Synthesis of 1*H*-1-(1-Alkynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-Dioxides: Alkynyl(aryl)iodonium Sulfonates with Heterocyclic Iodine

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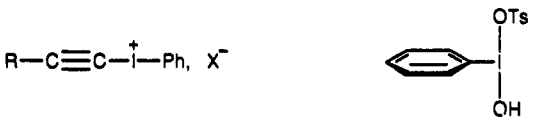
Prior to 1981, alkynyl(phenyl)iodonium compounds 1 were little more than structural curiosities, only two examples having been reported in the chemical literature.[1,2] The subsequent development of methods for the synthesis of alkynyl(phenyl)iodonium tosylates,[3] tetrafluoroborates,[4] and triflates[5] (i.e., X^- = TsO^-, BF_4^-, $CF_3SO_3^-$) has since stimulated considerable interest in the reactivity and synthetic utility of this class of iodonium salts.[5c,6]

The first tosylate compounds were prepared by the treatment of terminal alkynes, RC≡CH, with [hydroxy(tosyloxy)iodo]benzene (**2, HTIB**),[3a,b] typically in $CHCl_3$ at reflux.[3b] However, this approach is restricted to alkynes with aryl or bulky alkyl groups,[3b,7] and when R was *n*-Pr, *n*-Bu, *n*-C_5H_{11}, [β-(tosyloxy)vinyl](phenyl)iodonium tosylates **3** were obtained instead.[3b] The incorporation of



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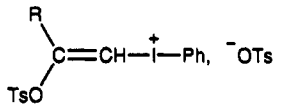

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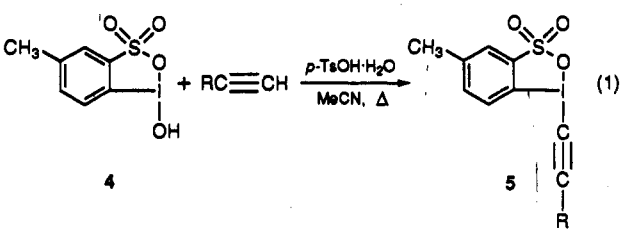
linear alkyl groups into 1 (X^- = TsO^-) was first achieved by the treatment of propyne and 1-hexyne with **HTIB** (CH_2Cl_2, rt) in the presence of a silica bead desiccant, but the yields (19%, 12%) were low.[3d] A much better procedure, based on the standard approach to tetrafluoroborate salts,[4a] entails the BF_3·Et_2O-induced coupling of (trimethylsilyl)alkynes, RC≡CSiMe_3, with iodosobenzene, PhI=O ($CHCl_3$, rt), and subsequent treatment of the resulting solutions at 0 °C with aqueous NaOTs.[3e] In this way, tosylate salts of 1 with R = Me, Et, *n*-Pr, and *n*-Bu have been obtained in 62–89% yields.

We now report the use of 1*H*-1-hydroxy-5-methyl-1,2,3-benziodoxathiole 3,3-dioxide (**4**), a cyclic analog of **HTIB**, for the direct synthesis of alkynyl(aryl)iodonium arenesulfonates from terminal alkynes; eq 1. The products are 1*H*-1-(1-alkynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-dioxides **5**;[8] more significantly, congeners of **5** with linear alkyl groups in the alkynyliodonio moiety can be readily obtained without the use of a desiccant or silyl activation of the alkyne The hydroxy sulfonyloxy iodane **4** is less reactive than **HTIB** toward terminal alkynes, and it proved expedient to facilitate the reactions shown in eq 1 with *p*-toluenesulfonic acid.



4 **5** (1)

Table I. 1-Alkynylbenziodoxathiole Dioxides 5 from Reactions of 4 with Terminal Alkynes

compound	R	molar ratio (alkyne/4)	isolated yield (%)
5a	*n*-Pr	5/1	61
5b	*n*-Bu	5/1	54
5c	*n*-C_6H_{11}	3/1	41
5d	*n*-C_6H_{13}	5/1	51
5e	*i*-Bu	5/1	66
5f	*s*-Bu	2.5/1	32
5g	*t*-Bu	5/1	70
5h	cyclohexyl	1.8/1	26
5i	Ph	5/1	51

