yellow liquid, b.p. 40–110° (0.5 mm.), but the pot residue, black and tarry, could not be further distilled. Addition of bromine to the distillate permitted isolation of a small quantity of 1,1,2-tribromo-2-phenylethane, m.p. 37–38°.[21]

**Ethynesulfonyl Chloride.**—A solution of 6.5 g. (0.0316 mole) of 1-bromoethene-1-sulfonyl chloride in 40 ml. of dry ether was cooled to −70°. A solution of 3.3 g. (0.0326 mole) of triethylamine in 25 ml. of ether was added below −60° in one-half hour. After an additional half-hour, the precipitated hydrobromide was filtered and washed with dry ether. After evaporation of the ether, the brown oil was distilled, giving 1.8 g., 46% yield of a yellow oil, b.p. 33–43° (0.5 mm.). The compound was a vicious lachrymator. Satisfactory analytical data have not yet been obtained; this product is doubtless contaminated with starting material. Its infrared spectrum was taken without solvent or in carbon disulfide or carbon tetrachloride on a Baird instrument in a cell 0.1 mm. thick.

ANN ARBOR, MICHIGAN

---

[21] R. Fittig and F. Binder, *Ann.*, **195**, 142 (1879).

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

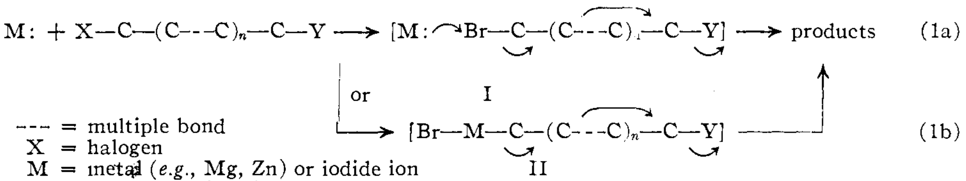
# The Action of Metals on Unsaturated 1,4-Dihalides and Derivatives. I. Synthesis and Some Properties of Butatriene[1]

BY W. M. SCHUBERT, THOMAS H. LIDDICOET AND WAYNE A. LANKA

RECEIVED OCTOBER 19, 1953

As part of a study of the elimination reactions of "vinylogous" 1,2-dihalides and derivatives, butatriene has been synthesized by the action of zinc on 1,4-dibromo-2-butyne or 1-bromo-4-phenoxy-2-butyne. Butatriene, a readily polymerizable volatile substance, has been thoroughly characterized and some of its chemical properties explored. On hydration in 78% sulfuric acid it yielded methyl vinyl ketone. When added in excess and in high dilution to bromine, butatriene gave mainly 1,2,3,4-tetrabromo-2-butene. A small amount of 1,4-dibromo-2-butyne and a very easily polymerized isomeric dibromo compound were also formed. Attempted nascent hydrogen reduction, reaction with phenyl azide, diazoacetic ester, maleic anhydride or cyclopentadiene yielded only polymeric materials.

A study is being made to determine the general nature of reactions of type 1 in which $n$ is greater than zero.[2] The general reaction 1 in which $n = 0$ is, of course, well-known. However, just a few isolated examples of the reaction 1 in which $n > 0$ are reported. For example, in 1899, Thiele found that 1,4-dibromo-2-butene and zinc in ethanol yielded 1,3-butadiene.[3] Later, 1,3-butadiene was obtained from 1,4-dibromo-2-butene and magnesium in ether[4,5] and from γ-phenoxycrotyl bromide and magnesium under the same conditions.[4] No Grignard reagent or coupling product was detected. Reid and Yost obtained cyclopentadiene in the reaction of magnesium and *cis*-3,5-dibromocyclopentene with magnesium in ether, whereas ethylmethylfulvenol is a reported product when the reaction was run in the presence of excess butanone.[6] The presence of reaction 1 probably also explains the failure to obtain a condensation product by treatment of the reaction mixture of magnesium and γ-methoxycrotyl bromide with the sodium salt of hydroxymethylene-β-ionone.[7] An example of the reaction 1 in which $n = 2$ is the formation of 1,3,5-hexatriene as an unstable liquid from the action of zinc on 1,6-dibromo-2,4-hexadiene.[8] Examples of reactions at least similar to 1 may exist in the tetraarylcumulene synthesis of Kuhn in which the α,ω-diols are treated with $P_2I_4$.[9]



