

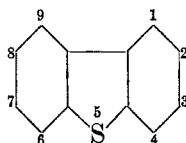
DIBENZOTHIOPHENE: ORIENTATION AND DERIVATIVES

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INTRODUCTION

The extensive studies by Courtot and by Cullinane have shown that halogenation¹, nitration,² and sulfonation³ involve the 2 position in dibenzothiophene.



This corresponds with related nuclear substitution reactions in the oxygen analog, dibenzofuran. However, nitration of dibenzofuran yields the 2- and the 3-nitro compounds, the latter greatly predominating. Disubstitution in dibenzothiophene proceeds symmetrically to give 2,8 derivatives like 2,8-dibromodibenzothiophene and 2-bromo-8-nitrodibenzothiophene.

Two other important nuclear substitution reactions are the Friedel-Crafts reaction and metalation. We have shown that acylation by the Friedel-Crafts reaction also involves the 2 position, as is the case with dibenzofuran.

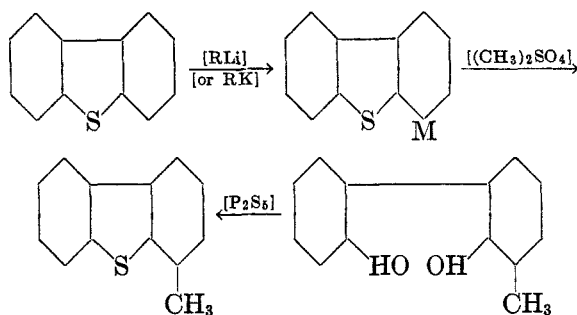
Metalation.—An examination of polynuclear heterocyclic compounds previously metalated, reveals that metalation of such types is unique in the sense that it makes possible the direct introduction of nuclear substituents into positions not otherwise available by direct substitution.⁴ Metalation of dibenzothiophene by RLi or RK compounds involves the 4 position, which again finds its counterpart in the dibenzofuran series. The structure of the new organolithium and -potassium compounds was established by the following sequence of reactions.

¹ COURTOT, NICOLAS, AND LIANG, *Compt. rend.*, **186**, 1624 (1928).

² COURTOT AND POMONIS, *ibid.*, **182**, 931 (1926); CULLINANE, DAVIES, AND DAVIES, *J. Chem. Soc.*, **1936**, 1435.

³ COURTOT AND KELNER, *Compt. rend.*, **198**, 2003 (1934).

⁴ See some leading references in the following paper.



The yields of 4-dibenzothiényllithium, or the corresponding dibenzothiophene-4-carboxylic acid obtained by carbonation, vary in a striking manner with the nature of the R group in the RLi compounds used as metalating agents.

METALATING AGENT	% YIELD OF 4-ACID
<i>n</i> -Butyllithium.....	55
Phenyllithium.....	12
α -Naphthyllithium.....	7.6
<i>p</i> -Anisyllithium.....	0

This series follows that obtained by Kharasch and co-workers⁵ in the cleavage of unsymmetrical organomercurials. However, the results obtained with *p*-anisyllithium may be anomolous, for the acid obtained subsequent to carbonation was shown to be largely 2-methoxy-5-bromobenzoic acid and only a small quantity of *p*-anisic acid was isolated.⁶ Apparently the *p*-anisyllithium metalates the unreacted *p*-bromoanisole used in its preparation. Metalation of dibenzothiophene by phenylcalcium iodide involves the 3 position. This is quite unlike the case of dibenzofuran which undergoes metalation in the 4 position by all metalating agents so far examined. Details on the metalation by phenylcalcium iodide are contained in the following paper.

1-Substituted dibenzothiophenes.—There is no method for the direct introduction of substituents into the 1 position. However, 1-substituted dibenzothiophenes were made available by the sequence of reactions shown on page 110.

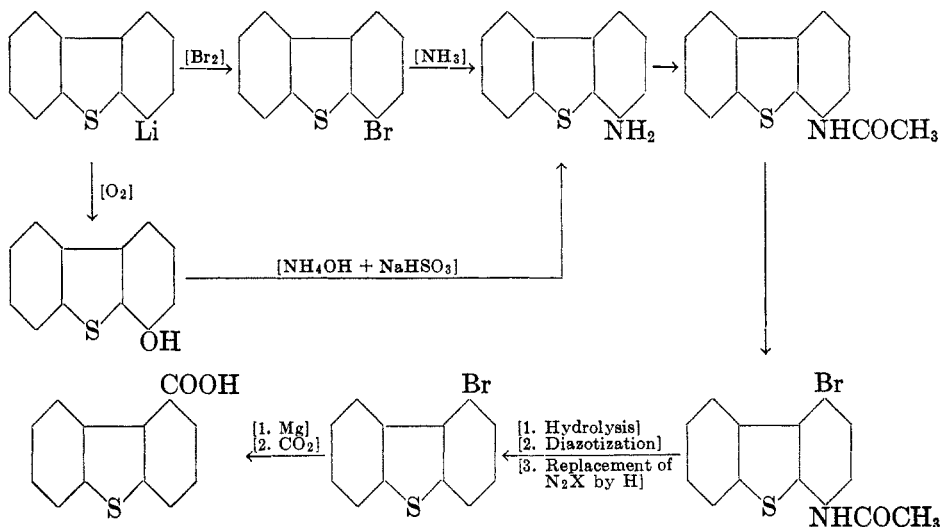
The constitution of the dibenzothiophenecarboxylic acid obtained in this manner was established by showing the acid to be unlike dibenzothiophene-3-carboxylic acid,⁷ the only possible alternative acid inasmuch as the struc-

