349(17) Å, $\alpha$ = 90°, $\beta$ = 102.746(14)°, $\gamma$ = 90°, $V$ = 1018.9(3) Å$^3$). The data collection was carried out using Mo K$\alpha$ radiation (graphite monochromator). The final set of reflections was collected within 3.112−27.488 range of 2$\theta$. The intensity data were corrected for absorption and decay using Texan 10.3b program.[13] The structure was solved using Bruker SHELXTL

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(13) TeXsan 10.3b. Rigaku Inc.. Tokyo, Japan, 1998.

software[14] and refined using CRYSTALS for Windows package.[15] The space group $P2_1/c$ was determined on the basis of systematic absences and intensity statistics. A direct-method solution provided the most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters unless stated otherwise. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R_1 = 0.0384$ and $wR_2 = 0.1051$ ($F^2$, $3\sigma$). For further details on the crystal structure of **8c**, see the CIF file (Supporting Information).

**1-Iodyl-2-butoxybenzene (8d).** Oxidation of 1-iodo-2-butoxybenzene **7d** (0.276 g, 1.0 mmol) according to the general procedure afforded 0.248 g (90%) of product **8d**, isolated as white crystals: mp 164−165 °C dec; [1H] NMR (CDCl$_3$) $\delta$ 7.90 (dd, $J = 8.1$, 1.5 Hz, 1H), 7.51 (td, $J = 7.8$, 1.5 Hz, 1H), 7.19 (t, $J = 7.8$ Hz, 1H), 7.00 (d, $J = 7.8$ Hz, 1H), 4.12 (t, $J = 6.7$ Hz, 2H), 1.82 (m, 2H), 1.48 (m, 2H), 0.98 (t, $J = 7.3$ Hz, 3H); [13C] NMR (CDCl$_3$) $\delta$ 156.8, 135.2, 134.9, 125.9, 122.5, 112.6, 69.7, 30.8, 19.1, 13.8; ESI HRMS $m/z$ 330.9789 (100) [M + Na]$^+$. Anal. Calcd for C$_{10}$H$_{13}$IO$_3$: C, 38.98; H, 4.25; I, 41.19. Found: C, 39.05; H, 4.35; I, 41.28.

A single crystal of **8d** suitable for X-ray crystallographic analysis was obtained by slow evaporation of its saturated methylene chloride solution. A crystal (approximate dimensions $0.80 \times 0.40 \times 0.05$ mm$^3$) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted for a data collection at 293(2) K. The unit cell dimensions were calculated from 25 reflections in the $\theta = 15−18°$ range ($a = 14.117(5)$ Å, $b = 12.342(3)$ Å, $c = 6.582(5)$ Å, $\alpha = 90°$, $\beta = 98.80(4)°$, $\gamma = 90°$, $V = 1133.3(10)$ Å$^3$). The data collection was carried out using Mo Kα radiation (graphite monochromator). The final set of reflections was collected within $0.993−26.925$ range of $2\theta$. The intensity data were corrected for absorption and decay using Texan 10.3b program.[13] The structure was solved using Bruker SHELXTL software[14] and refined using CRYSTALS for Windows package.[15] The space group $P2_1/n$ was determined on the basis of systematic absences and intensity statistics. A direct-methods solution provided the most of non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters unless stated otherwise. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R_1 = 0.0453$ and $wR_2 = 0.1043$ ($F^2$, $3\sigma$). For further details on crystal structure of **8d**, see the CIF file (Supporting Information).

**General Procedure for Oxidation of Sulfides by Reagents 8c and 8d.** To a vigorously stirred mixture of reagent **8** (0.3 mmol) in acetonitrile (5 mL) was added an appropriate sulfide (0.5 mmol), and the solution was refluxed. The reaction mixture was refluxed until complete disappearance of sulfide (monitored by TLC). Then the mixture was evaporated, and the residue was separated by column chromatography using an EtOAc/hexane mixture (1:2) as eluent to yield the final sulfoxide.

**General Procedure for Oxidation of Alcohols by Reagents 8c and 8d.** To a vigorously stirred mixture of reagent **8** (0.05 mmol) in freshly distilled and purified over basic aluminum oxide chloroform (0.7 mL) was added an appropriate alcohol (0.05 mmol), and the solution was refluxed. The reaction mixture was refluxed until complete disappearance of alcohol (monitored by TLC). A portion of the crude reaction mixture (0.1 mL) was passed through 1 cm of silica gel suspended in a pasteur pipet and eluted with CH$_2$Cl$_2$ (1 mL) and then diluted to 3 mL and analyzed by GC−MS.

**Supporting Information Available:** Details of the experimental procedures, spectroscopic data of the reaction products, and X-ray data for the compounds **8c** and **8d** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) SHELXTL-Plus V5.10, Bruker Analytical X-ray Systems, Madison, WI.

(15) Betteridge, P. W.; Carruthers, J. R.; Copper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487.