range (Figures 1 and 2, Table III), there are some deviations at relatively high concentrations of acid, the observed values being lower than those calculated for the monomethyl phosphate II, as was observed in the periodate oxidation of quinols,[11] but not of their carboxylic esters.[13] However, for the dimethyl ester the observed values are greater than those calculated (Table II), but because of the complex equilibria it is difficult to predict the sign or magnitude of what are probably kinetic or equilibrium electrolyte effects.

Relation with Periodate Oxidations of Quinols and Their Derivatives.—The reactions of *p*-quinol or its monomethyl ether with periodic acid are much faster than those of the undissociated phosphate esters, or the corresponding carboxylic esters.[11,13] For reaction of periodic acid with *p*-quinol the second-order rate constant is 71.7 l. mol^{-1} sec^{-1} at 25°,[11] whereas for *p*-hydroxyphenyl acetate[13] it is 19.6 × 10^{-4} l. mol^{-1} sec^{-1}, and for the phosphates I and II it is 0.26 l. mol^{-1} sec^{-1}. These low reactivities of the esters can be explained in part in terms of electron withdrawal by the acetyl and phosphoryl groups. (The σ_p values follow: $^{26}CH_3CO$, +0.50, and PO_3H^-, +0.26.) In addition, decomposition of intermediates requires an extensive molecular reorganization, much more than in the decomposition of the corresponding intermediates in the oxidation of *p*-quinol. This explanation implies that formation of the periodate intermediate in the ester oxidations is reversible, with an unfavorable equilibrium constant, because it would be difficult to explain the rate constants solely in terms of the electronic effects of the phosphoryl groups upon formation of a periodate ester.

Registry No.—I, 940-75-0; II lithium salt, 39478-13-2; III, 1665-78-7; IV, 39478-14-3; dimethyl phosphite, 868-85-9.

Sulfonium Salts. VI. The Halogenation of Thiophane. Reaction Products

G. EDWIN WILSON, JR.,* AND RICHARD ALBERT[1]

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

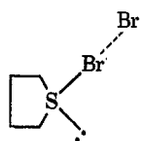
Received February 21, 1973

Bromination of thiophane in methylene chloride solution provides *trans*-2,3-dibromothiophane, isolated after methanolysis as *trans*-3-bromo-2-methoxythiophane (**3**). Chlorination of thiophane in methylene chloride solution provides 2-chlorothiophane (**10**) and 2,3-dichlorothiophane (**11**) identified after methanolysis as 2-methoxythiophane (**9**) and *trans*-3-chloro-2-methoxythiophane (**10**). The nmr spectrum of **3** suggests a highly favored conformation in solution with the substituents disposed diaxially on the thiophane ring.

The bromination of diethyl sulfide to produce unidentified fuming oils was described by Rathke in 1869.[2] The reaction was investigated by others, who obtained α-halo sulfides[3] and α,β-unsaturated sulfides[4] using a variety of halogenating agents. In some cases halogenation led to rupture of the carbon–sulfur bond with subsequent reactions ensuing from the sulfenyl halide generated.[3,5] In most cases such fragmentation appeared to be favored over α-substitution because decomposition of the halosulfonium salt intermediate could lead to a stable carbonium ion. We considered that a comparison of the results for halogenations of thiophanes with those of oxathiolanes[5a] would help in evaluating the importance of conformational effects on α-substitution in a five-membered ring and the importance of carbonium ion stabilization as an aid to carbon–sulfur bond fragmentation. Here we report results for the halogenation of the parent compound, thiophane, which indicate that α-substitution can be highly favorable in five-membered, sulfur-containing rings.

Results and Discussion

Bromination.—Bromination of thiophane in cold carbon tetrachloride solution provided an orange, crystalline adduct of sulfide with bromine. Recrystallization at low temperature from methylene chloride provided crystals whose molecular structure was found to be as shown.[6]



When the bromine complex of thiophane was allowed to react with cyclohexene, *trans*-1,2-dibromocyclohexane was produced. With water, the sulfoxide was formed. In methylene chloride solution at temperatures as low as 10°, hydrogen bromide was evolved and the orange color of the solution faded to a faint yellow. Thiophane could be readily identified by vpc as a reaction product, but the remaining materials were too unstable to handle. Removal of methylene chloride

(1) (a) Taken in part from the dissertation of Richard Albert, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn. (b) NASA Trainee, 1966–1969.

