(11,000); $[\alpha]^{23}D$ −44.2° (*c* 0.2, MeOH); ORD (MeOH) multiple Cotton effect with a peak at 335 mμ (Φ +8300°), crossover at 307 mμ, a trough at 290 mμ (Φ −7500°), crossover at 277 mμ, a shoulder at 265 mμ (Φ +5100°), and a peak at 238 mμ (Φ +30,500°); nmr ($CDCl_3$) 1.60 and 1.62 (s, 9, *tert*-BuO), 3.9–4.5 (m, 4, $C_{3'}$, $C_{4'}$, and $C_{5'}$ H's), 5.45 (d, 1, $J_{2',3'}$ = 8 Hz, $C_{2'}$ H), 5.67 and 5.82 (s, 1, $ArCHO_2$), 7.3–7.6 (m, 10, arom), 8.40 ppm (s, 1, C_6H).

Anal. Calcd for $C_{31}H_{36}N_2O_7$: C, 67.86; H, 6.61; N, 5.11. Found: C, 67.73; H, 6.76; N, 4.92.

The same compound was obtained by oxidation of **6a** in a similar way.

B.—A crude mixture of **5a** and **6a** (500 mg) in acetonitrile (30 ml) was stirred for 1 hr at room temperature with activated manganese dioxide (9 g). After filtration through Celite, the filtrates were evaporated to dryness leaving a chromatographically homogeneous, crystalline residue. Recrystallization from ethanol gave 219 mg (45%) of **13** identical with that above.

Metal Hydride Reduction of 13. A. Using Sodium Borohydride.—Sodium borohydride (7 mg) was slowly added to a slurry of **13** (45 mg) in methanol (2 ml). After 10 min the solvent was evaporated and the residue was partitioned between benzene and water. Evaporation of the benzene left a crystalline residue of almost pure **5a**. Quantitative tlc using carbon tetrachloride–acetone (85:15) showed the product to contain 94% **5a** and 6% **6a** with quantitative recovery.

B. Using $LiAlH_4$.—Lithium aluminum hydride (5 mg) was added to a solution of **13** (45 mg) in tetrahydrofuran (2 ml) and after 30 min the mixture was worked up as above giving crystalline, almost pure **5a** that was shown by tlc to be 96% **5a** and 4% **6a**.

5-(2,4:3,5-Di-*O*-benzylidene-1-keto-D-*ribo*-tetrahydroxypentyl)uracil (14).—A suspension of finely divided **13** (400 mg) in 80% acetic acid (5 ml) was stirred at 25° for 1.5 hr. During this time **13** dissolved and was replaced by fine needles of **14** (283 mg) which were removed by filtration. Addition of water to the filtrate gave a further 17 mg (total yield), 300 mg (94%) of **14** which was recrystallized from ethanol with mp 269–271° dec; λ_{max}^{MeOH} 290 mμ (ε 7400), 227 (sh, 5700); $[\alpha]^{23}D$ −91.4° (*c* 0.1, MeOH); ORD (MeOH) negative Cotton effect with a trough at 296 mμ (Φ −9000°), crossover at 278 mμ, and a peak at 262 mμ (Φ +4800°); nmr (pyridine-d_5) 4.0–4.6 (m, 3, $C_{4'}$ H and $C_{5'}$ H_2), 4.68 (t, 1, $J_{2',3'}$ = $J_{3',4'}$ = 9 Hz, $C_{3'}$ H), 5.92 and 6.23 (s, 1, $ArCHO_2$), 6.48 (d, 1, $J_{2',3'}$ = 9 Hz, $C_{2'}$ H), 7.2–7.8 (m, 10, arom), 8.21 ppm (s, 1, C_6H).

Anal. Calcd for $C_{23}H_{20}N_2O_7$: C, 63.30; H, 4.62; N, 6.42. Found: C, 63.15; H, 4.45; N, 6.04.

5-(D-*altro*-1-Acetamido-2,3,4,5-tetrahydroxypentyl)uracil (17).—A solution of **10b** (350 mg, 0.71 mmol) in methanol (5 ml) and concentrated ammonium hydroxide (5 ml) was kept at 23° for 5 hr and then evaporated to dryness *in vacuo*. Preparative tlc on three Avicel plates using 1-butanol–acetic acid–water (5:2:3) gave a major band moving just slower than α-pseudouridine. Elution with water and evaporation gave a syrup (4250 OD units at 260 mμ, 81%) that was dissolved in hot 90% methanol to remove some insoluble material, evaporated, and crystallized from 90% ethanol giving 122 mg (57%) of **17** with mp 223–224°; λ_{max}^{MeOH} 262 mμ (ε 7400); $[\alpha]^{23}D$ +52.4°; ORD (H_2O) negative Cotton effect with a trough at 258 mμ (Φ −11,600°), crossover at 242 mμ, and a peak at 230 mμ (Φ +6100°); nmr (DMSO-d_6–D_2O) 1.91 (s, 3, $C_{1'}$ NAc), 3.2–3.7 (m, 5, $C_{2'}$, $C_{3'}$, $C_{4'}$, and $C_{5'}$ H's), 5.15 (br, s, 1, $C_{1'}$ H), 7.29 ppm (s, 1, C_6 H). The compound consumed 3.0 equiv of periodate[22] with release of 1.0 equiv of formaldehyde.[23]

Anal. Calcd for $C_{11}H_{17}N_3O_7$: C, 43.56; H, 5.65; N, 13.86; O, 36.93. Found: C, 43.68; H, 5.84; N, 13.34; O, 36.91.

Registry No.—**1**, 1445-07-4; **1** 2′,3′,5′-tri-*O*-acetate, 24800-34-8; **2**, 1017-66-0; **2** 2′,3′,5′-tri-*O*-acetate, 28455-49-4; **4** methyl hemiacetal, 28399-55-5; **5a**, 28455-50-7; **6a**, 28399-56-6; **7a**, 28399-57-7; **7b**, 28399-58-8; **8a**, 28455-51-8; **8b**, 28399-59-9; **9a**, 28399-60-2; **9b**, 28399-61-3; **10a**, 13039-98-0; **10b**, 28399-63-5; **11**, 28399-64-6; **13**, 28399-65-7; **14**, 28399-66-8; **17**, 28399-67-9.

Acknowledgment.—We are most grateful to Mr. E. K. Hamamura for his ever-skillful assistance in parts of this work.

