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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE VIRGINIA POLYTECHNIC INSTITUTE]

Unsaturated Cyclic Sulfones. IV. Isomeric 2-Methyldihydrothiophene 1,1-Dioxides

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2-Methyl-2,5-dihydrothiophene 1,1-dioxide (I) has been carefully characterized, and from this sulfone the remaining two isomeric sulfones have been obtained. Isomerization of I in basic medium gives 2-methyl-4,5-dihydrothiophene 1,1-dioxide and the pyrolysis of the acetate from the alcohol from I gives 2-methyl-2,3-dihydrothiophene 1,1-dioxide.

The characterization of 2-methyl-2,5-dihydrothiophene 1,1-dioxide (I) and the development of reasonably simple methods of preparation of the remaining isomeric sulfones and their subsequent characterization are necessary to the study of the chemistry of the sulfones[2] of the 2-methyl series.

In 1943 Craig[3] reported the preparation of I from the reaction of 1,3-pentadiene and sulfur dioxide, and although he reported that he was able to distill the sulfone no physical constants were given for this product. In 1945 Morris and Finch[4] reported the density and refractive index of this sulfone. Although studies concerning this sulfone have been reported by Frank,[5] Drake,[6] and Grummitt and co-workers[7] no characterization of the compound was reported. Thus, the first objective of the present work is the purification and characterization of I. The sulfone was prepared by the reaction of sulfur dioxide and 1,3-pentadiene in the presence of hydroquinone, to give a colorless oil in 55% yield. Purification of I was effected by distillation at reduced pressure in an atmosphere of sulfur dioxide or more simply by the method described in detail in the Experimental section of this paper. The latter method was found to give as good a product and one which exhibits practically no absorption in the ultraviolet between 220 and 320 mμ at concentrations up to 1 g./liter in ethanol. The crude sulfone, as it moved through the purification scheme, showed a steady decrease in absorption at 220–230 and 280–300 mμ. The loss of absorptivity in these regions was found to be due to removal of traces of 1,3-pentadiene and sulfur dioxide, respectively. The infrared spectra of the distilled sulfone and the extracted sulfone are in excellent agreement.

Under refrigeration at 0° the decomposition of the purified sulfone becomes perceptible through the odor of sulfur dioxide after 11 days, and the sulfone undergoes complete dissociation at 100°. Previous studies in this laboratory demonstrated the utility of bromine adducts as aids in the characterization of certain unsaturated sulfones, hence, the dibromide from I was prepared. Actually, two dibromides from I appear to have been obtained, and it is suggested that these two dibromides are two racemic mixtures. The higher melting dibromide will be referred to as IIa and the lower melting substance as IIb. Sulfone I as well as adducts IIa and IIb are optically inactive; however, if one assumes the trans addition of bromine (see reaction conditions) to sulfone I four stereoisomers are indeed possible (two racemic mixtures). Quantitative analysis supports the formula $C_5H_8Br_2O_2S$ for IIa and IIb. While the infrared spectra of IIa and IIb are similar, the spectra are definitely not identical. Sulfone I was converted to the tetrahydro derivative, 2-methyltetrahydrothiophene 1,1-dioxide (III) in 91% The physical constants for III are in good agreement with those reported by Grishkevich-Trokhimovskii[8] who prepared this compound by the reaction of 1,4-dibromopentane and sodium sulfide, and the subsequent oxidation of the cyclic sulfide of the sulfone. The infrared spectrum of III appears in good agreement with the spectra of 3-methyltetrahydrothiophene 1,1-dioxide and with

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[2] For the previous paper see R. C. Krug, G. R. Tichelaar, and F. E. Didot, *J. Org. Chem.*, **23**, 212 (1958).

[3] D. Craig, *J. Am. Chem. Soc.*, **65**, 1006 (1943).

[4] R. C. Morris and H. deV. Finch (to Shell Development Co.), U. S. Patent **2,373,329**, April 10, 1945.

