



# Enhancing the solubility for hypervalent *ortho*-sulfonyl iodine compounds

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## ABSTRACT

The synthesis and characterization of new hypervalent iodine reagents ArINTs (**2a**), ArIO (**3a**), and ArIO<sub>2</sub> (**4a**) (Ar=2-*tert*-butylsulfonyl-5-*tert*-butylphenyl) are described. These reagents are compared to previously reported analogous set of reagents Ar=2-*tert*-butylsulfonylphenyl and found to have significantly enhanced solubility and similar chemical reactivity. The X-ray crystal structures of **4a** and of ArI (**1a**) (Ar=2-*tert*-butylsulfonyl-5-*tert*-butylphenyl) are discussed and compared. These reagents find use in atom and group transfer reactions.

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## 1. Introduction

Polyvalent organoiodine compounds are an extremely important class of compounds finding many uses for organic synthesis.<sup>1</sup> In 1999, we found that strategic placement of an *ortho-tert*-butyl sulfonyl group into the aromatic ring of polyvalent iodobenzenes could markedly improve their solubility in organic media and afford opportunities to study their crystal structures.<sup>2,3</sup> Their enhanced solubility have led others to capitalize on these favorable properties for improving selectivity and to better understand transition metal catalyzed atom and group transfer reactions involving organoiodine(III) reagents.<sup>4–21</sup> The strategy of introducing elements bringing intramolecular I⋯E bonds to influence the reactivity and physical properties of hypervalent iodine compounds has grown immensely.<sup>22,23</sup> In this contribution we present simple means for enhancing the solubility (and perhaps utility) of *ortho-tert*-butyl sulfonyl substituted polyvalent iodobenzenes.

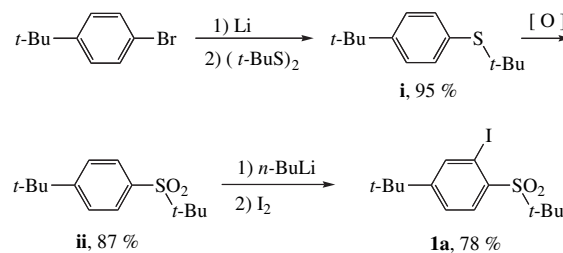
## 2. Results and discussion

Our original attempt at improving the solubility of *ortho-tert*-butyl sulfonyl substituted polyvalent iodobenzenes focused on placement of the *p*-CF<sub>3</sub> group onto the parent iodobenzene ring.<sup>24</sup> While a modest gain in solubility was obtained for the iodosylbenzene (ca. 3.7×), the ArI=NTs species was found to actually be less soluble. Furthermore, the *p*-CF<sub>3</sub> bearing iodosylbenzene was less stable than the parent compound. With the objective of further

promoting the solubility of these reagents (while maintaining the desired reactivity), we have thus examined the impact of a *tert*-butyl group in the 5-position on the phenyl ring. During this work it was important to make all steps easy and high yielding in order to maximize the utility of the reagent.

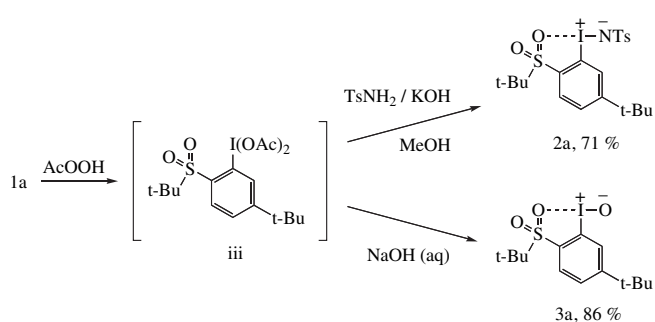
Iodoarene **1a** was prepared by the synthetic route outlined in Scheme 1. 4-*tert*-Butylbromobenzene was subjected to halogen/lithium exchange using Schumann's protocol and treated with di-*tert*-butyldisulfide (*t*-BuS)<sub>2</sub> to obtain intermediate **i** in 95% yield. Thioether **i** was easily oxidized to sulfone **ii** using excess peracetic acid. Sulfone **ii** was transformed to iodoarene **1a**, in good yields, by taking advantage of the *ortho*-metal directing ability of the *tert*-butylsulfone moiety.

Compound **1a** served as a convenient entryway to the desired polyvalent iodine compound. Specifically, it could be readily oxidized to the diacetoxyiodoarene **iii**, using peracetic acid. This intermediate was not isolated, but was prepared and used in situ to obtain (tosylimino)iodoarene **2a** and iodosylarene **3a** (Scheme 2). These new iodanes were readily identified and characterized by <sup>1</sup>H



Scheme 1.

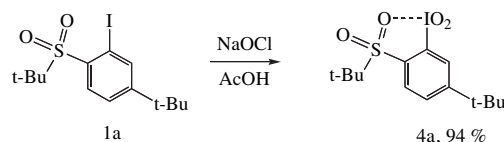
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Scheme 2.

and <sup>13</sup>C NMR spectroscopy, as well by elemental analysis. In particular, <sup>13</sup>C{<sup>1</sup>H} NMR spectral data for **2a** and **3a** in CDCl<sub>3</sub> display resonances shifted downfield for the *ipso*-aromatic carbon atoms at δ 115.7 and δ 117.8, respectively, relative to **1a** (δ 94.8) that signal oxidation of I(I) to I(III).

Iodanes **2a** and **3a** were found to have pronounced solubility in chloroform, ca. 8–13 times that of the original soluble analogues **2b** and **3b**, respectively (Table 1). Solutions of these oxidants could be



Scheme 3.

