Distillation yielded $CF_3CFHCCl_2OCH_3$, b.p. 50° (94 mm.), $n^{20}{}_D$ 1.3717, $d^{20}{}_4$ 1.5096. *Anal.* Calcd. for $C_4H_4Cl_2F_4O$: C, 22.30; H, 1.86; Cl, 33.3. Found: C, 22.14; H, 1.82; Cl, 33.72.

**Preparation of $CF_2ClCFHCCl_2OCH_3$.**—This was obtained from $CF_2ClCF{=}CCl_2$ and methanolic base. $CF_2ClCFHCCl_2OCH_3$, b.p. 78–80° (91 mm.), $n^{20}{}_D$ 1.4120, $d^{20}{}_4$ 1.5510. *Anal.* Calcd. for $C_4H_4Cl_3F_3O$: C, 20.3; H, 1.73; Cl, 45.99. Found: C, 21; H, 1.8; Cl, 45.87.

**Preparation of $CF_3CHClCO_2C_2H_5$.**—About 5 g. of $CF_3CHClCF_2OC_2H_5$ was added cautiously to twice its volume of 90% sulfuric acid, according to the method of Young and Tarrant.[9] When the addition was completed, the reaction product was cooled to room temperature and poured over a small amount of ice. The oily layer which separated was washed with ice-water and dried over anhydrous calcium chloride. Its physical properties compared closely with those of $CF_3CHClCO_2C_2H_5$ given above ($n^{20}{}_D$ 1.3637, $d^{20}{}_4$ 1.3222).

**Preparation of $CF_3CHFCO_2C_2H_5$.**—Two methods were used to accomplish the hydrolysis of $CF_3CHFCF_2OC_2H_5$ to $CF_3CHFCO_2C_2H_5$. In the first, about 100 g. of 90% sulfuric acid was placed in a three-neck flask containing a stirrer, dropping funnel and a reflux condenser. About 19.6 g. of $CF_3CHFCF_2OC_2H_5$ was dropped into the flask at a rate slow enough to prevent the reaction from getting out of hand. The evolved hydrogen fluoride gas was led from the top of the reflux condenser to a trap. When the last of the ether had been added, the reaction mixture was hydrolyzed by adding an excess of ice-water with continued stirring and cooling of the flask with an ice-bath. The oily layer was then separated, washed twice with ice-water, dried over anhydrous sodium sulfate and fractionated. The fraction boiling 103–104° (629 mm.) was $CF_3CHFCO_2C_2H_5$, yield 10.0 g. (57.4% of theory), $n^{20}{}_D$ 1.3288, $d^{20}{}_4$ 1.2884.

The second method developed from an attempt to decompose the $CF_3CHFCF_2OC_2H_5$ to $CF_3CHFCOF$ and $C_2H_5F$ by heating in a sealed tube. The desired products were not obtained and the only product which could be identified was $CF_3CHFCO_2C_2H_5$.

It is suggested that the fluoroether reacted with the silicon dioxide present in the walls of the sealed tube to form the ester and silicon tetrafluoride.

$$2\,CF_3CHFCF_2OC_2H_5 + SiO_2 \longrightarrow 2\,CF_3CHFCO_2C_2H_5 + SiF_4$$

About 20 g. of $CF_3CHFCF_2OC_2H_5$ was placed in a thick-walled Pyrex tube and carefully sealed. The tube was heated at 150° for 12 hours, then permitted to cool to room temperature. The tube was chilled by immersion in a Dry Ice–acetone-bath and opened. A considerable amount of non-condensable gas escaped, assumed to be silicon tetrafluoride. The remaining liquid was distilled directly from the opened tube, washed several times with ice-water to remove acid present, dried over anhydrous sodium sulfate and fractionated. The fraction boiling 103–104° (629 mm.) was $CF_3CHFCO_2C_2H_5$. About 8 g. was obtained which is 46% yield. Tar formation in the sealed tube and handling losses accounted for the rest of the material.

