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.

Acknowledgment.—This investigation was supported by the Public Health Service Research Grant No. CA-07351 from the National Cancer Institute.

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).

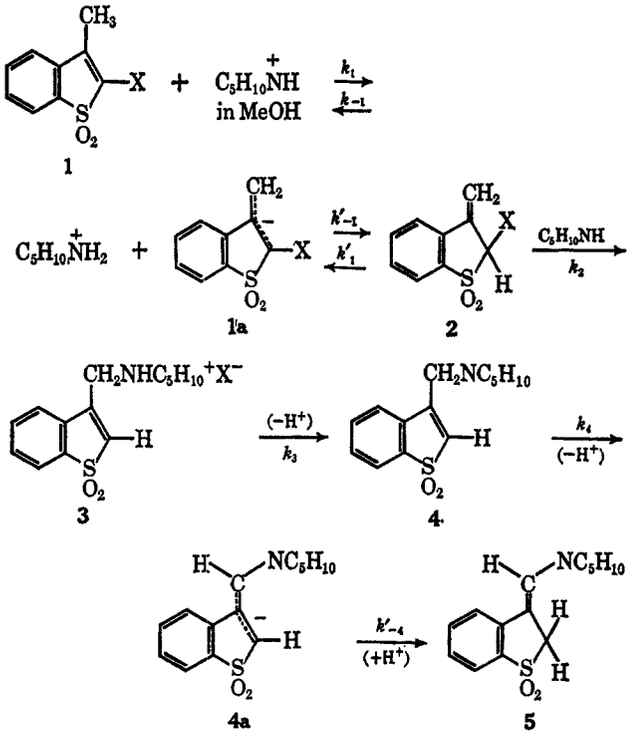


TABLE I

KINETIC DATA FOR THE REACTION OF 2-HALO-3-METHYLBENZO[*b*]THIOPHENE 1,1-DIOXIDES (1) WITH EXCESS PIPERIDINE IN ABSOLUTE METHANOL

Halide	Temp, °C	k_2, M^{-1} sec^{-1} [a]	E_a, kcal/mol	$\Delta S\neq$, eu
Cl	25.0	$1.04 \pm 0.02 \times 10^{-4}$		
	45.0	$5.46 \pm 0.04 \times 10^{-4}$	16	−24
	45.0	(5.48×10^{-4})[b]		
Br	25.0	$3.08 \pm 0.04 \times 10^{-4}$		
	45.0	$1.54 \pm 0.02 \times 10^{-3}$	15	−23
		(1.58×10^{-3})[b]		
I	25.0	$(1.40 \pm 0.15 \times 10^{-4})$[c]		
	25.0	(1.52×10^{-4})[d]	17	−19
	45.0	(8.46×10^{-4})[e]		
	45.0	$(8.60 \pm 0.06 \times 10^{-4})$[b]		

[a] From a plot of log $(R_t/R_t - R_\infty)$ *vs. t*. [b] Plotted by the Guggenheim method. [c] Runs made with 0.103 and 0.206 *M* piperidine. [d] Halide concentration doubled. [e] Single run.

TABLE II

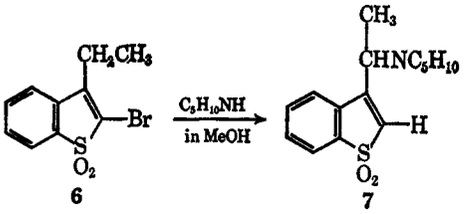
RATES OF FORMATION OF 3-(1-PIPERIDYLMETHYLENE)-2,3-DIHYDROBENZO[*b*]THIOPHENE 1,1-DIOXIDE (5) FROM 2-HALO-3-METHYLBENZO[*b*]THIOPHENE 1,1-DIOXIDES (1) AND PIPERIDINE IN METHANOL AT 45°

Halide	Piperidine concn, *M*	k_2, M^{-1} sec^{-1}[a]
Cl	0.315	$2.02 \pm 0.01 \times 10^{-4}$
Br	0.315	3.25×10^{-4}
	0.105	3.08×10^{-4}
I	0.315	2.29×10^{-4}

[a] Determined spectrophotometrically.

peridine protons at δ 2.5 and six piperidine protons at 1.5 developed at the same rate. The signal due to the 3-methyl of **1** diminished rapidly, but no absorptions attributable to **2** could be detected.

