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

Unsaturated Cyclic Sulfones. II. Displacement and Elimination Reactions

ROBERT C. KRUG AND TEH FU YEN[1]

Received June 25, 1956

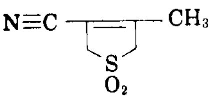
Some displacement reactions on 3-bromomethyl-2,5-dihydrothiophene 1,1-dioxide illustrating the allylic character of this bromide are described. The dehydrobromination of two isomeric dibromo compounds is found to give two new unsaturated cyclic sulfones.

In view of the reactive carbon-bromine bond in 3-bromomethyl-2,5-dihydrothiophene 1,1-dioxide[2] (I) the behavior of this compound in the presence of certain nucleophilic agents was studied. The substitution of iodine for bromine in I was accomplished by the action of sodium iodide in the presence of acetone to give 3-iodomethyl-2,5-dihydrothiophene 1,1-dioxide (II). The isothiuronium picrate from II was found by a mixture melting point determination to be identical with that obtained from I.

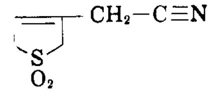
An attempted substitution of chlorine for iodine in II was performed according to the procedure of Oppenheim[3] for the conversion of allyl iodide to allyl chloride. Mercuric iodide was identified as a reaction product; however, the desired chloride was not isolated. A small amount of an unidentified oil was the only organic substance obtained from the attempted conversion.

The replacement of bromine by an hydroxy group in an allylic halide is of course well known. Attempted hydrolysis of I in the presence of 5% potassium hydroxide solution at 50–80° for 30 minutes gave a white, crystalline solid which resinified within 24 hours to a dark brown substance. The instability of the product prevented a reliable quantitative analysis. Although the compound was found to contain carbon, hydrogen, and oxygen, the ceric nitrate test for an hydroxy group was negative. It is not too unreasonable to suppose that an intermolecular dehydrobromination of I might have occurred to give a symmetrically substituted ethene. Treatment of I with a 10% potassium hydroxide solution at room temperature gave I unchanged. This result is interesting in view of the fact that 3-methyl-2,5-dihydrothiophene 1,1-dioxide under similar conditions gives the isomeric α-sulfone, 4-methyl-2,3-dihydrothiophene 1,1-dioxide. The replacement of bromine in I with an ethoxy group (Williamson ether synthesis) was accomplished by using the procedure of Miller, *et al.*[4] for 9,10-dichloromethylanthracene. The β-sulfone structure of the ether, 3-ethoxymethyl-2,5-dihydrothiophene 1,1-dioxide (III) was clearly established by the nickel hydroxide-paper test.[5]

The conversion of I to a nitrile was investigated under several different conditions. In benzene in the presence of copper$^{(I)}$ cyanide, I was recovered from the mixture unchanged. In 50% aqueous ethanol with potassium cyanide I gave a compound having the molecular formula $C_6H_7NO_2S$ (IV). The same substance was obtained from the action of potassium cyanide and copper$^{(I)}$ cyanide in 50% ethanol on I. There are two principal, alternative structures possible for IV, and they are:



IVa



IVb

From a consideration of the ultraviolet absorption spectra of 3-methyl-2,5-dihydrothiophene 1,1-dioxide, I and IV a tentative structural formula for IV is offered. The curves for the unsubstituted compound and for I are characteristic of isolated π-electron groups while the distinct maximum at 235 mμ for IV cannot be attributed to such isolated groups, *i.e.*, IV possesses a higher degree of conjugation. While the maximum of 235 mμ cannot be attributed to a π-σ-π-conjugation it may very well be accounted for in terms of a π-π-conjugation. Thus, tentatively, structure IVa is assigned to nitrile IV. The above interpretation of the ultraviolet spectra is supported by the theoretical argument of Lane, *et al.*[6] It should also be noted that recent evidence has shown that the cyano group exhibits a strong chromophoric action. For example, cyclohexene shows a maximum at 182 mμ[7] while the maximum for 1-cyanocyclohexene is shifted to 211 mμ.[8] The infrared spectrum of IV

---

[1] This work, taken from the Ph.D. dissertation of Teh Fu Yen, was performed under contract AF 18(600)-690 monitored by the Office of Scientific Research, Air Research and Development Command, Baltimore, Maryland.

