# SYNTHESIS AND INVESTIGATION OF CROSS-SHAPED AND SPIROCYCLIC HETEROORGANIC COMPOUNDS

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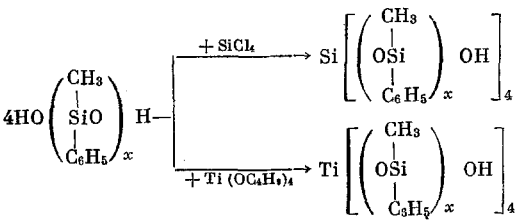
The study of the formation of branched cross-shaped heteroorganic compounds is of considerable theoretical interest. Compounds with the indicated structure have been little studied, and the mechanism of their chemical conversion is not yet clear.

This work discusses the synthesis and reactions of polycondensation of tetrakis(methylphenylsiloxanohydroxy)silanes and titanes. The above-mentioned compounds were produced by the reaction of the corresponding $\alpha,\omega$-dihydroxymethylphenylsiloxanes with $SiCl_4$ or tetrabutoxytitanium according to the following scheme



$x = 2, 3, 4$

The characteristics of the compounds obtained are cited in Table 1.

The polycondensation of tetrakis(methylphenylsiloxanohydroxy)silanes and titanes was conducted without catalysts. The first experiments indicated that the process occurs primarily with the formation of

TABLE 1. Tetrakis(methylphenylsiloxanohydroxy)silanes and Titanes

| Formula | Tglass, °C | Mol. wt. found | Mol. wt. calculated | Found, % OH | Found, % Si | Found, % Ti | Calculated, % OH | Calculated, % Si | Calculated, % Ti | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|
| $Si[(OSi)_2OH]_4$ | −22 | 1247 | 1185 | 5,45 | 21,36 | — | 5,73 | 21,31 | — | 49,0 |
| $Si[(OSi)_3OH]_4$ | −20 | 1858 | 1731 | 3,66 | 20,70 | — | 3,92 | 21,09 | — | 44,2 |
| $Si[(OSi)_4OH]_4$ | −19 | 2300 | 2276 | 2,82 | 20,73 | — | 2,99 | 20,91 | — | 30,0 |
| $Ti[(OSi)_2OH]_4$ | −42 | 1256 | 1206 | 5,42 | 18,42 | 3,88 | 5,65 | 18,60 | 3,80 | 46,5 |
| $Ti[(OSi)_3OH]_4$ | −33 | 1888 | 1751 | 3,66 | 19,01 | 2,64 | 3,88 | 19,25 | 2,70 | 45,2 |
| $Ti[(OSi)_4OH]_4$ | −27 | 2419 | 2296 | 2,81 | 19,17 | 2,24 | 2,98 | 19,57 | 2,08 | 47,8 |

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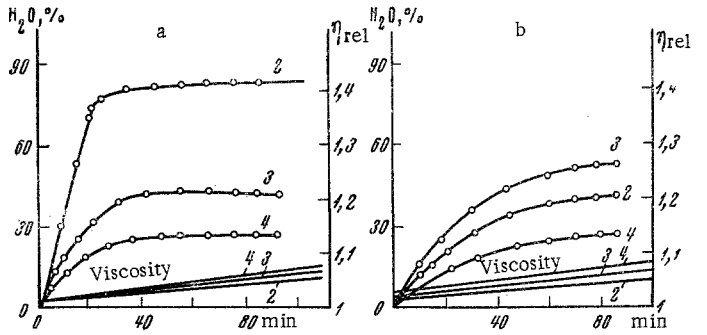
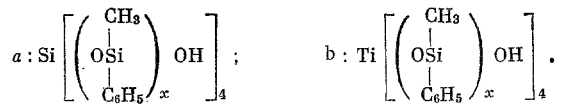



Fig. 1. Condensation of the simplest cross-shaped oligomers:



The numbers next to the curves represent values of x.

