1955

Some reactions of the dibenzothiophene nucleus

Gene Ray Wilder
Iowa State College

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SOME REACTIONS OF THE DIBENZOTHIOPHENE NUCLEUS

by

Gene Ray Wilder

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

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Dean of Graduate College

Iowa State College

1955
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INTRODUCTION

The most commonly accepted numbering system for dibenzothiophene is the one adopted by Chemical Abstracts in 1937, shown by I. Another system found in the literature is that represented by II. Other names for dibenzothiophene encountered frequently in the literature are biphenylene sulfide and diphenylene sulfide.

\[
\begin{align*}
\text{I} & \quad \begin{array}{c}
\begin{array}{c}
\text{II} \\
\end{array}
\end{array} \\
\end{align*}
\]

The literature in this country conforms to the numbering system (I); however, when consulting the literature of other countries, the usual care should be exercised, i.e., by comparing references to described compounds and also chemical and physical properties of representative compounds.

An excellent review of dibenzothiophene covering the literature through 1952 is to be found in Hartough and Meisel

---

and a brief review in Elderfield. Additional material may be obtained by consulting the works of Jacoby, Avakian, Nobis, Esmay, and Ingham.

The purpose of this study is inherent in the physico-chemical nature of dibenzothiophene. The aromatic system, the distortion of the rings, the activating influence of the sulfur, and the capability of the sulfide linkage to be oxidized to the sulfoxide or sulfone which possess completely different sets of properties, make dibenzothiophene and its derivatives an interesting study.

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HISTORICAL

In the following literature survey, material will be given so as to be pertinent to the experimental and discussion, by analogously aiding in the prediction of the products resulting from the reactions, and in the identification of the compounds synthesized. The literature has been covered thoroughly through 1953 and as completely as possible through May, 1955.

Preparation of Dibenzothiophene

Perhaps the best method for the preparation of dibenzothiophene is the reaction of biphenyl with sulfur in the presence of anhydrous aluminum chloride.\textsuperscript{8,9,10,11} Other laboratory methods of importance include the reaction of

\begin{itemize}
\item German Patent 579,917 [\textit{G. A.}, 28, 1053 (1934)].
\item Belgian Patent 390,439 [\textit{G. A.}, 27, 2696 (1933)].
\item F. Muth and B. Putzer, PBL 63,936, Fiat Microfilm Reel C60, PB 17,657.
\end{itemize}
phosphorus pentasulfide with 2,2'-dihydroxybiphenyl,\textsuperscript{12,13} and the tetrazotization of 2,2'-diaminobiphenyl followed by treatment with potassium hexathiocyanatochromate(III) and subsequently with potassium chloride.\textsuperscript{14} Another method involves the use of very basic reagents such as phenylsodium or phenyllithium on diphenyl sulfide.\textsuperscript{15} Additional procedures include the reduction of the 5-oxide with mild reagents such as stannous chloride and hydrochloric acid\textsuperscript{16}, by ethylmagnesium bromide\textsuperscript{17}, and by \textit{n}-butyllithium\textsuperscript{18}. The reduction of dibenzothiophene-5-dioxide is much more difficult and requires a strong reducing agent such as lithium aluminum hydride\textsuperscript{19}, or molten sulfur\textsuperscript{20}.

\textsuperscript{12}German Patent 330,833 [\textit{Chem. Zentr.}, 22, 265 (1921)].
\textsuperscript{13}N. Cullinane, C. Davies and G. Davies, \textit{J. Chem. Soc.}, 1435 (1936).
\textsuperscript{14}H. W. Schwesten, \textit{Ber.}, 65, 1608 (1932).
\textsuperscript{15}A. Luttinghaus and G. W. von Saßf, \textit{Ann.}, 557, 25 (1945).
\textsuperscript{17}C. Courtot and C. Pomonis, \textit{Compt. rend.}, 182, 893 (1928).
\textsuperscript{19}F. G. Bordwell and W. H. McKellin, \textit{ibid.}, 73, 2251 (1951).
Reduction of Dibenzothiophene

Dibenzothiophene may be reduced by sodium in liquid ammonia to yield 1,4-dihydridibenzothiophene.\textsuperscript{11} Catalytic reduction with hydrogen using cobalt sulfide or molybdenum sulfide yields partially and completely hydrogenated biphenyls.\textsuperscript{21} Biphenyl may be obtained by refluxing dibenzothiophene with an excess of Raney nickel in ethanol.\textsuperscript{22}

Oxidation of Dibenzothiophene

The two most common methods employed for the preparation of dibenzothiophene-5-oxide are by the controlled oxidation of dibenzothiophene with hydrogen peroxide in glacial acetic acid\textsuperscript{23}, and by the action of stoichiometric amounts of chlorine on dibenzothiophene in an inert solvent followed by hydrolysis\textsuperscript{16}. The 5-oxide is also obtained as a byproduct in the nitration of dibenzothiophene in yields generally equal to that of the nitrated product.\textsuperscript{17}


\textsuperscript{22}F. F. Blice and D. G. Sheets, \textit{J. Am. Chem. Soc.}, 71, 4010 (1949).

There are several good methods for the preparation of dibenzothiophene-5-dioxide. The most convenient procedure is the oxidation of dibenzothiophene with hydrogen peroxide in glacial acetic acid.\(^23^{,24,25}\) Chrome acid has also proved effective in the formation of the sulfone.\(^26,27\) Another method of some limitation is by the cyclization of biphenyl-2-sulfonyl chloride.\(^26\)

Alkyl and Aryl Derivatives

The only monomethyl derivative of dibenzothiophene which has been synthesized is the 4-isomer.\(^11\) This was prepared by the action of 4-dibenzothiophenyllithium on dimethyl sulfate, and also by the reaction of 3-methyl-2,2'-dihydroxypiphenyl with phosphorus pentasulfide.

Several 2-alkyl derivatives have been prepared from the corresponding acyl analogs by a Clemmenson reduction.\(^28\)

\(^{25}\)W. Herzog and J. Kreidl, *Ber.*, 85, 3394 (1922).
2-Vinyl dibenzothiophene has been prepared by the reduction of 2-acetyldibenzothiophene followed by dehydration of the resulting alcohol.\textsuperscript{29} This material was used in connection with polymerization studies.

No aryldibenzothiophene derivatives of known structure have been reported.

**Halogen Derivatives**

The only attempted chlorination of dibenzothiophene that has been reported was conducted at low temperatures in an inert solvent; however, this resulted in the formation of the chlorosulfonium chloride instead of any nuclear substitution.\textsuperscript{16} 1-Chlorodibenzothiophene has been prepared by the action of hydrochloric acid and ethanol on 1-nitro-2-acetamidodibenzothiophene or on 1-nitro-2-aminodibenzothiophene.\textsuperscript{30} It has also been prepared by the deamination of 1-chloro-2-aminodibenzothiophene.\textsuperscript{31} 2-Chlorodibenzothiophene has been prepared by the reaction of 2-nitrodibenzothiophene


\textsuperscript{30}H. Gilman and G. R. Wilder, *ibid.*, 76, 2906 (1954).

and thionyl chloride\textsuperscript{32,33}, and also from 2-aminodibenzothiophene by the Sandmeyer reaction\textsuperscript{32,34}.

All of the monobromodibenzothiophene isomers have been prepared. 1-Bromodibenzothiophene has been synthesized by the bromination of 4-acetamidodibenzothiophene followed by hydrolysis and deamination.\textsuperscript{11} It has also been prepared by the action of ethanolic hydrobromic acid on 1-nitro-2-acetaminodibenzothiophene or on 1-nitro-2-aminodibenzothiophene.\textsuperscript{30} The direct bromination of dibenzothiophene affords 2-bromodibenzothiophene.\textsuperscript{13,32,34,35} It has also been prepared from 2-aminodibenzothiophene by the Sandmeyer reaction\textsuperscript{13,32,34}, and by the action of thionyl bromide on 2-nitrodibenzothiophene.\textsuperscript{32} When more than one equivalent of bromine is used in the bromination of dibenzothiophene, the resulting product is 2,8-dibromodibenzothiophene\textsuperscript{32,36}, which also results when dibenzothiophene-5-oxide is treated with


\textsuperscript{34}C. Courtot, \textit{Compt. rend.}, \textbf{198}, 2260 (1934).

\textsuperscript{35}French Patent 768,052 [\textit{C. A.}, \textbf{29}, 475 (1935)].

bromine. 3-Bromodibenzothiophene has been synthesized by use of the Sandmeyer reaction on 3-aminodibenzothiophene and also by the reduction of 3-bromodibenzothiophene-5-dioxide with lithium aluminum hydride. The bromination of 2-acetamidodibenzothiophene followed by hydrolysis and deamination affords another route for the preparation of 3-bromodibenzothiophene. The reaction of 4-dibenzothienyllithium with bromine affords a method for the synthesis of 4-bromodibenzothiophene.

The preparation of 2-iododibenzothiophene has been accomplished by means of the Sandmeyer reaction on 2-aminodibenzothiophene. 4-Iododibenzothiophene has been prepared in a manner similar to that of its bromo analog from 4-dibenzothienyllithium and iodine.

Nitrogen Derivatives

Since the primary interest of this work is concerned with nuclear substitution, only nitrogen functional derivatives attached to the rings will be considered.

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The four monosubstituted nitrodibenzothiophenes have all been synthesized. The nitration of 2-acetamidodibenzothiophene gives 1-nitro-2-acetamidodibenzothiophene, which, when hydrolyzed and deaminated with sulfuric acid, ethanol and sodium nitrite yields 1-nitrodibenzothiophene. Dibenzothiophene is nitrated in the 2-position accompanied by the competitive oxidation of dibenzothiophene to the oxide, regardless of whether sulfuric or acetic acid is used as a solvent. The cyclization of 2-amino-4-nitrodiphenyl sulfide could be considered an unambiguous synthesis of 2-nitrodibenzothiophene. Dibenzothiophene-5-oxide or the corresponding sulfone can be nitrated with substitution taking place in the 3-position. 3-Nitrodibenzothiophene has been prepared by the reduction of its 5-oxide with hydrobromic acid in acetic acid.