[2] Krug and Yen, *J. Org. Chem.*, **21**, 1082 (1956).

[3] Oppenheim, *Ann.*, **140**, 204 (1866).

[4] Miller, Amidon, and Tawney, *J. Am. Chem. Soc.*, **77**, 2845 (1955).

[5] A black color developed upon the release of sulfur dioxide; see Feigl, *Spot Test*, Vol. II, Elsevier Publishing Co., Houston, 1954, p. 180 ff.

[6] Lane, Fentress, and Sherwood, *J. Am. Chem. Soc.*, **66**, 545 (1944).

[7] Platt, Klevens, and Price, *J. Chem. Phys.*, **17**, 466 (1949).

[8] Braude and Wheeler, *J. Chem. Soc.*, 320 (1955).

shows a nitrile band at 2250 cm.$^{-1}$; however, in view of the unknown effect of the sulfone linkage on the position of this band, no conclusion can be drawn as to the conjugation of the cyano group with the carbon to carbon double bond. The absence of a non-conjugative, carbon to carbon double bond stretching band is in agreement with structure IVa, since such a band is found in the case of 3-methyl, 3-bromomethyl and the unsubstituted cyclic sulfones where the double bond is in the 3,4-position.

Since the carbon-bromine bond in I is quite reactive because of the allylic properties of the molecule, the nucleophilic attack by nitrogenous bases should proceed with ease, and indeed this was found to be the case. The use of compounds such as piperidine brought about such a violent reaction that no quaternary salt could be isolated. Studies are continuing on this aspect of the work. The bases used in the work reported here are pyridine, quinoline, and benzo[*f*]quinoline, and the results of these studies are summarized in Table I.

TABLE I

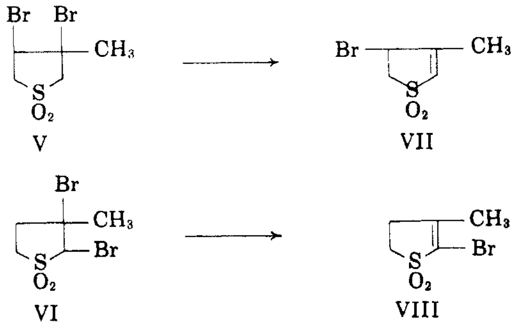
QUATERNARY SALTS FROM 3-BROMOMETHYL-2,5-DIHYDROTHIOPHENE 1,1-DIOXIDE

Base	Conditions	M.p., °C.
Pyridine	~25°; 1 day	153–155
Quinoline	~25°; 6 hours	200–202
Benzo[*f*]quinoline	~25°; 2 days	197

Not included in Table I is the isothiuronium salt from I[2] wherein one finds a displacement reaction which results in the formation of a carbon-sulfur bond.

In the displacement reactions studied only one case was found which involves a rearrangement and that case is the conversion of I to the rearranged nitrile. Thus, the appearance of rearranged and nonrearranged products of displacement reactions confirms the allylic properties of I and supports the anionotropic character of the mesomeric cation from I.

Our interest in the elimination reactions arose from two related points, namely, the utility of the new compounds so produced and the study of the mode of elimination, *i.e.*, positions in the sulfone molecule involved in the elimination reaction. In 1942 Backer and Blass[9] studied the dehydrobromination of 3,4-dibromotetrahydrothiophene 1,1-dioxide, and more recently Bailey and Cummins[10] improved the earlier procedure. No studies on the dehydrobromination of 3,4-dibromo-3-methyl (V) or 2,3-dibromo-3-methyl-tetrahydrothiophene 1,1-dioxides (VI) have hitherto been reported. It is of course realized that in these cases isomeric products could result depending upon the mode of elimination. The reactions are illustrated with the formation of VII and VIII. Compound V was prepared by the addition of bromine to 3-methyl-2,5-dihydrothiophene 1,1-dioxide, and compound VI was prepared by the addition of bromine to 4-methyl-2,3-dihydrothiophene 1,1-dioxide which was obtained from the base-catalyzed isomerization of the 2,5-dihydro isomer. The white, crystalline compound isolated from the dehydrobromination of VI was obtained in 4% yield and failed to react with ethanolic silver nitrate solution, even when heated. Thus, of the three possible structures which might be formed from the elimination reaction only one, VIII, is of the vinyl type and the structure has been so assigned. The remainder of the organic starting material from the dehydrobromination appeared to be a polymer. The product obtained from the dehydrobromination of V gave a positive test with ethanolic silver nitrate solution and easily formed an isothiuronium picrate. In addition to structure VII, tentatively assigned this product, two other allylic structures are initially plausible, one in which the bromine atom is attached to the quaternary carbon and the other which contains an exocyclic carbon-carbon double bond. Evidence in favor of structure VII was obtained from a comparison of the ultraviolet absorption spectra of 4-methyl-2,3-dihydrothiophene 1,1-dioxide, VIII and the compound assigned structure VII. The three absorption curves were quite similar; however, the curves from VIII and the product from V showed, respectively, displacement toward the longer wave lengths as compared with that from 4-methyl-2,3-dihydrothiophene 1,1-dioxide. It was expected[11] that VIII should show a definite bathochromic shift (π-σ- and π-p-conjugations) in comparison with the unsubstituted sulfone. The product from V was found to exhibit a $\lambda_{max.}$ of 217 mμ. Neither of the other plausible structures for this compound would show such a maximum. The similarity of the three curves is in agreement with the presence of an α-methyl-β-sulfonylethylenic unit assigned to each of the three compounds. The maximum at 217 mμ may be due to the



