An Abnormal Allylic Substitution Followed by a Novel Allylic Rearrangement[1]

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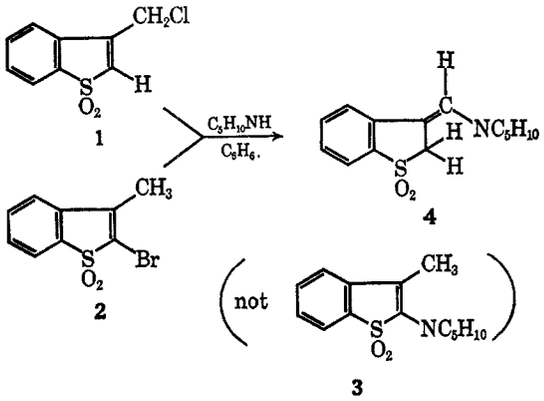
The products obtained from 2-halo-3-alkyl- and 3-α-chloroalkylbenzo[*b*]thiophene 1,1-dioxides with piperidine in benzene have been assigned structures using chemical methods combined with uv and nmr spectroscopy. Under these conditions 2-halo-3-alkylbenzo[*b*]thiophene 1,1-dioxides were found to undergo a tautomerism followed by a rapid abnormal allylic substitution. The 3-α-chloroethyl- and 3-(α-chloro-α-methylethyl)benzo[*b*]thiophene 1,1-dioxides were found to undergo an abnormal allylic substitution followed by an unusual ring opening and ring closing; the over-all result was molecular rearrangement.

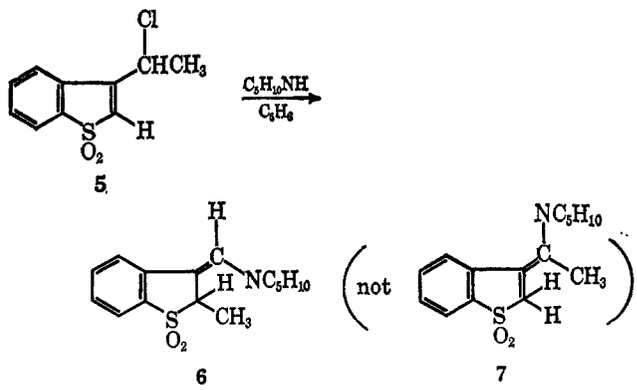
It was reported in a previous paper that 3-chloromethylbenzo[*b*]thiophene 1,1-dioxide (**1**) reacts with piperidine or morpholine in benzene, with sodium thiophenoxide in alcohol–benzene, and with thiourea in alcohol to give products in which the nitrogen atom or sulfur atom was attached to a vinylic carbon atom (from the uv spectra).[2] The reaction of 2-bromo-3-methylbenzo[*b*]thiophene 1,1-dioxide (**2**) with piperidine gave a product identical with that from **1**, but thiourea failed to react with **2**.[2] It appeared from these results that piperidine was effecting a displacement of the bromine atom in **2**, as is known to occur with 3-bromobenzo[*b*]thiophene 1,1-dioxide (which also fails to react with thiourea),[3] and was effecting an abnormal allylic substitution (SN2′) reaction on **1** to give the same product. The product from the piperidine experiment was believed, therefore, to be 2-piperidino-3-methylbenzo[*b*]thiophene 1,1-dioxide (**3**), and the other products obtained from **1** were assigned comparable structures. With the advent of nmr spectroscopy it immediately became apparent that this structure assignment was incorrrect. In place of the expected methyl singlet, the nmr spectrum of the product showed the presence of a vinylic proton and two other protons with a chemical shift and spin–spin splitting pattern consistent with allylic protons, as in structure **4**.



The nmr spectra of the products obtained from **1** and other nucleophiles (morpholine, sodium thiophenoxide, thiourea, sodium 2,4,6-trimethylthiophenoxide, sodium phenylmethanethiolate) showed that their structures were analogous to that of **4**.

Formation of **4** from **2** can be visualized as occurring by a 1,3-proton shift to form an allylic system followed by an SN2′ reaction.[4] Formation of **4** from **1** can be visualized as an SN2 displacement followed by a 1,3-proton shift, but this is an oversimplification, as will soon become apparent from a consideration of the behavior of the next higher homolog of **1**, 3-(α-chloroethyl)benzothiophenne 1,1-dioxide (**5**).

Reaction of **5** with piperidine in benzene occurs readily but, in sharp contrast to the behavior of **1**, **5** fails to react with thiourea in alcohol.[5] The nmr spectrum of the product showed, in addition to four phenyl protons and ten piperidine protons, a methyl doublet at δ 1.49 (J = 7.4 cps), a one-proton quartet at 4.11 (J = 7.4 cps), and a one-proton singlet at 6.67. This spectrum is consistent with structure **6**, but not with **7** (the product expected from SN2 displacement followed by a 1,3-proton shift).



The product has a high intensity maximum at 324 mμ, which is comparable with that of **4** (λ_{max} 325 mμ), and a strong band at 6.07 μ, which is characteristic of the enamine structure (**4** has a band at 6.11 μ).

The isomer of **6** with the enamine grouping in the 2 position is ruled out since its uv maximum should occur at a shorter wavelength.

Acid hydrolysis of the product gave a carbonyl compound, which was isolated as its 2,4-dinitrophenylhydrazone. The nmr spectrum of this product had eight protons in the δ 7.5–8.5 region (presumably seven phenyl protons and one aldehydic proton) which is consistent with structure **6a** (derived from **6**), but not with **8** (derived from the six-membered-ring isomer of **6**).

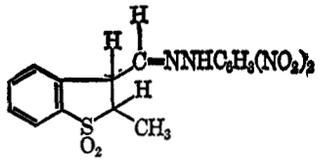
(1) Abstracted from the Ph.D. Dissertations of R. W. Hemwall, 1965, and D. A. Schexnayder, 1968. A preliminary account of part of this work has appeared: F. G. Bordwell, R. W. Hemwall, and D. A. Schexnayder, *J. Amer. Chem. Soc.*, **89**, 7144 (1967).

(2) F. G. Bordwell, F. Ross, and J. Weinstock, *ibid.*, **82**, 2878 (1960).

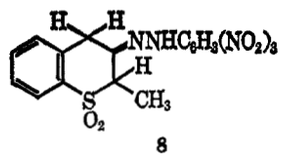
(3) F. G. Bordwell, B. B. Lampert, and W. H. McKellin, *ibid.*, **71**, 1702 (1949).

(4) The mechanism of this reaction is discussed in detail in the next paper of the present series: F. G. Bordwell, R. W. Hemwall, and D. A. Schexnayder, *J. Org. Chem.*, **33**, 3233 (1968).

(5) P. E. Sokol, Ph.D. Dissertation, Northwestern University, 1959.



6a



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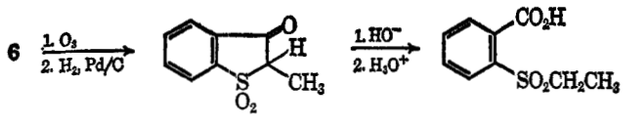
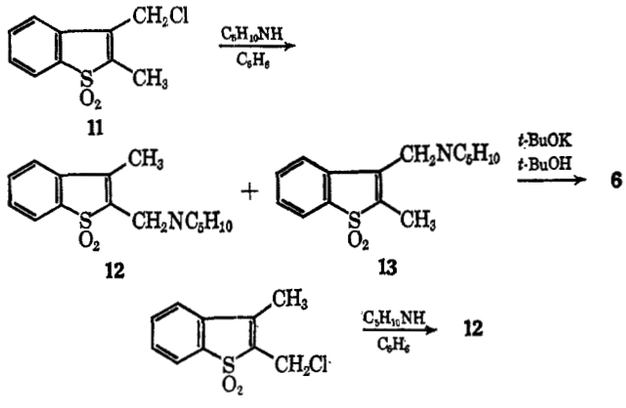
Ozonolysis of **6** gave the (known) ketone **9**,[6] which was cleaved by base to *o*-ethylsulfonylbenzoic (**10**).[7]



9 **10**

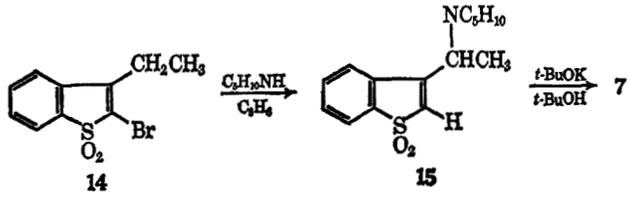
Synthesis of **6** was accomplished starting with 2-methyl-3-chloromethylbenzo[*b*]thiophene 1,1-dioxide (**11**). Treatment of **11** with piperidine in benzene afforded a mixture of 2-methyl-3-piperidinomethyl- and 3-methyl-2-piperidinomethylbenzothiophene 1,1-dioxides (**12** and **13**, respectively). The structures of these products, one or both of which presumably arise by addition of piperidine to a 1,3-diene, were assigned on the basis of their nmr spectra (see Table I).



