Synthesis and S_NV Reactions of 2-(Haloethenyl)benzo[*b*]thiophene 1,1-Dioxides

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The synthesis of a variety of 2-(haloethenyl)benzo[*b*]thiophenes from both substituted and unsubstituted benzo[*b*]thiophenes is described. Their corresponding 1,1-dioxides exhibited versatile reactivity via addition/conjugated elimination and direct substitution mechanisms with amine, thio, and alkoxy nucleophiles in good yield.

Introduction

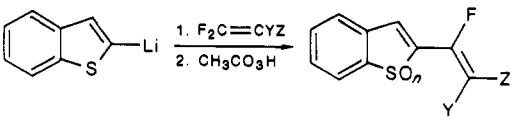
Mechanistic routes for nucleophilic vinylic substitution (S_NV) with vinyl halides are numerous and have been recently reviewed.[1] Furthermore, addition–elimination reactions of amines with 3-bromobenzo[*b*]thiophene 1,1-dioxide via direct displacement[2,3] and of allylic intermediates from benzo[*b*]thiophene 1,1-dioxides via an S_N2' reaction mechanism[4] are documented. However, anomalous displacement reactions of halovinyl heterocycles involving addition/conjugated elimination mechanisms have not been described. Initially, the nematocidal utility of heteroaromatic vinyl halides, e.g. 5-(2,2-dichloroethenyl)-2-thienylethanone,[5] prompted our investigation of the synthesis of 2-(haloethenyl)benzo[*b*]thiophenes. By comparison with 2-(haloethenyl)thiophene prototypes, the greater susceptibility of benzo[*b*]thiophenes to ring sulfur oxidation was inferred from field studies.[6] Interestingly, isolation of the corresponding benzo[*b*]thiophene 1,1-dioxides fostered our observation of their versatile reactivity to nucleophilic vinylic substitution via both addition/conjugated elimination and direct substitution mechanisms.

Results

A convenient synthesis of phenyl-substituted vinyl halides via phenyllithium addition to commercially available fluoro olefins has been described.[7-10] Thianaphthenyllithium addition to both hexafluoropropylene and 1,1-dichloro-2,2-difluoroethylene gave good yields of the corresponding 2-(haloethenyl)benzo[*b*]thiophenes (Table I). In the former case, the intermediate carbanion formed in the nucleophilic addition is stabilized by the trifluoromethyl group leading to **1** (*E* isomer), which exhibited a 128.8-Hz *trans*-vinyl fluorine coupling constant. Compound **2** and 2-(2,2-dichloro-1-fluoroethenyl)benzo[*b*]-thiophenes **5–18** (Table II) containing a variety of benzenoid ring substitutions were similarly prepared from 1,1-dichloro-2,2-difluoroethylene.

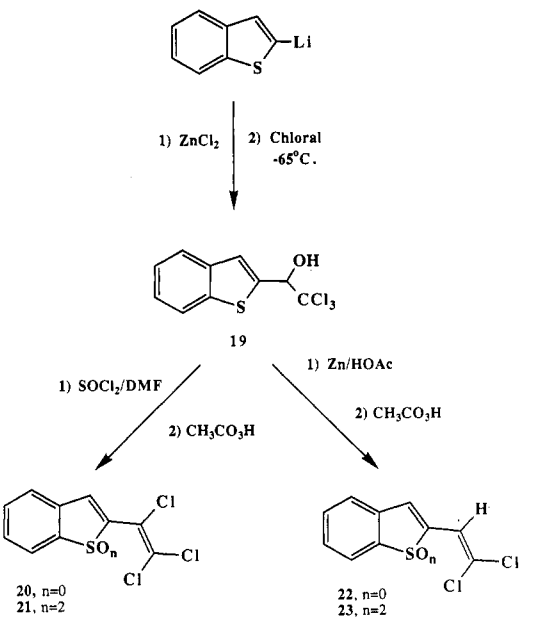
Alternative vinyl halide substitutions were derived from the 3,3,3-trihaloethanol intermediates **19** (Scheme I) and **24** (Scheme II). Substantial decomposition occurred in the reaction of chloral with thianaphthenyllithium; however, the thianaphthenylzinc reagent permitted the clean isolation of **19** in good yield. In contrast, the reaction of tribromoacetaldehyde with thianaphthenylzinc led to decomposition. Compound **24** was prepared by the in situ generation of tribromomethane anion[11] in DMSO and reaction with benzo[*b*]thiophene-2-carboxaldehyde.[12] The intermediate trihaloethanols **19** and **24** were halogenated with either thionyl chloride or (diethylamino)sulfur tri-

Table I. Synthesis of 2-(Haloethenyl)benzo[*b*]thiophenes and 1,1-Dioxides



compd	Y	Z	*n*
1	F	CF_3	0
2	Cl	Cl	0
3	Cl	Cl	2
4	F	CF_3	2

Scheme I



(1) Rapporport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309.
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(6) Gajewski, R. P., unpublished results.
(7) Dixon, S. *J. Org. Chem.* **1956**, *21*, 400.
(8) U.S. Patent 3,712,929 1973; cited in *Chem. Abstr.* **1973**, *78*, 124246q.
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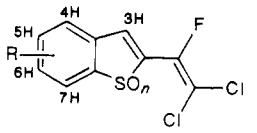
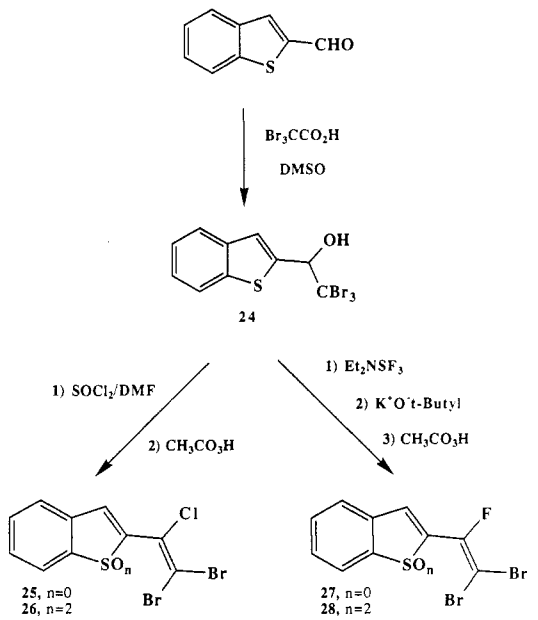
0022-3263/89/1954-3311$01.50/0