⁵ KHARASCH AND FLENNER, *J. Am. Chem. Soc.*, **54**, 674 (1932).

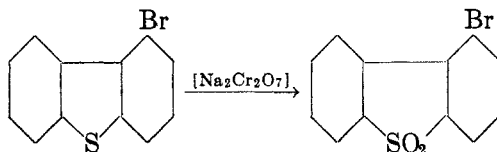
⁶ Studies by W. H. LANGHAM.

⁷ See following paper.

tures of the 2- and the 4-carboxylic acids were unequivocally established. Dibenzothiophene-2-carboxylic acid was prepared previously⁸ by carbonation of the Grignard reagent obtained from authentic 2-bromodibenzothiophene.



Also, the structure of the 1-bromodibenzothiophene was proved by oxidizing it to a bromodibenzothiophene-5-dioxide which was shown to be unlike the 2- and 3-bromodibenzothiophene-5-dioxides.



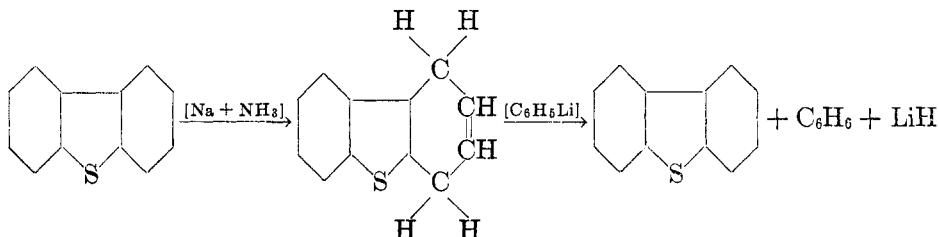
Dihydrodibenzothiophene.—Reduction of dibenzothiophene by sodium in liquid ammonia gives a dihydro compound which probably is 1,4-dihydrodibenzothiophene, by analogy to the behavior of dibenzofuran⁹ and naphthalene. The dihydro compound adds one molecule of bromine to give a dihydro-dibromide which loses hydrogen bromide to yield dibenzothiophene.

Of greater interest is the conversion of the dihydro compound to dibenzothiophene by means of organometallic compounds. When the dihydro-

⁸ COURTOT, NICOLAS, AND LIANG, *Compt. rend.*, **186**, 1624 (1928), and private communication from Professor Courtot.

⁹ STUDIES BY C. W. BRADLEY.

dibenzothiophene is treated with phenyllithium under conditions identical with those employed in metalations, a very smooth dehydrogenation occurs to yield dibenzothiophene, benzene, and lithium hydride.



The same dehydrogenation occurs with other highly reactive organo-metallic compounds such as RNa and RK types.

EXPERIMENTAL

Dibenzothiophene.—Dibenzothiophene was prepared in essential accordance with a method outlined in the patent literature.¹⁰ In a typical experiment, 500 g. of technical biphenyl and 208 g. of sulfur were melted together in a 5-l. round-bottomed flask, immersed in an oil bath. While the temperature of the bath was maintained at 115–120°, 25 g. of powdered, anhydrous aluminum chloride was added over a period of one and one-fourth hours. The temperature was kept at the 115–120° range until the end of the third hour and then gradually allowed to rise, reaching 240° at the end of the eighth or ninth hour. When cool, the mass in the reaction flask was extracted three times by boiling gently with 500 cc. of water, cooling, and decanting the water. Then eight alcohol extractions were made, boiling each time with a liter of alcohol and decanting hot. The combined extracts were digested with Norite and filtered immediately through a hot Büchner funnel. Upon cooling, almost colorless needles separated from the filtrate. Concentration of the liquors yielded additional dibenzothiophene. The crude compound usually melts as high as 98° and is suitable for many purposes. The yield is 65–70%. Distillation under reduced pressure (b.p., 152–154°/3 mm.) followed by crystallization from alcohol gives beautiful colorless needles melting at 99°. The highly purified compound prepared by distillation and recrystallization from alcohol gives maximum yields of metalation products and is strongly recommended for this type of nuclear substitution. The less pure compound was found satisfactory for other reactions.

