D,L-*threo*-1-Phenyl-1,2-propanediol Dibenzoate (VII) from D,L-*cis*-1-Phenyl-1,2-epoxypropane by Acid Hydrolysis.—A mixture of 3.00 g. of D,L-*cis*-1-phenyl-1,2-epoxypropane and 75 ml. of water was stirred vigorously for five minutes and then treated with 5 drops of perchloric acid (60%). After one hour of vigorous stirring at room temperature much unchanged starting material remained, so 50 ml. of water and 8 drops of perchloric acid were added to the mixture. One hour later, the mixture was only slightly turbid but a strong odor of epoxide was still noticeable. The mixture was stirred for two more hours and was allowed to stand overnight. The following morning the mixture was still turbid and the odor of starting material pronounced. Four drops of perchloric acid was added to the mixture and stirring was resumed for several hours. At the end of that period the mixture was still slightly turbid, but the odor of starting material weak. The mixture was saturated with sodium chloride, treated with excess sodium bicarbonate and extracted with ether. The ethereal extracts were washed with saturated sodium chloride solution, dried and evaporated. The residue was 3.57 g. of a colorless, viscous liquid, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.81s, 2.94m, 5.85w. Attempts to crystallize the residue were unsuccessful.

Two grams of the crude glycol in 9 ml. of pyridine, cooled in an ice-bath, was benzoylated with 3.68 g. of benzoyl chloride. Crystallization of the product from methanol yielded 2.64 g. (58.4% yield based on epoxide) of the *threo*-dibenzoate, m.p. 75.0–78.0°. Recrystallization from methanol afforded the analytical sample, m.p. 76.0–78.0°.

Anal. Calcd. for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.49; H, 5.70.

The compound was identical with the dibenzoate of VI according to mixed melting point determination and infrared spectrum.

Concentration of the mother liquor from the recrystallization of the dibenzoate (m.p. 75.0–78.0°) yielded 0.66 g. of colorless crystals, m.p. 68–103°.

D,L-*erythro*-1-Phenyl-1,2-propanediol Dibenzoate (IV) from *cis*-Propenylbenzene (II).—Careful fractionation of the mother liquors from the dibenzoate VII of the *threo*-glycol VI eventually led to pure dibenzoate IV of the *erythro*-glycol V. It was obtained from methanol as rosettes of short needles, m.p. 103–104°. The identity with IV was established by mixed melting point determination and by the infrared spectrum.

BETHESDA, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Chemistry of 1,4-Dithiadiene. III.[1] Preparation and Decomposition of Sulfoxides

BY H. HARRY SZMANT AND LUIS M. ALFONSO

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The monosulfoxides of 2,5-diphenyl-1,4-dithiadiene (I) and of the 3-nitro-, 3-bromo- and the 3-bromo-6-nitro derivatives of I were prepared. The sulfoxides are rather unstable and decompose to give substituted thiophenes. Possible mechanisms of the decomposition of the sulfoxide of I are suggested.

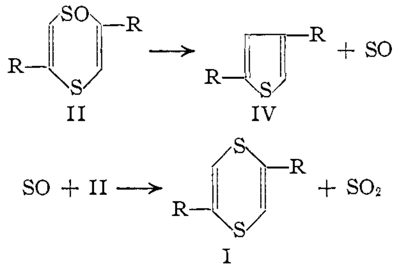
One of the remarkable reactions of 2,5-diphenyl-1,4-dithiadiene (I) and its derivatives is the formation of thiophenes during partial oxidation reactions. Parham[2] originally concluded that the formation of thiophenes proceeds by the loss of sulfur dioxide from an intermediate monosulfone of I. However, the thermal stability of the monosulfones of I[1] and of 2,5-diphenyl-3-bromo-1,4-dithiadiene[3] contradicts this conclusion. In our preceding publication[1] it was suggested that the monosulfoxide of I is the species which undergoes decomposition to a thiophene, and this paper provides experimental proof for this reaction path.

