at the carbonyl groups rather than at the tin–carbon bond.

Experimental[7]

Preparation of Starting Materials.—Trimethylphenylgermane was prepared in 75% yield by the reaction of C_6H_5MgBr with $(CH_3)_3GeI$ in an ether–toluene solvent system; b.p. 182–184° (lit.[8] 182°), $n^{25}D$ 1.5045.

Anal. Calcd. for $C_9H_{14}Ge$: C, 55.49; H, 7.24. Found: C, 55.65; H, 7.20.

Trimethylphenyltin was prepared in 78% yield by the reaction of CH_3MgBr with $C_6H_5SnCl_3$ (Metal & Thermit Corp.) in tetrahydrofuran; b.p. 76.5° at 0.9 mm., $n^{25}D$ 1.5330. This compound was prepared previously[9] in 35% yield, but no physical constants were recorded.

Trimethylsilylbenzene Chromium Tricarbonyl.—A mixture of $Cr(CO)_6$ (2.2 g., 10 mmoles) and 10 ml. of $(CH_3)_3SiC_6H_5$ was maintained at 170–175° for 36 hr. under an argon atmosphere in a flask equipped with an air condenser topped with a water-cooled condenser. During this time the $Cr(CO)_6$ which sublimed into the air condenser was periodically pushed back into the reaction flask with a long spatula. A yellow color developed slowly in the reaction mixture, and a small amount of solid formed. The mixture then was cooled and diluted with 100 ml. of ether. Filtration through a short column of deactivated alumina was followed by removal of volatiles at reduced pressure. The yellow crystalline residue was recrystallized from aqueous ethanol to give 0.56 g. (20%) of I, m.p. 72–73°. An analytical sample was sublimed at 60–65° at 0.01 mm.

Anal. Calcd. for $C_{12}H_{14}O_3SiCr$: C, 50.33; H, 4.93. Found: C, 50.83; H, 4.86.

The infrared spectrum (10% solution in cyclohexane) showed carbonyl absorption at 1987 and 1911 cm.⁻¹ (lit.[6] 1982 and 1911 cm.⁻¹), bands due to the trimethylsilyl group (1250, 840, and 757 cm.⁻¹), and a band characteristic of the Si–phenyl linkage at 1105 cm.⁻¹.[10]

Trimethylgermylbenzene Chromium Tricarbonyl.—Chromium hexacarbonyl (10 mmoles) and $(CH_3)_3GeC_6H_5$ (1.95 g., 10 mmoles) were heated under argon in anhydrous ethylene glycol dimethyl ether (10 ml.) at 155° for 26 hr., and the sublimed hexacarbonyl was returned to the flask in the usual manner. A green solid formed slowly. The residue obtained by filtration and evaporation of the filtrate at reduced pressure was recrystallized from ethanol–water. Yellow crystals of II, 1.12 g. (34%), m.p. 79–79.5°, were obtained. Sublimation (70°, 0.001 mm.) gave pure material, m.p. 79.5–80°.

Anal. Calcd. for $C_{12}H_{14}O_3GeCr$: C, 43.56; H, 4.27. Found: C, 43.37; H, 4.26.

Its infrared spectrum showed carbonyl absorption at 1985 and 1910 cm.⁻¹ and a band due to the Ge–phenyl linkage at 1082 cm.⁻¹.[10]

Trimethylstannylbenzene Chromium Tricarbonyl.—The procedure described above was used in the reaction of 10 mmoles of $Cr(CO)_6$ and 3.61 g. (15 mmoles) of $(CH_3)_3SnC_6H_5$ in 10 ml. of anhydrous ethylene glycol dimethyl ether. The heating period (155°) was 43 hr., and again green solid was formed. The crude residue was recrystallized from ethanol–water and from petroleum ether at −40° to give 1.28 g. (34%) of shiny yellow crystals of III, m.p. 77–77.5°. Further purification by slow sublimation at 65–70° at 0.001 mm. raised the m.p. to 78.5–79°.

(7) All reactions were carried out under an atmosphere of argon or prepurified nitrogen. Melting points are uncorrected. Analyses by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by A. Schoeller, Kronach, Ofr.

(8) H. Bauer and K. Burschkies, *Ber.*, **66**, 1156 (1933).

(9) R. H. Bullard and W. R. Robinson, *J. Am. Chem. Soc.*, **49**, 1368 (1927).

(10) Sharp absorptions characteristic of the Si–phenyl, Ge–phenyl, and Sn–phenyl linkages are reported to occur at 1100, 1080, and 1065 cm.⁻¹, respectively: M. C. Henry and J. G. Noltes, *J. Am. Chem. Soc.*, **82**, 555 (1960).