--- = multiple bond
X = halogen
M = metal (*e.g.*, Mg, Zn) or iodide ion
Y = electronegative element or group

**Preparation and Characterization of Butatriene.**—To determine whether the multiple bond of reaction 1 can be a triple bond a study of the action of metals and iodide ion on 1,4-dibromo-2-butyne was undertaken. The first experiments, with zinc in ethanol or water, produced a volatile gas which was largely 1,3-butadiene, as evidenced by infrared, ultraviolet and mass spectra. The spectra showed the presence of another substance, shown later to be butatriene, to the extent of 10–15% of the total product.[10] Chemical tests confirmed the absence of acetylenic hydrogen. There was evidence of polymer formation which did not take place in a similar preparation of 1,3-butadiene from 1,4-dibromo-2-butene and zinc. The mixture of volatile products when treated with excess bromine in carbon tetrachloride gave a crystalline mush which, though no longer unsaturated to bromine, readily reduced potassium permanganate. Apparently 1,2,3,4-tetrabromo-2-butene was present. On recrystallization, the crude bromination product gave fairly

---

[1] Supported in part by a Cottrell Grant of the Research Corporation.

[2] W. M. Schubert, W. A. Lanka and T. H. Liddicoet, *Science*, **116**, 124 (1952).

[3] J. Thiele, *Ann.*, **308**, 333 (1899).

[4] A. Lüttringhaus, G. V. Saaf and K. Hauschild, *Ber.*, **71**, 1673 (1938).

[5] G. N. Khitrik, *J. Gen. Chem.* (*U.S.S.R*), **10**, 2098 (1940).

[6] E. B. Reid and J. F. Yost, THIS JOURNAL, **72**, 1807 (1950).

[7] E. M. Schantz, *ibid.*, **68**, 2552 (1946).

[8] E. H. Farmer, B. Das Laroia, T. M. Switz and J. F. Thorpe, *J. Chem. Soc.*, 2937 (1927).

[9] R. Kuhn and H. Zahn, *Chem. Ber.*, **84**, 566 (1951).

[10] After this work was completed, C. Troyanowsky, *Compt. rend.*, **236**, 618 (1953), reported that 1,4-dibromo-2-butyne when treated with zinc and ethanol gave only 1,3-butadiene.

pure 1,2,3,4-tetrabromobutane, confirming that butadiene was the principal product of the debromination reaction.

To prevent reduction from occurring, attention was turned to the use of non-hydroxylic solvents. Johnson[11] had reported that the action of magnesium in ether on 1,4-dibromo-2-butyne deposited a solid on the surface of the magnesium which terminated the reaction. A faint positive test for the Grignard reagent was obtained with Michler ketone. In these laboratories, magnesium in tetrahydrofuran gave a vigorous exothermic reaction that yielded voluminous amounts of an insoluble polymeric substance. During the reaction, nitrogen was blown through the reaction mixture in order to entrain any volatile product. The nitrogen stream was led through water wash bottles and drying tubes to Dry Ice–acetone and liquid nitrogen-cooled traps. The cold traps condensed only a few drops of liquid which formed an intractable polymer on being warmed to room temperature. With the same apparatus and procedure, zinc dust in diethylene glycol diethyl ether solvent at 80° gave pure butatriene in yields up to 85%.[12] Acetonitrile, tried because in reactions of type 1 with acid chlorides it offered advantages over ethers (which undergo cleavage), was an equally effective solvent. The yield of monomer collected appeared to depend on the exclusion of air, and varied inversely with the amount of polymer that formed in the reaction mixture.

A readily polymerizable compound, said to be butatriene, is reported in a patent by Carothers and Berchet.[13] It was obtained as a small by-product in the treatment of 1-chloro-2,3-butadiene with potassium or sodium hydroxide to give vinylacetylene as the main product. No characterization of the compound was reported. In these laboratories, butatriene was characterized as follows. With excess bromine it yielded the known 1,2,3,4-tetrabromo-2-butene, obtained by the reaction of 1,4-dibromo-2-butyne with bromine. It was attempted to run a carbon–hydrogen analysis on the compound as a gas at atmospheric pressure but it polymerized in both liquid and gas phases before this pressure could be reached. The carbon–hydrogen ratio was determined on the gas at 200 mm. pressure, diluted to atmospheric pressure with helium. The molecular weight by the Dumas method on the gas at 250 mm. was 52.6, whereas the mass spectrum gave a large parent peak at mass 52. The infrared spectrum of the gas had two strong bands in the double bond region. A strong, very broad band at 860 cm.$^{-1}$ (11.6 $\mu$) contained a series of sharp Q branches whose rather wide spacing indicates one small principal moment of inertia, such as in a molecule with a linear carbon chain.[14]