**Preparation of $CF_3CHClCO_2C_2H_5$.**—About 10 g. of $CF_3CCl{=}CFOC_2H_5$ was hydrolyzed with 90% sulfuric acid in the same method used to hydrolyze the series of ethers $CF_3CCl{=}CClOR$ as described in the preparation of $CF_3CHClCO_2C_2H_5$ from $CF_3CHClCF_2OC_2H_5$ above. An ester, $CF_3CHClCO_2C_2H_5$, prepared elsewhere in this paper, was isolated, $n^{20}{}_D$ 1.3634, $d^{20}{}_4$ 1.3215.

**Preparation of $CF_3CHFCONH_2$.**—$CF_3CHFCO_2C_2H_5 + NH_4OH \rightarrow CF_3CHFCONH_2 + C_2H_5OH + H_2O$. About 2 g. of $CF_3CHFCO_2C_2H_5$ was treated with ammonium hydroxide and purified in the same manner as $CF_3CHClCO_2CH_3$ above. The amide isolated, $CF_3CHFCONH_2$, had a melting point of 57.0°. *Anal.* Calcd. for $C_3H_3F_4NO$: N, 9.65. Found: N, 9.51.

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BOULDER, COLORADO

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[CONTRIBUTION FROM THE DOW CORNING CORPORATION]

# The Synthesis and Polymerization of Organosilanes Containing Vinyl and Hydrogen Joined to the Same Silicon Atom

BY JAMES W. CURRY[1]

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Certain organosilanes containing vinyl and hydrogen joined to the same silicon atom were prepared and then polymerized to polysilethylenes at atmospheric pressure, using platinum, suspended on finely divided carbon, as the catalyst. In addition to the polymeric products, there were isolated in all cases lesser amounts of lower molecular weight materials, which were identified as the first authentic examples of the 1,4-disilacyclohexane ring system.

The continuing interest in organosilicon polymers, wherein the occurrence of alternating silicon atoms and difunctional organic groups[2] is a distinguishing structural feature of the polymer chain, led us to consider the possibility of synthesizing certain of these materials, namely, the polysilethylenes, in which the recurring silicon atoms are connected through ethylenic bridges. The general procedure, as visualized at the outset, involved the polymerization of compounds containing the vinyl group and the Si–H function within the same molecule through addition of Si–H to the carbon–carbon double bond of an adjacent molecule.

Dimethylvinylchlorosilane, diethylvinylchlorosilane, diphenylvinylchlorosilane and methylphenylvinylchlorosilane were used as starting materials for the preparation of the organosilicon monomers. The chloro compounds were reduced with lithium aluminum hydride[3] in the usual way to afford silanes containing vinyl and hydrogen joined to the same silicon atom.[4] The monomers thus prepared were heated at atmospheric pressure, in the absence of solvent, with a catalyst consisting of 0.06% by weight of platinum suspended on finely divided carbon.[5,6] Polymerization took place in all cases.

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[2] For a discussion of polymers of this general type, see E. G. Rochow, "An Introduction to the Chemistry of the Silicones," 2nd Edition, New York, N. Y., John Wiley and Sons, Inc., 1951, pp. 62–66.

(3) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **69**, 2692 (1947).

(4) S. Tannenbaum, S. Kaye and G. F. Lewenz, *ibid.*, **75**, 3753 (1953).

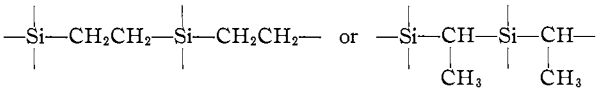
(5) G. H. Wagner (to Union Carbide and Carbon Corp.), U. S. Patent 2,637,738, May 5, 1953.

(6) Earlier, Wagner had reported the polymerization of vinyldichlorosilane under conditions of high temperature and pressure, using other types of platinum catalysts. The product was a liquid polymeric material containing no Si–H. See G. H. Wagner (to Union Carbide and Carbon Corp.), U. S. Patent 2,632,013, March 17, 1953.

