The NMR Spectra of Some Substituted Dibenzothiophenes (1)

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In order to use the NMR spectra of dibenzothiophenes to determine the position of substitution, a series of compounds has been prepared, most of which are new while some represent an improved method of preparation of previously reported compounds. With the exception of one, the structures of the compounds prepared were not in doubt, however the splitting patterns and chemical shifts presented here will facilitate future structure determinations of dibenzothiophenes.

Our interest in the synthesis of sulfur isosteres of some biologically active indole alkaloids and polycyclic midring heterocycles in general has led us to examine some of the basic chemistry of dibenzothiophene. Bromination of dibenzothiophene leads to 2-bromodibenzothiophene (I, X = Br) in good yield (2). Treatment of I (X = Br) with butyllithium gave the 2-lithio compound from which dibenzothiophene-2-carboxaldehyde (I, X = CHO) was formed by treatment with *N,N*-dimethylformamide. Similarly treatment of the 2-lithio compound with carbon dioxide, *N,N*-dimethylacetamide or methyl sulfate gave dibenzothiophene-2-carboxylic acid (I, X = COOH), 2-acetyldibenzothiophene (I, X = $COCH_3$) and 2-methyldibenzothiophene (I, X = CH_3) in high yields.

2-Acetyldibenzothiophene has been isolated in low yield from the Friedel-Craft acetylation of dibenzothiophene (3). In an earlier attempt to prepare I (X = $COCH_3$) from the 2-bromo compound (I, X = Br) the corresponding lithio derivative was reacted with ethyl acetate. The product isolated, was however, bis(2-dibenzothienyl)methylcarbinol (II). The infrared spectrum of the crude product exhibited a weak carbonyl absorption which was lost upon purification. It therefore seems likely that II arises by initial formation of 2-acetyldibenzothiophene which further reacts with the 2-lithio compound to give the observed bis-alcohol. Bromination of 2-methyldibenzothiophene (I, X = CH_3) gave 3-bromo-2-methyldibenzothiophene. Treatment of I (X = CHO) under Cannizzaro conditions gave I (X = COOH) and 2-hydroxymethyldibenzothiophene (I, X = CH_2OH). The alcohol (I, X = CH_2OH) was also formed by lithium aluminum hydride reduction of I (X = CHO). The acids (I, X = COOH) formed by the above two routes were identical and melted 21° higher than previously reported (4).

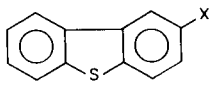
As a route to 3-substituted derivatives, 3-bromodibenzothiophene (III, X = Br) was prepared (5). However we experienced difficulty in repeating the work of Sandin (6) for the preparation of its precursor, 3-aminodibenzothiophene. The method calls for reduction of 3-nitrodibenzothiophene 5-oxide with stannous chloride and hydrochloric acid at room temperature. Upon repeating this reaction we isolated a low yield (18%) of 3-aminodibenzothiophene 5,5-dioxide (IV, X = NH_2) along with material melting over an 80° range from which 3-bromodibenzothiophene 5,5-dioxide (IV, X = Br) was isolated after treatment under Sandmeyer conditions. Reduction of IV (X = Br) with lithium aluminum hydride gave dibenzothiophene, in contrast to the reported reduction of 3,7-dibromodibenzothiophene 5,5-dioxide with lithium aluminum hydride which gave 3,7-dibromodibenzothiophene (7). We were finally able to isolate III (X = NH_2) by modifying the reduction conditions of 3-nitrodibenzothiophene 5-oxide. Treatment of III (X = Br) with butyllithium followed by *N,N*-dimethylformamide yielded dibenzothiophene-3-carboxaldehyde (III, X = CHO), from which 3-methyldibenzothiophene (8) (III, X = CH_3) was formed by Wolff-Kishner reduction. Likewise reaction of III (X = Br) with butyllithium and *N,N*-dimethylacetamide gave a low yield of 3-acetyldibenzothiophene. Reaction of 2-nitrodibenzothiophene with thionyl bromide is reported to yield 2-bromodibenzothiophene (9). Attempts to repeat this reaction with 3-nitrodibenzothiophene (6) gave unchanged starting material.

The yields of products derived from 3-lithiodibenzothiophene were lower than those from the 2-lithio compound, both sets of experiments being conducted at 0°. With the 3-lithio compound the chance of translithiation to the more stable 4-lithio derivative probably accounts for reduced yields and suggests that future lithiation work with 3-bromodibenzothiophene should be carried out

at lower temperatures.