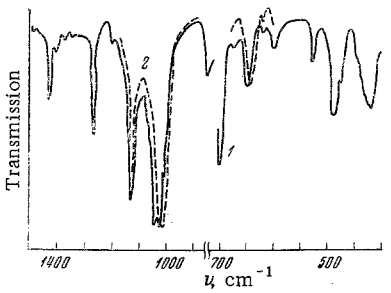



Fig. 2

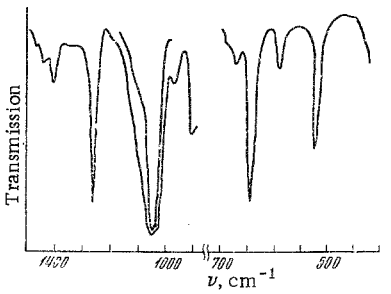



Fig. 3

Fig. 2. IR spectra: 1) dimethyl-2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxaspiro-(5,5)-undecane (IV); 2) trimethyltriphenylcyclotrisiloxane.

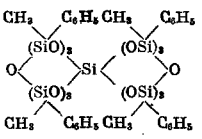
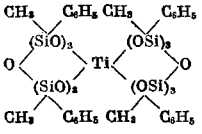
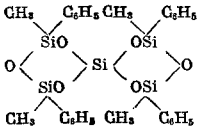
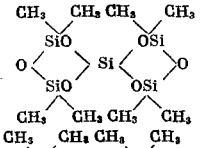
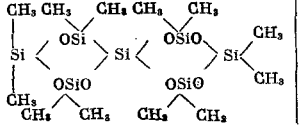
Fig. 3. IR spectrum of methylphenyl-2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxaspiro-(5,5)-undecane (III).

low-molecular products. In view of this, we were interested in conducting more thorough investigations of these reactions. The polycondensation of tetrakis(methylphenylsiloxanohydroxy)silanes and titanes was conducted at the temperature 150° in a stream of nitrogen. The course of the process was followed according to the amount of water liberated. The degree of drying of the nitrogen used to purge the system was evaluated in a blank experiment. The rate of passage of nitrogen was selected equal to 18-20 ml/min. Under these conditions the polycondensation of tetrakis(methylphenylsiloxanohydroxy)silanes and titanes occurs at a high rate, and after 2 h the degree of its completion with respect to the water liberated reaches more than 80%.

Figure 1 depicts the dependence of the amount of water liberated during the polycondensation process on the time and the change in the viscosity of the products to be concentrated. The second variation of the van't-Hoff differential method was used for the treatment of the experimental data and the determination of the reaction order. The experiments indicated that the reactions of polycondensation of tetrakis-(methylphenylsiloxanohydroxy)silanes have the same time order for all the oligomers, a fractional 2.7, while for the corresponding tetrakis(methylphenylsiloxanohydroxy)titanes the value is 1.7.

The formal rate constants of the polycondensation of tetrakis(methylphenylsiloxanohydroxy)silanes are equal to $k_1 = 1.2 \cdot 10^{-5}$ sec$^{-1}$ for oligomers with x = 2; $k_2 = 3.8 \cdot 10^{-7}$ sec$^{-1}$ for oligomers with x = 3; $k_3 = 2.0 \cdot 10^{-7}$ sec$^{-1}$ for oligomers with x = 4. For cross-shaped oligomers with a central titanium atom, the rate constant of polycondensation is equal to: for oligomers with x = 2 $k_4 = 1.59 \cdot 10^{-5}$ sec$^{-1}$; x = 3 $k_5 = 8.75 \cdot 10^{-6}$ sec$^{-1}$; x = 4 $k_6 = 2.96 \cdot 10^{-6}$ sec$^{-1}$.

