

1 Article

2 Synthesis of Siloxyalumoxanes and Alumosiloxanes 3 Based on Organosilicon Diols

4 Galina I. Shcherbakova *, Pavel A. Storozhenko and Alexander V. Kisin

5 State Research Institute for Chemistry and Technology of Organoelement Compounds, 105118,

6 Shosse Entuziastov 38, Moscow, Russia; info@eos.su (P.A.S.); kisin@eos.su (A.V.K.)

7 * Correspondence: galina7479@mail.ru; Tel.: +7-495-673-7230

8 1. Introduction

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

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

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

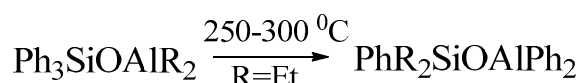
29 The nearest aspect of our work was the investigation performed by Andrew R. Barron's group,
30 they studied the synthesis, properties and structure of organosiloxyalumoxanes - precursors of
31 alumosilicate ceramics [16,17].

32 A considerable number of molecular alumosiloxanes and alumosilicates have been obtained
33 using aluminum halogenides, chalcogenides, hydrides, and organometallic compounds as starting
34 materials, by reacting them with the appropriate $R_nSi(OH)_{4-n}$ precursor [18]. The reaction of Al_2Cl_6
35 with an excess of $Ph_2Si(OH)_2$ in THF in the presence of pyridine yielded new anionic and cyclic
36 aluminosiloxanes: the structure of the anionic complex comprises separated pyridinium cations and
37 aluminosiloxane anions with a tetrahedral arrangement around the Al atom, which is similar to that in
38 natural aluminosilicates; the core of the cyclic aluminosiloxane is a twelve-membered $Al_2Si_4O_6$ ring
39 in a chair conformation, which contains a Cl group on each of the two Al atoms [19]. Reaction of
40 $Al(tBu)_3$ with neol-H₂ (2,2-dimethylpropane-1,3-diol) yields $[Al_2(tBu)_4(neol-H)_2]$. $[Al_2(tBu)_4(neol-H)_2]$
41 may be considered as bifunctional (two OH groups), tetradentate (4O) ligands as highlighted by its
42 reactivity with Group 13 hydrides and alkyls. Reaction of $[Al_2(tBu)_4(neol-H)_2]$ with $AlH_3(NMe_3)$,
43 $AlH_2Cl(NMe_3)$ and $AlMe_3$ yields the tri-aluminium compounds, $[Al_3(tBu)_4(X)(neol)_2]$ with X = H, Cl,
44 Me, respectively [20].

45 The main research on the synthetic and structural chemistry of alumosiloxanes is described in
46 the review [21]. Michael Veith's works describe the synthesis, physicochemical properties, crystal
47 structure and interaction of polycyclic $[Ph_2SiO]_8[AlO(OH)]_4$ with various chemical compounds [22–
48 25].

49 **2. Results and Discussion**

50 To investigate the mechanism of $\text{Al}(i\text{Bu})_3$ reaction with $\text{Ph}_2\text{Si}(\text{OH})_2$ we studied (by means of
 51 NMR spectroscopy) their interaction in hexadeuterobenzene (C_6D_6). In contrast to the reactions in
 52 benzene deuterobenzene solvent makes it possible to determine besides isobutyl groups benzene
 53 presence in ^1H and ^{13}C NMR spectra. In NMR spectra of the reaction mixture after $\text{Al}(i\text{Bu})_3$ interaction
 54 with $\text{Ph}_2\text{Si}(\text{OH})_2$, is completed, a proton signal was observed at 7.23 ppm, and a signal of ^{13}C nuclei
 55 of unlabeled benzene was observed at 128 ppm [26]. When siloxyalumoxane oligomer reaction
 56 product was released, the produced benzene was distilled along with a solvent (C_6D_6) and was
 57 recorded in NMR spectra of the distillate. Benzene may be produced in the result of phenyl and
 58 isobutyl groups exchange between silicon and aluminium. Earlier a few authors [27] observed phenyl
 59 and alkyl groups migration in triphenylsiloxyaluminiumalkyl at 250–300 °C (Figure 1).



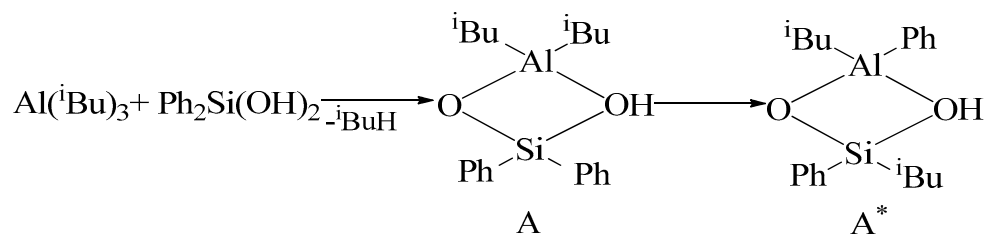
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61 **Figure 1.** Migration of the phenyl and alkyl groups in triphenylsiloxyaluminiumalkyl.

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

63 In ^{27}Al NMR spectra of the products of $\text{Al}(i\text{Bu})_3$ reaction with $\text{Ph}_2\text{Si}(\text{OH})_2$ in C_6D_6 at 25 °C broad
 64 signal typical for oligomer structures where aluminium coordination number is four was recorded at
 65 61,0 ppm.

