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The Addition of Silicon Hydrides to Olefinic Double Bonds. Part I. The Use of Phenylsilane, Diphenylsilane, Phenylmethylsilane, Amylsilane and Tribromosilane

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Phenylsilane adds to the double bond of certain compounds including octene-1, cyclohexene, allyl acetate, allyloxytrimethylsilane, diallyl ether, N-allylhexamethyldisilazane, *o*-allylphenyl acetate, methyl oleate, dicyclopentenyl acetate, acrolein diacetate, acrolein diethyl acetal, methyl 3-cyclohexenecarboxylate, *cis*-4-cyclohexene-1,2-dicarboxylic anhydride. Saturated phenylsilyl substituted derivatives were obtained. Diphenylsilane, methylphenylsilane and amylsilane reacted similarly. Tribromosilane adds very rapidly to the olefinic double bond in methyl *cis*-bicyclo[2.2.1]hept-5-ene-2-carboxylate. Some of the adducts obtained in this way were converted to derivatives or hydrolyzed to form a new type of polysiloxane structures possessing functionally substituted aliphatic groups attached to the silicon atoms.

Since about 1947, silicon hydrides such as trichlorosilane have been known to add to olefinic double bonds under the influence of peroxide catalysts,[1] azo catalysts,[2] platinum[3] and under the influence of elevated temperatures[4] (usually about 300°). Dichlorosilane also adds to olefins.[3b] Despite its usefulness, this reaction has not been applied to olefins containing an organofunctional substituent except for the addition of trichlorosilane to methyl undecylenate under the influence of acetyl peroxide[5] and of triphenylsilane to undecylenic acid using benzoyl peroxide as the catalyst.[6]

The use of tribromosilane was investigated briefly using a peroxide catalyst. Tribromosilane has been added to olefins under the influence of ultraviolet light[7] and also at elevated temperatures.[8] No examples were found of the use of tribromosilane with peroxide catalysts and no bromosilyl substituted organofunctional compounds have been prepared.

We found tribromosilane to be very reactive in the presence of *t*-butyl perbenzoate at about 100°, adding very rapidly with the liberation of much heat to methyl *cis*-bicyclo[2.2.1]hept-5-ene-2-carboxylate.

A large variety of organo-functional compounds may be synthesized in fair to excellent yields using silicon hydrides such as phenyl, diphenyl or amylsilane. Derivatives of alcohols, aldehydes, acids and amines may be obtained which possess silane hydrogen upon the silicon and may be hydrolyzed to form new families of polysiloxanes, having the typical reactivity of organic functional compounds and physical properties unknown to conventional polysiloxanes.

Examples to illustrate the scope of the synthetic procedure are presented in this paper. Later papers will describe the polymeric products and various derivatives in greater detail.

Experimental

The silanes used were prepared from chlorosilanes and lithium aluminum hydride.[9] Commercial amyltrichlorosilane, believed to be largely *n*-amyltrichlorosilane, was treated in a dibutyl ether with lithium aluminum hydride to form amylsilane in a yield of 80%, b.p. 79–80° at 744 mm., $d^{25}{}_4$ 0.6986, $n^{25}\text{D}$ 1.4022; R_D 0.3487, calcd. 0.3491. Phenylsilane was usually obtained in yields of about 70% having properties of b.p. 62° at 100 mm., $n^{25}\text{D}$ 1.5086, $d^{25}{}_4$ 0.8775; R_D 0.3400, calcd. 0.3405. Diphenylsilane was obtained in 78% yield, b.p. 95° at about 2 mm., $n^{25}\text{D}$ 1.5759, $d^{25}{}_4$ 0.996; R_D 0.3322, calcd. 0.3320.[10]

Tribromosilane was obtained by passing a mixture of equal volumes of hydrogen bromide and hydrogen through a column of granulated 98% Si containing 10% by weight of finely divided copper powder. The method is essentially that of Schumb and Young[11] except for the use of the copper powder. The presence of the copper caused the formation of tribromosilane to take place rapidly above about 210° and care was taken to prevent the heat of reaction from raising the temperature of the column above 250°. Tribromosilane was obtained in 60% yield based on the hydrogen bromide used with tetrabromosilane as the chief coproduct.

The olefinic compounds used were commercial materials or were prepared by commonly known methods.

Analyses.—Silane hydrogen (SiH) was determined by dissolving a sample of the silane in *n*-butyl alcohol in a small flask attached to a gas buret at room temperature. A small measured amount of sodium butoxide in butanol was added from an attached buret. This alkali catalyzed the evolution of hydrogen. The mixture was stirred with a magnetic stirrer until the volume of hydrogen produced remained constant at room temperature. The moles of hydrogen were calculated according to the gas laws. The procedure usually gave slightly low results on products which remained in solution and much lower results if a gel or precipitate formed.