Reactions of Diaryl Disulfides with Active, Nonnucleophilic Alkylating Agents[1]

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Reaction of diphenyl disulfide with triethyloxonium fluoroborate or diethoxycarbonium fluoroborate gave diethylphenylsulfonium fluoroborate and *S*-ethylsulfonium salts of ethyl *p*-thiophenoxyphenyl sulfide (**5**) and of a product assigned the structure of ethyl *p*-(*p*-thiophenoxyphenyl)thiophenoxyphenyl sulfide (**6**). Recovered diphenyl disulfide, thianthrene (**3**), and the *S*-ethylsulfonium salt of ethyl *o*-thiophenoxyphenyl sulfide (**4**) were also obtained in smaller amounts. The products obtained from alkylation of mixtures of diphenyl disulfide with diphenyl disulfide-d_{10} or anisole showed that formation of all products proceeded through intermolecular steps. Formation of all products of these reactions, as well as the reaction of di-β-naphthyl disulfide with trimethyloxonium fluoroborate to give dibenzothianthrene (**8**), could be explained as proceeding by S-alkylation of the disulfides, followed by nucleophilic attack upon the unalkylated sulfur atom by another disulfide molecule or by anisole.

The structural similarities between *sym*-diphenylhydrazines and diphenyl disulfides have prompted several research groups to react diphenyl disulfide with strong protonic acids[2,3] or with boron trifluoride,[2] in attempts to obtain rearrangements similar to the benzidine rearrangements of diphenylhydrazines.[4] These attempts have been unsuccessful, resulting either in no reaction[2] or in formation of ill-characterized polymers.[3] It has been suggested[3] that the polymeric materials may arise by oxidation and sulfonation of a 4,4′-dimercaptobiphenyl resulting from rearrangements of the benzidine type, but no concrete support for this proposal has been offered.

There are indeed excellent reasons why reactions analogous to the benzidine rearrangement are unlikely to occur during the reactions of diphenyl disulfides with proton acids. Benzidine rearrangements of most *sym*-diphenylhydrazines have been found to proceed from the diprotonated forms.[4] The very low basicity of disulfides, as compared to hydrazines, requires that much stronger acids must be used even for monopro-

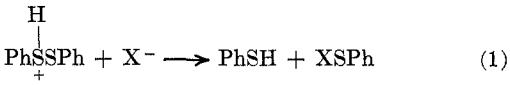
(1) Part of this work has been published as a preliminary communication: B. Miller and C.-H. Han, *Chem. Commun.*, 623 (1970).

(2) H. H. Szmant and R. L. Lapinski, *J. Org. Chem.*, **21**, 847 (1956).

(3) H. J. Shine and J. L. Baer, *Chem. Ind. (London)*, 565 (1957).

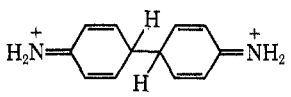
(4) D. V. Banthorpe in "Topics in Carbocyclic Chemistry," D. Lloyd, Ed., Logos Press, Ltd., London, 1969, pp 1–63.

tonation to occur, while diprotonation seems unlikely to occur at all. The use of very high concentrations of acid, particularly of sulfuric acid,[2,3] greatly increases the possibility of obtaining products of ring substitution or of oxidative cleavage of the S–S bond. The well-known susceptibility of the S–S bond to nucleophilic attack (presumably due to availability of d orbitals on sulfur for attack by the nucleophile)[5] should be greatly enhanced in a protonated disulfide, so that reactions such as that in eq 1 (which have analogies in the acid-catalyzed exchange reactions of disulfides)[5]



$$PhS(H^+)SPh + X^- \longrightarrow PhSH + XSPh \qquad (1)$$

must be avoided. Finally, and perhaps most important, the very low bond strength of a C=S double bond[6] makes it appear highly improbable that a sulfur analog of **1**, which presumably is an intermediate in the benzidine rearrangement (regardless of its detailed mechanism),[4] could form from a diphenyl disulfide.



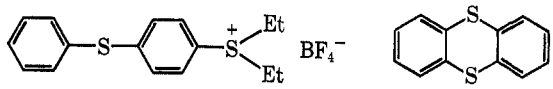
1

Despite these difficulties, the great interest in expanding our knowledge of the class of reactions represented by the benzidine rearrangement (which includes not only reactions leading to semidines and diphenylines[4] but also the acid-catalyzed rearrangements of quinamines[7] and, probably, of *O,N*-diphenylhydroxylamines[8]) encouraged us to reinvestigate the possibility of such rearrangements occuring.

Although divalent sulfur atoms are poor hydrogen bases, they are usually excellent carbon bases.[9] We therefore decided to employ "carbon acids" (alkylating agents) as the reagents for our attempted rearrangements. To minimize the possibility of bimolecular cleavage of an alkylated disulfide occurring, we decided to employ alkylating agents with as poorly nucleophilic leaving groups or counterions as possible. Trialkyloxonium salts, as well as the less common dialkoxycarbonium salts, were therefore chosen to react with diaryl disulfides.

Results

Reaction of diphenyl disulfide with triethyloxonium fluoroborate in refluxing chloroform proceeded slowly, requiring from 6 to 24 hr, depending on the concentration of the solution and the amount of alkylating agent employed. A large excess of the alkylating agent was necessary to obtain reasonably complete reaction, due to partial decomposition of the oxonium salts in the refluxing reaction mixture. Evaporation of the solvent at the end of the reaction left gummy mixtures which appeared to consist largely of sulfonium salts. Thin layer chromatography of the alkylation products on silica in a large variety of solvent systems showed the presence of several components which could not be completely separated. Attempts to isolate the products by column chromatography failed. However, careful extraction and preparative tlc procedures (see Experimental Section) resulted in the isolation of two crystalline products which were identified as diethyl phenylsulfonium fluoroborate and diethyl *p*-thiophenoxyphenylsulfonium fluoroborate (**2**), as will be discussed below. No other products could be isolated by these means.



2 **3**

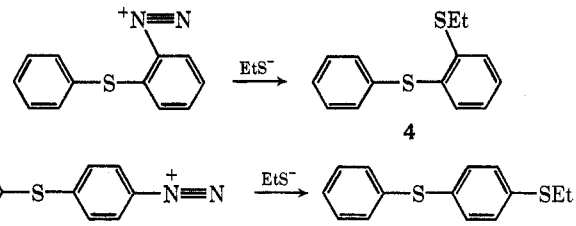
We therefore decided to convert the mixture of sulfonium salts to neutral sulfides, which we felt would be easier to isolate. Either pyrolysis of the crude alkylation product at 175° for 10 hr or hydrolysis in refluxing aqueous alkali yielded a product mixture which did not give a test for sulfonium salts.[10] Vpc analysis showed the pressure of seven components in this mixture. Essentially identical vpc analyses were obtained for the neutral mixtures obtained from pyrolysis and from hydrolysis of the sulfonium salts. Direct vpc analysis of the crude alkylation product showed the presence of the same seven peaks, but several of these peaks were much smaller when analysis was carried out before cleavage of the sulfonium salts. Apparently the sulfonium salts were only partially cleaved on the vpc column.

The first five components were isolated by preparative vpc on a 6 ft, 30% SE-30 column. The final two components, one of which appeared as a shoulder preceding the other, were obtained at much higher retention times than the other components. They could not be separated from one another but were collected as a mixture in approximately a 1:5 ratio.