The picrate, prepared in hot ethanol solution, crystallizes from ethanol as yellow needles melting at 125°.

Cullinane and Davies¹¹ reported recently the reduction of dibenzothiophene-5-dioxide to dibenzothiophene by means of sulfur. We were independently led to the same reaction by the observation of Courtot and Motamedi¹² that heating a mixture of selenium and diphenylene sulfone gave dibenzoselenophene. In a 25-cc.

¹⁰ TSCHUNKUR AND HIMMER, *D. R. P.* 579,917 (1933), [*C. A.*, **28**, 1053 (1934)].

¹¹ CULLINANE AND DAVIES, *Rec. trav. chim.*, **55**, 881 (1936).

¹² COURTOT AND MOTAMEDI, *Compt. rend.*, **199**, 531 (1934). Also, private communication from Professor Courtot.

Claisen flask was placed 5 g. (0.023 mole) of dibenzothiophene-5-dioxide and 0.9 g. (0.028 g. atom) of sulfur. A thermometer was dipped into the reaction mixture, and the flask was heated in a metal bath. The molten mass was heated at 320° for two and one-half hours, during which time sulfur dioxide and hydrogen sulfide were evolved. The temperature was then raised to 340° for an additional one-half hour, causing gentle boiling, and then heating was increased until 2.3 g. of distillate was collected. This crude product (m.p., 94–95°) was recrystallized and yielded 54% of dibenzothiophene.

2-Acetyldibenzothiophene.—A Friedel-Crafts reaction was carried out with 30 g. (0.16 mole) of dibenzothiophene, 225 cc. of dry carbon disulfide, 60 g. of powdered aluminum chloride and 13 g. (0.16 mole) of acetyl chloride to give a 70% yield of ketone, which when recrystallized from alcohol, melted at 111°.

Anal. Calc'd for $C_{14}H_{10}OS$: S, 14.2. Found: S, 14.1.

The oxime was prepared in almost quantitative yield by the procedure of Bachmann and Boatner,¹³ and melted at 160–161° after recrystallization from alcohol.

Anal. Calc'd for $C_{14}H_{11}NOS$: N, 5.81. Found: N, 5.55, 5.59.

2-Acetyldibenzothiophene was oxidized to dibenzothiophene-2-carboxylic acid by the method of Fuson and Tullock¹⁴ using iodine-potassium iodide and sodium hydroxide in dioxane as a medium. The acid (m.p., 253°) was converted to the methyl ester (m.p., 75°) by means of diazomethane, and identification was completed by comparison with an authentic specimen of the ester.

Methyl dibenzothiophene-2-carboxylate.—In the purification of 2-bromodibenzothiophene there is a significant loss by recrystallization. However, the less pure material, obtainable in 70% or greater yields, is satisfactory for reactions such as amination.

An activated magnesium was found desirable, but not necessary, for obtaining satisfactory yields of the corresponding Grignard reagent in reasonable time. Carbonation of the latter yields the 2-acid.

Methyl dibenzothiophene-2-carboxylate, prepared from the acid and diazomethane, melted at 74–75° after recrystallization from methanol.

Anal. Calc'd for $C_{14}H_{10}O_2S$: S, 13.2. Found: S, 13.5.

Dibenzothiophene-4-carboxylic acid by metalation.—Ten grams (0.054 mole) of dibenzothiophene in 75 cc. of ether was metalated by treatment with 0.1 mole of *n*-butyllithium in 75 cc. of ether. The reaction mixture was refluxed gently for 13 hours and then carbonated by pouring upon solid carbon dioxide. After removal of the excess carbon dioxide, the mixture was extracted with water, and the water layer was acidified with hydrochloric acid. Recrystallization from methanol gave a colorless acid melting at 252–253°.

Anal. Calc'd for $C_{13}H_8O_2S$: Neutral. equiv., 228.1; C, 68.38; H, 3.54; S, 14.1.

Found: Neutral. equiv., 237; C, 68.18; H, 3.80; S, 14.0.

The yield of acid is greatly diminished if the dibenzothiophene is not purified by distillation. When phenyllithium is used as the metalating agent the yield of acid is almost insignificant if the highly purified dibenzothiophene be not used. In the α -naphthyllithium metalation the α -naphthoic acid obtained subsequent to carbonation is readily removed from the dibenzothiophene-4-carboxylic acid by extraction with hot water.

Decarboxylation of dibenzothiophene-4-carboxylic acid.—About 0.1–0.2 g. of the acid was mixed with an equal quantity of copper powder and 2–3 cc. of quinoline

¹³ BACHMANN AND BOATNER, *J. Am. Chem. Soc.*, **58**, 2099 (1936).

¹⁴ FUSON AND TULLOCK, *ibid.*, **56**, 1638 (1934).

and heated in a test-tube immersed in a metal bath, in accordance with the usual procedure of Johnson. Gas evolution was apparent at 120°, and the bath was kept at 200° for one hour. Steam distillation from a solution acidified with sulfuric acid gave dibenzothiophene.