[5] E. J. Frank, *J. Am. Chem. Soc.*, **69**, 2313 (1947).

[6] S. P. Drake, *J. Am. Chem. Soc.*, **68**, 2521 (1946).

[7] O. Grummitt, A. E. Ardis, and J. Fick, *J. Am. Chem. Soc.*, **72**, 5167 (1950).

[8] E. Grishkevich-Trokhimovskii, *J. Russ. Phys. Chem. Soc.*, **48**, 901 (1916).

tetrahydrothiophene 1,1-dioxide with respect to the presence of the saturated ring system.

In view of previous studies[2] it seemed reasonable to expect that sulfone I in the presence of a strong base should undergo isomerization. Indeed, such was found to be the case and the reaction product was identified as 2-methyl-4,5-dihydrothiophene 1,1-dioxide (IV). The melting point of this sulfone and of its bromine adduct are in good agreement with the values given by Birch and McAllan.[9] These authors obtained a compound which they tentatively identified as sulfone IV by the oxidation of a minor reduction product from 2-methylthiophene. In 1953 Bacchetti and Fiecchi[10] prepared a compound having a melting point similar to that reported by Birch and McAllan for IV by the cyclization of 5-mercapto-2-pentanone to give the cyclic sulfide which was oxidized to the sulfone. In the present work, sulfone IV was converted to III in 81% with hydrogen in the presence of a catalyst. The infrared spectrum of IV supports the presence of the $-\mathrm{CH}{=}\overset{|}{\mathrm{C}}-$ type of double bond.

There remained of course the synthesis of the third isomer, 2-methyl-2,3-dihydrothiophene 1,1-dioxide. One of the most direct methods of synthesis appeared to be the hydration of sulfone I (depending on the location of the hydroxy group), conversion of the alcohol to the acetate, and the pyrolysis of the acetate. The alcohol was obtained in 18% yield by the action of aqueous potassium hydroxide on sulfone I. The position of the hydroxy group is assigned in agreement with the formula 4-hydroxy-2-methyltetrahydrothiophene 1,1-dioxide (V), as will be subsequently established. Sulfone V, a colorless oil, gave a 3,5-dinitrobenzoate and an acetate. The infrared spectrum of V was prepared; however, no information regarding the location of the hydroxy group was obtained. The alcohol was converted to its corresponding acetate (VI) in 81% yield. By means of the infrared spectra the relationship between V and VI was established. Thus, VI was assigned the formula in agreement with 4-acetoxy-2-methyltetrahydrothiophene 1,1-dioxide. Vapor phase pyrolysis of the acetate at 440–452° gave, after purification, a colorless oil (VII). Analytical data clearly support the formula $C_5H_8O_2S$, and the infrared spectrum of VII gave evidence of the presence of a symmetrical —CH=CH— ethylenic unit. Sulfone I and the pyrolysis product absorb strongly near 690 cm.$^{-1}$, while sulfone IV does not absorb in this region of the spectrum. Sulfone VII was converted to a dibromide, and catalytic reduction of VII gave II in 74% yield. Parenthetically, the trans addition of bromine to VII should give four stereoisomeric dibromides (two racemic mixtures); however, one dibromide m.p. 84–85° has thus far been identified. Thus, the formula of sulfone VII is established as 2-methyl-2,3-dihydrothiophene 1,1-dioxide, and the structures of sulfones V and VI are as indicated by their respective names.