V VII

VI VIII

---

[9] Backer and Blass, *Rec. trav. chim.*, **61**, 785 (1942).

[10] Bailey and Cummins, *J. Am. Chem. Soc.*, **76**, 1932 (1954).

[11] Braude, *Ann. Repts.* (*Chem. Soc. London*), **42**, 105 (1945).

stabilization of a polar excited form.[12] It should be mentioned that the assignment of structure VII to the product from V has its theoretical foundation. Both VIII and VII result from the preferential elimination of a bromine atom from a quaternary carbon atom; thus, the reaction may have proceeded *via* an E$_1$ process and the reaction products so assigned are in accordance with the Saytzeff rule that the most highly branched olefins are formed. The fact that elimination occurred from the 2,3- and not the 3,4-positions may be due to the conjugative effect of the sulfone group. In the thiophene series Karrer and Kieso[13] reported the formation of 3-methyl-2,5-dihydrothiophene by the action of sodium methoxide on 3-bromo-3-methyltetrahydrothiophene, but in the sulfone series Kharasch, *et al.*[14] found that the action of sodium hydroxide on 4-bromo-3-trichloromethyltetrahydrothiophene 1,1-dioxide gave 3-trichloromethyl - 2,3 - dihydrothiophene 1,1 - dioxide.

EXPERIMENTAL[15]

3-Iodomethyl-2,5-dihydrothiophene 1,1-dioxide (II). To 100 ml. of dry acetone were added 4.2 g. (0.020 mole) of I and 3.0 g. (0.020 mole) of sodium iodide, and the mixture was heated under reflux for 8 hours. The precipitated sodium bromide weighed 1.9 g. (theoretical amount, 2.0 g.). After the solvent had been removed, crude II was recrystallized from 95% ethanol to give 2.0 g. (56%) of lusterless flakes melting at 118–119°.

Anal. Calc'd for $C_5H_7IO_2S$: C, 23.27; H, 2.73; S, 12.42. Found: C, 23.59; H, 2.99; S, 12.57.

This substance, like I, is highly irritating to the skin and reacts instantaneously with ethanolic silver nitrate solution to form silver iodide. The isothiuronium picrate from II was prepared according to the procedure described for I.[2] The mixture melting point of this derivative with the isothiuronium picrate from I showed no depression.

Attempted hydrolysis of I. Compound I (2.1 g., 0.010 mole) was treated with 5% potassium hydroxide solution at 50–80° for 30 minutes. The clear solution then was extracted with ethyl ether and upon evaporation of the ether an oil was obtained. Trituration of the oil with petroleum ether gave a white, crystalline compound melting at 54–56°. This solid failed to give a positive ceric nitrate test and upon standing 24 hours apparently resinified giving a dark brown substance.

In another experiment, a 10% sodium hydroxide solution was used, with occasional stirring, to dissolve I. The clear solution was extracted with chloroform and from the extract there was isolated a solid melting at 82–84°. A mixture melting point of a sample of this solid with I showed no depression.