The nitration of 2-benzenesulfonamido or 2-benzamido-dibenzothiophene affords 2-amino-3-nitrodibenzothiophene

upon hydrolysis of the resulting amides. The nitration of 3-acetamidodibenzothiophene gives 4-nitro-3-acetamidodibenzothiophene, which when hydrolyzed and deaminated affords 4-nitrodibenzothiophene. 45

The catalytic reduction of 1-nitrodibenzothiophene described earlier with hydrogen, using Raney nickel as the catalyst, gives 1-aminodibenzothiophene. 30 Reduction of 2-nitrodibenzothiophene has been accomplished by several methods. Assuming one has pure nitro compound, the best method reported is by the catalytic reduction with hydrogen using Raney nickel. 7,41 Other methods for the reduction include zinc and ammonia, 13,17,32 tin and hydrochloric acid, 41 and also by iron filings and water. 13 Another method for the preparation of 2-aminodibenzothiophene is by the use of the Beckmann rearrangement on the oxime of 2-acetyldibenzothiophene and subsequent hydrolysis of the amide. 11,41,46 Direct displacement of 2-bromodibenzothiophene with ammonia in the presence of copper salts has also been reported. 10,11 The reduction of 2-nitrodibenzothiophene-5-dioxide to 2-aminodibenzothiophene-5-dioxide with stannous chloride and hydrochloric acid is reported to be nearly

quantitative.\textsuperscript{42} 3-Nitrodibenzothiophene-5-oxide can be reduced with stannous chloride and hydrochloric acid to give 3-aminodibenzothiophene.\textsuperscript{16} The synthesis of the 3-amino isomer has also been accomplished by the unusual reaction of 4-iododibenzothiophene with sodamide.\textsuperscript{24} The reaction of 4-dibenzothienyllithium and O-methylhydroxylamine affords good yields of 4-aminodibenzothiophene based upon the O-methylhydroxylamine used.\textsuperscript{39} 4-Aminodibenzothiophene has also been prepared by the Bucherer reaction on 4-hydroxydibenzothiophene\textsuperscript{11}, by the Hoffmann reaction on 4-dibenzothiophene-carboxylic acid amide\textsuperscript{23}, and also by the treatment of 4-bromodibenzothiophene with ammonia in the presence of copper salts\textsuperscript{11}.

**Hydroxyl Derivatives**

The synthesis of 2-hydroxydibenzothiophene has been accomplished by several methods. The reaction of 2-bromodibenzothiophene with alkali or alkaline earth hydroxide gives 2-hydroxydibenzothiophene.\textsuperscript{10,47,48} 2-Hydroxydibenzothiophene has also been prepared from 2-aminodibenzothiophene

\textsuperscript{47}German Patent 606,350 [C. A., 22, 1434 (1935)].

\textsuperscript{48}U. S. Patent 2,479,513 [C. A., 43, 9432 (1949)].
by treating an acid solution of the corresponding diazonium salt with superheated steam.\textsuperscript{10,13,49} An unambiguous synthesis was carried out by the cyclization of 2-amino-4'-methoxydiphenyl sulfide, followed by cleavage of the methyl group to give 2-hydroxydibenzothiophene. The oxidation of 4-dibenzothienyllithium with oxygen in the presence of either n-butylmagnesium bromide or ethylmagnesium bromide gives 4-hydroxydibenzothiophene.\textsuperscript{11}

**Carbonyl Derivatives**

No aldehydes of dibenzothiophene have been prepared.

The action of acetyl chloride in carbon disulfide in the presence of anhydrous aluminum chloride on dibenzothiophene gives as a major product 2-acetyldibenzothiophene and a small amount of 4-acetyldibenzothiophene.\textsuperscript{11,41,46,50} Several 2-acetyldibenzothiophenes have been prepared directly

\textsuperscript{49}German Patent 591,213 [Chem. Zentr., 115, 2196 (1934)].

by Friedel and Crafts-type reactions. The carbonation of 4-dibenzothienyllithium, which had been prepared by metalation with \( \text{\textit{N}} \)-butyllithium, gave as a by-product 4-valerilyldibenzothiophene. This was also prepared by the reaction of 4-dibenzothienyllithium on valeric anhydride.

Carboxyl Derivatives

All four monosubstituted carboxylic acids of dibenzothiophene are known.

The reaction of 1-bromodibenzothiophene with magnesium followed by carbonation affords 1-dibenzothiophene-carboxylic acid. The first preparation of 2-dibenzothiophene-carboxylic acid was accomplished by the treatment of 2-bromodibenzothiophene with magnesium followed by carbonation. The hydrolysis of 2-cyanodibenzothiophene, and the sodium

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52 Ng. Ph. Buu-Hoif et al., ibid., 68, 473 (1949).


54 French Patent 614,959 [Chem. Zentr., 95, 797 (1924)].

hypohalite oxidation of 2-acetyldibenzothiophene\textsuperscript{11} have
also been used for the preparation of the 2-acid. The
synthesis of 3-dibenzothiophenecarboxylic acid was achieved
by an apparent anomaly. The metalation of dibenzothiophene
with phenylcalcium iodide followed by carbonation yields the
3-acid, instead of the usual metalation product ortho to the
heterocatom.\textsuperscript{40} The treatment of dibenzothiophene with the
usual metalation reagents followed by carbonation affords
4-dibenzothiophenecarboxylic acid. The best results are
obtained by using \textit{n}-propyl- or \textit{n}-butyllithium.\textsuperscript{6,11,40,56,57}
The 4-acid has also been prepared by the oxidation of 4-
acetyldibenzothiophene.\textsuperscript{50}

Sulfur Derivatives

The sulfonation of dibenzothiophene gives 2-dibenzo-
thiophenesulfonic acid.\textsuperscript{34} The acid chloride of this compound
was reduced with zinc and acetic acid to the corresponding
thiophenol, and this subsequently benzoylated. This was
compared with the thiobenzoate obtained by another series
of reactions which involved treating the diazonium salt of


\textsuperscript{57}H. Gilman and G. G. Stuckwisch, \textit{ibid.}, 67, 877 (1945).
2-aminodibenzo thiophene with potassium ethylxanthate followed by benzoylation.\textsuperscript{58} 2-Dibenzothiophenesulfonyl chloride may be reduced with zinc and acetic acid to form the sulfinic acid, and this may be further reduced with zinc to form bis-(2-dibenzothiienyl) disulfide.\textsuperscript{58} The reaction of thionyl chloride, dibenzothiophene and 2-dibenzothiophene-sulfonyl chloride in carbon disulfide with anhydrous aluminum chloride as a catalyst yields bis-(2-dibenzothiienyl) sulfoxide.\textsuperscript{58}

**Metallic Derivatives**

The major portion of the work that has been done on dibenzothiophene involving metalation has been with reagents of the alkali and alkaline earth types. Metalation almost always takes place in the 4-position, the only exception occurs with phenylcalcium iodide which metalates in the 3-position.\textsuperscript{40} Several reagents have been used to metalate dibenzothiophene. Yields, after carbonation of the organo-metallic compound, were reported as 4-dibenzothiophene-carboxylic acid. \(n\)-Propyllithium when used as a metalation

reagent gave a 75% yield of the 4-acid, and n-butyllithium
effected a 55% yield of the 4-acid. Aryllithium compounds
were relatively ineffective as metalating agents.11,59
Metalation with n-amylsodium gave a 23% yield of the
4-acid.60 The organomagnesium compounds have been made of
1-bromo-, 2-bromo-, and 2,8-dibromodibenzothiophene.32 The
mercuration of dibenzothiophene with mercuric acetate gave
a product which was thought to be mostly the 2-derivative
with a slight amount of impurity.11 A number of quite
stable silyl derivatives of dibenzothiophene have been pre-
pared by either metalation followed by treatment with the
silyl halide or by halogen-metal interconversion followed
by its reaction with the silyl halide.38,61 The silyl
derivatives of dibenzothiophene are easily oxidized with
hydrogen peroxide to the corresponding sulfones. Cleavage
studies were made on the silyl derivatives which indicated
that the silyl derivatives of the sulfones were much more
stable to acid cleavage than their analogous sulfides.
4-Trimethyl-silyldibenzothiophene-5-dioxide was nitrated

60 H. Gilman and R. L. Bebb, ibid., 61, 109 (1938).
with fuming nitric acid to afford a nitro-4-trimethylsilyl-
dibenzothiophene-5-dioxide, further indicating the stability
of this type of compound. 60

The metalation of dibenzothiophene-5-oxide with $n$-
butyllithium gave a 36% yield of 4-dibenzothiophenecar-
boxylic acid and a 11% yield of dibenzothiophene subsequent
to carbonation. 18 Dibenzothiophene-5-dioxide can be either
monometalated or dimetalated with $n$-butyllithium. 59

Derivatives of Dibenzothiophene

Table 1 is an extension of the derivatives of dibenzo-
 thiophene which do not appear in the compilations of Nobis 5,
Esmay 6, and Ingham 7. The new compounds reported in the
Experimental section of this thesis are also included.
Table 1
Derivatives of Dibenzothiophene

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<tr>
<th>Name of Compound</th>
<th>M.P. °C</th>
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<td>1-Acetamidodibenzothiophene</td>
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62 See Experimental section of this thesis.

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<td>2,8-Dicyanodibenzo thiophene</td>
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<td>n-Propyl-N-(4-nitro-3-dibenzo-thienyl)-carbamate</td>
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Dibenzothiophene-5-dioxides

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<td>1-Chlorodibenzothiophene-5-dioxide</td>
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<td>1-Methyldibenzothiophene-5-dioxide</td>
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<td>4-Methyldibenzothiophene-5-dioxide</td>
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<td>1-Trimethylsilyldibenzothiophene-5-dioxide</td>
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<td>1-Nitro-2-acetamidodibenzothiophene-5-dioxide</td>
<td>267</td>
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EXPERIMENTAL

Work which has been carried out in this laboratory during the course of this study which has been previously published\textsuperscript{30,31,44} will not be included in the Experimental section. All melting points are uncorrected and all reactions involving organometallic compounds were carried out in an atmosphere of oxygen-free, dry nitrogen.

Dibenzothiophene Derivatives

**Preparation of 2,8-dicyanodibenzothiophene**

This compound was prepared in accordance with the method of Koelsch and Whitney\textsuperscript{65} by a substitution reaction on the corresponding dibromo compound using copper(I) cyanide in quinoline at elevated temperatures.

A mixture containing 51.0 g. (0.149 mole) of 2,8-dibromodibenzothiophene\textsuperscript{32}, 35.0 g. (0.39 mole) of copper(I) cyanide and 200 ml. of freshly distilled quinoline was heated at a temperature between 190-200° for 20 hours under

an atmosphere of nitrogen. The contents were decanted into 1 liter of 6 N hydrochloric acid. Filtration and drying of the resulting residue gave 26.1 g. (74.5%) of reddish-brown material melting between 265-278º. Crystallization of this material from tetrachloroethane, using Norit-A yielded 20.2 g. (57.8%) of 2,8-dicyanodibenzothiophene melting at 337-338º.

The infrared spectrum of this material gave an absorption band at 4.3 µ, indicative of the cyano group.66


**Attempted oxidation of 2,8-dicyanodibenzothiophene**

The attempted oxidation of 2,8-dicyanodibenzothiophene was carried out in accordance with the procedure of Emsay18, using 30% hydrogen peroxide in glacial acetic acid.

A mixture containing 5.0 g. (0.0214 mole) of 2,8-dicyanodibenzothiophene, 62 ml. (0.60 mole) of 30% hydrogen peroxide and 75 ml. of glacial acetic acid was heated and stirred for a period of 1.5 hours. The mixture was then

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66 All infrared spectra were run on a Baird infrared spectrophotometer, property of the Institute for Atomic Research, Ames, Ia.
decanted into 200 ml. of cold water and then filtered to yield 4.9 g. (98.0% recovery) of 2,8-dicyanodibenzothiophene which gave no depression in melting point when admixed with starting material.

Attempted preparation of 2,8-dicyanodibenzothiophene-5-oxide

The procedure of Brown, Christensen and Sandin16 was used in an attempt to prepare the 5-oxide. This involves the treatment of the sulfide with chlorine in an inert solvent to form first the chlorosulfonium chloride, which is then hydrolyzed to form the oxide.

