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Synthesis of Siloxyalumoxanes and Alumosiloxanes Based on Organosilicon Diols

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Abstract We have drawn a few interesting conclusions while studying reaction products of $Ph_2Si(OH)_2$ with $Al(^iBu)_3$ and tetraisobutylalumoxane. In the first place, this is the production (at $Ph_2Si(OH)_2$ and $Al(^iBu)_3$ equimolar ratio) of oligomer siloxyalumoxane structure with alternating four- and six-member rings, as well as isobutyl and phenyl groups migration between aluminum and silicon due to the formation of intramolecular four-member cyclic complex $[Ph_2(OH)SiO]Al(^iBu)_2 \rightarrow [(^iBu)Ph(OH)SiO]Al(^iBu)Ph$. $Ph_2Si(OH)_2$ interaction with $Al(^iBu)_3$ not only starts from intramolecular complex production, but the chain is terminated for the same reason, which in the case of $Ph_2Si(OH)_2$ reaction with tetraisobutylalumoxane results in failure of obtaining high-polymer siloxyalumoxane compounds. When $Al(^iBu)_3$ interacts with α- and γ-diols, no oligomer compounds are produced. $Al(^iBu)_3$ reaction with α, γ-diols results in monomer compounds that are likely to have cyclic structure. Notably at $Al(^iBu)_3$ interaction with α-diol only double excess of $Al(^iBu)_3$ allows full replacement of hydrogen in α-diol hydroxyl groups by aluminum alkyl residue with 1,3-bis(diisobutylalumoxymethyl)-1,1,3,3-tetramethyldisiloxane production. At equimolar ratio of initial reagents the second isobutyl radical at Al does not interact with the second hydroxyl group of α-diol, apparently due to the steric hindrance and 1-(diisobutylalumoxymethyl)-3-(hydroxymethyl)-1,1,3,3-tetramethyl-disiloxane is produced. $Al(^iBu)_3$ reactions with γ-diol also result in monomer compounds but the presence of a chain consisting of three CH_2-groups between Si and hydroxyl group facilitates interaction between the second hydroxyl group of γ-diol and the second isobutyl radical $Al(^iBu)_3$. Tetraisobutylalumoxane reaction with α- and γ-diols results in oligomer compounds.

Keywords: organosiloxyalumoxanes, organoalumosiloxanes, triisobutylaluminum, tetraisobutylalumoxane, diphenylsilanediol, α-diol, γ-diol

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1. Introduction

Organosiloxyalumoxane and organoalumoxanesiloxane oligomers were synthesized 30 years ago [1]. Their probable structure from conventional viewpoint looked like three-coordinated Al atom. These compounds are amorphous, therefore it did not seem possible to prove their structure by means of X-ray diffraction. But in the middle of 1980s papers dealing with nonclassical structure of alumoxane and alumosiloxane compounds with four-coordinated Al atom and three-coordinated oxygen atom were published [2–4]. The coordination number of Al atoms in bicyclic and oligomer alumoxanes and alumosiloxanes was shown to be 4 and may increase to 5 (or even to 6) [2]. The crystalline structure of alumosiloxane of $C_8H_{24}Al_3Br_5O_6Si_4$ composition was proved [5]. It was found that the molecule of crystalline alumosiloxane consisted of four condensed nuclei: two planar four-membered rings, built from two aluminum atoms and two oxygen atoms, and two "saddle-shaped" six-membered rings composed of alternating silicon, oxygen, and aluminum atoms. The Al atom, which belongs to all four rings, has a coordination number of 5. The remaining atoms of aluminum and silicon have tetrahedral coordination.

Based on the data of [2–5], the results of [1] were analyzed. In addition, the reaction of $Al(^iBu)_3$ with $Ph_2Si(OH)_2$ in hexadeuterobenzene was studied. The results obtained suggested a probable scheme for the interaction of $Al(^iBu)_3$ with $Ph_2Si(OH)_2$ and the possible structure of the oligomers obtained [6]. However these results were not published.

Since the beginning of the 1990s, detailed studies of the synthesis, properties, and structure of alkylalumoxanes have been carried out [7–14]. In 2013, works on this problem were summarized in the review [15].

The nearest aspect of our work was the investigation performed by Andrew R. Barron's group, they studied the synthesis, properties and structure of organosiloxyalumoxanes - precursors of alumosilicate ceramics [16,17].

A considerable number of molecular alumosiloxanes and alumosilicates have been obtained using aluminum halogenides, chalcogenides, hydrides, and organometallic compounds as starting materials, by reacting them with the appropriate $R_nSi(OH)_{4-n}$ precursor [18].The reaction of Al_2Cl_6 with an excess of $Ph_2Si(OH)_2$ in THF in the presence of pyridine yielded new anionic and cyclic aluminosiloxanes: the structure of the anionic complex comprises separated pyridinium cations and alumosiloxane anions with a tetrahedral arrangement around the Al atom, which is similar to that in natural aluminosilicates; the core of the cyclic aluminosiloxane is a twelve-membered $Al_2Si_4O_6$ ring in a chair conformation, which contains a Cl group on each of the two Al atoms [19]. Reaction of $Al(^tBu)_3$ with neol-H_2 (2,2-dimethylpropane-1,3-diol) yields

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[Al$_2$(^{t}Bu)$_4$(neol-H)$_2$]. [Al$_2$(^{t}Bu)$_4$(neol-H)$_2$] may be considered as bifunctional (two OH groups), tetradentate (*4O*) ligands as highlighted by its reactivity with Group 13 hydrides and alkyls. Reaction of [Al$_2$(^{t}Bu)$_4$(neol-H)$_2$] with AlH$_3$(NMe$_3$), AlH$_2$Cl(NMe$_3$) and AlMe$_3$ yields the tri-aluminium compounds, [Al$_3$(^{t}Bu)$_4$(X)(neol)$_2$] with X = H, Cl, Me, respectively [20].

The main research on the synthetic and structural chemistry of alumosiloxanes is described in the review [21]. Michael Veith's works describe the synthesis, physicochemical properties, crystal structure and interaction of polycyclic [Ph$_2$SiO]$_8$[AlO(OH)]$_4$ with various chemical compounds [22–25].

2. Results and Discussion

To investigate the mechanism of Al(^{i}Bu)$_3$ reaction with Ph$_2$Si(OH)$_2$ we studied (by means of NMR spectroscopy) their interaction in hexadeuterobenzene (C$_6$D$_6$). In contrast to the reactions in benzene deuterobenzene solvent makes it possible to determine besides isobutyl groups benzene presence in ^{1}H and ^{13}C NMR spectra. In NMR spectra of the reaction mixture after Al(^{i}Bu)$_3$ interaction with Ph$_2$Si(OH)$_2$, is completed, a proton signal was observed at 7.23 ppm, and a signal of ^{13}C nuclei of unlabeled benzene was observed at 128 ppm [26]. When siloxyalumoxane oligomer reaction product was released, the produced benzene was distilled along with a solvent (C$_6$D$_6$) and was recorded in NMR spectra of the distillate. Benzene may be produced in the result of phenyl and isobutyl groups exchange between silicon and aluminium. Earlier a few authors [27] observed phenyl and alkyl groups migration in triphenylsiloxyaluminiumalkyl at 250–300 °C (Figure 1).

Figure 1. Migration of the phenyl and alkyl groups in triphenylsiloxyaluminiumalkyl.

$$\mathrm{Ph_3SiOAlR_2} \xrightarrow[\mathrm{R=Et}]{250\text{-}300\ ^0\mathrm{C}} \mathrm{PhR_2SiOAlPh_2}$$

In our case such migration is observed even at 80 °C.