The resulting polymers varied considerably in viscosity according to the nature of the R groups on the silicon atom. Those in which both groups were alkyl were rather mobile, fluid substances, but the introduction of phenyl groups resulted in materials which were considerably more viscous. The organosilicon polymer containing two phenyl groups attached to each silicon was, in fact, a brittle, glassy solid at room temperature, although it would flow readily when heated to *ca.* 150°. Diphenylsiloxane polymers exhibit similar viscosity–temperature behavior.[7]

It has been observed repeatedly that dimethyl substituted organosilicon polymers containing difunctional organic groups in the polymer chain have higher viscosities at a given temperature than the corresponding polysiloxanes of comparable molecular weight.[8-10] The results of the present work further exemplify this general relationship. The average molecular weight of our polymer sample, by analysis of residual vinyl content, was found to be 1728. The viscosity at 25° was 1726 centistokes. By comparison, dimethylsilicone of approximately the same molecular size exhibits a viscosity of between 10 and 20 centistokes at the same temperature.[11]

The polymeric substances obtained were presumed to be of the polysilethylene type since, in reactions involving Si–H addition to a vinyl group, the silicon atom holding the hydrogen usually becomes attached to the terminal carbon atom of the unsaturated reactant.[12-16] Even so, the possibility that the polymer chain might consist of either one or both of the two possible isomeric forms, *i.e.*

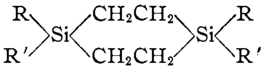


$$—\text{Si}—CH_2CH_2—\text{Si}—CH_2CH_2— \quad \text{or} \quad —\text{Si}—\underset{CH_3}{CH}—\text{Si}—\underset{CH_3}{CH}—$$

did not appear to us to be entirely ruled out prior to the acquisition of certain experimental evidence. Actually, infrared analysis indicated that all four polymers were constituted of the first of these forms to the exclusion of the other. Bands due to Si–$CH_2CH_2$–Si were found in all of the spectra, but in no instance was there observed any absorption which could be attributed to the isomeric arrangement.

Additional evidence in the form of an unequivocal synthesis provided added support for the polysilethylene structure in one case. When Sommer treated bis-(chloromethyl)-dimethylsilane with magnesium, he was able to isolate from the reaction mixture a polymeric material[17] which he identified as polydimethylsilethylene. Roberts and Dev[18] also obtained this same product, although inadvertently, when they treated bis-(iodomethyl)-dimethylsilane with magnesium. From a consideration of the mode of formation of such a polymer from a bis-(halomethyl)-silane, it is clear that the production of isomers is not possible. The structure of our product was proved conclusively, therefore, when it was shown that the infrared absorption spectrum of the material was identical in all important respects to that of the polydimethylsilethylene prepared by Sommer.

In addition to the polymers, there were isolated from the several reaction mixtures certain volatile by-products. While elemental analysis of these volatiles showed them to be of the same composition as the respective starting materials, molecular weight determinations gave values which were approximately double those found for the original monomers. The infrared spectra contained no absorption bands which could be attributed to $CH_2$=CH—Si or Si—H. Evidence for Si–$CH(CH_3)$–Si was also lacking in all cases. Although Si–$CH_2CH_2$–Si absorption was detected in only one instance, its apparent absence from the spectra of the other three compounds did not necessarily preclude the presence of this structural arrangement because the characteristic Si–$CH_2CH_2$–Si bands could be obscured if the structure were present in a symmetrical molecule.[19] On the basis of the foregoing evidence, together with the favorable molar refractivity data which were obtained, it is apparent that these compounds are cyclic dimers of the type



and as such they represent the first well-authenticated examples of the 1,4-disilacyclohexane ring system. It is not unlikely that Roberts and Dev[18] obtained 1,1,4,4-tetramethyl-1,4-disilacyclohexane among the distillable components from their reaction mixture, but they did not definitely establish that this substance was present.

## Experimental[20,21]

**Dimethylvinylchlorosilane.**—The dimethylvinylchlorosilane used was prepared by Weyenberg and exhibited the following physical properties[22]: b.p. 82–82.5°, $n^{25}_D$ 1.4141, $d^{25}_{25}$ 0.8744.

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[7] Reference 2, p. 102.

[8] L. H. Sommer, F. A. Mitch and G. M. Goldberg, THIS JOURNAL, **71**, 2746 (1949).

[9] E. L. Warrick, M. J. Hunter and A. J. Barry, *Ind. Eng. Chem.*, **44**, 2196 (1952).

[10] L. H. Sommer and G. R. Ansul, THIS JOURNAL, **77**, 2482 (1955).

[11] M. J. Hunter, E. L. Warrick, J. F. Hyde and C. C. Currie, *ibid.*, **68**, 2284 (1946).

