## ORGANIC PHOSPHOSILICON COMPOUNDS OF STEREOCYCLIC STRUCTURE

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It was shown earlier that condensation of methylphosphinic acid with diethoxydiorganosilanes and  $\alpha$ ,  $\omega$ diethoxyorganosiloxanes proceeds with the formation of organocyclophosphinoxysiloxanes [1, 2]. In the present work we made a study of the possibility of preparing organic phosphosilicon compounds of stereocyclic structure in the condensation of alkyltriethoxysilanes and dialkyltetraethoxydisiloxanes with methylphosphinic acid. A synthesis was made of alkyltrialkoxysilanes and alkylalkoxysiloxanes; some of them were reported for the first time. The properties of the compounds are given in Table 1. The compounds were identified by elementary analysis, molecular weights, and IR and PMR spectra. IR spectra confirmed the presence of the groups: R (2960, 2870 cm<sup>-1</sup>), C-C (815 cm<sup>-1</sup>), R-Si (1200 cm<sup>-1</sup>), OCH<sub>3</sub> (1075-1110 cm<sup>-1</sup>) (for methoxysiloxanes), and for ethoxysilanes OC<sub>2</sub>H<sub>5</sub> (960, 1095-1108 cm<sup>-1</sup>). An absorption band with a maximum at ~1020 cm<sup>-1</sup> corresponded to cyclotrisiloxanes.

The condensation of alkyltriethoxysilanes with methylphosphinic acid proceeded with the separation of alcohol (up to 95% of the theoretical amount). Distillation of reaction products in vacuo has shown that the

TABLE 1. Physicochemical Properties of Alkylethoxysilanes and Alkylethoxysiloxanes

Compound	Bp,°C (p, mm Hg)	d4 <sup>20</sup>	n <sup>20</sup> D	MR	
				found	calculated
$\begin{array}{c} \vdots - C_9 H_{19} Si (OCH_3)_3 \\ (n - C_6 H_{19})_2 Si (OC_2 H_5)_2 \\ (n - C_1 0H_{21})_2 Si (OC_2 H_5)_2 \\ C_6 H_{13} Si (OC_2 H_3)_2 Sl_2 O \\ [i - C_9 H_{19} (OCH_3)_2 Si]_2 O \\ [i - C_9 H_{19} (OCH_3)_2 Si]_2 O \\ [i - C_9 H_{19} (C_2 H_5 O)_2 Si]_2 O \\ [c_6 H_{13} Si (OC_2 H_5) O]_3 \\ [i - C_9 H_{19} Si (OC_2 H_5) O]_3 \\ \end{array}$	$\begin{array}{c} 91'-92\ (2)\\ 157\ (0,1)\\ 193-196\ (1-2)\\ 136-138\ (2)\\ 169-170\ (1)\\ 172-178\ (2)\\ 1173-175\ (2)\\ 199-200\ (0,1) \end{array}$	$\begin{array}{c} 0,9142\\ 0,8537\\ 0,9458\\ 0,9329\\ 0,9458\\ 0,9277\\ 0,9581\\ 0,9424 \end{array}$	1,4240 1,4385 1,4345 1,4270 1,4345 1,4368 1,4368 1,4340 1,4442	69,60 114,74 124,75 116,38 124,27 143,12 142,12 183,04	69,31 114,46 124,44 116,29 125,37 143,74 142,02 183,21

TABLE 2. Physicochemical Properties of Cyclomethylphosphinoxyorganosilsesquioxanes

