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Oxidation of Sulfides to Sulfoxides with Hypervalent (*tert*-Butylperoxy)iodanes

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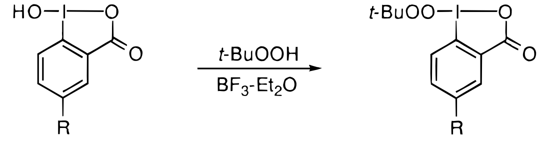
Oxidation of sulfides with the crystalline (alkylperoxy)iodanes, 1-(*tert*-butylperoxy)-1,2-benziodoxol-3(1*H*)-ones **2a** and **2b**, in acetonitrile−water or in dichloromethane, affords sulfoxides in high yields. Measurement of the relative rates of oxidation for a series of ring-substituted thioanisoles **3b** (*p*-MeO), **3c** (*p*-Me), and **3d** (*p*-Cl) in acetonitrile−water indicates that electron-releasing groups such as *p*-MeO and *p*-Me groups increase the rate of oxidation, and Hammett correlation of the relative rate factors with the substituent constants affords the reaction constants $\rho^+ = -2.23$ (σ^+, $r = 0.98$) for BF_3-catalyzed oxidation and $\rho = -3.32$ (σ, $r = 0.98$) for uncatalyzed oxidation. The effects of a free-radical scavenger, galvinoxyl, were examined. A mechanism involving the intermediary formation of the sulfonium species **11** by nucleophilic attack of sulfide toward the iodine(III) atom of **2** is proposed for the oxidation in acetonitrile−water in the presence and the absence of $BF_3 \cdot Et_2O$. On the other hand, the oxidation of sulfoxides in dichloromethane probably proceeds by a radical process, which involves the decomposition at room temperature of **2** via homolytic bond cleavage of the weak iodine(III)−peroxy bond, generating *tert*-butylperoxy radical and the [9-I-2] iodanyl radical **12**.

In spite of extensive studies on the chemistry of hypervalent organoiodanes, little is known about peroxyiodanes, probably because of their high tendency to decompose.[1] Milas and Plesnicar reported the reaction of iodosylbenzene with *tert*-butyl hydroperoxide in dichloromethane, and proposed the in situ generation of labile [bis(*tert*-butylperoxy)iodo]benzene, which decomposes homolytically even at −80 °C to give *tert*-butylperoxy radical and iodobenzene.[2] Plesnicar and Russell reported the first synthesis of (peraroyloxy)iodanes.[3] By the reaction of iodosylbenzene with perbenzoic acids, they obtained the symmetrically substituted [bis(perbenzoyloxy)iodo]benzenes as labile amorphous solids, which undergo spontaneous ignition or detonation upon manipulation in the solid state at room temperature. Recently, we found the Lewis acid-catalyzed ligand exchange of 1-hydroxy-1,2-benziodoxol-3(1*H*)-ones **1a**,**b** with *tert*-butyl hydroperoxide in chloroform affords the crystalline (alkylperoxy)iodanes, 1-(*tert*-butylperoxy)-1,2-benziodoxol-3(1*H*)-ones **2a** and **2b**.[4,5] The (alkylperoxy)iodane **2a** is stable in the solid state and can be safely stored at room temperature for an indefinite period of time.



1a,**b** **2a**,**b**

a: R = H; **b**: R = NO$_2$

The (*tert*-butylperoxy)iodane **2** oxidizes benzyl and allyl ethers to the esters at room temperature in the presence of alkali metal carbonates via a radical process.[4b] Because this reaction is compatible with other protecting groups such as MOM, THP, and TBDMS ethers, and acetoxy groups, and because esters are readily hydrolyzed under basic conditions, this method provides a convenient and effective alternative to the usual reductive deprotection of benzyl and allyl ethers. We report here the oxidation of sulfides with the (*tert*-butylperoxy)iodane **2** in acetonitrile−water or in dichloromethane, yielding sulfoxides in high yields. Substituent effects were examined for the oxidation of thioanisoles in acetonitrile−water in the presence of the absence of $BF_3 \cdot Et_2O$ as well as the effects of a free-radical scavenger, galvinoxyl.

Results and Discussion

Oxidation of Sulfides. Hypervalent organoiodanes such as iodosylbenzene[6] and [bis(acyloxy)iodo]benzenes[7] have been known to selectively oxidize sulfides to sulfoxides. Oxidation with (diacetoxyiodo)benzene in CH$_3$-

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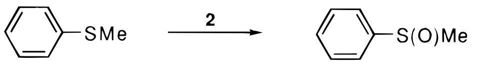
Table 1. Oxidation of Thioanisole (3a) with (*tert*-Butylperoxy)iodanes 2[a]

				conditions	product (yield,[b] %)			
entry	peroxyiodane **2** (equiv)	solvent	additive (equiv)	temp/°C, time/h	**4a**	**5**	**6**	**3a**
1	**2a** (1.2)	CH_2Cl_2[c]		25, 8.5	31	5	26	2
2	**2b** (1.3)	CH_2Cl_2[c]		25, 7.5	37	7	22	2
3	**2a** (1.2)	CH_2Cl_2	$BF_3 \cdot Et_2O$ (1.2)	25, 3	67 (63)	1	4	15
4	**2a** (1.2)	AcOEt−H_2O (5:1)[c]		25, 72	11			82
5	**2a** (1.2)	AcOEt−H_2O (5:1)[c]		50, 24	63			17
6	**2a** (1.1)	CH_3CN		25, 80	64 (48)	4		
7	**2a** (1.2)	CH_3CN		50, 10	60 (56)	3		13
8	**2a** (1.1)	CH_3CN-H_2O (5:1)		25, 80	94 (84)			
9	**2a** (1.1)	CH_3CN-H_2O (5:1)	$BF_3 \cdot Et_2O$ (0.3)	25, 3.5	100 (100)			
10	**2a** (1.2)	CH_3CN-H_2O (5:1)		50, 10	100 (97)			
11	**2a** (1.2)	CH_3CN-H_2O (5:1)[c]		50, 7.5	100 (100)			
12	**2b** (1.1)	CH_3CN-H_2O (5:1)[c]		50, 1	98 (61)			
13	**2a** (2.1)	CH_3CN-H_2O (5:1)[c]		50, 4	(81)			
14	**2a** (0.34)	CH_3CN-H_2O (5:1)[c]		50, 27	36			63
15	**2a** (2.5)	toluene		30, 96		(82)		

[a] Reactions were carried out under nitrogen, unless otherwise noted. [b] Yields were determined by GC. Yields in parentheses are based on pure isolated materials. [c] Reactions were carried out under atmospheric conditions.

