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SYNTHESIS AND PROPERTIES OF BIFUNCTIONAL DECAORGANYLCYCLOHEXASILOXANES

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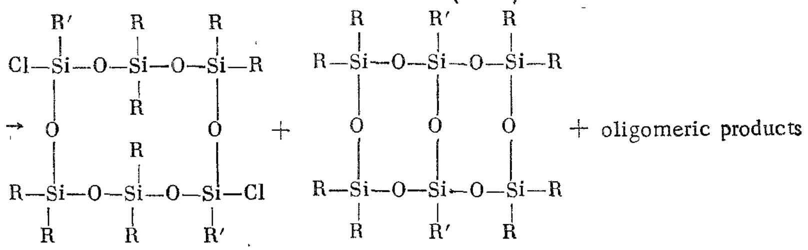
We have previously reported the synthesis of bifunctional organylcyclotetrasiloxanes [1] and polymethylcyclopenta-(and hexa-)siloxanes [2].

We here continue a study of the condensation of substituted trichlorosilanes with 1,3-dihydroxytetramethyldisiloxane (DHTMDS) and 1,3-dihydroxytetraphenyldisiloxane (DHTPDS), with the object of obtaining 2,8-dichlorodecaorganylcyclohexasiloxanes. The results confirm a previous report [3], according to which the one-step synthesis affords, in addition to chloropentaorganylcyclotrisiloxanes and 2,8-dichlorodecaorganylcyclosiloxanes, 1,1,7,7-tetrachlorohexaorganyltetrasiloxanes and 2,4-dichloro-2,4,6,6,8,8-hexaorganyltetrasiloxanes, and the reaction of DHTPDS with methyltrichlorosilane gives a structural isomer of 2,8-dichlorodecaorganylcyclohexasiloxane.

With these considerations in mind, the synthesis of 2,8-dichlorodecaorganylcyclohexasiloxanes was carried out by a two-step condensation, as follows:

$$2R'SiCl_3 + HO(R_2SiO)_2H \rightarrow \underset{(Ia\text{-}c)}{Cl_2(R')SiO(R_2SiO)_2Si(R')Cl_2} + HO(R_2SiO)_2H \rightarrow$$



(IIa—c)

(IIIa —c)

where

R = R' = Me (Ia); R = Me, R' = Ph (Ib); R = Ph, R' = Me (Ic); R = R' = Me (IIa); R = Me, R' = Ph (IIb); R = Ph, Me (IIc); R = R' = Me (IIIa); R = Me, R' = Ph (IIIb); R = Ph, R' = Me (IIIc).

Although the first step proceeds specifically to give (I) in 58-87% yields, the second step gives 22-48% of (II) accompanied by polysubstituted cyclosiloxanes which do not contain reactive groups, as shown by PMR and mass spectroscopy. The yields of compounds devoid of functional groups, according to GLC, vary from 3 to 20%. Fractionation of the products of the reaction of methyltrichlorosilane with DHTMDS gave chromatographically pure (IIa) (Table 1), whereas fractionation of the products of the reaction of phenyltrichlorosilane with DHTMDS gave (IIb) invariably accompanied by 3-10% of impurities.

Reaction of 1,1,7,7-tetrachloro-1,7-dimethyl-3,3,5,5-tetraphenyltetrasiloxane with DHTPDS gave a mixture which crystallized readily, recrystallization from heptane giving (IIc) (Table 1). From its PMR and mass spectra and its elemental analysis, (IIc) was identified as 2,8-di-

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TABLE 1. Characteristics of Bifunctional Organylcyclohexasiloxanes (IIa-c) and (VIa-c)