Table II. Benzenoid ^{1}H NMR Data of 2-(2,2-Dichloro-1-fluoroethenyl)benzo[*b*]thiophenes and 1,1-Dioxides



compd	R	*n*	3H	4H	7H	5H	6H
5	4-Me	0	7.8 s		7.6 d	7.2–7.3 m	
6	3-Me	2		7.6 m	7.7 d	7.6 m	7.5 d
7	7-Me	0	7.7 s	7.6 d		7.2–7.3 m	
8	7-Me	2	8.2 s	7.5 m		7.4–7.6 m	
9	4-Et	0	7.8 s		7.65 d	7.2 d	7.35 t
10	4-Et	2	7.7 s			7.4–7.55 m	
11	4-Ph	0					
12	4-Ph	2					
13	4-Cl	0	7.9 s		7.7 d	7.3–7.5 m	
14	4-Cl	2	7.8 s			7.5–7.7 m	
15	5-Cl	0	7.8 s	7.7 s	7.75 d		7.4 d
16	5-Cl	2	7.6 s	7.65 d	7.7 d		7.5 d
17	6-Cl	0	7.8 s	7.75 d	7.7 s	7.3 d	
18	6-Cl	2	7.7 s	7.6 d	7.55 s	7.4 d	

Scheme II



fluoride followed by dehydrohalogenation to give vinyl halides **20**, **25**, and **27**. Compound **19** was reduced with zinc/acetic acid to produce the 2,2-dichloroethenyl derivative **22**. Each of the above vinyl halides was labile to oxidation and was converted to the corresponding 1,1-dioxides (Tables I and II, Scheme I and II) with peroxyacetic acid.

The dioxides were susceptible to nucleophilic attack. Aminolysis of the dioxide **3** (Scheme III) with dimethylamine in DMF was expected to give, after hydrolysis, *N*,*N*-dimethylbenzo[*b*]thiophen-2-ylfluoroacetamide via nucleophilic attack at the terminus of the vinyl halide functionality, analogous to the phenylacetamide product reported by Fokin[13] from reaction of diethylamine with trifluoroethenylbenzene. However, X-ray analysis[14] of the product **30** (Figure 1) confirmed its structure as (*Z*)-2-(2-chloro-1-fluoroethenyl)-3-(dimethylamino)benzo[*b*]-thiophene 1,1-dioxide obtained via nucleophilic attack at the 3-position of the benzo[*b*]thiophene ring followed by

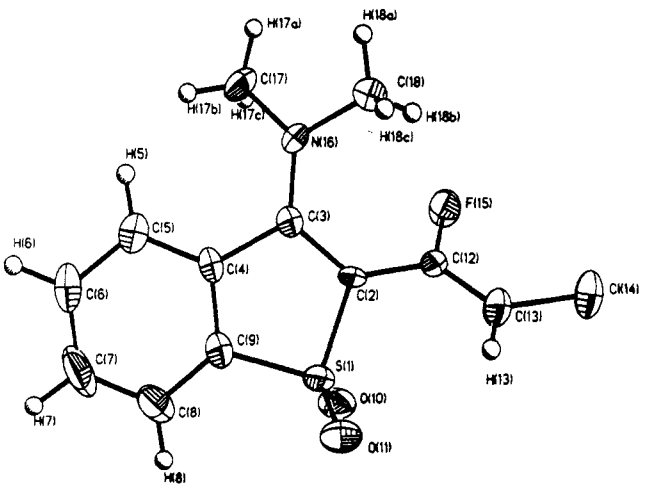
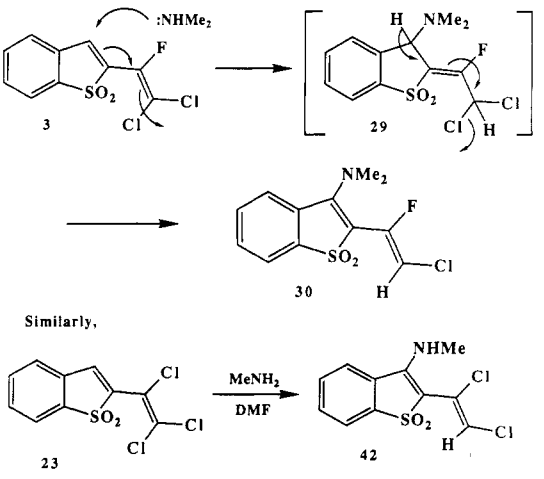


Figure 1. ORTEP plot of compound 30.

Scheme III



conjugated elimination of HCl (Scheme III). The ^{1}H NMR spectrum of **30** exhibited a vinyl proton absorption at 6.15 ppm with a *trans*-vinyl fluorine coupling constant of 22.4 Hz. Similarly, **23** reacted with methylamine to produce **42**, exhibiting a vinyl singlet at 6.8 ppm (Scheme III). Interestingly, the terminus of the vinyl halide functionality exhibited little reactivity since the 3-methyl-substituted analogue **6** (Table II) gave no reaction with methylamine at room temperature.

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(14) See experimental and supplementary data sections for details.

Scheme IV

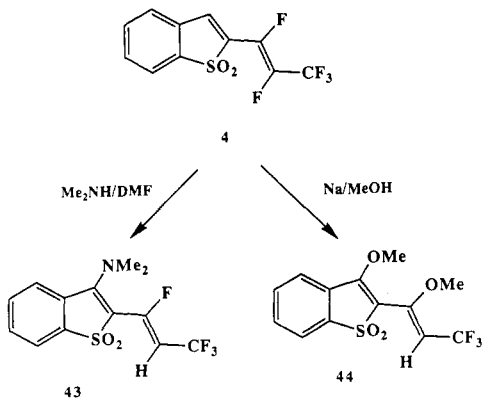
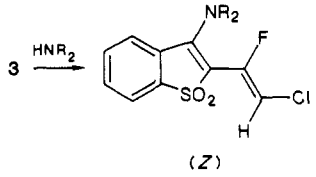
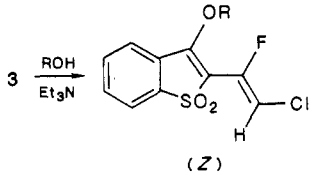


Table III. Amine S_NV Displacement Products



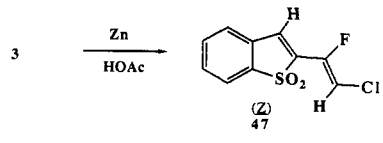
compd	NR_2	yield, %
30	NMe_2	60
31	NEt_2	19
32	*N*-(3-pyrrolino)	90
33	NHMe	79
34	NHEt	80
35	NH_2	86
36	*N*-morpholino	76
37	*N*-pyrrolidino	45
38	*N*-thiomorpholino	61
39	*N*-piperidino	61
40	1,2,3,6-tetrahydropyridino	80
41	*N*-(2-aminopropanol)-	57

Table IV. Alkoxy S_NV Displacement Products



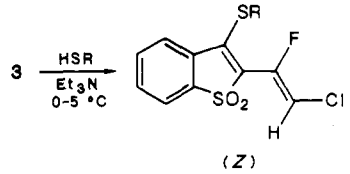
compd	R	yield, %
45	ethyl	76
46	*n*-propyl	54

The reaction of **4** with dimethylamine and sodium methoxide produced **43** and **44**, respectively (Scheme IV). The ^1H NMR spectrum of **43** exhibited a single vinyl proton as a doublet of quartets at 5.8 ppm due to coupling with both the *trans*-vinyl fluorine (J = 31.2 Hz) and trifluoromethyl group (J = 8.9 Hz). The ^1H NMR spectrum of **44** exhibited a vinyl proton quartet at 5.4 ppm (J = 7.0 Hz) from trifluoromethyl coupling (Scheme IV). Further examples (**30–41**) of the generality of the amine addition/elimination reaction are listed in Table III, and analogous alkoxy addition/elimination products **45** and **46** are listed in Table IV. The corresponding reduction product **47** from treatment of 3 with one equivalent of zinc dust in glacial acetic acid is shown in eq 1.



