peared at 4.55, 5.86 and 5.98 μ as well as other wave lengths.

Higher boiling fractions were obtained, b.p. 75–110° (2 mm.), which solidified to a crystalline solid. When recrystallized from petroleum ether (b.p. 30–60°) they gave 15.6 g. of 1,2,3,4-tetrabromobutene-2, m.p. 69–70°.

Addition of Excess Iodine to Butatriene.—Butatriene (1.0 g.) was treated with iodine (9.9 g.) in cold carbon tetrachloride (100 ml.). After evaporation of the solvent the residue was recrystallized from hexane and gave 7.2 g. of nearly white crystals, m.p. 97–102° with considerable charring and decomposition below that temperature. On being stored in the refrigerator for a few days it changed to an insoluble polymer which did not melt but exploded on being heated above 150°.

Anal. Calcd. for $C_4H_4I_4$: I, 90.7. Found: I, 88.5.

Hydration of Butatriene.—Butatriene (5.2 g.) was added in four portions to stirred ice-cooled 78% sulfuric acid (60 ml.). After an hour the mixture was poured on 500 g. of cracked ice and partly neutralized with sodium carbonate. The organic layer was separated and the aqueous layer extracted with ether. The combined organic layers were dried over anhydrous magnesium sulfate and the ether removed by distillation. Distillation of the residue through a modified Claisen head yielded 2.6 g. (37%) of methyl vinyl ketone, b.p. 29–32° (115–121 mm.), $n^{25}\text{D}$ 1.4110. The infrared spectrum of the product was identical with that of authentic methyl vinyl ketone and its semicarbazone, m.p. 140–143°, gave no depression in m.p. with methyl vinyl ketone semicarbazone.

Attempted Nascent Hydrogen Reduction of Butatriene.—The apparatus was similar to that used in the preparation of butatriene. A solution of butatriene (2 g.) in 60 ml. of absolute alcohol was added slowly to sodium slivers (10 g.) in 100 ml. of purified dioxane. Nitrogen was bubbled slowly through the reaction mixture during the addition and then more vigorously after the addition was complete. No volatile product collected in the cold traps. The reaction mixture after neutralization with hydrochloric acid and removal of the solvent yielded only a brown, insoluble polymeric material.

Attempted Reaction of Butatriene with Maleic Anhydride.—A solution of butatriene (1.0 g.) and maleic anhydride (5 g.) was allowed to stand for two weeks. Only maleic anhydride and a polymer which did not melt but did burn were recovered.

Attempted Reaction of Butatriene with Cyclopentadiene.—A solution of butatriene (5.2 g.) and cyclopentadiene (6.6 g.) in dry benzene (15 ml.) was allowed to stand for 60 days in the refrigerator. The benzene was removed by evaporation over nitrogen leaving a red molasses-like material which could not be distilled. On exposure to air it soon hardened to an orange wax-like material which, when heated, charred but did not melt.

Attempted Reaction with Diazoacetic Ester or Phenyl Azide.—When allowed to stand for long periods with diazoacetic ester and phenyl azide, butatriene yielded only starting materials and polymeric products.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Cyclic Dienes. III. The Synthesis of Thiophene 1-Dioxide[1,2]

BY WILLIAM J. BAILEY[3] AND EARL W. CUMMINS

RECEIVED AUGUST 6, 1953

Thiophene 1-dioxide (I) was synthesized in six steps from butadiene sulfone utilizing a stepwise exhaustive methylation. It was an unstable substance that could not be isolated in a pure form but was stable in solution. The structure of I was indicated by the method of synthesis, ultraviolet absorption and the ready addition of dimethylamine to form a known derivative.

Thiophene 1-dioxide (I) has attracted attention because knowledge of its aromatic character or lack of it would possibly shed light on the theoretical problems of whether sulfur could expand its valence shell beyond eight electrons and whether six electrons are necessary for aromatic resonance. In 1911, Lanfry[4] reported that the oxidation of thiophene with hydrogen peroxide produced the dioxide I as a water-insoluble oil boiling at 130°. Subsequent workers,[5] however, were unable to repeat his work. Although a whole series of thiophene 1-dioxide derivatives containing benzene rings have been prepared, the true nature of the thiophene 1-dioxide ring is obscured by the presence of other aromatic rings. Thus Backer, Bolt and Stevens[6] prepared 3,4-diphenylthiophene 1-dioxide by oxidation of the corresponding 3,4-diphenylthiophene. Similarly, Lanfry[7] prepared 2,3-benzothiophene 1-dioxide by the direct oxidation of benzothiophene. Both of these dioxides are stable compounds and that fact would indicate some degree of stabilization of thiophene 1-dioxide ring.

