[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY AT HARVARD UNIVERSITY]

Neopentyl Group Analogs. I. The Preparation and Some Cleavage Reactions of Trimethylsilylmethyl-substituted Tin Compounds

BY DIETMAR SEYFERTH*

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The preparation of $Me_3SiCH_2SnMe_3$, $(Me_3SiCH_2)_4Sn$ and $(Me_3SiCH_2)_2SnR_2$ (R = Me, Vi, *n*-Bu, C_6H_5) by the Grignard reaction in tetrahydrofuran solution is described. Cleavage of these compounds by iodine and bromine requires vigorous conditions. Cleavage by hydrogen bromide, mercuric bromide and trifluoroacetic acid also has been studied. Some reactions of $(Me_3SiCH_2)_2SnX_2$ (X = Br and I) are described.

We have previously investigated the synthesis of compounds containing neopentyl group analogs, $Me_3M^{IV}CH_2$–, where M^{IV} is a Group IV-B element, as well as the chemical consequences of introducing such groups into organosilicon compounds.[1] In order to obtain more information on the inductive and steric effects of the neopentyl group analogs as the quaternary atom is varied from C to Si to Ge to Sn, we are commencing a study of the synthesis, properties and reactions of compounds containing these groups. In Part I we are concerned with trimethylsilylmethyltin compounds and some of their reactions.

Trimethylsilylmethyltin compounds were conveniently prepared by the reaction of trimethylsilylmethylmagnesium chloride with the appropriate tin halide in refluxing tetrahydrofuran (THF) solution, *e.g.*

$$4Me_3SiCH_2MgCl + SnCl_4 \xrightarrow{THF} (Me_3SiCH_2)_4Sn + 4MgCl_2$$

Use of the relatively high-boiling, basic THF solvent readily permits complete tetrasubstitution and does not require the extra steps usually necessary to obtain good yields when diethyl ether is used as solvent.[2] Yields ranging from 84 to 94% were obtained in the preparation of the compounds listed in Table I.

TABLE I

TRIMETHYLSILYLMETHYL-SUBSTITUTED TIN COMPOUNDS

Compound	Formula	Boiling range °C.	Boiling range Mm.	$n^{25}D$	d^{25}_4	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
	$Me_3SiCH_2SnMe_3$	64–65	24	1.4594	1.136	33.49	33.54	8.03	8.26
I	$(Me_3SiCH_2)_4Sn$	94	0.2	1.4839	1.018	41.09	41.17	9.49	9.22
II	$(Me_3SiCH_2)_2SnMe_2$	55	0.7	1.4702	1.073	37.16	37.10	8.73	8.48
		62	1.3						
III	$(Me_3SiCH_2)_2Sn(Bu\text{-}n)_2$	98	0.45	1.4777	1.027	47.17	47.22	9.90	9.76
IV	$(Me_3SiCH_2)_2Sn(C_6H_5)_2$	137	.35	1.5499	1.149	53.69	53.92	7.21	6.91
		130–132	.2						
	$(Me_3SiCH_2)_2SnVi_2$[a]	93–94	3.4	1.4826	1.078	41.50	41.67	8.13	8.07

[a] Prepared from $(Me_3SiCH_2)_2SnBr_2$ and $CH_2{=}CHMgBr$; *cf.*, Experimental part.

NOTE ADDED IN PROOF: After this manuscript had been submitted, the work of S. Papetti and H. W. Post, *J. Org. Chem.*, **22**, 526 (1957), appeared. Their preparation of the compounds II, IV and $Me_3SiCH_2SnMe_3$, carried out in diethyl ether solution in yields of 51–58.5%, emphasizes the superiority of THF as a solvent for the Grignard preparation of tetraorganotin compounds. The values of $n^{25}D$ and d^{25}_4 for the compounds common to this study and those of Papetti and Post differ considerably in some cases, and we present molar refraction data in support of our values:

Compound	MR_D(found)	MR_D(calcd.)
$Me_3SiCH_2SnMe_3$	60.46	60.24
I	131.3	130.7
II	84.04	83.73
III	112.2	111.7
IV	124.0	122.7
$(Me_3SiCH_2)_2SnVi_2$	91.95	92.07

Molar refractions were calculated using bond refraction data of A. I. Vogel, *et al.*, *J. Phys. Chem.*, **58**, 174 (1954).