Treatment of **13** with potassium *t*-butoxide in *t*-butyl alcohol gave **6** (1,3-proton shift). The failure of the conversion **13** → **6** to occur with piperidine in benzene rules out the possibility of **13** being an intermediate in the conversion of **5** into **6**.

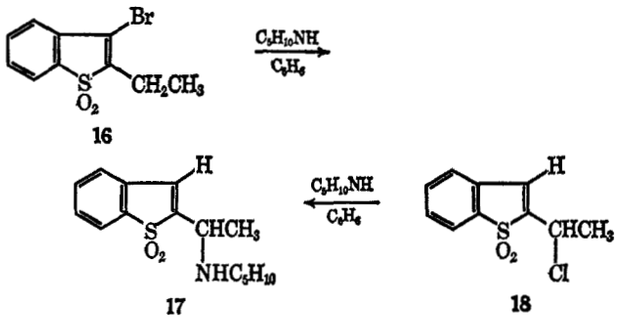
Treatment of 2-chloromethyl-3-methylbenzo[*b*]thiophene 1,1-dioxide with piperidine in benzene gave **12** as the only isolated product.

By analogy with the conversion of **2** into **4** one would expect the next higher homolog of **2**, 2-bromo-3-ethylbenzo[*b*]thiophene 1,1-dioxide (**14**) to react with piperidine to give **7**. Instead, this reaction gave 3-(α-piperidinoethyl)benzo[*b*]thiophene 1,1-dioxide (**15**) (the product expected from an SN2 reaction of **5** with piperidine). Treatment of **15** with potassium *t*-butoxide did give a compound believed to be **7**.



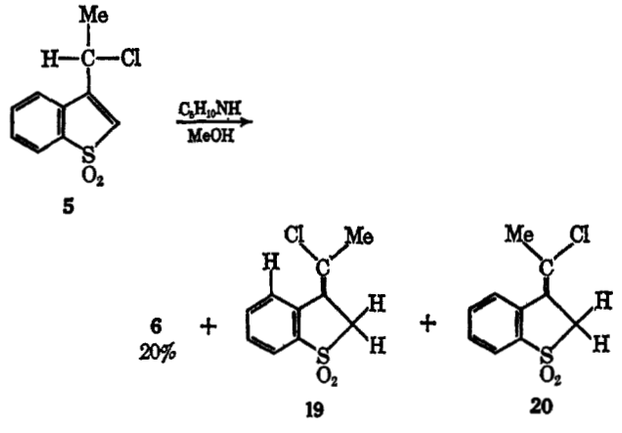
The failure of piperidine to effect the conversion of **15** into **6** rules out **15** as an intermediate in the conversion of **5** into **6**.

A reaction similar to the conversion **14** → **15** was observed on treatment of the isomer of **14**, 3-bromo-2-ethylbenzo[*b*]thiophene 1,1-dioxide (**16**), with piperidine in benzene.



The same product (**17**) was obtained from **18** under comparable conditions. This contrasts with the behavior of the 3-α-chloroethyl isomer (**5**), which gives a rearrangement product (see above).

The reaction of **5** with piperidine in methanol (0.5-hr reflux) gave only *ca.* 20% **6**. The remainder of the material was a mixture of the *cis* and *trans* tautomers of **5**, **19**, and **20**.



The chlorine atom is believed to be *cis* to the C-4 (*peri*) hydrogen atom in **19** on the basis of the nmr spectrum (Table II). Molecular models indicate that there is appreciable steric interference between the C-4 hydrogen atom and a *cis* group other than hydrogen in structures like **6**, **19**, and **20**. For this reason **6** and its analogs are assigned structures with the hydrogen atom *cis* to the C-4 hydrogen atom.

Pathways for the Reactions 2 → 4, 14 → 15, and 16 → 17.—For the reaction of 3-methyl-2-halobenzo[*b*]-thiophene 1,1-dioxides (**2**) with piperidine in benzene or methanol the sequence of steps appears to be (1) tautomerism to an allylic halide (**2a**), (2) an SN2′ re-

(6) E. W. McClelland and J. L. DaSilva, *J. Chem. Soc.*, 2972 (1931).

(7) For a comparable cleavage of 3-oxo-2,3-dihydrobenzo[b]thiophene 1,1-dioxide to *o*-methylsulfonylbenzoic acid, see F. Arndt and C. Martius, *Ann.*, **499**, 228 (1932).

TABLE I

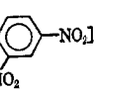
NMR PARAMETERS FOR SUBSTITUTED BENZO[*b*]THIOPHENE 1,1-DIOXIDES[a]

Substituent	Registry no.	Chemical shifts: =C(H)	(-CH₂-) (-CH-)	-CH₃	Other
None	325-44-5	6.86 (d, 7.0) 7.36 (d, 7.0)	...	...	
2-Br	5350-05-0	7.33 (s)	...	...	
3-Br	16957-97-4	7.00 (s)	...	...	
2-CH_3	6224-55-1	6.85 (q, 1.7)	...	2.17 (d, 1.7)	
3-CH_3	6406-91-3	6.58 (q, 1.5)	...	2.25 (d, 1.5)	
3-C_2H_5	16958-00-2	6.48 (t, 1.5)	2.63 (q, 7.5, 1.5)[b]	1.28 (t, 7.5)	
2,3-di-CH_3	16958-01-3	...	...	2.12 (s)	
2-Br-3-CH_3		...	...	2.25 (s)	
2-Br-3-C_2H_5		...	2.72 (q, 7.5)	1.23 (t, 7.5)	
2-C_2H_5-3-Br		...	2.73 (q, 8.0)	1.38 (t, 8.0)	
3-CH_2Cl		6.67 (t, 1.5)	4.47 (d, 1.5)	...	
2-CH_3-3-CH_2Cl		...	4.48 (s)	2.20 (s)	
2-CH_2Cl-3-CH_3	16958-02-4	...	4.55 (s)	2.28 (s)	
2-CH_3-3-$CH_2NC_5H_{10}$		...	3.43 (s)	2.20 (s)	Piperidine protons (σ, 2.45; β, γ, 1.50)
2-$CH_2NC_5H_{10}$-3-CH_3		...	3.49 (s)	2.28 (s)	Piperidine protons (σ, 2.48; β, γ, 1.50)
3-$CHOHCH_3$	16958-03-5	6.73 (d, 1.4)	4.98	1.52 (d, 7.0)	OH, 3.46 (d, 4.7)
3-$CHClCH_3$		6.72 (d, 1.3)	5.02 (q, 7.0, 1.3)[b]	1.82 (d, 7.0)	
2-$CHClCH_3$		7.25 (d, 1.5)	5.10 (q, 6.9, 1.5)[b]	1.98 (d, 6.9)	
3-$CH(NC_5H_{10})CH_3$		6.55 (s)	3.70 (q, 6.3)	1.28 (d, 6.3)	Piperidine protons (σ, 2.48; β, γ, 1.46)
2-$CH(NC_5H_{10})CH_3$		7.03	3.87 (q, 6.8, 1.1)[b]	1.42 (d, 6.8)	Piperidine protons (σ, 2.55; β, γ, 1.51)
3-CH_3O(*p*-anisoyl)	16958-04-6	6.75 (t, 2.0)	5.35 (d, 2.0)	...	OCH_3, 3.85 (s)
3-CH_2O(mesitoyl)	16958-05-7	6.77 (t, 1.7)	5.38 (d, 1.7)	...	*o,p*-CH_3, 2.29 (s)
3-$CH_2OCH_2CH_3$	16958-06-8	6.65 (t, 1.5)	4.48 (d, 1.5)	...	CH_2, 3.60 (q, 7.0) CH_3, 1.23 (t, 7.0)
3-$CH_2NC_5H_{10}$[c]	16958-07-9	6.84 (t, 1.5)	3.55 (d, 1.5)	...	Piperidine protons (α, 2.5; β, γ, 1.5)

[a] Chemical shifts are in δ values measured in parts per million (ppm) relative to TMS. The multiplicity and coupling constant (cps) are given in parentheses following the chemical shift (s = singlet, d = doublet, t = triplet, q = quartet). [b] Quartet of doublets. [c] Tentative assignment.

