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Preliminary communication

A novel silicon cage compound from the hydrolysis of 1,3,5-trichloro-1,3,5-trimethyl-1,3,5-trisilacyclohexane*

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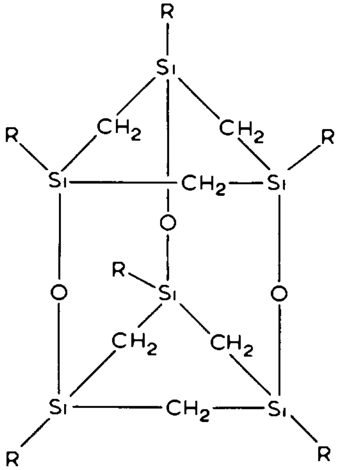
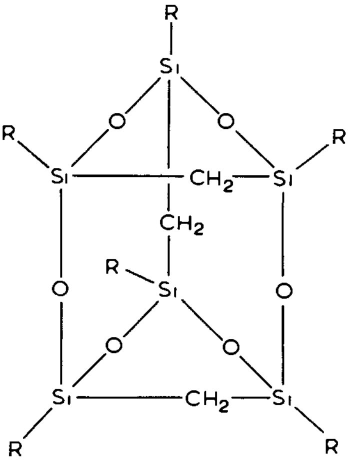
When $(ClCH_3SiCH_2)_3$ (I)[1] is hydrolyzed rapidly with relatively large quantities of water one usually obtains an intractable, nonvolatile polymer. We have found that controlled hydrolysis of (I) results in essentially quantitative formation of a novel crystalline cage compound (II), the proposed structure of which is shown.



(II)

R = Me



(III)

R = Me, Ph

This structure is similar to that of a cage compound (III) identified by Cooke *et al.*[2] Evidence in support of (II) was obtained by infrared, PMR, and mass spectrometry. The infrared spectrum of (II) shows only two major differences from that of (I), namely the appearance of a strong absorption band at 1110 cm^{-1} indicative of an Si–O–Si linkage

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and the absence of an Si–Cl peak at 550 cm^{-1}. In the PMR spectrum of (II) in $CDCl_3$ (Varian HA-100 using TMS as internal standard) three sets of peaks were observed, two doublets at τ 10.03 and 10.67, and a singlet at τ 10.01. This we interpret to be an ABX pattern resulting from nonequivalent methylene protons (J_{AB} 14 Hz) and the equivalent methyl protons. The integration of the spectrum showed a 1/1/3 (A/B/X) proton ratio which is in agreement with this interpretation. A similar argument of geminal splitting was proposed by Cooke *et al.*[2] for (III) in which the methylene protons are found to be in an orientation similar to those in (II). A mass spectrum of (II) was obtained on a Dupont 492 high resolution mass spectrometer with peak matching. Excellent agreement with the proposed compound was obtained (Table 1).

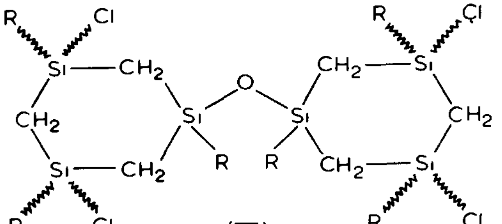
TABLE 1

MASS SPECTRAL DATA FOR $C_{12}H_{30}O_3Si_6$

	Found	Calculated
Parent peak	390.07850	390.08106
Base peak (–Me)	375.05610	375.05758
–2Me, H	359.02600	359.02627

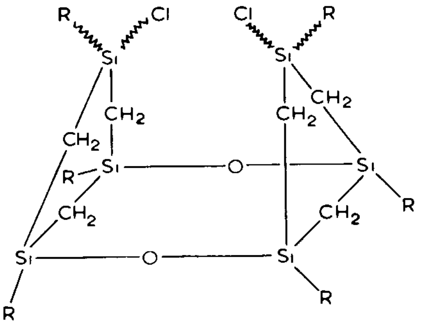
The best yields of (II) were obtained by refluxing dilute (0.06 *M*) tetrahydrofuran (THF) solutions of (I) in a nitrogen stream. In a typical experiment a solution of 4.05 g (14.5 mmol) of (I) in 250 ml of dry THF was refluxed for 105 h (when HCl evolution had ceased). A white solid formed on cooling the solution. The recrystallized (from THF) solid, 2.71 g (6.95 mmol, 95.8% yield), m.p. 285° (uncorrected), could be sublimed at 160° (2.5 mm). The success of this method apparently results from the slow introduction of moisture from the undried nitrogen and/or diffusion of humid air into the reflux apparatus through the joints. Experiments in which water was deliberately added to the nitrogen stream gave II in far lower yields (*e.g.* 10–23%). No evidence was found to indicate a reaction of (I) with THF.