In a typical experiment, a mixture of **4** (5.00 mmol), *p*-TsOH·H_2O (5.0 mmol), and 1-hexyne (25.0 mmol) in MeCN (40 mL) was heated under reflux for 20 h. The resulting solution was then concentrated, and the oil that remained was washed (in $CHCl_3$) with 5% $NaHCO_3$ and H_2O to remove toluenesulfonic acid. The solid, thus obtained, was recrystallized from a mixture of CH_2Cl_2, Et_2O, and hexanes to give 1*H*-1-(1-hexynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-dioxide (**5b**) in 54% yield. Similar treatment of eight other terminal alkynes with **4** gave the alkynylbenziodoxathiole dioxides shown in Table I, all of which were characterized by IR, NMR (^1H, ^{13}C), and elemental (C,H) analysis. The yields reported in Table I are those of the isolated, analytically pure compounds and appear to be regulated, at least to some extent, by the starting alkyne/**4** molar ratios.

The hydroxybenziodoxathiole **4** was prepared from 2-amino-5-methylbenzenesulfonic acid by diazotization ($NaNO_2$, HCl), iodination (NaI, H_2O, Δ), and oxidation (35% $MeCO_3H$) and was initially characterized by NMR

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(3) (a) Koser, G. F.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1981**, *46*, 4324. (b) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4700. (c) Stang, P. J.; Surber, B. W. *J. Am. Chem. Soc.* **1985**, *107*, 1452. (d) Stang, P. J.; Surber, B. W.; Chen, Z-C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228. (e) Kitamura, T.; Stang, P. J. *J. Org. Chem.* **1988**, *53*, 4105.
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(5) (a) Stang, P. J.; Arif, A. M.; Crittell, C. M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 287. (b) Stang, P. J.; Williamson, B. L.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1991**, *113*, 5870. (c) Williamson, B. L.; Stang, P. J.; Arif, A. M. *J. Am. Chem. Soc.* **1993**, *115*, 2590.
(6) (a) Stang, P. J. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 274 (Review). (b) Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH Publishers: New York, New York, 1992; pp 267–277.
(7) Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1990**, *55*, 1513.
(8) Three 1-alkynyl-1,2-benziodoxol-3(1*H*)-ones, cyclic carboxylate analogs of **5**, have recently been prepared from 1-hydroxy-1,2-benziodoxol-3(1*H*)-one; see Ochiai, M.; Masaki, Y.; Shiro, M. *J. Org. Chem.* **1991**, *56*, 5511.
(9) 1*H*-1-Hydroxy-1,2,3-benziodoxathiole 3,3-dioxide is known; see (a) Willgerodt, C. *Die Organischen Verbindungen mit Mehrwertigem Jod*, F. Enke: Stuttgart, 1914; p 166 (sodium salt reported). (b) Wettach, R. H., Ph.D. dissertation, The University of Akron, 1981, pp 156–157 (monohydrate described).

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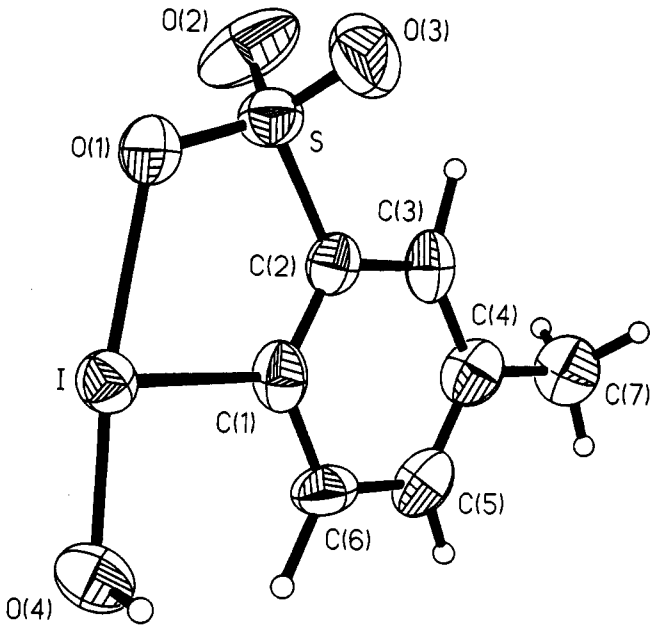


Figure 1. Thermal ellipsoid projection of 4.

