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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Received November 14, 1956

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:

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

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

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

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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TABLE I

PHYSICAL PROPERTIES

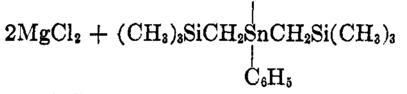
	M.P., °C.	B.P., °C.	Mm.	n_D^{25}	d_4^{25}	%
$(C_6H_5)_3SnCH_2Si(CH_3)_3$		162-163	2	1.5943	1.2369	62
$(CH_3)_3SnCH_2Si(CH_3)_3$		165-166	760	1.4569	1.1244	58.5
$(C_6H_5)_2Sn[CH_2Si(CH_3)_3]_2$		138–140	1.5	1.5425	1.1404	57
$(CH_3)_2Sn[CH_2Si(CH_3)_3]_2$		146.5–147.5	65	1.4644	1.0559	51
$(C_6H_5)3SiOSn(C_6H_5)_3$	138–139					67
$(C_6H_5)_3SnC_6H_4Si(CH_3)_3$-*p*	132.5–133.5					71.5
$(C_6H_5)2Sn[C_6H_4Si(CH_3)_3$-*p*$]_2$	95–96					23.5

In this paper are described the syntheses of seven compounds as listed in Table I.

These syntheses are illustrated below:

$$(CH_3)_3SiCH_2MgCl + (C_6H_5)_3SnCl \longrightarrow MgCl_2 + (C_6H_5)SnCH_2Si(CH_3)_3$$

$$2(CH_3)_3SiCH_2MgCl + (C_6H_5)_2SnCl_2 \longrightarrow$$



$$2MgCl_2 + (CH_3)_3SiCH_2\overset{C_6H_5}{\underset{C_6H_5}{Sn}}CH_2Si(CH_3)_3$$

$$(C_6H_5)_3SiONa + (C_6H_5)_3SiCl \longrightarrow NaCl + (C_6H_5)_3SnOSi(C_6H_5)_3$$

Trimethyl-*p*-bromophenylsilane has been prepared by the method of Campagna and Post.[7]

$$p\text{-}(CH_3)_3SiC_6H_4MgBr + (C_6H_5)_3SnCl \longrightarrow MgClBr + p\text{-}(CH_3)_3SiC_6H_4Sn(C_6H_5)_3$$

$$2p\text{-}(CH_3)_3SiC_6H_4MgBr + (C_6H_5)_2SnCl_2 \longrightarrow MgCl_2 + MgBr_2 + [p\text{-}(CH_3)_3SiC_6H_4]_2Sn(C_6H_5)_2$$

EXPERIMENTAL

Tetraphenylstannane was prepared by the interaction of stannic chloride and phenylmagnesium bromide,[8] triphenylchlorostannane by the method of Kozeschkow, Nadj, and Alexandrow[9] while diphenyldichlorostannane was obtained as described by Metal and Thermit Corp.[10] Chloromethyltrimethylsilane was prepared by the method of Whitmore and Sommer.[12] *p*-Bromophenyltrimethylsilane was made by the method of Burkhard.[15] Tetraphenylstannane, m.p. (found and literature)[8] 224–225°, yield 74%. Triphenylchlorostannane m.p. (found and literature)[9] 105–106°, yield 65%. Diphenyldichlorostannane m.p. 41–42° (lit.[10] 42°), yield 70%. Chloromethyltrimethylsilane, b.p. 96.5–97.5° (lit.[12] 97.1°, 743 mm.); n_D^{20} 1.4158 (lit.[12] 1.4180). *p*-Bromophenyltrimethylsilane, b.p. (found and lit.[7] 136–138°) (50 mm.), n_D^{25} (found and lit.[7] 1.5250).

Triphenyltriphenylsiloxystannane. According to the method of Gilman, Benedict, and Hartzfeld[11] for the preparation of the analogous silicon compound, a dry ether solution of triphenylchlorostannane (7.75 g., 0.02 mole) was added to 0.0218 mole of sodium triphenylsilanolate in 100 cc. of dry ether and refluxed for 14 hr. The product was hydrolyzed with water and the ethereal solution separated and concentrated. The resulting crystals of triphenyltriphenylsiloxystannane were recrystallized from ethyl alcohol, m.p. 138–139°, yield 67%.

Anal. Calcd. for $C_{36}H_{30}OSiSn$: Si, 4.49; Sn, 18.91. Found: Si, 4.61; Sn, 18.80.

