to 0.2%. The ratio of per cent reaction of I/II in the chemical and photochemical reaction is 1.1 and 1.4, respectively. The similarity of these two ratios suggest that singlet oxygen is the oxidant.[1a,d] Foote[1a] has presented relative reactivities for a series of olefins with singlet oxygen. With II as the common olefin in this series and the present data, I may be placed in the series. It is found that I is 0.034 times as reactive with singlet oxygen as tetramethylethylene, which is the most reactive monoolefin in the series. However, I is 720 times as reactive as *trans*-4-methyl-2-pentene, the least reactive olefin. The results indicate that allylic hydrogen atoms are not a prerequisite for facile reaction of singlet oxygen with an appropriately substituted olefin. The most reasonable mechanism for the reaction is *via* a 1,2-dioxetane intermediate as shown below.
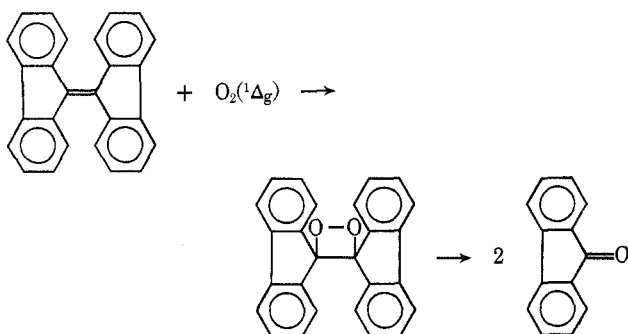
The generation of the 1,2-dioxetane by methods previously employed by us[7] and the initial electronic state of fluorenone are currently under investigation.

Experimental Section[10]

Materials.—9,9'-Bifluorenylidene (I) (Matheson Coleman and Bell), mp 193–194° (lit.[11] mp 188–190°), was used as received. The nmr spectrum of three multiplets centered at 7.12, 7.50, and 8.20 with relative areas of 2:1:1 was consistent with that previously reported.[12] The ir spectrum was void of significant absorption in the carbonyl region. The following chemicals were obtained from Matheson Coleman and Bell and were used without further purification: 2-methyl-2-butene (II), 30% hydrogen hydroperoxide, methylene blue chloride, and biphenyl. A 5% sodium hypochlorite (Purex) solution was used. The reagent grade solvents, methanol, dioxane, and methylene chloride, were used as received. Reagent grade tetrahydrofuran was distilled from calcium hydride.

Photosensitized Oxygenations.—An immersion photochemical reactor similar to the design given by Gollnick and Schenck[13] was used with circulating ice-cooled water. Oxygen was passed in a slow stream through a glass frit in the bottom of the reactor. Irradiation was carried out with a Sylvania Type DWY-625W tungsten–iodine lamp operated at 60 V. In a typical reaction, the reactor was charged with 0.3304 g (1.00 mmol) of I, 70.2 mg (1.00 mmol) of II, 50 mg of methylene blue, and 133.5 g of methylene chloride. Photooxygenation was conducted for 2.33 hr. At this time an aliquot was removed and weighed. Biphenyl and tetrahydrofuran (THF) were weighed into the aliquot as standards for glpc analysis. The samples were kept cool and immediately subjected to glpc analysis. Analyses for II and the

THF internal standard were carried out on a PAR-2, 5 ft × ⅛ in. column, operated at 103° (injector 220°, detector 250°) with a 29-ml/min flow of nitrogen. Retention times for a 1-μl injection were 10 and 19 min, respectively, for I and THF. Analyses for fluorenone and the biphenyl internal standard were performed on a 15% Apiezon L on Chromosorb G, 10 ft × ⅛ in. column, operated at 220° (injector 220°, detector 250°) with a 29-ml/min flow of nitrogen. Retention times for a 1-μl injection were 5.6 and 21 min, respectively, for biphenyl and fluorenone. Yields and per cent reaction, based on initial amounts of I and II, were calculated from the glpc data by comparison with standard mixtures of the solvent, II, fluorenone, and the internal standards. In one reaction with I, the methylene chloride solvent was removed on a rotary evaporator. The remaining mixture was triturated with ether and then filtered to remove methylene blue. The concentrated filtrate was subjected to column chromatography on Merck acid-washed alumina to give fluorenone, mp 82.5–83.5° (lit.[14] mp 83°). Nmr and ir spectra of the sample were identical with those given in the Sadler spectra.