2,8-Dibromodibenzothiophene (V, X = Br) has been prepared by refluxing dibenzothiophene in carbon disulfide with bromine for nine days (10). By reducing the amount of solvent the reaction was complete within 1 hour. Treatment of V (X = Br) with two equivalents of butyllithium and *N,N*-dimethylformamide gave dibenzothiophene-2,8-dicarboxaldehyde (V, X = CHO). Wolff-Kishner reduction of V (X = CHO) gave the known 2,8-dimethyldibenzothiophene (V, X = CH_3) (7).

CHART I



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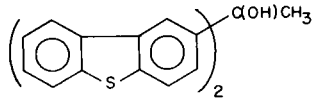
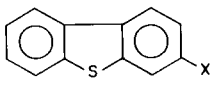
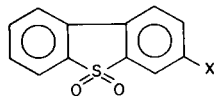


II

X = Br, CHO, COOH, $COCH_3$, CH_3, CH_2OH



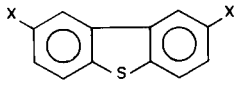
III



IV

X = NH_2, Br, CHO, CH_3, $COCH_3$

X = NH_2, Br



V

X = Br, CHO, CH_3

The low solubility of I (X = COOH) and V (X = Br or CHO) precluded the determination of their NMR spectra. In the following 100 MHz NMR analysis frequent reference to the schematic spectra (Figures I and II) will be helpful. *Meta*-couplings, usually less than 2 Hz, have not been shown but are referred to in the text as broadened resonances, and in all cases confirm the assignments made.

The 60 MHz NMR spectrum of dibenzothiophene has been determined by Faller (11), and consisted of three separate multiplets (Figure Ia). The first centered at δ 7.3 assigned to protons 2,3,7, and 8, the second centered at δ 7.7 assigned to protons 4 and 6 and the third centered at δ 8.0 assigned to protons 1 and 9. In the substituted compounds to be discussed, these multiplets, associated with the protons of the unsubstituted ring, are represented by blocks in the schematic spectra. The chemical shifts of protons in the substituted ring have in

FIGURE I

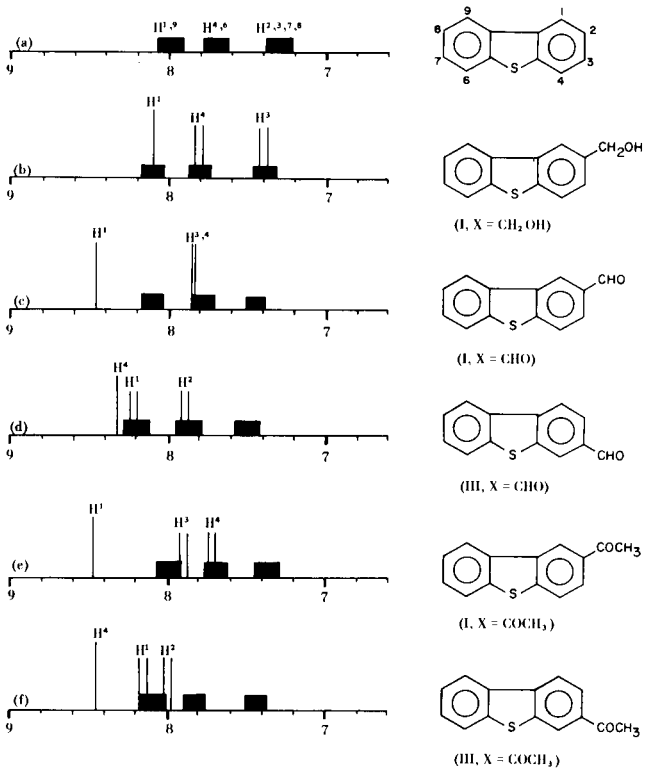
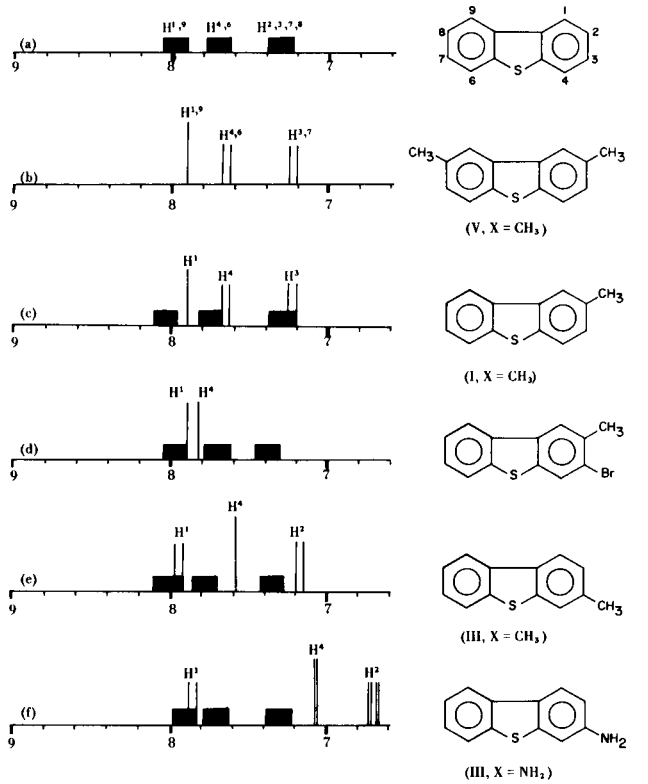


FIGURE II



all cases been measured from the center of the multiplet given by their counterparts in the unsubstituted ring.

