

**1,1,3,3-TETRAMETHYL-1,3-DISILA-2,6-DIOXACYCLOOCTANE AND  
1,1,3,3,9,9,11,11-OCTAMETHYL-1,3,9,11-TETRASILA-2,6,10,14-  
TETRAOXACYCLOHEXADECANE\***

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The title compounds were prepared by hydrolysis of bis[2-(dimethylchlorosilyl)ethyl] ether and were characterized by  $^1\text{H-NMR}$  and IR spectroscopy. Mass spectra of both compounds were interpreted in terms of interaction between silicon and oxygen atoms which leads to elimination of ethylene molecule. The character of fragmentation of the former compound is not affected by change of ionizing energy from 70 eV to 20 eV, while significant changes were observed in fragmentation of the latter compound.

The synthesis and properties of cyclocarbosiloxanes have recently been treated in reviews<sup>1,2</sup>. The compounds prepared in this work are the first example of 8- and 16-membered cyclic compounds containing both Si—O—Si and C—O—C groupings. Within the framework of our mass spectrometric study of carbofunctional silicon compounds<sup>3-5</sup> it was of interest to ascertain to what extent fragmentation of both compounds on electron impact is influenced by interaction between their silicon and oxygen atoms and whether relative importance of this interaction depends on the size of the cycle.

**EXPERIMENTAL**

*Bis[2-(dimethylchlorosilyl)ethyl] ether.* Divinyl ether (17.5 g, 0.25 mol), di-n-butyl ether (60 ml) and 0.5 ml of 0.001M hexachloroplatinic acid solution in isopropanol were placed in a three-necked 250 ml-flask equipped with a thermometer, a separating funnel with a pressure-equalizing arm and a reflux condenser which was topped with a dry ice-acetone trap. The apparatus was sealed by means of a bladder. The mixture was warmed up to 80°C and then dimethylchlorosilane (48 g, 0.5 mol) was added dropwise. The temperature of the reaction mixture gradually raised to 120°C. After completion of the addition, the mixture was maintained at this temperature for another 3 h and then it was rapidly distilled under reduced pressure (1 Torr). Bis[2-(dimethylchlorosilyl)ethyl] ether (45 g, 0.17 mol) was obtained by fractionation in 68% yield as a fraction boiling at 117°C/10 Torr. For  $\text{C}_8\text{H}_{20}\text{Cl}_2\text{OSi}_2$  (259.3) calculated: 27.35% Cl; found: 26.96% Cl.

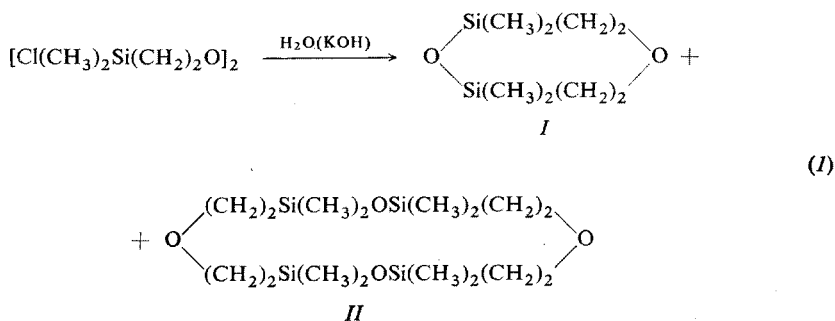
\* Part CXXXV in the series Organosilicon Compounds; Part CXXXIV: This Journal 41, 239 (1976).

