PENTAMETHYLDISILANE AND 1,1,2,2-TETRAMETHYLDISILANE AND THEIR ADDITION TO OLEFINS

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Research by Kumada[1-4] and MacDiarmid[5-8] and their co-workers has led to characterization of numerous polymethyldisilane derivatives. However, the compound 1,2-dimethyldisilane is the only hydride in this series whose chemistry has been described[5]. Recently, pentamethyldisilane[9] [$(CH_3)_5Si_2H$] and 1,1,2,2-tetramethyldisilane[10] [$(CH_3)_4Si_2H_2$] have been obtained in small amounts in reactions of other organosilicon systems. This paper reports the synthesis and characterization of $(CH_3)_5Si_2H$ and $(CH_3)_4Si_2H_2$, and a preliminary study of reactions which these hydrides undergo with olefins in the presence of various catalysts.

The two silanes were prepared by lithium aluminum hydride reduction of the corresponding chlorosilanes, which were obtained from hexamethyldisilane according to the method of Kumada and his co-workers. Both compounds are colorless liquids boiling below 100°, and showing infrared spectra consistent with the assigned structures.

The proton magnetic resonance spectra of the silanes, shown in Fig. 1, serve both to confirm the structures and to provide a theoretical problem of some difficulty and interest. The NMR spectrum of $(CH_3)_5Si_2H$ is normal, showing a singlet at 9.84 τ [$-Si(C\underline{H}_3)_3$], a doublet centered at 9.83 τ [$-Si(C\underline{H}_3)_2-$], and a septet centered at 6.22 τ ($Si-\underline{H}$). The coupling constant J between the dimethylsilyl protons and the silane proton has the value 4.7 cps and $J(^{29}Si-H)$ is 173 cps. The methyl proton resonance of $(CH_3)_4Si_2H_2$ also appears normal, consisting of a doublet centered at 9.85 τ and split by 4.7 cps., undoubtedly by coupling with the adjacent silane hydrogen. However, the silane hydrogen resonance pattern is not the simple septet found for the pentamethyl compound, but instead is a well-resolved pattern of nineteen lines (Fig. 1). The two silane hydrogens in $(CH_3)_4Si_2H_2$, though symmetry-equivalent, are magnetically non-equivalent[11], so that coupling between these two protons can influence the hyperfine splitting pattern. The observed resonance seems to consist of two overlapping septets further overlapped by a quintet (Fig. 1). The spin-coupling problem presented by this spectrum, of the type A_2X_{12}, is too complex for solution by manual methods by may yield to analysis by high-speed digital computer**.

The addition of $(CH_3)_5Si_2H$ to 1-octene in the presence of di-*tert*-butyl peroxide followed the expected course and led to a single product, *n*-octylpentamethyldisilane,

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** The problem is being investigated by Dr. JOHN BALDESCHWEILER at Harvard University. For a full discussion of the origin of complex spin coupling in molecules like $(CH_3)_4Si_2H_2$, see ref. 11.

