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

Nitro and Amino Derivatives of Dibenzothiophene

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Direct nitration of dibenzothiophene-5-oxide produces 3-nitro- and 3,7-dinitrodibenzothiophene-5-oxide which can be selectively reduced to the corresponding nitrosulfides with hydrobromic acid. Vigorous reduction yields the expected amine sulfides. Although 2-nitrodibenzothiophene was readily converted into 2-nitrodibenzothiophene-5-dioxide, all attempts to prepare 2-nitrobenzothiophene-5-oxide, 2,8-dinitrodibenzothiophene-5-oxide, and 2,8-dinitrodibenzothiophene-5-dioxide by direct oxidation of the corresponding sulfides, failed. This is in sharp contrast to the facile formation of both the sulfoxide and sulfone of those nitrodibenzothiophene derivatives in which the nitro groups are in the meta position with respect to the sulfur atom.

Much of the chemistry of dibenzothiophene has already been described in a number of excellent papers.[1-10] These have shown that nuclear halogenation,[7,9] nitration,[1-4] sulfonation[10] and acylation[4,8] of dibenzothiophene occur in the 2- and 8-positions in accordance with the ortho and para directive influence of the sulfide function, whereas the presence of the strongly electronegative sulfone group leads to substitution at positions 3 and 7 in dibenzothiophene-5-dioxide. The recent preparation of 3-nitrodibenzothiophene-5-oxide by the direct nitration of dibenzothiophene-5-oxide[11] is evidence that the sulfoxide group is similar to the sulfone group in its meta directing property.

Since sulfoxides, in sharp contrast to sulfones, are readily reduced to the sulfides[12] a route is thus made available to the preparation of 3-aminodibenzothiophene, somewhat simpler and in better yield than the elegant method devised by Gilman and Nobis.[6]

This paper presents additional information concerning derivatives of dibenzothiophene.

The symmetrical 3,7-dinitrodibenzothiophene-5-oxide has now been prepared both by further nitration of 3-nitrodibenzothiophene-5-oxide and by nitration of the dibenzothiophene-5-oxide. Its structure was confirmed by conversion to the sulfone which was found to be identical with the 3,7-dinitrodibenzothiophene-5-dioxide prepared by Cullinane, *et al.*[2] Reduction of 3,7-dinitrodibenzothiophene-5-oxide with stannous chloride gave the 3,7-diaminodibenzothiophene in good yield.

The reduction of 3-nitrodibenzothiophene-5-oxide with stannous chloride and concentrated hydrochloric[11] acid involves two competing reactions, one yielding 3-aminodibenzothiophene, while the other affords 3-nitrodibenzothiophene which is further reduced to the 3-aminodibenzothiophene. By carrying out the reduction below 40° and for a limited time, the 3-nitrodibenzothiophene can be isolated in 35% yield. However, the same compound can be obtained in high yield by treating 3-nitrodibenzothiophene-5-oxide with a mixture of concentrated hydrobromic acid and glacial acetic acid, a procedure by which the sulfoxide function is easily and preferably converted to the sulfide in the presence of the nitro group.[13] It is of interest to note that Fries and Vogt[14] have employed a solution of hydrobromic acid and glacial acetic acid to distinguish sulfoxides from sulfones. Reduction of 3,7-dinitrodibenzothiophene-5-oxide with hydrobromic acid gave, in excellent yield, 3,7-dinitrodibenzothiophene which was in turn reduced with stannous chloride to 3,7-diaminodibenzothiophene. Dichromate oxidation of 3,7-dinitrodibenzothiophene produced, quantitatively, the corresponding sulfone.

Conversion of the 2-nitrodibenzothiophene to the 2-nitrodibenzothiophene-5-oxide, followed by nitration in which advantage is taken of the meta directing effect of the sulfoxide group, should provide a route to the unsymmetrical 2,7-(or 3,8)-dinitrodibenzothiophene. However, attempts to prepare the 2-nitrodibenzothiophene-5-oxide were unsuccessful either by employing the theoretical amount of hydrogen peroxide in acetic acid as recommended by Price and Pohland in the preparation of the sulfoxide of β-(β-chloroethylthio)-ethyl ether,[15] or by addition of the theoretical amount of chlorine to the sulfur in 2-nitrodibenzothiophene followed by hydrolysis of the addition product, a method which readily converts dibenzothiophene to the sulfoxide.[11] By these methods only unchanged starting material was quantitatively recovered. It might be pointed out that iodosobenzene, employed by Ford-Moore to prepare sulfoxides of those compounds unaffected by hydrogen peroxide,[16] also proved fruitless although conversion of unsubstituted dibenzothiophene to dibenzothiophene-5-oxide was possible.