In ^{27}Al NMR spectra of the products of Al(^{i}Bu)$_3$ reaction with Ph$_2$Si(OH)$_2$ in C$_6$D$_6$ at 25 °C broad signal typical for oligomer structures where aluminium coordination number is four was recorded at 61,0 ppm.

According to the abovementioned we can propose the following mechanism of siloxyalumoxane oligomers production through an active intramolecular complex (A*), wherein isobutyl and phenyl groups exchange at aluminium and silicon is probable (Scheme 1).

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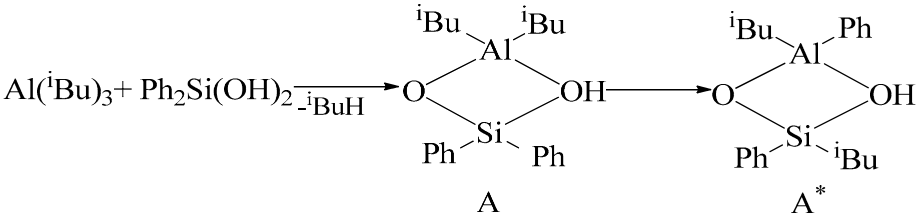
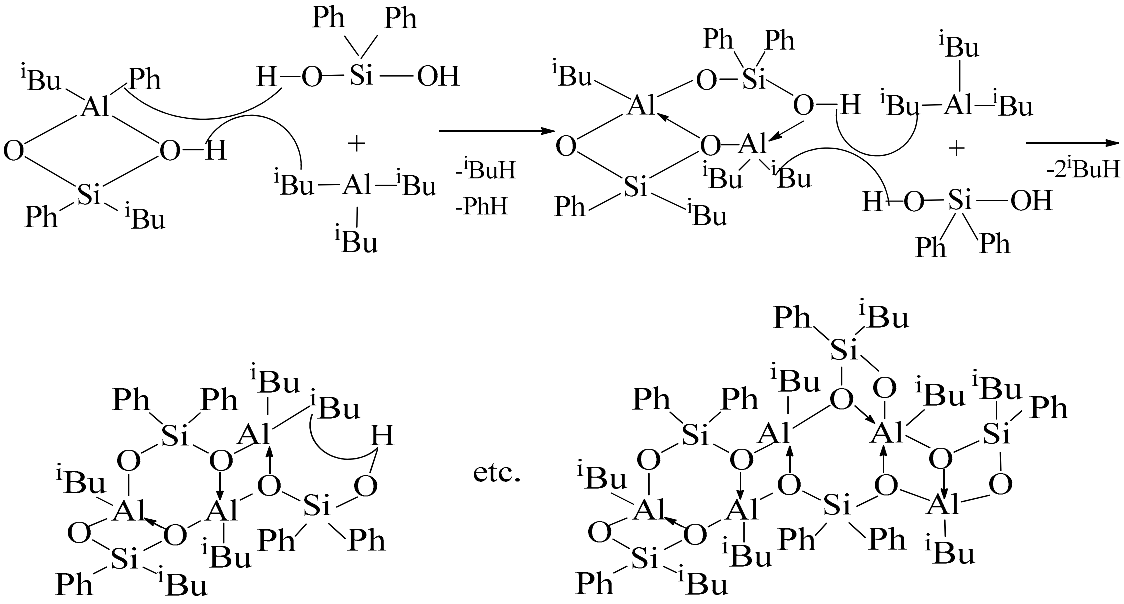
Scheme 1. The formation of active intramolecular complex (A*).



At equimolar ratio of the starting reagents hydrogen of the hydroxyl group reacts with ^{i}Bu-group of another Al(^{i}Bu)$_3$ molecule and one of the organic groups at aluminium (preferably phenyl one as it has more electronegative character than isobutyl group) interacts with hydrogen of OH group of the next Ph$_2$Si(OH)$_2$ molecule. Six-membered ring is formed, the ring in its turn has active sites able to react with the following Al(^{i}Bu)$_3$ and Ph$_2$Si(OH)$_2$ molecules, which results in four-membered alumoxane ring, then six-membered ring is formed again etc. (Scheme 2).

Scheme 2. The probable scheme of interaction of Al(^{i}Bu)$_3$ and Ph$_2$Si(OH)$_2$ at Al:Si=1:1.



1

The chain is terminated due to intramolecular A* complex.

So, siloxyalumoxane oligomer **1** is formed where one of the phenyl groups is substituted by an isobutyl group at three silicon atoms. Considering the amount of C_6D_6, taken for synthesis (at equimolar ratio of Al(^{i}Bu)$_3$: Ph$_2$Si(OH)$_2$ = 1:1), the distilled C_6D_6 must contain about 1.5 wt

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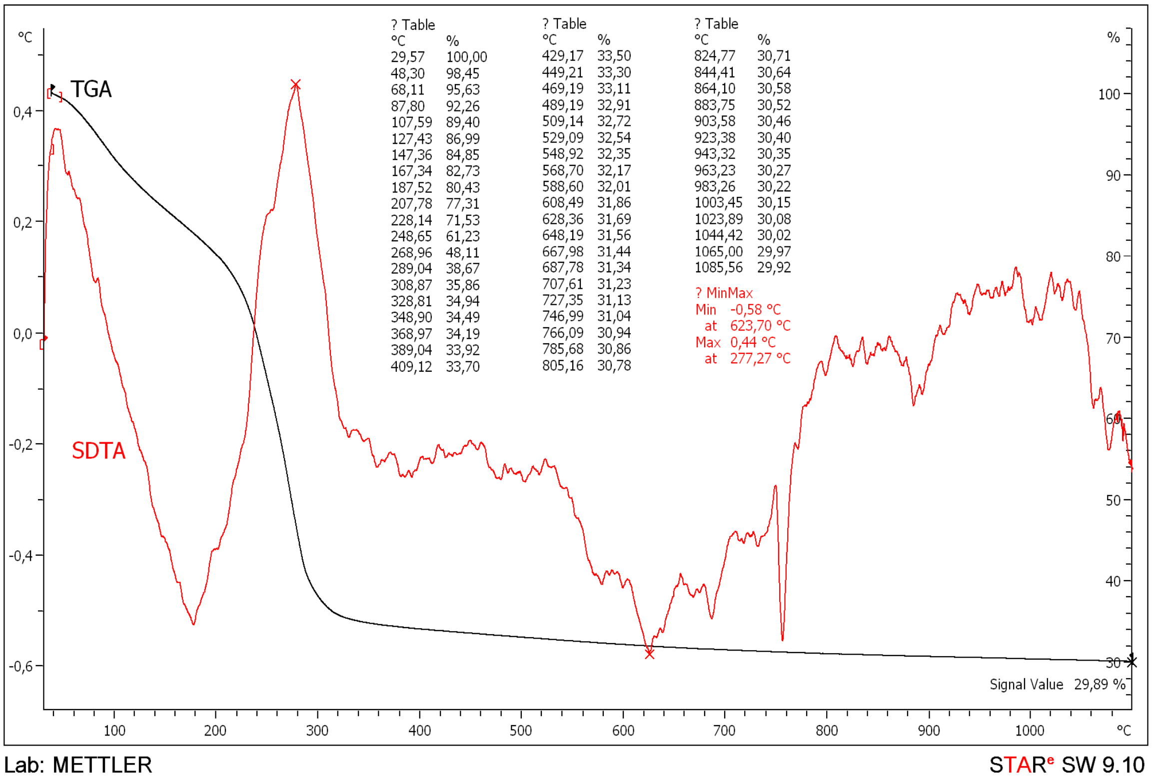
% of benzene. Mass spectrometric analysis of the distillate showed that along with the used solvent (C_6D_6) 1.6 wt % of benzene is distilled.