Compound		Yield, %	bp, ℃ (p, torr), or mp, ℃	Empirical formula	Found/calculated				$\frac{M^+-CH_3}{\text{mol. wt.}}$
					C	H	Si	Cl/OH	
(IIa)	R=R′=CH_3 X=Cl	50,6	55–57 (1–2)	$C_{10}H_{30}Si_6Cl_2O_6$	$\frac{25,22}{24,72}$	$\frac{6,32}{6,22}$	$\frac{34,41}{34,69}$	$\frac{14,67}{14,80}$	$\frac{469}{485,7}$
cis -(IIb)	R=CH_3 R′=C_6H_5 X=Cl	12,5	175–177 (1–1,5)	$C_{20}H_{34}Si_6Cl_2O_6$	$\frac{39,85}{39,39}$	$\frac{5,47}{5,62}$	$\frac{27,99}{27,63}$	$\frac{10,79}{11,62}$	$\frac{593}{609,8}$
trans -(IIb)	R=CH_3 R′=C_6H_5 X=Cl	14,5	89–91	$C_{20}H_{34}Si_6Cl_2O_6$	$\frac{39,85}{39,39}$	$\frac{5,77}{5,62}$	$\frac{27,40}{27,63}$	$\frac{10,97}{11,62}$	$\frac{593}{609,8}$
(IIc)	R=C_6H_5, R′=CH_3 X=Cl	27,2	315–317 ($2\cdot10^{-2}$)	$C_{50}H_{16}Si_6Cl_2O_6$	$\frac{61,81}{61,14}$	$\frac{4,92}{4,72}$	$\frac{17,61}{17,14}$	$\frac{6,17}{7,22}$	$\frac{965}{982,1}$
cis-(VIa)	R=R′=CH_3 X=OH	48,0	47–48	$C_{10}H_{32}Si_6O_8$	$\frac{27,24}{26,75}$	$\frac{7,36}{7,18}$	$\frac{37,49}{37,55}$	$\frac{7,58}{7,58}$	$\frac{-}{448,9}$
trans -(VIa)	R=R′=CH_3 X=OH	44,7	97–99	$C_{10}H_{32}Si_6O_8$	$\frac{27,48}{26,75}$	$\frac{7,40}{7,18}$	$\frac{37,07}{37,55}$	$\frac{7,70}{7,58}$	$\frac{-}{448,9}$
cis -(VIb)	R=CH_3 R′=C_6H_5 X=OH	89,0	87–88	$C_{20}H_{36}Si_6O_8$	$\frac{42,20}{41,92}$	$\frac{6,45}{6,33}$	$\frac{29,89}{29,41}$	$\frac{5,61}{5,93}$	$\frac{-}{572,9}$
trans-(VIb)	R=CH_3 R′=C_6H_5 X=OH	90,0	72–73	$C_{20}H_{36}Si_6O_8$	$\frac{42,37}{41,92}$	$\frac{6,51}{6,33}$	$\frac{29,73}{29,41}$	$\frac{5,75}{5,93}$	$\frac{-}{572,9}$
trans-(VIc)	R=C_6H_5 R′=CH_3 X=OH	77,0	217–219	$C_{50}H_{48}Si_6O_8$	$\frac{63,43}{63,53}$	$\frac{5,14}{5,12}$	$\frac{16,66}{17,81}$	$\frac{3,41}{3,60}$	$\frac{-}{945,2}$

TABLE 2. Characteristics of Decaorganylbicyclo[5.5.1]hexasiloxanes

Compound	Yield, %	mp, °C	Empirical formula	Found/calculated			M^+-CH_3	PMR spectrum, δCH_3, ppm
				C	H	Si	mol. wt.	
(IIIa)	28,0	48–49	$C_{10}H_{30}Si_6O_7$	28,10 27,88	7,08 7,02	38,45 39,11	415 430,8	0,089, 0,094, 0,116
(IIIb)	48,0	61–62	$C_{20}H_{34}Si_6O_7$	42,95 43,21	6,15 6,16	30,26 30,37	540 557,8	0,080, 0,210
(IIIc)	50,0	189–191	$C_{50}H_{46}Si_6O_7$	63,45 64,76	4,85 5,00	17,09 18,16	911 927,2	0,135

chloro-2,8-dimethyl-4,4,6,6,10,10,12,12-octaphenylcyclohexasiloxane, with a cis–trans ratio of 50:50. Distillation of (IIc) gave 80% of a compound with bp 315-317°C (1.10^{-2} torr), mp 209-211°C, cis–trans isomer ratio 30:70.