The first three components isolated were identified as ethyl phenyl sulfide, recovered diphenyl disulfide, and thianthrene (**3**). The fourth and fifth components were separated with appreciable difficulty, since the fourth component was a minor product which appeared at a retention time very close to that of the fifth component. Both compounds had analyses corresponding to the formula $C_{14}H_{14}S_2$. The two isomers had very similar nmr spectra, each showing the presence of an ethyl group on sulfur and of nine aromatic protons. The mass spectrum of each showed a parent peak at *m/e* 246 and a base peak at *m/e* 215, corresponding to loss of an ethyl group. The ir spectrum of each showed strong peaks at 690 and 740–750 cm^{-1}, indicating the presence of unsubstituted or ortho-substituted phenyl groups.[11] The spectrum of the major (fifth) component, but not that of the minor component, had, in addition, a medium intensity absorption at 820 cm^{-1}, suggesting the presence of a para-substituted benzene ring.[11] The major product was therefore tentatively assigned the structure ethyl *p*-thiophenoxyphenyl sulfide (**5**) and the minor product the structure ethyl *o*-thiophenoxyphenyl sulfide (**4**). The two isomers were independently synthesized by reaction of *o*- and *p*-thio-

(5) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).
(6) H. Mackle, *Tetrahedron*, **19**, 1159 (1963).
(7) B. Miller, *J. Amer. Chem. Soc.*, **86**, 1127 (1964).
(8) J. R. Cox, Jr., and M. F. Dunn, *Tetrahedron Lett.*, **No. 15**, 985 (1963).
(9) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, pp 159–162.
(10) H. Potratz and J. Rosen, *Anal. Chem.*, **21**, 1276 (1949).
(11) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, Chapter 5.

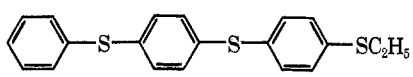
phenoxyphenyldiazonium chlorides with ethanethiol. The ir and nmr spectra and vpc retention times of the products were identical with those of **4** and **5**, respectively.



4

5

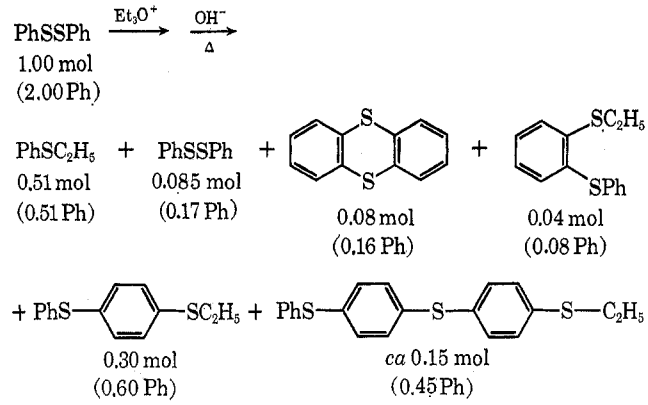
The sixth and seventh components of the mixture, as was mentioned above, could not be separated from one another, but were isolated as a mixture in the approximate ration 1:5. Although neither could be obtained in a pure state, we believe that a reasonable structural assignment for the major component, at least, can be based on the information given below. The mass spectrum showed a parent peak at m/e 354 (corresponding to the formula $C_{20}H_{18}S_3$) and a base peak at m/e 325. The nmr spectrum of the mixture showed the presence of one ethyl group attached to sulfur and of 13 aromatic protons. No other peaks could be detected. These facts suggest that the two compounds are isomers containing one S-ethyl group and three aromatic rings linked together by sulfide bonds. The ir spectrum of the mixture shows peaks at 685 and 735 cm^{-1}, characteristic of phenyl or ortho-substituted aromatic rings, and a strong peak (the most intense in the spectrum) at 813 cm^{-1}, characteristic of para-substituted aromatic compounds.[11] The intensity of the 813-cm^{-1} peak, compared to the peaks at lower frequency, suggests that two of the three rings are para substituted. We therefore propose that the structure of the main component in the mixture of high retention time isomers is **6**. The minor component is presumably an isomer with one ortho-substituted ring.



6

Synthetic mixtures of the compounds isolated from the reaction were prepared, and the mole fraction/area relationship for these components was determined. The mole ratios of the products of the reaction were obtained from the areas of peaks in the chromatogram of the reaction mixture after hydrolysis or pyrolysis. The number of moles of each product obtained from reaction of 1.00 mol of diphenyl disulfide is given in eq 2. Beneath these values, in parentheses, are listed the number of equivalents of phenyl groups (based on 2.00 phenyl equivalents in the starting diphenyl disulfide) in each product of the reaction. The number of phenyl equivalents obtained from this reaction adds up to 1.97. Although there is some uncertainty in this value, due to the impurity of the **6** obtained from the reaction, it does appear that we have isolated almost all the products of the reaction.

Thioethers **4** and **5** closely resemble the *o*- and *p*-thiosemidines obtained from benzidine rearrangements. In hope of determining whether these products are obtained by *intra*- or *inter*molecular reaction paths,

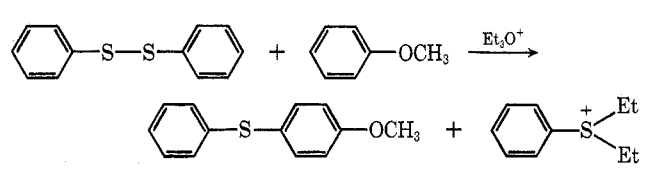


(2)

we reacted triethyloxonium fluoroborate with a mixture of phenyl disulfide and diphenyl disulfide-d_{10}. (Diphenyl disulfide-d_{10} was prepared by reacting phenyl-d_{10} magnesium bromide with sulfur and oxidizing the thiol thus prepared to the disulfide.) No apparent change in the course of reaction with the Meerwein reagent was observed when deuterated diphenyl disulfide was substituted for diphenyl disulfide. The products of the reaction were again isolated by preparative vpc, and the deuterium distribution in the products was determined from their mass spectra.

As can be seen from the results recorded in the Experimental Section, the mass spectra of all the products showed good agreement with the 1:2:1 undeuterated–half-deuterated–perdeuterated patterns expected for intermolecular rearrangements, if allowance is made for some exchange with the partially deuterated fluoroboric acid produced in the reaction. However, it can also be seen that the diphenyl disulfide recovered from the reaction had undergone complete exchange of phenyl groups between the deuterated and undeuterated species. Since exchange of phenyl groups in diphenyl disulfide under these conditions is therefore at least as fast as the rearrangements to **3**, **4**, and **5**, no conclusion can be drawn as to whether the formation of these products involves a second intermolecular step (other than that involved in exchange of phenyl groups among diphenyl disulfide molecules).