The preparation of the monosulfoxide of I (II) requires carefully controlled conditions because of the ease with which II is further oxidized and in view of its inherent instability. The use of peracetic acid and of a reaction time of two minutes permits the preparation of II in good yields (82%). The reduction of II by means of zinc yielded I, and the oxidation of II by peracetic acid gave a 72% yield of the monosulfone of I. The latter reaction is of interest since it indicates that the sulfoxide function of the heterocyclic ring of I is more susceptible to oxidation than the sulfide function.

The white crystals of II are rapidly discolored when exposed to light. Solutions of II were found to give upon heating either the molecular complex[1] III of I and 2,4-diphenylthiophene (IV) or only IV. The interesting feature in the formation of III is the apparent disproportionation of the sulfoxide. While the details of the mechanism of the decomposition of II are being currently investigated, we wish to suggest two possible paths by which II may produce either III or IV.

The first path may involve the loss of sulfur monoxide from II; the subsequent reduction of another molecule of II by the transient sulfur monoxide could produce I.

($R = C_6H_5$)



$$I + IV \longrightarrow III$$

The second possible path of the decomposition of II is visualized to proceed by way of a bimolecular complex of two sulfoxide molecules[4] and is represented symbolically as

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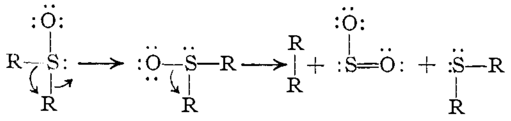
[1] For preceding paper see THIS JOURNAL, **78**, 1064 (1956).

[2] W. E. Parham and V. J. Traynelis, *ibid.*, **76**, 4960 (1954); **77**, 68 (1955).

[3] W. E. Parham, I. Nicholson and V. J. Traynelis, *ibid.*, **78**, 850 (1956).

[4] Association of sulfoxides was suggested by D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.*, 2442 (1949), to explain the differences in the infrared spectra of sulfoxides in solution and in the solid state; see also J. Cymerman and J. B. Willis, *ibid.*, 1332 (1951). F. G. Bordwell and B. M. Pitt, THIS JOURNAL, **77**, 572 (1955), suggest an association of sulfoxides with thionyl chloride (an inorganic "sulfoxide") during the reaction leading to the formation of a chloro sulfide and sulfur dioxide.



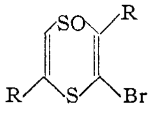
II + II IV I

$I + IV \longrightarrow III$

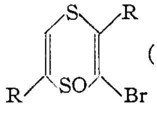
The formation of the resonance stabilized thiophene molecule would be expected to favor the elimination of sulfur dioxide from the bimolecular complex of II. It is possible that a mechanism such as that shown above may lead to disproportionation of sulfoxides *without* loss of sulfur dioxide in other systems lacking the proper driving force.

Present evidence indicates that both reaction paths may be operative in the decomposition of II and that the chosen reaction path may depend, in part, on the conditions of the reaction. Higher temperatures would be expected to favor the first of the suggested mechanisms and, if the temperature is such that the transient sulfur monoxide is removed or destroyed, the decomposition of II would then tend to produce IV rather than III. Lower temperatures, on the other hand, would be expected to favor the second of the suggested mechanisms, and the decomposition of II would then tend to produce III rather than IV. In support of these postulates are the following results. When solutions of II were warmed for a short time at 65–70° or at 90–95° only III could be isolated from the reaction mixtures, while from the reaction mixtures heated to 135° only IV could be obtained. Very significant results were obtained when dimethyl sulfoxide was employed as the solvent in the decomposition of II. The decomposition of II at 90–95° in dimethyl sulfoxide gave a 95% yield of IV and a gas which is believed to be dimethyl sulfide. Thus, at the same temperature at which a solution of II in toluene gave III, the reaction in dimethyl sulfoxide gave an almost quantitative yield of IV and the apparent reduction product of dimethyl sulfoxide. It is felt that the results of this experiment support the second mechanism modified to the extent that the bimolecular complex involves II and dimethyl sulfoxide. It is noteworthy that while I is known[2] to decompose to IV with the loss of sulfur, this reaction does not take place until higher temperatures (180°) are reached.

