SYNTHESIS AND NMR SPECTRA OF ORGANOBICYCLOSILOXANES

WITH AN ETHYLENE BRIDGE

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We have previously investigated the heterofunctional condensation reaction of alkylchlorosilanes with hydroxyl derivatives in order to obtain organocyclosiloxanes with a given configuration of functional groups in the ring (vinyl and SiH), from which it was possible to synthesize polymers of a defined structure and determine the effect of the monomer's structure on the properties of the oligomers and polymers [1, 2].

In the present work the heterofunctional condensation reaction has been used to obtain previously unknown organobicyclosiloxanes with an ethylene bridge between Si atoms. There is information in the literature about the isolation from the pyrolysis products of $[Me_2SiO]_2$. $[Ph_2SiO]_2$ cyclosiloxanes of a cyclotetrasiloxane with a phenylene bridge between Si atoms, the structure of which was proved only from its NMR, IR, and mass spectra [3]. We have investigated the reactions of bis(methyldichlorosilyl)ethane (A) with organosilicon dihydroxy derivatives





In the reaction of (A) with dihydroxysilanes, tetrasiloxane rings with an endo-ethylene bridge (I)-(V) are formed, while with dihydroxydisiloxanes a mixture of two isomeric products is formed - bis(pentaorganocyclotrisiloxanyl)ethanes (VII) and (IX) and organobicyclocarbosilox-anes (VI) and (VIII).

In the reaction of (A) with tetramethyldisiloxanediol, a fraction was isolated with bp 98-101°C (1 mm), which according to its NMR spectra consisted of a mixture of (VI) and (VII) in the ratio 3:1. On recrystallization of the mixture it was only possible to isolate (VI) in a pure form, the structure of which was confirmed by its NMR spectra and x-ray diffraction analysis [4]. Isomers (VIII) and (IX) were isolated in a pure form from the products of the reaction of (A) with tetraphenyldisiloxanediol, the initial ratio of isomers in the reaction products being 3:1. The properties of the compounds obtained are shown in Table 1.

In the IR spectra of (I)-(V) there is a displacement of the absorption bands due to deformation and symmetrical stretching vibrations of SiOSi to 620 and 1020-1030 cm⁻¹ respec-

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 657-662, March, 1988. Original article submitted April 10, 1986.

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Compound	Bp, °C (p, mm Hg)	Yiéld, %	Found Calculated		
	Mp, C		Si	C	H
Ma Mat Ma CH ₂ CH ₂ CH ₂ Ma Ma Ma	<u> </u>	23	<u>37.26</u> 38,17	<u>32,67</u> 32,61	<u>7,69</u> 7,47
(I) Vj Me Me CH ₂ CH ₂ Me Vi Me (II)	<u>96–100(10)</u> –	38	<u>34,14</u> 35,09	<u>37.74</u> 37,79	<u>6.90</u> 6,91
Et Et Me. CH ₂ CH ₂ Me Et Et (III)	<u>126–128 (10)</u> –	45	<u>31.70</u> <u>32,06</u>	41,15 41,10	<u>-8,72</u> 8,57
Ph Me Me CH ₂ CH ₂ Me Me Ph	<u>172-180(1)</u> _	30	<u>26.69</u> 26.85	51,64 51,65	<u>6,33</u> <u>6,21</u>
$M_{\theta} \xrightarrow{Ph} \xrightarrow{Ph} M_{\theta}$ $M_{\theta} \xrightarrow{CH_2CH_2} M_{\theta}$ $Ph \xrightarrow{Ph} Ph$ (V)	<u>290 (1)</u> 148–149	60	20.04 20.60	63,02 61,93	5.52 5,53
$Me_2 \qquad Me_2$ $Me \underbrace{CH_2CH_2}_{Me_2} Me$ $Me_2 \qquad Me_2$ Me_2	<u>98–102(1)</u> 49	38	<u>37.50</u> 38,01	<u>33.22</u> <u>32,53</u>	7.74 7,68
$Me_{2} \xrightarrow{Me_{2}} CH_{2}CH_{2} \xrightarrow{Me_{2}} Me_{2} \xrightarrow{Me_{2}} Me_{3}$	<u>98-102(1)</u> 41		For (VI	a mixture I) in the ra	of (VI) and atio 3:1

