neutral equivalent of the substance indicate it to be 2,2',4-tricarboxybiphenyl (II), a previously unreported compound.

Anal. Calcd. for $C_{15}H_{10}O_6$: C, 62.9; H, 3.5; neut. equiv., 95.4. Found: C, 62.4; H, 3.8; neut. equiv., 94.3.

2.—Different results were obtained when a sodium hypochlorite solution with a *p*H of about 10 (the *p*H of a 5% solution of the salt) was employed. The ketone (3.0 g.) and 400 ml. of the hypochlorite solution were refluxed under nitrogen for 9 hours. On cooling, a sodium salt precipitated which, on acidification, yielded 1.0 g. of 9,10-dihydrophenanthrene-2-carboxylic acid, m.p. 215.0–216.5°. Acidification of the aqueous solution yielded a mixture of acids weighing 1.0 g. Recrystallization from 50% acetic acid yielded another 0.3 g. of 9,10-dihydrophenanthrene-2-carboxylic acid, m.p. 215.0–216.5°, and 0.3 g. of the tricarboxybiphenyl, m.p. 262–268°.

Oxidation of 9,10-Phenanthrenequinone.—The quinone (4.0 g.) and 500 ml. of sodium hypochlorite solution were refluxed under nitrogen for 22 hours. The hot solution was treated with sodium bisulfite and acidified. Chilling the solution caused 1.70 g. of lustrous white crystals to precipitate. The aqueous solution was saturated with salt and extracted with ether. The extracts contained 2.61 g. of the product. The total, 4.31 g., constituted a 94% yield of crude diphenic acid, m.p. 219–222°. After recrystallization from water, the acid melted sharply at 220–221°.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.12; H, 4.13.

Oxidation of Benzil.—A mixture of benzil (5.0 g.) and 300 ml. of sodium hypochlorite solution were gently refluxed under nitrogen for 20 hours. The excess hypochlorite was destroyed and the solution acidified. There resulted 5.1 g. (88% yield) of benzoic acid (m.p. 121–122°, mixed m.p. 121–122°).

Oxidation of 6-Acetyltetralin.—6-Acetyltetralin (22.0 g.) and 0.58 *N* sodium hypochlorite (prepared by bubbling chlorine into 3 liters of water containing 260 g. of sodium hydroxide) were stirred under nitrogen at 86° for 14 hours. Acidification of the reaction mixture precipitated 3.9 g. of white crystals which were dissolved in benzene and percolated over silica gel using acetone as the eluent. The solid was then recrystallized from ethanol–water and shown to be the normal oxidation product, 6-tetralincarboxylic acid; calcd. neut. equiv. for $C_{11}H_{12}O_2$ 176, found 170; m.p. 153–156°, reported 154–155°.

Ether extraction of the acidified reaction mixture yielded 16.8 g. of a tan solid. Chromatographic treatment of the solid over silica gel using chloroform–acetone and then acetone as the eluents showed that two products other than the tetralincarboxylic acid were formed. They are 3-(2,4-dicarboxyphenyl)-propanoic acid (IV) and an isomer believed to be 3-(2,5-dicarboxyphenyl)-propanoic acid (V). The latter is the predominant product.

Anal. Calcd. or reported for $C_{11}H_{10}O_6$: C, 55.5; H, 4.2; neut. equiv., 79.4; m.p. 265–266° (for the 2,4-isomer; m.p. of 2,5-isomer is unknown). Predominant isomer: Found: C, 55.3; H, 4.4; m.p. 230–232°; neut. equiv., 80.1. Other isomer: Found: C, 55.2; H, 4.5; m.p. 251–257°.

Oxidation of *p*-Ethylacetophenone.—*p*-Ethylacetophenone (5.0 g.) and 800 ml. of sodium hypochlorite solution were refluxed gently under nitrogen for 44 hours. After destruction of the excess hypochlorite, acidification of the solution produced 5.24 g. (95% yield) of terephthalic acid.

Anal. Calcd. for $C_8H_6O_4$: C, 57.8; H, 3.64; neut. equiv., 83.1. Found: C, 57.5; H, 3.69; neut. equiv., 84.5.

The acid was identified further through its dichloride, prepared from the acid and phosphorus pentachloride; m.p. 77.5–79° reported m.p. 79–80°.