Compound	Bp, °C (p, mm Hg)	d4 <sup>20</sup>	Glass trans- ition tem- perature* °C	Yield (% of theoretical amount)
$ \begin{array}{l} & [C_2H_5SiO_{1.5}]_4[OP(O)CH_3]_8 \\ & [C_4H_9SiO_{1.5}]_4[OP(O)CH_3]_6 \\ & [C_6H_{15}SiO_{1.5}]_4[OP(O)CH_3]_6 \\ & [C_9H_{19}SiO_{1.5}]_4[OP(O)CH_3]_6 \\ & [C_9H_{19}SiO_{1.5}]_4[OP(O)CH_3]_6 \\ & [(C_2H_9SiO_2O]_2[OP(O)CH_3]_4 \\ & [(C_4H_9SiO_2O]_2[OP(O)CH_3]_4 \\ & [(C_6H_{13}SiO_3O]_5]_2[OP(O)CH_3]_4 \\ & [(C_6H_{13}SiO_3O]_5]_2[OP(O)CH_3]_4 \\ & [(C_6H_{13}SiO_3O]_5]_2[OP(O)CH_3]_4 \\ & [(C_6H_{13}SiO_3O]_5]_2[OP(O)CH_3]_6 \\ & [(C_6H_{1$	$\begin{array}{c} 311 \ (0,022) \\ 296-299 \ (0,011) \\ 304-306 \ (0,01) \\ 273 \ (0,006) \\ 316 \ (0,018) \\ 325 \ (0,05) \\ 258-260 \ (0,014) \\ 306 \ (0,005) \\ 300-303 \ (0,003) \\ 308-310 \ (0,004) \end{array}$	1,5091 1,2942 1,2258 1,1625 1,5402 1,2718 1,1918 1,1124 1,1773 1,1026	28 45 28 15 54 23 3 19 12	10,7 42,5 90,7 117,8 64,0 82,5 91,3 89,7 75,0

\* The glass transition temperature was determined on Kargin's balance.

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TABLE 3. Physicochemical Properties of Hexaalkylcyclotrisiloxanes

Compound	Bp, °C (p, mm Hg)	d4 <sup>20</sup>	<sup>n20</sup> D	MR	
				found	calculated
[(C <sub>9</sub> H <sub>19</sub> ) <sub>2</sub> SiO] <sub>3</sub> [C <sub>10</sub> H <sub>21</sub> ) <sub>2</sub> SiO] <sub>3</sub>	157 (0,1) 193—196 (0,1)	0,8537 0,9458	1,4385 1,4418	114,74 124,75	1114,46 124,44



amount of distillate strongly depends on the organic radical attached to silicon. The dependence of the yield of cyclic and polymeric products on the size of the radical attached to silicon is shown in Fig. 1. Curves 1 and 2 show that at  $R = CH_3$  only polymeric products are formed; at  $R = C_4H_9$  the formation of cyclic and polymeric products is equally probable; larger R give mainly cyclic products according to the reaction

$$4\text{RSi}(\text{OC}_{2}\text{H}_{5})_{3} + 6(\text{HO})_{2}\text{P}(\text{O})\text{CH}_{3} \rightarrow [\text{RSiO}_{1,5}]_{4}[\text{OP}(\text{O})\text{CH}_{3}]_{6} + 12\text{C}_{2}\text{H}_{5}\text{OH}$$
$$\text{R} = \text{C}_{4}\text{H}_{9}, \text{C}_{6}\text{H}_{13}, \text{C}_{9}\text{H}_{19}$$

Further on, a study was made of the cocondensing reaction of methylphosphinic acid with dialkyltetraethoxydisiloxanes. The reaction proceeded according to the scheme

$$\begin{aligned} & 2[\text{RSi}(\text{OC}_2\text{H}_5)_2]_2\text{O} + 4(\text{HO})_2\text{P}(\text{O})\text{CH}_3 \rightarrow 8\text{C}_2\text{H}_5\text{OH} + [(\text{RSiO})_2\text{O}]_2[\text{OP}(\text{O})\text{CH}_3]_4 \\ & \text{R} = \text{C}_4\text{H}_9, \text{ C}_6\text{H}_{13}, \text{ C}_9\text{H}_{19} \end{aligned}$$

As in the case of alkyltriethoxysilanes, the amount of alcohol yielded was high (up to 95%) and the formation of cyclic and polymeric products depended on the size of the radical attached to silicon. This dependence is shown

in Fig. 1 (curves 3 and 4). The condensation of alkylethoxycyclotrisiloxanes with methylphosphinic acid proceeded according to the equation