A solution of 5.0 g. (0.0214 mole) of 2,8-dicyanodibenzothiophene in 150 ml. of carbon tetrachloride was treated with 1.6 g. (0.025 mole) of chlorine. The mixture was allowed to stand for a period of 1.5 hours at room temperature and then shaken with 200 ml. of water. Concentration of the carbon tetrachloride layer afforded 4.7 g. (94.0% recovery) of material which gave no depression in melting point when admixed with the starting material.

Attempted preparation of 3-bromodibenzothiophene-5-oxide

The direct bromination of dibenzothiophene-5-oxide
yields 2-bromodibenzothiophene or 2,8-dibromodibenzothio-
phene as the main products depending upon the quantity of
bromine employed. The reduction of the 5-oxide is caused
by the hydrogen bromide formed by the initial bromination
of the oxide and then subsequently formed by the bromination
of dibenzothiophene itself. It was thought that, if some
oxidizing agent of sufficient strength to oxidize hydrogen
bromide at a more rapid rate than could the 5-oxide was
introduced, then bromination would take place, and in the
3-position. A reagent which has been used to oxidize hydroy-
gen bromide formed during the course of a reaction is
potassium chlorate. This was used in connection with
the bromination of ketones, where the presence of acid
promotes condensations.

A mixture containing 5.0 g. (0.025 mole) of dibenzo-
 thiophene-5-oxide, 1.2 g. (0.0083 mole) of potassium chlo-
rate, 50 ml. of glacial acetic acid and 5 ml. of water was
heated for a period of 3 hours. The mixture was then de-
canted into 100 ml. of water. Fractional crystallization
from an ethanol-methyl Cellosolve pair gave 3.1 g. (57.5%)
of material which melted at 228-229°, and gave no depression

in melting point when admixed with an authentic specimen of dibenzothiophene-5-dioxide. There was also obtained 0.6 g. (12.0% recovery) of dibenzothiophene-5-oxide.

**Preparation of 4-bromophenoxyacetic acid**

Since potassium chlorate in acetic acid was too strong as an oxidizing agent, another reagent was sought which would not oxidize dibenzothiophene-5-oxide but would oxidize bromide to bromine. Another sulfoxide was chosen because of its water solubility, low molecular weight and the ease with which its reduction product could be removed from the reaction system; this was dimethyl sulfoxide.

To establish the formation of some positive-type bromine radical resulting from the reaction of hydrobromic acid and dimethyl sulfoxide, phenol was introduced as a capture reagent, due to its ease of bromination.

A mixture containing 4.7 g. (0.05 mole) of phenol, 4.0 g. (0.051 mole) of dimethyl sulfoxide, 25.5 g. (0.15 mole) of 48% hydrobromic acid and 25 ml. of glacial acetic acid was refluxed for a period of 1 hour. The mixture was decanted into 75 ml. of saturated ammonium chloride solution

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68 The dimethyl sulfoxide was obtained as a gift from the Stephan Chemical Co., Chicago, Ill.
and the resulting mixture extracted with ether. The ether was removed by distillation leaving an oil. To the oily residue were added 9.5 g. (0.10 mole) of chloroacetic acid and sufficient 10% sodium hydroxide to make the mixture basic. The resulting solution was heated and the contents concentrated to near dryness. There was then added 50 ml. of water and the mixture was made acidic with dilute hydrochloric acid. The mixture was then filtered and the residue crystallized from water, using Norit-A to yield 5.9 g. (51.0%) of crude product melting between 139-152°. An additional recrystallization from water gave 4.2 g. (36.5%) of 4-bromophenoxyacetic acid melting at 158-160°, which gave no depression in melting point with an authentic specimen prepared by the reaction of 4-bromophenol, chloroacetic acid and sodium hydroxide. 69

Attempted oxidation of dibenzothiophene

Since both dibenzothiophene-5-oxide and dimethyl sulfoxide are of sufficient strength to convert bromide to bromine, there existed the possibility that dimethyl

sulfoxide could oxidize dibenzo thiophene. Although the equilibrium in solution might not be favorable for the formation of dibenzo thiophene-5-oxide, the volatility of dimethyl sulfide could effect the exchange reaction. The procedure of Bordwell\textsuperscript{70} was adapted for this experiment.

A mixture containing 5.0 g. (0.0274 mole) of dibenzo thiophene, 5.0 g. (0.064 mole) of dimethyl sulfoxide, 25 ml. of glacial acetic acid and 2 drops of concentrated sulfuric acid was refluxed for a period of 4 hours. The mixture was decanted into 75 ml. of water and the resulting residue was crystallized from ethanol to yield 3.7 g. (74.0\% recovery) of dibenzo thiophene melting at 97-98\textdegree.

\textbf{Attempted bromination of dibenzo thiophene}

Since the reaction of dimethyl sulfoxide, hydrobromic acid and phenol resulted in the formation of 4-bromophenol, it was thought that the reaction of dibenzo thiophene, hydrobromic acid and dimethyl sulfoxide might give 2-bromodi benzothiophene.

A mixture containing 9.2 g. (0.050 mole) of dibenzo thiophene, 4.0 g. (0.050 mole) of dimethyl sulfoxide, 25.5 g.

(0.15 mole) of 48% hydrobromic acid and 85 ml. of glacial acetic acid was heated at reflux for a period of 2 hours. The mixture was decanted into 150 ml. of water and the resulting precipitate filtered and dried to yield 6.7 g. of material which melted between 80-93°. This was crystallized from ethanol to give 5.4 g. (58.7% recovery) of dibenzothiophene which melted at 97-98°.

**Preparation of 1-methyldibenzothiophene**

Since the 1-derivatives of dibenzothiophene are rather inaccessible, the synthesis of 1-methyldibenzothiophene appeared to be best achieved by means of a halogen-metal interconversion reaction on 1-bromodibenzothiophene, in a manner used on 2-bromodibenzothiophene, and treating the resulting 1-lithio derivative with dimethylsulfate.

Into a 1-liter, three-necked, round-bottomed flask equipped with a mechanical stirrer and reflux condenser fitted to a nitrogen inlet were placed 15.5 g. (0.059 mole) of 1-bromodibenzothiophene and 250 ml. of anhydrous ether. To the mixture was added, at room temperature, over a 5-minute period, 0.060 mole of n-butyllithium contained in

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56 ml. of an ethereal solution. After 15 minutes, Color Test II\textsuperscript{72} was negative. One-half (0.029 mole) of this solution was added slowly to a mixture containing 5.0 ml. (0.054 mole) of dimethylsulfate dissolved in 100 ml. of ether. At the end of 30 minutes, Color Test I\textsuperscript{73} was negative. The mixture was hydrolyzed with water, the ethereal layer separated and dried over anhydrous sodium sulfate. The ether was removed by distillation to leave 3.5 g. of a semi-solid, which, upon recrystallization from ethanol gave a total of 2.5 g. (43.5\%) of 1-methyldibenzothiophene melting at 67-68°.

**Anal.** Calcd. for C\textsubscript{13}H\textsubscript{10}S: S, 16.17. Found: S, 16.01.

**Preparation of 1-dibenzothienyltrimethylesilane**

This compound was prepared in accordance with the procedure of Illuminati, Nobis and Gilman\textsuperscript{38}, used to prepare the isomeric 2- and 3-isomers. The 1-dibenzothienyllithium prepared in the previous experiment was used in this synthesis.

\textsuperscript{72}H. Gilman and J. Swiss, \textit{ibid.}, 62, 1847 (1940).

To 0.030 mole of 1-dibenzothienyllithium was added 7.0 g. (0.066 mole) of trimethylsilyl chloride contained in 30 ml. of anhydrous ether. The mixture was allowed to react at room temperature for a period of 3 hours after which time, Color Test I was negative. The mixture was hydrolyzed with water, the ethereal layer separated and dried over anhydrous sodium sulfate. The ether was removed by distillation and the oily residue vacuum distilled. The fraction boiling between 150-155°/0.25 mm. was collected to yield 4.1 g. (53.3%) of 1-dibenzothienyltrimethylsilane.

**Anal.** Calcd. for C\(_{15}\)H\(_{16}\)SiS: Si, 11.0. Found: Si, 10.8, 10.8.

**Preparation of 1-methyldibenzothiophene-5-dioxide**

The oxidation of 1-methyldibenzothiophene was carried out essentially in accordance with the procedure for the oxidation of dibenzothiophene, using 30% hydrogen peroxide in glacial acetic acid.\(^6\)

A mixture containing 1.5 g. (0.0076 mole) of 1-methyldibenzothiophene, 25 ml. of glacial acetic acid and 10 ml. of 30% hydrogen peroxide was refluxed for a period of 1 hour. The solution was then decanted into approximately 100 ml. of water and the resulting precipitate filtered.
The crude material was crystallized from ethanol to yield 1.5 g. (86.0%) of material melting between 190-192\(^\circ\). An analytical sample melted at 191-192\(^\circ\).

**Anal.** Calcd. for \(\text{C}_{13}\text{H}_{10}\text{O}_2\text{S}\): S, 13.92. Found: S, 13.78.

**Preparation of 1-Trimethylsilyldibenzothiophene-5-dioxide**

The oxidation of 1-dibenzothienyltrimethylsilane was carried out in a manner described previously.

A mixture containing 2.0 g. (0.0078 mole) of 1-dibenzothienyltrimethylsilane, 25 ml. of glacial acetic acid and 10 ml. of 30% hydrogen peroxide was refluxed for 1 hour and then decanted into 100 ml. of water. The crude residue was crystallized from ethanol to yield 2.1 g. of material melting between 109-119\(^\circ\). Recrystallization from methanol gave 1.9 g. (84.5%) of material melting at 138-139\(^\circ\).

**Anal.** Calcd. for \(\text{C}_{15}\text{H}_{16}\text{SiO}_2\text{S}\): Si, 9.74. Found: Si, 9.61, 9.54.

**Preparation of 2-Methyldibenzothiophene**

The 2-methyl derivative was prepared in a manner analogous to the synthesis of the 1-methyl derivative.
To a mixture containing 21.0 g. (0.080 mole) of 2-bromodibenzothiophene in 300 ml. of anhydrous ether was added 0.080 mole of n-butyllithium in 66 ml. of an ethereal solution. Color Test II was negative after 30 minutes. This mixture was added to a solution of 12.6 g. (0.1 mole) of dimethylsulfate in 150 ml. of anhydrous ether. Color Test I was negative after 30 minutes. The mixture was hydrolyzed with water and the ethereal layer separated and dried over anhydrous sodium sulfate. The ether was removed by distillation and the residue crystallized from ethanol to yield a total of 5.6 g. (35.4%) of 2-methyl dibenzothiophene melting at 88-89°.


Preparation of 2-methyl dibenzothiophene-5-dioxide

Two grams (0.010 mole) of 2-methyl dibenzothiophene, 50 ml. of glacial acetic acid and 10 ml. of 30% hydrogen peroxide were heated at reflux for 1 hour. The solution was decanted into approximately 100 ml. of water and the resulting precipitate filtered. The residue was crystallized from ethanol and then again from methanol to yield
1.2 g. (52.0%) of product melting at 199-200° and 1.0 g. of material melting between 197-199°.