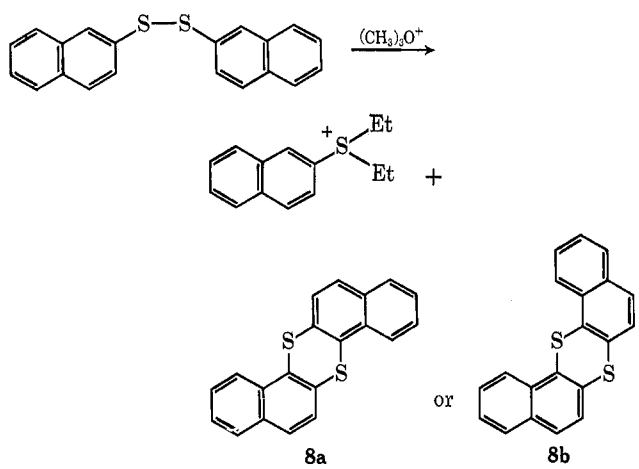
We then attempted to obtain indirect evidence that the major reaction product **5**, at least, can be formed intermolecularly by demonstrating that similar products can be obtained from clearly intermolecular electrophilic substitution processes. When anisole was added to the reaction mixture of diphenyl disulfide and triethyloxonium fluoroborate in chloroform, formation of the normal reaction products was almost entirely inhibited. Instead, a single new product was obtained, along with an equimolar amount of diethyl phenylsulfonium fluoroborate. The product was isolated by vpc and shown to be *p*-thiophenoxyanisole (**7**) by comparison with an authentic sample.[12]



7

(12) (a) O. Hinsberg, *Chem. Ber.*, **36**, 107 (1903); (b) W. E. Truce, D. P. Tate, and D. N. Burdge, *J. Amer. Chem. Soc.*, **82**, 2872 (1960).

In view of the exceptional reactivity of dinaphthylhydrazines in benzidine rearrangements,[4] we decided to examine the reactions of dinaphthyl disulfides with Meerwein reagents. However, we could discern no reaction between triethyloxonium fluoroborate or diethoxycarbonium fluoroborate and di-8-naphthyl disulfide even after long reaction times. Trimethyloxonium fluoroborate, on the other hand, did react with the disulfide in a reasonable time. Analogy with the corresponding benzidine rearrangement[4] suggested that the two α positions might become linked during the reaction. However, no evidence for formation of any compound with a new C–C bond could be obtained. Instead, a mixture of dimethyl naphthylsulfonium fluoroborate and a solid (mp 182–185°) with the formula $C_{20}H_{12}S_2$ was obtained. This product showed no evidence for the presence of a disulfide link, and its nmr spectrum showed only aromatic absorption. On this basis, the product was assigned the structure of one of the isomeric benzothianthrenes **8a** or **8b**, and, indeed,



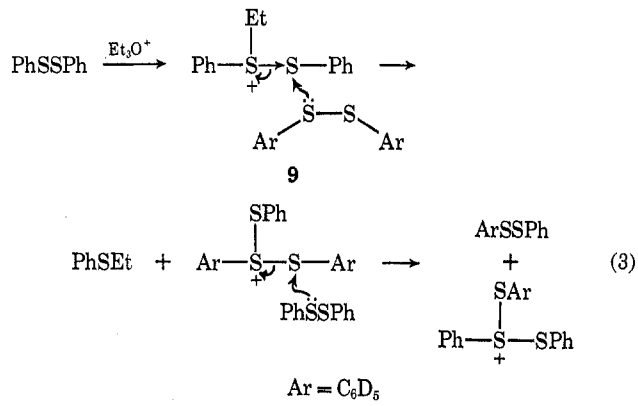
8a **8b**

was found to be identical with the compound (mp 184°) previously assigned structure **8b** by Fries and Volk.[13] Although the gross structure of the product is established however, the stereochemistry (which seems to have been assigned arbitrarily[13]) is still uncertain. Our attempts to determine the stereochemistry of the product by synthesis of one of the stereoisomers by unequivocal methods failed. However, on the basis of the presumed mechanism for its formation (see below), we favor structure **8a** for this product.

In contrast to the reaction of di-β-naphthyl disulfide, the reaction of di-α-naphthyl disulfide with trimethyloxonium fluoroborate gave a complex mixture from which no pure products could be isolated.

Discussion

Reaction of diphenyl disulfide with triethyloxonium fluoroborate gives products which closely resemble those of the semidine rearrangement of *sym*-diphenylhydrazines.[4] It is clearly of great interest to determine whether formation of these products proceeds by intermolecular or intramolecular paths. (It may be noted, by the way, that there is no direct evidence that semidine rearrangements actually proceed by intramolecular pathways, although it is commonly assumed that they do.[4]) The most direct attempt to demonstrate the nature of the pathways involved in formation of products **3**–**5**—the mixed rearrangement of deuterated and undeuterated diphenyl disulfide—failed, due to the fact that the disulfide itself undergoes exchange of the two aromatic rings during the reaction. The exchange is clearly catalyzed by triethyloxonium fluoroborate, since no exchange takes place in the absence of this reagent. A simple chain mechanism can be written for the exchange reaction, which has analogy in the proton-catalyzed exchanges observed in dialkyl disulfides.[5] This mechanism is outlined in eq 3. (Of



course, initial alkylation of deuterated disulfide would also occur.) We have written the actual exchange step as involving displacement on a sulfur atom in the alkylated disulfide **9**, in order to minimize the number of postulated intermediates in the reaction. The possibility that the actual electrophilic reagent is the phenylsulfenium cation, however, has not been eliminated. (It has been suggested[14] that sulfenium cations are intermediates in proton-catalyzed exchange reaction.)

