Thermal Decomposition of XVI.—The photodimer was heated under vacuum at 300° (bath) in a Pyrex test-tube for one hour. The oily drops of XV (m.p. and mixed m.p.) which accumulated in the upper part of the reaction vessel solidified after being allowed to cool in a vacuum.

Behavior of If, Ie and Ig toward the Action of Sunlight.—A solution of 1 g. of 2,3-dimethylthianaphthene-1,1-dioxide (If) in 30 ml. of dry benzene was exposed to sunlight for 15 days (November). When the reaction mixture was evaporated, it was recovered in an almost quantitative yield.

Similar results were obtained when a suspension of Ie and of VIII in 40 ml. of dry benzene each was exposed to sunlight for 15 days (November).

The exposure of a solution of 1 g. of phenyl vinyl sulfone in 30 ml. of benzene for 7 days (January) gave, after evaporation, an oily residue which upon washing with petroleum ether (60 ml., b.p. 60–80°) gave a colorless solid, identified as unchanged material. The petroleum ether washings gave upon evaporation an oily substance which is under further investigation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Bromination Studies with 5-Hydroxybenzothiophene

BY M. MARTIN-SMITH[1] AND MARSHALL GATES

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An investigation of the products formed by the action of successive molar quantities of bromine on 5-hydroxybenzothiophene in acetic acid was undertaken. Once both the 4- and 6-positions have undergone substitution, the nature of the product of further bromination depends on the presence or absence of sodium acetate in the reaction mixture.

Recently[2,3] it was shown that the product resulting from the action of two moles of bromine on 5-hydroxybenzothiophene in acetic acid in the presence of sodium acetate was not the 3,4-dibromo compound as postulated by earlier workers,[4] and this substance was reassigned the structure 4,6-dibromo-5-hydroxybenzothiophene.[3] Final proof that this assignment is correct has now been obtained by the decarboxylation of 4,6-dibromo-5-methoxybenzothiophene-2-carboxylic acid to 4,6-dibromo-5-methoxybenzothiophene, which was identical with the product resulting from the action of diazomethane on the dibromo compound, which consequently must be 4,6-dibromo-5-hydroxybenzothiophene (Chart I).

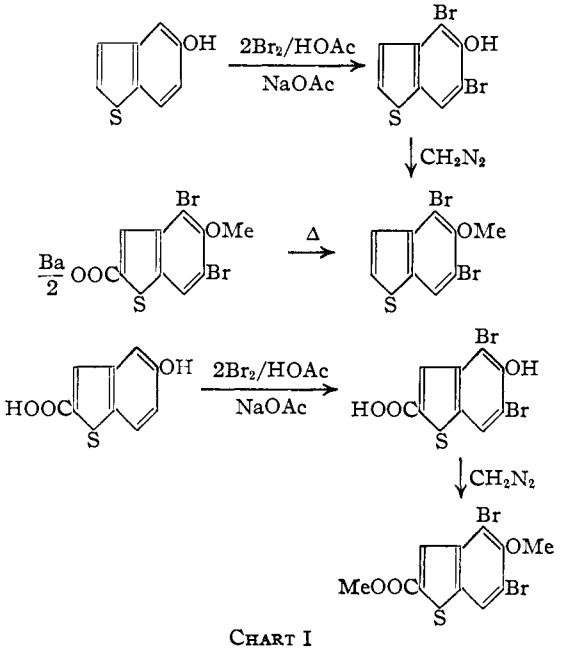

CHART I

Further treatment of 4,6-dibromo-5-hydroxybenzothiophene with one mole of bromine in acetic acid led to either of two products, depending on whether or not sodium acetate was present. In the absence of acetate ion the uptake of bromine was slow, yielding a compound which proved to be 5-hydroxy-3,4,6-tribromobenzothiophene, as it was identical with a specimen prepared by the action of bromine on 3,4-dibromo-5-hydroxybenzothiophene[2,3] in acetic acid in the presence of sodium acetate. On the other hand, the uptake of bromine was instantaneous in the presence of acetate ion to yield 4,5-dihydro-5-keto-4,4,6-tribromobenzothiophene[5] (Chart II). This compound was readily reconverted to 4,6-dibromo-5-hydroxybenzothiophene