The controlled oxidation of 2,5-diphenyl-3-bromo-1,4-dithiadiene gave a sulfoxide which may have either structure V or VI.



V

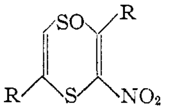


VI

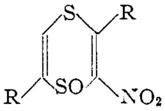
(R = C_6H_5)

Structure V is thought to be more probable than VI. The oxidation of the bromo sulfoxide gave the corresponding sulfone identical in melting point with that of the compound to which Parham[3] assigns the structure of 2,5-diphenyl-3-bromo-1,4-dithiadiene-1,1-dioxide. The results of the thermal decomposition of the bromo sulfoxide are inconclusive at this time and will be reported in the future.

The controlled oxidation of 2,5-diphenyl-3-nitro-1,4-dithiadiene gave a sulfoxide which may have the structure VII or VIII.



VII

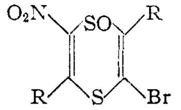


VIII

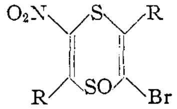
(R = C_6H_5)

It is suggested that structure VIII is more probable since it is obtained by the oxidation of the more electron-rich sulfur atom. Thermal decomposition of the above sulfoxide gave a 50% yield of product which appears to be the 2,4-diphenyl-3-nitrothiophene of Parham.[2]

The controlled oxidation of 2,5-diphenyl-3-nitro-6-bromo-1,4-dithiadiene gave a sulfoxide which may have structure IX or X.



IX



X

(R = C_6H_5)

It is suggested that IX is the more probable product for the same reason stated in connection with VIII. Thermal decomposition of the above sulfoxide gave a 51% yield of product which appears to be the 2,4-diphenyl-3-nitro-5-bromothiophene described by Parham.[3]

The infrared spectra of the new sulfoxides were examined and all compounds were found to possess the frequencies characteristic of sulfoxides.[5]

Experimental[6]

Preparation of 2,5-Diphenyl-1,4-dithiadiene-1-oxide (II).—A solution of 5 ml. of 40% peracetic acid in 25 ml. of ethyl acetate was added to a solution of 4 g. of I in 100 ml. of benzene. After two minutes the solution was washed with three 100-ml. volumes of water and the organic portion was dried over anhydrous calcium sulfate. Addition of 150 ml. of low boiling petroleum ether to the dried solution and chilling gave 3.5 g. (82%) of white crystals, m.p. 109° dec.

Anal. Calcd. for $C_{16}H_{12}OS_2$: C, 67.57; H, 4.25; S, 22.55. Found: C, 67.58; H, 4.27; S, 22.45.

Another experiment identical to the above except for the reaction time of 1.5 min. gave 2.8 g. (66%) of the product.

Reduction of II.—An excess of granular zinc was added to a solution of 0.50 g. of II in 25 ml. of glacial acetic acid, and the mixture was allowed to stand with occasional stirring for 3 days. The reaction mixture was then poured into water and the resulting mixture was extracted with benzene. The benzene extract was dried, concentrated, diluted with ethanol and again concentrated and deposited on standing 0.095 g. (20%) of I, m.p. and mixture m.p. 116–118°.

Oxidation of II.—A solution of 0.750 g. of II in 25 ml. of acetic acid was treated with 5 ml. of 40% peracetic acid, and the resulting solution was allowed to stand at room temperature for 2 hr. The reaction mixture was poured on ice and the white precipitate was collected, washed with water and dissolved in benzene. The benzene solution was diluted with isopropyl alcohol and concentrated to yield 0.565 g. (72%) of the monosulfone[1] of I, m.p. and mixture m.p. 152–154°.

