a −70 °C solution of LDA (from 0.84 mL (6 mmol) of diisopropylamine and 3.75 mL (6 mmol) of 1.6 M *n*-BuLi in hexane) in 10 mL of THF. The reaction mixture was allowed to stir with gradual warming to −45 °C over 2 h and was then cooled back to −70 °C. Iodomethane (1.24 mL, 20 mmol) was added, and the mixture was stirred at −70 °C for 1 h and then allowed to warm to room temperature. After dilution with ether, the mixture was washed with dilute aqueous HCl. The ether was dried (Na_2SO_4) and evaporated, and the residue was chromatographed on silica gel (medium pressure, 50% ethyl acetate–hexane) to afford 0.92 g of **23c**: mp 98–99 °C; NMR ($CDCl_3$) δ 8.14 (m, 1 H), 7.35 (m, 2 H), 7.01 (m, 1 H), 6.65 (d, 1 H, J = 7.9 Hz), 6.50 (m, 2 H), 5.87 (AB q, 2 H, J = 1.4 Hz), 4.38 (d, 1 H, J = 1.5 Hz), 3.12 (s, 3 H), 3.10 (dq, 1 H, J = 1.5, 7.1 Hz), 1.45 (d, 3 H, J = 7.1 Hz). Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.22; H, 5.76; N, 4.75. Found: C, 73.08; H, 5.83; N, 4.69.

***trans*-3-(1,3-Benzodioxol-5-yl)-2-methyl-4-(2-propenyl)-3,4-dihydro-1(2*H*)-isoquinolone (23e)**: mp 119–120 °C; NMR ($CDCl_3$) δ 8.15 (m, 1 H), 7.35 (m, 2 H), 6.98 (m, 1 H), 6.64 (d, 1 H, J = 8 Hz), 6.46 (m, 2 H), 5.88 (AB q, 2 H, J = 1.35 Hz), 5.86 (m, 1 H), 5.18 (dd, 1 H, J = 1, 9 Hz), 5.10 (dd, 1 H, J = 1, 16 Hz), 4.54 (s, 1 H), 3.10 (s, 3 H), 2.95 (t, 1 H, J = 6 Hz), 2.45 (m, 2 H); MS, m/e (relative intensity) 321 (82, M^+), 306 (13), 280 (100), 279 (68), 239 (61), 159 (78), 158 (95), 130 (95), 129 (88), 115 (63). Anal. Calcd for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.68; H, 6.92; N, 4.09.

***trans*- and *cis*-3-(1,3-Benzodioxol-5-yl)-2-methyl-4-(2-propenyl)-3,4-dihydro-1(2*H*)-isoquinolone (23e and 25).** *N,N*-Diethyl-2-(3-butenyl)benzamide (**24**) was prepared by reaction of *o*-toluic acid dianion[13] with allyl bromide followed by conversion to the acid chloride (oxalyl chloride) and treatment with diethylamine. A solution of **24** (2.3 g, 10 mmol) in 5 mL of THF was added to a −70 °C solution of LDA (from 1.7 mL (12 mmol) of diisopropylamine and 6.25 mL of 1.6 M *n*-BuLi in hexane) in 40 mL of THF. After 5 min, a solution of imine **12g** (1.96 g, 12 mmol) was added, and the resulting solution was stirred 10 min at −70 °C. Dilute aqueous HCl was added, and the mixture was allowed to warm to room temperature. The mixture was poured into aqueous HCl and extracted with ether. The ether extract was dried (Na_2SO_4) and evaporated to a mixture of crude isomers **23e** and **25**, which were separated by silica gel chromatography (30% ethyl acetate–hexane). The less polar isomer (**23e**, 0.28 g, 9%) was identical with that from Table II). The more polar isomer was the cis compound **25** (0.07 g, 2%): mp 116–118 °C; NMR ($CDCl_3$) δ 8.16 (dd, 1 H, J = 1.5, 7.3 Hz), 7.42 (m, 2 H), 7.22 (d, 1 H, J = 7.5 Hz), 6.60 (d, 1 H, J = 8 Hz), 6.45 (dd, 1 H, J = 1.8, 8 Hz), 6.35 (d, 1 H, J = 1.8 Hz), 5.94 (m, 1 H), 5.86 (AB q, 2 H, J = 1.35 Hz), 5.21 (dd, 1 H, J = 1, 9 Hz), 5.15 (dd, 1 H, J = 1, 15 Hz), 4.42 (d, 1 H, J = 5.9 Hz), 3.76 (m, 1 H), 3.06 (s, 3 H), 2.68 (m, 1 H), 2.08 (m, 1 H). Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.74; H, 5.96; N, 4.36. Found: C, 74.72; H, 6.00; N, 4.32.