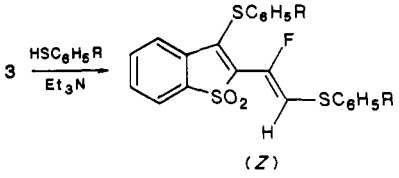
(1)

Table V. Monothio S_NV Displacement Products



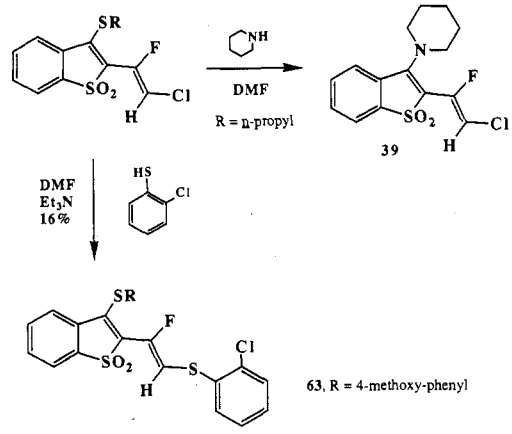
compd	R	yield, %
49	$4\text{-}MeOC_6H_5$	55
50	$4\text{-}MeC_6H_5$	27
51	ethyl	67
52	*n*-propyl	41
53	*iso*-propyl	50
54	*tert*-butyl	40
55	methyl	59

Table VI. Bis(thio) S_NV Displacement Products



compd	R	yield, %
56	2-Me	68
57	4-Me	74
58	3-Me	95
59	H	83
60	4-Cl	67
61	2-Cl	81
62	$3,4\text{-}Cl_2$	36

Scheme V

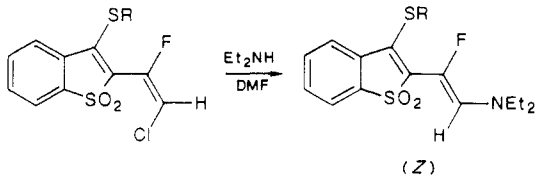


In contrast to the reaction with amine and alkoxy nucleophiles, reactions of **3** with 1 equiv of a thiophenol or an alkyl thiol gave mixtures of mono- and dithio S_NV displacement products. The monothio addition/elimination products **49–55** (Table V) could be isolated in low to moderate yield, generally as the *Z* isomers. The intermediate 3-(arylthio)benzo[*b*]thiophenes from reaction of **3** with thiophenols are activated and undergo addition/elimination with a second equivalent of thiophenol at the 2-chloroethenyl position to produce *Z* isomers of bis(arylthio) displacement products **56–62** (Table VI).

Attempts to react the intermediate 3-(arylthio)benzo[*b*]thiophenes above with amines or a second, dissimilar thiophenol anion generally gave complex mixtures of products resulting from displacement of the 3-position substituent, such as **39** and **63** (Scheme V).

However, reactions of intermediate 3-(alkylthio)benzo[*b*]thiophenes above with diethylamine were successful

Table VII. Thio-Amino S_NV Displacement Products



(Z)

compd	R	yield, %
64	*iso*-propyl	88
65	*tert*-butyl	70
66	*n*-propyl	69
67	ethyl	67
68	methyl	67

exceptions which produced single *Z* isomeric products **64–68** (Table VII) in high yield.

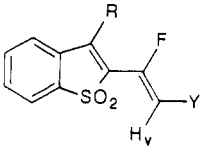
Discussion

^{1}H NMR chemical shifts in Table II were readily assigned from the variety of substituted benzenoid ring products and from observed splitting patterns, and they are consistent with proton magnetic resonance studies reported for 5-substituted benzo[*b*]thiophenes[15] and their dioxides. Generally, the 4H and 7H protons resonate at lower field than the 5H and 6H protons, and upon bis-oxidation the benzenoid ^{1}H NMR pattern exhibits a characteristic upfield shift of the 4H proton, for example, in pairs **7**/**8**, **15**/**16**, and **17**/**18**. The observation served as a model for the identification of oxidation regiochemistry in novel thieno[3,2-*b*][1]benzothiophenes.[16]

Each of the addition/elimination reactions with **3** yielded the *Z* isomer as evidenced by a single vinyl ^{1}H NMR absorption. Table VIII lists the key ^{1}H NMR and ^{19}F NMR chemical shifts of specific examples. The monosubstitution products **30**, **45**, **47**, **50**, and **53** exhibited a vinyl proton chemical shift from 6.15 to 6.55 ppm with a *trans*-vinyl fluorine coupling constant from 22 to 25 Hz. Disubstituted products **59** and **64** exhibited a similar vinyl proton chemical shift but with a larger coupling constant of about 34 Hz. The vinyl fluorine of each product exhibited an ^{19}F NMR chemical shift from −89 to −158 ppm with a comparable trans proton coupling constant.

In general mechanistic terms, similar β-additions of nucleophiles to a vinyl sulfone substructure followed by elimination of an allylic leaving group have been studied and utilized by several groups.[17–22] Furthermore, β-addition of trialkyl phosphites to α-bromovinyl sulfones is known to proceed with elimination of HBr to produce vinyl phosphonates.[23] However, β-addition to a vinyl sulfone substructure with subsequent conjugated elimination of hydrogen halide involving isomerization of the double bond back into conjugation with the sulfone moiety, as exemplified by the 2-(haloethenyl)benzo[*b*]thiophene 1,1-dioxides, is unique. Indeed, the lability of benzo[*b*]thiophenes to oxidation fostered the observation of unusual nucleophilic reactivity by comparison with 2-(haloethenyl)thiophene prototypes. From these results, it may be further argued that the mechanism of zinc reduction with **3** involves electron donation at the 3H position followed by HCl elimination in contrast with direct carbon–halogen bond fission and protonation.[24]

Table VIII. NMR Spectral Data of (*Z*)-2-(1-Fluoroethenyl)benzo[*b*]thiophene 1,1-Dioxides



compd	R	Y	H_v ^{1}H NMR, ppm (*J*, Hz)	^{19}F NMR, ppm (*J*, Hz)
30	Me_2N	Cl	6.15 (22.4)	−89.3 (22.2)
45	EtO	Cl	6.25 (23.7)	−89.0 (22.1)
47	H	Cl	6.45 (25.9)	−119.4 (27.4)
50	4-MeC_6H_5S	Cl	6.25 (25.0)	−104.4 (22.0)
53	2-C_3H_7S	Cl	6.55 (23.3)	−107.1 (23.6)
59	C_6H_5S	C_6H_5S	6.80 (34.2)	−107.2 (34.1)
64	2-C_3H_7S	NEt_2	6.60 (34.5)	−158.0 (32.0)

Experimental Section

Benzo[*b*]thiophenes were either commerically available or prepared by known methods.[25–28] ^{1}H NMR spectra were obtained on either a Varian T60, an IBM NR-80, or a Brucker 250-MHz spectrometer, and chemical shift data are reported in ppm relative to tetramethylsilane in deuteriochloroform solvent. All ^{19}F NMR data were obtained on an IBM NR-80 at 75.26 MHz, and chemical shifts are reported in ppm relative to $CFCl_3$ in chloroform solvent. Melting points were determined on a Mel-Temp and are uncorrected.

