bromoketone was mixed with 40 ml. of morpholine and warmed to 65° for 24 hr. and then allowed to stand at room temperature for the same length of time. Ether was added and 8.5 g. of morpholine hydrobromide removed by filtration. The filtrate was washed with water, dried and evaporated to give a solid residue which was recrystallized from aqueous methanol; wt. 2.9 g. (67% yield); yellow needles, m.p. 102–103°.

Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.46; N, 5.44. Found: C, 75.00; H, 7.20; N, 5.46.

(*b*) *From the α-bromoketone, IV.* Using conditions similar to those described under (a), 2.0 g. of the bromoketone IV produced 1.2 g. of the aminoketone, V.

1,3-Diketo-4,4-dimethyl-tetralin, VI. A 5.0 g. sample of the aminoketone, V, was dissolved in 20 ml. of 20% sulfuric acid, and heated for 2 hr. on the steam bath. The precipitated material was crystallized from aqueous methanol to give 3.5 g. (95% yield) of colorless crystals, m.p. 101–102.° The compound sublimes readily above 80° at 1 mm pressure.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.59; H, 6.54.

The 1,3-diketone, VI, gave a deep purple-brown color with ferric chloride in ethanol, and a very pale yellow color with titanous chloride (no color change) in methanol. The diketone dissolved in 5% sodium hydroxide to give a yellow solution. No reaction was obtained on refluxing the diketone with morpholine in the presence of a drop of concentrated hydrochloric acid. This 1,3-diketone was uneffected by periodic acid in a glacial acetic acid solution after 72 hr. at room temperature. No reaction of the 1,3-diketone took place with *o*-phenylenediamine or its hydrochloride in ethanol on heating on the steam bath for several hours.

Oxidation of VI with potassium hypochlorite. A 0.47 g. sample of VI was dissolved in a solution of 1.4 g. of potassium hydroxide in 10 ml. of water and chlorine passed in slowly for 1 hr. during which time the temperature of the reaction mixture rose to 40–50°. After standing for 24 hr. the mixture was filtered and acidified to give a solid, which was redissolved in aqueous alkali. This solution was decolorized with charcoal, saturated with carbon dioxide, and filtered. The filtrate was acidified to give colorless needles, m.p. 109–115°; recrystallized from aqueous ethanol, m.p. 123°. This product was found to be identical with an authentic sample of α,α-dimethylhomophthalic acid, VII.[17]

Epoxidation of 1,1-Dimethyl-2-keto-1,2-dihydronaphthalene, I. A solution of 3.7 g. of the unsaturated ketone I in 40 ml. of ethanol was warmed and 4 ml. of 30% hydrogen peroxide and 20 ml. of 4% sodium carbonate added. When the evolution of gas ceased, the mixture was worked up for the ether soluble portion. The epoxide VIII was not isolated and the ether solution containing it was divided into two equal portions for the following reactions.

(*a*) *With morpholine.* The ether was evaporated from one half of the above epoxide solution and the residue heated with 10 ml. of morpholine on the steam bath for 30 min. From this reaction was obtained 0.42 g. (22% based on ketone I) of pale yellow needles, m.p. 101–102°; mixed m.p. with V, 101–103°.

(*b*) *With sulfuric acid.* The second half of the ethereal epoxide solution was evaporated and the residue dissolved in concentrated sulfuric acid to give a red-brown homogeneous solution. This was cooled and crushed ice added to give a gummy solid which was recrystallized from methanol to give 0.45 g. (25% yield based on ketone I) of colorless crystals, m.p. 100–103°, identical with the 1,3-diketone, VI.

On attempting to isolate the pure epoxide in another experiment it was found that even an ethanol and water mixture at 80° for 30 min. converted the epoxide to the 1,3-diketone, VI.

4,4-Dimethyl-1-keto-2-methoxy-1,4-dihydronaphthalene, IX. A 7.1 g. sample of 2-bromo-4,4-dimethyl-1-keto-1,4-dihydronaphthalene[5,9] in methanol was heated with an excess of sodium methoxide on the steam bath for 12 hr. Acidification with hydrochloric acid produced 5.03 g. (88% yield) of crude IX, m.p. 108–116°; recrystallized from aqueous ethanol, m.p. 116–117°. The compound sublimed rapidly above 90°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.90; H, 6.77.