TABLE 2. Spirocyclic Compounds

| Number | Formula | Mp ($T_{glass}$), °C | Mol. wt | | Found, % | | | | Calculated, % | | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | found | calculated | Si | Ti | C | H | Si | Ti | C | H | |
| I |  | (—23) | 1610 | 1695 | 20,92 | — | 60,02 | 5,27 | 21,53 | — | 59,53 | 5,27 | 15,0 |
| II |  | (—38) | 1600 | 1715 | 19,00 | 2,75 | 58,91 | 5,50 | 19,59 | 2,79 | 58,84 | 5,64 | 10,0 |
| III |  | (—10) | 589 | 605 | 23,03 | — | 55,49 | 5,40 | 23,21 | — | 55,59 | 5,33 | 1,0 |
| IV |  | 121 | 360 | 357 | 39,50 | — | 26,89 | 6,46 | 39,37 | — | 26,94 | 6,78 | 9,9 |
| V |  | 31 | 520 | 505 | 38,50 | — | 29,50 | 7,26 | 38,93 | — | 28,54 | 7,19 | 2,7 |

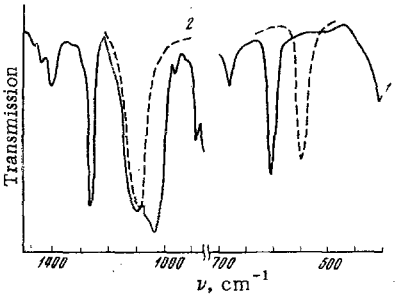



Fig. 4

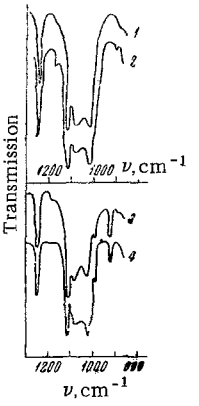


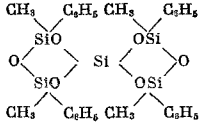
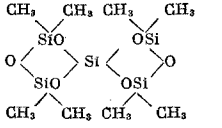
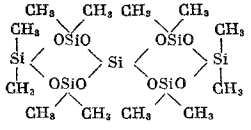
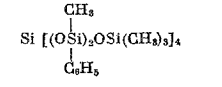
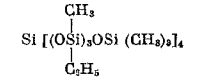
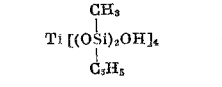
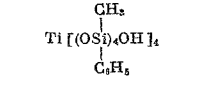
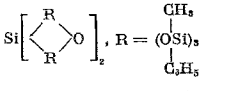
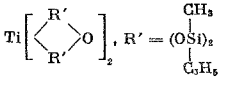
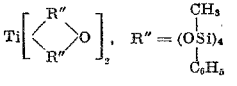

Fig. 5

Fig. 4. IR spectra: 1) dimethyl-2,4,6,8,10,12,14-heptasila-1,3,5,7,9,11,13,15-octaoxaspiro-(7,7)-pentadecane (V); 2) octamethylcyclotetrasiloxane.

Fig. 5. IR spectra: 1) tetrakis-(3,5,7,9,11,13-hexamethyl-3,5,7,9,11,13-hexaphenylhexasiloxano-13-trimethylsiloxy)silane; 3) tetrakis-(3,5,7-trimethyl-3,5,7-triphenyltrisiloxano-7-trimethylsiloxy)titane; 4) tetrakis-(3,5,7,9,11,13-hexamethyl-3,5,7,11,13-hexaphenylhexasiloxano-13-triphenylsiloxy)titane.

All this indicates a complexity of the reactions that occur, which will require further study before it can be explained. This complexity is also indicated by the composition of the products. All the condensation products, both obtained from tetrakis(methylphenylsiloxanohydroxy)silanes and from tetrakis(methylphenylsiloxanohydroxy)titanes, are transparent viscous liquids at room temperature, readily soluble in organic solvents, containing no hydroxyl groups. The absence of hydroxyl groups permits us to assume that