Synthesis of 2-(Haloethenyl)benzo[*b*]thiophenes. (*E*)-2-(1,2,3,3,3-Pentafluoro-1-propenyl)benzo[*b*]thiophene (1). To 230 mL of 2.1 M *n*-butyllithium in *n*-hexane (0.48 mol) was added 53.6 g (0.4 mol) of thianaphthene in 250 mL of diethyl ether with magnetic stirring in an ice bath. The mixture was allowed to warm to room temperature and was added dropwise to an ice-cold mixture of 102 g (0.68 mol) hexafluoropropene in 250 mL of diethyl ether with mechanical stirring under a CO_2/acetone condenser. The mixture was allowed to warm to room temperature, stirred overnight, and filtered, and the volatiles were removed by distillation. The residue was recrystallized from 95% ethanol to give 59.3 g of **1** (55%): mp 93–5 °C; ^{19}F NMR −63.30 ppm (dd, 3 F, *J* = 11.2, 22.6 Hz), −135.6 (dq, 1 F, *J* = 22.3, 128.9 Hz), −156.0 (dq, 1 F, *J* = 11.2, 128.8 Hz). Anal. Calcd for $C_{11}H_5F_5S$: C, 50.01; H, 1.91. Found: C, 49.73; H, 1.99.

2-(2,2-Dichloro-1-fluoroethenyl)benzo[*b*]thiophene (2). To 39 mL of 2.7 M *n*-butyllithium in *n*-hexane (0.105 mol) was added 13.4 g (0.10 mol) of thianaphthene in 60 mL of diethyl ether with magnetic stirring in an ice bath. The mixture was allowed to warm to room temperature and added dropwise to an ice-cold mixture

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of 26.6 g (0.20 mol) of 1,1-dichloro-2,2-difluoroethylene in 50 mL of diethyl ether under a CO_2/acetone condenser. The mixture was allowed to warm to room temperature and filtered, and the volatiles were evaporated under vacuum. The residue was crystallized from pentane to give 14.0 g (57%) of **2**: mp 67–9 °C; ^{1}H NMR (250 MHz) 7.37 ppm (m, 2 H), 7.71 (s, 1 H), 7.79 (m, 2 H); MS 250 (15), 248 (70), 246 (100), 176 (42). Anal. Calcd for $C_{10}H_5Cl_2FS$: C, 48.60; H, 2.04. Found: C, 48.39; H, 2.22.

Benzo[b]thiophenes from Table II were prepared similarly.

2-(2,2-Dichloro-1-fluoroethenyl)-4-methylbenzo[b]thiophene (5): mp 74–5 °C. Anal. Calcd for $C_{11}H_7Cl_2FS$: C, 50.59; H, 2.70. Found: C, 50.83; H, 2.95.

2-(2,2-Dichloro-1-fluoroethenyl)-7-methylbenzo[b]thiophene (7): mp 58–60 °C from 7-methylbenzo[b]thiophene.[27,28] Anal. Calcd for $C_{11}H_7Cl_2FS$: C, 50.59; H, 2.70. Found: C, 50.83; H, 2.44.

2-(2,2-Dichloro-1-fluoroethenyl)-4-ethylbenzo[b]thiophene (9): mp 143–5 °C from 4-ethylbenzo[b]thiophene.[25] Anal. Calcd for $C_{12}H_9Cl_2FS$: C, 52.38; H, 3.30. Found: C, 52.38; H, 3.31.

2-(2,2-Dichloro-1-fluoroethenyl)-4-phenylbenzo[b]thiophene (11): mp 93–5 °C from 4-phenylbenzo[b]thiophene.[25] Anal. Calcd for $C_{16}H_9Cl_2FS$: C, 59.46; H, 2.81. Found: C, 59.42; H, 2.85.

4-Chloro-2-(2,2-dichloro-1-fluoroethenyl)benzo[b]thiophene (13): mp 78 °C from 4-chlorobenzo[b]thiophene.[26] Anal. Calcd for $C_{10}H_4Cl_3FS$: C, 42.66; H, 1.43. Found: C, 42.87; H, 1.63.

5-Chloro-2-(2,2-dichloro-1-fluoroethenyl)benzo[b]thiophene (15): mp 98–100 °C from 5-chlorobenzo[b]thiophene.[26] Anal. Calcd for $C_{10}H_4Cl_3FS$: C, 42.66; H, 1.43. Found: C, 43.32; H, 1.51.

6-Chloro-2-(2,2-dichloro-1-fluoroethenyl)benzo[b]thiophene (17): mp 107–8 °C from 6-chlorobenzo[b]thiophene.[26] Anal. Calcd for $C_{10}H_4Cl_3FS$: C, 42.66; H, 1.43. Found: C, 42.88; H, 1.53.

1-(Benzo[b]thiophene-2-yl)-2,2,2-trichloroethanol (19). To thianaphthenyllithium [prepared from 300 mL of 2.6 M *n*-butyllithium (0.78 mol) and 80.0 g (0.60 mol) of thianaphthene in 300 mL of ether] was added portionwise 100 g (0.72 mol) of fused, anhydrous, and powdered $ZnCl_2$ with mechanical stirring. The mixture was cooled at 0–5 °C, and 104 g (0.72 mol) of anhydrous chloral was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight, and the organic layer was washed with excess ice-cold dilute HCl. The organic layer was washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated under vacuum. The residue was crystallized from cyclohexane to yield 105 g (62%) of **19**, mp 82–3 °C. Anal. Calcd for $C_{10}H_7Cl_3OS$: C, 42.65; H, 2.51. Found: C, 42.89; H, 2.31.

2-(Trichloroethenyl)benzo[b]thiophene (20). To 22.6 g (0.08 mol) of **19** in 125 mL of toluene was added dropwise 9.5 g (0.08 mol) of thionyl chloride. Two drops of dimethylformamide (DMF) were added, and the mixture was boiled under reflux overnight. The mixture was evaporated under vacuum, and the residue was quenched with ice. The product was filtered, washed with water, air-dried, and recrystallized from 95% ethanol to give 15.6 g (75%) of **20**, mp 109–10 °C. Anal. Calcd for $C_{10}H_5Cl_3S$: C, 40.64; H, 1.71. Found: C, 40.81; H, 1.78.