Oxidation of *m*- and *p*-Methylacetophenone.—The methylacetophenone (5.0 g.) and 800 ml. of sodium hypochlorite solution were treated exactly as described in the above experiment. The oxidation of the *m*-methylacetophenone yielded 0.8 g. (13% yield) of isophthalic acid while the *p*-isomer yielded 2.9 g. (47% yield) of terephthalic acid. The acids were identified by means of their dichlorides.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

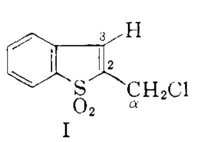
S_N2 and S_N2' Reactions of 2- and 3-Chloromethylbenzothiophene 1,1-Dioxides

BY F. G. BORDWELL, FRANK ROSS AND JOSEPH WEINSTOCK

RECEIVED MAY 20, 1959

The reactions of piperidine, thiourea and sodium thiophenoxide with 2-chloromethylbenzothiophene 1,1-dioxide (I) were found to be normal S_N2 displacements, but 3-chloromethylbenzothiophene 1,1-dioxide (II) was attacked by these reagents, and also by morpholine at the $C_2{=}C_3$ bond. The latter are the only known examples in which a primary allylic halide has been found to react with nucleophilic reagents by an S_N2' mechanism.

This study was initiated several years ago[1] on the basis that substitution of the strongly electron-attracting sulfonyl group[2] into the *β*- or *γ*-position of an allylic system, $\overset{\gamma}{C}{=}\overset{\beta}{C}{-}\overset{\alpha}{C}{-}X$, would probably reduce the electron density of the C=C bond, and thereby favor reaction of nucleophilic reagents at the *γ*-position resulting in reactions by S_N2' mechanisms. The 2- and 3-chloromethylbenzothiophene 1,1-dioxides (I and II) appeared to be compounds of the desired type. Earlier studies have shown that the $C_2{=}C_3$ bond in benzothiophene 1,1-dioxide is aliphatic in nature.[3] The allylic systems present in I and II are unique in that activation by the sulfonyl group in each can operate from a *β*- and/or a *γ*-position. Thus in I the sulfonyl group is attached to the *β*-carbon, but it can also exert its influence from the *γ*-position by operating through the benzene ring; the situation is just reversed for II.



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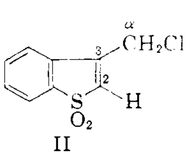

II

The desired chloromethyl sulfones I and II were readily prepared by the peracetic acid oxidation of the previously known 2-chloromethyl-[4] and 3-

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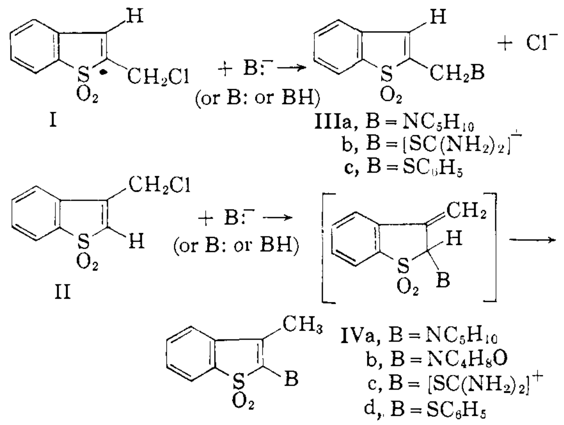
(1) An account of the work described in this paper was given at the 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953; see Abstracts, p. 60-O.

(2) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **73**, 5187 1951).

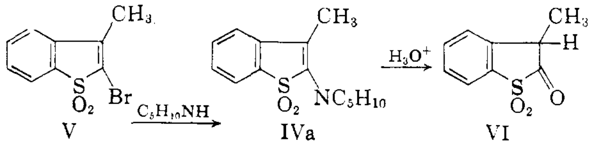
(3) F. G. Bordwell and W. H. McKellin, *ibid.*, **72**, 1985 (1950).

(4) F. F. Blicke and D. G. Sheets, *ibid.*, **71**, 2856 (1949).

chloromethylbenzothiophenes.[5] The reactions of I with piperidine, thiourea and sodium thiophenoxide and of II with these reagents and also morpholine are described herein. With each of the nucleophilic reagents compound I underwent simple S$_N$2 displacements whereas II in every instance gave products in which the reagent attacked the γ-position. The products from the latter reactions are formulated as arising by S$_N$2′ displacements followed by tautomerism.



