derivative and the bicyclo[2.2.2], 2,3 derivative. Furthermore, it is seen that the relative rates bear little relationship to freezing of internal rotations.

Variation in rates were obtained in three ways which had minimal effect on properties other than orientation. These ways were (a) change in the supporting superstructure, (b) addition of methyl groups to limit the rotation of the carboxyl, and (c) change of the O group to S with its longer C–S bond length. Not only were large changes in rate observed but within each category the rates sometimes increased and sometimes decreased. This is exactly the type of behavior one might expect for an orientation effect whereas compression, ring strain, solvation, etc., would seem to require a constant increase or decrease for any one agent.

It might still be argued that, although none of the alternatives to orientation are viable as a common explanation for all the results, they can be used in some combination not yet devised to explain these intriguing changes. It is difficult to dispute such a nontheory. One can only say that no satisfactory self-consistent set of alternate explanations has been devised and the orientation factor argument does provide a single and logical explanation for the observations made so far.

The empirical function which relates angles of approach to the velocity of reaction is too crude to be considered a theory as yet. To obtain a reasonable number of points molecules which allowed freedom of rotation (*e.g.*, the 2,3-norbornane derivatives) were included and their correlation using a single angle would lead to the assumption that this conformation was equally filled in the two compounds. Likewise, sulfur and oxygen compounds were included which would involve a tacit hypothesis that the preferred orbital orientations in sulfur were similar to oxygen, the differences in rate coming from the new imposed geometries caused by the longer C–S bond. There is no independent supporting evidence for either hypothesis but both are plausible. The overall fit of data to the dashed curve in Figure 1 is therefore intriguing and perhaps a good point of departure for further studies. The optimum angle of 98° which is derived empirically is also logical since it is midway between a perpendicular initial approach and a tetrahedral transition state. However, this should be taken only as an intriguing correlation at the present.

The hypothesis proposed earlier,[1,2] that reaction rates may be sensitive to orientation by factors of 10^4 even after juxtaposition of the reacting atoms, is given some further support by these experiments. It is perhaps worth emphasizing that the orbital steering concept, *i.e.*, that enzymes and intramolecular structures can achieve accelerated rates by steering the reacting atoms in preferred orientations, defines the factors in empirical terms. The added acceleration is that achieved over an unoriented reaction and its theoretical components may result from bond bending, nonbonded interaction, etc. In other papers we have dealt with some theoretical aspects of the components of this factor.[3,4] Recently Hoare has evaluated a further contribution of solvent orientation.[19] In this paper we record experiments which deal with the orientation factor as a whole and support the order of magnitude postulated. The integration achieved by appropriate experiments is vital since a steering which maximizes overlap in the forming bond while minimizing repulsive interactions involves differences between large forces, none of which is subject to highly precise calculation.

(19) D. G. Hoare, *Nature (London)*, **236**, 437 (1972).

Addition–Elimination and Rearrangement Reactions in Allylic Systems

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Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received October 8, 1971*

Abstract: Reactions of 3-(α-halo-α-methylethyl)benzo[*b*]thiophene 1,1-dioxide (**1**) with benzenesulfinate, thiophenoxide, cyanide, and azide salts in suitable solvents resulted in addition–elimination reactions. Evidence is presented to show that the reactions are best classified as ion-pair SN2′ from a mechanistic standpoint.

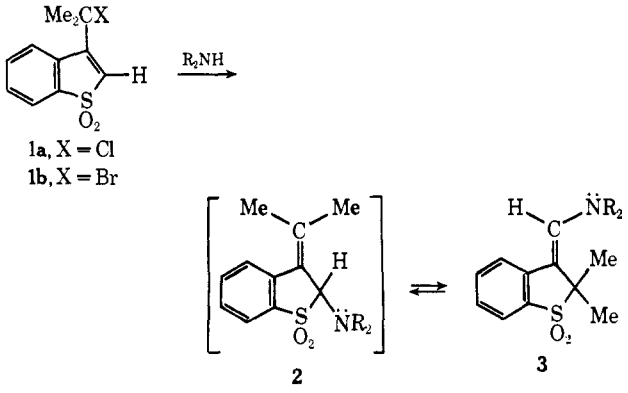
In earlier papers we have shown that treatment of 3-(α-chloro-α-methylethyl)benzo[*b*]thiophene 1,1-dioxide (**1a**) with piperidine resulted in an addition–elimination (SN2′ or SN2′-like) reaction to form **2** (not isolated), followed by a ring opening–ring closing isomerization to form **3**.[2] The electron pair on nitrogen was visualized as providing the driving force for the ring opening of **2** and the stabilizing factor causing **3** to predominate completely over **2** at equilibrium. It follows that reactions of **1a** with nucleophiles like $C_6H_5SO_2^-$ should stop at the first stage since an electron pair is not present in the addition–elimination product corresponding to **2**. The present paper describes reactions of this type which provide additional information concerning the addition–elimination and rearrangement steps in the above type of reaction sequence.