The structure of **4a** was conclusively established by an X-ray structural analysis performed on a crystal of **4a**·H<sub>2</sub>O grown from a solution in chloroform. As expected, secondary bonding was evident from one of the sulfonyl oxygen atoms (O3) to the electropositive iodine center (*d*<sub>I...O</sub>=2.704(4) Å) (Fig. 1). For comparative purposes, the X-ray structure of compound **1a** was also determined from a crystal grown from slow evaporation of a solution of **1a** in a 1:1 mixture of methanol/dichloromethane, and the results are shown in Figure 2. Clearly such an interaction is absent in **1a** (closest *d*<sub>I...O</sub>=3.190(4) Å). The intramolecular secondary bonding in **4a** induces the I1, C1, C2, S, and O3 atoms to be coplanar, thereby, closely resembling some cyclic iodyl structures (**4b** and **5b** Chart 1).<sup>27,28</sup> Compound **5a** is unusual in that the O3...I vector nearly bisects the O1–I–O2 angle. Most secondary bonds are directed so as to direct electron density into an I–O σ\* orbital.<sup>25,26</sup> Due to the

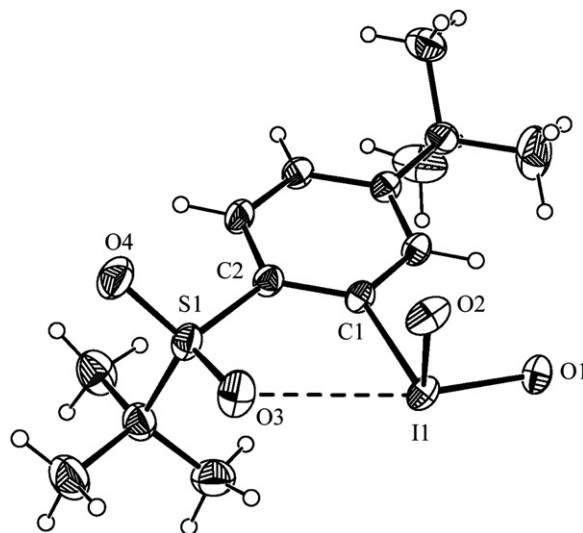
**Table 1**  
Comparative solubility data (data for **2b**, **3b** are from reference<sup>3</sup>, data for para-CF<sub>3</sub> compound are from reference<sup>24</sup>).

ArI=NTs	Solubility (M) CHCl <sub>3</sub>	Relative solubility	ArI=O	Solubility (M) CHCl <sub>3</sub>	Relative solubility
	0.14	1		0.08	1
	1.06	7.6		1.08	13.5
	0.05	0.36		0.30	3.7

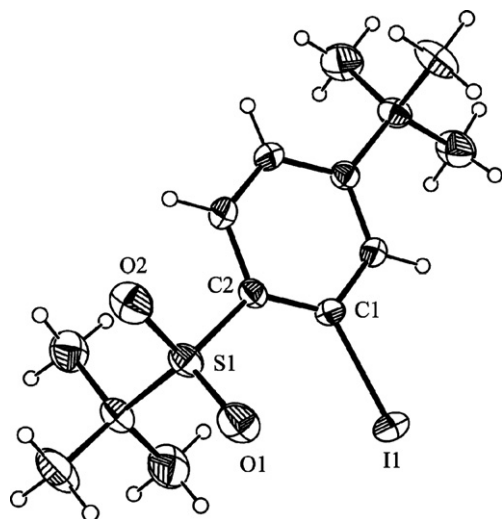
prepared up to 1 M in chloroform (as determined by integration in <sup>1</sup>H NMR spectra using 1,4-dimethoxybenzene as an internal standard). Solutions of **2a** were moderately stable in chloroform, showing some decomposition (<30%) when monitored over 24 h.

Solutions of **3a** in CDCl<sub>3</sub>, however, were found to rapidly disproportionate, to iodoarene **1a** and iodylarene **4a**, in the presence of 1,4-dimethoxybenzene. The solubility of iodosylarene **3a** was determined by measuring the amount of solvent required to form a homogeneous mixture with a known amount of **3a**. Iodanes **2a** and **3a**, however, did not display a significant increase in solubility in acetonitrile over compounds **2b** and **3b**, respectively. For example, a 0.05 M solution of **2a** could be prepared in acetonitrile, which is about twice that of **2b** in acetonitrile. It is unclear why the presence of 1,4-dimethoxybenzene should promote the disproportionation reaction of **3a**.

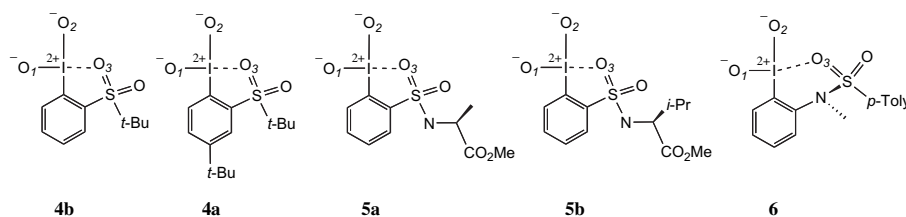
The iodylarene **4a** that results from the decomposition of **3a** can be produced more directly by oxidation of **1a** with bleach in acetic acid (Scheme 3) in near quantitative yield. Compound **4a** is reasonably soluble in chloroform, and the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **4a** in CDCl<sub>3</sub> display resonance shifted downfield for the *ipso*-aromatic carbon atoms at δ 146.8 relative to **1a** (δ 94.8) that indicate oxidation of I(I) to I(V).