The acidic aqueous layer from above was basified with NH_4OH and extracted with ether to afford 3 g of crude adduct **26**: oil; NMR ($CDCl_3$) δ 7.40–7.15 (m, 4 H), 6.90 (s, 1 H), 6.75 (br s, 2 H), 5.95 (s, 2 H), 5.30 (m, 1 H), 4.80 (m, 1 H), 4.70 (m, 1 H), 3.85 (m, 1 H), 3.52 (d, 1 H, J = 9 Hz), 3.30 (m, 1 H), 3.15 (m, 1 H), 3.00 (m, 1 H), 2.90 (m, 1 H), 2.20 (m, 2 H), 2.05 (s, 3 H), 1.30 (t, 3 H, J = 6 Hz), 1.10 (t, 3 H, J = 6 Hz). This material was heated at reflux in 50 mL of xylene with 0.1 g of *p*-toluenesulfonic acid for 48 h. TLC analysis showed conversion to trans isomer **23c** with only a trace amount of cis isomer **25** present. Silica gel chromatography (30% ethyl acetate–hexane) afforded 1.34 g (total yield 51%) of additional **23e**.

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Supplementary Material Available: Spectral and analytical data on compounds listed in Tables I and II (6 pages). Ordering information is given on any current masthead page.

Photostimulated $S_{RN}1$ Reactions of Halothiophenes with Benzenethiolate Ion in Acetonitrile

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The photostimulated reactions between benzenethiolate and 2-chloro-, 2-bromo-, 2-iodo-, and 3-bromothiophene in MeCN lead to rather complex product mixtures where the phenyl thienyl sulfide (ThSPh), the ipso-substitution product, represents the main component. The collected results agree well with the occurrence of an $S_{RN}1$ chain pathway. As to the obtainable yield of sulfide, the main drawback is represented by the fragmentation into ThS^- and $Ph^\bullet$ of the $ThSPh^{\bullet-}$ radical anion, formed either along the propagation cycle or by single-electron reduction of the sulfide itself. Optimization of the yield of ThSPh, although at the expense of the overall reaction rate, can be achieved by the employment of suitable electron acceptors. The overall reactivity orders (2-I > 2-Br > 2-Cl and 2-Br > 3-Br) are also discussed.

The behavior of various nitrothiophene derivatives to nucleophilic substitutions on a side-chain carbon atom via the $S_{RN}1$ mechanism has been widely studied, and the scope and limitations of such reactions have been defined sufficiently.[1] Conversely, notwithstanding its obvious value in synthesis, the aromatic $S_{RN}1$ reaction[2,3] in the thiophene series has received relatively little attention.[4,5] The available results,[4-6] however, suggest some remarkable differences with respect to other more extensively explored arene series: for instance, in spite of the presence of a good nucleofugal group and the use of very reactive $S_{RN}1$ nucleophiles,[2,3] the photoinduced reactions of 2-iodothiophene with ammonium benzenethiolate or potassium diethyl

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Table I. Photostimulated Reactions of Halothiophenes with Tetrabutylammonium Benzenethiolate in MeCN[a]

entry	substrt (ThX)	time, min	recovd[b] ThX, %	% yield[c] ThH	ThSPh	ThSMe	materl balnce,[d] %	ThH/ reacted ThX[c,e]	ThS⁻/ reacted ThX[c,f]	% yield of byproducts PhH	PhSPh	PhSSPh
1	**2c**	30	66	6	10	14	96	0.18	0.41	5	9	4
2	**2b**	30	41	9	26	17	93	0.15	0.29	7	13	7
3		90	11	13	28	30	82	0.15	0.34	14	21	9
4	**2i**	30	18	8	52	10	88	0.10	0.12	4	8	10
5		45	6	14	45	20	85	0.15	0.21	12	12	9
6	**3b**	30	57	3	26	12	98	0.07	0.28	9	9	4
7		60	37	4	35	15	91	0.06	0.24	13	12	5
8		90	25	5	38	18	86	0.07	0.24	18	14	5
9		120	20	5	39	18	82	0.06	0.23	20	15	5
10	**2p**	30	50	5		40	95	0.10	0.80	10	32	7
11	**3p**	30	90			8	98		0.80	10	10	9
12[g]	**2b**	30	47	7[h]	25	15	94	0.13[h]	0.28	6[h]	11[h]	7[h]
	3b		90		8		98					