(1) National Institutes of Health Predoctoral Fellow, 1968–1971.

(2) (a) F. G. Bordwell and D. A. Schexnayder, *J. Org. Chem.*, **33**, 3226 (1968); (b) F. G. Bordwell, D. A. Schexnayder, and R. H. Hemwall, *ibid.*, **33**, 3233 (1968); (c) F. G. Bordwell and D. A. Schexnayder, *ibid.*, **33**, 3236 (1968); (d) F. G. Bordwell and D. A. Schexnayder, *ibid.*, **33**, 3240 (1968).

Results

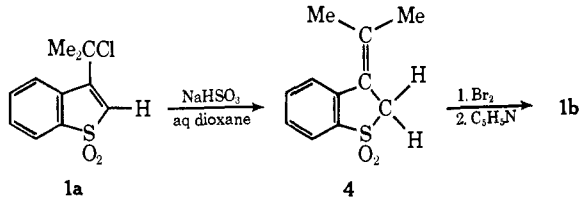
Preparation of the bromide **1b** was desired in order to test the k^{Br}/k^{Cl} leaving group effect in the addition–elimination reaction. The method used for synthesis



1a, X = Cl
1b, X = Br

2 ⇌ 3

of chloride **1a**[2] was unsuccessful, but the preparation was readily accomplished by the sequence of steps **1a → 4 → 1b**.



1a 4

The reduction of **1a** is no doubt the result of attack of HSO_3^- (or SO_3^{2-}) on chlorine to yield a carbanion intermediate, which is protonated by the medium forming **4**. Reaction of **4** with NaOMe–MeOD gave the α,α-dideuterio derivative, showing that **4** is more stable than its tautomer.[3]

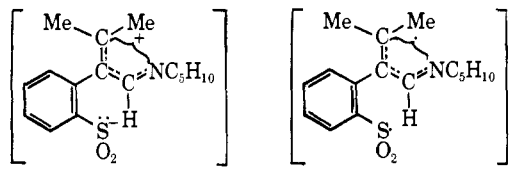
Bromide **1b** was inert to solvolysis, only 10% release of Br^- being realized in an 8-day reflux in methanol. It reacted readily with piperidine in benzene, methanol, or DMF to give enamine **3** in high yield. Comparable enamines were obtained in (slower) reactions with *n*-butylamine and cyclohexylamine in benzene. The structure of enamine **3** (R_2N = piperidino) has been established previously.[2a] The structures of the other two enamines were established from their nmr spectra and hydrolysis to a common aldehyde, which was identical with that obtained from **3** (R_2N = piperidino). The rates of reaction of **1a** and **1b** with excess piperidine in benzene, methanol, and DMF were measured spectrophotometrically by following the formation of enamine **3a**. The data are summarized in Table I.

The data in Table I show that the reactions of **1a** in benzene, methanol, and DMF and **1b** in methanol and DMF are overall second order (first order in piperidine and first order in **1a** or **1b**). This is consistent with rate-limiting formation of **2** in steady-state concentrations and rapid unimolecular rearrangement of **2** to **3**. Bromide **1b** showed a different kinetic behavior in benzene. Division of the observed pseudo-first-order constants by the piperidine concentration did *not* yield a second-order constant (Table I). Apparently the k^{Br}/k^{Cl} leaving group effect is large enough to make the rate of formation of **2** competitive with the unimolecular rearrangement of **2** to **3**, giving rise to mixed order kinetics.[4] In the better ionizing solvents methanol and DMF the reaction of **1b** with piperidine *did* follow second-order kinetics. Here the rate of the unimolecular rearrangement step, **2 → 3**, has increased to the point where it has outstripped the addition–elimination step, **1b → 2**, and no longer figures in the rate of appearance of **3**. This apparent acceleration of the rearrangement rate by better ionizing solvents supports the suggestion that this isomerization involves a dipolar ion intermediate **2a**[2] rather than a diradical intermediate **2b**.