Methyl dibenzothiophene-4-carboxylate.—The methyl ester, prepared by means of diazomethane, melted at 95° after recrystallization from methanol.

Anal. Calc'd for $C_{14}H_{10}O_2S$: S, 13.2. Found: S, 13.1.

4-Methylthiophene.—A. By metalation. The dibenzothiophenyl-4-lithium was prepared in the usual manner by means of *n*-butyllithium and treated with an ether solution of dimethyl sulfate at room temperature until there was a negative color test. The reaction mixture was worked up in a customary manner to give the 4-methylthiophene which melted at 65° after recrystallization from dilute methanol.

Anal. Calc'd for $C_{13}H_{12}S$: S, 16.0. Found: S, 16.1.

B. By ring closure. In a small Claisen flask was placed a mixture of 2 g. of 3-methyl-2,2'-dihydroxybiphenyl and 1 g. of phosphorus pentasulfide. The flask was heated in a metal bath, the temperature being raised gradually from 165° (at which evolution of hydrogen sulfide set in) to 400° in 45 minutes, after which the heating was increased until a small quantity of colorless liquid distilled. The liquid solidified, and the solid was recrystallized from methanol to give small needles melting at 66.5°. A mixture with the methyl compound obtained by metalation (m.p., 65°) melted at 65.5°.

4-Hydroxythiophene.—A mixture of 0.5 mole of dibenzothiophenyl-4-lithium and 0.5 mole of ethylmagnesium chloride in ether was treated with oxygen (Ivanoff's procedure¹⁵). The temperature was kept below 3° by regulating the intake of oxygen, and a negative color test after 5 hours showed the reaction to be complete. Alkaline extraction and then acidification gave a 33% yield of the phenol, melting at 157–159°. Recrystallization from dilute methanol gave fine, colorless needles melting at 167°. The phenol gives a green color with ferric chloride solution.

Anal. Calc'd for $C_{12}H_8OS$: S, 16.0. Found: S, 15.9.

Dinitro-4-hydroxythiophene.—A 77% yield of the dinitro phenol was obtained by nitrating 0.5 g. of 4-hydroxythiophene in glacial acetic acid by concentrated nitric acid. The dark-orange, crystalline powder melted with decomposition at 204°. Recrystallization from glacial acetic acid did not raise the melting point.

Anal. Calc'd for $C_{12}H_6N_2O_5S$: N, 9.65. Found: N, 9.45.

4-Methoxythiophene.—A 94% yield of the 4-methoxy compound was obtained by reaction of 4-hydroxythiophene, dimethyl sulfate and sodium hydroxide. Recrystallization from alcohol gave heavy, colorless crystals melting at 123°.

Anal. Calc'd for $C_{13}H_{10}SO$: S, 15.0. Found: S, 14.9.

4-Aminothiophene.—A. By the Bucherer reaction. In accordance with a procedure by Fieser and co-workers¹⁶, 1.5 g. of 4-hydroxythiophene, 7.5 g. of sodium bisulfite, 15 cc. of water, 15 cc. of concentrated aqueous ammonia, and 7.5 cc. of dioxane were sealed in a Carius tube and heated for 11 hours at 200–210°. Upon opening the tube no pressure was noted and there was no darkening of the contents. The mixture was transferred to a separatory funnel with a little more than an equal volume of water, and the whole was extracted with ether. The ether

¹⁵ IVANOFF, *Bull. soc. chim.*, **39**, 47 (1926).

¹⁶ FIESER AND CO-WORKERS, *J. Am. Chem. Soc.*, **59**, 478 (1937).

extracts were dried over solid sodium hydroxide, and from the ether was then precipitated by dry hydrogen chloride, 0.4 g. (25% yield) of amine hydrochloride. After one recrystallization of the hydrochloride the free base was obtained by treatment with ammonia. The melting point, 110°, was not raised by recrystallization from methanol.

Anal. Calc'd for $C_{12}H_9NS$: N, 7.04. Found: N, 7.02.

B. By amination of 4-bromodibenzofuran. Ninety-two grams (0.5 mole) of dibenzothiophene was metalated by *n*-butyllithium. The mixture was then cooled in an icebath while nitrogen containing bromine vapor was passed slowly over the stirred surface. The nitrogen was first passed through a wash-bottle containing about 80 g. of bromine, and a slight pressure was maintained on the system by allowing the excess nitrogen to escape through the condenser against a 10 mm. head of mercury. In two and one-half hours the reaction was complete, as indicated by a negative color test. Excess bromine was removed by a bisulfite wash, and the ether solution was freed of solvent by distillation. The crude product, weighing 90 g., was directly aminated in portions as described below.