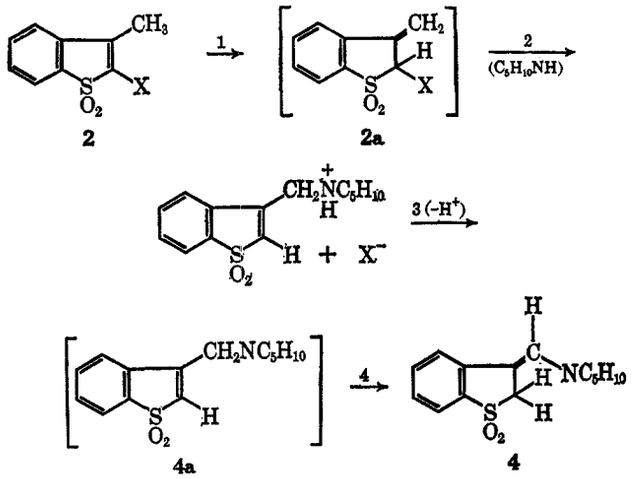
TABLE II

NMR PARAMETERS FOR SUBSTITUTED 2,3-DIHYDROBENZO[*b*]THIOPHENE 1,1-DIOXIDES[a]

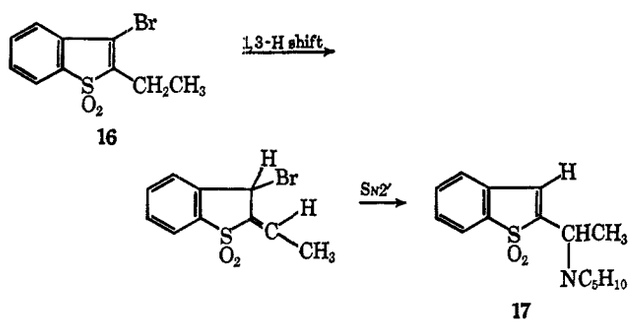
Substituent	Registry no.	Chemical shifts: =C(H)	(-CH₂-) (-CH-)	-CH₃	Other
None	14315-13-0	...	3.38 (s)	...	
3-(=CHCl)	16958-09-1	6.84 (t, 2.2)	4.12 (d, 2.2)	...	
2-CH_3-3-oxo		...	3.98 (q, 7.5)	1.66 (d, 7.5)	
3-[=CHS(mesityl)]	16958-10-4	6.72 (t, 2.3)	4.09 (d, 2.3)	...	*o*-CH_3, 2.46 (s) *p*-CH_3, 2.32 (s)
3-[=CH(N-morpholinyl)]	16958-11-5	6.87 (t, 1.7)	4.27 (d, 1.7)	...	O-CH_2, 3.8 N-CH_2, 3.3
3-[=CHSC$(NH_2)_2^+$]Cl^-	16958-12-6	*ca.* 7.9[b]	4.58 (d, 1.9)	...	C-4 proton, 8.4[c]
3-[=CH(NC_5H_{10})]	16934-29-5	6.82 (t, 1.6)	4.24 (d, 1.6)	...	Piperidine protons (α, 3.31; β, γ, 1.63)
3-[=CHS$CH_2C_6H_5$]	16958-14-8	6.99 (t, 2.2)	4.03 (d, 2.2)	...	CH_2, 4.11 (s)
3-[=CHO(mesitoyl)]	16958-15-9	8.39 (t, 2.3)	4.20 (d, 2.3)	...	*o*-CH_3, 2.37 (s) *p*-CH_3, 2.32 (s)
2-CH_3-3-[=CH(NC_5H_{10})]		6.67 (s)	4.11 (q, 7.4)	1.49 (d, 7.4)	Piperidine protons (α, 3.3; β, γ, 1.6)
3-(CH=N—NH—C_6H_5)	16958-16-0	*ca.* 7.8[b]	C-2, 3.98 (d, 6.7) C-3, 4.67 (q, 6.7)	...	N-H, 10.27 (s)
2-CH_3-3-[CH=N—NH— ]	16958-17-1	*ca.* 7.8[b]	4.2	1.55 (d, 6.5)	N-H, 11.79 (s)
3-(=C<$^{CH_3}_{NC_5H_{10}}$)[c]	16958-49-9	...	4.03 (s)	1.96 (s)	Piperidine protons (α, 2.9; β, γ, 1.6)
3-(=C<$^{Cl}_{CH_3}$)[c]		...	4.17 (q, 1.0)	2.37 (t, 1.0)	C-4 proton, 8.67[c]
3-(=C<$^{CH_3}_{Cl}$)[c]		...	4.31 (q, 1.8)	2.62 (t, 1.8)	
2-Cl-3-oxo	16958-50-2	...	5.94 (s)	...	
3-(=CH_2)[c]	16958-51-3	5.52 6.03	4.21 (t, 1.9)	...	

[a] Chemical shifts are in δ values measured in parts per million (ppm) relative to TMS. The multiplicity and coupling constant (cps) are given in parentheses following the chemical shift (s = singlet, d = doublet, t = triplet, q = quartet). [b] Obscured by the phenyl protons. [c] Tentative assignment; the isomer in which the signal for the C-4 proton appears at δ 8.67.

action initiated by piperidine, (3) loss of a proton to give **4a**, and (4) tautomerism to form an enamine (**4**).[4]



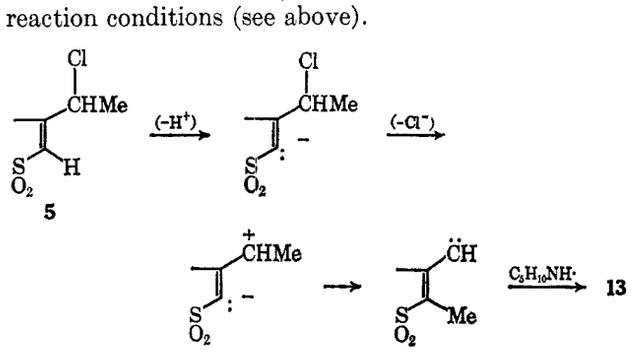
Comparable reaction paths are visualized for the conversion of **14** into **15** and of **16** into **17**, except that the final 1,3-proton shift fails to occur from **15** or **17** under the reaction conditions.



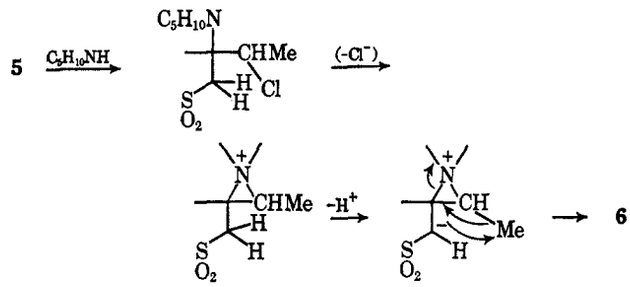
The formation of **17** from **18** shows that the latter takes the SN2 pathway in preference to the SN2′ pathway (in contrast to its isomer **5**, which has the α-chloroethyl group in the 3 position). This may be rationalized by noting that the SN2′ pathway for **18**, but not for **5**, requires the C=C bond to go out of conjugation with the benzene ring.