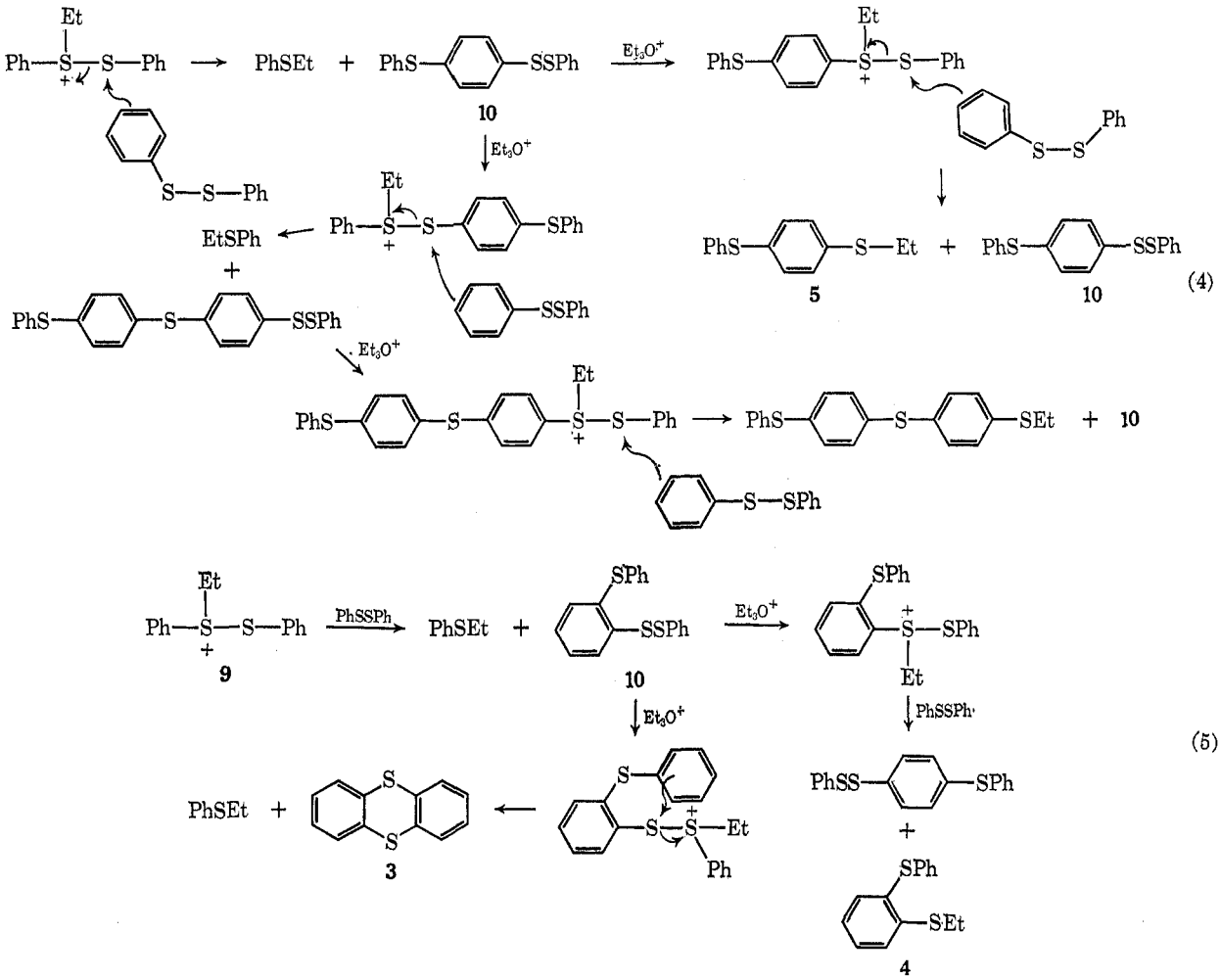
Although no conclusion about the intermolecular or intramolecular nature of the "rearrangement" steps leading to **4** and **5** can be drawn from the mixed reaction experiment, other evidence provides strong argument that these products are formed by intermolecular paths. Clearly, formation of at least one of the diaryl sulfide links in **6** must proceed by an intermolecular path. Since exactly the same sort of linkage is characteristic of each of the other products of the reaction, it seems superfluous to postulate a second, intramolecular path to form those bonds. A similar argument holds for formation of the diaryl sulfide linkage in **7**. The formation of **7**, to the essential exclusion of the normal reaction products of diphenyl disulfide with triethyloxonium fluoroborate, or of the meta or ortho isomers of **7**, is completely consistent with the reactivity expected of anisole in electrophilic substitution reactions[15] but quite different from its reactivity patterns in homolytic substitution reactions.[16] In all respects, formation of **7** appears to be a typical electrophilic aromatic substitution. It does not, of course, necessarily follow that formation of products **3**–**6** similarly follow electrophilic paths, but in view of the basic similarities of these products to **7**, there again seems no point in postulating very different reaction mechanisms to explain their formation.

(13) K. Fries and W. Volk, *Chem. Ber.*, **42**, 1170 (1909).

(14) R. E. Benesch and R. Benesch, *J. Amer. Chem. Soc.*, **80**, 1666 (1958).

(15) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960.

(16) P. B. D. De la Mare and J. H. Ridd, "Aromatic Substitution-Nitration and Halogenation," Academic Press, New York, N. Y., 1959.



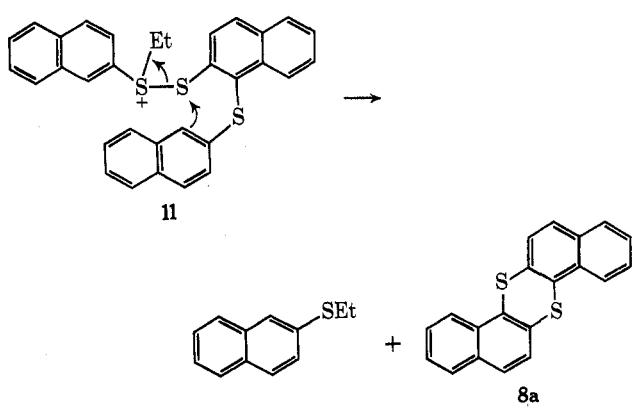
(4)

(5)

All the products of the reaction of diphenyl disulfide with triethyloxonium fluoroborate can be accounted for by electrophilic attack by the alkylated diphenyl disulfide **9** upon a diphenyl disulfide molecule. This mechanism is outlined in eq 4 for the formation of the major reaction products **5** and **6**, and in eq 5 for the formation of **3** and **4**.

In writing these mechanisms, we have assumed that the electrophilic agents were alkylated diaryl disulfides rather than free sulfenium ions. Some justification for this choice can be found in the high para/ortho ratios in the products of the reaction of phenyl disulfide with triethyloxonium fluoroborate. If the number of times reaction occurs at a para position to give **5** and **6** (counting two para attacks to form a molecule of **6**) is compared to the number of times attack occurs at an ortho position to give **3** and **4**, a para/ortho ratio of approximately 5:1 is obtained. This is quite a high ratio, particularly since the directing atom is a divalent sulfur. High para/ortho ratios are often characteristic of substitution upon rings bearing substituents with unshared electrons but high electronegativities, *e.g.*, fluorine.[16] In these instances, the inductive effect of the substituent reduces the reactivity of the ortho positions. A similar high para/ortho ratio would not be expected to result from substitution upon a ring bearing a divalent sulfur. Aromatic rings substituted with bromine and chlorine atoms, which have higher electronegativities than sulfur,[17] typically give para/ortho ratios of *ca.* 2:1 in halogenation and nitration reactions.[16] It is true that the ortho/para ratio can vary greatly with the nature of the attacking electrophile. Use of more reactive electrophiles, *e.g.*, the bromonium ion in place of molecular bromine, results in more indiscriminate attack at both ortho and para positions, while use of bulkier electrophiles results in more selective attack at the para position, presumably due to steric repulsions by the existing substituent.[16] On both grounds, the *S*-ethylsulfonium salt **9** seems more likely to give a high para/ortho ratio in attack upon a diphenyl disulfide molecule than does a simple sulfenium cation.