[12] L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *ibid.*, **69**, 188 (1947).

[13] E. W. Pietrusza, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 484 (1948).

[14] A. J. Barry, L. DePree, J. W. Gilkey and D. E. Hook, *ibid.*, **69**, 2916 (1947).

[15] C. A. Burkhard and R. H. Krieble, *ibid.*, **69**, 2687 (1947).

[16] D. G. White and E. G. Rochow, *ibid.*, **76**, 3897 (1954). These investigators polymerized vinylsilane by subjecting it to ultraviolet radiation. On the basis of analysis of residual Si–H content, they reported that the product which resulted was probably the parent polymer, polysilethylene.

[17] L. H. Sommer, unpublished data. The polymer which Sommer isolated was a high molecular weight, waxy solid.

[18] J. D. Roberts and S. Dev, THIS JOURNAL, **73**, 1879 (1951).

[19] F. A. Miller, in Gilman's "Organic Chemistry. An Advanced Treatise," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 122.

[20] Calculated molar refractivities were computed from bond refractivity values listed in the following references: A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *Chemistry and Industry*, 358 (1950), and A. I. Vogel, W. T. Cresswell and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

[21] Cryoscopic molecular weight determinations for the dialkylvinylsilanes were carried out in benzene, and for the 1,4-disilacyclohexanes, in camphor.

[22] D. R. Weyenberg, Dow Corning Corporation, private communication.

**Diethylvinylchlorosilane.**—To a solution of 436.1 g. (2.70 moles) of redistilled vinyltrichlorosilane in 750 ml. of dry ether was added, with stirring, 2 l. of an ether solution containing 720.0 g. (5.40 moles) of ethylmagnesium bromide at a rate sufficient to maintain vigorous refluxing of the solvent. The addition required 2.25 hours, following which the reaction mixture was stirred under reflux for an additional 45 minutes, then allowed to stand overnight. The combined filtered reaction mixture and ether washings were distilled at atmospheric pressure to remove ether. Fractionation of the liquid residue afforded diethylvinylchlorosilane, b.p. 139–141°, $n^{25}_{D}$ 1.4373, $d^{25}_{4}$ 0.9096 (reported[23] b.p. 138° (738 mm.), $n^{20}_{D}$ 1.4392, $d^{20}$ 0.9061), yield 274.4 g. (68.4%).

**Diphenylvinylchlorosilane.**—This compound was synthesized by the Grignard reaction from phenylvinyldichlorosilane rather than from vinyltrichlorosilane because of the unfavorable product distribution which results when the latter chlorosilane is employed as the starting material.[24] The reaction was carried out in a manner similar to that described previously, using 288.5 g. (1.42 moles) of phenylvinyldichlorosilane in 2 l. of ether and 194.4 g. (1.42 moles) of phenylmagnesium chloride in 1 l. of ether. The reaction mixture was stirred under reflux for 20 hours following the addition of the Grignard solution, then worked up in the manner described above. There was obtained, on fractionation *in vacuo*, diphenylvinylchlorosilane, b.p. 105–105.5° (0.17–0.18 mm.) (from Weyenberg's data[22] 172–175° (20 mm.)), $n^{25}_{D}$ 1.5793, $d^{25}_{4}$ 1.1035, yield 165.2 g. (47.6%).

*Anal.* Calcd. for $C_{14}H_{13}ClSi$: C, 68.69; Si, 11.47; Cl, 14.48; $MR_D$, 73.85. Found: C, 68.7; Si, 11.78; Cl, 14.16; $MR_D$, 73.75.

**Methylphenylvinylchlorosilane.**—The synthesis of this material was carried out under the slightly modified conditions described for the preparation of diphenylvinylchlorosilane, using 200.5 g. (1.42 moles) of methylvinyldichlorosilane in 2 l. of ether and 194.4 g. (1.42 moles) of phenylmagnesium chloride in 1 l. of ether. The crude product was fractionated under reduced pressure to afford methylphenylvinylchlorosilane, b.p. 79–79.5° (3–4 mm.), $n^{25}_{D}$ 1.5197, $d^{25}_{4}$ 1.0340, yield 105.8 g. (40.8%).