Overberger, Ligthelm and Swire[8] synthesized 2,5-diphenyl-3,4-diketo-2,3,4,5-tetrahydrothiophene 1-dioxide and deduced from its ultraviolet spectrum that it existed to a considerable extent in its enol form. In this case, it appears that the thiophene 1-dioxide ring is quite stable, but how much of this stability is due to the two phenyl groups cannot be determined.

Several thiophene 1-dioxides containing only aliphatic substituents have been reported, but in no case has the structure been unequivocally proved. Backer and Strating[9] reported that treatment of dimethylbutadiene sulfone dibromide with base produced 3,4-dimethylthiophene 1-dioxide. However, subsequent work showed that ozonolysis of the reaction product produced formic acid plus an unsaturated ketone.[10] Thus the structure of the reaction product was reassigned to 3-methylene-4-methyl-2,3-dihydrothiophene 1-dioxide. In this case there appears to be no driving force for the rearrangement of the double bonds to form a thiophene 1-dioxide ring.

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(1) This work was supported in part by the Office of Naval Research. Presented at the 118th Meeting of the American Chemical Society, Chicago, Illinois, September, 1950.

(2) Previous paper in this series, THIS JOURNAL, **75**, 5603 (1953).

(3) Department of Chemistry, University of Maryland, College Park, Maryland.

(4) M. Lanfry, *Compt. rend.*, **153**, 73, 821 (1911); **154**, 1090 (1912).

(5) (a) O. Hinsberg, *Ber.*, **48**, 1611 (1915); (b) W. Steinkopf, *Ann.*, **430**, 96 (1923); (c) H. J. Backer, W. Stevens and J. R. van der Bijl, *Rec. trav. chim.*, **59**, 1147 (1940).

(6) H. J. Backer, C. C. Bolt and W. Stevens, *ibid.*, **56**, 1063 (1937).

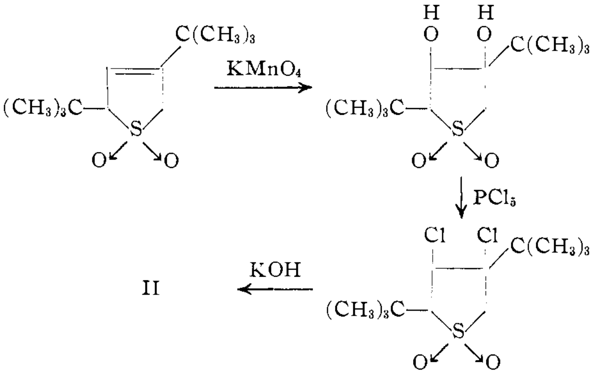
(7) M. Lanfry, *Compt. rend.* **154**, 519 (1912).

(8) C. G. Overberger, S. P. Ligthelm and E. A. Swire, THIS JOURNAL, **72**, 2856 (1950).

(9) H. J. Backer and J. Strating, *Rec. trav. chim.*, **53**, 525 (1934).

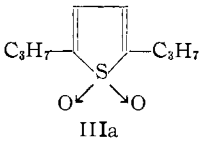
(10) H. J. Backer and J. Strating, *ibid.*, **54**, 170 (1935).

Backer and Strating[11] reported the synthesis of 2,4-di-*tert*-butylthiophene 1-dioxide (II) by the reactions

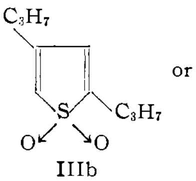


However, the structure of II was not rigorously proved and in view of the possibility for rearrangement might be questioned.

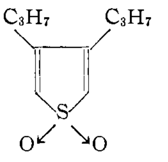
Marvel and Williams[12] obtained an unsaturated sulfone from the pyrolysis of the polysulfone from pentyne-1 and sulfur dioxide, to which they assigned the structure of a dipropylthiophene 1-dioxide (III).


IIIa

or


IIIb

or


IIIc

Using the same method, Young[13] claimed the synthesis of several disubstituted thiophene 1-dioxides, including a dimethyl derivative. The structure of these compounds, of course, was not fully established.

Since the present work was originally presented,[1] Melles and Backer[14] reported that the oxidation of 2,5-dimethylthiophene and 3,4-dimethylthiophene produced the corresponding stable crystalline sulfone derivatives. However, nothing further was reported about their chemical reactions. Because of the volume of confused literature that exists, it was considered highly desirable to synthesize thiophene 1-dioxide (I) itself and study its reactions.

