

Preliminary communication

Hindered silylenes

I. Isolation and characterization of decaisobutylcyclopentasilane

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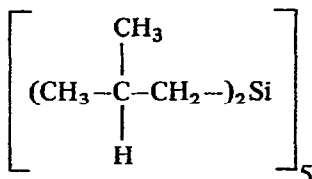
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(Received February 26th, 1971; by publisher April 27th, 1971)

Compounds of the cyclopolysilane series $(R_2Si)_n$ have been isolated from reductive coupling reactions utilizing alkali metals and dihalosilanes, R_2SiX_2 . Most comprehensive have been the studies of the series where $R = \text{phenyl}$; $n = 4, 5, 6$ ¹, and $R = \text{CH}_3$; $n = 5, 6, 7$ ². Presumably these cyclopolysilanes and the accompanying linear polymers arise either from intermediate silylene or silylmetallic species.

It was of interest to us to investigate the interaction of alkali metals with dialkyl-dihalosilanes where the alkyl substituent was of considerable steric bulk, *e.g.*, isobutyl and *tert*-butyl, in order to determine the effect of these larger groups on the ability of the intermediates to cyclize. Further, we envisaged that H-abstraction might play a major role in these reactions, perhaps leading to interesting heterocyclic compounds. Finally, the studies may lead to a better understanding of the nature of the intermediates involved in the coupling reaction. We now wish to report the preliminary findings of our study with diisobutylchlorosilane.

The reaction of diisobutylchlorosilane with potassium biphenylide results in the formation of complex polysilanes containing Si-H and Si-O linkages as evidenced by appropriate absorptions in the infrared region. The structures of these compounds, a complex series, have not yet been determined. However, the isolation of decaisobutylcyclopentasilane (I), although in small yield (1.4 percent), is of considerable interest.



The white crystalline solid (I) can be distilled (b.p. 250°/4 mm), sublimed under vacuum, or recrystallized from acetone or benzene (m.p. 178–180°). In contrast to the permethylated cyclopentasilane, (I) was stable in air.

Elemental analysis and molecular weight data consistent with (I) are shown in Table 1.

TABLE 1

ANALYTICAL DATA OF DECAISOBUTYLCYCLOPENTASILANE (I)

	C(%)	H(%)	Si(%)	mol.wt. ^b
Determined ^a	67.59	12.92	19.59	727
Calculated	67.51	12.75	19.24	712

^a Galbraith Laboratories. ^b Vapor osmometry in benzene.

The proton magnetic resonance spectrum in carbon tetrachloride determined on a Varian A60 Spectrometer is also consistent with (I). At room temperature, the spectrum consists of a methyl doublet ($\delta(\text{CH}_3)$ 1.97 ppm; $J \approx 5$ Hz); a methylene doublet ($\delta(\text{CH}_2)$ 0.77 ppm) with the lower field portion nearly buried in the methyl doublet; and a methine multiplet (centered near $\delta(\text{CH})$ 1.64 ppm). The integrated relative intensities of the absorptions indicates a methyl + methylene/methine $\approx 7.8/1$.

The infrared spectrum of the solid isobutyl compound (I) (KBr pellet) determined on a Perkin-Elmer 225 spectrometer, is strikingly similar to the spectra of the permethylated cyclopolysilanes². A comparison is shown in Table 2.

Aside from the similarity, it is notable that the characteristic doublet attributed to a geminal dimethyl group for isobutyl is absent from the solid state spectrum of (I). This doublet does appear, however, in solution spectrum in carbon tetrachloride as moderately strong absorptions at 1360 and 1375 cm^{-1} . Of further note is the fact that no absorptions occur in either the solid state or solution spectra of (I) which are characteristic of Si-H or Si-O bonds. Finally, of most importance, the Si-Si stretch of (I) (389 cm^{-1}) occurs at significantly lower energy than that of the permethylated analog (400 cm^{-1}).

TABLE 2

COMPARISON OF INFRARED SPECTRA (cm^{-1})

$\text{Me}_{10}\text{Si}_5$	$i\text{-Bu}_{10}\text{Si}_5$	$\text{Me}_{12}\text{Si}_6$
2950 s	2950 s	2950 s
2890 m	2890 m	2885 m
2795 w	2790 w	2790 w
1400 m	1400 m	1400 m
	1235 m	1240 m
1250 s	1250 s	1250 s
	1255 m	
845 m	840 s	845 m
830 m		830 m
800 vs	792 vs	800 vs
735 s		735 s
690 m	680 m	690 m
655 s	645 s	655 s
		630 w
400 w	389 w	383 w

The ultraviolet spectrum of (I) taken in cyclohexane solution using a Cary-14 spectrometer shows a hypsochromic shift in comparison with the permethylated analog. Spectral comparisons with the permethylcyclopolysilanes² are shown in Table 3.

TABLE 3

COMPARISON OF ULTRAVIOLET SPECTRA

	λ_{\max} (nm)	ϵ
Me ₁₀ Si ₅	261	1,100
	272	970
i-Bu ₁₀ Si ₅	231.4	19,000
	254.4	5,900
Me ₁₂ Si ₆	230.5	6,000
	252.5	1,200

If one compares the infrared ring absorptions and the ultraviolet absorption of (I) with the corresponding absorptions of the permethylated pentamer and hexamer, the effect of the isobutyl group on the σ - π -bonding system³ of the cyclopolysilanes becomes apparent. The strain placed on the five-membered ring system by the bulky groups results in ring distortion with concurrent diminution of orbital overlap and thus bond strength. This results in a lower energy infrared stretching vibration and increased energy for the ultraviolet transition in a fashion similar to that observed for cyclohexasilanes². The increased intensity of the electronic absorptions is not readily explained.

Preliminary studies of reactions of di-tert-butylchlorosilane with alkali metals gave numerous products, but no evidence of ring formation has been found. The one crystalline product isolated has infrared absorptions characteristic of hydroxy and Si-H groups.

Continuing research seeks not only to increase the yields and prepare new hindered cyclopolysilanes, but to identify the products derived from H-abstraction.

EXPERIMENTAL

Diisobutyldichlorosilane was prepared from isobutylmagnesium bromide and silicon tetrachloride⁴. The silane was purified to greater than 99% purity via gas chromatography on a 10% SE-30 column on silanized Chromosorb-W.

The reaction apparatus was flame-dried under vacuum and preflushed with high purity, dry nitrogen. All subsequent operations, prior to final hydrolysis, were carried out under nitrogen with careful exclusion of oxygen and moisture.

Fifty ml of tetrahydrofuran was distilled from lithium aluminum hydride directly into the reaction vessel. Sodium-potassium alloy (3.78 g; 22/78; 0.09 moles active metal) and 0.78 g biphenyl were transferred to the reaction vessel at room temperature. Stirring commenced immediately and the bright green of the biphenyl anion radical appeared. Ten g of diisobutyldichlorosilane (0.047 moles) was added dropwise over a period of two hours and the mixture was stirred for 46 hours. Mercury was then added and the excess alkali metal was removed as the amalgam. The remaining slurry

was added to water and the organic material was extracted with ether. Vacuum fractionation (0.4 mm) yielded 6.6 g of an uncharacterized mixture of carbosilanes and a solid fraction boiling at 250°. The solid could be recrystallized from benzene to give 95 mg of pure decaisobutylcyclopentasilane. Time and concentration variations in the reaction did not increase the yield of the cyclosilane.

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