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SYNTHESIS OF ORGANOBICYCLOSILOXANES WITH CARBOSILOXANE AND CARBOSILANE GROUPS BETWEEN THE RINGS

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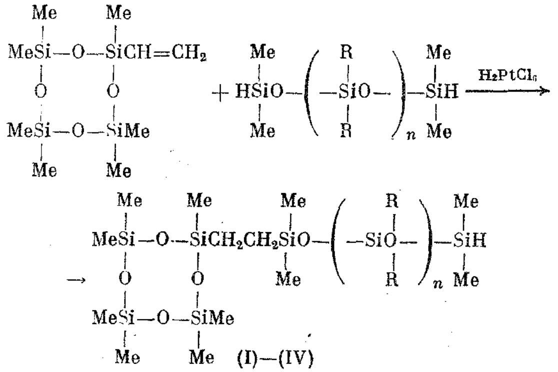
We have previously obtained bicyclocarbosiloxanes and bicyclocarbosilanes containing tri- or tetrasiloxane rings [1, 2]. It was of interest to synthesize bicyclocarbosiloxanes and bicyclocarbosilanes containing both six- and seven-membered siloxane rings, in order to examine their polymerization.

The synthesis of these organobicyclosiloxane groups between the rings was carried out stepwise. First, the monoaddition compounds were obtained by hydrosilylation of heptamethylvinylcyclotetrasiloxane with α-ω-dihydroorganosiloxanes in the presence of H_2PtCl_6, molar ratio of reactants 1:1.



(I)—(IV)

R = Me; $n = 0$ (I); R = Me; $n = 1$ (II); R = Me; $n = 2$ (III); R = Ph; $n = 1$ (IV).

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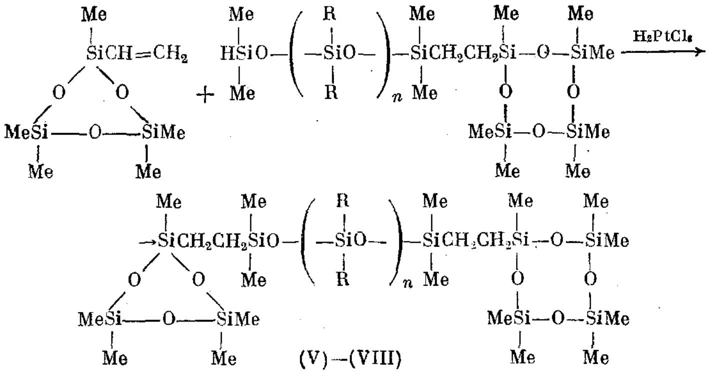
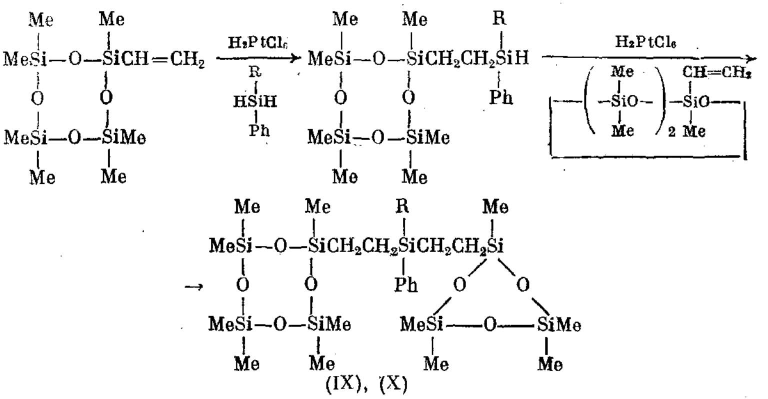
Next, hydrosilylation of pentamethylvinylcyclotrisiloxane with the compounds obtained (I-IV) afforded the bicyclocarbosiloxanes (V-VIII)



(V)-(VIII)

R = Me; $n = 0$ (V); R = Me; $n = 1$ (VI); R = Me, $n = 2$ (VII); R = Ph; $n = 1$ (VIII)

Bicyclocarbosilanes were also obtained by hydrosilylation, as follows*



(IX), (X)

R = Me (IX); Ph (X).