CN−H_2O or AcOH−H_2O have been shown to be acid catalyzed.[8] High yields of sulfoxides have been obtained by the sulfuric acid-catalyzed oxidation with 1-hydroxy-1,2-benziodoxol-3(1*H*)-one (**1a**), in which the recovered *o*-iodobenzoic acid can be reconverted into the oxidizing agent.[9] [Hydroxy(tosyloxy)iodo]benzene can effect the controlled oxidation of sulfides to sulfoxides.[10] (Dichloroiodo)benzene in aqueous pyridine also affords sulfoxides and/or sulfones, depending on the reaction conditions.[11] Catalytic oxidation of sulfides using metalloporphyrin and iodosylbenzene as a terminal oxidant gives sulfoxides in high yields.[12] Benzeneseleninic acid catalyzes oxidation of sulfides with iodosylbenzene, in which [hydroxy(benzeneseleninyloxy)iodo]benzene generated in situ has been proposed to be an active oxidant.[13]



3a **4a**

The results of oxidation of thioanisole (**3a**) with the (*tert*-butylperoxy)iodanes **2** under a variety of conditions are summarized in Table 1. Exposure of **3a** to the peroxyiodane **2a** in dichloromethane at room temperature afforded a mixture of products consisting of the sulfoxide **4a** (31%), methyl phenyl sulfone (**5**) (5%), and chloromethyl phenyl sulfoxide (**6**) (26%). A similar mixture of products was obtained when the (*p*-nitroperoxy)iodane **2b** was employed (Table 1, entry 2). Use of $BF_3 \cdot Et_2O$ as an additive led to selective formation of the sulfoxide **4a** in 67% yield (Table 1, entry 3). The choice of solvents is important in the reaction. Oxidation of **3a** in acetonitrile−water (5:1) at room temperature was very slow (80 h) but highly selective and gave rise to the sulfoxide **4a** in 94% yield. In the absence of water, further oxidation of **4a** to the sulfone **5** may compete to a small extent (compare entries 6 and 8). It has been reported that, in the oxidation of dibenzyl sulfide to the sulfoxide with hydrogen peroxide in isopropyl alcohol, the presence of water decreases the rate of further oxidation to the sulfone, presumably because of the specific solvation of the sulfoxide ground state by water.[14] This solvation results in a decrease in nucleophilicity of the sulfur atom, thereby lowering the reactivity of the sulfoxide toward peroxide oxidation.

The rate of oxidation was much increased either by the use of acid catalyst $BF_3 \cdot Et_2O$ (0.3 equiv) as an additive in acetonitrile−water (5:1) at room temperature (method A) or by carrying out the reaction at 50 °C in acetonitrile−water (5:1) (method B) (Table 1, entries 9−11). In spite of the presence of both a peroxy group and a trivalent iodine in the molecule, the experimental data on the stoichiometry (Table 1, entry 14) of the reaction indicate that the (*tert*-butylperoxy)iodane **2a** oxidizes 1 mol equivalent of the sulfides **3a** to the sulfoxide **4a**. Interestingly, use of toluene as a solvent and 2.5 equiv of **2a** gave the sulfone **5** in 82% yield, whereas other solvents such as benzene, fluorobenzene, acetone, ethyl acetate, and carbon tetrachloride gave poor results for oxidation to the sulfone **5**.

The uncatalyzed (50 °C) and the BF_3-catalyzed oxidations (25 °C) of a variety of sulfides with the (*tert*-butylperoxy)iodane **2a** in acetonitrile−water afforded the corresponding sulfoxides in high yields (Table 2). In general, oxidation of dialkyl sulfides is fast, being completed within 1 h. The rate of oxidation decreases in the order dialkyl > alkyl aryl > diaryl sulfides, which would suggest an electrophilic nature of the oxidant under these conditions.[15] Allylic oxidation[4b] as well as epoxidation[4a] of a double bond cannot compete with the sulfide oxidation (Table 2, entries 11 and 12). The oxidation of diphenyl sulfide (**3e**) under these conditions is very slow; for instance, even after 26 h at 50 °C (method B), a large amount of the sulfide **3e** was recovered unchanged (Table

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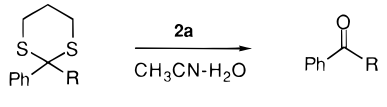
Table 2. Oxidation of Sulfides to Sulfoxides with (*tert*-Butylperoxy)iodane 2a

entry	sulfide	method[a]	time/h	yield,[b] %
1	*n*-$BuSCH_2Ph$	A	0.7	100
2	*n*-$BuSCH_2Ph$	B	0.25	78
3	*i*-$BuSCH_2Ph$	A	0.7	87
4	*i*-$BuSCH_2Ph$	B	0.25	80
5	*s*-$BuSCH_2Ph$	A	0.4	90
6	*s*-$BuSCH_2Ph$	B	0.25	75
7	$(PhCH_2)_2S$	A	0.5	85
8	$(PhCH_2)_2S$	B	0.7	78
9	$Me(CH_2)_4SPh$	A	3	99
10	$Me(CH_2)_4SPh$	B	2	82
11	$CH_2{=}CHCH_2SPh$	A	3.5	82
12	$CH_2{=}CHCH_2SPh$	B	2.5	77
13	*p*-$MeOC_6H_4SMe$ **3b**	A	3	79
14	*p*-$MeOC_6H_4SMe$ **3b**	B	2.25	90
15	*p*-MeC_6H_4SMe **3c**	A	3	75
16	*p*-MeC_6H_4SMe **3c**	B	2	97
17	*p*-ClC_6H_4SMe **3d**	A	6	92
18	*p*-$ClCC_6H_4SMe$ **3d**	B	8	87[c]
19	$PhSCH_2P(O)(OEt)_2$	A	38	82[c]
20	$PhSCH_2P(O)(OEt)_2$	B	11	69[c]
21	Ph_2S **3e**	A	28	98
22	Ph_2S **3e**	B	26	24[d]
23	Ph_2S **3e**	C	11	90
24	Ph_2S **3e**	C	4	74[e]
25	(*p*-$MeOC_6H_4)_2S$	C	5.5	69[f]
26	(*p*-$MeOC_6H_4)_2S$	C	77	86[g]
27	(*p*-$ClC_6H_4)_2S$	C	60	73[h]