**Figure 1.** X-ray crystal structure of iodylarene **4a**·H<sub>2</sub>O (H<sub>2</sub>O molecule omitted for clarity). Selected distances [Å] and angles [°]: I1–O1 1.800(3), I1–O2 1.803(3), I1...O3 2.704(4), I1–C1 2.158(4), S1–O3 1.436(3), S1–O4 1.439(3); C1–I1–O1 95.2(1), O1–I1–O2 99.3(1), C1–I1–O2 96.1(1), O(1)–I(1)–O(3) 168.2(2).



**Figure 2.** X-ray crystal structure of iodoarene **1a**. Selected distances [Å]: I1–C1 2.109 (4), S1–O1 1.427(3), S1–O2 1.440(3).



Bond Lengths	<b>4b</b> (ref 2)	<b>4a</b> (this work)	<b>5a*</b> (ref 27)	<b>5b</b> (ref 27)	<b>6</b> (ref 28)
d <sub>I-O1</sub> (Å)	1.796	1.806	1.845, 1.832	1.820	1.807
d <sub>I-O2</sub> (Å)	1.822	1.807	1.799, 1.793	1.795	1.786
d <sub>I-O3</sub> (Å)	2.693	2.709	3.084, 3.010	2.871	3.035

\*Two independent molecules per asymmetric unit

**Chart 1.** Comparison of intramolecular I⋯O=S secondary bonds in some iodylarenes.

increased ring pseudo-size (from 5 to 6 atoms), the geometry of **6** departs from the others in that the pseudo-ring cannot be planar. The two I–O bond lengths in **4a** were determined to be 1.800(3) Å and 1.803(3) Å, which is comparable to the range of such distances in related compounds having I⋯O=S contacts (Chart 1).<sup>28</sup> Compound **4a**, like other iodyl compounds, features additional intermolecular contacts in the crystal lattice that yield a pseudo octahedral geometry for the iodine center in **4a** (Fig. 3). Also of note, molecules of **4a** cocrystallize with one molecule of H<sub>2</sub>O, consistent with the results of elemental analysis. While hydrogen atoms on the oxygen atom of the included water were not successfully located, the shortest O⋯O distance (3.07 Å) involves O1, and could indicate possible HO–H⋯O–I hydrogen bonding.

Compounds **2a**, **3a**, and **4a** were studied as atom and group transfer sources in various reactions under conditions that we have previously reported, and products were identified by <sup>1</sup>H NMR spectroscopy in comparisons to authentic samples.<sup>3</sup> (Tosyliminoiodo)arene **2a** was found to act as a nitrene precursor under CuOTf catalysis yielding sulfimines in good yields (Scheme 4). Tri-*n*-

butylphosphine was instantaneously oxidized when treated with **2a** to afford 4-methyl-*N*-(tri-*n*-butyl phosphoranylidene)-benzenesulfonamide in good yields. Triphenylphosphine was also oxidized to 4-methyl-*N*-(triphenylphosphoranylidene)-benzenesulfonamide, although the reaction took 2 h for completion. CuOTf catalyzed aziridination of styrene and *trans*-stilbene using **2a** yielded *N*-(*para*-tolylsulfonyl)-2-phenylaziridine and *trans*-*N*-(*para*-tolylsulfonyl)-2,3-diphenylaziridine in yields comparable to that obtained by using **4a** or PhINTs.

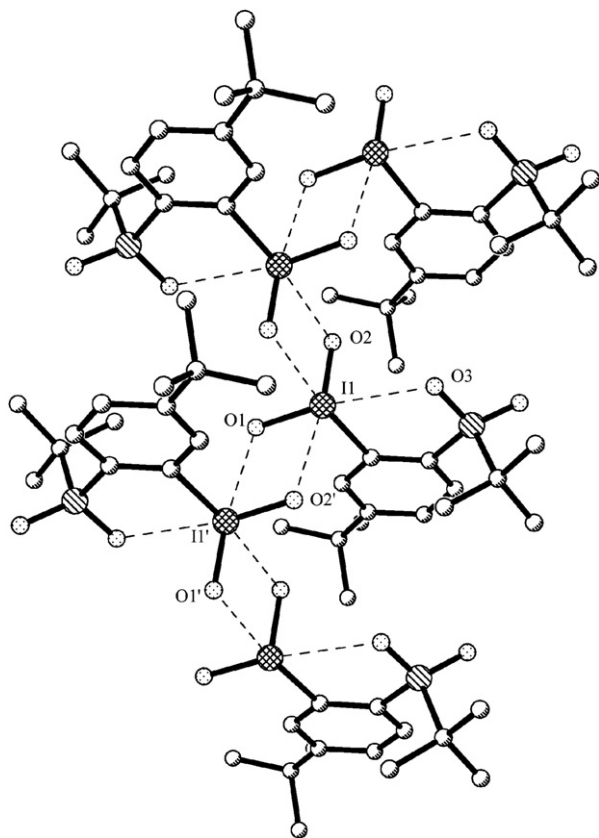
Iodosylarene **3a** was found to act as an effective oxo precursor, readily yielding sulfoxides and triphenylphosphine oxide (Scheme 5). Manganese catalyzed epoxidations of styrene and *trans*-stilbene using **3a** as oxidant slowly yielded the corresponding epoxides over a 2–4 day period. Elevated temperatures decreased reaction times to 6–12 h, but caused a drop in yields. These yields are comparable to those obtained by using iodosylarene **4b** as the oxidant under the same reaction conditions.