Oxygenation with Sodium Hypochlorite–Hydrogen Peroxide.—In a typical reaction, 15 ml of 5% Purex (0.67 *M*, 10 mmol) was added with mechanical stirring to an ice-cold solution of 0.3304 g (1.00 mmol) I, 74.6 mg (1.07 mmol) II, 2.1 ml of 30% hydrogen peroxide (9.4 *M*, 20 mmol), 20 ml of methanol, and 80 ml of dioxane. After a 7-min addition period, followed by stirring for 1 hr, an aliquot was withdrawn and subjected to glpc analysis for II as described in the previous section. Glpc analysis for fluorenone was carried out as described above, but after work-up by extracting with ether, drying over magnesium sulfate, and concentrating on a rotary evaporator. Fluorenone was identified in these reactions by comparison of glpc retention times and by thin layer chromatography.

(10) Gas–liquid partition chromatography (glpc) was performed on a Varian Aerograph Hy-F:III Series 1200 flame ionization instrument. Infrared spectra were measured in carbon tetrachloride with a Perkin-Elmer Model 621 spectrometer. Nmr spectra was determined in carbon tetrachloride solution with a Varian Model A-60 spectrometer. Chemical shifts are expressed in parts per million (ppm) relative to internal tetramethylsilane as 0 ppm (δ scale). All melting points are corrected and were determined with a Hoover–Thomas capillary melting point apparatus.

(11) R. C. Fuson and H. D. Porter, *J. Amer. Chem. Soc.*, **70**, 895 (1948).

(12) M. Rabinovitz, I. Agranat, and E. D. Bergmann, *Tetrahedron Lett.*, 1265 (1965).

(13) K. Gollnick and G. O. Schenck, in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press Inc., New York, N. Y., 1967, Chapter 10.

(14) M. Frankel and S. Patai, "Tables for Identification of Organic Compounds," The Chemical Rubber Co., Cleveland, Ohio, 1964.
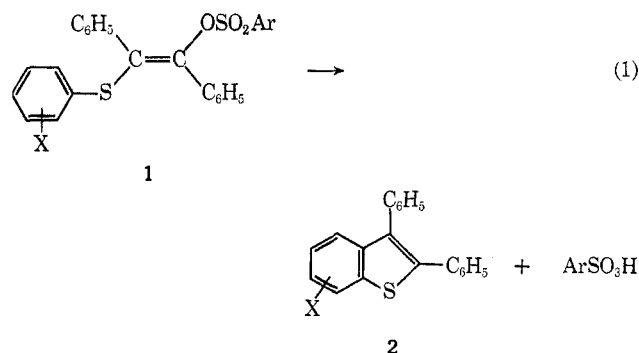

Cyclization of Arylthiovinyl Sulfonic Esters to Benzo[b]thiophenes. An Unusual 1,2-Sulfur Shift

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An unusual rearrangement was observed in the cyclization of some arylthiovinyl sulfonic esters **1** to benzo[b]thiophenes **2**[1] (eq 1).


