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ORIENTATION AND CLEAVAGE OF SOME SUBSTITUTED DIBENZOTHIOPHENES

by

John Francis Nobis

A Thesis Submitted to the Graduate Faculty
for the Degree of

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In Charge of Major Work

Head of Major Department

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INTRODUCTION

The interest in dibenzothiophene chemistry was initiated a few years ago in these laboratories by Jacoby and continued to some extent by Avakian. Substituted dibenzothiophenes are of interest for several reasons. First of all, the isosteric replacement of benzene and benzene derivatives by thiophene and thiophene derivatives has been demonstrated beyond doubt by Erlenmeyer[1], who initiated the concept that divalent sulfur contained a shell of valence electrons numerically equal to that of the group or "pseudoatom" - CH=CH-. Also, the replacement of oxygen by sulfur in certain organic compounds[2] has been observed to produce an increase in physiological action. Finally, dibenzothiophene and substituted dibenzothiophenes are easily oxidized to the corresponding sulfoxides and sulfones which are known to possess pharmacological action (e.g., $\underline{p},\underline{p}'$-diaminodiphenyl sulfone[3]).

Additional evidence for the concept of isosteric replace-

1. Erlenmeyer, Berger, and Leo, Helv. Chim. Acta, 16, 733 (1933); Erlenmeyer and Leo, ibid., 16, 1381 (1933).
2. Gilman and Pickens, J. Am. Chem. Soc., 47, 245 (1925); Tabern and Volwiler, ibid., 57, 1961 (1935).
3. (a) Buttle and Co-workers, Lancet, 1937 (I), 1331 /C. A., 31, 7118 (1937)_7; (b) Coggeshall, Maier, and Best, J. Am. Med. Assoc., 117, 1077 (1941); (c) Marshall, et al, J. Pharm. Exptl. Therap., 75, 89 (1942) /C. A., 60, 4196 (1942)_7.

ment was shown by Burger and co-workers[4] in their studies of the physical and pharmacological changes effected by introducing a thiophene nucleus into ring systems in place of an aromatic nucleus. Their results indicated that the amino alcohols derived from dibenzothiophene had about the same analgesic action as compounds derived by the introduction of similar substitutents into the dibenzofuran, carbazole, and phenanthrene nuclei. Burtner and Lehman[5] found that β-diethylaminoethyl 2-dibenzothiophenecarboxylate hydrochloride had a weak anesthetic action, although it was of short duration.

Gilman and Avakian[6] prepared some dialkylamino derivatives of dibenzothiophene and submitted them for antimalarial testing. No compounds were found active against avian malaria. This inactivity was attributed to the fact that the compounds contained only one nuclear substitutent in addition to the γ-diethylaminopropyl group.

Dibenzothiophene itself has shown promising results as an insecticide[7] and is toxic at a dilution of 3 parts per million[8].

4. (a) Burger, Wartman, and Lutz, J. Am. Chem. Soc., 60, 2628
    (1938); (b) Burger and Bryant, J. Org. Chem., 4, 119
    (1939); (c) Burger and Bryant, J. Am. Chem. Soc., 63, 1054
    (1941).
5. Burtner and Lehman, J. Am. Chem. Soc., 62, 527 (1940).
6. Gilman and Avakian, Ibid., 68, 1514 (1946).
7. Dudley, Bronson, and Harries, U. S. Dept. Agr. Bur. Entomol.
    Plant Quarantine, E-651, 10 pp. (1945) ⟋ C. A., 39, 3111
    (1945)⟋.
8. Fink and Smith, J. Econ. Entomol., 29804 (1936) ⟋ C. A., 30,
    7722 (1936)⟋.

The continued feeding of dibenzothiophene to young rats was found to lessen the growth rate[9].

Neumoyer and Amstutz[10] have prepared 2,8-diaminodibenzothiophene-5-dioxide as a possible antibiotic since they regarded it as derived from 4,4'-diaminodiphenyl sulfone. Actually, this diaminodibenzothiophene sulfone may be regarded as the closed model of 4,4'-diaminodiphenyl sulfone and was prepared independently during the course of this work as a possible antimalarial.

The objects of this work were to study the reaction between 4-iododibenzothiophene and sodamide in liquid ammonia; to prepare certain substituted dibenzothiophenes which might possess antimalarial activity; and to add to the knowledge of dibenzothiophene and silicon chemistry through the preparation and cleavage of some dibenzothiophene substituted silanes.

9. Thomas, De Eds, and Cox, Food Research, 7, 161 (1942) /C. A., 36, 4193 (1942)/.
10. Neumoyer and Amstutz, J. Am. Chem. Soc., 69, 1920 (1947).

HISTORICAL

Dibenzothiophene has been known since the year 1870 when it was first prepared by Stenhouse[11], who passed the vapors of diphenyl sulfide over iron nails in an iron tube. A glance at the known compounds of dibenzothiphene might leave one with the impression that a large amount of investigation had been carried out on this heterocycle. Actually, the chemical knowledge of dibenzothiophene is relatively incomplete when compared with the considerably more complete knowledge of the chemistry of the similar heterocycle, dibenzofuran.

A detailed survey of the chemistry of dibenzothiophene, with particular emphasis upon the structure proofs of various substituted dibenzothiophenes, has been given by Jacoby[12]. His survey covers the work done up to 1938. The following pages are devoted to the work done since that time with the inclusion of a few miscellaneous reactions not mentioned by Jacoby. Since there has been no complete literature survey of dibenzothiophene compounds, the following tables include, as nearly as possible, all derivatives of dibenzothiophene. Derivatives of some fused ring systems incorporating a dibenzothiophene nucleus have been omitted. The numbering system

11. Stenhouse, Ann., 156, 332 (1870).
12. Jacoby, Doctoral Dissertation, Iowa State College, 1938.

used in these laboratories and throughout this thesis is in accord with that approved by the International Rules for Numbering Organic Ring Systems[13]. The correct structure of dibenzothiophene, together with the approved numbering system, is
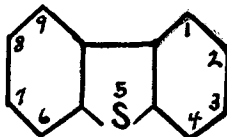
The German, French, and English literature frequently refers to dibenzothiophene as diphenylene sulfide and uses a different numbering system:
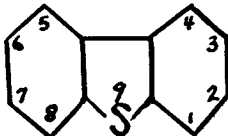
The naming and numbering system of all compounds in the following tables has been made to conform with the current Chemical Abstracts usage. The major references for each compound are given first but all literature mention of each compound is included, with the exception of dibenzothiophene itself.

13. Patterson, J. Am. Chem. Soc., 47, 543 (1925); Patterson and Capell, The Ring Index, Reinhold Publishing Corp., New York, (1940) p. 237; Patterson, Capell, and Magill, C. A., 39, 5875 (1945).

A brief glance at the literature on dibenzothiophene would impress one with the frequency of occurrence of the name Courtot. He carried out much of the fundamental research on orientation in the dibenzothiophene nucleus. He showed that halogenation[14], nitration[15], and sulfonation[16] all involved the 2-position. Gilman[17,18] and Cullinane[19] have also made important contributions to the knowledge of substitution in dibenzothiophene.

While ordinary nuclear substitution, including the Friedel-Crafts reaction, takes place in the 2-position or disubstitution in the 2,8-position[14], metalation with organoalkali compounds takes place in the 4-position[17]. The 3-position of dibenzothiophene was made available by metalation with phenylcalcium iodide and indirectly in the course of this research, by rearrangement of 4-iododibenzothiophene with sodamide in liquid ammonia to give the 3-aminodibenzothiophene. Metalation with phenylcalcium iodide is of little preparative value however, because of the extremely low yields.

There is no direct method for introducing substitutents into the 1-position of dibenzothiophene but by bromination of

14. Courtot, Nicolas, and Liang, Compt. rend., 186, 1624 (1928).
15. Courtot and Pomonis, ibid., 182, 931 (1926).
16. Courtot and Kelner, ibid., 198, 2003 (1934).
17. Gilman and Jacoby, J. Org. Chem., 3, 108 (1938).
18. Gilman, Jacoby, and Pacevitz, ibid., 3, 120 (1938).
19. Cullinane, Davies, and Davies, J. Chem. Soc., 1435 (1936).

4-acetaminodibenzothiophene followed by hydrolysis and
deamination, Gilman and Jacoby[17] have opened the route to this
position.

Burger and co-workers[4] isolated a small amount of 4-
acetyldibenzothiophene as a by-product in the preparation of
2-acetyldibenzothiophene. The structure of the 4-isomer was
determined through oxidation of the acetyl derivative to the
known 4-carboxylic acid and also by a Beckmann rearrangement
of the acetyl oxime to the known 4-acetamino derivative. Both
the 2-acetyldibenzothiophene and the 4-acetyldibenzothiophene
may be halogenated in the _alpha_ position to the carbonyl group[4b].
These ω-bromo ketones easily exchange halogen atoms with
tertiary amino groups to give aminoketones[4b,4c]. 2-Succinyl-
dibenzothiophene has been prepared[4b] by the reaction between
2-ω-bromoacetyldibenzothiophene and ethyl sodiomalonate
followed by hydrolysis and decarboxylation.

A number of patents[20,21,22,23,24,25] record the prepara-
tion of 2-hydroxy-3-dibenzothiophenecarboxylic acid through a
Kolbe reaction on 2-hydroxydibenzothiophene but no structure
proof is given in any of the references.

Gilman and Avakian[6] were able to prepare 2-amino-3-

20. German Patent 593506 /C. A., 28, 3422 (1934)_7.
21. French Patent 768,052 /C. A., 29, 475 (1935)7.
22. German Patent 606,350 /C. A., 29, 1434 (1935)_7.
23. German Patent 607,381 /C. A., 29, 1997 (1935)7.
24. U. S. Patent 2,157,796 /C. A., 33, 6346 (1939)_7.
25. U. S. Patent 2,189,367 /C. A., 34, 4283 (1940)_7.

bromodibenzothiophene by bromination of 2-acetaminodibenzothiophene followed by hydrolysis. The structure of the bromination product was proven by deamination and oxidation to the known 3-bromodibenzothiophene-5-dioxide.

In accordance with the copper powder catalyzed amination prodedure of Gilman and Jacoby[17] for the preparation of 2-aminodibenzothiophene from 2-bromodibenzothiophene, Neumoyer and Amstutz[10] were able to prepare 2,8-diaminodibenzothiophene from 2,8-dibromodibenzothiophene. They were unable to oxidize the 2,8-diacetamino compound to the corresponding sulfone so prepared the 2,8-diaminodibenzothiophene-5-dioxide by amination of the 2,8-dibromodibenzothiophene-5-dioxide. Independent studies during the course of this work established the structure of the 2,8-diaminodibenzothiophene-5-dioxide which was prepared by oxidation of the 2,8-diacetamino compound followed by hydrolysis. Neumoyer and Amstutz[10] have listed corrected melting points for 2,8-diaminodibenzothiophene and for 2,8-diacetaminodibenzothiophene. Their results agree with the studies in this laboratory.

Metalation of dibenzothiophene has been attempted with various organoalkali compounds, and various solvents have been used as reaction media; the most useful metalating agent is n-butyllithium in n-butyl ether[17,26]. Dibenzothiophene is not metalated as rapidly as dibenzofuran[27] but this was

26. Gilman and Bebb, J. Am. Chem. Soc., 61, 109 (1939).
27. Gilman, Van Ess, Willis, and Stuckwisch, J. Am. Chem. Soc., 62, 2606 (1940).

predictable since preferential metalation was noted in phenoxathiin, where lithium replaced the hydrogen on the carbon ortho to the oxygen rather than the hydrogen on the carbon ortho to the sulfur.

The action of aluminum chloride on a mixture of sulfur and biphenyl is the best method for the preparation of dibenzothiophene[17]. This procedure was developed by Gilman and Jacoby[17] from the vague directions of a German Patent[28] and modified somewhat during the course of this work.

Dibenzothiophene is smoothly converted to the sulfone (dibenzothiophene-5-dioxide) by the action of strong oxidizing agents[19]. While the sulfur atom in dibenzothiophene itself is strongly para directing, conversion to the dioxide changes the orientating ability of the sulfur to meta directing. This may be explained on the basis that the electromeric effect of the SO_2 group is towards the oxygen, resulting in a deactivation of the benzene ring. This effect is smallest in the meta position. As would then be expected, nitration[18] and bromination[19] of the sulfone give the 3- and 3,7-derivatives respectively.

Most of the substituted dibenzothiophenes can be oxidized to the corresponding sulfones but many of the sulfones listed in the tables were prepared by the more tedious route of ring closure of substituted biphenyls.

Considerable interesting research still remains to be

28. German Patent 579,917 /C. A., 28, 1053 (1934)_7.

done on dibenzothiophene and dibenzothiophene derivatives.
The pharmacological properties of dibenzothiophene compounds
have been investigated only slightly. The orientation of
disubstituted and trisubstituted derivatives of dibenzothio-
phene merits a great deal more study than has been given to
them thus far.

TABLE I

DERIVATIVES OF DIBENZOTHIOPHENE

Name of Compound	M.P.	Reference
Dibenzothiophene	99-100	(17,29,12,19)
Dibenzothiophene picrate	125	(12)
MONOSUBSTITUTED DIBENZOTHIOPHENES		
2-Acetaminodibenzothiophene	181-3	(17,12,4a)
3-Acetaminodibenzothiophene	199-200	(30,29a)
4-Acetaminodibenzothiophene	198	(17,12,4b)
2-(1-Acetoxyethyl)dibenzothiophene		(4c)
2-Acetyldibenzothiophene	111-2	(17,4a,12,31)
2-Acetyldibenzothiophene oxime	161-4	(17,12,4a)
2-Acetyldibenzothiophene semicarbazone	234-5	(4a)
4-Acetyldibenzothiophene	129-30	(4b,4a)
4-Acetyldibenzothiophene oxime	155-60	(4b)
4-Acetyldibenzothiophene oxime acetate	142-3	(4b)
4-Acetyldibenzothiophene semicarbazone	302-4	(4a)

29.   (a) This Thesis; (b) for absorption spectra of dibenzo-
      thiophene see Ley and Specker, Z. wiss. Phot., 38, 12
      (1939) /¯C. A., 34, 4992 (1940)¯7; (c) for Raman spectra
      of dibenzothiophene see Donzelot and Chaix, Compt. rend.,
      202, 851 (1936).
30.   Gilman and Nobis, J. Am. Chem. Soc., 67, 1479 (1945).
31.   Steinkopf and Engelman, Ann., 546, 205 (1941).

TABLE I (Continued)

Name of Compound	M.P.	Reference
2-Aminodibenzothiophene	133	(17,12,4a) (19,32,14)
3-Aminodibenzothiophene	121.5-22	(29a,30)
4-Aminodibenzothiophene	110	(17,33,12,6)
2-ω-Bromoacetyldibenzothiophene	115-6	(4b)
4-ω-Bromoacetyldibenzothiophene	149-151	(4b)
1-Bromodibenzothiophene	84	(17)
2-Bromodibenzothiophene	127	(19,14,21,12) (16,34a,34b)
o-Carbethoxy-(2-dibenzothenoyl)benzene	105-6	(17,12)
1-Carbomethoxydibenzothiophene	72-72.5	(17)
2-Carbomethoxydibenzothiophene	75	(12,17)
3-Carbomethoxydibenzothiophene	129-30	(18,12)
4-Carbomethoxydibenzothiophene	95	(17,12)
2-(4-Carboxy-2-quinolyl)dibenzothiophene	299-300	(31)
2-Chlorodibenzothiophene	113	(14,34a,34b)

32. Courtot and Pomonis, Compt. rend., 182, 893 (1926).
33. Avakian, Doctoral Dissertation, Iowa State College, 1944.
34. (a) Courtot, Compt. rend., 198, 2260 (1934); (b) for absorption spectra of 2-bromo-, 2-chloro-, and 2-nitrodibenzothiophene and 2,8-dibromo-, and 2,8-dichlorodibenzothiophene see Chaix, Compt. rend., 200, 1208 (1935); (c) for fluorescence of 2,8-dibenzothiophenedisulfonic acid see Deribere, Tiba, 15, 349 (1939) /C. A., 32, 1602 (1938)_7.

TABLE I (Continued)

Name of Compound	M.P.	Reference
2-Cyanodibenzothiophene	159-60	(4b)
o-(2-Dibenzothenoyl)benzoic acid		(17,12)
β-(2-Dibenzothenoyl)propionic acid	160.5-61	(17,12,35)
γ-(2-Dibenzothienyl)butyric acid	131	(17,12,35)
4-Dibenzothienyllithium		(17,26,30)(36)
1-Dibenzothiophenecarboxylic acid	176-7	(17)
2-Dibenzothiophenecarboxylic acid	255	(17,14,12)
3-Dibenzothiophenecarboxylic acid	300-305	(18,12)
4-Dibenzothiophenecarboxylic acid	261-2	(17,30,4b,12)
2-Dibenzothiophenesulfinic acid	121	(16)
2-Dibenzothiophenesulfinic acid (barium salt)		(16)
2-Dibenzothiophenesulfinic acid (sodium salt)		(16)
2-Dibenzothiophenesulfonic acid	172	(16)
2-Dibenzothiophenesulfonyl chloride	141	(34a)
2,2'-Didibenzothienyldisulfide	195	(16)
2,2'-Didibenzothienylsulfoxide	260	(16)
2-(2-Diethylamino-1-acetoxyethyl)-dibenzothiophene hydrochloride	188-92	(4c)

35. Buu-Hoi and Cagniant, Ber., 76B, 1269 (1943).
36. Gilman, Moore, and Baine, J. Am. Chem. Soc., 63, 2479 (1941).

TABLE I (Continued)

Name of Compound	M.P.	Reference
β-Diethylaminoethyl 2-dibenzothiophene-carboxylate	219	(5)
β-Diethylaminoethyl 4-dibenzothiophene-carboxylate	213	(5)
2-(2-Diethylamino-1-hydroxyethyl)-dibenzothiophene	59-60	(4c)
2-(2-Diethylamino-1-hydroxyethyl)-dibenzothiophene hydrochloride	163-4	(4c)
2-(γ-Diethylaminopropylamino)-dibenzothiophene	b.p.,280-2/ 2 mm.	(6)
4-(γ-Diethylaminopropylamino)-dibenzothiophene	b.p.,210-13/ 0.1 mm.	(6)
2-(2-Diethylamino-1-oxoethyl)-dibenzothiophene hydrochloride	214-15	(4b,4c)
2-(3-Diethylamino-1-oxopropyl)-dibenzothiophene hydrochloride	150-51	(4c)
2-(2-Dimethylamino-1-acetoxyethyl)-dibenzothiophene hydrochloride	214-15	(4c)
2-(2-Dimethylamino-1-hydroxyethyl)-dibenzothiophene hydrochloride	228-28.5	(4c)

TABLE I (Continued)

Name of Compound	M.P.	Reference
2-(2-Dimethylamino-1-oxoethyl)-dibenzothiophene hydrochloride	220-225	(4c)
2-(3-Dimethylamino-1-acetoxypropyl)-dibenzothiophene hydrochloride	149-50	(4c)
2-(3-Dimethylamino-1-hydroxypropyl)-dibenzothiophene	118	(4c)
2-(3-Dimethylamino-1-hydroxypropyl)-dibenzothiophene hydrochloride	192-5	(4c)
2-Ethyldibenzothiophene	93	(16)
2-Ethylmercaptodibenzothiophene	93	(16)
2-Hydroxydibenzothiophene	156	(19,34) (21,22)
4-Hydroxydibenzothiophene	167	(17,12)
2-(1-Hydroxyethyl)dibenzothiophene	76-7	(4c)
2-Iododibenzothiophene	87	(14)
4-Iododibenzothiophene	101-2	(30,29a)
2-Mercaptodibenzothiophene	81	(16)
4-Methoxydibenzothiophene	123	(17,12)

TABLE I (Continued)

