Flash Vacuum Pyrolysis (FVP) of 2,7-Dimethyl-2,3:7,8-diepoxy-5-silaspiro[4.4]nonane (I) with Cyclotrisiloxanes—Synthesis of Spirocyclosiloxanes. Characterization of Silica Formed by FVP of I

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Flash vacuum pyrolysis of 2,7-dimethyl-2,3:7,8-diepoxy-5-silaspiro[4.4]nonane (I) with cyclotrisiloxanes yields 2,4,6,8,10,12,14-heptasila-1,3,5,7,9,11,13,15-octaoxaspiro[7.7]pentadecanes (III) and 2,4,6,8,10,12,14,17-octasila-1,3,5,7,9,11,13,15,16,18-decaoxadispiro[5.3.5.3]octadecanes (IV). These spiro-cyclosiloxanes may result from the insertion of "[O=Si=O]" or an equivalent synthon into the Si—O single bond of the trapping reagents. The structures of these have been determined by ^{1}H, ^{13}C, and, in particular, ^{29}Si NMR. The structure of IVa has been confirmed by X-ray crystallography. In the absence of trapping agents silicon dioxide of high surface area is deposited. This material has been characterized by scanning and transmission electron microscopy.

We have reported previously that flash vacuum pyrolysis (FVP) of 6-oxa-3-silabicyclo[3.1.0]hexanes (II) provides a convenient route to reactive silicon–oxygen doubly bonded species (silanones).[2] The mechanism of the thermal decomposition of II to yield silanones has been studied.[3] Likewise, FVP of 2,7-dimethyl-2,3:7,8-diepoxy-5-silaspiro[4.4]nonane (I) was suggested to yield monomeric silicon dioxide [O=Si=O] on the basis of copyrolysis experiments of I with hexamethylcyclotrisiloxane (D$_3$) which gave isoprene and 2,2,4,4,6,6,10,10,12,12,14,14-dodecamethyl-2,4,6,8,10,12,14-heptasila-1,3,5,7,9,11,13,15-octaoxaspiro[7.7]pentadecane (IIIa).[2] [O=Si=O] has been produced by the reaction of silicon monoxide with atomic oxygen generated by microwave excitation in an argon matrix and its infrared spectrum recorded.[4] Silicon dioxide has also been detected by both negative and positive ion mass spectrometry in the upper atmosphere.[5,6]

We should like to report the results of several additional copyrolysis experiments carried out with I and other cyclic siloxanes which demonstrate the utility of this method for the synthesis of spirosiloxanes. A few spirosiloxanes have been prepared in very low yield by cohydrolysis of dimethyldichlorosilane and silicon tetrachloride.[7,8] Furthermore, we have found that the reaction of I with D$_3$ is more complicated than we had supposed. Finally, FVP of I in the absence of trapping agents has been carried out. The product of this reaction, impure silicon dioxide, has been characterized.

Let us consider first the copyrolysis of I and D$_3$. This reaction yields not only isoprene and IIIa but also a higher molecular weight compound (IVa) derived from IIIa and a second equivalent of "[O=Si=O]". Free "[O=Si=O]"

is probably not involved in this reaction which may occur in a stepwise fashion (Scheme I). Copyrolysis of IIIa and I leads to significantly higher yields of IVa. This suggests that IIIa is a precursor of IVa. On the basis of ^{1}H, ^{13}C, and ^{29}Si NMR data as well as its molecular weight determined by mass spectrometry we have suggested that the structure of IVa was 2,2,4,4,8,8,10,10,14,14,17,17-dodecamethyl-2,4,6,8,10,12,14,17-octasila-1,3,5,7,9,11,13,15,16,18-decaoxatricyclo[5.5.3.3]octadecane.[9,10] X-ray crystallography as well as more careful analysis of the ^{29}Si NMR data demonstrates that this structure is in fact incorrect and that the correct structure for IVa is 2,2,4,4,8,8,12,12,14,14,17,17-dodecamethyl-2,4,6,8,10,12,14,17-octasila-1,3,5,7,9,11,13,15,16,18-decaoxadispiro[5.3.5.3]octadecane (Scheme I, Figure 1, and Tables I–IV). The sequence of reactions leading to the generation of silicon–oxygen doubly bonded intermediates from I follows that reported for II.[3] The formation of IVa by reaction of "[O=Si=O]" with IIIa clearly involves major skeletal rearrangements.

A significant effect of ring size has been observed on the ^{29}Si NMR chemical shifts in cyclic siloxanes. Specifically, the ^{29}Si NMR chemical shift for D$_3$ occurs at -9.2 ppm while that for octamethylcyclotetrasiloxanes (D$_4$) comes at -20.0 ppm. Silicate silicon atoms have been observed at -105 ppm.[11] The ^{29}Si NMR data for IVa: (-6.092, -15.629, and -100.761 ppm) (2:1:1) are consistent with that expected for four magnetically equivalent silicon atoms in six-membered siloxane rings, two equivalent silicon atoms in eight-membered siloxane rings, and two identical silicate silicon atoms.