Table I. Second-Order Spectrophotometric Rate Constants for the Reaction of 3-(α-Halo-α-methylethyl)benzo[*b*]thiophene 1,1-Dioxides (**1a**, X = Cl; **1b**, X = Br) with Piperidine at 50°

Compd	X	Solvent	k_2,[a] M^{-1} sec^{-1}
1a	Cl	Benzene[b]	1.6×10^{-4}
1a	Cl	Benzene[c]	1.6×10^{-4}
1a	Cl	Methanol[b]	1.8×10^{-5}
1a	Cl	DMF[b]	6.5×10^{-4}
1b	Br	Benzene[d]	5.88×10^{-3}
1b	Br	Benzene[e,f]	1.96×10^{-3}
1b	Br	Methanol	4.7×10^{-4}
1b	Br	DMF	1.62×10^{-2}

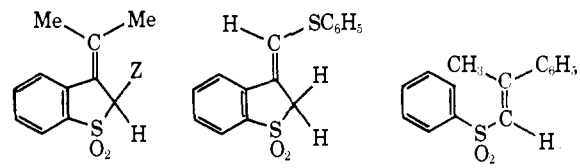
[a] Rate constants for the appearance of enamine **3** (R_2N = piperidino); unless noted otherwise, the rate constant is independent of piperidine concentration. [b] Reference 2. [c] The solution contained 0.01 *M* *m*-dinitrobenzene. [d] [Piperidine] = 0.0296 *M*; pseudo-first-order constant (k_1) = 1.74×10^{-4} sec^{-1}. [e] [Piperidine] = 0.355 *M*; $k_1 = 6.95 \times 10^{-4}$ sec^{-1}. [f] At 0.202 and 0.292 *M* piperidine concentrations the respective $10^4 k_1$ values were 6.48 and 6.47 sec^{-1}, while the $10^3 k_2$ values were 3.21 and 2.22 M^{-1} sec^{-1}.



2a 2b

Failure of *m*-dinitrobenzene, a radical inhibitor, to affect the rate for the reaction of **1a** with piperidine (Table I), and failure of light or oxygen to produce any observable influence on the reaction also argue against the intermediacy of **2b**.

Reaction of **1a** or **1b** with benzenesulfinate, thiophenoxide, cyanide, or azide salts in a suitable solvent gave in each instance an analog of **2**, which could be isolated and characterized (compounds **5a–5d**).



5a, Z = $SO_2C_6H_5$
5b, Z = SC_6H_5
5c, Z = CN
5d, Z = N_3

6 7

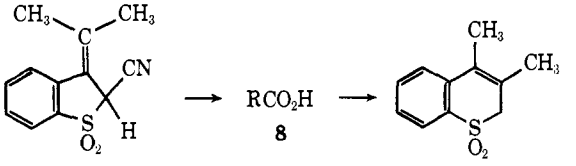
(3) This is expected since in an open-chain analog the ratio of $CH_2{=}CHCH_2SO_2CH_3/CH_3CH{=}CHSO_2CH_3$ at equilibrium is 44/56 (D. E. O'Connor and W. I. Lyness, *J. Amer. Chem. Soc.*, 86, 3840 (1964)) and in the benzothiophene 1,1-dioxide series the equilibrium is completely on the side of the isomer wherein the double bond is exocyclic even when only one methyl group is present at the γ position, *i.e.*, 3-ethylbenzothiophene 1,1-dioxide isomerizes completely to its CH_3-$CH{=}C<$ tautomer (D. A. Schexnayder, Ph.D. Dissertation, Northwestern University, 1968).

(4) Similar kinetic behavior was observed for 3-(α-chloroethyl)benzo[*b*]thiophene 1,1-dioxide, the secondary chloride analogous to **1a**, for which the titrimetric rate was second order, but the spectrophotometric rate was of mixed order.[2c] Here the unimolecular rearrangement is competitive in rate with addition–elimination, and the release of chloride ion (titrimetric rate) was faster than the observed rate of enamine formation.