Sommer and Whitmore[3] prepared unsymmetrical mercurials, $RHgCH_2SiMe_3$ (R = Me, *n*-hexyl, C_6H_5), and studied the cleavage of these compounds by hydrogen chloride in ethanol solution. Their results, which indicated that for this particular reaction the ease of cleavage of groups from the mercury atom varied $C_6H_5 > Me_3SiCH_2 > Me > n$-hexyl, prompted us to investigate the cleavage of tin compounds of the type $R_2Sn(CH_2SiMe_3)_2$ (R = Me, *n*-Bu, C_6H_5). Cleavage reagents used in this study included iodine, bromine, hydrogen bromide, mercuric bromide and trifluoroacetic acid. Our results are listed in Table II.

The resistance of these compounds to cleavage, very probably due to steric causes, is shown by the unusually harsh conditions necessary to effect cleavage with bromine and iodine. In iodine cleavage reactions of compounds such as *n*-amyltrimethyltin[4] or *n*-dodecyltriethyltin,[5] refluxing the reactants in diethyl ether solution for about ten hours served to give reasonable yields of triorganotin iodide. In the case of $(Me_3SiCH_2)_4Sn$, $(Me_3SiCH_2)_2SnMe_2$ and $(Me_3SiCH_2)_2Sn(Bu\text{-}n)_2$, reaction did not appear to occur even in refluxing xylene

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* Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Mass.

[1] (a) D. Seyferth and E. G. Rochow, THIS JOURNAL, **77**, 907 (1955); (b) **77**, 1302 (1955); (c) *J. Org. Chem.*, **20**, 250 (1955); (d) *J. Polymer Sci.*, **18**, 543 (1955).

[2] *E.g.*, G. J. M. van der Kerk and J. G. A. Luitjen, *Org. Syntheses*, **36**, 86 (1956).

[3] L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **68**, 481 (1946).

[4] Z. M. Manulkin, *J. Gen. Chem.* (*U.S.S.R.*), **13**, 42 (1943).

[5] G. J. M. van der Kerk and J. G. A. Luitjen, *J. Appl. Chem.*, **6**, 56 (1956).

TABLE II

CLEAVAGE OF $R_2Sn(CH_2SiMe_3)_2$ COMPOUNDS BY VARIOUS REAGENTS

R	Cleavage agent	Products isolated (yield, %)
Me	I_2	$(Me_3SiCH_2)_2MeSnI$ (81.4%)
n-Bu	I_2	$(Me_3SiCH_2)_2(n\text{-}Bu)SnI$ (93.5%)
C_6H_5	I_2	$(Me_3SiCH_2)_2SnI_2$ (83.0%), C_6H_5I (96.0%)
Me_3SiCH_2	I_2	$(Me_3SiCH_2)_3SnI$ (76.5%), Me_3SiCH_2I (78.5%)
Me	Br_2	$(Me_3SiCH_2)Me_2SnBr$ (31.4%), $(Me_3SiCH_2)_2MeSnBr$ (56.0%)
n-Bu	Br_2	$(Me_3SiCH_2)(n\text{-}Bu)_2SnBr$ + $(Me_3SiCH_2)_2(n\text{-}Bu)SnBr$ (equimolar mixture: not separable)
Me	HBr	$(Me_3SiCH_2)Me_2SnBr$ (52.0%), $(Me_3SiCH_2)_2MeSnBr$ (43.0%), Me_4Si (54.3%)
n-Bu	HBr	$(Me_3SiCH_2)(n\text{-}Bu)_2SnBr$ (97.0%), Me_4Si (98.0%)
C_6H_5	HBr	$(Me_3SiCH_2)_2SnBr_2$ (98.0%)
Me	$HgBr_2$	MeHgBr (94.0%)
n-Bu	CF_3CO_2H	$(Me_3SiCH_2)(n\text{-}Bu)_2SnO_2CCF_3$ (54.7%), Me_4Si (26.2%)