Oligomer **1** production is confirmed by thermo-gravimetric analysis results (Figure 2).

Figure 2. Thermogram of oligomer **1**.



? Table

°C	%
29,57	100,00
48,30	98,45
68,11	95,63
87,80	92,26
107,59	89,40
127,43	86,99
147,36	84,85
167,34	82,73
187,52	80,43
207,78	77,31
228,14	71,53
248,65	61,23
268,96	48,11
289,04	38,67
308,87	35,86
328,81	34,94
348,90	34,49
368,97	34,19
389,04	33,92
409,12	33,70

? Table

°C	%
429,17	33,50
449,21	33,30
469,19	33,11
489,19	32,91
509,14	32,72
529,09	32,54
548,92	32,35
568,70	32,17
588,60	32,01
608,49	31,86
628,36	31,69
648,19	31,56
667,98	31,44
687,78	31,34
707,61	31,23
727,35	31,13
746,99	31,04
766,09	30,94
785,68	30,86
805,16	30,78

? Table

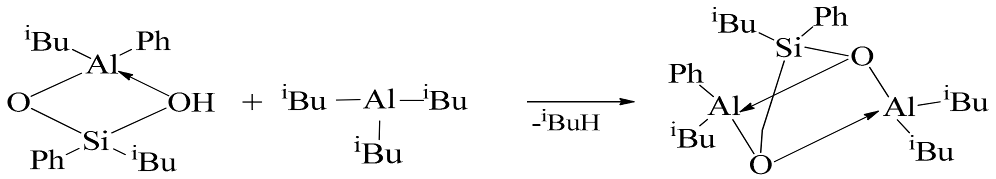
°C	%
824,77	30,71
844,41	30,64
864,10	30,58
883,75	30,52
903,58	30,46
923,38	30,40
943,32	30,35
963,23	30,27
983,26	30,22
1003,45	30,15
1023,89	30,08
1044,42	30,02
1065,00	29,97
1085,56	29,92

? MinMax
Min -0,58 °C
at 623,70 °C
Max 0,44 °C
at 277,27 °C

The TGA curve shows that in the temperature range of 30–230 °C the weight loss is about 30 wt %, while the SDTA curve shows an endo-effect at 180 °C. This corresponds to the complete removal of isobutyl groups in the form of isobutene (theoretically, the weight loss is 31.33 wt %). In the temperature range of 230–650 °C, the weight loss is about 40 wt. %, while the SDTA curve shows an exo-effect at 280 ºC. This corresponds to the complete removal of the phenyl groups in the form of benzene (theoretically the weight loss is 38.18 wt %). Further pyrolysis in an inert atmosphere (argon) to 1100 °C leads to the formation of an alumosilicate ceramic residue of 29.89 wt %, which actually coincides with the theoretically calculated value for oligomer **1** (30.42 wt %) (Figure 2).

At $Al(^iBu)_3$ (Al:Si = 2:1) excess the complex is stabilized due to the second $Al(^iBu)_3$ molecule attachment and formation of bis(diisobutylalumoxy)diphenylsilane; taking into account isobutyl and phenyl groups migration between aluminium and silicon the interaction mechanism can be presented as follows (Scheme 3).

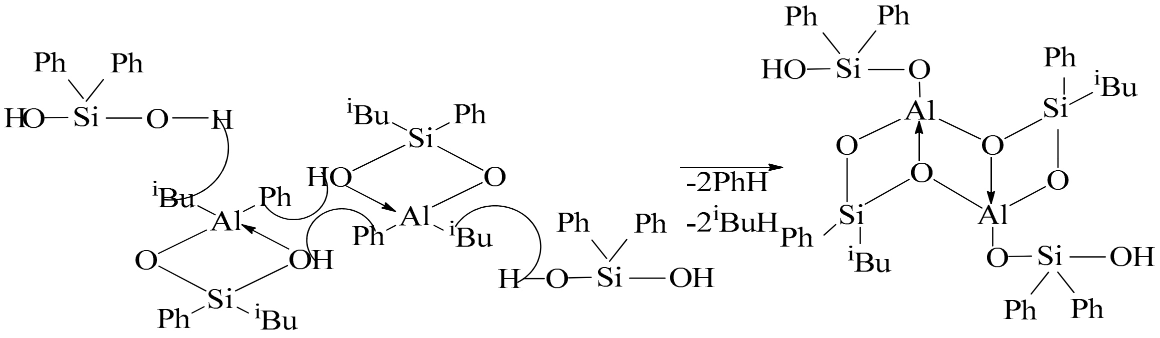
Scheme 3. The probable scheme of interaction of Al(^{i}Bu)$_3$ and Ph$_2$Si(OH)$_2$ at Al:Si=2:1.



2

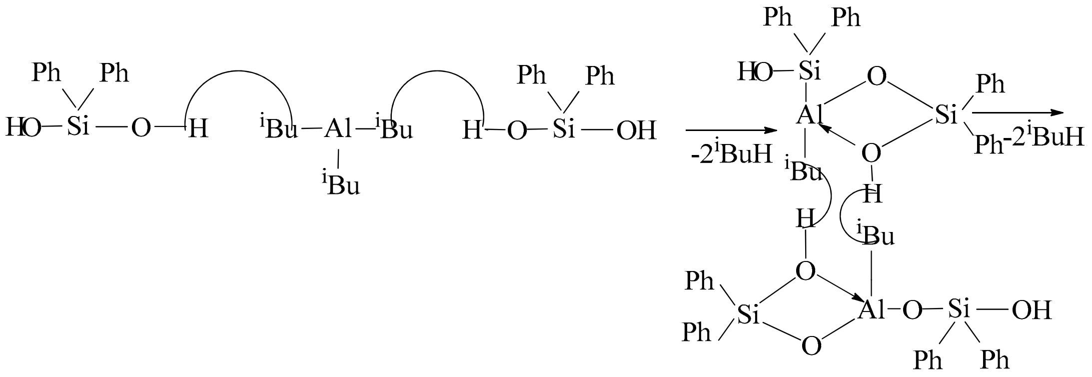
When the reaction proceeds at Ph$_2$Si(OH)$_2$ (Al:Si=1:2) excess, organosiloxyalumoxane formation may be presented in two ways (Scheme 4).

Scheme 4. The probable scheme of interaction of Al(^{i}Bu)$_3$ and Ph$_2$Si(OH)$_2$ at Al:Si=1:2.



3

(a)



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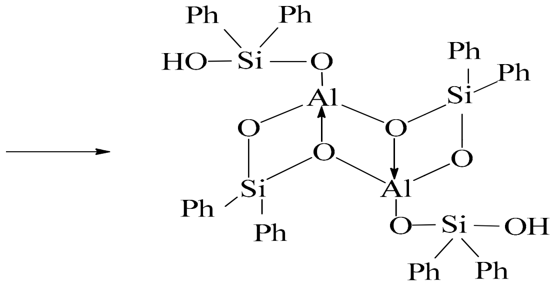
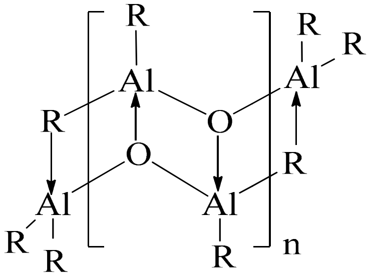


(**b**)

Way 4(**a**) is most probable. This is confirmed by the fact that in ^{1}H NMR spectra of siloxyalumoxane with molar ratio Al:Si = 1:2 low resolution signals of isobutyl groups protons at 1.05 ppm of CH_3 (^{i}Bu–Si); 1.4 ppm of CH_2 (^{i}Bu–Si) are observed. And moreover if one mole of Al(^{i}Bu)$_3$ interacts with two moles of $Ph_2Si(OH)_2$, the amount of gas released is much less as compared to the theory and amounts to less than 70 %, which corresponds to two isobutyl groups migration from aluminium to silicon.