The structures of IVa (B = NC_5H_{10}) and IVb (B = NC_4H_8O) were established: (1) by synthesis from 2-bromo-3-methylbenzothiophene 1,1-dioxide (V), (2) by acid hydrolysis to a highly reactive ketone (VI, isolated as its 2,4-dinitrophenylhydrazone), and (3) through their ultraviolet absorption spectra.



Reaction of V with piperidine to give IVa is expected by analogy with the behavior of 3-bromobenzothiophene 1,1-dioxide under these conditions.[6] The hydrolysis of IVa in acid medium to VI is comparable to the conversion of 3-piperidinobenzothiophene 1,1-dioxide to 3-keto-2,3-dihydrobenzothiophene 1,1-dioxide.[6] Little is known concerning the behavior of α-keto sulfones,[7] but one would expect the carbonyl group to be highly susceptible to attack by nucleophilic agents (compare α-diketones), and to be readily cleaved. Hydrolysis of IVa in the presence of 2,4-dinitrophenylhydrazine or semicarbazide gave high yields of the carbonyl derivatives of VI, but difficulty was encountered in attempts to isolate VI or its hydrolysis products in pure form.

Replacement of hydrogen on the benzene nucleus by NR_2, SR or OR groups results in strong bathochromic shifts of the high intensity benzene absorption maxima.[8] Similar shifts in absorption maxima would be expected for substitution at the 2- or 3-positions in the benzothiophene 1,1-dioxide nucleus. Realization of this expectation is demonstrated in Table I for several such compounds.

TABLE I

ULTRAVIOLET ABSCRPTION MAXIMA OF 2- AND 3-SUBSTITUTED BENZOTHIOPHENE 1,1-DIOXIDES

Benzothiophene 1,1-dioxide	Substituents 2-	3-	λ_{max}, mμ	log ϵ λ_{max}
	H	H	220	4.48
	H	CH_3	220	4.45
	H	NC_5H_{10}	252	4.04
	CH_3	H	222	4.37
I	CH_2Cl	H	225	4.49
IIIa	$CH_2NC_5H_{10}$	H	224	4.60
IIIb	$CH_2SC^+(NH_2)_2Cl^-$	H	225	4.50
IIIc	$CH_2SC_6H_5$	H	224	4.42
II	H	CH_2Cl	222	4.43
IVa	NC_5H_{10}	CH_3	325	4.44
IVc	$SC^+(NH_2)_2Cl^-$	CH_3	287	4.33
IVd	SC_6H_5	CH_3	315	4.36

From Table I it will be noted that the position of λ_{max} for 2-methylbenzothiophene 1,1-dioxide (222 mμ) remains essentially unchanged by replacement of a hydrogen of the methyl group by Cl, NC_5H_{10}, $SC^+(NH_2)_2$ or SC_6H_5 groups. This is expected since the methylene group insulates the C=C bond from the effect of these groups. The spectra of the products from I and nucleophilic reagents are therefore consistent with the assumed S$_N$2 displacement. Similarly, replacement of a hydrogen of the methyl group of 3-methylbenzothiophene 1,1-dioxide by chlorine (to give II) causes little effect in the position of λ_{max} (222 instead of 220 mμ). Simple S$_N$2 displacement of the chlorine in II should then lead to products with λ_{max} in the 220–225 mμ region. Instead, the products (IVa, IVc, IVd) have absorption maxima at much longer wave lengths (287–325 mμ). This supports the structures assigned for these compounds in which it has been assumed that the NC_5H_{10}, $\overset{+}{S}C(NH_2)_2$ and SC_6H_5 groups are conjugated with C=C. These products are believed to arise by S$_N$2′ displacement followed by tautomerism.

The absence of bands in the 287–325 mμ region for the products from I indicates that little or no S$_N$2′ displacement accompanies the S$_N$2 displacements with piperidine, thiourea and thiophenol. The high yield of product from II and thiourea or sodium thiophenoxide indicates that the S$_N$2′ reaction in this instance is also clean. With II and piperidine the yield of isolated product was lower, but, judging from the absorbancy at 325 mμ for the crude product, the yield is actually at least 81%. A similar check at 287 mμ for the crude thiouronium salt from II shows at least 92% of yield S$_N$2′ product.