The ^{29}Si NMR data for IIIa are also consistent with its structure. Thus three nonequivalent silicon signals are observed in a four to two to one ratio. The first two come at -17.570 and -18.768 ppm in the region expected for silicon atoms in eight-membered siloxane rings while the

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(2) Manuel, G.; Bertrand, G.; Weber, W. P.; Kazoura, S. A. *Organometallics* 1984, 3, 1340.
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(6) Viggiano, A. A.; Arnold, F.; Fahey, D. W.; Fehsenfeld, F. C.; Ferguson, E. E. *Planet. Space Sci.* 1982, 30, 499.
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Table I. Final Atomic Coordinates for IVa

atom	molecule 1			molecule 2		
	x	y	z	x	y	z
O(1)	0.7732 (8)	0.0104 (10)	0.3718 (12)	0.5508 (7)	0.4290 (9)	−0.1665 (10)
Si(2)	0.6973 (5)	0.0443 (6)	0.2624 (6)	0.6300 (4)	0.4305 (5)	−0.0366 (5)
O(3)	0.7539 (9)	0.1807 (11)	0.2091 (11)	0.7076 (8)	0.3737 (10)	−0.0934 (11)
Si(4)	0.8630 (5)	0.2786 (5)	0.2453 (5)	0.7165 (5)	0.3197 (6)	−0.2396 (6)
O(5)	0.9158 (8)	0.2137 (10)	0.3620 (11)	0.6316 (9)	0.3429 (11)	−0.3461 (10)
Si(6)	0.8874 (4)	0.0740 (6)	0.4122 (5)	0.5573 (4)	0.4154 (5)	−0.3258 (5)
O(7)	0.9109 (9)	0.0735 (12)	0.5753 (10)	0.4541 (8)	0.3401 (9)	−0.4001 (11)
Si(8)	0.9780 (4)	0.0582 (4)	0.7048 (5)	0.3729 (4)	0.3284 (5)	−0.5250 (5)
O(9)	1.0554 (9)	−0.0037 (12)	0.6580 (12)	0.5929 (9)	0.5493 (10)	−0.3870 (12)
C(10)	0.6615 (18)	−0.0733 (18)	0.1176 (20)	0.6931 (16)	0.5972 (16)	0.0210 (19)
C(11)	0.5914 (12)	0.0535 (20)	0.3477 (21)	0.5665 (13)	0.3289 (17)	0.0964 (16)
C(12)	0.8565 (14)	0.4304 (15)	0.3139 (18)	0.8402 (15)	0.4042 (25)	−0.2991 (22)
C(13)	0.9322 (14)	0.3058 (18)	0.0895 (17)	0.6944 (17)	0.1460 (17)	−0.2251 (23)
C(14)	1.0460 (14)	0.2147 (15)	0.7845 (19)	0.2546 (11)	0.3163 (16)	−0.4573 (19)
C(15)	0.9006 (14)	−0.0472 (18)	0.8226 (18)	0.3687 (14)	0.1915 (15)	−0.6329 (16)

Table II. Final Temperature Factors (×10³) for IVa

| atom	$U(11)$	$U(22)$	$U(33)$	$U(12)$	$U(13)$	$U(23)$
			(A) Molecule I			
O(1)	56 (10)	106 (10)	134 (11)	29 (8)	−11 (8)	63 (8)
Si(2)	75 (5)	92 (5)	97 (5)	25 (4)	−4 (4)	45 (4)
O(3)	72 (10)	96 (10)	114 (11)	32 (9)	−19 (8)	37 (9)
Si(4)	78 (5)	75 (4)	69 (4)	28 (4)	−10 (4)	19 (4)
O(5)	74 (9)	81 (9)	98 (10)	16 (8)	−28 (8)	28 (8)
Si(6)	66 (5)	90 (5)	57 (4)	50 (4)	3 (4)	18 (4)
O(7)	112 (11)	189 (13)	52 (9)	95 (11)	−40 (8)	24 (8)
Si(8)	65 (5)	76 (4)	56 (4)	32 (4)	1 (4)	13 (3)
O(9)	120 (12)	145 (12)	90 (10)	103 (12)	9 (8)	2 (8)
C(10)	195 (25)	112 (18)	109 (19)	−15 (18)	−39 (17)	−47 (15)
C(11)	36 (15)	193 (23)	194 (24)	60 (15)	59 (15)	84 (18)
C(12)	169 (22)	69 (14)	120 (17)	69 (15)	1 (16)	−2 (12)
C(13)	108 (18)	163 (20)	68 (14)	13 (16)	55 (14)	21 (13)
C(14)	131 (20)	60 (14)	130 (19)	−11 (14)	32 (15)	−51 (13)
C(15)	87 (16)	162 (19)	91 (15)	11 (15)	42 (13)	76 (14)
			(B) Molecule II			
O(1)	74 (9)	98 (9)	67 (9)	46 (8)	−16 (7)	5 (7)
Si(2)	72 (5)	96 (5)	51 (4)	43 (4)	−11 (4)	5 (4)
O(3)	96 (11)	112 (10)	66 (9)	53 (9)	−21 (8)	−3 (7)
Si(4)	102 (6)	111 (5)	65 (5)	62 (5)	−17 (4)	−2 (4)
O(5)	160 (13)	149 (12)	51 (8)	113 (11)	−3 (8)	−2 (8)
Si(6)	69 (5)	46 (4)	53 (4)	14 (4)	−15 (4)	13 (3)
O(7)	84 (10)	70 (9)	85 (9)	−25 (8)	−47 (8)	41 (7)
Si(8)	59 (5)	52 (4)	66 (4)	1 (3)	−13 (4)	21 (3)
O(9)	113 (11)	73 (9)	109 (10)	−14 (8)	−42 (9)	41 (8)
C(10)	175 (22)	70 (14)	122 (17)	38 (15)	−36 (16)	−64 (13)
C(11)	108 (17)	159 (18)	63 (13)	69 (15)	47 (12)	72 (12)
C(12)	73 (19)	297 (31)	139 (21)	68 (20)	49 (15)	76 (20)
C(13)	226 (27)	75 (16)	205 (25)	92 (18)	−69 (21)	−53 (16)
C(14)	38 (14)	111 (16)	151 (19)	33 (13)	43 (13)	11 (14)
C(15)	142 (19)	84 (14)	61 (13)	44 (14)	29 (12)	−22 (11)
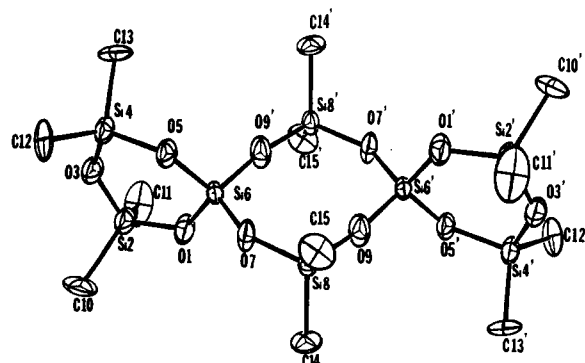
Figure 1. ORTEP diagram of IIIa.