2-(2,2-Dichloroethenyl)benzo[b]thiophene (22). To 5.2 g of zinc dust in 50 mL of glacial acetic acid was added portionwise 11.3 g (0.04 mol) of **19** with mechanical stirring at ambient temperature. The mixture was stirred overnight and poured into ice water. The product was filtered, washed with water, and recrystallized from 95% ethanol to give 4.5 g (50%) of **22**, mp 134 °C. Anal. Calcd for $C_{10}H_6Cl_2S$: C, 52.42; H, 2.64. Found: C, 54.42; H, 3.02.

1-(Benzo[b]thiophene-2-yl)-2,2,2-tribromoethanol (24). To 3.2 g (0.02 mol) of benzo[b]thiophene-2-carboxaldehyde[12] in 25 mL of dimethyl sulfoxide was added portionwise 8.9 g (0.03 mol) of tribromoacetic acid with stirring at ambient temperature. The mixture was stirred overnight, poured into ice water, filtered, and recrystallized from 95% ethanol to give 2.8 g (35%) of **24**, mp 98–100 °C. Anal. Calcd for $C_{10}H_7Br_3OS$: C, 28.95; H, 1.70. Found: C, 28.93; H, 1.49.

2-(1-Chloro-2,2-dibromoethenyl)benzo[b]thiophene (25). Three drops of DMF were added to 15 mL of thionyl chloride, and 3.0 g (0.0075 mol) of **24** was added portionwise with stirring at ambient temperature. After being stirred for 16 h, the mixture was evaporated under vacuum, and the residue was quenched with ice water. The product was filtered and recrystallized from pentane/ethyl acetate to give 0.85 g (32%) of **25**, mp 116–17 °C. Anal. Calcd for $C_{10}H_5Br_2ClS$: C, 34.08; H, 1.43. Found: C, 34.34; H, 1.51.

2-(2,2-Dibromo-1-fluoroethenyl)benzo[b]thiophene (27). To 1.5 g (0.0036 mol) of **24** in 25 mL of methylene chloride was added dropwise 0.75 g (0.0045 mol) of (diethylamino)sulfur trifluoride dropwise at ambient temperature. The solution was washed with ice water, dried over anhydrous sodium sulfate, and evaporated under vacuum. The residue was dissolved in 20 mL of tetrahydrofuran, and 1.0 g (0.009 mol) of potassium *tert*-butoxide was added portionwise with stirring at ambient temperature. The reaction mixture was evaporated to dryness under vacuum, and the residue was partitioned between diethyl ether and water. The organic layer was dried over sodium sulfate and evaporated under vacuum, and the residue was recrystallized from hexane to give 0.5 g (33%) of **27**, mp 82–3 °C. Anal. Calcd for $C_{10}H_6Br_3FS$: C, 35.75; H, 1.50. Found: C, 36.03; H, 1.62.

Synthesis of 2-(Haloethenyl)benzo[b]thiophene 1,1-Dioxides. 2-(2,2-Dichloro-1-fluoroethenyl)benzo[b]thiophene 1,1-Dioxide (3). To 200 mL of glacial acetic acid was added 38.0 g (0.15 mol) of **2**. The solution was heated on a steam bath, and 39.0 g (0.375 mol) of 30% H_2O_2 was added dropwise with occasional shaking. The mixture was poured into ice water, filtered, and recrystallized from 95% ethanol to give 36.1 g (87%) of **3**: mp 154–6 °C; ^{1}H NMR (250 MHz) 7.45 ppm (m, 1 H), 7.61 (m, 3 H), 7.72 (m, 1 H); MS 280 (12), 278 (14), 144 (33), 137 (100). Anal. Calcd for $C_{10}H_5Cl_2FO_2S$: C, 43.03; H, 1.81. Found: C, 43.14; H, 2.05.

Benzo[b]thiophene 1,1-dioxides **4**, **6**, **8**, **10**, **12**, **14**, **16**, **18**, **21**, **23**, **26**, and **28** were prepared similarly.

(*E*)-2-(1,2,3,3,3-Pentafluoro-1-propenyl)benzo[b]thiophene 1,1-dioxide (4): mp 133 °C. Anal. Calcd for $C_{11}H_5F_5O_2S$: C, 44.60; H, 1.70. Found: C, 44.69; H, 1.42.

2-(2,2-Dichloro-1-fluoroethenyl)-3-methylbenzo[b]thiophene 1,1-dioxide (6): mp 177–9 °C. Anal. Calcd for $C_{11}H_7Cl_2FO_2S$: C, 45.07; H, 2.41; Cl, 24.19. Found: C, 45.22; H, 2.52; Cl, 24.12.

2-(2,2-Dichloro-1-fluoroethenyl)-7-methylbenzo[b]thiophene 1,1-dioxide (8): mp 196–8 °C. Anal. Calcd for $C_{11}H_7Cl_2FO_2S$: C, 45.07; H, 2.41. Found: C, 45.21; H, 2.25.

2-(2,2-Dichloro-1-fluoroethenyl)-4-ethylbenzo[b]thiophene 1,1-dioxide (10): mp 121–3 °C. Anal. Calcd for $C_{12}H_9Cl_2FO_2S$: C, 46.92; H, 2.95; Cl, 23.08. Found: C, 46.91; H, 2.90; Cl, 23.23.

2-(2,2-Dichloro-1-fluoroethenyl)-4-phenylbenzo[b]thiophene 1,1-dioxide (12): mp 134–6 °C. Anal. Calcd for $C_{16}H_9Cl_2FO_2S$: C, 54.10; H, 2.55; Cl, 19.96; F, 5.35. Found: C, 54.36; H, 2.65; Cl, 19.95; F, 5.31.

4-Chloro-2-(2,2-dichloro-1-fluoroethenyl)benzo[b]thiophene 1,1-dioxide (14): mp 126–9 °C. Anal. Calcd for $C_{10}H_4Cl_3FO_2S$: C, 38.31; H, 1.29. Found: C, 38.59; H, 1.45.

5-Chloro-2-(2,2-dichloro-1-fluoroethenyl)benzo[b]thiophene 1,1-dioxide (16): mp 164–5 °C. Anal. Calcd for $C_{10}H_4Cl_3FO_2S$: C, 38.31; H, 1.29. Found: C, 38.49; H, 1.55.

6-Chloro-2-(2,2-dichloro-1-fluoroethenyl)benzo[b]thiophene 1,1-dioxide (18): mp 181–7 °C. Anal. Calcd for $C_{10}H_4Cl_3FO_2S$: C, 38.31; H, 1.29. Found: C, 38.54; H, 1.32.