EXPERIMENTAL[11]

2-Methyl-2,5-dihydrothiophene 1,1-dioxide (I). Commercial 1,3-pentadiene (90% pentadiene, Phillips Petroleum Co.) was enriched in the trans-1,3-pentadiene component by the method of Frank.[5] The crude diene showed a change in refractive index during enrichment from n_D^{20} 1.4326 to n_D^{20} 1.4290 (lit.[12]; cis, n_D^{20} 1.4359; trans n_D^{20} 1.4299). In a steel reaction vessel were placed 250 ml. (3.88 moles) of liquid sulfur dioxide 90.0 g. (1.32 moles) of the enriched 1,3-pentadiene (peroxide free), and 5.0 g. of hydroquinone. The vessel was sealed, and heated to 95° for 3 hr. The vessel was cooled, and the volatile components were vented to give 150 g. of a red colored oil. Of this oil 60.0 g. was added to 600 ml. of water, and the mixture was shaken thoroughly and refrigerated overnight. The supernatant liquid was decanted, filtered, and the filtrate was extracted with four portions of chloroform. The chloroform was evaporated from the combined extracts to give 48.0 g. of a yellow oil which was dissolved in 250 ml. of distilled water and refrigerated overnight. The aqueous phase was separated from the gum and extracted with four portions of chloroform under refrigerated (0°) conditions. Removal of chloroform from the combined extracts gave 38.1 g. of colorless oil, n_D^{20} 1.4942, d_4^{20} 1.2433. A sample of this oil, distilled under reduced pressure in an atmosphere of sulfur dioxide, gave the following: b.p. 85°/7 mm., n_D^{20} 1.4929, and d_4^{20} 1.2539. The yield of purified I based on the trans content of the diene as 86%[5] was 55%. Infrared spectra of the distilled product and the extracted product were entirely similar, and the principal frequencies are: 3040, 2970, 2930, 1615, 1450, 1409, 1380, 1348, 1305, 1250, 1223, 1128, 1077, 1008, 960, 916, 896, 830, 726, 704, and 657 cm.$^{-1}$

2-Methyl-3,4-dibromotetrahydrothiophene 1,1-dioxide (II). To a flask containing 16.0 g. (0.100 mole) of bromine and 0.146 g. of aluminum chloride was added 12.4 g. (0.094 mole) of I. After four days a slight sediment was filtered, and the chloroform was evaporated. The residue was continuously extracted with water for 33 hr. The solid which did not dissolve was recrystallized from ethanol to give 4.6 g. (17%) of IIa, m.p. 145.0–145.5°. The aqueous extract was chilled and the solid was recrystallized from methanol to give white crystals weighing 2.3 g. (8%), m.p. 89–90° (IIb).

Anal. Calcd. for $C_5H_8Br_2O_2S$: C, 20.56; H, 2.76; Br, 54.74; S, 10.98. Found (IIa): C, 20.26; H, 3.20; Br, 54.75; S, 11.12. Found (IIb): C, 20.49; H, 2.99; Br, 54.60; S, 10.94.

The infrared spectrum of IIa showed the following principal frequencies: 3000, 2930, 1448, 1399, 1380, 1318, 1300, 1280, 1230, 1221, 1190, 1175, 1133, 1109, 1083, 1071, 1043, 994, 936, 891, 881, 801, and 701 cm.$^{-1}$

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(9) F. F. Birch and D. T. McAllan, *J. Chem. Soc.*, 3411 (1951).

(10) T. Bacchetti and A. Fiecchi, *Gazz. chim. ital.*, **83**, 1037 (1953).

(11) All melting and boiling points are uncorrected. Analyses performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra prepared by Kendall Infrared Laboratories, Plainfield, N. J. Ultraviolet spectra were obtained with a Perkin-Elmer Spectracord. Anhydrous sulfur dioxide was supplied through the courtesy of the Virginia Smelting Co., West Norfolk, Va.

(12) F. D. Rossini *et al.*, Selected Values of Properties of Hydrocarbons, Nat. Bur. Stds. Circular C461, U. S. Gov't. Printing Office, Washington, D. C., 1947, p. 55.