last comes at −105.1488 ppm in the region in which silicate silicon atoms are found.

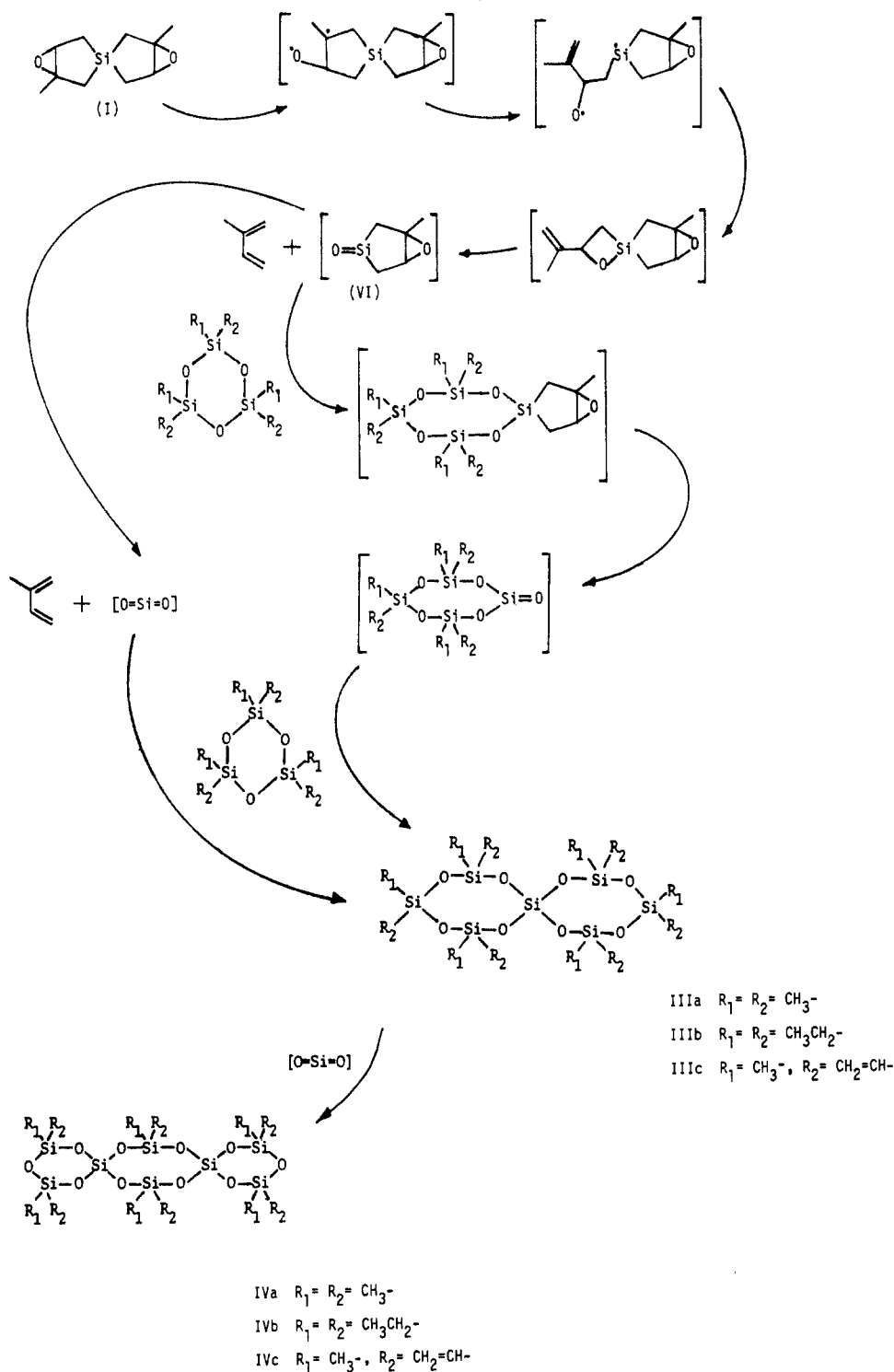In a similar manner, copyrolysis of I and hexaethyl-cyclotrisiloxane gave two products:

Table III. Bond Distances (Å) in IVa for Molecule I and II

	I	II
Si(2)–O(1)	1.621 (13)	1.651 (12)
Si(2)–O(3)	1.620 (14)	1.628 (13)
Si(4)–O(3)	1.636 (13)	1.611 (13)
Si(4)–O(5)	1.642 (13)	1.649 (14)
Si(6)–O(5)	1.601 (13)	1.603 (12)
Si(6)–O(7)	1.623 (14)	1.591 (12)
Si(6)–O(9′)	1.547 (14)	1.583 (13)
Si(8)–O(7)	1.592 (13)	1.613 (12)
Si(8)–O(9)	1.625 (14)	1.605 (13)
Si(2)–C(10)	1.886 (23)	1.888 (21)
Si(2)–C(11)	1.873 (21)	1.860 (19)
Si(4)–C(12)	1.899 (20)	1.907 (25)
Si(4)–C(13)	1.898 (20)	1.908 (23)
Si(8)–C(14)	1.874 (20)	1.887 (18)
Si(8)–C(15)	1.856 (20)	1.879 (18)

2,2,4,4,6,6,10,10,12,12,14,14-dodecaethyl-2,4,6,8,10,12,14-heptasila-1,3,5,7,9,11,13,15-octaoxaspiro[7.7]pentadecane (IIIb) and 2,2,4,4,8,8,12,12,14,14,17,17-dodecaethyl-

Scheme I

IIIa $R_1 = R_2 = CH_3-$

IIIb $R_1 = R_2 = CH_3CH_2-$

IIIc $R_1 = CH_3-$, $R_2 = CH_2=CH-$

IVa $R_1 = R_2 = CH_3-$

IVb $R_1 = R_2 = CH_3CH_2-$

IVc $R_1 = CH_3-$, $R_2 = CH_2=CH-$

2,4,6,8,10,12,14,17-octasila-1,3,5,7,9,11,13,15,16,18-decaoxadispiro[5.3.5.3]octadecane (IVb). The structures assigned to IIIb and IVb are based largely on their ^{29}Si NMR spectra. Thus the ^{29}Si NMR of IIIb exhibits three nonequivalent silicon signals in a ratio of 4:2:1. The first two signals are in the region expected for silicon atoms in eight-membered siloxane rings (−18.977 and −19.068 ppm) while the latter is in the region of silicate silicon atoms (−105.264 ppm). On the other hand, the ^{29}Si NMR of IVb has three nonequivalent silicon signals in a ratio of 2:1:1. The chemical shift of the first (−7.01 ppm) is consistent with silicon atoms in a six-membered siloxane ring while the second (−17.326 ppm) is in the region expected for silicon atoms in an eight-membered siloxane ring. The chemical shift of the final signal (−105.422 ppm) is in the
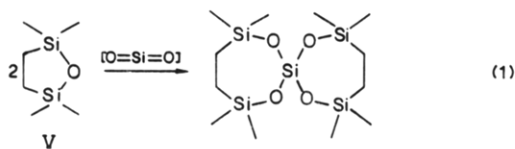
region where silicate silicon atoms are found.

Likewise, copyrolysis of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane with I yields two products: 2,4,6,10,12,14-hexavinyl-2,4,6,10,12,14-hexamethyl-2,4,6,8,10,12,14-heptasila-1,3,5,7,9,11,13,15-octaoxaspiro[7.7]pentadecane (IIIc) and 2,4,8,12,14,17-hexavinyl-2,4,8,12,14,17-hexamethyl-2,4,6,8,10,12,14,17-octasila-1,3,5,7,9,11,13,15,16,18-decaoxadispiro[5.3.5.3]octadecane (IVc). In the assignment of these structures, ^1H, ^{13}C and, in particular, ^{29}Si NMR spectra were especially useful. The ^{29}Si NMR spectrum of IIIc has three signals in a 4:2:1 ratio. The first and second are at −31.696 and −32.227 ppm, respectively, characteristic of monovinyl-substituted silicon atoms in eight-membered ring siloxanes. For example, the ^{29}Si NMR signal of the vinyl-substituted silicon atom in