2-(2,2-Dichloroethenyl)benzo[b]thiophene 1,1-dioxide (21): mp 128–30 °C. Anal. Calcd for $C_{10}H_6Cl_2O_2S$: C, 46.00; H, 2.32. Found: C, 46.28; H, 2.24.

2-(Trichloroethenyl)benzo[b]thiophene 1,1-dioxide (23): mp 83 °C. Anal. Calcd for $C_{10}H_5Cl_3O_2S$: C, 40.64; H, 1.71. Found: C, 40.81; H, 1.78.

2-(1-Chloro-2,2-dibromoethenyl)benzo[b]thiophene 1,1-dioxide (26): mp 143–5 °C. Anal. Calcd for $C_{10}H_5Br_2ClO_2S$: C, 31.24; H, 1.31. Found: C, 31.37; H, 1.40.

2-(2,2-Dibromo-1-fluoroethenyl)benzo[b]thiophene 1,1-dioxide (28): mp 186–7 °C. Anal. Calcd for $C_{10}H_5Br_2FO_2S$: C, 32.64; H, 1.37. Found: C, 32.61; H, 1.28.

(*Z*)-(2-Chloro-1-fluoroethenyl)benzo[b]thiophene 1,1-Dioxide (47). To 1.4 g (0.005 mol) of **3** was added 0.825 g (0.0125 mol) of zinc dust in 25 mL of glacial acetic acid. The mixture was heated on a steam bath with intermittent shaking for 1.5 h

and poured into ice water containing dilute HCl. The product was filtered and recrystallized from methanol to give 0.45 g (37%) of **47**: mp 162–4 °C; ^{1}H NMR (60 MHz) 6.45 ppm (d, 1 H, J = 25.9 Hz), 7.22 (s, 1 H), 7.46 (m, 1 H), 7.60 (m, 1 H), 7.76 (m, 1 H). Anal. Calcd for $C_{10}H_6ClFO_2S$: C, 48.98; H, 2.45. Found: C, 48.92; H, 2.54.

Synthesis of 3-Alkylamino Substitution Products. (*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(dimethylamino)benzo[*b*]thiophene 1,1-Dioxide (30). To 11.1 g (0.04 mol) of **3** in 75 mL of DMF was added 25 mL of 40% dimethylamine dropwise at ambient temperature. The mixture was stirred overnight, poured into ice water, filtered, and recrystallized from 95% ethanol to give 6.7 g (60%) of **30**: mp 164–5 °C; ^{1}H NMR (60 MHz) 3.15 ppm (s, 3 H), 3.25 (s, 3 H), 6.15 (d, 1 H, J = 22.4 Hz), 7.50 (m, 4 H). Anal. Calcd for $C_{12}H_{11}ClFNO_2S$: C, 50.09; H, 3.85; N, 4.87. Found: C, 49.85; H, 3.77; N, 4.70.

The 3-amino substitution products (Table III) were obtained similarly.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(diethylamino)benzo[*b*]thiophene 1,1-dioxide (31): mp 112–13 °C. Anal. Calcd for $C_{14}H_{15}ClFNO_2S$: C, 53.25; H, 4.79; N, 4.44. Found: C, 53.20; H, 4.75; N, 4.31.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(3,4-dihydropyrrolino)benzo[*b*]thiophene 1,1-dioxide (32): mp 136–38 °C. Anal. Calcd for $C_{14}H_{11}ClFNO_2S$: C, 53.94; H, 3.56; N, 4.49. Found: C, 53.82; H, 3.73; N, 4.60.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(methylamino)benzo[*b*]thiophene 1,1-dioxide (33): mp 213–15 °C dec. Anal. Calcd for $C_{11}H_9ClFNO_2S$: C, 48.35; H, 3.30; N, 5.13. Found: C, 48.05; H, 3.36; N, 5.11.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(ethylamino)benzo[*b*]thiophene 1,1-dioxide (34): mp 188–90 °C dec. Anal. Calcd for $C_{12}H_{11}ClFNO_2S$: C, 50.35; H, 3.85; N, 4.89. Found: C, 49.94; H, 3.73; N, 4.78.

(*Z*)-3-Amino-2-(2-chloro-1-fluoroethenyl)benzo[*b*]thiophene 1,1-dioxide (35): mp 170–73 °C. Anal. Calcd for $C_{10}H_7ClFNO_2S$: C, 46.25; H, 2.72; N, 5.39. Found: C, 46.35; H, 2.93; N, 5.65.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(*N*-morpholino)benzo[*b*]thiophene 1,1-dioxide (36): mp 178 °C. Anal. Calcd for $C_{14}H_{13}ClFNO_3S$: C, 51.06; H, 3.95. Found: C, 51.17; H, 3.65.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(*N*-pyrrolidino)benzo[*b*]thiophene 1,1-dioxide (37): mp 190 °C dec. Anal. Calcd for $C_{14}H_{13}ClFNO_2S$: C, 53.59; H, 4.18; N, 4.46. Found: C, 53.73; H, 4.27; N, 4.18.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(*N*-thiomorpholino)benzo[*b*]thiophene 1,1-dioxide (38): mp 170–1 °C. Anal. Calcd for $C_{14}H_{13}ClFNO_2S_2$: C, 48.62; H, 3.79; N, 4.05. Found: C, 48.76; H, 3.98; N, 3.77.

(*Z*)-2-(2-Chloro-1-fluorethenyl)-3-(*N*-piperidino)benzo[*b*]thiophene 1,1-dioxide (39): mp 162 °C. Anal. Calcd for $C_{15}H_{15}ClFNO_2S$: C, 54.96; H, 4.61; N, 4.27. Found: C, 55.17; H, 4.54; N, 4.24.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(1,2,3,6-tetrahydropyridino)benzo[*b*]thiophene 1,1-dioxide (40): mp 156–8 °C. Anal. Calcd for $H_{15}H_{13}ClFNO_2S$: C, 55.30; H, 4.02; N, 4.30. Found: C, 55.29; H, 3.83; N, 4.07.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-((1-hydroxyprop-2-yl)amino)benzo[*b*]thiophene 1,1-dioxide (41): mp 163–5 °C dec. Anal. Calcd for $C_{13}H_{13}ClFNO_3S$: C, 48.98; H, 4.10; N, 4.39. Found: C, 49.18; H, 4.16; N, 4.33.

(*Z*)-2-(1,2-Dichloroethenyl)-3-(methylamino)benzo[*b*]thiophene 1,1-dioxide (42): mp 200–1 °C from **23**; ^{1}H NMR (60 MHz) 7.7 ppm (m, 4 H), 6.8 (s, 1 H), 3.3 (s, 3 H), 3.0 (d, 1 H). Anal. Calcd for $C_{11}H_9Cl_2O_2S$: C, 45.55; H, 3.13; N, 4.83. Found: C, 45.74; H, 2.95; N, 4.72.