TABLE 1. Physicochemical Properties of Organocyclosiloxanes with endo-Ethylene Bridge between Si Atoms

TABLE 1 (continued)

Compound	Bp. C (p, mm Hg)	Yield th	Found Calculated		
Compound	Mp, °C	11010, 10	Si	C	. H
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	208	40	<u>17.63</u> 17,73	<u>65,80</u> 65,64	<u>5,49</u> 5,26
$\frac{\mathbf{p}\mathbf{h}_{s}}{\mathbf{p}\mathbf{h}_{s}} \underbrace{\frac{\mathbf{p}\mathbf{h}_{s}}{{\underset{\mathbf{M}e}}} \mathbf{p}\mathbf{h}_{s}}_{\mathbf{M}e} \underbrace{\mathbf{p}\mathbf{h}_{s}}_{\mathbf{M}e} \mathbf{p}\mathbf{h}_{s}}_{\mathbf{M}e}$	152-153	20	<u>17,32</u> 17,73	<u>65,12</u> 65,64	<u>5,77</u> <u>5,26</u>

TABLE 2. NMR Spectra of Organocyclosiloxanes with an Ethylene Bridge within the Ring

		ð ^{ss} si, ppm		Substituents at Si ¹		ð ¹³ C, ppm			
						substituents at Si ²			
Compo	und-	Si ¹	Si ²	СНз	$CH_3 \qquad CH_2 \qquad CH_4 \qquad CH_3 - CH_2 \\ CH_2 = CH \qquad CH_2 = CH$				
(I)	_	-13,21	-11,32	1,46	9,40	0,65 0,76			
(11)	a b	-12,13 -11,78	-25,41 $\{ -25,21$ $\{ -25,49$	-1,45 -1,45	9,53 9,39	-1,00 -0,83 -0.87	133,85; 135,92 133,17; 135,99 133,85: 136,42		
(III)	c	-11,39 -12,85	-25,30 -11,48	-1,45 -1,54	9,29 9,13	-0,73	133,30; 136,25 6,56; 7,04 6,56: 7,07		
(IV)	а	-11,91	-24,37	-140	9,58	-0,19		135,82; 133,46; 127,37; 129,44	
	Ъ	-11,25	$\left\{\begin{array}{c} -24.01 \\ -24.25 \end{array}\right.$	-140	9,39	-0,10		136.69; 132.98; 127,62; 129.68	
	с					0,00		137,39; 133,63; 127,76; 129,82	
(V)		-9,81	-37,74	-1,42	9,29			134,04; 133.82; 127,26; 129,59 135,18; 134.28; 127,64; 129,85	
(VI)		-22,02	-20,81	0,67	10,03	0,85 0,88			
(VII)		-9,70	-9,09	-1,32	7,98	0,88 0,94			
(VIII)		-19,29	-45,02	0,81	10,58			134,36; 134.14; 127,23; 129,42 135,53; 134,28; 127,48; 129,70	
(IX)		-6,26	-35,08	-1,33	7,79			134,60; 134,04; 127,56; 130,06	

tively. This may be due to the considerable strain in the rings of (I)-(V); the SiOSi angles in them are 134.4° [4], which is much less than in cyclotetrasiloxanes (142°) . For (VI) and (VIII) the bands due to the SiOSi bonds occur at 1100 and 520-540 cm⁻¹.

The structures of (I)-(IX) have been confirmed from their ¹³C and ²⁹Si NMR spectra (Table 2), For compounds of the type



with the same substituents at Si^2 , i.e., (I), (III), (V), (VI), and (VIII), in accordance with the molecular symmetry there are two signals in the ²⁹Si spectra, due to Si^1 and Si^2 , while in the ¹³C spectra there is one signal each from the two equivalent MeSi¹ and CH_2Si^1 groups as well as double signals from the carbons of the substituents at Si^2 . The substituents at the different Si^2 sites formidentical pairs; within the pairs the substituents have a different configuration relative to the skeleton of the bicyclic system.