Finally, we may note that application of the mechanism in eq 5 to di-β-naphthyl disulfide gives rise to the intermediate **11**. Cyclization of **11**, in the manner suggested for formation of **3**, should give rise to the "trans" dibenzothianthrene **8a**. As has been mentioned above,



(17) L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1948.

however, experimental confirmation for the geometry of this molecule has not yet been obtained.

Experimental Section

Unless otherwise noted, all nmr spectra were recorded in $CDCl_3$ solution. Melting points are corrected and boiling points are uncorrected. Mass spectra were taken on A.E.I. MS-9 mass spectrometers with probe inlets at 100–125°.[18] Coupling constants (J) are given in hertz.

Reaction of Diphenyl Disulfide with Triethyloxonium Fluoroborate.—A solution of diphenyl disulfide (6.39 g, 0.030 mol) and triethyloxonium fluoroborate (8.55 g, 0.044 mol) in 20 ml of chloroform was heated at reflux for 16 hr. The mixture was then cooled to room temperature and washed several times with small portions of water. The chloroform layer was dried over magnesium sulfate and the solvent evaporated to give 1.68 g of yellow oil. This could not be crystallized on standing. Tlc on silica plates showed the presence of several components which were not well resolved. A sample of the chloroform-soluble material was applied to a preparative tlc plate (silica, 20 × 20 cm) and the plate developed with a 9:1 mixture of acetone and ethyl acetate. The only well-developed spot appeared at R_f 0.9, with appreciable tailing. This was scraped off the plate and extracted with acetone. Evaporation of the acetone left a small amount of solid, which had ir spectra and tlc retention times identical with those of diethyl *p*-thiophenoxyphenylsulfonium fluoroborate (**2**).

The combined aqueous washes were extracted several times with chloroform. The chloroform extract was dried and the solvent evaporated to give a yellow oil, which partially crystallized on standing. The crystals were isolated and identified by melting point, mixture melting point, and ir spectra as diethyl phenylsulfonium fluoroborate.

In another urn, using 0.05 mol of diphenyl disulfide and 0.15 mol of triethyloxonium fluoroborate, the reaction was followed by vpc on a 5 ft, 3% SE-30 on Chromosorb W column at 200°. Essentially identical chromatograms were obtained after reaction times of 6, 12, and 17 hr. Significant peaks were observed at retention times of 0.7, 1.5, 2.3, 2.9, 3.5, 22 (shoulder), and 26.8 min. The reaction product was refluxed for 19 hr with 50 ml of 10 N sodium hydroxide solution. The same peaks as before hydrolysis were observed on vpc, but the relative areas of the peaks were somewhat different. The first five products eluted were isolated by preparative vpc on a 5 ft, 20% SE-30 on Chromosorb W column, at temperatures ranging from 150–250°, and were identified (in order of elution) as ethyl phenyl sulfide, phenyl disulfide, thianthrene (**3**), ethyl *o*-thiophenoxyphenyl sulfide (**4**), and ethyl *p*-thiophenoxyphenyl sulfide (**5**) by comparison of their ir and nmr spectra and vpc retention times with those of authentic samples. The products with the highest retention times could not be obtained from the same column as the other products but were collected from vpc on an 18 in., 30% SE-30 on Chromosorb W column at 250°. The main peak could not be collected free of the component immediately preceding it which appeared as a shoulder even in an analytical column. The ratio of the two components was approximately 5:1. The nmr spectrum of the mixture showed a triplet (3 H, J = 7.5) at 1.30 ppm, a quartet (2 H, J = 7.5) at 2.84 ppm, and a multiplet (13 H) around 7.25 ppm. Its ir spectrum had peaks at 1570 (m), 1470 (s), 1440 (s), 1387 (m), 1310 (m), 1255 (m), 1145 (m), 1095 (m–s), 1010 (m), 960 (w), 815 (vs), 735 (s), and 685 cm^{-1} (m). Its mass spectrum had major peaks at m/e 354 (M^+) and m/e 325.

Reaction of Diphenyl Disulfide with Diethoxycarbonium Fluoroborate.—Diphenyl disulfide (4.35 g, 0.02 mol) and diethoxycarbonium fluoroborate[19] (11.4 g, 0.06 mol) were dissolved in 20 ml of chloroform and the mixture was stirred at room temperature for 5.5 hr. Water was added and the mixture stirred for 0.5 hr, the layers were separated, and the chloroform layer was dried and evaporated to give 3.54 g of recovered diphenyl disulfide. In another run, using the same quantities of materials, the mixture was refluxed for 4 hr and then worked up in the manner described for the reaction of diphenyl disulfide with triethyloxonium fluoroborate. A gummy residue (3.79 g) was obtained, whose ir spectrum was identical with that of the crude product from the reaction with triethyloxonium fluoroborate. Part of the product (1.65 g) was refluxed with 5 ml of 10 N sodium hydroxide solution for 10 hr. The ir spectrum and vpc analysis of the product showed it to be essentially identical with that obtained from the reaction of diphenyl disulfide with triethyloxonium fluoroborate.

Ethyl *p*-Thiophenoxyphenyl Sulfide (**5**).—Phenyl *p*-aminophenyl sulfide[20] (6.6 g, 0.0328 mol) was dissolved in 95 ml of an 11% solution of sulfuric acid in water. The solution was kept at 0–5° while a solution of sodium nitrite (2.55 g, 0.037 mol) in 10 ml of water was added. The greenish-brown diazonium salt solution was then added to an ice-cold solution prepared by addition of ethanethiol (2.16 g, 0.0348 mol) to a solution of sodium hydroxide (4.2 g, 0.104 mol) in 25 ml of water. The reaction mixture was stirred for 4 hr at room temperature and extracted with three 50-ml portions of ether. The combined ether extract was washed with sodium carbonate solution and then with water and dried over magnesium sulfate. Evaporation of the ether gave an oil which was distilled under vacuum to give ethyl *p*-thiophenoxyphenyl sulfide (3.0 g, 37.0%), bp 144–145° (2.7 mm). Its ir spectrum showed absorptions at 1580 (m), 1480 (s), 1140 (m), 1390 (m), 1260 (m), 1100 (m), 1080 (m), 1020 (m), 1010 (m), 810 (m), 740 (s), and 690 cm^{-1} (s). Its nmr spectrum showed a triplet (J = 7.0) at 1.30 ppm (3 H), a quartet (J = 7.0) at 2.90 ppm (2 H), and a broad absorption at 7.3 ppm (9 H). Its molecular weight (mass spectrum) was 246.

Anal. Calcd for $C_{14}H_{14}S_2$: C, 68.3; H, 5.73; S, 26.0. Found: C, 68.0; H, 5.51; S, 26.3.