Upon substitution in the 2- or 3-position the protons of the substituted ring are separated into two adjacent protons which will couple (*ca.* 8 Hz) and one isolated proton which apart from a small *meta*-coupling (*ca.* 2 Hz) will be a singlet. In the absence of any shielding or deshielding of adjacent protons by the functional group that has been introduced into the ring the signals from these three protons will lie within the multiplets given by their counterparts in the unsubstituted ring. The only example encountered of this behavior was with I (X = CH_2OH) (Figure Ib).

In general, however, functional groups exert a marked shielding or deshielding of adjacent protons. This is illustrated by the spectra of the aldehydes I (X = CHO) and III (X = CHO). In the latter (Figure Id) the doublet associated with H-1 is superimposed upon the H-3 multiplet while the doublet of H-2 and the broadened singlet of H-4 are both deshielded by the adjacent formyl group (*ca.* 40 Hz). In the spectrum of I (X = CHO) (Figure Ic) the resonances of H-1 and H-3 are likewise deshielded, H-1 giving a broadened singlet at δ 8.45. However, the deshielding of H-3 (*ca.* 40 Hz) makes it magnetically identical to H-4 resulting in zero coupling between H-3 and H-4 and the formation of what are essentially singlets at δ 7.84 and 7.85. The acetyl function in I (X = $COCH_3$) (Figure Ie) exerts a greater deshielding effect on adjacent protons than does the corresponding aldehyde as seen by the broadened singlet of H-1 which is deshielded by 48 Hz from the H-9 multiplet. This enhanced effect is sufficient to carry the resonance of H-3 to lower field than the unperturbed H-4 resonance, doublets again being observed for these two protons. The spectrum of 3-acetyldibenzothiophene (III, X = $COCH_3$) (Figure If) shows a broadened singlet for H-4 (deshielded by *ca.* 55 Hz) and a broadened doublet for H-2 (deshielded by *ca.* 55 Hz). The doublet associated with H-1 appears along with the H-9 multiplet. 3-Carbonyl substitution results in a deshielding of the proton multiplets associated with the unsubstituted ring by *ca.* 0.1 ppm as compared to dibenzothiophene or 2-carbonyl substituted compounds (see Figures I-d, f).

In contrast to the deshielding influence of the carbonyl functional groups, methyl substitution results in the shielding of adjacent protons and to a lower extent *meta*-related protons. 2,8-Dimethyldibenzothiophene (V, X = CH_3) (Figure IIb) showed a broadened singlet for H-1,9 along with a broadened doublet for H-3,7 and a sharp doublet for H-4,5. The spectrum of 2-methyldibenzothiophene (I, X = CH_3) (Figure IIc) has identical resonances apart from the reintroduction of the multiplets associated with the unsubstituted ring (Figure IIa). The bromination product of I (X = CH_3) (Figure IId) exhibited sharp singlets at δ 7.9 and 7.84 associated with H-1 and H-4, although a definite assignment of signals cannot be made in this case. The disappearance of the H-3 broadened doublet and collapse of the H-4 doublet to a sharp singlet showed the product to be 3-bromo-2-methyldibenzothiophene, thus clearly showing the diagnostic value of this study.

The spectrum of 3-methyldibenzothiophene (Figure IIe) is as expected, showing a doublet at δ 7.97 associated with H-1, along with a broadened singlet for H-4 and a broadened doublet for H-2, the latter two resonances being shifted to higher field due to the *ortho*-methyl group.

The very large shielding effect of the amino group in 3 aminodibenzothiophene (III, X = NH_2) (Figure IIf) completely removed the resonances of H-2 and H-4 from the rest of the spectrum. A closely spaced doublet (J = 2.5 Hz) at δ 7.03 was assigned to H-4 and a double doublet at δ 6.75 to H-2. The H-1 doublet appeared at δ 7.86.

The foregoing discussion has dealt solely with 2- or 3-substituted dibenzothiophenes. Consideration of 1- or 4-substituted compounds was omitted due to their general inavailability. Complex patterns would however be anticipated for such compounds due to the superimposition of a shielded or deshielded ABC multiplet upon the normal resonances of the unsubstituted ring. The spectrum of 4-methyldibenzothiophene, previously prepared by Osborn (12) in fact gave two complex multiplets centered at δ 7.8 (H-1,6,9) and δ 7.2 (H-2,3,7,8) which were not interpretable by first order methods. The spectrum of 1,4-dimethyldibenzothiophene has recently been recorded by Goodman (13).