In the spectra of the dumbbell-shaped compounds (VII) and (IX) the number of signals must be the same as for the compounds reported above. The substituents at Si² are distinguished according to their cis and trans configuration relative to the ethylene bridge. In the ¹³C spectrum of (VII) there are two signals from the methyl groups at Si², whereas for (IX) the differences in ¹³C chemical shifts from the nonequivalent phenyl groups occur within the width of the lines.

The difference between (VII), (IX) and the corresponding isomers (VI), (VIII) is most clearly shown in the ²⁹Si spectra. The atoms of the first two form part of a six-membered cyclosiloxane. The ²⁹Si chemical shifts in [5] match up with them for this size of ring (in the case of (IX) a correction is made for the effect of the phenyl groups [6]). For (VI) and (VIII) the ²⁹Si chemical shifts that occur are characteristic of rings of a larger size. The ²⁹Si chemical shifts that occur are characteristic of rings of a nine-membered cyclocarbosiloxane, occupies an intermediate position between the ²⁹Si chemical shifts of octamethylcyclotetrasiloxane (20.0 ppm) and decamethylcyclopentasiloxane (22.8 ppm). It should be noted that the value of the ²⁹Si chemical shift from the Me₂Si fragment in (I) (part of a seven-membered cyclocarbosiloxane) also occurs between the chemical shifts of the corresponding fragments in six- and eight-membered cyclosiloxanes. Thus, the dependence of the ²⁹Si chemical shifts on the size of the ring also extends to the cyclocarbosiloxane studied in this work. For compounds having two different substituents at Si², the following isomers are possible



where $R = CH_2 = CH$ (II) and Ph (IV).

In isomers (a) and (c) the Si² atoms and the substituents at Si² are mutually equivalent as a result of their symmetry. Therefore, one Si² signal in the ²⁹Si spectrum and one set of signals each from carbon in the substituents at Si² in the ¹³C spectrum must correspond to each isomer. In isomer (b) the two Si² atoms and the substituents of one type (Me or R) at Si² occupy sterically nonequivalent positions. Therefore isomer (b) must give two Si² signals in the ²⁹Si spectrum and double sets of signals from substituents in the ¹³C spectrum. In all three isomers Si¹ and the substituents at Si¹ (CH₂ and Me) have a symmetrical configuration relative to the plane passing through the Si² atoms and the center of the C-C bond in the ethylene bridge. Hence, one Si¹ signal (²⁹Si spectrum) and one signal each from CH₂ and Me (¹³C spectrum) must correspond to each isomer.

The experimental spectra of (II) and (IV) are consistent with a mixture of isomers. The ²⁹Si spectrum of (II) contains three Si¹ signals and four Si² signals, while the ¹³C spectrum has three Si¹CH₂ signals and four sets of signals from Si²Me and CH₂CH-, which corresponds to a mixture of three isomers. It was possible to assign the signals from the (b) isomer from the intensity ratio and the doubling of certain signals. It made up 48% of the mixture. The content of the other two isomers in the mixture was 16 and 36%. Isomers (a) and (c) have the same number of nonequivalent atoms and groups and it is not possible to identify their signals in the spectra from this criterion. It may be assumed that the steric interaction of the two vinyl groups inhibits the formation of isomer (c) when (II) is obtained. Therefore, isomer (c) can be assigned the signals of the isomer with content 16%.

The ²⁹Si and ¹³C spectra of (IV) are consistent with a mixture of only two isomers — (b) and one or the other of (a) and (c). Their content in the mixture was 55 and 45% respectively. Isomer (c) is likely to be absent as its formation is inhibited by even bulkier substituents than for (II). In the case of (IV) there is a greater degree of distortion in the ratio of isomers that would occur if the statistical factor were to play a determining role in the formation of the isomers, namely, (a):(b):(c) = 1:2:1. Reinforcement of this tendency in the case of (IV) compared to (II) supports the validity of the principle used to assign the signals of isomers (a) and (c).

