Reactivity and Synthetic Utility of 1-(Arenesulfonyloxy)benziodoxolones

Takahito Muraki,[†] Hideo Togo,*[,†,‡] and Masataka Yokoyama[†,‡]

Graduate School of Science and Technology, and Department of Chemistry, Faculty of Science, Chiba University, Yayoi cho 1-33, Inage-ku, Chiba 263-8522, Japan

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The reactivity and synthetic use of 1-(arenesulfonyloxy)benziodoxolones were studied. In the presence of iodine, 1-(arenesulfonyloxy)benziodoxolones iodinated various aromatics to give iodoarenes in moderate to good yields. In particular, 1-(*p*-chlorobenzenesulfonyloxy)benziodoxolone showed the best reactivity. Using a halide salt such as lithium bromide or lithium chloride instead of iodine, the corresponding aryl bromides and chlorides were also obtained in good yields. In the absence of aromatics, 1-(arenesulfonyloxy)benziodoxolones gave rise to desulfonyloxyiodination reactions to give the corresponding aryl iodides via electrophilic ipso substitution on the aromatic rings. Furthermore, the 1-(*p*-toluenesulfonyloxy)benziodoxolone/iodine system iodotosyloxylated alkynes in good yields. These reactions proceeded via the formation of arenesulfonyl hypoiodites.

Introduction

Recently, intensive study of organohypervalent iodine compounds has been carried out;[1] in particular, the preparation and synthetic use of cyclic trivalent iodine compounds such as benziodoxole and benziodazolone skeletons are of interest. For example, 1-(alkanesulfonyloxy)benziodoxoles and -benziodoxolones and 1-(tosyloxy)-benziodoxolone (**1A**) were prepared by Zhdankin et al. in 1994, and the former compounds have been used for the synthesis of iodonium salts, while the latter compound has not been used as a synthetic tool.[2] Furthermore, 1-(alkylperoxy)benziodoxolones were reported as a useful oxidation reagent from benzyl ethers to benzoyl esters,[3] and 1-azido,[4] 1-cyano,[5] and 1-amido benziodoxoles[6] and -benziodoxolones could be used for the direct azidation, cyanation, and amidation of organic substrates. Here, we report our study on the reactivity and synthetic utility of various 1-(arenesulfonyloxy)benziodoxolones.

Results and Discussion

1. Halogenation of Aromatics. The preparation of aryl halides is a very important field in organic chemistry because aryl halides are precursors for various functional group transformations and are very valuable for organic synthesis; therefore, many halogenation reagents have been developed hitherto.[7] Today, it is known that a few trivalent iodine compounds, such as (diacetoxyiodo)-benzene (**2**),[8] [bis(trifluoroacetoxy)iodo]benzene (**3**),[9] and [hydroxy(tosyloxy)iodo]benzene (**4**, Koser's reagent),[10] have been used for the halogenation of aromatics. Accordingly, we attempted the halogenation reaction of

[†] Graduate School of Science and Technology.

[‡] Department of Chemistry.

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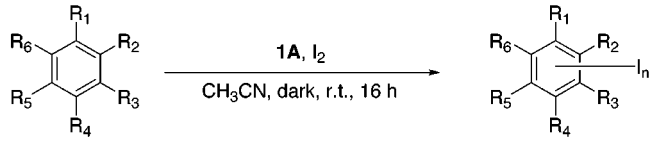
Table 1. Iodination of Aromatics 5 with Iodane 1A



5 6

entry	substituted groups (R_1−R_6)	5	ratio[a] (**5**/**1A**/I_2)	*n*	iodinated position	product	yield/%
1	1,3,5-trimethoxy	**5a**	A	3	2, 4, 6	**6a**	50
2	1,3,5-triisopropyl	**5b**	B	1	2	**6b**	87
3	1,3,5-trimethyl	**5c**	C	2	2, 4	**6c**	99
4	1-methoxy-4-methoxycarbonyl	**5d**	B	1	2	**6d**	85
5	1-methoxy-4-bromo	**5e**	B	1	2	**6e**	99
6	1,4-dimethyl	**5f**	C	2	2, 5	**6f**	96
7	1,3-dimethyl	**5g**	C	2	4, 6	**6g**	78
8	methoxy	**5h**	C	2	2, 4	**6h**	80
9	*tert*-butyl	**5i**	B	1	4	**6i**	79
10	chloro	**5j**		1	4	**6j**	40[b,c]
11	acetoxy	**5k**	D	1	4	**6k**	75[d]

[a] A: Ratio of **5**/**1A**/I_2 is 1.0/3.3/1.6. B: Ratio of **5**/**1A**/I_2 is 1.0/1.2/0.6. C: Ratio of **5**/**1A**/I_2 is 1.0/2.4/1.2. D: Ratio of **5**/**1A**/I_2 is 1.0/1.6/0.8. [b] Chlorobenzene was used as a solvent [c] Yield was determined based on **1A**. [d] Solvent was reduced to 1.5 mL.

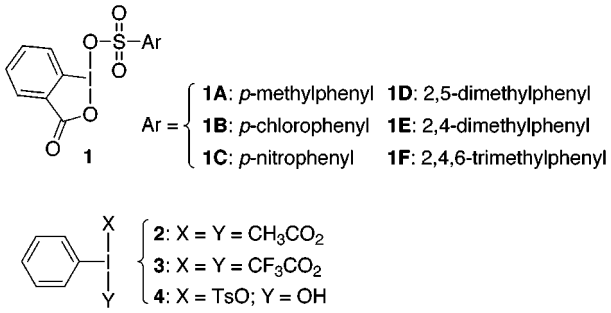


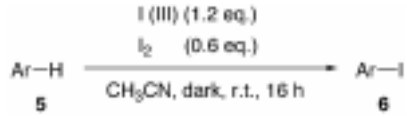
Figure 1.

aromatics using various 1-(arenesulfonyloxy)benziodoxolones (**1**).[11] Thus, various 1-(arenesulfonyloxy)-benziodoxolones (**1**) were prepared with Zhdankin's method and were obtained in ~70% yields (Figure 1).