In order to rationalize the high yield of (II) we must examine the most probable reactions that would occur and the most probable intermediate compounds formed. The initial hydrolysis of (I) would produce a silanol which on condensation with (I) would give (IV). There is low probability that silanol–silanol condensation would occur at the outset but it could become an important reaction as (I) decreases in concentration. A silanol

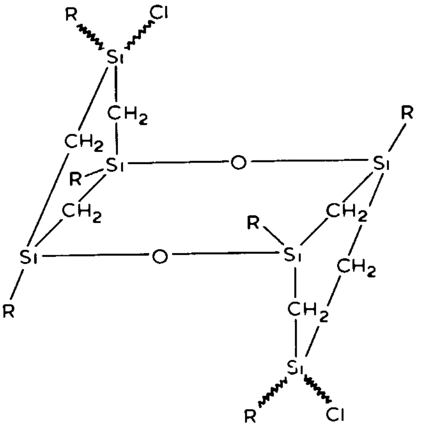


(IV)

formed from (IV) would have the Si–OH either *cis* or *trans* to the Si–O of the siloxane★. The *cis–trans* ratio would be in equilibrium via configuration inversion reactions. A *cis* configuration would favor an intramolecular condensation which could produce (V) or (VI). On examination models of the *cis* silanol of (IV) we conclude that the probability of

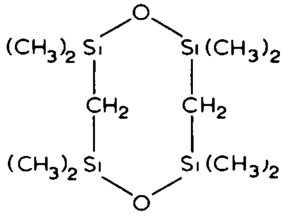


(V)



(VI)

formation of (V) and (VI) is equal unless there is a preferred orientation of the siloxane in THF. It is possible that cleavage of a siloxane bond could "equilibrate" (V) and (VI). In contradiction to this possibility, Wang *et al.*[3] conclude that the cyclosiloxane (VII) could not be polymerized by "equilibration". The same cyclosiloxane skeletal structure is present as the middle ring in (V) and (VI). Further investigation of the proposed ring cleavage reaction is necessary.



(VII)

The *trans* configuration of the silanol of (IV) would favor intermolecular condensation leading to high molecular weight species. Since little polymeric material was obtained under dilute conditions as long as the hydrolysis was slow, we can conclude that the configuration change to *cis* and further condensation of the *cis* form shifts the reaction in favor of the formation of (V) or (VI). In addition, any higher molecular weight

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★The *cis–trans* ratio of the starting material (I) has not been determined satisfactorily due to rapid hydrolysis on handling. Compound (I) was prepared[1] from $[(C_2H_5O)CH_3SiCH_2]_3$ which is found in a 1/3 *cis–trans* ratio.

siloxanes formed could be cleaved under acid conditions, again shifting the reaction toward the formation of (V) or (VI). Rapid hydrolysis even under identical dilutions produced considerable polymeric material which had limited solubility in THF and was not appreciably redistributed to (II) even on boiling the acid mixture several days.

An intramolecular condensation of a silanol of (V) having an Si–OH group *cis* to the Si–O bonds would result in the formation of (II). A facile conversion of a *trans* silanol to a *cis* configuration would again explain the low degree of intermolecular condensation as long as hydrolysis is slow. Redistribution of (II) by acid cleavage is apparently curtailed by dilution. It has yet to be demonstrated that the cage can be cleaved at all in acidic THF solutions.

We conclude that slow hydrolysis of dilute THF solutions of (I) to give nearly quantitative yields of (II) can be rationalized by well known reactions in silicon chemistry. We are currently attempting to make model compounds of (V) and (VI) in order to determine whether the compounds will undergo equilibration reactions under the experimental conditions used in this study.

ACKNOWLEDGMENT

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