Into a steel bomb of 500 cc. capacity was introduced 25 g. of crude 4-bromodibenzothiophene, 20 g. of freshly prepared cuprous bromide, and 500 cc. of concentrated aqueous ammonia. The bomb was heated for 10-11 hours at 210-220°. When cool, the contents were transferred to a separatory funnel and extracted with ether. The washed and dried ether extract gave 8.3 g. of amine hydrochloride when saturated with dry hydrogen chloride. This crude salt represented a 37% yield on the basis that the starting material was pure 4-bromodibenzothiophene. The free base was obtained by treatment with aqueous ammonia, and purification was effected by treating a hot methanol solution with Norite and a pinch of sodium hydrosulfite (to prevent darkening by oxidation). The methanol solution was filtered hot, and diluted with hot water just to the point of turbidity. Slow cooling gave the pure amine.

4-Acetamidodibenzothiophene.—A practically quantitative yield of 4-acetamidodibenzothiophene was obtained by allowing a solution of the amino compound and acetic anhydride in benzene to stand overnight. On recrystallization from benzene the compound melted at 198°.

Anal. Calc'd for $C_{14}H_{11}NOS$: N, 5.82. Found: N, 5.93.

1-Bromo-4-acetamidodibenzothiophene.—Five grams (0.021 mole) of 4-acetamidodibenzothiophene was dissolved in 175 cc. of glacial acetic acid and treated with 22 cc. of a 0.1 molar solution of bromine in acetic acid. The addition required 30 minutes, and the solution was then stirred an additional hour before pouring into 800 cc. of water to which a little sodium bisulfite had been added. The yield was 86%, and the melting point after recrystallization from acetic acid was 254°.

Anal. Calc'd for $C_{14}H_{10}BrNOS$: N, 4.38. Found: N, 4.28.

1-Bromo-4-Aminodibenzothiophene.—Six grams of the acetamido compound was hydrolyzed by refluxing in a mixture of 450 cc. of absolute alcohol and 150 cc. of concentrated hydrochloric acid for 6.5 hours. The yield of free base, obtained from the salt by treatment with aqueous ammonia, was 5.5 g. On recrystallization from alcohol the amine melted at 156°.

Anal. Calc'd for $C_{12}H_9BrNS$: N, 5.04. Found: N, 5.01.

1-Bromodibenzothiophene.—The procedure used for deamination was essentially that of Cullinane¹⁷. To a solution of 2.25 g. of 1-bromo-4-aminodibenzothiophene in 63 cc. of alcohol was added cautiously a mixture of 13 cc. of oleum (20% sulfur

¹⁷ CULLINANE, *J. Chem. Soc.*, 1932, 2367.

trioxide) and 10 cc. of water. While the resulting solution was kept at 80°, 6 g. of sodium nitrite was added slowly. The reaction was then completed by refluxing for 30 minutes. Dilution of the reaction mixture with water, and cooling, gave a red solid which was filtered out, extracted with hot dilute sodium hydroxide and then with boiling alcohol, a small amount of Norite being added. From the hot, filtered alcoholic extract, after careful dilution with water and cooling, was isolated a 47% yield of 1-bromodibenzothiophene melting at 84° after recrystallization from dilute alcohol.

Anal. Calc'd for $C_{12}H_7BrS$: S, 12.2. Found: S, 11.7, 11.8.

1-Bromodibenzothiophene-5-dioxide.—To a cool solution of 7 cc. glacial acetic acid, 3 drops of concentrated sulfuric acid, 2 drops of water and 0.05 g. of sodium dichromate, was added 0.035 g. of 1-bromodibenzothiophene. On working up the oxidation product in the usual manner, there was isolated 0.024 g. (61% yield) of the dioxide, which melted at 170–171° after recrystallization from ethanol.

Anal. Calc'd for $C_{12}H_7BrO_2S$: S, 10.84. Found: S, 10.73.

Dibenzothiophene-1-carboxylic acid.—The Grignard reagent was prepared in the customary manner from 1-bromodibenzothiophene, using an activated magnesium, and then carbonated to give the acid which melted at 176–177° after recrystallization from methanol.

Anal. Calc'd for $C_{12}H_8OS$: Neutral. equiv., 228; S, 14.05.

Found: Neutral. equiv., 229; S, 13.9.

One-tenth gram of the acid was decarboxylated in the usual manner to give dibenzothiophene.

Methyl dibenzothiophene-1-carboxylate, prepared from the acid and diazomethane, melted at 72–72.5° after recrystallization from methanol. Because the melting point of this methyl ester is close to that of the methyl ester of the 2-acid (75°), a mixture melting point determination was made, and a marked depression was noted.

Anal. Calc'd for $C_{14}H_{10}O_2S$: S, 13.2. Found: S, 13.2.

Mercuration of dibenzothiophene.—Two attempts to mercurate dibenzothiophene by refluxing an alcoholic solution of dibenzothiophene and mercuric acetate gave no mercurial. Mercurous acetate was formed to some extent, and a large proportion of the original dibenzothiophene was recovered unchanged.