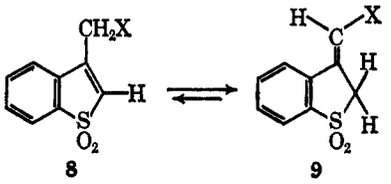
Formation of **4** as an intermediate is supported further by the behavior of 2-bromo-3-ethylbenzo[*b*]thiophene 1,1-dioxide (**6**), the next higher homolog of **1**. Here the SN2′ product (**7**) is the end result.[1] Evidently the presence of the methyl group in **7** greatly retards the rate of proton removal which controls the final tautomerism step. A similar result was obtained with 3-bromo-2-ethylbenzo[*b*]thiophene 1,1-dioxide.[1-3]



The low order of the halogen leaving group effect ($k_{Br}:k_{Cl} \cong 3:1$; $k_I:k_{Cl} \cong 1.4:1$) in the conductometric rates can be accounted for in one or more of the following ways: (a) equilibrium between **1** and **2** is established, but the concentration of **2** changes with changing halogen [*i.e.*, **2** (X = Cl) > **2** (X = Br) > **2** (X = I)] so as to offset the usual leaving group effect (I > Br > Cl);[4] (b) proton removal in the first step (**1** → **1a**) is rate controlling (*i.e.*, $k'_{-1} \gg k_{-1}$ and $k_2 \gg k'_1$ and k'_{-1}; in other words, equilibrium between **1** and **2** is not established); or (c) there is only a small leaving group effect in the SN2′ reaction of **1** with piperidine in methanol.

The first explanation can be ruled out because the positions of the tautomeric equilibria in a similar system, HCC=CX ⇄ C=CCHX, have been found to change in the *reverse manner* (vinylic chloride > vinylic bromide > vinylic iodide).[3] This requires that in the equilibrium **1** ⇄ **2** the change of X from Cl to Br favor **2**, which should give an apparent *increase* in the Br:Cl rate ratio.

The second explanation also appears to be inadmissable, because proton transfers from piperidinium ion to a carbanion like **1a** would be expected to be very rapid. Therefore, k_{-1} and k'_{-1} would be expected to be rapid relative to k_2. Nevertheless, the over-all rate does appear to be of a magnitude comparable with the rate of proton removal. Thus, the rate of proton removal for **8**, an isomer of **1**, by piperidine in methanol is *ca.* 6.5×10^{-2} *M* sec^{-1} at 25°.[3] That for **1** might be expected to be several powers of ten slower, which places it at the same order of magnitude as the observed conductometric rate (Table I).



In order to obtain additional evidence with regard to the rate-determining step the reaction of **1** with piperidine was studied in the presence of methoxide ion. The rate of proton abstraction by methoxide ion from **8** is

(2) Additional evidence for the intermediacy of **4** is provided by the observation that the spectrophotometric rate for **1** is the same as that for the reaction of 3-halomethylbenzo[*b*]thiophene 1,1-dioxides (**8**) with piperidine in methanol, where **5** is also the product. The intermediate **4** was also isolated in this reaction; its nmr spectrum agreed with that described herein.[3]

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

(4) Average values for $k_{Br}:k_{Cl} \cong 50:1$ and $k_I:k_{Br} \cong 4:1$: A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., New York, N. Y., 1962, p 29.

about 250 times that by piperidine.[3] If proton abstraction from **1** is rate determining, addition of methoxide ion should lead to a marked increase in rate. Titrimetric rate constants for the reaction of **1** with piperidine in benzene with and without added methoxide ion are summarized in Table III.

TABLE III

TITRIMETRIC RATES FOR THE REACTION OF 2-HALO-3-METHYLBENZO[*b*]THIOPHENE 1,1-DIOXIDE (**1**) WITH PIPERIDINE IN METHANOL AT 50°

Halide (X)[a]	$[C_5H_{10}NH]$, M	$[MeO^-]$, M	k, M^{-1} sec^{-1} [b]
Cl	0.1092	...	$8.7 \pm 0.5 \times 10^{-4}$
Cl	0.04775	0.075	$1.4 \pm 0.1 \times 10^{-3}$
Br	...	0.10	9.4×10^{-4}
Br	0.01910	0.037	1.00×10^{-2}
	0.03820	0.075	1.08×10^{-2}
	0.3350	0.090	1.13×10^{-2}
		Av	$1.07 \pm 0.05 \times 10^{-2}$
Br	0.06767	0.13	$(1.07 \pm 0.06 \times 10^{-2})$[c]

[a] The halide concentration was about 10^{-3} M in each instance. [b] Calculated from the pseudo-first-order constant by dividing by the piperidine concentration. [c] Spectrophotometric rate.