Hydrolysis of the methoxyketone, IX. A solution of 0.5 g. of IX in 0.5 g. of sulfuric acid and 4.5 ml. of glacial acetic acid was heated to boiling and then immediately poured into cold water. The precipitated oil was taken up in ether and this solution washed with water and extracted with 10% aqueous sodium hydroxide. The ether raffinate contained 0.396 g. (80%) of the starting methoxyketone, IX. Acidification of the sodium hydroxide extract gave 0.05 g. (10%) of 4,4-dimethyl-1,2-diketotetralin,[5] m.p. 65°.

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LINCOLN, NEB.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Synthesis of Some Dibenzothiophene Derivatives

HENRY GILMAN AND GENE R. WILDER

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Several dibenzothiophene derivatives have been synthesized by the use of a halogen-metal interconversion reaction on the corresponding bromo compound followed by a reaction with the desired precursor. The oxidation of dibenzothiophene compounds using 30% hydrogen peroxide in glacial acetic acid has been shown to be a convenient method for the synthesis of various sulfones. Several series of monosubstituted dibenzothiophene derivatives have been made complete by the synthesis of various sulfones and other hitherto rather inaccessible compounds.

During the course of a study of the chemical and physical properties of dibenzothiophene derivatives, it was found desirable to include the preparation of a number of the more fundamental type monosubstituted isomers. The 1- position of dibenzothiophene has been rather inaccessible because of the indirect route that had to be taken for the preparation of those derivatives. It has been shown that the action of hydrobromic acid in ethanol on 1-nitro-2-acetamidodibenzothiophene gives 1-bromodibenzothiophene.[1] This compound may

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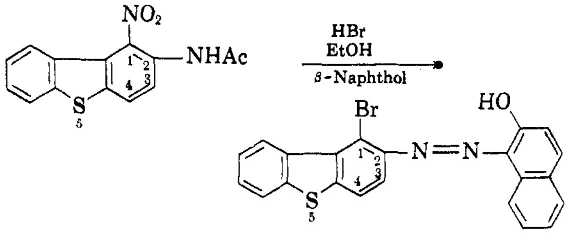
[1] H. Gilman and G. R. Wilder, *J. Am. Chem. Soc.*, **76**, 2906 (1954).

be treated with *n*-butyllithium in a manner described for the 2-bromo isomer[2] causing a halogen-metal interconversion, and the subsequently formed 1-lithio derivative used to introduce a variety of moities. The methyl derivatives described in this paper were prepared by treating the corresponding lithium derivative with dimethyl sulfate.[3] The oxidation of the described sulfides was carried out in essential accordance with the previously published method,[4] using 30% hydrogen peroxide in glacial acetic acid. The 1-trimethylsilyl derivative was prepared by treatment of the corresponding lithium compound with trimethylchlorosilane[2] as had been done previously in the preparation of the 2- and 3- isomers. A modified Ullmann reaction[5] was used in the preparation of 4,4′-bis(dibenzothiophene), which was used in connection with scintillation studies. The boronic acids were prepared by the treatment of the corresponding lithium derivatives with a tri-alkyl borate followed by hydrolysis of the ester to the acid.[6] These acids were prepared in connection with brain tumor studies.

The preparation of 1-bromo-2-(2-hydroxy-1-naphthaleneazo)dibenzothiophene was in essential accordance with the synthesis of its chloro analog.[1]



EXPERIMENTAL[7]

1-Methyldibenzothiophene. Into a 1-liter, three necked, round bottomed flask equipped with a mechanical stirrer and reflux condenser were placed 15.5 g. (0.059 mole) of 1 bromodibenzothiophene and 250 ml. of anhydrous ether. To the mixture was added, over a period of 5 min., 0.060 mole of *n*-butyllithium[8] contained in 56 ml. of an ethereal solution. After 15 min., Color Test II[9] was negative. One half (0.029 mole) of this solution was added slowly to a mixture containing 5.0 ml. (0.054 mole) of dimethyl sulfate dissolved in 100 ml. of ether. At the end of 30 min., Color Test I[10] was negative. The mixture was hydrolyzed with water, the ethereal solution separated and dried over anhydrous sodium sulfate. The ether was removed by distillation leaving 3.5 g. of a semi-solid, which, upon crystallization from ethanol, gave 2.5 g. (43.4%) of 1-methyldibenzothiophene melting at 67–68°.

Anal. Calcd. for $C_{13}H_{10}S$: S, 16.17. Found: S, 16.01.

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

Anal. Calcd. for $C_{15}H_{16}SiS$: Si, 11.0. Found: Si, 10.8, 10.8.

