

## ORGANOSILICON COMPOUNDS. XCVIII.\*

THE STRUCTURE OF 1-OXA-2-SILACYCLOHEXANES AND  
 $\alpha$ -TRIMETHYLSILYL- $\omega$ -TRIMETHYLSILOXYALKANES

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Relative basicity of the oxygen of the compounds  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$  ( $n = 1-4$ ) was studied by IR spectroscopy. By comparison with the basicity of  $(\text{CH}_3)_3\text{C}(\text{CH}_2)_4\text{OSi}(\text{CH}_3)_3$  it was established that the basicity of the above compounds is not decreased, which indicates that for  $n \geq 2$  the coordination interaction of the type  $\text{O} \rightarrow \text{Si}$  is insignificant. Relative basicities, measured by the same method, and dipole moments of the compounds  $(\text{C}_2\text{H}_5\text{O})_n(\text{CH}_3)_{2-n}\text{Si}(\text{CH}_2)_4\text{O}$  ( $n = 0-2$ ) are higher than the basicities and dipole moments of non-cyclic analogs,  $\text{RSi}(\text{OC}_2\text{H}_5)(\text{CH}_3)_2$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_4\text{H}_9$ ). On the basis of this comparison the conclusions were drawn concerning the structure of 1-oxa-2-silacyclohexanes.

The importance of a ( $p \rightarrow d$ ) $_{\sigma}$  intramolecular coordination of oxygen to silicon is influenced by properties of both interacting centres. In the case of terminal ethoxysilyl-substituted propoxy- and butoxytrimethylsilanes of the general formula  $(\text{C}_2\text{H}_5\text{O})_n(\text{CH}_3)_{3-n}\text{Si}(\text{CH}_2)_m\text{OSi}(\text{CH}_3)_3$  ( $n = 1-3; m = 3,4$ ) coordination of this type facilitates cyclization of these compounds<sup>1</sup>. Similar effect has not been however observed with trimethylsilylalkanols of the type  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OH}$  ( $n = 2-4$ )<sup>2</sup>. The aim of this work was to find to what extent this intramolecular coordination is influenced by nucleophilicity of the oxygen. For this purpose we measured relative basicities of oxygen atoms of the compounds  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$  ( $n = 1-4$ ) and compared them with the already reported basicities of trimethylsilylalkanols<sup>2</sup>. As the measure of the basicity we have chosen the strength of the hydrogen bond between the oxygen of studied compounds and hydroxylic hydrogen of phenol, indicated as in the case of trimethylsilylalkanols by IR spectroscopy. These data were compared also with the basicity of 1-trimethylsiloxy-5,5-dimethylhexane. The structure of six-membered heterocycles containing the silicon and oxygen atoms in adjacent position has not yet been studied. From measurements of the physical and chemical properties of compounds structurally alike it followed that, in contrast to 1-oxa-2-silacyclopentanes<sup>6</sup>, silacyclohexanes<sup>3-5</sup> are almost without angular strain.

In this work we studied the structure of 1-oxa-2-silacyclohexanes of the type  $(\text{C}_2\text{H}_5\text{O})_n(\text{CH}_3)_{2-n}\text{Si}(\text{CH}_2)_4\text{O}$  ( $n = 0-2$ ) by comparing their dipole moments and basicities with the data for non-cyclic analogs of the type  $(\text{C}_2\text{H}_5\text{O})_n(\text{CH}_3)_{3-n}\text{SiR}$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_4\text{H}_9, n = 1-3$ ) and tetrahydropyran.

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## EXPERIMENTAL

*Preparation of model compounds.* Trimethylsiloxyalkylsilanes  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$  ( $n = 1-4$ ) and 1-trimethylsiloxy-5,5-dimethylhexane were prepared by reaction of the corresponding alcohols  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OH}$  ( $n = 1-4$ )<sup>2</sup> and  $(\text{CH}_3)_3\text{C}(\text{CH}_2)_4\text{OH}$  with trimethylchlorosilane in light petroleum in the presence of pyridine at 0°C. Alkyl(ethoxy)methylsilanes  $\text{R}(\text{CH}_3)_n\text{Si}(\text{OC}_2\text{H}_5)_{3-n}$  ( $n = 0-2$ ;  $\text{R} = \text{C}_2\text{H}_5, \text{C}_4\text{H}_9$ ) were prepared by alkylation of the methyl(ethoxy)silanes  $(\text{CH}_3)_n\text{Si}(\text{OC}_2\text{H}_5)_{4-n}$  ( $n = 0-2$ ) with alkylmagnesium halogenide,  $\text{RMgX}$  ( $\text{R} = n\text{-C}_4\text{H}_9, \text{C}_2\text{H}_5$ ). Their physical properties and yields are recorded in Table I. The preparation and physical constants of the 1-oxa-2-silacyclohexanes  $(\text{C}_2\text{H}_5\text{O})_n(\text{CH}_3)_{2-n}\text{Si}(\text{CH}_2)_4\text{O}$  ( $n = 0-2$ ) were reported in a previous work<sup>1</sup>. Tetrahydropyran (Fluka, AG, Buchs SG) was dried with calcium chloride and distilled (b.p. 88–89°C).