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

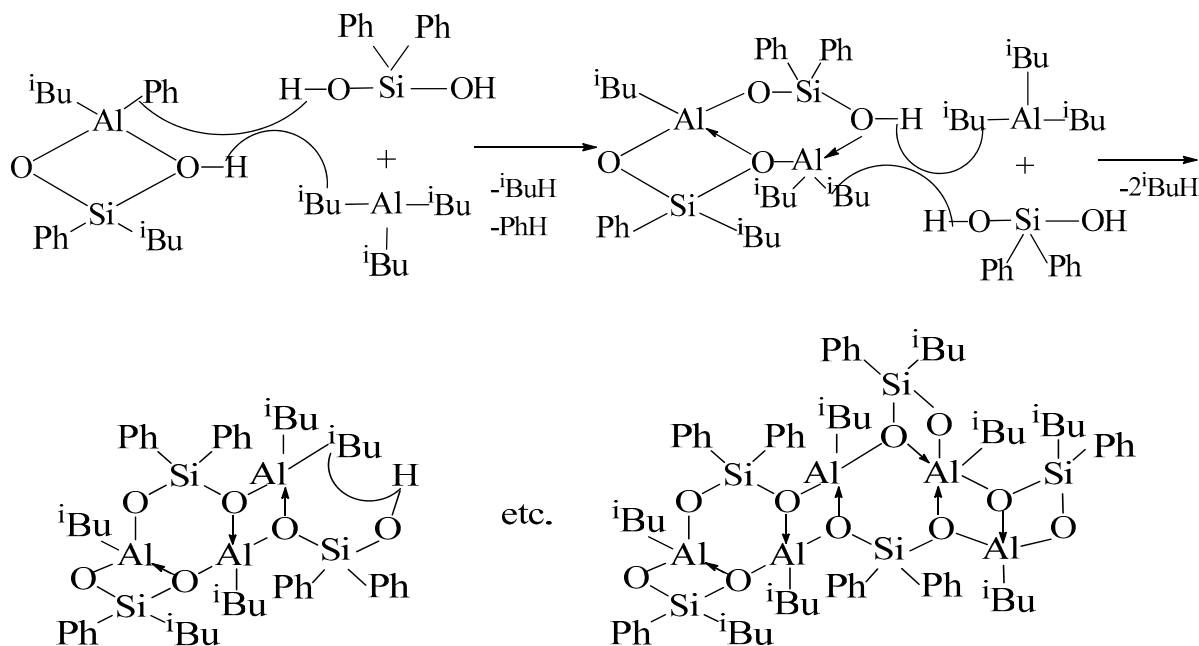


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Scheme 1. The formation of active intramolecular complex (A^*).

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



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

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 $\text{Al}(\text{iBu})_3 : \text{Ph}_2\text{Si}(\text{OH})_2 = 1:1$), the distilled C_6D_6 must contain about 1.5 wt % 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).

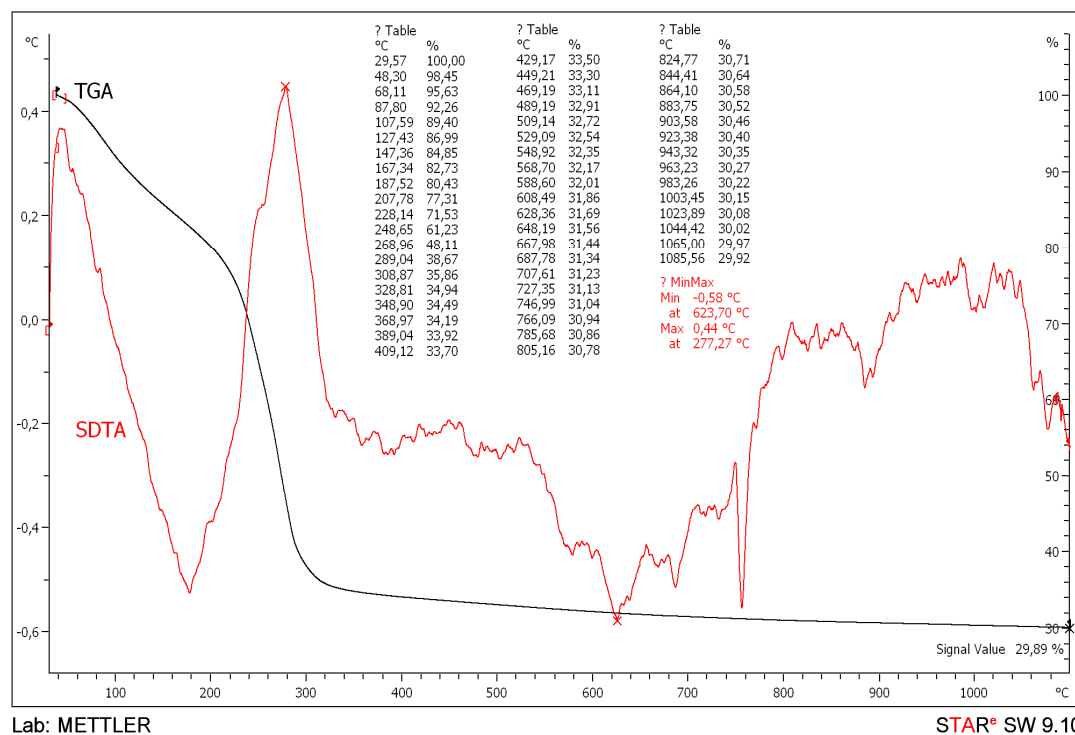
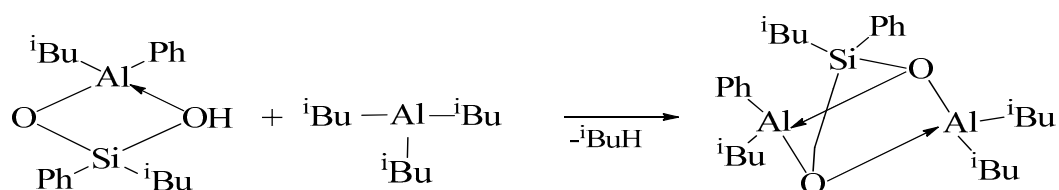


Figure 2. Thermogram of oligomer **1**.