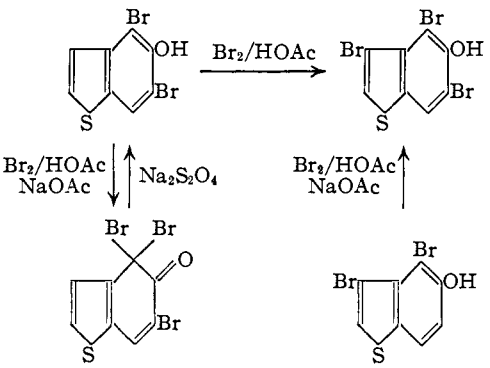

CHART II

by the action of sodium hydrosulfite in aqueous ethanol. On treatment with hydrobromic acid in acetic acid it gave a mixture of 4,6-dibromo-5-hydroxybenzothiophene and 5-hydroxy-3,4,6-tribromobenzothiophene.

Similarly, 5-hydroxy-3,4,6-tribromobenzothiophene on further treatment with one mole of bromine in acetic acid gave 5-hydroxy-2,3,4,6-tetrabromobenzothiophene in the absence of acetate ion with slow uptake of bromine. In the presence of acetate ion the product was 4,5-dihydro-5-keto-3,4,4,6-tetrabromobenzothiophene (Chart III).

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(2) F. G. Bordwell and H. Stange, THIS JOURNAL, **77**, 5939 (1955).

(3) M. Martin-Smith and M. Gates, *ibid.*, **78**, 5351 (1956).

(4) K. Fries, H. Heering, K. Hemmecke and G. Siebert, *Ann.*, **527**, 83 (1936).

(5) The infrared spectrum of this compound showed a strong carbonyl absorption at 6.03 μ and no absorption in the 3-μ region in accordance with the assigned structure.

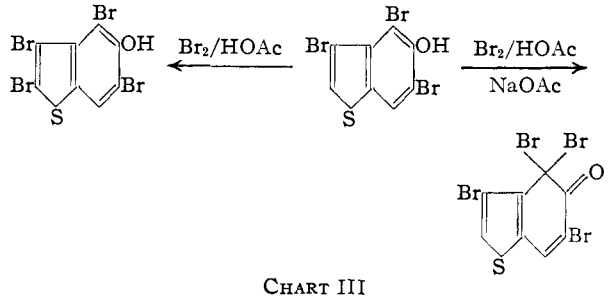
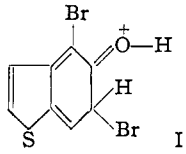
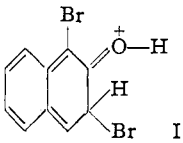


CHART III

From these results an interesting comparison between 5-hydroxybenzothiophene and its isostere 2-naphthol can be made. In accordance with earlier observations[2] it is clear that both positions *ortho* to the hydroxyl group in 5-hydroxybenzothiophene are subject to electrophilic attack, in contrast to the case of 2-naphthol where only the 1-position is reactive.[6-8] This difference in behavior between 5-hydroxybenzothiophene and 2-naphthol is a manifestation of the lower resonance energy of the thiophene ring as compared to the benzene ring.[9-13] Thus a transition state of type I, where the resonance of the thiophene ring is



I



II

destroyed, is quite evidently favored; whereas, as has been well established, a transition state such as II, in which the resonance of the non-substituted benzene ring is interrupted is energetically unfavorable. The resonance energy of the thiophene ring is thus low enough for 5-hydroxybenzothiophene to behave as a true phenol, and its reactions as far as have been studied are analogous to those of 6-hydroxytetralin.[14,15]

However, once the two reactive positions *ortho* to the hydroxyl group have been substituted by bromine in 5-hydroxybenzothiophene, the properties of the product are strictly analogous to the properties of 1-bromo-2-naphthol, where the only reactive position *ortho* to the hydroxyl group in 2-naphthol has been substituted. Thus 1-bromo-2-naphthol on bromination in acetic acid in the presence of acetate ion yields 1,1-dibromo-1,2-dihydro-2-ketonaphthalene,[16,17] whereas in the absence of acetate ion the product is 1,6-dibromo-2-naphthol.[18]