A six-step synthesis (indicated by heavy arrows on diagram) of thiophene 1-dioxide (I) was developed starting with butadiene sulfone (IV). IV was brominated in chloroform to 3,4-dibromotetrahydrothiophene 1-dioxide (V). Treatment of V with a tenfold excess of dimethylamine in benzene for 3 days produced a 95% yield of 3,4-bis-(dimethylamino)-tetrahydrothiophene 1-dioxide (VI). Standing at room temperature for 12 hours with an alcoholic solution of methyl iodide converted VI into 3,4-bis-(dimethylamino)-tetrahydrothiophene 1-dioxide methiodide (VII). Hofmann degradation of VII occurred at room temperature upon the addition of silver oxide to form 3-dimethylamino-2,3-dihydrothiophene 1-dioxide (VIII).

A more direct synthesis of VIII was attempted by first converting V to 3-bromo-2,3-dihydrothiophene 1-dioxide (IX) by reaction with pyridine. The structure of IX is indicated by the strong absorption in the ultraviolet. Treatment of IX with stronger bases gave a mixture of products which could not be identified. Even though the bromine in IX is allylic, it is deactivated by the sulfone group so that it does not give a precipitate with silver nitrate. Treatment of IX with dimethylamine did not produce the unsaturated amine VIII but gave, instead, the diamine VI. That the unsaturated amine VIII was not an intermediate in this reaction was shown by the fact that VIII does not add dimethylamine under these conditions. This proved that dimethylamine must first add to the double bond in IX to produce the intermediate bromoamine X, which reacts with a second dimethylamine molecule to give VI.

The structure of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide (VIII) was proved by analysis, ultraviolet absorption, preparation of a picrate derivative and hydrogenation to 3-dimethylaminotetrahydrothiophene 1-dioxide (XI).

The ultraviolet absorption of the key intermediate VIII showed a broad ϵ_{max} of 225 at 238 mμ, a slight ϵ_{min} of 175 at 229 mμ, and an increase to an ϵ of 258 at 220 mμ. The spectrum of 3,4-bis-(dimethylamino)-tetrahydrothiophene 1-dioxide (VI), on the other hand, showed no maximum or minimum above 220 mμ but increased from an ϵ of 31 at 240 mμ to an ϵ of 502 at 220 mμ. Comparison of the spectra of VIII, VI and 3-bromo-2,3-dihydrothiophene 1-dioxide (IX), which did not show a maximum or minimum above 220 mμ but increased from an ϵ of 31 at 270 mμ to an ϵ of 1770 at 220 mμ, shows that α,β-unsaturation shifts the absorption to longer wave lengths.

The structure of XI was proved by an independent synthesis starting from butadiene sulfone (IV). Refluxing IV with base caused a partial isomerization to 2,3-dihydrothiophene 1-dioxide (XII). Heating the mixture decomposed IV into butadiene and sulfur dioxide, leaving only the heat-stable XII. The presence of an α,β-unsaturated structure in XII was indicated by the fact that XII did not show a maximum or minimum in the ultraviolet spectrum above 220 mμ but increased to an ϵ of 26 at 220 mμ. Butadiene sulfone (IV) showed no appreciable absorption in this range. Addition of dimethylamine to XII produced the saturated amine XI. Both samples of XI, the one prepared by this independent method and the one formed by hydrogenation of VIII, were identical, as were their picrates XIII. Mixed melting points of the two picrates showed no depression.

Addition of methyl iodide to VIII produced 3-dimethylamino-2,3-dihydrothiophene 1-dioxide methiodide (XIV). The ultraviolet absorption of XIV did not show a maximum or minimum above 220 mμ but increased from an ϵ of 100 at 252 mμ to an ϵ of 14,800 at 220 mμ. The strong absorption near 220 mμ was very probably due almost entirely to the quaternary ammonium iodide structure, since 3,4-bis-(dimethylamino)-tetrahydrothiophene 1-dioxide monomethiodide (VIII) had almost the