TABLE III

TRIMETHYLSILYLMETHYL-SUBSTITUTED TIN HALIDES FROM CLEAVAGE REACTIONS

Formula	Boiling range °C.	Boiling range Mm.	$n^{25}D$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Halogen, % Calcd.	Halogen, % Found
$(Me_3SiCH_2)_2MeSnI$	85–86	0.35	1.5268	24.84	24.82	5.79	5.61	29.17	29.39
$(Me_3SiCH_2)_2(n\text{-}Bu)SnI$	105	.4	1.5257	30.20	30.38	6.55	6.31	26.60	26.61
$(Me_3SiCH_2)_3SnI$	105	.3	1.5237	28.41	28.43	6.56	6.32	25.02	25.31
$(Me_3SiCH_2)Me_2SnBr$	50	.35	1.5101	22.81	22.82	5.43	5.25	25.30	25.40
$(Me_3SiCH_2)_2MeSnBr$	73	.18	1.5018	27.85	28.12	6.49	6.42	20.59	20.79
$(Me_3SiCH_2)(n\text{-}Bu)_2SnBr$	91	.2	1.5037	36.02	35.90	7.31	7.15	19.98	20.20
$(Me_3SiCH_2)_2SnBr_2$	M.p. 38.6–39.8°			21.21	21.31	4.90	4.68	35.28	35.52
$(Me_3SiCH_2)_2SnI_2$	M.p. 34.6–35.4°			17.57	17.70	4.06	4.25	46.41	46.45
$(Me_3SiCH_2)(n\text{-}Bu)_2SnO_2CCF_3$	M.p. 62.0–63.4°			38.82	38.74	6.75	6.97		

solution. Only when most of the xylene had been distilled off and the reactants were heated at about 175° did cleavage take place at an appreciable rate. Similarly, bromine cleavage, in order to be of preparative usefulness, generally is carried out at −30 to −40°.[6] In contrast, $(Me_3SiCH_2)_2SnMe_2$ and $(Me_3SiCH_2)_2Sn(Bu\text{-}n)_2$ were not cleaved by bromine in carbon tetrachloride solution at 0° and reacted only very slowly at room temperature. However, cleavage by hydrogen bromide appeared to be fairly rapid even at −78°.

The conditions required for the cleavage of both phenyl groups from bis-(trimethylsilylmethyl)-diphenyltin were much milder. For instance, reaction with iodine occurred fairly rapidly in refluxing benzene solution, and hydrogen bromide removed both phenyl groups very rapidly at −78°. This was to be expected, since the rate of electrophilic cleavage of an aryl–metal bond is very much faster than that of an alkyl–metal bond.[7]

It would appear at first sight that the size of the attacking reagent is the crucial factor in the cleavage of compounds containing hindered groups such as trimethylsilylmethyl. Cleavage by iodine to give $(Me_3SiCH_2)_3SnI$ was observed in the case of tetrakis-(trimethylsilylmethyl)-tin, but with $(Me_3SiCH_2)_2SnMe_2$ and $(Me_3SiCH_2)_2Sn(Bu\text{-}n)_2$ only methyl and butyl group cleavage occurred. When bromine was used as cleavage agent, fission of both possible groups resulted, cleavage of the methyl group still being slightly favored. When cleavage with hydrogen bromide was carried out, trimethylsilylmethyl cleavage was now slightly favored in the case of $(Me_3SiCH_2)_2SnMe_2$, while with the butyl compound the cleavage preference was completely reversed, only Me_3SiCH_2-fission being observed. No firm conclusion concerning the mechanism of these cleavage reactions is possible at this time. The iodine cleavage at 175° may well be a free radical reaction, while the HBr and mercuric bromide cleavages very likely are true electrophilic substitution reactions.