At first, iodane **1A** was used for the iodination of various aromatics **5**, and results are shown in Table 1.

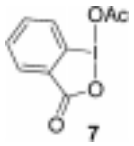
In entries 1−3 (Table 1), trisubstituted benzenes were iodinated. Aromatics **5a** gave the triiodinated compound in moderate yield. This iodination reaction also proceeded in methanol and 1,2-dichloroethane solvents. Thus, triisopropyliodobenzene (**6b**) was obtained in 78% and 98% yields, respectively, under the same conditions, while, an ethyl acetate solvent retarded this reaction (iodide **6b** was obtained in only 36% yield). 2,4-Diiodomesitylene was obtained in 99% yield under the condition C at rt. However, when the reaction was carried out in the presence of mesitylene at 0 °C, iodomesitylene was mainly obtained in 71% yield, though the reaction required a long reaction time (32 h). Next, iodination and chlorination of tri-*tert*-butylbenzene were attempted; however, the corresponding halides were not formed because of the large steric hindrance of the *tert*-butyl groups. Di- and monosubstituted aromatics having alkyl and alkoxy groups also gave the corresponding iodides in good yields (Table 1, entries 4−9). Iodide **6j** was obtained in 40% yield, using chlorobenzene (**5j**) as a solvent. Phenyl acetate (**5k**) was iodinated only in 39% yield under the standard conditions. Then, the amount of solvent was decreased from 5 to 1.5 mL to form iodinated product **6k** in 75% yield. However, iodination of ethyl benzoate did not proceed at all. The iodination ability of various iodanes **1A**, **1B**, **1C**, **2**, **3**, **4**, and 1-acetoxybenziodoxolone (**7**) was studied, and the results are shown in Table 2 and Figure 2.

Table 2. Reactivity for Iodination with Various Iodanes



	yields/%‘		
I (III)	**6b**	**6k**	**6l**[a]
1A	87	39	80
1B	85	68	83
1c	23	58	83
2	41	0	38
3	88	57	53
4	64	39	53
7[b]	0	0	0

[a] Iodonaphthalene. [b] 1-Acetoxybenziodoxolone.



As typical aromatics for iodination, triisopropylbenzene (**5b**), phenyl acetate (**5k**), and naphthalene (**5l**) were used, and the reactivity was compared. Here, it was seen that 1-(arenesulfonyloxy)benziodoxolones **1** gave the corresponding iodide **6** in moderate to good yields; in particular, 1-(*p*-chlorobenzenesulfonyloxy)benziodoxolone (**1B**) showed the best reactivity for the iodination of aromatics. Iodination and chlorination reactions using Koser's reagent **4** were previously reported by McNelis et al.;[10] however, yields were not so high as shown in Table 2. [Bis(trifluoroacetoxy)iodo]benzene (**3**) was a better iodination reagent than (diacetoxyiodo)benzene (**2**). Initially, we expected that iodane **7** would show moderate iodination ability, similar to that of iodane **2**, and we thought that these iodination species might be acetyl hypoiodite. However, iodinated compounds were not

(11) Preliminary communication: Muraki, T.; Togo, H.; Yokoyama, M. *Synlett* **1997**, 286.

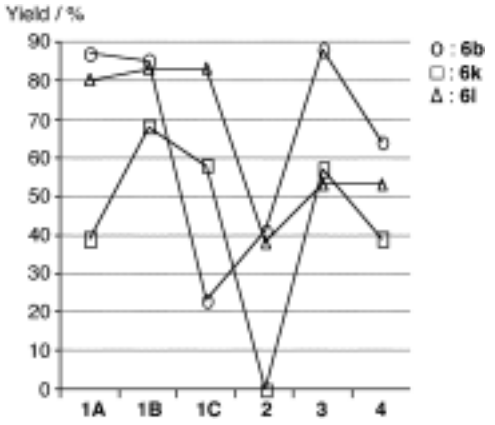
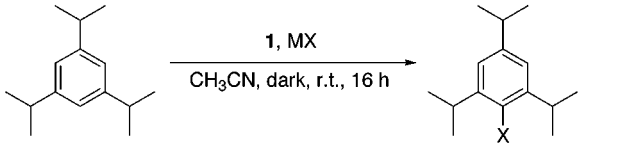


Figure 2.

Table 3. Halogenation of Aromatics 5b Using Halide Salts



5b

6b : X = I; **8b** : X = F
9b : X = Cl; **10b** : X = Br

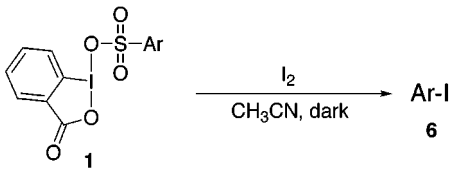
entry	1	MX	conditions[a]	product	yield/%
1	**1A**	Bu_4NF	A	**8b**	0
2	**1A**	Bu_4NCl	A	**9b**	73
3	**1A**	LiCl	A	**9b**	84
4	**1B**	LiCl	A	**9b**	78
5	**1C**	LiCl	A	**9b**	66
6	**1A**	Bu_4NBr	A	**10b**	68
7	**1A**	Bu_4NBr	B	**10b**	84
8	**1A**	LiBr	A	**10b**	79
9	**1B**	LiBr	A	**10b**	74
10	**1C**	LiBr	A	**10b**	66
11	**1A**	Bu_4NI	A	**6b**	0
12	**1A**	Bu_4NI	B	**6b**	71

[a] A: Ratio of **5b**/**1**/MX was 1.0/1.2/1.2. B: Ratio of **5b**/**1**/MX was 1.0/2.4/1.2.

obtained with iodane **7**. Though the difference between iodanes **2** and **7** in iodination ability is not clear, we speculated that the benziodoxolone skeleton should be very rigid, and so, the formation of acetyl hypoiodite would be retarded. Various halogenation reactions were then carried out using halide salts (Table 3).