Although 2-nitrodibenzothiophene-5-oxide could not be obtained, good yields of the 2-nitrodibenzothiophene-5-dioxide were realized by treating 2-nitrodibenzothiophene with excess hydrogen peroxide at reflux temperatures according to conventional procedures.[6] The failure of the sulfur atom in both 2-nitrodibenzothiophene and 2,8-dinitrodibenzothiophene to hold a *single* atom of oxygen whereas 3-nitrodibenzothiophene-5-oxide and 3,7-dinitrodibenzothiophene-5-oxide are both

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(1) C. Courtot and C. Pomonis, *Comp. rend.*, **182**, 893 (1926); *cf. C. A.*, **20**, 2155 (1926).

(2) N. M. Cullinane, C. G. Davies and G. I. Davies, *J. Chem. Soc.*, 1435 (1936).

(3) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938–1939).

(4) H. Gilman, A. L. Jacoby and H. A. Pacevitz, *ibid.*, **3**, 120 (1938–1939).

(5) H. Gilman and S. Avakian, THIS JOURNAL, **68**, 1514 (1946).

(6) H. Gilman and J. F. Nobis, *ibid.*, **67**, 1479 (1945).

(7) C. R. Neumoyer and E. D. Amstutz, *ibid.*, **69**, 1920 (1947).

(8) A. Burger, W. B. Wartmann and R. E. Lutz, *ibid.*, **60**, 2628 (1938).

(9) C. Courtot, L. Nicolas and T. H. Liang, *Compt. rend.*, **186**, 1624 (1928).

(10) C. Courtot and I. Kelner, *ibid.*, **198**, 2003 (1934).

(11) R. K. Brown, R. G. Christiansen and R. B. Sandin, THIS JOURNAL, **70**, 1748 (1948).

(12) Gilman, "Organic Chemistry," 2nd ed., Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1945, pp. 872, 877.

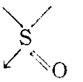
(13) Ref. 12, pp. 872–873.

(14) K. Fries and W. Vogt, *Ann.*, **381**, 346 (1911); *Ber.*, **44**, 759 (1911).

(15) C. C. Price and A. Pohland, *J. Org. Chem.*, **12**, 249 (1947).

(16) A. H. Ford-Moore, *J. Chem. Soc.*, 2126 (1949).

quite stable can be explained by the decrease in availability of the electrons about the sulfur atom due to the inductive effect of the nitro group situated para to the sulfur. On the other hand the successful addition of *two* oxygen atoms to 2-nitrodibenzothiophene to form the stable 2-nitrodibenzothiophene-5-dioxide is no doubt due to the remarkable and well-known stability of the sulfone group. Amstutz, Hunsberger and Chessick[17] have advanced the theory that stability of the sulfone function might reasonably arise from a resonating structure such as a and b, analogous to that accepted for the carboxylic acids. However, the combined effect of the *two* nitro groups in 2,8-dinitrodibenzothiophene was effective in preventing the formation of either the sulfone or the sulfoxide of this compound. Conversion to the 2,8-diaminodibenzothiophene has been shown to permit the formation of the corresponding diaminosulfone.[7] Furthermore, Bordwell and Albisetti[18] have reported the failure of either 30% hydrogen peroxide or sodium dichromate in sulfuric acid to oxidize 3-nitro-, 3,5-dinitro- and 3,5,7-trinitrobenzothiophene to their respective sulfones, whereas 30% hydrogen peroxide readily converted 5-nitrobenzothiophene to 5-nitrobenzothiophene-1-dioxide. Since the structures of these compounds resemble those of 2-nitro- and 2,8-dinitrodibenzothiophene the resistance to oxidation shown by both types of nitrated compounds must be similar in nature.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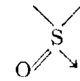
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Experimental

3-Nitrodibenzothiophene (II). Method A.—To a solution of 4 g. of 3-nitrodibenzothiophene-5-oxide[11] in 50 ml. of glacial acetic acid was added 25.7 g. of dihydrated stannous chloride previously dissolved in 33 ml. of concentrated hydrochloric acid. The solution was stirred and kept at a temperature of 30–40° until the heat of reaction had subsided. The thick yellow precipitate remained in contact with the reduction mixture for one hour at room temperature and was then removed by filtration and washed with a small amount of a mixture of glacial acetic acid and concentrated hydrochloric acid (1:1). The solid was then dispersed in excess dilute sodium hydroxide solution and the light yellow precipitate collected on a buchner and washed with water. The crude, air-dried material melted at 95–108°. Two crystallizations from diluted alcohol (Norit) produced 1.3 g. (35%) of a pale yellow compound melting at 151.5–152.5° (153–154° cor.).