(2) B. Rathke, *Justus Liebigs Ann. Chem.*, **152**, 181 (1869).

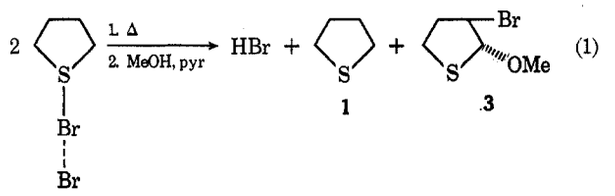
(3) For lead references, see G. E. Wilson, Jr., and M. G. Huang, *J. Org. Chem.*, **35**, 3002 (1970).

(4) H. Bohme and H. Gran, *Justus Liebigs Ann. Chem.*, **577**, 6B (1952).

(5) (a) G. E. Wilson, Jr., *J. Amer. Chem. Soc.*, **87**, 3785 (1965); (b) D. S. Tarbell and D. P. Harnish, *ibid.*, **74**, 1862 (1952); (c) D. C. Gregg, K. Hazelton, and T. F. McKeon, Jr., *J. Org. Chem.*, **18**, 36 (1953); (d) K. C. Schreiber and V. P. Fernandez, *ibid.*, **26**, 2478 (1961); (e) M. L. Wolfrom, H. G. Garg, and D. Horton, *ibid.*, **29**, 3280 (1964), and references cited therein; (f) H. Kwart and P. S. Strilko, *Chem. Commun.*, **767** (1967), and references cited therein; (g) J. M. Stewart and C. H. Burnside, *J. Amer. Chem. Soc.*, **75**, 243 (1953); (h) N. J. Leonard and G. E. Wilson, Jr., *ibid.*, **86**, 5307 (1964).

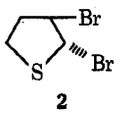
(6) G. Allegra, G. E. Wilson, Jr., E. Benedetti, C. Pedone, and R. Albert, *J. Amer. Chem. Soc.*, **92**, 4002 (1970).

at room temperature under vacuum led to decomposition of the products with evolution of hydrogen bromide. Addition of pyridine and methanol to the original reaction mixture provided pyridinium bromide and a solution containing equimolar quantities of thiophane (**1**) and an unknown methoxylated derivative (**3**) of the bromine-containing product (**2**). In subsequent experiments the hydrogen bromide was isolated as silver bromide, and the stoichiometry of the decomposition was established to be as shown in eq 1.



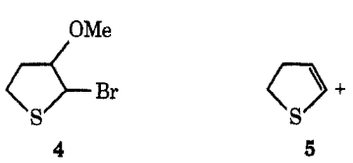
1 **3**

Spectral data for the bromination product and its methoxylated derivative were consistent with the assigned structures **2** and **3**. The nmr spectrum of **3**



2

consisted of a triplet of doublets for one proton at 4.45 (J = 3.2, 1.5 Hz), a one-proton doublet at 5.07 (J = 1.5 Hz), a three-proton singlet at 3.24, and two broad two-proton multiplets centered at 3.0 and 2.5 ppm downfield from TMS. The coupling patterns of the downfield protons and the existence of the two-proton resonance at 3.0 ppm, consistent with the normal position of methylene groups adjacent to sulfur atoms, appeared to rule out isomers other than **3** or **4**. The downfield resonances of **2** were a structured single peak at 5.02 ppm and a tightly coupled multiplet at 5.80 ppm. The mass spectral fragmentation pattern of **3** (M^+, 196, 198) showed loss of Br· (m/e 117, 95%) followed by loss of methanol (m/e 85, 100%) to give ion **5**. Alternatively, loss of the methoxy radical (m/e



4 **5**

165, 167; 41%, 40%) may have occurred first followed by loss of HBr to give ion **5**.

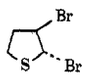
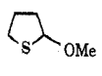
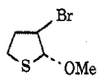
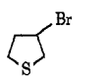
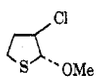
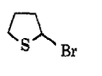
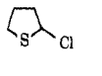
Dibromide **2** undergoes a very rapid reaction with iodide ion in DMF at room temperature to produce copious quantities of iodine. Under the conditions of the reaction, the dihydrothiophene formed apparently polymerizes. The rapidity of this reaction is noteworthy, for 1,2-dibromocyclopentane requires a reaction temperature of 75° before it reacts smoothly with iodide ion in methanol solution to produce cyclopentene.[7] We consider that this provides additional evidence for trans substitution in a rather rigid ring system (*vide infra*).

