[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Further Studies on Highly-Branched Aliphatic Organosilicon Compounds: Trimethylsilylmethyl Group[1]

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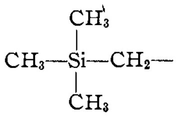
Syntheses of seven new compounds having the trimethylsilylmethyl group directly linked to silicon are described. These include all four of the compounds which can be derived from silicon tetrachloride by substitution of trimethylsilylmethyl for chlorine. From an investigation of the properties of the compounds obtained from hydrolysis or ammonolysis of chlorosilanes containing the trimethylsilylmethyl group it is concluded that in reactions involving the attack of bulky reagents, the steric effects of trimethylsilylmethyl are of a magnitude intermediate between the *n*-alkyl and *t*-butyl groups.

In previous work[2] we found that the presence of a *t*-butyl group in organosilicon structures has some remarkable steric effects on the chemistry of functional groups linked to silicon in these compounds, especially in the direction of blocking the ordinarily rapid self-condensation reactions characteristic of ordinary organosilanediols and organodiaminosilanes. For the purpose of providing additional data on the steric effects of highly-branched groups in aliphatic organosilicon compounds, we now report a study of compounds having the trimethylsilylmethyl group



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-CH_2-$$

directly linked to silicon. This group is of interest from two standpoints. Firstly, in comparison to *t*-butyl, the methyl branching is at a β-atom. Secondly, this highly-branched group possesses no carbon–carbon bonds.

In the present work a series of four compounds derived from progressive substitution of chlorine in silicon tetrachloride by trimethylsilylmethyl groups has been synthesized. Reaction of trimethylsilylmethylmagnesium chloride with silicon tetrachloride gave trimethylsilylmethyltrichlorosilane (I) in 58% yield.

$$Me_3SiCH_2MgCl + SiCl_4 \longrightarrow Me_3SiCH_2SiCl_3 \quad (I)$$

For the preparation of di-(trimethylsilylmethyl)-dichlorosilane (II), trimethylsilylmethyllithium in a pentane solvent was used, taking advantage of the greater reactivity of the lithium compound as compared to the Grignard reagent, and a yield of 40% was obtained.

$$2Me_3SiCH_2Li + SiCl_4 \longrightarrow (Me_3SiCH_2)_2SiCl_2 \quad (II)$$

From reaction of 1.1 moles of trimethylsilylmethyllithium with 0.2 mole of silicon tetrachloride at the boiling point of pentane (37°) for 72 hours, a 50% yield of tri-(trimethylsilylmethyl)-chlorosilane (III) was obtained.

$$3Me_3SiCH_2Li + SiCl_4 \longrightarrow (Me_3SiCH_2)_3SiCl \quad (III)$$

This reaction is in marked contrast to the results obtained from treatment of di-*t*-butyldichlorosilane with *t*-butyllithium over a temperature range of 75–160°. No tri-*t*-butylchlorosilane was formed.[3] Further, while tetraisopropylsilane does not result from reaction of silicon tetrachloride with isopropyllithium,[4] tetra-(trimethylsilylmethyl)-silane (IV) was prepared in the present work in 33% yield from reaction of trimethylsilylmethyllithium with silicon tetrachloride at 150° for 12 hours.

$$4Me_3SiCH_2Li + SiCl_4 \longrightarrow (Me_3SiCH_2)_4Si \quad (IV)$$

Compound IV is a white solid, m.p. 28.5°.

While the preparation of compound IV shows that four trimethylsilylmethyl groups can be introduced around a silicon atom, it is of some interest to note that the conditions required for this synthesis are considerably more vigorous than those needed for the preparation of tetra-*n*-alkylsilanes using organolithium compounds and silicon tetrachloride. These latter type reactions are virtually quantitative after short reaction times and temperatures not exceeding the boiling point of petroleum ether.[5] Thus, the facility with which trimethylsilylmethyl groups can be introduced into an organosilicon structure is intermediate between *n*-alkyl and *t*-butyl.