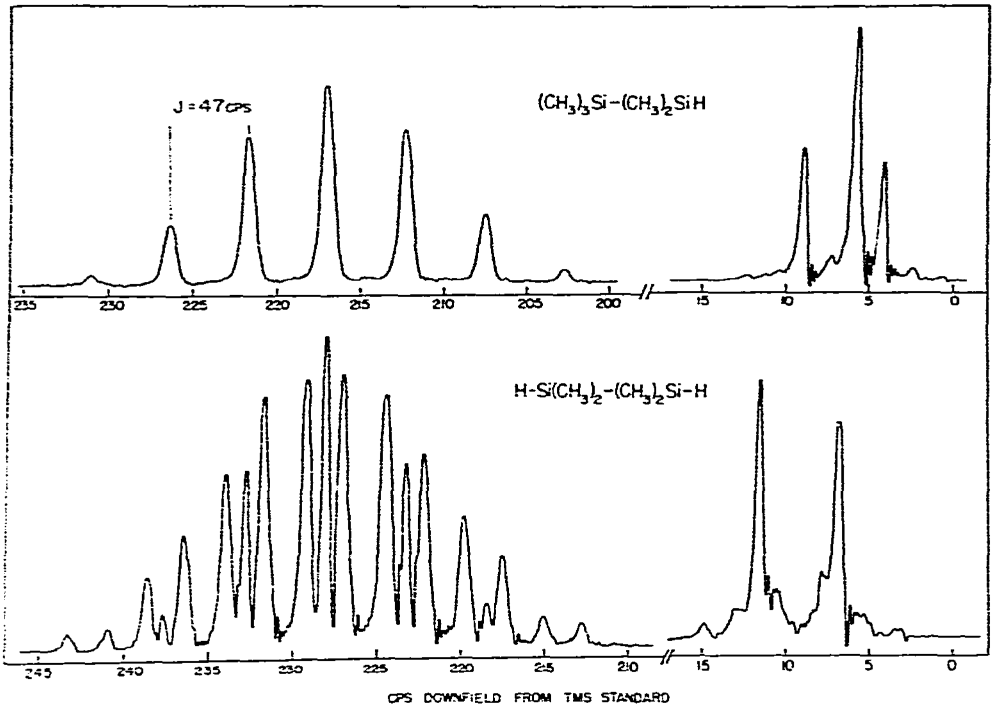


Fig. 1. Proton NMR spectra of pentamethyldisilane and 1,1,2,2-tetramethyldisilane.

in 78% yield. $(CH_3)_4Si_2H_2$ also reacted with 1-octene under the same conditions, yielding a mixture of products, including a compound believed to be 1,1,2,2-tetramethyl-2-*n*-octyldisilane, the product of normal terminal addition. A mixture of higher boiling products was also obtained, apparently consisting of telomers such as $C_{16}H_{33}Si(CH_3)_2Si(CH_3)_2H$. The normal terminal adduct probably arises via the free-radical chain process usually accepted for this addition reaction[12–15] and outlined as pathway (1) below. The telomers could arise from the reaction of the initially formed secondary radical with the olefin instead of with the disilanyl hydride[14, 15] (pathway 2):

Common to (1) and (2)

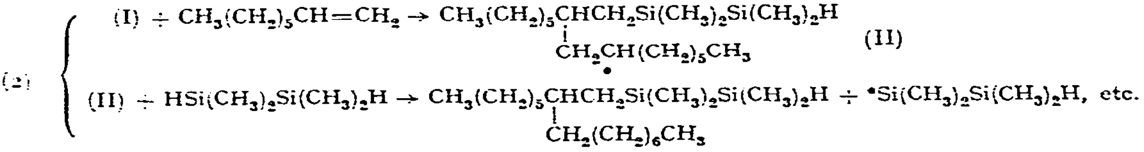
$$R^\bullet + HSi(CH_3)_2Si(CH_3)_2H \rightarrow RH + {}^\bullet Si(CH_3)_2Si(CH_3)_2H$$

$$CH_3(CH_2)_5CH{=}CH_2 + {}^\bullet Si(CH_3)_2Si(CH_3)_2H \rightarrow CH_3(CH_2)_5\overset{\bullet}{C}HCH_2Si(CH_3)_2Si(CH_3)_2H \qquad (I)$$

(1)

$$(I) + HSi(CH_3)_2Si(CH_3)_2H \rightarrow CH_3(CH_2)_7Si(CH_3)_2Si(CH_3)_2H + {}^\bullet Si(CH_3)_2Si(CH_3)_2H \quad \text{etc.}$$

(2)



$$(I) + CH_3(CH_2)_5CH{=}CH_2 \rightarrow CH_3(CH_2)_5\underset{\underset{\bullet}{CH_2CH}(CH_2)_5CH_3}{\underset{|}{C}}HCH_2Si(CH_3)_2Si(CH_3)_2H \qquad (II)$$

$$(II) + HSi(CH_3)_2Si(CH_3)_2H \rightarrow CH_3(CH_2)_5\underset{CH_2(CH_2)_6CH_3}{\underset{|}{C}}HCH_2Si(CH_3)_2Si(CH_3)_2H + {}^\bullet Si(CH_3)_2Si(CH_3)_2H, \text{ etc.}$$