**The Mechanism of the Elimination.**—The results reported do not enable a choice to be made between mechanisms 1a and 1b. The fact that the reaction proceeds well in acetonitrile shows that either II is not formed, or, if formed, decomposes faster to give butatriene than it can add to acetonitrile. A cyclic version of mechanism 1b is ruled out by the linear carbon chain of 1,4-dibromo-2-butyne and butatriene (hence presumably also of the transition state).

The group Y need not be halogen as shown in the elimination reactions of the halogen ethers. Since 1,4-dimethoxy-2-butene failed to react with zinc or magnesium, even after the addition of zinc chloride to provide a "pull" at one of the methoxy groups, it appears that one of the terminal groups need be halogen.

**Chemical Properties of Butatriene.**—Investigation of the chemical properties of butatriene was complicated by its easy polymerization. However, it could be kept indefinitely as a solid at liquid nitrogen temperature or a liquid at Dry Ice–acetone temperature. When allowed to warm the liquid began to turn yellow at about zero degrees and deposited a flocculent precipitate (the addition of inhibitors, of which hydroquinone appeared to be best, delayed this process somewhat). The polymerization became quite exothermic at this point and yielded a colored amorphous intractable solid that from one sample to the next varied in color from yellow to orange to green to blue and black. The polymer gained weight when exposed to air. When allowed to stand at room temperature in an open test-tube, butatriene was polymerized and oxidized rapidly, with spontaneous ignition. Exposed to air in a thin layer, it gave sometimes a rubbery, sometimes a paper-like white substance that did not melt and was insoluble in all solvents.

When butatriene was added very slowly in high dilution to less than a molar equivalent of bromine in cold chloroform, the only pure product isolated and identified was 1,2,3,4-tetrabromo-2-butene, in 36% yield based on bromine. Two lower boiling fractions were obtained in very small amount. The former of these polymerized in a few minutes to a material that gave a bromine analysis corresponding to $(C_4H_4Br_2)_x$. The monomer was evidently not 1,4-dibromo-2-butyne because the latter is fairly stable. The second fraction, judging from the infrared spectrum, was a mixture of 1,4-dibromo-2-butyne plus one or more other compounds which absorbed in the carbon–carbon triple bond or cumulative bond region.

Treatment of butatriene with 78% sulfuric acid yielded methyl vinyl ketone. Addition had to occur 1,2 or 2,3 for this product to form.

Attempted nascent hydrogen reduction of butatriene with sodium and alcohol yielded only polymer. This may mean that butatriene is not an intermediate in the formation of 1,3-butadiene from 1,4-dibromo-2-butyne and zinc in hydroxylic solvents. Treatment of butatriene with maleic anhydride, cyclopentadiene, diazoacetic ester or phenyl azide yielded polymers and no clean-cut products. Whether polymerization occurred before or after a possible reaction of these reagents with butatriene was not determined.

---

(11) A. W. Johnson, *J. Chem. Soc.*, 1009 (1946).

(12) W. M. Schubert, T. H. Liddicoet and W. A. Lanka, This Journal, **74**, 569 (1952).

(13) W. H. Carothers and G. J. Berchet, U. S. Patent 2,136,178 (Nov. 8, 1937).

(14) We wish to thank Dr. David Eggers for aid in interpreting the infrared spectrum. A detailed analysis of the spectral data will appear elsewhere.

## Experimental

**Preparation of Butatriene.**—The following procedure was used in most of the runs. The reaction vessel was a three-necked flask equipped with mechanical stirrer, dropping funnel, spiral condenser and a nitrogen inlet tube extending below the surface of the reaction mixture. Purified nitrogen gas was bubbled through the reaction mixture and led out the spiral condenser through four water wash bottles, the inlet tubes of which had fritted glass tips. The gases then led through a drying tube containing anhydrous calcium chloride, another tube containing indicator-type Drierite, thence into a Dry Ice–acetone trap and finally into a liquid nitrogen trap. Both traps contained a pinch of hydroquinone. The flow of nitrogen gas through the system was kept rapid by adjusting the nitrogen flow and by the application of a mild vacuum at the end of the system.