In the IR spectrum of (IIa-c), obtained in CCl_4 solution or KBr disks, absorption was present in the 1000-1100 cm^{-1} region (ν_{as} asymmetrical stretching vibrations of the Si–O–Si bond) at 1060-1070 cm^{-1} (IIa) and 108-1105 cm^{-1} (IIb and c). The spectrum of (IIc) also contained in this region very weak absorption bands at 1000 and 1032 cm^{-1}, and the IR spectra of (IIa-c) showed absorption characteristic of the $Si-CH_3$, $Si-C_6H_5$, and Si–Cl bonds at 1265, 1135, and 470 cm^{-1}, respectively.

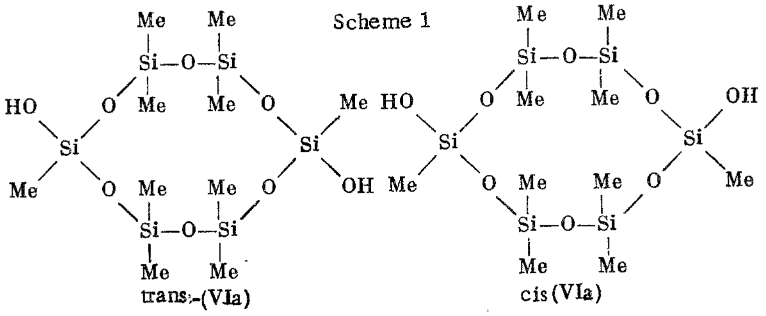
However, in [4] the absorption in the IR spectra of bifunctional dichloroorganocyclosiloxanes at 1025-1030 and 1045-1050 cm^{-1} was attributed to ν_{as} Si–O–Si asymmetrical stretching vibrations. In contrast, it was earlier reported that when the Si atom carries more than one phenyl substituent, then this absorption is stronger, appearing as a doublet at lower frequencies [5]. In order to assign correctly the absorption in the 1000-1100 cm^{-1} region, we synthesized some straight-chain and cyclic siloxanes containing diphenyl subtituents in the diorganylsiloxane moieties. Comparison of the IR spectra showed that (Ic), in addition to doublet splitting at 1030 and 1050 cm^{-1}, gave a band at 1065-1070 cm^{-1}. Three bands, at 1020, 1042, and 1070 cm^{-1}, are seen for bis(methyltetraphenylcyclotrisiloxy) oxide, the band at 1020 cm^{-1} being the strongest. In the IR spectra of 2,6-dichloro(and dihydroxy)-2,6-dimethyl-4,4,8,8-tetraphenylcyclotetrasiloxanes [1], absorption at 1040-1050 cm^{-1} is no longer present, a new band appearing at 1080-1090 cm^{-1}, whereas in the spectrum of dodecamethylcyclohexasiloxane the Si–O–Si ν_{as} absorption is seen at 1070-1075 cm^{-1}. Therefore, the assignment of the absorption at 1080-1100 cm^{-1} to Si–O–Si ν_{as} for (IIa-c) is evidently fully justified.

The PMR and mass spectra of (IIa-c) show the absence of methyl groups on the Si atoms carrying the two chlorine atoms and those in the methylsilsesquioxane groups. It may therefore be asserted that the compounds obtained (IIa-c) are 2,8-dichlorodecaorganylcyclohexasiloxanes.