Anal. Calcd. for $C_{12}H_{14}O_3SnCr$: C, 38.23; H, 3.74. Found: C, 38.25; H, 3.83.

The infrared spectrum of the product showed carbonyl absorption at 1984 and 1908 cm.⁻¹ and a band characteristic of the tin–phenyl system at 1066 cm.⁻¹.[10]

III, as well as its silicon and germanium analogs, appeared to be stable in air in the solid state. In solution, however, all three compounds were decomposed by air. None was very stable thermally; during the sublimations mentioned above, some decomposition always appeared to occur.


Contribution from the Department of Chemistry of the Massachusetts Institute of Technology, Cambridge, Massachusetts

The Cleavage of Hexamethyldisiloxane and Hexamethyldigermoxane by Methyllithium: A Convenient Preparation of Lithium Trimethylsilanolate and Lithium Trimethylgermanolate[1]

By Dietmar Seyferth[2a] and David L. Alleston[2b]

Although the cleavage of organosiloxanes by organolithium reagents is known,[3] this reaction has found no synthetic application to the preparation of lithium silanolates.

$$R_3SiOSiR_3 + R'Li \longrightarrow R_3SiOLi + R_3SiR'$$
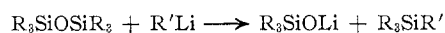
In the examples reported,[3] the siloxanes and lithium reagents used did not constitute a system favorable for synthetic purposes, since a tetraorganosilane of relatively high molecular weight also was formed in the reaction.

It seemed to us that this apparently general reaction could find synthetic utility, especially in the preparation of lithium trimethylsilanolate. None of the procedures for preparing alkali metal silanolates is wholly satisfactory.[4] Thus some methods are based on the use of trimethylsilanol, a silicon intermediate which is not commercially available, while the best method for sodium trimethylsilanolate based on the commercially available hexamethyldisiloxane requires a reaction in liquid ammonia.

We find that the cleavage of hexamethyldisiloxane with one molar equivalent of methyllithium in an

(1) Presented in part at the Colloque International de Chimie Organique du Centre de la Recherche Scientifique, Paris, Sept. 24–28, 1962.

(2) (a) Alfred P. Sloan Research Fellow; (b) Fellow of the M.I.T. School for Advanced Study, 1961–1962.

(3) H. Gilman, H. N. Benedict, and H. Hartzfeld, *J. Org. Chem.*, **19**, 419 (1954).

(4) For a review see C. Eaborn, "Organosilicon Compounds," Butterworth Publications Ltd., London, 1960, pp. 271–273.

ether–tetrahydrofuran solvent system produces lithium trimethylsilanolate in high yield.

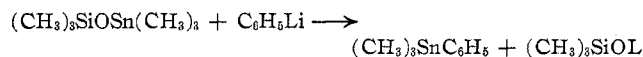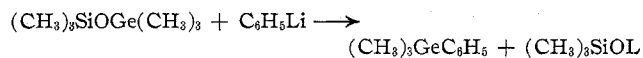$$(CH_3)_3SiOSi(CH_3)_3 + CH_3Li \longrightarrow (CH_3)_3SiOLi + (CH_3)_4Si$$
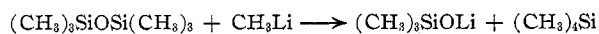
The tetramethylsilane (b.p. 26°) formed does not interfere in any way during subsequent reactions of the silanolate and in no way interferes in the work-up of the reaction mixtures. A number of siloxane preparations in 80–90% yield, based on the reaction of lithium trimethylsilanolate with chlorosilanes, established the value of this procedure. This siloxane cleavage reaction does not occur to any great extent in diethyl or di-*n*-butyl ether alone, and this provides another example of the large positive effect of tetrahydrofuran on the reactivity of methyllithium.

The procedure used for lithium trimethylsilanolate also serves well in the preparation of lithium trimethylgermanolate.

$$(CH_3)_3GeOGe(CH_3)_3 + CH_3Li \longrightarrow (CH_3)_3GeOLi + (CH_3)_4Ge$$
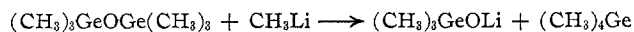
It is, however, much less practical, since the starting organogermanium compound must be prepared by the route $GeCl_4 \rightarrow (CH_3)_4Ge \rightarrow (CH_3)_3GeI \rightarrow (CH_3)_3-GeOGe(CH_3)_3$. Thus loss of one-half of the germanium in the form of tetramethylgermane cannot be tolerated. Moreover, recovery of the latter from the ether–tetrahydrofuran solvent system is difficult. The lithium trimethylgermanolate reacts normally (*e.g.*, with trimethylchlorosilane to give $(CH_3)_3SiOGe(CH_3)_3$ in 67% yield), and thus this procedure has utility in small-scale preparations.