Analyses were patterned after the procedures outlined by Gilman and King.[17]

Triphenyltrimethylsilylmethylstannane. To trimethylsilylmethylmagnesium chloride, prepared from 12.2 g. (0.1 mole) of chloromethyltrimethylsilane and 2.4 g. (0.1 mole) of magnesium in 50 cc. of dry ether, 9.3 g. (0.05 mole) of triphenylchlorostannane in 50 cc. of dry ether was added dropwise, at a rate sufficient to cause continual refluxing. After this addition, the system was stirred for 30 min. at room temperature while the brown color was disappearing, then refluxed for 3 hr. The product was hydrolyzed with 5% hydrochloric acid and the ethereal layer dried over calcium chloride and distilled giving triphenyltrimethylsilylmethylstannane, b.p. 162–163° (2 mm.), n_D^{25} 1.5943, d_4^{25} 1.2369, yield 62%.

Anal. Calcd. for $C_{22}H_{26}SiSn$: Si, 6.42; Sn, 27.06; M.R. 117.67. Found: Si, 6.47, 6.11; Sn, 26.99, 27.17; M.R. 120.04.

Methylchlorostannanes. Tetramethylstannane was prepared in accordance with the method of Edgell and Ward,[13] b.p. 76.7° (lit.[13] 76°); n_D^{25} 1.4405 (lit.[13] 1.4409); d_4^{25} 1.2900 (lit.[13] 1.2904); yield 47%. The product was converted to trimethylchlorostannane by reaction with mercuric chloride as described by Manulkin,[14] m.p. 36–38° (lit.[14] 37–38°); b.p. (found and lit.[14] 152–154°); yield 78%. In the same manner, but using different proportions of reactants, dimethyldichlorostannane was prepared, yield 81%.

Trimethyltrimethylsilylmethylstannane. By the same general procedure which was followed in the preparation of the triphenyl analog described above, the Grignard reagent from 12.2 g. (0.1 mole) of trimethylchloromethylsilane was allowed to react with 12.0 g. (0.06 mole) of trimethylchlorostannane, yielding trimethyltrimethylsilylmethylstannane, b.p. 165–166°, n_D^{25} 1.4569, d_4^{25} 1.1244, yield 58.5%.

Anal. Calcd. for $C_7H_{20}SiSn$: Si, 11.21; Sn, 47.13; M.R., 60.52. Found: Si, 11.10, 11.02; Sn, 47.27, 47.15; M.R., 60.67.

Diphenylbis(trimethylsilylmethyl)stannane. Similarly, 24.5 g. (0.2 mole) of trimethylchloromethylsilane, converted to the Grignard reagent, reacted with 20 g. (0.07 mole) of diphenyldichlorostannane forming diphenylbis(trimethylsilylmethyl)stannane, b.p. 138–140° (1.5 mm.), n_D^{25} 1.5425, d_4^{25} 1.1404, yield 57%.

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Anal. Calcd. for $C_{20}H_{32}Si_2Sn$: Si, 12.57; Sn, 26.44; M.R., 122.22. Found: Si, 12.35, 12.45; Sn, 26.33, 26.34; M.R., 123.51.

Dimethylbis(trimethylsilylmethyl)stannane. In the same manner, the Grignard reagent from 24.5 g. (0.2 mole) of chloromethyltrimethylsilane reacted with 11.0 g. (0.05 mole) of dimethyldichlorostannane yielding dimethylbis-(trimethylsilylmethyl)stannane, b.p. 146.5–147.3° (65 mm.), n_D^{25} 1.4644, d_4^{25} 1.0559, yield 51%.

Anal. Calcd. for $C_{10}H_{28}Si_2Sn$: Si, 17.45; Sn, 36.62; M.R., 84.12. Found: Si, 17.33, 17.07; Sn, 36.43, 36.41; M.R., 84.47.

Triphenyl-p-trimethylsilylphenylstannane. The corresponding disilicon compound has already been prepared.[16] Triphenyl-*p*-trimethylsilylphenylstannane could not be prepared by the interaction of trimethyl-*p*-bromosilane, triphenylchlorostannane and sodium in boiling toluene. The principal product obtained was hexaphenyldistannane. Accordingly, the Grignard reagent was prepared from the silicon compound, using the method of Campagna and Post,[7] from 22.9 g. (0.1 mole) of trimethyl-*p*-bromophenylsilane. After solution of the magnesium, 19.5 g. (0.05 mole) of triphenylchlorostannane was added dropwise and the mixture refluxed for 24 hr. The resulting system was hydrolyzed, the ethereal layer evaporated to dryness, and the residue recrystallized three times from alcohol, giving triphenyl-*p*-trimethylsilylphenylstannane, m.p. 132.5–133.5°, yield 71.5%.