Examination of Table III shows that inclusion of 0.075 M sodium methoxide caused a 61% increase in the titrimetric rate constant for chloride **1**. (The titrimetric rate constant is in reasonably good agreement with the conductometric rate constant, which is 8.1×10^{-4} M^{-1} sec^{-1} at 50°.) The titrimetric rate constant for bromide **1** is seen to be independent of methoxide concentration.

The fact that only a 61% increase in rate for chloride **1**, rather than a several-hundred-fold increase, occurs on addition of methoxide ion shows that equilibration of **1** and **2** must be nearly complete even in the presence of the much weaker base piperidine. Therefore, in the absence of methoxide ion, the conductometric (and titrimetric) rate constants are essentially equal to Kk_2, where K is the equilibrium constant for **1** $\rightleftarrows$ **2**. On the other hand, the spectrophotometric rate constant is determined primarily by k_4, the rate constant for the removal of a proton from **4** by piperidine to give carbanion **4a**. According to this analysis inclusion of methoxide ion should greatly accelerate the conversion of **4** into **4a**, and this step should no longer be rate determining. Indeed, it was found that in the presence of 0.13 M sodium methoxide the spectrophotometric rate constant for the reaction of bromide **1** with piperidine in methanol at 50° was 1.07×10^{-2} M^{-1} sec^{-1} (Table III) compared with 3.2×10^{-4} M^{-1} sec^{-1} at 45° in the absence of methoxide ion (Table II). Furthermore, in the presence of methoxide ion the titrimetric and spectrophotometric rates for bromide **1** were equal (Table III). These results clearly establish the pathway

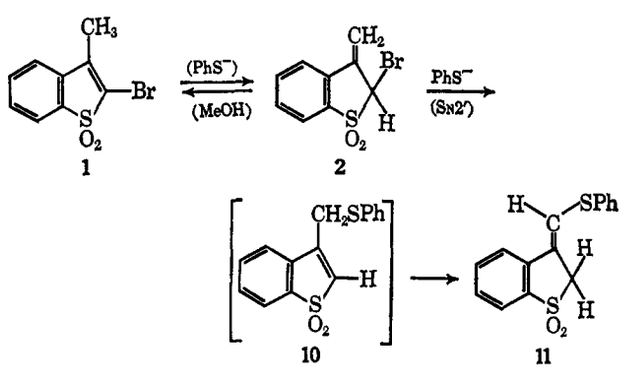
$$1 \rightleftarrows 2 \xrightarrow{k_2} 3 \longrightarrow 4 \xrightarrow{k_4} 5$$

for the reaction of **1** with piperidine in methanol, with k_2 being rate determining for halide loss and k_4 being rate determining for product formation.

A further point of interest is that inclusion of methoxide ion did not lead to the formation of a methyl ether. Instead, **5** remained as the product, even when the molar concentration of methoxide ion to piperidine was 2:1. This shows that piperidine must be at least one hundred times more effective as a nucleophile in attacking **2** in an SN2′-type reaction than is methoxide ion.

The relative rates of release of halide ion from **1**, as judged by the conductometric rate constants (Table I), are Cl:Br:I = 1.0:2.9:1.6. These leaving group effects are a composite, however, of the equilibrium constants for **1** $\rightleftarrows$ **2** and the k_2 values for the various halides **2** (X = Cl, Br, or I). The equilibrium constants for a somewhat analogous system, **8** $\rightleftarrows$ **9**, have been measured. Here the relative per cents of allylic halides (**8**) present at equilibrium are Cl:Br:I = 5.4:11:34.[3] Assuming comparable values for the **1** $\rightleftarrows$ **2** equilibria and correcting the k_{obsd} values gives relative k_2 values for Cl:Br:I of 1.0:1.4:0.25. Clearly, the leaving group effects for the conversion of **2** into **3** by abnormal allylic displacements are much smaller than for comparable SN2 displacements.[4-6]

Reaction of **1** with sodium thiophenoxide in methanol results in the formation of a product (**11**) having a structure analogous to that of **5**.[7,8] This product is no doubt formed in a comparable manner.