Partial hydrolysis of (IIb) with a trans:cis isomer ratio of 60:40 gave the trans isomer of (IIb) and a compound which, from its PMR, IR, and mass spectra, was identified as 1,7-diphenyl-3,3,5,5,9,9,11,11-octamethylbicyclo[5.5.1]hexasiloxane (IIIb) (Table 2). To confirm the structure of (IIb) and to determine the isomer ratio, (IIb) was reacted with DHTMDS. There were obtained (IV) and (V), showing that the reaction follows both intramolecular and intermolecular routes. A compound (IIIb) was also obtained which was identified by its GLC, PMR, and mass spectra (see Scheme 2).

The formation of (IIIb) in this reaction is unexpected. For this reason, a further examination of the possibility of separating the cis and trans isomers of (II) was carried out in order to assess the relative reactivities of their functional groups.

Scheme 1



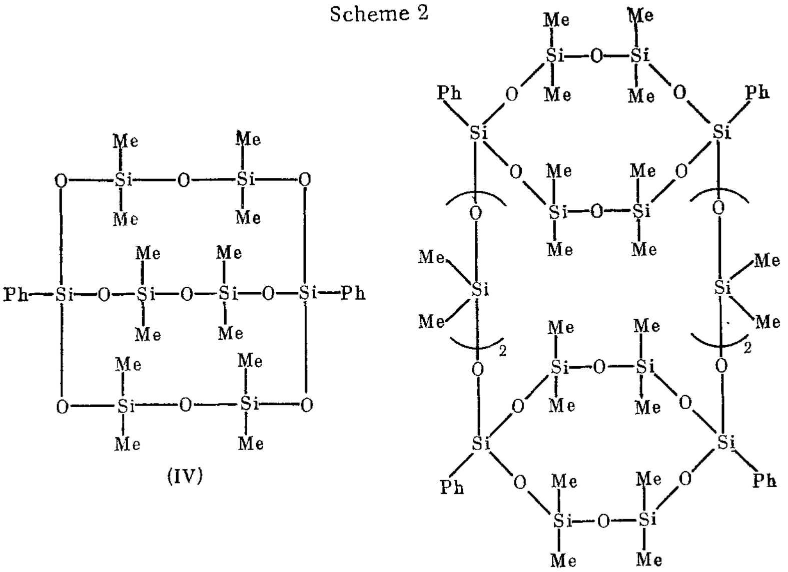
trans-(VIa) cis(VIa)

TABLE 3. Properties of 1,1,7,7,-Tetrachlorohexaorganyltetra-

Compound	Yield, %	bp, °C (p, torr)	n_D^{25}
$Cl_2(Me)SiO(Me_2SiO)_2Si(Me)Cl_2$ (Ia) *	76,5	225–227 (760)	1,4130
$Cl_2(Ph)SiO(Me_2SiO)_2Si(Ph)Cl_2$ (Ib)	58,0	140–142 ($2\cdot10^{-2}$)	1,4980
$Cl_2(Me)SiO(Ph_2SiO)_2Si(Me)Cl_2$ (Ic)	87,5	220–225 ($5\cdot10^{-2}$)	

*The data for (Ia) have been reported previously [2].

Scheme 2



(IV)

(V)

In the case of (IIa), it was found to be possible to enrich the trans isomer to 70-75%. However, hydrolysis of (IIa) in the presence of an HCl acceptor, and recrystallization from heptane, gave the chromatographically pure cis and trans isomers of (VIa) (see Scheme 1).

On storage, cis-(VIa) was converted into (IIIa), which was purified by sublimination and identified by its PMR, IR, and mass spectra as 1,3,3,5,5,7,9,9,11,11-decamethylbicyclo[5.5.1]-hexasiloxane (Table 2). Heating a 50% benzene solution of trans-(VIa) at 80°C for 16 h gave 18% of (IIIa).