 $2[R(C_2H_5O)SiO]_3 + 3(HO)_2P(O)CH_3 \rightarrow 6C_2H_5OH + [(RSiO)_3O_{1,5}]_2[OP(O)CH_3]_3$ 

$$R = C_6 H_{13}, C_9 H_{19}$$

All compounds obtained were colorless, very viscous, noncrystallizing, and readily converted into supercooled, glass-like substances of a fairly high density. Some physicochemical properties are given in Table 2. With the increase of the radical attached to silicon the density for the compounds of the same formula decreases and the glass transition temperature drops.

Compounds of composition  $[RSiO_{1.5}]_4[OP(O)CH_3]_6$  can be presented only by two structural formulas (Fig. 2, I, II). The most probable, according to our opinion, is structure I in which 8-membered organic phosphosilicon rings are linked by phosphinoxy groups. Structure II contains large 12-membered rings whose formation is less probable. Moreover, the formation of type II compounds assumes equal reactivity for all three ethoxy groups. However, it is known that the third alkoxy group possesses lower reactivity; consequently, the formation of structure II is less probable. For cyclohexamethylphosphinoxytetraisononyl-silsesquioxane, the IR spectrum shows absorption bands characteristic of groups (cm<sup>-1</sup>): 805 (Si - C), 1320 (P - CH<sub>3</sub>), 1220 (P = O), 2960, 2873 (CH<sub>3</sub>), 2930 (CH<sub>2</sub>). Two absorption bands were present in the region of valence vibrations of Si - O and P - O groups. The band with a maximum of 1125 cm<sup>-1</sup>, as described in [3].

characteristic of organosilses quioxanes, in our case is apparently caused by the presence of the Si-O group.

The band 1030-1080 cm<sup>-1</sup>, characteristic of 8-membered organosilicon and organic phosphosilicon (I) cyclic compounds, shows the presence of an 8-membered organic phosphosilicon ring. Thus, IR spectra also favor structure I.

Compounds of formula  $[(RSiO)_2O]_2$   $[OP(O)CH_3]_4$  can be presented by two structures (Fig. 2, III, IV). An analysis of structures on models has rejected structure IV. In the IR spectra recorded for cyclotetramethylphosphinoxytetrahexylsilsesquioxane and cyclotetramethylphosphinoxytetraisononylsilsesquioxane, absorption bands are present corresponding to bonds (cm<sup>-1</sup>): 805 (Si-C), 1320 (P-CH<sub>3</sub>), 1220 (P=O), 2960,

Fig. 1. Yield of cyclic (1, 3) and polymeric (2, 4) products as a function of the size of the radical attached to silicon.



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IV).

Fig. 2. Structure of inorganic backbone

of compounds of the type  $[RSiO_{1,5}]_4[OP(O)]$ 

 $\cdot$ CH<sub>3</sub>]<sub>6</sub> (I, II) and [(RSiO)<sub>2</sub>]<sub>2</sub>[OP(O)CH<sub>3</sub>]<sub>4</sub> (III,



Fig. 3. Model of cyclohexamethylphosphinoxytetranonylsilsesquioxane.

2873 (CH<sub>3</sub>) and 2930 (CH<sub>2</sub>). In the region of valence vibrations of Si-O and P-O bonds, a well defined peak is shown at 1025 cm<sup>-1</sup> (for cyclotetramethylphosphinoxytetranonylsilsesquioxane) and  $1035 \, \mathrm{cm}^{-1}$  (for cyclotetramethylphosphinoxytetrahexylsilsesquioxane). The peak suggests the presence of a 6-membered ring as well as the presence of a P-Obond. Moreover, absorption bands 1060-1130 and 1070-

1140 cm<sup>-1</sup> are caused by Si-O group. Figure 3 shows the

model of cyclohexamethylphosphinoxytetranonylsilsesquioxane.