89 The TGA curve shows that in the temperature range of 30–230 °C the weight loss is about 30 wt
 90 %, while the SDTA curve shows an endo-effect at 180 °C. This corresponds to the complete removal
 91 of isobutyl groups in the form of isobutene (theoretically, the weight loss is 31.33 wt %). In the
 92 temperature range of 230–650 °C, the weight loss is about 40 wt. %, while the SDTA curve shows an
 93 exo-effect at 280 °C. This corresponds to the complete removal of the phenyl groups in the form of
 94 benzene (theoretically the weight loss is 38.18 wt %). Further pyrolysis in an inert atmosphere (argon)
 95 to 1100 °C leads to the formation of an alumosilicate ceramic residue of 29.89 wt %, which actually
 96 coincides with the theoretically calculated value for oligomer **1** (30.42 wt %) (Figure 2).

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

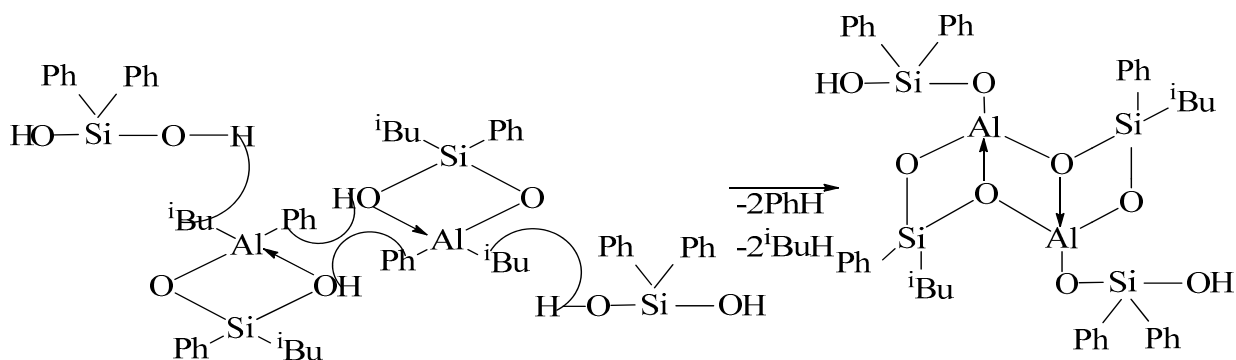


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Scheme 3. The probable scheme of interaction of Al(ⁱBu)₃ and Ph₂Si(OH)₂ at Al:Si=2:1.

103 When the reaction proceeds at Ph₂Si(OH)₂ (Al:Si=1:2) excess, organosiloxyalumoxane formation
 104 may be presented in two ways (Scheme 4).