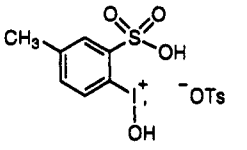
Table II. Selected Bond Distances and Angles for 1*H*-1-Hydroxy-5-methyl-1,2,3-benziodoxathiole 3,3-Dioxide (4)[a]

bond distance (Å)		bond angle (deg)	
I–O(1)	2.372(5)	O(1)–I–O(4)	168.6(2)
I–O(4)	1.933(5)	O(4)–I–C(1)	92.3(2)
S–O(1)	1.440(5)	O(1)–I–C(1)	76.9(2)
S–O(2)	1.406(6)	I–O(4)–H	98.7(1)
S–O(3)	1.415(9)	O(1)–S–O(2)	113.4(4)
H–O(4)	1.010	O(1)–S–O(3)	110.0(4)
I–C(1)	2.125(6)	O(2)–S–O(3)	114.0(4)
S–C(2)	1.759(6)		

[a] The numbering scheme in Table II refers to the thermal ellipsoid projection shown in Figure 1 and not to the numbering scheme employed to name compound 4.

(^{1}H, ^{13}C) and elemental (C,H) analysis.[9] In order to ascertain the influence of planar, cyclic vs nonplanar acyclic structures on the asymmetric [3c–4e] hypervalent bond[10] of hydroxy sulfonyloxy iodanes, a single crystal X-ray structure of 4 was also determined.[11a,b] As expected for a λ^3-iodane, molecules of 4 (Figure 1, Table II) are approximately T-shaped about the iodine atom, although the O–I–O triad in 4 (bond angle, 168.6°) is "less linear" than the O–I–O triad in **HTIB** (178.8°).[12] The I–OH bond distances in 4 (1.933 Å) and **HTIB** (1.940 Å)[12] are nearly the same and a bit shorter than the computed covalent distance of 1.99 Å for an I–O single bond. The I–O bond to the sulfonate ligand in 4 (2.372 Å) is elongated by 0.38 Å and appears to be endowed with ionic character, a conclusion which is corroborated by the near equivalence of the three sulfur–oxygen bond distances (1.406–1.440 Å). However, the iodine–sulfonate linkage in 4 is 0.1 Å shorter than it is in **HTIB** (2.473 Å).[12]

Compound 4 is insoluble in MeCN, even at reflux, and it seems likely that the "catalytic" action of *p*-TsOH is due to the protonation of 4 at the sulfonate ligand to give 6. Indeed, when 4 was treated with TsOH·H$_2$O in MeCN at reflux, the iodane "dissolved". However, when the solution was allowed to cool, only 4 separated and was recovered in 94% yield.



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Experimental Section

General. The NMR spectra reported herein were recorded at resonance frequencies of 300 (^{1}H) and 75 (^{13}C) MHz. ^{1}H Chemical shifts are expressed relative to residual protonated solvent in $CDCl_3$ (δ 7.24) and DMSO-d_6 (δ 2.49) and to DSS (δ 0.00) in D_2O. Coupling constants are reported in hertz. ^{13}C chemical shifts are expressed relative to $CDCl_3$ (δ 77.0), DMSO-d_6 (δ 39.5), and DSS (δ 0.00) in D_2O. FTIR samples were thin CH_2Cl_2 films; C≡C maxima were estimated (*ca.* ±5 cm^{-1}) relative to polystyrene at 1601 cm^{-1}. Melting points are uncorrected. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. The synthetic procedure for 1*H*-1-(1-hexynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-dioxide (**5b**) is given in detail and serves as a general example. Abbreviated procedures for the remaining compounds of this series are presented.

The ^{1}H NMR spectra of **5a–h** exhibit three multiplets in the aromatic region: δ 7.43–7.46, δ 7.83–7.90 (d, J = 8.5(5)–8.7(3) Hz), δ 7.95–8.00. The high-field and low-field aromatic multiplets of **5b** and **5d–h** closely resemble a doublet of doublets ($J \sim$ 8.4–8.9 Hz, 1.8–2.2 Hz) and a doublet ($J \sim$ 1.5–2.0 Hz), respectively, typically with a hint of fine structure that complicates the estimation of coupling constants. For **5a** and **5c**, these multiplets more nearly resemble a ddd (high field) and a dd (low field), the additional splitting being less than 1 Hz.