[a] Method A: **2a** (1.1 equiv), $BF_3\cdot Et_2O$ (0.3 equiv), CH_3CN-H_2O (5:1), 25 °C, N_2. Method B: **2a** (1.2 equiv), CH_3CN-H_2O (5:1), 50 °C, air. Method C: **2a** (1.2 equiv), CH_2Cl_2, 25 °C, N_2. [b] Yields are based on pure isolated materials. [c] A small amount of sulfides (3−6%) was recovered. [d] 66% of sulfide was recovered unchanged. [e] Instead of **2a**, **2b** was used. [f] 21% of sulfone was obtained. [g] Reaction was carried out using **2a** (1 equiv) at 0 °C. [h] 20% of sulfide was recovered unchanged.

2, entry 22), a finding that is compatible with the decreased nucleophilicity of aryl sulfides as compared to alkyl sulfides. However, in dichloromethane, oxidation of **3e** occurred smoothly even at room temperature (method C) and diphenyl sulfoxide (**4e**) was obtained in 90% yield after 11 h.

The (*tert*-butylperoxy)iodane **2a** was found to undergo deprotection of dithioacetals, regenerating the parent carbonyl function. For instance, treatment of dithioacetals **7** and **8** with **2a** in aqueous acetonitrile at room temperature or at 0 °C gave the parent ketones in good yields. Stork and Zhao reported that dithioacetals are efficiently cleaved to carbonyl compounds by [bis(trifluoroacetoxy)iodo]benzene at room temperature.[16] Their method is especially useful for selective deprotection and is compatible with a variety of other functional groups, such as amines, thioesters, alcohols, amides, alkenes, and nitriles.



7: R = Me
8: R = n-C_5H_{11}

Substituent Effects. To gain some insight into the mechanism of this oxidation of sulfides with the peroxyiodane **2a**, the relative rates of oxidation for a series of ring-substituted thioanisoles **3b** (*p*-MeO), **3c** (*p*-Me), and **3d** (*p*-Cl) were measured in acetonitrile−water either at 30 °C in the presence of $BF_3\cdot Et_2O$ or at 40 °C without an additive by examining competitive reactions in which a mixture of each 25-fold excess of two competing substrates was used. Table 2 shows that aryl methyl sulfoxides **4b**−**d** were formed in high yields under similar conditions, regardless of the substitution of the phenyl ring. The reaction rate was found to be very sensitive to the nature of substituents, and electron-releasing groups such as *p*-MeO and *p*-Me groups increased the rate of oxidation in both reaction conditions; the effect of substituents on the rate of oxidation is shown in Table 3.

Table 3. Relative Reactivity of Thioanisoles 3 to Peroxyiodane 2a

substrate		k_{rel} with BF_3[b]	k_{rel} without BF_3[c]	E_p[a]
3a	(H)	1.0	1.0	1.53
3b	(*p*-MeO)	31.25	13.38	1.26
3c	(*p*-Me)	3.70	3.17	1.41
3d	(*p*-Cl)	0.23	0.24	1.55

[a] One-electron oxidation potentials (V vs SCE in CH_3CN) reported by Oae.[17] [b] $BF_3\cdot Et_2O$ (0.3 equiv), CH_3CN-H_2O (5:1), 30 °C, 3 h, N_2. [c] CH_3CN-H_2O (5:1), 40 °C, 5 h, air.

The BF_3-catalyzed reaction exhibited a greater dependence on the nature of substituents as compared to the uncatalyzed reaction. A Hammett correlation plot for the BF_3-catalyzed oxidation of these thioanisoles **3** presented in Table 3 shows a better correlation of relative rate factors with the σ^+- rather than the σ-constants of substituents in the aromatic ring, and afforded a negative reaction constant $\varrho^+ = -2.23$ ($r = 0.98$).[18] The uncatalyzed oxidation of **3** also showed a large negative reaction constant $\varrho = -3.32$ (σ, $r = 0.98$). These negative ϱ values are greater than those found for the oxidation of **3** with (diacetoxyiodo)benzene in CH_3CN-H_2O ($\varrho = -0.8$),[8b] but appear to be comparable to that for the oxidation with N_2O_4 in carbon tetrachloride $\varrho = -2.7$,[19] with dimethylphenylsilyl hydrotrioxides in acetone $\varrho = -2.0$,[20] and with bromine in aqueous methanol $\varrho = -3.2$.[21] In these reactions with negative ϱ values, a mechanism involving the intermediacy of sulfonium species via nucleophilic attack of sulfides is proposed. The relatively large negative Hammett ϱ values obtained in our reactions indicate that the peroxyiodane **2a** is a highly electrophilic oxidant in acetonitrile−water.

Effects of Radical Inhibitors. We have reported that the benzylic and allylic oxidation of benzyl and allyl ethers to the esters with the alkylperoxyiodane **2a** proceeds via a radical mechanism involving the generation of α-oxy carbon-centered radicals, which were detected by nitroxyl radical trapping.[4b] These results suggest the occurrence of a radical process in this sulfide oxidation. Indeed, the alkylperoxyiodane oxidation of sulfides **3** in dichloromethane (method C) was exclusively inhibited by the use of a free-radical scavenger (Table 4, entries 6 and 7); thus, treatment of thioanisole (**3a**) or diphenyl sulfide (**3e**) with **2a** in the presence of 1.3−1.5 equiv of galvinoxyl[22] resulted in the recovery of more than

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Table 4. Effects of Added Galvinoxyl for Oxidation of Sulfides with (*tert*-Butylperoxy)iodane 2a[a]

entry	sulfide **3**	peroxyiodane **2a** (equiv)	solvent	additive (equiv)		conditions		product (yield,[b] %)	
				BF_3·Et_2O	galvinoxyl	temp/°C,	time/h	**4**	**3**
1	**3a**	1.2	CH_3CN-H_2O (5:1)		1.5	50	10	**4a** (72)	**3a** (28)
2	**3a**	1.1	CH_3CN-H_2O (5:1)	0.3	1.5	25	3.5	**4a** (87)	**3a** (2)
4	**3e**	1.2	CH_3CN-H_2O (5:1)		1.5	50	28	**4e** (3)	**3e** (97)
5	**3e**	1.1	CH_3CN-H_2O (5:1)	0.3	1.5	25	28	**4e** (71)	**3e** (31)
6	**3a**	1.0	CH_2Cl_2		1.3	25	8.5	**4a** (1)	**3a** (99)
7	**3e**	1.2	CH_2Cl_2		1.5	25	26	**4e** (2)	**3e** (98)

[a] Reactions were carried out under nitrogen. [b] Yields were determined by GC.