The separation of the cis and trans isomers of (IIb) was effected by cooling its solution in dry heptane. The crystalline product with mp 89-91°C was the trans isomer, and the liquid, the cis isomer. Hydrolysis of the chromatographically pure cis and trans isomers of (IIb) afforded the corresponding cis- and trans-dihydroxy derivatives of the decaorganylcyclohexasiloxane (VIb). There was no inversion of configuration on hydrolysis of the isomers. Storage of cis-(VIb) for 24 h resulted in the formation of crystals of a new form. Sublimination of these crystals *in vacuo* gave a compound, mp 61-62°C, identified by its PMR, IR, and mass spectra as 1,7-diphenyl-3,3,5,5,9,9,11,11-octamethylbicyclo[5.5.1]hexasiloxane (IIIb). Since the (IIIb) isolated had constants which differed from those previously reported [6], x-ray structural analysis was employed to establish its structure [7]. Compound (IIIb) was thereby shown to be cis-1,7-diphenyl-3,3,5,5,9,9,11,11-octamethylbicyclo[5.5.1]hexasiloxane, with the phenyl subtituents situated on the same side of the plane of the organylcyclotetrasiloxane.

In contrast to the extremely facile intramolecular cyclization of the cis-dihydroxy compound (VIb), when the trans-dihydroxy derivitive of (VIb) was heated at 110°C in toluene for 30 h, the trans isomer was recovered in 85% yield. There were no new PMR signals in the spectrum of the reaction mixture following heating.

siloxanes (Ia-c)

Empirical formula	Found/Calculated, %				PMR spectrum, δ (CH_3), ppm
	C	H	Si	Cl	
$C_6H_{18}Si_4O_3Cl_4$					0,355, 0,910
$C_{16}H_{22}Si_4O_3Cl_4$	$\frac{37,35}{37,20}$	$\frac{4,22}{4,29}$	$\frac{21,34}{21,75}$	$\frac{27,34}{27,46}$	0,244
$C_{26}H_{26}Si_4O_3Cl_4$	$\frac{48,92}{48,75}$	$\frac{4,01}{4,09}$	$\frac{16,89}{17,53}$	$\frac{21,70}{22,14}$	0,54

Hydrolysis of (IIc) gave a crystalline solid, which on fractional crystallization from hot benzene gave trans-(VIb), mp 217-219°C, identified by its PMR and IR* spectra, and a compound with mp 189-191°C which did not contain hydroxyl groups and which was identified by its PMR, IR, and mass spectra and elemental analysis as 1,7-dimethyl-3,3,5,5,9,9,11,11-octamethylbicyclo[5.5.1]hexasiloxane (IIIc) (Table 2).

The formation of organocyclohexasiloxanes (III) from bifunctional organylcyclohexasiloxanes containing either methyl or phenyl groups attached to silicon atoms bearing functional groups appears to result from transannular interactions of the substituents at the 2 and 8-Si atoms. Although in cyclic alkanes of moderate ring size the hydrogen atoms situated on opposite sides of the ring are closest to each other in 9- to 11-membered rings, in the organylcyclosiloxanes interaction between the substituents on the Si atoms can occur only in rings containing an even number of atoms, i.e., in 10-, 12-, and 14-membered rings (organylcyclopenta, organylcyclohexa-, and organylcycloheptasiloxanes). In order to confirm the absence of a transannular effect in bifunctional hexaorganylcyclotetrasiloxanes, homocondensation of the pure cis and trans isomers of dihydroxyhexaorganyltetrasiloxanes under the same conditions as for dihydroxydecaorganylcyclohexasiloxanes was carried out. Workup of the reaction mixture gave the starting materials.

It is reasonable to suppose that intramolecular cyclization at the 2,8 positions in bifunctional organylcyclohexasiloxanes is facilitated by the considerable flexibility of the molecule, which is favorable for the approach of the 2,8-Si atoms and the neighboring O atoms, and the transformation into the organylbicyclohexasiloxane results in the formation of thermodynamically favored and stable compounds. A check on the approach of the 2- and 8-Si atoms in decaorganylcyclohexasiloxanes by conformational calculations [8] shows that in the cis-dihydroxy derivatives such an approach can occur readily up to distances corresponding to the formation of hydrogen bonds between the OH groups. These hydrogen bonds facilitate an even closer approach of the 2- and 8-Si atoms in the ring, and since the proton in the OH group of (VIb) is more acidic than that in (VIa), the greater reactivity of the OH group in the cis isomer is quite logical. In the trans derivatives, on the other hand, such an approach is energetically disfavored, and it increases with increasing size of the substituents on the 2- and 8-Si atoms.