Iodylarene **4a** was also established to serve as a useful oxo donor. Triphenylphosphine was readily oxidized to triphenylphosphine oxide upon the addition of a solution of **4a** in CDCl<sub>3</sub>. Iodoxyarene **4a** oxidizes thioethers and olefins (under manganese

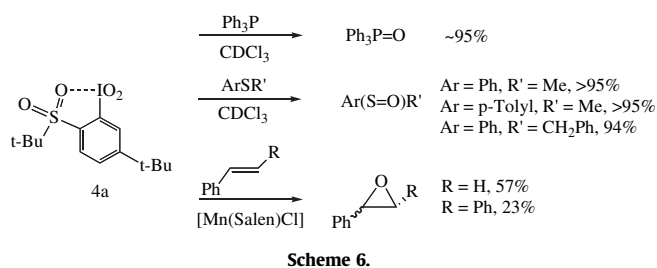
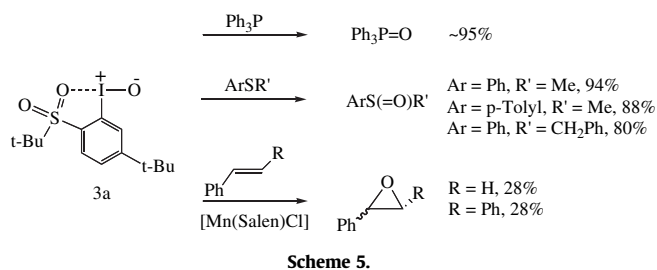
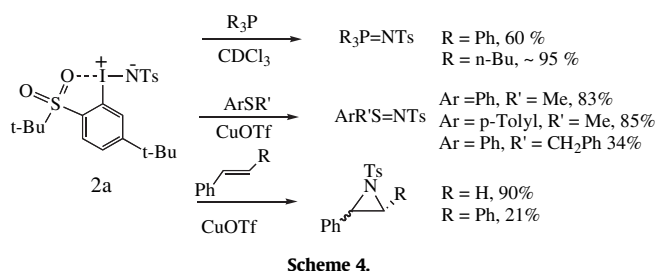
catalysis) to the corresponding sulfoxides and epoxides (Scheme 6). Epoxidation reactions required long reaction times (days) for complete consumption of the oxidant. An optimum yield of the styrene epoxide (57%) was obtained when the reaction was allowed to proceed for 4 days at room temperature. At elevated temperature (65 °C) the reaction was complete in 1 h but the yield of epoxide obtained was reduced to 33%. In the oxidation processes **4a** loses both its oxygen atoms, reducing back to iodoarene **1a**.

### 3. Conclusions

New soluble iodanes containing two substituents in the iodoarene residue were synthesized and assessed to be moderately effective oxidants. The added *tert*-butyl group in iodanes **2a** and **3a** provide greater solubility of iodosylarenes and (tosyliminoiodo)arenes, and importantly, does not significantly change the chemical reactivity of the reagents. The impact of this group was also evident in the solubility of iodylarene **4a**. This solubility of iodylarenes should facilitate the further study of these reagents as oxidants. Our



**Figure 3.** Packing diagram of iodylarene **4a** · H<sub>2</sub>O (hydrogen atoms and H<sub>2</sub>O molecules have been omitted for clarity). Selected distances [Å]: O1...O1' 2.672(4), O1...O2' 2.615(4).



strategy should also find merit for those seeking to further enhance the properties of other hypervalent reagents.

## 4. Experimental section

### 4.1. General procedures

Alkylolithium reagents were purchased from Aldrich and titrated with diphenylacetic acid prior to use. Reactions involving the manipulation of air and water sensitive reagents were performed under a nitrogen atmosphere using Schlenk techniques. THF was distilled from sodium benzophenone ketyl. CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN were distilled from calcium hydride. The identities of aziridines, sulfilimines, and phosphinimines synthesized in this work were confirmed by comparison of spectra and melting points with literature values. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on Varian XL200 or Varian XL 300 spectrometers. Chemical shifts were referenced internally to residual solvent signals (<sup>1</sup>H). HRMS spectra were recorded on a Carlo-Erba Mass Spectrometer. GC–MS spectra were recorded on an HP5890 Series II Gas Chromatograph equipped with an HP 5972 Mass Selective Detector. Elemental analyses were performed by Qualitative Technologies Inc. (QTI), Whitehouse, NJ.

### 4.2. 4-*tert*-Butylphenyl *tert*-butyl thioether (i)

This synthesis was adapted from a literature procedure. In a 100 mL two-neck flask fitted with a reflux condenser were placed Li wire (0.208 g, 30.0 mmol) and dry diethyl ether (25 mL) under argon. To this flask was added 4-*tert*-butylbromobenzene (2.6 g, 12 mmol) via syringe with constant stirring and the mixture maintained under reflux conditions to obtain a brown solution. This solution was then transferred dropwise via cannula into a flask containing di-*tert*-butyldisulfide (1.67 g, 9.36 mmol) and the resultant suspension was stirred at –40 °C for 2 h. The suspension was then allowed to warm to room temperature and 1 M HCl (10 mL) and water (10 mL) added. The organic layer was separated and the aqueous layer extracted with diethyl ether (3 × 10 mL). The combined organic extracts were washed with brine and dried over MgSO<sub>4</sub>. The solvents were removed in vacuo to obtain a pale yellow solid. Recrystallization from diethyl ether yielded a colorless **i**. Yield: 2.11 g (95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 7.46 (d, 2H, <sup>3</sup>J<sub>HH</sub>=8.6 Hz), 7.34 (d, 2H, <sup>3</sup>J<sub>HH</sub>=8.6 Hz), 1.33 (s, 9H), 1.29 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 50.2 MHz): δ 151.8, 137.2, 129.2, 125.5, 45.7, 34.7, 31.4, 31.0.