Considering alkylalumoxane reactions with $Ph_2Si(OH)_2$, we kept in mind that aluminium atom is four coordinated in alkylalumoxanes [2–15], whose schematic structural formulas are presented as follows: (at n=1 – tetraisobutylalumoxane, at n>1 – polyisobutylalumoxane) [3] (Figure 3).

Figure 3. Schematic structural formula of alkylalumoxanes.



It should be noted that at a temperature above 20 °C tetraisobutylalumoxane disproportionation takes place with triisobutylaluminium release [3,13] (Scheme 5).

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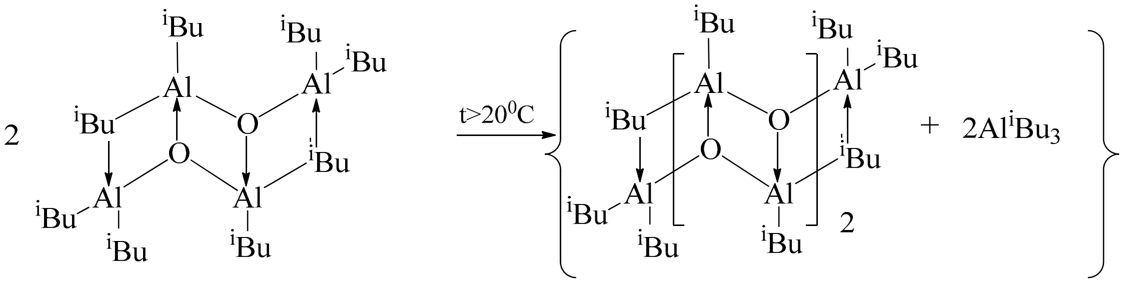
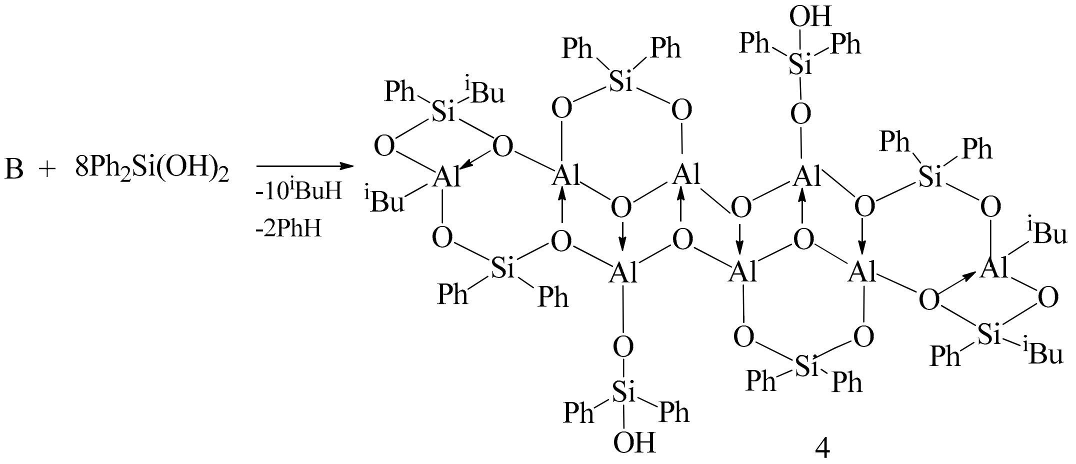
Scheme 5. Disproportionation of tetraisobutylalumoxane.



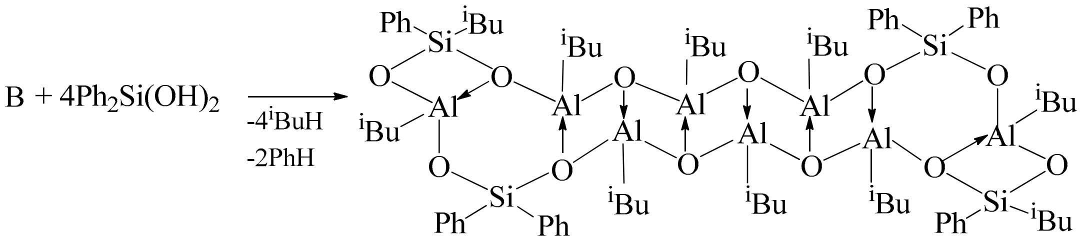
B

At a temperature of 80 °C a mixture of triisobutylaluminium and pentaisobutyltrialumoxane (B) reacts with $Ph_2Si(OH)_2$, therefore a part of $Ph_2Si(OH)_2$ interacts with Al(^{i}Bu)$_3$ forming intramolecular **A*** complex. The other part of $Ph_2Si(OH)_2$ reacts with double alumoxane chain, the alumoxane chain therewith is terminated by **A'** complex, which results in impossibility to obtain high-polymer siloxyalumoxane compounds from tetraisobutylalumoxane and $Ph_2Si(OH)_2$ (Scheme 6).

Scheme 6. Probable scheme of interaction of tetraisobutylalumoxane with $Ph_2Si(OH)_2$.



(**a**) Al:Si = 1:1 molar ratio in the reaction mixture



5

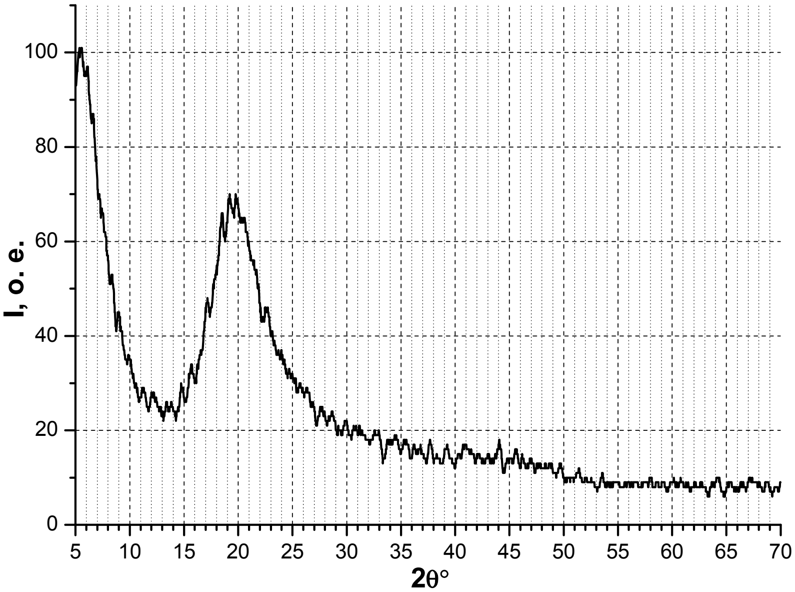
(**b**) Al:Si = 2:1 molar ratio in the reaction mixture

Siloxyalumoxane oligomers **4** or **5** containing four- and six-membered rings are produced.

Siloxyalumoxanes **1**–**5** were white, glassy, benzene-soluble oligomers with different molecular weights.

X-ray amorphism of siloxyalumoxane oligomers (Figure 4) did not allow determining their crystalline characteristics, but the presence of reduced structural units in formulas (1-5) was confirmed by multinuclear magnetic resonance, IR spectroscopy, TGA, and elemental analysis.