Fluorination reactions did not proceed (Table 3, entry 1), while chlorination (Table 3, entries 2−5) and bromination (Table 3, entries 6−10) reactions proceeded effectively, and the corresponding halides, **9b** and **10b** were obtained in good yields. Here, iodanes **1A**, **1B**, and **1C** show similar halogenation ability using halide salts. Compound **5e** was also halogenated with the iodane **1A**/lithium halide system, and the corresponding halides 2-chloro-4-bromoanisole (**9e**) and 2,4-dibromoanisole (**10e**) were obtained in 63% and 81% yields, respectively. In the bromination reactions of aromatics, the solution color turned to orange, after addition of bromide salts, so it suggests that the bromide anion might be oxidized to bromine (Br_2) with iodane **1**. Thus, bromination reactions would proceed through the formation of bromine. Actually, 1,3,5-triisopropylbenzene (**5b**) was converted to the corresponding bromide **10b** with bromine alone in 57% yield under the same conditions. In entry 7 of Table 3, the amount of iodane was increased to generate arenesulfonyl hypobromite. However, there was no remarkable difference in the bromination, while the iodide **6b** was not formed in entry 11 (Table 3). This suggests that iodane **1A** was completely consumed by the oxidation of iodide to iodine. However, iodine has no ability to iodinate aromatics; therefore, an iodination reaction did not occur. Practically, treatment of iodine alone and 1,3,5-triisopropylbenzene (**5b**) did not give the corresponding iodide **6b** at all. When the amount of iodane **1A** was doubled (Table 3, entry 12), the corresponding iodide **6b** was obtained in 71% yield. This suggests that the iodination species should be an arenesulfonyl hypoiodite species ($ArSO_3I$), not iodine.

Table 4. Desulfonyloxyiodination Reaction of Iodanes 1



1 **6**

entry	1	ratio (**1**/I_2)	conditions[a]	6	yield/%
1	**1A**	1.0/0.6	A	**6m**[b]	57
2	**1B**	1.0/0.6	B	**6j**	53
3	**1D**	1.0/1.2	A	**6c**	67
4	**1E**	1.0/1.2	A	**6f**	68
5	**1F**	1.0/1.2	A	**6g**	61

[a] A: Stirring at 20−30 °C for 16 h. B: Stirring at 55−65 °C for 8 h. [b] 4-Iodotoluene.

2. Desulfonyloxyiodination Reaction of Iodanes 1. To date, a few desulfonyloxyhalogenation reactions have been reported. One is the desulfonyloxyiodination reaction of aliphatic sulfonic acids with a triphenyl phosphine/iodine system via aliphatic thiols. However, aromatic sulfonic acids gave the corresponding thiols alone in this system.[12] In aromatic sulfonic acid, a desulfonyloxyiodination reaction was reported in 1991 with the $I_2-H_2SO_4-SO_3$ system; however, a mixture of many iodinated products was formed here, the yields were rather low, and the reaction requires strong acidic media.[13] Another desulfonyloxybromination reaction of aromatic sulfonic acids is the reaction of aromatic sulfonic acids having an electron-donating group such as an amino or a hydroxyl group on the aromatic ring, with bromine in aqueous solvent to give the corresponding polybrominated aromatics via electrophilic ipso-bromination.[14] As mentioned above, we attempted the iodination of ethyl benzoate with iodane **1A**. However, the corresponding iodinated ethyl benzoate was not formed, and instead, 4-iodotoluene (**6m**) was obtained in 56% yield. We thought this iodide **6m** should be derived from iodane **1A**. Thus, various iodanes **1** were stirred with iodine under various conditions to obtain the corresponding iodides via electrophilic ipso-substitution (Table 4).

Iodane **1A** gave the desulfonyloxyiodination product, iodide **6m**, in 57% yield (Table 4, entry 1). Iodane **1B** was treated under conditions B, and *p*-chloroiodobenzene (**6j**) was obtained in 53% yield; however, the same treatment at rt gave iodide **6j** only in 4% yield, while 1-(*p*-nitrobenzenesulfonyloxy)benziodoxolone (**1C**) did not give the corresponding desulfonyloxyiodination product. Iodanes **1D**−**F** gave the corresponding diiodinated aromat-

(12) Oae, S.; Togo, H. *Synthesis* **1981**, 371.
(13) Mattern, D. L.; Chen, X. *J. Org. Chem.* **1991**, *56*, 5903.
(14) Cannell, L. G. *J. Am. Chem. Soc.* **1957**, *79*, 2927 and 2932.

ics in moderate yields (Table 4, entries 4 ∼ 6). As competition reactions, when iodination of 4-bromoanisole (**5e**) using 1-(mesitylenesulfonyl)benziodoxolone (**1F**) and iodine was carried out, 2-iodo-4-bromoanisole (**6e**) was obtained only in 1% yield and desulfonyloxyiodination products, iodomesitylene and diiodomesitylene (**6c**), were formed in 50% and 22% yields, respectively. 4-Iodoanisole was obtained in 85% yield in the presence of anisole with iodane **1F** and iodine, together with iodomesitylene in 21% yield. Thus, iodane **1F** would iodinate electron-rich aromatics such as anisole via the corresponding sulfonyl hypoiodite, before desulfonyloxyiodination. Koser's reagent (**4**) gave a complex mixture, together with a small amount of 2,4-diiodotoluene by ^{1}H NMR. Using lithium bromide instead of iodine, with iodane **1A** under the same reaction conditions as entry 1, the corresponding bromide (4-bromotoluene) was not obtained. We believe these iodination reactions using iodanes **1** proceed via a similar reaction intermediate, a so-called "arenesulfonyl hypoiodite", which we attempted to trap with carbon−carbon multibonds as follows.