[a] [ThX] = 16.7 mM, $[Bu_4N^+PhS^-]$ = 83.5 mM. The reactions were carried out in Pyrex test tubes deaerated with argon. Irradiation was performed in a Rayonet RP 100 reactor equipped with a merry-go-round system and with eight "350-nm" lamps (reaction temperature around 35 °C). The reactions were quenched by addition of excess MeI and left overnight at room temperature in the dark before workup. [b] Near quantitative recoveries of starting material were obtained in the absence of light or in the light without added benzenethiolate ion. [c] Mean values of up to four GLC determinations of at least three independent experiments. [d] Material balance in thienyl derivatives. [e] Molar fraction of reacted substrate converted into ThH. [f] Molar fraction of reacted substrate converted into 2- or 3-thiophenethiolate anion. [g] Competitive experiment: [**2b**] = [**3b**] = 16.7 mM, $[Bu_4N^+PhS^-]$ = 83.5 mM. [h] Calculated as deriving only from **2b**.

Table II. Effect of Added Electron Acceptors (EA) in the Photostimulated Reactions of Halothiophenes with Tetrabutylammonium Benzenethiolate in MeCN[a]

entry	substrt (ThX)	EA	time, min	recovd ThX, %	% yield[b] ThH	ThSPh	ThSMe	materl balnce,[c] %	ThH/ reacted ThX[b,d]	ThS⁻/ reacted ThX[b,e]	% yield of byproducts PhH	PhSPh	PhSSPh
2	**2b**	None	30	41	9	26	17	93	0.15	0.29	7	13	7
3		None	90	11	13	28	30	82	0.15	0.34	14	21	9
13		PhCN	30	65	3	27	3	98	0.09	0.09	2	3	3
14		PhCN	60	41	6	41	6	94	0.10	0.10	4	6	4
15		PhCN	90	35	6	42	6	89	0.09	0.09	3	6	7
16		PhCN	120	25	7	46	7	85	0.09	0.09	2	8	7
17		$PhNO_2$	30	76	1	20	1	98	0.04	0.04		1	3
18		$PhNO_2$	60	55	1	35	2	93	0.02	0.04		2	5
6	**3b**	None	30	57	3	26	12	98	0.07	0.28	9	9	4
8		None	90	25	5	38	18	86	0.07	0.24	18	14	5
19		PhCN	30	81	1	15	1	98	0.05	0.05	1	2	3
20		PhCN	90	52	3	40	2	97	0.06	0.04	2	4	4
21		PhCN	150	39	4	49	3	95	0.07	0.05	2	6	3
22		PhCN	300	13	7	64	6	90	0.08	0.07	9	11	1

[a] [ThX] = 16.7 mM, $[Bu_4N^+PhS^-]$ = 83.5 mM, [EA] = 11.0 mM. Photostimulation and MeI quenching were carried out as for experiments in Table I: see footnote *a* of that table. [b,c,d,e] Refer respectively to footnotes *c*, *d*, *e*, and *f* in Table I.

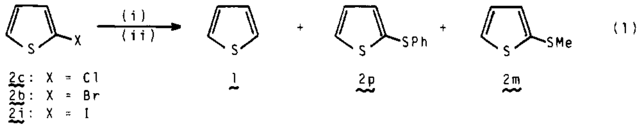
phosphite in liquid ammonia have been reported to fail to yield substantial substitution.[6]

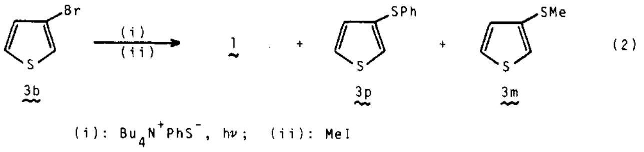
In line with our interest both in reductively activated nucleophilic substitutions[7] and in the reactivity of thiophene derivatives,[8] we studied the photostimulated reactions of 2-chloro- (**2c**), 2-bromo- (**2b**), 2-iodo- (**2i**), and 3-bromothiophene (**3b**) in MeCN with benzenethiolate. The results of this investigation are now reported.

Results and Discussion

Reactions were carried out under argon in MeCN solution, with a fivefold molar excess of tetrabutylammonium benzenethiolate. The results are collected in the Tables I and II, where the entry numbering is progressive, so that runs referred to in both tables maintain the same number.