(1) (a) G. Capozzi, G. Melloni, G. Modena, and M. Piscitelli, *Tetrahedron Lett.*, 4039 (1968); (b) G. Capozzi, A. Di Bello, G. Melloni, and G. Modena, *Ric. Sci.*, **39**, 267 (1969).
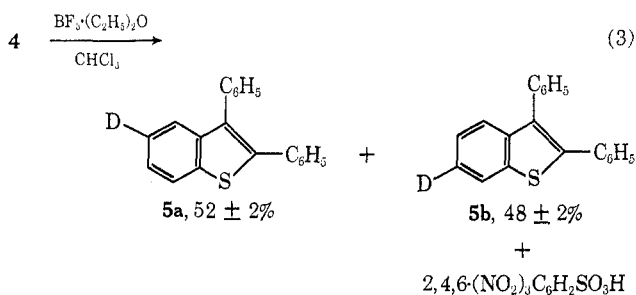
When the substituent X (CH₃, CH₃O, Cl, Br) in **1** was *para* to the vinylthio group, the benzo[*b*]thiophene formed had the substituent in the 6 position, *i.e.*, *meta* to the sulfur, instead of the expected 5 position. No "formal migration" of the substituent was observed when X (CH₃O, Cl) in **1** was *meta* to the vinylthio group. In this case, the expected 4- and 6-substituted benzo[*b*]thiophenes were formed.

In order to obtain further information on the mechanism of the rearrangement and a better understanding of the effect of the substituents, the cyclization of a deuterium-labeled arylthiovinyl sulfonic ester was studied.

Reaction of *p*-deuteriophenylsulfenyl chloride (**3**) with silver 2,4,6-trinitrobenzenesulfonate (AgTNBS) and tolane in methylene chloride afforded 1,2-diphenyl-2-*p*-deuteriophenylthiovinyl 2,4,6-trinitrobenzenesulfonate (**4**), probably of *trans* configuration[1a] (eq 2).

$$D-\!\!\!\!\bigcirc\!\!\!\!-SCl \ + \ AgTNBS \ + \ C_6H_5C\!\equiv\!CC_6H_5 \ \xrightarrow[-AgCl]{CH_2Cl_2}$$

$$\text{(2)}$$

4
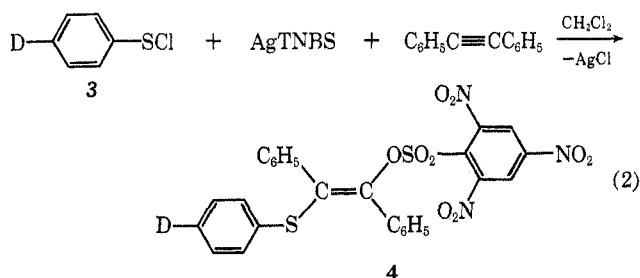
Cyclization of **4** in the presence of BF₃ etherate afforded in good yield a mixture of deuterated 2,3-diphenylbenzo[*b*]thiophenes **5** (eq 3).

$$\mathbf{4} \ \xrightarrow[CHCl_3]{BF_3\cdot(C_2H_5)_2O} \qquad\qquad (3)$$

5a, 52 ± 2%   **5b**, 48 ± 2%
+
$$2,4,6\text{-}(NO_2)_3C_6H_2SO_3H$$

To determine the position of the deuterium atom in the benzo[*b*]thiophenes formed, authentic 5- and 6-deuterio-2,3-diphenylbenzo[*b*]thiophenes were prepared from the corresponding bromo derivatives. Infrared analysis[2] of mixtures of the two model compounds, based on the different aromatic substitution patterns in the 900–600-cm⁻¹ region of their spectra, made it possible to ascertain that **5** was actually a mixture of 2,3-diphenyl-5-deuteriobenzo[*b*]thiophene (**5a**, 52 ± 2%) and 2,3-diphenyl-6-deuteriobenzo[*b*]thiophene (**5b**, 48 ± 2%).

Chemical and kinetic studies of the reactions of compounds **1** have suggested[1,3] that the rate-determining step of the reactions is the formation of a cationic species which can be formulated as **6a**, **6b**, or **6c**. The present results suggest that the cyclization may occur by two distinct pathways (a and b)[4] leading from **6** to benzo[*b*]thiophenes **5**, as illustrated in Scheme I.

(2) An attempt to analyze mixture **5** by means of nmr techniques failed owing to the complexity of the multiplets corresponding to the aromatic protons.