3. Iodotosyloxylation of Alkynes. The Koser reagent/iodine system has been used not only for iodination of aromatics[10] but also for migration reaction of alcohols having an alkyne unit.[15] However, the iodotosyloxylation reaction to alkynes with 1-(arenesulfonyloxy)benziodoxolones in the presence of iodine has not been studied. In organic synthesis, trap of a hypoiodite species with carbon−carbon multibonds and use of its functionalized adducts as synthetic intermediates have been carried out.[16] Therefore, we at first attempted to trap the arenesulfonyl hypoiodite species with alkenes such as cyclohexene and *trans*-stilbene; however, complex reaction mixtures were obtained. Then, alkynes were used as a trap of the *p*-toluenesulfonyl hypoiodite species (Table 5).

In entry 1, addition compound **12-I** was obtained in good yield (conditions A). Compared with conditions A and B, internal alkynes **11-I** and **11-II** gave the corresponding adducts **12-I** and **12-II** in similar yields, while in the terminal alkynes **11-V** and **11-VI**, condition A gave the corresponding alkenes in better yields than condition B. In entry 8, *gem*-diiodoalkene **13** was also obtained in 20% yield, and this compound would be derived from the double addition−elimination reaction of the tosyl hypoiodite species to alkyne **11-V**. Electron-deficient alkyne **11-III** did not react at all with iodane **1A** and iodine (entry 5), while terminal electron-deficient alkyne **11-VII** was converted to the corresponding alkene **12-VII** in 29% yield. Iodanes **4** and **7** were used in this addition reaction under the same reaction conditions as entry 1. Thus, Koser's reagent **4** gave the corresponding alkene **12-I** in 85% yield, while cyclic iodane having an acetoxy group **7** did not give the corresponding adduct. Bromotosyloxylation of alkyne **11-I** was attempted with iodane **1A**/Bu_4NBr or LiBr system; however, the corresponding adduct was not formed. The structure of compound **12-IV** was established by a single-crystal X-ray analysis (Figure 2).

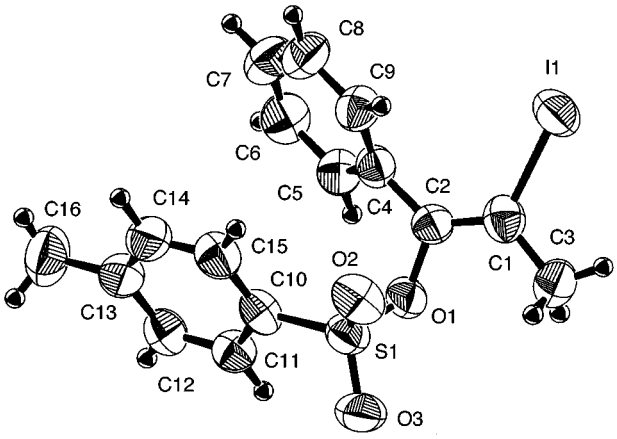
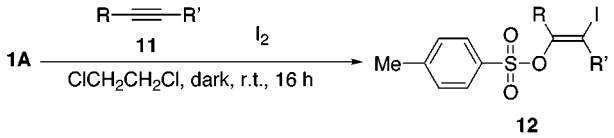


Figure 3.

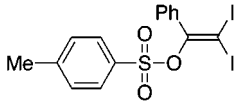
Table 5. Iodotosyloxylation of Alkynes with Iodane 1A



12

entry	R	R′	11	conditions[a]	yield/%
1	Ph	Ph	**11−I**	A	93
2	Ph	Ph	**11−I**	B	87
3	n-Pr	n-Pr	**11−II**	A	73
4	n-Pr	n-Pr	**11−II**	B	67
5	CO_2Et	CO_2Et	**11−III**	C	0[b]
6	Ph	Me	**11−IV**	B	84
7	Ph	H	**11−V**	A	69
8	Ph	H	**11−V**	B	42[c]
9	n-Bu	H	**11−VI**	A	83
10	n-Bu	H	**11−VI**	B	60
11	H	CO_2Et	**11−VII**	A	29

[a] A: Ratio of **1A**/**11**/I_2 was 1.0/5.0/1.2, and the amount of solvent was 5 mL. B: Ratio of **1A**/**11**/I_2 was 1.0/1.2/1.2, and the amount of solvent was 2.5 mL. C: Ratio of **1A**/**11**/I_2 was 1.0/2.4/1.2, and the amount of solvent was 2.5 mL. [b] 4-Iodotoluene was obtained in 4% yield. [c] Compound **13** was also obtained in 20% yield.



13

On the basis of the results of single-crystal X-ray analysis of compound **12-IV** and NMR spectral data of compounds **12-V** and **12-VI** ($\delta_{Cmethyne}$ = ∼70 ppm), this reaction proceeds via trans addition according to Markovnikov's rule. In all the reactions of Table 5, alkenes having an *o*-iodobenzoate group did not form.

In these three types of reactions, the plausible reaction pathways are shown in Scheme 1.

Iodanes **1** produced iodine from iodide, and the iodane **1** further oxidized iodine to arenesulfonyl hypoiodites ($ArSO_3I$), which iodinate aromatics to give iodoarenes. In the absence of aromatics, $ArSO_3I$ formed slowly, giving rise to electrophilic ipso-desulfonyloxyiodination on the aromatic ring to give iodoarenes. This arenesulfonyl hypoiodite species, which is formed in situ by the reaction of iodane **1** and iodine, reacts with alkynes to give the corresponding 1,2-iodotosyloxylated adducts **12** in good yields. The mixture of tetrabutylammonium *p*-toluene-

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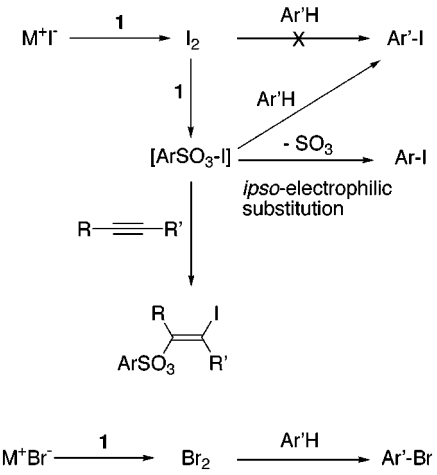
(16) (a) Review: Rodriguez, J.; Dulcère, J.-P. *Synthesis* **1993**, 1177. (b) Iodoacetoxylation: Kirschning, A.; Plumeier, C.; Rose L. *Chem. Commun.* **1998**, 33 and references therein.