Mechanisms for the Reaction 5 → 6.—Of the various mechanisms that can be envisioned for the transformation of **5** to **6**, one has already been ruled out. The failure of **15** to form **6** under the reaction conditions shows that the sequence is not an SN2 reaction to form **15** followed by shift of a methyl group and the C=C bond.

A mechanism involving carbene formation and methyl migration can be imagined, but this leads to **13** and, although **13** can be converted into **6** by the action of *t*-butoxide ion, it does not form **6** under the reaction conditions (see above).

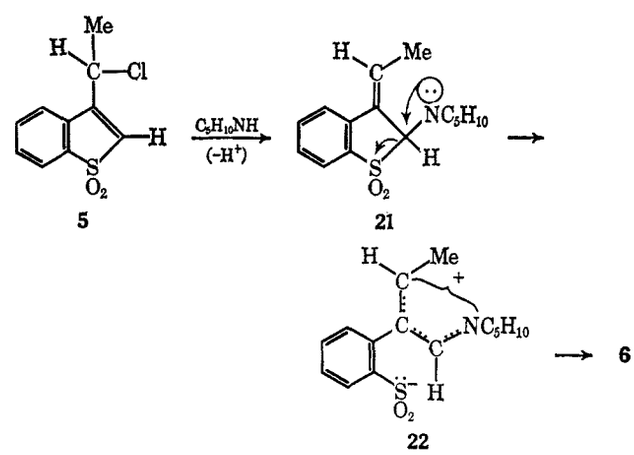


Another possibility is that piperidine adds to the double bond of **5** and that this adduct reacts in a series of steps to give **6**. The only evidence against this

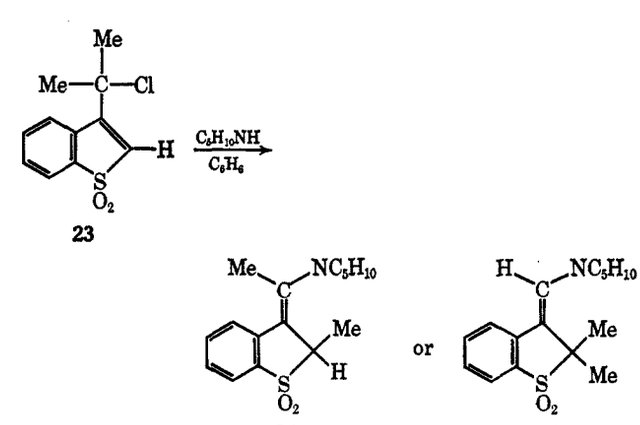


sequence is that 3-methylbenzo[*b*]thiophene 1,1-dioxide fails to add piperidine;[8a] addition occurs very readily with the parent heterocycle in 95% ethanol but not in benzene.[8b]

A final possibility is that **5** undergoes an SN2′ reaction and that the product (**21**) thus obtained rearranges by a ring opening to form a dipolar ion (**22**) which closes the ring in a different position.

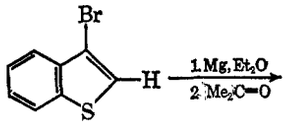


It is possible to distinguish between the mechanisms involving methyl migration and that involving ring opening and ring closing by putting a label at C-2 or on the side chain. This was accomplished by synthesis of **23**, which has an additional methyl group on the side chain. Methyl migration during reaction with piperidine would give **24** (or the *cis* isomer), whereas the interchange mechanism would give **25**.



(8) (a) F. Ross, Ph.D. Dissertation, Northwestern University, June 1952. (b) W. H. McKellin, Ph.D. Dissertation, Northwestern University, June 1950.

The desired chloride (**23**) was prepared from 3-bromobenzo[*b*]thiophene (**26**) in a conventional manner.



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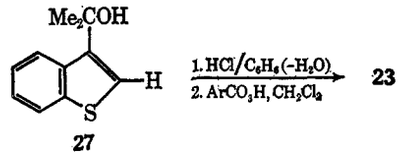

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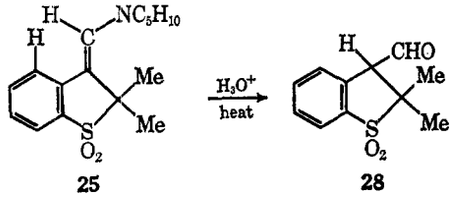
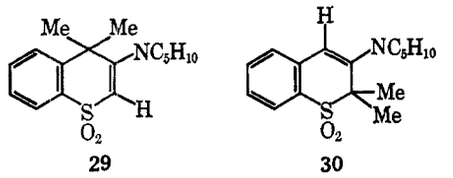
Treatment of **23** with piperidine in refluxing benzene, ethanol, or acetone gave a high yield of an enamine [λ_{max} 332 mμ (ϵ_{max} 11,100)]. Its nmr spectrum revealed four aromatic protons, ten piperidino protons, and a dimethyl singlet (δ 1.52, 6 H). This is the spectrum expected for **25**. Structure **24** should have two distinct methyl groups, one of which should appear as a doublet. Acid hydrolysis of the enamine gave a carbonyl compound whose ir spectrum revealed an aldehydic hydrogen (λ_{max} 3.50, 3.60 μ) and whose nmr spectrum differed from that of the enamine only in that the signals for the vinyl and piperidino protons were replaced by those of an aldehydic and a methinyl hydrogen [doublet at δ 9.72 (1 H) coupled (J = 3.7 cps) with a doublet at 3.87 (1 H, J = 3.7 cps)]. This is consistent with the transformation of **25** to **28**.

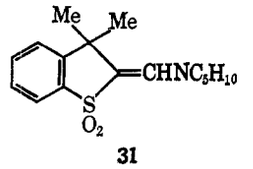


25 **28**

The isomeric enamine structures **29** and **30**, which might be considered to be consistent with the nmr spectrum, are ruled out since they would give ketones on hydrolysis. Structure **31** is eliminated by the uv data.



29 **30**



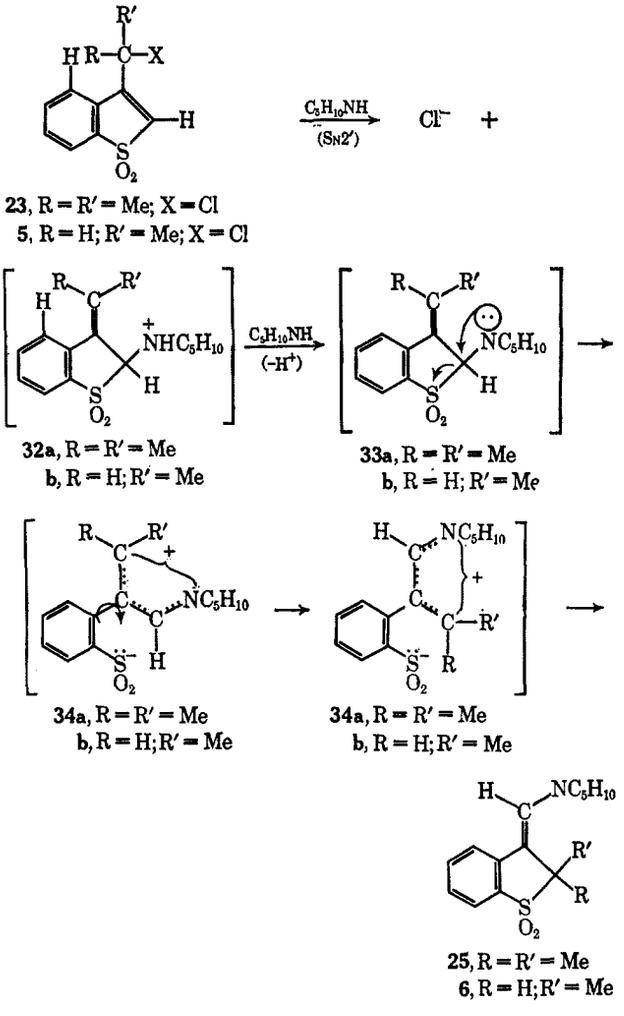
31

The assignment of structure **25** to the enamine is supported further by the similarity of its properties and behavior to that of **6**, the structure of which has been firmly established (see above).