1,1,3,3-Tetramethyl-1,3-disila-2,6-dioxacyclooctane (I) and 1,1,3,3,9,9,11,11-octamethyl-1,3,9,11-tetrasil-2,6,10,14-tetraoxacyclohexadecane (II). Bis[2-(dimethylchlorosilyl)ethyl] ether was hydrolysed in a three-necked 4 l-flask equipped with a stirrer and two separating funnels (with pressure-equalizing arms) topped with a bladder. The flask was charged with 2 l of dry dioxane and the contents were cooled by a dry ice-acetone mixture to  $-10^{\circ}\text{C}$ . Bis[2-(dimethylchlorosilyl)ethyl] ether (45 g, 0.17 mol) and a mixture of water (3.5 g, 0.17 mol) and KOH (19 g, 0.34 mol), both dissolved in 500 ml of dry dioxane, were added separately and at the same rate from the separating funnels (20 h) to the stirred and cooled dioxane. The reaction mixture was then poured onto 3 l of water and the product was extracted with diethyl ether. The organic layer was separated, washed until it was neutral and dried over anhydrous calcium dichloride. The diethyl ether was evaporated *in vacuo* and compounds I and II were obtained by rectification as fractions boiling at  $81-82^{\circ}\text{C}/7$  Torr (29% yield) and  $198-200^{\circ}\text{C}/5$  Torr (8% yield), respectively. For  $\text{C}_8\text{H}_{20}\text{O}_2\cdot\text{Si}_2$  (I, 204.4) calculated: 47.00% C, 9.86% H, 27.49% Si; found: m.wt. 205, 47.02% C, 9.80% H, 27.36% Si;  $n_D^{20}$  1.4370. For  $\text{C}_{16}\text{H}_{40}\text{O}_4\text{Si}_4$  (II, 408.9) found: m.wt. 415, m.p.  $76-77^{\circ}\text{C}$ ; 46.72% C, 9.76% H, 27.38% Si. Both compounds were characterized by  $^1\text{H-NMR}$  and IR spectra of their solutions in tetrachloromethane (I, II): the chemical shift ( $\tau$ ) in p.p.m. (benzene as an external reference)  $\text{CH}_3$ : 9.96, 10.03;  $\text{CH}_3(\text{Si})$ : 9.37, 9.20 (triplet);  $\text{CH}_2(\text{O})$ : 6.59, 6.64 (triplet);  $J^{1,3}$  (C—H) for  $\text{CH}_3$  group 118.16 Hz, 118.68 Hz;  $\delta_s(\text{CH}_3)$  1258  $\text{cm}^{-1}$ , 1257  $\text{cm}^{-1}$ ,  $\nu(\text{C—O—C})$  1093  $\text{cm}^{-1}$ , 1098  $\text{cm}^{-1}$ ;  $\nu(\text{Si—O—Si})$  1041  $\text{cm}^{-1}$ ;  $\rho(\text{CH}_3)$  845  $\text{cm}^{-1}$ , 843  $\text{cm}^{-1}$ .

$^1\text{H-NMR}$  spectra were measured with a modified Tesla BS-477 spectrometer (60 MHz), IR spectra were recorded with a double-beam Zeiss UR-20 spectrophotometer (Jena, GDR). Mass spectra were recorded with MS 902 spectrometer and molecular weights were determined cryoscopically for benzene solutions of the compounds with the use of Knauer apparatus.

## RESULTS AND DISCUSSION

Slow hydrolysis of bis[2-(dimethylchlorosilyl)ethyl] ether by potassium hydroxide in dioxane produces 1,1,3,3-tetramethyl-1,3-disila-2,6-dioxacyclooctane (I) and 1,1,3,3,9,9,11,11-octamethyl-1,3,9,11-tetrasil-2,6,10,14-tetraoxacyclohexadecane (II) (equation (I)).  $^1\text{H-NMR}$  spectra of both cycles are essentially identical, small changes are likely due to conformational population. Preliminary assignment of the vibrations for both compounds was based on the IR spectra of bis(ethylidimethyl)disiloxane<sup>6</sup> and bis[2-(4-trimethylsilyl)ethyl] ether<sup>7</sup>.