The attack of organolithium reagents on unsymmetrical hexaorganodisiloxanes occurs at the more electrophilic silicon atom of the siloxane linkage. For example, action of *p*-tolyllithium on $(C_6H_5)_3-SiOSi(C_6H_4CH_3-p)_3$ gave triphenyl-*p*-tolylsilane and lithium tris-*p*-tolylsilanolate.[3] We have examined the reactions of phenyllithium with the mixed group IV oxides $(CH_3)_3SiOGe(CH_3)_3$ and $(CH_3)_3SiOSn(CH_3)_3$, and have found that here also nucleophilic attack by phenyllithium occurs exclusively at the more electrophilic group IV atom

$$(CH_3)_3SiOGe(CH_3)_3 + C_6H_5Li \longrightarrow$$
$$(CH_3)_3GeC_6H_5 + (CH_3)_3SiOL$$

$$(CH_3)_3SiOSn(CH_3)_3 + C_6H_5Li \longrightarrow$$
$$(CH_3)_3SnC_6H_5 + (CH_3)_3SiOL$$

The compound $(CH_3)_3GeOSn(CH_3)_3$ obviously would be of interest in this connection, but our attempts at its preparation were not successful, apparently because of its facile disproportionation to the symmetrical hexamethyldimetaloxanes. It should be noted that phenyllithium attacks silicon readily when there are no more electrophilic metal atoms in the dimetaloxane molecule, *i.e.*, when hexamethyldisiloxane is the substrate. The action of phenyllithium on hexamethyldisiloxane under conditions comparable to those used for the mixed metal oxides gave trimethylphenylsilane in 74% yield.

Preparation of Lithium Trimethylsilanolate.—An ethereal solution of CH_3Li (1 molar equivalent) was added slowly from a storage buret to a stirred solution of hexamethyldisiloxane (Dow Corning Corp.) in anhydrous tetrahydrofuran (THF). A slightly exothermic reaction occurred, causing the solvent to reflux gently. Tetramethylsilane, ether, and some THF (all identified by gas chromatography) were distilled from the reaction mixture until the temperature at the distillation head reached 65°. The resulting solution was heated under reflux and with stirring overnight to complete the reaction (Gilman Color Test I negative). This procedure gave a slightly brownish yellow solution of the reagent.

Preparation of Siloxanes Using Lithium Trimethylsilanolate.—Dimethyldichlorosilane (Silicone Products Dept., General Electric Co.) (6.45 g., 50 mmoles) in 25 ml. of THF was added to a stirred solution of 100 mmoles of $(CH_3)_3SiOLi$ (prepared from 110 ml. of 0.91 M CH_3Li and 16.24 g. of hexamethyldisiloxane in 100 ml. of THF). A fairly exothermic reaction ensued which caused moderate refluxing of the solution. Lithium chloride was precipitated during the addition. The mixture was heated at reflux for 2 hr. and then hydrolyzed with 50 ml. of 2% HCl. Fractional distillation of the organic layer gave a fraction of boiling range 150–157°. This was washed with water, dried, and redistilled to give 10.8 g. (91%) of octamethyltrisiloxane, b.p. 153–154°, $n^{20}D$ 1.3849 (lit.[6] b.p. 152°, $n^{20}D$ 1.3848).

Similar reactions of lithium trimethylsilanolate with the appropriate chlorosilane gave: (1) **Pentamethylvinyldisiloxane** (80% yield), b.p. 122°, $n^{25}D$ 1.3929 (lit.[7] b.p. 120°, $n^{25}D$ 1.3930). *Anal.* Calcd. for $C_7H_{18}OSi_2$: C, 48.20; H, 10.40. Found: C, 48.66; H, 10.29. The infrared spectrum of the product showed bands characteristic of the vinyl group ($\nu_{C=C}$ 1595 cm.$^{-1}$), trimethylsilyl group (1257, 845, and 756 cm.$^{-1}$), and the siloxane linkage (1060 cm.$^{-1}$). (2) **Allyltris-(trimethylsiloxy)-silane** (82% yield), b.p. 105–106° at 1.7 mm., $n^{25}D$ 1.4009. *Anal.* Calcd. for $C_{12}H_{32}O_3Si_4$: C, 42.80; H, 9.58. Found: C, 42.95; H, 9.68. Its infrared spectrum showed bands characteristic of the allyl group ($\nu_{C=C}$ 1633 cm.$^{-1}$), the trimethylsilyl group, and the siloxane linkage.