Scheme 1



sulfonate and iodine was used in the iodotosyloxylation of alkynes instead of iodane **1A** as a tosyloxy source under the same conditions as entry 1 (Table 5). However, iodotosyloxylated alkene **12-I** was not obtained. Thus, iodotosyloxylation of alkynes did not proceed with an iodine and tosylate anion system. In the bromination reaction with bromide and iodanes **1**, the reaction intermediate is mainly bromine; thus, bromination of aromatics occurred. However, the desulfonyloxybromination reaction of iodane **1** and bromotosyloxylation reaction to alkyne do not occur, since the formation of $ArSO_3Br$ does not occur.

Conclusion

In the presence of iodine, 1-(arenesulfonyloxy)benziodoxolones **1** iodinated various aromatics in moderate to good yields. Especially, 1-(*p*-chlorobenzenesulfonyloxy)-benziodoxolone (**1B**) showed good iodination ability of aromatics and was also used for bromination and chlorination with bromide and chloride, respectively, instead of iodine, to give aryl bromides and chlorides in good yields. In the absence of aromatics, desulfonyloxyiodination reactions of iodanes **1** via $ArSO_3I$ occurred to give the corresponding aryl iodides. Furthermore, the iodanes **1**/iodine system produced the functionalized iodotosyloxylated alkenes from alkynes effectively. On the basis of these results, we propose the present three types of reactions proceeded via arenesulfonyl hypoiodites.

Experimental Section

General Methods. All reactions were performed under an argon atmosphere. ^{1}H NMR spectra were recorded on 400 and 500 MHz spectrometers, and ^{13}C NMR spectra were recorded on 100 and 125 MHz spectrometers. Chemical shifts are reported as ppm downfield from tetramethylsilane (TMS) in δ units. *J* values are given in Hz. The matrix of mass spectra (FAB) used 3-nitrobenzyl alcohol. Melting points were determined on an electrothermal apparatus in open capillary tubes and are uncorrected. Kieselgel 60 F254 (Merck) was used for TLC, and Wakogel B-5F was used for pTLC.

Materials. The iodanes **2**−**4**, aromatics **5** (except for **5d**), and alkynes **11** were commercially available. Iodanes **1** were prepared according to Zhdankin's method.[2] Aromatic **5d** was prepared with *p*-methoxybenzoic acid and methanol. Benziodoxolone derivative **7** was prepared on the basis of the literature method.[17] Iodides **6j**, **6l**, and **6m** and 4-iodoanisole were compared with commercially available samples.

1-(*p*-Chlorobenzenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one (**1B**): 74%; mp 172−173 °C dec; IR (KBr) 3080, 1610, 1230, 1180, 760 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.36 (2H, d, *J* = 8.5 Hz), 7.59 (2H, d, *J* = 8.2), 7.68 (1H, td, *J* = 7.3, 1.0 Hz), 7.83 (1H, d, *J* = 7.5 Hz), 7.94 (1H, td, *J* = 7.3, 1.7 Hz), 8.00 (1H, dd, *J* = 7.6, 1.5 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 120.37 (q), 126.25 (t), 127.42 (t), 127.64 (t), 130.31 (t), 131.04 (t), 131.48 (q), 132.93 (q), 134.42 (t), 147.16 (q), 167.68 (q). Anal. Calcd for $C_{13}H_6ClIO_5S$: C, 35.60; H, 1.84. Found: C, 35.72; H, 1.92.

1-(*p*-Nitrobenzenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one (**1C**): 70%; mp 180−181 °C dec; IR (KBr) 3080, 1610, 1510, 1240, 1120, 740 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.68 (1H, t, *J* = 7.1 Hz), 7.81−7.85 (3H, m), 7.94 (1H, td, *J* = 7.5, 1.5 Hz), 7.99 (1H, dd, *J* = 7.5, 1.3 Hz), 8.18 (1H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 120.41 (q), 123.33 (t), 126.28 (t), 126.90 (t), 130.36 (t), 131.03 (t), 131.48 (q), 134.47 (t), 147.27 (q), 154.22 (q), 167.74 (q). Anal. Calcd for $C_{13}H_8INO_7S$: C, 34.76; H, 1.80; N, 3.12. Found: C, 34.55; H, 2.01; N, 2.97.

1-(2′,5′-Dimethylbenzenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one (**1D**): 72%; mp 158−159 °C dec; IR (KBr) 2920, 1680, 1610, 1300, 1180, 1100, 820 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.28 (3H, s), 2.49 (3H, s), 7.04 (2H, s), 7.58 (1H, s), 7.73 (1H, t, *J* = 7.3 Hz), 7.87 (1H, d, *J* = 8.1 Hz), 7.99 (1H, t, *J* = 7.6 Hz), 8.04 (1H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 19.62 (p), 20.55 (p), 120.42 (q), 126.30 (t), 127.10 (t), 129.09 (t), 130.36 (t), 130.59 (t), 131.08 (t), 131.50 (q), 132.29 (q), 133.59 (q), 134.47 (t), 145.70 (q), 167.74 (q). Anal. Calcd for $C_{15}H_{13}IO_5S$: C, 41.68; H, 3.03. Found: C, 41.39; H, 3.22.

1-(2′,4′-Dimethylbenzenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one (**1E**): 70%; mp 177−179 °C dec; IR (KBr) 2920, 1690, 1610, 1200, 1100, 820 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.26 (3H, s), 2.49 (3H, s), 6.92 (1H, d, *J* = 7.8 Hz), 6.96 (1H, s), 7.61 (1H, d, *J* = 7.9 Hz), 7.71 (1H, t, *J* = 7.3 Hz), 7.85 (1H, d, *J* = 8.0 Hz), 7.97 (1H, td, *J* = 8.0, 1.4 Hz), 8.02 (1H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 19.96 (p), 20.57 (p), 120.41 (q), 125.10 (t), 126.28 (t), 126.60 (t), 130.35 (t), 131.08 (t), 131.27 (t), 131.50 (q), 134.47 (t), 135.31 (q), 137.85 (q), 143.40 (q), 167.73 (q). Anal. Calcd for $C_{15}H_{13}IO_5S$: C, 41.68; H, 3.03. Found: C, 41.63; H, 3.19.