Similarly, the action of nitric acid in acetic acid on 1-bromo-2-naphthols to give 1-bromo-1,2-dihydro-2-keto-1-nitronaphthalene,[17,19,20] which can be decomposed to the *o*-naphthoquinones, appears to have its counterpart in 4,6-dibromo-5-hydroxybenzothiophene, although with this latter compound the intermediate 4,6-dibromo-4,5-dihydro-5-keto-4-nitrobenzothiophene could not be isolated. Thus when 4,6-dibromo-5-hydroxybenzothiophene in acetic acid was treated with concentrated nitric acid and the mixture diluted with water, crude 6-bromo-5-hydroxy-4-nitrobenzothiophene separated. The red mother liquor on shaking with ethyl cyanoacetate, triethylamine and aqueous potassium ferricyanide went deep green, indicating the formation of a 7-[cyanocarbethoxymethyl]-benzothiophene-4,5-quinone.[3,21]

The formation of 1-nitro-2-naphthols from 1-bromo-1,2-dihydro-2-keto-1-nitronaphthalenes under the influence of base is well established,[19] and it is to be presumed that, owing to greater instability factors, 4,6-dibromo-4,5-dihydro-5-keto-4-nitrobenzothiophene decomposes in dilute acetic acid by hydrolysis.

It was possible, however, to obtain 4-bromo-4,5-dihydro-5-keto-4-nitro derivatives as unstable orange crystalline solids from 3,4-dibromo-5-hydroxybenzothiophene,[3] 5-hydroxy-3,4,6-tribromobenzothiophene and 5-hydroxy-2,3,4,6-tetrabromobenzothiophene on treatment with nitric acid in acetic acid. On boiling in benzene these gave off red fumes and yielded the corresponding 4,5-quinones,[22] which all gave a green Craven test.[23]

It was discovered that in many of the bromination reactions with 5-hydroxybenzothiophenes, traces of the 4,5-quinone were formed, imparting a red color to the mother liquors of the reaction. Thus in the formation of 4,6-dibromo-5-hydroxybenzothiophene-2-carboxylic acid, the mother liquor after dilution with water and shaking with excess triethylamine, ethyl cyanoacetate and aqueous potassium ferricyanide solution afforded a sample of 2-carboxy-7-[cyanocarbethoxymethyl]-benzothiophene-4,5-quinone identical with an authentic specimen.[3] In other cases the Craven test[23] alone was used to prove the presence of quinone.[24]

Fries and co-workers reported[4] that the action of two moles of chlorine on 5-hydroxybenzothiophene in acetic acid in the presence of sodium acetate gave 4,4-dichloro-4,5-dihydro-5-ketobenzothio-