As an example of a dichlorosilane containing only one trimethylsilylmethyl group, methyltrimethylsilylmethyldichlorosilane (V) was prepared from the reaction of trimethylsilylmethyllithium with methyltrichlorosilane.

$$Me_3SiCH_2Li + MeSiCl_3 \longrightarrow Me(Me_3SiCH_2)SiCl_2 \quad (V)$$

In this reaction, $Me(Me_3SiCH_2)_2SiCl$ (VI) was obtained as a by-product.

Recently we reported the synthesis of three di-*n*-alkylsilanediols, *i.e.*, diethyl-, di-*n*-propyl- and di-*n*-butylsilanediol, by controlled hydrolysis of the corresponding dichlorosilanes with 1.5 *N* alkali using low temperatures and short reaction times to favor diol and hinder siloxane formation. These diols are white solids which readily give quantitative dehydration to siloxanes in benzene solution containing iodine after two hours of refluxing.[6] In sharp contrast to this condensation of di-*n*-alkylsilanediols, di-*t*-butylsilanediol could not be condensed with more effective dehydrating agents under a wide variety of more vigorous conditions.[2]

In the present work, di-(trimethylsilylmethyl)-silanediol (VII), m.p. 93°, was prepared in 83% yield from the dichlorosilane by the method employed for the di-*n*-alkylsilanediols. Treatment of

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[1] Paper 43 in a series on organosilicon chemistry. For Paper 42 see THIS JOURNAL, **76**, 1613 (1954).

[2] L. H. Sommer and L. J. Tyler, THIS JOURNAL, **76**, 1030 (1954).

[3] L. J. Tyler, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2876 (1948).

[4] H. Gilman and R. N. Clark, *ibid.*, **69**, 1499 (1947). However, these authors used the boiling point of petroleum ether as their maximum reaction temperature.

[5] H. Gilman and R. N. Clark, *ibid.*, **68**, 1675 (1946).

[6] P. D. George, L. H. Sommer and F. C. Whitmore, *ibid.*, **75**, 1585 (1953).

compound VII with benzene and iodine at the boiling point by the procedure used for the quantitative dehydration of the di-*n*-alkylsilanediols gave less than 20% reaction after 16 hours. However, after 16 hours at reflux, a xylene solution containing iodine and β-naphthalenesulfonic acid gave 95% dehydration. This diol was further characterized by a determination for active hydrogen using lithium aluminum hydride in *n*-butyl ether.

Our previous studies on steric effects of the *t*-butyl group in organosilicon compounds revealed that di-*t*-butyldiaminosilane is readily available from treatment of the corresponding dichlorosilane with liquid ammonia and that this diaminosilane is exceedingly stable and can be distilled without decomposition at 190°.[2] It was also found that the presence of even a *single t*-butyl group permits the formation of a stable dialkyldiaminosilane, *e.g.*, *t*-butylmethyldiaminosilane. In contrast, di-*n*-alkyldichlorosilanes on treatment with liquid ammonia give silazanes (compounds having Si–NH–Si groupings) and none of the monomeric dialkyldiaminosilane.[2] In the present work di-(trimethylsilylmethyl)-dichlorosilanes gave no diaminosilane. Instead, a mixture of silazanes was obtained.

Taken together the above facts clearly show the far greater steric effect of branching at an atom alpha to silicon (*e.g.*, in the *t*-group) as compared to branching at the β-atom (*e.g.* in the trimethylsilylmethyl group) *when the attacking reagent is a bulky one*—in condensation reactions and in the progressive introduction of bulky groups by means of organometallic compounds. Comparison of Fisher–Hirschfelder molecular models of siloxanes and silazanes containing *t*-butyl groups with analogous compounds containing trimethylsilylmethyl groups clearly indicates greater "crowding" in the *t*-butyl compounds.

The situation concerning steric effects of groups such as *t*-butyl- and trimethylsilylmethyl in displacement reactions at a silicon atom which involve reagents of a smaller size is of theoretical interest for more exact comparison with steric effects in purely organic compounds Studies in this direction are now under way in this Laboratory.