2-Methyldibenzothiophene. This compound was prepared in a manner described for the preparation of the 1-isomer, using 21.0 g. (0.080 mole) of 2-bromodibenzothiophene in 300 ml. of anhydrous ether. There was obtained 5.6 g. (35.4%) of 2-methyldibenzothiophene melting at 88–89°.[11]

Anal. Calcd. for $C_{13}H_{10}S$: S, 16.17. Found: S, 15.91, 16.03.

3-Methyldibenzothiophene. This compound was prepared in an analogous manner from 3-bromodibenzothiophene[12] by the use of a halogen-metal interconversion reaction followed by treatment with dimethyl sulfate. A mixture containing 9.1 g. (0.035 mole) of 3-bromodibenzothiophene and 150 ml. of anhydrous ether was treated with 0.040 mole of *n*-butyllithium in 41 ml. of an ethereal solution, and this subsequently reacted with 5.0 g. (0.040 mole) of dimethyl sulfate. There was obtained 3.1 g. (45.2%) of 3-methyldibenzothiophene melting at 78–79°.

Anal. Calcd. for $C_{13}H_{10}S$: S, 16.17. Found: S, 16.25.

2,8-Dimethyldibenzothiophene. To a stirred mixture containing 25.0 g. (0.073 mole) of 2,8-dibromodibenzothiophene in 300 ml. of anhydrous ether was added 0.15 mole of *n*-butyllithium. After 30 min., Color Test II was negative. To this solution was added 9.2 g. (0.073 mole) of dimethyl sulfate dissolved in 100 ml. of ether. A negative Color Test I was obtained almost immediately after the dimethyl sulfate had been added. Work-up in the usual manner afforded 5.1 g. (32.8%) of 2,8-dimethyldibenzothiophene melting at 122–123°.[13]

Anal. Calcd. for $C_{14}H_{12}S$: S, 15.11. Found: S, 15.15, 15.24.

1-Methyldibenzothiophene-5-dioxide. A mixture containing 1.5 g. (0.0076 mole) of 1-methyldibenzothiophene, 25 ml. of glacial acetic acid, and 10 ml. of 30% hydrogen peroxide was refluxed for 1 hr. This was decanted into approximately 100 ml. of water and the resulting precipitate filtered. Crystallization from ethanol, gave 1.5 g. (86.0%) of 1-methyldibenzothiophene-5-dioxide melting at 191–192°.

Anal. Calcd. for $C_{13}H_{10}O_2S$: S, 13.92. Found: S, 13.78.

This procedure also was employed for the preparation of 2-methyl-, 3-methyl-, 4-methyl-, 2,8-dimethyl-, and 1-chlorodibenzothiophene-5-dioxide; data for these compounds are summarized in Table I.

1-Iododibenzothiophene. A mixture containing 0.019 mole of 1-dibenzothienyllithium contained in 220 ml. of an ethereal solution (prepared from 1-bromodibenzothiophene and *n*-butyllithium) was added to a solution containing 6.0 g.

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[2] G. Illuminati J. F. Nobis, and H. Gilman, *J. Am. Chem. Soc.*, **73**, 5887 (1951).

[3] H. Gilman and J. A. Jacoby, *J. Org. Chem.*, **3**, 108 (1938).

[4] H. Gilman and D. L. Esmay *J. Am. Chem. Soc.*, **74**, 266 (1952).

[5] P. E. Fanta *Chem. Revs.*, **38**, 139 (1946).

[6] Unpublished studies of J. J. Goodman.

[7] All melting points are uncorrected and all reactions involving organometallic compounds were run in an atmosphere of oxygen-free, dry nitrogen.

[8] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

[9] H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

[10] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

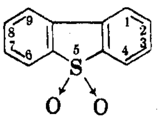
[11] D. F. DeTar and S. V. Sagmanli, *J. Am. Chem. Soc.*, **72**, 965 (1950), reported a methyldibenzothiophene which melted at 85–86°; although this compound was reported as 3-methyldibenzothiophene, it was probably the 2-methyl compound.

[12] H. Gilman and S. Avakian, *J. Am. Chem. Soc.*, **68**, 1514 (1946).

[13] 2,8-Dimethyldibenzothiophene was prepared by K. Fuchs, *Monatsh.*, **53** and **54**, 483 (1929); it was erroneously described as the 1,9-dimethyl derivative.