The experimental data to this point could also be reconciled with an alternative pair of structures (**6** and **7**) for the dibrominated product and the methoxyl-

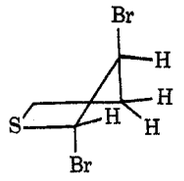
6 **7**

ated derivative, respectively;[8] however, these were eliminated from consideration when bromination of dihydrothiophene was demonstrated to produce products identical with those obtained by bromination of thiophane. Assignment of structure **3** rather than **4** is based on the high reactivity of α-halo sulfides to nucleophilic substitution reactions[9] and comparison of the chemical shifts of the methinyl protons with those of model compounds (Table I).

TABLE I
DOWNFIELD CHEMICAL SHIFTS OF METHINE PROTONS α AND β TO SULFUR IN THIOPHANES

Compd	δ in CCl4, ppm α	δ in CCl4, ppm β	Compd	δ in CCl4, ppm α	δ in CCl4, ppm β
	5.80	5.02		5.04	
	5.07	4.45			4.72
	5.03	4.45		5.63	
				5.65	

The nmr spectra of the 2-methoxy-3-halothiophanes and 2,3-dibromothiophane indicate a system with a strongly preferred conformation and they are instrumental in assigning the trans stereochemistry. If rapid and complete pseudorotation through equienergy conformations were occurring in any of these compounds, the vicinal coupling constant between the methine protons would be in the range of 5–8 Hz for either cis or trans disubstitution. The small magnitude of this coupling, 1.5 Hz in **3** and less than 1.0 Hz in 2-methoxy-3-chlorothiophane (**10**), requires that there be *highly* favored conformations restricted so that the dihedral angle between the methine protons be close to 90°. This can be true only for trans-1,2-disubstitution and only if the substituents are diaxially disposed on a thiophane ring which itself is very nearly of C_2 symmetry[10] (see structure below). In the favored conformation the dihedral angles between the β proton and both β′ protons are equal, thus explaining the triplet of doublets for the β proton.



(7) J. Weinstock, S. N. Lewis, and F. G. Bordwell, *J. Amer. Chem. Soc.*, **78**, 6072 (1956).

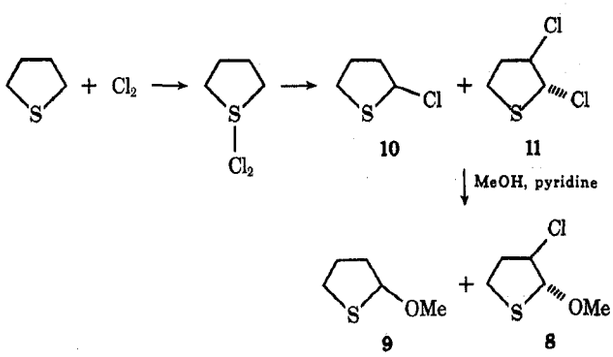
(8) G. E. Wilson, Jr., and R. Albert, *Tetrahedron Lett.*, 6271 (1968).

(9) F. G. Bordwell and W. T. Brannen, Jr., *J. Amer. Chem. Soc.*, **86**, 4645 (1964).

(10) The coupling constants are also certainly in line with that envelope conformation with the flap atom at the 2 position. This represents only a negligible distortion of the proposed most favorable conformation.

Chlorination.—Chlorination of thiophane in carbon tetrachloride produced a complex believed to be of 1:1 stoichiometry similar to that with bromine. This material is stable at −20° at pressures as low as 10^{-5} Torr, but it decomposes as it warms to room temperature with the evolution of hydrogen chloride. Decomposition ensues even when the material is formed at low temperature on the vacuum line and overlayered with an atmosphere of argon before the sample temperature is allowed to increase.[11]