Name of Compound	M.P.	Reference
4-Methyldibenzothiophene	65	(17,12)
2-Nitrodibenzothiophene	186	(19,32,14) (29a)
2-(2-Piperidino-1-acetoxyethyl)- dibenzothiophene hydrochloride	220-25	(4c)
2-(3-Piperidino-1-acetoxypropyl)- dibenzothiophene hydrochloride	185-6	(4c)
2-(2-Piperidino-1-hydroxyethyl)- dibenzothiophene	88-9	(4c)
2-(2-Piperidino-1-hydroxyethyl)- dibenzothiophene hydrochloride	225-29	(4c)
4-(3-Piperidino-1-hydroxypropyl)- dibenzothiophene	105	(4c)
2-(3-Piperidino-1-hydroxypropyl)- dibenzothiophene	102	(4c)
2-(3-Piperidino-1-hydroxypropyl)- dibenzothiophene hydrochloride	201-201.5	(4c)
2-(2-Piperidino-1-oxoethyl)- dibenzothiophene	117	(4c)
2-(2-Piperidino-1-oxoethyl)- dibenzothiophene hydrochloride	245-6	(4b)

TABLE I (Continued)

Name of Compound	M.P.	Reference
4-(2-Piperidino-1-oxoethyl)- dibenzothiophene hydrochloride	258-60	(4b)
2-(3-Piperidino-1-oxopropyl)- dibenzothiophene hydrochloride	201-3	(4c)
4-(3-Piperidino-1-oxopropyl)- dibenzothiophene	112	(4c)
4-(3-Piperidino-1-oxopropyl)- dibenzothiophene hydrochloride	229-32	(4c)
2-Propionyldibenzothiophene	72-72.5	(4c)
2-Propionyldibenzothiophene semicarbazone	196-8	(4c)
2-(2-Quinolyl)dibenzothiophene	144-5	(31)
2-Stearyldibenzothiophene	69-70	(37)
2-Succinyldibenzothiophene	158-9	(4b)
2-/¯3-(1,2,3,4-Tetrahydroisoquinolino- 1-acetoxypropyl)_7dibenzothiophene hydrochloride	193-6	(4c)
2-/¯2-(1,2,3,4-Tetrahydroisoquinolino- 1-hydroxyethyl)_7dibenzothiophene	106-7	(4c)

37. Ralston and Christensen, _Ind. Eng. Chem._, 29, 194 (1937).

TABLE I (Continued)

Name of Compound	M.P.	Reference
2-∠2-(1,2,3,4-Tetrahydroisoquinolino-1-hydroxyethyl)_7dibenzothiophene hydrobromide	250-52	(4c)
2-∠2-(1,2,3,4-Tetrahydroisoquinolino-1-hydroxyethyl)_7dibenzothiophene hydrochloride	243-4	(4c)
2-∠3-(1,2,3,4-Tetrahydroisoquinolino-1-hydroxypropyl)_7dibenzothiophene	136	(4c)
2-∠3-(1,2,3,4-Tetrahydroisoquinolino-1-hydroxypropyl)_7dibenzothiophene hydrochloride	183-5	(4c)
2-∠2-(1,2,3,4-Tetrahydroisoquinolino-1-oxoethyl)_7dibenzothiophene	122-25	(4c)
2-∠2-(1,2,3,4-Tetrahydroisoquinolino-1-oxoethyl)_7dibenzothiophene hydrobromide	257-59	(4c)
2-∠2-(1,2,3,4-Tetrahydroisoquinolino-1-oxoethyl)_7dibenzothiophene hydrochloride	244-46	(4c)
2-∠3-(1,2,3,4-Tetrahydroisoquinolino-1-oxopropyl)_7dibenzothiophene	106-7	(4c)

TABLE I (Continued)

Name of Compound	M.P.	Reference
2-/ 3-(1,2,3,4-Tetrahydroisoquinolino-1-oxopropyl) 7dibenzothiophene hydrochloride	197-8	(4c)
2-Thioacetoxydibenzothiophene	122	(16)
2-Thiobenzoxydibenzothiophene	116	(16)
4-Trimethylsilyldibenzothiophene	b.p.,135-7/ 0.8 mm.	(29)

DISUBSTITUTED DIBENZOTHIOPHENES

Name of Compound	M.P.	Reference
2-Acetamino-3-bromodibenzothiophene	199-200	(6)
2-Acetamino-3-chlorodibenzothiophene	199.5-200	(6)
2-Amino-3-bromodibenzothiophene	135-135.5	(6)
2-Amino-3-chlorodibenzothiophene	118-9	(6)
1-Amino-4-methoxydibenzothiophene	101-2	(6)
2-Acetamino-3(?)-nitrodibenzothiophene	208.5-9	(12)
2-Acetamino-8(?)-nitrodibenzothiophene	250	(12)
2,8-bis(4-Carboxy-2-quinolyl)-dibenzothiophene	330-340	(31)
1-Bromo-4-acetaminodibenzothiophene	254	(17,12)
1-Bromo-4-aminodibenzothiophene	156	(17)
2-Bromo-8-aminodibenzothiophene	150-51	(14)

No 2 NH₂ ?NH₂ [handwritten annotation]

TABLE I (Continued)

Name of Compound	M.P.	Reference
1-Bromo-4-(ɤ diethylaminopropylamino)-dibenzothiophene	b.p.,263-6/ 0.3 mm.	(6)
2-Bromo-8-nitrodibenzothiophene	264-5	(14,16)
N-4-Carbazoyl-2-hydroxy-3-dibenzothiophene-carboxamide	300	(23,24)
4'-Chloro-2-hydroxy-3-dibenzothiophene-carboxanilide	304	(23,24)
4'-Chloro-2',5'-dimethoxy-2-hydroxy-3-dibenzothiophenecarboxanilide	233	(23,24)
5'-Chloro-2',4'-dimethoxy-2-hydroxy-3-dibenzothiophenecarboxanilide	257	(23,24)
4'-Chloro-2-hydroxy-2'-methoxy-3-dibenzo-thiophenecarboxanilide	234	(23)
5'-Chloro-2-hydroxy-2'-methoxy-3-dibenzo-thiophenecarboxanilide	250	(23,24)
4'-Chloro-2-hydroxy-2'-methyl-3-dibenzo-thiophenecarboxanilide	268	(23,24)
5'-Chloro-2-hydroxy-2'-methyl-3-dibenzo-thiophenecarboxanilide	233	(23,24)
2,8-Diacetaminodibenzothiophene	304-5.5	(10,29a) (4a,32)

TABLE I (Continued)

Name of Compound	M.P.	Reference
1,4-Diacetoxydibenzothiophene	126	(38)
2,8-Diacetyldibenzothiophene	208-9	(4a,29a) (31)
2,8-Diacetyldibenzothiophene oxime	272	(4a,29)
2,8-Diaminodibenzothiophene	199.5-201.5	(10,29a,4a) (32,15)
2,8-Dibenzothiophenedicarboxylic acid	320	(14)
2,8-Dibenzothiophenedisulfonic acid		(32a,34c)
2,8-Dibromodibenzothiophene	229	(16,34a,34b) (10,14)
2,8-Dichlorodibenzothiophene	212	(34a,34b,14)
3',4'-Dichloro-2-hydroxy-3-dibenzo-thiophenecarboxanilide	288	(23,24)
2-(β-Diethylaminoethylamino)-8-methyldibenzothiophene	b.p.,235/ 1 mm.	(39)
1-(γ-Diethylaminopropylamino)-4-methoxydibenzothiophene	b.p.,251-4/ 0.15 mm.	(6)

38. Hinsberg, Ber., 56B, 2008 (1923).
39. German Patent 550,327 /C. A., 26, 4063 (1932)/.

TABLE I (Continued)

Name of Compound	M.P.	Reference
2-(γ-Diethylaminopropylamino)-3-bromo- dibenzothiophene	b.p., 275-280/ 0.5 mm.	(6)
2-(γ-Diethylaminopropylamino)-3-chloro- dibenzothiophene	b.p., 215-20/ 0.1 mm.	(6)
2,2''-Dihydroxy-4,4'''-bi-3-dibenzothiophene- carbox-o-aniside /N,N'-(3,3'-dimethoxy- 4,4'-biphenylene)bis/2-hydroxy-3-dibenzo- thiophenecarboxamide_7_7	336	(23,24)
2,8-Diiododibenzothiophene	219-220	(14)
2,8-Dimethyldibenzothiophene		(40)
2,8-Dinitrodibenzothiophene	324-5	(32,29a)
2,8-Di(2-quinolyl)dibenzothiophene	206-7	(31)
N-(6-Ethoxy-2-benzothiazolyl)-2-hydroxy- 3-dibenzothiophenecarboxamide	270	(23,24)
2-Hydroxy-3-dibenzothiophenecarboxylic acid	283	(21,20,25)
2-Hydroxy-3-dibenzothiophenecarboxanilide	289	(23,24)
2-Hydroxy-2',4'-dimethoxy-3-dibenzothio- phenecarboxanilide	260	(23,24)
2-Hydroxy-2',5'-dimethoxy-3-dibenzo- thiophenecarboxanilide	203	(23,24)

40. Fuchs, Monatsh., 53/54, 438 (1929).

TABLE I (Continued)

Name of Compound	M.P.	Reference
2-Hydroxy-2',5'-dimethyl-3-dibenzothiophenecarboxanilide	190	(23,24)
2-Hydroxy-2'-ethoxy-3-dibenzothiophenecarboxanilide	205	(23,24)
2-Hydroxy-4'-ethoxy-3-dibenzothiophenecarboxanilide	265	(23,24)
2-Hydroxy-2'-methoxy-3-dibenzothiophenecarboxanilide	195	(23,24)
2-Hydroxy-4'-methoxy-3-dibenzothiophenecarboxanilide	255	(23,24)
2-Hydroxy-4'-methoxy-2'-methyl-3-dibenzothiophenecarboxanilide	244	(23,24)
2-Hydroxy-4'-methoxy-3'-methyl-3-dibenzothiophenecarboxanilide	245	(23,24)
2-Hydroxy-2'-methyl-3-dibenzothiophenecarboxanilide	207	(23,24)
2-Hydroxy-4'-methyl-3-dibenzothiophenecarboxanilide	295	(23,24)
2-Hydroxy-1'-naphthyl-3-dibenzothiophenecarboxanilide	238	(23,24)

TABLE I (Continued)

Name of Compound	M.P.	Reference
2-Hydroxy-2'-nitro-3-dibenzothiophene-carboxanilide	233	(23,24)
2-Hydroxy-3'-nitro-3-dibenzothiophene-carboxanilide	302	(23,24)
1-Nitro-4-methoxydibenzothiophene	161-2	(6)
2-Nitro-8-dibenzothiophenesulfonyl chloride	257	(16)
TRISUBSTITUTED DIBENZOTHIOPHENES		
1(?),3(?)-Dinitro-4-hydroxydibenzothiophene	204	(12)

TABLE II

DERIVATIVES OF DIBENZOTHIOPHENE-5-OXIDE
(DIBENZOTHIOPHENE SULFOXIDE)

Name of Compound	M.P.	Reference
Dibenzothiophene-5-oxide	188-88.5	(32)
MONOSUBSTITUTED DIBENZOTHIOPHENE-5-OXIDES		
2-Bromodibenzothiophene-5-oxide	171-2	(14)
2-Hydroxydibenzothiophene-5-oxide	147	(21)
DISUBSTITUTED DIBENZOTHIOPHENE-5-OXIDES		
1,4-Diacetoxydibenzothiophene-5-oxide	185	(38)
2-Hydroxy-3-carboxydibenzothiophene-5-oxide	258	(21)

TABLE III

DERIVATIVES OF DIBENZOTHIOPHENE-5-DIOXIDE
(DIBENZOTHIOPHENE SULFONE)

Name of Compound	M.P.	Reference
Dibenzothiophene-5-dioxide	235	(30,29a,41) (19,42)
MONOSUBSTITUTED DIBENZOTHIOPHENE-5-DIOXIDES		
3-Acetaminodibenzothiophene-5-dioxide	325-7	(30,29a)
2-Acetoxydibenzothiophene-5-dioxide	269	(34a)
3-Aminodibenzothiophene-5-dioxide	259-60	(18)
2-Benzoxydibenzothiophene-5-dioxide	176	(34a)
1-Bromodibenzothiophene-5-dioxide	170-1	(17)
2-Bromodibenzothiophene-5-dioxide	266-7	(34a,43)
3-Bromodibenzothiophene-5-dioxide	224-5	(6,18)
2-Chlorodibenzothiophene-5-dioxide	249	(34a,43)
2-Dibenzothiophenesulfonic acid 5-dioxide	276	(34a)
2-Dibenzothiophenesulfonyl chloride 5-dioxide	234-5	(34a)
2-Hydroxydibenzothiophene-5-dioxide	264	(21,34a)
2-Nitrodibenzothiophene-5-dioxide	258	(19,29a)

41. Courtot and Evain, Bull. soc. chim., 49, 1555 (1931).
42. Cullinane and Davies, Rec. trav. chim., 55, 881 (1936).
43. Chaix and Rochebovet, Bull. soc. chim., /5/ 2, 273 (1935).

TABLE III (Continued)

Name of Compound	M.P.	Reference
3-Nitrodibenzothiophene-5-dioxide	265-6	(18)
DISUBSTITUTED DIBENZOTHIOPHENE-5-DIOXIDES		
2,8-Diacetaminodibenzothiophene-5-dioxide	356-7	(29a,32,10)
2,8-Diaminodibenzothiophene-5-dioxide	329-31	(10,29a)
3,7-Diaminodibenzothiophene-5-dioxide	327	(19,44,42)
2,8-Dibenzothiophenedisulfonyl chloride 5-dioxide	333-340	(34a)
3,7-Dibenzothiophenedisulfonyl chloride 5-dioxide	236	(45)
3,7-Dibenzothiophenedisulfonanilide 5-dioxide	207	(45)
2,8-Dibenzoxydibenzothiophene-5-dioxide	227-8	(34a)
2,8-Dibromodibenzothiophene-5-dioxide	361-2	(10,34a)
3,7-Dibromodibenzothiophene-5-dioxide	315	(19,46,41)
2,8-Dichlorodibenzothiophene-5-dioxide	340	(34a)
3,7-Dichlorodibenzothiophene-5-dioxide	295-6	(41)
2,8-Dihydroxydibenzothiophene-5-dioxide	331	(34a)

44. Courtot and Chaix, Compt. rend., 192, 1667 (1931).
45. Pollak, Kauss, Katscher, and Lustig, Monatsh., 55, 358 (1930).
46. Courtot and Lin, Bull. soc. chim., /4/ 49, 1047 (1931).

TABLE III (Continued)

Name of Compound	M.P.	Reference
2-Hydroxy-3-dibenzothiophenecarboxylic acid 5-dioxide	284	(21)
2,8-Dimethyldibenzothiophene-5-dioxide	287-8	(47)
3,7-Dinitrodibenzothiophene-5-dioxide	290	(19,18)
2'-Methoxy-4'-chloro-2-hydroxy-3-dibenzothiophencarboxanilide 5-dioxide	300	(23)

HEXASUBSTITUTED DIBENZOTHIOPHENE-5-DIOXIDES

2,3,7,8-Tetramethoxy-1(?)-9(?)-dinitro-dibenzothiophene-5-dioxide	238	(48)

47. Fuchs and Grosz, Ber., 63, 1009 (1930).
48. Koch and Stukenbrock, Ann., 468, 162 (1929).
Fries

EXPERIMENTAL

A. Dibenzothiophene Compounds

Dibenzothiophene.[30]— The dibenzothiophene used during the course of this research was prepared in essential accordance with the directions of Gilman and Jacoby[17]. However, it was found that the crude yield previously obtained by eight alcoholic extractions of the reaction mixture, could be dupli- cated by the use of two extractions of one liter each of absolute ethanol. The yield of pure dibenzothiophene after distillation and recrystallization was 47 %.

4-Iododibenzothiophene.[30] - 4-Dibenzothienyllithium[17] was prepared by refluxing a mixture of 134 g. (0.73 mole) of di-benzothiophene and 0.88 mole of n-butyllithium[49,50] in 1500 cc. of ether for nineteen hours. At the end of this time, a negative Color Test II[51] showed that the alkyllithium compound had been used up. To the solution of 4-dibenzothienyllithium was slowly added 190 g. (0.75 mole) of powdered iodine. When the addition was complete, the reaction mixture was refluxed for one hour, and a negative Color Test I[52] at the end of this

49. Gilman and Stuckwisch, J. Am. Chem. Soc., 65, 1462 (1943).
50. The titer of the n-butyllithium was determined according
     to the method of Gilman and Haubein, ibid., 66, 1515 (1944).
51. Gilman and Swiss, ibid., 62, 1847 (1940).
52. Gilman and Schulze, ibid., 47, 2002 (1925).

time showed the absence of any organometallic compound. The solution was poured into water and the ether layer separated. The ether layer was treated with sodium bisulfite to remove the unreacted iodine and then dried over sodium sulfate. After removal of the ether by distillation, the residual oil was distilled under reduced pressure to give 100 g. (44 %) of crude product boiling from 160-170° / 1 mm. and melting over the range 90-100°. Recrystallization of the crude product from petroleum ether (b.p., 63-78°) to a constant melting point of 101-102° reduced the yield to 50 g. (22 %).

In following preparations, the iodine was dissolved in ether before being added to the organolithium compound. This procedure was found to be without advantage and involves the handling of an unnecessarily large volume of solvent. It was also found impractical to attempt recrystallization before distillation since any unreacted dibenzothiophene is more effectively separated from the 4-iododibenzothiophene by preliminary distillation under reduced pressure. The yield in the preparation in which this procedure was used was 20 %.

Anal. Calcd. for $C_{12}H_7IS$: I, 41.0.

Found: I, 41.1.

3-Aminodibenzothiophene[30].- A solution of sodamide in liquid ammonia was prepared according to the directions of

Vaughn, Vogt, and Nieuwland[53] from 4.6 g. (0.2 g. atom) of sodium and 0.5 g. of ferric nitrate in 250 cc. of liquid ammonia. Eighteen g. (0.058 mole) of 4-iododibenzothiophene was added to the sodamide solution over a period of fifteen minutes. If the addition of the 4-iododibenzothiophene was too rapid the reaction became violent. The reaction mixture was stirred mechanically for thirty minutes and the unreacted sodamide decomposed with ammonium chloride. The solution was allowed to warm to room temperature in order to facilitate evaporation of the ammonia. The residue was extracted with benzene and the benzene extracts treated with dry hydrogen chloride to precipitate the amine as the hydrochloride. Treatment of the amine hydrochloride with ammonium hydroxide liberated 8.5 g. (74 %) of the crude amine. (When 4-bromodibenzothiophene was used the crude yield was only 5 %). The amine was purified by dissolving it in hot methanol, treating the methanol solution with decolorizing carbon, filtering, and adding water to the filtrate until a 50-50 mixture resulted. There was obtained 5.7 g. (49.5%) of 3-aminodibenzothiophene melting at 114-119°. Repetition of this procedure raised the melting point to 121.5-122°.

Anal. Calcd. for $C_{12}H_9NS$: N, 7.05.

Found: N, 7.22.

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53. Vaughn, Vogt, and Nieuwland, J. Am. Chem. Soc., 56, 2120 (1934).

3-Acetaminodibenzothiophene[30].- A mixture of 3 g. (0.015 mole) of 3-aminodibenzothiophene and 2 g. (0.019 mole) of acetic anhydride in 20 cc. of benzene was refluxed for one hour. There was obtained by filtration 3 g. (83.5 %) of the acetamino derivative melting at 197-198°. Recrystallization from dilute ethanol raised the melting point to 199-200°.

Anal. Calcd. for $C_{14}H_{11}ONS$: N, 5.82.

Found: N, 6.02.

A mixed melting point with 4-acetaminodibenzothiophene (m.p. 198°) melted over the range of 170-190°.