TABLE I

DIBENZOTHIOPHENE-5-DIOXIDES



Substituent	M.P., °C.	Yield, %	Molecular Formula	Analyses, % Sulfur Calcd.	Found
1-Methyl-	191–192	86.0	$C_{13}H_{10}O_2S$	13.92	13.78
2-Methyl-	197–199	52.0	$C_{13}H_{10}O_2S$	13.92	13.85, 14.08
3-Methyl-	184–185	79.4	$C_{13}H_{10}O_2S$	13.92	13.81
4-Methyl-[a]	204–205	47.0	$C_{13}H_{10}O_2S$	13.92	13.69
2,8-Dimethyl-[b]	290–292	52.1	$C_{14}H_{12}O_2S$	13.14	13.05, 13.28
1-Chloro-	187	87.5	$C_{12}H_7ClO_2S$	14.14	13.75, 13.91

[a] For the preparation of 4-methyldibenzothiophene, see ref. 3. [b] Recrystallized from methyl Cellosolve.

(0.024 mole) of iodine and 150 ml. of anhydrous ether. The resulting solution was stirred at room temperature for 1 hr. and then hydrolyzed with water. The ethereal layer was separated, washed with sodium bisulfite and then dried over anhydrous sodium sulfate. Removal of the ether followed by crystallization gave 1.6 g. (27.1%) of 1-iododibenzothiophene melting at 78–79°.

Anal. Calcd. for $C_{12}H_7IS$: S, 10.34. Found: S, 10.51, 10.56.

3-Iododibenzothiophene. A mixture containing 10.0 g. (0.055 mole) of 3-aminodibenzothiophene,[14] 3.5 ml. of concentrated sulfuric acid, and 50 ml. of water was cooled to 0–5°. This was treated with 3.45 g. of sodium nitrite dissolved in 15 ml. of water, and then stirred for 30 min. The solution was decanted into a mixture containing 15 g. of potassium iodide, a small amount of copper bronze, and 75 ml. of water. This was then heated on a steam bath for 30 min. and worked-up in the usual manner using ethanol for crystallization to give 2.1 g. (13.5%) of 3-iododibenzothiophene melting at 112–113°.

Anal. Calcd. for $C_{12}H_7IS$: S, 10.34. Found: S, 10.56, 10.81.

1-Chlorodibenzothiophene. Into a 250-ml. beaker were placed 4.0 g. (0.021 mole) of 1-aminodibenzothiophene, 100 ml. of water, and 30 ml. of concentrated hydrochloric acid. The mixture was cooled to 0–5° and 1.4 g. of sodium nitrite contained in 15 ml. of water was added slowly. After stirring the mixture for 15 min. it was added to a solution containing 6.0 g. of cuprous chloride dissolved in 50 ml. of concentrated hydrochloric acid, and then heated for 30 min. on a steam bath. The resulting residue was crystallized from ethanol to give 0.71 g. (16.8%) of 1-chlorodibenzothiophene melting at 88° and showing no depression in a mixture melting point with an authentic specimen.[1]

3-Chlorodibenzothiophene. Into a 250-ml. beaker were placed 5.0 g. (0.025 mole) of 3-aminodibenzothiophene and 60 ml. of glacial acetic acid. This was added slowly to 15 ml. of sulfuric acid containing nitrosyl sulfuric acid[15] (10% in excess of the added amine). This was stirred for 15 min. and then decanted into a solution containing 4.0 g. of cuprous chloride in 60 ml. of concentrated hydrochloric acid. The mixture was heated on a steam bath for 30 min. and then decanted into 150 ml. of water. The resulting precipitate was crystallized from ethanol to give 0.72 g. (13.3%) of 3-chlorodibenzothiophene melting at 80–81°.

Anal. Calcd. for $C_{12}H_7ClS$: Cl, 16.21. Found: Cl, 16.17, 16.06.

4-Chlorodibenzothiophene. This compound was prepared in a manner described for the 3-isomer starting with 6.0 g. (0.030 mole) of 4-aminodibenzothiophene.[12] There was obtained 1.2 g. (18.4%) of 4-chlorodibenzothiophene melting at 84–85°.

Anal. Calcd. for $C_{12}H_7ClS$: Cl, 16.21. Found: Cl, 16.08, 16.31.