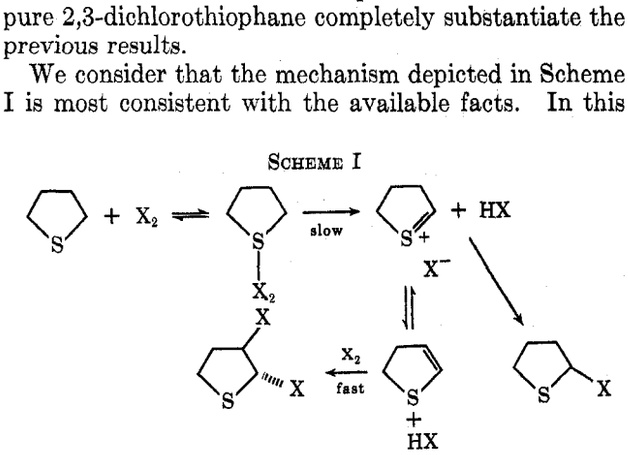
Two products in addition to thiophane were obtained when a methylene chloride solution of the chlorine complex of thiophane was warmed. These were immediately converted to methoxylated derivatives for identification. The first was identified as 2-methoxythiophane (**9**) by spectroscopic methods, and by comparison to an authentic sample generated by addition of hydrogen chloride to dihydrothiophene. The second product was identified as 2-methoxy-3-chlorothiophane (**8**) based on spectral similarities to the bromo compound **3**. Thus the precursors must be α-chlorothiophane (**10**) and 2,3-dichlorothiophane (**11**).



Bordwell and Pitt[12] suggested that **11** was produced by treatment of thiophane with sulfuryl chloride. They isolated in 2% yield a material considered to be 2-phenyl-3-chlorosulfolane (**12**), mp 154–155°, with an analysis consistent with the empirical formula $C_{10}H_{11}ClO_2S$ after treatment of the chlorinated thiophane with phenylmagnesium bromide and oxidation to a sulfone. Our results on a sample known to be almost pure 2,3-dichlorothiophane completely substantiate the previous results.

We consider that the mechanism depicted in Scheme I is most consistent with the available facts. In this

SCHEME I



context and particularly germane for synthetic applications is the fact that modification of the bromination reaction by addition of triethylamine to the reaction medium results in formation of nearly pure α-bromothiophane. We believe that the course of the bromination is altered in this way because the amine ties up the available halogen and thus retards the bromination of the dihydrothiophene.

Experimental Section[13]

1-Bromothiophanium Bromide.—To a solution of 8.8 g (0.10 mol) of thiophane in 50 ml of carbon tetrachloride at 4° was added dropwise and with stirring 16.0 g (0.10 mol) of bromine in 25 ml of cold carbon tetrachloride, causing a deposition of orange crystals. The crystals were removed by filtration, washed with cold carbon tetrachloride, and dried under vacuum: mp 80–81°; uv $\lambda_{max}^{CH_2Cl_2}$ 285 nm (ε 1800); ir ν_{max}^{KBr} 3420, 2930, 1411, 1312, 1265, 1194, and 1137 cm^{-1}; nmr ($CDCl_3$) τ 6.47 (4 H, m) and 7.59 (4 H, m); nmr (CD_3CN) τ 6.13 (4 H, m) and 7.58 (4 H, m). A satisfactory analysis could not be obtained, probably because of the instability of 1-bromothiophanium bromide at room temperature even when stored in a sealed ampoule under nitrogen or *in vacuo*. The structure was confirmed by single-crystal X-ray techniques.[6]

Reaction of 1-Bromothiophanium Bromide with Cyclohexene.—To 0.25 ml of cyclohexene in 10 ml of cold methylene chloride was added an unmeasured quantity of solid 1-bromothiophanium bromide. The solution was immediately decolorized. A sample of the solution was then injected into the vpc (20% SE-30, 9 ft × 0.25 in., Chromosorb P, 60/80 mesh) column; and the product peak corresponding to *trans*-1,2-dibromocyclohexane was identified by mixed injection with an authentic sample.