Silicon determinations were made by digesting the sample with concentrated sulfuric acid, fuming the acid away slowly and igniting in a muffle furnace and weighing the residue as SiO_2. The specific refraction values were calculated using the data of Warrick.[12]

Addition of Phenylsilane to Octene-1.—Phenylsilane (32 g., 0.3 mole) was heated on a steam-bath to about 90°. Octene-1 (16 g., 0.14 mole) mixed with *t*-butyl perbenzoate (2.8 g., 0.014 mole) was then added dropwise through the top of the reflux condenser. A slow stream of nitrogen was passed through a glass tube extending about half-way down the reflux condenser. After the addition of reagents was complete, the mixture was heated under a nitrogen atmosphere overnight and distilled.

Phenylsilane (19 g., 0.18 mole) was recovered followed

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(1) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, THIS JOURNAL, **69**, 188 (1947); **70**, 484 (1948); R. H. Krieble, U. S. Patent 2,524,529, October 3, 1950; C. A. Burkhard and R. H. Krieble, *ibid.*, **69**, 2687 (1947).

(2) R. V. Lipscomb, U. S. Patent 2,570,462, October 9 (1951).

(3) (a) G. H. Wagner and C. O. Strother, British Patent 670,617, April 23, 1952; U. S. Patent 2,632,013, March 17, 1953; (b) G. H. Wagner, U. S. Patent 2,637,738, May 5 (1953).

(4) A. J. Barry, L. De Pree, J. W. Gilkey and D. E. Hook, *ibid.*, **69**, 2916 (1947); A. J. Barry, L. De Pree and D. E. Hook, British Patent 633,732, Dec. 19, 1949; Belgian Patent 473,674, July 31, 1947.

(5) R. Calas and N. Duffaut, *Oleagineux*, 8 (1953).

(6) G. N. Gadsby, *Research*, **3**, 338 (1950).

(7) A. V. Topchiev, N. S. Nametkin and O. P. Solovova, *Doklady Akad. Nauk. S.S.S.R.*, **86**, 965 (1952).

(8) A. J. Barry and D. E. Hook, U. S. Patent 2,626,271, January 20, 1953.

(9) W. H. Nebergall, THIS JOURNAL, **72**, 4702 (1950); A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947).

(10) R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 648 (1952), reported b.p. 75–76° at 0.5 mm., $n^{20}\text{D}$ 1.5795, $d^{22}{}_4$ 0.9969.

(11) W. C. Schumb and R. C. Young, *ibid.*, **52**, 1463 (1930).

(12) E. L. Warrick, *ibid.*, **68**, 2455 (1946).

by octylphenylsilane (23 g., 0.104 mole, 69% yield based on octene, 87% based on unrecovered phenylsilane). About 5 g. of higher boiling material also was obtained. The octylphenylsilane had the properties: b.p. about 161° at 21 mm., n^{25}_{D} 1.495, d^{25}_{4} 0.875; R_{D} 0.333, calcd. 0.334.

Anal. Calcd. for $C_8H_{17}C_6H_5SiH_2$: SiH, 0.915. Found: SiH, 0.930.

Under the same conditions phenylsilane (32 g., 0.3 mole), octene-1 (72 g., 0.6 mole) and *t*-butyl perbenzoate (5.6 g., 0.03 mole) yielded no recovered phenylsilane. Octene-1 was recovered (17 g., 0.15 mole) followed by a small impure fraction of octylphenylsilane, and dioctylphenylsilane (18 g., 0.06 mole), b.p. 200–223° at 22 mm., n^{25}_{D} 1.4885, d^{25}_{4} 0.8704; R_{D} 0.3314, calcd. 0.3319.

Anal. Calcd. for $(C_8H_{17})_2C_6H_4SiH$: Si, 8.43. Found: Si, 8.30.

A fraction of trioctylphenylsilane (18 g., 0.04 mole) was also obtained, b.p. about 210–253° at 2.4–4.5 mm., n^{25}_{D} 1.4880, d^{25}_{4} 0.8682; R_{D} 0.3319, calcd. 0.3308.

Anal. Calcd. for $(C_8H_{17})_3C_6H_5Si$: Si, 6.31; SiH, 0.00. Found: Si, 6.7; SiH, 0.0.