Preparation of Trimethyl-(trimethylsiloxy)-tin.—Trimethyltin bromide (24.4 g., 100 mmoles) in 50 ml. of THF was added with stirring to a solution of 100 mmoles of $(CH_3)_3SiOLi$ in 125 ml. of THF. The reaction mixture was heated at reflux for 2 hr., and then all volatiles were distilled off at reduced pressure. Fractional distillation of the distillate gave 15.4 g. (61%) of $(CH_3)_3-SiOSn(CH_3)_3$, b.p. 144° (lit.[8] 141° at 720 mm.). Gas chromatographic analysis showed the product to be essentially pure except for a trace of THF. The product, an evil smelling liquid, underwent rapid hydrolysis in laboratory air, depositing solid trimethyltin hydroxide.

Preparation of Trimethyl-(trimethylsiloxy)-germane via $(CH_3)_3-GeOLi$.—To 18.9 g. (75 mmoles) of hexamethyldigermoxane[9] (prepared by basic hydrolysis of $(CH_3)_3GeI^{10}$) in 125 ml. of THF was added slowly with stirring 75 mmoles of ethereal methyllithium. A reaction more noticeably exothermic than that occurring between CH_3Li and the siloxane commenced. Ether, THF, and tetramethylgermane (identified by gas chromatography) were distilled from the mixture until a head temperature of 65° was reached. The clear, brownish yellow solution was heated at reflux for 7 hr. To this solution was added 8.15 g. (75 mmoles) of trimethylchlorosilane (Dow Corning Corp.), and the mixture was heated at reflux for 3 hr. Vacuum distillation of the mixture, followed by fractional distillation of the distillate, gave

(5) All reactions were carried out under an atmosphere of prepurified nitrogen. Analyses by the Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and A. Schoeller, Kronach, Ofr.

(6) W. I. Patnode and D. F. Wilcock, *J. Am. Chem. Soc.*, **68**, 358 (1946).

(7) R. M. Pike and D. L. Bailey, *J. Polymer Sci.*, **22**, 55 (1956).

(8) H. Schmidbaur and M. Schmidt, *J. Am. Chem. Soc.*, **83**, 2963 (1961).

(9) M. P. Brown, R. Okawara, and E. G. Rochow, *Spectrochim. Acta*, **16**, 595 (1960).

(10) D. Seyferth and N. Kahlen, *J. Org. Chem.*, **25**, 809 (1960).

three fractions: (1) 1.8 g., b.p. 110–118°, *ca.* 10% (CH₃)₃-SiOSi(CH₃)₃, 45% product, and 45% THF, by gas chromatography; (2) 8.5 g., b.p. 118–122°, essentially pure product[11] (lit.[12] b.p. 116–117°); (3) 2.2 g., b.p. above 122°, *ca.* 50% product and 50% (CH₃)₃GeOGe(CH₃)₃; total yield of product, 10.4 g. (67%). This compound also was readily hydrolyzed by atmospheric moisture.

The Reaction of Phenyllithium with (CH₃)₃SiOGe(CH₃)₃ and with (CH₃)₃SiOSn(CH₃)₃.—An ethereal solution of C₆H₅Li (*ca.* 20 ml. of 0.1 *M* solution) was added to 20 mmoles of the hexamethyldimetaloxane in 50 ml. of THF. Ether and THF were distilled from the mixture until the temperature at the distillation head was 65°. The resulting solution was heated at reflux overnight. Water then was added, the layers were separated, and the aqueous layer was extracted with THF. The combined organic layers were dried over anhydrous CaSO₄ and distilled into a single receiver. The more volatile material was collected at atmospheric pressure, while the high boilers were collected at reduced pressure (bath temperature *ca.* 200° at 0.1 mm.). The resulting solutions were analyzed first qualitatively by gas chromatography. Peaks corresponding to the trimethylphenylmetal derivative and the hexamethyldimetaloxane formed were collected and identified by comparison of their infrared spectra with those of authentic samples. Quantitative gas chromatographic analysis of the trimethylphenylmetal compounds was carried out on a Dow Corning 710 silicone fluid-on-Chromosorb P column with jacket temperature 200° and 15 p.s.i. helium carrier gas. Indene was used as internal standard. These results were obtained: **(CH₃)₃SiOGe(CH₃)₃.** Only (CH₃)₃GeC₆H₅ and (CH₃)₃SiOSi-(CH₃)₃ were formed; the former compound was formed in 93.3 and 95% yield in the two runs carried out. One mole % of (CH₃)₃SiC₆H₅ would have been detected under the conditions of the analysis if this compound had been formed. **(CH₃)₃SiOSn-(CH₃)₃.** Only (CH₃)₃SnC₆H₅ and (CH₃)₃SiOSi(CH₃)₃ were detected in the gas chromatographic analysis. In four runs the former compound was formed in yields of 64.2, 66.8, 69.9, and 79.0%. The significant feature of both sets of experiments is the absence of (CH₃)₃SiC₆H₅.