### 4.3. 4-*tert*-Butylphenyl *tert*-butylsulfone (ii)

To a 100 mL beaker charged with **i** (1.5 g, 6.7 mmol) were added 30% H<sub>2</sub>O<sub>2</sub> (3 mL) and glacial AcOH (3 mL) and the suspension stirred at 80 °C for 3 h. This mixture was allowed to cool to room temperature and crushed ice was added to precipitate a white solid. The solid was isolated by filtration, washed successively with water and cold hexanes. Recrystallization from EtOH afforded a colorless **ii**. Yield: 1.5 g (87%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.79 (d, 2H, <sup>3</sup>J<sub>HH</sub>=8.6 Hz), 7.55 (d, 2H, <sup>3</sup>J<sub>HH</sub>=8.6 Hz), 1.35 (s, 18H).

### 4.4. 2-(*tert*-Butylsulfonyl)-5-*tert*-butyliodobenzene (**1a**)

To a solution of **ii** (0.500 g, 1.96 mmol) in THF (30 mL) cooled to –78 °C was added *n*-BuLi (0.91 mL of 2.5 M solution in hexanes, 2.3 mmol) dropwise with vigorous stirring. The yellow reaction mixture was stirred at –78 °C for 1 h and a solution of iodine (0.730 g, 2.85 mmol) in THF (20 mL) slowly added via cannula. The dark brown reaction mixture was stirred at –78 °C for 1 h and allowed to warm to room temperature. Excess iodine was quenched with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The organic layer separated and the

aqueous layer extracted with diethyl ether (3×20 mL). The combined organic extracts were washed with brine and dried over MgSO<sub>4</sub>. The solvents were removed in vacuo to obtain a yellow solid. Recrystallization of this material from EtOH yielded a colorless **1a**. Yield: 0.586 g (78%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.11 (d, 1H, <sup>4</sup>J<sub>HH</sub>=2.0 Hz), 7.98 (d, 1H, <sup>3</sup>J<sub>HH</sub>=8.4 Hz), 7.52 (dd, 1H, <sup>4</sup>J<sub>HH</sub>=1.9 Hz, <sup>3</sup>J<sub>HH</sub>=8.4 Hz), 1.42 (s, 9H), 1.33 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.5 MHz): δ 158.3, 141.1, 134.8, 134.2, 125.5, 94.8, 62.4, 34.9, 30.9, 24.3. Anal. Calcd for C<sub>14</sub>H<sub>21</sub>O<sub>2</sub>IS: C, 44.22; H, 5.56. Found C, 44.31; H, 5.83.

#### 4.5. 2-(*tert*-Butylsulfonyl)-5-*tert*-butyl-(tosylimino)iodobenzene (**2a**)

Acetic anhydride (2.4 mL) and 30% H<sub>2</sub>O<sub>2</sub> (0.6 mL) were stirred at 42 °C for 4 h. To the resulting solution was added **1a** (0.729 g, 1.92 mmol) and the reaction mixture stirred at 30 °C for 24 h resulting in a pale yellow solution. The progress of the reaction was monitored by TLC (benzene/silica gel plate) to ensure complete oxidation of **1a**. The solvents were removed in vacuo and the white pasty solid obtained was treated with an ice-cooled solution of *para*-toluenesulfonamide (0.342 g, 2.01 mmol) and KOH (0.360 g, 6.40 mmol) in MeOH (10 mL). The reaction mixture was stirred for 1 h at 0 °C and for 1 h at room temperature to give a pale yellow precipitate. This material was washed with water and diethyl ether and dried in vacuo to obtain a yellow solid. Yield: 0.749 g (71%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 8.44 (d, 1H, <sup>4</sup>J<sub>HH</sub>=1.18 Hz), 7.85–7.79 (m, 3H), 7.70–7.66 (m, 1H), 7.27–7.21 (m, 2H), 2.39 (s, 3H), 1.45 (s, 9H), 1.41 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.5 MHz): δ 161.5, 142.0, 140.5, 133.3, 129.4, 128.8, 128.0, 126.8, 125.9, 115.7, 63.4, 36.5, 30.9, 23.5, and 21.5. Anal. Calcd for C<sub>21</sub>H<sub>28</sub>O<sub>4</sub>NIS<sub>2</sub>: C, 45.90; H, 5.13; N, 2.55. Found: C, 45.77; H, 5.09; N, 2.41. Solubility extent: 0.18 mL of CDCl<sub>3</sub> was required to completely dissolve 105 mg of **4**. Thus a 1.06 M solution of **2a** in CDCl<sub>3</sub> could be prepared.