The IR spectra of (V)-(X) show strong absorption at 1080 and 1020 cm^{-1} for the stretching vibrations of the Si–O bond in organocyclotetra- and organosilotrisiloxanes respectively. The spectra of (I)-(V) show weak absorption of 2890-2880 cm^{-1}, due to symmetrical stretching vibrations of the methylene CH group, which are absent in the spectra of the starting materials. Furthermore, absorption at 1140 cm^{-1} is seen in compounds (I)-(III) and (V)-(VII), assigned to fan vibrations of the CH_2 groups in the $SiCH_2CH_2Si$ grouping [3]. These findings show that hydrosiloxanes add to the β-carbon of the ring vinyl group. Absorption at 1140 cm^{-1} in the spectra of (IV) and (VIII)-(X) is obscured by absorption at 1125 cm^{-1} due to the SiPh bond.

The PMR spectra of (I)-(X) show signals at 0-0.25 ppm for the SiMe groups, and at 0.44-0.48 ppm for the $SiCH_2CH_2Si$ groups. In addition, the spectra of (I)-(IV) show signals at 4.2-4.7 ppm for the SiH groups, and in (IV) and (VIII)-(X) signals at 7.0-7.5 ppm for the Ph protons. The occurrence of all these signals, and the ratios of the integral intensities of the Me, CH_2CH_2. Ph and H protons for the compounds are close to the values calculated for compounds with structural formulas (I)-(X). The physicochemical properties and elemental analyses for the compounds obtained are given in Table 1.

Chromatograms of the monoaddition compounds (I)-(III) with methyl groups attached to the Si atom show two peaks, and the diaddition products (V)-(VII) three peaks. The occurrence of more than one peak may be rationalized by assuming that hydrosiloxanes add to some extent to the α-carbon atom in addition to the β-carbon of the ring vinyl groups. This would afford two and three isomers respectively in these compounds. To confirm this suggestion, an analogous disiloxane containing two pentamethylcyclotrisiloxanylethyl groups was subjected to separation, together with the compound obtained by hydride addition of 1,3-dihydrotetramethyldisiloxane to pentamethylvinylcyclotrisiloxane, the ratio of components being 1:2 [1]. This compound was chosen for study for the reason that, according to GLC, it contained the greatest amount (34%) of a compound corresponding to the second peak on the chromatogram. We assign the following structure to this compound

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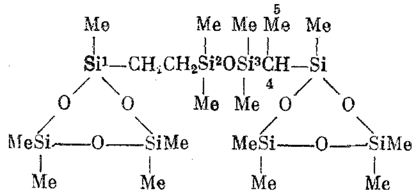
* The physicochemical properties of the monoaddition products have been reported [2].