98% of the sulfides unchanged, and the corresponding sulfoxides were obtained in less than 2% yield. (Compare these results with Table 1, entry 1, and Table 2, entry 23.)

On the other hand, for the reaction of **3a** in CH_3CN-H_2O, addition of the radical scavenger only slightly inhibited oxidation. Uncatalyzed reaction of **3a** in CH_3CN-H_2O at 50 °C in the presence of added galvinoxyl afforded the sulfoxide **4a** in 72% yield with the 28% recovered sulfide **3a** (Table 4, entry 1). The BF_3-catalyzed oxidation of **3a** to **4a** in CH_3CN-H_2O at 25 °C is even less sensitive to the radical scavenger, and only a trace amount of **3a** was recovered (Table 4, entry 2). Similarly, the BF_3-catalyzed oxidation of **3e** in CH_3CN-H_2O is less sensitive to the radical scavenger than the uncatalyzed oxidation, although the oxidations of **3e** are more effectively inhibited by the added galvinoxyl than those of **3a**. These results imply that the oxidation of sulfides **3a** and **3e** in dichloromethane proceeds exclusively by a radical process, while a nonradical process becomes important for the oxidation of **3a** in CH_3CN-H_2O, especially in the BF_3-catalyzed oxidation.

Reaction of Thioanisole (3a) with Hydroxyiodane 1a and/or *tert*-Butyl Hydroperoxide. We have reported a ligand exchange of the *tert*-butylperoxy group of **2a** with an alcohol: for instance, treatment of **2a** with methanol at room temperature for 2 days gives the methoxyiodane **9** in 50% yield.[4b] It seems reasonable to assume, therefore, that in CH_3CN-H_2O the peroxyiodane **2a** undergoes a ligand exchange with water on the hypervalent iodine atom, generating the hydroxyiodane **1a** and *tert*-butyl hydroperoxide. Furthermore, these species generated in situ may oxidize the sulfides to the sulfoxides under the conditions used here. As mentioned above, it has been reported that the hydroxyiodane **1a** oxidizes of thioanisole (**3a**) in acetic acid to give **4a** in 71% yield, although the reaction requires sulfuric acid as a catalyst.[9] Similarly, *tert*-butyl hydroperoxide can effect the oxidation of alkyl sulfides to the corresponding sulfoxides; in such reactions, the addition of acids increases the rate of oxidation.[23]

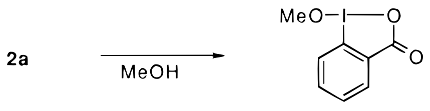

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Table 5. Reaction of Thioanisole (3a) with Hydroxyiodane 1a and/or *tert*-Butyl Hydroperoxide[a]

entry	iodane **1a** (equiv)	*t*-BuOOH (equiv)	additive (equiv)	yield,[b] %	
				3a	**4a**
1	1	0		92	1
2	0	1		93	2
3	1.2	0	*o*-$IC_6H_4CO_2H$ (1)	94	1
4	0	1.2	*o*-$IC_6H_4CO_2H$ (1.2)	98	2
5	1.2	1.2		0	98
6	0.6	1.2		56	34
7[c]	1.2	0.6		0	90
8[d]	1.1	0	BF_3·Et_2O (0.3)	47	53

[a] Reactions were carried out in CH_3CN-H_2O (5:1) at 50 °C for 7.5 h under atmospheric conditions, unless otherwise noted. [b] Yields are determined by GC. [c] Reaction time: 49 h. [d] Reaction was carried out in CH_3CN-H_2O (5:1) at 25 °C for 3.5 h under nitrogen.

The results of the attempted oxidation of thioanisole (**3a**) with the hydroxyiodane **1a** and/or *tert*-butyl hydroperoxide are summarized in Table 5. Exposure of **3a** to either the hydroxyiodane **1a** or *tert*-butyl hydroperoxide in CH_3CN-H_2O (5:1) at 50 °C for 7.5 h resulted in the recovery of a large amount of the sulfide **3a** unchanged, and only a trace amount of **4a** (less than 2%) was detected. In the oxidation of sulfides to sulfoxides shown in Table 2, the oxidant **2a** was always converted to *o*-iodobenzoic acid; therefore, this acid may catalyze the oxidation with **1a** or *tert*-butyl hydroperoxide, because *o*-iodobenzoic acid is known to be a relatively strong acid with a pK_a value of 2.85.[24,25] However, this acid was not able to catalyze the reaction of **3a** with **1a** or *tert*-butyl hydroperoxide under these conditions (Table 5, entries 3 and 4). A moderate yield of the sulfoxide **4a** was obtained by the reaction with **1a** when BF_3·Et_2O was used as an acid catalyst (Table 5, entry 8).

It is noteworthy that a combination of the hydroxyiodane **1a** and *tert*-butyl hydroperoxide makes the oxidation of the sulfide **3a** possible (Table 5, entry 5). Thus, reaction of **3a** with **2a** (1.2 equiv) and *tert*-butyl hydroperoxide (1.2 equiv) in CH_3CN-H_2O (5:1) at 50 °C for 7.5 h afforded the sulfoxide **4a** in 98% yield. Using less **1a** or *tert*-butyl hydroperoxide led to less effective oxidation of **3a** (Table 5, entries 6 and 7).