In general therefore, the structure of any 2- or 3-substituted dibenzothiophene can be assigned or confirmed by reference to its 100 MHz NMR spectrum, and the position of further substitution readily determined.

EXPERIMENTAL

Melting points were determined on a Meltemp melting point apparatus and are corrected. Infrared spectra were measured in potassium bromide mulls on an Infracord Spectrometer, Model 137-B. The 100 MHz NMR spectra were determined in deuteriochloroform on a Varian HA100 instrument at 20°, tetramethylsilane being used as internal standard throughout. The drying agent used was anhydrous magnesium sulfate. The butyllithium used was a 15% solution in hexane. In reporting the NMR spectra the following abbreviations have been used. s = singlet; d = doublet; dd = double doublet; m = multiplet. δ Values for multiplets refer to the center of the resonances.

Dibenzothiophene-2-carboxaldehyde (I, X = CHO).

2-Lithiodibenzothiophene was prepared by treating a suspension of 2-bromodibenzothiophene (2) (70.4 g., 0.2715 mole) in ether (650 ml.) with butyllithium (169.2 ml., 0.2715 mole) under a dry atmosphere of nitrogen for 2 minutes at 0°. *N,N*-Dimethylformamide (20.7 ml., 0.2715 mole) was added, and the mixture

was allowed to reflux gently for 3 hours. Water (1 l.) was added and the solution was extracted with ether (4 x 1 l.). Removal of the solvent from the combined extracts under reduced pressure gave a solid which was crystallized from ethanol yielding I (X = CHO) (40 g., 71%), m.p. 104-105°. An analytical sample from 95% ethanol had m.p. 107.5-108.5°; IR 5.95 (CHO), 6.3 (C=C), 13.25. 13.8 and 14.45 μ (unassigned); NMR δ 7.44 (m, H-7,8), 7.78 (m, H-6), 7.84 and 7.85 (s,s, H-3,4), 8.12 (m, H-9) and 8.45 (s, H-1) and 10.05 (s, CHO).

Anal. Calcd. for $C_{13}H_8OS \cdot \frac{1}{2}H_2O$: C, 70.6; H, 4.1; S, 14.5. Found: C, 70.5; H, 3.8; S, 14.2.

2-Methyldibenzothiophene (I, X = CH_3).

Methyl sulfate (2.36 ml., 0.025 mole) was added with stirring to a solution of 2-lithiodibenzothiophene (0.02 mole) in ether (50 ml.) and the resultant clear solution kept at 20° for 1 hour. Water (100 ml.) was added, the organic phase separated and the aqueous phase extracted with a further 50 ml. of ether. The combined extracts were dried and the solvent evaporated yielding I (X = CH_3) as a semi-solid which crystallized from ethanol as needles (3.5 g., 92%), m.p. 77-80°. An analytical sample from ethanol had m.p. 84.5-85.5°; NMR δ 2.48 (s, 2-CH_3), 7.19 (dd, $J_{3,4}$ 9 Hz, $J_{3,1}$ 1.5 Hz, H-3), 7.38 (m, H-7,8), 7.65 (d, $J_{4,3}$ 9 Hz, H-4), 7.76 (m, H-6), 7.88 (d, $J_{1,3}$ 1.5 Hz, H-1) 8.04 (m, H-9).

Anal. Calcd. for $C_{13}H_{10}S$: C, 78.75; H, 5.1. Found: C, 79.0; H, 5.2.

2-Acetyldibenzothiophene (I, X = $COCH_3$).

Freshly distilled *N,N*-dimethylacetamide (0.681 ml., 0.0073 mole) was added to a solution of 2-lithiodibenzothiophene (0.0073 mole) in ether (50 ml.) and the resultant cloudy solution refluxed for 2.5 hours. Hydrochloric acid (18%, 3 ml.) was added and the mixture was stirred for 5 minutes. Water (*ca.* 10 ml.) was added until the solution clarified. The organic phase was separated and combined with two further ether extractions of the aqueous phase. The combined extracts were washed with sodium bicarbonate, water and dried. Evaporation of the solvent yielded I (X = $COCH_3$) as crystals, m.p. 92-98° (1.5 g., 98%). Crystallization from ethanol gave the product (1.17 g., 71%), m.p. 109-111° (Lit. (3) m.p. 111-112°); IR 6.05 (C = O), 7.15, 8.18, 12.4, 13.2 and 13.7 μ (unassigned); NMR δ 2.59 (s, CH_3), 7.34 (m; H-7,8), 7.74 (d; $J_{4,3}$ 9 Hz H-4), 7.67 (m, H-6), 7.85 (dd, $J_{3,4}$ 9 Hz, $J_{3,1}$ 2 Hz; H-3), 8.0 (m; H-9) and 8.48 (d; $J_{1,3}$ 2 Hz, H-1).