The reaction of $(CH_3)_5Si_2H$ with 1-methylcyclohexene was also studied using peroxide catalysis. A single product was obtained in 80–90% yield whose properties were consistent with those for the expected adduct, (1-methylcyclohexyl)pentamethyldisilane. $(CH_3)_5Si_2H_2$ and 1-methylcyclohexene gave the same compound in fair yield upon irradiation with ultraviolet light, and in poor yield when heated together to 300° in the absence of a catalyst. The reaction appears to be highly stereoselective, for in each case the product gave a single peak on gas chromatography indicating that it consisted of a single isomer. However, the stereochemistry of the product was not established. Radical additions to olefins generally take place by stereospecific *trans* addition to give *cis* products[16,17], and so it might be argued by analogy that the product obtained has the *cis* arrangement. On the other hand, addition of trichlorosilane to 1-methylcyclohexene is only moderately stereoselective, giving 15 % of *trans*-(1-methylcyclohexyl)trichlorosilane along with 85 % of the *cis* isomer[18]. Possibly the greater steric requirement of the pentamethyldisilanyl group might lead to predominant formation of the less-hindered *trans* isomer of (1-methylcyclohexyl)pentamethyldisilane.

The addition of $(CH_3)_5Si_2H$ to 1-octene and to 1-methylcyclohexene was also attempted using chloroplatinic acid in isopropyl alcohol as a catalyst. However, this reaction does not follow a normal course. When the usual small amounts of catalyst are used[19,20], the starting materials are recovered unchanged. When large amounts of catalyst are present, the principal reaction is cleavage of the Si–Si bond in the disilane, leading to trimethylsilane and isopropoxysilicon compounds. Only traces of addition product could be isolated from either reaction; these were *n*-octylpentamethyldisilane and the same isomer of (1-methylcyclohexyl)pentamethyldisilane as obtained in the free-radical catalyzed reaction. The mechanism of the platinum-catalyzed addition reaction is poorly understood, but it seems probable that an intermediate with a Pt–Si bond is formed, with which the olefin may also be complexed[20,21]. This intermediate may lead principally to olefin addition in the case of monosilanes and principally to cleavage in the case of disilanes.

EXPERIMENTAL

Infrared spectra were determined on a Perkin-Elmer Model 237 Infracord grating spectrometer. NMR spectra were obtained using a Varian A60 spectrometer. A spinning-band distillation column (Nester and Faust Co., Semimicro) was used for all fractional distillations. Gas chromatographic separations and tests of purity were carried out on an Aerograph A700 chromatograph, using a 20′ column packed with 30 % DC-550 Silicone oil on 60–80 mesh firebrick. Analyses and molecular weight determinations were performed by Galbraith Laboratories, Knoxville, Tenn., U.S.A.

Starting materials

Hexamethyldisilane was obtained by treating a mixture of methylchlorodisilanes with methylmagnesium bromide. Conversion to chloropentamethyldisilane and to 1,1,2,2-tetramethyl-1,2-dichlorodisilane was effected by treating the hexamethyldisilane with concentrated sulfuric acid and ammonium chloride, according to the directions of Kumada and his co-workers[1].