The results of our hydrogen bromide cleavage reactions are in essential agreement with those of Sommer and Whitmore,[3] obtained in a very different system. The ready cleavage of the trimethylsilylmethyl group by HBr and HCl is not surprising. The positive inductive effect of the trimethylsilylmethyl group[8] at one side, and of the trialkylstannyl group at another, should make the methylene carbon linking the silicon and tin atoms more negative than other α-carbon atoms, hence more susceptible to electrophilic cleavage.

The organotin halides which resulted from these cleavages are listed in Table III. The bis-(trimethylsilylmethyl)-tin dihalides are white crystalline solids, easily soluble in organic solvents, but not soluble in water. The steric effect of the two Me_3SiCH_2– groups is shown by the fact that pyridine appears to form no addition compound with $(Me_3SiCH_2)_2SnBr_2$. In comparison, when pyridine is added to an ether solution of dimethyltin dibromide, the addition compound $Me_2SnBr_2{\cdot}2C_5H_5N$ precipitates immediately, while the $n\text{-}Bu_2SnBr_2$–pyridine addition compound is precipitated when the methanolic solution of the reactants is chilled.

Basic hydrolysis of $(Me_3SiCH_2)_2SnBr_2$ appears to give the polymeric oxide, $[(Me_3SiCH_2)_2SnO]_n$. In view of the apparent stability of di-*t*-butyltin and di-*t*-amyltin dihydroxides,[9] it might have been expected that it would be possible to isolate $(Me_3SiCH_2)_2Sn(OH)_2$. Apparently, however, there is not sufficient steric hindrance in this hydroxide to prevent condensation to the polymeric oxide.

Experimental[10]

(1) **Analyses** were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York. Melting points were determined using a Hershberg melting point apparatus.

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[6] G. Grüttner and E. Krause, *Ber.*, **50**, 1802 (1917).

[7] See S. Winstein and T. G. Traylor, THIS JOURNAL, **77**, 3747 (1955), for experimental results and a discussion of this point.

[8] (a) L. H. Sommer, J. R. Gold, G. Goldberg and N. S. Marans, THIS JOURNAL, **71**, 1509 (1949); (b) C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 939 (1954); (c) J. E. Noll, B. F. Daubert and J. L. Speier, THIS JOURNAL, **73**, 3871 (1951); (d) L. H. Sommer and J. Rockett, *ibid.*, **73**, 5130 (1951).

[9] E. Krause and K. Weinberg, *Ber.*, **63**, 381 (1930).

[10] See Table I for key to Roman numeral designations.

(2) **Starting Materials.**—Chloromethyltrimethylsilane, b.p. 98–99°, was prepared by methylation of chloromethyldimethylchlorosilane with methylmagnesium bromide in diethyl ether solution. Dimethyltin dichloride was obtained by the direct reaction between methyl chloride and tin metal,[11] trimethyltin bromide by the low temperature bromination of tetramethyltin, and diphenyltin dichloride by the redistribution of tetraphenyltin with tin tetrachloride at 190°. Other metal halides were commercial products. Tetrahydrofuran was distilled from lithium aluminum hydride prior to use.

(3) **Reaction of Trimethylsilylmethylmagnesium Chloride with Tin Halides.**—The preparation of II is given as an example of the procedure used.