*Anal.* Calcd. for $C_9H_{11}ClSi$: C, 59.16; Si, 15.37; Cl, 19.40; $MR_D$, 53.83. Found: C, 59.05; Si, 16.60; Cl, 18.82; $MR_D$, 53.70.

**Dimethylvinylsilane.**—To a stirred slurry of 25.0 g. (0.66 mole) of lithium aluminum hydride in 300 ml. of freshly redistilled dibutyl ether was added a solution of 316.5 g. (2.64 moles) of dimethylvinylchlorosilane in 150 ml. of the purified dibutyl ether, dropwise, over a period of 4.75 hours. The reaction mixture was then heated slightly with continued stirring for 18.5 hours, following which the product was distilled directly from the reaction mixture. The crude distillate was washed free of acid with cold water, dried over anhydrous sodium sulfate, then fractionated at atmospheric pressure. There was obtained dimethylvinylsilane, b.p. 36.7° (738 mm.), $n^{25}_{D}$ 1.3855, $d^{25}_{4}$ 0.6744, yield 78.6 g. (34.6%).

*Anal.* Calcd. for $C_4H_{10}Si$: C, 55.73; Si, 32.58; mol. wt., 86.2; $MR_D$, 29.98. Found: C, 55.45; Si, 32.67; mol. wt., 91.2; $MR_D$, 29.99.

The infrared spectrum showed $CH_2{=}CH{-}Si$ absorption bands at 6.27, 9.90 and 10.53 μ, and an Si–H band at 4.69 μ.

**Diethylvinylsilane.**—To a stirred slurry of 11.8 g. (0.31 mole) of lithium aluminum hydride in 100 ml. of dry ether was added a solution of 180.0 g. (1.21 moles) of diethylvinylchlorosilane in 300 ml. of dry ether over a period of 2 hours. The mixture was stirred under reflux for an additional 3.25 hours, then allowed to stand overnight. Water, 180 ml., was added dropwise to hydrolyze the inorganic halides. The aqueous phase was separated, and the ether layer was washed neutral with water and dried over anhydrous sodium sulfate. Following removal of ether by distillation, the liquid residue was fractionated at atmospheric pressure to afford diethylvinylsilane, b.p. 100.5° (744 mm.), $n^{25}_{D}$ 1.4186, $d^{25}_{4}$ 0.7354, yield 72.0 g. (52.1%).

*Anal.* Calcd. for $C_6H_{14}Si$: C, 63.07; Si, 24.58; mol. wt., 114; $MR_D$, 39.28. Found: C, 62.7; Si, 24.61; mol. wt., 135; $MR_D$, 39.20.

The infrared spectrum exhibited the following important absorption bands: $CH_2{=}CH{-}Si$, 6.29, 9.92, and 10.52 μ; Si–H, 4.73 μ.

**Diphenylvinylsilane.**—This compound was prepared under conditions similar to those described for diethylvinylsilane, using 5.8 g. (0.153 mole) of lithium aluminum hydride in 200 ml. of dry ether and 150.0 g. (0.613 mole) of diphenylvinylchlorosilane in 300 ml. of dry ether. The reaction mixture was stirred under reflux for 16.25 hours following the addition of the chlorosilane, then worked up as described previously. Vacuum fractionation gave the purified diphenylvinylsilane, b.p. 79.5–80.5° (0.015–0.02 mm.), $n^{25}_{D}$ 1.5768, $d^{25}_{4}$ 0.9979, yield 91.1 g. (70.7%).

*Anal.* Calcd. for $C_{14}H_{14}Si$: C, 79.93; H, 6.71; Si, 13.35; mol. wt., 210; $MR_D$, 69.78. Found: C, 79.95; H, 6.75; Si, 13.37; mol. wt., 160; $MR_D$, 69.84.

The infrared spectrum showed absorption bands at 6.31, 9.95 and 10.48 μ, characteristic of $CH_2{=}CH{-}Si$, and a band at 4.71 μ, characteristic of Si–H.