3-Acetaminodibenzothiophene-5-dioxide[30]. /A/ From 3-Acetaminodibenzothiophene.- To 1.25 g. (0.005 mole) of 3-acetaminodibenzothiophene in 20 cc. of glacial acetic acid was added 10 cc. (0.08 mole) of 30 % hydrogen peroxide. The reaction mixture was heated for three hours on a boiling water bath. The orange-colored solid that settled out was removed by filtration after the mixture had cooled. The yield of product melting at 324-326° was one gram (70.5 %). The yield was decreased considerably when the reactants were refluxed. If the reaction mixture was poured into water rather than filtering directly, recrystallization from ethanol was necessary. The yield obtained when this method was used was 61 %.

/ B / From 3-Aminodibenzothiophene-5-dioxide. - A mixture of

0.1 g. (0.004 mole) of 3-aminodibenzothiophene-5-dioxide and a

few drops of acetic anhydride in 5 cc. of benzene was heated

for one-half hour at reflux temperature. There was obtained

0.1 g. (96 %) of the 3-acetaminodibenzothiophene-5-dioxide

melting at 325-327°. A mixed melting point determination with

the product obtained by the oxidation of 3-acetaminodibenzo-

thiophene was not depressed.

Anal. Calcd. for $C_{14}H_{11}O_3NS$: N, 5.13.

Found: N, 5.05.

Dibenzothiophene-5-dioxide[30].- One-tenth mole (18.4 g.)

of dibenzothiophene was dissolved in 100 cc. of glacial acetic

acid and the mixture was warmed to 80°. To this solution was

added 30 cc. of 30 % hydrogen peroxide and the mixture heated

at 90° for one hour, and refluxed for one-half hour. The

sulfone soon separated, and an additional 10 cc. of hydrogen

peroxide was added. At the end of another thirty minutes the

flame was removed and the reaction mixture allowed to cool.

The white sulfone was removed by filtration and washed well with

water. The yield of product melting at 233-234° was 20.7 g.

(96 %).[54]

A four-hour reflux period had no advantage and actually

lowered the yield to 92 %. However, a small amount of crude

material was obtained by dilution of the filtrate in this

preparation.

54. Unpublished studies of G. A. Martin.

When the reactants were refluxed for one hour immediately after the addition of the peroxide, and the reaction mixture allowed to stand overnight, the yield was 97.5 %.

Methyl 4-Dibenzothiophenecarboxylate[30].- 4-Dibenzothienyllithium was prepared by refluxing 5 g. (0.0161 mole) of 4-iododibenzothiophene and 0.28 g. (0.04 g. atom) of finely cut lithium in 50 cc. of ether. The reaction was kept under an atmosphere of nitrogen. Color Test I[52] was positive at the end of one hour and an acid-titration analysis[55] made at the end of three hours of refluxing showed the yield of aryllithium compound to be 75 %. The solution was poured on Dry Ice for the purpose of carbonation. The crude material that was obtained was recrystallized from dilute methanol to give a 55 % yield of acid melting at 245-250°. A second recrystallization raised the melting point to 248-251°, and sublimation at reduced pressure gave a melting point of 255-257°. The melting point reported by Gilman and Jacoby[17] was 252-253°. The acid was converted to the methyl ester by reaction with diazomethane and the ester was shown to be identical with an authentic specimen by a mixed melting point.

2-Nitrodibenzothiophene.- Cullinane[19] has reported a 40 % yield of 2-nitrodibenzothiophene by nitration of dibenzothiophene with fuming nitric acid. All attempts to duplicate

this yield resulted in yields below 20 %. In one particular
preparation the temperature was kept below 30°, as compared
to a temperature of 40° reported by Cullinane, but the yield
was only 15.5 %. In another attempt the theoretical amount
of fuming nitric acid was used rather than the fourfold
excess of Cullinane. The yield in this preparation was 3.3 %.
The most successful preparation involved the nitration of
10 g. (0.0544 mole) of dibenzothiophene in 80 cc. of glacial
acetic acid with 10 cc. of fuming nitric acid. The glacial
acetic acid solution of dibenzothiophene was kept at 30°
during the 30 minute addition of the nitric acid. When the
addition was complete the reaction mixture was stirred at
room temperature for one hour and then filtered directly.
In all previous runs the nitration mixture had been poured
into water. The nitration product was refluxed for several
hours with 100 cc. of ethyl alcohol. The insoluble 2-nitro-
dibenzothiophene was removed by filtering the hot solution.
The melting point was 186-187° and the yield was 3.5 g. (28.2 %).

2-Nitrodibenzothiophene-5-dioxide[19].- To a suspension of
15 g. (0.065 mole) of 2-nitrodibenzothiophene in 125 cc. of
glacial acetic acid at 100° was added 100 cc. (0.88 mole) of
30 % hydrogen peroxide. The reaction mixture was slowly
heated to reflux temperature and held at this temperature for
four hours. While the nitro compound was not completely

soluble in the acetic acid, it was possible to notice a
change in the crystal structure during the reflux period.
There was obtained by filtration 15 g. (88 %) of crude 2-
nitrodibenzothiophene-5-dioxide melting at 245-248°. Re-
crystallization of the crude product from dioxane gave a
melting point of 248-251°. A second recrystallization from
acetone raised the melting point to 255-256°. Cullinane[19]
prepared this compound by oxidation of 2-nitrodibenzo-
thiophene with a mixture of dichromate and sulfuric acid and
obtained a 90 % yield of product after recrystallization from
acetone. He also mentions that a similar yield was obtained
by oxidation with hydrogen peroxide but gives no details.

2-Acetyldibenzothiophene.- Burger and Bryant[4b] reported
that they were unable to repeat the results of Gilman and
Jacoby[17] in obtaining a 70 % yield of 2-acetyldibenzo-
thiophene from dibenzothiophene and acetyl chloride in the
presence of aluminum chloride. During the course of this re-
search it was necessary to prepare this compound and a 78 %
crude yield was obtained. The material was purified by a
new procedure and a value obtained for the final pure yield
not previously reported. Incidentally, Dr. R. R. Burtner was
also able to obtain the yield of Gilman and Jacoby in some
unpublished studies.

One-hundred and twenty g. (0.64 mole) of dibenzothio-
phene in 900 cc. of dry carbon disulfide was treated with

52 g. (0.64 mole) of acetyl chloride according to the directions
of Gilman and Jacoby[17]. The reaction product was purified by
distillation at reduced pressure and the observed boiling point
was 183-185°/ 1 mm. This material melted at 60-80° and there
was obtained 112.5 g. (78 %). Gilman and Jacoby listed the
yield as 70 % after this treatment. The crude material was re-
fluxed for two hours with two successive portions of 500 cc. of
ether. The melting point was 109-110° after this treatment.
Recrystallization from methanol gave 60 g. (41.5 %) of pure
product melting at 111-111.5°.

Burger, Wartman, and Lutz obtained a 25 % yield of pure
product melting at 111-112°. Gilman and Jacoby recrystallized
the distilled material from methanol several times to obtain
pure material melting at 111°.

2-Aminodibenzothiophene. /¯A¯/ From 2-Nitrodibenzothiophene.-
A suspension of 13.5 g. (0.059 mole) of 2-nitrodibenzothiophene
and one and one-half teaspoon of Raney nickel catalyst in 150
cc. of absolute ethanol was treated with hydrogen in a small
bomb. The reaction mixture was shaken overnight and a total
of 18 pounds of hydrogen was adsorbed. The solution was warmed
slightly and filtered. There was obtained 3.7 g. of very pure
amine melting at 133°. The filtrate was heated to reflux
temperature and diluted with water to the turbidity point. An
additional 7 g. of product melting at 129-131° was obtained.
The total yield was 10.7 g. (91.5 %). The best yield of

2-aminodibenzothiophene obtained by reduction with tin and hydrochloric acid was 66.7 % and the product melted at 125-126° after three recrystallizations from dilute ethanol.

/ B / From 2-Acetyldibenzothiophene Oxime. - A Beckmann rearrangement of 18 g. (0.075 mole) of the oxime of 2-acetyldibenzothiophene (prepared according to the method of Gilman and Jacoby[17]) in 250 cc. of benzene gave a quantitative yield of crude 2-acetaminodibenzothiophene. This crude product was refluxed with 500 cc. of 1:1 hydrochloric acid for four hours. The solution was filtered hot and the residue extracted with two liters of boiling water. The free amine was liberated from the extracts by treatment with ammonium hydroxide. The yield was 10.7 g. (72 %) melting at 129-131°. Gilman and Jacoby[17] prepared the acetamino compound in 70 % yield by this method but did not hydrolyze it to the free amine. Burger, Wartman, and Lutz[4a] used dry hydrogen chloride in a similar Beckmann rearrangement but listed no yield of product.

2-Aminodibenzothiophene-5-dioxide. - A mixture of 9 g. (0.034 mole) of 2-nitrodibenzothiophene-5-dioxide, 23 g. of granular tin metal, 115 cc. of hydrochloric acid, and 100 cc. of ethanol was stirred at reflux temperature until a clear solution resulted. After a few minutes the white crystals of amine hydrochloride began to settle out. Heating and mechanical stirring were continued for one hour. When the reaction mixture

had cooled to room temperature, the amine hydrochloride was removed by filtration. Treatment of the amine hydrochloride with ammonium hydroxide gave 6.86 g. (87 %) of 2-aminodibenzothiophene-5-dioxide melting at 274-276°. Recrystallization from methanol raised the melting point to 278-280° but reduced the yield to 4.7 g. (59.5 %).

Anal. Calcd. for $C_{12}H_9O_2NS$: S, 13.84.

Found: S, 13.50.

2-Hydroxydibenzothiophene. /‾A‾7 From 2-Aminodibenzothiophene.- A mixture of 9.7 g. (0.049 mole) of 2-aminodibenzothiophene, and 10.2 g. (0.103 mole) of concentrated sulfuric acid in 95 cc. of water was heated gently with stirring. When the amine sulfate had formed, the solution was cooled to -5° and 3.7 g. of sodium nitrite in 15 cc. of water was slowly added. The reaction mixture was allowed to stir for ten minutes after the addition was complete and the slight excess of nitrous acid was destroyed with a small amount of urea. The reaction mixture was then heated on a water bath at 50-60° for 3 hours. The mixture was extracted with one liter of ether in small portions and the extracts dried over sodium sulfate. The ether was removed by distillation and the remaining oil extracted with sodium hydroxide solution. Acidification of the extracts gave 2 g. (20 %) of crude phenol. Crystallization from dilute ethanol gave a product melting at 130-140°. Recrystallization

from petroleum ether (b.p., 68-75°) followed by two recrystal-
lizations from dilute ethanol raised the melting point to 158°.

/B/ Attempted From 2-Bromodibenzothiophene. - A mixture of
18.4 g. (0.1 mole) of 2-bromodibenzothiophene, 22 g. of sodium
hydroxide, 8 g. of copper sulfate, 22 g. of copper turnings,
2.5 g. of copper-bronze powder, and 65 cc. of water were
sealed in an autoclave. The bomb was heated at approximately
300° for six hours. The solid mass that resulted was worked
up in the usual manner but no phenolic material could be isolated.

Cullinane[19] prepared 2-hydroxydibenzothiophene by diazatiza-
tion of the amine hydrochloride and obtained a 20 % yield. He
purified the phenol by distillation with super-heated steam.

2,8-Diacetyldibenzothiophene. - The essential directions of
Burger, Wartman, and Lutz[4a] were followed but their method of
purification of the crude product was improved upon.

To a mixture of 22.6 g. (0.1 mole) of 2-acetyldibenzo-
thiophene and 53 g. (0.4 mole) of aluminum chloride in 500 cc.
of dry carbon disulfide was added 7.8 g. (0.1 mole) of acetyl
chloride over a period of ten minutes. The reaction mixture
was stirred under reflux conditions for six hours. At the end
of this time the suspension was poured onto a mixture of ice
and hydrochloric acid and the resulting mixture stirred for one
hour. A quantitative yield of crude product was obtained by
filtration since it is insoluble in carbon disulfide. The

crude white solid was washed with 50 cc. of benzene and recrystallized from ethanol to give 20.5 g. (76.5 %) of the 2,8-diacetyldibenzothiophene melting at 206-208°. If the crude product is refluxed with one liter of ethanol (an insufficient amount for complete solution) the yield is 77 %.

Burger, Wartman, and Lutz[4a] reported a yield of 90 % on a one gram run but do not specify as to whether that was the yield of pure or crude product. They removed the carbon disulfide from the original reaction mixture by steam distillation. The residue was extracted with chloroform; the chloroform extracts were evaporated; the residue was treated with cold benzene; and, the insoluble portion was recrystallized from ethanol. When these same researchers treated dibenzothiophene with two equivalents of acetyl chloride they obtained only a 19 % yield of 2,8-diacetyl-dibenzothiophene.

2,8-Diacetyldibenzothiophene Dioxime.- One-tenth mole (26.8 g.) of 2,8-diacetyldibenzothiophene, 27.2 g. (0.4 mole) of hydroxylamine hydrochloride, and 60 cc. of pyridine in 250 cc. of absolute ethanol were stirred under reflux conditions for 3 hours. The solution was evaporated to one-half the volume and the remaining viscous liquid poured into 1600 cc. of water. The white solid that formed was removed by filtration and washed well with water. There was

by dinitration of dibenzothiophene according to the directions of Courtot[32] gave only 12 % of the 2-nitrodibenzothiophene. Courtot reported a yield of 45% of the dinitrodibenzothiophene and a 40 % yield of mononitrodibenzothiophene.

2,8-Diaminodibenzothiophene.- A mixture of 1.1 g. (0.004 mole) of 2,8-dinitrodibenzothiophene, 20 cc. of hydrochloric acid, 4 g. of tin, 20 cc. of ethanol, and 40 cc. of water was refluxed for four and one-half hours. The insoluble dinitro compound gradually disappeared and a clear solution resulted. This solution was filtered hot to remove the small amount of insoluble material and the filtrate neutralized with ammonium hydroxide. The crude amine was removed by filtration and dissolved in hot ethyl alcohol. The resulting solution was filtered to remove the insoluble tin salts. Dilution of the hot filtrate gave 0.3 g. (35 %) of the 2,8-diaminodibenzothiophene melting at 180-195°. The melting point of this small amount could not be improved by crystallization from either dilute methanol or dilute ethanol.

In a second preparation 3.2 g. (0.0117 mole) of 2,8-dinitrodibenzothiophene was dissolved in 100 cc. of absolute ethanol and one teaspoon of Raney nickel catalyst was added. The mixture was warmed slightly and the reaction flask attached to a hydrogenation apparatus. The flask was allowed to remain in the shaking apparatus until no more hydrogen was adsorbed. The reaction mixture was heated to about 80° and

filtered hot. There was obtained 0.7 g. of 2,8-diaminodibenzothiophene melting at 194-196°. An additional 0.45 g. of diamine was obtained by dilution of the filtrate. The total yield was 46 %. A mixed melting point with the diaminodibenzothiophene (m.p., 199.5-200°) obtained by a Beckmann rearrangement (see following preparation) of 2,8-diacetyldibenzothiophene dioxime followed by hydrolysis, was not depressed.

Courtot and Pomonis[32] prepared this compound by reduction of the 2,8-dinitrodibenzothiophene but listed no details of the method employed. They reported the melting point as 178°. Burger, Wartman, and Lutz[4a] prepared the compound by a Beckmann rearrangement of the dioxime of 2,8-diacetyldibenzothiophene followed by hydrolysis of the resulting diacetamino compound. They purified their product by sublimation and recorded the melting point as 193-194°. Neumoyer and Amstutz[10], in some recent studies, prepared 2,8-diaminodibenzothiophene from 2,8-dibromodibenzothiophene by a copper-catalyzed ammination reaction and obtained pure product melting at 199.5-201.5°. No yields were reported in any of these references but this is understandable since the

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obtained 28.5 g. (95.5 %) of 2,8-diacetyldibenzothiophene dioxime melting at 266-267°. Recrystallization from ethanol raised the melting point to 268-270°.

Burger, Wartman, and Lutz[4a] prepared this compound by

reacting the acetyl compound for seven hours with hydroxyl-

benzene at 40° was added 60 g. (0.287 mole) of phosphorous
pentachloride at such a rate as to cause the benzene to re-
flux gently. When reaction had subsided, the mixture was
poured on ice, and the resulting mixture made alkaline with
sodium carbonate. There was obtained 25 g. (93.5 %) of
crude 2,8-diacetaminodibenzothiophene melting at 240-280°.

Burger, Wartman, and Lutz[4a] dissolved their dioxime in
acetic anhydride and effected the rearrangement by saturat-
ing the solution with dry hydrogen chloride. They listed
no yield but purified the crude material by vacuum sublima-
tion and recrystallization from methanol. The melting point
was 252-253°. When their procedure was followed in these
laboratories only a 30 % yield of crude product was obtained
melting from 220-280°.

The crude diacetamino compound (0.84 mole) was refluxed
with 800 cc. of 18 % hydrochloric acid for four hours. The
resulting solution was diluted to 1600 cc. and heated again
to boiling subsequent to hot filtration. There was obtained
13.7 g. (76 %) of 2,8-diaminodibenzothiophene melting at
182-192°. Recrystallization from ethanol and treatment with
decolorizing carbon raised the melting point to 197-198°.
A further recrystallization from ethanol gave white crystals
melting at 199.5-200°. As mentioned above Burger[4a] listed
the melting point as 193-194° and Courtot[32] as 178°. How-
ever, a mixed melting point, as indicated previously, with

the material prepared by reduction of the 2,8-dinitrodibenzothiophene, was not depressed.

Anal. Calcd. for $C_{12}H_{10}N_2S$: S, 14.95.

Found: S, 14.90.

To 0.1 g. (0.0004 mole) of 2,8-diaminodibenzothiophene dissolved in 25 cc. of benzene was added a few drops of acetic anhydride and the mixture refluxed for one hour. When the reaction mixture had cooled to room temperature, the benzene was removed by filtration. There was obtained 0.11 g. (92 %) of 2,8-diacetaminodibenzothiophene melting at 299-301°. Recrystallization from dilute ethanol raised the melting point to 303°. Neumoyer and Amstutz[10] using essentially the same procedure obtained a product melting at 304-305.5°. Burger, Wartman, and Lutz[4a] listed the melting point as 252-253° and Courtot recorded it as 237°.

Anal. Calcd. for $C_{16}H_{14}O_2N_2S$: N, 9.39.

Found: N, 9.44.

/_B_7 From 2,8-Diaminodibenzothiophene Prepared from Dinitrodibenzothiophene.- One-tenth g. (0.0004 mole) of 2,8-diaminodibenzothiophene (prepared by reduction of the 2,8-dinitrodibenzothiophene) was treated with acetic anhydride as above and gave 0.1 g. of 2,8-diacetaminodibenzothiophene melting at 298-300°. Recrystallization from dilute methanol raised the melting point to 301-302°. A mixed melting point with the material prepared above was not depressed.

<u>2,8-Diacetaminodibenzothiophene-5-dioxide.-</u> One g.
(0.003 mole) of 2,8-diacetaminodibenzothiophene was dissolved
in 20 cc. of glacial acetic acid by warming to 70°. To this
solution was added 2 cc. of 30 % hydrogen peroxide and the
temperature slowly raised to 93° and held at that temperature
for three hours. An additional 2 cc. of hydrogen peroxide
had been added during this heating period. The reaction
mixture was poured on ice and the tan solid removed by
filtration. The yield of dioxide melting at 330-331° was
1 g. (95 %). This solid was refluxed with 75 cc. of ethanol
to remove any unreacted 2,8-diacetaminodibenzothiophene and
the melting point of the 2,8-diacetaminodibenzothiophene-5-
dioxide was raised to 339-341°. A similar treatment with
100 cc. of dioxane gave a melting point of 356-357°. Treat-
ment with boiling acetone did not change the melting point.