Trimethylsilylmethylmagnesium chloride was prepared from 40 g. (0.327 mole) of chloromethyltrimethylsilane and 7.55 g. (0.31 g. atom) of magnesium turnings in 200 ml. of THF. The reaction was initiated with a few drops of ethyl bromide. To the Grignard solution then was added a solution of 27.5 g. (0.125 mole) of dimethyltin dichloride in 70 ml. of THF at such a rate that a gentle reflux was maintained. The reaction mixture was heated at reflux for 20 hr. after the addition was completed. It was then allowed to cool to room temperature and was subsequently hydrolyzed with 60 ml. of saturated aqueous ammonium chloride solution. The organic layer was decanted and the residual salts were washed with several portions of diethyl ether, the washings being added to the organic layer. After the solvents had been distilled off at atmospheric pressure, the residue was fractionally distilled at reduced pressure to give 37.8 g. (94%) of II, b.p. 49–52° at 0.35 mm.

Experimental data for other preparations are listed in Table IV.

TABLE IV

REACTION OF Me_3SiCH_2MgCl WITH TIN HALIDES, EXPERIMENTAL

Tin halide	moles	Me_3SiCH_2-MgCl, moles	Product	Yield, %
Me_3SnBr	0.15	0.205	$Me_3SiCH_2SnMe_3$	86.2
$SnCl_4$[a]	.11	.654	I	83.5
Me_2SnCl_2	.125	.31	II	94.0
n-Bu_2SnCl_2	.165	.40	III	91.0
$(C_6H_5)_2SnCl_2$	.25	.62	IV	88.4

[a] Added as a solution in 25 ml. of benzene.

Bis-(trimethylsilylmethyl)-divinyltin was prepared by the reaction of 0.083 mole of $(Me_3SiCH_2)_2SnBr_2$ and 0.35 mole of vinylmagnesium bromide in 79.5% yield, using the method outlined previously.[12]

(4) **Cleavage Reactions with Iodine.** (a) **Compounds I, II and III.**—Essentially the same method was used in the reaction of iodine and I, II and III, and the procedure used for II is given as an example.

To a solution of 30.5 g. (0.0944 mole) of II in 400 ml. of diethyl ether was added 24.0 g. (0.0944 mole) of iodine. The mixture was refluxed for 18 hr., but no reaction appeared to occur. The ether solvent was replaced with benzene. As before, no reaction occurred at this higher reflux temperature. Therefore 250 ml. of xylene was added and most of the benzene was distilled off. No reaction occurred even at the temperature of the refluxing xylene solution. Only when most of the xylene had been distilled away (pot temperature *ca.* 175°) did reaction take place. Distillation of the residual liquid gave 33.4 g. of $(Me_3SiCH_2)_2MeSnI$, b.p. 85–86° at 0.35 mm.

Compound III reacted during a 15.5-hr. reflux period when a small amount of xylene solvent was used. No solvent was used in the cleavage of I with iodine at 175°. In the latter reaction, the other cleavage fragment, Me_3SiCH_2I, b.p. 137–138° at atmospheric pressure, $n^{25}D$ 1.4906, was isolated in 78.5% yield. Sommer and Whitmore[3] report b.p. 140° at 744 mm., $n^{20}D$ 1.4917 for this compound.

(b) **Compound IV.**—To 30 g. (0.067 mole) of IV, dissolved in 150 ml. of benzene, was added 34.2 g. (0.134 mole) of iodine. The reaction mixture was refluxed overnight. The benzene then was removed at atmospheric pressure, and the iodobenzene resulting from the cleavage (26.1 g., 96% yield) at reduced pressure. The residue was diluted with 30–60° petroleum ether, treated with decolorizing charcoal and subsequently crystallized at −78° to give 30.5 g. (83%) of $(Me_3SiCH_2)_2SnI_2$. A small portion was recrystallized to give analytically pure material, m.p. 34.6–35.4°.