While control experiments indicated no appreciable reaction in the dark, consumption of the substrate occurred under photostimulation with 350-nm light, the overall reactivity order being **2i** > **2b** > **3b** > **2c**, as judged from the recovered unchanged halothiophene (cf. entries 1, 2, 4, and 6). Analysis of the reaction mixture, carried out by GLC after quenching with methyl iodide, always gave a good material balance, showing, besides benzene, diphenyl sulfide, diphenyl disulfide, and thioanisole (directly derived from quenching of the excess benzenethiolate), the formation in each case (eq 1 and 2) of three thiophene ring containing compounds in variable yields: thiophene (**1**), 2- or 3-(phenylthio)thiophene (**2p** or **3p**), and 2- or 3-(methylthio)thiophene (**2m** or **3m**). The formation of **2p**, **3p**, **2m**, and **3m** was confirmed also by isolation of these





(i): $Bu_4N^+PhS^-$, hν; (ii): MeI

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products from large-scale experiments, followed by oxidation to the corresponding sulfones and comparison (^{1}H NMR and mixed mp) with authentic samples prepared as reported in the literature (see Experimental Section).

Mechanistic Aspects. The expected[4,5,9] occurrence of an $S_{RN}1$ mechanism in the present reactions is in good agreement with both the catalytic effect of light and the reactivity order of the 2-haloderivatives (I > Br > Cl), which matches the order commonly found in similar processes in different aromatic systems.[2,3] An explanation of the differential reactivity of **2b** and **3b** is not straightforward and will be dealt with later in the discussion. Further substantiation of the involvement of an $S_{RN}1$ mechanism comes from the outcome of a typical recognition test,[2,3] viz., the employment of electron acceptors. Comparison of, e.g., entry 2 with 13 or 17 for **2b** and of entry 6 with 19 for **3b** indicates a substantial retardation of substrate conversion brought about by either PhCN or $PhNO_2$, with accompanying effects on the product composition which will be rationalized in a following section. Accordingly, the step sequence for the $S_{RN}1$ mechanism, as adapted to the present case, is sketched in Scheme I, where the Th abbreviation (as so forth in the text, unless specified) stands for either the 2- or the 3-thienyl moiety.

Scheme I

$$ThX + PhS^- \xrightarrow{h\nu} ThX^{\bullet-} + PhS^\bullet \qquad (M1)$$

$$ThX^{\bullet-} \rightarrow Th^\bullet + X^- \qquad (M2)$$

$$Th^\bullet + PhS^- \rightarrow ThSPh^{\bullet-} \qquad (M3)$$

$$ThSPh^{\bullet-} + ThX \rightleftharpoons ThSPh + ThX^{\bullet-} \qquad (M4)$$

The initiation step is believed to occur by photostimulated transfer of an electron from the thiolate anion[9] to the thienyl halide (step M1): accordingly, the substrate radical anion provides the access to the propagation cycle while the thiyl radical eventually leads to diphenyl disulfide. In the first two steps of the propagation cycle the $ThX^{\bullet-}$ radical anion ejects a halide ion (step M2), and the resulting thienyl radical adds (step M3) to the benzenethiolate ion to form the radical anion $ThSPh^{\bullet-}$. The cycle is then completed by the electron transfer from $ThSPh^{\bullet-}$ to substrate (step M4).

Conceivable termination steps for the present systems are reported in reactions M5 and M7. Steps M5 + M6 or M7 account for the formation of thiophene, the hydrodehalogenation product.

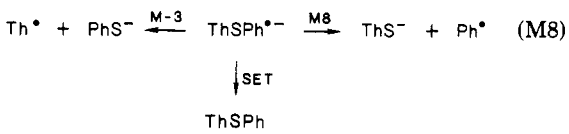
$$Th^\bullet + e \rightarrow Th^- \qquad (M5)$$

$$Th^- + AH \rightarrow ThH + A^+ \qquad (M6)$$

$$Th^\bullet + DH \rightarrow ThH + D^\bullet \qquad (M7)$$

In the first case the thienyl radical is reduced to thienyl anion by any oxidable species present in the reaction medium.[10] Protonation of Th^- by a proton donor AH (the solvent, the tetrabutylammonium ion used as the counterion of benzenethiolate, or adventitious water) then gives thiophene (step M6). In the second case (step M7), which in organic solvents is supposed to predominate over the above (M5 + M6) pathway,[10,11] thiophene is formed via H-atom transfer to the thienyl radical from a donor, which can herein be represented by either the solvent[9b,e,11] or the tetrabutylammonium cation.[9e]