Table IV. Bond Angles (deg) IVa for Molecules I and II

	I	II
(A) Angles around Silicon		
O(1)–Si(2)–O(3)	106.2 (7)	106.3 (6)
O(1)–Si(2)–C(10)	109.2 (9)	107.9 (8)
O(1)–Si(2)–C(11)	109.8 (8)	109.0 (7)
O(3)–Si(2)–C(10)	110.2 (9)	109.5 (8)
O(3)–Si(2)–C(11)	109.3 (8)	109.5 (8)
C(10)–Si(2)–C(11)	112.9 (10)	114.3 (9)
O(3)–Si(4)–O(5)	106.2 (7)	107.2 (7)
O(3)–Si(4)–C(12)	109.9 (8)	110.5 (9)
O(3)–Si(4)–C(13)	110.4 (8)	108.1 (9)
O(5)–Si(4)–C(12)	110.0 (8)	109.6 (9)
O(5)–Si(4)–C(13)	109.7 (8)	109.7 (9)
C(12)–Si(4)–C(13)	110.6 (9)	111.6 (10)
O(1)–Si(6)–O(5)	106.8 (7)	108.1 (7)
O(1)–Si(6)–O(7)	109.7 (7)	110.5 (6)
O(1)–Si(6)–O(9')	110.5 (7)	109.0 (7)
O(5)–Si(6)–O(7)	109.9 (7)	109.6 (7)
O(5)–Si(6)–O(9')	110.1 (7)	110.9 (7)
O(7)–Si(6)–O(9')	109.7 (7)	108.7 (7)
O(7)–Si(8)–O(9)	109.1 (7)	108.4 (7)
O(7)–Si(8)–C(14)	109.3 (8)	109.4 (7)
O(7)–Si(8)–C(15)	108.4 (8)	106.9 (7)
O(9)–Si(8)–C(14)	108.6 (8)	109.3 (8)
O(9)–Si(8)–C(15)	108.9 (8)	108.3 (8)
C(14)–Si(8)–C(15)	112.4 (9)	114.3 (8)
(B) Angles around Oxygen		
Si(2)–O(1)–Si(6)	132.7 (8)	130.3 (7)
Si(2)–O(3)–Si(4)	133.2 (8)	133.1 (8)
Si(4)–O(5)–Si(6)	131.4 (8)	130.7 (8)
Si(6)–O(7)–Si(8)	150.7 (9)	148.5 (8)
Si(8)–O(9)–Si(6)	167.8 (10)	169.5 (9)

Figure 2. Scanning electron micrograph (5 K magnification; 2.0 μm/cm).
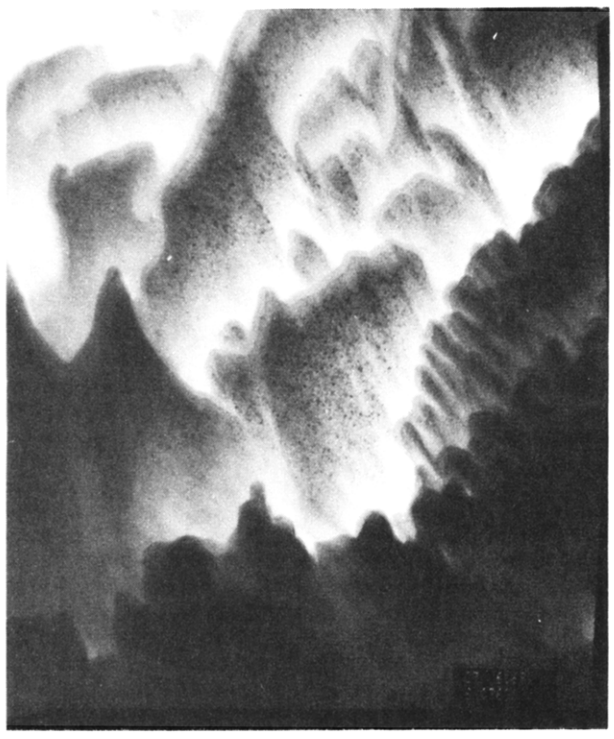
Figure 3. Transmission electron micrograph (36 K magnification; 0.28 μm/cm).

vinylheptamethylcyclotetrasiloxane comes at −33.475 ppm.[12] The last is at −106.102 ppm characteristic of a silicate silicon atom. Likewise, the ^{29}Si NMR of IVc has three signals which are in a ratio of 4:2:2. The first at −20.765 ppm is characteristic of monovinyl-substituted silicon atoms in a six-membered siloxane ring. For comparison, the ^{29}Si NMR signal of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane comes at −22.666 ppm. The second is at −30.79 ppm characteristic of monovinyl-substituted silicon atoms in an eight-membered siloxane ring. Note that the difference in silicon chemical shift between a six- and eight-membered cyclic siloxane is approximately 8 ppm when each silicon is substituted with a single vinyl substituent. The silicon chemical shift difference between D_3 and D_4, for comparison, is almost 11 ppm. The last absorption is at −101.369 ppm characteristic of silicate silicon atoms. The starting material as well as the products in this case are mixtures of stereoisomers. We were unsuccessful in attempts to separate them.