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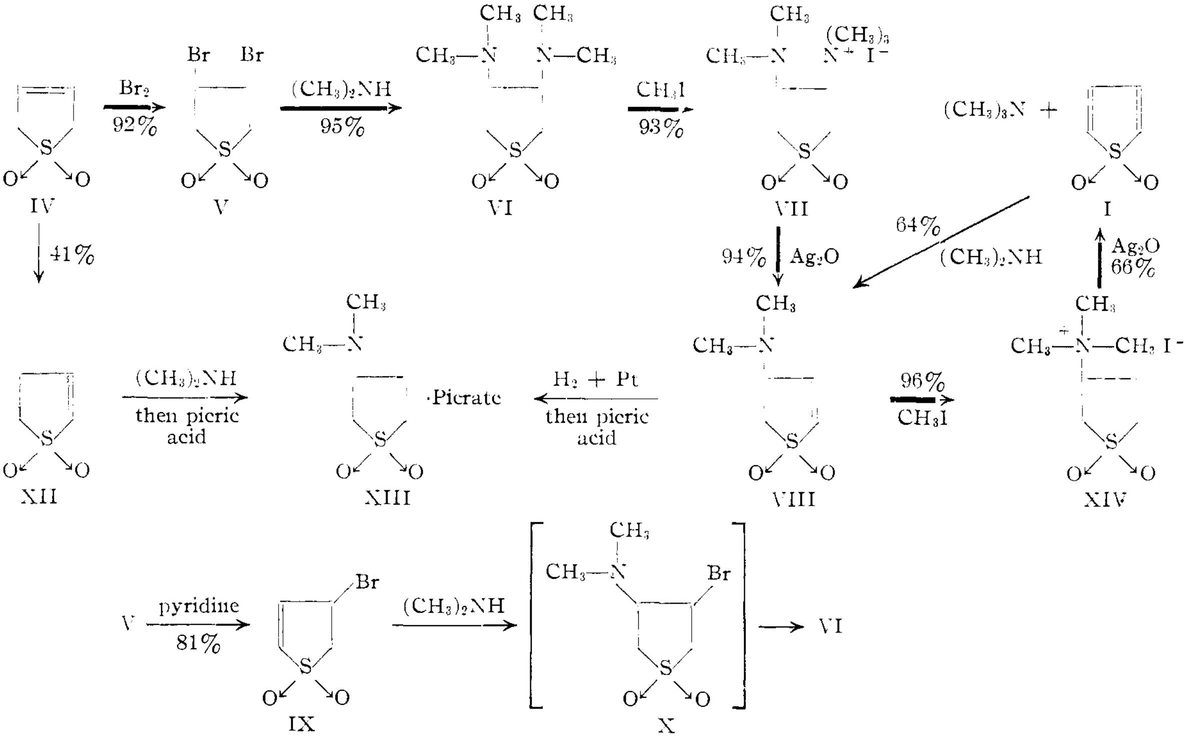
[11] H. J. Backer and J. Strating, *Rec. trav. chim.*, **56**, 1069 (1937).

[12] C. S. Marvel and W. W. Williams, THIS JOURNAL, **61**, 2714 (1939).

[13] D. W. Young, U. S. Patent 2,456,354 (1948).

[14] J. L. Melles and H. J. Backer, *Rec. trav. chim.*, **72**, 314 (1953).



same absorption as did XIV. When a suspension of XIV in ice–water mixture was treated with silver oxide, trimethylamine was liberated instantaneously. Extractions of this solution with chloroform produced a solution of thiophene 1-dioxide (I). It could not be isolated in the pure state because of the strong tendency to form a dimer with the loss of sulfur dioxide. This dimerization reaction will be discussed in the following paper.[15] If the chloroform solution was evaporated under reduced pressure, just before the last bit of solvent was removed, the residue became warm and sulfur dioxide was liberated. Even if a carbon tetrachloride solution of I was frozen and the solvent sublimed, sulfur dioxide was liberated from the solid residue upon warming to near room temperature. However, the chloroform solution of the dioxide could be stored at 5° for several weeks without any appreciable decomposition. The structure of thiophene 1-dioxide (I) was therefore deduced from its physical properties and its chemical reactions.

That thiophene 1-dioxide (I) was indeed present in this solution was indicated by its conversion to known derivatives. When a solution of the dioxide was treated with dimethylamine, the unsaturated amine VIII was produced in an over-all yield of 66% (based on the XIV used). Mixed melting point with an authentic sample of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide (VIII) showed no depression. Other chemical reactions are described in the following papers.[15]

The ultraviolet absorption spectrum of I indicates an $\epsilon_{\max}$ at 289 mμ of 1230 and an $\epsilon_{\min}$ at 254 mμ of 450 rising to an ϵ of 2010 at 220 mμ (assuming 6.6×10^{-4} mole of I produced from 10^{-3} mole of XIV). The general shape of the curve is similar to cyclopentadiene[16] ($\epsilon_{\max}$ of 2500 at 243 mμ) and cyclohexadiene[17] ($\epsilon_{\max}$ of 7940 at 256 mμ). It seems that this type of curve is general for a pair of conjugated double bonds in a ring. The presence of the conjugated sulfone shifts the maximum to longer wave lengths and lowers the intensity. It is significant that the absorption curve for 2,3-dihydrothiophene 1-dioxide (XII) is completely different.