(3) G. Modena and U. Tonellato, *Chem. Commun.*, 1676 (1968).

SCHEME I
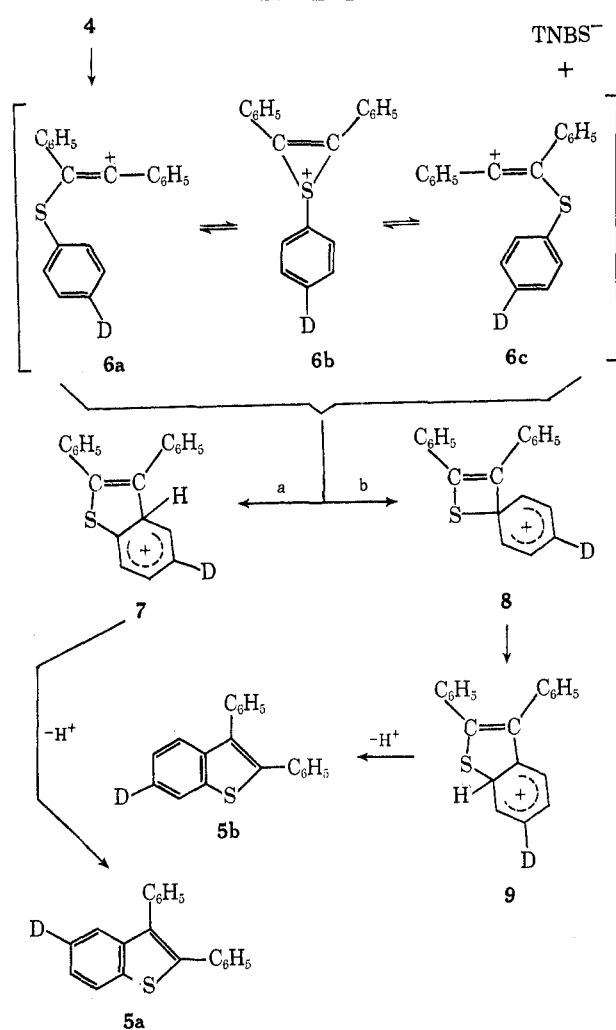
Path a is a Friedel–Crafts-like internal attack of the positive center at either *ortho* position adjacent to the sulfur of the phenylthio nucleus to give **7**, which then suffers loss of a proton. Path b implies attack of the positive center at the 1 position of the phenylthio nucleus[5] followed by a 1,2-sulfur shift and loss of a proton.

In our opinion, breaking of the S–phenyl bond before the formation of the new C–phenyl bond is unlikely and would have caused randomization of the label in all positions of the phenylthio nucleus or some loss in the deuterium content of the cyclization products, contrary to the experimental results.

The results indicate that paths a and b are almost equally probable in the unsubstituted derivative, and that even a small perturbing factor, like a substituent in the *meta* or *para* position with respect to sulfur, causes a distinct unbalance in the system, favoring either path a or b. This is consistent with the general scheme proposed for the reactions of compounds **1**, which considers the product-forming step as fast.

(4) In principle, one could also formulate a transition state common to both pathways in which the positive charge is distributed among the vinyl carbon, the sulfur, and the three apical carbons of the phenylthio nucleus in a kind of nonclassical ion. In any event, for the sake of simplicity, we will carry on the discussion on the basis of pathways a and b, which represent the limiting cases.

(5) This step, as well as the formation of **7** in path a, could also be formulated as a ring enlargement of the cyclic sulfonium cation **6b**.

Since the cationic intermediate is a highly reactive species, it is expected that it reacts by a transition state very "reactantlike," or in other terms that it is more sensitive to the charge distribution in the initial state than to the stability of the products.