EXPERIMENTAL

NMR spectra were recorded on a Bruker WP-200SY spectrometer at 50.31 MHz for ¹³C and 39.76 MHz for ²⁹Si. The samples were used as 5% solutions in CCl₄ with the addition of 10-15% C₆D₆, with TMS as internal standard. In order to obtain spectra with intensities that were not distorted, pulsed suppression at the proton frequencies (inversed decoupling) and long delay times (20-30 sec) were used. To assign the ²⁹Si signals in specific cases spectra were recorded without proton decoupling. In order to assign certain ¹³C signals the pulsed DEPT was used.

<u>1,3,3,5,7,7-Hexamethylbicyclo[3.2.3]tetrasila-2,4,6,8-oxane (I).</u> To a solution of 28.3 g (0.358 mole) of pyridine in 100 ml of ether at 0°C were added dropwise for 2 h 20.8 g (0.081 mole) of tetrachloride (A) in 300 ml of ether and 15.0 g (0.163 mole) of dimethyldihydroxysilane in 350 ml of ether. After separation of the precipitate the mixture was washed with water, dried over Na₂O₄, and fractionated. From 18 g of oil was obtained 6.8 g (28%) of (I) with bp 85°C (10 mm).

<u>1,3,5,7-Tetramethyl-3,7-divinylbicyclo[3.2.3]1,3,5,7-tetrasila-2,4,6,8-oxane (II).</u> To a solution of 40.0 g (0.505 mole) of pyridine in 150 ml of ether with agitation at 0°C were introduced 30.6 g (0.119 mole) of (A) in 300 ml of ether and 24.9 g (0.239 mole) of methylvinyldihydroxysilane in 300 ml of ether. The precipitate was filtered off, and the reaction mixture was washed with water, dried, and distilled. The fraction with bp 95-120°C (10 mm) containing 14 g (38%) of (II) was selected.

<u>1,5-Dimethyl-3,3,7,7-tetraethylbicyclo[3.2.3]1,3,5,7-tetrasila-2,4,6,8-oxane (III)</u>. To a solution of 23.1 g (0.293 mole) of pyridine in 200 ml of ether at 0°C were added dropwise 17.1 g (0.066 mole) of (A) in 200 ml of ether and 16.0 g (0.133 mole) of diethyldihydroxysilane in 200 ml of ether. The mixture was treated in the same way as indicated above. From 18 g of oil taken for distillation 9.2 g (45%) of (III) was obtained, with bp 110-120°C (3-4 mm).

<u>1,3,5,7-Tetramethyl-3,7-diphenylbicyclo[3.2.3]1,3,5,7-tetrasila-2,4,6,8-oxane (IV).</u> To a solution of 19.9 g (0.25 mole) of pyridine in 130 ml of ether at 0°C were introduced 14.7 g (57 mmoles) of (A) in 200 ml of ether and 15.4 g (0.114 mole) of methylphenyldihydroxysilane in 200 ml of ether. The mixture was treated in the same way as indicated above. From 19 g of oil was isolated 7.6 g (32%) of (IV), with bp 175-183°C (1 mm).

<u>1,5-Dimethyl-3,3,7,7-tetraphenylbicyclo[3.2.3]1,3,5,7-tetrasila-2,4,6,8-oxane (V).</u> To a solution of 12.8 g (0.05 mole) of (A) in 200 ml of ether at 10°C were added dropwise a solution of 23.3 g (0.1 mole) of diphenyldihydroxysilane in 300 ml of ether and 17.4 g (0.22 mole) of pyridine in 350 ml of ether. The mixture was treated in the same way as indicated above. After distillation, the fraction with bp 170-190°C (1 mm) was selected, containing 14.5 g (54%) of product (V), which was recrystallized from an ether-pentane (1:1) mixture, bp 148-149°C.