**Anal.** Calcd. for C_{13}H_{10}O_{2}S: S, 13.93. Found: S, 13.85, 14.08.

**Preparation of 3-methyldibenzothiophene**

The 3-methyl derivative was made in a manner described previously. A halogen-metal interconversion was carried out on 3-bromodibenzothiophene and the resulting product treated with dimethylsulfate.

A mixture containing 9.1 g. (0.0346 mole) of 3-bromodibenzothiophene and 150 ml. of anhydrous ether was treated with 0.040 mole of n-butyllithium contained in 41 ml. of an ethereal solution. This gave a negative Color Test II after 30 minutes. The mixture was then added to a solution containing 5.0 g. (0.040 mole) of dimethylsulfate in 75 ml. of anhydrous ether. This was stirred for 1 hour, at the end of which time, Color Test I was negative. The product was worked up in the manner described previously to give 3.1 g. (45.2%) of 3-methyldibenzothiophene melting at 78-79°.

Preparation of 3-methyldibenzothiophene-5-dioxide

A mixture of 1.5 g. (0.0076 mole) of 3-methyldibenzothiophene, 10 ml. of 30% hydrogen peroxide and 20 ml. of glacial acetic acid was heated for 1 hour. This was treated with water and the resulting residue was filtered. This material was recrystallized twice from ethanol and once from methanol to yield a total of 1.3 g. (79.4%) of 3-methyldibenzothiophene-5-dioxide melting at 184-185°.


Preparation of 4-methyldibenzothiophene-5-dioxide

4-Methyldibenzothiophene was prepared by Jacoby³, however, the corresponding sulfone was not synthesized. A sample of Jacoby's 4-methyl derivative was purified and used in the following preparation.

Into a 125-ml. Erlenmeyer flask equipped with a reflux condenser were placed 0.57 g. (0.0029 mole) of 4-methyldibenzothiophene, 25 ml. of glacial acetic acid and 10 ml. of 30% hydrogen peroxide. The mixture was heated for 1 hour, decanted into water and the resulting precipitate filtered. Recrystallization from ethanol and then from methanol
yielded 0.31 g. (47.0%) of 4-methyldibenzothiophene-5-dioxide melting at 204-205°C.


Preparation of 2,8-dimethyldibenzothiophene

Into a 500-ml. three-necked, round-bottomed flask equipped with a mechanical stirrer and a reflux condenser fitted with a nitrogen inlet were placed 25.0 g. (0.073 mole) of 2,8-dibromodibenzothiophene and 300 ml. of anhydrous ether. To the stirred solution was added 0.15 mole of n-butyllithium. At the end of 30 minutes Color Test II was negative. To this solution was then added a mixture containing 9.2 g. (0.073 mole) of dimethylsulfate dissolved in 100 ml. of anhydrous ether. A negative Color Test I was obtained immediately after the dimethylsulfate had been added. The solution was hydrolyzed with water, the ethereal layer separated and washed with water. The ethereal solution was then dried over anhydrous sodium sulfate, filtered and the ether was removed by distillation. The oily product was crystallized from ethanol to yield 5.1 g. (32.8%) of crystals melting at 122-123°C.

Preparation of 2,8-dimethyldibenzothiophene-5-dioxide

Two grams (0.0094 mole) of 2,8-dimethyldibenzothiophene were refluxed with a solution containing 30 ml. of glacial acetic acid and 10 ml. of 30% hydrogen peroxide. The mixture was treated with water and the resulting residue was crystallized from methyl Cellosolve to yield 1.2 g. (52.1%) of 2,8-dimethyldibenzothiophene-5-dioxide melting at 290-292°C.


Preparation of 4,4'-bis(dibenzo thiophene)

This compound was prepared by two different methods. The first synthesis involved the use of the Ullmann reaction on 4-iododibenzothiophene\textsuperscript{74}, and the other method used was a modification of the procedure of Hall, Lesslie and Turner\textsuperscript{75}, using an organometallic compound on copper(II) chloride.

\textsuperscript{74} D. Fanta, Chem. Rev., 38, 139 (1946).
Run I. Into a flask, suspended in an oil-bath was placed 20.0 g. (0.00645 mole) of 4-iododibenzothiophene. The bath was heated, such that the temperature of the 4-iododibenzothiophene was about 200-210°. To this was added, in small portions, 8.5 g. (0.134 g. atom) of copper bronze over a period of 30 minutes. The reaction temperature was held at 200-220° for 2 hours and then the contents were decanted into sand. The resulting mixture was ground and then refluxed with ethanol. The residue that was not soluble in ethanol was refluxed with methyl Cellosolve and filtered. The filtrate was treated with Norit-A and refiltered. There was obtained 2.2 g. (18.7%) of 4,4'-bis(dibenzothiophene) melting at 189-90°.

Anal. Calcd. for C_{12}H_{8}S: S, 17.50. Found: S, 18.50, 17.63, 17.76.

Run II. A run with similar quantities of 4-iododibenzothiophene and copper bronze was made using a reaction temperature of about 260°. There was obtained 3.6 g. (30.5%) of 4,4'-bis(dibenzothiophene) melting at 189-190°.

Run III. Into a 1-liter, three-necked, round-bottomed flask equipped with a mechanical stirrer and a reflux condenser were placed 25.0 g. (0.136 mole) of dibenzothiophene and 200 ml. of anhydrous ether. To this was added 138 ml. of an ethereal solution containing 0.15 mole of n-butyllithium.
This mixture was allowed to react at room temperature for a period of 20 hours, at the end of which time, a negative Color Test II was obtained. This solution was added to a suspension of 18.6 g. (0.14 mole) of copper(II) chloride in 100 ml. of anhydrous ether. The mixture was refluxed for two hours and then 150 ml. of the ether was distilled from the flask. The concentrated mixture was refluxed for 30 minutes more, at the end of which time, a negative Color Test I was obtained. The contents were hydrolyzed with dilute hydrochloric acid and the remainder of the ether was allowed to evaporate. The residue was treated with several portions of dilute hydrochloric acid to remove remaining copper salts. The crude material was refluxed with ethanol and the residue containing the product was taken up in refluxing methyl Celloxolve and treated with Norit-A. There was obtained a total of 1.2 g. (4.8%) of 4,4'-bis(dibenzo-thiophene) melting at 189-190°, which gave no depression in a mixed melting point determination with the product obtained by the reaction of 4-iododibenzo thiophene and copper bronze.

**Preparation of 9,10-bis(4-dibenzo thienvl)9,10-enthradiol**

Into a 1-liter, three-necked, round-bottomed flask equipped with a mechanical stirrer and a reflux condenser
were placed 10.0 g. (0.048 mole) of 9,10-anthraquinone and 300 ml. of anhydrous ether. To the stirring slurry was added 0.1 mole of 4-dibenzothienyllithium (theoretical yield prepared by the metalation of dibenzothiophene with n-butyl-lithium) contained in 235 ml. of ether. The mixture was stirred at room temperature for 20 hours and then 200 ml. of ether was removed by distillation. To the system was added 100 ml. of anhydrous petroleum ether, b.p., 120-130°. The solution was refluxed for 8 hours, at the end of which time, a negative Color Test I was obtained. Hydrolysis with dilute hydrochloric acid followed by evaporation of the ethereal layer afforded 22.0 g. (79.8%) of crude product melting between 254°-257°. Crystallization from methyl Cellosolve gave 15.1 g. (54.5%) of material melting at 297-298°. Infrared analysis of this compound gave an absorption band at 2.9 μ, indicative of the -OH group and no band in the vicinity of 6 μ, indicating the absence of a carbonyl group.

**Anal. Calcd. for C_{19}H_{12}O_{8}: S, 11.12. Found: S, 10.85, 10.92.**

**Preparation of 1-chlorodibenzothiophene**

The synthesis of 1-chlorodibenzothiophene has been
accomplished by three different methods. 1-Nitro-2-acetamidodibenzothiophene or its corresponding amine may be refluxed with ethanol and hydrochloric acid to give 1-chlorodibenzothiophene. 2-Acetamidodibenzothiophene is chlorinated by sulfuryl chloride in chloroform to give 1-chloro-2-acetamidodibenzothiophene, which may be hydrolyzed and deaminated, to give the desired product. 1-Nitro-2-aminodibenzothiophene may be deaminated with a mixture containing ethanol, sulfuric acid and sodium nitrite to give 1-nitrodibenzothiophene, which in turn may be reduced to the corresponding amine. The amine may be used in a Sandmeyer reaction to give the 1-chloro isomer.

**From 1-chloro-2-aminodibenzothiophene.** Into a 250-ml. beaker were placed 2.5 g. (0.011 mole) of 1-chloro-2-aminodibenzothiophene, 50 ml. of ethanol, 20 ml. of water and 20 ml. of concentrated sulfuric acid. The mixture was warmed to approximately 60° and then 3.0 g. of sodium nitrite was added slowly. The mixture was transferred to a 250 ml. Erlenmeyer flask equipped with a reflux condenser and heated at total reflux for 30 minutes. This solution was decanted into 200 ml. of water and the resulting precipitate, filtered. The crude material was crystallized from ethanol using Norit-A to yield a total of 0.42 g. (17.5%) of 1-chlorodibenzothiophene melting at 88° and which gave no depression
in a mixed melting point determination with a sample of 1-chlorodibenzothiophene obtained by the ethanolic hydrochloric acid treatment of 1-nitro-2-acetamidodibenzothiophene.

From 1-aminodibenzothiophene. Into a 250-ml. beaker were placed 4.0 g. (0.0205 mole) of 1-aminodibenzothiophene, 100 ml. of water and 30 ml. of concentrated hydrochloric acid. The solution was cooled to approximately 0-5° and 1.4 g. of sodium nitrite contained in 15 ml. of water was added slowly. After stirring this solution for 15 minutes, it was added to a solution containing 6 g. of copper(I) chloride dissolved in 50 ml. of dilute hydrochloric acid. The combined mixture was heated for 30 minutes and then allowed to cool. The residue which formed was filtered and crystallized from ethanol to yield 0.71 g. (16.8%) of 1-chlorodibenzothiophene melting at 88°.

Preparation of 1-chlorodibenzothiophene-5-dioxide

A mixture containing 0.40 g. (0.0018 mole) of 1-chlorodibenzothiophene, 20 ml. of glacial acetic acid and 10 ml. of 30% hydrogen peroxide was refluxed for a period of 1 hour. The solution was decanted into water, the resulting precipitate filtered and crystallized from
ethanol to yield 0.40 g. (87.5%) of 1-chlorodibenzothiophene-5-dioxide melting at 187\(^\circ\).


**Preparation of 2-chlorodibenzothiophene**

This compound has been prepared by Courtot\(^{34}\), however, the melting point of his product did not correspond with the chloro isomer obtained by the deamination of 2-chloro-3-aminodibenzothiophene. The infrared spectrum of the chloro amine was almost identical with the infrared spectrum of 2-bromo-3-aminodibenzothiophene.\(^{44}\) The oxidation of the 2-chlorodibenzothiophene obtained by deamination afforded a sulfone which did correspond to the one obtained by Courtot, thus indicating that his 2-chloro product was impure.