Stereoisomers (*cis*, *trans*) are possible for **25**. Examination of molecular models shows, however, that there will be steric interference between the *peri* hydrogen (shown) at C-4 and the 1-piperidyl grouping in the isomer in which these groups are *cis*. Therefore, these groups are placed *trans* in the assigned structure **25**.

The most likely route for formation of **25** from tertiary chloride **23** by reaction with piperidine in benzene appears to be (1) abnormal substitution (S$_N$2′) to form **32a**, (2) loss of a proton to give **33a**, and (3) rearrangement of **33a** by way of dipolar intermediate **34a** to **25**. The route for the formation of **6** from the secondary chloride **5** under comparable conditions would be **5** → **32b** → **33b** → **34b** → **6** (see Scheme I).

SCHEME I



23, R = R′ = Me; X = Cl
5, R = H; R′ = Me; X = Cl

32a, R = R′ = Me
b, R = H; R′ = Me

33a, R = R′ = Me
b, R = H; R′ = Me

34a, R = R′ = Me
b, R = H; R′ = Me

34a, R = R′ = Me
b, R = H; R′ = Me

25, R = R′ = Me
6, R = H; R′ = Me

Experimental Section[9]

Nmr Spectra of Substituted Benzo[*b*]thiophene 1,1-Dioxides.—Examination of the nmr spectra of a variety of compounds in this series (Tables I and II) has revealed the following correlations useful for structural assignments. (1) The C-3 proton in the 2-substituted compounds absorb at least 0.3 ppm downfield from the analogous C-2 proton in the 3-substituted isomers. (2) Protons at the α position of C-3 alkyl group usually absorb downfield (*ca.* 1 ppm) from comparable protons of a C-2 alkyl group. (3) Coupling of 0.5–2 cps between the α- and γ-carbon atoms of the allylic system was observed in most instances.

Ozonolysis of 2-Methyl-3-(1-piperidyl)methylene-2,3-dihydrobenzo[*b*]thiophene 1,1-Dioxide (4).—Ozone was bubbled through a solution of 1.0 g (0.0036 mol) of **4** in 30 ml of ethyl acetate at −78° until no further reaction occurred. The ozonide was then decomposed by hydrogenation at room temperature, using a 5% palladium-on-charcoal catalyst. Filtration and distillation of the solvent at reduced pressure gave a yellow oil. Trituration of the oil with 95% ethanol gave 0.24 g (41%) of 2-methyl-3-oxo-2,3-dihydrobenzothiophene 1,1-dioxide (**9**), as white crystals, mp 108–110°. Recrystallization from ethanol raised the melting

(9) Microanalyses were by Micro-Tech Laboratories, Inc., Skokie, Ill.

point to 109.5–110° (lit.[6] mp 110–111°). An additional 0.15 g (21%) of product melting at 107–110° was obtained by concentration of the mother liquor.

An authentic sample of **9** was prepared by refluxing a solution of 0.2 g (80 mmol) of 2-methyl-3-acetoxybenzo[*b*]thiophene 1,1-dioxide[10] in 10 ml of methanol and 1 ml of concentrated hydrochloric acid for 1 hr. Partial evaporation of the solvent and cooling in an ice bath gave 0.09 g (57%) of **9**: mp 109.5–110°, mmp 110–110.5°. The infrared spectra of the two samples were superimposable.

Basic Hydrolysis of 4.—A mixture of 10 ml of a 20% aqueous sodium hydroxide solution and 0.1 g of **4** was heated on a steam bath for 30 min, during which time the solid slowly dissolved. The solution was then acidified with concentrated hydrochloric acid, and evaporated to give an oily, solid residue, which was extracted with benzene. Filtration, and evaporation of the filtrate, gave a water-soluble oil, which would not crystallize from hexane, ether–hexane, ether, methanol, or methanol–water. The nmr spectrum of the oil showed four phenyl protons, a broad, one-proton singlet at δ 10.48 (carboxyl proton), a two-proton quartet at 3.67 (methylene protons) (J = 7.5 cps), and a three-proton triplet at 1.32 (methyl protons) (J = 7.5 cps). This spectrum is consistent with that expected for *o*-ethylsulfonylbenzoic acid (**10**).

Reaction of 3-Chloromethylbenzo[*b*]thiophene 1,1-Dioxide (1) with Thiophenoxide Ion.—A solution of 0.4 g (0.01 mol) of sodium hydroxide and 1.1 g (0.01 mol) of thiophenol in 20 ml of absolute ethanol was heated for 10 min on a steam bath. The solution was then treated with 0.51 g (0.002 mol) of **1**, refluxed for 4 hr, and poured into 300 ml of cold water. Recrystallization from methanol of the resulting amorphous, brown solid gave 0.35 g (56%) of yellow crystals melting at 162–164.5°. Further recrystallization methanol, with charcoal decolorization, gave white crystals, mp 164.5–166° (lit.[2] mp 165–167°).

Reaction of 2-Bromo-3-methylbenzo[*b*]thiophene 1,1-Dioxide (2) with Thiophenoxide in Alcohol.—A solution of 0.06 g (0.0015 mol) of sodium hydroxide and 0.165 g (0.0015 mol) of thiophenol in 10 ml of absolute ethanol was treated with 0.26 g (0.001 mol) of **2** and refluxed for 0.5 hr. Processing as above gave 0.07 g (25%) of white crystals, mp 164.5–165.5°. The product was identical, by infrared spectra and mixture melting point with the product of **1** with thiophenoxide ion.

Reaction of 2 with Piperidine in Methanol.—2-Bromo-3-methylbenzothiophene 1,1-dioxide (100 mg, 0.386 mmol) was dissolved in 4 ml of hot absolute methanol, and piperidine (197 mg, 2.32 mmol) was added with 1 ml of methanol. The yellow solution was heated at reflux for 16 hr. Cooling and filtering afforded long yellow needles (73.7 mg, 72.7%), mp 177.7–182.7°; the mixture melting point with authentic 3-(1-piperidyl)methylene-2,3-dihydrobenzothiophene 1,1-dioxide[2] was undepressed.

2-Chloro-3-methylbenzo[*b*]thiophene 1,1-Dioxide.—A suspension of 21 g (0.05 mol) of 2-mercuriacetoxy-3-methylbenzothiophene in 200 ml of chloroform was treated with a solution of 3.6 g (0.05 mol) of chlorine in 70 ml of chloroform, added dropwise with ice-bath cooling. After stirring at room temperature overnight, the mixture was filtered and the solvent was removed *in vacuo*. The resulting brown oil was dissolved in 35 ml of glacial acetic acid and 30 ml of acetic anhydride and treated with 30 ml of 30% hydrogen peroxide. After cooling to room temperature, the solution was poured over 300 g of crushed ice. Chromatography of the resulting yellow solid (3 g; mp 115–150°) on a 60 × 3 cm silica gel column (eluted with 20% ether–hexane) gave 1.3 g (12%) of product, mp 152–154°. Recrystallization from methanol followed by vacuum sublimation gave the analytical sample, mp 152–154.5°.

Anal. Calcd for $C_9H_7ClO_2S$: C, 50.37; H, 3.23. Found: C, 50.73; H, 3.22.

Preparation of 3-(α-Hydroxyethyl)benzo[*b*]thiophene 1,1-Dioxide.—A solution of 3.6 g (0.02 mol) of 3-(α-hydroxyethyl)-benzothiophene[5] in 10 ml of chloroform was treated with a solution of 8.9 g (0.044 mol) of 85% *m*-chloroperoxybenzoic acid in 90 ml of chloroform, added dropwise with stirring. The reaction temperature was kept below 40° by controlling the rate of addition. Stirring was continued for 15 hr. The excess per acid was then destroyed with aqueous sodium sulfite, and the mixture was filtered. The filtrate was washed with 5% aqueous sodium bicarbonate and water and dried over magnesium sulfate. The solvent was distilled at reduced pressure, leaving a yellow oil which crystallized upon trituration with cold 95% ethanol. Two recrystallizations from 95% ethanol gave 2.16 g. (51%) of 3-(α-hydroxyethyl)benzothiophene 1,1-dioxide as white crystals, mp 109–110°.

