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Decamethylcyclopentasilane and tetradecamethylcycloheptasilane

The cyclic perphenylpolysilanes $(Ph_2Si)_n$ where $n = 4$–6 are known and have recently been well characterized[1–5]. However, the only known cyclic permethylpolysilane is the six-membered ring species, dodecamethylcyclohexasilane. This compound was first prepared by Burkhard[6] and later synthesized in better yields by Stolberg[7], Gilman[8], and others. Attempts to obtain other cyclic compounds in the permethyl series have been unsuccessful*, but Gilman and Tomasi have reported observation of additional peaks thought to be due to cyclic species in gas chromatography of $[Si(CH_3)_2]_6$[8].

We now report the synthesis and characterization of the five and seven membered cyclic species, decamethylcyclopentasilane and tetradecamethylcycloheptasilane. These compounds are present in small amounts in the dodecamethylcyclohexasilane prepared from dimethyldichlorosilane and sodium–potassium alloy according to the method of Stolberg[7]. We consistently found 3–5 % of $Me_{10}Si_5$ and 1–2 % of $Me_{14}Si_7$ along with $Me_{12}Si_6$ in the crystalline fraction obtained from this reaction. However, detection and separation of these new cyclic compounds was greatly aided by the fortuitous discovery that the amounts of both 5- and 7-membered cyclosilanes are much increased if the initial reaction product is worked up immediately after addition of Me_2SiCl_2 is completed, without refluxing. Upon mild hydrolysis and filtration both high polymer and crystalline solids were obtained; the latter consists of about 20–27 % $Me_{10}Si_5$, 70–75 % $Me_{12}Si_6$, and 4–5 % $Me_{14}Si_7$. If desired, the cyclopentasilane content of a given sample can be further increased by slow vacuum sublimation. The ultimate separation is best made by preparative gas chromatography of a hydrocarbon solution of the cyclic compounds**.

Both $Me_{10}Si_5$ and $Me_{14}Si_7$, like $Me_{12}Si_6$, showed only singlet proton NMR absorption, indicating that all of the hydrogens in each compound have identical environments on a time-average basis. Ultraviolet spectra of the two new compounds are also closely similar to that of $Me_{12}Si_6$[9]; $Me_{10}Si_5$ shows $\lambda_{max} = 210$ mμ (shoulder on end absorption), 261 mμ ($\varepsilon = 1100$) and 272 mμ ($\varepsilon = 970$), while $Me_{14}Si_7$ shows $\lambda_{max} =$

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* Decamethylcyclopentasilane may have been synthesized in the laboratories of M. Kumada by another route, but the sample was not obtained in pure form. Private communication from M. Kumada.

** Good separations were obtained using a 3/8" × 25' column packed with 30 % SE-30 silicone on chromosorb W, and a helium flow rate of 150 cc/min.

TABLE 1

PROPERTIES OF CYCLIC PERMETHYLPOLYSILANES

Compound	*M.p.*	*NMR, ppm* (δ)	*Anal.*[a]			*Mol. wt.*	
			C	*H*	*Si*	*Calcd.*	*Found*
$Me_{10}Si_5$	186–189	−0.135	41.09	10.29	48.39	290.8	285[b] 290[c]
$Me_{12}Si_6$	252–255	−0.132	41.19	10.41	48.33	349	341[b]
$Me_{14}Si_7$	228–232	−0.125	41.08	10.40	—	407	400[b]

[a] Calcd. for $(C_2H_6Si)_n$: C, 41.30; H, 10.40; Si, 48.30. [b] By osmometry. [c] By mass spectroscopy

217 mμ (shoulder on end absorption) and λ_{max} 242 mμ ($\varepsilon = 2100$). The infrared spectra of both compounds show no absorption in the siloxane region, but the cyclopentasilane undergoes air oxidation easily with appearance of a siloxane infrared band at 1050 cm^{-1}. Some properties of the cyclic permethylpolysilanes are summarized in Table 1.

Preliminary experiments, indicate that $Me_{10}Si_5$ forms a delocalized anion-radical like that obtained from $Me_{12}Si_6$[10].

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The redistribution of chlorine, fluorine, or methoxy with hydrogen on silicon

Several studies during recent years have dealt with the distribution of products at equilibrium in the redistribution of ligands about a silicon atom*. These studies have generally shown a random distribution of products when both redistributing ligands are organic substituents[2a,3] or hydrogen[2b]. Quite nonrandom distributions are observed with many other combinations such as the redistribution of an alkoxy or an

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* For recent reviews of this subject see reference 1.