4,4'-Bis(dibenzothiophene). Into a flask suspended in an oil bath was placed 20.0 g. (0.0645 mole) of 4-iododibenzothiophene. The bath was heated such that the temperature of the 4-iododibenzothiophene was about 260°. To this was added 8.5 g. (0.13 g. atom) of copper bronze over a period of 30 min. The mixture was held at 260° for two hr. and then the contents were decanted onto sand. The resulting solid was ground and then refluxed with ethanol to remove any unreacted 4-iododibenzothiophene. The residue was refluxed with methyl Cellosolve and filtered. The filtrate was treated with Norit-A and refiltered. There was obtained 3.6 g. (30.5%) of 4,4'-bis(dibenzothiophene) melting at 189–190°.

Anal. Calcd. for $C_{24}H_{14}S_2$: S, 17.50. Found: S, 17.63, 17.76.

2-Dibenzothiopheneboronic acid. Into a 1-l., three necked round bottomed flask equipped with a mechanical stirrer and reflux condenser were placed 13.0 g. (0.049 mole) of 2-bromodibenzothiophene and 200 ml. of anhydrous ether. To this mixture was added, at room temperature, 0.050 mole of *n*-butyllithium in 38 ml. of an ethereal solution. Color Test II was negative after 15 min. The organometallic compound was slowly added to a mixture containing 20.0 g. (0.107 mole) of triisopropyl borate in 200 ml. of ether, maintaining a reaction temperature of −60° by means of a dry ice–acetone bath. Within 30 min. after the organometallic compound had been added, Color Test I was negative. The mixture was allowed to warm to room temperature and then hydrolyzed with water and the two layers separated. The ethereal layer was extracted with portions of dilute sodium hydroxide and the basic solutions combined. This was heated to expel dissolved ether, allowed to cool, and then acidified. The resulting residue was crystallized from an acetone-water pair to yield 2.5 g. (22.3%) of 2-dibenzothiopheneboronic acid melting at 277–278°.

Anal. Calcd. for $C_{12}H_9BO_2S$: S, 14.06; neut. equiv., 228.1. Found: S, 14.22; neut. equiv., 230.1, 233.2.

4-Dibenzothiopheneboronic acid. Forty-six g. (0.25 mole) of dibenzothiophene in 500 ml. of anhydrous ether was metalated with *n*-butyllithium (0.26 mole in 170 ml. of an ethereal solution) at room temperature. A negative Color Test II was obtained after 20 hr. This solution was then added to a mixture containing 92.0 g. (0.40 mole) of tri-*n*-butyl borate in 300 ml. of anhydrous ether, maintaining a reaction temperature below −65°. After addition of the organometallic compound, Color Test I was negative. The mixture was hydrolyzed with 10% sulfuric acid, the ethereal layer separated, and the ether distilled. The residue was made basic with 15% potassium hydroxide and the butyl

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(14) R. K. Brown, R. G. Christiansen, and R. B. Sandin, *J. Am. Chem. Soc.*, **70**, 1748 (1948).

(15) H. H. Hodgson and J. Walker, *J. Chem. Soc.*, 1620 (1933).

alcohol removed by steam distillation. The remaining aqueous solution was filtered to remove any unreacted dibenzothiophene and the filtrate acidified. The resulting precipitate was crystallized from an acetone-water pair to yield a total of 18.0 g. (31.6%) of 4-dibenzothiopheneboronic acid which melted at 337–339°. The infrared spectrum of this acid had an absorption band at 2.7 μ, indicative of an —OH group; however, a sample of this acid which was heated at approximately 120° for 3 min. gave no band in the infrared region which would infer the presence of an acid. The observed melting point then is probably that of an anhydride.

Anal. Calcd. for $C_{12}H_9BO_2S$: S, 14.06; neut. equiv., 228.1. Found: S, 14.13, 14.28; neut. equiv., 232.4, 232.8.

1-Bromo-2-(2-hydroxy-1-naphthaleneazo)dibenzothiophene. The synthesis of this compound was accomplished in a manner described for the analogous chloro compound in a previous paper.[1] Into a 125-ml. Erlenmeyer flask equipped with a reflux condenser were placed 1.6 g. (0.0056 mole) of 1-nitro-2-acetamidodibenzothiophene, 0.8 g. (0.0056 mole) of β-naphthol, 40 ml. of ethanol, and 30 ml. of 30% hydrobromic acid. The mixture was refluxed for 20 min. and then allowed to cool. The resulting precipitate was crystallized from methyl Cellosolve to give 1.1 g. (36.9%) of a dark red product which melted at 246–247°. The infrared spectrum of this compound was quite similar to that of 1-chloro-2-(2-hydroxy-1-naphthaleneazo)dibenzothiophene.