Before concluding that abnormal products have arisen by S$_N$2′ mechanisms it is necessary to make sure: (1) that the halides have not rearranged prior to reaction, (2) that initially formed S$_N$2 products have not rearranged subsequently to S$_N$2′ products, and (3) that the reaction is first order in halide and nucleophile.[9]

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[5] W. J. King and F. F. Nord, *J. Org. Chem.*, **13**, 635 (1948).

[6] F. G. Bordwell and C. J. Albisetti, THIS JOURNAL, **70**, 1558 (1948).

[7] E. P. Kohler and his students prepared a number of α-keto sulfones [see E. P. Kohler and M. B. MacDonald, *Am. Chem. J.*, **22**, 219 (1899)], but this work apparently has never been published.

[8] L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947).

[9] R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 769 (1956).

Halide II is inert to solvolysis, which is not surprising in view of the presence of the strongly electron-withdrawing sulfonyl group; therefore rearrangement of II prior to the SN2′ reaction is ruled out (also, 2-bromo-3-methylbenzothiophene 1,1-dioxide, the bromine analog of the probable rearrangement product, is inert to thiourea). The possibility that II reacts by a normal SN2 process and that the product thus formed rearranges to the observed SN2′ product is highly unlikely, since the inertness of II to solvolysis mitigates against such rearrangements of an SN2 product. Furthermore, the SN2 products from I are stable under these conditions, which makes it highly unlikely that the similarly constituted SN2 products from II would rearrange, once formed. The kinetics for the reactions of I and II with thiourea are described in the accompanying paper.

From the yield data we judge that the SN2′ reaction of II with piperidine, thiourea and thiophenoxide predominates over the SN2 reaction by a factor of at least ten to one. This is of particular interest since, to our knowledge, this is the only primary allylic halide in which the SN2′ reaction is favored over SN2. We believe that the strong electron-withdrawing effect of the sulfonyl group in II permits easy access to the C=C bond, and makes attack of the nucleophile as feasible by SN2′ as by SN2 mechanisms. This point will be discussed further in the next paper.

Experimental

2-Chloromethylbenzothiophene 1,1-Dioxide.—To a solution of 24.4 g. (0.134 mole) of crude 2-chloromethylbenzothiophene[4] in 100 ml. of glacial acetic acid there was slowly added with cooling 70 ml. of an acetic acid solution of 6.3 *N* peracetic acid (0.44 mole). After standing overnight at room temperature the reaction mixture was poured onto an equal volume of washed ice, the solid thus formed was filtered, washed with cold water, and dried in a steam-oven. This gave 26.9 g. (93%) of a white product, m.p. 102–109°. Two recrystallizations from benzene–hexane gave white crystals, m.p. 109–110°.

Anal. Calcd. for $C_9H_7SO_2Cl$: C, 50.35; H, 3.29. Found: C, 50.37; H, 3.33.

3-Chloromethylbenzothiophene 1,1-Dioxide.—To a solution of 36.5 g. (0.2 mole) of 3-chloromethylbenzothiophene[5] in 150 ml. of glacial acetic acid there was slowly added 100 ml. of 40% peracetic acid while the reaction mixture was kept at room temperature by cooling with ice. After 24 hours the product was obtained by adding one liter of cold water, filtering and washing with cold water. On drying in a steam-oven 39.4 g. (91.8%) of a white product, m.p. 122.5–124.5°, was obtained. On recrystallization from methanol white crystals were obtained, m.p. 125–127.5°.

Anal. Calcd for $C_9H_7O_2SCl$: C, 50.35; H, 3.29. Found: C, 50.72; H, 3.57.

2,3-Dibromo-2,3-dihydro-3-methylbenzothiophene 1,1-Dioxide.—To a suspension of 5.15 g. (0.029 mole) of 3-methylbenzothiophene 1,1-dioxide[10] in 50 ml. of carbon tetrachloride there was added 4.95 g. (0.031 mole) of bromine and the mixture shaken for one-half hour. The reaction mixture was then made homogeneous by the addition of 15 ml. of methanol and then allowed to stand at room temperature for 2 hours. Evaporation of the excess bromine and solvent followed by the addition of methanol and chilling gave 7.19 g. (77.5%) of product, m.p. 105–116°. Two recrystallizations from methanol gave white crystals, m.p. 116–117° and then 119–120°.