Pentamethyldisilane

In a three-necked flask equipped with a reflux condenser, a mechanical stirrer and a pressure-equalizing dropping funnel was placed a slurry of lithium aluminum hydride (4.6 g, 0.122 mole) in anhydrous diethyl ether. Pentamethylchlorodisilane (40.8 g, 0.244 mole) was then added dropwise while the mixture was stirred. After addition of the chloride was complete the reaction mixture was stirred and refluxed for five hours. The mixture was then hydrolyzed by pouring into ice-water and the resulting two layers were separated. The water layer was washed once with ether and the ethereal extracts and washings were combined and dried over anhydrous sodium sulfate. The ether was distilled away and the residue was fractionated to give pentamethyldisilane (24.1 g, 72%), b.p. 98.5–98.7°, n_D^{25} 1.4217, d_{25}^{4} 0.7093. (Found: C, 45.60; H, 12.40; Si, 42.16; M.R. 47.40. $C_5H_{16}Si_2$ calcd.: C, 45.37; H, 12.19; Si, 42.44%; M.R. 46.96.) The infrared absorption spectrum, recorded on a thin film of liquid between two sodium chloride plates, showed the following bands (given in cm^{-1}): 2960 vs C–H str., 2900 m C–H str., 2800 sh, 2090 vs Si–H str., 1440 sh CH_3 def., 1410 m CH_3 def., 1305 w, 1248 vs CH_3 def., 885 vs Si–H def., 845 sh, 825 vs, 740 sh, 725 s, 690 s, 660 s. The bands from 845 to 660 cm^{-1} are due mainly to CH_3 rocking and Si–C stretching modes.

1,1,2,2-Tetramethyldisilane

In the apparatus described above 35.4 g (0.190 mole) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane was added dropwise to 7.2 g (0.190 mole) of lithium aluminum hydride in anhydrous diethyl ether. After complete addition of the dichloride the ethereal solution was refluxed for six hours and then the reaction mixture was hydrolyzed and worked up as described above to give 1,1,2,2-tetramethyldisilane (12.0 g, 54%) of b.p. 85.5–86°, n_D^{25} 1.4260, d_{25}^{4} 0.7076. (Found: C, 40.42; H, 11.82; Si, 47.20; M.R. 42.84. $C_4H_{14}Si_2$ calcd.: C, 40.60; H, 11.92; Si, 47.38%; M.R. 42.55.)

The infrared absorption spectrum, recorded on a thin film of liquid between two sodium chloride plates, showed the following bands (given in cm^{-1}): 2970 vs C–H str., 2910 m C–H str., 2810 sh, 2102 vs, Si–H str., 1425 sh CH_3 def., 1412 m CH_3 def., 1250 vs CH_3 def., 887 vs Si–H def., 855 vs, 830 vs, 745 s, 755 s, 703 s, 670 s, 640 s. The bands from 855 to 640 cm^{-1} are due mainly to CH_3 rocking and Si–C stretching modes.

Peroxide-catalyzed addition of pentamethyldisilane to 1-octene

A 125 ml flask was fitted with a magnetic stirring bar, a thermometer, a pressure equalizing dropping funnel, a gas inlet tube and a reflux condenser which was connected to a mercury valve. After sweeping the system with nitrogen, 14.2 g (0.107 mole) of pentamethyldisilane and 3.0 g (0.027 mole) of 1-octene were charged to the flask. In the dropping funnel was placed 1.0 g (0.006 mole) of di-*tert*-butyl peroxide dissolved in a further 3.0 g of 1-octene. The mixture in the reaction flask was heated to reflux (102°) and then the contents of the dropping funnel were added dropwise with stirring. After complete addition of the peroxide solution the reaction mixture was refluxed for 96 h during which time the reflux temperature increased to 107° and remained constant at this temperature for twenty-four hours. Fractionation of the mixture gave: (*a*) liquid of b.p. 74–87° (2.1 ml) which the infrared spectrum indicated to be a mixture of acetone, *tert*-butyl alcohol and pentamethyldisilane, (*b*) unreacted pentamethyldisilane (2.0 ml) and (*c*) an oily residue. Fractionation of the oily residue gave *n*-octylpentamethyldisilane (10.2 g, 78% yield based on the amount of olefin employed) of b.p. 93.5–94°/5 mm, d_{25}^{4} 0.7791, n_D^{25} 1.4486. The product was shown to be a single isomer by gas chromatography. (Found: C, 63.92; H, 13.28; Si, 23.14; mol. wt., 237. $C_{13}H_{32}Si_2$ calcd.: C, 63.84; H, 13.19; Si, 22.97%; mol. wt., 245.)