Thus the method of synthesis, its chemical reactions and its ultraviolet spectrum substantiate the proposed structure of I and indicate that it is a high reactive molecule that is stable only in solution.

Experimental[18]

2,5-Dihydrothiophene 1-Dioxide (Butadiene Sulfone) (IV).—Butadiene sulfone (IV) was prepared by a modification of the method of Staudinger and Ritzenthaler,[19] using a mixture of chloroform and ether for recrystallization. The yield of IV, m.p. 64.5–65.5°, was 84%.

3,4-Dibromotetrahydrothiophene 1-Dioxide (V).—A solution of 700 g. (5.92 moles) of 2,5-dihydrothiophene 1-dioxide (IV) in 1 l. of dry chloroform was placed in a 3-l., three-necked, round-bottom flask, fitted with a reflux condenser protected by a drying tube, a mechanical stirrer, and a dropping funnel. After the mixture was heated to boiling, a solution of 948 g. (5.92 moles) of dry bromine in 750 ml. of dry chloroform was added, in ten equal portions, over a period of 7 hours. Each portion of the bromine solution required about 15 to 20 minutes for addition and the next portion was not added until most of the previous portion had reacted. (After the addition of the seventh portion of the bromine solution, crystalline materials appeared in the reaction solution.) When the addition of bromine was complete, the heating and stirring of the reaction mixture were continued for an additional 2 hours and then the mixture was allowed to stand at room temperature overnight. The bright red reaction mixture was filtered, the residue washed

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[15] W. J. Bailey and E. W. Cummins, This Journal, **76**, 1936, 1940 (1954).

[16] L. W. Pickett, E. Paddock and E. Sackler, *ibid.*, **63**, 1073 (1941).

[17] V. Henri and L. W. Pickett, *J. Chem. Phys.*, **7**, 439 (1939).

[18] The authors are indebted to Vivian Kapuscinski, James French, Robert Keen and Arthur Tomasewski for the analyses. All melting points are corrected.

[19] H. Staudinger and B. Ritzenthaler, *Ber.*, **68**, 470 (1935).

with chloroform until colorless, and dried to give 1396 g. of V as pure white plates, m.p. 141.0–141.8°. An additional 113 g. of V was obtained by working up the mother liquors. In all, the yield of 3,4-dibromotetrahydrothiophene 1-dioxide (V) was 1509 g. (92%). A mixed melting point with a sample prepared by the method of Staudinger and Ritzenthaler[19] using water as a solvent showed no depression.

3,4-Bis-(dimethylamino)-tetrahydrothiophene 1-Dioxide (VI). A. From 3,4-Dibromotetrahydrothiophene 1-Dioxide (V).—A solution of 590 g. (13.1 moles) of dimethylamine in 3200 ml. of dry benzene was placed in a 5-l., round-bottom flask and cooled to 5°. While the reaction was maintained below 20°, 200 g. (0.719 mole) of 3,4-dibromotetrahydrothiophene 1-dioxide (V) was added in small portions, during one-half hour. (The addition of V in large portions resulted in the loss of large amounts of dimethylamine.) After standing for 3 days, with occasional shaking, the reaction mixture was filtered to remove the precipitated solids. The light red filtrate was evaporated under a partial vacuum to remove excess dimethylamine, and then extracted with 15% hydrochloric acid. The acid aqueous extracts, on standing for about 15 minutes, deposited a considerable amount of white powder which was filtered off. The acidic filtrate was extracted with chloroform, to remove non-basic materials, and then made basic with a concentrated solution of sodium hydroxide (220 g. of sodium hydroxide in 250 ml. of water) while the reaction temperature was maintained below 30°. The resulting alkaline solution was extracted several times with chloroform. These combined chloroform extracts were washed with water, dried over magnesium sulfate and evaporated to dryness under reduced pressure, while the pot temperature was maintained below 30°, to give a bright red oil which crystallized on standing. Recrystallization from an ether–petroleum ether mixture produced 140 g. (95%) of 3,4-bis-(dimethylamino-)-tetrahydrothiophene 1-dioxide (VI), m.p. 63.4–63.6°.

Anal. Calcd. for $C_8H_{18}N_2O_2S$: C, 46.60; H, 8.74; N, 13.59. Found: C, 46.56; H, 8.57; N, 13.41.