Scheme II



$$\begin{array}{c} Th^\bullet + PhS^- \xleftarrow{M-3} ThSPh^{\bullet-} \xrightarrow{M8} ThS^- + Ph^\bullet \qquad (M8) \\ \downarrow \text{SET} \\ ThSPh \end{array}$$

The formation of the other secondary products found in the studied reactions can be accounted for by the occurrence of the M8 fragmentation step (Scheme II), which is based upon several reports showing the possibility for diaryl sulfides radical anions to cleave into an aryl radical and arenethiolate ion.[9a,c,e,f,12,13] Thus, the radical anion intermediate formed in step M3 can suffer three competitive reactions (Scheme II), i.e., single-electron transfer (SET) to give the substitution product (step M4) and fragmentation to either starting materials (step M–3, viz., the reverse of M3) or to thiophenethiolate ion and phenyl radical (step M8).[14]

On this grounds, 2-(methylthio)- (**2m**) or 3-(methylthio)thiophene (**3m**) can be envisaged to form from the trapping of the 2- or 3-thiophenethiolate anion, respectively, by the methyl iodide intentionally used to quench the reactions. The possibility that $Th^\bullet$ can combine with ThS^- to form $ThSTh^{\bullet-}$ and ultimately dithienyl sulfide ThSTh is statistically disfavored with respect to the coupling of the same radical with the more abundant benzenethiolate anion; accordingly no trace of either 2,2′- or 3,3′-dithienyl sulfide was detected by GLC. The formation of benzene and diphenyl sulfide[15] can finally be easily explained by considering that the phenyl radical produced in reaction M8 can suffer a fate similar to that of the thienyl radical, i.e., either H-atom transfer to yield benzene or trapping by benzenethiolate to give ultimately diphenyl sulfide, most likely via electron transfer from the intermediate $PhSPh^{\bullet-}$ radical anion to ThX. It should be noted that this last reaction represents an alternative initiation step of the M2 + M3 + M4 propagation cycle.

Further Analysis of the Experimental Data. The yield of a given product through a chain process depends on the competition between the propagation steps and possible alternative routes for the chain-carrying intermediates.[10,14] It goes by itself that, other factors being constant, the faster the rotation of the propagation cycle, the lower the yield of byproducts. Accordingly, the data

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(9) For the intervening aptitude of arenethiolates in aromatic $S_{RN}1$ substitutions, see ref 3, p 80, ref 7a–c, and the following: (a) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1975**, *40*, 3740. (b) Bunnett, J. F.; Scamehorn, R. G.; Traber, R. P. *Ibid.* **1976**, *41*, 3677. (c) Galli, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 7140. (d) van Tilborg, W. J. M.; Smit, C. J.; Scheele, J. J. *Tetrahedron Lett.* **1977**, *24*, 2113. (e) Swartz, J. E.; Stenzel, T. T. *J. Am. Chem. Soc.* **1984**, *106*, 2520. (f) Amatore, C.; Combellas, C.; Pinson, J.; Oturan, M. A.; Robveille, S.; Saveant, J. M.; Thiebault, A. *Ibid.* **1985**, *107*, 4846.

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(14) For a comprehensive treatment about the competition between electron transfer and fragmentation routes for the radical anion of the substitution product in the course of aromatic $S_{RN}1$ reactions, see ref 2d and 3, p 205–224.

(15) The stoichiometry of step M8 requires that the yield of ThSMe and the sum of those of PhH and PhSPh be equal; however, the data of the tables show that the latter is always somehow higher than the former. A partial explanation of this outcome could arise from the results of a control experiment showing the formation of a trace amount of benzene (together with diphenyl disulfide) by irradiation of tetrabutylammonium benzenethiolate alone under typical reaction conditions.

of Table I (cf. entries 1, 2, and 4) show that on going from **2c** to **2b** and **2i**, i.e., toward faster and faster propagation cycles, the molar fraction of substrate converted into ThH + ThS^- decreases from 0.59 to 0.44 and to 0.22.

