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Unsaturated Cyclic Sulfones. III. Some Halogen-Containing Derivatives

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Hydrogen bromide, hydrogen chloride, nitrosyl chloride, and iodine monochloride add to the carbon-carbon double bond in 3-methyl-2,5-dihydrothiophene 1,1-dioxide; however, only hydrogen bromide was found to add to the isomeric 4-methyl-2,3-dihydrothiophene 1,1-dioxide. Hydrogen bromide and hydrogen chloride fail to add to 2,5-dihydrothiophene 1,1-dioxide and to its isomer, 2,3-dihydrothiophene 1,1-dioxide. The preparation of 3-iodo- and 3-chloro-2,3-dihydrothiophene 1,1-dioxides is described.

In the continuation of the study of the chemistry of the five-membered unsaturated cyclic sulfones[3] emphasis in the present work is placed upon the preparation of halogen derivatives by reactions at the carbon-carbon double bond together with the two halogen derivatives obtained from displacement reactions on 3-bromo-2,3-dihydrothiophene 1,1-dioxide.

An intensive study of the addition of hydrogen bromide and of hydrogen chloride to 2,5- and to 2,3-dihydrothiophene 1,1-dioxides (I and II, respectively) and to 3-methyl-2,5- and 4-methyl-2,3-dihydrothiophene 1,1-dioxides (III and IV, respectively) was undertaken in this laboratory. It is of considerable interest that no evidence of the addition of hydrogen bromide or hydrogen chloride was found in the case of I or II. The starting sulfones were recovered; however, the weight recoveries of I at temperatures above 75° were low because of the reverse Diels-Alder reaction which evolved sulfur dioxide and 1,3-butadiene during the attempted reactions. Parenthetically, it should be recalled that mercaptans, alcohols, and water have been found to add to I in the presence of bases, presumably *via* a nucleophilic attack.

Hydrogen bromide adds to III in 55% yield in the presence of zinc bromide and hydrobromic acid with an excess of hydrogen bromide at 60°, whereas no adduct is found under similar conditions in the absence of hydrogen bromide. The structure of the adduct corresponds to 3-bromo-3-methyltetrahydrothiophene 1,1-dioxide (V). Under similar conditions hydrogen bromide adds to IV in 35% yield to give an adduct which is identical with that obtained from III. The action of hydrogen bromide on III, as described above, at 50° gave 25% of V.

Hydrogen chloride adds to III in 35% yield in hydrochloric acid-zinc chloride solution in the presence of hydrogen chloride, whereas the yield of adduct is 4% when the reaction is performed in benzene with hydrogen chloride in the presence of tin (IV) chloride. The structure of the adduct is assigned as 3-chloro-3-methyltetrahydrothiophene, 1,1-dioxide (VI) on the basis of the excellent agreement of its infrared spectrum with that of V. Addition of hydrogen bromide to III failed to occur in benzene in the presence of tin(IV) bromide. At temperatures above 50°, namely 60° and 75°, no hydrogen chloride adduct was isolated from III; however, IV was isolated in yields up to 60%. Thus, it is suspected that addition occurred followed by the elimination of hydrogen chloride at these higher temperatures. No acid catalyzed isomerization of III to IV has been reported in the literature.

The above-mentioned addition reactions are seen to follow the expected Markownikoff rule. Of particular interest is the tremendous effect of the methyl group whose inductive and/or hyperconjugative effects apparently overcome the strong electron withdrawing effect of the sulfone group thus making addition possible in III as compared with the result obtained with I.

With carbon tetrachloride as the solvent, iodine monochloride was found to add to III at room temperature in 91% yield. The adduct is assigned the structure corresponding to 3-chloro-4-iodo-3-methyltetrahydrothiophene 1,1-dioxide (VII). It seems quite reasonable to suggest that addition occurred in the manner claimed in view of the work of Ingle[4] with styrene and of Ingold and Geoffrey[5] with ethylenesulfonic acid. From the observations of the addition of the hydrogen halides to III and of nitrosyl chloride to III as will be discussed later, it should be expected that ionic addition will occur here with the positive iodine attacking at the 4-position, the more electron dense of the two carbon atoms in the double bond.

In the presence of sodium borohydride VII is quantitatively converted to III while the use of lithium aluminum hydride gives only 22% of III with some degradation of the molecule. Hydriodic acid converts VII to III in 100% yield, and the action of sodium thiosulfate solution on VII gives

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(3) For the previous paper in this series see R. C. Krug and T. F. Yen, *J. Org. Chem.*, 21, 1441 (1956).