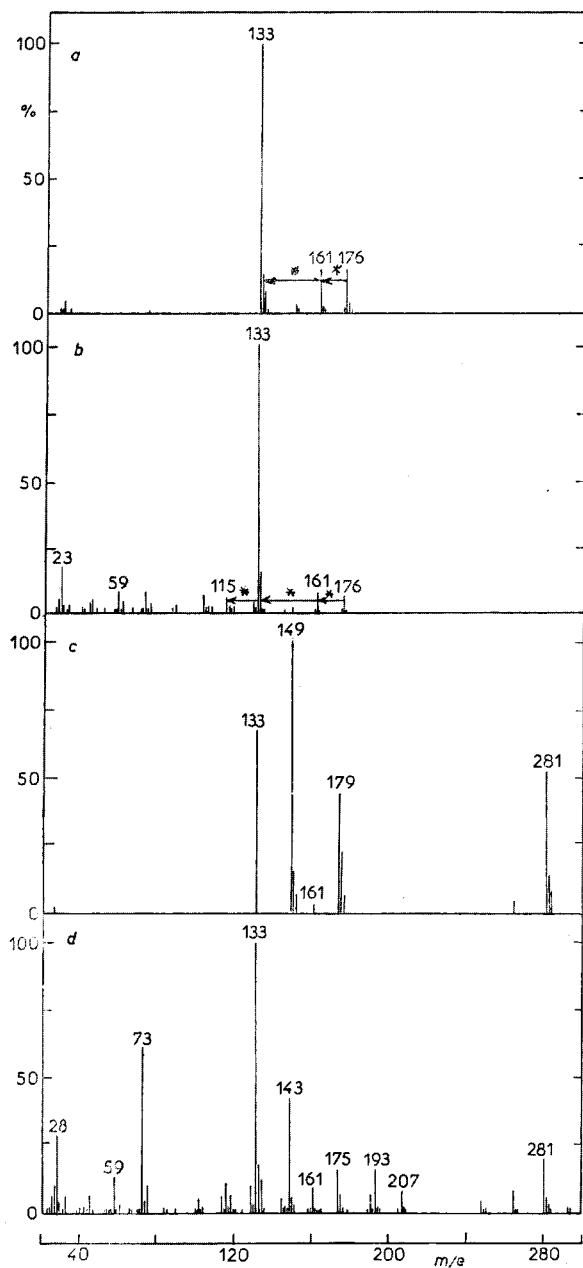
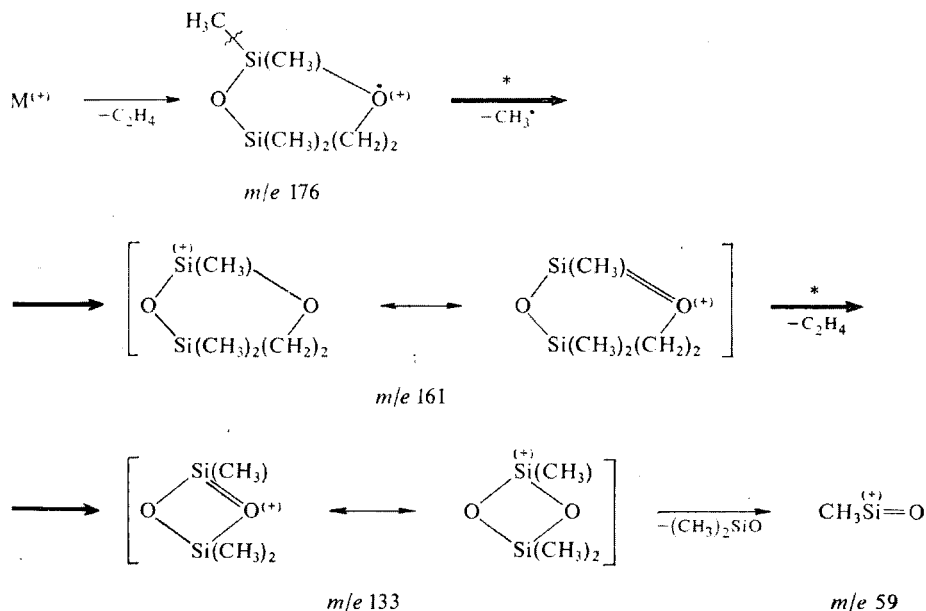


FIG. 1

Mass Spectra of Compounds I (*a* 70 eV, *b* 20 eV) and II (*c* 70 eV, *d* 20 eV)

Asterisks denote formation of metastable ions.

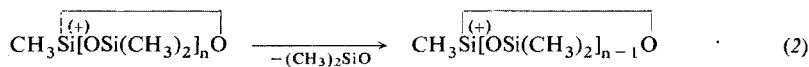
Dominant fragmentation which determines mass spectra of the cycles *I* and *II* at 70 eV (Fig. 1) is the release of ethylene molecules which is conditioned by interaction between oxygen and silicon atoms (the great mobility of silyl groups in carbofunctional compounds on electron impact was already established earlier<sup>3,5,8-10</sup>, migration of the hetero atom to the silicon in carbofunctional silanes was also evidenced<sup>11</sup>; because of the  $\beta$ -elimination<sup>12</sup>,  $\beta$ -carbofunctional compounds occupy quite exceptional position among the compounds of this class). Fragmentation of the cycle *I* (very low intensity of the molecular ion, low relative intensities of the ions at  $m/e$  176, 161 and 59 as well as the base peak at  $m/e$  133) may be visualized by Scheme 1. The correctness of this scheme is supported by the occurrence of metastable