Figure 4. Typical diffractogram of siloxyalumoxane oligomers (**1**–**6**).



In contrast to starting Al(*ⁱ*Bu)$_3$, tetraisobutylalumoxane and Ph$_2$Si(OH)$_2$ their interaction products in IR spectra have highly intense broad absorption band in the region of 1050 – 1075 cm^{-1} typical for Al–O–Si bonds as well as absorption band of medium intensity in the region of 820–840 cm^{-1}, corresponding to valence vibrations of Al–O–Al bond (bridge). Presence or

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absence of a wide absorption band in the region of 3400–3500 cm^{-1} typical for hydroxyl group valence vibrations confirms probable oligomer **1–5** structures.

In ^{1}H NMR spectra of the reaction mixture after the completion of $Al(^iBu)_3$ (tetraisobutylalumoxane) reaction with $Ph_2Si(OH)_2$ in benzene, isobutyl group proton signals were observed as low resolution multiplets in the region of 0.5 to 2.5 ppm.

^{1}H NMR spectrum of the concentrated isobutylalumoxanephenylsiloxane oligomer in C_6D_6 had a broadened signal at 7.5 ppm typical for phenyl group protons and another signal at 1.5 ppm, corresponding to isobutyl group protons.

Therefore organoaluminium compounds reactions with diphenylsilanediol result in organosiloxyalumoxane compounds with alternating four- and six-membered rings containing aluminium atoms with the coordination number equal to 4. Isobutyl and phenyl groups at aluminium and silicon may migrate in the process of reaction.

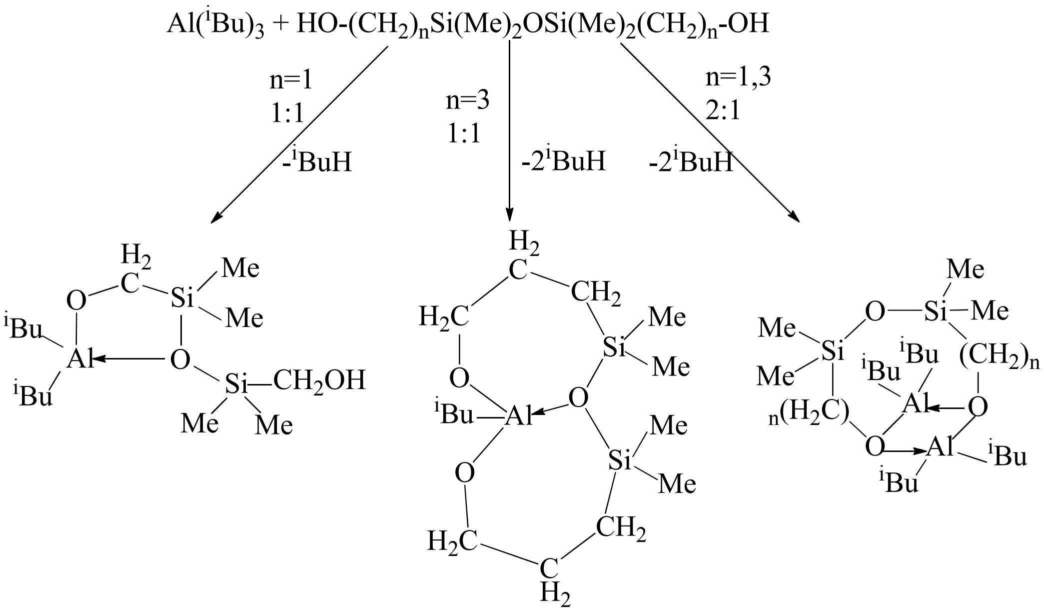
Such structure of the alumoxanesiloxane oligomers is confirmed by [16,17] where it is shown that the hydrolytically stable alumoxanes of the formula $[Al(O)_x(OH)_y(X)_z]_n$ (X = $OSiR_3$, O_2CR) are neither linear nor ring structures, but are spatial clusters. These alumoxanes have isostructural center (nucleus) similar to minerals - boehmite and diaspore $\{[Al(O)(OH)]_n\}$, wherein central aluminium atoms are six-coordinated, in case of siloxy derivatives four-coordinated aluminium atoms are present circumferentially [16,17].

Triisobutylaluminium and tetraisobutylalumoxane reactions with α-diol and γ-diol were conducted in benzene at different temperature (20° and 80 °C) and given molar ratio Al:Si (1:1; 2:1; 3:1; 1:2). $Al(^iBu)_3$ interaction with α - and γ-diols occurred already at 20 °C, but full gas release was observed only at 80 °C. The resulting products were viscous colorless or yellow clear liquids readily soluble in hydrocarbon solvents and readily hydrolyzing in air [1,6].

Elemental analysis data as well as molecular weight of the synthesized compounds suggest, that depending on mole ratio of starting reagents, $Al(^iBu)_3$ reactions with α, γ-diols result in compounds **(6-11)** probably having cyclic structure. Moreover, when $Al(^iBu)_3$ interacts with α-diol, only double excess of $Al(^iBu)_3$ allows full replacement of hydroxyl group hydrogen in α-diol with aluminiumalkyl residue to form 1,3-bis(diisobutylalumoxymethyl)-1,1,3,3-tetramethyldisiloxane **(7)**. At equimolar ratio of the starting reagents the second isobutyl radical at Al does not react with the second hydroxyl group of α-diol probably due to steric hindrance and 1-(diisobutylalumoxymethyl)-3-(hydroxymethyl)-1,1,3,3-tetramethyldisiloxane **(6)** is produced.

$Al(^iBu)_3$ reactions with *γ*-diol also result in monomer compounds (**8, 9**), but the presence of a chain comprising three CH_2-groups between *Si* atom and a hydroxyl group simplifies the interaction between the second hydroxyl group of *γ*-diol and the second isobutyl radical $Al(^iBu)_3$. Triisobutylaluminium reactions with α, γ-diols may be presented by scheme 7:

Scheme 7. Probable scheme of interaction of $Al(^iBu)_3$ with α, γ-diols



6 8 7,9

The comparison of IR spectra of 1-(diisobutylalumoxymethyl)-3-(hydroxymethyl)-1,1,3,3-tetramethyldisiloxane **(6)** and 1,3-bis(diisobutylalumoxymethyl)-1,1,3,3-tetramethyldisiloxane (**7**) with IR spectrum of the starting α-diol confirms our assumptions. In IR spectrum of compound (**6**) there is a wide absorption band in the region of 660 cm^{-1} corresponding to valence vibrations ν(Al–C), and the intensity of an absorption band in the region of 3400 cm^{-1} ν(OH) significantly decreases. In IR spectrum of compound (**7**) there is no absorption in the region of 3400 cm^{-1}, and an intense absorption band in the region of 665cm^{-1} ν(Al–C) appears. Moreover, in both cases the intense absorption band broadens in the region of 1060 cm^{-1} ν(Si–O–Si) and has a shoulder of 1015 cm^{-1} *ν*(Al–O–C).

In contrast to ^1H NMR spectrum of the starting *α*-diol, wherein proton signals at 0.38 ppm (CH_3); 3.5 ppm (CH_2) and 4.62 ppm (OH) were recorded, in the spectra of compounds **(6,7)** proton signals of isobutyl groups were observed at 0.4 ppm (CH_2), 1.07 ppm (CH_3) 1.45 ppm (CH), but protons signal of CH_2 groups of *α*-diol was shifted to weaker field and is manifested at 3.65 ppm.