As a matter of fact, if the course of the reaction is determined by the position of attack of the electrophilic center to the arylthio nucleus and independent of the energy and the fate of intermediates **7** and **8**, the results hitherto obtained may be rationalized on the basis of the directing effect of the substituents. Those so far studied are indeed of the *ortho,para*-directing type, and consequently when they are *para* they direct the attack at the 1 position (rearrangement), whereas when they are *meta* they direct the attack at the 2,6-positions (no rearrangement) of the phenylthio nucleus.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were determined in carbon disulfide solution on a Perkin-Elmer Model 225 spectrophotometer.

p-**Bromophenyl** *t*-**butyl sulfide** was prepared in 61% yield by the method previously reported for the synthesis of phenyl *t*-butyl sulfide[6] as a colorless liquid, bp 153–155° (20 mm).

Anal. Calcd for $C_{10}H_{13}BrS$: C, 48.99; H, 5.34; Br, 32.59; S, 13.08. Found: C, 48.98; H, 5.24; Br, 32.22; S, 12.93.

p-**Deuteriophenyl** *t*-**Butyl Sulfide.**—*p*-(*t*-Butylthio)phenylmagnesium bromide from 9.5 g of *p*-bromophenyl *t*-butyl sulfide and 1.2 g of magnesium in 40 ml of anhydrous ether was hydrolyzed with a 15% solution of deuterium chloride in deuterium oxide. The ether solution was separated and dried (Na_2SO_4) and the solvent was removed. The liquid residue was distilled twice to give 4.6 g (71% yield) of *p*-deuteriophenyl *t*-butyl sulfide, bp 106–107° (20 mm) [lit.[6] bp 73° (5 mm) for phenyl *t*-butyl sulfide]; the corresponding sulfone was obtained, mp 99–100° (lit.[6] mp 98–99° for pheny *t*-butyl sulfone).

p-**Deuteriophenylsulfenyl chloride** (3) was prepared by chlorinolysis of *p*-deuteriophenyl *t*-butyl sulfide (4.6 g) by chlorine in carbon tetrachloride at −10°, following a modification of the procedure reported by Kharasch and Langford[7] for the synthesis of 2,4-dinitrophenylsulfenyl chloride, and purified by distillation. There were obtained 3.5 g (87% yield) of **3**, bp 90–92° (20 mm), identical with that of a sample of phenylsulfenyl chloride prepared by the same method.

1,2-Diphenyl-2-*p*-deuteriophenylthiovinyl 2,4,6-Trinitrobenzenesulfonate (4).—Tolane (1.78 g, 10 mmol) was dissolved in 60 ml of anhydrous methylene chloride, silver 2,4,6-trinitrobenzenesulfonate (acetonitrile complex,[8] 5.23 g, 10 mmol) was added, and the suspension was stirred for a few minutes. A solution of **3** (1.45 g, 10 mmol) in 15 ml of methylene chloride was added dropwise at 15° and the reaction mixture was stirred for 10 min. Filtration of the insoluble AgCl followed by addition of pentane to the clear solution resulted in the precipitation of **4** (2.8 g, 48% yield) as a yellow, crystalline solid, which was purified by crystallization from methylene chloride–pentane, mp 109–110° dec. A mixture melting point with 1,2-diphenyl-2-phenylthiovinyl 2,4,6-trinitrobenzenesulfonate (prepared by the same method)[1a] was 109–110° dec.

2,3-Diphenyl-5-bromobenzo[*b*]thiophene was prepared in 53% yield by cyclization of 2-phenyl-2-*p*-bromophenylthioacetophenone in polyphosphoric acid.[1a] Chromatography on silica gel (hexane) and recrystallization from ethanol gave white crystals, mp 175–176°.

Anal. Calcd for $C_{20}H_{13}BrS$: C, 65.75; H, 3.59; Br, 21.88; S, 8.78. Found: C, 66.04; H, 3.59; Br, 21.77; S, 8.77.