The IR spectra of  $[(C_6H_{13}SiO)_3O_{1,5}][OP(O)CH_3]_3$  and  $[(C_9H_{19}SiO)_3O_{1,5}]_2[OP(O)CH_3]$  had absorption bands (cm<sup>-1</sup>): 1020 (caused by the presence of 6-membered siloxane ring), 1125 (characteristic of Si-O group);

1230 (P = O), 1325 (P - CH<sub>3</sub>), 2580 (CH<sub>3</sub>), 2935 (CH<sub>2</sub>).

Our data suggest the following reaction mechanism. Alkoxy groups containing organic phosphosilicon rings are first formed.



Such cyclic organic phosphosilicon compounds were obtained earlier in the condensation of dialkyldiethoxysilanes with methylphosphinic acid [1, 2].

The resulting cyclic compounds react with methylphosphinic acid in the positions of the remaining ethoxy groups.



Fig. 4. PMR spectra of a mixture of nonyltriethoxysilane with methylphosphinic acid (a) and of the product obtained in the reaction of ethyl alcohol (b) and cyclohexamethyl-phosphinoxytetranonylsilsesquioxane (c).



The voluminous organic groups attached to the silicon atom make difficult the intermolecular condensation and, as a result, the reaction proceeds mainly intramolecularly and leads to the formation of stereocyclic structures. A study was made of the hydrolytic stability of the reaction products. Experiments show that with the increase of the organic radical attached to silicon the hydrolytic stability somewhat increases.

It appeared of interest to clarify the possibility of preparing organic borosilicon compounds of similar stereocyclic structure. The reaction of isononyltriethoxysilane with boric acid proceeded with the formation of an organic borosilicon polymer. The condensation of boric acid with dinonyldiethoxysilane and didecyldiethoxysilane proceeded according to the scheme described earlier for diethyldiethoxysilane [4]:

$$\begin{aligned} 3R_2Si(OC_2H_5)_2 + 2(HO)_3B &\rightarrow [R_2SiO]_3 + 3H_2O + 2B(OC_2H_5)_3 \\ R &= C_9H_{19}, \ C_{10}H_{21} \end{aligned}$$

Distillation of the reaction products gave new compounds: hexanonylcyclotrisiloxane and hexadecylcyclotrisiloxane, whose structure and composition were established by elementary analysis, molecular weight determination, and IR spectra. The properties of the compounds are given in Table 3.



Fig. 5. PMR spectra of a mixture of nonyltriethoxysilane with phenylboric acid (a) and of reaction products: ethylphenyl borate (b), triphenylboroxole (c), and nonylsilsesquioxane (d).

The reaction of phenylboric acid with isononyltriethoxysilane and with hexyltriethoxysilane yielded ethylphenylborate, ethyl alcohol (in a small amount), triphenylboroxole and distillable alkylsilsesquioxanes; undistallable products, 3-4%. In the case of ethyltriethoxysilane, the yield of ethyl alcohol was 74.3%, of the theoretical amount, and the yield of undistallable polyethylsiloxane was 98.3%. Phenylboric acid was completely converted into its ethyl ester and triphenylboroxole. No organic borosilicon stereocyclic compounds were obtained.

In order to elucidate the processes occurring in the reactions of nonyltriethoxysilane with methylphosphinic and phenylboric acids a study was made of PMR spectra of the reagents, reaction mixtures, and all reaction products.\* Figure 4 shows PMR spectrum of the reaction mixture of nonyltriethoxysilane with methylphosphinic acid and PMR spectra of substances formed as a result of the reaction of alcohol with cyclohexamethylphosphinoxytetranonylsilsesquioxane. An examination of these spectra leads to the following conclusions: 1) the reaction proceeds with the separation of alcohol and simultaneous formation of  $CH_3$ -P and  $Si - C_9H_{19}$  groups; 2) PMR spectra of cyclohexamethylphosphinoxytetranonylsilsesquioxane shows two types of proton: H in  $Si - C_9H_{19}$  group and  $CH_3$  in  $P - CH_3$  group, the absence of other protons indicates the absence of end groups (OH,  $OC_2H_5$ ) and is a proof of the cyclic structure of the compound.