Structure assignments for **5a–5d** were made on the basis of nmr spectra. Each exhibited *two nonequivalent methyl* resonances (δ 1.0–2.2), a methinyl signal (1 H) in the 3.5–5.5 region, and a multiplet (4 H) for the aromatic region (7.5–7.8). These spectra are similar to that of **3** except that the signal for the vinyl proton in **3** is farther downfield than that of the methinyl protons in **5a–5d** (δ 6.18 *vs.* 3.5–5.5) and the methyl signal in **3** appears as a *singlet*.[2a] At the outset the product from thiophenoxide was assigned a structure analogous to **3** because in chloroform only a single methyl peak was observed. This peak was resolved into a doublet in benzene solution, however, leading to the assignment of structure **5b**. This assignment was supported further by conversion of **5b** to **5a** by oxidation.

The structure assignment was supported by the observation that the methinyl protons in **5a**, **5b**, **5c**, and **5d** were exchanged much more rapidly in CH_3ONa–CH_3OD than the vinyl protons in **3**, **6**, or **7**. Comparison of **5b** with **6** is particularly pertinent. For **5b** deuterium exchange of the methinyl proton was complete at room temperature within 20 sec in 0.005 *M* NaOMe–MeOD, whereas after 20 min in 0.01 *M* NaOMe–MeOD exchange occurred at only the methylene position in **6**. There was no exchange of the vinyl hydrogen of **6** (or **7**). Similarly, **3** gave less than 5% exchange with 0.01 *M* NaOMe–MeOH at 25° in 20 min.

Nitrile **5c** was hydrolyzed to a carboxamide and then to a carboxylic acid, **8**. Decarboxylation of **8** was accomplished by a 2.5-day reflux in quinoline. The product was not, however, the expected **4**, but, instead, an isomer of **4** to which we have tentatively assigned structure **9**.[5]

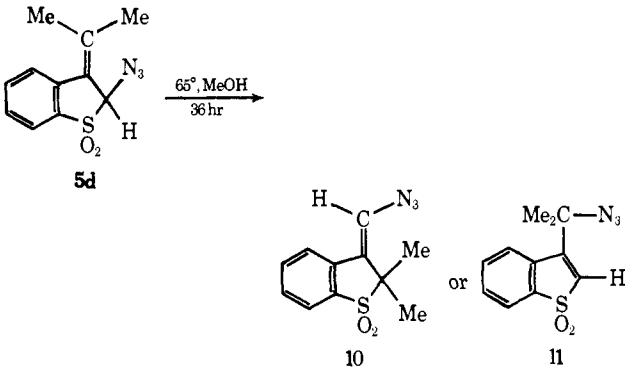


5c **8** **9**

Reaction of chloride **1a** with potassium thiophenoxide in ethanol gave 55% of **5b** and 45% of **4**. In contrast, a comparable reaction in methanol gave only **5b**. Similar results were obtained with bromide **1b** (77% of **5b** and 23% of **4** in EtOH; 100% **5b** in MeOH). Evidently nucleophilic attack on halogen *vs.* carbon is promoted by the solvent with poorer hydrogen bonding characteristics, namely ethanol.

Reactions with chloride **1a** in methanol or ethanol occurred readily only with powerful nucleophiles such as piperidine or thiophenoxide ion. Sodium benzenesulfinate, sodium cyanide, sodium thiocyanate, and ethyl sodiomalonate failed to elicit reaction in these solvents, even after extended reaction times. For example, no reaction was observed with sodium benzenesulfinate after a 48-hr reflux in aqueous ethanol, whereas the reaction was essentially complete in DMF at 100° in 7 hr. Reactions with sodium cyanide and lithium azide were also only successful in DMF or DMF–EtOH.

Compounds **5a**, **5b**, and **5c** appear to be highly stable to thermal or solvolytic rearrangement. Heating **5a** in refluxing acetonitrile for 10 days caused no rearrangement, and **5b** was recovered unchanged after 20 days of reflux in methanol. Refluxing **5c** with 0.2 *M* NaOMe in MeOH for 20 hr caused no change. On the other hand, azide **5d** isomerized in refluxing methanol to the extent of about 50% in 36 hr ($k \cong 5 \times 10^{-5}$ sec^{-1}). It is uncertain, however, whether the rearrangement product is **10** (from a ring opening–ring



5d **10** **11**

closing isomerization[2]) or **11** (from an intramolecular migration of the azide[6]). Rearrangement of **5d** appears to be only slightly slower in $CHCl_3$ or DMF than in MeOH. This insensitivity of rearrangement rate to solvent effects is more in line with intramolecular migration of the azide grouping (and double bond)[6] than the ring opening–ring closing isomerization of **2**, which is sensitive to solvent changes (see above).

