[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF HARVARD UNIVERSITY AND THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Neopentyl Group Analogs. II. Tris-(trimethylsilylmethyl) Compounds of Phosphorus, Arsenic, Antimony and Bismuth and their Derivatives[1]

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The tris-(trimethylsilylmethyl) compounds of phosphorus, arsenic, antimony and bismuth have been prepared in good yield by the reaction of trimethylsilylmethylmagnesium chloride in tetrahydrofuran solution with the appropriate trihalide. Adducts of these new compounds with methyl, ethyl and trimethylsilylmethyl iodides, bromine, iodine and mercuric chloride are described. Tris-(trimethylsilylmethyl)-bismuth appears to have no donor properties.

Continuing our investigation of the chemistry of compounds containing neopentyl group analogs, $Me_3M^{IV}CH_2^-$, where M^{IV} is one of the Group IV-B elements, we have prepared and studied some reactions of the tris-(trimethylsilylmethyl) compounds of phosphorus, arsenic, antimony and bismuth. All four of these compounds were prepared in good yield by the reaction of trimethylsilylmethylmagnesium chloride with the appropriate Group V trichloride (or tribromide in the case of phosphorus) in refluxing tetrahydrofuran (THF) solution. This method was used previously with good advantage in the preparation of trimethylsilylmethyl-substituted tin compounds.[1]

$$3Me_3SiCH_2MgCl + M^vCl_3 \xrightarrow{THF} (Me_3SiCH_2)_3M^v + 3MgCl_2$$

$$(M^v = P, As, Sb \text{ or } Bi)$$

The Group V tris-(trimethylsilylmethyl) compounds are all white, nicely crystalline solids. The melting points of the first three members of the series prepared in this study are practically identical: phosphine, 66–69°; arsine, 67–68.5°; stibine, 64–65°. All, with the exception of the arsine, are quite reactive toward oxygen despite the presence of the three relatively bulky silico-neopentyl groups on the central atoms. Tris-(trimethylsilylmethyl)-stibine, on exposure to air, immediately melts due to the heat of oxidation and at times bursts into flame. The stibine will cause ignition of any combustible substance, such as paper, cloth or wood, that it comes in contact with in the presence of air. The corresponding phosphine is somewhat less reactive toward oxygen. Tris-(trimethylsilylmethyl)-bismuth appears to be unstable; even in an atmosphere of nitrogen the originally white crystalline product darkens on standing and a bismuth mirror forms on the flask walls on longer storage. In air the compound gives off dense grey-green fumes before finally igniting. An analytically pure sample was not obtained.

The steric hindrance of the three silico-neopentyl groups is not sufficient to hinder the usual reactions of these Group V compounds such as formation of quaternary "onium" iodides with methyl, ethyl or trimethylsilylmethyl iodides

$$(Me_3SiCH_2)_3P + Me_3SiCH_2I \longrightarrow [(Me_3SiCH_2)_4P]I,$$

addition of halogens

$$(Me_3SiCH_2)_3Sb + Br_2 \longrightarrow (Me_3SiCH_2)_3SbBr_2$$

and formation of crystalline addition compounds with mercuric chloride

$$(Me_3SiCH_2)_3As + HgCl_2 \longrightarrow (Me_3SiCH_2)_3As \cdot HgCl_2$$

However, some of these reactions, particularly "onium" compound formation, are perceptibly slower in rate with the tris-(trimethylsilylmethyl) compounds than with the tri-*n*-butyl derivatives of the Group V elements.

Tris-(trimethylsilylmethyl)-bismuth formed no quaternary compounds with methyl or trimethylsilylmethyl iodides, nor an adduct with mercuric chloride. This parallels the behavior of trimethylbismuth, which is totally devoid of donor properties.[3]

Experimental[4]

1. **Starting Materials.**—Chloromethyltrimethylsilane was prepared as described in Part I of this series.[1] Iodomethyltrimethylsilane was prepared using the method of Sommer and Whitmore.[5]

2. **Tris-(trimethylsilylmethyl) Compounds of P, As, Sb and Bi.**—The same general procedure was used in the preparation of the tris-(trimethylsilylmethyl) compounds of As, Sb and Bi, and is described in detail only for the arsine preparation. All operations were carried out under an atmosphere of prepurified nitrogen.

To 0.4 mole of trimethylsilylmethylmagnesium chloride in 200 ml. of THF[1] was added 18.1 g. (0.1 mole) of arsenic trichloride, diluted with 20 ml. of benzene, at such a rate that a moderate reflux was maintained. The reaction mixture was refluxed for 4.5 hr. after the addition was completed. The mixture was then allowed to cool to room temperature and was subsequently hydrolyzed with 70 ml. of saturated ammonium chloride solution. The organic layer was decanted and the residual salts were washed with diethyl ether, the washings being added to the organic layer. The solvents were distilled at atmospheric pressure. The residue on cooling formed white needles. These were treated with decolorizing charcoal and recrystallized from diethyl ether. A yield of 27 g. (80%) of recrystallized tris-(trimethylsilylmethyl)-arsine, m.p. 67–68.5°, was obtained.