#### 4.6. 2-(*tert*-Butylsulfonyl)-5-*tert*-butyliodosylbenzene (**3a**)

Acetic anhydride (6.36 mL, 67.4 mmol) and 30% H<sub>2</sub>O<sub>2</sub> (1.45 mL, 14.2 mmol) were stirred at 42 °C for 4 h. To the resulting solution was added **1a** (2.01 g, 5.28 mmol) and the reaction mixture stirred at 30 °C for 24 h to result in a pale yellow solution. The progress of the reaction was monitored by TLC (benzene/silica gel plate) to ensure complete oxidation of **1a**. The solvents were removed in vacuo and the white pasty solid obtained was treated with aqueous 3 N NaOH (5 mL) at 0 °C to obtain a yellow precipitate. The reaction mixture was stirred at 0 °C for 1 h and allowed to warm to room temperature. The yellow solid was isolated by filtration, washed with water and diethyl ether and air-dried. Yield: 1.801 g (86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 8.06 (d, 1H, <sup>4</sup>J<sub>HH</sub>=1.7 Hz), 7.77 (d, 1H, <sup>2</sup>J<sub>HH</sub>=8.1 Hz), 7.60 (dd, 1H, <sup>4</sup>J<sub>HH</sub>=1.7 Hz, <sup>2</sup>J<sub>HH</sub>=8.1 Hz), 1.41 (s, 18H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.5 MHz): δ 160.4, 132.5, 128.8, 127.0, 124.2, 117.8, 63.2, 36.3, 30.9, 23.5. Anal. Calcd for C<sub>15</sub>H<sub>22</sub>O<sub>3</sub>Cl<sub>3</sub>IS·CHCl<sub>3</sub>: C, 34.94; H, 4.3. Found: C, 35.26; H, 4.71.

#### 4.7. 2-(*tert*-Butylsulfonyl)-5-*tert*-butyliodylbenzene (**4a**)

This synthetic procedure was adapted from the literature. To a vigorously stirred suspension of **1a** (0.500 g, 1.37 mmol) in commercial bleach (5.25% aqueous NaOCl, 3.3 mL, 2.3 mmol) was added glacial acetic acid (0.66 mL). A white precipitate was seen immediately. The reaction mixture was stirred for 16 h at room temperature, and the white solid isolated by filtration, washed with water (3×25 mL), acetone, diethyl ether, and air-dried. Yield: 0.508 g (94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 8.69 (s, 1H), 7.76 (m, 2H), 1.40 (s, 18H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.5 MHz): δ 160.7, 146.8, 131.4, 129.7,

123.3, 62.1, 36.7, 31.2, 23.9. Anal. Calcd for C<sub>14</sub>H<sub>19</sub>O<sub>3</sub>SI·H<sub>2</sub>O: C, 40.78; H, 5.13. Found: C, 39.59; H, 5.14.

### 4.8. Reactions involving **2a**

4.8.1. *N*-(*para*-Tolylsulfonyl)-2-phenylaziridine. To a suspension of **2a** (0.100 g, 0.18 mmol), styrene (0.11 mL, 0.91 mmol), and 4 Å molecular sieves in CH<sub>3</sub>CN (1 mL) was injected a solution of CuOTf·½C<sub>6</sub>H<sub>6</sub> (4.5 mg, 9 μmol) in toluene (1 mL) to result in a green suspension. The reaction mixture was stirred at room temperature for 3 h until all of **2a** was consumed and diethyl ether (5 mL) added to it. The suspension was filtered through a plug of silica gel and eluted with diethyl ether (5 mL). The solvents were removed in vacuo and the yield of *N*-(*para*-tolylsulfonyl)-2-phenylaziridine was determined by the addition of 1,4-dimethoxybenzene as an internal standard to be 90%.

4.8.2. *trans-N*-(*para*-Tolylsulfonyl)-2,3-diphenylaziridine. To a suspension of **2a** (0.08 g, 0.14 mmol), stilbene (0.131 g, 0.729 mmol), and 4 Å molecular sieves in CH<sub>3</sub>CN (1 mL) was added via syringe a solution of CuOTf·½C<sub>6</sub>H<sub>6</sub> (3.6 mg, 7.3 μmol) in toluene (1 mL) to result in a green suspension. The reaction mixture was stirred at room temperature for 3 h until all of **2a** was consumed and diethyl ether (5 mL) added to it. The suspension was filtered through a plug of silica gel and eluted with diethyl ether (5 mL). The solvents were removed in vacuo and the yield of *N*-(*para*-tolylsulfonyl)-2,3-diphenylaziridine determined by <sup>1</sup>H NMR integration by using 1,4-dimethoxybenzene as an internal standard to be 21%.

4.8.3. *Methyl phenyl sulfimine*. To a solution of **2a** (0.08 g, 0.14 mmol) and thioanisole (18.0 mg, 0.15 mmol) in dichloromethane (2 mL) was added via syringe a solution of CuOTf·½C<sub>6</sub>H<sub>6</sub> (3.7 mg, 7.3 μmol) in toluene (0.4 mL) to result in a pale yellow colored solution. The reaction mixture was stirred at room temperature for 48 h, diluted with diethyl ether (2 mL), and passed through a short plug of silica gel to remove the copper catalyst. The solvents were removed in vacuo and the yield of methyl phenyl sulfimine determined by <sup>1</sup>H NMR spectrum integration using 1,4-dimethoxybenzene as an internal standard to be 83%.

4.8.4. *Benzyl phenyl sulfimine*. To a solution of **2a** (0.08 g, 0.14 mmol) and benzyl phenyl sulfide (29.2 mg, 0.15 mmol) in dichloromethane (2 mL) was added via syringe a solution of CuOTf·½C<sub>6</sub>H<sub>6</sub> (3.7 mg, 7.3 μmol) in toluene (0.4 mL) to result in a pale yellow colored solution. The reaction mixture was stirred at room temperature for 48 h, diluted with diethyl ether (2 mL), and passed through a short plug of silica gel to remove the copper catalyst. The solvents were removed in vacuo and the yield of benzyl phenyl sulfimine determined by <sup>1</sup>H NMR spectrum integration using 1,4-dimethoxybenzene as an internal standard to be 34%.

