SYNTHESIS OF BICYCLIC ORGANOSILICON COMPOUNDS WITH AN ETHYLENE BRIDGE BETWEEN THE RINGS

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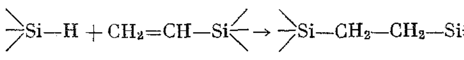
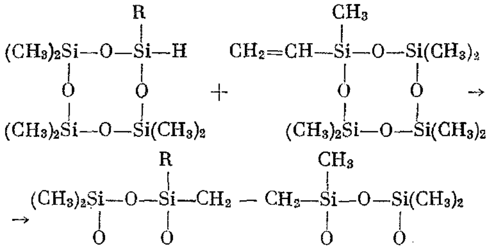
Addition reactions in accordance with the scheme



in presence of platinum catalysts—platinized charcoal [1] and chloroplatinic acid [2]—have been investigated in their application to various organosilicon compounds, including the case in which one of the reacting compounds is cyclic [3, 4]. In the present investigation this reaction was brought about for compounds in which the reacting groups are attached to silicon atoms contained in organosiloxane rings.



R=CH_3 (IV); R = C_6H_5 (V)

For the study of this reaction we used the previously prepared heptamethylvinylcyclotetrasiloxane (I) and heptamethylcyclotetrasiloxane (II), and also the newly prepared 2,2,4,4,6,6-hexamethyl-8-phenylcyclotetrasiloxane (III). The properties of the resulting bicyclic compounds with an ethylene bridge between the rings are given in Table 1.

Ethylenebis[heptamethylcyclotetrasiloxane] (IV) has been synthesized previously [5] by another method: by the action of benzoyl peroxide on octamethylcyclotetrasiloxane. 2-Methyl-2'-phenyl-2,2'-ethylenebis[hexamethylcyclotetrasiloxane] (V) was prepared for the first time.

In the case of the oligomeric cyclic hydride and vinyl organosilicon compounds reaction is less vigorous than in the case of monomeric compounds, which is evidenced by the small exothermic effect and the low yields of addition products (10-30%). This is probably to be explained by steric hindrance due to the presence of bulky cyclic groupings on the silicon atoms to which the reacting groups are directly attached.

We studied the IR spectra of the original monocyclic compounds and of the bicyclic compounds prepared from them. The IR spectra of (I) and (II) (Fig. 1) contain bands at (frequencies always in cm^{-1}) 550-560 (s) and 1080 (v.s) characteristic for Si—O bonds of cyclotetrasiloxane and also bands at 810 (s), 1268 (m), 1414 (w), 2906 (m), and 2967 (s) belonging to an Si-methyl group [6, 7]. The bands at 965, 1602, 3017, and 3056 in the spectrum of (I) belong to the Si-vinyl group [8-11], and the bands at about 830 (s), 915 (m), and 2165 (s) in the spectrum of (II) belong to the Si—H bond [12-14].

In the IR spectrum of (IV) the bands at 553 and 1090 belonging to the Si—O bond in the tetrasiloxane ring have approximately the same position as in the spectra of the original monocyclic compounds. The bands characteristic for the vinyl group and the Si-hydrogen atom are absent, and there are new bands at 2920, 2887, 1451, 1141, and 1055 due to the structural element $-CH_2-CH_2-$.

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TABLE 1. Bicyclic Organosilicon Compounds with an Ethylene Bridge between the Rings

Compound	B.p., °C (p, mm)	n_D^{20}	d_4^{20}	Found					Calculated				
				C, %	H, %	Si, %	mol. wt.	*MR*	C, %	H, %	Si, %	mol. wt.	*MR*
Ethylenebis[heptamethylcyclotetrasiloxane] (IV)	—	—	—	32.64 32.49	7.86 7.90	38.47 38.49	579	—	32.50	7.86	38.0	591	—
2-Methyl-2'-phenyl-2,2'-ethylenebis[hexamethylcyclotetrasiloxane] (V)	155—157 (1.5)	1.4440	1.0399	39.12 39.24	7.60 7.71	34.80 39.24	649	166.01	38.60	7.42	34.39	653	166.81

The difference of the spectrum of (V) from the spectra of the starting compounds (Fig. 2) is analogous to that considered above. The bands at 830, 870, and 2170 belonging to the Si—H bond and present in the spectrum of (III) are absent from the spectrum of (V), and this applies also to the bands enumerated above in the spectrum of (I) which are characteristic for an Si-vinyl group. The bands at 560 and 1090, characteristic for cyclotetrasiloxanes, are preserved. As in the spectrum of (III), there are bands at 810, 1268, 1415, 2905, and 2964 in the spectrum of (V) belonging to the Si-methyl group and also at about 485-500, 700, 742, 1433, 1595, 3004, 3024, 3052, and 3071 belonging to the Si-phenyl group. The spectrum of (V) contains new bands, not present in the spectra of (I) and (III), at 2920, 2887, 1451, 1141, and about 1060 (this band is poorly resolved from the band at 1090, belonging to the cyclotetrasiloxane ring, as a result of the high intensities of the two bands), which confirms the presence of the $-CH_2-CH_2-$ group.