Neumoyer and Amstutz[10] reported that they were unable to
oxidize their 2,8-diacetaminodibenzothiophene to the correspond-
ing dioxide with the use of hydrogen peroxide. They treated
2,8-diaminodibenzothiophene with an excess of acetic anhydride
and suggested that they had obtained the tetracetyl compound.
However, no attempt was made to purify this doubtful compound
nor the resulting dioxide that was obtained after treatment
with hydrogen peroxide. They hydrolyzed this tetracetyl
dioxide to 2,8-diaminodibenzothiophene-5-dioxide and recorded
a melting point that is in agreement with the melting point

of the same compound prepared during the course of this research.

Anal. Calcd. for $C_{16}H_{14}O_4N_2S$: S, 9.70.

Found: S, 9.65.

Ten g. (0.0335 mole) of crude 2,8-diacetaminodibenzothiophene (m.p., 275-280°) was suspended in 300 cc. of glacial acetic acid at 80°. One-hundred cc. of freshly prepared sodium hypochlorite solution (prepared according to the directions of Weijlard[55]) was added over a period of fifteen minutes. The reaction mixture darkened considerably during the following fifteen minutes that it was allowed to stir. A quantitative crude yield was obtained by pouring the reaction mixture into one liter of water and removing the product by filtration. The crude 2,8-diacetaminodibenzothiophene-5-dioxide was used for the preparation of the 2,8-diaminodibenzothiophene-5-dioxide.

2,8-Diaminodibenzothiophene-5-dioxide.- A mixture of 0.8 g. (0.0024 mole) of 2,8-diacetaminodibenzothiophene-5-dioxide was refluxed for thirty minutes with 100 cc. of 18 % hydrochloric acid. The diacetaminodibenzothiophene-5-dioxide was insoluble in the dilute hydrochloric acid solution but as the hydrolysis proceeded the solution became clear. The reaction mixture was diluted to twice the volume with water and refluxed for an additional fifteen minutes. The solution

55. Weijlard, J. Am. Chem. Soc., 67, 1031 (1945).

was filtered hot to remove the small amount of insoluble material and the filtrate nuetralized with ammonium hydroxide. There was obtained 0.6 g. of material melting at 306-308°. This crude material was dissolved in 200 cc. of hot ethanol. The ethanol solution was treated with decolorizing carbon and filtered hot. The yield of pure 2,8-diaminodibenzothiophene-5-dioxide melting at 327-328° was 0.3 g. or 51 %.

In another preparation, the crude 2,8-diacetaminodibenzothiophene, prepared by the hypochlorite oxidation of 2,8-diacetaminodibenzothiophene, was refluxed for two hours with 300 cc. of 18 % hydrochloric acid and allowed to stand overnight. The insoluble material was extracted twice with one liter of water and the combined extracts treated with decolorizing carbon to remove the dark red color. The solution of the diamine dihydrochloride was treated with ammonium hydroxide to give 4 g. (48.5 % yield based on the amount of 2,8-diacetaminodibenzothiophene used in the hypochlorite oxidation) of 2,8-diaminodibenzothiophene-5-dioxide melting at 325-326°.

Neumoyer and Amstutz[10] prepared this compound in 82 % yield by amination of 2,8-dibromodibenzothiophene-5-dioxide in the presence of copper-bronze powder. They recrystallized the crude product from water to obtain pure material melting at 329-331°.

<u>Anal</u>. Calcd. for $C_{12}H_{10}O_2N$ S : S, 13.0.

Found: S, 13.4.

<u>4-Methoxydibenzothiophene-5-dioxide.</u>- To a hot solution of 8.1 g. (0.038 mole) of 4-methoxydibenzothiophene in 50 cc. of glacial acetic acid was added 12 cc. (0.1 mole) of 30 % hydrogen peroxide. A precipitate formed after the addition but almost immediately redissolved. After the addition of 15 cc. more of hydrogen peroxide the solution was refluxed for three and one-half hours. After cooling and filtering, 6.6 g. (70.5 %) of product melting at 189-192° was obtained. An additional 1.3 g. of product was obtained by dilution of the filtrate and this increased the yield to 85 %. Recrystallization from ethanol raised the melting point to 191-192°.

<u>Anal</u>. Calcd. for $C_{13}H_{10}O_3S$: S, 13.00.

Found: S, 13.33.

<u>Reaction of Dibenzothiophene with Aluminum Chloride.</u>- One-tenth mole (18.4 g.) of dibenzothiophene and 0.3 mole (40 g.) of aluminum chloride was sealed in a Carius tube under an atmosphere of nitrogen. The tube was heated at 200-210° for 72 hours. A considerable amount of hydrogen sulfide burst from the tube when it was cracked open. The dark tarry contents were extracted with 150 cc. of dry benzene and the extracts treated with carbon dioxide at the reflux temperature of benzene for eight hours. No dibenzothiophenecarboxylic acid could be isolated from the reaction mixture and it would appear that the high temperature caused

cleavage rather than metalation.

Reaction of Dibenzothiophene With Aluminum Bromide.-
One-tenth mole of dibenzothiophene was treated with 0.3
mole of aluminum bromide in a Carius tube at 150° for three
days. The reaction mixture was worked up in the same
manner as the previous reaction but no acid could be iso-
lated.

Another attempt was made to metalate dibenzothiophene
with aluminum bromide at 120-125° for 48 hours but no acid
could be isolated on subsequent carbonation. In all the
experiments a large volume of hydrogen sulfide was present
when the Carius tubes were opened.

Reaction of Dibenzothiophene with Aluminum Iodide.-
The same negative results were obtained as in the two pre-
ceding experiments when 0.05 mole of dibenzothiophene was
heated at 130-135° with 0.142 mole of aluminum iodide.

4-Trimethylsilyldibenzothiophene.- 4-Dibenzothienyl-
lithium was prepared in the usual manner from 37.8 g.
(0.2 mole) of dibenzothiophene and 0.23 mole of n-butyl-
lithium. The reaction flask was cooled in an ice bath and
21.6 g. (0.2 mole) of trimethylsilyl chloride in 50 cc.
of ether was added dropwise. The reaction mixture was
slowly brought to reflux temperature and held there for 48
hours. Color Test I[52] was positive at the end of twenty-
four and forty-eight hours but a previous preparation had

shown that additional refluxing or the addition of a large excess of the trimethylsilyl chloride had no effect on the small amount of organometallic compound remaining. Water was added to the mixture to decompose the unreacted 4-dibenzothienyllithium. The ether layer was removed and dried. After removal of the ether, the remaining oil was distilled at reduced pressure. The crude 4-trimethylsilyldibenzothiophene boiled at $180°/$ 5 mm. Other observed boiling points were $215-217°/$ 20 mm., $135-137°/$ 0.5 mm., and $142-143°/$ 0.8 mm. Three fractionations were necessary to remove the unreacted dibenzothiophene. The pure yield was 27 g. (53 %). The following constants were obtained for this compound: n_D^{20} 1.6354; d_4^{20} 1.112; MR_D calcd. 80.5; and MR_D found 82.4. (The molecular refraction was calculated from the values of Warrick[56] and the value given by Lange[56] for the R-S-R linkage. The bond refraction of the R-S-R linkage in a cyclic compound like dibenzothiophene has not been determined as far as the author can ascertain.)

(2-Trimethylsilyldibenzothiophene has recently been prepared in these laboratories by Mr. John Irwin and was found to be a solid melting at $43°$ so we could not determine whether the discrepancy between the calculated and found

56. Warrick, J. Am. Chem. Soc., 68, 2455 (1946); Lange, Handbook of Chemistry, 5th Edition 1946, Handbook Publishers, Sandusky, Ohio, p. 1025; see also Sauer, J. Am. Chem. Soc., 68, 954 (1946).

molecular refraction in 4-trimethylsilyldibenzothiophene
also occurred in other liquid dibenzothiophene compounds.)

<u>Anal</u>. Calcd. for $C_{15}H_{16}SSi$: Si, 10.94.

Found: Si, 10.50.

<u>Cleavage of 4-Trimethylsilyldibenzothiophene</u>.- Anhydrous
hydrogen chloride was slowly passed through a refluxing
solution of 5.2 g. (0.2 mole) of 4-trimethylsilyldibenzo-
thiophene in 100 cc. of glacial acetic acid for fifteen
hours. The outlet of the condenser was connected to a Dry-
Ice acetone cooled trap. The reaction mixture was poured in-
to water at the end of the fifteen hours. There was obtained
3.2 g. (87 %) of dibenzothiophene melting at 89-91°. Re-
crystallization from ethanol raised the melting point to
95-96°. A mixed melting point with an authentic specimen of
dibenzothiophene was not depressed.

The trap contained 1 g. (48 %) of trimethylsilyl
chloride which was identified by preparation of the addition
compound with thiourea. The melting point was 111-113° and
a mixed melting point with an authentic specimen (m.p. 117°)
was not depressed. The proof of identity of this addition
product is being determined by Mr. Wm. Meikle.

<u>4-Trimethylsilyldibenzothiophene-5-dioxide</u>.- To 5.2 g.
(0.2 mole) of 4-trimethylsilyldibenzothiophene in 50 cc. of
glacial acetic acid was added 10 cc. of 30 % hydrogen
peroxide in 15 cc. of glacial acetic acid. The mixture was

kept at a temperature of 100° for 2 hours and after the addition of an additional 10 cc. of hydrogen peroxide was refluxed for two hours. The reaction mixture was poured into water and a quantitative yield of crude produce melting at $125-130^o$ was obtained. Recrystallization from ethanol gave a melting point of $140-143^o$. A second recrystallization from petroleum ether (b.p., $65-78^o$) raised the melting point to $146-147^o$. The yield was 2.5 g. (42 %).

Anal. Calcd. for $C_{15}H_{16}O_2SSi$: Si, 9.74.

Found: Si, 9.75.

Cleavage of 4-Trimethylsilyldibenzothiophene-5-dioxide.-
One g. (0.0035 mole) of 4-trimethylsilyldibenzothiophene-5-dioxide in 50 cc. of glacial acetic acid was treated with dry hydrogen chloride in the same manner as was the 4-trimethylsilyldibenzothiophene. At the end of fifteen hours the reaction mixture was poured into water and there was obtained a quantitative yield of starting material.

Nitration of 4-Trimethylsilyldibenzothiophene-5-dioxide.-
To a mixture of 4 cc. of glacial acetic acid and 4 cc. of concentrated sulfuric acid was added 1 g. (0.0035 mole) of 4-trimethylsilyldibenzothiophene-5-dioxide. The mixture was cooled to 5° and 6 cc. of fuming nitric acid added dropwise. The nitration mixture was stirred at 5° for onehalf hour. However, during this time the temperature was

allowed to reach 20° for 5 minutes. The reaction mixture was poured into water and there was obtained 1.1 g. (95 %) of a product melting at 180-200°. Recrystallization from ethanol raised the melting point to 223-224°. The yield of pure material was 0.4 g. (34 %).

Anal.   Calcd. for $C_{15}H_{15}O_4NSSi$:   Si,   8.43.
                                            N,   4.21

Found: Si,   8.72.
             N,   4.10.

Thanks are due to Mr. John Irwin for the nitrogen analysis.

4-Triphenylsilyldibenzothiophene. - Triphenylethoxy-silane was prepared by the method of Clark[57] from 41.6 g. (0.2 mole) of tetraethyl orthosilicate and 0.6 mole of phenyllithium in 600 cc. of ether. 4-Dibenzothienyllithium was prepared from 55.3 g. (0.3 mole) of dibenzothiophene and 0.29 mole of n-butyllithium. To the solution of triphenyl-ethoxysilane was added the 4-dibenzothienyllithium solution in a dropwise manner. The ensuing reaction was sufficient to reflux the ether for the first five minutes of the addition. When all of the 4-dibenzothienyllithium had been added the solution was refluxed for twenty-one hours. Color Test I[52] was positive at the end of this time, but since an excess of the 4-dibenzothienyllithium was probably present, the reaction mixture was hydrolyzed with water and dilute hydrochloric acid. The ether layer was separated and dried

57.   Clark, Doctoral Dissertation, Iowa State College, 1946.

over calcium chloride. After removal of the ether by distillation, a yellow oil remained. The oil solidified almost completely after standing overnight. This solid was refluxed with 100 cc. of ethyl acetate and 50 cc. of glacial acetic acid. The hot solvent was removed by filtration and the remaining white solid (7.5 g.) melted at 181-186°. A small amount of this crude material was recrystallized from dilute acetic acid and the melting point was raised to 190-192°. One gram of the crude material was refluxed with ethyl alcohol to give a melting point (after filtration) of 192-194°. Recrystallization from ethyl acetate gave a melting point of 193-194°. The remaining crude material, and the crude material obtained by dilution of the filtrates, was recrystallized from ethyl acetate to give a total pure yield of 6 g. (6.8 %).

In another preparation of the same size, the crude material was distilled at 1 mm. pressure in hopes of more efficient removal of the unreacted dibenzothiophene. From the material distilling at 200-250°, there was isolated only 1.4 g. of 4-triphenylsilyldibenzothiophene.

Anal. Calcd. for $C_{30}H_{22}SSi$: Si, 6.34.

Found: Si, 6.06, 6.11.

4-Triphenylsilyldibenzothiophene-5-dioxide.- To 1.5 (0.0034 mole) of 4-triphenylsilyldibenzothiophene in 20 cc. of glacial acetic acid was added 10 cc. of 30 % hydrogen

peroxide. The solution was refluxed for four hours and then
allowed to cool to room temperature. There was obtained 1.5
g. (93 %) of the 5-dioxide melting at 195-210°. Two re-
crystallizations from ethyl acetate raised the melting point
to 212-213°.

Anal. Calcd. for $C_{30}H_{22}O_2SSi$: Si, 5.95.

Found: Si, 5.75.

Cleavage of 4-Triphenylsilyldibenzothiophene.- Anhydrous
hydrogen chloride was passed through a refluxing solution
of 5 g. (0.011 mole) of 4-triphenylsilyldibenzothiophene in
120 cc. of glacial acetic acid for 16 hours. The solution
was allowed to cool to room temperature and the solid re-
moved by filtration. There was obtained 2.75 g. (55 %) of
4-triphenylsilyldibenzothiophene melting at 187-191°. No
cleavage products were isolated. The 4-triphenylsilyldi-
benzothiophene was identified by means of a melting point
determination with an authentic specimen.

Reaction between 4-Triphenylsilyldibenzothiophene and
Bromine.- A refluxing solution of 1.2 g. (0.0027 mole) of 4-
triphenylsilyldibenzothiophene in 20 cc. of glacial acetic
acid was treated dropwise with 0.435 g. (0.0027 mole) of
bromine. The reaction mixture was refluxed for three hours.
Subsequent treatment with 50 cc. of water gave a yellow-
brown solid melting at 40-70°. The material was probably a
mixture of triphenylsilanol and 4-bromodibenzothiophene.

(A sodium fusion test verified the presence of bromine.)
Recrystallizations from petroleum ether (b.p., 65-78°)
would not raise the melting point above 60-85°.

Attempted Preparation of 4-Tri-n-butylsilyldibenzo-
thiophene.- To 20.8 g. (0.1 mole) of tetraethyl orthosili-
cate in 50 cc. of ether was added 417 cc. (0.3 mole) of n-
butyllithium. When the addition was complete the solution
was refluxed for twenty-four hours, at the end of which time
Color Test II[51] was negative. To this solution was added
a solution of 4-dibenzothienyllithium prepared from 18.4 g.
(0.1 mole) of dibenzothiophene and 0.13 mole of n-butyl-
lithium. The reaction mixture was refluxed for 50 hours
and then hydrolyzed with water and dilute hydrochloric acid.
The ether layer was separated, dried over calcium chloride,
and the ether removed by distillation. The remaining solid
was crystallized from glacial acetic acid to give 14 g.
(72 %) of unreacted dibenzothiophene.

Attempted Preparation of 2-Tri-n-butylsilyldibenzo-
thiophene.- Tri-n-butylsilyl chloride was prepared by the
addition of 0.132 mole of n-butyllithium in 110 cc. of ether
to 7.5 g. (0.044 mole) of silicon tetrachloride in 100 cc. of
ether. Color Test II[51] was negative immediately after the
addition was complete.

To the solution of tri-n-butylsilyl chloride was added
a solution of 2-dibenzothienyllithium prepared by the

addition of 0.044 mole of n-butyllithium to 11.5 g. (0.044 mole) of 2-bromodibenzothiophene in 50 cc. of ether. Color Test I[52] was negative after the addition was complete. The reaction mixture was treated with water; the ether layer removed and dried; and the ether removed by distillation. The oil that remained was distilled under reduced pressure and a clear liquid was collected at 111-112°/3 mm. A white solid distilled at 140-170°/3 mm. that was subsequently found to be dibenzothiophene. The liquid distillate was refractionated and boiled at 90-91°/1.5 mm. The index of refraction was n^{20}_D 1.4496. Marshall[58] observed the boiling point of tri-n-butylsilanol to be 80°/0.3 mm. and recorded the index of refraction as n^{20}_D 1.4449, so it is probable that the material obtained here was slightly impure tri-n-butylsilanol.

Attempted Preparation of Triethoxy-4-dibenzothienyl-silane.- To 0.1 mole of triethoxysilyl chloride in 50 cc. of dry ether was added an ether solution of 4-dibenzothienyllithium prepared from 18.4 g. (0.1 mole) of dibenzothiophene in 100 cc. of ether and 0.2 mole of n-butyllithium. Color Test I[52] was negative one-half hour after the addition was complete. The lithium chloride was removed by filtration and the ether removed from the filtrate by distillation. The viscous oil that remained was distilled under vacuum

58. Marshall, Doctoral Dissertation, Iowa State College, 1948.

and a solid was obtained boiling at 160°/ 1 mm. This
material was found to be dibenzothiophene.

B. Organosilicon Compounds

Triphenyl-β-styrylsilane.- Twenty-five g. (0.096
mole) of triphenylsilanol was suspended in 200 cc. of an-
hydrous ether in a 500 cc. three-necked flask fitted with an
efficient stirrer, a gas inlet tube, and a calcium chloride
tube. Anhydrous hydrogen chloride was passed through the
vigorously stirred solution until one-half of the volume of
ether had been carried away. The gas inlet tube was re-
moved and the remainder of the ether drawn off on the water
aspirator. The final traces of ether were removed by heat-
ing the reaction flask containing the product on a water
bath at 70° under the vacuum of the water aspirator. The
product was recrystallized from petroleum ether (b.p., 95-
110°) to give 23 g. (86 %) of triphenylsilyl chloride melt-
ing at 91-94°. If a purer product is desired the material
can be crystallized again from the petroleum ether.

To 1.26 g. (0.18 g. atom) of very finely cut lithium
in 10 cc. of ether was added 9.15 g. (0.05 mole) of freshly
distilled β-bromostyrene (b.p., 127°/ 15 mm.) in 50 cc. of

ether[59]. The solution turned a blood red color during the fifteen minutes required for the addition. The reaction mixture was stirred five minutes at room temperature after the addition was complete. Another preparation of the same size was made simultaneously in another reaction flask since it was found that larger runs than the one described give predominantly α-lithio-β-bromostyrene, which loses lithium bromide to give phenyl acetylene[59].

To 17 g. (0.6 mole) of the freshly prepared triphenylsilyl chloride in 100 cc. of ether was rapidly added the β-styryllithium. The blood red color of the styryllithium disappeared during the addition of the first half of the solution but remained thereafter. The second preparation was rapidly added immediately after the first. Color Test I[52] was negative after the reaction mixture had been refluxed for three hours. The solution was treated with water; the ether layer removed and dried; and the ether removed by distillation. A yellow oil remained containing particles of solid. The material was cooled and the solid removed by filtration. After recrystallization from petroleum ether (b.p., 65-78°) there was obtained 10 g. (47 %) of triphenyl-β-styrylsilane melting at 140-143°. Recrystallization from ethanol raised the melting point to 146-147°.

59. Wright, J. Org. Chem., 1, 457 (1936); Gilman, Zoellner, and Selby, J. Am. Chem. Soc., 55, 1257 (1933); Gilman, Langham, and Moore, Ibid. 62, 2327 (1940); Wittig and Witt, Ber., 74B, 1474 (1941).

mineral acids, and the material was probably a mixture of various styrene polymers.