TABLE 3. IR Spectra of the Investigated Substances

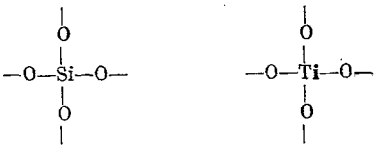
| Number | Formula of substance | Assignment of frequencies* | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | ν (OH) | $\nu_{CH}$ in the aromatic ring | | | $\nu_{as}$ $(CH_3)_3$ | $\nu_s$ $(CH)_3$ | $C_6H_5$—(Si) | δ $CH_3$—(Si) | | | $\nu_{as}$ (SiOSi) | | | Si—O—Ti | | | | $\nu_s$ $(SiC_3)$ $\nu_s$(SiO—Si) | | | | | δ (O—Si—$CH_3$) |
| I |  | — | 3070 s | 3050 s | 3023 m | 2961 s | 2910 w | 1432 m | 1409 w | 1268 s | 1130 s | — | 1039 s | 1028 s | 1000 w | — | 700 m | 675 w | 642 m | 592 w | — | 523 m | 485 s | 415 s |
| II |  | — | — | — | — | 2962 s | 2906 w | — | 1409 w | 1269 s | — | — | 1046 s | 1036 s | — | — | 700 m | 675 w | 644 m | 594 w | — | 524 m | — | 415 s |
| III |  | — | — | — | — | 2960 s | 2906 w | — | 1408 w | 1267 s | — | 1090 m | — | 1029 s | — | — | — | 686 w | — | 608 s | — | 523 m | — | 410 m |
| IV |  | — | 3068 s | 3049 s | 3020 m | 2960 s | 2906 w | 1430 | 1409 w | 1267 s | 1131 s | 1080 s | — | 1022 s | 1000 w | — | 700 m | 685 | 644 m | 600—618 w | 550 v. w | 523 w | 481 s | 414 m |
| V |  | — | 3070 s | 3050 s | 3023 m | 2963 s | 2910 w | 1432 m | 1410 w | 1269 s | 1131 s | 1087 s | 1068 s | 1028 s | 1000 w | — | 700 m | 688 | 644 w | 600—618 w | 541 w | 521 v. w | 480 486 s | 415 |
| VI |  | 3400 3600 w | 3070 s | 3049 s | 3021 m | 2960 s | 2910 w | 1430 | 1410 w | 1263 s | 1131 | 1090 s | — | 1030 s | 1000 w | 927 m | 700 m | 688 | 645 w | 618 w | 550 w | 521 m | 482 s | 415 m |
| VII |  | 3400 3600 v. w | 3069 s | 3050 s | 3023 m | 2961 s | 2908 w | 1430 m | 1410 w | 1265 s | 1128 s | 1080 s | — | 1027 s | 1000 w | 928 m | 700 m | 686 | 645 w | — | 550 w | 524 w | 482 s | 415 m |
| VIII |  | — | 3069 s | 3050 s | 3022 m | 2961 s | 2906 w | 1431 m | 1408 w | 1267 s | 1130 s | 1084 s. b | — | 1026 s | 1000 w | — | 700 m | 685 | 644 v. w | 590 w. b | 540—550 w | 522 w | 483 s | — |
| IX |  | — | 3069 s | 3050 s | 3023 m | 2962 s | 2908 w | 1431 | 1410 w | 1268 | 1130 | 1092 s | 1070 s | 1026 v. s | 1000 w | 926 m | 700 m | 686 | 642 w | — | 550 v. w | 522 w | 481 s | 414 m |
| X |  | — | 3070 s | 3050 s | 3022 m | 2962 s | 2910 w | 1430 | 1408 w | 1266 | 1130 | 1085 s. b | — | 1022 s | 1000 w | 924 m | 700 m | 686 w | 642 w | — | 540 w | 521 w | 483 s | 415 m |

* The frequencies are expressed in $cm^{-1}$; s) strong, m) medium, v. w) very weak, w) weak, v. s) very strong, b) broad.

these products have a cyclic structure. Exposure of the condensation products at the temperature 25° for 10 days led to their partial crystallization, but the crystalline portion formed could not be separated by filtration. Compounds, the composition and molecular weight of which correspond to spirocyclic compounds (Table 2, Nos. I, II), were obtained by fractional addition of the condensation products, followed by their sublimation at 60° and a residual pressure of 0.5 mm. The unsublimed products are identical in composition with the sublimed products and have an average mol. wt. 2300-2500. These data show that the polycondensation process proceeds primarily intramolecularly and leads to spirocyclic compounds. The compounds obtained were investigated by the methods of IR spectroscopy and x-ray diffraction study. Such compounds were first mentioned in [1-4].