2,3-Diphenyl-5-deuteriobenzo[*b*]thiophene (5a).—The Grignard reagent prepared from 1.0 g of 2,3-diphenyl-5-bromobenzo[*b*]-thiophene and 0.15 g of magnesium in 100 ml of anhydrous ether was hydrolyzed with a 15% solution of deuterium chloride in deuterium oxide. The ether solution was separated, the solvent was removed, and the residue was chromatographed on silica gel. Elution with hexane gave 0.6 g (76% yield) of **5a**, which was recrystallized from ethanol, mp 113–114°.[9]

Mass spectrometric data indicated a deuterium content of 0.89 ± 0.02 atoms per molecule.

2,3-Diphenyl-6-bromobenzo[*b*]thiophene was prepared in 89% yield by cyclization of 1,2-diphenyl-2-*p*-bromophenylthiovinyl 2,4,6-trinitrobenzenesulfonate in the presence of gaseous BF_3.[1a] Recrystallization from ethanol gave white crystals, mp 169–171°.[1b]

Anal. Calcd for $C_{20}H_{13}BrS$: C, 65.75; H, 3.59; Br, 21.88; S, 8.78. Found: C, 66.25; H, 3.53; Br, 21.88; S, 8.72.

2,3-Diphenyl-6-deuteriobenzo[*b*]thiophene (5b) was prepared in 73% yield from 2,3-diphenyl-6-bromobenzo[*b*]thiophene by the same procedure reported for the preparation of **5a**, mp 113–114°.[9]

Mass spectrometric data indicated a deuterium content of 0.90 ± 0.02 atoms per molecule.

Treatment of 4 with BF_3 Etherate.—**4** (2.5 g, 4.3 mmol) was dissolved in 200 ml of anhydrous methylene chloride, 20 ml of boron trifluoride diethyletherate was added, and the reaction mixture was allowed to stand for 24 hr at room temperature. The 2,4,6-trinitrobenzenesulfonic acid formed was filtered, and the solution was washed with water and dried (Na_2SO_4). The solvent was evaporated and the residue was chromatographed on silica gel. Elution with hexane gave, after recrystallization from ethanol, 1.05 g (85% yield) of a mixture of deuterated 2,3-diphenylbenzo[*b*]thiophenes **5**, mp 113–114°.[9]

Mass spectrometric data indicated a total deuterium content of 0.90 ± 0.02 atoms per molecule.

The infrared analysis of the mixture was performed by means of calibration curves, based on a band at 821 cm^{-1} for **5a** and a band at 640 cm^{-1} for **5b**, obtained from mixtures of the two model compounds in various ratios.

(6) V. N. Ipatieff, H. Pines, and B. S. Friedman, *J. Amer. Chem. Soc.*, **60**, 2731 (1938).

(7) N. Kharasch and R. B. Langford, *J. Org. Chem.*, **28**, 1903 (1963).

(8) D. J. Pettitt and G. K. Helmkamp, *ibid.*, **29**, 2702 (1964).

(9) Identical with that of an authentic sample of 2,3-diphenylbenzo[*b*]-thiophene.[1]

The Photoreactions of 2,4-Dimethoxyacetanilide[1-3]

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Aryl esters and N-arylamides have been found to undergo photo Fries rearrangements.[4-6] Recently, we reported that, when 2,4-dimethoxyphenyl acetate (I) was irradiated, not only a normal photo-Fries rearrangement to the unoccupied *ortho* position took place but

(1) Supported by the Research Division, Brigham Young University, and the United Fund of Utah County.

(2) Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer purchased under the National Science Foundation Grant GP-6837.

(3) Presented at the Pacific Northwest Regional Meeting, Salt Lake City, Utah, June 1969.

(4) (a) J. C. Anderson and C. B. Reese, *Proc. Chem. Soc.*, 217 (1960); (b) J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781, (1963).

(5) See D. Bellus and P. Hrdlovic, *Chem. Rev.*, **67**, 599 (1967), for a review of the photo-Fries and related reactions.

(6) (a) D. Elad, *Tetrahedron Lett.*, 873 (1963); (b) D. Elad, D. V. Rao, and V. I. Stenberg, *J. Org. Chem.*, **30**, 3252 (1965).