**Methylphenylvinylsilane.**—This material was synthesized under the slightly modified conditions described above for diphenylvinylsilane, starting from 4.2 g. (0.111 mole) of lithium aluminum hydride in 200 ml. of dry ether and 80.0 g. (0.438 mole) of methylphenylvinylchlorosilane in 300 ml. of dry ether. Fractionation of the crude product under reduced pressure gave methylphenylvinylsilane, b.p. 56–56.5° (6.5–8 mm.), $n^{25}_{D}$ 1.5115, $d^{25}_{4}$ 0.8912, yield 53.9 g. (83.1%).

*Anal.* Calcd. for $C_9H_{12}Si$: C, 72.90; H, 8.16; Si, 18.94; mol. wt., 148; $MR_D$, 49.89. Found: C, 72.5; H, 8.4; Si, 19.15; mol. wt., 163; $MR_D$, 49.88.

Bands at 6.26, 9.93 and 10.50 μ, denoting $CH_2{=}CH{-}Si$ absorption, were found in the infrared spectrum. Absorption due to Si–H was noted at 4.70 μ.

**Polydimethylsilethylene and 1,1,4,4-Tetramethyl-1,4-disilacyclohexane.**—A mixture of 29.8 g. (0.346 mole) of dimethylvinylsilane and 0.35 g. of 0.06% platinum on finely divided carbon was heated under reflux for a total of 4.5 hours. The polymerization proceeded slowly during the first 3.5 hours, then more rapidly in the final hour of the heating period. When the reaction temperature reached 199°, heating was discontinued. The reaction mixture was cooled and diluted with ether, and the catalyst was removed by filtration. The combined filtrate and ether washings were distilled at atmospheric pressure to a pot temperature of 130°. Removal of volatile reaction products was effected by heating to 190° under reduced pressure and, finally, by heating to 173.5° *in vacuo*. The volatiles amounted to 5.7 g. (19.1%). The residue was filtered to afford polydimethylsilethylene, $n^{25}_{D}$ 1.4883, viscosity (centistokes at 25°) 1726, yield 20.3 g. (68.2%).

*Anal.* Calcd. for $(C_4H_{10}Si)_n$: C, 55.73; H, 11.69; Si, 32.58. Found: C, 55.9; H, 11.5; Si, 32.56; vinyl, 1.565. The average molecular weight, calculated from the residual vinyl content, was 1728, and the degree of polymerization, 20.0.

Infrared analysis revealed the presence of Si–H absorption at 4.74 μ (weak). Bands were noted at 8.82 and 9.45 μ, and at 8.03 μ, characteristic of $Si{-}CH_2CH_2{-}Si$ and $CH_3{-}Si$ absorption, respectively.

The volatiles were fractionated at atmospheric pressure. There was obtained 1,1,4,4-tetramethyl-1,4-disilacyclohexane, b.p. 168–169° (744 mm.), $n^{25}_{D}$ 1.4531, $d^{25}_{4}$ 0.8277, yield 5.3 g. (17.8%).

*Anal.* Calcd. for $C_8H_{20}Si_2$: C, 55.73; H, 11.69; Si, 32.58; mol. wt., 172; $MR_D$, 56.27. Found: C, 56.0; H, 11.7; Si, 32.88; mol. wt., 180; $MR_D$, 56.32.

Infrared analysis indicated that the proposed structure was correct. The symmetry of the molecule appeared to prevent detection of the $Si{-}CH_2CH_2{-}Si$ bands, but no absorption due to residual $CH_2{=}CH{-}Si$ or Si–H was noted. There was no particular evidence for $Si{-}CH(CH_3){-}Si$. A band due to $CH_3{-}Si$ was found at 8.03 μ.

**Polydiethylsilethylene and 1,1,4,4-Tetraethyl-1,4-disilacyclohexane.**—The polymerization was effected under refluxing conditions similar to those described above, using 29.0 g. (0.257 mole) of diethylvinylsilane and 0.26 g. of the Wagner platinum-on-carbon catalyst. The total heating time was 1.33 hours. The reaction took place rather slowly

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[23] L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans and F. C. Whitmore, THIS JOURNAL, **76**, 1613 (1954).

[24] G. L. Constan and R. L. Przybyla, Dow Corning Corporation, unpublished data.

during the first 20 minutes, then proceeded at a progressively more rapid rate. External heating was discontinued when the temperature reached 190°, and the reaction mixture was cooled and worked up according to the procedure described above. Devolatilization was accomplished to 180° under reduced pressure, then to 175° *in vacuo*. In addition to the volatiles (7.9 g., 27.2%), there was obtained polydiethylsilethylene, $n^{25}\text{D}$ 1.4977, viscosity (centistokes at 25°) 378.6, yield 16.6 g. (57.3%).