Sodium 2-Iodo-5-methylbenzenesulfonate. A solution of $NaNO_2$ (18 g, 0.26 mol) in H_2O (40 mL) was added dropwise to a stirred, cold (0–5 °C) mixture of 2-amino-5-methylbenzenesulfonic acid (46.80 g, 250 mmol) in concd HCl (63 mL). The resulting mixture was stirred and kept at 0–5 °C for at least 30 min and was then treated with urea (*ca.* 0.5 g). A solution of NaI (39 g, 0.26 mol) in H_2O (40 mL) was then added slowly to the stirred, cold mixture. After the addition was complete, stirring was continued while the reaction mixture was kept for 2 h at 0–5 °C, 1 h at rt, and 13 h at *ca.* 50 °C (i.e., until N_2 evolution had nearly ceased). The mixture was then refrigerated, and the insoluble solid component was isolated and washed with MeCN. This material (peach-colored) was treated with boiling EtOH (some MeOH and Et_2O then added) and, after the mixture was allowed to cool, the insoluble solid was isolated, washed with EtOH and Et_2O, and identified as the monohydrate of the title compound (grayish-white powder, 47.6 g). Concentration of the aqueous filtrate from the first filtration, extraction of the residual solid with MeOH, and concentration of the MeOH extract gave 17 g more of product: combined yield, 64.6 g (76%); mp > 380 °C dec; ^{1}H NMR (D_2O, DSS) δ 2.30 (s, 3 H), 7.01 (dd, 8.0, 2.2 Hz, 1 H), 7.83 (d, 2.1 Hz, 1 H), 7.92 (d, 8.0 Hz, 1 H); ^{13}C NMR (D_2O, DSS) δ 22.8, 89.4, 131.6(5), 135.9, 141.9, 144.5, 147.1. Anal. Calcd for $C_7H_6INaO_3S·H_2O$: C, 24.87; H, 2.38. Found: C, 24.33; H, 2.57.

2-Iodo-5-methylbenzenesulfonic Acid. H_2O was added slowly to a stirred mixture of sodium 2-iodo-5-methylbenzenesulfonate monohydrate (18.10 g, 53.5 mmol) in concd HCl (*ca.*

(10) See Koser, G. F. In *The Chemistry of the Functional Groups*, Supplement D; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, 1983; Chapter 18, pp 729–740 and references cited therein.

(11) (a) Compound 4 (colorless parallelepiped, 0.4 x 0.5 x 0.7 mm) crystallized in the monoclinic space group $P2_1/n$: a = 5.064(1) Å, b = 11.972(2) Å, c = 15.493(3) Å, β = 94.88(3)°, v = 935.9(3) Å^3, Z = 4, D_C = 2.229 g/cm^3; μ = 3.576 mm^{-1}, $F(000)$ = 600. A total of 1640 reflections were recorded at room temperature on a Syntex $P2_1$ diffractometer using Mo Kα radiation (λ = 0.71073 Å) in the range 3.5° ≤ 2θ ≤ 45°. All calculations were performed using SHELXTL PLUS (PC version). The final agreement indices are R = 4.88% and R_w = 8.67% for 125 refined parameters and 1134 unique observed reflections. (b) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(12) Koser, G. F.; Wettach, R. H.; Troup, J. M.; Frenz, B. A. *J. Org. Chem.* **1976**, *41*, 3609.

140 mL) until a homogeneous solution was obtained. More concd HCl (30 mL) was added, and the solution was stirred for 3 h at rt (cloudy), 2 h at *ca.* 50 °C, and overnight at rt. The cloudy mixture was then concentrated *in vacuo* at ~ 50–60 °C. The solid that remained was treated with hot MeCN (2 × 30 mL), and the mixture was filtered to give 3.30 g of NaCl (mostly). Treatment of the filtrate with Et_2O and hexanes led to the recovery of 0.8 g (4%) of the unprotonated sodium arenesulfonate. Concentration of the second filtrate gave an oil which gradually solidified. This material was treated with $CHCl_3$ (10 mL) and hexanes. The mixture was kept overnight at rt and filtered to give a white solid which was washed with hexanes and identified as the dihydrate of the title compound: yield, 11.62 g (65%); mp 112–114 °C; ^1H NMR (D_2O, DSS) δ 2.30 (s, 3 H), 7.01 (m, 1 H), 7.83 ("d", 2.1 Hz, 1 H), 7.92 (d, 8.0 Hz, 1 H); ^{13}C NMR (D_2O, DSS) δ 22.8, 89.4, 131.7, 135.9, 141.9, 144.5, 147.1. Anal. Calcd for $C_7H_7IO_3S \cdot 2H_2O$: C, 25.16; H, 3.32. Found: C, 24.86; H, 3.03.