(6) W. Marckwald, *Ann.*, **279**, 1 (1894).
(7) T. Zincke, *Ber.*, **21**, 3378, 3540 (1888).
(8) L. F. Fieser and W. C. Lothrop, THIS JOURNAL, **57**, 1459 (1935).
(9) V. Schomaker and L. Pauling, *ibid.*, **61**, 1769 (1939).
(10) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1953).
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(13) H. Grasshof, *Ber.*, **84**, 916 (1951).
(14) S. I. Sergievskaya and A. E. Gavrilova, *J. Gen. Chem. (U.S.S.R.)*, **11**, 1027 (1941) (*C. A.*, **39**, 4601 (1945)).
(15) G. Schroeter, *Ann.*, **426**, 83 (1922).
(16) K. Fries and H. Engel, *ibid.*, **439**, 232 (1924).
(17) K. Fries and K. Schimmelschmidt, *ibid.*, **484**, 245 (1930).
(18) H. Franzen and G. Stauble, *J. prakt. Chem.*, **103**, 352 (1922).
(19) H. E. Armstrong and E. C. Rossiter, *Proc. Chem. Soc.*, 89 (1891).
(20) L. F. Fieser and J. L. Hartwell, THIS JOURNAL, **57**, 1479 (1935).
(21) It is to be noted that when 4,6-dibromo-5-hydroxybenzothiophene is shaken with nitric acid in chloroform a good yield of 6-bromobenzothiophene-4,5-quinone results directly.[4]
(22) The fact that 2,3,6-tribromobenzothiophene-4,5-quinone obtained from 5-hydroxy-2,3,4,6-tetrabromobenzothiophene in this manner did not yield bromide ion on boiling with sodium ethoxide provided proof of the constitution of these two compounds. A bromine atom in the 7-position would be cleaved in the same way as a halogen in the 4-position of the corresponding orthonaphthoquinones (H. Hirsch, *Ber.*, **33**, 2412 (1900)).
(23) R. Craven, *J. Chem. Soc.*, 1605 (1931).
(24) In this respect it is to be noted that although all of the 4,4-dibromo-4,5-dihydro-5-ketobenzothiophenes prepared gave a green coloration with triethylamine and cyanoacetic ester, it was possible to distinguish this test from that given by the quinones as the color was destroyed by the addition of aqueous potassium ferricyanide solution, and no cyanocarbethoxymethyl derivative could be isolated.

phene, but no experimental details were given. This seemed surprising in view of the reactions with bromine, and we re-investigated this reaction. After many attempts we were unable to obtain a homogeneous product. The infrared spectrum of the crude product indicated that it was a mixture and, surprisingly, two distinct peaks of equal intensity were to be found in the carbonyl region at 5.74 and 5.93 μ. The only component obtained in the pure state was a white crystalline solid which was purified by way of its sodium salt. This by analogy with the bromination product must be 4,6-dichloro-5-hydroxybenzothiophene.

Experimental[25,26]

Methyl 4,6-Dibromo-5-methoxybenzothiophene-2-carboxylate.—4,6 - Dibromo - 5 - hydroxybenzothiophene - 2-carboxylic acid[3] (1.0 g.) was suspended in 100 ml. of cold ether and an excess of an ethereal solution of diazomethane added. There was an immediate vigorous evolution of nitrogen and when this ceased the solution was concentrated to about 50 ml. On cooling 980 mg. (92.5%) of colorless feathery needles separated, m.p. 140–142°. The compound is soluble in acetone and ethyl acetate and insoluble in water. A sample was recrystallized from aqueous ethanol for analysis.

Anal. Calcd. for $C_{11}H_8O_3Br_2S$: C, 34.76; H, 2.12. Found: C, 34.69; H, 2.16.

4,6-Dibromo-5-methoxybenzothiophene-2-carboxylic Acid.—Methyl 4,6-dibromo-5-methoxybenzothiophene-2-carboxylate (800 mg.) was refluxed with 5.0 g. of potassium hydroxide in 50 ml. of ethanol and 100 ml. of water for 2.5 hours. The solution was then boiled down to half-volume to drive off the ethanol and on cooling white needles of potassium 4,6-dibromo-5-methoxybenzothiophene-2-carboxylate were deposited, 600 mg. (70.5%). The sparingly soluble potassium salt was dissolved in 500 ml. of boiling water and the free acid liberated by the addition of sulfuric acid. The white amorphous solid which separated was collected and recrystallized twice from ethanol. The acid crystallizes in small colorless needles, m.p. 308–310° with decomposition and some preliminary sublimation. This compound gains a pink tinge after a period of time.

Anal. Calcd. for $C_{10}H_6O_3Br_2S$: C, 32.81; H, 1.65. Found: C, 32.94; H, 1.79.

4,6-Dibromo-5-methoxybenzothiophene. (a) **From 4,6-Dibromo - 5 - hydroxybenzothiophene.**—4,6 - Dibromo - 5-hydroxybenzothiophene (225 mg.) was dissolved in 30 ml. of ether and treated with an excess of diazomethane in ether. The reaction mixture after standing for 16 hours was taken to dryness under reduced pressure. The residue was crystallized twice from absolute ethanol as 180 mg. of long colorless needles, m.p. 102–103°.