Anal. Calcd. for $C_9H_8O_2SBr_2$: C, 31.79; H, 2.37. Found: C, 31.83; H, 2.63.

2-Bromo-3-methylbenzothiophene 1,1-Dioxide.—To a solution of 4.2 g. (0.051 mole) of sodium acetate dissolved in a mixture of 50 ml. of methanol, 3 ml. of water and 35 ml. of acetone there was added 4.79 g. (0.0141 mole) of 2,3-dibromo-2,3-dihydro-3-methylbenzothiophene 1,1-dioxide. The solvent was slowly evaporated to near dryness on a steam-bath and then 70 ml. of cold water added. This gave 3.54 g. (97%) of white crystals, m.p. 154–159°. Recrystallization from methanol gave white crystals, m.p. 157–158°.

Anal. Calcd. for $C_9H_7O_2SBr$: C, 41.71; H, 2.71. Found: C, 41.77; H, 2.95.

Reactions of Nucleophilic Reagents with 2-Bromo-3-methylbenzothiophene 1,1-Dioxide. (a) Piperidine.—A solution of 12.96 g. (0.05 mole) of 2-bromo-3-methylbenzothiophene 1,1-dioxide and 30 ml. (0.30 mole) of piperidine in 100 ml. of benzene was heated under reflux for 2.25 hours. After removing the precipitated piperidine hydrobromide (7.5 g., 90%), the benzene solution was evaporated to small volume on a steam-bath and chilled to yield 11.4 g. (86%) of a yellow product, m.p. 172–177°. Recrystallization from methanol and acetone–water gave yellow needles, m.p. 179.5–180.5°.

Anal. Calcd. for $C_{14}H_{17}O_2NS$: C, 63.85; H, 6.41; N, 5.32. Found: C, 64.08; H, 6.37; N, 5.34.

Refluxing the same quantities of reactants in 400 ml. of absolute ethanol for 2 hours gave a quantitative yield of product, m.p. 172–180°.

Hydrolysis of the product was accomplished by heating a solution containing 0.65 g. (0.0025 mole) with 5 ml. of 6 *N* sulfuric acid on a steam-bath for 20 minutes. To this was then added a freshly prepared solution of 0.5 g. (0.0025 mole) of 2,4-dinitrophenylhydrazine in 2.2 ml. of concentrated sulfuric acid and 3.5 ml. of water. There resulted 0.86 g. (91.5%) of a yellow product, m.p. 222–227° dec. Three recrystallizations from nitromethane gave a yellow product, m.p. 239°, which is the **2,4-dinitrophenylhydrazone of 2-keto-3-methyl-2,3-dihydrobenzothiophene 1,1-dioxide.**

Anal. Calcd. for $C_{15}H_{12}O_6N_4S$: C, 47.87; H, 3.21; N, 14.89. Found: C, 48.16; H, 3.28; N, 14.90.

(b) **Morpholine.**—A solution of 5.88 g. (0.023 mole) of 2-bromo-3-methylbenzothiophene 1,1-dioxide in 40 ml. of benzene was heated under reflux for 18 hours with 10 ml. (0.115 mole) of morpholine. Evaporation of the solvent gave a yellow oil which on washing with water gave 5.60 g. (91%) of a yellow product, m.p. 195–222° dec. Recrystallization from methanol, benzene and absolute ethanol gave yellow crystals, m.p. 223–224°.

Anal. Calcd. for $C_{13}H_{15}O_3NS$: C, 58.85; H, 5.70; N, 5.28. Found: C, 59.25; H, 5.74; N, 5.03.

Hydrolysis of this product was accomplished by heating 0.5 g. with 10 ml. of 6 *N* hydrochloric acid on a steam-bath for 20 minutes. On treatment with 2,4-dinitrophenylhydrazine in the manner described above, 0.68 g. (92%) of a yellow product was obtained, m.p. 236–238°, undepressed on admixture of the product obtained from the acid-catalyzed hydrolysis of the piperidino compound.

(c) **Sodium Thiophenoxide.**—A solution containing 1.30 g. (0.005 mole) of 2-bromo-3-methylbenzothiophene 1,1-dioxide, 0.4 g. (0.01 mole) of potassium hydroxide and 1.5 g. (0.02 mole) of thiophenol in 20 ml. of methanol was refluxed on a steam-bath for one hour. On cooling and adding water 1.17 g. (81%) of white crystals, m.p. 150–165°, was obtained. Recrystallization from ethanol gave white needles, m.p. 165–167°.