The ^1H and ^{13}C NMR spectra (D_2O) of the sulfonic acid and its sodium salt are virtually identical.

1*H*-1-Hydroxy-5-methyl-1,2,3-benziodoxathiole 3,3-Dioxide (4). Peroxyacetic acid (35%, 58 mL) was added dropwise to a stirred mixture of 2-iodo-5-methylbenzenesulfonic acid dihydrate (25.05 g, 75.0 mmol) in glacial acetic acid (70 mL) maintained at 10–15 °C; a clear solution initially resulted. The reaction mixture was stirred for 1 h at 15 °C and overnight at rt. A white solid separated and was isolated by filtration and washed with Et_2O (yield, 23.32 g). A mixture of this material in hot MeCN (300 mL) was treated with hot H_2O (*ca.* 150 mL) until most of the solid dissolved. The hot mixture was filtered, and the filtrate was kept overnight at rt. Compound **4** separated as a colorless crystalline solid and was isolated by filtration. The filtrate, upon evaporation to a volume of about 50 mL, gave a second fraction of product: combined yield, 21.98 g (93%); mp 144–146 °C dec; ^1H NMR (DMSO-d_6) δ 2.46 (s, 3 H), 7.55–7.74 (arom m's; lines at 7.57, 7.60, 7.70, 7.72; 3 H), 10.06 (br s, 1 H); ^{13}C NMR (DMSO-d_6) δ 20.1, 109.6, 125.8, 128.5, 134.3, 141.2, 141.9. Anal. Calcd for $C_7H_7IO_4S$: C, 26.77; H, 2.25. Found: C, 26.93; H, 2.32.

1*H*-1-(1-Hexynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-Dioxide (5b, R = *n*-Bu). A mixture of **4** (1.57 g, 5.00 mmol), $TsOH \cdot H_2O$ (0.95 g, 5.0 mmol), and 1-hexyne (2.05 g, 25.0 mmol) in MeCN (40 mL) was stirred and heated under reflux for 20 h; the resulting solution was concentrated (rotary evaporator) to an oil. A solution of the oil in $CHCl_3$ (200 mL) was washed with 5% $NaHCO_3$ (80 mL) and H_2O (3 × 50 mL) and concentrated to a solid (1.57 g). Recrystallization of this material from a mixture of CH_2Cl_2 (30 mL), Et_2O (*ca.* 100 mL), and hexanes (*ca.* 60 mL) gave **5b** as an off-white solid: yield, 1.02 g (54%); mp 179–181 °C dec; IR 2164 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3 H), 1.45 (m, 2 H), 1.64 (m, 2 H), 2.46 (s, 3 H), 2.69 (t, 7.1 Hz, 2 H), 7.44 (dd, 1 H), 7.89 (d, 8.7 Hz, 1 H), 7.96 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.4, 20.5, 20.7, 21.9(5), 28.2, 29.8, 105.6, 115.4, 126.8, 130.6, 135.0, 141.5, 143.6. Anal. Calcd for $C_{13}H_{15}IO_3S$: C, 41.28; H, 4.00. Found: C, 41.47; H, 4.01.

1*H*-1-(1-Pentynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-Dioxide (5a, R = *n*-Pr): from **4** (2.20 g, 7.00 mmol), $TsOH \cdot H_2O$ (1.33 g, 7.00 mmol), 1-pentyne (2.38 g, 34.9 mmol), and MeCN (50 mL); 17 h, reflux; aqueous workup; crude solid (2.00 g) recrystallized from CH_2Cl_2 (40 mL) with Et_2O and again from CH_2Cl_2 (30 mL) and Et_2O (*ca.* 100 mL) to give **5a** as a yellowish solid: yield, 1.55 g (61%); mp 159–161 °C dec; IR 2168 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 1.06 (t, 7.4 Hz, 3 H), 1.71 (m, 2 H), 2.48 (s, 3 H), 2.68 (t, 7.1 Hz, 2 H), 7.46 (ddd, 1 H), 7.89 (d, 1 H), 8.00 (dd, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.5, 20.7, 21.4(5), 22.7, 28.4, 105.6, 115.2, 126.9, 130.6, 135.0, 141.5, 143.6. Anal. Calcd for $C_{12}H_{13}IO_3S$: C, 39.57; H, 3.60. Found: C, 39.66; H, 3.60.