Anal. Calcd. for $C_9H_6OSBr_2$: C, 33.57; H, 1.88. Found: C, 33.70; H, 1.95.

(b) **From Barium 4,6-Dibromo-5-methoxybenzothiophene-2-carboxylate.**—Potassium 4,6-dibromo-5-methoxybenzothiophene-2-carboxylate (400 mg.) was dissolved in 500 ml. of boiling water and excess saturated aqueous barium hydroxide solution added. The insoluble barium salt was collected and after drying was mixed with three times its weight of solid barium hydroxide. The mixture was heated to 360° under 10^{-4} mm. pressure in a sublimation apparatus. The white solid (200 mg.) which had collected on the cold finger on recrystallization from ethanol gave colorless needles, whose m.p. both alone and in admixture with the material prepared by the action of diazomethane on 4,6-dibromo-5-hydroxybenzothiophene was 102–103°.

5-Hydroxy-3,4,6-tribromobenzothiophene. (a) **From 3-Bromo - 5 - hydroxybenzothiophene.**—3 - Bromo - 5 - hydroxybenzothiophene (100 mg.) was dissolved in 5 ml. of acetic acid containing 200 mg. of sodium acetate, and to the solution was added 140 mg. of bromine (2-mole proportion) in 1.14 ml. of acetic acid. The bromine was instantly decolorized and the pale yellow solution on careful dilution with water threw down a yellowish solid. On recrystallization from heptane with treatment with activated carbon, 85 mg. of colorless needles (69%), m.p. 189–194°, was obtained. Further recrystallization raised the m.p. to 193–195°.

Anal. Calcd. for $C_8H_3OSBr_3$: C, 24.83; H, 0.78. Found: C, 25.01; H, 0.81.

The compound is soluble in acetone and acetic acid. It is sparingly soluble in ethanol, heptane and chloroform and insoluble in water. This same compound is obtained by the action of one mole of bromine in acetic acid on 3,4-dibromo-5-hydroxybenzothiophene in the presence of sodium acetate, using the same conditions as described above.

(b) **From 4,6-Dibromo-5-hydroxybenzothiophene.**—4,6-Dibromo-5-hydroxybenzothiophene (1.0 g.) was dissolved in 25 ml. of acetic acid and to the solution was added 520 mg. of bromine (1-mole proportion) contained in 2.54 ml. of acetic acid. The uptake of bromine was slow. The solution was warmed on the steam-bath for 20 minutes. On cooling, the light orange solution deposited colorless needles, 300 mg. (24%). The mother liquor on dilution with water yielded mainly unchanged starting material.

The tribromo compound after two recrystallizations from heptane melted 191–194° and gave no depression in melting point with a specimen prepared from 3-bromo-5-hydroxybenzothiophene.

A sample of the compound was suspended in acetic acid and concentrated nitric acid was added. On warming, the solid dissolved to give a yellow-orange solution. Careful dilution of the solution with water threw down an orange solid. This on boiling in benzene gave off red fumes, and the cooled solution gave a positive Craven test.[28] No attempt was made to isolate this 7-(cyanocarbethoxymethyl]-benzothiophene-4,5-quinone, its quinone precursor or the 4-bromo-4-nitro-5-keto intermediate.

4,5-Dihydro-5-keto-4,4,6-tribromobenzothiophene.—4,6-Dibromo-5-hydroxybenzothiophene (0.50 g.) was dissolved in 10 ml. of acetic acid together with 0.25 g. of crystalline sodium acetate by warming, and the solution cooled in ice. To the solution was then added with constant swirling 0.26 g. of bromine in 4.8 ml. of acetic acid (1 mole of bromine). When the addition of the bromine was complete, an orange solid separated. Careful dilution with water deposited more material. The product was collected, washed well with water and dried under vacuum at 10^{-2} mm.; 0.55 g. (88%), m.p. 82–87° dec. The compound is unstable, decomposing at room temperature. It can be preserved at 0° for a short time. It cannot be recrystallized. A sample of material dried as above was submitted for analysis.