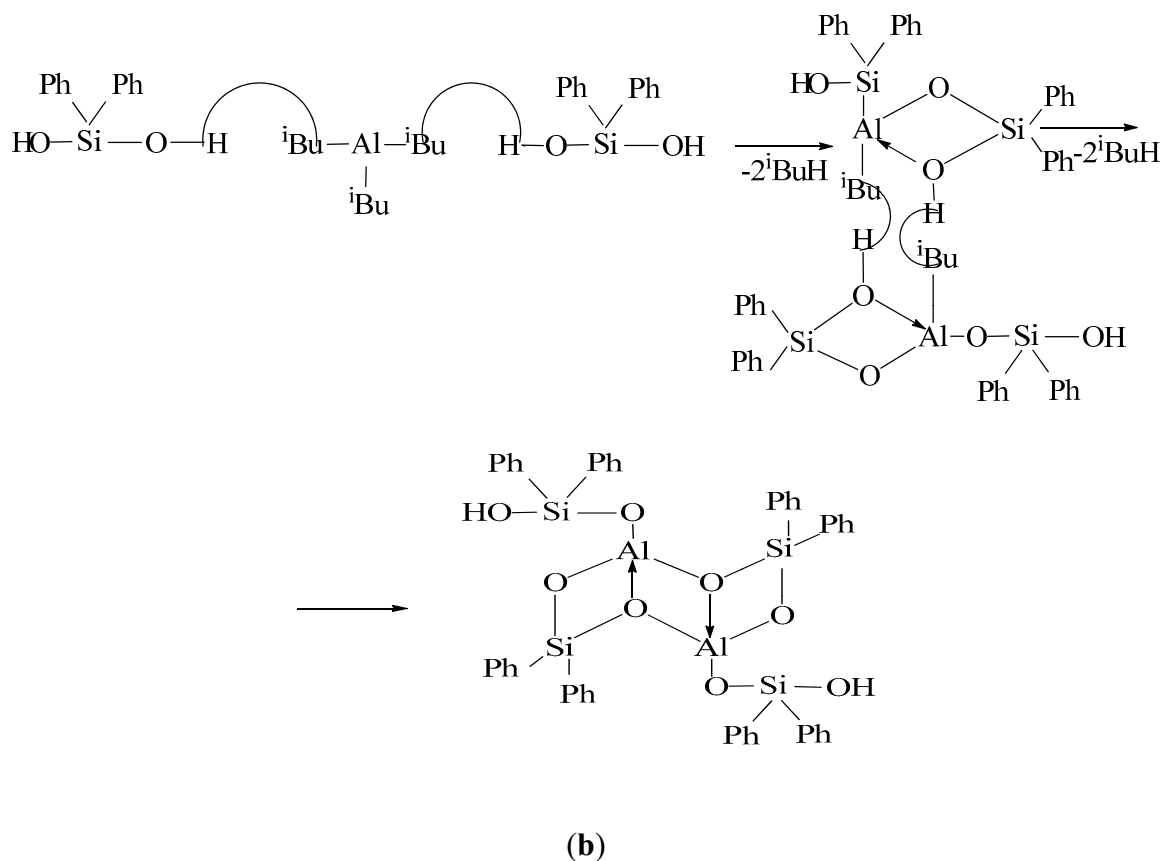


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(a)

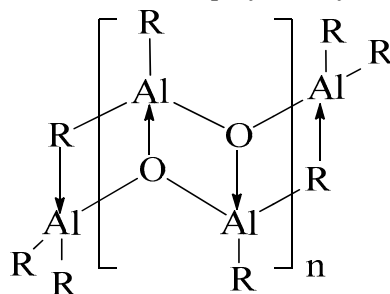
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111 **Scheme 4.** The probable scheme of interaction of $\text{Al}(\text{iBu})_3$ and $\text{Ph}_2\text{Si}(\text{OH})_2$ at $\text{Al}:\text{Si}=1:2$.

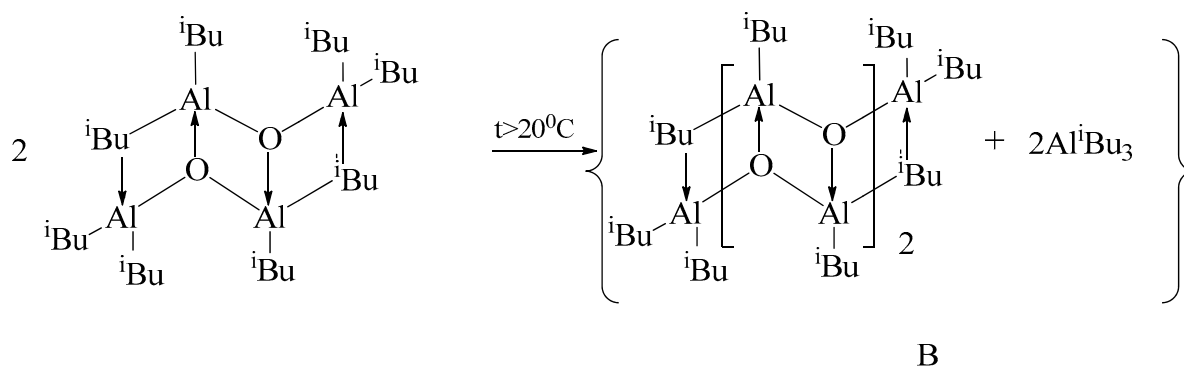
112 Way 4(a) is most probable. This is confirmed by the fact that in ^1H NMR spectra of
 113 siloxyalumoxane with molar ratio $\text{Al}:\text{Si} = 1:2$ low resolution signals of isobutyl groups protons at 1.05
 114 ppm of CH_3 ($^i\text{Bu}-\text{Si}$); 1.4 ppm of CH_2 ($^i\text{Bu}-\text{Si}$) are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

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

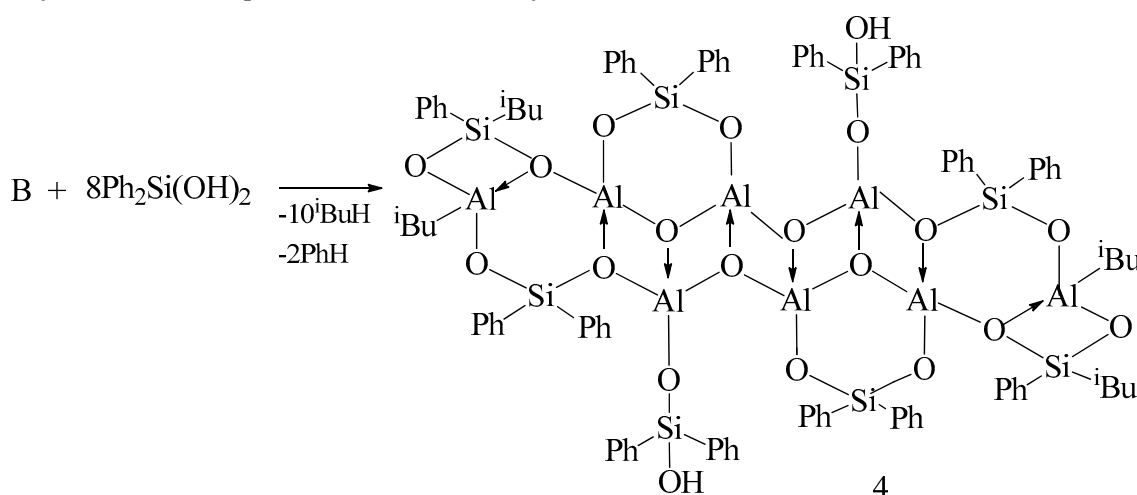


123 **Figure 3.** Schematic structural formula of alkylalumoxanes.

124 It should be noted that at a temperature above $20\text{ }^\circ\text{C}$ tetraisobutylalumoxane disproportionation
 takes place with triisobutylaluminium release [3,13] (Scheme 5).