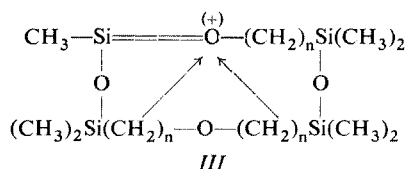
SCHEME 1

fragments (denoted by asterisk) and by the structure of the fragment at  $m/e$  133 ( $\text{Si}_2\text{O}_3\text{H}_9\text{O}_2$ ) which was derived from the ratio of the intensities of peaks at  $m/e$  134 and 133 (0.145). Fragmentation of the cycle *II* (the ion with the highest  $m/e$  value at 281 and further fragments at  $m/e$  207, 133) can again be explained by elimination of ethylene molecules which gives rise to a siloxane fragment ( $m/e$  281). The fragment at  $m/e$  133 has the same structure as in the case of fragmentation of the cycle *I*. The ratio of the intensities of peaks at  $m/e$  134 and 133 (0.180) could indicate, however, that the peak at  $m/e$  133 is formed to a small extent also by the double-charged fragment  $\text{Si}_4\text{C}_{16}\text{H}_{18}\text{O}_4^{2-}$  whose occurrence was observed in the spectrum of octa-

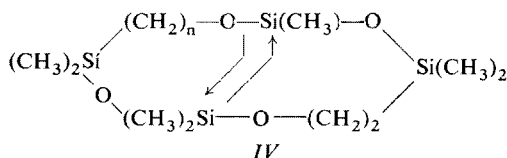
methylecycloctetrasiloxane<sup>11</sup>. Occurrence of the fragment at  $m/e$  133 in the spectrum of the cycle *II* could be described by equation (2), in agreement with the fragmentation of octamethylcycloctetrasiloxane<sup>13</sup>. The much greater intensity of this peak in the spectrum of the cycle *II* compared to the spectrum of octamethylcycloctetrasiloxane<sup>13</sup> is likely due to simultaneous formation of the above fragment as a result of interaction of the silicon atoms with the electron-deficient oxygen in the fragment *III* ( $n = 0$  or 2).



$m/e$  281 ( $n = 3$ ), 207 ( $n = 2$ ), 133 ( $n = 1$ )



The peak at  $m/e$  161 could belong to a fragment formed *via* intramolecular interaction between the oxygen and the silicon in formula *IV* ( $n = 0$  or 2).



The structure of fragments at  $m/e$  175 and 149 was determined by high precision measurements of the  $m/e$  ratio. Experimental values of  $m/e$  so obtained correspond to  $\text{C}_6\text{H}_{15}\text{Si}_2\text{O}_2$  ( $m/e$  175.0613) and  $\text{C}_4\text{H}_{13}\text{Si}_2\text{O}_2$  ( $m/e$  149.0453), respectively. It seems likely that the latter fragment arises from the former *via* loss of one acetylene molecule.

At 20 eV ionizing energy (Fig. 1) the mass spectra of both compounds differ from one another. While the pattern of fragmentation of the cycle *I* remains the same as at 70 eV, fragmentation of the cycle *II* is determined above all by formation of the ions  $\text{C}_6\text{H}_{15}\text{Si}_2\text{O}$  and  $\text{C}_5\text{H}_{13}\text{Si}_2\text{O}_2$  and the fragmentation which is dominant at 70 eV and involves elimination of ethylene molecules (and  $(\text{CH}_3)_2\text{SiO}$  units) is now minor.

The mass spectra of the cyclic compounds *I* and *II* at 70 eV, and especially at 20 eV, are thus the evidence for and the first example of the effect of the size of the cycle (and presumably also its conformation) on the mode of fragmentation of equi-structural carbofunctional silicon derivatives. The deeper insight into the mass

spectrometric fragmentation described in the present work might be provided by the study of pyrolysis of both compounds, since frequent parallelity in molecular transformations during electron impact and pyrolysis has often been stressed<sup>14</sup>.

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