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

Unsaturated Cyclic Sulfones. I. 3-Bromomethyl-2,5-dihydrothiophene 1,1-Dioxide

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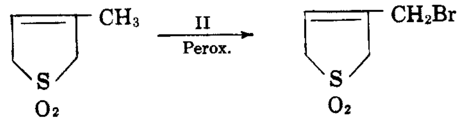
The synthesis and some properties of 3-bromomethyl-2,5-dihydrothiophene 1,1-dioxide are described for the first time. The pyrolysis of this compound is found to give a monobromodiene and a dibromoalkene.

In 1948 Backer, Stevens and Dost[2] reported that no reaction occurred between 3-methyl-2,5-dihydrothiophene 1,1-dioxide (I) and N-bromosuccinimide (II) in carbon tetrachloride in the presence of benzoyl peroxide. The brominations attempted in this laboratory were performed in chloroform since this compound appears to be an excellent solvent for I as well as for other sulfones of this type. The bromination did indeed yield a monobromide together with a viscous, bromine-containing oil which has resisted all attempts at crystallization. This oil distills with extensive decomposition at pressures as low as 1 mm. The monobromide (III) has been assigned the structure shown.



I III

The 3-bromomethyl-2,5-dihydrothiophene 1,1-dioxide (III) is a white, crystalline solid which is soluble in many organic solvents. On treatment with aqueous sodium hydroxide or carbonate solutions, III yields a polymeric substance. Further, III is a potent skin irritant and reacts readily with alcoholic silver nitrate solution.

Evidence supporting the structure assigned to III has been obtained from physical and chemical studies. An analysis of the infrared spectra of III and I shown in Figures 1 and 2 respectively has been made. Since the interpretation of these spectra is offered in support of structure III, several significant points are given here. (a) The C—Br bond in III with characteristic absorption frequencies at 525–475 cm.$^{-1}$ cannot be detected within the range of the present spectra. (b) The two characteristic C—H stretching frequencies, *viz.*, 2960 and 2870 cm.$^{-1}$, of the methyl group are very pronounced in I, but greatly reduced in III. This is further supported by the disappearance of both asymmetric and symmetric C—H deformation of the methyl group at 1450 and 1338 cm.$^{-1}$ in III while these maxima appear in I. (c) Both spectra possess the characteristic frequencies of the sulfone group and they are very intense. (d) Compounds I and III possess a tertiary substituted ethylenic unit with only one hydrogen attached. This structure is indicated by the characteristic absorption frequencies at 3010 and 798 cm.$^{-1}$ for I. The absorption maxima of the former compound are much weaker than those of the latter. This result is in agreement with the postulate that the electron density at the ethylenic linkage decreases due to the introduction of a negative group such as bromine. (e) Both I and III possess the characteristic C=C stretching of the non-conjugated type at 1650 and 1664 cm.$^{-1}$, respectively. The conjugated C=C stretching appears at 1626 cm.$^{-1}$ for III while in I the band appears broad.

The same conditions used in the synthesis of III were applied to sulfone I with N-bromoacetamide (IV). In this case there was no monobromo compound isolated; however, a dibromo compound was obtained. This compound was shown to be 3-methyl-3,4-dibromotetrahydrothiophene 1,1-dioxide (V).

The conventional chlorination[3] employing sulfuryl chloride in the presence of benzoyl peroxide gave no side-chain chlorination although 3-methyl-3,4-dichlorotetrahydrothiophene 1,1-dioxide (VI) was isolated in good yield. The structure of VI is supported by quantitative elementary analysis and by the results of qualitative tests for unsaturation. In the absence of peroxides the original sulfone I was recovered unchanged, thus the radical attack here is indispensable. It is to be noted that a chlorine-substituted product such as obtained in the thiophene series[4] was not isolated here.

It is striking that the action of II on I gives a monobromosulfone and that no dibromosulfone could be isolated, whereas, IV gives solely the dibromosulfone. It is of further interest to note that in the case of II with 2,5-dihydrothiophene 1,1-di-

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(2) Backer, Stevens, and Dost, *Rec. trav. chim.*, **67**, 451 (1948).

(3) Goerner and Nametz, *J. Am. Chem. Soc.*, **73**, 2940 (1951).

(4) Campaigne and LeSuer, *J. Am. Chem. Soc.*, **70**, 415 (1948).