4.8.5. *Methyl para-tolyl sulfimine*. To a solution of **2a** (0.08 g, 0.14 mmol) and methyl *para*-tolyl sulfide (29.2 mg, 0.15 mmol) in dichloromethane (2 mL) was added via syringe a solution of CuOTf·½C<sub>6</sub>H<sub>6</sub> (3.7 mg, 7.3 μmol) in toluene (0.4 mL) to result in a pale yellow colored solution. The reaction mixture was stirred at room temperature for 48 h, diluted with diethyl ether (2 mL), and passed through a short plug of silica gel to remove the copper catalyst. The solvents were removed in vacuo and the yield of methyl *para*-tolyl sulfimine determined by <sup>1</sup>H NMR spectrum integration using 1,4-dimethoxybenzene as an internal standard to be 85%.

4.8.6. *4-Methyl-N-(tri-*n*-butylphosphoranylidene)-benzenesulfonamide*. To a solution of **2a** (93 mg, 0.17 mmol) in CDCl<sub>3</sub> (0.4 mL) was added tri-*n*-butylphosphine (5.0 μL, 0.2 mmol)

via syringe.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum recorded after mixing the reagents indicated instantaneous oxidation. 1,4-Dimethoxybenzene (8.0 mg, 0.05 mmol) was added as an internal standard and yield was determined by  $^1\text{H}$  NMR spectrum integration to be >95%.

**4.8.7. 4-Methyl-N-(triphenylphosphoranylidene)-benzenesulfonamide.** To a solution of **2a** (0.01 g, 0.02 mmol) in  $\text{CDCl}_3$  (0.4 mL) was added triphenylphosphine (8.0 mg, 0.03 mmol) and the progress of reaction monitored by periodically recording its  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra. The reaction required several hours to complete at room temperature and the yield of 4-methyl-N-(triphenylphosphoranylidene)-benzenesulfonamide was determined to be 60% by  $^1\text{H}$  NMR spectral analysis.

#### 4.9. Reactions involving **3a**

**4.9.1. Epoxidation of styrene.** To a suspension of styrene (0.14 mL, 1.3 mmol) and (1*R*,2*R*)-(–)-[1,2-cyclohexanediamino-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)]manganese(III) chloride (7.9 mg, 12  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added **3a** (0.100 g, 0.254 mmol), and the resulting dark brown solution stirred at room temperature (for 2 days), until all of **3a** was consumed. To the solution was added hexane (10 mL), and passed through a short column of silica gel to remove the catalyst. The column was eluted with of 1:1 mixture of diethyl ether/hexanes (10 mL). The solvents were removed in vacuo and to the solid obtained was added 1,4-dimethoxybenzene as an internal standard and the yield of styrene epoxide determined by  $^1\text{H}$  NMR spectrum integration to be 28%.

**4.9.2. Epoxidation of stilbene.** To a suspension of *trans*-stilbene (0.225 g, 1.25 mmol) and (1*R*,2*R*)-(–)-[1,2-cyclohexanediamino-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)]manganese(III) chloride (7.9 mg, 12  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added **3a** (0.100 g, 0.254 mmol), and the resulting dark brown mixture stirred at room temperature for 4 days. To the solution was added hexane (10 mL) and passed through a short column of silica gel, to remove the catalyst. The column was eluted with 1:1 mixture of diethyl ether/hexanes (10 mL). The solvents were removed in vacuo and to the solid obtained was added 1,4-dimethoxybenzene as an internal standard and the yield of stilbene epoxide determined by  $^1\text{H}$  NMR spectrum integration to be 28%.

**4.9.3. Methyl phenyl sulfoxide.** To a solution of **3a** (25 mg, 0.06 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added thioanisole (7.6  $\mu\text{L}$ , 0.07 mmol) and the resulting solution stirred at room temperature for 8 h until all the oxidant was consumed. To the clear solution was added a measured amount of 1,4-dimethoxybenzene as an internal standard, and the solvents removed in vacuo. The solid obtained was dissolved in  $\text{CDCl}_3$  (0.8 mL) and the yield of methyl phenyl sulfoxide determined by  $^1\text{H}$  NMR integration to be 94%.

**4.9.4. Methyl para-tolyl sulfoxide.** To a solution of **3a** (20 mg, 0.05 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added methyl *para*-tolyl sulfide (7.1  $\mu\text{L}$ , 0.05 mmol), and the resulting solution stirred at room temperature for 5 h until all of the oxidant was consumed. To the clear solution was added a measured amount of 1,4-dimethoxybenzene as an internal standard, and the solvents removed in vacuo. The solid obtained was dissolved in  $\text{CDCl}_3$  (0.8 mL) and the yield of methyl *para*-tolyl sulfoxide determined by  $^1\text{H}$  NMR integration to be 88%.

**4.9.5. Triphenylphosphine oxide.** To a solution of **3a** (12 mg, 0.03 mmol) in  $\text{CDCl}_3$  was added triphenylphosphine (15 mg, 0.06 mmol) and  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra recorded after mixing. The phosphine was instantaneously oxidized to

triphenylphosphine oxide in near quantitative yield. **3a** was observed to have completely reduced to iodoarene **1a** from the  $^1\text{H}$  NMR spectrum.