Anal. Calcd for $C_{10}H_{10}O_3S$: C, 57.12; H, 4.79. Found: C, 56.91; H, 4.70.

Preparation of 3-(α-Chloroethyl)benzo[*b*]thiophene 1,1-Dioxide (5).[5]—A solution of 20.95 g (0.118 mol) of 3-(α-hydroxyethyl)benzothiophene[5] in 50 ml of chloroform was cooled in an ice bath while 16.5 g (0.14 mol) of thionyl chloride was added in small portions with stirring. The solution was then refluxed for 2 hr. The solvent and excess thionyl chloride were distilled under reduced pressure, leaving a brown oil. The oil was dissolved in 30 ml of ether, and a solution of 53 g (0.26 mol) of 85% *m*-chloroperoxybenzoic acid in 150 ml of ether was added dropwise, with stirring, over an 8-hr period. Stirring was continued for an additional 12 hr. Processing as before gave 19.02 g (70%) of yellow solid, mp 97–104°. An additional recrystallization from 95% ethanol raised the melting point to 107.5–108.5° (lit.[5] mp 108–109°).

Reaction of 5 with Piperidine in Dry Benzene.—A solution of 0.91 g (0.004 mol) of **5** and 1.7 g (0.02 mol) of piperidine in 15 ml of dry benzene was refluxed for 2 hr. Cooling and filtration gave 0.44 g (91%) of piperidine hydrochloride. The filtrate was evaporated to a gummy, brown oil under an air jet. Trituration with cold methanol gave 0.78 g (70%) of 2-methyl-3-(1-piperidyl)methylene-2,3-dihydrobenzothiophene 1,1-dioxide (**6**) as yellow crystals: mp 142–143°, mp 144–145° after two recrystallizations from 95% ethanol; λ_{max} 323 mμ (ε 22,900), 6.07 and 6.27μ).

Reaction of 5 with Piperidine in Absolute Methanol.—A solution of 0.92 g (0.004 mol) of **5** and 1.7 g (0.02 mol) of piperidine in 15 ml of absolute methanol was refluxed. After 0.5 hr, the dark-brown solution was evaporated yielding an oily solid, and the residue was treated with 20 ml of dry benzene. Piperidine hydrochloride (0.20 g; 41%) was collected and the filtrate was evaporated. The residue was crystallized from 95% ethanol, giving 0.27 g of a yellow solid, mp 120–145°. Recrystallization from ethanol did not improve the melting point. The nmr spectrum of the product showed the mixture to be composed of three compounds, one of which was **6**, in *ca.* 20% yield based on the isolated product mixture. The other two compounds appeared to be the *cis* and *trans* isomers of 3-(α-chloroethylidene)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (**19** and **20**) in *ca.* a 2:1 ratio, comprising about 80% of the isolated product.

2-Bromo-3-ethylbenzothiophene 1,1-Dioxide.[5]—To a suspension of 1.94 g (0.010 mol) of 3-ethylbenzothiophene 1,1-dioxide[11] in 20 ml of carbon tetrachloride was added 1.76 g (0.011 mol) of bromine and the reaction mixture was shaken about 10 min and allowed to stand at room temperature for 2 hr. The oil obtained on evaporation was dissolved in 20 ml of acetone and treated with a solution consisting of 2 g of sodium acetate, 5 ml of methanol, 20 ml of water, and 10 ml of acetone. Heating and evaporating on a steam bath followed by addition of cold water gave 2.3 g (85%) of a colorless solid melting at 133–138°. Two recrystallizations from ethanol–water mixtures gave an analytical sample, mp 147.5–148.5°.

Anal. Calcd for $C_{10}H_9BrO_2S$: C, 43.97; H, 3.32. Found: C 43.74; H, 3.39.

Reaction of 2-Bromo-3-ethylbenzo[*b*]thiophene 1,1-Dioxide (14) with Piperidine.—A solution of 0.54 g (0.002 mol) of 2-bromo-3-ethylbenzothiophene 1,1-dioxide and 0.85 g (0.01 mol) of piperidine in 10 ml of dry benzene was refluxed for 22 hr. Cooling and filtration gave 0.32 g (96%) of piperidine hydrobromide. Trituration of the oil obtained on evaporation with cold, aqueous methanol gave 0.32 g (58%) of 3-[α-(1-piperidyl)ethyl]benzothiophene 1,1-dioxide (**15**), as pale yellow crystals, mp 93–95°. Two recrystallizations from hexane raised the melting point to 94–95° [λ_{max} 221 mμ (ε 28,700), no strong absorption in the 6.0–6.4-μ region of the infrared spectrum].

Anal. Calcd for $C_{15}H_{19}NO_2S$: C, 64.95; H, 6.90. Found: C, 65.14; H, 7.02.

Preparation of 2-Ethyl-3-bromobenzo[*b*]thiophene 1,1-Dioxide (16).—A sample of 8 g of 2-ethylbenzo[*b*]thiophene, prepared by the method of Shirley and Cameron,[12] was dissolved in 20 ml of chloroform and treated with a solution of 8.0 g (0.05 mol) of

(10) J. D. Spainhour, Ph.D. Dissertation, Northwestern University, 1957.

(11) J. C. Petropoulus, M. A. McCall, and D. S. Tarbell, *J. Amer. Chem. Soc.*, **75**, 1133 (1953).

(12) D. A. Shirley and M. D. Cameron, *ibid.*, **74**, 664 (1952).

bromine in 40 ml of chloroform, added dropwise with stirring. After stirring for 10 hr, the solvent was distilled under reduced pressure, leaving a brown, oily solid, which was dissolved in 60 ml of 1:1 acetic acid–acetic anhydride and treated with 30 ml of 30% hydrogen peroxide. The solution was stirred for 4 hr, then poured over 300 g of crushed ice. Crystallization of the resulting yellow solid gave 1.7 g (12.5%) of **16**, mp 100–102°. Recrystallization from ethanol raised the melting point to 103–104°.

Anal. Calcd for $C_{10}H_9BrO_2S$: C, 43.97; H, 3.32. Found: C, 43.86; H, 3.51.

Reaction of 16 with Piperidine.—A solution of 0.54 g (0.002 mol) of **16** and 0.85 g (0.01 mol) of piperidine in 15 ml of dry benzene was refluxed for 8 hr (81% of piperidine hydrobromide). The filtrate was evaporated under an air jet, leaving a pale yellow, solid residue. Recrystallization from methanol gave 0.31 g (55%) of 2-[α-(1-piperidylethyl]benzo[*b*]thiophene 1,1-dioxide (**17**), as lustrous, white crystals, mp 162–165°. Two recrystallizations from ethanol raised the melting point to 167–168°.

Anal. Calcd for $C_{15}H_{19}NO_2S$: C, 64.95; H, 6.90. Found: C, 64.72; H, 7.11.

Preparation of 2-(α-Chloroethyl)benzo[*b*]thiophene 1,1-Dioxide (18).—A solution of 6.7 g (0.05 mol) of benzothiophene in 70 ml of anhydrous ether, under nitrogen, was treated at 0° with 35.5 ml (0.055 mol) of 1.55 *N* butyllithium in hexane. The mixture was stirred for 15 min, then treated with a solution of 2.4 g (0.055 mol) of acetaldehyde in 40 ml of anhydrous ether, added dropwise. After 10 min of additional stirring, water was added, the layers were separated, and the water layer was extracted with ether. The combined organic extracts were washed with water and dried over magnesium sulfate. Removal of the solvent gave a yellow oil which solidified on standing. The solid was recrystallized from ether–hexane, giving 4.33 g (49%) of 2-(α-hydroxyethyl)benzothiophene, melting at 56–60°. An additional recrystallization from ether–hexane raised the melting point to 60–61°. The nmr spectrum was consistent with the assigned structure. A solution of 3.01 g (0.017 mol) of 2-(α-hydroxyethyl)benzo[*b*]thiophene in 30 ml of chloroform was treated with 2.4 g (0.02 mol) of thionyl chloride. The solution was refluxed for 1.5 hr, and solvent and excess thionyl chloride were then distilled under reduced pressure, leaving a brown oil. The oil was dissolved in 10 ml of chloroform and oxidized with a solution of 7.5 g (0.037 mol) of 85% *m*-chloroperoxybenzoic acid in 78 ml of chloroform as described above. Trituration of the resulting oil with cold ethanol gave 1.53 g (39%) of **18** as pale yellow crystals, mp 53–54°. Two recrystallizations from ethanol raised the melting point to 54–55°.