In the region of the stretching vibrations of $>$CH no frequencies can be observed in the spectra of (IV) and (V), which is indicative of the nonformation of a $\underset{\mathrm{CH_3}}{\underset{|}{-\mathrm{CH}-}}$ interring bridge in the reaction between the hydride and vinyl cyclosiloxanes.

Study of the IR spectra shows that the addition of hydride cyclosiloxanes goes in the direction opposite to that required by the Markovnikov rule, with formation of a $-CH_2-CH_2-$ link between the rings, as usually occurs in reactions between hydride and vinyl organosilicon compounds. The presence of an ethylene bridge between the organocyclotetrasiloxane rings does not affect the energy state of the latter.

EXPERIMENTAL

Synthesis of 2,2,4,4,6,6-Hexamethyl-8-phenylcyclotetrasiloxane (III). A three-necked flask fitted with oil-sealed stirrer, thermometer, and dropping funnel was charged with 340 g of distilled water and 170 g of ether, and the mixture was cooled to 0°. A solution of 110 g of dichlorodimethylsilane and 60 g of dichlorophenylsilane in 170 g of ether was added dropwise from the funnel with stirring. During the addition of the solution of organochlorosilanes the temperature in the flask was maintained between -2 and +1° by means of a cooling bath. When the whole of the solution of organochlorosilanes had been added, the cooling bath was removed, and the reaction mixture was stirred for 1 h, during which time the temperature of the mixture rose to that of the room. The organic layer was separated from the aqueous layer and washed with water until the washings were neutral to universal indicator. The cohydrolysis product was dried with $CaCl_2$, and then, after removal of solvent, vacuum-fractionated. We obtained 42.76 g of a product of b.p. 94-101° (2 mm), and in the refractionation of this we isolated 29.9 g (about 29%) of (III); b.p. 98° (2 mm); n_D^{20} 1.4505; d_4^{20} 1.0317. Found: C 41.57, 41.63; H 7.15, 7.18; Si 32.41, 32.34; H_{Si-H} 0.309, 0.301%; mol. wt. 351; MR 91.57. $C_{12}H_{24}Si_4O_4$. Calculated: C 41.81; H 7.03; Si 32.59; H_{Si-H} 0.290%; mol. wt. 344.7; MR 90.25.

Heptamethylcyclotetrasiloxane (II) was prepared by the cohydrolysis of dichlorodimethylsilane and dichloromethylsilane at a molar ratio of 3 : 1. The cohydrolysis was conducted in an ether medium at 0-1°. In the vacuum fractionation of the reaction products we isolated heptamethylcyclotetrasiloxane; b.p. 60-62° (10 mm); n_D^{20} 1.3995. [17] gives: b.p. 84.5° (50 mm); n_D^{20} 1.3965. Found: H_{Si-H} 0.291; 0.294%; mol. wt. 283; 289. $C_7H_{22}Si_4O_4$. Calculated: H_{Si-H} 0.354%; mol. wt. 282.7.

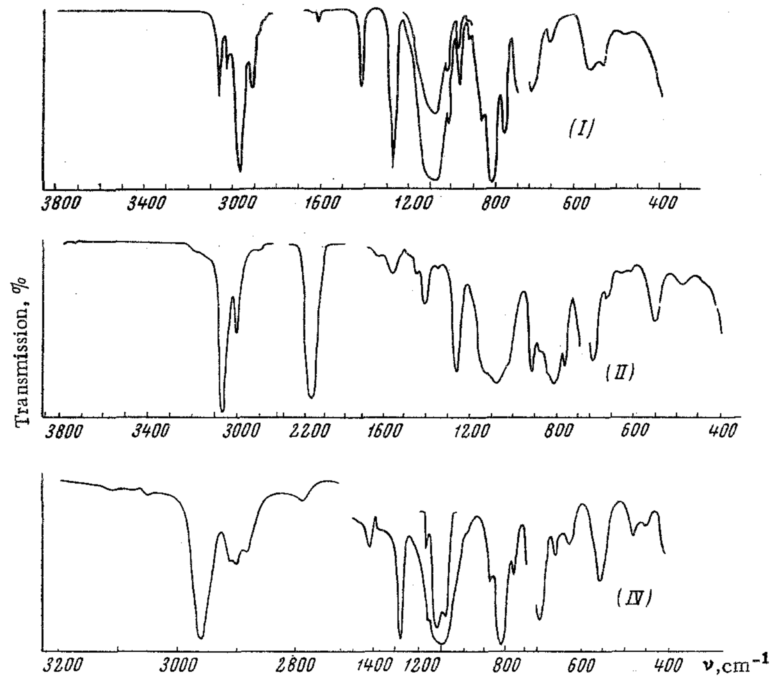

Fig. 1. IR spectra of heptamethylvinylcyclotetrasiloxane (I), heptamethylcyclotetrasiloxane (II), and ethylenebis[heptamethylcyclotetrasiloxane] (IV).