(5) **Cleavage with Bromine.** (a) **Compound II.**—A solution of 25 g. (0.0774 mole) of II in 65 ml. of CCl_4 was cooled to 0°, and about 0.5 ml. of bromine was added dropwise. No reaction appeared to occur. The bromine was consumed very slowly after the reaction mixture had been allowed to come to room temperature. The rest of the bromine (12.4 g. total, 0.0774 mole), dissolved in 40 ml. of CCl_4, was then added in small portions over a period of 4 hr. After the bromine had reacted, the solvent was distilled off and the residue was fractionally distilled at reduced pressure to give 7.7 g. (31.4%) of $(Me_3SiCH_2)Me_2SnBr$, b.p. 47–50° at 0.35 mm., a small center cut and 16.8 g. (56%) of $(Me_3SiCH_2)_2MeSnBr$, b.p. 71° at 0.2 mm. to 73° at 0.18 mm.

(b) **Compound III.**—The reaction between 30 g. (0.0737 mole) of III and 11.8 g. (0.0737 mole) of bromine in 105 ml. of CCl_4 was carried out as described above. Fractional distillation, after removal of the solvent, gave only one fraction, b.p. 89–90° at 0.2 mm., 28.7 g., $n^{25}D$ 1.5018.

Anal. Found: C, 34.60; H, 7.10. Calcd. for $(Me_3SiCH_2)_2(C_4H_9)SnBr$: C, 33.50; H, 7.26. Calcd. for $Me_3SiCH_2(C_4H_9)_2SnBr$: C, 36.02; H, 7.31. Calcd. for an equimolar mixture of these products: C, 34.76; H, 7.28.

Assuming the % C values to be significant, analysis indicates that an approximately equimolar mixture of the two possible cleavage products has resulted.

Indirect confirmation was given by the butylation of the product mixture of the bromine cleavage of III. To 0.144 mole of n-C_4H_9MgBr in 150 ml. of THF was added 26.7 g. of the product mixture described above. The Grignard reaction mixture was refluxed for 20 hr., hydrolyzed with saturated ammonium chloride solution, and the organic layer was distilled to give 24.5 g. of liquid boiling 86–94° at 0.23 mm.

Anal. Found: C, 49.24; H, 9.86. Calcd. for $(Me_3SiCH_2)_2(C_4H_9)_2Sn$: C, 47.17; H, 9.90. Calcd. for $Me_3SiCH_2(C_4H_9)_3Sn$: C, 50.94; H, 10.15. Calcd. for an equimolar mixture of these compounds: C, 49.05; H, 10.02.

Again, agreement of the % C values for an approximately equimolar mixture of the two possible products is good. It should be pointed out that the molecular weights of the two possible bromine cleavage products, 430.2 and 400.1, differ by less than 10%, hence their boiling points would be expected to be too close to permit separation by fractional distillation using the equipment available to us.

(6) **Cleavage with Hydrogen Bromide.** (a) **Compounds II and III.**—The same procedure was used for II and III, and the experimental details are given only for the former.

Eight grams of HBr gas was absorbed in 20 ml. of chloroform at −78°, and this solution was then added in small portions to 27.1 g. (0.084 mole) of II at −78°. The reaction mixture was kept at −78° until gas evolution became very slow and was then warmed very cautiously to room temperature. Distillation gave first a 25–35° fraction, then the chloroform solvent, and finally, at reduced pressure, 13.8 g. of $(Me_3SiCH_2)Me_2SnBr$, a small intermediate cut and 14.0 g. of $(Me_3SiCH_2)_2MeSnBr$. The 25–35° fraction was diluted with 20 ml. of xylene and was redistilled to give 4.0 g. of tetramethylsilane, b.p. 26–27°, identified by comparison of its infrared absorption spectrum with that of an authentic sample.