TABLE I  
Yields and Physical Constants of Alkoxysilanes

Product	Yield %	B.p., °C/Torr	$n_D^{20}$	
			found	lit.
$(\text{CH}_3)_3\text{SiCH}_2\text{OSi}(\text{CH}_3)_3^a$	70	131–132	1.3991	—
		129.8/738	1.3971	—
$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_2\text{OSi}(\text{CH}_3)_3^b$	73	60–63/22	1.4100	—
		—	—	—
$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{OSi}(\text{CH}_3)_3^c$	85	78–79/24	1.4143	—
		81/25	1.4120 <sup>d</sup>	—
$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_4\text{OSi}(\text{CH}_3)_3^e$	74	90–92/24	1.4185	—
		94/24	1.4166 <sup>d</sup>	—
$(\text{CH}_3)_3\text{C}(\text{CH}_2)_4\text{OSi}(\text{CH}_3)_3^e$	86	86–88/20	1.4128	—
		—	—	—
$\text{C}_4\text{H}_9\text{Si}(\text{OC}_2\text{H}_5)_3^f$	60	117/70	1.4010	—
		190–193	1.4011	0.8883
$\text{C}_4\text{H}_9\text{SiCH}_3(\text{OC}_2\text{H}_5)_2^g$	57	115.5/115	1.4037	—
		—	—	—
$\text{C}_4\text{H}_9\text{Si}(\text{CH}_3)_2\text{OC}_4\text{H}_5^h$	53	112/200	1.4040	—
		—	—	—
$\text{C}_2\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3^i$	65	158	1.3906	0.9152 <sup>l</sup>
		150–151	1.3869	0.8963
$\text{C}_2\text{H}_5\text{SiCH}_3(\text{OC}_2\text{H}_5)_2^j$	60	137.5	1.3912	0.8476 <sup>l</sup>
		134–135	1.3925	0.8440
$\text{C}_2\text{H}_5\text{Si}(\text{CH}_3)_2\text{OC}_2\text{H}_5^k$	56	101.5	1.3910	0.7813 <sup>l</sup>
		106	1.3888	—

<sup>a</sup> Ref.<sup>7</sup>; <sup>b</sup> for  $\text{C}_8\text{H}_{22}\text{OSi}_2$  calculated: 50.45% C, 11.64% H; found 50.78% C, 11.58% H; <sup>c</sup> ref.<sup>8</sup>; <sup>d</sup>  $n_D^{25}$ ; <sup>e</sup> for  $\text{C}_{11}\text{H}_{26}\text{OSi}$  calculated: 65.27% C, 12.95% H; found: 65.46% C, 13.01% H; <sup>f</sup> ref.<sup>9</sup>; <sup>g</sup> for  $\text{C}_9\text{H}_{22}\text{O}_2\text{Si}$  calculated: 14.76% Si; found: 14.74% Si; <sup>h</sup> for  $\text{C}_8\text{H}_{20}\text{OSi}$  calculated: 17.52% Si; found: 16.90% Si; <sup>i</sup> ref.<sup>10</sup>; <sup>j</sup> ref.<sup>11</sup>; <sup>k</sup> ref.<sup>12</sup>; <sup>l</sup>  $d_4^{24}$ .

*Dipole moment measurements.* Dipole moments of 1-oxa-2-silacyclohexanes (Table II) were determined by measuring concentration dependence of the dielectric constant and specific volume of  $10^{-2}$ – $10^{-3}$ M benzene solutions of these compounds. Dielectric constants were measured by resonance method, using the instrument after LeFèvre and Russell<sup>13</sup>, which was equipped with quartz-crystal vibrating with the frequency of 545 kc/s. The resonance was indicated by galvanometer working with maximum sensitivity of  $7.7 \cdot 10^9 \text{ \AA}$ . Densities were measured in Sprengel-Oswald pycnometers at  $25 \pm 0.05^\circ\text{C}$ . Dipole moments were calculated from experimental data according to Halverstadt and Kumler<sup>14</sup>.