Finally, the copyrolysis of I and 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (V) was carried out. In addition to isoprene and recovered V the only product found was 2,2,5,5,9,9,12,12-octamethyl-2,5,7,9,12-pentasila-1,6,8,13-tetraoxaspiro[6.6]tridecane (eq 1). Two signals

(1)

in a 4:1 ratio were observed in the ^{29}Si NMR spectrum of this compound. The first at 12.28 ppm is quite close to that reported for hexamethyldisiloxane at 7.20 ppm. The other signal is at −95.91 ppm in the region in which signals for silicate silicon atoms are found.
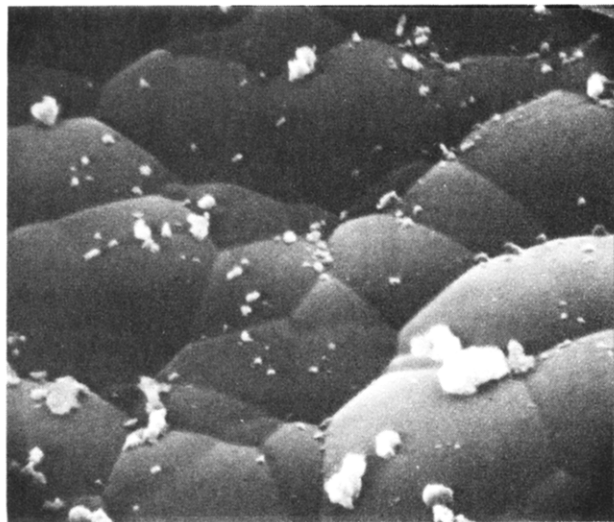
Flash vacuum pyrolysis of I in the absence of a trapping agent results in the deposition of a finely divided white to yellowish white material on the inside of the pyrolysis tube. This material is tightly bonded to the quartz or glass surface. It can be removed by scraping with a stainless-steel spatula. The surface area of this material as determined by differential gas adsorption of nitrogen vs. helium and was found to be 310 m²/g.[13] This high surface area is approximately that found for fumed silica.[14] This material was also characterized by scanning electron microscopy at a resolution of 100 Å on a Phillips EM-420 (Figure 2). The small, bright, white irregular particles on the rounded hill-like structures apparently result from

(12) Juengst, C., private communication.

(13) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.

(14) Cab-O-Sil Properties and Functions, Cabot Corp., 1983.

damage to the sample when it is scraped from the walls of the pyrolysis tube. The electron diffraction pattern and transmission electron microscopy at a resolution of 2.4 Å were determined on a Cambridge F-4-10 instrument (Figure 3). The regular electron diffraction pattern indicates a crystalline structure for the sample. The transmission electron micrographs show areas of crystallinity as well as dark areas of amorphous material. Consistent with this finding is the fact that elemental analysis indicates that the SiO_2 is not pure but contains variable amounts of carbon (up to ten percent in some samples). This supports the previous suggestion (see Scheme I) that I decomposes in a stepwise manner. Apparently, the silanone intermediate VI is capable of inserting into either the strained Si–O–Si bonds or the Si–OH bonds at the surface of the pyrolysis tube. These reactions of silicon–oxygen doubly bonded intermediates with the surface of the pyrolysis tube in competition with the Si–O bonds of the trapping reagents results in decreased yields of spirosiloxane products.

In conclusion, FVP of I and cyclic siloxanes yields spirosiloxane compounds which are virtually inaccessible by traditional synthetic methods.[6,7] This work also provides several examples which demonstrate the value of ^{29}Si chemical shifts for the elucidation of siloxane structure.

Experimental Section

^1H and ^{13}C NMR spectra were obtained on an IBM WP-270-SY or a JEOL FX-90-Q spectrometer operating in the FT mode using 5% and 15% solutions in chloroform-d, respectively. Chloroform was utilized as an internal standard. ^{29}Si NMR spectra were obtained on the IBM WP-270-SY spectrometer using Me_4Si as an external standard. ^{29}Si NMR spectra were run with gated broad band proton decoupling with a 100-s pulse delay in order to minimize the NOE effect. ^{29}Si NMR data are presented and discussed in the text. IR spectra were obtained on a Perkin-Elmer 281 spectrometer of 5% chloroform solutions. Low-resolution mass spectra were obtained on a Hewlett-Packard 5985 GC-MS at an ionizing voltage of 70 eV. A 20 in. × $^1/_8$ in. 2% OV-101 on 100/120 mesh Chromosorb W column was used in the gas chromatographic inlet of the mass spectrometer. In all cases, 2 g of I was utilized. Thus the theoretical amount of [O=Si=O] is 0.6 g (10 mmol). The percent yield of spirosiloxane products is based on the amount of [O=Si=O] produced after correction for the amount of this reactive intermediate which reacts with the surface of the pyrolysis tube. This value was determined by weighing the pyrolysis tube before and after the reaction. After the reaction, the pyrolysis tube was placed in a furnace at 560 °C and heated overnight in an atmosphere of air before it was reweighed. The usual weight gain of the pyrolysis tube was about 0.36 g. Yields of spirosiloxane products are thus calculated on the basis of 0.24 g (4 mmol) of [O=Si=O] available and were generally found to be in the range of 20–30%. ^1H NMR of the crude pyrolysis mixture was carried out to determine if any unreacted I was still present. In most reactions none was observed. Dodecane was added as an internal standard for GLPC analysis. This were performed on a Hewlett-Packard F&M 700 GC equipped with either a 18 in. × $^1/_4$ in. 20% SE-30 on 60/80 mesh Chromosorb W column (A) or a 18 in. × $^1/_4$ in. 5% OV-101 on 100/120 mesh Chromosorb W column (B). The columns were deactivated by silylation with hexamethyldisilazane immediately before use. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. High-resolution mass spectra were obtained on an A.E.I. MS-902 at an ionizing voltage of 70 eV. Exact masses were determined by peak matching against known masses of perfluoro kerosene.