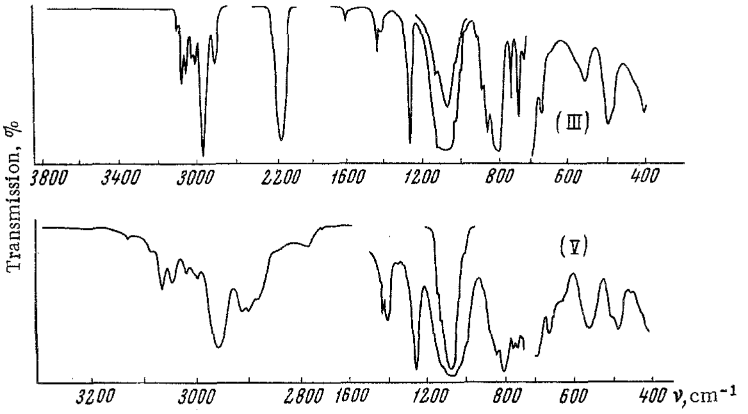

Fig. 2. IR spectra of 2,2,4,4,6,6-hexamethyl-8-phenylcyclotetrasiloxane (III) and 2-methyl-2'-phenyl-2,2'-ethylenebis[hexamethylcyclotetrasiloxane] (V).

Heptamethylvinylcyclotetrasiloxane (I) was prepared analogously by the cohydrolysis of dichlorodimethylsilane and dichloromethylvinylsilane at a molar ratio of 3 : 1. B.p. 78-79° (10 mm); n_D^{20} 1.4072 [8] gives: b.p. 62-64° (11 mm); n_D^{20} 1.4035. Found: bromine value 48.44, 48.72. $C_9H_{24}Si_4O_4$. Calculated: bromine value 51.77.

Synthesis of Ethylenebis[heptamethylcyclotetrasiloxane] (IV). A flask fitted with oil-sealed stirrer, thermometer, and dropping funnel was charged with 10 g of heptamethylvinylcyclotetrasiloxane and 0.1 ml of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol. The contents of the flask were heated to 100°, after which the supply of heat to the flask was switched off and 9.15 g of heptamethylcyclotetrasiloxane was added dropwise from the dropping funnel. By the end of the addition of the heptamethylcyclotetrasiloxane the temperature of the reaction mixture had risen spontaneously to 114.5°. The contents were then heated for 3 h at 150°. Unchanged reactants were vacuum-distilled off, and the residue crystallized on standing; the yield of crude (IV) was 6.17 g.

The crystalline product was dissolved in 23.4 g of acetone, and 9 ml of distilled water was added to the solution. The mixture was carefully stirred, and it was then transferred to a separating funnel and left for 3 days to settle. An oily liquid then separated. It was removed and dissolved in 15 g of acetone, and the solution was filtered and dried over P_2O_5. After the removal of solvent the product was recrystallized from acetone. The yield of purified (IV) was 5.14 g. The analytical results are given in Table 1.

Synthesis of 2-Methyl-2'-phenyl-2,2'-ethylenebis[hexamethylcyclotetrasiloxane] (V). Reaction was conducted as described above with 10 g of heptamethylvinylcyclotetrasiloxane and 11.2 g of (III) (catalyst 0.1 ml of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol). The reaction product was vacuum-fractionated. We isolated a fraction of b.p. 140-150° (2 mm), by the refractionation of which we obtained 7.1 g of a substance of b.p. 146-147° (1 mm). This product was distilled once more. We obtained 4 g of (V), b.p. 155-157° (1.5 mm). Its properties are given in Table 1.

CONCLUSIONS

1. A study was made of the reaction between hydride and vinyl organocyclosiloxanes in presence of chloroplatinic acid. Addition goes in the direction contrary to that required by the Markovnikov rule with formation of an ethylene bridge between the rings.

2. The new bicyclic organosilicon compound 2-methyl-2'-phenyl-2,2'-ethylenebis[hexamethylcyclotetrasiloxane] was synthesized and characterized.

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