*Relative basicities* were determined from the spectra of hydrogen bonds in the region of 3100 to  $3700 \text{ cm}^{-1}$  in NaCl cells which were 0.1 cm thick. Concentrations of proton acceptors in spectrograde  $\text{CCl}_4$  were 0.2–0.5M. Phenol (0.02M) and pyrrole (0.01M) were used as proton donors. Wave-numbers of absorption band maxima were obtained as the average of three measurements.

## RESULTS AND DISCUSSION

From measurements of properties of the compounds  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$  ( $n = 1-4$ ) (Table III) it follows that the basicity of oxygen is the highest in trimethylsiloxy(trimethylsilyl)methane and decreases with increasing number of the methylene groups separating the silicon from the oxygen. This can be explained by inductive effect of the trimethylsilyl group, similarly as in the case of the compounds  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OH}$  ( $n = 1-4$ )<sup>2</sup>. Basicity of the oxygen in the compounds  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$  ( $n = 3, 4$ ) is comparable with the basicity of  $(\text{CH}_3)_3\text{C}(\text{CH}_2)_4\text{OSi}(\text{CH}_3)_3$ . It is therefore possible to state that in the compounds  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$  ( $n = 3, 4$ ) theoretically possible coordination of the type O—Si (structure I) does not occur to a significant extent (similarly as in trimethylsilylalkanol<sup>2</sup>), even though such interaction in the compounds of this type is more

TABLE II

Properties of 1-Oxa-2-silacyclohexanes

$\alpha$  and  $\beta$  is the slope of the linear dependence of the dielectric constant and of the specific volume of benzene solution, respectively, on concentration of dissolved compound,  $P_\infty$  is the molar polarization of dissolved compound, extrapolated to infinite dilution and  $R$  is the molar refraction of dissolved compound.

Quantity	$(\text{C}_2\text{H}_5\text{O})_2\text{Si}(\text{CH}_2)_4\text{O}$	$\text{C}_2\text{H}_5\text{O}(\text{CH}_3)\text{Si}(\text{CH}_2)_4\text{O}$	$(\text{CH}_3)_2\text{Si}(\text{CH}_2)_4\text{O}$
$\alpha$	4.299	5.000	4.848
$\beta$	-0.269	-0.196	-0.122
$P_\infty, \text{cm}^3$	117.945	108.539	89.089
$R, \text{cm}^3$	49.00	43.00	38.10
$\mu, \text{D}$	1.84	1.78	1.58
$n_D^{20}$	1.4283	1.4289	1.4282
$d_4^{24}$	1.0207	0.9472	0.8810



oxygen in silacyclohexane may be expected not to lead to significant increase in angular strain so that the character of the Si—O bond would not differ much from the character of the same bond of the non-cyclic compounds. The six membered rings with silicon adjacent to oxygen seem therefore to be without significant angular strain. The  $\Delta\nu$  values obtained can however be interpreted similarly as the basicities of cyclosiloxanes, in which case the higher basicity of hexamethylcyclotrisiloxane relative to octamethylcyclotetrasiloxane is connected with different SiOSi bond angles (for  $[(\text{CH}_3)_2\text{SiO}]_3$ :  $125 \pm 5^\circ$  (ref.<sup>17</sup>); for  $[(\text{CH}_3)_2\text{SiO}]_4$ :  $142.5^\circ$  (ref.<sup>18</sup>)) and, in contrast to octamethylcyclotetrasiloxane, the planar structure of hexamethylcyclotrisiloxane makes the ( $p \rightarrow d$ )  $\pi$  bond formation between silicon and oxygen by far more difficult. From higher basicities of the oxygen of 1-oxa-2-silacyclohexanes by comparison with reference compounds one can also conclude that the  $\pi$ -character of the silicon—oxygen bond in these compounds is relatively less important. The higher basicity of 1-oxa-2,2-dimethyl-2-silacyclohexanes relative to tetrahydropyran can hardly be explained otherwise than by the polarity of the Si—O bond and by inductive effects of the methyl groups. Comparatively higher polarization of the Si—O bond in 1-oxa-2-silacyclohexanes by comparison with the non-cyclic analogues may be taken as the reason for observed differences between dipole moments of these compounds. Hence, the smaller ( $p \rightarrow d$ )  $\pi$  interaction of the silicon with the oxygen may be interpreted under the assumption that during hypothetical transformation of the reference compound to the cyclic 1-oxa-2-silacyclohexane the Si—O—C bond angle is decreased and thus the oxygen is rehybridized from the  $sp^2$  towards the  $sp^3$  state.

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