These products were not obtained pure, but their identity seems reasonably certain, thus illustrating that all three of the hydrogens bonded to silicon are capable of addition to an olefinic double bond. A semi-solid residue of about 10 g. remained.

Phenylsilane (8.2 g., 0.75 mole) and octene-1 (5.8 g., 0.052 mole) were sealed into a Pyrex pressure tube and heated to 200° for 18 hr. Distillation yielded a mixture of phenylsilane and octene-1 followed by octylphenylsilane (6 g., 53% yield), b.p. 159–161° at 25 mm., n^{25}_{D} 1.490, d^{25}_{4} 0.862; R_{D} 0.335, calcd. 0.334.

Anal. Calcd. for $(C_8H_{17})C_6H_5SiH_2$: Si, 12.73; SiH, 0.92. Found: Si, 12.63; SiH, 0.98.

Addition of Amylsilane to Octene-1.—Amylsilane (15 g., 0.148 mole) under a nitrogen atmosphere as described above was mixed with octene-1 (8.3 g., 0.074 mole) and *t*-butyl perbenzoate (1.4 g., 0.007 mole) and heated overnight at about 90°. On distillation, amyloctylsilane (9.5 g., 60% yield) was obtained, b.p. 140–141° at 25 mm., n^{25}_{D} 1.4400, d^{25}_{4} 0.7813; R_{D} 0.3373, calcd. 0.3378.

Anal. Calcd. for $(C_5H_{11})C_8H_{17}SiH_2$: SiH, 0.94. Found: SiH, 0.98.

About 5 g. of dark liquid residue was obtained.

Addition of Phenylsilane to Cyclohexene.—Phenylsilane (43 g., 0.4 mole), cyclohexene (16.5 g., 0.2 mole) and *t*-butyl perbenzoate (3.7 g. 0.02 mole) were mixed and heated under nitrogen overnight at about 90°. There was obtained in addition to recovered phenylsilane (33 g., 77%), cyclohexylphenylsilane (10 g., 0.052 mole), b.p. 135° at about 20 mm., n^{26}_{D} 1.5255, d^{25}_{4} 0.9356, R_{D} 0.3278, calcd. 0.3256.

Anal. Calcd. for $(C_6H_{11})C_6H_5SiH_2$: Si, 14.7; SiH, 1.05. Found: Si, 14.2, 14.1; SiH, 1.07.

Addition of Phenylsilane to Methyl Oleate.—Phenylsilane (32 g., 0.3 mole), methyl oleate (44.5 g., 0.15 mole) and *t*-butyl perbenzoate (2.8 g., 0.015 mole) were mixed and heated under nitrogen for 18 hr. at 90°. All volatile materials were removed up to 150° at 0.5 mm. The residue taken as $C_6H_5H_2SiC_{17}H_{34}COOMe$ weighed 61 g., 100% of theory and was a viscous light colored fluid, n^{25}_{D} 1.4896, d^{25}_{4} 0.940; R_{D} 0.307, calcd. 0.312.

Anal. Calcd. for $C_6H_5H_2SiC_{17}H_{34}COOMe$: Si, 6.93. Found: Si, 6.83.

Erratic results were obtained in efforts to determine the Si–H content, due presumably to the saponification of the COOMe group by the BuOH/NaOBu mixture used to determine the Si–H content and to the formation of an insoluble gelatinous precipitate.

Addition of Phenylsilane to *cis*-4-Cyclohexene-1,2-dicarboxylic Anhydride.—Phenylsilane (32.5 g., 0.3 mole), *cis*-4-cyclohexene-1,2-dicarboxylic anhydride (22.8 g., 0.15 mole) and *t*-butyl perbenzoate (2.8 g., 0.014 mole) and 20 g. of hexane were heated to reflux for four hours. The temperature of the mixture remained near 100°. All volatile material was then evaporated, finally up to 150° at less than 1 mm. pressure. This left a very viscous liquid weighing 38.5 g., 95% of theory for the desired addition product. This product had n^{25}_{D} 1.549, d^{25}_{4} 1.179; R_{D} 0.270, calcd. 0.2738.

Anal. Calcd. for $C_6H_5H_2Si(C_6H_9C_2O_3)$: Si, 10.82; SiH, 0.77; neut. equiv., 130. Found: Si, 10.1; SiH, 0.69; neut. equiv., 131.5, 135.

The neutral equivalents were obtained by dissolving a weighed amount of sample in known excess sodium hydroxide in dioxane, adding water to the point of incipient turbidity and back titrating the excess alkali. The use of alcohol as a solvent led to very high results presumably due to the formation of esters from the carboxylic anhydride.