(11) *Anal.* Calcd. for C₆H₁₈OSiGe: C, 34.83; H, 8.77. Found: C, 34.44; H, 8.27.

(12) H. Schmidbaur and M. Schmidt, *Chem. Ber.*, **94**, 1138 (1961).

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida

The Reaction of Iodine Monochloride and HICl₂ with Hexaphenylcyclotriphosphazene[1]

By R. D. Whitaker,[2] J. C. Carleton,[3] and H. H. Sisler

The existence of addition compounds of iodine monochloride and ordinary heterocyclic amines[4] has been established. Since Shaw and co-workers[5] have found

that the basicity of fully substituted aminocyclophosphazenes is comparable with that of free amines, it would seem that information about the basicity of cyclophosphazenes could be gained by studying the interaction of iodine monochloride with one of the cyclophosphazenes. It has been assumed by these workers that the ring nitrogen atoms are the basic centers rather than the exocyclic nitrogen atoms.

We decided to study a fully substituted cyclophosphazene which does not contain exocyclic nitrogen atoms so that any Lewis acid–base interaction would more definitely involve the ring nitrogen atoms. Furthermore, a cyclotriphosphazene was used because the ring is planar and thus is somewhat analogous to the ordinary aromatic heterocyclic amines.

We have found that hexaphenylcyclotriphosphazene and iodine monochloride do not react directly in dry carbon tetrachloride to give a solid adduct. The presence of moisture, however, results in the formation of hydrogen chloride by the hydrolysis of iodine monochloride and causes precipitation of a small amount of crystalline solid having the empirical formula [(C₆H₅)₂-PN]₃·HICl₂. The addition of hydrogen chloride to the solution of iodine monochloride causes a significant increase in the yield of this crystalline substance. The heterogeneous reaction of the pure phosphazene and pure iodine monochloride carried out in the strict absence of moisture yields [(C₆H₅)₂PN]₃·2ICl. Structural studies on these two new adducts of hexaphenylcyclotriphosphazene have not been carried out. However, in view of the known basicity of the phosphazene ring established by Shaw and his co-workers,[5] it seems reasonable to formulate [(C₆H₅)₂PN]₃·HCl·ICl as ([(C₆H₅)₂PN]₃H)⁺ICl₂⁻. Since the two compounds have similar superficial characteristics the structure ([(C₆H₅)₂PN]₃I)⁺ICl₂⁻ is a reasonable possibility for the compound [(C₆H₅)₂PN]₃·2ICl.

Bode, Bütow, and Lienau[6] reported the formation of a salt from the reaction of hexachlorocyclotriphosphazene and perchloric acid. Hence we carried out a similar experiment with ICl and also with HICl₂ using the triphenyltrichlorocyclotriphosphazene. However, we observed no reaction between 2,4,6-trichloro-2,4,6-triphenylcyclotriphosphazene[7] and ICl or HICl₂ in carbon tetrachloride.

Our results can be interpreted in terms of the assumption that the ring nitrogen atoms in the cyclotriphosphazenes are basic centers and that in the absence of strongly electronegative substituents on the phosphorus atoms their basicity is similar to that of ordinary aromatic heterocyclic amines. Furthermore, it appears that the introduction of electronegative substituents on the phosphorus atoms sharply reduces this basicity.

Experimental

Chemicals.—Iodine monochloride (m.p. 26.5°; lit.[8] 27.2°)

(1) Trimer of diphenylphosphonitrile.

(2) N. S. F. Summer Research Participant.

(3) Participant in N. S. F. Summer Research Institute for Secondary School Students.

(4) R. D. Whitaker, J. R. Ambrose, and C. W. Hickam, *J. Inorg. Nucl. Chem.*, **17**, 254 (1961).

(5) S. K. Ray and R. A. Shaw, *Chem. Ind.* (London), 1173 (1961); D. Feakins, W. A. Last, and R. A. Shaw, *ibid.*, 510 (1962).

(6) H. Bode, K. Bütow, and G. Lienau, *Chem. Ber.*, **81**, 547 (1948).

(7) Private communication from Dr. B. Gruschkin, W. R. Grace and Co., indicates that this compound is probably the *trans* isomer.