Diethyl *p*-Thiophenoxyphenylsulfonium Fluoroborate (**2**).—Ethyl *p*-thiophenoxyphenyl sulfide (1.25 g, 5.08 × 10^{-3} mol) was added to triethyloxonium fluoroborate (1.45 g, 7.63 × 10^{-3} mol) in 5 ml of chloroform. The mixture was refluxed for 16 hr and cooled, and 5 ml of water added to the reaction mixture. The aqueous layer was separated and washed with three 3-ml portions of chloroform. The combined chloroform layer was dried over magnesium sulfate and the solvent evaporated. The residue was twice recrystallized from ethanol, giving 1.0 g (54.5%) of diethyl *p*-thiophenoxyphenylsulfonium fluoroborate as pale yellow rods, mp 104–106°. Its ir spectrum (Nujol mull) had peaks at 1570 (s), 1480 (s), 1440 (s), 1400 (m), 1290 (m), 1210 (w), 1050 (s), 820 (m), 750 (s), and 690 cm^{-1} (m). Its nmr spectrum showed a triplet (6 H, J = 7.0) at 1.30 ppm, a quartet (4 H, J = 7.0) at 3.70 ppm, and multiplets (*ca.* 7 H and 2 H, respectively) at 7.25–7.7 and 7.7–8.1 ppm.

Anal. Calcd for $C_{16}H_{19}S_2BF_4$: C, 53.0; H, 5.29; S, 17.7. Found: C, 53.3; H, 5.48; S, 17.5.

Ethyl *p*-Phenylsulfonylphenyl Sulfone.—Hydrogen peroxide (30% solution, 1.8 g) was added drop by drop to a solution of ethyl *p*-thiophenoxyphenyl sulfide (1.23 g, 0.005 mol) in 2 ml of glacial acetic acid. The mixture was heated under reflux for 3 hr and was then poured into 10 ml of water. The mixture was extracted with three 5-ml portions of chloroform and the chloroform extract dried over magnesium sulfate. Evaporation of the solvent and recrystallization of the residue from ethanol gave ethyl *p*-phenylsulfonylphenyl sulfone as white plates, mp 114–116°. Its ir spectrum (Nujol mull) had strong peaks at 1160 and 1320 cm^{-1}.

Anal. Calcd for $C_{14}H_{14}O_4S_2$: C, 54.2; H, 4.55; S, 20.7. Found: C, 54.5; H, 4.64; C, 20.8.

Ethyl *o*-thiophenoxyphenyl sulfide (**4**) was prepared by a procedure similar to that used for the preparation of ethyl *p*-thiophenoxyphenyl sulfide, starting with 7.0 g (0.0348 mol) of phenyl *o*-aminophenyl sulfide.[20] Distillation of the product gave ethyl *o*-thiophenoxyphenyl sulfide as a yellow oil, bp 141–142° (3 mm), in 43% yield. Its ir spectrum had peaks at 1570 (m), 1480 (s), 1440 (s), 1370 (w), 1250 (m), 1100 (w), 1040 (m), 1420 (m), 750 (s), and 690 cm^{-1} (s). Its nmr spectrum showed a triplet (3 H, J = 7.0) at 1.30 ppm, a quartet (2 H, J = 7.0) at 2.90 ppm, and a broad absorption (9 H) around 7.3 ppm. Its molecular weight (mass spectrum) was 246.

Anal. Calcd for $C_{14}H_{14}S_2$: C, 68.3; H, 5.73; S, 26.0. Found: C, 67.8; H, 5.80; S, 26.1.

Diethyl *o*-thiophenoxyphenylsulfonium fluoroborate was prepared in the same manner as diethyl *p*-thiophenoxyphenylsulfonium fluoroborate, starting with 1.25 g (5.08 × 10^{-3} mol) of ethyl *o*-thiophenoxyphenyl sulfide. The product (obtained in 66% yield) was recrystallized from ethanol and melted at 99–101°. Its ir spectrum (Nujol mull) had peaks at 1580 (m), 1290

(18) We wish to express our thanks to Mr. Thomas Mead, American Cyanamid Co., Stamford, Conn., and Dr. Arthur Kluge, Cornell University, for the mass spectroscopic analyses.

(19) R. F. Borch, *J. Org. Chem.*, **34**, 627 (1969).

(20) E. Bourgeois and P. Huber, *Recl. Trav. Chim. Pay-Bas*, **31**, 30 (1912).

(m), 1260 (m), 1050 (s), 800 (w), 770 (s), 730 (w), 710 (w), and 700 cm^{-1} (m). Its nmr spectrum showed a triplet (3 H, J = 7.0) at 1.30 ppm, a quartet (4 H, J = 7.0) at 3.75 ppm, and multiplets at 7.25–7.65 (8 H) and 7.7–8.1 (1 H) ppm.

Preparation of Diphenyl Disulfide-d_{10}.—Phenyl-d_5-magnesium bromide was prepared in the usual manner from 10.0 g (0.063 mol) of bromobenzene-d_5[21] and 1.66 g (0.0693 g-atom) of magnesium in 40 ml of ether. Sulfur powder (2.0 g, 0.0625 mol) was added slowly to the mixture, which was stirred at room temperature according to the procedure of Leuckart.[22] After completion of the addition, the mixture was stirred for an additional 6 hr. The reaction was then quenched by the addition of water and then of dilute hydrochloric acid, and the ether layer was separated, dried over magnesium sulfate, and evaporated under vacuum to give a yellow fluid residue. The residue was stirred while a solution of ferric chloride (3.55 g, 0.0219 mol) in 8 ml of water was slowly added. The mixture was stirred for 1 hr and filtered, and the collected solids were washed with water and with dilute hydrochloric acid. Recrystallization of the product from ethanol gave 2.67 g (40.5%) of diphenyl disulfide-d_{10} as small needles, mp 60–61°. It showed essentially no absorption in the proton nmr region. Its ir spectrum showed peaks at 1550 (m), 1340 (s), 1320 (m), 1030 (m), 870 (w), and 820 cm^{-1} (m). Its mass spectrum showed peaks at m/e 228 and 227 in the ratio 95.2:4.8.

Reaction of Diphenyl Disulfide-d_{10} with Triethyloxonium Fluoroborate.—A mixture of diphenyl disulfide-d_{10} (0.5 g, 0.0022 mol) and triethyloxonium fluoroborate (0.00876 mol) in chloroform was refluxed and worked up as described for the undeuterated disulfide. The vpc retention times of the products were identical with those of the undeuterated products. Ethyl p-thiophenoxyphenyl sulfide-d_9 was isolated by vpc. Its mass spectrum showed the following parent peaks.

m/e	Mol %
255 ($C_{14}H_5D_9S_2$)	81
254 ($C_{14}H_6D_8S_2$)	16
253 ($C_{14}H_7D_7S_2$)	3

Reaction of Diphenyl Disulfide and Diphenyl Disulfide-d_{10} with Triethyloxonium Fluoroborate.—A mixture of diphenyl disulfide (0.25 g, 0.00115 mol) and diphenyl disulfide-d_{10} (0.25 g, 0.00110 mol) was allowed to react with 1.76 g of triethyloxonium fluoroborate and worked up as usual. The ethyl p-thiophenoxyphenyl sulfide fraction was isolated by vpc. Parent peaks of the mass spectrum are shown in Table I. The reaction was repeated using