Addition of Diphenylsilane to *cis*-4-Cyclohexene-1,2-dicarboxylic Anhydride.—Under the same conditions employed in the preceding experiment, diphenylsilane (55 g., 0.3 mole), the anhydride (22.8 g., 0.15 mole) and *t*-butyl perbenzoate (2.8 g., 0.015 mole) produced a glass-like solid product weighing 39 g., 95% of the theoretical weight for the addition product. This glassy product, having a neut. equiv. of 192, calcd. 168, was hydrolyzed in a mixture of acetone and water in an unsuccessful effort to get a crystalline product which could be purified as the dicarboxylic acid. However, another glassy product was obtained. This was treated with excess alkali in acetone to convert it to a silanol, acidified with hydrochloric acid and diluted with water to produce a solid which also was a glass. This product, thought to be either 4-(hydroxydiphenylsilyl)-cyclohexyl-1,2-dicarboxylic acid or the corresponding disiloxane, was dissolved in acetone, decolorized with Nuchar and obtained on evaporation of the acetone as a brittle colorless glass. Efforts to crystallize this from a variety of solvents led always to the same end. This glass softened at about 145° and melted at 155–165°. It was soluble in dilute aqueous alkali, acetone and alcohol, but insoluble in benzene, hexane and ether.

Anal. Calcd. for $(C_6H_5)_2HOSiC_6H_9(COOH)_2$: Si, 7.55; neut. equiv., 186. Found: Si, 7.97, 8.04; neut. equiv., 193, 196.

Addition of Phenylsilane to Methyl 3-Cyclohexenecarboxylate.—Phenylsilane (200 g., 1.86 moles), methyl 3-cyclohexenecarboxylate (130 g., 0.93 mole) and *t*-butyl perbenzoate (2 g., 0.01 mole) were heated to about 90° on a steam-bath. After 45 minutes, the temperature rose to 106° because of the exothermic addition reaction and slowly returned to about 90° where it remained overnight. Distillation yielded phenylsilane, followed by 151 g., 66% yield, of methyl phenylsilylcyclohexylcarboxylate, b.p. about 159° at 5 mm., n^{25}_{D} 1.5238, d^{25}_{4} 1.036; R_{D} 0.2952, calcd. 0.2958.

Anal. Calcd. for $C_6H_5H_2SiC_6H_{10}COOMe$: Si, 11.30. Found: Si, 11.5.

A portion of this product was dissolved in alcohol and made just alkaline with sodium hydroxide. Evolution of hydrogen took place vigorously. As soon as this subsided the mixture was diluted with dilute aqueous hydrochloric acid to precipitate a very viscous polysiloxane believed to be $[OC_6H_5SiC_6H_{10}COOMe]_x$.

Anal. Calcd. for $[OC_6H_5SiC_6H_{10}COOMe]_x$: Si, 10.34. Found: Si, 10.43, 10.49.

Addition of Phenylsilane to Diallyl Ether.—Phenylsilane (43 g., 0.4 mole), diallyl ether (14 g., 0.14 mole) and *t*-butyl perbenzoate (2.8 g., 0.014 mole) were heated together under nitrogen overnight at about 90° and distilled.

Phenylsilane (27 g., 63%) was recovered followed by phenylsilylpropyl allyl ether (18.5 g., 0.09 mole, 60% yield based on diallyl ether), b.p. 160–164° at 25 mm., n^{25}_{D} 1.4984, d^{25}_{4} 0.928; R_{D} 0.3161, calcd. for $C_6H_5H_2Si(C_3H_6)\text{-}OCH_2CH{=}CH_2$, 0.3189; calcd. for $C_6H_5HS\underbracket{iC_3H_6\text{–}OC_3H_6}$, 0.3096.

Anal. Calcd. for $C_6H_5H_2SiC_3H_6OC_3H_5$: SiH, 0.97. Calcd. for $C_6H_5HSi\underbracket{(CH_2)_3O(CH_2)_3}$: SiH, 0.48. Found: SiH, 0.90.

Addition of Phenylsilane to Allyl Acetate.—Phenylsilane (43 g., 0.4 mole), hexane (43 g.), allyl acetate (20 g., 0.2 mole) and *t*-butyl perbenzoate (0.2 g., 0.001 mole) were heated to reflux under nitrogen to a maximum flask temperature of 86° for about four hours and distilled. Hexane was recovered followed by phenylsilane (25.5 g., 59%). No allyl acetate was recovered. Phenylsilylpropyl acetate (32 g., 77% yield based on allyl acetate, 95% based on unrecovered phenylsilane) was obtained leaving a very viscous residue weighing 11 g. Phenylsilylpropyl acetate had the properties: b.p. 156° at 25 mm., n^{25}_{D} 1.5040–1.5050, d^{25}_{4} 1.00; R_{D} 0.296 to 0.297, calcd. 0.2960.