__Triphenylphenylethinylsilane__[60].- Triphenylphenylethinyl-silane was prepared according to the method of Plunket[60] from 12.94 g. (0.0915 mole) of silicon tetrachloride, 0.2715 mole of phenyllithium in 259 cc. of ether, and 0.0915 mole of phenylethinyllithium /prepared from 9.35 g. (0.0915 mole) of phenylacetylene and 0.0915 mole of phenyllithium in 86 cc. of ether7. The yield of pure material melting at 96-98° was 30 %.

When the same preparation was attempted using 0.03 mole of triphenylethoxysilane and 0.3 mole of phenylethinyl-lithium the yield of triphenylphenylethinylsilane was 10 %. An attempt to prepare phenylethinyltriethoxysilane according to method of Andrianov[61] resulted in failure.

__Hydrogen Chloride Cleavage of Triphenylphenylethinyl-silane__.- Dry hydrogen chloride was passed through a refluxing solution of 4.5 g. (0.012 mole) of triphenylphenylethinyl-silane in 100 cc. of glacial acetic acid for 15 hours. At the end of this time the clear solution was poured into water. The water solution was extracted with ether; the ether extracts were dried over sodium sulfate; and the ether was removed by distillation. The residue was distilled

60. Plunket, Doctoral Dissertation, Iowa State College, 1947.
61. Andrianov, _J_. _Gen_. _Chem_., (U.S.S.R.) 8, 1255 (1938).

under reduced pressure to give 1 g. (67 %) of acetophenone, identified by preparation of the 2,4-dinitrophenyl hydrazone (m.p. 245-246°). A mixed melting point with an authentic specimen of the 2,4-dinitrophenyl hydrazone of acetophenone was not depressed.

The solid residue remaining after removal of the acetophenone was dissolved in xylene. The xylene solution was treated with petroleum ether (b.p., 95-110°) until solid material settled out. Two recrystallizations from benzene gave a melting point of 223-224°. A mixed melting point with hexaphenyldisiloxane was not depressed. The yield of hexaphenyldisiloxane was 1 g. (32 %).

Triphenyl-α-chloroethylsilane.- To 17.5 g. (0.0887 mole) of α-chloroethyltrichlorosilane (prepared according to the directions of Sommer and Whitmore[62]) in 50 cc. of ether was added 0.267 mole of phenyllithium in 216 cc. of ether. The rate of addition was approximately 4 cc. per minute, and the reaction flask was well cooled in ice during the addition. Color Test I[52] was positive when the addition was complete but negative after the reaction mixture was stirred mechanically at room temperature for thirty minutes. Water was added to the solution and the ether layer removed and dried. The ether was removed by distillation and a yellow oily residue remained. The residue

62. (a) Sommer and Whitmore, J. Am. Chem. Soc., 68, 485 (1946); (b) for a discussion of the general use of sulfuryl chloride see Kharasch and Brown, ibid., 62, 926 (1940).

partially solidified on standing overnight at a temperature
of 10°. The melting point of the 6 g. (21 % yield) of solid
material was 90-110°. Recrystallization from petroleum
ether (b.p., 65-78°), ethanol, and petroleum ether, in the
order given, gave a melting point of 129-130°. It was ob-
served that if only sufficient solvent was used to dissolve
the material, the melting point was improved very slowly.
However, if a 10 % excess of solvent was used only two
recrystallizations were necessary to obtain pure material.

<u>Anal</u>. Calcd. for $C_{20}H_{19}ClSi$: Si, 8.67.

Cl, 10.90.

Found: Si, 8.69.

Cl, 11.01

<u>Reaction of Triphenyl-α-chloroethylsilane with Sodium
Hydroxide</u>.- One-half g. (0.0015 mole) of triphenyl-α-
chloroethylsilane was refluxed for one hour with 20 cc. of
10 % sodium hydroxide. The reaction mixture was allowed to
cool to room temperature and there was obtained by filtra-
tion 0.5 g. of material melting at 110-115°. Recrystal-
lization from ethanol raised the melting point to 130-132°.
A mixed melting point with the starting material was not
depressed.

<u>Reaction of Triphenyl-α-chloroethylsilane with
Magnesium</u>.- To 0.181 g. (0.007 mole) of magnesium in 10
cc. of dry ether was added 2.4 g. (0.007 mole) of pure
triphenyl-α-chloroethylsilane in 50 cc. of ether. There

was no immediate reaction so a few drops of methylmagnesium iodide were added. The solution became somewhat turbid and after refluxing overnight the amount of magnesium apparently was diminished. The reaction mixture was poured jetwise onto Dry Ice and the resulting mixture treated with 3 % sodium hydroxide after it had reached room temperature. Acidification of the sodium hydroxide extracts gave no solid material. The ether solution gave an oil after removal of the ether. This oil was crystallized by allowing it to stand overnight in a few cc. of petroleum ether (b.p., 65-78°). The melting point was 90-111°. Recrystallization from petroleum ether gave a melting point of 126-128° that was not depressed when mixed with starting material. The amount recovered was 0.4 g. (12.5 %) but it is entirely possible that mechanical losses of such a small size preparation would account for at least a similar percentage of material.

Triphenylethylsilane[63,64].- To 104 g. (0.5 mole) of tetraethylorthosilicate in 200 cc. of ether was added 1.5 mole of phenyllithium in 1300 cc. of ether. The addition was at such a rate as to cause only very gentle refluxing of the ether or no refluxing at all. Rapid addition increased the formation of the tetraphenylsilane impurity and reduced the yield of triphenylethoxysilane.

One-half mole of ethyllithium (prepared just previous to use from one mole of ethyl bromide in 200 cc. of ether and two g.,

63. Ladenburg, Ber., 40, 2278 (1907).
64. Marsden and Kipping, J. Chem. Soc., 93, 209 (1908).

atoms of finely cut lithium in 400 cc. of ether) was added
rapidly to the solution of triphenylethoxysilane. Color Test
I[52] was negative after three hours of mechanical stirring. The
reaction mixture was hydrolyzed with water; the ether layer
separated and dried over sodium sulfate; and, the ether re-
moved by distillation. The residue was treated with 100 cc.
of hot petroleum ether (b.p., 65-78°) and the solution filtered
hot. There was obtained 5 g. of material melting at 60-160°.
Recrystallization from benzene gave 3.5 g. of tetraphenylsilane
melting at 225-228°. The petroleum ether filtrate was evaporat-
ed to one-half the volume to give 50 g. (35 %) of triphenyl-
ethylsilane melting at 60-65°. Recrystallization from petroleum
ether followed by a second recrystallization from a small amount
of benzene (the triphenylethylsilane is quite soluble in
benzene) gave a yield of 32 g. (22.2 %) melting at 70-72. The
melting point previously reported was 72-74° [64]. This compound
has been prepared in almost quantitative yields from triphenyl-
silyl chloride and ethylmagnesium bromide[64]. Ladenburg[63] pre-
pared it from triphenylsilyl bromide and diethyl zinc but gave
no yield.

Reaction of Triphenylethylsilane with Sulfuryl Chloride.-
A mixture of 28.8 g. (0.1 mole) of triphenylethylsilane, 7 cc.
of sulfuryl chloride[62], 0.5 g. of benzoyl peroxide, and 30 cc.
of carbon tetrachloride was refluxed for eight hours. The

reaction vessel was protected from moisture by a phosphorous pentoxide tube. After standing overnight at room temperature, the carbon tetrachloride was removed from the reaction mixture by distillation at reduced pressure. The remaining liquid was dissolved in 50 cc. of petroleum ether (b.p., 65-78°) and there was obtained 16 g. of material melting at 60-110°. This material was recrystallized from ethanol to raise the melting point to 100-110°. Another recrystallization from petroleum ether and one from ethanol gave a melting point of 133-134°. A mixed melting point with an authentic specimen of triphenyl-__-chloroethylsilane (prepared by the reaction of phenyllithium on __-chloroethyltrichlorosilane) was not depressed. The combined filtrates fro the various recrystallizations were combined and the crude solid obtained from them was subjected to vacuum distillation. The material distilling at 90-100°/2 mm. melted at 122-125° after crystallization from ethanol and petroleum ether. The total yield was 3.5 g. or 11 %.

Triphenyl-β-chloroethylsilane.- To 13.35 g. (0.0675 mole) of β-chloroethyltrichlorosilane (prepared[62] from ethyltrichloro-silane and sulfuryl chloride) was added three equivalents of phenyllithium (0.203 mole) in 155 cc. of ether. The reaction flask was well cooled in ice during the addition. Color Test I[52] was negative when the addition was complete. The reaction mixture was treated with 20 cc. of water and the ether layer

was removed and dried. A brown oil remained after removal of the ether. Part of this oil solidified after standing over night at a temperature of 10°. The melting point was 110-115° but was raised to $124\text{-}125^\circ$ after two recrystallizations from petroleum ether (b.p., $65\text{-}78^\circ$). The yield was 1 g. (5.2 %). A mixed melting point determination with triphenyl-α-chloroethylsilane melted at $90\text{-}100^\circ$.

Anal. Calcd. for $C_{20}H_{19}ClSi$: Si, 8.67.

Found: Si, 8.60.

Reaction of Tetraethylsilane with Sulfuryl Chloride.-
Five g. (0.035 mole) of tetraethylsilane /‾prepared in 93.5 % yield from 10.4 g. of ethylsilicate in 100 cc. of ether and 0.23 mole of ethyllithium in 1500 cc. of petroleum ether (b.p., $28\text{-}35^\circ$)_7, 4.7 g. of sulfuryl chloride, 0.5 g. of benzoyl peroxide, and 20 cc. of carbon tetrachloride were refluxed for 12 hours. The system was protected from moisture by a phosphorous pentoxide tube. Fractionation of the reaction mixture gave no constant boiling product but since no tetraethylsilane was recovered it indicated that chlorination did take place.

Reaction of Triphenylmethylsilane with Sulfuryl Chloride.-
A mixture of 5 g. (0.018 mole) of triphenylmethylsilane, 2.44 g. (0.018 mole) of sulfuryl chloride, 0.5 g. of benzoyl peroxide, and 10 cc. of carbon tetrachloride were refluxed for six hours. The carbon tetrachloride was removed by distillation and the solid residue crystallized from petroleum ether

(b.p., 65-78°). The melting point was 55-80°. Recrystalliza-
tion from the same solvent gave 1.25 g. (20 %) of product melt-
ing at 94-99°. A second recrystallization from petroleum
ether raised the melting point to 98-99°. The silicon analysis
would indicate that the product was triphenyldichloromethyl-
silane but apparently it was a mixture of triphenylchloro-
methylsilane and triphenyldichloromethylsilane since the
chlorine analysis was in between the theoretical for the two
possibilities.

An attempt to throw further light on this perplexing re-
sult was made recently in these laboratories by Mr. John Irwin.
He used a slight excess of sulfuryl chloride and increased the
reflux period to twenty-four hours. However, he also obtained
a mixture of chlorinated products from which no pure material
could be isolated.

Anal. Calcd. for $C_{19}H_{17}ClSi$: Si, 9.07; Cl, 11.55.

Calcd. for $C_{19}H_{16}Cl_2Si$: Si, 8.16; Cl, 20.4.

Found: Si, 7.95, 8.05; Cl, 13.07, 14.32.

2-Triphenylsilyldibenzofuran.- 2-Dibenzofuryllithium[65] was
prepared from 4.2 g. (0.0168 mole) of 2-bromodibenzofuran and
0.0168 mole of n-butyllithium. To the solution of 2-dibenzofuryl-
lithium was added 4.0 g. (0.0135 mole) of triphenylsilyl

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65. Gilman, Langham, and Willis, J. Am. Chem. Soc., 62, 346
    (1940).

chloride. Color Test I[52] was negative after the reaction
mixture had been refluxed for one hour. The solution was
treated with water and the ether layer removed and dried.
After removal of the ether there remained a dark oil. This
dark oil was extracted with 25 cc. of absolute ethanol leaving
a light oil that crystallized on cooling. Recrystallization
from petroleum ether (b.p., 95-110°) gave 0.5 g. (8.7 %) of
4-triphenylsilyldibenzofuran melting at 124-125°.

Anal. Calcd. for $C_{30}H_{22}OSi$;   Si,   6.58.

Found: Si,   6.59.

Attempted Preparation of 4-Triphenylsilyldibenzofuran.-
A solution of triphenylsilyl chloride was prepared from 20.1
g. (0.123 mole) of silicon tetrachloride in 50 cc. of ether
and 0.369 mole of phenyllithium in 386 cc. of ether. To this
solution was added a solution of 4-dibibenzofuryllithium pre-
pared from 16.8 g. (0.1 mole) of dibenzofuran and 0.15 mole
of n-butyllithium. When the addition was complete the reaction
mixture was refluxed for two hours, at the end of which time
Color Test I[52] was negative. The solution was hydrolyzed with
water and the ether layer separated and dried. As usual in
such preparations an oil resulted after removal of the ether.
The oil was crystallized from ethanol to give a solid melting
at 90-95°. Various methods were used in an attempt to purify
this material but all were unsuccessful.

Trimethyl-o-anisylsilane.- To 27 g. (0.25 mole) of tri-
methylsilyl chloride in 100 cc. of ether was slowly added a
solution of o-anisyllithium[66] prepared from 52 g. (0.277 mole)
of o-bromoanisole in 200 cc. of ether and 4 g. (0.554 g. atom)
of lithium in 100 cc. of ether. Color Test I[52] was negative
one-half hour after the addition was complete. The reaction
mixture was worked up in the usual manner to give 35 g. (71 %)
of trimethyl-o-anisylsilane distilling at 91-93°/15 mm.
Fractionation of the product at reduced pressure would not
separate it from the small amount of o-bromoanisole that was
present so the silane was fractionated at atmospheric pressure
(b.p., 205-206°/733 mm.). The following constants were de-
termined: n_D^{20} 1.5055; d_4^{20} 0.9587; MR_D calcd.,[56] 56.47; and
MR_D found, 55.80.

Anal. Calcd. for $C_{10}H_{16}OSi$: Si, 15.55.
Found: Si, 15.32.

Trimethyl-p-anisylsilane.- To 27 g. (0.25 mole) of tri-
methylsilyl chloride in 100 cc. of ether was added a solution
of p-anisyllithium[66] (approximately 0.25 mole) prepared from 6
g. (0.831 g. atom) of lithium in 200 cc. of ether and 52 g.
(0.277 mole) of p-bromoanisole in 300 cc. of ether. The re-
action mixture was allowed to stir overnight and then treated
with water in the usual manner. The ether was removed from

66. Gilman, Langham, and Jacoby, J. Am. Chem. Soc., 61, 106
(1939).

the product by distillation and the residue distilled at 118-120°/ 30 mm. The crude product was contaminated with unreacted p-bromoanisole. Fractional distillation at atmospheric pressure, steam distillation of the crude product, and freezing the solution were attempted in hopes of separating the product from the p-bromoanisole but all were unsuccessful. As a last resort, the contaminated product was extracted with 500 cc. of water in 50 cc. portions. Fractionation of this material gave 18 g. (40 %) of pure trimethyl-p-anisylsilane boiling at 220°/740 mm.; n_D^{20} 1.5014; d_4^{20} 0.9398; MR_D calcd.,[56] 56.47; and MR_D found, 56.46.

Anal. Calcd. for $C_{10}H_{16}OSi$: Si, 15.55.

Found: Si, 15.48.

Trimethyl-p-bromophenylsilane.- To 47.55 g. (0.28 mole) of silicon tetrachloride in 100 cc. of cold ether was added 0.84 mole of methyllithium in 900 cc. of ether. The rate of addition was controlled at 3-4 cc. per minute. Color Test I[52] was negative at the end of the addition. A solution of p-bromophenyllithium, prepared in accordance with the procedure of Gilman, Langham, and Moore[67] from 0.15 mole of p-dibromobenzene and 0.35 mole of n-butyllithium, was rapidly added to the solution of trimethylsilyl chloride. (This compound was prepared before trimethylsilyl chloride became commercially

67. Gilman, Langham, and Moore, J. Am. Chem. Soc., 62, 2327 (1940).

available. It can now be purchased from the General Electric Co. or the Anderson Laboratories.) The solution was refluxed overnight and then hydrolyzed with water. The ether layer was dried and the ether removed by distillation. The residue was fractionated under reduced pressure to give 35 g. (55 %) of crude trimethyl-p-bromophenylsilane boiling at $103-107^\circ/$ 14 mm. The crude product was refractionated twice to give pure material distilling at $104-105^\circ/$ 14 mm. The following constants were observed: n_D^{20} 1.5221; d_4^{20} 1.2015; MR_D calcd., 57.52; and MR_D found, 57.32. This compound has recently been prepared[57,68] in 45 % and 53 % yields from p-bromophenyltrichlorosilane and methyllithium, and from p-bromophenylmagnesium bromide and trimethylsilyl chloride. It distilled at $146-148^\circ/$ 50 mm. or $95-96^\circ/$ 3 mm; d_4^{20} 1.2022 and 1.2197; n_D^{20} 1.5271 and 1.5302; MR_D 57.48 and 58.03.

There was also obtained 8 g. of trimethyl-n-butylsilane distilling at $122-123^\circ/742$ mm.: n_D^{20} 1.4020. Clark[57] lists the boiling point as $115^\circ/760$ mm. and n_D^{20} 1.4030. A small amount of material boiling at $165-180^\circ$ was also present and was probably trimethylphenylsilane but it could not be purified sufficiently for identification.

Attempted Preparation of Trimethyl-o-hydroxyphenylsilane.-
_[A_] From Trimethylsilyl Chloride and Lithium o-lithiophenoxide.- To the reaction mixture from 17.3 g. (0.1 mole of o-

68. Burkhard, J. Am. Chem. Soc., 68, 2103 (1946).

bromophenol[69] in 50 cc. of ether and 0.2 mole of lithium in 400 cc. of ether was added 5.4 g. (0.05 mole) of trimethylsilyl chloride. There was no apparent reaction during the addition. The resulting solution was refluxed overnight and treated with water. The ether layer contained less than 1 g. of a mixture (b.p., 90-95°) suspected of being trimethylsilanol and hexamethyldisiloxane. (Sauer[70] reports that trimethylsilanol and hexamethyldisiloxane form an azeotropic mixture boiling at 91-92°.) Acidification of the water layer gave an oil that was extracted with ether. The ether was removed and the residue distilled. There was obtained 10 g. of phenol distilling at 175-180°. No other phenolic material was isolated.

$\boxed{B}$ By Sodium Cleavage of Trimethyl-o-anisylsilane in Pyridine.- To 18 g. (0.1 mole) of trimethyl-o-anisylsilane in 250 cc. of pyridine was added 10 g. of sodium in small portions according to the method of Prey[71]. The reaction mixture was slowly heated to boiling and refluxed overnight. The system was kept under an atmosphere of nitrogen except during the addition of the sodium. After the reaction mixture had cooled to room temperature, it was treated with pyridine, pyridine-water, and water, in the order

69. For the preparation of lithium lithiophenoxides see Gilman and Amtzen, J. Am. Chem. Soc., 69, 1537 (1947).
70. Sauer, ibid., 66, 1707 (1944).
71. Prey, Ber., 76B, 156 (1943).

given, to remove any unreacted sodium. The dark solution was worked up in search of trimethyl-o-hydroxyphenylsilane but no phenolic material was isolated.