Into a 125-ml. Erlenmeyer flask equipped with a reflux condenser were placed 1.0 g. (0.0043 mole) of 2-chloro-3-aminodibenzothiophene, 30 ml. of ethanol, 6 ml. of concentrated sulfuric acid and 4 ml. of water. To the refluxing solution was added 2.5 g. of sodium nitrite and the mixture heated for 30 minutes. The resulting sodium sulfate was filtered off and the crude chloro compound was precipitated
by the addition of water. This material melted at 116-119\(^\circ\); however, an additional recrystallization afforded 0.41 g. (43.0\%) of 2-chlorodibenzothiophene melting at 121-122\(^\circ\).

A small sample of this material was oxidized with 30\% hydrogen peroxide in acetic acid to give a compound which melted at 241-242\(^\circ\).

**Preparation of 3-chlorodibenzothiophene**

The synthesis of this compound was accomplished by means of a Sandmeyer reaction on 3-aminodibenzothiophene. The copper(I) chloride was freshly prepared by the procedure of Vogel.\(^76\) The nitrosyl sulfuric acid was prepared by the method of Hodgson and Walker.\(^77\)

Into a 250-ml. beaker were placed 5.0 g. (0.025 mole) of 3-aminodibenzothiophene and 60 ml. of glacial acetic acid. This mixture was added slowly, not allowing the temperature to rise above 10\(^\circ\), to 15 ml. of concentrated sulfuric acid containing 2.0 g. of sodium nitrite. This was stirred in an ice-bath for 15 minutes and then decanted

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into a solution containing 4.0 g. of copper(I) chloride in 60 ml. of concentrated hydrochloric acid. This was heated for a period of 30 minutes on a steam-bath and then decanted into 150 ml. of water. The residue thus formed was filtered and crystallized from ethanol to yield 0.72 g. (13.3%) of 3-chlorodibenzothiophene melting at 80-81°.


Preparation of 4-chlorodibenzothiophene

The 4-chloro isomer was prepared in a manner analogous to the preparation of the 3-isomer.

Into a 250-ml. beaker were placed 6.0 g. (0.03 mole) of 4-aminodibenzothiophene and 70 ml. of glacial acetic acid. This was added to a cooled solution of nitrosyl sulfuric acid (10% in excess of the amine), not allowing the temperature to rise above 10°. This mixture was added to a solution containing 5.0 g. of copper(I) chloride dissolved in 60 ml. of concentrated hydrochloric acid and heated on a steam-bath for 1 hour. The contents were then decanted into 300 ml. of water and the resulting residue was filtered and crystallized, using Norit-A to yield a total of 1.2 g. (18.4%) of 4-chlorodibenzothiophene melting at 84-85°.
**Anal.** Calcd. for C₁₂H₇Cl₂S: Cl, 16.21. Found: Cl, 16.08, 16.31.

**Preparation of 1-iododibenzothiophene**

This compound was prepared from 1-bromodibenzothiophene, by means of a halogen-metal interconversion followed by treatment of the 1-lithio derivative with iodine\(^{24}\).

Into a 500-ml., three-necked, round-bottomed flask equipped with a mechanical stirrer and a reflux condenser were placed 5.0 g. (0.019 mole) of 1-bromodibenzothiophene and 200 ml. of anhydrous ether. To the stirring solution was added 18 ml. of an ethereal solution containing 0.020 mole of \(n\)-butyllithium. After stirring for 5 minutes at room temperature, a negative Color Test II was obtained. This mixture was added to a solution containing 6.0 g. of iodine in 150 ml. of anhydrous ether and then allowed to react for an additional hour. Hydrolysis was effected with water and the ethereal layer separated. This layer was washed with sodium bisulfite and then dried over anhydrous sodium sulfate. The ether was removed by distillation leaving a semi-solid which was crystallized from ethanol to yield a total of 1.6 g. (27.1\%) of 1-iododibenzothiophene melting at 78-79\°.
Anal. Calcd. for C_{12}H_{7}S: S, 10.34. Found: S, 10.51, 10.56.

Preparation of 3-iododibenzothiophene

Into a 250-ml. beaker were placed 10.0 g. (0.0545 mole) of 3-aminodibenzothiophene and a solution of 3.5 ml. of concentrated sulfuric acid in 50 ml. of water. The mixture was cooled to 0-5° and then 3.45 g. of sodium nitrite, dissolved in 10 ml. of water, was added slowly from a burette. This mixture was stirred for 30 minutes and then decanted into a hot solution containing 15.0 g. of potassium iodide dissolved in 50 ml. of water. A small amount of copper bronze was added to catalyze the reaction and the contents were heated on a steam-bath for 1 hour. This was cooled and extracted with carbon tetrachloride. The extract was separated and washed with sodium bisulfite solution and the solvent subsequently stripped from the product. Several recrystallizations from ethanol yielded 2.1 g. (13.5%) of 3-iododibenzothiophene melting at 112-113°.

Anal. Calcd. for C_{12}H_{7}S: S, 10.34. Found: S, 10.56, 10.81.
Preparation of 2-nitrodibenzothiophene

This compound has been reported by Courtot and co-workers\textsuperscript{17,32}, but no experimental details were given. Cullinane and co-workers\textsuperscript{13} reported a 40% yield of 2-nitrodibenzothiophene using fuming nitric acid, however, Gilman and Nobis\textsuperscript{41} obtained yields in the range of 20-25%. Ingham\textsuperscript{7}, with a slight modification, obtained a yield of 30%. The following is a modification of Ingham’s procedure.

A suspension of 150 g. (0.815 mole) of dibenzothiophene in 1 liter of glacial acetic acid was cooled to approximately 20° in an ice-bath. To this was added 210 ml. of nitric acid (90%) over a period of 45 minutes, not allowing the temperature of the reaction mixture to rise above 23°. The mixture was allowed to react at this temperature for 2 hours and then at room temperature for an additional 1 hour. The resulting mixture was filtered and the residue washed by forming a slurry with ethanol and refiltering. The crude product was washed on the Böchner funnel with small portions of ethanol, and then dried to yield 60.1 g. (32.0%) of material melting between 183-185°. Pure 2-nitrodibenzothiophene has a melting point of 186°; however, the material obtained in the above manner is suitable for reduction with tin(II) chloride and hydrochloric acid.
Preparation of 2-aminodibenzothiophene

The reduction of 2-nitrodibenzothiophene has been carried out in several ways; however, the best yields from the nitro compound are obtained by the catalytic reduction using Raney nickel and hydrogen. This preparation has certain limitations with respect to the size of the run that may be carried out due to restrictions on the size of the hydrogenation facilities available. Another limitation to the use of catalytic hydrogenation is that, unless quite pure 2-nitrodibenzothiophene is used, the reduction appears to stop at some intermediate stage. The following is a modification that has been used to reduce 3-nitrodibenzothiophene-5-oxide to 3-aminodibenzothiophene.

To a mixture containing 35.0 g. (0.153 mole) of 2-nitrodibenzothiophene, m.p. 183-185°, and 200 ml. of glacial acetic acid was added a solution containing 139 g. (0.618 mole) of tin(II) chloride dihydrate in 140 ml. of concentrated hydrochloric acid. This mixture was heated to near reflux and stirred for 1 hour. It was then cooled in an ice-bath and the resulting precipitate filtered and washed with a mixture of concentrated hydrochloric and glacial acetic acids (1:1). The residue was treated with 300 ml. of water to which had been added 40 g. of sodium hydroxide.
The free base was collected by means of filtration through a sintered glass funnel. The crude amine was crystallized from ethanol to yield 22.6 g. (74.0%) of 2-aminodibenzothiophene melting at 120-121.5°. This material gave no depression in mixed melting point with an authentic specimen prepared by the catalytic reduction of 2-nitrodibenzothiophene.

Preparation of 2-diacetamidodibenzothiophene

This compound was prepared according to the procedure of Vogel76, for the preparation of diacetyl amides. Since some diacetamido compounds are unstable, the synthesis was undertaken to determine if a representative nuclear amine of dibenzothiophene could be diacetylated. It was also prepared to study its relative directive influence to electrophilic attack, as compared to the monoacetyl derivative.

A mixture containing 5.0 g. (0.0252 mole) of 2-aminodibenzothiophene, 50 ml. of benzene and 50 ml. of acetic anhydride was heated at reflux for 2 hours. Carbon tetrachloride was added to the system and the mixture distilled to remove excess acetic anhydride. The process was repeated with petroleum ether (b.p. 90-118°). Cooling followed by filtration and drying gave 4.5 g. (63.5%) of 2-diacetamido-
dibenzothiophene melting at 115-116°. The infrared spectrum of this compound gave no evidence for the presence of an -NH band.

**Anal.** Calcd. for C₁₆H₁₃NO₂S: C, 67.84; H, 4.62; N, 4.95. Found: C, 67.75, 67.77; H, 4.60, 4.68; N, 4.99, 4.87.

**Nitration of 2-diacetamidodibenzothiophene**

The nitration of 2-diacetamidodibenzothiophene was studied to investigate the added deactivation induced by a second acetyl group placed on 2-aminodibenzothiophene and to examine any noted difference in electrophilic substitution due to increased steric factors about the 2-position.

**Run I.** A mixture containing 3.5 g. (0.0124 mole) of 2-diacetamidodibenzothiophene, 130 ml. of glacial acetic acid and 2.6 ml. of nitric acid (90%) was stirred at room temperature for a period of 30 minutes. The mixture was decanted into 150 ml. of water and the resulting precipitate filtered and dried to give 1.1 g. (31.4% recovery) of 2-diacetamidodibenzothiophene, which gave no depression in melting point when admixed with the starting material.

**Run II.** A mixture containing 1.6 g. (0.0057 mole) of 2-diacetamidodibenzothiophene, 25 ml. of glacial acetic acid and 2.5 ml. of nitric acid (90%) was stirred at room
temperature for 1 hour. The mixture was decanted into 100 ml. of water and filtered. The residue weighed 0.3 g. (18.5%) and melted at 208–209°. This material gave no depression in melting point when admixed with an authentic specimen of 1-nitro-2-acetamidodibenzothiophene.\(^{30}\)

**Preparation of 1-bromo-2-(2-hydroxy-1-naphthaleneazo)dibenzothiophene**

The synthesis of this compound was accomplished in a manner analogous to the corresponding chloro compound.\(^{30}\)

Into a 125-ml. Erlenmeyer flask equipped with a reflux condenser were placed 1.8 g. (0.0056 mole) of 1-nitro-2-acetamidodibenzothiophene, 0.8 g. (0.0056 mole) of naphthol-2, 40 ml. of ethanol and 30 ml. of hydrobromic acid (30%). The mixture was refluxed for 20 minutes and then allowed to cool. The resulting precipitate was crystallized from methyl Cellosolve to give 1.1 g. (36.9%) of dark-red product which melted at 246–247°. The infrared spectrum of this compound was quite similar to that of 1-chloro-2-(2-hydroxy-1-naphthaleneazo)dibenzothiophene.\(^{30}\)

**Anal.** Calcd. for \(C_{22}H_{13}BrN_{2}O_S\): Br, 14.99. Found: Br, 14.87, 14.80.
Relative reaction times for the formation of 1-chloro-2-(2-hydroxy-1-naphthalenesazo)dibenzothiophene

To elucidate the reaction mechanism for the formation of this product from 1-nitro-2-acetamidodibenzothiophene, ethanol and hydrochloric acid, it was essential that the reaction be nitrite-catalyzed. This was accomplished by measuring the rate of formation of the red precipitate of product resulting from the coupling reaction.