Figure 5 shows PMR spectra of the reaction mass of nonyltriethoxysilane with phenylboric acid and PMR spectra of the reaction products: ethylphenyl borate, triphenylboroxole, and nonylsilsesquioxane. An analysis of these spectra shows that: 1) the formation of ethylphenyl borate is only possible at the expense of substitution reactions of the functional groups; 2) no compounds are formed which contain simul-taneously  $C_6H_5$  and  $C_9H_{19}$  groups, i.e., no organic borosilicon compounds are formed and, consequently, no heterofunctional condensation reaction takes place. Thus, PMR spectra confirm the earlier assumption of the difference in the mechanisms of the reaction of nonyltriethoxysilane with methylphosphinic and phenylboric acids. The resulting data suggest the following reaction mechanism: in the case of phenylboric and boric acids there is apparently an exchange reaction of functional groups

 $2RSi(OC_2H_5)_3 + (HO)_2BC_6H_5 \rightarrow 2RSi(OH)(OC_2H_5)_2 + C_6H_5B(OC_2H_5)_2$ 

Further on, the hydroxyls at silicon are readily condensed

$$2RSi(OH)(OC_2H_5)_2 \rightarrow [RSi(OC_2H_5)_2]_2O + H_2O$$

The water which is separated hydrolyzes the ester to an acid which on heating is converted into triphenylboroxole

$$3(\mathrm{HO})_{2}\mathrm{BC}_{6}\mathrm{H}_{5}\longrightarrow [\mathrm{C}_{6}\mathrm{H}_{5}\mathrm{BO}]_{3} + 3\mathrm{H}_{2}\mathrm{O}$$

## EXPERIMENTAL

Dinonyldiethoxysilane and didecyldiethoxysilane were obtained by the Grignard reaction as described in [5]. The yield of dinonyldiethoxysilane was 19.7% of the theoretical amount. Found: C 71.22; H 12.75;

\* PMR spectra were taken with a MMR-5335 instrument, operating frequency 20 HMz in chloroform with tetramethylsilane as an internal standard.

Si 7.05%; mol.wt. 358.  $C_{22}H_{48}SiO_2$ . Calculated: C 70.88; H 13.01; Si 7.59%; mol.wt. 372. Didecylethoxy-silane gave a yield of 7.7% of the theoretical amount. Found: C 70.90; H 12.60; Si 6.33%; mol.wt. 413.3.  $C_{24}H_{52}SiO_2$ . Calculated: C 71.91; H 13.08; Si 7.00%; mol.wt. 400.8.

The remaining alkyltriethoxysilanes and alkylethoxysiloxanes were obtained by the esterification of the appropriate alkyltrichlorosilanes. Blowing-off of hydrogen chloride was carried out by undried nitrogen, thus yielding simultaneously the lower alkylalkoxysiloxanes. From 170 g of hexyltrichlorosilane, we obtained: 42.3 g of hexyltriethoxysilane, 51.4 g of dihexyltetraethoxydisiloxane, and 32.5 g of trihexyltriethoxy-cyclotrisiloxane. For dihexyltetraethoxydisiloxane. Found: C 56.04; H 10.89; Si 13.63%; mol.wt. 461.  $C_{20}H_{46}Si_2O_5$ . Calculated: C 55.56; H 10.87; Si 13.24%; mol.wt. 422. For trihexyltriethoxycyclotrisiloxane. Found: C 55.06; H 10.31; Si 15.96%; mol.wt. 519.  $C_{24}H_{54}Si_3O_6$ . Calculated: C 55.04; H 10.32; Si 16.05%; mol. wt. 523.