Anal. Calcd. for $C_{14}H_{10}OS$: C, 74.3; H, 4.45. Found: C, 74.0; H, 4.4.

2-Acetyldibenzothiophene Oxime.

2-Acetyldibenzothiophene (0.22 g., 0.001 mole) was added to a solution of hydroxylamine hydrochloride (0.5 g.) in water (2 ml.). Sodium hydroxide (10%, 2 ml.) was added followed by ethanol (7.5 ml.) and the mixture was refluxed for 15 minutes. Upon cooling colorless crystals of the product separated (0.18 g., 84%), m.p. 157-159°. An analytical sample from ethanol-water had m.p. 159-160°; IR 3.2 (OH), 9.9, 10.8, 11.4, 12.1, 13.3 and 13.9 μ (unassigned).

Anal. Calcd. for $C_{14}H_{11}NOS$: C, 69.7; H, 4.6; N, 5.8. Found: C, 69.45; H, 4.6; N, 5.6.

Dibenzothiophene-2-carboxylic Acid (I, X = COOH).

A solution of 2-lithiodibenzothiophene (0.0125 mole) in ether (25 ml.) was poured over solid carbon dioxide, and excess carbon dioxide and the solvent was allowed to evaporate leaving a colorless solid which was treated with hydrochloric acid (9%, 30 ml.). The aqueous solution was stirred with ether (1,000 ml.). Evaporation of the ether gave I (X = COOH) as a colorless solid (2.21 g., 97%), m.p. 263-266°, raised to 276-278° after crystallization from aqueous methanol (Lit. (4), m.p. 253-255°). This product was identical to the acid formed by the Cannizzaro reaction of dibenzothiophene-2-carboxaldehyde (see below).

Bis(2-dibenzothienyl)methylcarbonol (II).

Ethyl acetate (0.497 ml., 0.75 equivalents) in ether (10 ml.) was added to a solution of 2-lithiodibenzothiophene (0.0066 mole) in ether (15 ml.) and the solution refluxed for 1.5 hours. The reaction solution was added to water (20 ml.) and the ether layer was separated. The aqueous phase was further extracted with ether (10 ml.) and the combined extracts were dried and evaporated. The resultant oil was crystallized from aqueous ethanol (0.75 g., 50%), m.p. 162-165°. An analytical sample had m.p. 169-171°; IR 2.9 (OH), 13.2 and 13.7 μ (strong, unassigned); NMR (integral values given after assignments) δ 2.08 (s, CH_3, 3H), 2.46 (s, OH, 1H), 7.36 (m, H-2,7,8, 6H), 7.86 (d, $J_{4,3}$ 8 Hz, H-4, 2H), 7.96 (m, H-6, 2H), 8.06 (m, H-9, 2H) and 8.26 (d, $J_{1,3}$ 2 Hz, H-1, 2H).

Anal. Calcd. for $C_{26}H_{18}OS_2$: C, 76.1; H, 4.4. Found: C, 75.9; H, 4.6.

Reactions of Dibenzothiophene-2-carboxaldehyde (I, X = CHO).

A. Cannizzaro Reaction.

A solution of I (X = CHO) (3 g., 0.01415 mole) in ethanol (30 ml.) was treated with aqueous potassium hydroxide (50%, 30 ml.) under reflux for 1 hour. The solution was diluted with water (1 l.) and extracted with ether (1 l.). The ether layer was washed with water (2 x 100 ml.) and the water layer was washed with ether (2 x 100 ml.). The combined ether extracts were treated with Norit, dried and reduced to *ca.* 10 ml. Addition of hexane (50 ml.) produced fine needles of I (X = CH_2OH) (0.95 g., 63%), m.p. 105-107°. Crystallization from hexane raised, the m.p. to 108-108.5°; IR 3.1 (OH), 6.34 (C=C), 12.4, 13.3 and 13.9 μ (unassigned); NMR δ 4.83 (s, CH_2), 7.4 (m, H-7,8), 7.4 (d, $J_{3,4}$ 8 Hz, H-3), 7.78 (d, $J_{4,3}$ 8 Hz, H-4), 7.8 (m, H-6), 8.1 (s, H-1), 8.1 (m, H-9).

Anal. Calcd. for $C_{13}H_{10}OS$: C, 72.9; H, 4.7. Found: C, 72.4; H, 4.9.