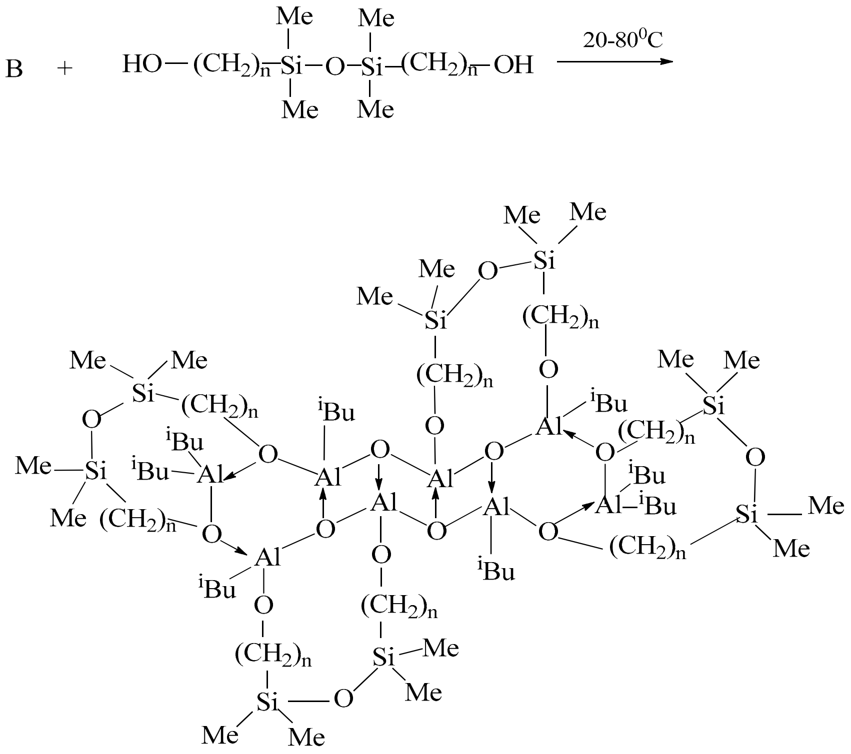
Comparison of IR spectra of 2-isobutyl-7,7,9,9-tetramethyl-1,3,8-trioxa-7,9-disila-2-alumacyclododecane (**8**) and 1,3-bis(diisobutylalumoxypropyl)-1,1,3,3-tetramethyldisiloxane (**9**) with IR spectrum of the starting *γ*-diol shows that there is no absorption band in the region of 3400 cm^{-1} typical for ν(OH), but a broad intense band appears in the region of 670 cm^{-1}, typical for valence vibrations of ν(Al–C) bond , as well as a shoulder in the region of 1010 - 1020cm^{-1}, corresponding to ν(Al–O–C) vibrations is clearly manifested.

The ^{1}H NMR spectrum of the γ-diol has proton signals at 0.25 ppm (CH_3); 0.75 ppm (α-CH_2); 1.8 ppm (β-CH_2); 3.75 ppm (γ-CH_2) and 4.4 ppm (OH). In ^{1}H NMR spectra of compounds **8** and **9** signals corresponding to isobutyl group protons and *γ*-diol protons are overlapped.

Tetraisobutylalumoxane (B) reactions with *α*- and *γ*-diols result in oligomer compounds, but here also, as in the case with diphenylsilanediol molecular weight growth is due to isobutyl radicals replacement with oxyorganosiloxane groupings. The resulting oligomers are white glassy products readily soluble in benzene. Compounds synthesized from tetraisobutylalumoxane and α-diol dissolved in heptane as well, but compounds synthesized from tetraisobutylalumoxane and γ-diol did not dissolve in heptane. Elemental analysis data and molecular mass of the obtained oligomers are presented in Table 3.

The formation of alumoxanes comprising oxyorganosiloxane fragments may be presented by scheme 8:

Scheme 8. Probable scheme of interaction of isobutylalumoxane with α, γ-diols



10 (n=1), 11 (n=3)

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^{1}H NMR and IR spectra of the reaction products of tetraisobutylalumoxane reaction with α- and γ-diols were similar to those of the compounds produced by Al(^{i}Bu)$_3$ reaction with α- and γ-diols, they confirmed hydroxyl group absence in the resulting compounds, the presence of isobutyl group, Al–C, Al–O–C bonds and oxyorganosiloxane fragments; molecular weight of the synthesized oxyorganosiloxane-containing alumoxanes depended on the molecular weight of the starting alkylalumoxane.

3 Experimental

3.1. General Methods

Triisobutylaluminium, tetraisobutylalumoxane, diphenylsilanediol, 1,3-bis(hydroxymethyl)-1,1,3,3- tetramethyldisiloxane (α-diol) and 1,3-bis(hydroxypropyl)-1,1,3,3-tetramethyldisiloxane (γ-diol) were purchased at Pilot Plant in Redkino. The solvent (benzene-D$_6$) used was acquired from «Galakhim» JSC. The solvent (benzene) used was purchased at "Component-Reaktiv" JSC. All synthesis processes were performed in dry argon (the content of O_2 and H_2O < 0.005 wt %). The aluminium content was determined by trilonometry. Silicon content was determined spectrophotometrically as a silicon molybdenum complex at a wavelength of 400 nm. Carbon and hydrogen were determined gravimetrically by burning a weighed sample in oxygen flow. The content of hydroxyl groups in the organosiloxyalumoxanes and organoalumosiloxanes was found by a gasometric method. Molecular weights of the obtained compounds were determined by the cryoscopic method. Gas volume released in the reactions was determined by gas volumetric method. Mass spectrometric analysis of the distillate was conducted on Agilent 240 GC mass-spectrometer /MS Ion Trap at ionizing voltage of 70 eV. The IR spectra of organosiloxyalumoxanes and organoalumosiloxanes were recorded on a Perkin-Elmer spectrometer, model 180 within the range of 400–4000 cm^{-1}. The ^{1}H and ^{27}Al NMR spectra of organosiloxyalumoxanes were obtained using a Bruker AM-360 NMR spectrometer (360 MHz for ^{1}H NMR and 93.8 MHz for ^{27}Al NMR) using solutions in C_6D_6. $[Al(H_2O)_6]^{3+}$ was used as an external standard. ^{1}H NMR spectra of organosilicon diols: 1,3-bis-(hydroxymethyl)-1,1,3,3-tetramethyldisiloxane (α-diol) and 1,3-bis-(hydroxypropyl)-1,1,3,3-tetramethyldisiloxane (γ-diol) were obtained using a Varian T-60A NMR spectrometer (60 MHz for ^{1}H NMR) using solutions in C_6D_6. Tetramethylsilane was used as internal standard. Phase compositions were determined by X-ray diffraction at room temperature on a Shimadzu XRD-6000 vertical X-ray diffractometer with CuKα radiation ($\lambda_{K\alpha cp}=(2\lambda_{K\alpha 1}+ \lambda_{K\alpha 2})/3=1.54178$ [Å]).

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The crystalline and amorphous phases present were identified using ICDD PDF Release 2003 data.

3.2. Synthetic Procedures

3.2.1. General Procedure for the Preparation of Organosiloxyalumoxanes

The interaction of organoaluminium compounds (OAC) – Al(^{i}Bu)$_3$ and tetraisobutylalumoxane with diphenylsilanediol Ph$_2$Si(OH)$_2$ was carried out in deuterobenzene C$_6$D$_6$. Ph$_2$Si(OH)$_2$ suspension in C$_6$D$_6$ was heated to 60–80 °C. The calculated amount of OAC (10–20 wt %, solution in deuterobenzene) was added under stirring, and isobutane (^{i}BuH) gas was released therewith, the gas was collected in a gas meter. Upon completion of OAC feed the reaction mixture was held for 1–2 hours at 80 °C, and then it was cooled to room temperature. The reaction mass was a colorless transparent liquid. The solvent was distilled hereafter. Light yellow or white solid glassy products were obtained. The yield of the target products was 85–99 wt %. Specific reaction conditions are presented in Table 1.