^1H NMR experiments indicated that an extensive ligand exchange of the (*tert*-butylperoxy)iodane **2a** with water takes place in CD_3CN-D_2O (5:1); after heating for 5.5 h at 50 °C, formation of a large amount of *tert*-butyl hydroperoxide was observed along with deposition of a white precipitate of the hydroxyiodane **1a**, and the ratio of *tert*-butyl hydroperoxide to **2a** was found to be 97:3. On the other hand, a mixture of **1a** and *tert*-butyl hydroperoxide in CD_3CN-D_2O under the same conditions resulted in the formation of **2a** in 2% yield. These results

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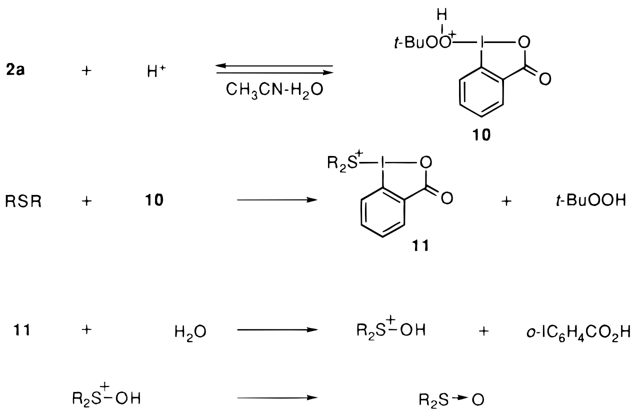
(23) (a) Bateman, L.; Hargrave, K. R. *Proc. R. Soc. A* **1954**, *224*, 389. (b) Bateman, L.; Hargrave, K. R. *Proc. R. Soc. A* **1954**, *224*, 399. (c) Oae, S.; Asada, K.; Yoshimura, T. *Tetrahedron Lett.* **1983**, *24*, 1265. (d) Madesclaire, M. *Tetrahedron* **1986**, *42*, 5459.

(24) Lide, D. R., Ed. CRC *Handbook of Chemistry and Physics*, 73rd ed; CRC Press: Boca Raton, FL, 1992; pp 8–39.

(25) The cyclic hydroxyiodane **1a** with a pK_a of 7.0 is less acidic than *o*-iodobenzoic acid and the estimated pK_a of the noncyclic tautomer, 2-iodosylbenzoic acid *o*-$OIC_6H_4CO_2H$, is 3.7. The iodane **1a** has been shown to exist predominantly in this cyclic structure, both in solution and in the solid state. See: (a) Katritzky, A. R.; Savage, G. P.; Palenik, G. J.; Qian, K.; Zhang, Z. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1657. (b) Moss, R. A.; Kim, K. Y.; Swarup, S. *J. Am. Chem. Soc.* **1986**, *108*, 788.

Scheme 1. Ionic Mechanism for Reaction in CH_3CN-H_2O



imply that an equilibrium between **2a** and **1a**, which strongly favors formation of **1a**, is probably established under these conditions.

$$\mathbf{2a} + H_2O \rightleftarrows \mathbf{1a} + t\text{-BuOOH}$$

Reaction Mechanism. A. Oxidation in Acetonitrile−Water. The fact that neither the hydroxyiodane **1a** nor *tert*-butyl hydroperoxide itself undergoes oxidation of the sulfide **3a** to the sulfoxide **4a** in CH_3CN-H_2O at 50 °C, and a combination of **1a** and *tert*-butyl hydroperoxide is required for the oxidation, combined with the existence of an equilibrium between **2a** and **1a** under these conditions, strongly suggest that the (*tert*-butylperoxy)iodane **2a** or its activated species is responsible for the oxidation as the actual oxidant.

A mechanism shown in Scheme 1, which is consistent with our results, involves formation of the activated peroxyiodane **10** by protonation to the apical oxygen atom of **2a**. The protonation increases the leaving group ability of *tert*-butylperoxy group as well as a positive charge on the hypervalent iodine. Formation of the activated peroxyiodane **10** is anticipated by considering the polarization of **2a** expected by a theory for electronic structure of hypervalent molecules in which the hypervalent bond (the three-center, four-electron bond) has an accumulation of negative charge on the apical ligands and positive charge on the central atom.[26] The BF_3-catalyzed reaction (method A) will lead to a higher concentration of the activated species **10** than the uncatalyzed reaction (method B), in which the resulting *o*-iodobenzoic acid with a pK_a value of 2.85 will act as a mild acid catalyst. Ligand exchange of the peroxyiodane **10** by nucleophilic attack of sulfides toward the iodine(III) atom would produce the sulfonium species **11**, which, in turn, reacts with water to give sulfoxides. Formation of the iodine(III)−sulfonium ions like **11** has been proposed for the oxidation of sulfides with [bis(acyloxy)iodo]benzenes,[8] 1-hydroxy-1,2-benziodoxol-3(1*H*)-one (**1a**),[9] and [bis(trifluoroacetoxy)-iodo]benzene.[27]

The large negative Hammett ϱ values observed for the oxidation of thioanisoles **3** in CH_3CN-H_2O ($\varrho^+ = -2.23$ for the BF_3-catalyzed and $\varrho = -3.32$ for the uncatalyzed reactions) are in good agreement with a mechanism shown in Scheme 1, involving the intermediacy of the sulfonium species **11**. These data may further suggest that formation of the sulfonium species **11** is likely to be the rate-determining step for the oxidation to the sulfoxides.