Flash vacuum pyrolysis was carried out as follows. A quartz tube, 40 in. long with an i.d. of 5 mm and an o.d. of 7 mm, was wrapped in the form of a helical spiral whose diameter was 0.75 in. and whose length was 12 in. Standard taper ground quartz joints were connected to either end of this quartz helix to complete the pyrolysis tube. The tube was placed in a tube furnace, 13 in. in length and having a heated zone 1 in. in diameter. The

temperature in the oven was determined by use of an iron-constantan thermocouple connected to an Omega 871 digital thermometer. Pyrolysis reactions were carried out at 520 °C. One end of the pyrolysis tube was connected to a round bottom flask in which were placed I and the particular cyclic siloxane trapping reagent. The other end of the pyrolysis tube was connected to a cold finger trap which was cooled by liquid nitrogen. This in turn was connected to a high vacuum line (10^{-4} mmHg). The reactant mixture was passed through the pyrolysis tube over the course of about 1 h.

Hexamethylcyclotrisiloxane (D_3), hexaethylcyclotrisiloxane, 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (V), and 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane were obtained from Petrarch Systems Inc.

2,7-Dimethyl-2,3:7,8-diepoxy-5-silaspiro[4.4]nonane (I) was prepared by literature methods.[2,15] It had spectral properties in complete agreement with those reported.

Copyrolysis of I and D_3. Copyrolysis of I (2 g, 10.2 mmol) and D_3 (12 g, 45 mmol) was carried out as above. The products consists of isoprene, recovered D_3, D_4, IIIa (18%), and IVa (6%). IIIa and IVa were separated by preparative GLPC on column A.

Copyrolysis of I and IIIa. Copyrolysis of I (1 g, 5.1 mmol) and IIIa (252 mg, 0.5 mmol) was carried out as above. The products consisted of isoprene, a small amount of IIIa, and IVa (40%).

IIIa had properties in agreement with those reported.[2]

IVa was a crystalline solid, mp 68.5 °C. It had the following spectral properties: ^1H NMR δ 0.1589 (s, 24 H), 0.1526 (s, 12 H); ^{13}C NMR δ 0.563 (8 C), 0.075 (4 C); IR ν 1100, and 1060 cm^{-1} (SiO); mass spectrum, m/e (relative intensity) 549 (32, M – 15$^+$), 489 (40), 401 (49). High-resolution mass spectrum of the (M – 15)$^+$ ion: calcd for $C_{11}H_{33}O_{10}Si_8$, 549.0228; found, 549.0198.

X-ray Structure Analysis of IVa. Unit cell parameters were derived from the angular settings of 15 well-centered reflections. Data were measured at room temperature by using a Nicolet/Syntex P2$_1$ diffractometer with Mo Kα radiation and a maximum 2θ of 45°. Compound IVa crystallizes in space group $P\bar{1}$ (triclinic) with unit cell parameters a = 14.716 (14) Å, b = 11.417 (13) Å, c = 9.919 (14) Å, α = 89.77 (10)°, β = 95.30 (10)°, γ = 109.13 (8)°, V = 1567 Å^3, and Z = 2. The structure was solved from 1501 reflections by using direct methods. Two independent half molecules were found, each situated on a crystallographic center of symmetry (center of inversion). Full-matrix least-squares refinement resulted in an R factor of 8.7, and a weighed R factor of 7.5.

Copyrolysis of I and 2,2,5,5-Tetramethyl-2,5-disila-1-oxacyclopentane (V). I (2 g, 10.2 mmol) and V (4.9 g, 30.6 mmol) were copyrolyzed as above. The products were isoprene, recovered V, and 2,2,5,5,9,9,12,12-octamethyl-2,5,7,9,12-pentasila-1,6,8,13-tetraoxaspiro[6.6]tridecane (20%). It had the following spectral properties: ^1H NMR δ 0.733 (s, 8 H), 0.085 (s, 24 H); ^{13}C NMR δ 10.44 (8 C), -0.560 (4 C); IR ν 1100 cm^{-1}. Anal. Calcd for $C_{12}H_{32}Si_5O_4$: C, 37.85; H, 8.47. Found: C, 38.07; H, 8.60.

Copyrolysis of I and Hexaethylcyclotrisiloxane. I (2 g, 10.2 mmol) and hexaethylcyclotrisiloxane (6.25 g, 20.2 mmol) were copyrolyzed as above. The products were isoprene, recovered hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, IIIb (14%), and IVb (8%).

IIIb had the following spectra properties: ^1H NMR δ 1.08–0.906 (m, 36 H), 0.699–0.601 (m, 24 H); ^{13}C NMR δ 7.885 (12 C), 6.477 (12 C); IR ν 1100 cm^{-1} (SiO); mass spectrum, m/e (relative intensity) 643 (100, M – 29$^+$), 499 (94), 439 (15), 276 (50). High-resolution mass spectrum: calcd for $C_{22}H_{55}Si_7O_8$, 643.2282; found, 643.2285. Anal. Calcd for $C_{24}H_{60}Si_7O_8$: C, 42.81; H, 8.98. Found: C, 42.61; H, 8.75.