1 **2** **10** **11**

Discussion

The failure of appearance of vinylic hydrogens characteristic of **2** in the nmr spectrum during the reaction of **1** with piperidine is not surprising since the equilibrium should strongly favor **1**. The α,β-unsaturated isomer is favored for 3-methyldihydrothiophene 1,1-dioxide (92:8),[9] and the same is true for 3-methylbenzo[*b*]thiophene 1,1-dioxide. For the latter the equilibrium appears to be *ca.* 3:1.[3] By analogy with the equilibrium **8** $\rightleftarrows$ **9**, the presence of the halogen should favor **1** over **2** by an additional factor (about 95:5 for the chloride and about 90:10 for the bromide). The equilibrium **1** $\rightleftarrows$ **2** should, then, favor **1** by a factor of over 50:1 for the chloride and over 25:1 for the bromide. This places the value of k_2, the SN2′ displacement rate of **2** with piperidine in methanol, at *ca.* 7×10^{-2} M^{-1} sec^{-1} for the chloride at 50° and *ca.* 2.7×10^{-1} M^{-1} sec^{-1} for the bromide ($k_{obsd} \times K$ in Table II). Comparison of

(5) F. G. Bordwell, P. E. Sokol, and J. D. Spainhour [*J. Amer. Chem. Soc.*, **82**, 2881 (1960)] reported a normal Br:Cl leaving group effect in an SN2′ reaction, but this conclusion was invalidated by later results.[1]

(6) N. H. Cromwell, unpublished results privately communicated, has found a small Br:Cl ratio for an SN2′ reaction of a similar type in which the activating group is carbonyl rather than sulfonyl.

(7) The product was originally believed to be 3-methyl-2-phenylthiobenzo[*b*]thiophene 1,1-dioxide,[8] but later work showed that this structure assignment was incorrect.[1]

(8) F. G. Bordwell, F. Ross, and J. Weinstock, *J. Amer. Chem. Soc.*, **82**, 2878 (1960).

(9) D. E. O'Conner and W. I. Lyness, *ibid.*, **86**, 3840 (1964).

these values with those for analogous SN2′ reactions will be made in the next paper in this series and the mechanism will be discussed therein.

Experimental Section

Reaction of 2-Bromo-3-methylbenzo[b]thiophene 1,1-Dioxide (1, X = Br) with Piperidine in Absolute Methanol in the Presence of Sodium Methoxide.—To a solution of 259.1 mg (1.00 mmol) of 1 (X = Br) in 10 ml of absolute methanol there was added 341 mg (4.00 mmol) of piperidine and 432 mg (8.00 mmol) of sodium methoxide. The mixture was refluxed 1 hr. Cooling to room temperature and filtering gave 160.6 mg (64.1%) of yellow needles, mp 178.8–181.8°; a mixture melting point with authentic 5[3] was undepressed.

Kinetic Procedures.—Piperidine solutions were prepared from freshly distilled reagent grade piperidine (bp 106°) and standardized by titrating with potassium biphthalate, using a pH meter to determine the end point.

A. Conductometric Determination.—An appropriate weight of halide was placed in one arm of a Y-shaped conductance cell, and dissolved in a known volume of absolute methanol, delivered by volumetric pipet. An appropriate volume of standard piperidine solution was then delivered into the other arm by volumetric pipette. After allowing 20 min for temperature equilibration in a bath controlled to ±0.05° with a thermoregulator, the contents of the two arms were thoroughly mixed and drained into the arm containing the platinized platinum electrodes. The resistance of the solution was then recorded as a function of time.

A plot of log $(R_t/R_t - R_\infty)$ *vs.* time gave straight lines. The slope of the line times 2.303 gave the pseudo-first-order rate constant. The second-order rate constants were then obtained by dividing the pseudo-first-order rate constants by the piperidine concentration. The infinity point was chosen to be between ten and twelve half-lives. For the Guggenheim procedure, the time interval was chosen to be about two to three half-lives. A plot of log $(1/R_{\Delta t} - 1/R_t)$ *vs.* time gave straight lines. Second-order rate constants were then derived from the slope of the line, as described above.