Conversely, the parallelism between overall reactivity and efficiency of the process would not seem to hold when comparing **2b** and **3b**: within the same reaction time (cf. entries 2 and 6), notwithstanding a higher conversion percentage of the former, in front of the same yield of substitution product lower yields of ThH and ThS^- are observed for the latter. Rationalization of this result could be offered, at least in part, by the stability in our reaction conditions of sulfides **2p** and **3p**. Control experiments (entries 10 and 11) show that under the same conditions used for halothiophenes (entries 1, 2, 4, and 6), 50% of 2-ThSPh disappears to give ThH and 2-ThS^- whereas the 3-isomer is more stable (90% recovery). In regard to this it must be recalled that diaryl sulfides are themselves suitable substrates in $S_{RN}1$ reactions,[9a,c,f,13] with a leaving group ability for PhS^-, as evaluated, e.g., in the benzene series with acetone enolate as the nucleophile,[13b] in between those of Br^- and Cl^-. Therefore, in the overall economy of the process, the possibility of the occurrence of step M9 has to be taken into account, whose incidence, other factors being equal, will anyway be negligible at low conversion percentages, given a statistically more favorable encounter of PhS^- with unreacted substrate rather than with the just formed sulfide. As far as the $ThSPh^{\bullet -}$ radical anion is efficiently oxidized via step M4, reaction M9 represents nothing but yet another initiation step of the M2 + M3 + M4 propagation cycle. However, when M4 is made less competitive (i.e., at high conversions, when less substrate is available in order to accomplish reoxidation, or with more negatively reducible substrates), step M9 will definitely result in higher yields of ThS^- and ThH through the sequence of reactions M9 + M8 or M9 + M−3 + M7. Thus the decomposition of **2p** cannot be prevented unless conversion is restricted to rather low percentages and very good yields of substitution from 2-halothiophenes are difficult to obtain under the present experimental conditions: an increase in the reaction time unavoidably results in a decrease in the relative yield of **2p** (cf. entry 2 with 3 and 4 with 5). On the other hand, because of the higher stability of **3p**, as far as **3b** is concerned, an increase in the reaction time does not cause any substantial variation in the product composition (entries 6–9). Nonetheless, a further drawback common to all the systems herein examined is represented by a trend to a decrease in the material balance with longer reaction times: darkening is observed, with formation (TLC) of tarry materials (perhaps from reductive cleavage of the thiophene ring[16]) and no new volatile product is detected by GLC. Because of this, in any case the absolute yield of substitution product reaches a limit value which cannot be improved by increasing the reaction time.

$$\mathrm{ThSPh} + \mathrm{PhS}^- \xrightarrow{h\nu} \mathrm{ThSPh}^{\bullet -} + \mathrm{PhS}^{\bullet} \qquad \text{(M9)}$$

Effect of Added Electron Acceptors. As evidenced by the discussion above, the system herein is considerably hampered by the fragmentation of the $ThSPh^{\bullet -}$ radical anion via step M8. Since this unimolecular process is in competition with the bimolecular[9d,17] process of oxidation of $ThSPh^{\bullet -}$ to substitution product (Scheme II), we postulated[9e,18] that the addition of a suitable electron acceptor (EA) to the reaction mixture would play a favorable role on the yield of ThSPh. In fact, provided that EA is more easily reducible than ThSPh, the occurrence of reaction M4′ is expected to ensure (coupled with M4) an overall faster oxidation of $ThSPh^{\bullet -}$ to the detriment of its competing fragmentation.

$$\mathrm{ThSPh}^{\bullet -} + \mathrm{EA} \rightleftharpoons \mathrm{ThSPh} + \mathrm{EA}^{\bullet -} \qquad \text{(M4}'\text{)}$$

Accordingly, we tested the effect of benzonitrile on the reactions of both **2b** and **3b** and of nitrobenzene on the reaction of **2b** (Table II). The choice was dictated by the consideration that these substances (a) do not interfere with the GLC analysis of the reaction mixtures, (b) give relatively stable radical anions,[19] and (c) do not lead to complete inhibition of the reactions[9e,20] by acting as electron sinks.[2a,21]

In agreement with the above expectations, the results reported in entries 13–22 show that the addition of PhCN or $PhNO_2$ to the reactions of **2b** or **3b** with benzenethiolate brings about a substantial improvement of the relative yields of the substitution products. In particular, comparison of entries 2, 13, and 17 and of 6 with 19 shows that, at the same irradiation time, the molar fraction of bromothiophene devolved to the formation of ThH + ThS^- decreases from 0.44 to 0.18 and to 0.08 for **2b** and from 0.35 to 0.10 for **3b**. It is interesting to note that such decrease occurs mainly at the expenses of ThS^- (actually with **3b** the molar fraction of ThX converted into ThH remains practically constant), to further substantiation of an effective inhibition of M8 by the added EA.