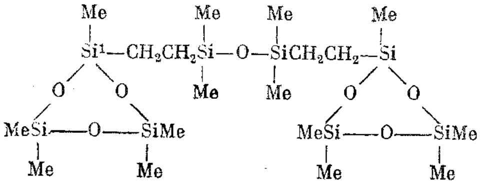
TABLE 1

Compound	Yield, %	Bp, °C (2 mm Hg)	d_4^{20}	n_D^{20}	MR, found/calculated	Empirical formula	Found/Calculated, %		
							C	H	Si
(I)	68,0	105–108	0,9529	1,4155	116,54/117,77	$C_{13}H_{38}Si_6O_5$	34,97/35,25	8,66/8,65	36,69/38,04
(II)	69,5	132–135	0,9561	1,4168	135,91/136,57	$C_{15}H_{44}Si_7O_6$	35,29/34.84	8,47/8,58	37,38/38,02
(III)	61,8	148–150	0,9602	1,4172	154,91/155,30	$C_{17}H_{48}Si_8O_7$	33,68/34,55	8,21/8,52	37,55/38,00
(IV)	60,6	185–188	1,0185	1,4707	175,89/176,21	$C_{25}H_{48}Si_7O_6$	47,34/46,83	7,60/7,54	30,32/30,66
(V)	74,9	172–175	0,9845	1,4248	175,86/176,40	$C_{20}H_{56}Si_9O_8$	35,22/35,46	8,29/8,33	37,57/37,31
(VI)	71,2	188–192	0,9816	1,4217	194,45/195,20	$C_{22}H_{62}Si_{10}O_9$	35,37/35,16	8,17/8,31	36,81/36,78
(VII)	72,8	207–210	0,9802	1,4200	213,17/214,00	$C_{24}H_{66}Si_{11}O_{10}$	35,15/34,91	8,17/8,29	36,87/37,41
(VIII)	69,3	235–238	1,0298	1,4632	234,29/234,84	$C_{32}H_{66}Si_{10}O_9$	43,88/43,89	7,64/7,60	31.85/32,07
(IX)	72,4	185–187	1,0159	1,4582	176,90/177,42	$C_{23}H_{52}Si_8O_7$	41,87/41,52	7,80/7,88	33,69/33,77
(X)	73,1	220–223	1,0514	1,4831	197,58/197,24	$C_{28}H_{54}Si_8O_7$	46,97/46,23	7,53/7,48	30,26/30,88



(XI) (β, α-position)

and to the compound corresponding to the first peak (63%), the structure



(XII) (β, β-position)

The compound corresponding to the third peak on the chromatogram (3%) could not be isolated in the pure state.

The PMR spectrum of (XII) in $CDCl_3$ consisted of signals for the CH_2CH_2 protons (δ 0.48 ppm), $Me_2SiOSiMe_2$ (δ, 0.44 ppm), Si^1Me (δ 0.146 ppm), and the remaining methyl groups of the cyclotrisiloxanes (δ 0.170 ppm). The ratios of the integral intensities were in agreement with the assigned structure. The spectrum of (XI) in CCl_4 showed signals for the protons of the CH_2CH_2 group (δ 0.44 ppm), a doublet for Me^5 (δ 1.04 ppm), and a quartet for CH (δ −0.05 ppm, $J_{CH_3CH} = 7.7$ Hz). The spectrum of the Si^1Me protons was more complex than in (XII), since in this molecule there is an asymmetric center at C^4, the presence of which renders all the SiMe groups nonequivalent, but in the event it apparently affects only its immediate environment, the left-hand half of the molecule being unaffected. This follows from the fact that the H atoms of the CH_2CH_2 group do not display nonequivalence. On the basis of the above, and taking into account the values of the chemical shifts in the spectrum of (XII), together with the ratios of the intensities in the spectrum of (XI), the following assignments can be made:

$\delta Si^2Me_2 = 0.047$ ppm, $\delta Si^3Me = 0.078$ ppm, $\delta Si^3Me = 0.89$ ppm and $\delta Si^1Me = 0.103$ ppm. The signals with δ = 0.122 and 0.126 ppm correspond to the methyl groups of the cyclotrisiloxane moieties, except for Si^1Me, the ratio of intensities being ~4:5. Hence, the PMR data fully confirm structures (XI) and (XII).

Since the chromatograms of the bicyclic compounds obtained are analogous to that of bicyclocarbosiloxane, it may be concluded that the first peak corresponds to compounds in which addition had taken place in the β,β positions with respect to the carbon atom of the vinyl group, and the second peak in the β, α-positions. According to GLC, in the preparation of the mono- and diaddition products (I)-(III) and (V)-(VII), the hydrosiloxanes add mainly to the β-carbon of the vinyl group, and the yields of β-addition products are in excess of 75%. No clear separation of isomers was observed in the chromatograms of compounds containing phenyl groups (IV), (VIII)-(X).