EXPERIMENTAL

PMR spectra were obtained in CCl_4 solution on a Hitachi–Perkin–Elmer R-20 spectrometer (60 MHz), internal standard TMS. For same of the compounds, PMR and NMR spectra were obtained in $CCl_4 + CDCl_3$ solution on a Bruker 200SY spectrometer. The mass spectra of (IIa, b) and (IIIa, b) were obtained on an AEI-MS-30 (England) instrument using the DS-50 system for processing the data, and of (IIc) and (IIIc), on a Varian MAT-311A instrument, ionizing electron energy 70 eV, temperature of the direct introduction system 25 and 30°C, respectively.

1,1,7,7-Tetrachlorohexamethyltetrasiloxane (Ia). To 65.8 g (0.440 mole) of methyltrichlorosilane in 525 ml of dry ether was added with stirring and cooling to –5°C 34.5 g (0.206 mole) of DHTMDS and 41.0 g (0.440 mole) of aniline in 250 ml of dry ether, over 2 h. The solid was filtered off, and the solvent distilled off. Distillation of 77.2 g of the product gave 61.9 g (76.5%) of (Ia). Compounds (Ib) and (Ic) were obtained similarly. The properties of (Ia-c) are shown in Table 3.

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*Assignment of the cis and trans structures to (VIa-c) was carried out from the changes in absorption at 3300-3600 cm^{-1}, characteristic of ν_{OH} stretching vibrations in dilute solution [2].

2,8-Dichloro-2,8-diphenyl-4,4,6,6,10,10,12,12-Octamethylcyclohexasiloxane (IIb). To 300 ml of dry ether, with stirring and cooling at —5°C, were added simultaneously from two dropping funnels 55.5 g (0.107 mole) of (Ib) in 100 ml of dry ether and 17.9 g (0.107 mole) of DHTMS and 19.9 g (0.214 mole) of aniline in 100 ml of dry ether. After 2 h, the solid was filtered off, and the solvent removed. Distillation of 59.9 g of the product gave 31.2 g (47.9%) of (IIb), bp 182-184°C ($2\cdot10^{-2}$ torr), which from GLC and its PMR and mass spectra contained ∿3% of (IIIb) (Tables 1 and 2).

Recrystallization of 31.0 g from heptane with cooling gave 6.4 g of trans-(IIb), mp 89-91°C. On keeping, the mother liquors afforded a further 5.1 g of trans-(IIb), and distillation of the residue afforded 14.3 g (46%) of the liquid cis-(IIb). PMR spectrum (δ, ppm): trans-(IIb) 0.192 ($\mathrm{Me}^{4,6',10',12}$), 0.134 ($\mathrm{Me}^{4',6,10,12'}$); cis-(IIb) 0.267 ($\mathrm{Me}^{4,6,10,12}$), 0.069 ($\mathrm{Me}^{4',6',10',12'}$).

Compounds (IIa) and (IIc) were obtained similarly. PMR spectrum (δ, ppm): trans-(IIa) 0.428 ($\mathrm{Me}^{2',8}$), 0.174 ($\mathrm{Me}^{4,6',10',12}$), 0.140 ($\mathrm{Me}^{4',6,10,12'}$); cis-(IIa) 0.422 ($\mathrm{Me}^{2',8'}$), 0.192 ($\mathrm{Me}^{4,6,10,12}$), 0.129 ($\mathrm{Me}^{4',6',10',12'}$); trans-(IIc) 0.092 ($\mathrm{Me}^{2',8}$), cis-(IIc) 0.152 ($\mathrm{Me}^{2',8'}$).