B. From 3-Bromo-2,3-dihydrothiophene 1-Dioxide (IX).—A solution of 90 g. (2 moles) of dimethylamine in 500 ml. of dry benzene was placed in a 1-l., round-bottom flask and cooled to 5°. Keeping the temperature below 20°, 19.4 g. (0.10 mole) of 3-bromo-2,3-dihydrothiophene 1-dioxide was added in small portions. After standing for 3 days the reaction mixture was worked up as above to yield 16.8 g. (82%) of 3,4-bis-(dimethylamino)-tetrahydrothiophene 1-dioxide (VI), m.p. 63.0–63.5°. Mixed melting point with an authentic sample prepared from V showed no depression.

3-Bromo-2,3-dihydrothiophene 1-Dioxide (IX).—Using a modification of the procedure described by Backer and Blass,[20] a solution of 60 g. (0.215 mole) of 3,4-dibromotetrahydrothiophene 1-dioxide (V) in 420 ml. of dry actone was placed in a 1-l., round-bottom flask equipped with a drying tube. Within 2 hours after 33.0 g. (0.417 mole) of dry pyridine was added, the solution began to deposit crystals of pyridine hydrobromide. After an additional 14 hours the mixture was filtered to give 28.0 g. (80.6%) of pure white crystals of pyridine hydrobromide.

The colorless filtrate was evaporated to dryness under reduced pressure at room temperature to give 50.5 g. of colorless oil containing considerable pyridine. Trituration of this oil with petroleum ether removed a small amount of a dark, evil smelling oil.

The petroleum ether-insoluble oil was triturated with hot benzene to separate the product from a large amount of insoluble polymeric substances. The combined triturates were dried over magnesium sulfate, filtered and evaporated to dryness to give 30.9 g. of white powder. Recrystallization from water gave 24.3 g. (56%) of large white crystals of 3-bromo-2,3-dihydrothiophene 1-dioxide (IX), m.p. 63.5–64° (reported[20] 64.5–65°).

3,4-Bis-(dimethylamino)-tetrahydrothiophene 1-Dioxide Monomethiodide (VII).—A solution of 106.5 g. (0.517 mole) of 3,4-bis-(dimethylamino)-tetrahydrothiophene 1-dioxide (VI) in 450 ml. of absolute alcohol was placed in a 1-l. flask, which was fitted with a reflux condenser containing a drying tube, and 73.5 g. (0.517 mole) of methyl iodide was added in one portion. Crystalline material formed almost immediately and the reaction mixture boiled vigorously for a few minutes. After standing for 12 hours at room temperature, the reaction mixture was cooled to 0° and filtered. The residue was washed with cold ethanol, peroxide-free ether, and finally recrystallized from an ethanol–water mixture to yield 168 g. (93%) of very light yellow needles of 3,4-bis-(dimethylamino)-tetrahydrothiophene 1-dioxide monomethiodide (VII), m.p. 156° dec.

Anal. Calcd. for $C_9H_{21}IN_2O_2S$: C, 31.03; H, 6.03; N, 8.05; I, 36.41. Found: C, 31.24; H, 5.88; N, 8.09; I, 36.39.

3-Dimethylamino-2,3-dihydrothiophene 1-Dioxide (VIII). A. From 3,4-Bis-(dimethylamino)-tetrahydrothiophene 1-Dioxide Monomethiodide (VII).—A solution of 167.5 g. (0.481 mole) of 3,4-bis-(dimethylamino)-tetrahydrothiophene 1-dioxide monomethiodide (VII) in 2.5 l. of distilled water was placed in a 5-l., two-necked flask, fitted with a mechanical stirrer and powder funnel. Freshly prepared silver oxide suspension (from 254.0 g. (1.49 moles) of silver nitrate) was added, through the powder funnel, to the well-agitated solution during a period of 10 minutes. The first portion of silver oxide resulted in the liberation of trimethylamine. After the reaction had continued for an additional 30 minutes, the insoluble mixture of silver oxide and silver iodide was filtered off and washed with water.

The combined filtrate and washings were extracted with chloroform. These chloroform extracts were combined, dried over magnesium sulfate, filtered and evaporated to dryness, under partial vacuum, while the pot temperature was maintained below 30°. The residue was recrystallized from ether–petroleum ether to give 72.5 g. (94%) of white needles of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide (VIII), m.p. 64.2–64.8°.

Anal. Calcd. for $C_6H_{11}NO_2S$: C, 44.70; H, 6.83; N, 8.69; mol. wt., 161. Found: C, 44.78; H, 6.91; N, 8.72; mol. wt., 165 (cryoscopic in benzene).