Figures 2-4 give the IR spectra of dimethyl-2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxaspiro-(5,5)-undecane (IV), methylphenyl-2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxaspiro-(5,5)-undecane (III), and dimethyl-2,4,6,8,10,12,14-heptasila-1,3,5,7,9,11,13,15-octaoxaspiro-(7,7)-pentadecane (V) (see Table 2). The IR spectrum of spiro-compounds differs most appreciably from the IR spectrum of organocyclosiloxanes in the frequencies of the skeletal vibrations of the siloxane chain of the molecule: the frequency of the asymmetrical valence vibration $\nu_{as}$(SiOSi) of trimethyltriphenylcyclotrisiloxane is 1019 $cm^{-1}$ [1], while a very intense band with two peaks: 1036 and 1046 $cm^{-1}$ (III) and 1028 and 1039 $cm^{-1}$ in (IV) is observed in the spectrum of the spiro-compounds (IV) and (III) in this region. The frequencies of the symmetrical valence vibrations $\nu_{s}$(SiOSi) of organocyclotrisiloxanes and the spiro-cycle are very close. The frequency $\nu_{as}$(SiOSi) of octamethylcyclotetrasiloxane is 1087 $cm^{-1}$ [1], while in the IR spectrum of the spiro-compound (V) a band is observed with two maxima 1090 and 1029 $cm^{-1}$. At the same time, $\nu_{s}$(SiOSi) is increased by 58 $cm^{-1}$ in comparison with the corresponding vibration in octamethylcyclotetrasiloxane. Thus, in the IR spectra of spiro-compounds, splitting of the asymmetrical valence vibration and a shift of the symmetrical valence vibration of (SiOSi) are observed.

We were interested in comparing the IR spectra of spirocyclic compounds with the IR spectra of tetrakis(methylphenylsiloxanohydroxy)silanes and titanes and the products of their thermal condensation, containing the groups



In the IR spectra of the compounds cited in Table 3, possessing a branched central atom (silicone or titanium), doubling of the band $\nu_{as}$ (SiOSi) into two maxima is observed, where the intensity of the long-wave maximum increases with decreasing size of the methylphenylsiloxane branch (Fig. 5). The nature of the terminal groups (–OH or $-OSiR_3$) has no appreciable influence (see Table 3). The peculiarities of the IR spectra of the compounds studied, both spirocyclic and cross-shaped, and their condensation products are evidently associated with the vibrations of the (Si–O–Si) groups adjoining the central atom and comprising on the whole the structural nucleus, which is preserved in all the compounds.

X-ray diffraction studies of tetrakis(methylphenylsiloxanohydroxy)silane and its condensation product indicated that tetrakis(methylphenylsiloxanohydroxy)silane is amorphous at room temperature when cooled to –120°, while the condensation product – a spirocyclic compound – has a pronounced crystalline structure. The absence of crystallization in tetrakis(methylphenylsiloxanohydroxy)silanes and titanes is probably due to the presence of hydrogen bonds.

## EXPERIMENTAL METHOD

Production of 2,2,4,4,8,8,10,10-Octamethyl-2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxaspiro-(5,5)-undecane. In a four-necked flask equipped with a mixer, two burettes, and a reflux condenser, we placed 50 ml of anhydrous benzene and 0.1 g (two drops) of pyridine. The reaction flask was cooled with ice. Then, with vigorous mixing, the first and second solutions were added from the two burettes simultaneously at the same rate to the contents of the flask over a period of 5 min. The first solution contained 2.21 g $SiCl_4$ in benzene; the second contained 4.32 g 1,3-dihydroxytetramethyldisiloxane and 4.11 g pyridine in benzene. The first and second solutions were prepared in amounts such that the final volume of each was equal to 30 ml. The reagents were carefully protected from atmospheric moisture. The temperature in the reaction mixture was kept at ~40°. After the introduction of the entire contents of the burettes, the

reaction mass was mixed for 1.5 h. Then the pyridine hydrochloride precipitate was removed on a No. 4 Schott filter, the benzene solution washed to remove traces of pyridine with respect to bromothymol blue, dried with calcined $K_2CO_3$, and the solvent distilled off under vacuum. A crystalline mass with mp 117-122° was formed. From it we isolated 0.46 g (9.97% of the theoretical) 2,2,4,4,8,8,10,10-octamethyl-2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxaspiro-(3,5)-undecane with mp 121° by sublimation at 50° (0.5 mm). Found: Si 39.09; 39.50; C 26.89; H 6.46%; mol. wt. 360. $C_8H_{24}O_6Si_5$. Calculated: Si 39.37; C 26.94; H 6.78% mol. wt. 357.