3-Ethoxymethyl-2,5-dihydrothiophene 1,1-dioxide (III). In 200 ml. of anhydrous ethanol were dissolved 5.5 g. (0.10 mole) of 85% potassium hydroxide. To the stirred solution was added 6.3 g. (0.030 mole) of I, and the mixture then was heated at 90° for one hour with stirring. The suspension was filtered while hot and 3 g. (85%) of potassium bromide was obtained. Ethanol was removed from the filtrate under reduced pressure and an oil remained which upon cooling crystallized as white plates, 2.5 g. (42%). The crude product was recrystallized twice from 95% ethanol to give white plates, m.p. 75–77°.

Anal. Calc'd for $C_7H_{12}O_3S$: C, 47.70; H, 6.86; S, 18.19. Found: C, 47.59; H, 6.77; S, 18.29.

3-Cyano-4-methyl-2,5-dihydrothiophene 1,1-dioxide (IV). To 100 ml. of 50% aqueous ethanol were added 5 g. (0.020 mole) of I and 1 g. (0.020 mole) of potassium cyanide. The mixture was heated under reflux for 3.5 hours and then was filtered to remove inorganic substances. Upon evaporation of the solvent, white plates melting at 130–134° were obtained which upon recrystallization from 95% ethanol gave 1.1 g. (30%) of fine plates, melting at 136–137°.

Anal. Calc'd for $C_6H_7NO_2S$: C, 45.84; H, 4.48; S, 20.40. Found: C, 45.91; H, 4.42; S, 20.37.

A modification of the above procedure using 3 g. of potassium cyanide and 0.5 g. of copper$^{(I)}$ cyanide was employed. The product obtained in this case (34%) was shown by mixture melting point to be identical with that obtained in the use of potassium cyanide as described above.

1-(1,1-Dioxy-2,5-dihydro-3-thenyl)pyridinium bromide. To 79 g. (1.0 mole) of anhydrous pyridine was added 21 g. (0.10 mole) of I and the system was protected from moisture by a calcium chloride drying tube. As soon as I dissolved an exothermic reaction occurred and the wall of the container became coated with a white solid. The reaction mixture was allowed to stand for one day. The clear liquid was decanted and the white solid was dried *in vacuo* for 20 minutes to remove pyridine. Subsequently the solid was washed with benzene and petroleum ether and stored under petroleum ether. The crude solid was recrystallized from 99% ethanol to give 24 g. (83%) of white, small plates melting at 153–155°. This compound was very hygroscopic.

Anal. Calc'd for $C_{10}H_{12}BrO_2S$: C, 41.38; 4.16; N, 4.82; S, 11.05. Found: C, 41.43; H, 4.28; N, 4.80; S, 11.08.

1-(1,1-Dioxy-2,5-dihydro-3-thenyl)quinolinium bromide. To 6.3 g. (0.030 mole) of I was added *ca.* 12 ml. of quinoline and the mixture was shaken occasionally. After six hours pink crystals formed. The crystals were washed with benzene and petroleum ether to remove the quinoline. After two recrystallizations from 99% ethanol 7 g. (70%) of pink plates melting at 200–202° were obtained.

Anal. Calc'd for $C_{14}H_{14}BrNO_2S$: N, 4.12; S, 9.42. Found: N, 4.07; S, 9.43.

4-(1,1-Dioxy-2,5-dihydro-3-thenyl)benzo[f]quinolinium bromide. To 10 ml. of chloroform were added 4.2 g. (0.020 mole) of I and 5.4 g. (0.030 mole) of benzo[*f*]quinoline. The mixture, with occasional shaking, was warmed with a water-bath. After the mixture had been allowed to stand at room temperature for 2 days yellow-colored crystals appeared which upon recrystallization from 99% ethanol gave felted, yellow crystals which melted at 197°; yield 5 g. (65%).

Anal. Calc'd for $C_{18}H_{16}BrNO_2S$: C, 55.39; H, 4.13; S, 8.21. Found: C, 55.21; H, 4.09; S, 8.27.

3,4-Dibromo-3-methyltetrahydrothiophene 1,1-dioxide (V). The bromination of 3-methyl-2,5-dihydrothiophene 1,1-dioxide was accomplished by the addition of bromine to a solution of the sulfone in carbon tetrachloride. The solid was recrystallized from ethanol to give a 78% yield of white plates melting at 126–127°. Eigenberger[16] reported a melting point of 127° for V.