Anal. Calcd. for $C_{15}H_{12}S_2O_2$: C, 62.48; H, 4.20. Found: C, 62.47; H, 4.37.

(d) **Thiourea.**—No reaction could be detected when equivalent amounts of thiourea and 2-bromo-3-methylbenzothiophene 1,1-dioxide in alcohol were refluxed for two hours as evidenced by melting points and mixed melting points of the recovered materials.

Reactions of 3-Chloromethylbenzothiophene 1,1-Dioxide with Nucleophilic Reagents. (a) Piperidine.—A solution of 2.15 g. (0.01 mole) of 3-chloromethylbenzothiophene 1,1-dioxide, 1.70 g. (0.02 mole) of piperidine and 15 ml. of benzene was refluxed for two hours. Cooling and filtration gave 1.2 g. (100%) of piperidine hydrochloride. Evaporation of solvent under a stream of air afforded an oil which on recrystallization from methanol yielded 1.2 g. (45%) of yellow crystals, m.p. 175–180° undepressed on admixture

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[10] E. G. Werner, *Rec. trav. chim.*, **68**, 509 (1949).

with the compound prepared from 2-bromo-3-methylbenzothiophene 1,1-dioxide. Concentration of the mother liquors afforded an additional 0.1 g., m.p. 170–178°, to raise the yield to 49%.

In a subsequent experiment carried out in absolute ethanol as solvent an aliquot was withdrawn, diluted to the appropriate volume and the absorbance at 325 mμ was observed in a Beckman DU spectrophotometer using in the reference cell an ethanolic piperidine solution of comparable piperidine concentration. The observed absorbance corresponded to a yield of 81% of 2-piperidine-3-methylbenzothiophene 1,1-dioxide (IVa).

(b) **Morpholine.**—A solution of 2.15 g. (0.01 mole) of 3-chloromethylbenzothiophene 1,1-dioxide and 5 ml. (0.06 mole) of morpholine in 20 ml. of benzene was heated under reflux for one hour. Evaporation of the solvent followed by washing the residue with water gave a green gum which on crystallization from ethanol gave 0.68 g. (25%) of a product, m.p. 205–220°. Recrystallization from ethanol gave yellow needles, m.p. 222–224°, undepressed on admixture of 2-morpholino-3-methylbenzothiophene 1,1-dioxide prepared from 2-bromo-3-methylbenzothiophene 1,1-dioxide.

(c) **Sodium Thiophenoxide.**—To a solution of 2.15 g. (0.01 mole) of 3-chloromethylbenzothiophene 1,1-dioxide in 10 ml. of benzene was added a fourfold excess of sodium thiophenoxide in absolute ethanol aand the reaction mixture refluxed for 3 hours. The reaction mixture was cooled and poured into cold water to give 2.56 g. (89%) of a light yellow solid, m.p. 163–167°. Recrystallization from ethanol which included a decolorization with Norite A gave white needles, m.p. 165–167°, identical with the product from the reaction of sodium thiophenoxide and 2-bromo-3-methylbenzothiophene 1,1-dioxide.

(d) **Thiourea.**—A solution of 1.0 g. (0.013 mole) of thiourea and 1.0 g. (0.0038 mole) of 3-chloromethylbenzothiophene 1,1-dioxide in 20 ml. of absolute ethanol was refluxed for 2 hours. On cooling, 1.22 g. (90%) of product was obtained, m.p. 215–230°, soften 209°. Recrystallization from a benzene–methanol mixture gave white crystals, m.p. 217–222°, soften 210°.

An ethanolic solution of the product from the reaction of 3-chloromethyl compound and thiourea had an absorbance at 287 mμ corresponding to a yield of 92% of SN2' product.

Anal. Calcd. for $C_{10}H_{11}S_2O_2N_2Cl$: C, 41.30, H, 3.81. Found: C, 41.08; H, 3.77.

(e) **Attempted Solvolysis.**—It was possible to recover as much as 90% of 3-chloromethylbenzothiophene 1,1-dioxide from solutions of 95% alcohol or glacial acetic acid which had been refluxed for periods up to 5 days in length.