From 94.4 g of nonyltrichlorosilane, we obtained 21.8 g of nonyltriethoxysilane, 20.7 g of dinonyltetraethoxydisiloxane, and 18 g of trinonyltriethoxycyclotrisiloxane. For dinonyltetraethoxydisiloxane. Found: C 60.99; H 10.51; Si 11.11;  $OC_2H_5$  35.30%; mol.wt. 537.  $C_{26}H_{58}Si_2O_5$ . Calculated: C 61.19; H 11.33; Si 11.04;  $OC_2H_5$  35.55%; mol. wt. 507.0. For trinonyltriethoxycyclotrisiloxane. Found: C 61.33; H 10.94; Si 12.68%; mol. wt. 650.  $C_{33}H_{72}Si_3O_6$ . Calculated: C 61.04; H 11.18; Si 12.98%; mol. wt. 649. The constants cited above for ethoxysilanes and ethoxysiloxanes agree with the literature data.

From 169 g of isononyltrichlorosilane, we obtained 100.4 g of isononyltrimethoxysilane and 10.2 g of dinonyltetramethoxydisiloxane. For isononyltrimethoxysilane. Found: C 57.52; H 11.08; Si 12.45%; mol. wt. 228.  $C_{12}H_{28}SiO_3$ . Calculated: C 58.01; H 11.36; Si 11.30%; mol. wt. 248. For dinonyltetramethoxydisiloxane. Found: C 58.40; H 10.50; Si 12.73; OCH<sub>3</sub> 28.16%; mol. wt. 439.  $C_{20}H_{50}Si_2O_7$ . Calculated: C 58.61; H 11.18; Si 12.46; OCH<sub>3</sub> 27.54%; mol. wt. 450.

The condensation of alkylalkoxysilanes with methylphosphinic acid was carried out by one procedure: the reagents were placed into a Wurtz flask with a magnetic stirrer and heated slowly to 200°; alcohol was distilled off and then the reaction products were distilled in vacuo. The condensation of 22.36 g of butyltriethoxysilane and 14.16 g of methylphosphinic acid gave 9.59 g of cyclohexamethylphosphinoxytetrabutylsilsesquioxane. Found: C 27.84; H 6.18; Si 11.91; P 21.12%; mol. wt. 908.  $C_{22}H_{54}Si_4P_6O_{18}$ . Calculated: C 29.20; H 6.02; Si 12.42; P 20.54%; mol. w t. 904.9. The reaction of 19.5 g of hexyltriethoxysilane with 10.8 g of methylphosphinic acid gave 18.0 g of cyclohexamethylphosphinoxytetrahexylsilsesquioxane. Found: Si 11.15; P 18.46%; mol. wt. 1036.  $C_{30}H_{70}Si_4P_6O_{18}$ . Calculated: Si 11.04; P 18.25%; mol. wt. 1017. Condensation of 37.7 g of nonyltriethoxysilane with 18 g of methylphosphinic acid gave 34.4 g of cyclohexamethylphosphinoxytetraisononylsilsesquioxane. Found: C 41.33; H 7.99; Si 10.14; P 14.70%; mol. wt. 1078.  $C_{24}H_{94}$ ·Si<sub>4</sub>P<sub>6</sub>O<sub>18</sub>. Calculated: C 42.55; H 7.99; Si 9.47; P 15.67%; mol. wt. 1185.