In a typical run with diethylene glycol diethyl ether solvent (purified in a manner similar to that used for dioxane[15]), 1,4-dibromo-2-butyne (85 g., 0.4 mole) in 50 ml. of solvent was added dropwise over a period of two hours to a stirred mixture of zinc (131 g., 2.0 gram atoms) and 100 ml. of solvent maintained at 80°. The flow of nitrogen was continued for an hour after the addition was complete. At the conclusion of the reaction, the Dry Ice–acetone trap contained several ml. of a colorless liquid and the liquid nitrogen trap contained a solid which liquefied at Dry Ice temperature. After a bulb to bulb distillation under reduced pressure (1 mm.) the yield of low-boiling liquid butatriene was 10.6 g., 52%. In several runs the yields of monomer varied from 10 to 85%, the yields being generally quite good if air was carefully excluded. The by-product was principally a polymer that formed in the reaction flask. A similar run with 1,2,3,4-tetrabromo-2-butene (38.2 g.) in 100 ml. of solvent, added to zinc dust (32.2 g.) in 50 ml. of solvent at 90° gave 3.4 g. (65%) of butatriene.

Acetonitrile also could be used as the solvent with comparable results. The conditions were the same except that it was unnecessary to heat the reaction mixture during the addition of the 1,4-dibromo-2-butyne because of the exothermic nature of the reaction. With tetrahydrofuran solvent only polymer was formed with magnesium or zinc and either 1,4-dibromo- or 1,4-dichloro-2-butyne.

The carbon–hydrogen ratio was obtained on a sample of the gas at 200 mm. pressure to which helium was added to atmospheric pressure. The butatriene–helium mixture then was led from a gas buret to the carbon–hydrogen train.

*Anal.* Calcd. C/H ratio for $C_4H_4$: 92.26/7.74. Found: 92.29/7.74 and 91.82/8.18. Calcd. mol. wt., 52.1. Found: (Dumas method, 250 mm. gas pressure), 52.6.

**Mass Spectrum.**—The principal peaks in the mass spectrum of two separate samples are listed in Table I. The large parent peak at mass 52 indicates the product is largely butatriene. It is difficult to account for the large mass 53 peak, since peaks above mass 54 were negligibly small, except perhaps on the basis of a synthesis during the spectral run.

TABLE I

MASS SPECTRUM OF SAMPLES OF BUTATRIENE[a]

| Mass no. | Relative intensity |  | Mass no. | Relative intensity |  |
|---|---|---|---|---|---|
|  | Sample I | Sample II |  | Sample 1 | Sample 1I |
| 26 | 21.2 | .. | 51 | 72.2 | 80.0 |
| 27 | 10.0 | .. | 52 | 100.0 | 100.0 |
| 37 | 9.1 | 10.9 | 53 | 22.2 | 14.7 |
| 44 | .. | 23.3 | 54 | 2.7 | 1.1 |
| 49 | 23.9 | 24.0 | 55 | 0.1 | 0 |
| 50 | 54.1 | 54.0 |  |  |  |

[a] Measured in a Consolidated Engineering Corporation Mass Spectrometer, type 21–103.

**Infrared Spectrum.**—The gas (100 mm. pressure, 10-cm. cell) showed strong absorption bands at 2990, 1708, 1610 and a broad band at 860 cm.$^{-1}$. The latter band was very broad and contained a series of sharp Q branches.[14]

**Ultraviolet Spectrum.**—In acetonitrile solvent butatriene showed a strong peak at 228 m$\mu$ ($\epsilon$ 1.25 × $10^4$) and a weak peak at 438 m$\mu$ ($\epsilon$ 13.7).

**1-Bromo-4-phenoxy-2-butyne.**—A solution of phenol (26.6 g.), potassium hydroxide (16 g.) and ethanol (400 ml.) was added slowly to a stirred solution of 1,4-dibromo-2-butyne (60 g.) in ethanol (180 ml.). Then the mixture was heated to reflux for four hours. The cooled mixture was poured into water (1 liter) and extracted with ether. The ether solution was dried over anhydrous magnesium sulfate and the ether removed by distillation. The residue was distilled under reduced pressure in a modified Claisen flask. The yield was 28 g. (44%), b.p. 114–119° at 0.7 mm., $n^{25}$D 1.5699.