B. From Thiophene 1-Dioxide (I).—To the cold chloroform extracts resulting from the decomposition of 20.75 g. (0.0685 mole) of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide methiodide (XIV) (presumably containing 5.2 g. (0.045 mole) of thiophene 1-dioxide (I)) was added 12.25 g. (0.272 mole) of dimethylamine and the resulting solution allowed to stand for 3 days at room temperature. A light yellow solution (containing a small amount of insoluble oil on the surface of the solution) was obtained and evaporated to a volume of 50 to 75 ml. under a slight vacuum. After the insoluble oil was separated and discarded, the chloroform solution was extracted with 10% hydrochloride acid. The acidic extracts were then made basic with a concentrated sodium hydroxide solution, while the temperature was maintained below 25°, and extracted with chloroform. The chloroform extracts were combined, washed with water, dried over magnesium sulfate, and evaporated to dryness at room temperature, under highly reduced pressure, to give 4.2 g. (40% based on the original XIV or 64% based on I in solution) of light yellow crystalline 3-dimethylamino-2,3-dihydrothiophene 1-dioxide (VIII), m.p. 64–65°. A mixed melting point with an authentic sample of VIII prepared from VII showed no depression, melting at 64–65°.

In a similar experiment, 3-dimethylamino-2,3-dihydrothiophene 1-dioxide (VIII) failed to add another molecule of dimethylamine and was recovered unchanged from the reaction mixture.

Picrate of 3-Dimethylamino-2,3-dihydrothiophene 1-Dioxide.—The picrate of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide was prepared by the method of Shriner and Fuson[21] and gave small yellow needles when recrystallized from an ethanol–water mixture, m.p. 159–160°.

Anal. Calcd. for $C_{12}H_{14}N_4O_9S$: C, 36.93; H, 3.59. Found: C, 36.67; H, 3.41.

2,3-Dihydrothiophene 1-Dioxide (XII).—A modification of the procedure by van Zuydewijn[22] was used, eliminating the evaporation of a large volume of aqueous solution, a high vacuum distillation, and irradiation with ultraviolet light. A solution of 50.0 g. (0.424 mole) of butadiene sulfone (IV) in 1 l. of 0.5 *N* potassium hydroxide was allowed to stand for 15 hours at room temperature and then acidified with 50 ml. of concentrated hydrochloric acid. The acidic aqueous layer was then extracted several times with chloroform. The combined extracts were dried over magnesium sulfate,

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(20) H. J. Backer and Th. A. H. Blass, *Rec. trav. chim.*, **61**, 785 (1942).

(21) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 180.

(22) E. de Roy van Zuydewijn, *Rec. trav. chim.*, **57**, 445 (1938).

filtered and evaporated to dryness to give 41.7 g. of light yellow oil. Heating at 180° under a pressure of 20 to 25 mm. resulted in the decomposition of the unreacted IV into butadiene and sulfur dioxide. When the evolution of gases had ceased, heating was discontinued. Recrystallization of the residue from a mixture of benzene and petroleum ether gave 20.5 g. (41%) of pure white needles of 2,3-dihydrothiophene 1-dioxide (XII), m.p. 48–49° (reported[22] 48.5–49.5°).

3-Dimethylaminotetrahydrothiophene 1-Dioxide Picrate (XIII). A. From 2,3-Dihydrothiophene 1-Dioxide (XII).—A solution of 0.50 g. (0.0042 mole) of 2,3-dihydrothiophene 1-dioxide (XIII) in 10 ml. of dry benzene and 1.90 g. (0.042 mole) of dimethylamine were placed in a tightly stoppered flask. After standing for 4 days at room temperature the solution was evaporated to near dryness, taken up in chloroform, and extracted with 5% hydrochloric acid. The acidic aqueous solution was cooled to 0° and made basic with sodium hydroxide and again extracted with chloroform. The chloroform extracts were combined, dried over magnesium sulfate, filtered and evaporated to dryness under vacuum at room temperature to give 0.65 g. (93%) 3-dimethylaminotetrahydrothiophene 1-dioxide (XI) as a very light yellow oil which could not be induced to crystallize. It was therefore converted into a picrate, by the method of Shriner and Fuson.[21] Recrystallization from an ethanol–water mixture produced the pure picrate of 3-dimethylaminotetrahydrothiophene 1-dioxide (XIII), m.p. 193–194° (without decomposition).

Anal. Calcd. for $C_{12}H_{16}N_4O_9S$: C, 37.19; H, 4.08. Found: C, 37.01; H, 3.90.