(b) **Compound IV.**—To a solution of 30 g. (0.067 mole) of IV in 15 ml. of dichloromethane at −78° was added about 6.5 g. of hydrogen bromide as a solution in 20 ml. of dichloromethane at −78°. A vigorous reaction commenced immediately, and within 5 min. the reaction mixture was a thick crystal slush. It was left to stand at −78° for one hr., then was allowed to warm up to room temperature. The mixture was filtered. The filtrate was concentrated to about one-half of its original volume, cooled to −78° and filtered again. This procedure was carried out one more time. A total of 13.5 g. of white crystalline material was obtained in this manner. The residual oil was diluted with about an equal volume of 30–60° petroleum ether, cooled to −78°, and more HBr was bubbled into the solution to

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[11] A. C. Smith, Jr., and E. G. Rochow, THIS JOURNAL, **75**, 4103 (1953).

[12] D. Seyferth and F. G. A. Stone, *ibid.*, **79**, 515 (1957).

give an additional 13.1 g. of solid product. The $(Me_3SiCH_2)_2SnBr_2$ so obtained was dissolved in 30–60° petroleum ether, treated with decolorizing charcoal, and recrystallized at −78°.

(7) **Cleavage with Trifluoroacetic Acid.**—To 26.5 g. (0.065 mole) of III in a three-necked flask, equipped with a mechanical stirrer, a dropping funnel and a reflux condenser, was added 7.4 g. (0.065 mole) of CF_3CO_2H. The open end of the condenser was connected to a cold trap in order to catch any volatile products. A mildly exothermic reaction developed as the acid was added. The mixture was stirred at room temperature for one-half hr., then at 60° for 2 hr. and finally for 3 hr. at 80°. The reaction mixture solidified on cooling to give a waxy semi-solid material. Recrystallization from 30–60° petroleum ether yielded 15.4 g. of white crystals, m.p. 62–63.4°, identified by analysis as di-*n*-butyl-(trimethylsilylmethyl)-tin trifluoroacetate. Dilution of the liquid in the cold trap with 20 ml. of xylene, followed by fractional distillation yielded 1.5 g. of tetramethylsilane.

(8) **Cleavage with Mercuric Bromide.**—A solution of 5.58 g. (0.0155 mole) of mercuric bromide in 50 ml. of absolute ethanol was added to 5.0 g. (0.0155 mole) of II. The mixture was refluxed for 45 hr. A small amount of reduction occurred, as evidenced by the presence of a few small droplets of mercury in the bottom of the reaction flask. Typical white, glistening RHgX-type crystals formed when the reaction mixture was cooled. These were filtered and the filtrate was concentrated to about one-half of its original volume and cooled again to give additional solid. In this manner 4.3 g. of CH_3HgBr, m.p. 157–158°, a yield of 94%, was obtained. A m.p. of 161.1° has been reported[13] for pure CH_3HgBr.

Anal. Calcd. for CH_3BrHg: Hg, 67.87. Found: Hg, 67.73.

(9) **Reactions of $(Me_2SiCH_2)_2SnX_2$ Compounds.** (a) $(Me_3SiCH_2)_2SnO$.—Solutions of 1.12 g. (0.02 mole) of KOH in 10 ml. of water and 4.5 g. (0.01 mole) of $(Me_3SiCH_2)_2SnBr_2$ in 15 ml. of diethyl ether were shaken together in a separatory funnel. The ethereal layer was diluted with 30–60° petroleum ether and separated from the aqueous phase. Evaporation of the organic solvents gave white amorphous solid, polymeric $(Me_3SiCH_2)_2SnO$, which was dried in the steam oven.

Anal. Calcd. for $C_8H_{22}OSi_2Sn$: C, 31.08; H, 7.17. Found: C, 30.95; H, 7.16. The polymeric oxide softens and melts over the range 145–160°.

(b) $(Me_3SiCH_2)_2SnS$.—$(Me_3SiCH_2)_2SnI_2$, 5.0 g. (0.0091 mole), was dissolved in ethanol and the solution was saturated with H_2S gas. No precipitate resulted. To the solution then was added 2.2 g. (0.0091 mole) of $Na_2S{\cdot}9H_2O$ and the H_2S addition was continued until white solid came out of solution. This was washed repeatedly with cold ethanol to give 2.0 g. of product. Recrystallization from ethanol gave as a small first fraction very fluffy white solid, melting range, 150–165°.