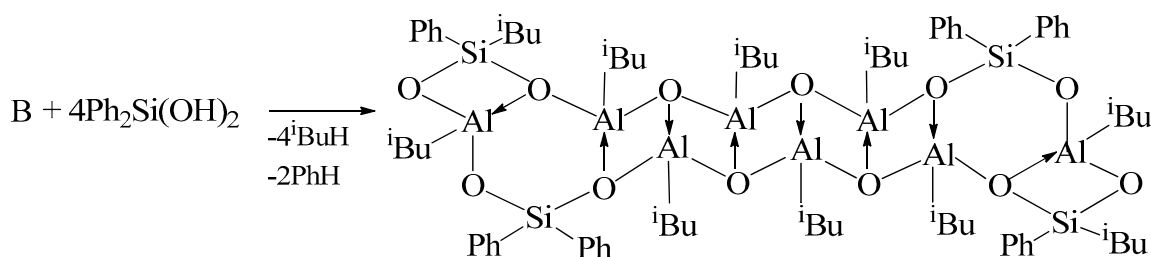
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126**Scheme 5.** Disproportionation of tetraisobutylalumoxane.

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



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

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

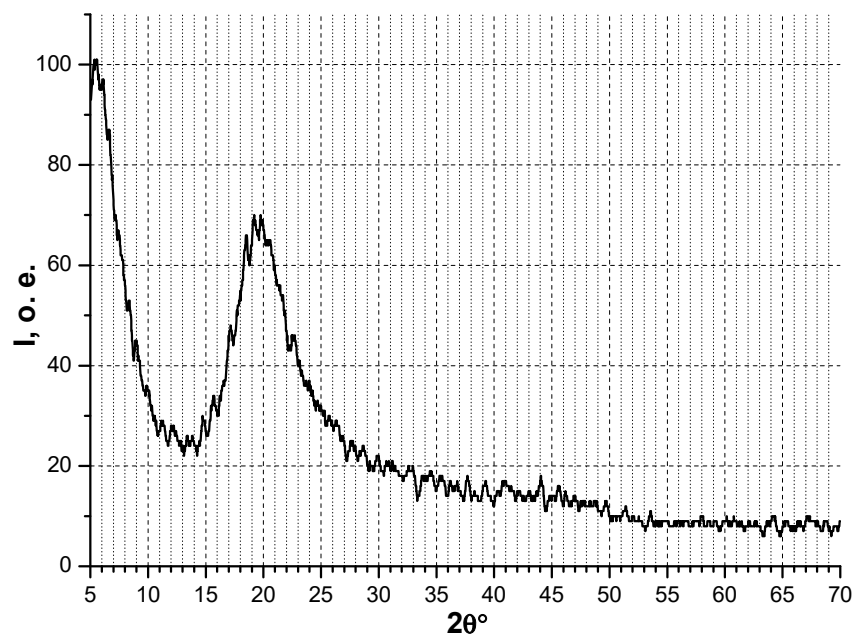
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Scheme 6. Probable scheme of interaction of tetraisobutylalumoxane with $\text{Ph}_2\text{Si}(\text{OH})_2$.

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

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

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



143

144

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

145 In contrast to starting $\text{Al}(\text{iBu})_3$, tetraisobutylalumoxane and $\text{Ph}_2\text{Si}(\text{OH})_2$ their interaction
 146 products in IR spectra have highly intense broad absorption band in the region of $1050 - 1075 \text{ cm}^{-1}$
 147 typical for Al–O–Si bonds as well as absorption band of medium intensity in the region of $820 - 840$
 148 cm^{-1} , corresponding to valence vibrations of Al–O–Al bond (bridge). Presence or absence of a wide
 149 absorption band in the region of $3400 - 3500 \text{ cm}^{-1}$ typical for hydroxyl group valence vibrations
 150 confirms probable oligomer 1–5 structures.

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

154 ^1H NMR spectrum of the concentrated isobutylalumoxanephenylosiloxane oligomer in C_6D_6 had
 155 a broadened signal at 7.5 ppm typical for phenyl group protons and another signal at 1.5 ppm,
 156 corresponding to isobutyl group protons.