The rates of reaction of azide with **1a** and **1b** in DMF followed spectrophotometrically by observing the disappearance of starting material (Table II). The rate for **1b** in methanol was obtained titrimetrically (Table II).

Table II. Second-Order Rate Constants for Reaction of **1a** and **1b** with Lithium Azide at 50°

Compd	Solvent	μ	k, M^{-1} sec^{-1}
1a	DMF	0.1	$3.9 \pm 0.1 \times 10^{-3}$
1b	DMF	0.1	$1.6 \pm 0.05 \times 10^{-1}$
1b	MeOH	0.3	$8.9 \pm 0.05 \times 10^{-5}$

Discussion

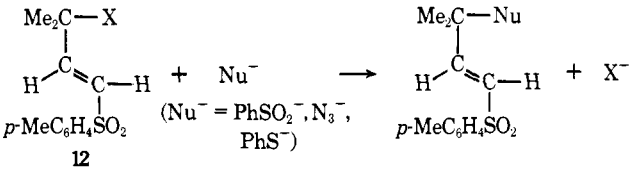
The kinetic behavior of bromide **1b** with piperidine, as described above, strongly supports the intermediacy of α-amino sulfone **2** in the conversion of **1b** to enamine **3**. This reaction sequence is supported also by the formation of α-phenylsulfonyl, α-phenylthio, α-cyano, and α-azido sulfones **5a–5d**, which are analogs of **2**, when **1b** reacts with other nucleophiles. The failure of α-disulfone **5a** and α-cyano sulfone **5c** to rearrange to analogs of **3** is understandable since they lack the electron pair on Z believed to provide the driving force for the rearrangement of **2** (**5** with Z = piperidino) to **3**. α-Phenylthio sulfone **5b** fails to rearrange, although it does have the requisite electron pair.

These experiments provide some additional insight into the mechanisms of attack of nucleophiles on tertiary allylic halides of type **1**. The parent tertiary allylic chloride analog of **1**, CH_2=$CHC(Cl)Me_2$, as a

(5) The course of this rearrangement is under investigation.

(6) Intramolecular rearrangements of CH_2=$CHC(Me)_2N_3$ in EtOH occurs about four times as fast at 25° as does that of **5d** in MeOH at 65°: see A. Gagneux, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, **82**, 5956 (1960).

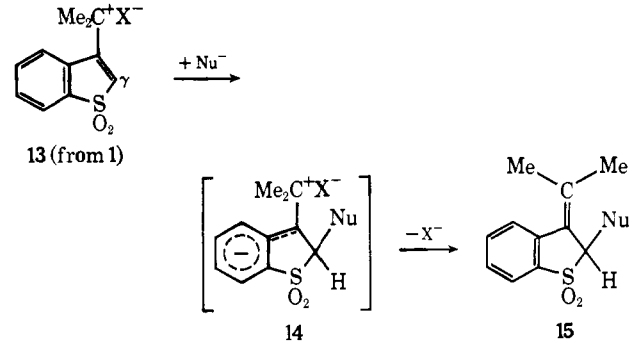
consequence of its high susceptibility to ionization,[7] reacts with nucleophiles primarily by carbonium ion type mechanisms. On the other hand, the presence of the sulfone group in **1** renders it relatively inert to solvolysis and more susceptible to nucleophilic attack. There are potentially three sites for nucleophilic attack on **1**: (a) the halogen atom, (b) the tertiary carbon atom (SN2 reaction), and (c) the γ-vinylic carbon atom (SN2′-like reaction). The halogen atom is attacked only by nucleophiles with a high reduction potential (HSO_3^- or $C_6H_5S^-$) in a protic solvent (EtOH > MeOH). Other nucleophiles appear to initiate attack primarily at the γ-vinylic carbon atom.[9] Nucleophilic attack at the tertiary carbon atom in **1** was not observed. This contrasts sharply with the behavior of **12**,



an open-chain analog of **1**, which suffers nucleophilic attack *only* at the tertiary center.[10]