1*H*-1-(1-Heptynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-Dioxide (5c, R = *n*-C_5H_{11}): from **4** (1.26 g, 4.01 mmol), $TsOH \cdot H_2O$ (0.76 g, 4.0 mmol), 1-heptyne (1.15 g, 12.0 mmol), and MeCN (40 mL); 20.5 h, reflux; aqueous workup; crude solid (1.12 g) recrystallized from CH_2Cl_2 (20 mL), Et_2O (*ca.* 100 mL), and hexanes (*ca.* 50 mL) to give **5c** as a pale-yellow solid: yield, 0.65 g (41%); mp 170–172 °C dec; IR 2163 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 0.89 ("t", 7.1 Hz, 3 H), 1.36 (m, 4 H), 1.65 (m, 2 H), 2.46 (s, 3 H), 2.68 (t, 7.2 Hz, 2 H), 7.43 (ddd, 1 H), 7.89 (d, 2 H), 7.95(5) (dd, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 20.7, 20.8, 22.0, 27.5, 28.2, 30.9, 105.6, 115.4, 126.9, 130.5, 134.9, 141.5, 143.5. Anal. Calcd for $C_{14}H_{17}IO_3S$: C, 42.87; H, 4.37. Found: C, 42.56; H, 4.36.

1*H*-1-(1-Octynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-Dioxide (5d, R = *n*-C_6H_{13}): from **4** (1.57 g, 5.00 mmol), $TsOH \cdot H_2O$ (0.95 g, 5.0 mmol), 1-octyne (2.75 g, 25.0 mmol), and MeCN (40 mL); 14 h, reflux; aqueous workup; crude solid (1.69 g) recrystallized from CH_2Cl_2 (50 mL), Et_2O (*ca.* 200 mL), hexanes (*ca.* 150 mL) to give **5d** as a pale yellow solid: yield, 1.04 g (51%); mp 152–154 °C dec; IR 2167 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 0.88 ("t", 3 H), 1.2–1.5 (closely spaced m's at δ 1.30, 1.42, 6 H), 1.65 (m, 2 H), 2.46(5) (s, 3 H), 2.68 (t, 7.1 Hz, 2 H), 7.43 (dd, 1 H), 7.89 (d, 1 H), 7.97 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 20.7, 20.8, 22.4, 27.8, 28.3, 28.5, 31.1, 105.6, 115.4, 126.8, 130.6, 134.9, 141.5, 143.6. Anal. Calcd for $C_{15}H_{19}IO_3S$: C, 44.34; H, 4.71. Found: C, 44.34; H, 4.61.

1*H*-1-(4-Methyl-1-pentynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-Dioxide (5e, R = *i*-Bu): from **4** (1.57 g, 5.00 mmol), $TsOH \cdot H_2O$ (0.95 g, 5.0 mmol), 4-methyl-1-pentyne (2.05 g, 25.0 mmol), and MeCN (40 mL); 23 h, reflux; aqueous workup; crude solid (1.58 g) recrystallized from CH_2Cl_2 (30 mL) and Et_2O (*ca.* 100 mL) to give **5e** as a tan solid: yield, 1.25 g (66%); mp 193–195 °C dec; IR 2164 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 1.04 (d, 6.65 Hz, 6 H), 1.98 (septet, 6.6 Hz, 1 H), 2.46 (s, 3 H), 2.59 (d, 6.5 Hz, 2 H), 7.44 (dd, 1 H), 7.90 (d, 1 H), 7.96 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 22.0, 27.9, 28.9, 29.8, 105.7, 114.4, 126.8(5), 130.6, 135.0, 141.5, 143.6. Anal. Calcd for $C_{13}H_{15}IO_3S$: C, 41.28; H, 4.00. Found: C, 41.02; H, 3.95.