Table 1. OAC interaction with Ph$_2$Si(OH)$_2$.
(reaction conditions: solvent – hexadeuterobenzene, T = 80 °C, τ = 1–2 hour)

No	OAC	Al:Si molar ratio in the reaction mixture	Amount of gas released in the reaction, ml		Product yield, wt %
			Calculated	Experiment	
1	Al(^{i}Bu)$_3$	1:1	223.28	210	94.0
2	Al(^{i}Bu)$_3$	2:1	77.75	80	99.3
3	Al(^{i}Bu)$_3$	1:2	299. 04	258	86.3
4	tetraisobutylalumoxane	1:1	279. 11	280	99.6
5	tetraisobutylalumoxane	2:1	93.70	93	99.3

3.2.2. General procedure for the preparation of organoalumosiloxanes and organoalumoxanesiloxanes

The interaction of organoaluminium compounds (OAC) – Al(^{i}Bu)$_3$ and tetraisobutylalumoxane with 1,3-bis(hydroxymethyl)-1,1,3,3-tetramethyldisiloxane (α-diol) and with 1,3-bis(3-hydroxypropyl)-1,1,3,3- tetramethyldisiloxane (γ-diol) was performed in benzene. 20 wt % solution of α-diol (γ-diol) in benzene were prepared. Under stirring at a temperature of 20 °C a calculated amount of OAC (20 wt %, solution in benzene) was added, depending on the specified Al:Si (1:1; 2:1; 1:2) mole ratio. Then the reaction mass was heated to 80 °C and held at 80 °C under stirring (after gas release completion) for an hour. The yield of desired products amounted to 74–100 wt %. Specific reaction conditions are presented in Table 2.

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Table 2. OAC interaction with α- and γ-diols.

(reaction conditions: solvent – benzene, T = 20–80 °C, τ = 1–2 hours)

No	OAC	OSC	Molar ratio		Amount of gas released in the reaction, ml		Product yield, wt %
			OAC:OSC	Al:Si	Calculated	Experiment	
6	$Al(^{i}Bu)_3$	α-diol	1:1	1:2	155.50	115	74.0
7	$Al(^{i}Bu)_3$	α- diol	2:1	1:1	75.75	76	95.5
8	$Al(^{i}Bu)_3$	γ- diol	1:1	1:2	239.23	203	85.0
9	$Al(^{i}Bu)_3$	γ- diol	2:1	1:1	207.30	194	93.4
10	tetraisobutylalumoxane	α- diol	1:1	1:1	149.52	150	99.9
11	tetraisobutylalumoxane	γ- diol	1:1	1:1	193.70	200	99.3

$[(^{i}BuPhSiO)_3(PhSiO)_2(^{i}BuAlO)_5]$ (**1**). Yield: 94.0 %; ^{1}H-NMR (360 MHz, C_6D_6): broad m 0.5-2.5 ppm (^{i}Bu); broad m 6.7-8.0 ppm (aromatic protons); ^{27}Al-NMR (93.8 MHz, C_6D_6): broad 61 ppm; IR (cm^{-1}), 2970-2850 ν(C−H); 1470, 1380 δ(C−H); 1130 ν(ring C_6H_5); 1070 ν(Si−O−Al); 820 ν(Al−O−Al); 720, 700 (Si−Ph); 670 ν(Al−C); 520, 480; Anal. Calculated for $C_{74}H_{107}Al_5Si_5O_{10}$: M_n, 1430; C, 62.10; H, 7.48; Al, 9.44; Si, 9.79, Found: M_n, 1470; C, 60.15; H, 7.47; Al, 9.24; Si, 9.89.

$[^{i}BuPhSiO_2Al_2(^{i}Bu)_3Ph]$ (**2**). Yield: 99.3 %; ^{1}H-NMR (60 MHz, C_6D_6): broad m 0.7 ppm CH_2 (^{i}Bu−Al); broad m 1.2 ppm CH_3 (^{i}Bu−Al); broad m 1.6 ppm CH_3(^{i}Bu−Si); broad m 1.8 ppm CH (^{i}Bu−Si); IR (cm^{-1}), 2960-2840 ν(C−H); 1470, 1435, 1380 δ(C−H), 1120 ν(ring C_6H_5), 1070 ν(Si−O−Al); 830 ν (Al−O−Al); 740, 720, 700 (Si−Ph); 670 ν(Al−C); 520, 480; Anal. Calculated for $C_{28}H_{46}Al_2SiO_2$: M_n, 496; C, 67.74; H, 9.27; Al, 10.89; Si, 5.65, Found: M_n, 504; C, 67.21; H, 9.08; Al, 10.80; Si, 5.60.

$[(^{i}BuPhSiO)_2(Ph_2Si(OH)O)_2(Al_2O_2)]$ (**3**). Yield: 86.3 %; ^{1}H-NMR (60 MHz, C_6D_6): 1.05 ppm, d, J=6 Hz, CH_3 (^{i}Bu−Si); 1.4 ppm d, J=6 Hz, CH_2 (^{i}Bu−Si); IR (cm^{-1}), 3300 ν(O−H); 2980-2860 ν(C−H); 1470, 1380 δ(C−H); 1120 ν(ring C_6H_5); 1070 ν(Si−O−Al); 1030 ν(Si−O) 820 ν(Al−O−Al); 720, 700 (Si−Ph); 520, 480; Anal. Calculated for $C_{44}H_{54}Al_2Si_4O_8$: M_n, 872; C, 60.55; H, 6.19; Al, 6.19; Si, 12.84; OH, 3.90, Found: M_n, 920; C, 60.22; H, 6.36; Al, 6.50; Si, 12.90; OH, 4.20.

$[(^{i}BuPhSiO)_2(Ph_2SiO_2)_4(Ph_2Si(OH)O)_2(^{i}BuAl_2O)_2(Al_2O_2)_2]$ (**4**). Yield: 99.6 %; ^{1}H-NMR (60 MHz, C_6D_6): 1.05 ppm, d, J=6 Hz, CH_3 (^{i}Bu−Al); 1.8 ppm m, CH_3(^{i}Bu−Si); IR (cm^{-1}), 3350 ν(O−H); 2970-2860 ν(C−H); 1460, 1375 δ(C−H); 1120 ν(ring C_6H_5); 1070-1020 ν(Si−O−Al); 810 ν(Al−O−Al); 710, 690 (Si−Ph); 670 ν(Al−C); 520, 480; Anal. Calculated for

$C_{100}H_{108}Al_8Si_8O_{20}$: M$_n$, 2068; C, 58.03; H, 5.22; Al, 10.44; Si, 10.83; OH, 1.40, Found: M$_n$, 2100; C, 57.83; H, 5.17; Al, 10.10; Si, 10.47, OH, 1.64.