Another point worth noting in the experiments carried out on **2b** is that, unlike the reactions where EA is absent, no variation in the product distribution with increasing reaction time (attributed, as discussed in the previous section, to the instability of **2p**) is observed along entries 13–18. This outcome, coupled with a concurrent slight decrease in the molar fraction of **2b** converted into ThH, is in agreement with the fact that the competitive decomposition of **2p**, as a consequence of reaction M9, is in turn completely inhibited by the presence of the more easily reducible added substance.

The same results, however, show that such a favorable effect is counterbalanced by a decrease in the overall reaction rate. As already mentioned, the comparison of experiments quenched at the same time (cf. entry 2 with 13 and 17, 3 with 15, 6 with 19, and 8 with 20) shows that the addition of PhCN or $PhNO_2$ to the reactions of **2b** or **3b** brings about a depression of the rate of disappearance of ThX, which is more marked with the latter than with the former EA. Although such a decrease in the overall reaction rate by EA's is quite a general effect in $S_{RN}1$ processes,[2,3,21] in our opinion, a proper explanation of it would herein at least require an exact knowledge of the relative efficiencies of EA and substrate as electron acceptors under photostimulation. In any case, the added EA, inhibiting the $ThSPh^{\bullet -}$ fragmentation of step M8 and therefore the formation of $Ph^{\bullet}$, eventually prevents the alternative initiation represented by the electron transfer from $PhSPh^{\bullet -}$ to substrate (see above), to the detriment of the overall rate of ThX consumption.

Differential Reactivity of 2b and 3b. While, as mentioned above, a reactivity comparison within the 2-halothiophene series is straightforward, the differential

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behavior of **2b** and **3b**, i.e., the somewhat lower overall reactivity of the latter (cf. entries 2 and 6) is subject to a number of additional variables which make interpretation more difficult.

In this regard it must be pointed out that the relative reactivities displayed in our system (**2b** > **3b**) are the reverse of the order found in, e.g., the photon or solvated electron-stimulated reactions with acetone enolate in liquid ammonia.[4] In the case of solvated-electron induction the higher reactivity of the 3-isomer has been attributed in turn to an easier fragmentation of the substrate radical anion[4] (step M2 herein) or to a higher electrophilicity of the resulting thienyl radical,[22] facilitating the successive radical/anion coupling (step M3 herein). On the other hand, no rationalization has been attempted in the photostimulated reactions, where, according to Bunnett and Gloor,[4] the overall reactivity of **2b** and **3b** can be affected by rate differences of both initiation, propagation, and termination steps. Furthermore, differences in the reaction conditions between the present and the cited systems[4] are so substantial that any attempt of comparison would be at the moment rather unwarranted.

To attain a deeper insight into our own results, we carried out an experiment (entry 12), in which equimolar amounts of **2b** and **3b** were allowed to compete for benzenethiolate under typical reaction conditions (entries 2 or 6). The outcome of such competition is represented by an apparent[23] reactivity difference between the two substrates which is more marked than that observed when they are reacted separately; instead of only 10% conversion of **3b**, 53% of **2b** reacts to give ThH, 2-ThSPh, and 2-ThSMe in yields which closely match those of entry 2. These facts[23] could find a rationale in an easier reducibility of the 2-isomer. Accordingly, in the competitive experiment the **2p**$^{\bullet-}$ and **3p**$^{\bullet-}$ anion radicals, generated within the propagation cycles relevant to **2b** and **3b**, would preferably act as electron-transfer agents towards **2b** rather than **3b**. In other words, **2b** acts as inhibitor of the **3b** propagation cycle, masking the actual reactivity difference of the two substrates but providing us with a sounding conclusion about the relative power of the two isomers as electron acceptors under photostimulation. Such conclusion, though, does not help us much in making conjectures on relative rotation rates of the two propagation cycles. Rather, a more favorable initiation step for **2b** can be reasonably guessed.

Experimental Section

General. Gas chromatographic analyses were performed on a Carlo Erba HRGC chromatograph equipped with a flame ionization detector and an Alltech fused-silica capillary column (30 m × 0.25 mm; liquid phase: RSL 150). Injection port and detector were maintained at 200 °C, while the column was operated at 20 °C for 4 min and then up to 200 °C with a heating rate of 8 °C/min. Quantitative analyses were conducted with naphthalene as internal standard and areas were corrected for molar response as determined from standard solutions of the products and the standard.