The above combined aqueous solution was acidified with dilute acetic acid and the precipitated I (X = COOH) filtered (1.23 g., 75%), 250-256°. Repeated recrystallization from aqueous methanol raised the m.p. to 276-278°. (Lit. (4), m.p. 253-255°); IR 3.3 (OH) and 6.05 μ (C=O).

Anal. Calcd. for $C_{13}H_8O_2S$: C, 68.4; H, 3.5. Found: C, 68.0; H, 3.6.

B. Lithium Aluminum Hydride Reduction.

A solution of I (X = CHO) (2.12 g., 0.01 mole) in dry ether (100 ml.) was treated with an excess of lithium aluminum hydride at room temperature for 1.5 hours followed by refluxing for 1 hour. The reaction mixture was worked up in the usual manner to yield 2-hydroxymethyldibenzothiophene (1.05 g., 49%), m.p. 107°. This sample was identical to the previously prepared alcohol.

Reduction of 3-Nitrodibenzothiophene 5-Oxide.

To a solution of 3-nitrodibenzothiophene 5-oxide (10 g.) (6) in glacial acetic acid (100 ml.) was added a solution of hydrated stannous chloride (51 g.) in concentrated hydrochloric acid (65 ml.). The reaction was exothermic and a solid formed. After standing at room temperature for 12 hours the solid was filtered and washed with a mixture of equal parts glacial acetic acid and concentrated hydrochloric acid. The filtered hydrochloride was

liberated with dilute sodium hydroxide giving a yellow solid (6.5 g.), m.p. 107-109° (partial) and 180° (Lit. (6) m.p. 113-117°). This material could not be purified by crystallization. Treatment of this material under Sandmeyer conditions as described for 3-aminodibenzothiophene (5) (the expected product) gave 3-bromodibenzothiophene 5,5-dioxide (IV, X = Br) (18%), m.p. 224-225° (Lit. (14) m.p. 224-225°).

Anal. Calcd. for $C_{12}H_7BrO_2S$: C, 48.8; H, 2.4; S, 10.9. Found: C, 48.9; H, 2.6; S, 11.1.

The acidic filtrate of the reduction was basified with dilute sodium hydroxide and extracted with ether (3 x 500 ml.). Removal of the solvent gave yellow needles of 3-aminodibenzothiophene 5,5-dioxide (IV, X = NH_2) (2 g., 19%), m.p. 257-259° (Lit. (14) m.p. 259-260°).

Anal. Calcd. for $C_{12}H_9NO_2S$: C, 62.3; H, 3.95; N, 6.0; S, 13.8. Found: C, 61.9; H, 4.0; N, 6.2; S, 14.2.

3-Aminodibenzothiophene (III, X = NH_2).

This was obtained by modifying the above reduction. The method of Sandin (6) was followed with the addition of a 2.5-hour reflux period before the prescribed 12 hours standing at room temperature. A yield of 45% (3.6 g.) of 3-aminodibenzothiophene, m.p. 121-122° was thus obtained; NMR δ 3.77 (s, NH_2), 6.74 (dd, $J_{2,1}$ 8 Hz, $J_{2,4}$ 2.5 Hz, H-2), 7.03 (d, $J_{4,2}$ 2.5 Hz, H-4), 7.32 (m, H-7,8), 7.74 (m, H-6), 7.86 (d; $J_{1,2}$ 8Hz, H-1) and 7.92 (m, H-9).

Reduction of 3-Bromodibenzothiophene 5,5-Dioxide.

A solution of the previously prepared 3-bromodibenzothiophene 5,5-dioxide (50 mg.) in tetrahydrofuran (5 ml.) was treated with an excess of lithium aluminum hydride at room temperature over 1 hour. Water (30 ml.) was added slowly and the tetrahydrofuran was removed in an air stream. Extraction of the remaining aqueous solution with benzene (4 x 20 ml.) gave, upon evaporation, dibenzothiophene (28 mg., 91%), m.p. 93-95°, identified by comparison with an authentic sample.

3-Bromo-2-methyldibenzothiophene.

To a solution of 2-methyldibenzothiophene (1.75 g., 0.00882 mole) in carbon disulfide (20 ml.) was added a solution of bromine (0.48 ml., 0.00882 mole) in carbon disulfide (6 ml.) and the mixture was kept at room temperature for 18 hours. After a further 2-hour reflux the solvent was removed leaving a colorless semi-solid. Crystallization from ethanol gave the product as plates, m.p. 110-114°, (0.63 g., 26%). A further crystallization from ethanol raised the m.p. to 124-125° (0.43 g., 18%); NMR δ 2.51 (s, 2-CH_3), 7.37 (m, H-7,8), 7.73 (m, H-6), 7.84 (s, H-4), 7.90 (s, H-1), 8.0 (m, H-9).