TABLE I

m/e	Mol %	m/e	Mol %
255 ($C_{14}H_5D_9S_2$)	13.6	250 ($C_{14}H_{10}D_4S_2$)	21.6
254 ($C_{14}H_6D_8S_2$)	6.1	249 ($C_{14}H_{11}D_3S_2$)	4.4
253 ($C_{14}H_7D_7S_2$)	2.7	248 ($C_{14}H_{12}D_2S_2$)	1.7
252 ($C_{14}H_6D_6S_2$)	3.1	247 ($C_{14}H_{13}DS_2$)	4.7
251 ($C_{14}H_9D_5S_2$)	22.0	246 ($C_{14}H_{14}S_2$)	20.1

0.5 g of diphenyl disulfide (0.00231 mol) and 0.54 g (0.00237 mol) of diphenyl disulfide-d_{10}. Recovered diphenyl disulfides, **3**, and **4** were isolated by vpc. The parent peaks of their mass spectra are shown in Table II.

Reaction of Diphenyl Disulfide with Triethyloxonium Fluoroborate in the Presence of Anisole.—A mixture of diphenyl disulfide (2.18 g, 0.01 mol), anisole (2.16 g, 0.02 mol), and triethyloxonium fluoroborate (8.02 g, 0.05 mol) in 10 ml of chloroform was refluxed for 2.5 hr. It was then washed with water, the chloroform layer dried, and the solvent evaporated. The residue was refluxed with 10 ml of 10 N sodium hydroxide solution for 10 hr and (after cooling in ice) extracted with chloroform. The chloroform layer was washed with water, dried, and evaporated to give 4.4 g of yellow oil. The components of the product mixture were isolated by vpc on a 5 ft, 20% SE-30 on Chromosorb W column and identified by their vpc retention times and ir spectra as recovered anisole, ethyl phenyl sulfide, and χ-thiophenoxyanisole.[12] A sample of p-thiophenoxyanisole was prepared for comparison by the method of Truce.[12b] Comparison

(21) Obtained from Diaprep, Inc., Atlanta, Ga.

(22) R. Leuckart, *J. Prakt. Chem.*, **41**, 179 (1890).

TABLE II

Diphenyl Disulfide

m/e	Mol %	m/e	Mol %
228 ($C_{12}D_{10}S_2$)	16.1	222 ($C_{12}H_6D_4S_2$)	3.8
227 ($C_{12}HD_9S_2$)	3.4	221 ($C_{12}H_7D_3S_2$)	2.0
226 ($C_{12}H_2D_8S_2$)	2.1	220 ($C_{12}H_8D_2S_2$)	3.8
225 ($C_{12}H_3D_7S_2$)	3.8	219 ($C_{12}H_9DS_2$)	6.3
224 ($C_{12}H_4D_6S_2$)	7.2	218 ($C_{12}H_{10}S_2$)	18.6
223 ($C_{12}H_5D_5S_2$)	32.6		

Thianthrene (**3**)

224 ($C_{12}D_8S_2$)	18.7	219 ($C_{12}H_5D_3S_2$)	8.2
223 ($C_{12}HD_7S_2$)	6.3	218 ($C_{12}H_6D_2S_2$)	3.7
222 ($C_{12}H_2D_6S_2$)	3.2	217 ($C_{12}H_7DS_2$)	5.6
221 ($C_{12}H_3D_5S_2$)	4.6	216 ($C_{12}H_8S_2$)	16.4
220 ($C_{12}H_4D_4S_2$)	33.3		

Ethyl o-Thiophenoxyphenyl Sulfide (**4**)

255	16.7	250	18.7
254	7.4	249	5.4
253	1.7	248	4.0
252	2.1	247	2.8
251	23.3	246	17.7

with synthetic mixtures showed that ethyl phenyl sulfide and p-thiophenoxyanisole were present in a 1:1 molar ratio.

Reaction of Di-β-naphthyl Disulfide with Trimethyloxonium Fluoroborate.—Di-β-naphthyl disulfide (5.0 g, 0.0158 mol) was added slowly to a suspension of trimethyloxonium fluoroborate[23a] (11.6 g, 0.0785 mol) in 50 ml of a 3:1 mixture of methylene chloride and nitromethane. The mixture was then heated under reflux for 24 hr, first becoming dark green and then changing to dark blue. The mixture was washed with water, the organic layer dried over magnesium sulfate, and the solvent evaporated. The residue was triturated with chloroform, and the insoluble solids (2.85 g) were extracted with acetone. The acetone-insoluble solids (0.49 g) could not be dissolved in any solvent tested and were not further investigated. Partial evaporation of the acetone resulted in precipitation of a solid, which was recrystallized from acetone–chloroform to give 1.76 g (0.0078 mol, 49%) of dimethyl-β-naphthylsulfonium fluoroborate, mp 126–128°, as colorless prisms. It was identified by comparison with a synthetic sample (see below). Further evaporation of the acetone mother liquors gave a second solid which was recrystallized from chloroform–acetone and then sublimed under vacuum to give 0.76 g (38%) of **8a** as colorless needles, mp 184–186°. Its nmr spectrum showed a multiplet from 7.50–7.75 ppm.

Anal. Calcd for $C_{20}H_{12}S_2$: C, 76.0; H, 3.80; S, 20.2. Found: C, 75.8; H, 3.98; S, 20.1.

Preparation of Dimethyl β-Naphthylsulfonium Fluoroborate.—Methyl β-naphthyl sulfide[23b] (2.0 g, 0.015 mol) was added slowly to a refluxing suspension of trimethyloxonium fluoroborate in 3:1 methylene chloride–nitromethane. After 3 hr, the mixture was washed with water, dried with magnesium sulfate, and evaporated. The residue was recrystallized twice from acetone–ether to give 1.5 g (0.0055 mol, 37%) of dimethyl β-naphthylsulfonium fluoroborate, mp 126–128°. Its nmr spectrum (in deuterioacetone) showed a singlet (6 H) at 2.85 ppm and a multiplet (7 H) at 7.0–8.2 ppm.

Registry No.—**2**, 28443-97-2; **4**, 28443-99-4; **5**, 28444-00-0; **8a**, 226-59-5; diphenyl disulfide, 882-33-7; triethyloxonium fluoroborate, 368-39-8; diethoxycarbonium fluoroborate, 1478-41-7; ethyl p-phenylsulfonylphenyl sulfone, 28443-98-3; diethyl-o-thiophenoxyphenylsulfoniumfluoroborate, 28444-01-1; dimethyl-β-naphthylsulfonium fluoroborate, 28444-03-3.

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(23) (a) H. Meerwein, *Org. Syn.*, **46**, 120 (1966); (b) J. Jacques, *Bull. Soc. Chim. Fr.*, 231 (1955).