Anal. Calcd for $C_{10}H_9ClO_2S$: C, 52.51; H, 3.97. Found: C, 52.60; H, 4.09.

Reaction of 18 with Piperidine.—A solution of 0.46 g (0.002 mol) of **18** and 0.85 g (0.02 mol) of piperidine in 10 ml of dry benzene was refluxed for 30 min (99% piperidine hydrobromide). Crystallization of the product from 95% ethanol gave 0.16 g (29%) of **17**, mp 162–164°. The melting point of recrystallized material was not depressed upon mixture with a sample of **17** obtained from **16** (see above).

2-Chloromethyl-3-methylbenzo[*b*]thiophene 1,1-Dioxide.—A solution of 3.07 g (0.017 mol) of 2-hydroxymethyl-3-methylbenzothiophene[13] in 30 ml of chloroform was treated with 2.4 g (0.02 mole) of thionyl chloride. Processing and oxidation in the manner described above for **18** gave 2.63 g (67%) of material, mp 128–131°. Two additional recrytallizations from 95% ethanol gave the analytical sample, mp 132–133°.

Anal. Calcd for $C_{10}H_9ClO_2S$: C, 52.51; H, 3.97. Found: C, 52.72; H, 4.19.

Reaction of 2-Chloromethyl-3-methylbenzo[*b*]thiophene 1,1-Dioxide with Piperidine.—A solution of 0.46 g (0.002 mol) of the chloride and 0.85 g (0.01 mol) of piperidine in 10 ml of dry benzene was refluxed for 1 hr (99% of piperidine hydrochloride). Recrystallization of the residue from ether–hexane gave 0.44 g (79%) of 2-(1-piperidyl)methyl-3-methylbenzothiophene 1,1-dioxide (**12**) as white crystals, mp 98.5–99.5°. Recrystallization from ether–hexane raised the melting point to 99–100°.

Anal. Calcd for $C_{15}H_{19}NO_2S$: C, 64.95; H, 6.90. Found: C, 64.86; H, 6.83.

2-Methyl-3-chloromethylbenzo[*b*]thiophene 1,1-Dioxide (11).[10]—Chloromethylation of 30 g of 2-methylbenzo[*b*]thiophene[12] gave a 45% yield of 3-chloromethyl-2-methylbenzo[*b*]thiophene, mp 69.5° (hexane).

Anal. Calcd for $C_{10}H_9ClS$: C, 61.06; H, 4.61. Found: C, 60.80; H, 4.38.

Oxidation with 40% peracetic acid gave a 68% yield of **11**, mp 138–139° (ethanol).

Anal. Calcd for $C_{10}H_9ClO_2S$: C, 52.52; H, 3.97. Found: C, 52.35; H, 3.96.

Reaction of 11 with Piperidine.—A solution of 1.4 g (0.006 mol) of **11** dioxide and 2.5 g (0.03 mol) of piperidine in 15 ml of dry benzene was refluxed for 30 min (85% of piperidine hydrochloride). Trituration of the oil obtained on evaporation with cold methanol gave 0.12 g (7%) of 2-methyl-3-(1-piperidyl)-methylbenzothiophene 1,1-dioxide (**13**), mp 141–142° (lit.[10] mp 145–146°). Concentration of the reaction solution gave 0.35 g (20%) of a product, mp 92–98°; the mixture melting point with **12** undepressed.

Base-Catalyzed Isomerization of 13 to 6.—A solution of 2.5 mmol of potassium *t*-butoxide in 10 ml of *t*-butyl alcohol was treated with 0.055 g of **13**. After 30 min at room temperature, the alcohol was partially distilled under reduced pressure and then evaporated under an air jet, leaving an oily residue. The residue was dissolved in 5 ml of 95% ethanol; cooling gave 0.12 g (22%) of **6**, mp 145–146°; the mixture melting point was undepressed and the ir spectra were identical.

Isomerization of 3-[α-(1-piperidyl)ethyl]benzothiophene 1,1-Dioxide (15).—A solution of 2.5 mmol of potassium *t*-butoxide in 10 ml *t*-butyl alcohol containing 0.10 g of **15** was heated on a steam bath for 22 hr. The solvent was partially evaporated, and the solution was diluted with 10 ml of water and cooled in an ice bath. The nmr spectrum of the solid (0.04 g), mp 118–120°, showed, in addition to ten piperidine protons and four phenyl protons, a broad three-proton singlet at δ 1.96 (methyl protons) and a broad two-proton singlet at 4.03 (methylene protons). The product is tentatively identified as 3-[α-(1-piperidyl)ethylidene]-2,3-dihydrobenzothiophene 1,1-dioxide (**7**).

3-(α-Hydroxy-α-methylethyl)benzo[*b*]thiophene 1,1-Dioxide.—Reaction of the Grignard reagent prepared from 20 g (94.3 mmol) of 3-bromobenzo[*b*]thiophene with 17.3 ml (0.2 mol) of dry acetone gave 10.6 g (61%) of tertiary alcohol, mp 74–78°. Recrystallization from hexane gave material with mp 83.5–84.3°. A 3-g (15.7 mmol) sample of this alcohol was oxidized with 5.7 g (35.7 mmol) of 85% *m*-chloroperoxybenzoic acid in 60 ml of methylene chloride at room temperature for 13 hr. The filtrate obtained from this mixture was washed successively with 30-ml portions of 10% aqueous sodium sulfite, 10% sodium hydroxide (twice), and water. After drying, concentration gave 3.1 g (88.6%) of sulfone alcohol, mp 124.5–126.5°. An analytical sample crystallized from methanol melted at 133.5–135°: nmr ($CDCl_3$), δ 7.5–8.2 (4 H multiplet), 6.72 (1 H singlet), 3.1 (1 H singlet, temperature dependent), 1.64 (6 H singlet).

Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.92; H, 5.37. Found: C, 59.20; H, 5.36.

3-(α-Chloro-α-methylethyl)benzo[*b*]thiophene 1,1-Dioxide (23).—A solution of 6.0 g (31.4 mmol) of 3-(α-hydroxy-α-methylethyl)-benzo[*b*]thiophene in 80 ml of dry benzene was saturated with hydrogen chloride. The benzene–water azeotrope was distilled over a period of 20 min while the introduction of hydrogen chloride was continued. The solution was cooled to room temperature and saturated with hydrogen chloride, and the solvent was removed under reduced pressure. The yellow oil was dissolved in 20 ml of anhydrous CH_2Cl_2 and added to a solution of 12.5 g (63 mmol) of 85% *m*-chloroperoxybenzoic acid in 140 ml of dry CH_2Cl_2 at 10° with stirring. After 30 min the temperature was allowed to rise to 20°. After 30 min the solution was filtered and the filtrate was washed with 40-ml portions of 10% NaOH, 10% Na_2SO_3, saturated $NaHCO_3$, and water. After drying over $CaCl_2$, filtering, and removing the solvent, there remained a pale yellow oil; the oil solidified upon trituration with methanol. Crystallization (MeOH) gave 3.4 g (50%) of colorless solid, mp 136–140°. Successive recrystallizations (benzene–hexane; ethyl acetate; benzene–hexane) gave **23**: mp 141–142°; nmr ($CDCl_3$), δ 7.43–8.09 (4 H multiplet), 6.64 (1 H singlet), 1.95 (6 H singlet); uv, λ_{max}^{MeOH} 299 mμ (ε 2.36 × 10³), 237.5 (2.26 × 10⁴); ir ($CHCl_3$), 7.63 (s), 8.42 (s), 8.55 μ (s).

Anal. Calcd for $C_{11}H_{11}ClO_2S$: C, 54.43; H, 4.57. Found: C, 54.63; H, 4.62.