Experimental

Trimethylsilylmethyltrichlorosilane (I).—Trimethylsilylmethylmagnesium chloride, 1 mole in 600 ml. of ether, was added to a stirred solution of silicon tetrachloride, 1.1 mole, in 900 ml. of ether and the reaction mixture was heated to reflux on the steam-bath for 12 hours. Filtering of the magnesium chloride and ether extraction followed by fractionation gave compound I, 130.5 g., 0.59 mole, b.p. 167° at 738 mm.

Anal. Calcd. for $C_4H_{11}Si_2Cl_3$: Si, 25.3; Cl, 48.1. Found: Si, 25.0; Cl, 47.7.

Di-(trimethylsilylmethyl)-dichlorosilane (II).—Trimethylsilylmethyllithium, 1 mole, in 200 ml. of pentane was prepared in 66% yield from chloromethyltrimethylsilane. After separation of the lithium chloride, the lithium compound was added to a solution of 85 g., 0.5 mole, of silicon tetrachloride dissolved in 100 ml. of pentane. The addition was carried out during a two-hour period and the reaction mixture was heated at reflux temperature for 12 hours. Removal of lithium chloride was followed by slow distillation of the pentane solvent until the flask contents attained a temperature of 80°. The reaction mixture was heated at this temperature for four hours and then 20 g. of excess silicon tetrachloride was added to ensure complete reaction of the lithium compound. After filtering to remove lithium chloride, fractionation gave 55.8 g., 0.204 mole, of compound II, b.p. 92° at 9 mm., 40% yield.

Anal. Calcd. for $C_8H_{22}Si_3Cl_2$: Si, 30.8; Cl, 26.0. Found: Si, 30.8; Cl, 26.1.

Tri-(trimethylsilylmethyl)-chlorosilane (III).—Silicon tetrachloride, 34 g., 0.2 mole, was added during one hour to a solution of trimethylsilylmethyllithium, 1 mole, in 1000 ml. of pentane and the reaction mixture was refluxed for 72 hours. After cooling, the contents of the flask was poured onto 260 g. of cracked ice. The layers were separated, the water layer extracted with 100 ml. of pentane, and the pentane solution of the product was dried over anhydrous potassium carbonate. Fractionation gave 32.6 g., 0.1 mole, of compound III, b.p. 112° at 4 mm., m.p. 13–14°, $n^{20}{}_D$ 1.4600, d^{20} 0.8900, MR_D 99.7 (calcd. 100.5), a 50% yield based on the silicon tetrachloride used.

Anal. Calcd. for $C_{12}H_{33}Si_4Cl$: Si, 34.5; Cl, 10.9; mol. wt., 325. Found: Si, 34.7; Cl, 11.2; mol. wt. in benzene, 316.

Compound III is fairly unreactive toward water as indicated by the above preparation in which the reaction product was poured onto ice. However, this is probably largely a matter of insolubility in water due to the high molecular weight. While compound III gave no apparent reaction with aqueous silver nitrate, treatment with alcoholic silver nitrate gave an immediate and copious precipitate of silver chloride. In fact, Volhard titration of an ethanol solution of compound III gave quantitative reaction of the silicon–chlorine bond.

Tetra-(trimethylsilylmethyl)-silane (IV).—To a refluxing solution of trimethylsilylmethyllithium, 1.2 moles, in 600 ml. of pentane there was added during one hour 26 g., 0.175 mole, of silicon tetrachloride. The reaction mixture was refluxed for 12 hours, followed by a slow distillation of pentane from the reaction vessel until the temperature of the flask was 90°. A slow stream of nitrogen was then introduced into the flask (above the liquid level), and the solvent was distilled until the temperature reached 150°, where it was maintained for 12 hours. After cooling, the contents of the flask were poured onto 600 g. of cracked ice. Extraction with pentane and drying over anhydrous potassium carbonate were followed by fractionation to give 21.3 g., 0.06 mole, of compound IV, b.p. 154° at 23 mm., m.p. 28.5°, a 33% yield based on the silicon tetrachloride used.

Anal. Calcd. for $C_{16}H_{44}Si_5$: Si, 37.2; mol. wt., 376. Found: Si, 37.4; mol. wt. in benzene, 381.