B. **From 3-Dimethylamino-2,3-dihydrothiophene 1-Dioxide (VIII).**—A solution of 0.50 g. (0.0031 mole) of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide (VIII) in 50 ml. of glacial acetic acid plus 0.1 g. of prereduced PtO_2 catalyst was subjected to low pressure hydrogenation. The hydrogen uptake was 60.2 ml. (86% of theory) in 12 hours. The catalyst was filtered off and 10 ml. of a saturated solution of picric acid in 95% ethanol was added to the filtrate. The resulting precipitate was purified by four recrystallizations from dilute ethanol to give the picrate of 3-dimethylaminotetrahydrothiophene 1-dioxide (XIII), m.p. 193–194°. A mixed melting point with the picrate XIII, prepared from XII in part A above, showed no depression, melting at 193–194°.

3-Dimethylamino-2,3-dihydrothiophene 1-Dioxide Methiodide (XIV).—A solution of 72.5 g. (0.450 mole) of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide (VIII) in 200 ml. of absolute alcohol was placed in a 500-ml. flask, equipped with a reflux condenser protected with a drying tube, and 64.5 g. (0.454 mole) of methyl iodide was added. Crystalline material formed almost immediately and the reaction mixture boiled vigorously for a few minutes. The reaction mixture was allowed to stand for 1.5 hours and then cooled to 0°. The cold mixture was filtered, washed with 100 ml. of cold alcohol and then with peroxide-free ether to give 116.5 g. of XIV. An additional 9.5 g. of XIV could be obtained by working up the mother liquors and washings. Recrystallization from ethanol gave 125 g. (96%) of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide methiodide (XIV) as pure white microcrystals, m.p. 184–185° dec.

Anal. Calcd. for $C_7H_{14}INO_2S$: C, 27.72; H, 4.63; N, 4.62; I, 41.86. Found: C, 27.85; H, 4.50; N, 4.77; I, 42.11.

Thiophene 1-Dioxide (I).—A solution of 10.0 g. (0.033 mole) of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide methiodide (XIV) in 150 ml. of distilled water was placed in a 300-ml., two-necked flask, fitted with a mechanical stirrer and powder funnel, and cooled to 0–5°. This resulted in the crystallization of a considerable amount of XIV. However, since the decomposition reaction went to completion rapidly no further addition of water was made, because of the desirability of keeping the final volume of the aqueous phase as small as possible for extraction purposes. The addition of freshly prepared silver oxide suspension from 11.22 g. (0.066 mole) of silver nitrate to this mixture, during a 15-minute period, resulted in the instantaneous liberation of trimethylamine. The reaction was allowed to proceed for an additional 15 minutes while the temperature was maintained between 0–5°. It was then filtered through a buchner funnel, containing ice, into an ice-cooled flask (no appreciable amount of iodide ion was present in either the residue or filtrate). The filtrate was transferred to a separatory funnel, also containing ice, and extracted with chloroform. The chloroform extracts were collected in an erlenmeyer flask, dried over magnesium sulfate, and used in this form for all subsequent reactions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Cyclic Dienes. IV. The Dimerization of Thiophene 1-Dioxide[1,2]

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In concentrated solution even below room temperature, thiophene 1-dioxide (I) dimerizes by a Diels-Alder reaction with the loss of sulfur dioxide to form 3a,7a-dihydrobenzothiophene 1-dioxide (II). The structure of II was proved by ultraviolet absorption, hydrogenation and independent synthesis of the hydrogenation product. Bromination of I proceeds very slowly to give bromination products of both I and II, indicating that I exists in solution largely as a monomer and not as a dissociating dimer.

Thiophene 1-dioxide (I) was synthesized[2] in order to determine whether it was aromatic or aliphatic. It was found, however, that it could not be isolated in a pure state. All attempts to obtain a concentrated form of the dioxide I, even at low temperatures, resulted in a spontaneous decomposition with the liberation of sulfur dioxide. From the reaction mixture was isolated a white crystalline solid II that analyzed for $C_8H_8O_2S$. II absorbed 3 moles of hydrogen to yield a saturated sulfone III. The similarity of the ultraviolet absorption spectrum of II, which indicates an ϵ maximum of 3550 at 266 mμ and an ϵ minimum of 1260 at 228 mμ, with that of cyclohexadiene-1,3 suggests the presence of conjugated double bonds in a six-membered ring. Thus II can be represented as 3a,7a-dihydrobenzothiophene 1-dioxide and III as octahydrobenzothiophene 1-dioxide. The formation of II can be rationalized by assuming that I dimerized with one molecule acting as the diene and the other as a dienophile to form the unstable Diels–Alder adduct IV, which spontaneously lost the bridged sulfone group to form II. The structure of III was proved by independent synthesis. Butadiene (V) was added to 2,3-dihydrothiophene 1-dioxide (VI) to produce Δ^5-hexahydrobenzothiophene 1-dioxide (VII). Hydrogenation of VII produced the octa-

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