Anal. Calcd. for $C_{12}H_7O_2NS$: S, 13.98. Found: S, 13.92.

Method B.—To a warm solution of 3 g. of 3-nitrodibenzothiophene-5-oxide in 20 ml. of glacial acetic acid was added 7.2 ml. of concentrated hydrobromic acid (sp. gr. 1.38). The reduction, accompanied by the liberation of bromine, was allowed to proceed for 30 min. at 40° whereupon the yellow precipitate was removed, washed with water and air dried. The crude material weighed 2.4 g. and melted at 149–151°. Dilution of the filtrate yielded an additional 0.4 g. (m.p. 140–150°). One recrystallization from diluted alcohol gave 2.5 g. (89%) of 3-nitrodibenzothiophene of m.p. 153–154° cor. A mixed melting point with the product from Method A showed no depression.

Anal. Calcd. for $C_{12}H_7O_2NS$: S, 13.98. Found: S, 13.95.

3,7-Dinitrodibenzothiophene-5-oxide (III). From 3-Nitrodibenzothiophene-5-oxide.—A solution of 20 g. of 3-nitrodibenzothiophene-5-oxide in 68 ml. of concentrated sulfuric acid was cooled to 12° and 34 ml. of 100% nitric acid was added slowly so that the reaction temperature remained at 10–15°. The mixture was left at this temperature for 30 minutes and then allowed to come to room temperature over a 30-minute period. The precipitate obtained by pouring the nitration mixture on ice, was collected on a buchner, washed with water and air dried. The crude material (27 g., m.p. 246–253°) when crystallized from acetone gave 21.5 g. (91%) of pure material which melted at 258–259° (267–268° cor.).

Anal. Calcd. for $C_{12}H_6O_5N_2S$: S, 11.05. Found: S, 11.08.

From **Dibenzothiophene-5-oxide.**—The dibenzothiophene (20 g.), treated in a manner identical to that employed in the preceding preparation, gave 21 g. (73%) of pure 3,7-dinitrobenzothiophene-5-oxide melting at 257–258° (266–267° cor.).

The 3,7-dinitrodibenzothiophene-5-oxide when heated with a mixture of sodium dichromate and acetic acid according to the method of Gilman, *et al.*,[4] was converted almost quantitatively to the corresponding sulfone giving a product melting at 273–275° (283–285° cor.). Reduction of an acetic acid solution of the 3,7-dinitrodibenzothiophene-5-dioxide with stannous chloride and concentrated hydrochloric acid, following the directions given by Gilman and Avakian[5] gave 3,7-diaminodibenzothiophene-5-dioxide of melting point 318–320° (330–332° cor.) identical with the diaminosulfone reported by Cullinane, Davies and Davies.[2]

3,7-Dinitrodibenzothiophene (IV).—To a solution of 5 g. of 3,7-dinitrodibenzothiophene-5-oxide in 130 ml. of glacial acetic acid at 80° was added 10 ml. of concentrated hydrobromic acid. The vessel was placed in a water-bath to moderate the temperature of the reaction which was allowed to proceed for 30 minutes. The copious yellow precipitate was removed, washed with water, and air dried. The crude material (5 g., m.p. 338–341°) was crystallized from benzene giving a quantitative yield of pure 3,7-dinitrodibenzothiophene of m.p. 342–344° (354–356° cor.).

Anal. Calcd. for $C_{12}H_6O_4N_2S$: S, 11.70. Found: S, 11.73.

3,7-Diaminodibenzothiophene (VII).—The procedure described by Gilman and Avakian for the preparation of 3-aminodibenzothiophene[5] was followed with minor modification.

To a suspension of 3,7-dinitrodibenzothiophene-5-oxide (5 g.) in glacial acetic acid (80 ml.) was added 40 g. of stannous chloride dihydrate dissolved in 60 ml. of concentrated hydrochloric acid. The mixture was allowed to stand for two hours while reduction progressed, and then heated for one hour on a boiling water-bath. The solid, which had assumed a grayish color, was collected on a buchner, washed with brine and dispersed in water. Addition of 40% caustic soda liberated the diamine. Crystallization from dilute alcohol (Norit) gave 3.0 g. (83%) of pale yellow material melting sharply at 169–170° (172–173° cor.).

Anal. Calcd. for $C_{12}H_{10}N_2S$: S, 14.98. Found: S, 15.08.