The NMR spectrum showed a sharp singlet at 9.97 τ [–Si($C\underline{H}_3$)$_2$–] and at 9.93 τ [–Si($C\underline{H}_3$)$_3$] as well as alkyl proton resonances at 9.09 and 8.70 τ.

Peroxide-catalyzed addition of 1,1,2,2-tetramethyldisilane to 1-octene

The reaction was carried out in the apparatus described above. After sweeping the system with nitrogen there was charged to the reaction flask 9.2 g (0.078 mole) of 1,1,2,2-tetramethyldisilane and 2.2 g (0.0195 mole) of 1-octene. From the additional funnel was added dropwise a mixture of 2.2 g of 1-octene and 0.6 g (0.0039 mole) of d-*tert*-butyl peroxide. After complete addition of the peroxide solution the reaction mixture was refluxed for 96 h during which time the temperature increased from 96° to 106°. Fractionation of the reaction mixture gave: (*a*) 4.7 ml of a mixture of b.p. 68–84° shown by infrared spectrum to be *tert*-butyl alcohol, acetone and unreacted 1,1,2,2-tetramethyldisilane and (*b*) high boiling oily residue. This residue was fractionated to give: (*a*) 1,1,2,2-tetramethyl-2-*n*-octyldisilane (3.5 g, 39% yield based on the amount of olefin used: of b.p. 80.5–81.5°/3.5 mm, n_D^{25} 1.4505, d_{25}^{4} 0.7819. (Found: C, 62.31; H, 13.10; Si, 24.52; mol. wt., 235. $C_{12}H_{30}Si_2$ calcd.: C, 62.51; H, 13.12; Si, 24.37%; mol. wt., 230.5.) The infrared spectrum showed very strong absorptions at 2095 cm^{-1} (Si–H stretch)[22] and 880 cm^{-1} (Si–H def.)[22]. Vapor phase chromatography (20 ft. column) showed that the compound was pure and not a mixture of isomers. (*b*) A mixture of telomers of b.p. 145–150°/5 mm which appeared to consist mainly of the compound $H[CH_3(CH_2)_5CHCH_2]_2Si(CH_3)_2Si(CH_3)_2H$, mol. wt., 352 (calcd.: 342.75). The infrared spectrum showed strong absorptions at 2098 and 883 cm^{-1}, indicating the presence of silanic hydrogen.

The NMR spectrum of 1,1,2,2-tetramethyl-2-*n*-octyldisilane showed two resonances in the methylsilane region, a singlet at 9.81 and a doublet at 9.90 τ, split by 4.6 cps. A five-line pattern is found with the proper position and intensity for a single silane hydrogen at 6.32 τ, also split by J = 4.6 cps. Other alkyl proton resonances are found centered at 8.70 and 9.08 τ.

Peroxide-catalyzed addition of pentamethyldisilane to 1-methylcyclohexene

Under the conditions described above, 22.7 g (0.171 mole) of pentamethyldisilane and 8.2 g (0.086 mole) of 1-methylcyclohexene were treated with 1.2 g (0.008 mole) of di-*tert*-butyl peroxide. After the reaction mixture had been heated to reflux for 96 h fractionation of the mixture gave: (*a*) a mixture of acetone, *tert*-butyl alcohol and pentamethyldisilane (2.2 ml), (*b*) unreacted pentamethyldisilane (10.0 ml), (*c*) a high boiling oily residue. Fractionation of the oily residue gave (1-methylcyclohexyl)pentamethyldisilane (16.5 g, 84% yield based on the amount of olefin used) of b.p. 83–84°/5 mm, n_D^{25} 1.4812, d_{25}^{4} 0.8449. Only a single peak was observed upon gas chromatography. (Found: C, 63.14; H, 12.25; Si, 24.69; mol. wt., 230. $C_{12}H_{28}Si_2$ calcd.: C, 63.07; H, 12.35; Si, 24.58%; mol. wt., 228.52.) The NMR spectrum showed a doublet at 9.97 τ [–Si($C\underline{H}_3$)$_2$–] and a singlet at 9.93 τ [–Si($C\underline{H}_3$)$_3$]. Sharp peaks are also found at 9.09 and 8.97 τ, along with a cluster centering at 8.53 τ, attributable to protons of the methylcyclohexyl moiety.