Attempted Preparation of Trimethyl-p-hydroxyphenylsilane.-
$\sqrt{A\,}$ From Trimethylsilyl Chloride and Lithium p-lithiophenoxide.- To 43 g. (0.25 mole) of p-bromophenol in 200 cc. of ether was rapidly added 0.5 mole of n-butyllithium in 470 cc. of ether. Color Test II[51] was negative after the reaction mixture had been refluxed for ninety minutes. To this solution was added 21.6 g. (0.2 mole) of trimethylsilyl chloride in 25 cc. of ether. The reaction mixture was refluxed for two hours and Color Test I[52] showed the absence of any organometallic compound. The solution was hydrolyzed with water and dilute hydrochloric acid and the ether layer removed and dried. The ether was removed by distillation and the residue distilled at reduced pressure. There was obtained one fraction boiling at 81-86°/ 25 mm. and another boiling at 86-120°/ 25 mm. Both fractions gave positive phenol tests and positive halogen tests. Redistillation at atmospheric pressure gave the following fractions: 164-168°, 168-170°, 170-173°, 175-186°, 186-200°, and 210-220°. The lower boiling fractions were identified as phenol and the higher fraction (210-220°) was found to be p-bromophenol. The identification was by means of the aryloxyacetic acids. Mixed melting point determinations with authentic specimens were

the final proof of identity.

[B] By Sodium Cleavage of Trimethyl-p-anisylsilane in Pyridine.- To 13 g. (0.072 mole) of trimethyl-p-anisyl-silane in 50 cc. of dry pyridine was added 7 g. of sodium according to the method of Prey[71]. The reaction mixture was refluxed overnight and then treated with pyridine, pyridine-water, and finally water to dissolve any unreacted sodium that may still have been present. A large amount of carbonaceous material was present that was insoluble in water and organic solvents. No organic material of any kind could be isolated from the reaction mixture.

[C] By Oxidation of Trimethyl-p-lithiophenylsilane.- A solution of trimethyl-p-lithiophenylsilane was prepared from 1 g. (0. 14 g. atom) of lithium in 20 cc. of ether and 16 g. (0.07 mole) of trimethyl-p-bromophenylsilane in 100 cc. of ether according to the method of Clark[57]. To this solution was added 0.07 mole of n-butylmagnesium bromide. The mixture was cooled to $-10°$ and dry air passed through the solution for three hours. Color Test I[52] was negative at the end of this time. The reaction mixture was hydrolyzed with water and dilute hydrochloric acid. The ether layer was removed and the water layer extracted twice with ether. The combined ether extracts were treated with 200 cc. of 3 % sodium hydroxide solution in 50 cc. portions. The basic extracts were acidified with hydrochloric acid and the solution extracted with ether. The ether was removed and

the residue distilled at reduced pressure to give 3 g.
(25%) of product distilling at 80-82°/ 15 mm. This material
was identified as phenol by preparation of the phenoxyacetic
acid. A mixed melting point with an authentic specimen was
not depressed.

In part $\sqrt{A\_7}$ of this attempted preparation, the ab-
sence of a Color Test I after interaction of the lithium
p-lithiophenoxide and trimethylsilyl chloride indicates
that trimethyl-p-hydroxyphenylsilane probably was formed
but may have been cleaved during the attempted isolation.
The negative Color Test I in part $\sqrt{C\_7}$ in the oxidation
of trimethyl-p-lithiophenylsilane shows that the lithium
salt of trimethyl-p-hydroxyphenylsilane must have existed
in solution but again may have been cleaved during the sub-
sequent operations. This same reasoning can be applied to
the attempted preparation of trimethyl-o-hydroxyphenylsilane.

It is difficult to explain the presence of the phenol
isolated in these experiments unless one attributes it to
the cleavage of the trimethylhydroxyphenylsilanes. It could
not have come from the lithium lithiophenoxides by hydrolysis
since the Color Test I showed the absence of any organo-
metallic compound.

Apparently, these trimethylhydroxyphenylsilanes are
very unstable compounds and are easily cleaved by dilute
acids. Benkeser noted in some unpublished studies that

trimethyl-p-aminophenylsilane was also a very unstable compound. When he attempted to prepare the diazonium salt under very mild conditions, aniline was isolated as one of the cleavage products.

Attempted Preparation of Trimethyl-p-aminophenylsilane[72].- To 43 g. (0.25 mole) of p-bromoaniline in 100 cc. of ether was added 0.5 mole of n-butyllithium[73] in 650 cc. of ether. Color Test II[51] was negative at the end of the addition. To this solution was added 27 g. (0.25 mole) of trimethylsilyl chloride in 100 cc. of ether. The ether refluxed gently during the addition. The reaction mixture was allowed to stir at room temperature for two hours and then let stand overnight before treating with water. The ether layer was separated and dried before distillation. The residue remaining after removal of the ether was distilled to give some p-bromoaniline distilling at 95-100°/0.7 mm. A small

72. Benkeser, Doctoral Dissertation, Iowa State College, 1947.
73. The use of two or three equivalents of n-butyllithium for the interconversion reaction with p-bromoaniline has never been definitely settled. Gilman and Stuckwisch /‾see J. Am. Chem. Soc., 63, 2844 (1941)‾/ reported the use of three equivalents of n-butyllithium and obtained a yield of 68 % of p-lithio-N,N-dilithioaniline. Clark (see ref. 57) used two equivalents for the interconversion reaction with p-bromoaniline and used the lithium compound for reaction with ethyl silicate. He obtained a 27 % yield of p-aminophenyltriethoxysilane. Gainer (see Gainer, Doctoral Dissertation, Iowa State College, 1946) reported the use of three equivalents of n-butyllithium for the same interconversion reaction. See also Gilman and Gainer, J. Am. Chem. Soc., 69, 1946 (1947).

amount of lower boiling material (75°/ 0.7 mm.) was obtained but it did not contain silicon and was too small to attempt identification. It was thought to be aniline.

Reaction Between Trimethylbenzylsilane and t-Butyl Chloride.- Five g. (0.03 mole) of trimethylbenzylsilane, 1.2 g. (0.1 mole) of aluminum chloride and 5 cc. of carbon disulfide were mixed together in a small flask and cooled to 10°. To this mixture was slowly added 2.5 g. (0.027 mole) of t-butyl chloride. The reaction mixture was slowly warmed to room temperature while being stirred rapidly. Small amounts of hydrogen chloride were given off during this warming period. At the end of one hour the reaction mixture was hydrolyzed with water and the layers separated. The water layer was extracted with ether and the ether extracts combined with the carbon disulfide layer. The ether and carbon disulfide were removed and the residue fractionated. A variety of high boiling fractions was obtained but no cleavage products (toluene, trimethylsilanol) nor unreacted starting material were obtained. It would seem that a Friedel-Crafts reaction may have taken place but purification and identification of the small amounts present was impossible. Melvin[74] has treated triphenylsilanol with acetyl chloride and benzoyl chloride in the presence of aluminum chloride and other less active catalysts. He obtained no alkylated

74. Unpublished studies of H. Melvin.

triphenylsilanols nor any isolable material when the catalyst was aluminum chloride. Only starting material was obtained when less active catalysts were used.

C. Pyrrole Compounds

2-(2,5-Dimethylpyrryl-1)-pyridine[75].— A mixture of 57 g. (0.5 mole) of acetonylacetone, 37 g. (0.5 mole) of 2-aminopyridine, and 3 cc. of hydrochloric acid was refluxed for four hours. The resulting water layer was removed and the oil distilled at reduced pressure. The material distilling at 146°/ 15 mm. was found to be 2-(2,5-dimethylpyrryl-1)-pyridine. The yield was 50 g. (57 %). The following constants were observed: n_D^{25} 1.5710; d_4^{29} 1.058; MR_D calcd. 53.17; and MR_D found 53.40.

Anal. Calcd. for $C_{11}H_{12}N_2$: N, 16.28

Found: N, 16.30.

The compound formed a picrate melting at $114-115^{\circ}$ after recrystallization from ethanol.

Anal. Calcd. for $C_{17}H_{15}O_7N$: N, 17.50

Found: N, 17.56.

1-(4'-Benzenesulfonamido)-2,5-dimethylpyrrole[75].— A solution of 10 g. (0.067 mole) of p-aminobenzenesulfonamide, 7.8 g. of acetonylacetone, and 3 cc. of glacial acetic acid in 15 cc. of ethanol was refluxed for five hours. The solid

75. Gilman, Stuckwisch, and Nobis, J. Am. Chem. Soc., 68, 326 (1946).

that precipitated was removed by filtration and melted at 134-135° after recrystallization from ethanol. The yield was 5 g. (33 %).

Anal. Calcd. for $C_{12}H_{14}O_2N_2S$: N, 11.20.

Found: N, 11.31.

1-(γ-Diethylaminopropyl)-2,5-dimethylpyrrole[75].-

Ten g. (0.07 mole) of γ-diethylaminopropylamine was refluxed for two hours with 14 g. (0.122 mole) of acetonylacetone. At the end of this time the reaction material was subjected to distillation at reduced pressure. There was obtained 16 g. distilling at 144-146°/ 15 mm. Redistillation gave 8 g. (50 %) boiling at 146°/ 16 mm.

Anal. Calcd. for $C_{13}H_{24}N_2$: N, 13.46.

Found; N, 13.45.

2-(2,5-Dimethylpyrryl-1)-6-(p-dimethylaminophenyl)-pyridine.- A solution of p-dimethylaminophenyllithium was prepared from 22 g. (0.1 mole) of p-bromoaniline in 40 cc. of ether and 1 g. (0.14 g. atom) of lithium in 35 cc. of ether. This solution was filtered through glass wool and to the filtrate was added 17 g. (0.1 mole) of 2-(2,5-dimethylpyrryl-1)-pyridine in 35 cc. of ether. Color Test I[52] was positive shortly after the addition was complete, but negative after the reaction mixture had been refluxed for two hours. The dihydro compound was oxidized by passing dry air over the solution for four hours. The solution

2-_[p-(2,5-Dimethylpyrryl-1)-phenyl_]quinoline.-[75] p-
(2,5-Dimethylpyrryl-1)-phenyllithium was prepared as in the
previous preparation from 125 g. (0.5 mole) of p-(2,5-dimethyl-
pyrryl-1)-bromobenzene in 200 cc. of ether and 7.0 g. (1.0
g. atom) of lithium in 100 cc. of ether. To the solution
of the pyrrylphenyllithium was added 65 g. (0.5 mole) of
quinoline in 100 cc. of ether over a period of one hour. The
solution was allowed to stir for three hours and then poured
on ice to give the dihydro compound. The dihydro compound
was refluxed for two hours with 100 cc. of nitrobenzene and
the nitrobenzene removed by steam distillation. The brown
solid that remained was crystallized from ethanol to give
7 g. (5 %) of the desired product melting at 149-150°. The
product was shown to be identical (mixed melting point)
with 2-_[p-(2,5-dimethylpyrryl-1)-phenyl_]-quinoline pre-
pared[77] earlier by condensation of 2-(p-aminophenyl)-
quinoline with acetonylacetone.

Anal. Calcd. for $C_{21}H_{18}N_2$:   N, 9.51.

Found: N, 9.53.

The compound formed a picrate which melted at 176-177°
after recrystallization from ethanol.

Anal. Calcd. for $C_{27}H_{21}O_7N_5$:   N, 13.20.

Found: N, 13.20.

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77. Unpublished studies of S. M. Spatz.

<u>1-(2'-Chlorophenyl)-2,5-dimethylpyrrole.</u>- A mixture
of 64 g. (0.5 mole) of <u>o</u>-chloroaniline, 57 g. (0.5 mole) of
acetonylacetone, and 10 cc. of glacial acetic acid was
refluxed for four hours in essential accordance with the
method of Hazelwood[76]. The product was obtained by vacuum
distillation of the reaction mixture. 1-(2'-Chlorophenyl)-
2,5-dimethylpyrrole boils at 180-182°/15 mm. (as compared
to a boiling point of 130°/15 mm. recorded by Hazelwood)
and was obtained in 55 % yield.

<u>1-Anilino-2,5-dimethylpyrrole.</u>- A mixture of 57 g.
(0.5 mole) of acetonylacetone, 50 cc. (0.5 mole) of
phenylhydrazine, and 5 cc. of hydrochloric acid was re-
fluxed for four hours. The reaction mixture was distilled
at reduced pressure and there was obtained a solid boiling
at 151°/15 mm. Recrystallization from petroleum ether
(b.p., 95-110°) gave 7 g. (7.5 %) of 1-anilino-2,5-
dimethylpyrrole melting at 94°. This procedure was simpler
than the method used by Knorr[78]. After heating equimolar
amounts of acetonylacetone and phenyl hydrazine, Knorr
poured the reaction mixture into water and separated his
product by steam distillation. He listed no yield.

<u>1-(p-Bromophenyl)-2-methyl-5-phenylpyrrole.</u>- Phenacyl-
acetone was prepared in 40 % yield according to the method
of Helberger[79] from levulinic acid and benzene. A mixture

78. Knorr, <u>Ber.</u>, <u>22</u>, 170 (1889).
79. Helberger, <u>Ann.</u>, <u>522</u>, 264 (1936); <u>Ann.</u>, <u>522</u>, 273 (1936).

of 30 g. (0.17 mole) of phenacylacetone, 29.2 g. (0.17 mole) of p-bromoaniline, and 0.5 cc. of hydrochloric acid was refluxed for two hours. The reaction mixture solidified when it was allowed to cool to room temperature. Recrystallization from ethanol gave 45 g. (85 %) of the desired pyrrole melting at 119-120°.

Anal. Calcd. for $C_{17}H_{14}NBr$: Br, 25.60; N, 4.48.

Found: Br, 25.70, 26.00; N, 4.38.

2-(2-Methyl-5-phenylpyrryl-1)-pyridine.- A mixture of 21 g. (0.119 mole) of phenacylacetone, 9.4 g. (0.114 mole) of 2-aminopyridine, 13 cc. of glacial acetic acid, and 1 cc. of hydrochloric acid was refluxed for fifteen hours. The reaction mixture was allowed to reach room temperature and then poured on ice. The addition of a few drops of hydrochloric acid to the resulting oil caused solidification of this oil. Recrystallization of the solid from ethanol gave 9 g. (33.7 %) of product melting at 94.5-96°.

Anal. Calcd. for $C_{16}H_{14}N_2$: N, 11.96.

Found: N, 11.82.

The 2-(2-methyl-5-phenylpyrryl-1)-pyridine formed a picrate that melted at 153.5-155° after recrystallization from ethanol.

Anal. Calcd. for $C_{22}H_{17}N_5O_7$: N, 15.11.

Found: N, 14.91.

1-(p-Carboxyphenyl)-2-methyl-5-phenylpyrrole.- /A_7

From Phenacylacetone and p-Aminobenzoic Acid.- To a mixture

of 10 g. (0.057 mole) of phenacylacetone and 7.8 g. (0.057

mole) of p-aminobenzoic acid was added 15 cc. of glacial

acetic acid. The mixture was heated at 120° for three

hours. The solid pyrrole was removed by filtration and re-

crystallized from glacial acetic acid. There was obtained

10.4 g. (67.5 %) of product melting at 210-211°.

/B_7 By Carbonation of 4-(2-Methyl-5-phenylpyrryl-1)-

phenyllithium.- 4-(2-Methyl-5-phenylpyrryl-1)-phenyllithium

was prepared from 7.25 g. (0.023 mole) of 1-(p-bromo-

phenyl)-2-methyl-5-phenylpyrrole in 25 cc. of ether and

0.023 mole of n-butyllithium in 50 cc. of ether. /4-(2-

Methyl-5-phenylpyrryl-1)-phenyllithium may also be pre-

pared by the interaction of the bromophenylpyrrole with

lithium metal_7 The solution of 4-(2-methyl-5-phenyl-

pyrryl-1)-phenyllithium was poured jet-wise on a suspension

of Dry Ice in ether. When the carbonation mixture had

warmed to room temperature 100 cc. of water was added and

the ether layer removed. Acidification of the water solu-

tion gave 3.36 g. (52.3 %) of crude acid melting at 206-

209°. Recrystallization from glacial acetic acid raised

the melting point to 209-210°. A mixed melting point with

the previously prepared 1-(p-carboxyphenyl)-2-methyl-5-

phenylpyrrole was not depressed.

8-(2-Methyl-5-phenylpyrryl-1)-6-methoxyquinoline.-

A mixture of 8.7 g. (0.05 mole) of 6-methoxy-8-amino-
quinoline and 9 g. (0.05 mole) of phenacylacetone was re-
fluxed for two hours at 120-130°. At the end of this time
10 drops of hydrochloric acid was added and the temperature
raised to 160° for two hours. The reaction mixture was
poured on ice and the yellow oil solidified on the addi-
tion of 3 drops of hydrochloric acid. Recrystallization
from ethanol gave 9.4 g. (60 %) melting at 139-140°.

Anal. Calcd. for $C_{21}H_{18}ON_2$: N, 8.93.

Found: N, 9.10.

DISCUSSION

A. Dibenzothiophene

Experimental evidence of orientation in the dibenzo-
thiophene nucleus shows excellent agreement with the modern
theory of aromatic substitution. However, there is no
modern detailed discussion of the competing factors present
in hetero-polynuclear systems[80a]. Cullinane[80b] in 1932
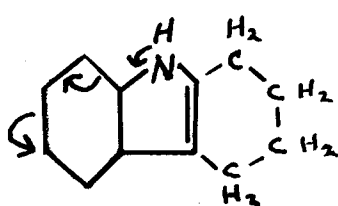made the following statements regarding the similar hetero-
cycle dibenzofuran.

"Modern electronic theory would lead one to ex-
pect the oxygen atom in dibenzofuran to be op-direct-
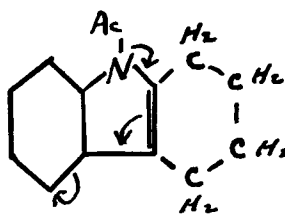ing (II), yet the main mononitration product is the
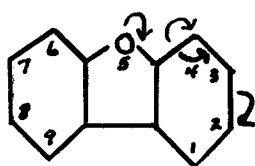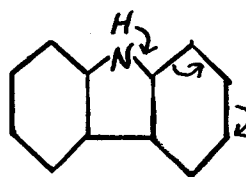
II III

IV V

80. (a) For a discussion of substitution in condensed
homocyclic ring systems see Waters and Lowry, Physical
Aspects of Organic Chemistry, D. Van Nostrand Co., 1937,
p. 462; (b) Cullinane, J. Chem. Soc., 2365 (1932);
(c) For a detailed discussion of substitution in
diphenyl see ref. 80a, p. 465.

3-nitrodibenzofuran. Professor R. Robinson has
suggested the following explanation. The nitration
of carbazole proceeds normally (III) and thus there
is a direct electromeric system involving the aro-
matic nucleus that is substituted and the imino-group.
The same thing appears to hold true for tetrahydro-
carbazole (IV), but if the imino-group is acetylated
or benzoylated nitration occurs in the position indi-
cated (V), and it was suggested by Robinson /see
Perkin and Plant, J., 123, 684 (1923)_7 that this
anomalous orientation is the result of the route
selected for the electromeric changes. In any aro-
matic system comprised of fused homocyclic aro-
matic groups such as naphthalene, anthracene, and
phenanthrene, no alteration in the results to be ex-
pected can be made by altering the route taken by the
electromeric changes. But the case is different when-
ever one of the fused rings comprises an odd number
of atoms, and the result obtained in the present work
can be accounted for by the electromeric change in the
course of nitration taking the route indicated (VI
or VII).
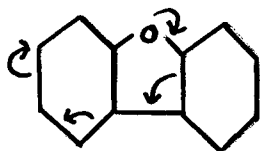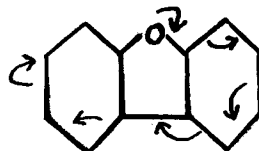
VI   VII

    In all probability bromination is a more facile
process than nitration and can take advantage of a
smaller degree of polarization occurring more fre-
quently than the activations of greater amplitude
required to facilitate nitration: dibenzofuran, there-
fore is brominated normally giving the 2-bromo de-
rivative. The substitution of the second nitro group
in dibenzofuran proceeds normally, for the positive
field of the first nitro group will inhibit any
electromeric changes from passing out of the nucleus
containing it."