Mercuration was effected when the calculated quantity of mercuric acetate was slowly added to a melt of dibenzothiophene at 140–145°. Unfortunately, the product was much more difficult to purify than the products of mercuration of dibenzofuran. A milky suspension, which changed to an amber glassy resin, was obtained when the melt was poured into hot propanol. A more tractable solid was obtained when the material precipitated from propanol was digested briefly with chloroform. This product melted with decomposition at 215° and was probably the monomercorial admixed with some di-mercurial.

Anal. Calc'd for $C_{14}H_{16}HgO_2S$: Hg, 45.3. Found: Hg, 47.7, 48.5.

2-Acetamidodibenzothiophene.—A. By nitration, reduction and acetylation. This is the procedure first used by Courtot and Pomonis². However, since they gave no experimental details and since the melting point of our product was different from that of theirs, an outline of the procedure is given. The 2-nitrodibenzothiophene prepared in accordance with their directions was reduced to the 2-amino compound by treatment of a suspension of the nitro compound in alcoholic ammonia with zinc dust and ammonium chloride. A solution of 1.5 g. of the amine thus obtained, in 50 cc. of benzene, was treated with 1 cc. of acetic anhydride. On standing, the acetamido derivative separated and was removed by filtration. The compound

melted at 178° after recrystallization from benzene. It is possible that their reported melting point (168°) is due to a typographical error.

Anal. Calc'd for $C_{14}H_{11}NOS$: N, 5.81. Found: N, 5.64, 5.72.

B. By amination of 2-bromodibenzothiophene followed by acetylation. A mixture of 2 g. of 2-bromodibenzothiophene, 2 g. of cuprous bromide, and 15 cc. of concentrated aqueous ammonia was heated in a sealed tube for 8 hours at 200–225°. When cool, the contents of the tube were washed out, extracted with ether, and the ether extract was saturated with gaseous hydrogen chloride. A 62% yield of the amine hydrochloride was isolated. Aqueous ammonia liberated the amine which melted at 129° after recrystallization from methanol. The amine was acetylated as described above.

C. By the Beckmann rearrangement of the oxime of 2-acetyldibenzothiophene. A quantitative yield of crude acetamido compound was obtained when 40 g. of the oxime in 500 cc. of dry benzene warmed to 40° was treated with an equal quantity of phosphorus pentachloride. Crystallization of the acetamido compound from benzene containing a few drops of acetic anhydride to reconvert any free base to the acetyl derivative, gave yields of pure acetamino compound which averaged above 70%.

Nitro-2-acetaminodibenzothiophene.—Twenty grams (0.083 mole) of 2-acetamidodibenzothiophene was dissolved in 800 cc. of acetic anhydride by warming slightly. The solution was then cooled to 25°. Some solid separated during the cooling. Then with stirring, 15 cc. (0.36 mole) of fuming nitric acid was added over a 5 minute period, keeping the temperature at 25–27°. The red solution was allowed to stand 25 minutes and then poured into about 3 l. of ice and water. Recrystallization from methanol yielded 16 g. or 67% of nitro-acetamido compound melting at 208.5–209°. In several experiments, a less soluble material (3 to 4% yield) separated first from the methanol as yellow needles, and this melted at 250° with decomposition, after recrystallization from acetic acid.

Anal. (Compound, m.p., 208.5–209°) Calc'd for $C_{14}H_{10}N_2O_3S$: N, 9.79. Found: N, 9.74 and 9.80. (Compound, m.p. 250°): Calc'd for $C_{12}H_8N_2O_2S$: N, 11.5. Found: N, 11.3, 11.6.

The nitro-2-acetamidodibenzothiophene (m.p. 208.5–209°) was hydrolyzed in an attempt to determine whether the compound melting at 250° was the nitro-amino product. Five-tenths of a gram of the nitro-acetamido compound was refluxed for one and one-half hours in a mixture of 20 cc. of absolute alcohol and 20 cc. of concentrated hydrochloric acid. At the start all of the material was in solution, but the mixture gradually became turbid. An odor resembling acetaldehyde was noticeable at the top of the condenser. The mixture was poured into cold water, made alkaline with ammonium hydroxide, and the reddish solid was separated by filtration. The product (yellow needles) melted at 85–86° when first crystallized from methanol; then recrystallization from dilute acetic acid gave a colorless compound melting at 88° and free of nitrogen.

Anal. Found: S, 22.4, 22.4; C, 65.74, 65.78; H, 3.29, 3.32.

1,4-Dihydrodibenzothiophene.—To a solution of 10 g. (about 40% excess) of sodium in 600 cc. of liquid ammonia was added, slowly and with stirring, 30 g. (0.16 mole) of dibenzothiophene. The excess sodium and reaction products were ammonolyzed by the cautious addition of 50 g. of solid ammonium nitrate. The crude product, 26 g. or an 85% yield, was collected at 160–165°/6 mm. Losses upon recrystallization are large, and the melting point after recrystallization from methanol is 76°.