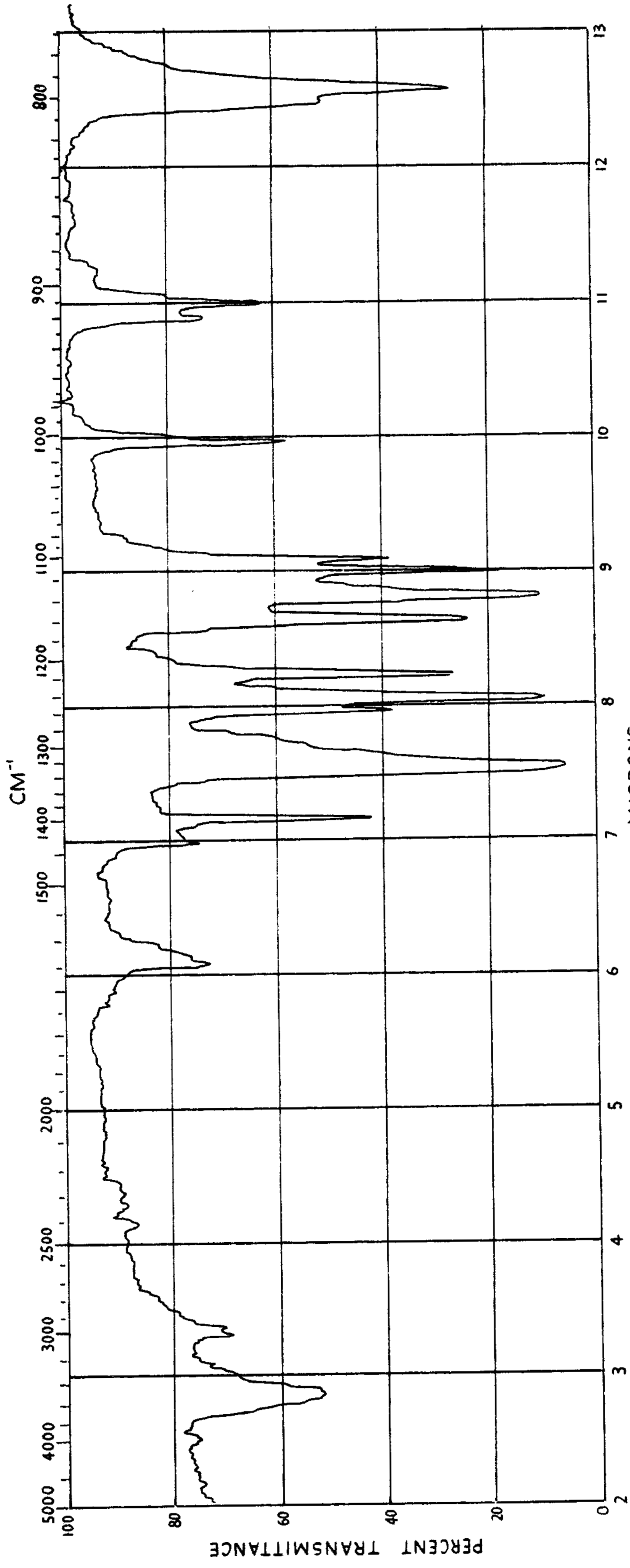


FIG. 1.—INFRARED SPECTRUM OF 3-BROMOMETHYL-2,5-DIHYDROTHIOPHENE 1,1-DIOXIDE. Concentration: 0.5% in KBr. Cell Thickness 0.5 Mm.