In marked contrast to **2a**, the hydroxyiodane **1a** does not undergo oxidation of the sulfide **3a** in CH_3CN-H_2O at 50 °C even in the presence of *o*-iodobenzoic acid (Table 5). This reactivity difference between the hydroxyiodane **1a** and the (*tert*-butylperoxy)iodane **2a** for the oxidation is partly attributable to the limited solubility of **1a** under these conditions. Furthermore, the more acidic nature of *tert*-butyl hydroperoxide ($pK_a = 12.8$ in water) compared to water ($pK_a = 15.7$) may make the *tert*-butylperoxy group a better leaving group than the hydroxy group.[28]

As an alternative mechanism, single electron transfer (SET) process from the sulfides to the peroxyiodane **2a** or to the activated species **10** could be envisioned. Oxidation of substituted thioanisoles **3a**−**d** by a reconstituted system of purified cytochrome P-450 to give sulfoxides involves one-electron transfer from the sulfides to the active species of the enzyme, generating the sulfide cation radical.[17] This SET oxidation shows a small negative reaction constant $\varrho^+ = -0.16$ (σ^+), which is in marked contrast to the large negative values in the BF_3-catalyzed ($\varrho^+ = -2.23$) and the uncatalyzed oxidations ($\varrho = -3.32$) by **2a**.[29] Logarithms of relative reactivity of thioanisoles **3a**−**d** toward **2a**, however, were found to be correlated linearly with the reported one-electron oxidation potentials of the sulfides,[17] shown in Table 3, with the following correlation coefficients: $r = 0.97$ (with BF_3) and 0.95 (without BF_3). Furthermore, the oxidation of **3a** with **2a** at 50 °C was considerably inhibited by the addition of SET quencher 1,4-dimethoxybenzene (the oxidation potential $E_p = 1.28$ V vs SCE in CH_3CN),[30] but not by the addition of methoxybenzene ($E_p = 1.96$ V vs SCE in CH_3CN).[31]

$$\mathbf{3a} \xrightarrow[\substack{CH_3CN\text{-}H_2O \\ 50\ °C,\ 7.5\ h}]{\mathbf{2a}\ (1.2\ \text{equiv})} \mathbf{4a} + \mathbf{3a}$$

additive:	4a	3a
p-$(MeO)_2C_6H_4$	33%	64%
$MeOC_6H_5$	97%	3%

The negligible effect (see Table 4, entry 2) of the added free-radical scavenger in the BF_3-catalyzed oxidation (method A) of **3a** suggests these ionic mechanisms. Inhibition of the uncatalyzed oxidation (method B) of **3a**, and the catalyzed and uncatalyzed oxidation of **3e** with added galvinoxyl to a small but discernible extent, may suggest a simultaneous occurrence of a radical process as a competing pathway.

B. Oxidation in Dichloromethane. The attempted oxidation of diphenyl sulfide (**3e**) with the hydroxyiodane **1a** or *tert*-butyl hydroperoxide in dichloromethane resulted in the recovery of a large amount (more than 80%) of the sulfide **3e** and only 1−2% yield of diphenyl sulfoxide (**4e**). A 24% yield of the sulfoxide **4e** was obtained in a similar reaction using a combination of the

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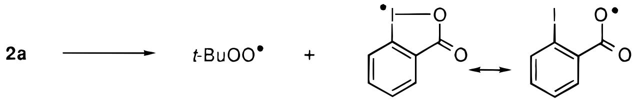
hydroxyiodane **1a** and *tert*-butyl hydroperoxide in dichloromethane. These results again suggest that the actual oxidant for the reaction in dichloromethane is (*tert*-butylperoxy)iodane **2a** rather than the hydroxyiodane **1a** and *tert*-butyl hydroperoxide.

In marked contrast to the reaction in CH_3CN-H_2O, the radical nature of the oxidation of **3a** and **3e** in dichloromethane was substantiated by the exclusive inhibition of the reaction with the added free-radical scavenger (Table 4). The (*tert*-butylperoxy)iodane **2a** could generate iodine-centered radicals at room temperature in solution, and the first-order rate constant for the decomposition of **2a** in dichloromethane at 30 °C has been reported to be $k_{obsd} = 2.62 \times 10^{-5}\ s^{-1}$.[4b] The initial step of the decomposition of **2a** would involve the homolytic bond cleavage of the weak iodine(III)−peroxy bond, generating *tert*-butylperoxy radical and the [9-I-2] iodanyl radical **12**. In analogy to a mechanism recently shown to occur in the oxidation of sulfides to sulfoxides by hydroxy[32] and peroxy radicals,[33] addition of these radicals to sulfides leading to the intermediary formation of the [9-S-3] sulfuranyl radicals **13**−**15** might constitute one of the possible reaction pathways. The *tert*-butylperoxy radical has been shown to be an efficient radical oxidant with the highly electrophilic nature for the conversion of sulfides to sulfoxides.[34]



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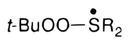

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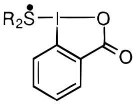

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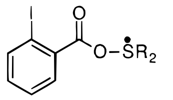

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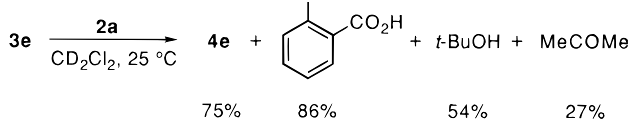
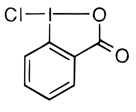
To investigate the fate of the *tert*-butylperoxy group of **2a**, ^1H NMR experiments were carried out in dichloromethane-d_2 at room temperature, and the products from the reaction of **3e** with **2a** were carefully analyzed: in addition to formation of the sulfoxide **4e** (75%) and *o*-iodobenzoic acid (86%), a 27% yield of acetone and a 54% yield of *tert*-butyl alcohol were detected. The *tert*-butoxy radical could be generated from *tert*-butylperoxy radical and is well-known to (1) undergo β-scission yielding acetone and methyl radical, or (2) to abstract a hydrogen atom yielding *tert*-butyl alcohol.[35] Thus, the formation of acetone as well as *tert*-butyl alcohol provides firm evidence for the intervention of *tert*-butoxy radical in this reaction.



The formation of a considerable amount of the α-chloromethyl sulfoxide **6** in the oxidation of thioanisole (**3a**) in dichloromethane deserves attention. The decomposition of **2a** in chloroform at room temperature affords 1-chloro-1,2-benziodoxol-3(1*H*)-one (**16**) through ligand exchange in high yield.[4a] Furthermore, it has been shown that alkyl sulfides undergo α-monochlorination with (dichloroiodo)arenes, which act as a controlled source of chlorine, to give α-chloro sulfides and α-chloro sulfoxides.[36] Therefore, it seems reasonable to assume that the chloroiodane **16** generated in situ from **2a** in dichloromethane could be responsible for the formation of the α-chloromethyl sulfoxide **6**.