Production of 2,2,4,4,6,6,10,10,12,12,14,14-Dodecamethyl-2,4,6,8,10,12,14-hexasila-1,3,5,7,9,11,15-octaoxaspiro-(7,7)-pentadecane. Analogously, when we mixed three solutions: the first (2.45 g $SiCl_4$ in benzene), the second (6.94 g 1,5-dihydroxyhexamethyltrisiloxane, 4.57 g pyridine, and benzene), and the third (0.1 g pyridine in 50 ml benzene), we obtained 0.19 g (2.66% of a product with mp 31°. Found: Si 38.5; C 29.5; H 7.26% mol. wt. 520. $C_{12}H_{36}O_8Si_7$. Calculated: Si 38.93; C 28.54; H 7.19%; mol. wt. 505.

Production of 2,4,8,10-Tetramethyl-2,4,8,10-tetraphenyl-2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxaspiro-(5,5)-undecane. Analogously, when three solutions are mixed: the first (1.76 g $SiCl_4$ in benzene), the second (6.00 g 1,3-dihydroxy-1,3-dimethyl-1,3-diphenyldisiloxane and 3.27 g pyridine) and the third (0.1 g pyridine in 80 ml benzene), we obtained 0.07 g (1.04%) of a crystalline product by sublimation at 60° (1 mm). Found: Si 22.38; 23.03%; mol. wt. 589. $C_{28}H_{32}O_6Si_5$. Calculated: Si 23.21%. No hydroxyl group.

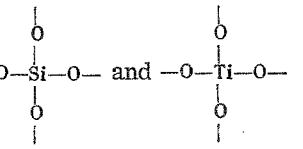
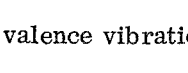
Production of the Spirocyclic Compound (I). In a three-necked flask, equipped with a thermometer, mixer, and bubbler, we placed 7.75 g tetrakis(3,5,7-trimethyl-3,5,7-triphenylsiloxano-7-hydroxy)silane. The contents of the flask were heated to 150° with mixing in a stream of nitrogen and kept at this temperature for 10. As a result a viscous liquid was formed, from which 1.14 g (15.0%) of a product with a vitrification point of −23° was obtained by sublimation at 60° and a residual pressure of 0.5 mm. Found: C 60.02; H 5.27; Si 20.92%; mol. wt. 1610. $C_{84}H_{96}O_{14}Si_{13}$. Calculated: C 59.53; H 5.27; Si 21.53%; mol. wt. 1695.

Production of the Spirocyclic Compound (II). According to the procedure indicated above, we obtained 0.77 g (10%) of a product with vitrification point −38° from 7.89 g tetrakis-(3,5,7-trimethyl-3,5,7-triphenyltrisiloxano-7-hydroxy)titane. Found: C 58.91; H 5.50; Si 19.00; Ti 2.75%; mol. wt. 1600. $C_{84}H_{96}O_{14}Si_{12}Ti$. Calculated: C 58.84; H 5.64; Si 19.59; Ti 2.79%; mol. wt. 1715.

## CONCLUSIONS

1. The polycondensation of tetrakis(methylphenylsiloxanohydroxy)titanes and silanes proceeds according to a complex mechanism.

2. Several spirocyclic compounds with central silicone and titanium atoms and with dimethyl or methylphenyl framing at the silicone atoms in the siloxane chain were isolated.

3. The IR spectra were investigated. For all the compounds possessing the  and  groups, splitting of the asymmetrical valence vibrations of  is observed.

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