Anal. Calcd. for $C_{13}H_9BrS$: C, 56.3; H, 3.3; Br, 28.8. Found: C, 56.0; H, 3.3; Br, 29.0.

3-Acetyldibenzothiophene (III, X = $COCH_3$).

3-Lithiodibenzothiophene was prepared by treating a stirred solution of 3-bromodibenzothiophene (5) (0.4 g., 0.00152 mole) in ether (10 ml.) under an atmosphere of dry nitrogen at 0° with butyllithium (0.92 ml., 0.00152 mole) for 2 minutes. *N,N*-Dimethylacetamide (0.142 ml., 0.00152 mole) was then introduced and the solution refluxed for 2 hours. A mixture of water (10 ml.) and hydrochloric acid (18% 1.5 ml.) was added and the ether layer was separated. The aqueous phase was washed with ether (3 x 50 ml.) and the combined extracts successively washed with sodium bicarbonate solution and water. After drying the solvent was removed yielding III (X = $COCH_3$) as an oil which crystallized from benzene light petroleum (0.15 g., 44%), m.p. 106-113°. Crystallization from ethanol water raised the m.p. to 133.5-134.5; IR 6.0 (C=O), 6.3 (C=C), 12.0, 13.1, 13.6 and 14.2 μ (unassigned); NMR δ 2.67 (s, CH_3), 7.46 (m, H-7,8), 7.84 (m, H-6), 8.1 (m, H-9), 8.0 (d, $J_{1,2}$ 8 Hz, H-1), 8.16 (d, $J_{2,1}$ 8 Hz, H-2) and 8.43 (s, H-4).

Anal. Calcd. for $C_{14}H_{10}OS$: C, 74.3; H, 4.45. Found: C, 73.1; H, 4.5. (Insufficient sample for resubmission). M. W. (mass spectrometry) Calcd. 226. Found: 226.

Dibenzothiophene-3-carboxaldehyde (III, X = CHO).

N,N-Dimethylformamide (0.175 g., 0.185 ml., 0.0024 mole) in ether (5 ml.) was added to a solution of 3-lithiodibenzothiophene (0.0022 mole) in ether (5 ml.) and the mixture refluxed for 2 hours. The resultant solution was hydrolyzed with 3 *N* hydrochloric acid (2 ml.) extracted with ether (3 x 20 ml.) and the ether extracts were washed with 1 *N* hydrochloric acid and sodium bicarbonate. The extract was dried and the solvent removed. The resultant oil was crystallized from ethanol to yield III (X = CHO) as a pale yellow solid (0.17 g., 41%), m.p. 114-116°. An analytical sample from ethanol had m.p. 118-121°; IR 3.7 (aldehyde CH), 5.95 μ (C=O); NMR δ 7.5 (m, H-7,8), 7.86 (m, H-6), 7.91 (d, $J_{2,1}$ 8 Hz, H-2), 8.17 (m, H-9), 8.2 (d, $J_{1,2}$ 8 Hz, H-1), and 8.31 (s, H-4), 10.08 (s, CHO).

Anal. Calcd. for $C_{13}H_8OS$: C, 73.5; H, 3.8. Found: C, 73.4; H, 3.8.

3-Methyldibenzothiophene (III, X = CH_3).

A mixture of dibenzothiophene-3-carboxaldehyde (0.182 g., 0.000857 mole) and hydrazine hydrate (88% aqueous solution, 0.55 ml.) in diethylene glycol (2 ml.) was heated in an open vessel on a Woods metal bath until the temperature of the solution reached 160°. The solution was cooled to 60° and finely ground potassium hydroxide (0.173 g.) was added. The solution was refluxed for a further 1.5 hours (160-180°), poured into ice-water (50 ml.), extracted with ether (2 x 50 ml.) and the ethereal extracts dried. Removal of the solvent gave the product (0.145 g., 88%), m.p. 77-79°. An analytical sample from ethanol-water had m.p. 82-82.5°; NMR δ 2.45 (s, 3-CH_3), 7.2 (d, $J_{2,1}$ 7 Hz, H-2), 7.35 (m, H-7,8), 7.58), 7.58 (s, H-4), 7.78 (m, H-6), 7.97 (d, $J_{1,2}$ 7 Hz, H-1), 8.04 (m, H-9).

Anal. Calcd. for $C_{13}H_{10}S$: C, 78.75; H, 5.1. Found: C, 79.0. H, 5.1.

2,8-Dibromodibenzothiophene (V, X = Br).

To a solution of dibenzothiophene (10 g., 0.053 mole) in carbon disulphide (17 ml.) was added bromine (11 ml., 0.106 mole) over a period of 10 minutes with occasional cooling. The mixture was kept at room temperature for 1 hour, filtered and washed with ethanol. The filtered product (12.6 g., 67%) had m.p. 215-220°. Crystallization from acetic anhydride gave needles (11.5 g., 62%), m.p. 224-225° (Lit. (10) m.p. 225-226°).