The reactions of **12** with nucleophiles are second order, like those of **1**. A detailed study indicates that these reactions are occurring by ion-pair SN2 mechanisms, at least in protic media.[10] The rate for tertiary bromide **12** reacting with LiN_3 in MeOH is ten times faster than for tertiary bromide **1b**. This means that reaction at the tertiary center of **1b** is a minimum of 10^3 times slower than that at the tertiary center of **12**. If we assume that **1b** is also reacting by an ion-pair mechanism the retardation of the overall rate may be attributed to a marked increase in the electron-withdrawing effect of the sulfonyl group at C_α in **1**, caused by transmission through the benzene ring, as well as through the side-chain C=C double bond.[11] It is not entirely clear, however, why the nucleophile should attack the ion pair **13** from **1** exclusively at the γ position, whereas it attacks the ion pair from **12** exclusively at the α position. One contributing factor may be increased steric hindrance for attack at C_α in **1** (or **13**) caused by a steric effect of the peri hydrogen atom. A second factor may be stabilization of intermediate **14**, derived from attack of the nucleophile (*e.g.*, N_3^-) at C_γ of **13**, caused by delocalization of the negative charge of the benzene ring. Comparable delocalization is not possible for the intermediate derived from **12**.

One would expect loss of bromide ion from **14** to be fast, which means that attack of Nu^- on ion-pair **13** would be rate limiting. This would be consistent with the k^{Br}/k^{Cl} leaving group effects observed since the concentration of ion-pair **13** will depend on the nature



of X. The k^{Br}/k^{Cl} leaving group ratios for reactions of **1** are 25/1 for piperidine in DMF, 41/1 for LiN_3 in DMF, and 26/1 for piperidine in MeOH. While these leaving group effects are substantial, they are appreciably smaller than those observed in SN2 reactions.[12]

A concerted SN2′ mechanism with simultaneous formation of Nu–C and C_β–C_α bonds and breaking of C_γ–C_β and C–X bonds is a possible alternative.[16] We do not favor this mechanism for reasons given earlier,[17] and in the succeeding paper.[10]

The acceleration in rate on changing from MeOH to DMF (36- and 34-fold for chloride **1a** and bromide **1b**, respectively, with piperidine; 1800 for **1b** with lithium azide) is probably caused primarily by increased reactivity of the nucleophile in DMF.[15]

Experimental Section

3-(α-Methylethylidene)-2,3-dihydrobenzo[*b*]thiophene 1,1-Dioxide (4). A solution of 2.0 g (8.5 mmol) of 3-(α-chloro-α-methylethyl)-benzo[*b*]thiophene 1,1-dioxide (**1a**) and 7.0 g (55 mmol) of sodium bisulfite in 60% (v/v) dioxane–water was refluxed for 24 hr, and then poured into 3 l. of brine. The combined organic phase from seven extractions with 500-ml portions of chloroform was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting oil was taken up in hot acetone–hexane and the solution allowed to cool slowly, yielding 1.4 g (79%) of **4**: mp 193–194°; $\lambda_{max}^{95\%\,EtOH}$ 259 nm (ϵ 1.54 × 10^4); ir (μ) 6.1 (m), 7.85 (s), 8.7 (s), 8.95 (s); nmr δ 1.9 (s, 3 H), 2.14 (s, 3 H), 4.03 (br s, 2 H), 7.45 (m, 4 H).

Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81. Found: C, 63.52; H, 5.71.

Refluxing **4** in 0.027 *M* NaOMe for 17 hr caused no change, but use of methanol-d_1 caused the δ 4.03 peak to disappear. Additional experiments showed that this deuterium exchange was complete in less than 2 hr.

3-(α-Bromo-α-methylethyl)benzo[*b*]thiophene 1,1-Dioxide (1b). A solution of 0.52 g (3.24 mmol) of bromine in 20 ml of CCl_4 was added to a solution of 0.17 g (3.24 mmol) of **4**. Crystallization of the resulting 3-(α-bromo-α-methylethyl)-3-bromo-2,3-dihydrobenzo[*b*]-thiophene 1,1-dioxide from methanol gave 1.07 g (97%): mp 149–150.5°; nmr δ 2.0 (d, J = 3 Hz, 6 H), 4.4 (m, 2 H), 7.7 (m, 4 H).

(7) For example, in 50% EtOH its solvolysis rate is 260 times that of *t*-BuCl.[8]

(8) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, Table 35, p 78.