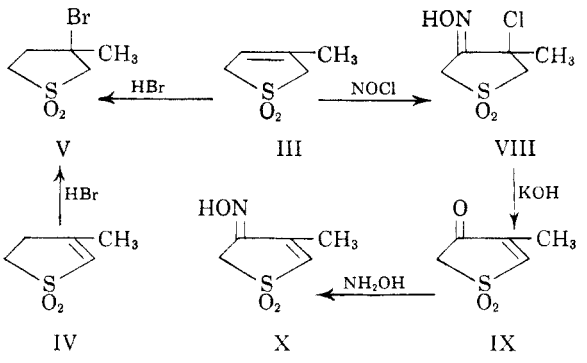
(4) H. Ingle, *J. Soc. Chem. Ind. (London)*, 21, 591 (1902).

(5) C. K. Ingold and H. Goeffrey, *J. Chem. Soc.*, 2742 (1931).

III as the only isolable product. Aqueous potassium hydroxide on VII gives tars and a small amount of III. The action of weaker bases such as pyridine and *N,N*-dimethylaniline causes the formation of tars and resinous substances from VII.

Under conditions similar to those employed for the addition of iodine monochloride to III, no addition product could be isolated or detected in the attempts to form the corresponding adduct from IV. In each case IV was recovered.

In the studies involving the reaction of nitrosyl chloride and the sulfones, copper (I) chloride was employed as suggested by Beckham.[6] In the present study moisture was found to be a necessary component of the reaction system. In the presence of chloroform as the solvent, nitrosyl chloride reacted with III to give a quantitative yield of an adduct whose structure is assigned as 3-chloro-4-oxo-3-methyltetrahydrothiophene 1,1-dioxide oxime (VIII).



In the presence of alcoholic potassium hydroxide VIII was converted in 34% yield to IX which melted at 164–165° as compared with the value of 163° reported by Backer and Strating[7] for IX prepared by a different method. In order to establish the structure assigned to IX, this compound was treated with hydroxylamine according to the procedure of Backer and Strating[7] and X was obtained in 36% yield. The reported melting point for this oxime was *circa* 146–148° as compared with the presently found value of *circa* 143–145°. Thus, the structure of the nitrosyl chloride adduct is definitely established. Nitrosyl chloride failed to add to IV under similar or slightly modified conditions employed with III.

The free radical-catalyzed addition of hydrogen bromide to I and III was extensively studied, with the greater number of experiments having been performed with III. Although solvents such as benzene, carbon tetrachloride, ethylbenzene, anhydrous sulfur dioxide, and chloroform were used at temperatures from −20° to 95° and peroxides such as benzoyl peroxide and acetyl peroxide were employed, no evidence for the peroxide effect in the addition of hydrogen bromide was obtained. A small amount of V was isolated in one case as was a small amount of 3,4-dibromo-3-methyltetrahydrothiophene 1,1-dioxide. The latter compound was obtained when large amounts of peroxide were employed. These substances were identified by means of mixed melting point determinations with authentic samples. The use of ultraviolet light with or without peroxide likewise failed to effect addition of hydrogen bromide to III in a Vycor tube. Except as noted, when addition failed the starting sulfone was recovered unchanged. This failure of the peroxide effect is rather strange since other free radical-catalyzed additions with I and III have been observed.[8,9] The dehydrobromination of 3,4-dibromotetrahydrothiophene 1,1-dioxide in the presence of pyridine to give 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XI) was first reported by Backer and Blaas[10] and more recently studied by Bailey and Cummins[11] in an attempt to prepare thiophene 1,1-dioxide. In addition to XI polymer was formed in the dehydrobromination. In the present study it was found that no polymer was formed if the reaction solution was first acidified before the removal of the solvent. This procedure increased the yield of XI 20–25% above the previous y reported values.

In the presence of sodium iodide in anhydrous acetone, XI was converted to 3-iodo-2,3-dihydrothiophene 1,1-dioxide (XII). The bromide XI was so reactive that at room temperature the immediate precipitation of sodium bromide was realized in 94% yield. Pure XII was obtained in 53% yield. Upon standing in air XII gradually decomposes. The structure of XI has been established[10] and the comparison of the infrared spectra of XI and XII clearly demonstrates the structural similarities of these two compounds.