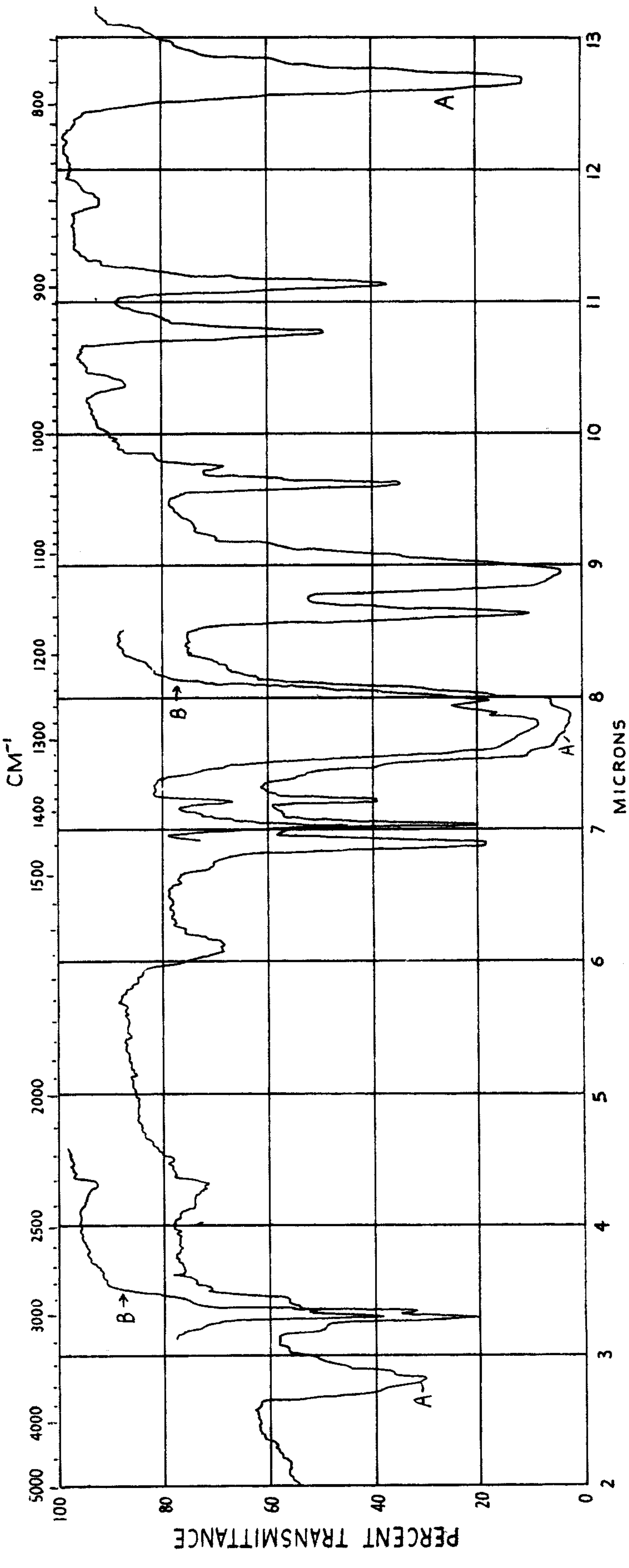
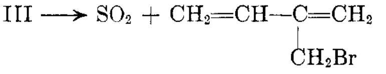


Fig. 2.—Infrared Spectrum of 3-Methyl-2,5-dihydrothiophene 1,1-Dioxide. Concentration: A, 0.6% in KBr; B, 0.25% in KBr. Cell Thickness: A, 0.05 Mm.; B, 0.4 Mm.

oxide the main product is 3,4-dibromotetrahydrothiophene 1,1-dioxide.[5] No bromine-substituted product was isolated in this instance.

As mentioned earlier the C—Br bond in III is very reactive, characteristic of an allylic bromide. It is known that a reverse Diels-Alder reaction occurs when sulfones such as I are heated. In fact, this reaction has been adapted to industrial operations for the purification of dienes. Thus, the pyrolysis of III should give 2-bromomethyl-1,3-butadiene (VII). This latter compound has never been isolated in pure form, although Petrov[6] reported it



$$III \longrightarrow SO_2 + CH_2{=}CH{-}\underset{\displaystyle CH_2Br}{\underset{|}{C}}{=}CH_2$$

VII

to be present in a mixture obtained from the dehydration of 1-bromo-2-methyl-3-buten-2-ol. Since the four isomeric monobromo-2-methyl-1,3-butadienes possess similar physical properties, the structure VII was confirmed by a study of the infrared spectrum of the diene from the pyrolysis of III. The spectrum, not shown here, conclusively revealed the presence of an unsymmetrically disubstituted ethylenic unit ($-\overset{|}{C}{=}CH_2$) and the absence of both a symmetrically disubstituted unit ($-CH{=}CH-$) and a trisubstituted ethylenic unit. In further support of VII, an alcoholic solution of silver nitrate reacted instantaneously with VII with the formation of silver bromide. Lastly, a comparison of the ultraviolet absorption spectra of VII and 2-methyl-1,3-butadiene supports the assigned structure for VII.