Anal. Calcd. for $C_6H_5H_2SiC_3H_6OAc$: SiH, 0.960. Found: SiH, 0.963.

A sample of phenylsilylpropyl acetate was hydrolyzed and saponified in methanolic alkali. After 0.5 hour at reflux the solution was diluted with water and the methanol was evaporated on a steam-bath. A viscous fluid separated from the alkaline water. The fluid was washed with water and dried to form a colorless viscous fluid believed to be a mixture of linear polysiloxane diols of the formula $HO-[C_6H_5Si(C_3H_6OH)O]_xH$.

Anal. Calcd. for $[C_6H_5Si(C_3H_6OH)O]_x$: Si, 15.6. Calcd. for $C_6H_5Si(C_3H_6OH)(OH)_2$: Si, 14.2. Found: Si, 14.9.

Addition of Methylphenylsilane to Allyl Acetate.—Methylphenylsilane (49 g., 0.4 mole), allyl acetate (20.4 g., 0.2 mole) and *t*-butyl perbenzoate (1.5 g., 0.008 mole) were heated together in a water-bath at 90°. After about 45 minutes the temperature of the mixture rose spontaneously to 125° and slowly returned to 90°. After 1.5 hr. distillation yielded methylphenylsilylpropyl acetate, b.p. about 158° at 25 mm., $n^{25}{}_D$ 1.5000, $d^{25}{}_4$ 0.9910; R_D 0.2968, calcd. 0.2968; yield of pure material was 19 g., 43%.

Anal. Calcd. for $C_6H_5MeHSiC_3H_6OAc$: SiH, 0.450. Found: SiH, 0.48.

A small sample of methylphenylsilylpropyl acetate was dissolved in methanol and kept slightly alkaline with dilute aqueous potassium hydroxide on a steam-bath for 1.5 hr. Most of the solvent was evaporated. The residue was filtered and freed of all volatile material leaving a sweet smelling liquid, disiloxane $O[C_6H_5MeSiC_3H_6OH]_2$.

Anal. Calcd. for $C_{20}H_{30}O_3Si_2$: Si, 14.98. Found: Si, 14.5, 14.9.

Addition of Phenylsilane to Allyloxytrimethylsilane.—Phenylsilane (32 g., 3 moles), allyloxytrimethylsilane (19.5 g., 0.15 mole) and *t*-butyl perbenzoate (2.8 g., 0.014 mole) were heated under nitrogen on a steam-bath at about 90°. After five minutes at 90° the temperature rose spontaneously to 122° and slowly subsided to 90° which was maintained 0.5 hour. Distillation recovered phenylsilane (17 g.) followed by (phenylsilylpropoxy)-trimethylsilane (24 g., 67% yield), b.p. about 130° at 25 mm., $n^{25}{}_D$ 1.4886, $d^{25}{}_4$ 0.921; R_D 0.313, calcd. 0.3129.

Anal. Calcd. for $C_6H_5SiH_2C_3H_6OSiMe_3$: SiH, 0.836. Found: SiH, 0.827.

A sample of this material was hydrolyzed in aqueous acetone solution containing one drop of hydrochloric acid. The solution was stirred about one hour and diluted with water to precipitate a viscous fluid phenylsilylpropyl alcohol. This was dissolved in ether and dried over sodium sulfate. Evaporation, finally under vacuum (less than 1 mm.) removed the ether and any hexamethyldisiloxane which was a co-product of the hydrolysis. The colorless product had the properties: $n^{25}{}_D$ 1.5277, $d^{25}{}_4$ 0.9835; R_D 0.3129, calcd. for $C_6H_5SiH_2C_3H_6OH$. 0.3138. Bubbles of gas formed continuously in the liquid presumably due to reaction of the hydroxyl group with the silane hydrogen.

In an effort to obtain a stable product, the alcohol was taken up in hexane and treated with α-naphthyl isocyanate on the steam-bath. A crystalline precipitate formed having a slightly yellow color. These crystals were recrystallized from hot hexane to a constant m.p. They were then pure white needle-like crystals, m.p. 77–78°; yield of α-naphthylurethan, 40% over-all.

Anal. Calcd. for $C_{20}H_{21}O_2NSi$: Si, 8.37. Found: Si, 8.44.