*Anal.* Calcd. for $C_{10}H_9OBr$: C, 53.36; H, 4.03. Found: C, 53.43; H, 4.31.

**Butatriene from 1-Bromo-4-phenoxy-2-butyne.**—The apparatus and procedure described above were used. A solution of 1-bromo-4-phenoxy-2-butyne (20 g., 0.089 mole) in 40 ml. of diethylene glycol diethyl ether was added to zinc dust (29 g.) in 60 ml. of diethylene glycol diethyl ether at 100°. The butatriene obtained was added to excess bromine in carbon tetrachloride, the solid product isolated and recrystallized. The yield of 1,2,3,4-tetrabromo-2-butene was 22.7 g. (69%), m.p. 67–69°, no depression in m.p. with authentic tetrabromide.

**Attempted Reaction of 1,4-Dimethoxy-2-butene with Metals.**—The apparatus and procedure were as described above. To a mixture of zinc dust (28 g.) and 100 ml. of purified diethylene glycol diethyl ether at 90° was added dropwise 1,4-dimethoxy-2-butene[11] (10 g.). No volatile product formed. The temperature was raised to 115° and later anhydrous zinc chloride (0.5 g.) was added and heating continued for an hour. No product was collected in the cold traps.

An attempt was made using magnesium in refluxing purified tetrahydrofuran. No discernible reaction occurred, even after addition of preformed butylmagnesium bromide.

**Reaction of 1,4-Dibromo-2-butyne with Zinc in Ethanol or Water.**—The apparatus and procedure described above were used. Zinc dust (38 g.) and absolute ethanol (50 ml.) were stirred as 1,4-dibromobutyne (21.2 g.) was added dropwise. A vigorous exothermic reaction caused the mixture to reflux gently until the addition was complete. The mixture was stirred for two hours and was then heated to reflux for ten minutes. The yield of volatile product collected in the cold traps was 4.6 g. When a sample was allowed to evaporate a small quantity of an amorphous intractable polymer was deposited. The infrared, ultraviolet and mass spectra showed the volatile product to be 85 to 90% butadiene with 10–15% of another gas, later shown to be butatriene. A similar mixture was obtained in a run made in water (40 ml.) with 38 g. of zinc, 10 g. of calcium carbonate and 21.2 g. of 1,4-dibromo-2-butyne.

The mixture gave negative tests for acetylenic hydrogen with alkaline mercuric iodide, mercuric oxide in glacial acetic acid and alcoholic silver nitrate. A portion of the trap contents was treated with excess bromine in carbon tetrachloride and the resulting crystalline product recrystallized from petroleum ether (30–60°). The material melted at 111–113°, and gave no depression in m.p. with authentic 1,2,3,4-tetrabromobutane.

**Addition of Bromine to Butatriene.**—Butatriene (1.0 g.) when treated with excess bromine in carbon tetrachloride yielded 7.0 g. (95%) of 1,2,3,4-tetrabromo-2-butene, m.p. 68–69.5°.

In a high dilution run, bromine (0.116 mole) in 500 ml. of chloroform was added over a 90-hour period to a rapidly stirred solution of butatriene (8.6 g., 0.165 mole) in two liters of chloroform at 0°. The solvent was removed by fractionation through a 16-inch glass helices column. A small amount of fine white polymer separated from the hydroquinone-inhibited pot mixture during the distillation. The residual brown oil was distilled under 2 mm. pressure through a small modified Claisen head. The first fraction, 0.4 g., b.p. 25–30° (2 mm.), changed in a few minutes to a high melting polymer.

*Anal.* Calcd. for $(C_4H_4Br_2)_x$: Br, 75.5. Found: Br, 75.8.

The second fraction, 0.50 g. of a yellow oil, boiled at 40–61° (2 mm.). The infrared spectrum showed points of similarity to 1,4-dibromo-2-butyne, such as absorption bands at 3.36, 4.43, 5.80 and 6.11 $\mu$. However, new bands ap-

---

(15) L. F. Fieser, "Experiments in Organic Chemistry," Ed. II, D. C. Heath and Company, New York, N. Y., 1941, p. 368.

peared at 4.55, 5.86 and 5.98 $\mu$ 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.), $n^{25}D$ 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.

---

[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).