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Experimental Section

IR spectra were recorded on JASCO IRA-1 and Perkin Elmer 1720 FT-IR spectrometers. ^1H and ^{13}C NMR were recorded on JEOL FX-200 and JMN-GCX 400 spectrometers. Chemical shifts were reported in parts per million (ppm) downfield from internal Me_4Si. Mass spectra (MS) were obtained on a JEOL JMS-DX300 spectrometer. Melting points were determined with a Yanaco micro melting points apparatus and are uncorrected. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-14A gas chromatograph with a column (1 or 3 m) of 15% FFAP and 20% Silicon GE SF-96 on Chromosorb W-AWDMCS. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, silica gel F-254). Kielselgel 60 (Merck, 230−400 mesh) was used for flash chromatography.

Purification of solvents was carried out under nitrogen. Acetonitrile and dichloromethane were dried over CaH_2 and distilled. Toluene was distilled from sodium benzophenone ketyl. BF_3-Et_2O was distilled from CaH_2. Hydroxyiodane (**1a**), thioanisoles **3a**−**d**, diphenyl sulfide (**3e**), and dibenzyl sulfide are commercially available. Commercially unavailable phenyl and benzyl sulfides were prepared by reactions of alkyl halides with potassium salts of thiols in methanol or ethanol. Phenyl (diethoxyphosphinyl)methyl sulfide was prepared according to literature procedure.[37]

General Procedure for Oxidation of Thioanisole (3a) with (*tert*-Butylperoxy)iodanes (2). To a stirred solution (4 mL) of peroxyiodane **2a**[4] or **2b**[5] was added thioanisole (**3a**) (25 mg, 0.20 mmol), and the mixture was stirred for the conditions shown in Table 1. Water was added and the mixture was extracted with dichloromethane three times, and the combined organic phase was washed with water and brine. The yields of methyl phenyl sulfoxide (**4a**), methyl phenyl sulfone (**5**), and chloromethyl phenyl sulfoxide (**6**) were determined by analytical GC using a column of 15% FFAP (200 °C, eicosane as the internal standard), and are given in Table 1. These products were isolated by preparative TLC (1:1:1 hexane−dichloromethane−diethyl ether). **4a**:[38] colorless oil; IR (film) 3056, 1718, 1444, 1090, 1049, 749, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.74−7.44 (m, 5H), 2.74 (s, 3H); MS *m/z* (relative intensity) 140 (93, M^+), 125 (100), 97 (51), 77 (62), 51 (56). **5**:[38] colorless plates; mp 88−89 °C (recrystallized from dichloromethane−diethyl ether−hexane); IR (KBr) 3024, 1449, 1285, 751, 690, 529 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.02−7.87 (m, 2H),

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7.73−7.48 (m, 3H), 3.06 (s, 3H); MS *m/z* (relative intensity) 156 (26, M$^+$), 141 (29), 94 (35), 77 (100), 51 (26). **6**: colorless oil; IR (film) 3003, 2935, 1445, 1087, 1054, 759, 741, 690, 518 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.82−7.40 (m, 5H), 4.40 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 140.89 (s), 132.18 (d), 129.35 (d), 124.80 (d), 61.33 (t); MS *m/z* (relative intensity) 174 (28, M$^+$), 125 (100), 97 (91), 91 (38), 77 (100), 51 (81). HRMS Calcd for C_7H_7ClOS (M$^+$) 173.9906. Found 173.9836. The authentic sample of **6** was prepared by oxidation of thioanisole (**3a**) with (dichloroiodo)benzene according to literature procedure.[39]

General Procedure for Oxidation of Sulfides to Sulfoxides with (*tert*-Butylperoxy)iodane (2a). (a) Method A. To a stirred solution of peroxyiodane **2a** (74 mg, 0.22 mmol) in 4.8 mL of CH_3CN-H_2O (5:1) were added a sulfide (0.2 mmol) and BF_3-Et_2O (9 mg, 0.06 mmol) under nitrogen at room temperature, and the mixture was stirred for the periods shown in Table 2. Water was added, the mixture was extracted with dichloromethane three times, and the combined organic phase was washed with 5% aqueous NaOH solution, water, and then brine. The solution was dried over anhydrous Na_2SO_4 and concentrated to give an oil, which was purified by preparative TLC (1:1 hexane−ethyl acetate). The yields of pure products are given in Table 2.

(b) Method B. To a stirred solution of peroxyiodane **2a** (81 mg, 0.24 mmol) in 4.8 mL of CH_3CN-H_2O (5:1) was added a sulfide (0.2 mmol) under atmosphere at room temperature, and the mixture was stirred for the periods shown in Table 2 at 50 °C. A finely dispersed precipitate appeared during the first 0.5 h. The isolated yields of pure products are given in Table 2.

(c) Method C. To a stirred solution of peroxyiodane **2a** (40 mg, 0.12 mmol) in dichloromethane (3 mL) was added a sulfide (0.1 mmol) under nitrogen at room temperature, and the mixture was stirred for the periods shown in Table 2. The isolated yields of pure products are given in Table 2.

Oxidative Deprotection of Acetophenone Dithioacetal (7). To a stirred solution of peroxyiodane **2a** (353 mg, 1.05 mmol) in 6 mL of CH_3CN-H_2O (9:1) was added a solution of dithioacetal **7** (105 mg, 0.50 mmol) in 7 mL of CH_3CN-H_2O (9:1) under nitrogen at 0 °C, and the mixture was stirred for 5 h. Analytical GC using a column of 15% FFAP (200 °C, eicosane as the internal standard) showed the formation of acetophenone in 84% yield.

Oxidative Deprotection of Hexanophenone Dithioacetal (8). To a stirred solution of peroxyiodane **2a** (50 mg, 0.15 mmol) in 3 mL of CH_3CN-H_2O (9:1) was added a solution of dithioacetal **8** (27 mg, 0.10 mmol) in 2 mL of CH_3CN-H_2O (9:1) under nitrogen at room temperature, and the mixture was stirred for 3 h. Analytical GC using a column of 20% Silicon GE SF-96 (150 °C, *n*-hexadecane as the internal standard) showed the formation of hexanophenone in 77% yield.