Anal. Calcd. for $C_8H_{22}SSi_2Sn$: C, 29.54; H, 6.82. Found: C, 29.37; H, 6.69.

The more soluble portion, obtained as a second fraction after concentration of the alcoholic solution, was obtained in the form of large, well-defined crystals, m.p. 74.4–75.5°.

Anal. Found: C, 29.81; H, 6.71.

Thus both fractions consist of the desired sulfide. The second fraction apparently is mainly composed of the trimer (mol. wt. 976) and tetramer (mol. wt. 1301), since the molecular weight of this fraction was determined to be 1105. It is likely that the less soluble portion is a higher polymer.

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CAMBRIDGE 38, MASSACHUSETTS

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[13] T. H. Vaughn, R. J. Spahr and J. A. Nieuwland, THIS JOURNAL, **55**, 4206 (1933).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY AT HARVARD UNIVERSITY]

Vinyl Derivatives of the Metals. VI. Preparation, Properties and Some Reactions of Trivinyl Compounds of Group V Elements[1,2]

BY LUDWIG MAIER, DIETMAR SEYFERTH, F. G. A. STONE AND EUGENE G. ROCHOW

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Trivinyl compounds of Group V elements have been prepared by the reaction between vinyl Grignard reagent and the appropriate trihalide. Some physical properties of these trivinyl derivatives are reported, and several new addition compounds of the type $[(CH_2{:}CH)_3RM^{V}]X$ are described. The ability to form "onium" type adducts decreases in passing from trivinylphosphine to trivinylbismuth. Trivinylarsine and -stibine form complex compounds $[(CH_2{:}CH)_3M^{V}]_2PtCl_2$. Thermal decomposition of trivinylarsine- and trivinylstibine diiodides yielded the corresponding divinyliodo derivatives. Redistribution reactions occur when trivinylarsine and trivinylstibine are mixed with their respective trichlorides or tribromides. In this manner the new compounds $(CH_2{:}CH)AsBr_2$, $(CH_2{:}CH)_2AsBr$, $(CH_2{:}CH)AsCl_2$, $(CH_2{:}CH)_2SbBr$ and $(CH_2{:}CH)_2SbCl$ were obtained, as well as certain *n*-butyl derivatives, *n*-$BuAs(CH{:}CH_2)_2$, *n*-$Bu_2AsCH{:}CH_2$ and *n*-$Bu_2SbCH{:}CH_2$. Vinylhaloarsines were also obtained by mixed redistribution reactions using *n*-$Bu_2Sn(CH{:}CH_2)_2$ and arsenic trichloride or tribromide. When mixed in the correct proportions, arsenic tribromide and triethylarsine also react exothermally giving ethyldibromoarsine.

The first vinyl derivatives of phosphorus and arsenic, prepared by dehydrohalogenation of β-bromoethylphosphonium and arsonium salts, were reported by Hofmann 97 years ago.[3] Vinylphosphorus compounds of the type $CH_2{:}CHP(O)(OR)_2$ have been described more recently,[4] and some sub-

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[1] Paper V in this series: D. Seyferth, *J. Org. Chem.*, **22**, 1252 (1957).

[2] For a preliminary communication see: L. Maier, D. Seyferth, F. G. A. Stone and E. G. Rochow, *Z. Naturforsch.*, **12b**, 263 (1957).

[3] A. W. Hofmann, *Ann. Suppl.*, **1**, 145, 275 (1860); see also R. Hunt and R. R. Renshaw, *J. Pharmacol. Exp. Therap.*, **25**, 315 (1925).

[4] (a) M. I. Kabachnik, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 97 (1947); (b) G. M. Kosolapoff, THIS JOURNAL, **70**, 1971 (1948); (c) A. H. Ford-Moore and J. H. Williams, *J. Chem. Soc.*, 1465 (1947).