Photoaddition of pentamethyldisilane to 1-methylcyclohexene

A 60 ml quartz flask which was attached to a reflux condenser was charged with 7.8 g (0.059 mole) of pentamethyldisilane and 5.7 g (0.059 mole) of 1-methylcyclohexene. The flask was then irradiated by means of a Hanovia low pressure mercury lamp for a period of 67 h. The heat from the lamp caused the material in the flask to reflux and at the end of this time the reaction mixture was yellow. Distillation gave: (*a*) a mixture of unreacted pentamethyldisilane and 1-methylcyclohexene of b.p. 92–106° (4.0 ml) and (*b*) an oily residue. Fractionation of the oily residue gave (1-methylcyclohexyl)pentamethyldisilane (5.9 g, 44 % yield, based on the amount of olefin used) of b.p. 85.5–86°/5 mm, n_D^{25} 1.4812. The infrared spectrum of this material was identical to that of (1-methylcyclohexyl)pentamethyldisilane obtained in the peroxide-catalyzed reaction.

Thermal reaction of pentamethyldisilane with 1-methylcyclohexene

A thick-walled pyrex tube was loaded with 9.9 g (0.075 mole) of pentamethyldisilane and 7.2 g (0.075 mole) of 1-methylcyclohexene. The tube was heated at 300° for 48 h in a hydrogenation bomb. The tube was then opened and the contents were fractionated to give: (*a*) a mixture of unreacted pentamethyldisilane and 1-methylcyclohexene of b.p. 90–106° (19.0 ml), and (*b*) higher boiling oily residue (4.1 ml). This oil was gas chromatographed and found to contain pentamethyldisilane, 1-methylcyclohexene and another material which was shown by infrared spectrum to be (1-methylcyclohexyl)pentamethyldisilane.

Platinum-catalyzed reaction of pentamethyldisilane with 1-methylcyclohexene

A 125 ml flask was equipped with a magnetic stirring bar, a gas inlet tube, a pressure equalizing dropping funnel, a thermometer and a reflux condenser to which was attached a —78° trap. The entire system was swept with nitrogen and 11.0 g (0.083 mole) of pentamethyldisilane and 2.4 g (0.025 mole) of 1-methylcyclohexene were charged to the reaction flask and stirred vigorously. A mixture of 0.0398 g of chloroplatinic acid (7.7×10^{-5} g-atom of platinum) dissolved in 4.0 ml of isopropyl alcohol and 2.4 g of 1-methylcyclohexene was added dropwise. An exothermic reaction commenced; the mixture in the flask turned dark and gas was evolved. After addition was complete the mixture was stirred and refluxed for 96 h. At the end of this time there was collected in the —78° trap 2.5 ml of trimethylsilane [infrared spectrum in vapor phase identical to $(CH_3)_3SiH$][24]. The material in the reaction flask was fractionated to give: (*a*) Dimethylisopropoxysilane, $H(CH_3)_2SiOCH(CH_3)_2$, 1.8 ml, b.p. 68–70°, n_D^{25} 1.2700. (Found: C, 49.63; H, 11.68; Si, 25.28; O by difference, 13.41. $C_5H_{14}SiO$ calcd.: C, 50.78; H, 11.93; Si, 23.75; O, 13.53 %.) The infrared spectrum showed a Si–H stretch at 2110 cm^{-1}, and $SiOCH(CH_3)_2$ vibrations[22] at 1130 cm^{-1} and 1035 cm^{-1}. (*b*) A mixture of isopropanol and pentamethyldisilane (1.5 ml) of b.p. 80–95°. (*c*) Unreacted pentamethyldisilane (5.0 ml) of b.p. 95–100°. (*d*) A mixture of pentamethyldisilane and 1-methylcyclohexene (8.0 ml) of b.p. 101–106°. (*e*) A black oily residue (3.0 ml). This oily residue was separated into two components by gas chromatography. The component with low retention time, which constituted 67 % of the mixture, appeared to be an organosilicon isopropoxy compound. Elemental analysis indicated the empirical formula $C_{11}H_{24}SiO$. The infrared spectrum showed $SiOCH(CH_3)_2$ vibrations at 1130 cm^{-1} and 1035 cm^{-1}. The component with larger retention time constituted 33 % of the mixture and was found to be (1-methylcyclohexyl)pentamethyldisilane, n_D^{25} 1.4805, infrared spectrum identical to that of (1-methylcyclohexyl)pentamethyldisilane prepared previously by other methods.