Thermal Decomposition of II. (A).—A solution of 0.700 g. of II in 30 ml. of dry toluene was maintained at 90–95° for 25 min., and the resulting solution was cooled and chromatographed on alumina (Fisher, 80–200 mesh). The yellow eluate was concentrated, diluted with ethanol and again concentrated and gave 0.345 g. (56%) of yellow

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(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co., London, 1954, p. 295.

(6) All melting points are uncorrected. Microanalyses by Dr. A. Elek, Los Angeles, California.

crystals, m.p. 112–121°. One recrystallization from a mixture of benzene and ethanol gave III, m.p. and mixture m.p. 128–129°.

(B).—A solution of 0.500 g. of II in 25 ml. of 2-ethoxyethanol (Cellosolve, b.p. 135°) was boiled for 1 min. and then poured into water. The solid was collected by filtration and was recrystallized from a mixture of benzene and isopropyl alcohol to give 0.265 g. (58%) of yellowish crystals, m.p. 110–115°. One crystallization from isopropyl alcohol gave colorless plates, m.p. 120–122°, which did not depress the m.p. of authentic IV.

(C).—A solution of 0.700 g. of II in 30 ml. of dimethyl sulfoxide was maintained at 90–95° for 1 hr. while nitrogen was used to sweep the gaseous products into a 6% solution of mercuric chloride in water. The reaction mixture was poured into 700 cc. of water, and the resulting solution was extracted with three 100-ml. volumes of low boiling petroleum ether. The extract was concentrated with addition of ethanol and gave 0.55 g. (95%) of white plates, m.p. 120–122°, which did not depress the m.p. of authentic IV. The solution containing mercuric chloride was filtered and there was obtained 0.654 g. of white solid, m.p. 156–157°.[7]

(D).—A solution of 0.500 g. of II in 25 ml. of ethyl acetate was maintained at 65–70° for 1 hour, cooled and chromatographed on alumina. The yellow eluate was concentrated to give 0.355 g. (76%) of III, m.p. and mixture m.p. 128–129°.

Oxidation of 2,5-Diphenyl-3-bromo-1,4-dithiadiene.—A solution of 1.5 g. of the bromo compound[1,3] in 100 ml. of benzene was treated with a solution of 5 ml. of 40% peracetic acid in 25 ml. of ethyl acetate. The solution became colorless in 2.5 min. at room temperature and was immediately washed with three 100-ml. volumes of water. The organic layer was dried over anhydrous calcium sulfate, and upon dilution with low boiling petroleum ether and cooling, there was obtained 0.87 g. (61%) of white crystals, m.p. 115–116° dec., thought to be 3-bromo-2,5-diphenyl-1,4-dithiadiene-1-oxide (V).

Anal. Calcd. for $C_{16}H_{11}OS_2Br$: C, 52.89; H, 3.05; Br, 22.00. Found: C, 52.83; H, 3.14; Br, 21.61.

A solution of 0.310 g. of the above sulfoxide in 15 ml. of acetic acid was treated with 5 ml. of 40% peracetic acid, and the resulting solution was allowed to stand at room temperature for 9 hr. The reaction mixture was poured into water and extracted with several portions of 300 ml. of benzene. The benzene extract was washed with water, dried, diluted with ethanol and concentrated to yield 0.180 g. (55%) of long white needles m.p. 176–178° (lit.[3] m.p. 176.5–178.5°).

Oxidation of 2,5-Diphenyl-3-nitro-1,4-dithiadiene.—A solution of 0.600 g. of the nitro compound[3] in 100 ml. of benzene was treated with a solution of 5 ml. of 40% peracetic acid in 25 ml. of ethyl acetate. The color of the solution changed from red to yellow in 35 min. at room temperature, and the solution was washed then with three 100-ml. volumes of water. The organic layer was dried over anhydrous calcium sulfate, diluted with low boiling petroleum ether and chilled to give 0.350 g. (57%) of yellow crystals, m.p. 108° dec., thought to be 2,5-diphenyl-3-nitro-1,4-dithiadiene-4-oxide (VIII).