Methyltrimethylsilylmethyldichlorosilane (V).—Trimethylsilylmethyllithium, 1.34 moles, in 800 ml. of pentane was added with stirring to a solution of methyltrichlorosilane, 1.34 moles, in 100 ml. of pentane during six hours, and the reaction mixture was stirred for an additional 12 hours without external heating. After removal of the lithium chloride, fractionation gave compound V, 68 g., 0.34 mole, b.p. 63° at 20 mm., 25% yield, and methyldi-(trimethylsilylmethyl)-chlorosilane, 64 g., 0.26 mole, b.p. 110° at 20 mm., 20% yield.

Anal. Calcd. for $C_5H_{14}Si_2Cl_2$: Si, 27.9; Cl, 35.2. Found: Si, 28.0; Cl, 35.1.

Anal. Calcd. for $C_9H_{25}Si_3Cl$: Si, 33.2; Cl, 14.0. Found: Si, 33.2; Cl, 13.9.

Di-(trimethylsilylmethyl)-silanediol (VII).—Compound II, 22 g., dissolved in 200 ml. of ether was added during five minutes with stirring to 110 ml. of 1.5 *N* sodium hydroxide while cooling the reaction mixture in an ice-bath. Immediately after completion of the addition, the water layer was separated from the product-containing ether layer and then extracted for additional product with three 50-ml. portions of ether. The ether solution was dried over anhydrous potassium carbonate for 15 minutes and evaporated to a volume of 50 ml. by heating on the steam-bath. Pentane, 100 ml., was then added and the volume again taken to 50 ml. Upon cooling, white, needle-like crystals formed. After drying under an infrared lamp, 17.3 g. of diol, 91% yield, m.p. 89–90°, was obtained. Recrystallization from ethanol gave m.p. 92°.

Anal. Calcd. for $C_8H_{24}Si_3O_2$: Si, 35.5. Found: Si, 36.1.

Compound VII was further characterized as a diol by an active hydrogen determination using lithium aluminum hydride in *n*-butyl ether. This procedure gave an equivalent weight of 121 (calcd. 118.5).

Some Properties of Compound VII.—A 13.1-g. sample of the diol was heated for 16 hours with 200 ml. of boiling benzene containing 0.5 g. of iodine and the water formed, 0.11 ml. (calcd. 1.00 ml.), was measured in a Stark–Dean water trap. Refluxing a 5.25-g. sample with 250 ml. of xylene containing 0.5 g. of iodine and 0.5 g. of β-naphthalenesulfonic acid gave 0.38 ml. of water (calcd. 0.40 ml.) after 16 hours.

In contrast to the more ordinary di-*n*-alkylsilanediols, *e.g.*, diethylsilanediol, whose heat sensitivity required a special procedure for melting point determinations involving preheating of the melting point bath to 75° and then raising the temperature at the rate of 5° per minute,[6] compound VII gave reproducible melting points by using an ordinary procedure employing a conventional melting point block and raising the temperature at the rate of 2° per minute. Thus, compound VII is somewhat more heat stable than diethylsilanediol but far less stable than di-*t*-butylsilanediol which distils without decomposition at 210°. Compound VII gave extensive condensation when held at 150° for several hours in a melting point capillary.

Reaction of Compound II with Liquid Ammonia.—Liquid ammonia, 150 g., was placed in a flask cooled in a Dry Ice–methanol-bath, and a solution of 57 g., 0.24 mole, of compound II in 200 ml. of dry pentane was added slowly over a two-hour period. After 12 hours of stirring and slow evaporation of the excess ammonia, the ammonium chloride, 23 g. (calcd. 23 g.), was separated by successive decantations and washings. Fractionation under vacuum gave no monomeric diaminosilane; the product boiled over a wide range, 92° at 10 mm., to 208° at 1 mm., and no constant-boiling material was obtained.

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The Preparation of Amides of Arylphosphonic Acids. I. Diamides of Primary Aromatic and Heterocyclic Amines[1]

BY G. O. DOAK AND LEON D. FREEDMAN

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p-Nitrophenylphosphonic dichloride was readily prepared by the action of phosphorus pentachloride on the appropriate acid. Condensation of this acid chloride with primary aromatic or heterocyclic amines gave a series of *p*-nitrophenylphosphonic diamides. Two different condensation procedures are described. The nitro-substituted amides were reduced with Raney nickel to the corresponding amino compounds.