Anal. Calcd. for $C_{22}H_{13}BrN_2OS$: Br, 14.99. Found: Br, 14.87, 14.80.

Acknowledgment. The authors wish to express their appreciation to Dr. V. A. Fassel and to Mr. Robert McCord of the Institute for Atomic Research for the infrared analyses. We also wish to acknowledge the financial support of the Division of Biology and Medicine of the United States Atomic Energy Commission who have made part of this work possible. The results of the biological testing of these compounds will be reported by Dr. Otho D. Easterday of the Brookhaven National Laboratory.

AMES, IOWA

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

Studies in Silico-Organic Compounds. XXXIII. Organosilicon Compounds Containing Tin

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Trimethylsilylmethylmagnesium chloride reacts with certain chlorostannanes to form organosilicon stannanes. Four such products are described here, namely triphenyltrimethylsilylmethylstannane, trimethyltrimethylsilylmethylstannane, diphenylbis(trimethylsilylmethyl)stannane, and dimethylbis(trimethylsilylmethyl)stannane.

Sodium triphenylsilanolate reacts with triphenylchlorostannane to form triphenyltriphenylsiloxystannane.

p-Trimethylsilylphenylmagnesium bromide reacts with triphenylchlorostannane to form triphenyl-*p*-trimethylsilylphenylstannane and with diphenyldichlorostannane giving diphenylbis(*p*-trimethylsilylphenyl)stannane.

Tetraphenylstannane results from the interaction of phenylmagnesium bromide and stannic chloride. By interchange with more stannic chloride, triphenylchlorostannane and diphenyldichlorostannane are formed.

Although the literature contains many examples of compounds containing silicon atoms connected through one or more carbon atoms, only a few examples of similar compounds of silicon, tin, and carbon are to be found.[1,2] Greer[1] has prepared compounds of the general formula $[(CH_3)_2SnCH_2]_x$ by the interaction of dimethyldisodiostannane and methylene dichloride. Session[2] and Krause and Wiernik[3] allowed *p*-dichlorobenzene to react with trimethylsodiostannane forming *p*-bis(trimethylstanni)benzene, m.p. 123–124.° This compound reacted with iodine forming *p*-diiodobenzene and trimethyliodostannane. In addition the following reactions were carried out:

$$2(C_2H_5)3Sn(CH_2)_5Br + Mg \longrightarrow MgBr_2 + (C_2H_5)_3Sn(CH_2)_{10}Sn(C_2H_5)_3$$

$$3(CH_3)_3SnNa + CHCl_3 \longrightarrow 3NaCl + CH[Sn(CH_3)_3]_3$$

$$2CH[Sn(CH_3)_3]_3 \text{ (heated)} \longrightarrow 2(CH_3)_3SnSn(CH_3)_3 + \underset{\text{b.p. } 194\text{–}5°}{(CH_3)_3SnCH = CHSn(CH_3)_3}$$

The last compound was easily split by bromine.

Kraus and Eatough[4] treated triphenyllithiosilane with trimethylchlorostannane, obtaining trimethyltriphenylsilylstannane.

Grüttner and Krause[5] treated *p*-triethylsilylphenylmagnesium bromide with triethylbromostannane to form triethyl-*p*-triethylsilylphenylstannane. Tin and silicon are found in the same molecule as the result of several syntheses recently reported by Seyferth and Rochow[6]:

$$(CH_3)_3SnCH_2MgCl + CH_3SiCl_3 \longrightarrow MgCl_2 + (CH_3)_3SnCH_2Si(CH_3)Cl_2$$

$$(CH_3)_3SnCH_2MgCl + CH_3Si(OCH_3)_3 \longrightarrow CH_3OMgCl + (CH_3)_3SnCH_2Si(OCH_3)_2CH_3$$

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(1) W. N. Greer, thesis, *The Dimethyltin Group and Some of Its Reactions*, Eschenbach Printing Co., Easton, Pa., 1925.

(2) W. V. Session, thesis, *A Study of the Trimethyltin Group*, Eschenbach Printing Co., Easton, Pa., 1925.

(3) M. Krause and E. Wiernik, *Ber.*, **50**, 1549 (1917).

(4) C. A. Kraus and H. Eatough, *J. Am. Chem. Soc.*, **55**, 5008 (1933).

(5) G. Grüttner and E. Krause, *Ber.*, **50**, 1559 (1917).

(6) D. Seyferth and E. G. Rochow, *J. Org. Chem.*, **20**, 250 (1955).