No such explanation is necessary in dibenzothiophene
however, since all substitution is in accordance with the
direct prediction as is the bromination of dibenzofuran. (The
metalation of dibenzothiophene by phenylcalcium iodide in the
3-position is an exception to this generalization.) The fol-
lowing discussion is a compilation of the existing views on
aromatic substitution and the experimental evidence of re-
lated compounds.

It is generally recognized the ordinary aromatic sub-
stitution is brought about by the attack of electrophilic
reagents and therefore accelerated by the presence of electron-
releasing groups within the molecule. Substitution also de-
pends on the relative extent to which various ring positions
become activated. Of particular importance in the fused
ring systems is the fact that the presence of electron-
attracting groups (i.e., nitro groups) will impede substitu-
tion and the attacking group will enter another ring where
possible.

There are two electron-releasing groups competing for
position activation in dibenzothiophene. The directive in-
fluence of one benzenoid ring upon the other in dibenzothio-
phene would be comparable to the effects existing in diphenyl[80c].
The other effect would be the sulfide linkage (a) joining the
benzene rings in the position <u>ortho</u> to the phenyl group (b).
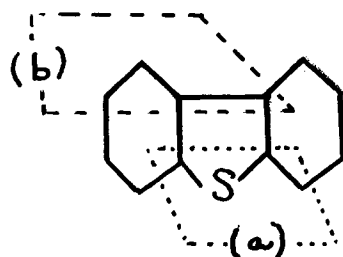
A study of substitution in diphenyl shows that monosubstitution takes place chiefly in the para position due to the extended conjugation possible between the two benzene rings. It is also of interest to note that substituted diphenyls containing a strong ortho and para directing group in the 4-position, will nitrate in the same ring ortho to the hydroxyl group, rather than ortho to the phenyl group[81].
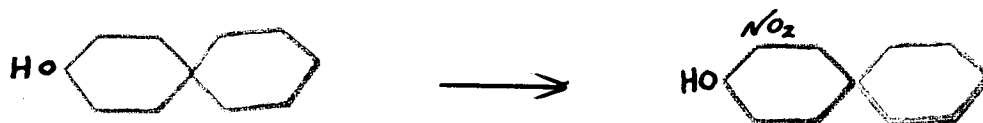
Experimental evidence[82] has shown that the methyl mercapto group (as in methyl phenyl sulfide) will give 90-95 % of the para isomer on bromination or sulfonation. When a methyl mercapto group competes with an alkyl group for position activation, the thiomethyl group has the greater activation effect[83].

81. See reference 80a, p. 468.
82. Van Hove, Bull, sci. acad. roy. Belg. [5], 12, 929 (1926).
83. Van Hove, Ibid., 13, 206 (1927).

From a study of benzene derivatives containing competing groups Robinson[84] has postulated that when a substitutent possesses unshared electrons on the atom next to the benzene ring, it will compete successfully for control of direction.

Application of the preceding evidence to dibenzothiophene would lead to the prediction that the 2-position would be the most active for monosubstitution and the 2,8-positions most active for disubstitution. The 2-position would be more active than the 3-position because of the greater activity of the sulfide linkage and the resulting mesomeric shift of the electrons from the sulfur atom. This effect would overshadow the effects of the phenyl linkage.
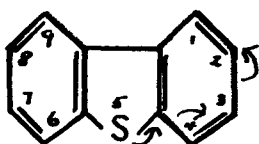
The observed orientation of dibenzothiophene (see historical section of this thesis) is in complete accord with these theoretical considerations. It has been demonstrated that monosubstitution (nitration, halogenation, sulfonation, as well as acylation by the Friedel-Crafts reaction) takes place

84. Robinson, Outline of Electrochemical Theory of the Course of Organic Reactions, The Institute of Chemistry of Great Britain and Ireland, p. 41.

in the 2-position and that disubstitution takes place in the 2,8-positions. The only recorded case of direct substitution by any of the common reagents in the 4-position is Burger's[4] isolation of a very small amount of 4-acetyldibenzothiophene from the reaction of acetyl chloride with dibenzothiophene in the presence of aluminum chloride. The main reaction product was 2-acetyldibenzothiophene.

As one would expect, the electron-attracting nitro group and sulfonic acid group deactivates the nucleus that contains them and further substitution takes place in the corresponding position of the opposite ring. It is also reasonable to predict that a uninuclear substituted dibenzothiophene containing a strong _ortho_ and _para_ directing group (electron-releasing group) would direct further substitution to the same nucleus. This prediction has been verified by halogenation of 2-acetamino-dibenzothiophene to obtain 2-acetamino-3-bromodibenzothio-phene[6]. As further evidence of ring activation in dibenzothiophene by electron-releasing groups, the preparation of 1-nitro-4-acetaminodibenzothiophene by nitration of 4-acetamino-dibenzothiophene should be mentioned.

The metalation of dibenzothiophene in the 4-position is entirely in agreement with the recent theories. According to Morton[85], _n_-butyllithium and organometallic compounds in general,

85. Morton, _J. Am. Chem. Soc._, _69_, 969 (1947).

attack the aromatic nucleus in an electrophilic manner. The position ortho to a group containing free electrons is preferred in the attack since this position offers the possibility of coordinate ring formation.
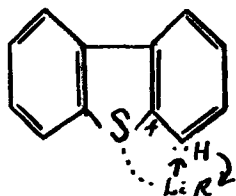
One apparent anomaly to this mechanism is the metalation of dibenzothiophene by phenylcalcium iodide in the 3-position. However, no such exception to the theory exists in the related heterocycle, dibenzofuran, where all metalating agents attack the 4 position.

Gilman and Avakian[86] have shown that ortho halogenated ethers react with sodamide in liquid ammonia solution to give meta amino ethers. The types of ethers employed in support of this rearrangement were 4-iododibenzofuran, 4-bromodibenzofuran, o-halogenated anisoles, and 2-iododiphenyl ether. These halogen ethers all gave the meta amino ethers on treatment with sodamide in liquid ammonia. This rearrangement has been extended to include thioethers in the course of this work. 4-Iododibenzothiophene was found to give 3-aminodibenzothiophene

86. Gilman and Avakian, J. Am. Chem. Soc., 67, 349 (1945).

when treated with sodamide in liquid ammonia. The aminodi-
benzothiophene was converted to the acetaminodibenzothiophene-
5-dioxide. This 5-dioxide was shown to be identical with an
authentic specimen of 3-acetaminodibenzothiophene-5-dioxide
prepared by nitration of dibenzothiophene-5-dioxide followed
by reduction and acetylation.
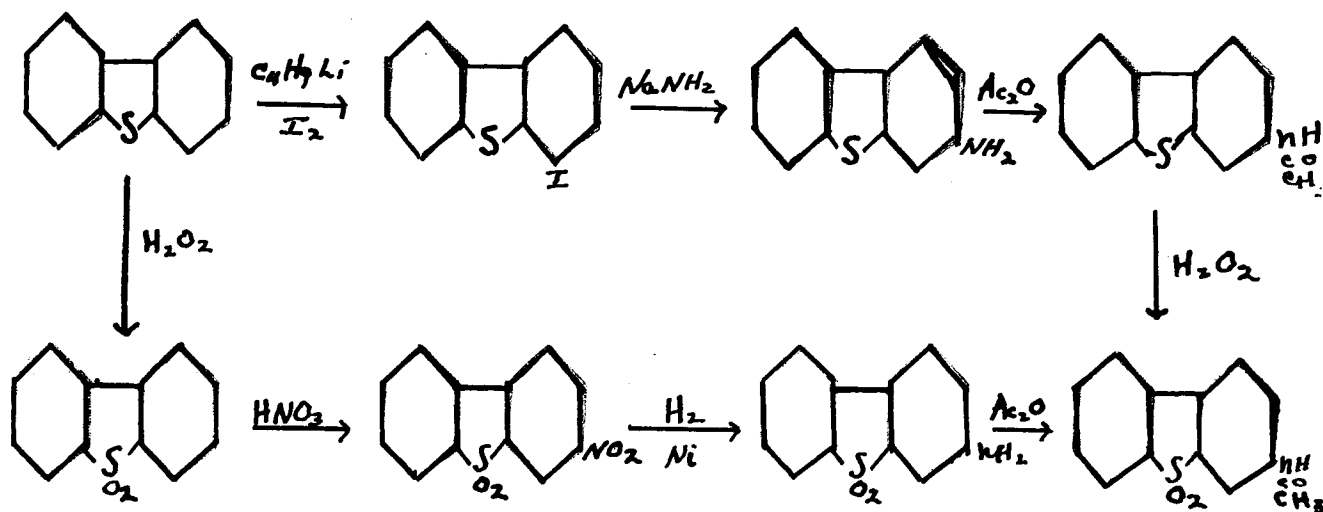
Since the 4-iododibenzothiophene was a new compound, it
was converted to the known methyl 4-dibenzothiophenecarboxylate
by reaction with lithium followed by carbonation and esterifi-
cation of the acid resulting by hydrolysis with diazomethane.
A mixed melting point with an authentic specimen was not de-
pressed. 4-Dibenzothiophenecarboxylic acid is difficult to
purify by recrystallization so sublimation at reduced pressure
was effected to prepare the pure acid.

Incidentally these rearrangements with sodamide have been

since extended to include the preparation of β-diethylamino-
naphthalene[87], m-diethylaminoanisole[88], and other diethyl-
amino compounds by the interaction of lithium diethylamide
and ortho halogenated ethers in dry ether.

In the course of this research, hydrogen peroxide was
found to be a reagent of choice for converting dibenzothiophene
and substituted dibenzothiophenes to the corresponding 5-
dioxides. The use of oxidizing agents such as potassium
dichromate and sulfuric acid is impractical for converting
acetaminodibenzothiophenes to the 5-dioxides because of the
formation of nitroso compounds. Hydrogen peroxide gave good
yields of the acetaminodibenzothiophene-5-dioxides if the re-
action temperature did not exceed 100°. The use of hypochlorous
acid was also investigated and found to be slightly superior
to hydrogen peroxide for the oxidation of 2,8-diacetamino-
dibenzothiophene to 2,8-diacetaminodibenzothiophene-5-dioxide.

Burger and Bryant[4a] reported that they were unable to
obtain the 70 % yield of 2-acetyldibenzothiophene reported by
Gilman and Jacoby[17]. The procedure of these latter researchers
was followed carefully during the course of this research and
a 78 % crude yield of the controversial compound was obtained.

87. Gilman, Crouse, Massie, Benkeser, and Spatz, J. Am. Chem.
    Soc., 67, 2106 (1945).
88. Gilman, Kyle, and Benkeser, ibid., 68, 143 (1946).

The pure yield not reported by Gilman and Jacoby was found to be 41.5 %. Burger and Bryant obtained a pure yield of 25 %. Incidentally, Dr. R. R. Burtner, in some unpublished studies, was also able to obtain the yield reported by Gilman and Jacoby.

2-Acetyldibenzothiophene is an important compound since it gives almost quantitative yields of the oxime, which can be transformed into 2-aminodibenzothiophene in 72 % yield by a Beckmann rearrangement followed by hydrolysis of the resulting acetamine compound. Although this desirable amine can be prepared by nitration of the parent heterocycle followed by reduction, the yields of 2-nitrodibenzothiophene are very poor. These low yields are accounted for by the fact that appreciable amounts of dibenzothiophene-5-oxide, dibenzothiophene-5-dioxide, 3-nitrodibenzothiophene-5-oxide, and 3-nitrodibenzothiophene-5-dioxide are formed under the conditions necessary for nitration. These by-products make isolation of the desired nitro compound exceedingly difficult.

Apparently, catalytic reduction of 2-nitrodibenzothiophene has been overlooked up to this time, but it was found that pure 2-aminodibenzothiophene could be obtained in 91 % yield by this method as compared to a 67 % yield of less pure material resulting from reduction with tin and hydrochloric acid.

2-Acetyldibenzothiophene is also an important starting material for the preparation of 2,8-diacetyldibenzothiophene.

2,8-Diacetyldibenzothiophene was prepared in 77 % yield in essential accordance with the directions of Burger, Wartman, and Lutz[4a] but the method of purification was changed somewhat. They reported a yield of 90 % on a one gram run (as opposed to a 22 gram run made here) but do not specify as to whether or not that was the yield of pure compound.

Since Burger and co-workers were the first to prepare this diacetyl compound they were concerned with the proof of structure. The second acetyl group was shown to be in the 8-position by rearrangement of the diacetyldibenzothiophene dioxime to the diacetamino compound. This diacetamino compound melted at 253-255° as opposed to a melting point of 237-239° reported by Courtot and Pomonis[32]. Courtot and Pomonis prepared their compound by dinitration of dibenzothiophene followed by reduction and acetylation. The 2,8-diacetaminodibenzothiophene prepared here by the methods of both of the above mentioned groups melted at 303°. A mixed melting point determination established the identity. The preparation of such an authentic specimen was apparently neglected by Burger and co-workers. Neumoyer and Amstutz[10] have recently prepared this compound by amination of 2,8-dibromodibenzothiophene followed by acetylation. They reported a melting point of 304-305°.

As further proof of structure Burger and co-workers hydrolyzed their diacetamino compound to the diaminodibenzothiophene and obtained a crude product melting at 178° which

agreed with the melting point of Courtot and Pomonis for
2,8-diaminodibenzothiophene. However, upon further purifi-
cation Burger's group obtained a melting point of 193-194°.
They did not mention that an authentic specimen had been
prepared. Neumoyer and Amstutz listed the melting point
of 2,8-diaminodibenzothiophene was 199.5-201.5°. The melt-
ing point of the diamino compound prepared during the course
of this research was 199.5-200°. This melting point was
obtained when the compound was prepared either by the method
of Burger and co-workers or by the method of Courtot and
Pomonis. A mixed melting point was not depressed. The com-
pound was analyzed and the percentage of sulfur found was in
excellent agreement with the theoretical percentage.

The 2,8-diacetyldibenzothiophene is an important com-
pound since it offers an alternate route to the preparation
of 2,8-diaminodibenzothiophene. The diacetyl compound will
form the dioxime in 96 % yield and a Beckmann rearrangement
of this dioxime in the presence of phosphorus pentachloride
gave 94 % of 2,8-diacetaminodibenzothiophene. The yield ob-
tained when the procedure of Burger and co-workers[4a] was
followed was 30 %. The 2,8-diacetaminodibenzothiophene gave
76 % of 2,8-diaminodibenzothiophene upon hydrolysis. As
mentioned previously, this diamino compound can also be pre-
pared in considerably lower yields by nitration of dibenzo-
thiophene followed by catalytic reduction of the dinitro com-
pound.

Neumoyer and Amstutz[10] were unable to oxidize their 2,8-diacetaminodibenzothiophene to the corresponding dioxide with the use of hydrogen peroxide. They prepared 2,8-diaminodibenzothiophene-5-dioxide by amination of 2,8-dibromodibenzothiophene-5-dioxide rather than by oxidation of the diacetamino derivative. It has been found here that this oxidation is possible with the use of either hydrogen peroxide or hypochlorous acid. The crude yield of 5-dioxide was 90 % when hydrogen peroxide was used. The hypochlorite oxidation method of Weijlard[55] gave even better results. Whereas the hydrogen peroxide oxidation followed by hydrolysis gave an overall yield of 40 % of 2,8-diaminodibenzothiophene-5-dioxide from 2,8-diacetaminodibenzothiophene, the oxidation of the diacetamino compound with hypochlorous acid followed by hydrolysis gave an overall yield of 49 % of the diamino 5-dioxide.

In connection with the studies of Gilman and Haubein[89] on the reaction between dibenzofuran and aluminum iodide to give an organometallic compound, a study was made of the reaction of aluminum halides with dibenzothiophene. Gilman and Haubein had isolated a small amount of 2-dibenzofurancarboxylic acid after carbonation of the reaction mixture. Although the reaction conditions between dibenzothiophene and the various

89. Gilman and Haubein, J. Am. Chem. Soc., 67, 1033 (1945).

aluminum halides were varied considerably, no dibenzothiophenecarboxylic acid could be isolated. It is known, however, that dibenzothiophene is less active towards metalating agents than is dibenzofuran so these results were not completely unexpected. Nevertheless, had the 2-dibenzothiophenecarboxylic acid been formed, it would have contributed somewhat to further the theory that metalation with aluminum halides is a possible mechanism for the Friedel-Crafts reaction.

The organosilicon derivatives of dibenzothiophene were prepared in the conventional manner[57] from the appropriate dibenzothienyllithium compounds and the trisubstituted silicon halides. The preparation of all dibenzothienyl-silanes involved the difficulty of separation of the unreacted dibenzothiophene*. The triphenylsilyl derivatives were almost impossible to isolate. The 5-dioxides of the compounds were prepared by oxidation with hydrogen peroxide in excellent yields.

Cleavage of the dibenzothienylsilanes with anhydrous hydrogen chloride gave results that were in agreement with the findings of Marshall[58]. 4-Trimethylsilyldibenzothiophene was cleaved in 87 % yield while the corresponding 5-dioxide was completely resistant to treatment with hydrogen chloride. Apparently the formation of the 5-dioxide stabilized the molecule to a considerable extent. Additional evidence of

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* The unreacted dibenzothiophene results from the incomplete metalation of dibenzothiophene by n-butyllithium.

this stability was noted by the fact that it was possible
to obtain a mononitro derivative of 4-trimethylsilyldibenzo-
thiophene-5-dioxide. Time did not permit a structure proof
of the nitro compound but it is very probably 3-nitro-4-
trimethylsilyldibenzothiophene-5-dioxide. This structure
is based on the assumption that the electrophilic attack-
ing group would prefer the 3-position, which is activated by
the 5-dioxide group, the trimethylsilyl group, and the phenyl
group.

4-Triphenylsilyldibenzothiophene was fairly stable to
treatment with anhydrous hydrogen chloride since 55% of the
material was recovered unchanged. Marshall[58] also observed
that the trimethylsilyl groups would cleave more easily
than the corresponding triphenylsilyl groups, when attached
to the same nucleus.

Since the chemistry of dibenzothiophene is analogous in
many respects to the chemistry of dibenzofuran, a comparison
of melting points of similar compounds in the related
heterocycles has been included in the following Table. The
melting point of the substituted dibenzofuran has been given
first and the melting point of the similar dibenzothiophene
compound (if known) follows it in parentheses.

From a study of Table IV the following generalizations
are apparent. 1. Most dibenzothiophene derivatives con-
taining the same functional group in the analogous position

to the dibenzofuran derivative melt higher. 2. The melting points of the substituted dibenzofuran compounds increase from the 1-position to the 2-position to the 3-position

TABLE IV.

MELTING POINTS OF SOME MONOSUBSTITUTED DIBENZO-
FURAN COMPOUNDS AND ANALOGOUS DIBENZOTHIOPHENE COMPOUNDS

	Br-	HO-	NH_2-	$NHCOCH_3$-	COOH-	$COOCH_3$-
1-	67 (84)	140	74	205	233(177)	63 (72)
2-	110(127)	134(156)	128(133)	163(183)	249(255)	83 (75)
3-	120(100)*138		101(122)	178(200)	272(305)	138(130)
4-	72	102(167)	85(110)	172(198)	210(262)	94 (95)

with the melting point of the 4-isomer usually lower than that of the 3-isomer. This same phenomenon seems to be borne out in the dibenzothiophene series.

* Unpublished studies of Dr. G. Illuminati.

B. Organosilicon Compounds

In 1939 Kharasch and Brown[62b] found that sulfuryl chloride in the presence of catalytic amounts of organic peroxides could serve as a source of chlorine atoms for the introduction of chlorine into paraffin hydrocarbons, side chains of aromatic hydrocarbons, aliphatic acids, and aliphatic ketones. Previous to this discovery, sulfuryl chloride had served as a source of molecular chlorine and was used almost exclusively for the chlorination of aromatic nuclei in the presence of halogen carriers.

Chlorination of aliphatic compounds with sulfuryl chloride shows a preference for secondary hydrogens over primary hydrogens and the presence of a halogen on a carbon atom increases the difficulty of further substitution. The opposite generality is true in the case of photochemical chlorination.