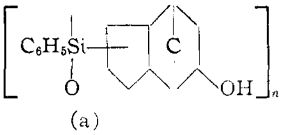
Addition of Phenylsilane to *o*-Allylphenyl Acetate.—Phenylsilane (54 g., 0.5 mole) was heated under N_2 to 100° as a mixture of *o*-allylphenyl acetate (44 g., 0.25 mole) and *t*-butyl perbenzoate (3.5 g., 0.025 mole) was added slowly. The temperature rose spontaneously to 108° and then was maintained between 90 and 105° for two hours. Distillation yielded 22 g. of phenylsilane followed by $o-(C_6H_5H_2SiC_3H_6)C_6H_4OAc$, *o*-(phenylsilylpropyl)-phenyl acetate (22 g., 50% of theory), b.p. 187–189° at 3.5 mm., $n^{25}{}_D$ 1.5472, $d^{25}{}_4$ 1.046; R_D 0.3032, calcd. 0.3025.

Anal. Calcd. for $o-(C_6H_5H_2SiC_3H_6)C_6H_4OAc$: SiH, 0.704. Found: SiH, 0.694.

Addition of Phenylsilane to Dicyclopentenyl Acetate.—Under the same conditions phenylsilane (194.4 g., 1.8 moles), dicyclopentyl acetate (174 g., 0.9 g.) and *t*-butyl perbenzoate (10 g., 0.05 mole) yielded a product boiling too high to be distilled (218 g., 81% of theory) $n^{25}{}_D$ 1.5412, $d^{25}{}_4$ 1.079; R_D 0.2913, calcd. 0.2903.

Anal. Calcd. for $C_{18}H_{24}O_2Si$: SiH, 0.663; Si, 9.34; sapn. equiv., 301. Found: SiH, 0.578, 0.592; Si, 9.22; sapn. equiv., 300.

A sample was saponified by refluxing in methanolic potassium hydroxide for several hours. The mixture was washed out with dilute acid to form a thermoplastic polysiloxane believed to be (a); yield 100%. *Anal.* Calcd.: Si, 10.06. Found: Si, 10.1.



(a)

Addition of Phenylsilane to Allylidene Diacetate.—Phenylsilane (32 g., 0.3 mole), allylidene diacetate (24 g., 0.15 mole) and *t*-butyl perbenzoate (2.8 g., 0.014 mole) were heated together under nitrogen at 90° overnight and distilled. Phenylsilane was recovered (16 g. 50%) followed by (15 g., 38% yield) phenylsilylpropyl-1,1-diacetate, b.p. 152° at about 2 mm., $n^{25}{}_D$ 1.4948, $d^{25}{}_4$ 1.07; R_D 0.273, calcd. 0.2726.

Anal. Calcd. for $C_6H_5H_2SiC_2H_4CH(OAc)_2$: Si, 10.53; SiH, 0.75. Found: Si, 10.43, 10.45; SiH, 0.62.

Addition of Phenylsilane to Acrolein Diethylacetal.—Phenylsilane (81 g., 0.75 mole), acrolein diethyl acetal (40 g., 0.306 mole) and *t*-butyl perbenzoate (3 g., 0.015 mole) were heated under nitrogen to 95–113° for 22 hr. and distilled. (1,1-Diethoxypropyl)-phenylsilane was obtained (39.5 g., 0.166 mole, 54.5% yield), b.p. 162° at 25 mm., $n^{25}{}_D$ 1.4872, $d^{25}{}_4$ 0.944, R_D 0.305, calcd. 0.305.

Anal. Calcd. for $(EtO)_2CHC_2H_4SiC_6H_5H_2$: SiH, 0.85; Si, 11.80. Found: SiH, 0.87; Si, 11.86.

Hydrolysis of this material (12 g., 0.05 mole) in dilute alcoholic alkali followed by dilute aqueous alcoholic hydrochloric acid produced a viscous fluid believed to be essentially $(HO)_2C_6H_5SiCH_2CH_2CHO$; yield 9.0 g., 91%.

Anal. Calcd. for $(HO)_2C_6H_5SiCH_2CH_2CHO$: Si, 14.2. Found: Si, 14.5.

Preparation of Allylaminotrimethylsilane.—Anhydrous allylamine and hexamethyldisilazane were mixed in a molar ratio of about 2/1 and heated to reflux overnight in the presence of a small amount of ammonium sulfate catalyst. Ammonia was produced at a fairly rapid rate for some time and then at a decreasing rate. The mixture was distilled and yielded allylaminotrimethylsilane, b.p. 109.5° at 731 mm., $n^{25}{}_D$ 1.4127, $d^{25}{}_4$ 0.768; R_D 0.3244, calcd. 0.3252.