Anal. Calcd. for $C_8H_3OSBr_3$: C, 24.83; H, 0.78. Found: C, 25.17; H, 0.88.

The compound is slightly soluble in cold ethanol to give an orange solution. On warming an aqueous alcoholic solution of the compound with sodium hydrosulfite the color is completely discharged, and 4,6-dibromo-5-hydroxybenzothiophene is obtained in 70% yield. The ethanolic solution with triethylamine and ethyl cyanoacetate gives a green color but, unlike that shown by the benzothiophene-4,5-quinones, it is destroyed on the addition of aqueous potassium ferricyanide.

5-Hydroxy-2,3,4,6-tetrabromobenzothiophene.—4,6-Dibromo-5-hydroxybenzothiophene (1.0 g.) was dissolved in 20 ml. of acetic acid and treated with 1.632 g. of bromine (3 mole proportion) dissolved in 10 ml. of acetic acid. The solution was warmed on the steam-bath for 20 minutes, at the end of which crystalline material had been deposited. On cooling, more material crystallized. The product was collected; 900 mg. (75%) of colorless needles, m.p. 185–190°. Further recrystallization gave colorless needles, m.p. 202–204°. This compound is moderately soluble in acetic acid and acetone, sparingly soluble in hexane and ethanol and insoluble in water.

Anal. Calcd. for $C_8H_2SOBr_4$: C, 20.63; H, 0.43. Found: C, 20.61; H, 0.43.

4,5-Dihydro-5-keto-3,4,4,6-tetrabromobenzothiophene.—5-Hydroxy-3,4,6-tribromobenzothiophene (100 mg.) was dissolved in 11 ml. of acetic acid together with 100 mg. of sodium acetate by warming. The solution was cooled until solid material first became visible. Then 41.3 mg. (1-mole proportion) of bromine in 0.25 ml. of acetic acid was

(25) All melting points are uncorrected.

(26) Microanalyses by Miss V. Williams, Miss A. Smith and H. Seguin. Infrared spectra by C. A. Whiteman.

added to the solution, which turned bright yellow. On careful dilution with water and external cooling in ice, an orange solid separated. This was collected, washed well with water and dried under 5×10^{-3} mm. for one hour, m.p. 133–134°. This compound appeared relatively stable and no decomposition was observed at the end of two weeks. The infrared spectrum showed no absorption in the 3 μ region. It shows a carbonyl peak at 5.97 μ.

Anal. Calcd. for $C_8H_2SOBr_4$: C, 20.63; H, 0.43. Found: C, 20.56; H, 0.41.

2,3,6-Tribromobenzothiophene-4,5-quinone.—5-Hydroxy-2,3,4,6-tetrabromobenzothiophene (750 mg.) was finely divided and suspended in 15 ml. of acetic acid. To the suspension was added 7.5 ml. of concentrated nitric acid and the mixture gently warmed with swirling. The starting material dissolved to give an orange solution which on cooling and careful dilution with water threw down the orange 4,5-dihydro-5-keto-4-nitro-2,3,4,6-tetrabromobenzothiophene. This was collected and dried at the water-pump. It was then dissolved in 20 ml. of benzene and the solution boiled. Red fumes were evolved, and on concentrating the deep red solution 400 mg. (62%) of dark needles were deposited, m.p. 185–191°. After two recrystallizations from benzene and three recrystallizations from ethyl acetate, deep violet iodine-colored needles were obtained, m.p. 203–206° with sublimation occurring slightly below the m.p.

Anal. Calcd. for $C_8HO_2SBr_3$: C, 23.96; H, 0.25. Found: C, 23.83; H, 0.22.

The compound is soluble in benzene, ethyl acetate and acetone. It is sparingly soluble in ethanol. Its solution in concentrated sulfuric acid is blue. Application of the Craven test[22] gives a green color. After boiling the compound in ethanol with sodium ethoxide, a negative test for bromide ion results.