Dibenzothiophene-2,8-dicarboxaldehyde (V, X = CHO).

A suspension of finely ground 2,8-dibromodibenzothiophene (3.42 g., 0.01 mole) in dry ether (50 ml.) stirred at 0° under nitrogen was treated with butyllithium (12 ml., 0.02 mole) for 5 minutes. *N,N*-dimethylformamide (1.69 ml., 0.022 mole) was added and the resultant mixture was refluxed for 1.5 hours and then allowed to stir at room temperature overnight. The solution was treated with hydrochloric acid (18%, 10 ml.) and water (50 ml.) and the ether removed in an air stream. The resultant yellow solid was filtered and washed with water (2.32 g., 97%), m.p. 214-220°. Crystallization from ethanol gave yellow needles (1.6 g., 69%) m.p. 230-231° (if placed in block at 220°). If the sample

was slowly heated melting did not occur by 360°; IR 6.0 (CHO), 6.4 μ (C=C).

Anal. Calcd. for $C_{14}H_8O_2S$: C, 69.9; H, 3.4. Found: C, 69.8; H, 3.5.

2,8-Dimethyldibenzothiophene (V, X = CH_3).

A mixture of dibenzothiophene-2,8-dicarboxaldehyde (0.412 g., 0.001714 mole) in diethylene glycol (4 ml.) and hydrazine hydrate (2.2 ml., 88% aqueous solution) was heated slowly in a Woods metal bath until the reaction solution reached 160°. The solution was cooled to 60° and finely ground sodium hydroxide (0.69 g.) was added. The mixture was gently refluxed for 1 hour, after which the solution was poured over ice (50 ml.) and extracted with ether (2 x 50 ml.). Removal of the solvent yielded the product which was crystallized from aqueous ethanol as plates (300 mg., 84%), m.p. 112-113°. An analytical sample had m.p. 119.5-121.5° (Lit. (7) m.p. 120.5-121.5°); NMR δ 2.51 (s, CH_3), 7.21 (dd, $J_{3,4}$ 7 Hz, $J_{3,1}$ 2 Hz, H-3,6), 7.66 (d, $J_{4,3}$ 7 Hz, H-4,6) and 7.88 (d, $J_{1,3}$ 2 Hz, H-1,9).

REFERENCES

(1) Contribution No. 1716, supported by a Public Health Service Grant GM-10366, to Indiana University. Since the completion of this study a paper on dibenzothiophenes has appeared by G. Vasiliu, A. Gioaba and O. Maior, (Univ. Bucharest, Bucharest, Rom.) *An. Univer. Bucuresti, Ser. Stiint. Natur., Chim.* 1966, 15 (2), 33-40 (Rom); *Chem. Abstr.*, 70, 77686F, (1969).

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

(3) A. Burger, W. B. Wartman and R. E. Lutz, *J. Am. Chem. Soc.*, 60, 2628 (1938); A. Burger and H. W. Bryant, *J. Org. Chem.*, 4, 119 (1939).

(4) H. Gilman and A. L. Jacoby, *ibid.*, 3, 108 (1938).

(5) G. Illuminati, J. Nobis and H. Gilman, *J. Am. Chem. Soc.*, 73, 5887 (1951).

(6) R. K. Brown, R. G. Christiansen and R. B. Sandin, *ibid.*, 70, 1748 (1948).

(7) R. Gerdil and E. A. C. Lucken, *ibid.*, 87, 213 (1965). Removal of aromatic halogens during lithium aluminum hydride reductions, while not common, has been encountered occasionally (*cf.*, E. Campaigne and R. C. Bourgeois, *J. Am. Chem. Soc.*, 76, 2445 (1954).

(8) A section of the infrared spectrum of this compound is reported without further details of source or physical constants by F. R. McDonald and G. L. Cook, U. S. Bureau of Mines, Rep. Invest., 6911 (1967).

(9) Ch. Courtot, L. Nicholas and T. H. Liang, *Compt. Rend.*, 186, 1624 (1928).

(10) E. D. Amstutz and C. R. Neumoyer, *J. Am. Chem. Soc.*, 69, 1925 (1947) and Ref. 9.

(11) P. Faller, *Bull. Soc. Chim. France*, 387 (1967).

(12) S. W. Osborn, Ph.D. Thesis, Indiana University, 1962.

(13) A. N. Fujiwara, E. M. Acton and L. Goodman, *J. Heterocyclic Chem.*, 5, 853 (1968).

(14) H. Gilman, A. L. Jacoby and H. A. Pacevitz, *J. Org. Chem.*, 3, 120 (1938).

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