Irradiation was conducted with a Rayonet RPR-100 photochemical reactor equipped with a merry-go-round apparatus and with eight lamps emitting maximally at 350 nm.

Materials. Spectrophotometric grade acetonitrile (Fluka) was used as received after drying over molecular sieves (type 4A). 2-Chloro-, 2-bromo-, 2-iodo-, and 3-bromothiophene, benzonitrile, and nitrobenzene were commercial samples, purified by distillation. Tetrabutylammonium benzenethiolate was prepared by addition of freshly distilled benzenethiol (1.13 mL, 11 mmol) to 40% aqueous tetrabutylammonium hydroxide (6.55 mL, 10 mmol). The water was evaporated off under reduced pressure and the residue worked up as previously described[24] for the preparation of solid sodium benzenethiolate.

For the analysis of the reaction products authentic samples of the following compounds were synthesized as reported in the literature: 2-(methylthio)-,[25] 3-(methylthio)-,[26] 2-(phenylthio)-,[27] 3-(phenylthio)-,[28] 2-(methylsulfonyl)-,[29] 3-(methylsulfonyl)-,[26] 2-(phenylsulfonyl)-,[27] and 3-(phenylsulfonyl)thiophene[28] and 2,2′-dithienyl[30] and 3,3′-dithienyl sulfide.[30]

Photostimulated Reactions of Halothiophenes with Tetrabutylammonium Benzenethiolate. Aliquots of 0.1 M solutions in acetonitrile of halothiophenes **2c**, **2b**, **2i**, or **3b** (1.5 mL, 0.15 mmol) and of tetrabutylammonium benzenethiolate (7.5 mL, 0.75 mmol) were mixed together in Pyrex test tubes. The reaction solutions were deaerated with argon using three freeze–pump–thaw cycles and stoppered with rubber septa. In the experiments carried out in the presence of electron acceptors, benzonitrile (10 μL, 0.098 mmol) or nitrobenzene (10 μL, 0.098 mmol) were added through the septum by means of a microsyringe. Dark reactions were carried out in test tubes wrapped in aluminium foil and placed in the photochemical reactor besides the corresponding photostimulated reactions.

Reactions were quenched by addition of methyl iodide (65 μL, ca. 1 mmol) and left overnight in the dark at room temperature. Usual workup then involved pouring into brine (30 mL), addition of a known amount of a 7 mM ether solution of naphthalene (used as internal standard), and extraction with ether (3 × 25 mL). The combined ether phases were washed with 10% NaOH (2 × 10 mL) and with water (2 × 10 mL) and dried over sodium sulfate prior to GLC analysis.

Identification of Products. All products were identified and quantified (GLC) by comparison of their retention times with those of authentic samples.

Large-scale experiments were performed on **2b** or **3b** in order to confirm the formation of 2- or 3-(methylthio)- and 2- or 3-(phenylthio)thiophene and of diphenyl sulfide also via isolation of the corresponding sulfones. Thus the ether extract, obtained as above, was evaporated off under reduced pressure and the residue oxidized in acetic acid at 100 °C with excess 36% hydrogen peroxide. After usual workup the mixture of sulfones was separated into its components by preparative HPLC. The various sulfones were identified by comparison (^{1}H NMR and mixed mp) with authentic samples prepared as reported in the literature (see above).

Registry No. 1, 110-02-1; **2b**, 1003-09-4; **2c**, 96-43-5; **2i**, 3437-95-4; **2m**, 5780-36-9; **2p**, 16718-12-0; **3b**, 872-31-1; **3m**, 20731-74-2; **3p**, 16718-11-9; $Bu_4N^+PhS^-$, 4670-62-6; PhH, 71-43-2; PhSPh, 139-66-2; PhSSPh, 882-33-7; PhCN, 100-47-0; $PhNO_2$, 98-95-3; PhS^-, 13133-62-5; 2-thiophenethiolate, 110487-97-3; 3-thiophenethiolate, 110487-98-4; 2-(phenylthio)thiophene radical anion, 110487-99-5; 3-(phenylthio)thiophene radical anion, 110488-00-1.

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(22) Reference 3, p 164.

(23) As to the significance and possible implications of competitive experiments in $S_{RN}1$ processes see, e.g., ref 3, p 232.

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