(*Z*)-3-(Dimethylamino)-2-(1,3,3,3-tetrafluoropropen-1-yl)benzo[*b*]thiophene 1,1-dioxide (43): mp 172–4 °C from **4**; ^{1}H NMR (250 MHz) 7.8 ppm (m, 2 H), 7.6 (m, 2 H), 5.8 (q, J = 8.9 Hz, d, J = 31.2 Hz, 1 H), 3.1 (s, 6 H). Anal. Calcd for $C_{13}H_{11}F_4NO_2S$: C, 48.60; H, 3.45; N, 4.36. Found: C, 48.46; H, 3.20; N, 4.17.

Synthesis of Alkoxy Substitution Products. 3-Methoxy-2-(1-methoxy-3,3,3-trifluoropropenyl)benzo[*b*]thiophene 1,1-Dioxide (44). Sodium methoxide solution was prepared with 0.5 g (0.022 mol) of sodium in 25 mL of anhydrous methanol. At −65 °C, 3.0 g (0.01 mol) of **4** was added portionwise with magnetic stirring. The mixture was allowed to warm to room temperature, poured over ice, filtered, and recrystallized from 95% ethanol to give 1.0 g (31%) of **44**: mp 151–3 °C; ^{1}H NMR (60 MHz) 7.8 ppm (m, 4 H), 5.4 (q, 1 H, J = 7.0 Hz), 4.1 (s, 3 H), 3.7 (s, 3 H). Anal. Calcd for $C_{13}H_{11}F_3O_4S$: C, 48.75; H, 3.46. Found: C, 49.00; H, 3.31.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-ethoxybenzo[*b*]thiophene (45). To 2.8 g (0.01 mol) of **3** in 40 mL of absolute ethanol was added 2.5 g (0.025 mol) of triethylamine. The mixture was boiled under reflux for 6 h, added to ice water containing dilute HCl, and filtered. The product was recrystallized from 95% ethanol to give 2.2 g (76%) of **45**: mp 153 °C; ^{1}H NMR (60 MHz) 1.50 ppm (t, 3 H, J = 8.6 Hz) 5.50 (q, 2 H, J = 8.4 Hz), 6.25 (d, 1 H, J = 23.7 Hz), 7.60–7.80 (m, 4 H). Anal. Calcd for $C_{12}H_{10}ClFO_3S$: C, 49.92; H, 3.49. Found: C, 49.67; H, 3.43.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-propoxybenzo[*b*]thiophene (46): mp 103 °C from **3** in 1-propanol and triethylamine. Anal. Calcd for $C_{13}H_{12}ClFO_3S$: C, 51.57; H, 4.00. Found: C, 51.78; H, 4.13.

Synthesis of 3-Alkyl or 3-Arylthio Substitution Products. (*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(2-propylthio)benzo[*b*]thiophene 1,1-Dioxide (53). To 2.8 g (0.01 mol) of **3** in 20 mL of DMF at 0 °C was added 0.8 g (0.01 mol) of 2-propanethiol. To the mixture was added dropwise 1.0 g (0.01 mol) of triethylamine, and the reaction mixture was allowed to warm to room temperature and poured into ice containing dilute HCl. The product was extracted with diethyl ether, dried over sodium sulfate, and chromatographed on silica gel with 10% ethyl acetate/pentane. The product was crystallized from pentane to give 1.6 g (50%) of **53**: mp 70–1 °C; ^{1}H NMR (60 MHz) 1.38 ppm (d, 6 H), 3.75 (m, 1 H), 6.55 (d, 1 H, J = 23.3 Hz), 7.60 (m, 2 H), 7.76 (m, 2 H). Anal. Calcd for $C_{13}H_{12}ClFO_2S_2$: C, 48.98; H, 3.79. Found: C, 49.03; H, 3.87.

The 3-Alkylthio substitution products (Table V) were obtained similarly.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-[(4-methoxyphenyl)thio]benzo[*b*]thiophene 1,1-dioxide (49): mp 171–173 °C. Anal. Calcd for $C_{17}H_{12}ClFO_3S_2$: C, 53.33; H, 3.16. Found: C, 53.60; H, 3.40.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-[(4-methylphenyl)thio]benzo[*b*]thiophene 1,1-dioxide (50): mp 134–35 °C. Anal. Calcd for $C_{17}H_{12}ClFO_2S_2$: C, 55.66; H, 3.30. Found: C, 55.89; H, 3.58.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(ethylthio)benzo[*b*]thiophene 1,1-dioxide (51): mp 127 °C. Anal. Calcd for $C_{12}H_{10}ClFO_2S_2$: C, 48.98; H, 3.79. Found: C, 47.17; H, 3.50.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(1-propylthio)benzo[*b*]thiophene 1,1-dioxide (52): mp 69–71 °C. Anal. Calcd for $C_{13}H_{12}ClFO_2S_2$: C, 48.98; H, 3.79. Found: C, 48.91; H, 3.97.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(4-*tert*-butylthio)benzo[*b*]thiophene 1,1-dioxide (54): mp 140 °C. Anal. Calcd for $C_{14}H_{14}ClFO_2S_2$: C, 50.52; H, 4.24. Found: C, 50.77; H, 4.27.

(*Z*)-2-(2-Chloro-1-fluoroethenyl)-3-(methylthio)benzo[*b*]thiophene 1,1-dioxide (55): mp 131 °C. Anal. Calcd for $C_{11}H_8ClFO_2S_2$: C, 45.44; H, 2.77. Found: C, 45.17; H, 2.74.

Synthesis of Bis(arylthio) Substitution Products. (*Z*)-2-[1-Fluoro-2-(phenylthio)ethenyl]-3-(phenylthio)benzo[*b*]thiophene 1,1-Dioxide (59). To 2.8 g (0.01 mol) of **3** in 25 mL of dimethylformamide was added 2.2 g (0.02 mol) of thiophenol and 2.0 g (0.02 mol) of triethylamine. The mixture was heated on a steam bath for 10 min, poured into ice water, and acidified with concentrated HCl. The solid product was filtered, washed with water, and recrystallized from 95% ethanol to yield 3.55 g (83%) of **59**: mp 139–40 °C; ^{1}H NMR (60 MHz) 6.80 ppm (d, 1 H, J = 34.2 Hz), 7.28–7.55 (m, 13 H), 7.72 (m, 1 H). Anal. Calcd for $C_{22}H_{15}FO_2S_3$: C, 61.97; H, 3.52. Found: C, 62.26; H, 3.73.

The bis(arylthio) substitution products (Table VI) were prepared similarly.

(*Z*)-2-[1-Fluoro-2-(2-tolylthio)ethenyl]-3-(2-tolylthio)benzo[*b*]thiophene 1,1-dioxide (56): mp 176–9 °C. Anal. Calcd for $C_{24}H_{19}FO_2S_3$: C, 63.41; H, 4.21. Found: C, 63.66; H, 4.46.

(*Z*)-2-[1-Fluoro-2-(4-tolylthio)ethenyl]-3-(4-tolylthio)benzo[*b*]thiophene 1,1-dioxide (57): mp 153–5 °C. Anal. Calcd for $C_{24}H_{19}FO_2S_3$: C, 63.41; H, 4.21. Found: C, 63.33; H, 4.21.