[(^{i}BuPhSiO)$_2$(Ph$_2$SiO$_2$)$_2$(^{i}Bu$_2$Al$_2$O)$_2$(^{i}Bu$_2$Al$_2$O$_2$)$_2$] (**5**). Yield: 99.5 %; ^{1}H-NMR (60 MHz, C_6D_6): 1.1 ppm, d, J=6 Hz, CH_3 (^{i}Bu−Al); 1.35 ppm d, J=7 Hz, CH_3 (^{i}Bu−Si); 2.3 ppm, m, CH_3(^{i}Bu−Al); IR (cm^{-1}), 2980-2860 ν(C−H); 1470, 1380 δ(C−H); 1130 ν(ring C_6H_5); 1070-1030 ν(Si−O−Al); 805 ν(Al−O−Al); 720, 700 (Si−Ph); 670 ν(Al−C); 520, 480; Anal. Calculated for $C_{76}H_{120}Al_8Si_4O_{12}$: M$_n$, 1552; C, 58.76; H, 7.73; Al, 13.92; Si, 7.22, Found: M$_n$, 1520; C, 58.13; H, 7.96; Al, 14.19; Si, 7.62.

1-(Diisobutylalumoxymethyl)-3-(hydroxymethyl)-1,1,3,3-tetramethyldisiloxane (**6**). Yield: 74.0 %; IR (cm^{-1}), 3400 ν(O−H); 2980, 2860 ν(C−H); 1470, 1395, 1370 δ(C−H); 1260 ν(Si−CH_3); 1060-1015 ν(Si−O−Si); ν(C−O−Al); 860, 800 ν(O−Si−(CH_3)$_2$); 665 ν(Al−C); Anal. Calculated for $C_{14}H_{35}AlSi_2O_3$: M$_n$, 334; C, 50.30; H, 10.48; Al, 8.08; Si, 16.77; OH, 5.09, Found: M$_n$, 330; C, 50.63; H, 10.59; Al, 8.30; Si, 16.30, OH, 5.20.

1,3-Bis(diisobutylalumoxymethyl)-1,1,3,3-tetramethyldisiloxane (**7**). Yield: 95.5 %; ^{1}H-NMR (60 MHz, C_6D_6): 0.4 ppm, s, ((CH_3)$_2$Si, α-diol); 0.5 ppm, broad m, (CH_2,^{i}Bu, olyg); 1.05 ppm, d, J=6 Hz, CH_3 (^{i}Bu−Al); 1.5 ppm, broad m, CH(^{i}Bu−Al, olyg); 3.7 ppm, s, (CH_2O-α-diol); IR (cm^{-1}), 2980, 2860 ν(C−H); 1465, 1395, 1360 δ(C−H); 1260 ν(Si−CH_3); 1060-1015 ν(Si−O−Si); ν(C−O−Al); 860, 800 (O−Si−(CH_3)$_2$); 665 ν(Al−C); Anal. Calculated for $C_{22}H_{52}Al_2Si_2O_3$: M$_n$, 474; C, 55.70; H, 10.97; Al, 11.39; Si, 11.81, Found: M$_n$, 480; C, 55.42; H, 10.34; Al, 11.10; Si, 11.40.

2-Isobutyl-7,7,9,9-tetramethyl-1,3,8-trioxa-7,9-disila-2-alumacyclododecane (**8**). Yield: 85.0 %; IR (cm^{-1}), 2980, 2860 ν(C−H); 1465, 1380, 1360, 1320 δ(C−H); 1255 ν(Si−CH_3); 1060-1010 ν(Si−O−Si); ν(C−O−Al); 860, 800 ν(O−Si−(CH_3)$_2$); 670 ν(Al−C); Anal. Calculated for $C_{14}H_{33}AlSi_2O_3$: M$_n$, 332; C, 50.60; H, 9.94; Al, 8.13; Si, 16.87, Found: M$_n$, 330; C, 48.98; H, 9.90; Al, 7.94; Si, 16.46.

1,3-Bis(diisobutylalumoxypropyl)-1,1,3,3-tetramethyldisiloxane (**9**). Yield: 93.4 %; ^{1}H-NMR (60 MHz, C_6D_6): 0.3 ppm, s, ((CH_3)$_2$Si, γ-diol); 0.5 ppm, broad m, (CH_2,^{i}Bu, olyg); 1.05 ppm, d, J=6 Hz, CH_3 (^{i}Bu−Al); 1.4 ppm, broad m, (α-CH_2, γ-diol); 2 ppm, broad m, (β-CH_2, γ-diol); 3.7 ppm, broad m, (γ-CH_2, γ-diol); IR (cm^{-1}), 2980, 2860 ν(C−H); 1465, 1400, 1365, 1320 δ(C−H); 1255 ν(Si−CH_3); 1060-1020 ν(Si−O−Si); ν(C−O−Al); 840, 800 ν(O−Si−(CH_3)$_2$); 670 ν(Al−C); Anal.

Calculated for $C_{26}H_{60}Al_2Si_2O_3$: M_n, 530; C, 58.87; H, 11.32; Al, 10.19; Si, 10.57, Found: M_n, 500; C, 58.54; H, 11.00; Al, 9.90; Si, 10.10.

{[Me$_4$(O)Si$_2$(CH$_2$)$_2$O$_2$]$_4$(^{i}Bu$_2$Al)$_2$(^{i}BuAl)$_2$(^{i}BuAl$_2$O$_2$)$_2$} (**10**). Yield: 99.9 %; IR (cm^{-1}), 2980, 2860 ν(C−H); 1460, 1395, 1360 δ(C−H); 1255 ν(Si−CH$_3$); 1060-1020 ν(Si−O−Si); ν(C−O−Al); 860, 800 (O−Si−(CH$_3$)$_2$); 750 ν(Al−O−Al); 660 ν(Al−C); Anal. Calculated for $C_{56}H_{136}Al_8Si_8O_{16}$: M_n, 1504; C, 44.68; H, 9.04; Al, 14.36; Si, 14.89, Found: M_n, 1490; C, 44.34; H, 9.23; Al, 14.70; Si, 15.10.

{[Me$_4$(O)Si$_2$(CH$_2$CH$_2$CH$_2$)$_2$O$_2$]$_4$(^{i}Bu$_2$Al)$_2$(^{i}BuAl)$_2$(^{i}BuAl$_2$O$_2$)$_2$} (**11**). Yield: 99.3 %; IR (cm^{-1}), 2980, 2860 ν(C−H); 1465, 1380, 1360, 1320 δ(C−H); 1260 ν(Si−CH$_3$); 1065-1015 ν(Si−O−Si); ν(C−O−Al); 840, 800, 770 (O−Si−(CH$_3$)$_2$), ν(Al−O−Al); 670 ν(Al−C); Anal. Calculated for $C_{72}H_{168}Al_8Si_8O_{16}$: M_n, 1728; C, 50.00; H, 9.72; Al, 12.50; Si, 12.96, Found: M_n, 1680; C, 49.19; H, 9.31; Al, 12.10; Si, 12.60.

4. Conclusion

Triisobutylaluminium interaction with diphenylsilanediol results in oligomer products only at the equimolar ratio of the starting Al(^{i}Bu)$_3$ and $Ph_2Si(OH)_2$. During the reaction, the isobutyl and phenyl groups at aluminium and silicon may migrate. In the interaction of alkylalumoxanes with diphenylsilane diol, the increase in molecular weight occurs not due to chain growth, but only due to the replacement of alkyl radicals by diphenylsilanol groups. When Al(^{i}Bu)$_3$ interacts with α- and γ-diols no oligomer compounds are produced. Tetraisobutylalumoxane reaction with α- and γ-diols results in oligomer compounds, and yet, as in the case of diphenylsilanediol, the increase in the molecular weight is due only to the replacement of isobutyl radicals by oxyorganosiloxane groupings.

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Galina I. Shcherbakova conceived and designed the experiments; performed the experiments; analyzed the data; Galina I. Shcherbakova and Pavel A. Storozhenko wrote the paper; Alexander V. Kisin conducted physicochemical studies of the synthesized oligomers and construed the data obtained.

Conflict of Interest

The authors declare no conflict of interest.

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