There is considerable evidence that *p*-aminophenylphosphonic acid (phosphanilic acid) possesses chemotherapeutic properties similar to the sulfa drugs and acts on bacteria by antagonizing *p*-aminobenzoic acid.[2] Since conversion of sulfanilic acid to an amide greatly enhances the activity of the parent compound, particularly when the amide group is suitably substituted, it seemed a matter of considerable interest to find out whether amides of phosphanilic acid comprise a class of potentially useful antibacterial agents.

Only one amide of phosphanilic acid has been reported in the literature. Limaye and Bhide prepared *p*-aminophenylphosphonic diamide (phosphanilamide)[3] in small yield by heating *p*-bromophenylphosphonic diamide with aqueous ammonia in the presence of cuprous oxide. They were unable, however, to extend this synthesis to the preparation of the phosphorus analog of sulfathiazole.

Since a satisfactory method for the preparation of *p*-nitrophenylphosphonic acid has recently been described,[4] we decided to use this compound as an intermediate in the preparation of a series of amides of phosphanilic acid. The following reaction sequence was employed

$$p\text{-}O_2NC_6H_4PO_3H_2 + 2PCl_5 \longrightarrow p\text{-}O_2NC_6H_4POCl_2 + 2POCl_3 + 2HCl \quad (1)$$

$$p\text{-}O_2NC_6H_4POCl_2 + 4RNH_2 \longrightarrow p\text{-}O_2NC_6H_4PO(NHR)_2 + 2RNH_3Cl \quad (2)$$

$$p\text{-}O_2NC_6H_4PO(NHR)_2 + 3H_2 \xrightarrow{Ni} p\text{-}NH_2C_6H_4PO(NHR)_2 + 2H_2O \quad (3)$$

p-Nitrophenylphosphonic dichloride was prepared without difficulty according to equation 1. Two general procedures were then investigated for the preparation of the nitro-substituted amides from this acid chloride. Procedure 1, which was similar to a method used by Buchner and Lockhart,[5] consisted of refluxing one mole of *p*-nitrophenylphosphonic dichloride with four moles of amine in an organic solvent and isolating the crude amide from the reaction mixture. The majority of the amides were insoluble in the reaction solvent and precipitated from solution together with the amine hydrochloride. In those cases in which the amide was soluble in the reaction solvent, the amine salt was removed by filtration and the crude amide obtained by evaporating the filtrate. Procedure 1 is probably more generally applicable than procedure 2 and gives higher yields and more easily purified materials; furthermore, if the required amine is scarce or expensive, the condensation can be performed with one mole of the acid chloride, only two moles of amine and two (or more) moles of pyridine.

Procedure 2 (based on a method described by Michaelis[6]) consisted of melting together a mixture

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[1] The organophosphorus nomenclature in this paper is that proposed by the Organic Division's Advisory Committee on the Nomenclature of Organic Phosphorus Compounds; *cf. Chem. Eng. News*, **30**, 4515 (1952).

[2] R. Kuhn, E. F. Möller, G. Wendt and H. Beinert, *Ber.*, **75**, 711 (1942); J. D. Thayer, H. J. Magnuson and M. S. Gravett, *Antibiotics and Chemotherapy*, **3**, 256 (1953).

[3] N. S. Limaye and B. V. Bhide, *J. Indian Chem. Soc.*, **25**, 251 (1948). The purity of their preparation is open to question, since they were unable to obtain satisfactory analyses on this compound.

[4] (a) G. O. Doak and L. D. Freedman, THIS JOURNAL, **73**, 5658 (1951); (b) see also L. D. Freedman and G. O. Doak, *ibid.*, **75**, 4905 (1953).

[5] B. Buchner and L. B. Lockhart, Jr., *ibid.*, **73**, 755 (1951). Somewhat similar reaction conditions were used earlier by A. Michaelis, *cf.* ref. 6.

[6] A. Michaelis, *Ann.*, **293**, 193 (1896).