Anal. Calcd. for $C_{12}H_{33}Si_3As$: C, 42.82; H, 10.01; mol. wt., 337. Found: C, 42.90; H, 10.08; mol. wt., 325.

The arsine did not oxidize rapidly in air and could be kept in a brown screw-cap bottle for several months. The compound has a distinctly unpleasant odor.

Tris-(trimethylsilylmethyl)-phosphine required a modification of the above procedure. To the Grignard reagent prepared from 50 g. (0.41 mole) of Me_3SiCH_2Cl and 9.7 g. of Mg turnings in a mixed solvent (50 ml. of THF and 150 ml. of diethyl ether) was added dropwise a solution of 27 g. (0.1 mole) of phosphorus tribromide in 30 ml. of diethyl ether. After the addition had been completed, about 160

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[1] Part I: D. Seyferth, THIS JOURNAL, **79**, 5881 (1957); *cf.* Abstracts of papers presented at the 132nd A. C. S. Meeting, New York, September, 1957, p. 35-S.

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[3] G. E. Coates, "Organo-metallic Compounds," Methuen, London, 1956, p. 158.

[4] Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York. Melting points were determined using a Hershberg melting point apparatus.

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

ml. of solvent was removed by distillation and the residue was heated at 100–120° for 20 hr. After the reaction mixture had cooled, 50 ml. of diethyl ethyl ether and 50 ml. of 30–60° petroleum ether was added and the resulting solution was hydrolyzed with 60 ml. of saturated ammonium chloride solution. The organic layer was separated from the salts and subsequently was evaporated at reduced pressure. A whitish crystalline residue (19.5 g., 66.5% yield) of the crude phosphine remained; this was extracted with 30–60° petroleum ether. The solid remaining after removal of the petroleum ether solvent from the extracts was sublimed at reduced pressure (*ca.* 1–2 mm. at 70–80°) to give white crystals of the pure phosphine, m.p. 66–69° (sealed tube). The yellow sublimation residue usually amounted to 15–20% of the total solids.

Anal. Calcd. for $C_{12}H_{33}Si_3P$: C, 49.24; H, 11.37; P, 10.34. Found: C, 48.90, 49.12; H, 11.48, 11.56; P, 10.37.

The small amount of petroleum ether insoluble material was taken up in methanol. Partial vacuum evaporation of the methanol gave about 2–3 g. of white crystalline solid, m.p. 168–172°, shown by analysis to be the phosphine oxide, $(Me_3SiCH_2)_3PO$.

Anal. Calcd. for $C_{12}H_{33}OSi_3P$: C, 46.70; H, 10.78. Found: C, 47.30; H, 10.74.

The phosphine, like the arsine, had a distinctly unpleasant odor. It fumed and, due to the heat of oxidation, melted in air. When in contact with combustible material it caused ignition of the latter in the presence of air.

Tris-(trimethylsilylmethyl)-stibine was prepared in the manner described for the arsine from 0.4 mole of Me_3SiCH_2MgCl and 0.1 mole of antimony trichloride. Extreme precautions had to be taken because of the facile oxidation of the stibine. The white crystalline stibine was recrystallized from a petroleum ether–methanol mixture to give a 74% yield of pure compound, m.p. 64–5° (sealed tube).

Anal. Calcd. for $C_{12}H_{33}Si_3Sb$: C, 37.58; H, 8.68., Found: C, 37.29; H, 8.62.

Tris-(trimethylsilylmethyl)-bismuth was prepared using the procedure described above from 0.4 mole of Me_3SiCH_2MgCl and 0.1 mole of bismuth trichloride in 35% yield. Extensive decomposition occurred during removal of the solvent. The grey crystalline residue was dissolved in diethyl ether, filtered through Filter-Aid, and the ether solvent was removed *in vacuo*. The residue was slurried in methanol, filtered and dried *in vacuo* to give white crystals of the bismuth compound.

Anal. Calcd. for $C_{12}H_{33}Si_3Bi$: C, 30.62; H, 7.07. Found: C, 26.97; H, 6.20.

The impure product became partially liquid at 107–109°; at 140° decomposition occurred.

3. The Preparation of Quaternary "Onium" Iodides.—In all cases a sample of the tris-(trimethylsilylmethyl) compound was dissolved in an excess of the organic iodide, and the mixture was refluxed under nitrogen for 2–4 hr. Excess of organic iodide was removed at reduced pressure, and the residue, usually crystalline, was dissolved in a minimum amount of ethanol. Addition of diethyl ether precipitated white crystals of the "onium" compound. Another precipitation usually served to give analytically pure material. The new compounds thus obtained are listed in Table I.