Distillation of reaction products obtained as a result of condensing 26.9 g of ethyltriethoxysilane and 20.1 g of methylphosphinic acid gave a fraction with bp 311° (0.022 mm), 2.96 g. Found: C 19.63; H 5.05; Si 12.11; P 27.9%. C<sub>8</sub>H<sub>22</sub>Si<sub>2</sub>P<sub>4</sub>O<sub>11</sub>. Calculated: C 20.3; H 4.67; Si 11.85; P 26.1%. The reaction of 14.64 g of methyltriethoxysilane with 11.92 g of methylphosphinic acid gave 13.05 g of organic phosphosilicon polymer. Found: Si 14.92; P 25.98%. C<sub>5</sub>H<sub>15</sub>Si<sub>2</sub>P<sub>3</sub>O<sub>9</sub>. Calculated: Si 15.2; P 25.3%. Condensation of 23.1 g of dibutyltetraethoxydisiloxane with 12.1 g of methylphosphinic acid gave 15.4 g of cyclotetramethylphosphinoxytetrabutylsilsesquioxane. Found: C 31.08; H 7.47; Si 14.81; P 16.38%. C<sub>20</sub>H<sub>45</sub>Si<sub>4</sub>P<sub>4</sub>O<sub>14</sub>. Calculated: C 32.12; H 6.47; Si 14.87; P 16.57%. The reaction of 23.11 g of dihexyltetraethoxydisiloxane with 10.1 g of methylphosphinic acid gave 19.5 g of cyclotetramethylphosphinoxytetrahexylsilsesquioxane. Found: C 39.42; H 7.68; Si 13.38; P 14.87%; mol. wt. 836. C<sub>28</sub>H<sub>64</sub>Si<sub>4</sub>P<sub>4</sub>O<sub>14</sub>. Calculated: C 39.05; H 7.49; Si 13.05; P 14.39%; mol. wt. 861. Condensation of 20.24 g of diisononyltetraexthoxydisiloxane with 7.98 g of methylphosphinic acid gave 18.9 g of cyclotetramethylphosphinoxytetranonylsilsesquioxane. Found: Si 10.23; P 12.28%; mol. wt. 1080. C<sub>40</sub>H<sub>88</sub>Si<sub>4</sub>P<sub>4</sub>O<sub>14</sub>. Calculated: Si 10.91; P 12.03%; mol. wt. 1029. Distillation of reaction products obtained as a result of condensing 16.81 g of diethyltetraethoxydisiloxane with 15.51 g of methylphosphinic acid gave a fraction of bp 316° (0.018 mm). Found: Si 15.30; P 21.89%. C<sub>7</sub>H<sub>19</sub>Si<sub>2</sub>P<sub>3</sub>O<sub>9</sub>. Calculated: Si 14.15; P 23.45%. Condensation of 19.9 g of trihexyltriethoxycyclotrisiloxane with 8.05 g of methylphosphinic acid gave 18.02 g of cyclotrimethylphosphinoxyhexahexylsilsesquioxane. Found: Si 14.13; P 8.25%; mol. wt. 1064. C39HgrSi6 ·P<sub>3</sub>O<sub>15</sub>. Calculated: Si 15.93; P 8.78%; mol. wt. 1057. The reaction of 16.1 g of trinonyltriethoxycyclotrisiloxane with 5.35 g of methylphosphinic acid gave 12.2 g of cyclotrimethylphosphinoxyhexanonylsilsesquioxane. Found: Si 12.05; P 8.41%; mol. wt. 1338. C<sub>57</sub>H<sub>123</sub>Si<sub>6</sub>P<sub>3</sub>O<sub>15</sub>. Calculated: Si 12.87; P 7.09%; mol. wt. 1308.

Condensation of 21.2 g of dinonyldiethoxysilane with 2.35 g of boric acid gave 12.72 g of hexanonyl-cyclotrisiloxane. Found: C 72.15; H 12.95; Si 8.67%; mol. wt. 1009.  $C_{54}H_{114}Si_3O_3$ . Calculated: C 72.40; H 12.83; Si 9.41%; mol. wt. 893. The reaction of 10.64 g of didecyldiethoxysilane with 1.46 g of boric acid gave 5.62 g of hexanonylcyclotrisiloxane. Found: C 71.90; H 12.54; Si 9.32%; mol. wt. 1090.  $C_{60}H_{126}Si_3O_3$ . Calculated: C 73.53; H 12.96; Si 8.60%; mol. wt. 1010.

## CONCLUSIONS

1. The condensation of alkyltriethoxysilanes and dialkyltetraexthoxysiloxanes with methylphosphinic and phenylboric acids has been studied. With methylphosphinic acid the reaction proceeds with the formation of organic phosphosilicon compounds of a stereocyclic structure in a yield depending on the size of the radical attached to silicon.

2. The reaction mechanism and the structure of the reaction products have been proposed.

3. In the case of phenylboric acid, the reaction results in an exchange of functional groups and no organic borosilicon compounds are formed.

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