The 3-chloro-2,3-dihydrothiophene 1,1-dioxide XIII was obtained by the action of mercury(II) chloride in absolute ethanol on XII in 42% yield. Again, a comparison of the infrared spectra of XI, XII, and XIII definitely establishes the common structural relationship of these compounds. Compound XII gives an immediate reaction with silver nitrate solution while the bromide XI requires several seconds and the chloride XIII does not give a positive test after standing for 15 hours at room temperature.

(6) L. T. Beckham (To Solvay Process Co.), U. S. Pat. 2,417,675, Mar. 18, 1947.

(7) H. J. Backer and J. Strating, *Rec. trav. chim.*, **54**, 170 (1935).

(8) M. S. Kharasch, M. Freeman, and W. H. Urry, *J. Org. Chem.*, **13**, 570 (1948).

(9) R. C. Krug and T. F. Yen, *J. Org. Chem.*, **21**, 1082 (1956).

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

(11) W. J. Bailey and E. W. Cummins, *J. Am. Chem. Soc.*, **76**, 1932 (1954).

EXPERIMENTAL[12]

2,5-Dihydrothiophene 1,1-dioxide (I). Anhydrous sulfur dioxide and 1,3-butadiene (The Matheson Co., Inc.) were used. The procedure was that of Grummitt, Ardis, and Fick[13]; however, contact time was reduced to 4 hr. at 100–105°. Crude I was purified by recrystallization from water to give pure I; m.p. 64–65° (lit.,[13] 64.5–65.0°), 85–93% yields.

2,3-Dihydrothiophene 1,1-dioxide (II). A modification of the procedure described by Bailey and Cummins[11] was employed. A solution of 50.0 g. (0.423 mole) of I in 1 liter of 0.5*N* potassium hydroxide was irradiated at room temperature with ultraviolet light for 20 hr. The resulting solution was submitted to continuous extraction with chloroform for 2 days, and upon the evaporation of the chloroform from the extract 35.4 g. of light brown-colored oil was obtained. This oil was heated to 180° at 15–20 mm. to remove unchanged I. The residual oil was purified by crystallization from benzene–petroleum ether or by distillation at reduced pressure. The latter procedure is recommended since 3-hydroxytetrahydrothiophene 1,1-dioxide, an impurity, is difficult to remove by the former procedure. The yield of pure II b.p.$_1$ 114–116°, m.p. 49–50° (lit.,[14] 48.5–49.5°) was 24.6 g. (49%). It was found that acidification of the basic, irradiated solution prior to the extraction with chloroform gave only 24% of pure II.

4-Methyl-2,3-dihydrothiophene 1,1-dioxide (IV). To 1000 ml. of 0.5*N* potassium hydroxide was added 60 g. (0.45 mole) of 3-methyl-2,5-dihydrothiophene 1,1-dioxide (III),[3] and the solution was stirred for 20 hr. at 30°. This solution was then extracted with 6 portions of chloroform, and the removal of solvent from the combined extracts gave a solid. This solid was recrystallized from ethanol to yield 42 g. (79%) of long, needle-shaped crystals; m.p. 77–78° (lit.,[10] 79°). Upon reducing the volume of the ethanolic mother liquor, 5.0 g. (8%) of III was obtained.

Addition of hydrogen bromide to 3-methyl-2,5-dihydrothiophene 1,1-dioxide (III). Zinc bromide was prepared by dissolving 32.7 g. (0.50 mole) of zinc in 171 ml. of 48% hydrobromic acid. After all of the zinc had reacted 10 g. (0.076 mole) of III was added. For 2 hr. hydrogen bromide was passed into the stirred solution which was heated to 50°. Heating was continued for 2 more hours and the solution was allowed to stand overnight at room temperature. The contents of the flask was then poured into 100 ml. of water, and this solution was extracted with 4 portions of chloroform. The extracts were combined and the chloroform was removed under reduced pressure to give an oil which was then dissolved in ethanol. Upon cooling the ethanolic solutions, 9.0 g. (55%) of small, white, needle-shaped crystals of 3-bromo-3-methyltetrahydrothiophene 1,1-dioxide (V), m.p. 95–96°, were obtained.

Anal. Calcd. for $C_5H_9BrO_2S$: C, 28.18; H, 4.25; Br, 37.50; S, 15.05. Found: C, 28.38; H, 4.18; Br, 37.72; S, 15.21.