***trans*-2-Methoxy-3-bromothiophane (3).**—To a solution of 5.0 g (0.057 mol) of thiophane in 150 ml of methylene chloride at −10° was added dropwise and with stirring 9.0 g (0.057 mol) of bromine. An orange, crystalline precipitate formed which dissolved when the solution was warmed to 40°. Stirring was continued under a nitrogen current at 40° until hydrogen bromide gas was no longer evolved. In another run the hydrogen bromide evolved was conducted through silver nitrate solution, where it produced 9.5 g (0.05 mol) of silver bromide. The solution was cooled to ambient temperature, and to it was added with stirring 2.0 g (0.063 mol) of methanol followed by 5.0 g (0.063 mol) of pyridine in small portions. The mixture was allowed to stand overnight, and the deposited crystals of pyridinium bromide were removed by filtration. The filtrate was then washed several times with 100-ml portions of water. The separated organic layer was then dried over sodium sulfate, and the solvent was removed on the rotary evaporator. From the 4.87 g (87% yield) of crude product, pure 2-methoxy-3-bromothiophane (2.96 g) was obtained by chromatography on 100 g of silica gel (Fisher Scientific Co., Grade 923 ASTM D 1319-61T, 100–200 mesh) in a column 1.8 × 60.0 cm. The crude material was added neat and then eluted using methylene chloride. The first six 50-ml fractions were combined, and the eluent was removed by rotary evaporation, resulting in 2.57 g (98% yield) of analytically pure 2-methoxy-3-bromothiophane: $n^{25}D$ 1.5430; uv λ_{max}^{EtOH} 212 nm (ε 720); ir ν_{max}^{neat} 2994 (CH), 2946 (CH), 2823, 1441, and 1075 cm^{-1} (OCH_3); nmr (CCl_4) τ 4.92 (1 H, d), 5.52 (1 H, t-d), 6.77 (3 H, s), 7.02 (2 H, m), and 7.57 (2 H, m).

Anal. Calcd for C_5H_9OSBr: C, 30.46; H, 4.60; S, 16.25; mol wt, 197.109. Found: C, 30.84; H, 4.60; S, 16.55; mol wt, 196, 198 (mass spectrum, molecular ion).

***trans*-2-Methoxy-3-chlorothiophane (8).**—To a deep yellow solution of 5.0 g (0.057 mol) of thiophane in 100 ml of liquid sulfur dioxide at −10° was added 4.0 g (0.057 mol) of chlorine in a stream of nitrogen and with stirring. The color disappeared immediately. Stirring was continued at −10° for 2 days, then the sulfur dioxide was replaced with 40 ml of methylene chloride,

(11) We wish to thank Dr. Thomas Bazzone for performing these experiments.

(12) F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.*, **77**, 572 (1955).

(13) Nmr spectra were obtained using a Varian Associates Model A-60 spectrometer equipped with a variable-temperature probe, and chemical shifts were measured using tetramethylsilane as an internal standard. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E mass spectrometer. Infrared spectra were obtained using a Perkin-Elmer automatic recording infrared spectrometer, Model 521. All elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn. An Aerograph Model 200B gas chromotograph with 0.25 in. × 9 ft columns packed with 15% SE-30 on Chromosorb P 60/80 A/W was employed for vpc analyses unless otherwise stated.

and the solution was allowed to reach ambient temperature. To this was added with stirring 10.0 g (0.315 mol) of methanol followed by 10.0 g (0.126 mol) of pyridine in small portions. The mixture was allowed to stand overnight, and the deposited crystals of pyridinium chloride were removed by filtration. The filtrate was washed several times with 100-ml portions of water. The separated organic layer was dried over sodium sulfate, and the solvent was removed on the rotary evaporator. The volatile portion of the product was shown by vpc to consist of 2.1 g (66%) of *trans*-2-methoxy-3-chlorothiophane. An analytical sample was obtained by preparative vpc: ir ν_{max}^{neat} 2932 (CH), 2826 (OCH_3), 1481, and 1080 cm^{-1} (OCH_3); nmr (CCl_4) τ 4.97 (1 H), 5.55 (1 H), 6.74 (5 H), and 7.72 (2 H).

Anal. Calcd for C_5H_9ClOS: C, 39.34; H, 5.94; Cl, 23.22; S, 21.00; mol wt, 152.65. Found: C, 39.37; H, 5.94; Cl, 23.24; S, 20.96; mol wt, 152, 154 (mass spectrum, molecular ion).

α-Methoxythiophane (9).—To a solution of 5.0 g (0.057 mol) of thiophane in 150 ml of carbon tetrachloride at 4° was added in a stream of nitrogen and with stirring 4.0 g (0.057 mol) of chlorine. A fluffy white precipitate formed which dissolved when the mixture was warmed to 40°. Stirring was continued at 40° until hydrogen chloride gas was no longer evolved in the nitrogen stream when the solution was cooled to ambient temperature, and to it was added with stirring 2.0 g (0.063 mol) of pyridine in small portions. The mixture was allowed to stand overnight, and the deposited crystals of pyridinium chloride were removed by filtration, the filtrate having been washed several times with 100-ml portions of water. The separated organic layer was dried over sodium sulfate and the solvent was removed on the rotary evaporator. The crude material was shown by vpc to consist of 5.6 g (80% yield) of α-methoxythiophane. An analytical sample was obtained by preparative vpc: $n^{20}D$ 1.496; ir ν_{max}^{neat} 2950 (CH), 2860 (OCH_3), 1437, and 1252 cm^{-1} (OCH_3); nmr (CCl_4) τ 5.00 (1 H, m), 6.82 (2 H, m), 7.15 (3 H, s), and 7.95 (4 H, m).