Anal. Calcd. for $C_{27}H_{28}SiSn$: Si, 5.63; Sn, 23.77. Found: Si, 5.60, 5.43; Sn, 23.71, 23.57.

Diphenylbis(p-trimethylsilylphenyl)stannane. The same method used for the preparation of triphenyl-*p*-trimethylsilylstannane was followed here with the following materials: 45.8 g. (0.2 mole) of the trimethyl-*p*-bromophenylsilane, 4.8 g. (0.2 g. atom) of magnesium and 17.2 g. (0.05 mole) of diphenyldichlorostannane. The ethereal solution, after hydrolysis, was dried over calcium chloride and fractionated yielding needle like crystals of diphenylbis(*p*-trimethylsilylphenyl)stannane, m.p. 95–96°, yield 23.5%.

Anal. Calcd. for $C_{30}H_{38}Si_2Sn$: Si, 9.82; Sn, 20.62. Found: Si, 9.90, 9.92; Sn, 20.50, 20.47.

Analytical. The analyses of these compounds were carried out by a determination of the total weight of the metallic oxides (silicon and tin oxides), obtained by the method of Gilman and King[17] and then determining the percentage of tin from the mixture of oxides by gravimetric or iodometric method.

The percentage of silicon was calculated from these results.

The gravimetric method consists in separating stannic oxide from silica by treating the mixture of oxides with sodium hydroxide and sulfur whereupon soluble sodium thiostannate was formed and solution filtered.

Stannic sulfide was precipitated from the boiling filtrate by the action of acetic acid. Then with sodium hydroxide the sulfide was converted once more to sodium thiostannate, soluble, while the excess of insoluble sulfur was filtered off.

Sodium thiostannate was oxidized to sodium stannate by hydrogen peroxide (boiling) and its solution neutralized with nitric acid using methyl orange and ammonium nitrate. Stannic acid precipitated quantitatively and was converted by heat to stannic oxide.

Iodometrically the tin was determined by extraction of the oxides with sodium hydroxide and collecting the sodium stannate and silicate formed in an Erlenmeyer flask, with the help of a stream of hot water.

The solution was treated with excess of 6*N* HCl (sodium stannate passed to stannic chloride and sodium silicate to insoluble silicic acid), and Sn^{4+} was reduced to Sn^{2+} by the action of nickel wire, in carbon dioxide ambient, boiling for 0.5 hr. Sn^{+2} was titrated with a standard solution of iodine.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Studies in the Dibenzobicyclo[2.2.2]octadiene System

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Received November 5, 1956

A number of 2- and 2,3-oxygenated derivatives of dibenzobicyclo[2.2.2]octadiene have been prepared, and the anomalous reactions encountered when attempts to rearrange them to derivatives of 9,10-methano-9,10-dihydroanthracene (dibenzobicyclo[2.2.1]heptadiene) failed are described. Especially noteworthy is the unusually mild alkaline cleavage of the 2,3-diketo derivative to give 9,10-dihydroanthracene and oxalate ion.

In a preliminary study of approaches to the synthesis of 9,10-methano-9,10-dihydroanthracene[3,4] three molecular rearrangements were considered: the benzilic acid rearrangement applied to dibenzobicyclo[2.2.2]octadiene-2,3-dione (I), the pinacol rearrangement applied to the *cis* glycol (II) derivable therefrom, and the pyrolysis of the sulfite ester (III) of II. As will appear in the sequel these approaches did not afford the desired methanoanthracene structure, but a number of interesting reactions were encountered.

The preparation of I involved selenium dioxide oxidation of dibenzobicyclo[2.2.2]octadien-2-one (IV), an independent synthesis[5] of which appeared subsequent to our isolation of the compound. Both procedures involve Oppenauer oxidation of the corresponding carbinol, the published one[5] employing cyclohexanone and ours employing benzoquinone. The carbinol in turn was obtained essentially by the procedure of Alder and Rickert[6] by

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