(9) This is true for amines, benzenesulfinate ion, cyanide ion, azide ion, and thiophenoxide ion in a suitable solvent. Mixtures of products that were not easily separable were obtained from reactions with sodium methoxide in methanol.

(10) F. G. Bordwell and T. G. Mecca, *J. Amer. Chem. Soc.*, **94**, 2119 (1972); **94**, 5829 (1972).

(11) One would expect this effect also to cause a marked retarding effect on the solvolysis rate for **1**. This is observed. Bromide **1b** undergoes methanolysis at a rate at least 100 times slower than does bromide **12**.[10]

(12) A k^{Br}/k^{Cl} leaving group of *ca.* 44 has been observed for the reaction of allyl halides with piperidine in methanol at 50°;[2c,13] it is *ca.* 90 for a comparable reaction of 3-halomethylbenzothiophene 1,1-dioxides.[14] A k^{Br}/k^{Cl} rate ratio of 250 has been reported for the reaction of lithium azide with methyl halides in DMF at 25°.[15]

(13) The rate for the reaction of piperidine with allyl chloride is 5.3 × 10^{-4} M^{-1} sec^{-1} rather than the rate of 5.3 × 10^{-3} M^{-1} sec^{-1} reported in ref 2c.[14]

(14) D. A. Schexnayder, Ph.D. Dissertation, Northwestern University, 1968.

(15) A. J. Parker, *Chem. Rev.*, **69**, 1 (1968).

(16) A mechanism in which Nu^- attacks **1** to form a carbanion intermediate is also an attractive alternative. It is difficult to account for the leaving group effects using a carbanion mechanism, however. These could be explained by reversible carbanion formation, but it seems unlikely that Nu would be lost from a carbanion intermediate in preference to X. (This was pointed out by a referee.) Rapid carbanion formation and slow loss of halide ion would not fit the kinetics. Slow carbanion formation and rapid loss of halide ion would not satisfy the leaving group effect unless the relative effects of bromine and chlorine in stabilizing the carbanion are unusual.

(17) F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).

Table III. Products from Substitution Reactions of **1a**

Reagent	Solvent	T, °C	Time, hr	Yield, %	Product (mp (°C))	Calcd C	Calcd H	Found C	Found H
$C_6H_5SO_2Na$	DMF	100	15	80	**5a** (206–207)	58.60	4.63	58.46	4.61
$C_6H_5S^-Et_3NH^+$	C_6H_6[a]	80	8	88	**5b** (137.5–139)	64.53	5.10	64.65	5.23
C_6H_5SK	MeOH[a]	65	13	55	**5b**, 45% of **4**				
NaCN	10% (v/v) DMF–EtOH	*b*	20	42	**5c** (177–178)	61.77[c]	4.75	61.62[c]	4.71
LiN_3	DMF	65	8	*d*	**5d** (122–124 dec)	52.99	4.85	52.98	4.55

[a] Flushed with nitrogen. [b] At reflux. [c] Calcd: N, 6.00. Found: N, 5.83. [d] A mixture of **5d** and **10** (or **11**) in a proportion of 68:32%; pure **5d** was obtained by fractional crystallization.

Anal. Calcd for $C_{11}H_{12}O_2Br_2S$: C, 35.89; H, 3.29. Found: C, 35.71; H, 3.23.

Dehydrobromination with excess pyridine by refluxing in benzene for 4 hr gave 0.71 g (90%) of **1b**: mp 149–150°; nmr δ 2.14 (s, 6 H), 6.56 (s, 1 H), 7.65 (m, 4 H); ir essentially identical with that of **1a**.[2a]

Anal. Calcd for $C_{11}H_{11}O_2BrS$: C, 46.00; H, 3.86. Found: C, 45.93; H, 3.95.

Substitution Reactions of 3-(α-Chloro-α-methylethyl)benzo[*b*]thiophene 1,1-Dioxide (1a). These are summarized in Table III.

Deuterium Exchange Experiments. Complete exchange of the protons in the α positions of **5a, 5b,** and **5c** was effected under the following conditions: **5a**, 0.001 *M* NaOD in 80% (v/v) dioxane–D_2O for 3 min at 25°; **5b**, 0.005 *M* NaOMe in MeOD at 25° for 20 sec; **5c**, 0.01 *M* NaOMe in MeOD at 25° for 20 min. Under comparable conditions the vinyl protons in enamine **3**, 3-(1-thiophenylmethylene)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (**6**), or C_6H_5-$C(CH_3)$=$CHSO_2C_6H_5$ (**7**) failed to exchange to any appreciable extent.