Anal. Calcd. for $C_3H_5NHSiMe_3$: neut. equiv., 129.3. Found: neut. equiv., 135.

Preparation of N-Allylhexamethyldisilazane.—The allylaminotrimethylsilane was refluxed overnight in the presence of ammonium sulfate and distilled very slowly to yield allylamine followed by N-allylhexamethyldisilazane (77% yield over-all, based upon hexamethyldisilazane used above), b.p. 179° at 741 mm., $n^{25}{}_D$ 1.4363, $d^{25}{}_4$ 0.820; R_D 0.319, calcd. 0.322.

Anal. Calcd. for $(Me_3Si)_2NC_3H_5$: neut. equiv., 201. Found: neut. equiv., 198.

Addition of Phenylsilane to N-Allylhexamethyldisilazane.—Phenylsilane (43 g., 0.4 mole), N-allylhexamethyldisilazane (40 g., 9.2 mole) and *t*-butyl perbenzoate (3.7 g., 0.02 mole) were heated under nitrogen at 90° overnight. On distillation phenylsilane (25 g., 58%) was recovered followed by N-(phenylsilylpropyl)-hexamethyldisilazane (48.5 g., 0.14 mole, 70% yield), b.p. 184° at 25 mm., $n^{25}{}_D$ 1.4900, $d^{25}{}_4$ 0.896; R_D 0.324, calcd. 0.323.

Anal. Calcd. for $C_6H_5H_2SiC_3H_6N(SiMe_3)_2$: SiH, 0.647. Found: SiH, 0.656.

Preparation of Dimethoxyphenylsilylpropylamine.—To N-(phenylsilylpropyl)-hexamethyldisilazane (77.3 g., 0.25 mole) was added anhydrous methanol (80 g., 2.5 moles). Hydrogen was evolved with little evolution of heat. The mixture stood overnight before distillation. A reaction occurred according to the equation

$$C_6H_5H_2SiC_3H_6N(SiMe_3)_2 + 4MeOH \longrightarrow 2Me_3SiOMe + C_6H_5(MeO)_2SiC_3H_6NH_2 + 2H_2$$

Distillation removed the methoxytrimethylsilane and methanol followed by phenyl-(dimethoxy)-silylpropylamine (56 g., 0.25 mole, 100% yield), b.p. 160° at 25 mm., $n^{25}{}_D$ 1.5065, $d^{25}{}_4$ 1.042; R_D 0.2854, calcd. 0.2843.

Anal. Calcd. for $(MeO)_2C_6H_5SiC_3H_6NH_2$: neut. equiv., 225. Found: neut. equiv., 222.

Hydrolysis of this in alcohol yielded a viscous fluid polysiloxane. This was acidified with hydrochloric acid to form a water-soluble material. When dry, this was a brittle glassy material; yield 97%. The product is probably a mixture of linear polysiloxane diols.

Anal. Calcd. for $[OC_6H_5SiC_3H_6NH_2 \cdot HCl]_x$: Si, 13.1; Cl, 16.5. Calcd. for $H[OC_6H_5SiC_3H_6NH_2 \cdot HCl]_2OH$: Si, 12.5; Cl, 15.8. Found: Si, 12.8; Cl, 15.6.

Use of Other Olefinic Compounds.—Attempts to use certain other unsaturated compounds were unsuccessful for a variety of reasons. Acrylonitrile, methyl acrylate and styrene, under the influence of the peroxide catalyst polymerized rapidly. Each of these led to the formation of viscous polymers containing small amounts of combined silicon, presumably as chain-terminating silyl groups in the organic polymer.[13] Other compounds did not add phenylsilane under the conditions employed. The reasons for these failures are not clear in each case but they included allyl cyanide, (allylmercapto)-trimethylsilane, allyl chloride, allylamine and allyl alcohol. The last three of these seem to react with the Si-H bonds to produce complex products. The first two led to no reaction of any kind.

Addition of Tribromosilane to Methyl *cis*-Bicyclo[2.2.1]-hept-5-ene-2-carboxylate.—Tribromosilane (241 g., 0.9 mole) was heated to 90° under a nitrogen atmosphere as methyl *cis*-bicyclo[2.2.1]hept-5-ene-2-carboxylate (106.4 g., 0.7 mole) containing *t*-butyl perbenzoate (2.8 g., 0.014 mole) was added slowly over a period of 3 hours. Much heat was produced and care was needed to keep the reactants below 100°. The mixture was kept at 100° for 1 hour after the addition was complete. Xylene (125 ml.) was added and the mixture was distilled well into the xylene plateau to ensure the complete removal of all excess tribromosilane.