The infrared spectrum of V showed the following principal frequencies: 2930, 1445, 1415, 1400, 1378, 1310, 1275, 1185, 1150, 1118, 1095, 1035, 913, 860, 790, and 765 cm.$^{-1}$

Addition of hydrogen chloride to III in the presence of zinc chloride. To 42 ml. of concentrated hydrochloric acid was added 68 g. (0.50 mole) of zinc chloride, followed by the addition of 10 g. (0.076 mole) of III, and solution of the components was effected at 50°. Hydrogen chloride was slowly passed into the solution for 2 hr. at 50° with stirring. After 22 hr. at 50° the liquid was poured into 150 ml. of water. The aqueous solution was extracted 3 times with 50-ml. portions of chloroform. The extracts were combined and the chloroform was removed under reduced pressure to give an oil. The oil was dissolved in ethanol, and upon cooling the solution crystals appeared which were recrystallized from ethanol to give 4.5 g. (35%) of small, white needle-shaped crystals of 3-chloro-3-methyltetrahydrothiophene 1,1-dioxide (VI); m.p. 95–96°.

Anal. Calcd. for $C_5H_9ClO_2S$: C, 35.61; H, 5.38; Cl, 21.02; S, 19.01. Found: C, 35.34; H, 5.25; Cl, 21.16; S, 19.17.

The infrared spectrum of VI showed the following principal frequencies: 2930, 1445, 1405, 1395, 1370, 1300, 1270, 1190, 1150, 1118, 1095, 1038, 910, 863, 791, and 767 cm.$^{-1}$

Addition of hydrogen chloride to III in the presence of tin(IV) chloride. To 100 ml. of anhydrous benzene were added 10 g. (0.076 mole) of III and 8.9 g. (0.029 mole) of freshly prepared tin(IV) chloride. Anhydrous hydrogen chloride was passed into the solution for 1 hr. at room temperature. After allowing the solution to stand for 72 hr., with the occasional passage of hydrogen chloride to keep the solution saturated, the benzene phase was separated and washed with water to remove the tin(IV) chloride. The aqueous phase was extracted once with benzene and this extract was combined with the original benzene layer, and the volume of benzene was reduced under vacuum. Crystals formed upon cooling the residual liquid. By fractional crystallization from ethanol, 9.5 g. (95%) of III and 0.5 g. (4%) of 3-chloro-3-methyltetrahydrothiophene 1,1-dioxide, VI (m.p. 95–96°) were obtained.

Addition of hydrogen bromide to 4-methyl-2,3-dihydrothiophene 1,1-dioxide (IV). Zinc bromide was freshly prepared by dissolving 16.4 g. (0.25 mole) of zinc in 85 ml. of 48% hydrobromic acid. After all of the zinc had reacted 5.0 g. (0.038 mole) of IV was dissolved in the solution. For 2 hr. hydrogen bromide was passed into the stirred solution which was heated to 50°. Heating was continued for 11 hr. After 7 hr. at room temperature the solution was poured into 100 ml. of water, and this aqueous solution was extracted 4 times with chloroform. The chloroform was removed from the combined extracts under reduced pressure, and the residual oil was dissolved in ethanol. Upon cooling the ethanolic solution, 4.5 g. (55%) of small, white, needle-shaped crystals of V, m.p. 95–96°, were obtained. A mixed melting point determination of this solid with that from the addition of hydrogen bromide to III showed no depression.

3-Chloro-4-iodo-3-methyltetrahydrothiophene 1,1-dioxide (VII). To a solution of 20 g. (0.15 mole) of III in 100 ml. of carbon tetrachloride was added dropwise approximately 8 ml. (slight excess) of iodine monochloride. To prevent the contents from overheating, the flask was immersed in cold water. After addition was complete, the solution was brought to reflux for 2 hr. Upon cooling the solution the heavy precipitate which formed was filtered, washed with petroleum ether to remove most of the purple color, and recrystallized from absolute ethanol. A total of 40 g. (91%) of VII, m.p. 107–108°, was obtained.

Anal. Calcd. for $C_5H_8ClIO_2S$: C, 20.39; H, 2.74; Cl, 12.04; I, 43.09; S, 10.88. Found: C, 20.08; H, 2.95; Cl, 11.86; I, 42.87; S, 10.80.