4-Methyl-2,3-dihydrothiophene 1,1-dioxide. To 250 ml. of a 5% sodium hydroxide solution was added 53 g. (0.40 mole) of 3-methyl-2,5-dihydrothiophene 1,1-dioxide and the mixture was heated at 80° overnight, with stirring. The solution was cooled and extracted with three 50-ml. portions of chloroform. The extract was dried and the solvent was evaporated to give a white solid. Recrystallization of this solid from ethanol gave 25 g. (47%) of long, needle-shaped

---

[12] Koch, *J. Chem. Soc.*, 408 (1949).

[13] Karrer and Kieso, *Helv. Chim. Acta*, **27**, 1285 (1944).

[14] Kharasch, Freiman, and Urry, *J. Org. Chem.*, **13**, 570 (1948); Kharasch, U. S. Patent 2,482,088 (United States Rubber Co.), Sept. 20, 1949.

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

[16] Eigenberger, *J. prakt. Chem.*, [2], **127**, 307 (1930).

crystals melting at 77–78°. Eigenberger[17] reported a value of 78°.

2,3-Dibromo-3-methyltetrahydrothiophene 1,1-dioxide (VI). The procedure used here was essentially that employed for the preparation of V. The product was an oil as reported by van Zuydewijn.[18] The oil distilled at 140° at 4 mm., n^{25}_{D} 1.5748 (crude yield, 58%).

3-Bromo-4-methyl-2,3-dihydrothiophene 1,1-dioxide (VII). A solution of 23 g. (0.079 mole) of V in 150 ml. of dry acetone was placed in round-bottomed flask protected with a drying tube. Within two hours after 12.5 g. (0.58 mole) of anhydrous pyridine was introduced into the flask, the crystalline pyridinium bromide began to precipitate. The reaction mixture was allowed to stand overnight. Approximately 9 g. of pyridinium bromide was filtered and the acetone was removed. The solid residue was recrystallized from 95% ethanol to give puffy platelets melting at 73–74°; 8.8 g. (53%). This compound gave a positive test with an ethanolic solution of silver nitrate.

Anal. Calc'd for $C_5H_7BrO_2S$: C, 28.45; H, 3.34; Br, 37.86. Found: C, 28.46; H, 3.43; Br, 37.76.

S-(1,1-Dioxy-4-methyl-2,3-dihydro-3-thienyl)isothiuronium picrate. In 6 ml. of 95% ethanol were dissolved 0.6 g. (0.005 mole) of VII and 0.7 g. (0.01 mole) of thiourea. The solution was heated to boiling for 2 minutes. A solution of 1 g. (0.005 mole) of picric acid in the minimum amount of boiling ethanol was prepared and the boiling solutions were mixed. Yellow-colored crystals formed immediately. After two recrystallizations from 95% ethanol the crystals melted at 214–215°.

Anal. Calc'd for $C_{12}H_{14}N_5O_9S$: C, 33.02; H, 3.23; N, 16.04. Found: C, 32.91; H, 3.06; N, 16.00.

2-Bromo-3-methyl-4,5-dihydrothiophene 1,1-dioxide (VIII). Into 45 ml. of dry acetone were introduced 7 g. (0.02 mole) of VI and 3.2 g. (0.041 mole) of anhydrous pyridine. After standing overnight the pyridinium bromide was filtered and the acetone was removed. The residual oil was triturated with petroleum ether to remove the last traces of pyridine. The oil was then extracted with hot benzene and a relatively large amount of an apparently polymeric substance precipitated. The solid was filtered and the filtrate was heated to remove the benzene whereupon white crystals formed. Recrystallization from 95% ethanol gave 40 mg. (4%) of white platelets melting at 112.5–113.5°. This solid failed to react with ethanolic silver nitrate solution even when warmed.

Anal. Calc'd for $C_5H_7BrO_2S$: C, 28.45; H, 3.34; Br, 37.86. Found: C, 28.49; H, 3.45; Br, 37.80.

BLACKSBURG, VIRGINIA

---

(17) Eigenberger, *J. prakt. Chem.*, [2], **129**, 312 (1931).

(18) van Zuydewijn, *Rec. trav. chim.*, **57**, 445 (1938).