*Anal.* Calcd. for $(C_6H_{14}Si)_n$: C, 63.07; H, 12.35; Si, 24.58. Found: C, 63.15; H, 12.8; Si, 25.04; vinyl, 3.59. The average molecular weight, calculated from the residual vinyl content, was 753, and the degree of polymerization, 6.59.

The presence of the polysilethylene structure was confirmed by infrared analysis. Bands due to $Si–CH_2CH_2–Si$ were found at 8.82 and 9.45 μ. There were $C_2H_5–Si$ bands at 6.86, 7.08 and 8.12 μ, and weak Si–H absorption appeared at 4.78 μ.

Fractionation of the volatile components afforded 1,1,4,4-tetraethyl-1,4-disilacyclohexane, b.p. 117–118° (6 mm.), $n^{25}\text{D}$ 1.4734, $d^{25}{}_4$ 0.8610, yield 5.7 g. (19.7%).

*Anal.* Calcd. for $C_{12}H_{28}Si_2$: C, 63.07; H, 12.35; Si, 24.58; mol. wt., 228; *MR*D, 74.86. Found: C, 62.7; H, 12.55; Si, 24.63; mol. wt., 210; *MR*D, 74.52.

Examination of the infrared spectrum revealed the presence of $Si–CH_2CH_2–Si$ absorption at 8.82 and 9.45 μ; bands due to $C_2H_5–Si$ were found at 8.11, 9.90 and 10.40 μ. There appeared to be no $CH_2{=}CH—Si$ or Si–H absorption.

**Polydiphenylsilethylene and 1,1,4,4-Tetraphenyl-1,4-disilacyclohexane.**—A mixture of 37.7 g. (0.179 mole) of diphenylvinylsilane and 0.18 g. of the Wagner catalyst was stirred accompanied by external heating for 4 hours. The monomer reacted slowly over the period of the first 3 hours, then more rapidly in the ensuing 30 minutes during which time the reaction temperature rose from 146.5 to 216°. The temperature then dropped to 183° during the final 30 minutes. The reaction mixture was worked up in the manner outlined previously. Devolatilization *in vacuo* to a pot temperature of 245° gave 1.8 g. (4.8%) of liquid volatiles. The residue solidified to a glass on cooling to room temperature. The material was taken up in toluene, filtered twice, then freed of toluene *in vacuo* at *ca.* 150° for 3 hours. There was obtained polydiphenylsilethylene, yield 23.2 g. (61.6%).

*Anal.* Calcd. for $(C_{14}H_{14}Si)_n$: C, 79.93; H, 6.71; Si, 13.35. Found: C, 79.55; H, 6.85; Si, 13.28.

The infrared spectrum showed the following absorption bands: $Si–CH_2CH_2–Si$, 8.85 and 9.50 μ; $C_6H_5–Si$, 7.01 and 9.00 μ; Si–H (weak), 4.73 μ.

Remaining on the filter from the filtration operations was a crude, crystalline solid amounting to 2.1 g. This material was twice resublimed *in vacuo* to afford 1,1,4,4-tetraphenyl-1,4-disilacyclohexane, m.p. 131–134.5° (uncor.), yield 0.55 g. (1.46%).

*Anal.* Calcd. for $C_{28}H_{28}Si_2$: Si, 13.35; mol. wt., 421. Found: Si, 13.05; mol. wt., 343.

Infrared analysis confirmed the proposed structure. The bands due to $Si–CH_2CH_2–Si$ were not apparent, but there was no evidence for $CH_2{=}CH—Si$ or Si–H, nor for $Si–CH(CH_3)–Si$. Bands at 7.00 and 8.98 μ indicated the presence of $C_6H_5–Si$.

Infrared data on the liquid volatiles showed these materials to be lower molecular weight, linear molecules.