A high-boiling unsaturated oil (b.p.$_{12}$ 90°) was obtained from the fractionation of the pyrolysate from III. This oil, empirical formula, $C_5H_8Br_2$ (VIII) gave a positive silver nitrate test and a positive phloroglucinol-hydrochloric acid test. Compound VIII may have resulted from the addition of hydrogen bromide (formed as a result of a side reaction) to VII.

$$\underset{}{VII + HBr} \longrightarrow \underset{VIII}{C_5H_8Br_2}$$

Should this be the case the following structures, each of which possesses an allylic bromine, are plausible: (a) $CH_3CH{=}C(CH_2Br)_2$, (b) $CH_3C(CH_2Br){=}CHCH_2Br$, (c) $CH_3CHBrC(CH_2Br){=}CH_2$, (d) $CH_2{=}CHC(Br)(CH_2Br)CH_3$, (e) $CH_2{=}C(CH_2Br)CH_2CH_2Br$, and (f) $CH_2{=}CH{-}CH(CH_2Br)CH_2Br$. Only (b) (*cis* and *trans* forms) has been reported,[7] and the properties of (b) (trans) agree with those found for VIII. Several significant points from the infrared spectrum of VIII, which support structure (b), are presented. The strong absorption at 11.8 and 12.7 μ indicates the presence of a trisubstituted ethylenic unit, thus eliminating structures (c), (d), (e), and (f). The strong CH_2 in plane deformation is shifted to 6.95 μ in agreement with the presence of the $-\overset{|}{C}{=}\overset{|}{C}{-}CH_2\text{-}X$ unit. There is a strong band at 8.30 μ in agreement with the structural unit $-\overset{|}{C}{=}CH{-}CH_2Br$. If the *alpha*-hydrogen in the latter unit is replaced (as in a) the band usually disappears or shifts to 8.13 μ. The fact that there is no such shift in this band strongly supports structure (b). This assignment is also in agreement with the theoretical deduction of Ingold.[8]

EXPERIMENTAL[9]

3-Methyl-2,5-dihydrothiophene 1,1-dioxide (I). Freshly-distilled, peroxide-free 2-methyl-1,3-butadiene[10] (Phillips Petroleum Co.) was used. The procedure was based on that of Frank and Seven;[11] however, crude I did not require treatment with Norit. One recrystallization from methanol gave pure I, m.p. 63–64°, 84% yield.

3-Bromomethyl-2,5-dihydrothiophene 1,1-dioxide (III). From 1.5 to 1.8 l. of dry chloroform was added to a mixture of 132 g. (1.0 mole) of I, 178 g. (1.0 mole) of N-bromosuccinimide, and 12 g. (0.05 mole) of benzoyl peroxide. The mixture was stirred and heated to 75° for 2 hours during which time the white suspension changed to a red-colored solution. Within the next 6 hours the color changed from red to yellow, and the total reaction time was 16–20 hours. The solution was allowed to cool to room temperature and crystals of succinimide collected at the surface of the solution. This solid was filtered and the remaining solution was subjected to reduced pressure to remove most of the chloroform (*ca.* 1.2 l.).[12] The concentrated solution, with succinimide floating on the surface was cooled in a refrigerator and the succinimide was filtered again. The combined succinimide (89 g.) was equivalent to a 90% yield. The last trace of chloroform in the viscous brown oil was removed at reduced pressure and to the residual oil was added 1.5 volumes of 95% ethanol. The solution was placed in a refrigerator, and crystals of III appeared within 2–3 days.[13] The yield of crude III, m.p. 78–84°, was 80 g. (38%). Five recrystallizations from 95% ethanol gave pure III, m.p. 87–88°.

Anal. Calc'd for $C_5H_7BrO_2S$: C, 28.45; H, 3.34; Br; 37.86. Found: C, 28.45; H, 3.44; Br, 37.66.

S-1,1-Dioxy-2,5-dihydro-3-thenyl isothiuronium picrate. In 12 ml. of 95% ethanol were dissolved 1.2 g. (0.010 mole) of III and 1.4 g. (0.020 mole) of thiourea. The mixture was heated to boiling for 2 min. and there was added a boiling solution of 2 g. (0.010 mole) of picric acid in the minimum

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[5] Unpublished work of Robert C. Krug and George R. Tichelaar.