(Z)-2-[1-Fluoro-2-(3-tolylthio)ethenyl]-3-(3-tolylthio)benzo[b]thiophene 1,1-dioxide (58): mp 120–1 °C. Anal. Calcd for $C_{24}H_{19}FO_2S_3$: C, 63.41; H, 4.21. Found: C, 64.15; H, 4.52.

(Z)-2-[1-Fluoro-2-[(4-chlorophenyl)thio]ethenyl]-3-[(4-chlorophenyl)thio]benzo[b]thiophene 1,1-dioxide (60): mp 150 °C. Anal. Calcd for $C_{22}H_{13}Cl_2FO_2S_3$: C, 53.34; H, 2.64. Found: C, 53.43; H, 2.80.

(Z)-2-[1-Fluoro-2-[(2-chlorophenyl)thio]ethenyl]-3-[(2-chlorophenyl)thio]benzo[b]thiophene 1,1-dioxide (61): mp 171 °C. Anal. Calcd for $C_{22}H_{13}Cl_2FO_2S_3$: C, 53.34; H, 2.64. Found: C, 53.21; H, 2.89.

(Z)-2-[1-Fluoro-2-[(3,4-dichlorophenyl)thio]ethenyl]-3-[(3,4-dichlorophenyl)thio]benzo[b]thiophene 1,1-dioxide (62): mp 168–70 °C. Anal. Calcd for $C_{22}H_{11}Cl_4FO_2S_3$: C, 46.82; H, 1.96. Found: C, 47.07; H, 1.95.

Diethylamino Substitution of 3-Alkylthio Substrates. (Z)-2-[2-(Diethylamino)-1-fluoroethenyl]-3-(2-propylthio)benzo[b]thiophene 1,1-Dioxide (64). To 1.0 g (0.0032 mol) of **53** in 20 mL of DMF was added 0.5 g (0.01 mol) of anhydrous diethylamine at room temperature. The product was stirred overnight and poured into ice water containing dilute HCl. The product was filtered and air-dried to give 1.0 g (88%) of **64**: mp 75–9 °C; ^{1}H NMR (60 MHz) 1.28 ppm (m, 12 H), 3.36 (m, 5 H), 6.60 (d, 1 H, J = 34.5 Hz), 7.30 (m, 1 H), 7.50–7.72 (m, 3 H). Anal. Calcd for $C_{17}H_{22}FNO_2S_2$: C, 57.44; H, 6.29; N, 3.94. Found: C, 57.67; H, 6.22; N, 3.82.

The diethylamino substitution products (Table VII) were prepared similarly.

(Z)-2-[2-(Diethylamino)-1-fluoroethenyl]-3-(*tert*-butylthio)benzo[b]thiophene 1,1-dioxide (65): mp 110–11 °C. Anal. Calcd for $C_{18}H_{24}FNO_2S_2$: C, 58.51; H, 6.55; N, 3.79. Found: C, 58.71; H, 6.80; N, 3.89.

(Z)-2-[2-(Diethylamino)-1-fluoroethenyl]-3-(1-propylthio)benzo[b]thiophene 1,1-dioxide (66): oil. Anal. Calcd for $C_{17}H_{22}FNO_2S_2$: C, 57.44; H, 6.24; N, 3.94. Found: C, 57.69; H, 6.17; N, 3.75.

(Z)-2-[2-(Diethylamino)-1-fluoroethenyl]-3-(ethylthio)benzo[b]thiophene 1,1-dioxide (67): mp 88 °C. Anal. Calcd for $C_{16}H_{20}FNO_2S_2$: C, 56.28; H, 5.90; N, 4.10. Found: C, 56.51; H, 6.02; N, 4.05.

(Z)-2-[2-(Diethylamino)-1-fluoroethenyl]-3-(methylthio)benzo[b]thiophene 1,1-dioxide (68): mp 119–120 °C. Anal. Calcd for $C_{15}H_{18}FNO_2S_2$: C, 55.02; H, 5.54; N, 4.28. Found: C, 54.93; H, 5.60; N, 4.15.

(Z)-2-[2-[(2-Chlorophenyl)thio]-1-fluoroethenyl]-3-[(4-methoxyphenyl)thio]benzo[b]thiophene 1,1-dioxide (63): mp 137–8 °C. Anal. Calcd for $C_{23}H_{16}ClFO_3S_3$: C, 56.26; H, 3.28. Found: C, 56.24; H, 3.23.

X-ray Crystallography of Compound 30. Compound **30** crystallized in the space group $P2_1/n$, with four molecules in a unit cell having the dimensions a = 12.798 (4) Å, b = 10.158 (2) Å, c = 9.722 (3) Å, β = 91.81 (2)°, and a calculated density of 1.51 g cm^{-3}. A total of 1597 unique reflections with 2θ less than 116.0° were measured on an automated four-circle diffractometer using monochromatic copper radiation. The structure was solved using the direct methods routine SOLV of the SHELXTL program library[29] and was refined by the least-squares method with anisotropic temperature factors for all atoms except hydrogen. All hydrogen atoms were included with isotropic temperature factors at calculated positions. The final R factor was 0.088 for 1723 observed reflections. Figure 1 shows an ORTEP plot of the molecule and Tables IX–XIV in the supplementary material give the atomic coordinates, bond lengths, bond angles, and anisotropic temperature factors.

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Supplementary Material Available: Tables of atom coordinates, bond lengths, bond angles, anisotropic temperature factors, hydrogen coordinates, and nonbonded distances for **30** (7 pages). Ordering information is given on any current masthead page.

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Solvolysis of 2-Propyl 4-Nitrobenzenesulfonate in 1,1,1,3,3,3-Hexafluoro-2-propanol

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The reaction of the halide nucleophiles and of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) with methyl 4-nitrobenzenesulfonate (methyl nosylate) and 2-propyl nosylate was examined in the solvent 1,1,1,3,3,3-hexafluoro-2-propanol. A plot of the logarithm of the second-order rate constant, k_{nuc}, for reaction of the halides and solvent with 2-propyl nosylate against log k_{nuc} for reaction with methyl nosylate is linear and has a slope of 0.34. The point corresponding to the reaction with HFIP falls on the same line as the halide nucleophiles. On the basis of these results, it is suggested that the solvolysis in HFIP of the simple secondary compound 2-propyl nosylate may be occurring by a concerted S_N2 mechanism and may not involve an ion-pair intermediate.

Secondary carbon compounds are known to solvolyze in the borderline region[1] and show characteristics of both the S_N1 and S_N2 mechanisms.[2] It is often suggested that the solvolysis of simple secondary carbon compounds occurs through the formation of an intermediate,[2-9] such as an ion-pair intermediate.[2,5-7,9] However, there is no conclusive evidence for the existence of an intermediate carbocation during the solvolysis of a simple secondary substrate in solvents of moderate nucleophilicity.[10,11] Most of the

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