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

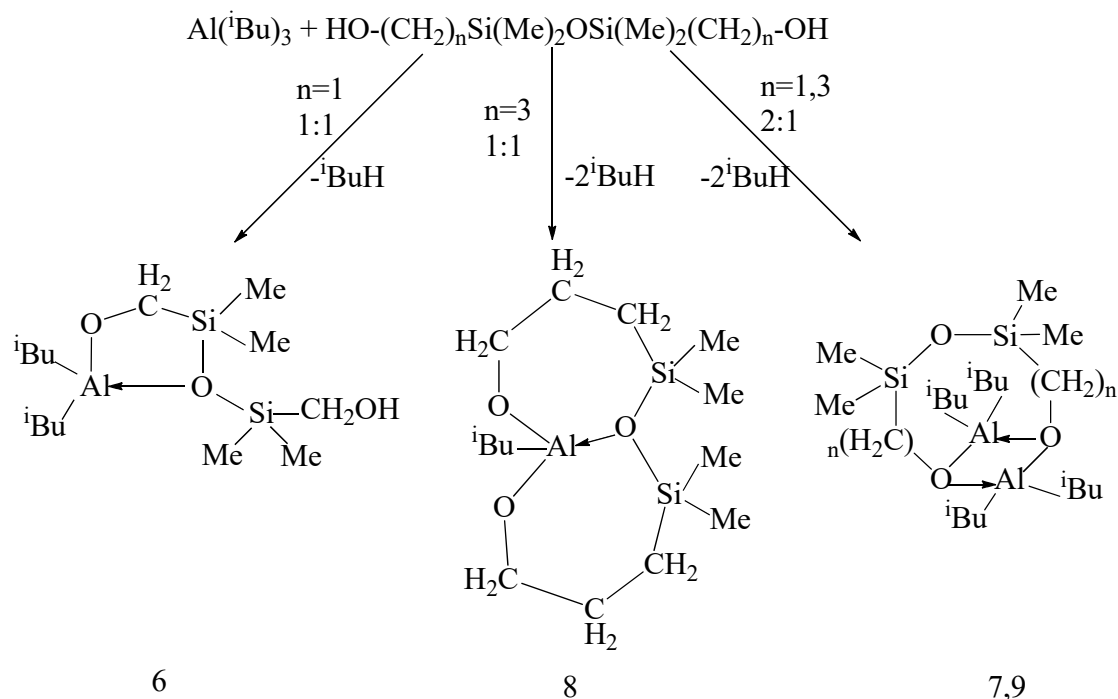
161 Such structure of the alumoxanesiloxane oligomers is confirmed by [16,17] where it is shown
 162 that the hydrolytically stable alumoxanes of the formula $[\text{Al}(\text{O})_x(\text{OH})_y(\text{X})_z]_n$ ($\text{X} = \text{OSiR}_3, \text{O}_2\text{CR}$) are
 163 neither linear nor ring structures, but are spatial clusters. These alumoxanes have isostructural center
 164 (nucleus) similar to minerals - boehmite and diasporite $[\text{Al}(\text{O})(\text{OH})]_n$, wherein central aluminium
 165 atoms are six-coordinated, in case of siloxy derivatives four-coordinated aluminium atoms are
 166 present circumferentially [16,17].

167 Triisobutylaluminium and tetraisobutylalumoxane reactions with α -diol and γ -diol were
 168 conducted in benzene at different temperature (20° and 80°C) and given molar ratio Al:Si (1:1; 2:1;
 169 3:1; 1:2). $\text{Al}(\text{iBu})_3$ interaction with α - and γ -diols occurred already at 20°C , but full gas release was
 170 observed only at 80°C . The resulting products were viscous colorless or yellow clear liquids readily
 171 soluble in hydrocarbon solvents and readily hydrolyzing in air [1,6].

172 Elemental analysis data as well as molecular weight of the synthesized compounds suggest,
 173 that depending on mole ratio of starting reagents, $\text{Al}(\text{iBu})_3$ reactions with α , γ -diols result in

174 compounds (6-11) probably having cyclic structure. Moreover, when $\text{Al}(\text{iBu})_3$ interacts with α -diol,
 175 only double excess of $\text{Al}(\text{iBu})_3$ allows full replacement of hydroxyl group hydrogen in α -diol with
 176 aluminiumalkyl residue to form 1,3-bis(diisobutylalumoxymethyl)-1,1,3,3-tetramethyldisiloxane (7).
 177 At equimolar ratio of the starting reagents the second isobutyl radical at Al does not react with the
 178 second hydroxyl group of α -diol probably due to steric hindrance and 1-
 179 (diisobutylalumoxymethyl)-3-(hydroxymethyl)-1,1,3,3-tetramethyldisiloxane (6) is produced.

180 $\text{Al}(\text{iBu})_3$ reactions with γ -diol also result in monomer compounds (8, 9), but the presence of a
 181 chain comprising three CH_2 -groups between Si atom and a hydroxyl group simplifies the interaction
 182 between the second hydroxyl group of γ -diol and the second isobutyl radical $\text{Al}(\text{iBu})_3$.
 183 Triisobutylaluminium reactions with α , γ -diols may be presented by scheme 7:



184

185

Scheme 7. Probable scheme of interaction of $\text{Al}(\text{iBu})_3$ with α , γ -diols