Run I. To a nearly boiling mixture containing 0.8 g. (0.0056 mole) of naphthol-2, 40 ml. of ethanol and 30 ml. of concentrated hydrochloric acid was quickly added 0.8 g. (0.0028 mole) of 1-nitro-2-acetamidodibenzothiophene. This solution was immediately refluxed and the time measured from the introduction of the nitro compound to the formation of a red precipitate was approximately 6.5 minutes.

Run II. This run was similar to that of run I in all respects with the exception that 10 mg. of sodium nitrite was introduced 30 seconds after the nitro compound. The time measured from the introduction to the formation of the red precipitate was approximately 3.0 minutes.
Preparation of 1-nitro-2-acetamidodibenzothiophene-5-dioxide

This compound was prepared essentially in accordance with the method used for the oxidation of dibenzothiophene to dibenzothiophene-5-dioxide.18

A mixture containing 2.0 g. (0.0070 mole) of 1-nitro-2-acetamidodibenzothiophene, 15 ml. of 30% hydrogen peroxide and 35 ml. of glacial acetic acid was refluxed for 1 hour. This was decanted into 100 ml. of water and the resulting precipitate crystallized from ethanol to yield 1.7 g. (76.5%) of material which melted at 266-267°.

Anal. Calcd. for C14H10N2O5S: N, 8.82; S, 10.08. Found: N, 8.40, 8.50; S, 9.90, 9.89.

Preparation of 4-aminodibenzothiophene

This compound was prepared according to the procedure of Avakian39, with a slight modification and a slightly improved yield.

Run I. Into a 2-liter, three-necked, round-bottomed flask equipped with a reflux condenser and mechanical stirrer were placed 73.6 g. (0.40 mole) of dibenzothiophene and 300 ml. of anhydrous ether. To this mixture was added 0.43 mole of n-butyllithium contained in 306 ml. of an ethereal
solution. The reaction mixture gave a negative Color Test II after 24 hours. The contents were cooled to 0-5°C and added was 7.5 g. (0.16 mole) of O-methylhydroxylamine dissolved in 100 ml. of ether. This mixture was allowed to react for 2 hours and then hydrolyzed with water. The two layers were separated and the ethereal layer was dried over sodium sulfate. Dry hydrogen chloride was passed through the ethereal solution and the resulting hydrochloride filtered and dried to give 27.2 g. (86.7%) of 4-aminodibenzothiophene hydrochloride, melting with decomposition at 233-235°C. The hydrochloride was placed in water and made basic to liberate the free amine. This was crystallized from petroleum ether (b.p. 90-118°C) to yield 19.1 g. (72.4%) of 4-aminodibenzothiophene melting at 109-110°C.

**Run II.** Into a three-necked, round-bottomed, 1 liter flask equipped with a mechanical stirrer and reflux condenser fitted to a nitrogen inlet were placed 18.4 g. (0.10 mole) of dibenzothiophene and 300 ml. of anhydrous ether. To this mixture was added 0.11 mole of n-butyllithium contained in 76 ml. of an ethereal solution. Color Test II was negative after 20 hours. The 4-dibenzothienyllithium was added to a solution containing 8.4 g. (0.10 mole) of O-methylhydroxylamine hydrochloride in 200 ml. of anhydrous ether to which had been added 160 ml. of n-butyllithium
solution containing 0.3 equivalents of total base. A negative Color Test I was obtained 15 minutes after the addition of 4-dibenzothienyllithium and the mixture was then hydrolyzed. The ethereal layer was separated and dried over sodium sulfate. Dry hydrogen chloride was passed into the ethereal solution which resulted in the formation of a solid and an oil. The oil was separated and made basic with dilute sodium hydroxide. The oil which separated was distilled to give 2.1 g., (b.p. 75-77\(^\circ\)) of liquid which was not identified, but, which was believed to be \(n\)-butylamine. The solid obtained as a result of passing dry hydrogen chloride through the ethereal solution was worked up in the usual manner to give 3.5 g. (17.5\%) of 4-aminodibenzothiophene melting at 109-110\(^\circ\).

**Preparation of 4-benzoxyldibenzothiophene**

To a mixture containing 40.0 g. (0.39 mole) of benzonitrile in 300 ml. of anhydrous ether was added 0.248 mole of 4-dibenzothienyllithium (theoretical yield based upon original amount of dibenzothiophene metalated) contained in 435 ml. of an ethereal solution. The mixture became red and a precipitate formed; Color Test I was negative after 15 minutes. The mixture was then hydrolyzed with dilute hydro-
chloric acid. The ether was removed by distillation and the crude product crystallized from methyl Cellosolve to yield a total of 31.5 g. (44.0%) of 4-benzoyldibenzothiophene melting at 159-160°.


Preparation of 2-dibenzothiopheneboronic acid

This compound was prepared from 2-bromodibenzothiophene by first a halogen-metal interconversion reaction followed by treatment of the lithium derivative with triisopropyl borate.

Into a 1-liter, three-necked, round-bottomed flask equipped with a mechanical stirrer and reflux condenser were placed 13.0 g. (0.049 mole) of 2-bromodibenzothiophene and 200 ml. of anhydrous ether. To this mixture was added at room temperature, 0.050 mole of n-butyllithium in 38 ml. of an ethereal solution. Color Test II was negative after 15 minutes. The organometallic compound was slowly added to a mixture containing 20.0 g. (0.107 mole) of triisopropyl borate in 200 ml. of anhydrous ether, maintaining a reaction temperature of -60° by means of a Dry Ice-acetone bath. Within 30 minutes after the organometallic compound had
been added, Color Test I was negative. The mixture was allowed to come to room temperature and then hydrolyzed with water and the two layers separated. The ethereal layer was extracted with portions of dilute base and the basic solutions combined. This solution was heated to expel residual ether, allowed to cool and then acidified. The resulting precipitate was filtered and dried to yield 4.4 g. of crude material melting between 230-253°. This was crystallized from an acetone-water pair to yield 2.5 g. (22.3%) of 2-dibenzothiopheneboronic acid melting at 277-278°.

Anal. Calcd. for C\textsubscript{12}H\textsubscript{9}BO\textsubscript{2}: S, 14.06; neutral equivalent, 228.1. Found: S, 14.22; neutral equivalent, 230.1, 233.2.

**Preparation of 4-dibenzothiopheneboronic acid**

Forty-six grams (0.25 mole) of dibenzothiophene in 500 ml. of anhydrous ether was metalted with n-butyllithium (0.26 mole in 170 ml. of an ethereal solution). After a negative Color Test II had been obtained this solution was added slowly to a mixture containing 92.0 g. (0.40 mole) of tri-n-butyl borate in 300 ml. of anhydrous ether, maintaining a reaction temperature below -65°. At the end of the addition of the organometallic compound, Color Test I was
negative. The mixture was hydrolyzed with 10% sulfuric acid, the ethereal layer separated and the ether distilled off. The residue was made basic with 15% potassium hydroxide and the butanol removed by steam distillation. The remaining aqueous solution was filtered to remove any unreacted dibenzo-thiophene and the filtrate acidified. The residue was crystallized from an acetone-water pair to yield a total of 18.0 g. (31.6%) of material which melted at 337-339°. The infrared spectrum of this acid had an absorption band at 2.7 μ, indicative of an -OH group; however, a sample of the acid that was heated at approximately 120° for about 3 minutes gave no band in its infrared spectrum which would infer the presence of an acid. Therefore the observed melting point is probably that of the anhydride.

DISCUSSION

Structural Proofs

The problems concerning the structural proofs for dibenzothiophene derivatives, is for the most part, one involving position isomerism.

Structural characterizations for dibenzothiophene derivatives may be classified into five headings, namely ring closure methods from known derivatives of diphenyl sulfide or biphenyl, ring openings to known derivatives of biphenyl, direct synthesis of dibenzothiophene derivatives from known derivatives, indirect synthesis from compounds completing a series and by physical methods.

By ring closure

Viewing the structure of dibenzothiophene with regard to ring closure possibilities, the best routes appear to be those which start with either a derivative of diphenyl sulfide or a derivative of biphenyl. Since many compounds of both of these two molecular systems are known, they offer a good starting point for structure elucidations.
2-Nitro dibenzothiophene, which is usually prepared by the direct nitration of dibenzothiophene, has also been synthesized from a diphenyl sulfide derivative by Cullinane and co-workers.\textsuperscript{13}

\[
\begin{array}{c}
\text{H}_2\text{N} \quad \text{NO}_2 \\
\text{S} \\
\text{1. Diazotize} \quad \rightarrow \\
\text{2. Couple}
\end{array}
\]

Another reaction involving diazotization of a diphenyl sulfide derivative is the synthesis of 2-hydroxydibenzothiophene from 2-amino-4'-methoxydiphenyl sulfide.\textsuperscript{10} The synthesis of 2-nitro-4'-iodo-8-ethoxydibenzothiophene from 4'-ethoxy-2',6'-diiodo-4'-nitrodiphenyl sulfide and potassium hydroxide is another example of a synthesis through a diphenyl sulfide derivative.\textsuperscript{78}

Syntheses involving the use of a biphenyl derivative include the preparation of 4-methyl dibenzothiophene from 2,2'-dihydroxy-3-methylbiphenyl and phosphorus pentasulfide.\textsuperscript{11}

\[
\begin{array}{c}
\text{OH} \quad \text{HO} \quad \text{CH}_3 \\
\text{P}_2\text{S}_5 \\
\rightarrow \\
\text{CH}_3
\end{array}
\]

The synthesis of dibenzothiophene-5-dioxide has been accomplished by a Friedel and Crafts-type reaction on 2-biphenylsulfonyl chloride with aluminum chloride in carbon disulfide. Use was made of this reaction for the preparation of 2-bromodibenzothiophene-5-dioxide from 2-amino-5-bromobiphenyl. 79

1. Diazotize

\[
\text{Br} \quad \text{NH}_2
\]

2. KSCN

3. KMnO₄

4. PCl₃

\[
\text{Br} \quad \text{SO}_2\text{Cl}
\]

\[
\text{AlCl}_3
\]

The addition of chlorosulfonic acid to 4,4'-dibromobiphenyl gives 3,7-dibromodibenzothiophene-5-dioxide. 80


By ring opening

Dibenzothiophene-5-dioxide may be cleaved by sodium hydroxide to give sodium 2-biphenyl sulfonate, or under more drastic conditions with sodium hydroxide, 2-hydroxybiphenyl. Use of this reaction has been applied to the degradation of 2,8-dibromodibenzothiophene to 3,3'-dibromobiphenyl by first oxidation to the sulfone followed by cleavage to the sulfonic acid derivative and then by acid hydrolysis to 3,3'-dibromobiphenyl.

\[
\begin{align*}
1. & \quad \text{H}_2\text{O}_2, \text{HOAc} \\
2. & \quad \text{NaOH, heat} \quad \text{Br} \\
3. & \quad \text{HBr}
\end{align*}
\]

A reaction which may prove of some value in the degradation of dibenzothiophene derivatives is the use of Raney nickel in ethanol with the dibenzothiophene derivative to give the corresponding biphenyl.