Anal. Calc'd for $C_{12}H_{10}S$: C, 77.36; H, 5.42.

Found: C, 77.44; H, 5.50.

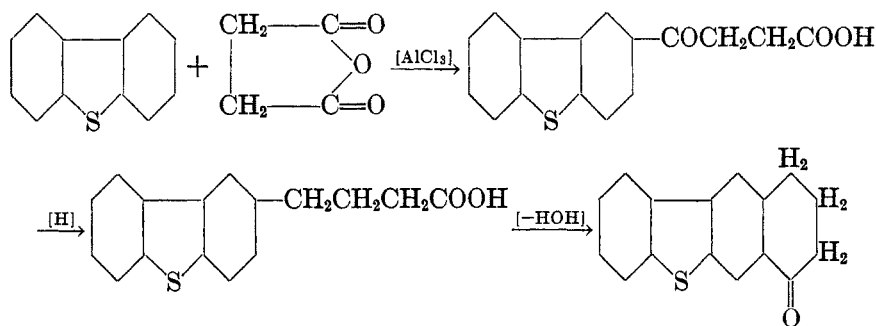
The picrate (red needles) melts at 105° after recrystallization from alcohol. Aqueous ammonia regenerates the dihydrodibenzothiophene.

One-half gram of the dihydro compound in 10 cc. of chloroform was cooled in an ice bath and treated cautiously with a solution of bromine in carbon tetrachloride until the faint color of bromine persisted. Nearly the theoretical amount of bromine was absorbed, and no hydrogen bromide was evolved. In one experiment when the solvents were removed under diminished pressure, and the residue was recrystallized from methanol, a nearly quantitative yield of dibenzothiophene was obtained. In another experiment the solvents were removed carefully and the oil remaining was kept cool for a long time without signs of crystallization. Evidently the bromine addition product is unstable and loses hydrogen bromide easily, as in the case of dihydronaphthalene.¹⁸

Dehydrogenation of 1,4-dihydrodibenzothiophene with RM compounds.—A. With phenyllithium. A filtered ether solution of phenyllithium (about 0.15 mole) was added to 10 g. (0.054 mole) of dihydrodibenzothiophene in 75 cc. of ether. The mixture was kept at 0° under nitrogen and immediately assumed a red color, which deepened during the first hour. After two hours a fine precipitate was visible, and after three hours the ice bath was removed, and the mixture was allowed to come to room temperature and remain there for one hour. It was then heated to reflux gently for 4 hours, cooled, and carbonated. The products isolated were 5 g. of benzoic acid, 1 g. of benzene (identified by its dinitro derivative) and 9 g. of dibenzothiophene.

B. With phenylisopropylpotassium. To 3 g. (0.016 mole) of 1,4-dihydrodibenzothiophene was added the phenylisopropylpotassium prepared from 0.035 mole of 2-phenylisopropyl methyl ether in accordance with the directions of Ziegler¹⁹. The mixture was refluxed for 7 hours, carbonated, and worked up in the usual manner to give 1 g. of dibenzothiophene. There was also obtained 2.8 g. of a crude acidic material which could not be crystallized to definite compounds. By analogy with dibenzofuran it appears quite probable that dehydrogenation first took place, followed by metalation of the resulting dibenzothiophene by the excess RK compound which, because of its high reactivity, may have given both mono- and polymetalation and therefore mono- and polybasic acids.

Keto-tetrahydrothiobrazan.—An interest in the biological properties of some polynuclear thienyl types, prompted the synthesis of thiobrazan derivatives. One of these was prepared by the following sequence of reactions.



¹⁸ BAMBERGER AND LODTER, *Ber.*, **20**, 1706 (1887).

¹⁹ ZIEGLER AND CO-WORKERS, *Ann.*, **473**, 18 (1929).

A. β -2-Dibenzothienylpropionic acid. Reaction was carried out with 92 g. (0.5 mole) of dibenzothiophene, 55 g. (0.55 mole) of succinic anhydride, suspended in a mixture of 400 cc. of tetrachloroethane and 200 cc. of nitrobenzene, and 150 g. (1.1 mole) of aluminum chloride. The temperature throughout the preparation was 0-5°, and hydrolysis was effected by ice and concentrated hydrochloric acid. The yield of pure β -2-dibenzothienylpropionic acid was 74 g. or 66%, and the compound melted at 160.5-161° after recrystallization from a large volume of ethyl acetate.

Anal. Calc'd for $C_{16}H_{12}O_3S$: Neutral. equiv., 284.2; S, 11.3.

Found: Neutral. equiv., 285; S, 11.1.