General Procedure for the Competition Experiments. (a) In the Presence of BF_3-Et_2O. To a stirred solution of thioanisole (**3a**) (155 mg, 1.25 mmol) and a substituted thioanisole (1.25 mmol) in 3 mL of CH_3CN-H_2O (5:1) were added a solution of peroxyiodane **2a** (17 mg, 0.05 mmol) in 3 mL of CH_3CN-H_2O (5:1) and then BF_3-Et_2O (2.1 mg, 0.015 mmol) under nitrogen. The reaction was allowed to proceed at 30 ± 0.2 °C for 3 h. After addition of 10% aqueous $Na_2S_2O_3$ solution at 0 °C, the mixture was stirred for 10 min and analyzed for the two sulfoxides by GC using a column of 15% FFAP (200 °C, docosane as the internal standard). The results are reported in Table 3.

(b) Without BF_3-Et_2O. To a stirred solution of thioanisole (**3a**) (155 mg, 1.25 mmol) and a substituted thioanisole (1.25 mmol) in 6 mL of CH_3CN-H_2O (5:1) was added peroxyiodane **2a** (17 mg, 0.05 mmol) under atmosphere. The reaction was allowed to proceed at 40 ± 0.2 °C for 5 h. After addition of 10% aqueous $Na_2S_2O_3$ solution at 0 °C, the mixture was stirred for 10 min and analyzed for the two sulfoxides by GC using a column of 15% FFAP. The results are reported in Table 3.

General Procedure for Oxidation of Sulfides with 2a in the Presence of Radical Inhibitors. To a stirred solution (3 mL) of sulfide **3** (0.2 mmol) and galvinoxyl (127 mg, 0.3 mmol) was added a solution (3 mL) of peroxyiodane **2a** (0.24 mmol) under nitrogen, and the mixture was stirred for the periods shown in Table 4. The yields of products were determined by analytical GC and are given in Table 4.

Reaction of Thioanisole (3a) with Hydroxyiodane 1a and *tert*-Butyl Hydroperoxide. To a stirred suspension of hydroxyiodane **1a** (63 mg, 0.24 mmol) in 4 mL of CH_3CN-H_2O (5:1) were added thioanisole (**3a**) (25 mg, 0.20 mmol) and 70% aqueous *tert*-butyl hydroperoxide (31 mg, 0.24 mmol) at 50 °C under atmosphere, and the mixture was stirred for 7.5 h. Analytical GC using a column of 15% FFAP showed the formation of **4a** in 98% yield (Table 5, entry 5).

Ligand Exchange of Peroxyiodane 2a with Water. A solution of peroxyiodane **2a** (34 mg, 0.1 mmol) in 2.4 mL of CD_3CN-D_2O (5:1) was heated at 50 °C under atmosphere. A finely dispersed precipitate of hydroxyiodane **1a** appeared during the first 0.5 h. Formation of *tert*-butyl hydroperoxide-d_1 by ligand exchange of **2a** with D_2O was detected by ^{1}H NMR spectra, and the reaction time and the ratios of peroxyiodane **2a** to *tert*-butyl hydroperoxide are as follows: 0.5 h, 83:17; 1 h, 5:95; 5.5 h, 3:97; 8.5 h, 3:97; 13 h, 3:97. In a separate experiment, hydroxyiodane **1a** was isolated in 80% yield by heating at 50 °C for 5.5 h.

Ligand Exchange of Hydroxyiodane 1a with *tert*-Butyl Hydroperoxide. A suspension of hydroxyiodane **1a** (26 mg, 0.10 mmol) and 70% aqueous *tert*-butyl hydroperoxide (13 mg, 0.10 mmol) in 2.4 mL of CD_3CN-D_2O (5:1) was heated at 50 °C under atmosphere. Formation of a small amount of peroxyiodane **2a** was detected by ^{1}H NMR spectra, and the reaction time and the ratios of peroxyiodane **2a** to *tert*-butyl hydroperoxide-*d* are as follows: 0.3 h, 2:98; 5.5 h, 2:98; 10 h, 2:98.

Oxidation of Thioanisole (3a) in the Presence of 1,4-Dimethoxybenzene. To a stirred solution of thioanisole (**3a**) (12 mg, 0.10 mmol) and 1,4-dimethoxybenzene (17 mg, 0.12 mmol) in 2.5 mL of CH_3CN-H_2O (5:1) was added a solution of peroxyiodane **2a** (47 mg, 0.12 mmol) in 2 mL of CH_3CN-H_2O (5:1) under atmosphere at 50 °C, and the mixture was stirred for 7.5 h. Analytical GC using a column of 15% FFAP showed the formation of sulfoxide **4a** (33%) along with the recovered **3a** (64%).

Oxidation of Thioanisole (3a) in the Presence of Methoxybenzene. To a stirred solution of thioanisole (**3a**) (12 mg, 0.1 mmol) and methoxybenzene (13 mg, 0.12 mmol) in 2.5 mL of CH_3CN-H_2O (5:1) was added a solution of peroxyiodane **2a** (47 mg, 0.12 mmol) in 2 mL of CH_3CN-H_2O (5:1) under atmosphere at 50 °C, and the mixture was stirred for 7.5 h. Analysis by GC indicated a 97% yield of sulfoxide **4a** and a small amount of **3a** (3%).

Oxidation of Diphenyl Sulfide (3e) with 2a in Dichloromethane-d_2. Oxidation of diphenyl sulfide (**3e**) (9 mg, 0.05 mmol) with peroxyiodane **2a** (17 mg, 0.05 mmol) in CD_2Cl_2 (0.5 mL) was carried in NMR tube at room temperature, and the mixture was allowed to stand for 11 days with occasional shaking. ^{1}H NMR analysis showed the formation of sulfoxide **4e** (75%), *o*-iodobenzoic acid (86%), *tert*-butyl alcohol (54%), and acetone (27%).

Supporting Information Available: Spectroscopic data for **4b−e**, benzyl *n*-butyl sulfoxide, benzyl isobutyl sulfoxide, benzyl *sec*-butyl sulfoxide, dibenzyl sulfoxide, *n*-pentyl phenyl sulfoxide, allyl phenyl sulfoxide, phenyl (diethoxyphosphinyl)methyl sulfoxide, bis(*p*-methoxyphenyl) sulfoxide, bis(*p*-chlorophenyl) sulfoxide, and bis(*p*-methoxyphenyl) sulfone (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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