[6] Petrov, *Zhur. Obschei Khim.*, **13**, 481 (1943).

[7] Petrov, *Zhur. Obschei Khim.*, **13**, 741 (1943).

[8] Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, 1953, p. 653.

[9] All melting and boiling points are uncorrected. Analyses performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[10] Commercial grade isoprene donated by the Enjay Co. gave results comparable to those obtained with the 99% isoprene from the Phillips Petroleum Co.

[11] Frank and Seven, *Org. Syntheses*, **Coll. Vol. 3**, 499 (1955).

[12] At this stage if too much solvent were removed, the residue would solidify thus making difficult the isolation of the desired product.

[13] Crystals of III could be obtained overnight if the solution were seeded.

amount of 95% ethanol. Yellow needles appeared at once. This solid, recrystallized from 95% ethanol, gave fine, yellow needles, m.p. 184–185°.

Anal. Calc'd for $C_{12}H_{14}N_5O_9S_2$: N, 16.04; S, 14.70. Found: N, 16.02; S, 14.86.

N-Bromoacetamide with I. The reaction was performed as described for III using 26.4 g. (0.20 mole) of I, 26.8 g. (0.20 mole) of N-bromoacetamide, and 2.4 g. (0.010 mole) of benzoyl peroxide in 400 ml. of dry chloroform. After the reaction mixture was heated to reflux for 5 hours, the cooled solution was extracted with water. The chloroform phase was dried and distilled at reduced pressure whereupon the residue solidified. This solid, recrystallized from 95% ethanol, m.p. 125–126°, in admixture with an authentic sample of 3-methyl-3,4-dibromotetrahydrothiophene 1,1-dioxide showed no depression upon melting. The yield of the dibromide was 11 g. (38% based on IV).

3-Methyl-3,4-dichlorotetrahydrothiophene 1,1-dioxide (VI). A mixture of 19.8 g. (0.14 mole) of I, 20.2 g. (0.15 mole) of sulfuryl chloride, 2.4 g. (0.010 mole) of benzoyl peroxide, and 400 ml. of chloroform was heated to reflux for 20 hours to give an orange-colored solution. The solvent was distilled at reduced pressure and the residual liquid solidified upon cooling. The solid was recrystallized four times from 95% ethanol to give 20.3 g. (66%) of VI, m.p. 129–130°.

Anal. Calc'd for $C_5H_8Cl_2O_2S$: C, 29.55; H, 3.95; Cl, 34.90. Found: C, 29.75; H, 4.16; Cl, 34.78.

2-Bromomethyl-1,3-butadiene (VII). A mixture of 42 g. (0.20 mole) of III and a small amount of hydroquinone was heated under reduced pressure in a flask connected to an ice-cooled receiver. Sulfur dioxide was evolved and the following distillates were obtained: (*a*) b.p.$_{100}$ 80–90°, (*b*) b.p.$_{30}$ 90–120°. Fraction *a* was twice distilled to give 8.8 g. (30%) of VII, a center fraction, b.p.$_{80}$ 68°, n_D^{25} 1.5130, d_4^{25} 1.348, of which was reserved for the infrared study. This diene was highly lachrymatory, readily decolorized bromine, and gave positive silver nitrate and phlorglucinol-hydrochloric acid[14] tests.

Anal. Calc'd for C_5H_7Br: C, 40.84; H, 4.80; Br, 54.35. Found: C, 40.76; H, 4.87; Br, 54.36.

1,4-Dibromo-2-methyl-2-butene (VIIIb). The higher-boiling portions from fraction *a* and fraction *b* from VII were combined and twice distilled. A center fraction, b.p.$_{12}$ 90°, n_D^{25} 1.5512, d_4^{25} 1.795, from the last distillation was reserved for the infrared study. The yield of VIIIb was *ca.* 4 g. This olefin was highly lachrymatory, readily decolorized bromine, and gave positive silver nitrate and phloroglucinol-hydrochloric acid tests.

Anal. Calc'd for $C_5H_8Br_2$; C, 26.34; H, 3.53; Br, 70.12. Found: C, 26.45; H, 3.93; Br, 69.78.

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[14] A yellow color is characteristic of an allylic linkage. See Feigl *Spot Test,* Vol. II, Elsevier Publishing Co., Houston, 1954, p. 226.