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Preliminary communication

PREPARATION OF PERMETHYLOCTADECASILANE AND PERMETHYLTETRACOSASILANE

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Summary

The synthesis and characterization of $Me(SiMe_2)_{18}Me$ and $Me(SiMe_2)_{24}Me$, reported herein, significantly extends the series of known linear permethylpolysilanes.

The extensively studied [1—6], short chain linear permethylated polysilanes have been prepared most conveniently by alkalimetal condensation of methylhalosilanes. Using this method, Kumada, Ishikawa and Maeda [1] were able to prepare the permethylpolysilanes up to and including the permethyldodecasilane by coupling of mono- and dichloro-di- and -tri-silanes. We wish to report the synthesis and characterization of two higher permethylpolysilanes, permethyloctadecasilane ($Me(SiMe_2)_{18}Me$) and permethyltetracosasilane ($Me(SiMe_2)_{24}Me$).

The intermediate species, dodecamethylcyclohexasilane [7], 1,6-dichloropermethylhexasilane [3], and 1-chloropermethylhexasilane [8] were prepared by published methods. Under a nitrogen atmosphere, 12.4 mmoles of methylmagnesium iodide in ethyl ether (2.0 *M*) was added to a solution of 12.4 mmoles of 1,6-dichloropermethylhexasilane in 20 ml of ethyl ether at a rate which maintained gentle refluxing. The ether was pumped off at room temperature and the resulting solid was extracted with two 20 ml portions of benzene. (Previous work [8] shows that the extract contains mostly 1-chloropermethylhexasilane.) An additional 6.2 mmoles of 1,6-dichloropermethylhexasilane was added to the benzene solution. This solution was then added to a 250 ml round bottom flask containing 50 ml of heptane and 24.0 mmoles of potassium. The mixture was stirred under nitrogen for 6 h, refluxed for 48 h, and then cooled to room temperature. For the destruction of any remaining Si—Cl groups, methylmagnesium iodide (10 mmoles) in ethyl ether was added and stirring continued for 15 minutes. Ethanol/acetic acid (1/1,

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20 ml) and then ethanol/water (1/1, 50 ml) were added. A solid polymer (3.10 g) was filtered off and the organic layer of the filtrate was separated. The heptane/benzene solvent was removed by rotary evaporation and the resulting solid (3.46 g) was dissolved in hexane. The solution was cooled to 5°, extracted with concentrated sulfuric acid, and washed until neutral to litmus. The hexane was removed and the resulting material was placed in 200 ml of ethanol and heated on a steam bath for 30 minutes. The hot solution was filtered. A white solid (0.88 g) was collected and washed with three 20 ml portions of hot ethanol. The solid was recrystallized three time from 1/1 cyclohexane/ethanol, giving 0.47 g $Me(SiMe_2)_{18}Me$ (m.p. 192—19 This compound was identified by molecular weight, determination of number of Si—Si bonds, and the integrated NMR spectrum: The molecular weig as determined by vapor-phase osmometry in carbon tetrachloride solution v 1104 (calcd. 1077). The value for the number of silicon—silicon bonds per molecule was found to be 16.8 (calcd. 17) by cleavage by bromine [9]. The ratio of $(SiMe_2)$-methyl protons (δ 0.148, 0.169, and 0.230) to $SiMe_3$-metl protons (δ 0.099) was 5.17/1 (calcd. 5.33/1). Absorptions in the ultraviolet were seen for this compound at 291 (a 4.4 × 10^4), 270 (a 4.0 × 10^4) and 225 nm (a 3.5 × 10^4). Concentration of the above ethanolic supernatant an wash solutions led to 0.63 g $Me(SiMe_2)_{12}Me$ (m.p. 150—152°, lit. [1] 153°)

The solid material which was insoluble in the benzene/heptane mixtur was heated in carbon tetrachloride (100 ml) for 15 minutes. The solution w filtered hot, The filtrate was cooled to room temperature and ethanol (100 ml) was added. The resulting white precipitate was filtered off and recrystallized twice from carbon tetrachloride. The product, $Me(SiMe_2)_{24}Me$ (0.21 g; m.p. 219—222° C), was characterized as above by molecular weight (found 1382, calcd. 1426), determination of the number of Si—Si bonds (found 23.2, calcd. 23.0), and the integrated NMR spectrum ($SiMe_2$ - meth protons/$SiMe_3$-methyl protons: found 7.21, calcd. 7.33) ($\delta(SiMe_2)$ 0.130, 0.168, and 0.242, $\delta(SiMe_3)$ 0.100). Absorptions in the ultraviolet occur at 293 (a 4.6 × 10^4), 228 (a 2.8 × 10^4) and 210 nm (a 2.8 × 10^4).

In progress are further studies of the physical and chemical properties of these newly isolated long-chain permethylpolysilanes.

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