1*H*-1-(3-Methyl-1-pentynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-Dioxide (5f, R = *s*-Bu): from **4** (1.57 g, 5.00 mmol), $TsOH \cdot H_2O$ (0.95 g, 5.0 mmol), 3-methyl-1-pentyne (1.02 g, 12.4 mmol), and MeCN (40 mL); 23 h, reflux; aqueous workup; crude solid (0.94 g) recrystallized from CH_2Cl_2 (20 mL), Et_2O (*ca.* 100 mL) to give **5f** as a pale-yellow solid: yield, 0.61 g (32%); mp 159–161 °C dec; IR 2154 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 1.03(5) (t, 7.4 Hz, 3 H), 1.30 (d, 7.0 Hz, 3 H), 1.61 (quintet, 2 H), 2.46 (s, 3 H), 2.85 (m, 1 H), 7.45 (dd, 1 H), 7.88 (d, 1 H), 7.97 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.6(5), 19.8, 20.7, 28.5, 29.2, 29.8, 105.7, 119.4, 126.6, 130.6, 135.0, 141.5, 143.6. Anal. Calcd for $C_{13}H_{15}IO_3S$: C, 41.28; H, 4.00. Found: C, 41.30; H, 4.05.

1*H*-1-(3,3-Dimethyl-1-butynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-Dioxide (5g, R = *t*-Bu): from **4** (1.26 g, 4.01 mmol), $TsOH \cdot H_2O$ (0.76 g, 4.0 mmol), 3,3-dimethyl-1-butyne (1.64 g, 20.0 mmol), and MeCN (30 mL); 16.5 h, reflux; aqueous workup; crude solid (1.25 g) recrystallized from CH_2Cl_2 (20 mL) and Et_2O (*ca.* 60 mL) to give **5g** as a white solid: yield, 1.06 g (70%); mp 212–214 °C; IR 2135, 2173 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 1.36 (s, 9 H), 2.46 (s, 3 H), 7.46 (dd, 1 H), 7.83 (d, 1 H), 7.97 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 27.6, 30.1, 30.2, 105.6, 122.7, 126.4, 130.6, 135.0, 141.5, 143.5. Anal. Calcd for $C_{13}H_{15}IO_3S$: C, 41.28; H, 4.00. Found: C, 41.12; H, 3.98.

1*H*-1-(Cyclohexylethynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-Dioxide (5h, R = cyclohexyl): from **4** (1.57 g, 5.00 mmol), $TsOH \cdot H_2O$ (0.95 g, 5.0 mmol), cyclohexylacetylene (0.95 g, 8.8 mmol), and MeCN (40 mL); 16 h, reflux; aqueous workup; residual material treated with warm Et_2O (20 mL) to give crude solid (0.82 g); solid recrystallized from CH_2Cl_2 (30 mL) and Et_2O (*ca.* 150 mL) to give **5h** as a tan solid: yield, 0.52 g (26%); mp 199–201 °C dec; IR 2155 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 1.25–2.00 (four closely spaced, poorly resolved m's, 10 H), 2.46 (s, 3 H), 2.86 (m, 1 H), 7.45 (dd, 1 H), 7.88 (d, 1 H), 7.97 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 24.6, 25.3, 28.3, 31.1, 31.8, 105.7, 119.1, 126.6, 130.6, 135.0, 141.5, 143.5(5). Anal. Calcd for $C_{15}H_{17}IO_3S$: C, 44.56; H, 4.24. Found: C, 44.34; H, 4.18.

1*H*-1-(Phenylethynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-Dioxide (5i, R = Ph): from **4** (1.26 g, 4.01 mmol), $TsOH \cdot H_2O$ (0.76 g, 4.0 mmol), phenylacetylene (2.04 g, 20.0 mmol), and MeCN (40 mL); 7 h, reflux (product separated from solvent); reaction mixture treated with Et_2O (10 mL), kept in an ice bath for 2 h, and filtered to give **5i** as a white solid (washed with Et_2O, dried in air): yield, 0.81 g (51%); mp 221–223 °C dec; IR 2154 cm^{-1} (C≡C); ^1H NMR (DMSO-d_6) δ 2.43(5) (s, 3 H), 7.5–7.66 (m, 4 H), 7.73–7.81 (m, 3 H), 8.10 (d, 8.5 Hz, 1 H); ^{13}C NMR (DMSO-d_6) δ 20.2, 41.3, 107.2, 107.7, 119.4, 128.8(5), 129.09, 129.14, 131.6, 133.0, 135.0, 142.4, 142.6. Anal. Calcd for $C_{15}H_{11}IO_3S$: C, 45.24; H, 2.78. Found: C, 45.12; H, 2.80.