B. Spectrophotometric Determination.—Solutions of twice the desired concentration of halide and piperidine were placed in separate arms of a Y-shaped cell. After allowing 20 min for temperature equilibration in a water bath at 45.0°, the contents of the arms were thoroughly mixed. At appropriate times, 1.00-ml aliquots were withdrawn and diluted to 25.00 ml with absolute methanol. The absorbances of these solutions at 324 mμ were then determined in a Beckman DU spectrophotometer.

Alternatively, 3-ml samples of standard piperidine solutions were equilibrated in the spectrophotometer cuvettes contained in a thermostated cell holder. A 20–50-μl sample of halide solution was then added and the change of absorbance was followed with time.

A plot of log $(D_\infty/D_\infty - D_t)$ *vs.* time gave straight lines. The infinity point was chosen to be between ten and twelve half-lives. The second-order rate constants were then calculated from the slope of the line as described above.

C. Titrimetric Determinations.—Standard solutions of piperidine (100 ml) in 250-ml volumetric flasks with Teflon screw caps were equilibrated 1 hr in a bath controlled to ± 0.02° with a thermoregulator. Halide solutions were prepared by weighing appropriate amounts and dissolving these samples in 25 ml of the desired solvent. Portions (4–10 ml) of the halide solutions were added to the standard piperidine solutions and mixed thoroughly. Aliquots were withdrawn, quenched with 10 ml of 0.25 *M* HNO_3, and titrated with 1.5×10^{-3} *M* silver nitrate solution, using an autotitrator. The volume of titrant was then recorded as a function of time.

A plot of $\log(V_\infty - V_t)$ *vs.* time gave straight lines. The slope of the lines times 2.303 gave the pseudo-first-order rate constant. The second-order rate contants were then obtained by dividing the first-order rate constants by the piperidine concentration. The infinity point was chosen to be at ten or more half-lives.

Registry No.—1 (X = Br), 16934-26-2; 1 (X = Cl), 16934-27-3; 1 (X = I), 16934-28-4; piperidine, 110-89-4; 5, 16934-29-5.

Acknowledgment.—This investigation was supported by the Public Health Service Research Grant No. CA-07351 from the National Cancer Institute.

Rates of SN2′ and SNi′ Rearrangements in 3-(α-Haloalkyl)benzo[b]thiophene 1,1-Dioxides[1]

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Rate constants have been determined for the reactions of 3-(α-chloroethyl)- and 3-(α-chloro-α-methylethyl)-benzo[b]thiophene 1,1-dioxides (**1a** and **1b**, respectively) with piperidine in benzene. For **1a** the rate of (enamine) product formation (spectrophotometric rate) is slower than the rate of chloride release (titrimetric rate) indicating that the SNi′ type of rearrangement is rate determining. This kinetic analysis predicts formation of an intermediate, and evidence is presented to show that such is formed. For **1b** the rate of (enamine) product formation is equal to the rate of halide release indicating that in this instance the SN2′ step, rather than the SNi′ step, is rate determining.

In a previous paper the reaction of secondary and tertiary chlorides **1a** and **1b** with piperidine in benzene was shown to give the enamines **5a** and **5b**, respectively. The suggested pathway involved intermediates **2**, **3**, and **4**.[2] The present paper provides additional experimental evidence for this route and considers the mechanisms of two of the steps in some detail.

The kinetics of the reaction of **1a** and **1b** with excess piperidine in benzene were examined under pseudo-first-order conditions by following the rates of release of chloride ion (titrimetric rates) and the rates of formation of enamines **5a** and **5b** (spectrophotometric rates). The results are summarized in Tables I and II.

Examination of Tables I and II reveals that for tertiary chloride **1b** the titrimetric and spectrophotometric rates are equal within experimental error. In terms of the suggested reaction scheme this requires that the abnormal allylic displacement (**1b** → **2b**) be rate determining and that the rearrangement steps (**3b** → **4b** → **5b**) be rapid. (Proton removal from **2b** to give **3b** is expected to be fast.) Variation of the piperidine con-

(1) 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, R. W. Hemwall, and D. A. Schexnayder, *J. Org. Chem.*, **33**, 3233 (1968).