Anal. Calcd for $C_5H_{10}OS$: C, 50.81; H, 8.52; S, 27.13, mol wt, 118.20. Found: C, 50.79; H, 8.51; S, 27.16; mol wt, 118 (mass spectrum, molecular ion).

2-Phenyl-3-chlorosulfolane (12).—A three-step procedure was carried out in order to convert 2,3-dichlorothiophane into a stable derivative the physical properties of which could be compared to those of the material prepared by Bordwell and Pitt.[12]

To a solution of 2,3-dichlorothiophane, prepared from 5.0 g (0.056 mol) of thiophane, in carbon tetrachloride was added with stirring 0.1 mol of phenylmagnesium bromide in 60 ml of ether. Stirring was continued at ambient temperature overnight, and then the excess Grignard reagent was hydrolyzed with 4 ml of water, extracted with ether, and dried over anhydrous potassium carbonate. The solvent was removed on a rotary evaporator, yielding 6 g of residue. The residue was taken up in 100 ml of glacial acetic acid containing 30 ml of 30% hydrogen peroxide and heated under reflux for 15 min, after which it was diluted with water and extracted with methylene chloride. The organic layer was dried and the solid residue after removal of solvent was dissolved in a minimum amount of benzene and allowed to crystallize under external cooling with an ice bath. The product, 2-phenyl-3-chlorothiophane, was collected as microcrystals: 0.267 g (4% yield); mp 153–154° (lit. mp 154–155°);[12] uv λ_{max}^{EtOH} 218 nm (ϵ 7000) and 259 (300); ir ν_{max}^{Nujol} 1310 and 1120 cm^{-1} ($-SO_2$); nmr ($CDCl_3$) τ 2.51 (6 H, s), 5.41 (1 H, m), 5.64 (1 H, m), 6.61 (2 H, m), and 7.31 (2 H, m).

Anal. Calcd for $C_{10}H_{11}ClOS$: C, 52.06; H, 4.80; S, 13.90; mol wt, 230.721. Found: C, 52.22; H, 4.67; S, 13.53; mol wt, 230 (molecular ion, mass spectrum).

3-Hydroxythiophane.—To a solution of 5.0 g (0.049 mol) of 3-thiophanone in 50 ml of methanol precooled to 4° was added with stirring a solution of 8.4 g (0.10 mol) of sodium acetate and 4.0 g (0.104 mol) of sodium borohydride in 30 ml of water at such a rate that the solution temperature remained between 4 and 10°. After addition was complete, the solution was stirred at 4° for 1 hr and then neutralized with several milliliters of concentrated sulfuric acid, and the product, in three 50-ml portions, was extracted into ether. The ether extract was dried over magnesium sulfate and the solvent was removed by rotary evaporation, leaving 4.3 g (83% yield) of 3-hydroxythiophane. The product was purified by distillation, bp 53° (0.25 mm), giving 3.8 g (72% yield) of 3-hydroxythiophane: $n^{20}D$ 1.5374; ir ν_{max}^{neat} 3382 (OH), 2943 (CH), 1451, 1336, 1262, 1195, 1027, 956, and 830 cm^{-1}; nmr (neat) τ 5.52 (q, 1 H, J = 4 Hz), 5.37 (s, 1 H), 7.00 (m, 4 H), and 7.92 (m, 2 H).

Anal. Calcd for C_4H_8OS: C, 46.12; H, 7.74; S, 30.78; mol wt, 104.17. Found: C, 46.16; H, 7.74; S, 30.75; mol wt, 104 (mass spectrum, molecular ion).