The neutralization and saponification equivalents of the residue which still contained most of the xylene was determined to be 191 and 139.5, respectively. The ratio 139.5/191 = 0.734. The theoretical value of this ratio if nothing acidic or saponifiable were present in the xylene except $Br_3SiC_7H_{10}COOMe$ is 0.75. The yield calculated upon this assumption is quantitative based upon the unsaturated ester used.

A portion (100 g.) of the xylene solution was distilled to yield 64 g., 82% of theory of the methyl tribromosilylbicyclo[2.2.1]heptylcarboxylate, b.p. 150–152° at about 2 mm., n^{25}_D 1.5430, d^{25}_4 1.829; R_D 0.1724, calcd. 0.1727.

Anal. Calcd. for $Br_3SiC_7H_{10}COOMe$: neut. equiv., 140.3. Found: neut. equiv., 144.

Twenty grams was hydrolyzed in 50 ml. of benzene by shaking with cold water. Two clear layers resulted. The benzene layer was separated, washed free of acid and evaporated to dryness leaving a putty-like product which was heated at 100° for 2.5 days to form a brittle light tan solid polymer.

Anal. Calcd. for $O_{3/2}SiC_7H_{10}COOMe$: Si, 13.7. Found: Si, 13.4.

This sample ground to a fine powder and heated an additional 16 hr. at 110° contained 13.9% Si.

Discussion

The addition reactions described here seem to have occurred in such a way that the silicon atom became attached to the terminal carbon atom when this was possible, in certain cases at least. The products obtained by addition to allyl acetate and to acrolein diethyl acetal, appeared to be essentially pure compounds having the structures $C_6H_5SiH_2(CH_2)_3OAc$, $C_6H_5H_2Si(CH_2)_2CH(OEt)_2$ and $C_6H_5MeHSi(CH_2)_3OAc$. Hydrolysis of these under either alkaline or acidic conditions gave no evidence of any appreciable cleavage of the Si–C bond. The hydrolysates were in each case fluids. Cleavage of Si–C bonds on hydrolysis would have produced cross-linked resins containing considerably higher silicon contents than those found.

In general, it is known that organic groups attached to siloxane structures are more readily cleaved under hydrolytic conditions than those attached to trialkylsilyl groups [for example, $\mathrm{Me_3SiCH_2}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{CH_3}$]. One would, therefore, expect the siloxanes to be readily cleaved if they possessed structures such as HOCHCH(Me)Si—O— or O=CHCH(Me)Si—O—, and resistant to cleavage if the structure were $HO(CH_2)_3SiO$— and O=CH-$(CH_2)_2$Si—O—. Compounds having oxygen, hydroxyl or other electronegative substituents in a position beta to a silicon atom are known to cleave very readily and $\mathrm{Me_3SiCH_2}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{CH_3}$ was cleaved by refluxing ethanol.[14] Structures having halogen[15] in the β-position and alcohols having the SiCCOH configuration also cleave readily. Cleavage reactions of β-oxygenated silicon compounds have been discussed.[16] β-Substituted amines of the type $SiCCNH_2$, are known to be resistant to cleavage.[17] The silylpropylamines prepared may have the structure of either $\mathrm{SiC{-}}\underset{\substack{| \\ \mathrm{C}}}{\mathrm{C}}\mathrm{NH_2}$ or $SiCCCNH_2$ or be a mixture of these. The criterion of ease of hydrolytic cleavage would not apply to these structures. No evidence of the presence of a mixture was observed during distillation and, by analogy with the products derived from allyl acetate, the $SiCCCNH_2$ structure seems most probable for the silylpropylamines.

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(13) Masao Monnage, Kunihiko Iino, Japanese Patent Publication No. 5645 (1954) showed that styrene in the presence of $HSiCl_3$ formed polymers of the type $Cl_3Si(CH_2CHC_6H_5)_xH$ in which the average value of x is a function of the molar ratio of trichlorosilane/styrene employed.

(14) C. R. Hauser and C. R. Hance, THIS JOURNAL, **74**, 5091 (1952).

(15) L. H. Sommer and F. C. Whitmore, *ibid.*, **68**, 485 (1946).

(16) F. C. Whitmore, L. H. Sommer, J. Gold and R. E. Van Strien, *bid.*, **69**, 1551 (1947).

(17) L. H. Sommer, N. S. Marans, G. M. Goldberg, J. Rockett and R. P. Pioch, J. Kerlin, *ibid.*, **73**, 882 (1951); **75**, 2932 (1953).