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81 C. Courtot and M. Chaix, Compt. rend., 192, 1687 (1931).
By direct synthesis

Perhaps more derivatives of dibenzothiophene have been prepared in this manner than by any other method. If the structure of a certain isomer is known, whose functional group is attached to one of the rings, then reactions may be employed to bring about a replacement with a high degree of certainty. Since the four isomeric mono-bromo compounds have been synthesized, they afford a convenient route for the synthesis of other derivatives. The bromide ion may be displaced by certain other strong bases such as hydroxide or amide or a halogen-metal interconversion reaction may be run on the bromo compound. Since the rate of halogen-metal interconversion is more rapid than metalation it is safe to say that rearrangement to the 4-position is unlikely. Thus, a very reactive negative center is placed on any one of the four positions of dibenzothiophene to be used in an unambiguous synthesis. It has also the advantage of usually giving rather good yields of product. Since all of the mono substituted amines are known, they also afford a convenient method for the introduction of negative substituents by use of Sandmeyer-type reactions. Although the yields are not always impressive, it does afford an unambiguous synthesis.
The direct electrophilic attack on dibenzothiophene, the 5-oxide or the 5-dioxide may not be classified as unambiguous; however, it is of interest to note that with only one exception, all electrophilic reagents that have been tried on dibenzothiophene have substituted in the 2-position, and that all electrophilic attacks on the 5-oxide or 5-dioxide, providing they do not reduce the oxide to the sulfide linkage have entered in the 3-position. There are limitations to the use of dibenzothiophene-5-oxide in that it is easily reduced to the sulfide, which if in a solution with electrophilic reagents would be attacked in the 2-position. The limitation to the use of the 5-dioxide is that the rings are deactivated to such an extent that reagents such as bromine in acetic acid will not react with it. Driving conditions with strong electrophiles will react to give the 3-isomer.

*By indirect synthesis*

By indirect synthesis is meant here that the compound in question was the only mono derivative which had not been prepared or had been prepared from a compound which was the last in a series to be prepared. The structure of 3-dibenzo-thiophene carboxylic acid has not been established by any
type of unambiguous synthesis. It was prepared by the metala-
tion of dibenzothiophene by phenylcalcium iodide followed by
carbonation. At that time the other three mono carboxylic
acids as well as their esters were known. Since no geomet-
rical isomerism could exist, plus the fact that the elemental
analysis, the neutral equivalent, the infrared spectrum and
the fact that its methyl ester was different from the other
three esters, presented a very strong argument for the
existence of the 3-isomer.

The evidence for the structure of 1-chlorodibenzothiophene is indirect, as it has not been synthesized by
ring closure or ring opening. 2-Acetimidodibenzothiophene
was nitrated to give a compound which analyzed for a nitro-
acetimidodibenzothiophene. In an attempt to hydrolyze this
compound to the corresponding amine, there was obtained a
product which contained no nitrogen. Elemental analysis of
this material indicated a chlorodibenzothiophene had been
obtained. Since the only mono chloro isomer known at that
time was the 2-derivative, the reaction of nitro-2-acet-
amidodibenzothiophene with ethanolic-hydrobromic acid was
carried out. The product obtained from this reaction
proved to be 1-bromodibenzothiophene. The previously men-
tioned chlorodibenzothiophene obtained by the hydrolysis
of the nitro-acetimidodibenzothiophene gave an infrared
spectrum almost identical with that of 1-bromodibenzothio-
phene. Thus it was assumed the chloro product was 1-chloro-
dibenzothiophene. One way that the hydrolysis product could
be accounted for was to assume that the nitration of 2-
acetamidodibenzothiophene gave a 1-nitro derivative and that
a displacement of the nitro group had taken place. Hydroly-
sis could be effected to yield a nitro-2-aminodibenzothio-
phene if hydriodic acid or sodium hydroxide were used. This
amine could be deaminated to yield a nitrodibenzothiophene
which was different than the 2- or 3-isomers. Reduction of
the nitrodibenzothiophene gave an amine which was different
than the three known mono amines, and acetylation of the
amine gave an acetamidodibenzothiophene which was different
from the three other known isomers. The supposed 1-aminod-
dibenzothiophene was treated by a Sandmeyer reaction to give
a chlorodibenzothiophene which was the same as the chloro
compound obtained by the reaction of ethanolic-hydrochloric
acid on 1-nitro-2-acetamidodibenzothiophene. Perhaps the
best method for the establishment of a 1-isomer would be
by degradation rather than synthesis because the precursors
for any ring closure type reaction would involve a consider-
able amount of time and expense without any particular
advantage. The compound which would best lend itself to
degradation would be 1-methyl dibenzothiophene which,
upon treatment with Raney nickel would give 2-methylbiphenyl.

By physical methods

Besides the use of mixed melting point determinations for identification of dibenzothiophene derivatives, the use of spectrograms has been of considerable help in confirming structures.

Compounds containing the same number of π-electrons, with approximately the same geometrical arrangement and bound about equally tightly, in a planar conjugated system are called iso-π-electronic molecules. Analogous derivatives of iso-π-electronic molecules are spectrally similar. The ultraviolet spectrum of carbazole and dibenzothiophene are quite similar. The ultraviolet spectrum of

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4-nitrodibenzothiophene and that of 1-nitrocarbazole\textsuperscript{83} are very similar. The same holds true for 3-nitrocarbazole and 2-nitrodibenzothiophene. In like manner the infrared spectrum of 1-chloro- and 1-bromodibenzothiophene are almost identical. Some spectra of comparable dibenzothiophene and dibenzofuran compounds are also quite similar. Considering the great number of absorption bands given by any particular compound, the use of this spectral comparison should be classified as good evidence for a particular structure.

**Mechanistic Studies**

The nature of some reactions of dibenzothiophene derivatives has lead to the study of the course of these reactions. The previously mentioned reaction of 1-nitro-2-acetamidodibenzothiophene with ethanolic-hydrochloric or hydrobromic acids to give the corresponding 1-chloro- or 1-bromodibenzothiophene was studied to elucidate the mechanism.\textsuperscript{30} The identification of the products and reactants used was done by the use of indirect synthesis and by the use of infrared analysis. The reaction was first run with ethanolic-hydrochloric acid to give a mono-chloro product.

\textsuperscript{83}The 1-position of carbazole is equivalent to the 4-position of dibenzothiophene.
The reaction was then tried with ethanolic-hydrobromic acid to give a monobromodibenzothiophene which proved to be the 1-bromo isomer. The infrared spectrum of the chloro-isomer and the bromo-isomer were almost identical, therefore, it was assumed the chloro product was 1-chlorodibenzothiophene. Treatment of the nitro-2-acetamidodibenzothiophene with either ethanolic-hydriodic acid or with sodium hydroxide gave the normal product, namely, nitro-2-aminodibenzothiophene. As mentioned previously this nitro amine could be deaminated to give, upon subsequent reactions, several isomers of series that were completed with the exception of the 1-derivative. It was assumed then that nitration took place in the 1-position. During the course of the reaction between 1-nitro-2-acetamidodibenzothiophene and ethanolic-hydrochloric acid, the formation of acetaldehyde was noticed and this product was identified. The reaction of diazonium salts with ethanol to give acetaldehyde and reduction of the diazonium salt to the hydrocarbon is well known. Thus it was thought that a diazonium ion did play a role in the formation of 1-chlorodibenzothiophene. The reaction of 2-naphthol with diazonium salts is quite rapid, thus, 2-naphthol was added to the reaction mixture with the formation of a red product which analyzed correctly for 1-chloro-2-[2-hydroxy-1-naphthaleneazo]-dibenzothiophene. Since no
other source of nitrite was available for diazotization, it must have come from the nitro compound. Displacements of nitro groups during diazotization are to be found in the literature. 84-89 Recently it has been found that certain nitro amines undergo a chain reaction initiated by the displacement of a nitro group from the conjugate acid of nitro amines. 90-92 The formation of 1-chlorodibenzothiophene from 1-nitro-2-acetamidodibenzothiophene may be illustrated as follows:

\[
\begin{align*}
\text{\begin{figure}
\includegraphics[width=\textwidth]{image.png}
\end{figure}}
\end{align*}
\]

\[
\begin{align*}
\text{(1)}
\end{align*}
\]

85 G. T. Morgan, *ibid.*, 81, 1377 (1902).
91 L. Sihlbom, *ibid.*, 5, 790 (1953).
92 L. Sihlbom, *ibid.*, 5, 1197 (1953).
Equations (2) and (4) both are nitrite ion releasing; however, since very few reactions are known as that represented by equation (2) it can be safely assumed that it is a very slow reaction. Thus, the addition of nitrite ion at the start of the reaction should increase the rate at which
the 1-chlorodiazonium ion is formed. This was found to be true by the introduction of 2-naphthol to mixtures with and without the addition of nitrite. The reaction represented by equation (5) is one of the slow steps in the reaction as evidenced by coupling taking place in preference to reduction when 2-naphthol is added to the system.

Another reaction of dibenzothiophene derivatives of some interest is the reduction of the 5-oxide by hydrogen bromide to give dibenzothiophene, which if left in solution is brominated in the 2-position. The direct halogenation of dibenzothiophene-5-oxide in the 3-position would be very helpful from a synthesis viewpoint. If an oxidizing agent were added to a mixture of bromine and dibenzothiophene-5-oxide such that the hydrogen bromide formed during the bromination could be oxidized at a faster rate than it could reduce the 5-oxide, then bromination would probably be effected, and in the 3-position. Potassium chlorate proved to be too strong as it oxidized the 5-oxide to the dioxide and dimethyl sulfoxide was not strong enough as an oxidizing agent in the bromination of dibenzothiophene. A mixture of dimethyl sulfoxide and hydrobromic acid was however effective in brominating phenol. If a sulfoxide exists which will aid in the bromination of dibenzothiophene-5-oxide, there will
probably be groups attached to the sulfur, somewhat electron withdrawing.

Another problem of some interest involves the nitration of dibenzothiophene and the resulting formation of approximately equal amounts of nitro compound and 5-oxide. If some reagent could be added that would be oxidized at a more rapid rate than dibenzothiophene and yet not be nitrated or consume the nitronium ion, then nitration would give higher yields of the nitro compound. A sulfinic acid or a dialkyl sulfide may be compounds of choice.

The reduction of dibenzothiophene-5-dioxide with sulfur proved to be a more complex reaction than originally anticipated. Reduction using the isotope of sulfur with an atomic weight of 35 gave dibenzothiophene containing radioactive sulfur. Less than 4% of the radioactive sulfur could be accounted for in the sulfur dioxide evolved. The replacement rather than simple reduction takes place.