<u>1,3,3,5,5,7,9,9,11,11-Decamethylbicyclo[4.2.4]1,3,5,7,9,11-hexasila-2,6,8,10,12-oxane</u> (VI). To a solution of 17.4 g (0.22 mole) of pyridine in 100 ml of ether at 0°C were introduced 1.6 g (0.1 mole) of tetramethyldihydroxydisiloxane in 200 ml of ether and 12.8 g (5 mmoles) of (A) in 200 ml of ether. After separation of the precipitate and distillation of the solvent the mixture (17.5 g) was fractionated. The fraction with bp 98-102°C (1 mm) containing 8.5 g (38%) was selected, mp 38-45°C. According to NMR this was a mixture of (VI) and (VII) (3:1). Recrystallization from pentane gave 4.2 g of (VI); (VII) was not isolated in pure form.

<u>1,7-Dimethyl-3,3,5,5,9,9,11,11-octaphenylbicyclo[4.2.4]1,3,5,7,9,11-hexasila-2,6,8,12-oxane (VIII).</u> To a solution of 9.22 g (58 mmoles) of pyridine in 75 ml of ether at 0°C were introduced a solution of 6.75 g (26.4 mmoles) of (A) in 150 ml of ether and 21.9 g (52.8 mmoles) of tetraphenyldihydroxydisiloxane in 150 ml of ether. The mixture was filtered, washed with water, and dried, and the solvent was distilled off. From 19.4 g of crystalline product 8 g (40%) of (VIII) was isolated by recrystallization from benzene, with mp 208°C, and 4 g of (IX) with mp 152-153°C was obtained from a benzene-pentane (2:1) mixture. The initial reaction product mixture, according to NMR, contained (VIII) and (IX) in the ratio 3:1.

CONCLUSIONS

The heterofunctional condensation reaction gave for the first time organocyclosiloxanes with an endo-ethylene bridge between Si atoms; their structures were confirmed by ²⁹Si and ¹³C NMR spectroscopy.

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AMMONOLYSIS AND AMINOLYSIS OF ORGANOCHLOROSILANES

WITH THE TRICYCLODECENYL RADICAL AT THE SILICON ATOM

UDC 542,958,3:547.1'128

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The reactions of organochlorosilanes, containing tricyclodecenyl groups at the Si atom, with NH₃, amines, and hexamethyldisilazane were studied in the present work. The initial organochlorosilanes were synthesized according to [1, 2].

$$\bigcirc + R_2 R'SiH \rightarrow C_{10}H_{13}SiR_2R'$$

where R = Me, R' = Cl; R = Cl, R' = Me.

The ammonolysis of tricyclo $[5.2.1.0^{2,6}]$ -dec-4-en-8-yldimethylchlorosilane (TDMCS) with dry NH₃ in benzene and the aminolysis with diethylamine by boiling in benzene give high yields (86-88%) of the aminosilanes (I) and (II).

 $C_{10}H_{13}SiMe_{2}CI \longrightarrow \begin{bmatrix} NH_{3} & C_{10}H_{13}SiMe_{2}NH_{2} \\ -NH_{4}CI & (I) \\ Et_{7}NH & (I) \\ -Et_{2}NH \cdot HCI & (II) \end{bmatrix}$

The absence of secondary conversions is explained by the shielding effect of the bulky substituent at the Si atom. The ammonolysis of tricyclo[$5.2.1.0.^{2,6}$]-dec-4-en-8-ylmethyldi-chlorosilane (TMDCS) under the conditions indicated above led to the isolation, by fractionation, of 1,3-diamino-1,3-bis(methyltricyclo[$5.2.1.0^{2,6}$]-dec-4-en-8-yl)disilazane (III) and 1,3,5-tris(tricyclo[$5.2.1.0^{2,6}$]-dec-4-en-8-yl)-1,3,5-trimethylcyclotrisilazane (IV).

$$nC_{10}H_{13}SiMeCl_2 + nNH_3 \xrightarrow{-NH_4Cl} [C_{10}H_{13}SiMe(NH_2)]_2NH + [C_{10}H_{13}SiMeNH]_3$$
(III) (IV)

The trans-silylation of TMDCS with hexamethyldisilazane at 70°C will give the product of the partial silylation – tricyclo- $[5.2.1.0^2, ^6]$ -dec-4-en-8-yl-(trimethylsilylamino)chloro-silane (V) – due to the significant steric hindrance of the bulky substituent at the Si atom.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 663-665, March, 1988. Original article submitted October 27, 1986.