Si^{29} NMR spectrum (δ, ppm): trans- and cis-(IIc) —44.33, —44.48 (SiMeCl), —45.19, —45.24 ($\mathrm{SiPh_2O}$).

Hydrolysis of trans-(IIb). To 30 ml of ether, 2 g of water, and 1.34 g (0.014 mole) of aniline was added slowly 4.40 g (0.007 mole) of trans-(IIb) in 20 ml of ether at 20°C. Two hours after the ether solution had been added, the solution was washed with water, and the solvent removed to give 3.7 g (89.6%) of residue, recrystallization of which from heptane gave 2.8 g of trans-(VIb), mp 72-73°C (Table 1). PMR spectrum (δ, ppm): trans-(VIb) 0.110 ($\mathrm{Me}^{4,6',10',12}$), 0.130 ($\mathrm{Me}^{4',6,10,12'}$).

Hydrolysis of cis(IIb). To 35 ml of ether, 3 g of water, and 0.76 g (0.008 mole) of aniline was added 2.5 g (0.004 mole) of cis-(IIb) in 15 ml of ether at 0°C. The ether solution was washed repeatedly with water, and the solvent removed to give 1.8 g of a viscous liquid. Crystallization gave acicular crystals, mp 87-88°C, identified as cis-(VIb). From the PMR spectrum, the ratio of cis-(VIb) to (IIIb) was 2:1 24 h after the reaction. PMR spectrum (δ, ppm): cis-(VIb) 0.078 ($\mathrm{Me}^{4,6,10,12}$), 0.115 ($\mathrm{Me}^{4',6',10',12'}$). Compounds (VIa) and (VIc) were obtained similarly. PMR spectra (δ, ppm): trans-(VIa) 0.136 ($\mathrm{Me}^{2',8}$), 0.119 and 0.128 ($\mathrm{Me_{rem}}$), 4.60 (OH); cis-(VIa) 0.071 ($\mathrm{Me}^{2',8'}$), 0.100 ($\mathrm{Me_{rem}}$), 5.71 (OH); trans-(VIc) —0.21 ($\mathrm{Me}^{2',8}$) cis-(VIc) 0.032 ($\mathrm{Me}^{2',8'}$).

1,7-Diphenyl-3,3,5,5,9,9,11,11,14,14,16,16-Dodecamethylbicyclo[5.5.1]octasiloxane. To 25 ml of dry ether was added with cooling at —10°C from two dropping funnels 14.2 g (0.023 mole) of (IIb) in 100 ml of dry ether and 2.58 g (0.015 mole) of DHTMDS, 3.11 g (0.031 mole) of triethylamine in 100 ml of ether over 1 h. After a further hour, the solid was filtered off, the ether solution washed repeatedly with water, and the solvent distilled off. Distillation of 9.6 g of product gave 2.4 g (25%) of (IV), bp 170-173°C ($6\cdot10^{-3}$ torr). PMR spectrum of (IV) (δ, ppm): 0.11 (Me), $\mathrm{M^+ - CH_3}$ = 687. Fractionation also gave 0.85 g (8.8%) of (V), bp 285-290°C ($6\cdot10^{-3}$ torr). Found: C 40.54; H 6.59; Si 31.88%; $\mathrm{H_{CH_3}:H_{C_6H_5}}$ = 3.34:1.00. $\mathrm{C_{48}H_{92}Si_{16}O_{18}}$. Calculated: C 40.99; H 6.59; Si 31.94%; $\mathrm{H_{CH_3}:H_{C_6H_5}}$ = 3.60:1.00.