Methyl-tris-(trimethylsilylmethyl)-arsonium mercuriiodide, $[(Me_3SiCH_2)_3MeAs]HgI_3$, was prepared by refluxing an ethanolic solution of methyl-tris-(trimethylsilylmethyl)-arsonium iodide in contact with the equivalent amount of red mercuric iodide. The latter gradually went into solution on heating. Light needles of the mercuriiodide crystallized when the yellow solution was cooled. A yield of 91% was thus obtained.

TABLE I

QUATERNARY "ONIUM" IODIDES

Compound	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
$[(Me_3SiCH_2)_4P]I$	136.5–138	37.91	37.77	8.75	8.75[a]
$[(Me_3SiCH_2)_3MeP]I$	175–177 dec.	35.92	36.20	8.35	8.69
$[(Me_2SiCH_2)_3EtP]I$	125.5–127	37.48	38.18	8.54	8.70
$[(Me_3SiCH_2)_4As]I$	143.5–145	34.89	34.93	8.05	8.06
$[(Me_3SiCH_2)_3MeAs]I$	193–195 dec.	32.63	32.84	7.58	7.39
$[(Me_3SiCH_2)_3EtAs]I$	112–115	34.13	34.05	7.78	7.60
$[(Me_3SiCH_2)_3MeSb]I$	147–148	29.72	29.98	6.91	6.85
$[(Me_3SiCH_2)_3MeAs]HgI_3$	134–135	16.73	16.81	3.89	4.07

[a] Calcd. iodine, 25.04; found, 25.00.

4. Reaction of the Tris-(trimethylsilylmethyl) Compounds with Bromine and Iodine. a. Tris-(trimethylsilylmethyl)-phosphine.—The dropwise addition of an equivalent quantity of bromine to a solution of the phosphine in petroleum ether solution resulted in an exothermic reaction which gave a light yellow precipitate. This solid, very probably the desired $(Me_3SiCH_2)_3PBr_2$, was very hygroscopic; it fumed in air and quickly became pasty. Its isolation in analytical purity was not attempted.

Similarly, mixing of equivalent quantities of the phosphine and iodine in methylene chloride solution resulted in an exothermic reaction and instantaneous decolorization of the iodine solution. Evaporation of the solvent gave yellow-brown extremely hygroscopic $(Me_3SiCH_2)_3PI_2$. Isolation of pure compound was not attempted.

b. **Tris-(trimethylsilylmethyl)-arsine.**—The reaction with bromine was carried out as described above with 0.003 mole of the arsine. The white precipitate was washed with cold petroleum ether and dried *in vacuo* to give pure $(Me_3SiCH_2)_3AsBr_2$, m.p. 118–120° dec.

Anal. Calcd. for $C_{12}H_{33}Br_2Si_3As$: C, 29.03; H, 6.70. Found: C, 29.22; H, 6.37.

Tris-(trimethylsilylmethyl)-arsenic diiodide was prepared by mixing equivalent amounts of the arsine and iodine in methylene chloride solution and evaporating the solvent. The golden yellow platelets, m.p. 118–120° with decomposition to a red liquid, decomposed on storage in a brown bottle.

Anal. Calcd. for $C_{12}H_{33}I_2Si_3As$: C, 24.41; H, 5.64. Found: C, 24.60; H, 5.64.

c. **Tris-(trimethylsilylmethyl)-stibine.**—Treatment of 1.0 g. of the stibine with an equivalent of bromine in petroleum ether at 0° under an atmosphere of nitrogen gave white solid $(Me_3SiCH_2)_3SbBr_2$, m.p. 158–160°.

Anal. Calcd. for $C_{12}H_{33}Br_2Si_3Sb$: C, 26.53; H, 6.12. Found: C, 27.52; H, 6.23.

5. Mercuric Chloride Adducts.—A solution of 0.005 mole of mercuric chloride in hot ethanol was added to an ethanolic solution of the tris-(trimethylsilylmethyl) compound. On cooling the mixture small white crystals of the addition compound came out of solution. These were filtered, washed with cold ethanol and dried. The adducts were acetone-soluble. The following were isolated in analytical purity: $(Me_3SiCH_2)_3P \cdot HgCl_2$, decomp. point 175–177°.

Anal. Calcd. for $C_{12}H_{33}Cl_2Si_3PHg$: C, 25.54; H, 5.90. Found: C, 25.74; H, 5.90.

$(Me_3SiCH_2)_3As \cdot HgCl_2$, decomp. point 176–176.8°.

Anal. Calcd. for $C_{12}H_{33}Cl_2Si_3AsHg$: C, 23.74; H, 5.48. Found: C, 23.82; H, 5.31.

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