3-(1-Piperidylmethylene)-2,2-dimethyl-2,3-dihydrobenzo[*b*]-thiophene 1,1-Dioxide (25).—A solution of 483.4 mg (2.0

(13) R. Gaertner, *J. Am. Chemer. Soc.*, **74**, 2185 (1952).

mmol) of **23** and 1.022 g (12 mmol) of piperidine in 10 ml of benzene was refluxed for 4 hr. Filtration gave 238.3 mg (98%) of piperidinium chloride. Evaporation of the filtrate gave 594 mg of crystals, mp 148–152°. After crystallization (MeOH), the yield of **25** was 81%, mp 150–155° (nmr analysis of the residue from the mother liquor indicated a total yield of 97%). An analytical sample prepared by additional crystallizations (EtOH, benzene–hexane) melted at 154–155°: nmr ($CDCl_3$), δ 7.2–7.9 (4 H multiplet), 6.18 (1 H singlet), 2.94 (4 H multiplet, 1.67 (6 H multiplet), 1.52 (6 H singlet, partially superimposed with δ 1.67 signal); uv, λ_{max}^{MeOH} 332 mμ (ϵ 11,900); ir ($CHCl_3$), 3.31 (m), 3.38 (m), 3.48 (w), 3.52 (w), 6.05 (s), 6.23 (m), 6.81 (s), 7.22 (m), 7.77 (vs), 8.11 (m), 8.22 (m), 8.56 (m), 8.99 μ (vs).

Anal. Calcd for $C_{16}H_{21}NO_2S$: C, 65.94; H, 7.26. Found: C, 66.31, 66.27; H, 7.51, 7.32.

A similar reaction was carried out using 100 mg (0.412 mmol) of **23** and 851 mg (10 mmol) of piperidine in 10 ml of benzene at 33.8° for 3 hr (*ca.* one half-life). After processing as before there was obtained 97 mg of an amphorous solid. The nmr ($CDCl_3$) peaks could all be accounted for as being due to starting chloride **23** and enamine **25**; from the ratio of the vinyl proton singlet of **23** (δ 6.65) to that of **25** (δ 6.13) and from the ratio of the methyl singlet of **23** (δ 1.95) to the multiplet for the α-piperidino protons of **25** (δ 2.92) the relative amounts of **23**:**25** was 1:1.

A reaction mixture from **23** and piperidine (1:6 molar ratio) in absolute ethanol (7.5 hr reflux) ws concentrated with the aid of an air jet. The residue was extracted with benzene and the solid obtained from the filtrate was crystallized from methanol to give 70% of **25**, mp 146–153° (mmp 149.5–154°). Nmr analysis of the mother liquors indicated a total yield of 84%. A comparable result was obtained after an 11.5-hr reflux in acetone.

Hydrolysis of 25.—When 50 mg (0.2 mmol) of **25** was added to 3 ml of 6 *N* hydrochloric acid on the steam bath, solution occurred immediately, and an oil separated within 10 min. After 15 min the solution was cooled and extracted with *ca.* 0.2 ml of $CDCl_3$ and the extract was dried over $CaCl_2$: nmr ($CDCl_3$), δ 9.72 (1 H doublet, J = 3.7 cps), 7.3–8.4 (4 H multiplet), 3.87 (1 H doublet, J = 3.7 cps), 1.55 (3 H singlet), 1.53 (3 H singlet). The integration for the aldehydic and methinyl protons was low (relative to the aromatic protons) and an additional peak (0.7 H) was present at δ 1.58 (methyl singlet for the enol). Evaporation of the solvent left 25.7 mg (60%) of clear oil: ir (neat), 2.98 [m (broad, enol H)], 3.51 (w), 3.64 (w), 4.4 (w), 5.8 (s), 5.97 (m), 6.26 (m), 6.81 (s), 7.19 (m), 7.30 (m), 7.74 (s), 8.5 (m), 8.7 μ (s).

In a separate run 70 mg (0.24 mmol) of **5** was hydrolyzed as above; the solution was then treated with 52 mg (0.26 mmol) of 2,4-dinitrophenylhydrazine in 4.5 ml of ethanol containing 0.7 ml of sulfuric acid. The derivative was obtained as fine yellow needles, mp 218–221°, after two recrystallizations from ethanol–nitromethane: nmr ($CDCl_3$), δ 11.30 (1 H singlet), 8.21 (1 H doublet, J = 2.6 cps), 7.32–8.65 (8 H multiplet) 4.18 (1 H doublet, J = 8.4 cps), 1.57 (3 H singlet), 1.52 (3 H singlet).

Anal. Calcd for $C_{17}H_{16}N_4O_6S$: C, 50.49; H, 3.99; N, 13.85. Found: C, 49.90; H, 4.16; N, 13.35.

Registry No.—**1**, 16957-75-8; **2**, 16934-26-2; **4**, 16957-77-0; **5**, 16934-30-8; **9**, 16957-79-2; **11**, 16957-80-5; **12**, 16957-81-6; **13**, 16957-82-7; **14**, 16957-83-8; **15**, 16957-84-9; **16**, 16957-85-0; **17**, 16957-86-1; **18**, 16957-87-2; **19**, 16958-18-2; **20**, 16957-88-3; 2-chloro-3-methylbenzo[*b*]-thiophene 1,1-dioxide, 16934-27-3; 3-chloromethyl-2-methylbenzo[*b*]thiophene, 16957-90-7; **23**, 16934-31-9; **25**, 16957-92-9; **28** (2,4-dinitrophenylhydrazone), 16957-93-0; 3-(α-hydroxy-α-methylethyl)benzo[*b*]thiophene 1,1-dioxide, 16957-94-1.

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An Abnormal Allylic Displacement in the Reaction of 2-Halo-3-methylbenzo[*b*]thiophene 1,1-Dioxides with Piperidine

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A kinetic study has shown that the reaction of 2-halo-3-methylbenzo[*b*]thiophene 1,1-dioxides (**1**) with piperidine in methanol to give 3-(1-piperidylmethylene)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (**5**) occurs in the following steps: (1) rapid tautomeric equilibration to form the allylic halide **2**, (2) SN2′ displacement, (3) loss of a proton to give **4**, and (4) tautomerism to **5** (rate controlling). In the presence of added methoxide ion step 2 becomes rate controlling. The Br:Cl rate ratio for SN2′ displacement is estimated to be *ca.* 1.4:1.0.

In a previous paper it was shown that 3-methyl-2-bromobenzo[*b*]thiophene 1,1-dioxide (**1**) undergoes reaction with piperidine in benzene to give 3-(1-piperidylmethylene)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (**5**).[1] The reaction course suggested was (1) base-catalyzed tautomerism to 3-methylene-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (**2**), (2) abnormal allylic (SN2′) displacement to give **3**, (3) loss of a proton, and (4) base-catalyzed tautomerism to give **5**.

In order to obtain additional information concerning the mechanism of this reaction the rates of halide ion release from the reaction of piperidine with **1** (X = Cl, Br, and I) in methanol were followed conductometrically (Table I). In addition, the rates of formation of the product (**5**) from these halides were determined spectrophotometrically (Table II).

It will be observed that both the conductometric and spectrophotometric rates are first order in piperidine (second order over-all), but that the latter are two to five times slower than the former. No product formation was detected from **1** in the ultraviolet (uv) until three or four conductometric half-lives had elapsed. After this "induction" period, a steady rate of product formation (**5**) took place. These observations suggest the formation of an intermediate (**4**), which reacts slowly to form **5**. This interpretation was supported by examination of the changes in the nmr spectrum of **1** in deuteriochloroform containing piperidine. Absorption at δ 3.52 (doublet, J = 1.5 cps) and 6.77 (triplet, J = 1.5 cps) with peak areas of approximately 2:1, respectively, began to develop within 2 min after the reactants were mixed. The signal at δ 3.52 is in the region expected for the $-CH_2-N$ group of **4** and the signal at 6.77 is in the region expected for the vinyl proton of **4**. Absorptions due to approximately four pi-

(1) F. G. Bordwell, R. W. Hemwall, and D. A. Schexnayder, *J. Org. Chem.*, **33**, 3226 (1968).