Reaction of Methyltrichlorosilane with DHTPDS. To 100 ml of dry toluene was added with stirring 7.5 g (0.05 mole) of methyltrichlorosilane in 200 ml of toluene, and 20.7 g (0.05 mole) of DHTPDS and 7.9 g (0.10 mole) of pyridine in 200 ml of toluene. After 24 h, the solid was separated, and fractionation of 25.8 g of reaction product gave: 1) 15.2 g (62.3%) of 2-chloro-2-methyl-4,4,6,6-tetraphenylcyclotrisiloxane (VII), bp 208-210°C ($5\cdot10^{-3}$ torr). PMR spectrum of (VII) (δ, ppm): 0.625 (Me). IR spectrum (ν, $\mathrm{cm^{-1}}$): 1000 ($\mathrm{C_6H_5}$), 1025 (Si—O), 1042 ($\mathrm{C_6H_5}$), 1122 and 1135 ($\mathrm{Si{-}C_6H_5}$), 1270 ($\mathrm{Si{-}CH_3}$), 2) 4 g (16.4%) of a mixture of (IIc) and its structural isomer, bp 300-303°C ($3\cdot10^{-2}$ torr). Si^{29} NMR spectrum (δ, ppm): —18.05 ($\mathrm{SiMeCl_2}$), —34.56 ($\mathrm{SiPh_2O}$ ring), —44.96 ($\mathrm{SiPh_2}$, straight ch.), —56.48 ($\mathrm{SiPh_2}$ ring), —44.30 and —44.43 (SiMeCl) (IIb), —45.15; —45.19 ($\mathrm{SiPh_2}$) (IIc); IR spectrum (ν, $\mathrm{cm^{-1}}$): 1000 ($\mathrm{C_6H_5}$), 1023 (Si—O), 1042 ($\mathrm{C_6H_5}$), 1090 (Si—O), 1135 ($\mathrm{Si{-}C_6H_5}$), 1270 ($\mathrm{Si{-}CH_3}$).

Hydrolysis of (VII). To 0.36 ml (0.02 mole) of water and 1.86 g (0.02 mole) of aniline in 15 ml of ether was added 7.4 g (0.015 mole) of (VII) in 25 ml of ether. The solid was filtered off, the ether solution washed with water, the solvent removed, and the solid recrystallized from heptane to give 6.8 g (96.5%) of a compound mp 74-76°C. PMR spectrum (δ, ppm): 0.30 (Me); 3.71 (OH). IR spectrum (ν, $\mathrm{cm^{-1}}$): 1000 ($\mathrm{C_6H_5}$), 1020 (Si—O), 1042 ($\mathrm{C_6H_5}$), 1120 and 1135 ($\mathrm{Si{-}C_6H_5}$), 1270 ($\mathrm{Si{-}CH_3}$).

Bis(methyltetraphenylcyclotrisilyloxy) Oxide (VIII). To 7.12 g (0.014 mole) of (VII) in 25 ml of ether was added with stirring 6.80 g (0.014 mole) of 2-hydroxy-2-methyl-4,4,6,6-tetraphenylcyclotrisiloxane and 1.5 g (0.015 mole) of aniline in 30 ml of ether. The solid was separated, and the ether solution washed with water. Crystallization from alcohol gave 6.0 g (43.6%) of (VIII), mp 152-154°C. PMR spectrum (δ, ppm): 0.009 (Me): $M^+ - CH_3 = 911$. IR spectrum (ν, cm^{-1}): 1000 (C_6H_5), 1020 (Si—O), 1042 (C_6H_5), 1070 (Si—O), 1120 and 1135 (Si—C_6H_5), 1270 (Si—CH_3).

CONCLUSIONS

1. Stepwise condensation of organyltrichlorosilanes with 1,3-dihydroxytetraorganyldisiloxanes affords 2,8-dichlorodecaorganylcyclohexasiloxanes, the dihydroxy derivatives of which have been separated into the cis and trans isomers.

2. All the cis-2,8-dihydroxydecaorganylcyclohexasiloxanes, irrespective of the substituents on the silicon atoms either in the diorganylsiloxane moiety or bonded to the functional group, undergo intramolecular cyclization to give decaorganylbicyclo[5.5.1]hexasiloxanes as a result of transannular interaction of the substituents at silicon atoms 2 and 8.

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