Formation of 3,4-Dimethylbenzo[*b*]thiacyclohex-3-ene 1,1-Dioxide 9) from 2-Cyano-3-isopropylidene-2,3-dihydrobenzo[*b*]thiophene 1,1-Dioxide (5c). A 0.5-g (2 mmol) sample of **5c** was hydrolyzed by refluxing with 0.2 *M* KOH in aqueous ethanol for 4 days to give 0.44 g of carboxylic acid (oil). An amide, mp 244–245°, was isolated from another experiment stopped after 1 day. The acid and amide had nmr spectra consistent with those expected for hydrolysis products of **5c**. Decarboxylation of the acid by refluxing in dry quinoline under a nitrogen atmosphere for 2.5 days gave 0.4 g of **9**: mp 229–231° (from EtOH); nmr δ 2.0 (t, J = 1.5 Hz, 3 H), 2.4 (t, J = 2.0 Hz, 3 H), 3.9 (br s, 2 H), 7.6 (m, 5 H); ir (μ) 3.45 (m), 6.06 (m), 6.27 (w), 6.8 (m), 6.9 (m), 7.25 (m), 7.8 (s), 8.68 (s), 8.8 (s), 8.86 (s), 9.4 (s), 13.02 (s), 13.8 (s), 14.1 (s), 15.32 (s).

Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.48; H, 5.81. Found: C, 63.18; H, 5.77.

Attempts to rearrange **4** to **9** by heating with *t*-BuOK in pyridine at 200° for 3 days gave recovered **4**.

Catalytic hydrogenation of **9** in EtOH using Pd/C gave a dihydro derivative: mp 127–128°; nmr δ 1.11 (d, J = 6 Hz, 3 H), 1.32 (d, J = 6 Hz, 3 H), 2.0–2.6 (m, 2 H), 3.2 (m, 2 H), 7.6 (m, 4 H).

Similar hydrogenation of **4** gave an oil: nmr δ 0.82 (d, J = 7 Hz, 3 H), 1.08 (d, J = 7 Hz, 3 H), 2.2–2.7 (m, 2 H), 3.4 (m, 2 H), 7.6 (m, 4 H).

Nucleophilic Substitutions in Allylic Systems. Further Evidence against the Existence of the Concerted SN2′ Mechanism

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Abstract: Attempts to discover systems susceptible to SN2′ reactions have led to the synthesis of *exo*- and *endo*-2-chloro-2-phenylsulfonyl-3-methylenebicyclo[2.2.1]hept-5-enes (**2a** and **2b**) and γ-*p*-tolylsulfonylallyl, -α-methylallyl, and -α,α-dimethylallyl halides (or methanesulfonates) (**5**, **4**, and **3**, respectively). Halides **2a** and **2b** proved to be relatively inert to nucleophilic attack. Halides **5** and **4** underwent SN2 displacement, usually accompanied by tautomerism of the starting halide or product. Halides (or mesylate) **3** underwent SN2-type displacements with protic solvents (Table I) or nucleophiles (Table II) accompanied by small amounts of elimination reactions. Despite the incorporation of structural features that should favor SN2′ displacements, none such were observed. The results cast further doubt concerning the existence of concerted SN2′ reactions.

A variety of nucleophiles have been shown to initiate attack at the γ position of tertiary allylic halides in the benzo[*b*]thiophene 1,1-dioxide series (**1**) leading to addition–elimination reactions.[2] Although it is difficult to rule out the (concerted) SN2′ mechanism for these reactions, we favor a mechanism (SN2′-like) involving reversible formation of an ion-pair intermediate.[2b] In fact, we have come to question the very existence of the concerted SN2′ mechanism.[3] The successful attack of nucleophiles at the C=C bond in **1** is no doubt due to: (a) the relative electron deficiency of the C=C bond caused by electron withdrawal from both the γ and β positions by the sulfonyl group, and (b) stabilization of the negative charge in the β position in the intermediate (or transition state) by delocalization to the sulfonyl group. It was of interest to examine the behavior toward nucleophiles of analogous systems where activation by the sulfonyl group is restricted to the α position (**2**)

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