Reactions of 2-Chloromethylbenzothiophene 1,1-Dioxide with Nucleophilic Reagents. (a) **Piperidine.**—To a solution of 1.08 g. (0.005 mole) of 2-chloromethylbenzothiophene 1,1-dioxide in 10 ml. of benzene there was added 2.52 g. (0.03 mole) of piperidine. An immediate evolution of heat occurred. After 2 hours at room temperature the reaction mixture was filtered to yield 0.60 g. (98%) of piperidine hydrochloride. Evaporation of the filtrate to dryness followed by the addition of methanol gave 0.5 g. (40%) of product, m.p. 116–123°. Recrystallization from methanol gave white needles, m.p. 124–126°.

Anal. Calcd. for $C_{14}H_{17}O_2NS$: C, 63.85; H, 6.51; N, 5.32. Found: C, 64.34; H, 6.49; N, 5.24.

In an attempted **hydrolysis** 0.5 g. (0.002 mole) of this product dissolved in 10 ml. of 2 *N* hydrochloric acid was heated on a steam-bath for 18 hours, cooled, and neutralized with sodium hydroxide solution. This returned 0.49 g. of starting material, m.p. 123–124°, undepressed on admixture of authentic starting material.

(b) **Sodium Thiophenoxide.**—To a solution of 2.15 g. (0.01 mole) of 2-chloromethylbenzothiophene 1,1-dioxide in 10 ml. of dry benzene there was added a twofold excess of sodium thiophenoxide in absolute ethanol and the mixture refluxed for 3 hours. On cooling and adding water, 2.05 g. (71%) of product was obtained in two crops, m.p. 88–94°. Recrystallization from methanol gave white crystals, m.p. 93–95°.

Anal. Calcd. for $C_{15}H_{12}S_2O_2$: C, 62.48; H, 4.20. Found: C, 62.82; H, 4.35.

(c) **Thiourea.**—A solution of 0.5 g. (0.0025 mole) of 2-chloromethylbenzothiophene 1,1-dioxide and 0.5 g. (0.0065 mole) of thiourea in 5 ml. of benzene and 5 ml. of 95% ethanol was refluxed for 2 hours. On cooling, 0.49 g. (73%) product was obtained, m.p. 200–207° dec. Recrystallization from a methanol–benzene mixture gave white plates, m.p. 203–207° dec.

Anal. Calcd. for $C_{10}H_{11}S_2O_2N_2Cl$: C, 41.30; H, 3.81. Found: C, 41.63; H, 3.85.

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EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Effect of the Leaving Group on the Rates of SN2 and SN2' Reactions in Allylic Systems

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The rates of the displacement reaction with thiourea in methanol of the chlorides, bromides and iodides have been measured in the systems: (1) 2-halomethylbenzothiophene 1,1-dioxide (I), (2) 3-halomethylbenzothiophene 1,1-dioxide (II), (3) 3-halo-1-*p*-toluenesulfonyl-1-propene (III), (4) allyl halide and (5) *n*-propyl halide. The halides II undergo SN2' displacement, whereas the others undergo SN2 displacement. The RBr/RCl ratios for all of the allylic systems (I, II, III and the allyl halides) are in the range of 28 to 82. The high RBr/RCl ratio (79) for system II shows that this SN2' reaction, and by analogy other SN2' reactions, is concerted. The geometry of halides I and II is such that SN2 displacement can occur only by utilizing a transition state in which the C–X bond is parallel to the orbitals of the π-bond system. The fact that the energies and entropies of activation are remarkably similar for the reactions of I, II, III and the simple allylic halides indicates that allylic systems in general utilize this transition state. Experimental evidence is thereby produced for a transition state for SN2 and SN2' reactions, which has been favored by several schools on theoretical grounds.

In the previous paper in this series[1] it was suggested on the basis of product analysis that 2-chloromethylbenzothiophene 1,1-dioxide (Ia) reacts with a number of nucleophilic reagents by an SN2 mechanism, whereas 3-chloromethylbenzothiophene 1,1-dioxide (IIa) reacts with these same reagents by an SN2' mechanism. A comparison of the rates of reaction of these chlorides and the corresponding bromides and iodides with thiourea has now been made in order to gain further information concerning the course of these reactions. Extension of the study to the open-chain analog III, and comparison of the rates with those of the corresponding allyl and propyl compounds has

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[1] F. G. Bordwell, F. Ross and J. Weinstock, THIS JOURNAL, **82**, 2878 (1960).