2-Nitrodibenzothiophene-5-dioxide (VIII).—A solution of 3 g. of 2-nitrodibenzothiophene[2] in 70 ml. of glacial acetic acid was refluxed with 15 ml. of 30% hydrogen peroxide following the directions supplied by Gilman and Nobis.[6] After 30 minutes a second quantity (10 ml.) of hydrogen peroxide was added and refluxing continued for an additional 20 minutes. The solid, removed from the cooled mixture and washed with a small amount of cold acetic acid, yielded 3.3 g. (95%) of crude, air-dried material melting at 249–250° (257–258° cor.). Recrystallization from acetone failed to raise the melting point. A sulfoxide test gave negative results.[12]

Anal. Calcd. for $C_{12}H_7O_4NS$: S, 12.27. Found: S, 12.23.

2-Aminodibenzothiophene-5-dioxide (IX).—To a solution of 2 g. of 2-nitrodibenzothiophene-5-dioxide in 60 ml. of glacial acetic acid was added 20 g. of dihydrated stannous

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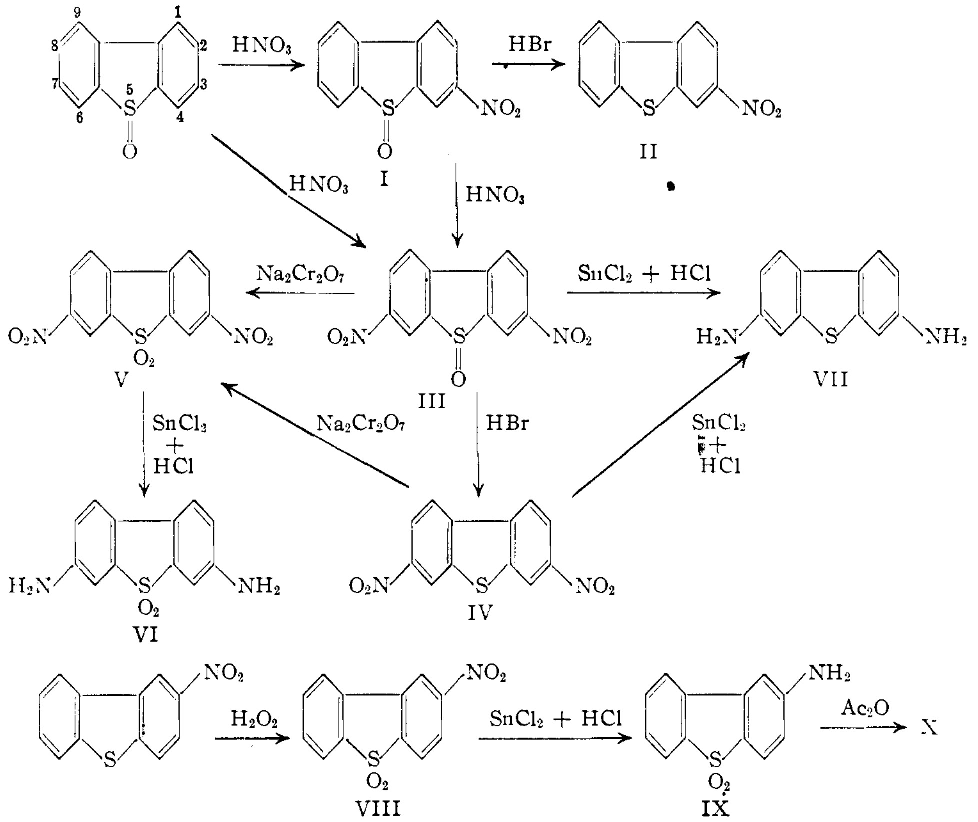
(17) E. D. Amstutz, I. M. Hunsberger and J. J. Chessick, THIS JOURNAL, **73**, 1220 (1951).

(18) F. G. Bordwell and C. J. Albisetti, *ibid.*, **70**, 1955 (1948).



chloride dissolved in 25 ml. of concentrated hydrochloric acid. A clear solution resulted which, upon heating at 100° for one hour after the initial heat of reaction had subsided, deposited a precipitate. The solid was removed from the cooled solution, dispersed in water, and basified with excess sodium hydroxide. The almost colorless amine was filtered free of liquid, washed with water and air dried, yielding 1.7 g. of material melting at 270–271° (278–279° cor.). Crystallization from alcohol failed to raise the melting point.

Anal. Calcd. for $C_{12}H_9O_2NS$: S, 13.87. Found: S, 13.87.

2-Acetamidodibenzothiophene-5-dioxide (X).—Acetic anhydride (1 ml.) was added to a solution of 2-aminodibenzothiophene-5-dioxide (0.75 g.) in 75 ml. of glacial acetic acid. After standing for two hours at room temperature, the solution deposited a precipitate which was removed and washed with cold acetic acid. Recrystallization from acetic acid gave 0.8 g. (90%) of substance melting at 265–266° (273–274° cor.).

Anal. Calcd. for $C_{14}H_{11}O_3NS$: S, 11.73. Found: S, 11.83.

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