6-Bromo-5-hydroxy-4-nitrobenzothiophene.—4,6-Dibromo-5-hydroxybenzothiophene (200 mg.) was suspended in 4.5 ml. of acetic acid and 2 ml. of concentrated nitric acid added, giving a blood-red solution. On careful dilution with water a brownish solid separated and was collected. The red mother liquor on shaking with excess triethylamine, potassium ferricyanide and ethyl cyanoacetate gave a positive Craven test,[23] showing the presence of a benzothiophene-4,5-quinone. The brown solid was crystallized from dilute ethanol several times; 100 mg. (43%) of bright yellow needles, m.p. 128–130°.

Anal. Calcd. for $C_8H_4O_3NBrS$: C, 35.37; H, 1.50. Found: C, 35.15; H, 1.45.

Fifty milligrams of the compound was dissolved in 7 ml. of ethanol and hydrogenated on the microhydrogenator, using Raney nickel catalyst. The theoretical uptake of 12.4 ml. of hydrogen (3 moles) was observed after 20 minutes. The solution was filtered free of catalyst under nitrogen directly into a solution of 0.5 ml. of triethylamine and one drop of ethyl cyanoacetate in 5 ml. of ethanol. The resulting colorless solution gave a deep purple color on the addition of an aqueous solution of potassium ferricyanide, indicating the formation of a 7-[cyanocarbethoxymethyl]-benzothiophene-4,5-quinone,[3] and so proving the constitution of 6-bromo-5-hydroxy-4-nitrobenzothiophene.

4,6-Dichloro-5-hydroxybenzothiophene.—Two hundred and fifty milligrams of 5-hydroxybenzothiophene together with 750 mg. of crystalline sodium acetate was dissolved in 10 ml. of acetic acid in the cold. To the mixture was added 238 mg. of chlorine (2 moles) contained in a standard solution of chlorine in acetic acid. The solution turned orange, and on cooling in ice sodium chloride separated. The solution was filtered free of this inorganic material, but no organic material was deposited after prolonged standing. Addition of water to a test sample threw down a brown solid, which, however, was not homogeneous. The infrared spectrum of the dried material showed absorption in the 3-μ region and two carbonyl peaks at 5.74 and 5.93 μ.

The red reaction liquor was taken to dryness at room temperature under reduced pressure, using a slow stream of nitrogen to produce smooth ebullition. The bright red gum resulting was taken up in ether. Satisfactory crystallization of the material was not possible with a wide variety of solvents. The ethereal solution was therefore shaken with dilute aqueous sodium hydroxide solution and the material passed into the aqueous phase to give a purple solution. This was treated with activated carbon, filtered, acidified and again extracted with ether. The ethereal solution was taken to dryness and the tarry residue extracted with hexane. On concentrating the hexane solution crystalline material separated (10 mg.). This was again crystallized from hexane as long colorless needles, iridescent under polarized light, m.p. 93–94°.

Anal. Calcd. for $C_8H_4OCl_2S$: C, 43.85; H, 1.84. Found: C, 43.70; H, 2.24.

2-Carboxy-7-[cyanocarbethoxymethyl]-benzothiophene-4,5-quinone from 5-Hydroxybenzothiophene-2-carboxylic Acid.—5-Hydroxybenzothiophene-2-carboxylic acid (825 mg.) was converted to the 4,6-dibromo derivative as described previously.[3] After the product had been collected, 1.04 g. (70%), the mother liquor was diluted with water, turning deep red. This red solution was shaken with 1 ml. of ethyl cyanoacetate and excess triethylamine in a separatory funnel, and the mixture turned deep green. A solution of 1.0 g. of potassium ferricyanide in 50 ml. of water was added and shaking continued for 10 minutes. The solution was acidified with hydrochloric acid and extracted with ether. The orange ethereal solution was extracted with aqueous sodium carbonate, and the green aqueous layer separated. On acidification with sulfuric acid an orange oil separated which soon solidified. One crystallization from ethyl acetate gave 170 mg. of orange microscopic needles, m.p. 257–259° dec. Two further crystallizations from the same solvent gave material of m.p. 268–270°, either alone or in admixture with authentic 2-carboxy-7-[cyanocarbethoxymethyl]-benzothiophene 4,5-quinone.[3]

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