A reaction which is yet not definitely established is the mode of metalation of dibenzothiophene-5-oxide with n-butyllithium. The oxide is reduced and metalated to give upon carbonation dibenzothiophene and 4-dibenzothiophene-carboxylic acid. A coordination complex was postulated for the metalation instead of reduction followed by metalation because dibenzothiophene is not metalated under the conditions of the experiment. The oxidation of
n-butyllithium should result in the formation of n-butanol, however, none has ever been isolated. A reaction that should be tried before excluding the reduction followed by metalation possibility, is the metalation of dibenzothiophene in the presence of an equivalent amount of lithium butoxide.

**Directive Influence of Substituents**

As a general rule, when considering electrophilic attack on mono substituted dibenzothiophene derivatives, the attack will be in the same ring if the substituent present is electron donating and will occur in the other ring if the group is electron withdrawing. Border-line cases such as halogens direct to the other ring even though they are ortho- and para-directing. It would be of some interest to study the effects of alkyl substituents. If the group is electron withdrawing the incoming electrophile is directed to the 8-position, which is comparable to the 2-position in the ring previously substituted.

Substitutions within the same ring have been studied to a greater extent than those involving substitution in both rings. A group which is very convenient to study is the acetamido group because of its relative ease of removal after substitution has been accomplished. Electrophilic
substitutions on 1-acetamidodibenzothiophene have not been studied; however, it might be predicted that chlorination and nitration would go predominantly in the 2-position and bromination in the 4-position by analogy to the 3-isomer. 2-Acetamidodibenzothiophene is chlorinated and nitrated in the 1-position and brominated in the 3-position. 2-Benzamidodibenzothiophene is chlorinated, nitrated and brominated in the 3-position. 3-Acetamidodibenzothiophene is nitrated in the 4-position, brominated in the 2-position and chlorinated to give approximately equal amounts of the 2- and the 4-isomers. The same holds true for 3-benzamidodibenzothiophene. 4-Acetamidodibenzothiophene is brominated in the 1-position.

Thus, it appears that if a bulky group, which is electron donating, is in the 2-position, electrophilic substitution will take place in the 3-position. If the group is not large, but yet electron donating, small electrophiles will be directed to the 1-position and large electrophiles to the 3-position. If the electron donating group is in the 3-position, large electrophiles will be directed to the 2-position and small electrophiles will yield mixed isomers. Since the sulfoxide has such a profound effect, it would be of interest to nitrate 2- and 3-acetamido derivatives of dibenzothiophene-5-oxide.
Synthetic Procedures

1-Position

The best methods available to synthesize 1-isomers is by electrophilic attack on the 2- or 4- acetamido derivatives followed by deamination or by a halogen-metal interconversion of 1-bromodibenzothiophene and subsequent reaction of the lithium compound with another reagent.

2-Position

The most direct method available is by an electrophilic attack on dibenzothiophene or by a halogen-metal interconversion followed by its reaction with the desired precursor.

3-Position

These isomers are obtained by an electrophilic attack on dibenzothiophene-5-oxide or the sulfone, followed by reduction with mild reducing agents for the oxide and lithium aluminum hydride for the sulfone derivatives. Another method of some importance is the reaction of 4-iodo-dibenzothiophene with sodamide in liquid ammonia to give
3-aminodibenzothiophene, from which several other isomers may be made.

4-Position

The most direct method involves the use of metalation and subsequent use of the organometallic compound. Another method of some use is by an electrophilic attack on 3-acetimidodibenzothiophene.

Melting Point Relationships

Since compilations of dibenzothiophene, dibenzothiophene-5-dioxide and dibenzofuran have been given considerable attention in the theses of Cheney93, Swislowsky94, Willis95, Hogg96, Esmary6, Ingham7, and Johnson97, monoderivatives

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common to the three will be included in Table 2. They will be listed in the order of dibenzofuran, dibenzothiophene and dibenzothiophene-5-dioxide for each respective position. Since only a small number of dibenzothiophene-5-oxide derivatives are known, they will be discussed separately.

In the following discussion concerning Table 2 the various mono functional groups will be considered with respect to the individual heterocyclic systems followed by a general resume.

Relationships in dibenzothiophene

As a general rule in comparing melting points in the dibenzothiophene series, the 1- and the 4- isomers have melting points within approximately 20° of one another. Exceptions to this occur in the carboxylic acids where the 4-isomer melts about 90° higher than the 1-derivative and in the nitro compound in which the 4-isomer is higher melting by some 60°. One other case worthy of mention is 1-acetamido-dibenzothiophene which melts some 30° higher than the 4-isomer. In all derivatives with the exception of the one just mentioned the 4-isomer is the higher melting of the two. Very polar groups such as the carboxyl and the nitro attached to the 4-position generally impart abnormally high
Table 2

Melting Points of Derivatives of Dibenzoferan, Dibenzothiophene and Dibenzothiophene-5-dioxide

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Heterocycle</th>
<th>M.P. (°C) of Position-</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>(-\text{NHCOCH}_3) \text{-O}</td>
<td>205</td>
<td>166</td>
</tr>
<tr>
<td>(-\text{NHCOCH}_3) \text{-S}</td>
<td>227</td>
<td>178</td>
</tr>
<tr>
<td>(-\text{NHCOCH}_3) \text{-SO}_2</td>
<td>\text{-}</td>
<td>274</td>
</tr>
<tr>
<td>(-\text{COCH}_3) \text{-O}</td>
<td>\text{-}</td>
<td>81</td>
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<tr>
<td>(-\text{COCH}_3) \text{-S}</td>
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<td>111</td>
</tr>
<tr>
<td>(-\text{NH}_2) \text{-O}</td>
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<td>130</td>
</tr>
<tr>
<td>(-\text{NH}_2) \text{-S}</td>
<td>97</td>
<td>132</td>
</tr>
<tr>
<td>(-\text{NH}_2) \text{-SO}_2</td>
<td>\text{-}</td>
<td>265</td>
</tr>
<tr>
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<td>110</td>
</tr>
<tr>
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<td>127</td>
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<tr>
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</tr>
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<td>(-\text{CO}_2\text{H}) \text{-S}</td>
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<td>253</td>
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Table 2 (Continued)

<table>
<thead>
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<th>M.P. (°C) of Position-</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>-S</td>
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<td>-I</td>
<td>-0</td>
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</tr>
<tr>
<td></td>
<td>-S</td>
<td>79</td>
</tr>
<tr>
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<td></td>
<td>-S</td>
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</tr>
<tr>
<td></td>
<td>-SO₂</td>
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<tr>
<td>-Si(CH₃)₃</td>
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<tr>
<td></td>
<td>-S</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-SO₂</td>
<td>132</td>
</tr>
</tbody>
</table>
deviations from what might be expected. The 2- and the 3-
isomers generally have higher melting points than the 1- or
4-isomers with the exceptions of the 1-acetamido, 4-carboxy
and the 4-nitro. Considering the 2- and the 3-isomers,
large groups such as the benzamido, the acetamido, the iodo
and the carbomethoxy impart a higher melting point to the
molecule when in the 3-position, and small functional groups
such as chloro, methyl and amino give higher melting points
when in the 2-position. As might be expected, polar groups
such as the carboxyl and the nitro have high melting points
for any one position.

Relationships in dibenzothiophene-5-dioxide

With the known isomers in this series, the 1- and the
4-derivatives have the lowest melting points, and of these
two positions, the 4-isomers melt higher. Considering the
2- and the 3-isomers, the more polar functional groups such
as the carboxyl and the nitro have higher melting points
when in the 3-position. Relatively large groups such as
the acetamido and the trimethylsilyl cause the molecule to
have higher melting points when in the 3-position.
Relationships in dibenzofuran

The 1- and the 4-isomers in dibenzofuran appear to have the lowest melting points. A notable exception to this fact as seen also in dibenzothiophene was that of the 1- and 4-acetamido derivatives. The more polar groups, such as the carboxyl and the nitro, when placed in the 1-position generally melt higher than in the 4-position. With the exception of the amino and methyl groups, the 3-isomers of dibenzofuran melt higher than the 2-derivatives.

General relationships

In comparing the individual positions of like functional groups between dibenzothiophene and dibenzofuran there appears to be some correlation. As a general rule the dibenzothiophene derivatives have about a 10° higher melting point than the corresponding dibenzofuran derivative. A notable exception to this lies in the carbomethoxy groups which have about a 5° higher melting point in the dibenzofuran series for the 2-, 3- and 4-isomers. An exception lies also in the nitro compounds in which the 1- and 3-isomers of dibenzofuran melt higher.
The comparison of dibenzothiophene and dibenzothiophene-5-dioxide is quite pronounced in that for almost any isomer of dibenzothiophene the melting point is raised from 100–130° by oxidizing it to the sulfoxide.

There are four known derivatives of dibenzothiophene-5-oxide, namely the 3-acetamido, 3-amino, 2-bromo and 3-nitro dibenzothiophene-5-oxides which melt at 267°, 209°, 172°, and 210°, respectively. This represents, for all but the bromo compound an elevation of approximately 65° from the dibenzothiophene compound to the corresponding 5-oxide. The melting point of the bromo derivative is only elevated some 45°.

Suggested Studies

Dibenzothiophene should be metalated in the presence of lithium butoxide to determine whether the formation of butanol in the reaction of n-butyllithium with dibenzothiophene-5-oxide acts as a catalyst.

The nitration of 2-acetamidodibenzenothiophene-5-oxide would be of interest because of the competing influences on the molecule.

The reaction of dimethyl sulfoxide with hydrochloric and hydrobromic acids should be investigated further.
The possibility of disproportionation of dibenzothiophene-5-oxide at elevated temperatures may prove of interest.

Electrophilic substitution reactions on alkyl dibenzothiophenes would prove of interest to study the effects of functional groups on the ring substituted by the attacking reagent.

Other negatively substituted sulfoxides should be tried as oxidizing reagents in the bromination of dibenzothiophene-5-oxide.

The reaction of organometallic compounds with O-methylhydroxylamine should be studied with respect to the addition of the organometallic compound to the dilithio derivative of O-methylhydroxylamine.
SUMMARY

An historical review of dibenzothiophene substitution has been presented, with emphasis placed on functional groups.

A supplementary listing of dibenzothiophene compounds has been made up to this date.

2,8-Dicyanodibenzothiophene has been shown to be resistant to some normal oxidation methods.

Unsuccessful attempts were made to synthesize directly 3-bromodibenzothiophene-5-oxide from dibenzothiophene-5-oxide.

The reaction of hydrobromic acid, dimethyl sulfoxide, and phenol in glacial acetic acid was found to give 4-bromophenol.

The hydrolysis of 1-nitro-2-acetamidodibenzothiophene, using hydrochloric acid in ethanol was found to give 1-chlorodibenzothiophene, and the mechanism of this interesting reaction was elucidated.

A number of dibenzothiophene derivatives has been synthesized.

A review of the methods used for structural proofs of dibenzothiophene derivatives has been given.
Melting points of a number of mono-derivatives of dibenzofuran, dibenzothiophene, dibenzothiophene-5-oxide, and dibenzothiophene-5-dioxide were presented and generalizations were made concerning the effect on melting points of the positions and polarity of functional groups.
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