**Polymethylphenylsilethylene and 1,4-Dimethyl-1,4-diphenyl-1,4-disilacyclohexane.**—A mixture of 30.5 g. (0.206 mole) of methylphenylvinylsilane and 0.21 g. of the Wagner catalyst was heated with stirring. After reaching 95°, the temperature rose to 255° during the following 3 minutes. The total heating period was 1 hour, by the end of which time the temperature had dropped to 164.5°. The reaction mixture was worked up in the usual way (devolatilization to 205° *in vacuo*) to yield 6.9 g. (22.6%) of volatiles. The polymeric residue was taken up in toluene and filtered twice to effect clarification. Toluene was then removed by heating *in vacuo* at *ca.* 150° for 3 hours to afford polymethylphenylsilethylene, $n^{25}\text{D}$ 1.5870, yield 18.8 g. (61.6%).

*Anal.* Calcd. for $(C_9H_{12}Si)_n$: C, 72.90; H, 8.16; Si, 18.94. Found: C, 71.8; H, 8.35; Si, 19.14.

Infrared analysis indicated the presence of the following bands: $Si–CH_2CH_2–Si$, 8.83 and 9.48 μ; $C_6H_5–Si$, 7.02 and 9.00 μ; $CH_3–Si$, 8.02 μ; Si–H (very weak), 4.75 μ.

The volatile portion of the polymerization mixture was fractionally distilled *in vacuo*. There was obtained 1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohexane (probably a mixture of the two possible isomers), b.p. 135–137° (0.26–0.275 mm.), $n^{25}\text{D}$ 1.5692, $d^{25}{}_4$ 1.0117, yield 6.0 g. (19.7%).

*Anal.* Calcd. for $C_{18}H_{24}Si_2$: C, 72.90; H, 8.16; Si, 18.94; mol. wt., 297; *MR*D, 96.08. Found: C, 71.3; H, 7.95; Si, 19.15; mol. wt., 262; *MR*D, 96.06.

Absorption bands characteristic of $CH_3–Si$ and $C_6H_5–Si$ were found to be present at 8.02 μ, and at 7.01, 9.75 and 10.02 μ, respectively, in the infrared spectrum.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# Some Tetraarylsilanes Containing Functional Groups

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A new method of introducing functional groups into tetraarylsilanes is presented. Triphenyl-(*p*-tolyl)-silane was brominated with N-bromosuccinimide to yield *p*-(triphenylsilyl)-benzyl bromide and *p*-(triphenylsilyl)-benzal bromide. The monobromination product was hydrolyzed to *p*-(triphenylsilyl)-benzyl alcohol and the alcohol was oxidized to *p*-(triphenylsilyl)-benzoic acid. The dibromination product was hydrolyzed to *p*-(triphenylsilyl)-benzaldehyde; treatment of this aldehyde with N-bromosuccinimide followed by hydrolysis gave *p*-(triphenylsilyl)-benzoic acid, a product also obtained by the chromic acid oxidation of triphenyl-(*p*-tolyl)-silane. Attempts to similarly brominate and oxidize tri-1-naphthyl-(*p*-tolyl)-silane were unsuccessful.

The introduction of functional groups to an aromatic ring of tetraphenylsilane has been achieved by the nitration of this compound.[1] This reaction, however, results in a mixture of isomers that are not easily separated. We are reporting a different and perhaps better method for the incorporation of such groupings, involving the lateral bromination of triphenyl-(*p*-tolyl)-silane using N-bromosuccinimide[2];

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[1] A. Polis, *Ber.*, **19**, 1016 (1886); F. S. Kipping and L. L. Lloyd, *J. Chem. Soc.*, **79**, 449 (1901); D. Vorlander, *Ber.*, **55**, 1900 (1922); F. S. Kipping and J. C. Blackburn, *J. Chem. Soc.*, 2200 (1932); F. S. Kipping and N. W. Cusa, *ibid.*, 1089 (1935).

[2] *p*-(Triphenylsilyl)-benzyl bromide was reported by H. Gilman, R. K. Ingham and R. D. Gorsich, WADC Technical Report 53-426, Part I, Wright Air Development Center, 1953, p. 91. M. Maienthal, M. Hellmann, C. P. Haber, L. A. Hymo, S. Carpenter and A. J. Carr, THIS JOURNAL, **76**, 6392 (1954), recently have reported the preparation of this compound by a similar procedure.