PREPARATION OF ISOMERIC 1,3- AND 1,5-(o-PHENYLENE)-HEXAMETHYLCYCLOTETRASILOXANES AND INVESTIGATION OF THEIR SPECTRAL CHARACTERISTICS

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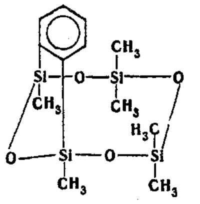
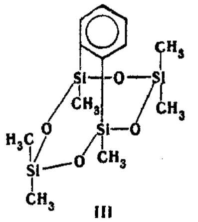
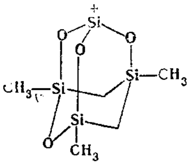
Workup of the mixture of products of pyrolysis of cyclotetrasiloxane $(Me_2SiO)_2(MePhSiO)_2$ yielded 1,3- (I) and 1,5-(o-phenylene)cyclosiloxane (II), the structures of which were established on the basis of data from their IR, PMR, and mass spectra.

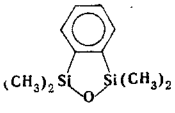
Cyclosiloxanes containing an o-phenylene bridge between the silicon atoms have not been previously synthesized, but on the basis of indirect data it has been assumed [1] that 1,3-(o-phenylene)-1,3,5,5,7,7-hexamethylcyclotetrasiloxane (II) and 1,5-(o-phenylene)-1,3,3,5,7,7-hexamethylcyclotetrasiloxane (III) are formed in the pyrolysis of a mixture of structural and spatial isomers of cyclotetrasiloxane $(Me_2SiO)_2(MePhSiO)_2$ (I). The present paper is devoted to the isolation of individual isomers II and III and to proof of their structures on the basis of data from their IR, PMR, and mass spectra.


II


III

A narrow fraction with bp 112-114°C (2 mm), which began to crystallize on standing, was distilled from the mixture of products of pyrolysis of cyclotetrasiloxane I (pyrolysis at 690°C, contact time 30 sec). Two individual white crystalline substances with different retention times during gas–liquid chromatography (GLC) were isolated from this mixture by repeated recrystallization. The mass spectra of the two products were identical. The molecular ion peak is found at m/e 342 (1%), i.e., 78 amu less than the molecular weight of siloxane I. Thus the compounds obtained are isomers and are formed as a result of intramolecular ejection of a molecule of benzene from the starting cyclotetrasiloxane during pyrolysis. The principal fragment ions in the mass spectra of II and III are typical for cyclosiloxanes containing methyl groups attached to the silicon atoms [2]: ions **a** ($[M - CH_3]^+$) with m/e 327 (100%), $[a - CH_2]^+$ with m/e 313 (2%), $[a - CH_4]^+$ with m/e 311 (3%), and $[a - C_2H_6]^+$ with m/e 297 (2%). We should especially dwell on the $[a - C_6H_6]^+$ ion with m/e 249 (6%), the formation of which requires the cleavage of no less than four bonds. We assume that this process is accompanied by complex skeletal rearrangements and leads to the formation of stable 3,5,7-trimethyl-1,3,5,7-tetrasila-2,4,6,8-tetraoxaadamantyl cation **b**. The **a** → **b** conversion was confirmed by the presence of a metastable peak at m*/e 189.8 (as compared with 189.6 calculated for the process $327^+ \rightarrow 249^+$).


b, *m/e* 249


IV

Ministry of the Chemical Industry of the USSR, Moscow 101000. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 24-25, January, 1978. Original article submitted February 8, 1977.

The assignment of structures II and III to the compounds obtained was made on the basis of the IR spectroscopic data. It is known [3] that the band of the stretching vibrations of the Si–O bond in 1,1,3,3-tetramethyl-1,3-disila-2-oxaindan (IV) is shifted strongly to the long-wave region as compared with the corresponding band in the spectra of cyclosiloxanes and gives a signal at 930 cm^{-1}. A band at 920 cm^{-1} is observed in addition to the band typical for siloxanes at 1020-1080 cm^{-1} in the IR spectrum of the compound that has a shorter retention time during GLC; consequently, this compound is also a disilaoxaindan derivative and has structure II. Only one band at 1035 cm^{-1} (in the region of stretching vibrations of the Si–O bond) is observed in the IR spectrum of the compound with the longer retention time. Thus structure III should be assigned to this compound.

Definite confirmation of the structures of products II and III was obtained during a study of their PMR spectra, which were of the same type. Each spectrum contains a symmetrical multiplet of an AA'BB' system of phenylene ring protons at 7.3-7.6 ppm and three singlet peaks of methyl groups at –0.3 to + 0.5 ppm (intensity ratio 4 : 6 : 6 : 6). The form of the signals of the aromatic protons provides evidence that the investigated compounds contain o-phenylene groupings (in the case of meta substitution we would have observed a more complex and unsymmetrical A_2BC system, and in the case of para substitution the four phenylene protons would be equivalent and would appear in the spectrum in the form of a sharp singlet). The signals of the protons of the methyl groups were assigned as follows: The chemical shifts of these protons are determined primarily by the diamagnetic anisotropy of the benzene rings and the resonance signals of the methyl groups near the axis perpendicular to the plane of the benzene ring, i.e., in the zone of increased shielding, should be observed at strongest field: the methyl groups in the cis-5 and cis-7 positions for II (δ –0.26 ppm) and cis-3 and cis-7 for III (δ –0.22 ppm). The signals of the protons of the methyl groups located near the plane of the benzene ring, i.e., in the zone of deshielding of the 1 and 3 positions for II (δ 0.39 ppm) and 1 and 5 positions for III (δ 0.47 ppm), should be found at weakest field. The methyl groups that are far removed from the benzene ring [the trans-5 and trans-7 positions in II (δ 0.10 ppm) and the trans-3 and trans-7 positions in III (δ 0.21 ppm)] have intermediate chemical shifts.

The mass spectra were recorded with an MKh-1303 mass spectrometer at 200°C and an ionizing voltage of 30 V. The IR spectra were recorded with a Perkin–Elmer model 457 spectrometer. The PMR spectra were recorded with a Varian XL-100 spectrometer.

LITERATURE CITED

1. V. N. Bochkarev, A. N. Polivanov, N. P. Telegina, N. A. Palamarchuk, V. S. Lozovskaya, E. A. Chernyshev, and T. I. Agapova, Zh. Obshch. Khim., 44, 1175 (1974).
2. V. Yu. Orlov, Zh. Obshch. Khim., 37, 2300 (1967).
3. N. A. Chumaevskii, Vibrational Spectra of Heteroorganic Compounds of Group IVB and VB Elements [in Russian], Nauka, Moscow (1971), p. 60.