1-(2′,4′,6′-Trimethylbenzenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one (**1F**): 68%; mp 145−146 °C dec; IR (KBr) 2980, 1680, 1600, 1210, 1190, 810 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.17 (3H, s), 2.49 (6H, s), 6.76 (2H, s), 7.69 (1H, t, *J* = 7.3 Hz), 7.83 (1H, d, *J* = 8.1 Hz), 7.95 (1H, td, *J* = 7.1, 1.2 Hz), 8.00 (1H, dd, *J* = 7.3, 1.4 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.27 (p), 22.67 (p), 120.42 (q), 126.29 (t), 129.94 (t), 130.36 (t), 131.08 (t), 131.50 (q), 134.47 (t), 135.96 (q), 136.64 (q), 142.12 (q), 167.74 (q). Anal. Calcd for $C_{16}H_{15}IO_5S$: C, 43.06; H, 3.39. Found: C, 42.89; H, 3.56.

Typical Procedures. All reactions (halogenation of aromatics, desulfonyloxyiodination, and iodotosyloxylation) were carried out in heterogeneous solution.

Iodination of Aromatics. The iodane **1A** (0.6 mmol) and iodine (0.3 mmol) were added to a solution (CH_3CN, 5 mL) of **5b** (0.5 mmol), and the mixture was vigorously stirred overnight (ca. 16 h) under dark conditions at rt. Then the reaction mixture was poured into saturated aqueous Na_2SO_3 solution and extracted with ethyl acetate (20 mL × 3). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel using hexane as an eluent. 2,4,6-Triisopropyliodobenzene **6b** was obtained in 87% yield.

1,3,5-Triiodo-2,4,6-trimethoxybenzene (**6a**): mp 178−179 °C; IR (KBr) 2920, 1520, 1440, 1360, 1080 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 60.80 (p), 82.69 (q), 161.33 (q). Anal. Calcd for $C_9H_9I_3O_3$: C,

(17) Baker, G. P.; Mann, F. G.; Sheppared, N.; Tetlow, A. J. *J. Chem. Soc.* **1965,** 3721.

19.80; H, 1.66. Found: C, 19.90; H, 1.68. MS (EI) found M^+ = 546, calcd for $C_9H_9O_3I_3$ M = 546.

1-Iodo-2,4,6-triisopropyl benzene (**6b**); oil, bp = 115 °C/2.5 mmHg (lit.[18] 173−175 °C/28 mmHg); IR (neat) 2950, 1565, 1460, 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.24 (12H, d, J = 6.8 Hz), 1.25 (6H, d, J = 7.0 Hz), 2.87 (1H, sept, J = 7.0 Hz), 3.39 (2H, sept, J = 7.0 Hz), 6.95 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.43 (p), 23.98 (p), 33.88 (t), 39.26 (t), 105.71 (q), 122.07, (t), 148.83 (q), 150.77 (q); MS (EI) found: M^+ = 330, calcd for $C_{15}H_{22}I$ M = 330.

Diiodomesitylene (**6c**): mp 79−80 °C (lit.[19] 82 °C); IR (KBr) 2975, 1440, 1375, 860 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.42 (6H, s), 2.92 (3H, s), 7.00 (1H, s); MS (EI) found M^+ = 372, calcd for $C_9H_{10}I_2$ M = 372.

Iodomesitylene: mp 30−31 °C (lit.[20] mp 30.5−31 °C); IR (KBr) 2975, 1440, 1375, 860 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.23 (3H, s), 2.43 (6H, s), 6.88 (2H, s); MS (EI) found M^+ = 292, calcd for $C_9H_{11}I$ M = 246.

Methyl 3-iodo-4-methoxybenzoate (**6d**): mp 93−94 °C; IR (KBr) 2940, 1710, 1590, 1490, 1270, 820 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.89 (3H, s), 3.94 (3H, s), 6.83 (1H, d, J = 8.7 Hz), 8.02 (1H, dd, J = 8.7, 2.0 Hz), 8.46 (1H, d, J = 2.0 Hz); HRMS (EI) found M^+ = 291.9594, calcd for $C_9H_9O_3I$ M = 291.9596.

4-Bromo-2-iodo-1-methoxybenzene (**6e**): oil (lit.[21] mp 64 °C); IR (neat) 2930, 1570, 1470, 1280, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.86 (3H, s), 6.62 (1H, d, J = 8.9 Hz), 7.34 (1H, dd, J = 8.9, 2.4 Hz), 7.80 (1H, d, J = 2.4 Hz); MS (EI) found M^+ = 312, calcd for $C_7H_6O^{79}BrI$ M = 312. Anal. Calcd for C_7H_6OBrI; C, 26.87; H, 1.93. Found: C, 26.64%; H, 1.93.

2,5-Diiodo-*p*-xylene (**6f**): mp 102−103 °C (lit.[22] mp 103−104 °C); IR (KBr) 2980, 1470, 1330, 880 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.34 (6H, s), 7.65 (2H, s); MS (EI) found M^+ = 358, calcd for $C_8H_8I_2$ M = 358.

4,6-Diiodo-*m*-xylene (**6g**): mp 70−71 °C (lit.[23] mp 71−72 °C); IR (KBr) 2980, 1470, 1330, 880 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 2.37 (6H, s), 7.09 (1H, s), 8.17 (1H, s); MS (EI) found M^+ = 358, calcd for $C_8H_8I_2$ M = 358.