Sommer and Whitmore[90] have made excellent use of the peroxide catalyzed sulfuryl chloride chlorination method for the introduction of chlorine into a series of alkylsilanes. These chloroalkylsilanes have shown many interesting properties and have contributed considerable valuable information to the organic chemistry of silicon.
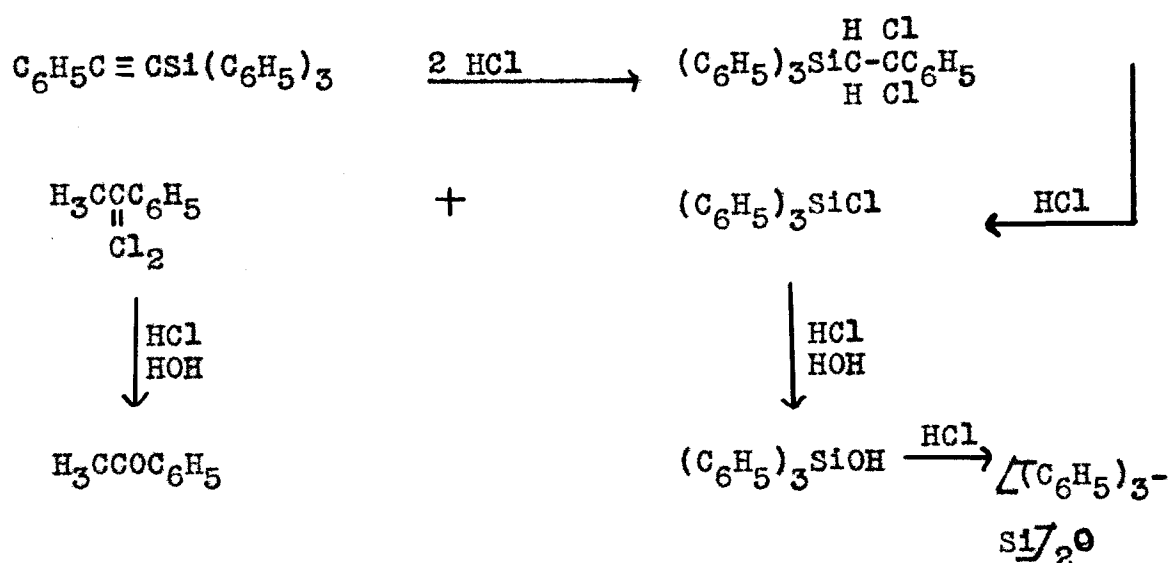
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90. Sommer, Whitmore, and co-workers, ibid., 68, 481, 485, 488, 1083, 1881 (1946).

In the course of this research several new chloralkyl-silanes were prepared. Triphenyl-α-chloroethylsilane and triphenyl-β-chloroethylsilane were prepared from the α- and β-chloroethyl trichlorosilanes and phenyllithium. Triphenyl-α-chloroethylsilane was also prepared by chlorination of triphenylethylsilane with sulfuryl chloride. This alpha-chlorine was found to be quite unreactive. The compound would not form a Grignard reagent and was recovered unchanged when refluxed with 10 % sodium hydroxide.

Although it is reported to be impossible to introduce chlorine atoms by the use of sulfuryl chloride into the methyl groups of compounds like methyltrichlorosilane, acetic acid or acetyl chloride, studies here have shown that replacement of the chlorine atoms by phenyl groups removes the deactivating effect of the $-SiCl_3$ group. When triphenylmethylsilane was treated with sulfuryl chloride in the presence of benzoyl peroxide, a chlorinated compound was obtained. Time did not permit a thorough study of the reaction but indications were that the product was a mixture of triphenyldichloromethyl-silane and triphenylchloromethylsilane.

Hydrogen chloride cleavage of triphenyl-β-styrylsilane and triphenylphenylethinylsilane gave interesting results. The latter compound was cleaved rather easily to give aceto-phenone and hexaphenyldisiloxane. The following steps are suggested as a possible mechanism for the cleavage reaction.

$$C_6H_5C \equiv CSi(C_6H_5)_3 \xrightarrow{\text{2 HCl}} (C_6H_5)_3Si\underset{\substack{| \\ H \ Cl}}{\overset{\substack{H \ Cl \\ |}}{C}}-CC_6H_5$$

$$\underset{Cl_2}{H_3C\overset{||}{C}C_6H_5} \qquad + \qquad (C_6H_5)_3SiCl \xleftarrow{\text{HCl}}$$

$$\Big\downarrow \substack{HCl \\ HOH} \qquad\qquad\qquad \Big\downarrow \substack{HCl \\ HOH}$$

$$H_3CCOC_6H_5 \qquad\qquad (C_6H_5)_3SiOH \xrightarrow{HCl} /(C_6H_5)_3\text{-}Si/_2O$$
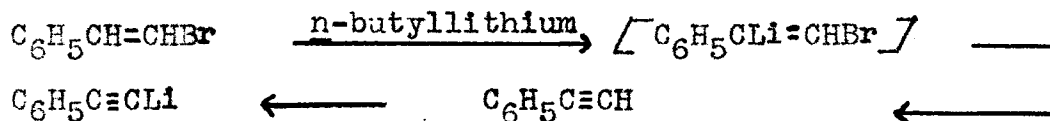
It is possible that in the first stage the silicon to carbon linkage may be broken before addition of the hydrogen chloride to the acetylenic linkage to give triphenylsilyl chloride and phenylacetylene. The following steps, however, would lead to the same products. It is known that phenyl-acetylene and styrene[91a,91b] will add halogen acids according to Markownikoff's rule so the production of acetophenone dichloride is nothing unusual. Acetophenone dichloride and similar compounds are easily hydrolyzed to the corresponding ketones in the presence of mineral acids[91c]. Phenylacetylene itself forms acetophenone when heated with a dilute solution of sulfuric acid[91a]. The cleavage products of triphenyl-__ -

91. (a) Richter, The Chemistry of the Carbon Compounds, Vol. III, Elsevier Publishing Co., New York, N. Y., 1946; (b) Schramm, Ber., 26, 1709 (1890); (c) Erlenmeyer, Ber., 14, 323 (1878).

styrylsilane were hexaphenyldisiloxane and what was thought to be a polymer of styrene.

The preparation of triphenyl-β-styrylsilane presented somewhat of a problem since β-styryllithium is very unstable and can be prepared only in low yields[59]. It has been suggested[59] that initial lateral metalation of the β-bromostyrene takes place, followed by the loss of lithium bromide.

$$C_6H_5CH{=}CHBr \xrightarrow{\text{n-butyllithium}} \left[C_6H_5CLi{=}CHBr \right]$$
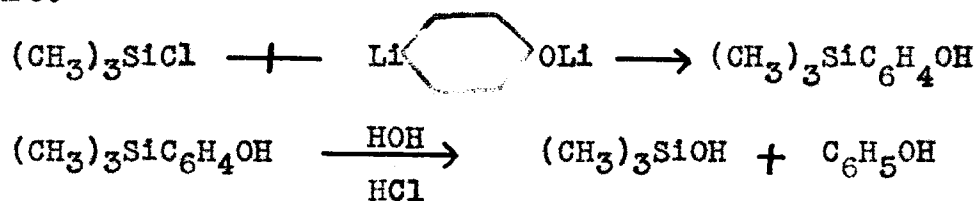
$$C_6H_5C{\equiv}CLi \longleftarrow C_6H_5C{\equiv}CH$$

This mechanism was verified to some extent by the isolation of triphenylphenylethinylsilane from one attempted preparation of triphenyl-β-styrylsilane from triphenylchlorosilane and what was thought to be β-styryllithium. This result indicated that Wright's[58] procedure for the preparation of β-styryllithium is useful only for small runs. The attempted preparation of β-styryllithium from 0.25 mole of β-bromostyrene gave no β-styryllithium. It would seem that the longer reaction time allowed for complete formation of the styryllithium also allowed lateral metalation of the unreacted β-bromostyrene which lost lithium bromide to give phenylacetylene. The phenylacetylene would proceed to react with the lithium present to give phenylethinyllithium. When 0.05 mole of β-bromostyrene was treated with n-butyllithium and

the reaction mixture used within a period of twenty minutes, β-styryllithium was obtained as shown by a 47 % yield of triphenyl-β-styrylsilane.

Several attempts were made to prepare some triphenylsilyldibenzofurans for cleavage studies but the same difficulties were encountered as in the dibenzothiophene series.

Various routes were used in attempts to prepare the trimethylhydroxyphenylsilanes. However, the results indicated that these compounds though initially formed were not stable. The reaction between trimethylsilyl chloride and lithium p-lithiophenoxide gave copious amounts of phenol although no organometallic compound was present, as evidenced by a negative Color Test I, when the isolation of the product was attempted. The presence of phenol can be explained only by admitting that the trimethyl-p-hydroxyphenylsilane formed with subsequent cleavage upon hydrolysis of the reaction mixture.

$$(CH_3)_3SiCl \quad +\!\!\!\!\!- \quad Li\langle \bigcirc \rangle OLi \quad \longrightarrow \quad (CH_3)_3SiC_6H_4OH$$

$$(CH_3)_3SiC_6H_4OH \quad \xrightarrow[HCl]{HOH} \quad (CH_3)_3SiOH \quad + \quad C_6H_5OH$$

Additional proof of this theory was found in the attempted preparation of trimethyl-p-hydroxyphenylsilane by oxidation of trimethyl-p-lithiophenylsilane. The only phenolic compound isolated from this reaction was phenol itself. The lithium salt of trimethyl-p-hydroxyphenylsilane must have existed in

solution since a Color Test I was negative before any attempt was made to isolate the products. Apparently, trimethyl-p-hydroxyphenylsilane is very unstable and was cleaved during isolation producing phenol.

Attempts to prepare the desired phenols from the corresponding ethers (trimethyl-o-anisylsilane and trimethyl-p-anisylsilane) by cleavage with sodium in pyridine[71] also resulted in failure.

The preparation of the anisylsilanes offered some difficulty since the products were contaminated with small amounts of unreacted bromoanisoles. This same difficulty was encountered by Marshall[58] in the preparation of other trimethyl substituted silanes so is possibly general for these compounds.

C. Pyrrole Compounds

Incidental to some war research problems it was shown that 6-methoxy-8-(2,5-dimethylpyrryl-1)-quinoline was moderately active against avian malaria[92]. A series of various

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92. Wiselogle, A Survey of Anti-Malarial Drugs 1941-1945, J. W. Edwards Co., Ann Arbor, Mich., 1946.

pyrryl derivatives[93] has been prepared to determine whether the activity of the above mentioned compound was aided by the introduction of the pyrrole group. The antimalarial activity of these compounds is not available since the testing was carried out under the auspices of the Office of Scientific Research and Development during the wartime period.

The discovery that acetonylacetone would enolize sufficiently to condense with primary amines was made by Paal and Schneider[94] in 1886. This condensation was more or less neglected until 1938, when Hazelwood, Hughes, and Lyons[76] made an extensive study of the optimum experimental conditions and limitations of this reaction. They found that a small amount of hydrochloric acid or glacial acetic acid was a necessary catalyst in the condensation. Studies in these laboratories have shown that some amines will condense in good yields with 1,4-diketones without the aid of these

93. A number of compounds containing the pyrrole nucleus were prepared in these laboratories. For further information see Gilman and O'Donnell, J. Am. Chem. Soc., 66, 840 (1944); Gilman and Karmas, Ibid., 67, 343 (1945); Gilman and Tolman, ibid., 67, 1847 (1945); Gilman, Stuckwisch, and Nobis, Ibid., 68, 326 (1946); Gilman, Tolman, Yeoman, Woods, Shirley, and Avakian, ibid., 426 (1946); Gilman and Fullhart, ibid., 68, 978 (1946); Gilman and Gainer, ibid., 69, 1946 (1947); and, Gilman and Broadbent, ibid., 69, 2053 (1947).
94. Paal and Schneider, Ber., 19, 558 (1886).

catalysts.

The simple 2,5-dimethylpyrryl type compounds studied
in this research were prepared by condensation of the appro-
priate amine with acetonylacetone. The 2-methyl-5-phenyl-
pyrryl compounds were prepared similarly by condensation of
amines with phenacylacetone. The phenacylacetone is best
prepared from levulinyl chloride and benzene in a Friedel-
Crafts type reaction[79].

Several interesting compounds were prepared by the addi-
tion of p-(2,5-dimethylpyrryl-1)-phenyllithium[95] to pyridine
and quinoline. The resulting dihydro compounds, formed by
the addition of the organometallic compound to the anil
linkage, were oxidized by passing dry air through the rapidly
stirred solutions.

It was also possible to react organolithium compounds
with the anil linkage in 2-(2,5-dimethylpyrryl-1)-pyridine.
The dihydro compound was oxidized subsequent to hydrolysis by
refluxing with nitrobenzene[96].

4-(2-Methyl-5-phenylpyrryl-1)-bromobenzene reacted quite
readily with lithium. Carbonation of the resulting organo-
metallic compound gave 52 % of 1-(p-carboxyphenyl)-2-methyl-

95. Gilman and O'Donnell, J. Am. Chem. Soc., 66, 840 (1944).
96. According to the method of Dr. L. A. Woods.

5-phenylpyrrole. This compound was also prepared by con-
densation of p-aminobenzoic acid with phenacylacetone.

SUMMARY

1. A survey of the known derivatives of dibenzothiophene has been presented.

2. A number of new dibenzothiophene compounds have been prepared. The structures of these new compounds have been proven, and final proof of structure for some previously reported compounds has been presented.

3. Some dibenzothienylsilanes have been prepared and studies made on the rates of cleavage of these compounds.

4. A number of new silicon compounds were prepared and the stability of the carbon to silicon linkage studied. Mechanisms of some cleavage reactions have been examined.

5. A series of attempts to introduce functional groups into some arylsilanes was made.

6. A number of special pyrrole compounds were prepared incidental to some war research problems.

APPENDIX

The following is a copy of a letter received from Dr.
Leonard T. Capell concerning an inquiry on the correct nomen-
clature of some substituted amides of 2-hydroxy-3-dibenzo-
thiophenecarboxylic acid:

Mr. John F. Nobis,
Iowa State College,
Ames, Iowa

Dear Mr. Nobis:

I have written the names of the compounds in your letter.
If you have further questions regarding these names I will be
glad to answer them.

Sincerely yours,

(Signed) Leonard T. Capell

German Patent 606,350 /¯C. A., 29, 1997 (1935)_7 and U. S.
Patent 2,157,796 /¯C. A., 33, 6346 (1939)_7 record the prepara-
tion of the following amides of 2-hydroxy-3-dibenzothiophene-
carboxylic acid. I have listed the names that I might use.

1. 2-Hydroxy-3-dibenzothiophenecarboxylic acid anilide

   "2-Hydroxy-3-dibenzothiophenecarboxanilide"

2. 2-Hydroxy-3-dibenzothiophenecarboxylic acid 2'-anisidide

   "2-Hydroxy-3-dibenzothiophenecarbox-o-anisidide"

3. bis-(2-Hydroxy-3-dibenzothiophenecarboxylic acid)
   bianisidide

   "Our name under our present practice is 2,2''-Dihydroxy-
   4,4'''-bi-3-dibenzothiophenecarbox-o-anisidide or, as
   entered in the 3rd Decennial Index, the name would be
   N,N'-(3,3'-dimethoxy-4,4'-biphenylene)bis/¯2-hydroxy-
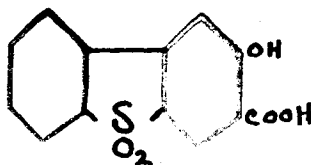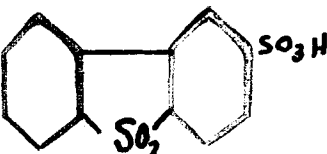   3-dibenzothiophenecarboxamide_7"

4. 2-Hydroxy-3-dibenzothiophenecarboxylic acid 1'-carbazole-
   amide

   "N-4-Carbazolyl-2-hydroxy-3-dibenzothiophenecarbox-
   amide"

5. 2-Hydroxy-3-dibenzothiophenecarboxylic acid 4'-chloroanilide

   "4'-Chloro-2-hydroxy-3-dibenzothiophenecarboxanilide"

6. 2-Hydroxy-3-dibenzothiophenecarboxylic acid 2',4'-dimethoxyanilide

   "2-Hydroxy-2',4'-dimethoxy-3-dibenzothiophene-carboxanilide"

7. 2-Hydroxy-3-dibenzothiophenecarboxylic acid 6'-ethoxy-2'-benzothiazoleamide

   "N-(6-Ethoxy-2-benzothiazolyl)-2-hydroxy-3-dibenzothiophenecarboxamide"

8. 2-Hydroxy-3-dibenzothiophenecarboxylic acid α-naphthylamide

   "2-Hydroxy-N-1-naphthyl-3-dibenzothiophenecarboxamide"

9. 2-Hydroxy-3-dibenzothiophenecarboxylic acid 4'-ethoxyanilide

   "2-Hydroxy-3-dibenzothiophenecarboxy-p-phenetidide"

The above compounds are representative of the various types. They are referred to in the subject index C. A., 29, 9080 (1935), but the names given there omit the position of the hydroxy and carboxamido groups. Some of the names used are more or less confusing.

I would also like to know the approved names for:

1.

   "2-Hydroxy-3-dibenzothiophene-carboxylic acid 5-dioxide"

2.

   "2-Dibenzothiophenesulfonic acid 5-dioxide"
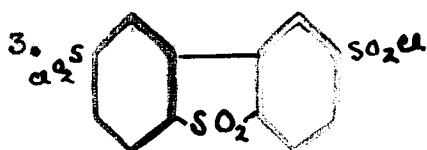
3.

"2,8-Dibenzothiophenedi-
sulfonyl chloride 5-dioxide"

4.
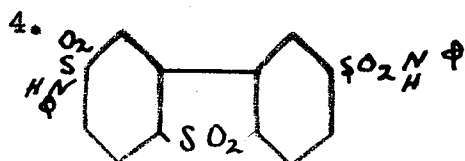
"2,8-Dibenzothiophenedi-
sulfonanilide 5-dioxide"

5. Is it best to use 5-dioxide or sulfone for the SO_2 group?

"We consider 5-oxide and 5-dioxide as the correct forms when the S is a part of the heterocyclic ring. One would not say dimethyl sulfide sulfone, which would be analogous to dibenzothiophene sulfone."

6. The compounds listed in the second above mentioned reference were listed in the subject index in C. A., 33, 6346 (1939) only as "dibenzothiophenecarboxamide, hydroxy-, deriv.".

"Since these compounds were indexed from C. A., 29, 1997 (1935), it was not considered necessary to reindex them from the Patent in C. A., 33, 6346 (1939) which is a duplicate of the German Patent. Only general entries were made from the duplicate Patent."

This second letter is a reply received from Dr. Leonard T. Capell following a further inquiry regarding the order of the substituents in the above letter.

Mr. John F. Nobis
Department of Chemistry
Iowa State College
Ames, Iowa

Dear Mr. Nobis:

Chemical Abstracts uses the alphabetic order of sub-stituents, which accounts for the apparent discrepancy in the

names given for the compounds. The parent compound in each
case is 3-dibenzothiophenecarboxanilide. The names of the
substituting groups are given in alphabetic order regard-
less of whether they are in the dibenzothiophene or in the
benzene ring of the carboxanilide, and regardless of the
number of any particular group (dimethoxy is alphabeted with
respect to other substituents as methoxy). The dibenzothio-
phene numbers are plan numbers, the anilide numbers are
primed numbers, so that any other order than the alphabetic
one does not add to the clarity of the name.

Chemical Abstracts prefers the alphabetic order because
no one as far as we know has been able to devise simple
rules for any other order. An explanation of this is given
in Section 77, page 5878 of the Introduction to the Volume
39 Index.

Very truly yours,

(Signed) Leonard T. Capell

LTC/mm