B. γ -2-Dibenzothiénylbutyric acid. Reduction of the keto acid was effected by Martin's²⁰ modification of the Clemmensen method. A mixture of 50 g. of amalgamated mossy zinc, 25 g. of the dibenzothienylpropionic acid, 38 cc. of water, 88 cc. of concentrated hydrochloric acid, 75 cc. of toluene and 3 cc. of glacial acetic acid was refluxed for 30 hours. At approximately 6-hour intervals, three 25-cc. portions of concentrated hydrochloric acid were added through the condenser. The solid obtained, after removing the toluene by steam distillation, was recrystallized from dilute methanol to yield 16 g. or 67% of acid melting at 131°. In addition, 3 g. of the original keto-acid was recovered.

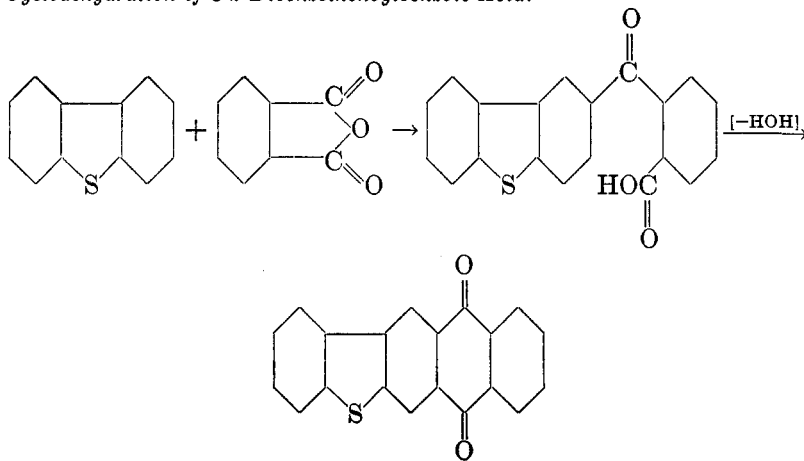
Anal. Calc'd for $C_{16}H_{14}O_2S$: Neutral. equiv., 270.2; S, 11.9.

Found: Neutral. equiv., 270; S, 11.4.

C. Cyclization of γ -2-Dibenzothiénylbutyric acid. Four grams of dibenzothiénylbutyric acid was dissolved in 100 cc. of 88% sulfuric acid and stirred for 15 minutes at room temperature. The deep-red solution was then poured upon ice and, after standing, the dilute acid was decanted from the green, tarry precipitate, which was washed with dilute sodium hydroxide, filtered, and dried. The thiobrazan melted at 178° after recrystallization from alcohol. Ring closure of the acid could lead to either the β - or γ -thiobrazan, the former by cyclization in the 3 position of dibenzothiophene and the latter by cyclization in the 1 position. In the reactions pictured at the beginning of this section we have indicated the more probable cyclization: namely, that in the 3 position leading to 1-keto-1,2,3,4-tetrahydro- β -thiobrazan.

Anal. Calc'd for $C_{16}H_{12}OS$: S, 12.7. Found: S, 12.6.

Cyclodehydration of o-2-Dibenzothienylbenzoic Acid.—



²⁰ MARTIN, *J. Am. Chem. Soc.*, **58**, 1438 (1936).

Reaction between 92 g. (0.5 mole) of dibenzothiophene, 82 g. (0.55 mole) of phthalic anhydride and 100 g. of aluminum chloride was carried out as in the preparation of the thio brazan. The crude *o*-2-dibenzothienoylbenzoic acid, melting with frothing at 120-125° and weighing 135 g. was probably an unstable hydrate. Part of it was converted to the ethyl ester by means of diazoethane. Recrystallization from petroleum ether (b.p., 60-68°) gave ethyl *o*-2-dibenzothienoylbenzoate melting at 105-106°.

Anal. Calc'd for $C_{22}H_{16}O_3S$: S, 8.91. Found: S, 9.04.

The *o*-2-dibenzothienoylbenzoic acid (3 g.) was cyclized by the procedure of Fieser and Fieser,²¹ by addition to a fused mixture of 4.16 g. of sodium chloride and 20.8 g. of aluminum chloride kept at 100-110°. The mixture was then heated at 150° for one-half hour. The benzothienyl-anthraquinone melted at 285-286° after recrystallization from glacial acetic acid.

Anal. Calc'd for $C_{20}H_{10}O_2S$: S, 10.2. Found: S, 10.2. As is the case with the thio brazan, cyclodehydration might occur in either or both of two positions. The reactions illustrated at the beginning of this section indicate the linear formula.

SUMMARY

The 1, 3, and 4 positions of dibenzothiophene have been made accessible, the latter two by metalation reactions. Organoalkali compounds have been used for the smooth dehydrogenation of 1, 4-dihydrodibenzothiophene to dibenzothiophene.

²¹ FIESER AND FIESER, *J. Am. Chem. Soc.*, **54**, 3749 (1932).