2,4-Diiodo-1-methoxybenzene (**6h**): mp 67.5−68.5 °C (lit.[24] mp 68−69 °C); IR (KBr) 2930, 1565, 1470, 1280, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.85 (3H, s), 6.58 (1H, d, J = 8.7 Hz), 7.57 (1H, dd, J = 8.7, 1.9 Hz), 8.04 (1H, d, 2.2 Hz); MS (EI) found M^+ = 360, calcd for $C_7H_6OI_2$ M = 360.

4-Iodo-*tert*-butylbenzene (**6i**): oil; bp 90 °C/12.5 mmHg (lit.[19] bp 258 °C/760 mmHg); IR (neat) 2960, 1490, 1395, 820 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (9H, s), 7.06 (2H, d, J = 8.7 Hz), 7.53 (2H, d, J = 8.7 Hz); MS (EI) found M^+ = 260, calcd for $C_{10}H_{13}I$ M = 260.

4-Iodophenyl acetate (**6k**): oil; IR (neat) 2975, 1760, 1580, 1480, 1370, 840 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.29 (3H, s), 6.79 (2H, d, J = 9.0 Hz), 7.60 (2H, d, J = 8.7 Hz); HRMS (EI) found M^+ = 261.9494, calcd for $C_8H_7O_2I$ M = 261.9491.

Bromination of Aromatics. Iodane **1A** (0.6 mmol) and lithium bromide (0.6 mmol) were added to a solution (CH_3CN, 5 mL) of **5e** (0.5 mmol), and then the solution turned orange and was vigorously stirred overnight (ca. 16 h) under dark conditions at rt. Then the reaction mixture was poured into saturated aqueous Na_2SO_3 solution and extracted with ethyl acetate (20 mL × 3). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel using hexane/toluene (5:1) as an eluent. 2,4-Dibromoanisole **10e** was obtained in 81% yield.

1-Chloro-2,4,6-triisopropylbenzene (**9b**): oil; IR (neat) 2960, 1580, 1460, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.24 (18H, d, J = 7.0 Hz), 2.87 (1H, sept, J = 7.0 Hz), 3.47 (2H, sept, J = 7.0 Hz), 6.99 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.88 (p), 24.06 (p), 30.62 (t), 34.09 (t), 121.95, (t), 130.04 (q), 145.58 (q), 147.07 (q); HRMS (EI) found M^+ = 238.1486, calcd for $C_{15}H_{22}{}^{35}Cl$ M = 238.1488.

4-Bromo-2-chloro-1-methoxybenzene (**9e**): oil; IR (neat) 2980, 1580, 1480, 1290, 810 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.88 (3H, s), 6.80 (1H, d, J = 8.7 Hz), 7.35 (1H, dd, J = 8.9, 2.4 Hz), 7.50 (1H, d, J = 2.4 Hz); HRMS (EI) found M^+ = 219.9302, calcd for $C_7H_6O^{79}Br^{35}Cl$ M = 219.9291.

1-Bromo-2,4,6-triisopropylbenzene (**10b**): oil; bp = 106 °C/3.0 mmHg (lit.[25] bp 153−154 °C/21 mmHg); IR (neat) 2960, 1580, 1460, 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.24 (18H, d, J = 7.0 Hz), 2.86 (1H, sept, J = 7.0 Hz), 3.48 (2H, sept, J = 7.0 Hz), 6.98 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.09 (p), 24.00 (p), 33.54 (t), 34.03 (t), 122.28, (t), 123.57 (q), 147.39 (q), 147.81 (q); MS (EI) found M^+ = 282, 284, calcd for $C_{15}H_{22}{}^{79}Br$ M = 282.

2,4-Dibromo-1-methoxybenzene (**10e**): mp 61−62 °C (lit.[26] mp 61−62 °C); IR (KBr) 2980, 1580, 1480, 1290, 810 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.88 (3H, s), 6.77 (1H, d, J = 8.9 Hz), 7.38 (1H, dd, J = 8.7, 2.1 Hz), 7.66 (1H, d, J = 1.9 Hz); MS (EI) found M^+ = 264, calcd for $C_7H_6O^{79}Br_2$ M = 264.

Desulfonyloxyiodination Reaction of Iodanes 1. A solution (CH_3CN, 5 mL) of iodane **1A** (0.5 mmol) and iodine (0.3 mmol) was stirred for 16 h under dark conditions at rt. The reaction mixture was poured into saturated aqueous Na_2SO_3 solution and extracted with ethyl acetate (20 mL × 3). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel using hexane as an eluent. 4-Iodotoluene (**6m**) was obtained in 57% yield.

Iodotosyloxylation Reaction for Alkynes. Iodane **1A** (0.5 mmol) and iodine (0.6 mmol) were added to a solution ($ClCH_2CH_2Cl$, 5 mL) of **11-I** (2.5 mmol), and the mixture was stirred overnight (ca. 16 h) under dark conditions at rt. Then the reaction mixture was poured into saturated aqueous Na_2SO_3 solution and extracted with chloroform (20 mL × 3). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel using hexane/ethyl acetate (8:1) as an eluent. 1,2-Diphenyl-1-iodo-2-(*p*-toluenesulfonyloxy)-ethylene **12-I** was obtained in 93% yield.

(*E*)-1-Iodo-2-(*p*-toluenesulfonyloxy)stilbene (**12-I**): mp 107−108 °C; IR (KBr) 3060, 1640, 1600, 1370, 1180, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.33 (3H, s), 6.98 (2H, d, J = 8.0 Hz), 7.17 (2H, d, J = 8.5 Hz), 7.25−7.33 (6H, m), 7.42 (2H, dd, J = 6.8, 1.7 Hz), 7.50 (2H, dd, J = 7.9, 1.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.51 (p), 93.45 (q), 127.69 (t), 127.84 (t), 128.03 (t), 128.39 (t), 129.18 (t), 129.22 (t), 129.49 (t), 130.45 (t), 133.46 (q), 135.30 (q), 139.84 (q), 144.34 (q), 145.22(q); MS (FAB) found M^+ = 476, calcd for $C_{21}H_{17}IO_3S$ M = 476. Anal. Calcd for $C_{21}H_{17}IO_3S$: C, 52.95; H, 3.60. Found: C, 52.97; H, 3.44.