Anal. Calcd. for $C_{16}H_{11}O_3S_2N$: C, 58.34; H, 3.37; N, 4.25. Found: C, 57.60; H, 3.48; N, 4.20.

Attempts to dry the product *in vacuo* caused extensive decomposition, and it is believed that the analytical sample contained traces of moisture (calcd. for $C_{16}H_{11}O_3S_2N \cdot {}^1/_4 H_2O$: C, 57.60; H, 3.48; N, 4.20).

Thermal Decomposition of the Sulfoxide of 2,5-Diphenyl-3-nitro-1,4-dithiadiene.—A solution of 0.22 g. of the above sulfoxide in 15 ml. of toluene was maintained at the boiling point for 5 min., cooled and chromatographed on alumina. The column was eluted with benzene and the yellow fraction was concentrated, diluted with ethanol and again concentrated. The product (50%) was isolated as pale yellow crystals, m.p. 114–115° (lit.[3] m.p. 113–115°), and is thought to be 2,4-diphenyl-3-nitrothiophene.

Anal. Calcd. for $C_{16}H_{11}O_2SN$: C, 68.30; H, 3.94; N, 4.98. Found: C, 68.14; H, 3.91; N, 5.21.

Oxidation of 2,5-Diphenyl-3-bromo-6-nitro-1,4-dithiadiene.—A solution of 0.66 g. of the bromonitro compound[3] in 70 ml. of benzene was treated with a solution of 5 ml. of 40% peracetic acid in 25 ml. of ethyl acetate. The color of the solution changed from red to yellow in 2.5 hr. at room temperature, and the reaction mixture was then washed with three 100-ml. volumes of water. The organic layer was dried over anhydrous calcium sulfate, diluted with low boiling petroleum ether and chilled to give 0.30 g. (43%) of yellow orange crystals, m.p. 124–125° dec., thought to be 2,5-diphenyl-3-bromo-6-nitro-1,4-dithiadiene-1-oxide (IX).

Anal. Calcd. for $C_{16}H_{10}O_3S_2NBr$: C, 47.07; H, 2.47; N, 3.43. Found: C, 46.32; H, 2.61; N, 3.21.

Attempts to dry this material *in vacuo* caused extensive decomposition, and it is believed that the analytical sample contained traces of moisture (calcd. for $C_{16}H_{10}O_3S_2NBr \cdot {}^1/_4 H_2O$: C, 46.55; H, 2.56; N, 3.39).

Thermal Decomposition of the Sulfoxide of 2,5-Diphenyl-3-bromo-6-nitro-1,4-dithiadiene.—A solution of 0.11 g. of the above sulfoxide in 10 ml. of toluene was maintained at the boiling point for 5 min., cooled and chromatographed on alumina. The yellow fraction was concentrated, diluted with ethanol and again concentrated to give 51% of yellow needles, m.p. 102.5–103.5° (lit.[3] m.p. 103–103.5°).

Anal. Calcd. for $C_{16}H_{10}O_2SNBr$: C, 53.36; H, 2.80; N, 3.90. Found: C, 53.95; H, 2.65; N, 3.52.

Infrared Spectra.—The frequencies near 1050 cm.$^{-1}$ are listed in Table I.

TABLE I

Compound	Medium	Frequencies (cm.$^{-1}$) and intensity
II	$CHCl_3$	1040 (v.s.)
V (or VI ?)	Nujol	1030 (v.s.)
VIII (or VII ?)	Nujol	1020 (v.s.); 1030 (v.s.); 1045 (s.)
IX (or X ?)	Nujol	1034 (s.); 1050 (v.s.)

Acknowledgments.—We wish to thank Dr. Foil Miller for the determination of the infrared spectra in Nujol and The Stephan Chemical Company for the gift of dimethyl sulfoxide.

PITTSBURGH 19, PA.

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[7] The dimethyl sulfide–mercuric chloride complex is reported to melt at 150–151° by W. F. Faragher, J. C. Morell and S. Comay, THIS JOURNAL, 51, 2779 (1929).