186 The comparison of IR spectra of 1-(diisobutylalumoxymethyl)-3-(hydroxymethyl)-1,1,3,3-
 187 tetramethyldisiloxane (6) and 1,3-bis(diisobutylalumoxymethyl)-1,1,3,3-tetramethyldisiloxane (7)
 188 with IR spectrum of the starting α -diol confirms our assumptions. In IR spectrum of compound (6)
 189 there is a wide absorption band in the region of 660 cm^{-1} corresponding to valence vibrations $\nu(\text{Al}-\text{C})$,
 190 and the intensity of an absorption band in the region of 3400 cm^{-1} $\nu(\text{OH})$ significantly decreases.
 191 In IR spectrum of compound (7) there is no absorption in the region of 3400 cm^{-1} , and an intense
 192 absorption band in the region of 665 cm^{-1} $\nu(\text{Al}-\text{C})$ appears. Moreover, in both cases the intense
 193 absorption band broadens in the region of 1060 cm^{-1} $\nu(\text{Si}-\text{O}-\text{Si})$ and has a shoulder of 1015 cm^{-1} $\nu(\text{Al}-\text{O}-\text{C})$.
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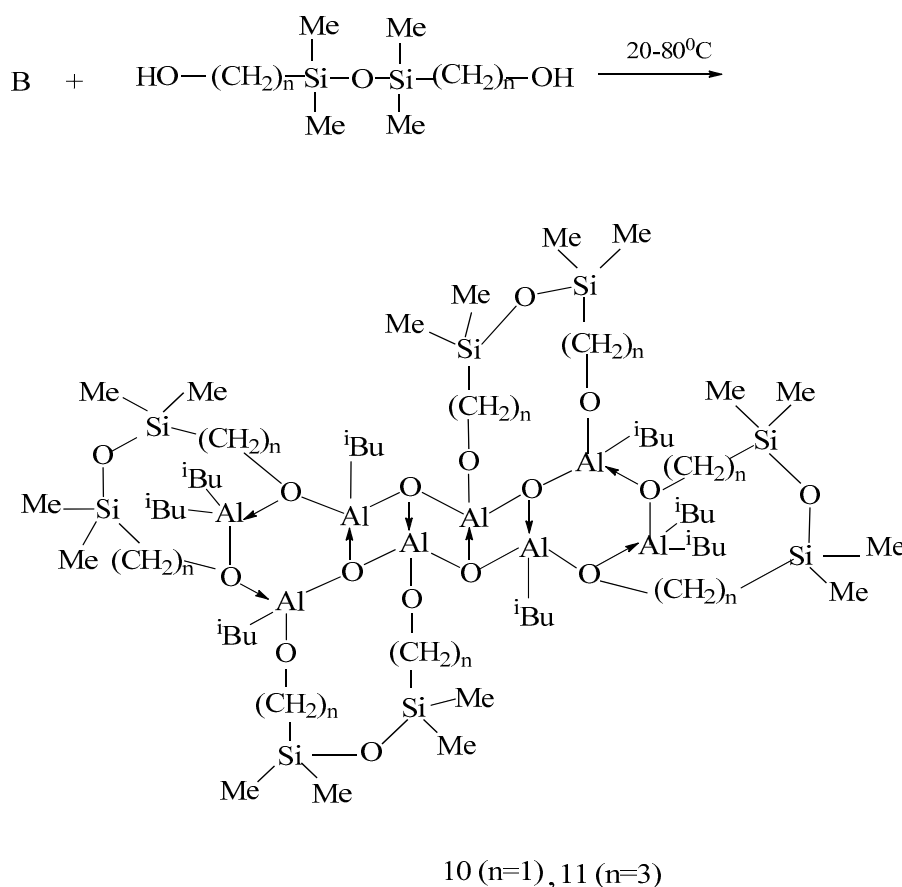
195 In contrast to ^1H NMR spectrum of the starting α -diol, wherein proton signals at 0.38 ppm (CH_3);
 196 3.5 ppm (CH_2) and 4.62 ppm (OH) were recorded, in the spectra of compounds (6,7) proton signals
 197 of isobutyl groups were observed at 0.4 ppm (CH_2), 1.07 ppm (CH_3) 1.45 ppm (CH), but protons signal
 198 of CH_2 groups of α -diol was shifted to weaker field and is manifested at 3.65 ppm.

199 Comparison of IR spectra of 2-isobutyl-7,7,9,9-tetramethyl-1,3,8-trioxa-7,9-disila-2-
 200 alumacyclododecane (8) and 1,3-bis(diisobutylalumoxypropyl)-1,1,3,3-tetramethyldisiloxane (9)
 201 with IR spectrum of the starting γ -diol shows that there is no absorption band in the region of 3400 cm^{-1}
 202 typical for $\nu(\text{OH})$, but a broad intense band appears in the region of 670 cm^{-1} , typical for valence
 203 vibrations of $\nu(\text{Al}-\text{C})$ bond, as well as a shoulder in the region of $1010 - 1020\text{ cm}^{-1}$, corresponding to
 204 $\nu(\text{Al}-\text{O}-\text{C})$ vibrations is clearly manifested.

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

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

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



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

219 ^1H NMR and IR spectra of the reaction products of tetraisobutylalumoxane reaction with α - and
 220 γ -diols were similar to those of the compounds produced by $\text{Al}(\text{iBu})_3$ reaction with α - and γ -diols,
 221 they confirmed hydroxyl group absence in the resulting compounds, the presence of isobutyl group,
 222 Al-C, Al-O-C bonds and oxyorganosiloxane fragments; molecular weight of the synthesized
 223 oxyorganosiloxane-containing alumoxanes depended on the molecular weight of the starting
 224 alkylalumoxane.

225 3 Experimental

226 3.1. General Methods

227 Triisobutylaluminium, tetraisobutylalumoxane, diphenylsilanediol, 1,3-bis(hydroxymethyl)-
 228 1,1,3,3-tetramethyldisiloxane (α -diol) and 1,3-bis(hydroxypropyl)-1,1,3,3-tetramethyldisiloxane (γ -
 229 diol) were purchased at Pilot Plant in Redkino. The solvent (benzene- D_6) used was acquired from