Alcoholic potassium hydroxide and VII. To a solution of 3.0 g. (0.010 mole) of VII in absolute ethanol was added dropwise a solution of 0.57 g. (0.010 mole) of potassium hydroxide in 50 ml. of absolute ethanol. After 2 hr. the yellow-colored mixture was filtered to remove inorganic salts (potassium chloride and iodide). The volume of the filtrate was reduced under vacuum and the residual oil was crystallized and purified to give 0.10 g. (8%) of III. In this and other experiments the identity of III was established by means of mixed melting point determination with an authentic sample. No other organic substance was isolated.

Sodium thiosulfate and VII. To a solution of 4.0 g. (0.014 mole) of VII in 200 ml. of 50% ethanol was added a solution of 4.3 g. (0.027 mole) of sodium thiosulfate in a small amount of water. After 2 min. the solution turned dark

(12) All melting and boiling points are uncorrected. Analyses performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

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

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

suddenly. The solution was found to be acidic and aqueous potassium hydroxide was added to *p*H 7. The resulting colorless solution was extracted with chloroform, and upon removal of the chloroform under reduced pressure a solid remained. The solid was recrystallized from ethanol to give 1.3 g. (70%) of III.

Sodium borohydride and VII. The procedure of Brown and Subba Rao[15] was followed with certain modifications. To 1.0 g. (0.0034 mole) of VII in 15 ml. of methanol was slowly added a solution of 0.15 g. (0.0040 mole) of sodium borohydride in 100 ml. of methanol. After 15 min. the solution turned dark brown in color. The solvent was removed under vacuum, the remaining oil was taken up in chloroform, and the chloroform solution was washed with 5% aqueous sodium thiosulfate. The chloroform phase was separated, and the chloroform was removed at reduced pressure. The residue was recrystallized from ethanol to give 100% of III.

Hydriodic acid and VII. Three grams (0.010 mole) of VII was dissolved in 75 ml. of colorless 50% hydriodic acid. After 3–4 hr. the solution was extracted with several portions of chloroform. The extracts were combined and washed with 5% aqueous sodium thiosulfate. The chloroform was removed under vacuum leaving a solid which upon recrystallization from ethanol gave a quantitative yield of III.

3-Chloro-4-oxo-3-methyltetrahydrothiophene 1,1-dioxide oxime (VIII). In a flask equipped with a stirrer was placed 20 g. (0.15 mole) of III dissolved in 100 ml. of chloroform. As the solution was stirred at room temperature approximately 0.5 g. of copper (I) chloride was added followed by a few drops of water, and nitrosyl chloride was passed into the solution for 2 hr. A precipitate appeared 6 hr. later. The experiment was continued for 1 week, with daily passage of gas to keep the solution saturated with nitrosyl chloride, and a few drops of water were added at least once a day. After 1 week the mixture was filtered. The solid was recrystallized from absolute ethanol and subsequently from chloroform. A quantitative yield of VIII, m.p. *circa* 148–152°d, was obtained.

Anal. Calcd. for $C_5H_8ClNO_2S$: Cl, 17.94; N, 7.09; S, 16.23. Found: Cl, 17.31; N, 6.87; S, 15.70.

Alcoholic potassium hydroxide on VIII. To a solution of 8.0 g. (0.040 mole) of VIII in 180 ml. of absolute ethanol at 30° a solution of 2.3 g. (0.040 mole) of potassium hydroxide in 200 ml. of absolute ethanol was added dropwise with vigorous stirring. Six hours after the addition was complete a precipitate appeared. This solid, which was identified as potassium chloride, was filtered and the filtrate was reduced in volume under vacuum. The residual alcoholic solution was cooled, and crystals formed which upon recrystallization from 95% ethanol gave 2.0 g. (34%) of 3-oxo-4-methyl-2,3-dihydrothiophene 1,1-dioxide (IX) as white needles; m.p. 164–165° (lit.,[7] 163°).

The oxime from IX was prepared according to the procedure described by Backer and Strating.[7] The crude oxime was recrystallized from water, then from chloroform to give 0.2 g. (36%) of X melting *circa* 143–145° (lit.,[7] 146–148°).

Attempted free radical addition of hydrogen bromide to 3-methyl-2,5-dihydrothiophene 1,1-dioxide (III). In a typical experiment, 10 g. (0.076 mole) of III (previously dried over sulfuric acid *in vacuo*) was dissolved in the selected solvent (anhydrous benzene in this case), and 1.2 g. (0.0050 mole) of benzoyl peroxide was added. Dry hydrogen bromide was passed into the solution for 2 hr. at the desired temperature (room temperature here). The solution was allowed to stand for 46 hr. or a shorter period. The solvent (benzene) was removed under reduced pressure and the residual oil was crystallized from ethanol. The recovered III weighed 9.0 g. (90%). The compound was identified by a mixed melting point determination with an authentic sample.