Platinum-catalyzed reaction of pentamethyldisilane with 1-octene

The apparatus was the same as that employed above except that the —78° trap was omitted. After sweeping the system with dry nitrogen a solution of 0.0093 g of chloroplatinic acid (1.8×10^{-5} g-atom of platinum) dissolved in 1.0 ml of isopropyl alcohol and 3.2 g (0.029 mole) of 1-octene were charged to the reaction flask. Then dropwise from the addition funnel was added a mixture of 11.0 g (0.083 mole) of pentamethyldisilane and 3.2 g of 1-octene. An immediate reaction occurred as evidenced by volatile material [$(CH_3)_3SiH$] bubbling out the mercury valve, an increase in temperature in the reaction flask and the reaction mixture turning dark in color. After addition was complete the reaction mixture was refluxed and stirred for 96 h. Fractionation of the reaction mixture gave: (*a*) 1.0 ml of liquid of b.p. 70–90°, (*b*) 10.2 ml of unreacted pentamethyldisilane of b.p. 90–98.5°, (*c*) 2.2 ml of a mixture of pentamethyldisilane and 1-octene of b.p. 100–120°, (*d*) 5.5 ml of unreacted 1-octene of b.p. 120–120.5° and (*e*) 4.5 ml of an oily high boiling residue. From the amount of 1-octene collected it was calculated that for approximately every 0.015 mole of olefin to react 1.8×10^{-5} g-atom of platinum were required. The unreacted materials which were collected above were again charged to the reaction flask and a solution of 0.0254 g of chloroplatinic acid (4.9×10^{-5} g-atom of platinum) dissolved in 2.0 ml of isopropyl alcohol were dropped in from the addition funnel. Again a reaction occurred as above and after complete addition of the platinum solution the reaction mixture was stirred and refluxed for 30 h and then fractionated to give: (*a*) 2.0 ml of liquid of b.p. 65–90°, (*b*) 5.8 ml of unreacted pentamethyldisilane of b.p. 90–98.5°, (*c*) 5.2 ml of unreacted oily residues which were combined and separated by gas chromatography into two components. The lower boiling component (36 % of the mixture) appeared from its infrared spectrum to be an isopropoxysilicon compound (Si–O bands at 1130 and 1035 cm^{-1}). The compound with longer retention time (64 %) was found to be *n*-octylpentamethyldisilane (n_D^{25} 1.4482, infrared spectrum identical to *n*-octylpentamethyldisilane prepared in the peroxide-catalyzed addition of pentamethyldisilane to 1-octene).

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SUMMARY

The compounds pentamethyldisilane and 1,1,2,2-tetramethyldisilane have been prepared and characterized. Pentamethyldisilane adds to 1-octene and methylcylohexene in the presence of peroxides or ultraviolet light in the normal way to give high yields of alkylpentamethyldisilanes. 1,1,2,2-Tetramethyldisilane also adds to 1-octene

in the presence of peroxides to give the normal 1:1 addition product and a mixture of telomers. Chloroplatinic acid-catalyzed reaction of pentamethyldisilane with olefins resulted in much cleavage of the Si–Si bond and yielded only traces of the expected addition product.

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