Fractional polymerization of bicyclosiloxanes with carbosiloxane and carbosilane groups between the rings was carried out in the presence of basic polymerization initiators. In most instances, the final polymerization products were spatially cross-linked polymers. Under mild conditions, however, soluble polymers were obtained. Thus, polymerization of (IX) in the presence of 0.05% of α, ω-bis(tetramethylammonio)polydimethyl(methylphenyl)siloxane (calculated on tetramethylammonium) at 60°C for 11 h afforded a polymer with η_{sp} 0.13. When a 15% benzene solution of (V) is polymerized under the same conditions, a polymer is formed which after reprecipitation from methanol has η_{sp} 0.05. It is likely that the polymerization of organosilicon compounds containing both cyclotri- and cyclotetrasiloxane fragments under mild conditions proceeds mainly via fission of the six-membered siloxane rings to give polysiloxanes containing cyclotetrasiloxanylethyl groups in the siloxane chain framework.

EXPERIMENTAL

1-Hydro-1,1,3,3-tetramethyl-3-[2-(heptamethylcyclotetrasiloxanyl)ethyl]disiloxane (I). To 7 g (0.023 mole) of heptamethylvinylcyclotetrasiloxane at 50°C under argon was added H_2PtCl_6, followed by dropwise addition of 3.10 g (0.023 mole) of tetramethyldisiloxane. The mixture was stirred for 3 h at 80°C, and distilled in vacuo.

Similarly obtained at 80°C, reactant ratio 1:1, were 1-hydro-1,1,3,3-5,5-hexamethyl-5-[2-(heptamethylcyclotetrasiloxanyl)ethyl]-trisiloxane (II), 1-hydro-1,1,3,3,5,5,7,7-octamethyl-7-[2-(heptamethylcyclotetrasiloxanyl)ethyl]tetrasiloxane (III), 1-hydro-1,1,5,5-tetramethyl-3,3-diphenyl-5-[2-(heptamethylcyclotetrasiloxanyl)ethyl]trisiloxane (IV), 1,1,3,3-tetramethyl-1-[2-(pentamethylcyclotrisiloxanyl)ethyl]-3-[2-(heptamethylcyclotetrasiloxanyl)ethyl]disiloxane (V), 1,1,3,3,5,5-hexamethyl-1-[2-(pentamethylcyclotrisiloxanyl)ethyl]-5-[2-(heptamethylcyclotetrasiloxanyl)ethyl]-trisiloxane (VI), 1,1,3,3,5,5,7,7-octamethyl-1-[2-(pentamethylcyclotrisiloxanyl)ethyl]-7-[2-(heptamethylcyclotetrasiloxanyl)ethyl]tetrasiloxane (VII), 1,1,3,3-tetramethyl-3,3-diphenyl-1-[2-pentamethylcyclotrisiloxanyl)-ethyl]trisiloxane (VIII), [2-(pentamethylcyclotrisiloxanyl)ethyl]-[2-(heptamethylcyclotetrasiloxanyl)ethyl]methylphenylsilane (IX), and [2-(pentamethylcyclotrisiloxanyl)ethyl]-[2-(heptamethylcyclotetrasiloxanyl)ethyl]diphenylsilane (X).

PMR spectra were obtained on a Bruker WP-200SY relative to TMS. Separation of isomers was carried out on a Khrom-3 preparative chromatograph (d = 3 mm, l = 3 m, stationary phase Chromaton N-AW 0.2-0.25 mm, liquid phase 12% OV-17, column temperature 220°C).

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CONCLUSIONS

1. Hydrosilylation of methylvinylsiloxanes with dihydrosiloxanes and dihydrosilanes in the presence of H_2PtCl_6 has given bicyclocarbosiloxanes and bicyclocarbosilanes containing six- and seven-membered siloxane rings.

2. Addition of dihydrosiloxanes occurs to some extent at the α-carbon atom of the ring vinyl group, in addition to the β-position.

3. Polymerization of bicyclocarbosiloxanes and bicyclocarbosilanes in the presence of basic polymerization initiators under severe conditions affords polymers with spatially cross-linked structures, but under mild conditions soluble polymers are obtained.

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