#### 4.10. Reactions involving **4a**

**4.10.1. Epoxidation of styrene.** To a suspension of styrene (0.14 mL, 1.3 mmol) and (1*R*,2*R*)-(–)-[1,2-cyclohexanediamino-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)]manganese(III) chloride (7.9 mg, 12  $\mu\text{mol}$ ) in  $\text{CHCl}_3$  (5 mL) was added **4a** (0.10 g, 0.24 mmol) and the resulting dark brown solution stirred at room temperature for 4 days until all of **4a** was consumed. To the solution was added hexane (10 mL) and passed through a short column of silica gel to remove the catalyst. The column was eluted with 1:1 mixture of diethyl ether/hexanes (10 mL). The solvents were removed in vacuo and to the solid obtained was added 1,4-dimethoxybenzene as an internal standard and the yield of styrene epoxide determined by  $^1\text{H}$  NMR integration to be 57%.

**4.10.2. Epoxidation of stilbene.** To a suspension of *trans*-stilbene (0.225 g, 1.27 mmol) and (1*R*,2*R*)-(–)-[1,2-cyclohexanediamino-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)]manganese(III) chloride (7.9 mg, 12  $\mu\text{mol}$ ) in  $\text{CHCl}_3$  (5 mL) was added **4a** (0.100 g, 0.24 mmol), and the resulting dark brown mixture stirred at 65 °C for 4 days. To the solution was added 10 mL hexane and passed through a short column of silica gel to remove the catalyst. The column was eluted with 1:1 mixture of diethyl ether/hexanes (10 mL). The solvents were removed in vacuo and to the solid obtained was added 1,4-dimethoxybenzene as an internal standard, and the yield of epoxide determined by  $^1\text{H}$  NMR integration to be 23%.

**4.10.3. Methyl phenyl sulfoxide (method a).** To a solution of **4a** (18.8 mg, 0.046 mmol) in  $\text{CDCl}_3$  (0.8 mL) placed in an NMR tube was added thioanisole (5.3  $\mu\text{L}$ , 0.05 mmol) and the tube placed in an oil bath held at 65 °C. The progress of the reaction was monitored by periodically recording the  $^1\text{H}$  NMR spectrum. In 48 h all of thioanisole was oxidized to methyl phenyl sulfoxide and 50% of **4a** remained unreacted.

**4.10.4. Methyl phenyl sulfoxide (method b).** To a solution of **4a** (14.3 mg, 0.035 mmol) in  $\text{CDCl}_3$  (0.8 mL) placed in an NMR tube was added thioanisole (8.2  $\mu\text{L}$ , 0.07 mmol) and the tube placed in an oil bath held at 65 °C. The progress of the reaction was monitored by periodically recording the  $^1\text{H}$  NMR spectrum. In 12 h all of **4a** was consumed to quantitatively oxidize thioanisole to methyl phenyl sulfoxide.

**4.10.5. Methyl para-tolyl sulfoxide (method a).** To a solution of **4a** (15.6 mg, 0.038 mmol) in  $\text{CDCl}_3$  (0.8 mL) placed in an NMR tube was added methyl *para*-tolyl sulfide (5.1  $\mu\text{L}$ , 0.04 mmol) and the tube placed in an oil bath held at 65 °C. The progress of the reaction was monitored by periodically recording the  $^1\text{H}$  NMR spectrum. In 48 h all of thioanisole was oxidized to methyl *para*-tolyl sulfoxide and 50% of **6** remained unreacted.

**4.10.6. Methyl para-tolyl sulfoxide (method b).** To a solution of **4a** (15.2 mg, 0.036 mmol) in  $\text{CDCl}_3$  (0.8 mL) placed in an NMR tube was added methyl *para*-tolyl sulfide (9.9  $\mu\text{L}$ , 0.07 mmol) and the tube placed in an oil bath held at 65 °C. The progress of the reaction was monitored by periodically recording the  $^1\text{H}$  NMR spectrum. In 12 h all of **4a** was consumed to quantitatively oxidize thioanisole to methyl *para*-tolyl sulfoxide.

**4.10.7. Triphenylphosphine oxide.** To a solution of **4a** (15 mg, 0.04 mmol) in  $\text{CDCl}_3$  (0.4 mL) was added triphenylphosphine

(19 mg, 0.07 mmol) and  $^1\text{H}$  and  $^{31}\text{P}\{\text{H}\}$  NMR spectra recorded after mixing. The phosphine was instantaneously oxidized to triphenylphosphine oxide in near quantitative yield. Compound **4a** was observed to have completely reduced to iodoarene **1a** from the  $^1\text{H}$  NMR spectrum.

#### 4.11. X-ray crystallography

Data were collected with a Bruker P4 diffractometer (Mo  $K\alpha$  radiation  $\lambda=0.71073$  Å). Crystals were mounted at the end of a glass fiber with superglue. Crystals were judged to be acceptable based on  $\omega$  scans and rotation photography. Random search located reflections to generate reduced primitive cells, cell lengths being corroborated by axial photography. Additional reflections with  $2\theta$  values between  $24.5^\circ$  and  $25^\circ$  were appended to the reflection arrays and yielded the refined cell constants. The symmetry of the unit cells was confirmed by further examination on the diffractometer. Data were corrected for absorption (empirical  $\psi$  scan). Direct methods (Siemens SHELXTL PLUS, Version 5.1) revealed all of the non-hydrogen atoms for **1a** and **4a**. All non-hydrogen atoms were refined anisotropically for **1a** and **4a**, and full crystallographic details for compounds **1a** and **4a** are provided within the cif files as Supplementary data.

#### 5. Supplementary data available

Supplementary X-ray structural data for **1a** and **4a** are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, England (fax: +44 1223 336033), on request quoting the deposition numbers CCDC 768414 and CCDC 768415.

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