(*E*)-4-Iodo-5-(*p*-toluenesulfonyloxy)-4-octene (**12-II**): oil; IR (neat) 2960, 1650, 1600, 1370, 1190, 910 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.81 (3H, t, J = 7.3 Hz), 0.85 (3H, t, J = 7.3 Hz), 1.41 (2H, sixtet, J = 7.3 Hz), 1.47 (2H, sixtet, J = 7.3 Hz), 2.29 (2H, t, J = 7.3 Hz), 2.46 (3H, s), 2.62 (2H, t, J = 7.3 Hz), 7.36 (2H, d, J = 7.9 Hz), 7.82 (2H, d, J = 8.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.90 (p), 13.30 (p), 19.98 (s), 21.76 (p, tosyl), 22.80 (s), 37.92 (s), 39.46 (s), 100.87 (q), 127.96 (t), 129.94 (t), 134.09 (q), 145.29 (q), 147.30 (q); HRMS (FAB) found M^+ = 408.0217, calcd for $C_{15}H_{21}IO_3S$ M = 408.0256.

(*E*)-1-Phenyl-1-(*p*-toluenesulfonyloxy)-2-iodo-1-propene (**12-IV**): mp 90−91 °C; IR (KBr) 3060, 2920, 1650, 1600, 1370, 1180, 830 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.34 (3H, s), 2.67 (3H, s), 7.06 (2H, d, J = 8.5 Hz), 7.13−7.28 (5H, m), 7.41 (2H, d, J = 8.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.53 (p), 28.10 (p), 92.37 (q), 127.61 (t), 127.90 (t), 128.98 (t), 129.32 (t), 130.25 (t), 133.63 (q), 135.02 (q), 144.64 (q), 145.12

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(q); MS (FAB) found $M^+ = 414$, calcd for $C_{16}H_{15}IO_3S$ M = 414. Anal. Calcd for $C_{16}H_{15}IO_3S$: C, 46.39; H, 3.65. Found: C, 46.58; H, 3.78. Crystal data for **12-IV** (Mo Kα radiation, Rigaku RAXIS-II diffractometer): $C_{16}H_{15}O_3SI$, FW = 414.26, a = 17.19(1) Å, b = 7.522(3) Å, c = 12.950(9) Å, orthorhombic, $Pca2_1$, Z = 4, V = 1674(1) Å^3, D_c = 1.643 g cm^{-3}. R factor = 0.044 for 1601 independent observed reflections ($I > 2\sigma(I)$); weighted R_w factor = 0.048.

(*E*)-1-Iodo-2-phenyl-2-(*p*-toluenesulfonyloxy)-1-ethene (**12-V**): mp 67−68 °C; IR (KBr) 3060, 1620, 1600, 1380, 1180, 990, 840 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (3H, s), 6.56 (1H, s), 7.18 (2H, d, J = 8.1 Hz), 7.22−7.31 (3H, m), 7.41 (2H, d, J = 6.8 Hz), 7.61 (2H, d, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.63 (p), 70.46 (t), 127.93 (t), 128.34 (t), 129.28 (t), 129.60 (t), 129.68 (t), 132.91 (q), 132.95 (q), 145.25 (q), 149.79 (q). MS (FAB) found $(M + H)^+ = 401$, calcd for $C_{15}H_{14}IO_3S$ M = 401. Anal. Calcd for $C_{15}H_{13}IO_3S$: C, 45.01; H, 3.27. Found: C, 45.13; H, 3.38.

(*E*)-1-Iodo-2-(*p*-toluenesulfonyloxy)-1-hexene (**12-VI**): oil; IR (neat) 2960, 1625, 1600, 1380, 1180, 820 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (3H, t, J = 7.3 Hz), 1.27 (2H, sixtet, J = 7.6 Hz), 1.43 (2H, quint, J = 7.3 Hz), 2.40 (2H, t, J = 7.8 Hz), 2.47 (3H, s), 6.01 (1H, s), 7.36 (2H, d, J = 8.0 Hz), 7.80 (2H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.74 (p), 21.73 (s), 21.86 (p), 27.92 (s), 33.35 (s), 69.59 (t), 128.29 (t), 129.88 (t), 132.94 (q), 145.51 (q), 153.71 (q); HRMS (FAB) found $(M + H)^+ = 380.9992$, calcd for $C_{13}H_{18}IO_3S$ M + H = 381.0021.

Ethyl (*E*)-2-iodo-3-(*p*-toluenesulfonyloxy)propenate (**12-VII**): oil; IR (neat) 2980, 1720, 1610, 1390, 1180, 820 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, J = 7.0 Hz), 2.47 (3H, s), 4.18 (2H, q, J = 7.1 Hz), 7.36 (1H, s), 7.39 (2H, d, J = 8.3 Hz), 7.82 (2H, d, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.91 (p), 21.73 (p), 62.65 (s), 75.31 (q), 128.00 (t), 130.16 (t), 132.00 (q), 145.53 (t), 146.23 (q), 161.44 (q); HRMS (FAB) found $(M + H)^+ = 396.9614$, calcd for $C_{12}H_{14}IO_5S$ M + H = 396.9607.

1,1-Diiodo-2-phenyl-2-(*p*-toluenesulfonyloxy)-1-ethene (**13**): mp 130−132 °C; IR (KBr) 1600, 1380, 1180, 860 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (3H, s), 7.09 (2H, d, J = 8.0 Hz), 7.19 (2H, t, J = 7.8 Hz), 7.28−7.32 (3H, m), 7.45 (2H, d, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.28 (q), 21.60 (p), 127.97 (t), 128.14 (t), 129.38 (t), 129.78 (t), 130.06 (t), 132.64 (q), 133.51 (q), 145.00 (q), 152.73 (q); HRMS (FAB) found $M^+ = 525.8560$, calcd for $C_{15}H_{12}I_2O_3S$ M = 525.8597.

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Supporting Information Available: Copies of ^{1}H NMR spectra and X-ray data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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