IVb had the following spectral properties: ^1H NMR (acetone-d_6) δ 0.897–0.985 (m, 36 H), 0.474–0.586 (m, 24 H); ^{13}C NMR (acetone-d_6) δ 7.854, 7.692, 7.529, 6.473; IR ν 1090 cm^{-1} (SiO); mass spectrum (relative intensity), m/e 703 (100, M – 29$^+$), 643 (19), 559 (35), 499 (18). High-resolution mass spectrum of the (M – 29)$^+$ ion: calcd for $C_{22}H_{55}Si_8O_{10}$, 703.1950; found, 703.1953.

Copyrolysis of I and 1,3,5-Trimethyl-1,3,5-trivinylcyclotrisiloxane (VI). I (2 g, 10.0 mmol) and VI (8.0 g, 30.6 mmol)

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were copyrolyzed as above. The products were isoprene, recovered VI, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, IIIc (15%), and IVc (8%).

IIIc is a liquid. It had the following spectral properties: ^1H NMR δ 6.01–5.84 (m, CH=CH$_2$), 0.248–0.154 (m, CH$_3$); ^{13}C NMR δ 136.13, 135.82, 133.65, 133.45, 133.36 (vinyl carbons), –0.976, –1.106 (methyl carbons); IR ν 1100, 1040 (SiO), 1600 cm^{-1} (C=C); mass spectrum, m/e (relative intensities) 576 (30, M$^+\cdot$), 561 (100, M – 15$^+$), 549 (35), 449 (43), 437 (72). High-resolution mass spectrum of the M$^+\cdot$ ion: calcd for C$_{18}$H$_{36}$Si$_7$O$_8$, 576.0795; found, 576.0790. Anal. Calcd for C$_{18}$H$_{36}$Si$_7$O$_8$: C, 37.47; H, 6.29. Found: C, 37.44; H, 6.24.

IVc is a liquid which has the following spectral properties: ^1H NMR δ 6.065–5.88 (m, CH=CH$_2$), 0.26–0.16 (m, CH$_3$); ^{13}C NMR δ 135.78, 135.09, 134.60, 134.49, 134.23, 133.64, 133.46 (vinyl carbons), –0.96, –1.17, –1.44 (methyl carbons); IR ν 1100, 1040 cm^{-1} (SiO), 1600 cm^{-1} (C=C). Anal. Calcd for C$_{18}$H$_{36}$Si$_8$O$_{10}$: C, 33.93; H, 5.68. Found: C, 33.83; H, 5.38.

Preparation and C–N Cleavage Reactions of Bis[(dimethylphosphino)ethane]ruthenium Isocyanide Complexes

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Received January 20, 1986

The thermal reaction of (DMPE)$_2$Ru(naphthyl)H [DMPE = bis(dimethylphosphino)ethane] with isocyanides is described. Thermolysis in the presence of excess neopentyl isocyanide at 60 °C in benzene solution results in the formation of the simple substitution complex (DMPE)$_2$Ru(CNCH$_2$CMe$_3$) plus naphthalene. Thermolysis in the presence of excess phenyl isocyanide results in the formation of the unusual monodentate DMPE complex Ru(η^2-DMPE)(η^1-DMPE)(CNPh)$_2$. Continued heating ultimately forms Ru(DMPE)$_2$(CNPh) plus phenyl isocyanide polymer. Thermolysis with ethyl isocyanide leads to the formation of Ru(DMPE)$_2$(CNEt). Thermolysis in the presence of *tert*-butyl isocyanide produces two organometallic products, Ru(DMPE)$_2$(CN)$_2$ and Ru(DMPE)$_2$(CN)H, plus four organic products, trimethylacetonitrile, naphthalene, isobutylene, and isobutane. A mechanism is suggested for the formation of these rearrangement and C–N bond cleavage products. The dicyanide molecule Ru(DMPE)$_2$(CN)$_2$ was found to crystallize in the orthorhombic space group *Pccn* with a = 9.2842 (14) Å, b = 14.1091 (30) Å, c = 16.3641 (50) Å, V = 2143.6 (1.4) Å^3, and Z = 4.

Introduction

Isocyanide complexes have been known for many years as isoelectronic analogues of carbon monoxide complexes. The chemistry of the coordinated isocyanide ligand, however, shows some distinct differences from that of CO with regard to reactions at both the metal–carbon linkage and the heteroatom. For example, the isocyanide ligand is generally believed to insert more readily into metal–alkyl bonds than is CO and often undergoes multiple insertions.[1] Isocyanides have also been observed to insert into the metal–hydrogen bond to generate formamyls.[2] More recently, isocyanide ligands have been observed to couple, forming new carbon–carbon bonds.[3]

The exclusive chemistry of the isocyanide ligand also extends to the chemistry of the C–N single bond. Isocyanide ligands can be formed by alkylation of a cyanide ligand.[4] Similarly, cyanide and hydride complexes have been formed by decomposition reactions of the coordinated

isocyanide, usually in cationic complexes, although the true nature of these interconversions were never elucidated.[5]

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