The infrared spectrum of IIb showed the following principal frequencies: 3000, 2930, 1453, 1409, 1383, 1311, 1278, 1250, 1221, 1192, 1179, 1132, 1122, 1082, 1071, 1043, 1024, 981, 911, 887, 818, and 718 cm.$^{-1}$

2-Methyl-4,5-dihydrothiophene 1,1-dioxide (IV). To 500 ml. of 0.5N potassium hydroxide was added 25.0 g. (0.189 mole) of I, and the mixture was stirred at 30° for 30 hr. after which time it was chilled and filtered. The residue was recrystallized from ethanol to give 11.1 g. (45%) white needles, m.p. 128.0–128.5° (lit.,[9,10] 128°, and 128–129°).

The bromine adduct from IV was prepared by the procedure described from the preparation of II. The crude product was extracted with hot water and the residue was recrystallized from ethanol, m.p. 69.5–70.0° (lit.,[9] 68–69°).

4-Hydroxy-2-methyltetrahydrothiophene 1,1-dioxide (V). An emulsion of 26.4 g. (0.199 mole) of I in 100 ml. of water was added very slowly to 300 ml. of 9.3N potassium hydroxide. The mixture was allowed to stir for 14 hr. after which time it was chilled and filtered. The solid, weighing 13.6 g. was recrystallized from ethanol, m.p. 128–129°. The filtrate was neutralized with hydrochloric acid, and the water was evaporated. The residue was extracted with four portions of acetone and the acetone was evaporated. The residual oil was dissolved in 30 ml. of water and extracted with five portions of chloroform. The water raffinate was concentrated and the residue was distilled *in vacuo* to yield 5.5 g. (18%) of a colorless oil, b.p. 128–130°/1 mm., n_D^{25} 1.4951, d_4^{25} 1.317.

Anal. Calcd. for $C_5H_{10}O_3S$: C, 39.98; H, 6.17; S, 21.35. Found: C, 39.54; H, 6.75; S, 22.43.

The 3,5-dinitrobenzoate from V was prepared by the method of Shriner and Fuson,[13] utilizing pyridine. After recrystallization from ethanol, the product melted 190–191°.

Anal. Calcd. for $C_{12}H_{12}N_2O_8S$: C, 41.86; H, 3.51; N, 8.14; S, 9.31. Found: C, 41.98; H, 3.29; N, 8.13; S, 9.19.

The infrared spectrum of V showed the following principal frequencies: 3460, 2930, 1453, 1400, 1340, 1300, 1258, 1207, 1193, 1135, 1111, 1070, 1030, 1015, 982, 935, 913, and 794 cm.$^{-1}$

4-Acetoxy-2-methyltetrahydrothiophene 1,1-dioxide (VI). Twenty-five grams (0.32 mole) of acetyl chloride was slowly added to a flask containing 16.0 g. (0.107 mole) of V. The reaction mixture was cooled externally and stirred for 30 min. The mixture was then poured into 140 ml. of distilled water, and the water was extracted with four portions of chloroform. Upon evaporation of the chloroform there remained an oil which was distilled under reduced pressure to give 18.0 g. (81%) of VI, b.p. 100°/1 mm.

Anal. Calcd. for $C_7H_{12}O_4S$: C, 43.73; H, 6.29; S, 16.68. Found: C, 43.72; H, 6.09; S, 16.78.

The infrared spectrum of VI showed the following principal frequencies: 2940, 1738, 1640, 1500, 1450, 1404, 1372, 1309, 1235, 1181, 1137, 1120, 1072, 1042, 1022, 983, 947, 931, 893, 855, and 779 cm.$^{-1}$