Under similar conditions the attempted peroxide catalyzed addition of hydrogen bromide to I was unsuccessful.

3-Bromo-2,3-dihydrothiophene 1,1-dioxide (XI). The procedure described here, based on the work of Backer and Blaas[10] and of Bailey and Cummins,[11] was found to give XI an improved yield. In a 1-liter round-bottomed flask was placed a solution of 60 g. (0.22 mole) of 3,4-dibromotetrahydrothiophene 1,1-dioxide[16] in 250 ml. of dry acetone. To this solution was added 33 g. (0.42 mole) of dry pyridine and the system was protected with a drying tube. Within 20 min., at room temperature, crystals of pyridinium bromide began to appear. After 14 hr. the mixture was filtered to give 35.4 g. of pyridinium bromide. The filtrate was acidified with concentrated hydrochloric acid and the resulting aqueous phase removed. The acetone-rich phase was subjected to reduced pressure to remove the acetone. The residue (oil and small amount of water) was extracted with 50 ml. of benzene from which 24.7 g. of a white solid was obtained. Extraction of the combined aqueous phases with three 25-ml. portions of benzene gave an additional 12.3 g. of white solid. The solids were combined and purified by recrystallization from ethanol to give 33.1 g. (76%) of white crystals; m.p. 63–64° (lit.,[10] 64–65°).

The infrared spectrum of XI showed the following principal frequencies: 3050, 3000, 2930, 1600, 1400, 1285, 1218, 1130, 1103, 1030, 950, 920, 895, 883, 762, and 715 cm.$^{-1}$

3-Iodo-2,3-dihydrothiophene 1,1-dioxide (XII). To a solution of 9.9 g. (0.05 mole) of XI in 50 ml. of dry acetone was added a solution of 11.3 g. (0.075 mole) of sodium iodide in dry acetone. A precipitate formed immediately and the solution turned a light yellow color. After 15 min. the solution began to darken and the solid was filtered. The solid, 4.8 g. (94%), was sodium bromide and was found to be free of iodide. The filtrate was shaken with a saturated solution of sodium thiosulfate and was dried over magnesium sulfate. The acetone was removed at room temperature under reduced pressure and the residue (oil plus a small amount of water) was extracted with chloroform. Removal of the chloroform gave 9.9 g. of crude oil which solidified upon standing. Recrystallization from methanol–petroleum ether gave 6.5 g. (53%) pure XII; m.p. 72.0–72.5°.

Anal. Calcd. for $C_4H_5IO_2S$: C, 19.68; H, 2.07. Found: C, 19.85; H, 1.93.

The infrared spectrum of XII showed the following principal frequencies: 3110, 3000, 2955, 1580, 1395, 1290, 1218, 1135, 1100, 1020, 955, 915, 895, 865, 747, and 710 cm.$^{-1}$

3-Chloro-2,3-dihydrothiophene 1,1-dioxide (XIII). To 3.9 g. (0.016 mole) of XII in 50 ml. of hot, absolute ethanol was added a solution of 4.4 g. (0.016 mole) of mercury (II) chloride in 50 ml. of hot, absolute ethanol. The resulting solution was allowed to stand overnight at room temperature after which time the solution was heated to reflux for 8 hr. Distillation of about two thirds of the ethanol caused the precipitation of 2 g. of mercury (II) iodide which was removed by filtration. The removal of the remainder of the ethanol gave a mixture of mercury (II) iodide, mercury (II) chloride, and XIII. Fractional crystallization of this mixture from ethanol gave 1.0 g. (42%) pure XIII; m.p. 82.5–83.0°.

Anal. Calcd. for $C_4H_5ClO_2S$: C, 31.48; H, 3.30. Found: C, 31.30; H, 3.33.

The infrared spectrum of XIII showed the following principal frequencies: 3070, 3000, 2950, 1610, 1400, 1285, 1230, 1130, 1105, 1030, 955, 920, 900, 885, 765, 715 cm.$^{-1}$

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(15) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 2582 (1956).

(16) This compound was prepared by the bromination of I in chloroform, a modification of the method of Bailey and Cummins.[11]