3-Bromothiophane.—To a solution of 4.0 g (0.0385 mol) of 3-thiophanol in 30 ml of methylene chloride was added slowly with stirring 10.5 g (0.0385 mol) of phosphorus tribromide. Upon completion of the phosphorus tribromide addition, the reaction mixture was allowed to reach ambient temperature over a period of 12 hr. The reaction mixture was washed twice with 50-ml portions of 10% aqueous sodium bicarbonate. The organic layer was separated and dried over sodium sulfate; the solvent was removed by rotary evaporation and the residue was distilled, bp 33° (0.4 mm), yielding 4.74 g (71% yield) of 3-bromothiophane: ir ν_{max}^{neat} 2944 (CH), 2862, 1421, 1372, 1233, 891, 735, 692, 656, and 515 cm^{-1}; nmr (CCl_4) τ 5.27 (q, 1 H, J = 6 Hz), 6.85 (m, 4 H), and 7.50 (t, 2 H, J = 6 Hz).

Anal. Calcd for C_4H_7BrS: C, 28.75; H, 4.24; S, 19.19; mol wt, 167.10. Found: C, 28.77; H, 4.19; S, 19.26; mol wt, 166, 168 (mass spectrum, molecular ion).

Dihydrothiophene.—A solution of 10.4 g (0.10 mol) of tetramethylene sulfoxide and 22.6 g (0.10 mol) of benzoic anhydride in 60 ml of benzene was heated under reflux for 5 hr, then cooled. The benzoic acid was then extracted with several 100-ml portions of 5% aqueous sodium bicarbonate. The separated organic layer was dried over sodium sulfate, and the solvent was removed on the rotary evaporator. The residue, 20.1 g of crude 2-benzoyloxythiophane, was distilled through a 15-cm Vigreux column at 80° (760 mm) yielding 2.0 g (23% yield) of dihydrothiophene: nmr (C_6H_6) τ 4.05 (doublet of triplets, 1 H, J = 6.0, 2.0 Hz), 4.72 (1 H, J = 6.0, 2.0 Hz), 7.02 (m, 1 H), and 7.29 (m, 1 H). The nmr (CCl_4) τ 3.94 (doublet of triplets, 1 H, J = 6.0, 2.0 Hz), 4.52 (m, 1 H, J = 5.8, 2.2 Hz), 6.92 (m, 1 H), and 7.38 (m, 1 H) (lit. J = 6.06, 2.2 Hz) was identical with that of the compound prepared by the method of Korver, *et al.*[14]

Addition of Chlorine and Bromine to Dihydrothiophene.—To 86 mg (1 mmol) of dihydrothiophene was added 1.25 ml of 1.25 *N* chlorine in $DCCl_3$ solution at 40°. The two envelopes at τ 3.94 and 4.52 were replaced by two new envelopes at τ 4.31 (m, 1 H, J = 8 Hz) and 5.19 (m, 1 H). Addition of 0.8 ml of 1.25 *N* bromine in CCl_4 solution led at first to a cloudy precipitate that dissolved and produced peaks at τ 4.15 (m, 1 H, J = 1 Hz) and 5.05 (m, 1 H).

Saturating the solution of 86 mg (1 mmol) of dihydrothiophene in 1 ml of carbon tetrachloride with chlorine gas annihilated the absorptions at τ 4.31, and the multiplet at 5.19 collapsed to a doublet of doublets. The resulting spectrum was similar to the one obtained from treating thiophane with excess chlorine.

Addition of Hydrogen Chloride to Dihydrothiophene.—Saturating a solution of 86 mg (1 mmol) of dihydrothiophene in 1 ml of carbon tetrachloride with hydrogen chloride annihilated the absorptions at τ 3.94 and 4.52 and formed a new multiplet at 4.32 giving a spectrum identical with that of 2-chlorothiophane.

Registry No.—**1**, 110-01-0; **3**, 39010-39-4; **8**, 39010-40-7; **9**, 33794-77-3; **11**, 39010-41-8; **12**, 39013-63-3; 1-bromothiophanium bromide, 22053-77-6; 3-thiophanone, 1003-04-9; 3-hydroxythiophane, 3334-05-2; 3-bromothiophane, 39013-66-6; tetramethylene sulfoxide, 1600-44-8; benzoic anhydride, 93-97-0; dihydrothiophene, 1120-59-8.

Acknowledgment.—We thank the donors of the Petroleum Research Fund, admimistered by the American Chemical Society, for a grant in partial support of this work. A NASA graduate traineeship awarded to R. A. is gratefully acknowledged.

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