2-Methyl-2,3-dihydrothiophene 1,1-dioxide (VII). The apparatus involved in this experiment consisted of a separatory funnel (with necessary gas lines) attached to a vertically mounted glass tube which passed through a furnace 12 inches in length. The tube was packed with glass wool for a length of 6 inches in the furnace zone. The tube was connected in series to a water-cooled condenser and a receiver cooled in an ice salt bath. Before each run the system was swept with nitrogen, and a very low flow of nitrogen was maintained during the run. The portion of the tube containing the glass wool was maintained at 440–452° during the pyrolysis. A solution of 15.0 g. (0.078 mole) of VI in 35 ml. of benzene was introduced into the reaction tube at a rate of 25 drops per min. After the addition of the solution was complete, the reaction tube was flushed by the introduction of benzene followed by a small amount of acetone. The liquid in the receiver was warmed to remove solvents. The residue was distilled and a fraction was collected $b_{.1}$ 87–95°. The residue was recycled through the furnace. Distillation and the recycling of the residue was continued until the conversion of the residue was complete. The pyrolysis products were collectively distilled through a 5-inch Vigreux column at 82–87° at 1 mm. This latter fraction (8.5 g.) was redistilled to give a colorless liquid, b.p. 75–77.5°/1 mm., m.p. 25–26°, n_D^{20} 1.4949, d_4^{20} 1.2504. The yield of crude product ($b_{.1}$ 82–87°) was 83%.

Anal. Calcd. for $C_5H_8O_2S$: C, 45.43; H, 6.10; S, 24.21. Found: C, 45.44; H, 6.02; S, 24.08.

The infrared spectrum of VII showed the following principal frequencies: 3050, 2950, 2900, 1600, 1500, 1450, 1433, 1380, 1311, 1290, 1236, 1176, 1132, 1077, 1073, 1011, 950, 910, 895, 829, and 704 cm.$^{-1}$

2-Methyl-4,5-dibromotetrahydrothiophene 1,1-dioxide (VIII). The procedure described for the preparation of the bromine adduct from I was employed. The oil was crystallized from ethanol and subsequently recrystallized from ethanol to give VIII in 27%, m.p. 85–86°.

Anal. Calcd. for $C_5H_8Br_2O_2S$: C, 20.56; H, 2.76; Br, 54.74; S, 10.98. Found: C, 20.66; H, 3.37; Br, 54.49; S, 10.84.

The infrared spectrum of VIII showed the following principal frequencies: 2970, 2920, 2890, 1450, 1320, 1307, 1290, 1257, 1207, 1180, 1150, 1144, 1111, 1105, 1090, 1032, 1000, 942, 913, 877, 816, 790, and 708 cm.$^{-1}$

The ethanolic liquors from the above mentioned recrystallizations were combined, and the ethanol was evaporated at reduced pressure. The residue was washed with a small amount of ethanol and filtered. This residue was dissolved in the minimum amount of ethanol and allowed to stand overnight at room temperature. The mixture was then filtered (crystals m.p. 78–83°) and the filtrate was refrigerated. The resulting precipitate was filtered and vacuum dried, m.p. 56–58°. This solid was not further characterized.

2-Methyltetrahydrothiophene 1,1-dioxide (III). In a Parr hydrogenation apparatus 13.2 g. (0.100 mole) of I in 220 ml. of chloroform was reduced with hydrogen (42 p.s.i.) in the presence of 0.5 g. of 10% palladium on charcoal. After the reaction mixture was filtered, the chloroform was evaporated. The residue was heated to 130° for 1 hr. to remove unreacted I, and subsequent distillation of the residue gave 12.0 g. (91%) of III, b.p. 70°/1 mm., 273–274°/701 mm., n_D^{20} 1.4801, d_4^{20} 1.2055 (lit.,[8] b.p. 279–280°/758 mm., n_D^{20} 1.4801, d_4^{20} 1.207). Under similar conditions IV gave 81% of III, $b_{.1}$ 70°, n_D^{20} 1.4817. The reduction of VII resulted in a 74% yield of III, b.p. 58–60°/1 mm., n_D^{20} 1.4809, d^{20} 1.2027.

The principal frequencies observed for III are: 2940, 2870, 1640, 1452, 1419, 1380, 1300, 1252, 1208, 1139, 1111, 1072, 1065, 1021, 1000, 967, 949, 886, 833, and 723 cm.$^{-1}$

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[13] R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, New York, 1948, p. 164