230 «Galakhim» JSC. The solvent (benzene) used was purchased at “Component-Reaktiv” JSC. All
 231 synthesis processes were performed in dry argon (the content of O₂ and H₂O < 0.005 wt %). The
 232 aluminium content was determined by trilonometry. Silicon content was determined
 233 spectrophotometrically as a silicon molybdenum complex at a wavelength of 400 nm. Carbon and
 234 hydrogen were determined gravimetrically by burning a weighed sample in oxygen flow. The
 235 content of hydroxyl groups in the organosiloxyalumoxanes and organoalumosiloxanes was found by
 236 a gasometric method. Molecular weights of the obtained compounds were determined by the
 237 cryoscopic method. Gas volume released in the reactions was determined by gas volumetric method.
 238 Mass spectrometric analysis of the distillate was conducted on Agilent 240 GC mass-spectrometer
 239 /MS Ion Trap at ionizing voltage of 70 eV. The IR spectra of organosiloxyalumoxanes and
 240 organoalumosiloxanes were recorded on a Perkin-Elmer spectrometer, model 180 within the range
 241 of 400–4000 cm⁻¹. The ¹H and ²⁷Al NMR spectra of organosiloxyalumoxanes were obtained using a
 242 Bruker AM-360 NMR spectrometer (360 MHz for ¹H NMR and 93.8 MHz for ²⁷Al NMR) using
 243 solutions in C₆D₆. [Al(H₂O)₆]³⁺ was used as an external standard. ¹H NMR spectra of organosilicon
 244 diols: 1,3-bis-(hydroxymethyl)-1,1,3,3-tetramethyldisiloxane (α-diol) and 1,3-bis-(hydroxypropyl)-
 245 1,1,3,3-tetramethyldisiloxane (γ-diol) were obtained using a Varian T-60A NMR spectrometer (60
 246 MHz for ¹H NMR) using solutions in C₆D₆. Tetramethylsilane was used as internal standard. Phase
 247 compositions were determined by X-ray diffraction at room temperature on a Shimadzu XRD-6000
 248 vertical X-ray diffractometer with CuKα radiation ($\lambda_{K\alpha p}=(2\lambda_{K\alpha 1}+ \lambda_{K\alpha 2})/3=1.54178$ [Å]). The crystalline
 249 and amorphous phases present were identified using ICDD PDF Release 2003 data.

250 3.2. Synthetic Procedures

251 3.2.1. General Procedure for the Preparation of Organosiloxyalumoxanes

252 The interaction of organoaluminium compounds (OAC) – Al(^tBu)₃ and tetraisobutylalumoxane
 253 with diphenylsilanediol Ph₂Si(OH)₂ was carried out in deuterobenzene C₆D₆. Ph₂Si(OH)₂ suspension
 254 in C₆D₆ was heated to 60–80 °C. The calculated amount of OAC (10–20 wt %, solution in
 255 deuterobenzene) was added under stirring, and isobutane (^tBuH) gas was released therewith, the gas
 256 was collected in a gas meter. Upon completion of OAC feed the reaction mixture was held for 1–2
 257 hours at 80 °C, and then it was cooled to room temperature. The reaction mass was a colorless
 258 transparent liquid. The solvent was distilled hereafter. Light yellow or white solid glassy products
 259 were obtained. The yield of the target products was 85–99 wt %. Specific reaction conditions are
 260 presented in Table 1.

261 **Table 1.** OAC interaction with Ph₂Si(OH)₂. (reaction conditions: solvent – hexadeuterobenzene, T =
 262 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(^t Bu) ₃	1:1	223.28	210	94.0
2	Al(^t Bu) ₃	2:1	77.75	80	99.3
3	Al(^t 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

263 3.2.2. General procedure for the preparation of organoalumosiloxanes and 264 organoalumosiloxanes

265 The interaction of organoaluminium compounds (OAC) – Al(^tBu)₃ and tetraisobutylalumoxane
 266 with 1,3-bis(hydroxymethyl)-1,1,3,3-tetramethyldisiloxane (α-diol) and with 1,3-bis(3-
 267 hydroxypropyl)-1,1,3,3-tetramethyldisiloxane (γ-diol) was performed in benzene. 20 wt % solution
 268 of α-diol (γ-diol) in benzene were prepared. Under stirring at a temperature of 20 °C a calculated

269 amount of OAC (20 wt %, solution in benzene) was added, depending on the specified Al:Si (1:1; 2:1;
270 1:2) mole ratio. Then the reaction mass was heated to 80 °C and held at 80 °C under stirring (after gas
271 release completion) for an hour. The yield of desired products amounted to 74–100 wt %. Specific
272 reaction conditions are presented in Table 2.

273 **Table 2.** OAC interaction with α - and γ -diols. (reaction conditions: solvent – benzene, T = 20–80 °C, τ
274 = 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(^t Bu) ₃	α -diol	1:1	1:2	155.50	115	74.0
7	Al(^t Bu) ₃	α -diol	2:1	1:1	75.75	76	95.5
8	Al(^t Bu) ₃	γ -diol	1:1	1:2	239.23	203	85.0
9	Al(^t 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

275 [^tBuPhSiO)₃(PhSiO)₂(^tBuAlO)₅] (1). Yield: 94.0 %; ¹H-NMR (360 MHz, C₆D₆): broad m 0.5-2.5 ppm
276 (^tBu); broad m 6.7-8.0 ppm (aromatic protons); ²⁷Al-NMR (93.8 MHz, C₆D₆): broad 61 ppm; IR (cm⁻¹),
277 2970-2850 ν (C-H); 1470, 1380 δ (C-H); 1130 ν (ring C₆H₅); 1070 ν (Si-O-Al); 820 ν (Al-O-Al); 720, 700
278 (Si-Ph); 670 ν (Al-C); 520, 480; Anal. Calculated for C₇₄H₁₀₇Al₅Si₅O₁₀: M_n, 1430; C, 62.10; H, 7.48; Al,
279 9.44; Si, 9.79, Found: M_n, 1470; C, 60.15; H, 7.47; Al, 9.24; Si, 9.89.

280 [^tBuPhSiO)₂Al₂(^tBu)₃Ph] (2). Yield: 99.3 %; ¹H-NMR (60 MHz, C₆D₆): broad m 0.7 ppm CH₂
281 (^tBu-Al); broad m 1.2 ppm CH₃ (^tBu-Al); broad m 1.6 ppm CH₃ (^tBu-Si); broad m 1.8 ppm CH (^tBu-Si);
282 IR (cm⁻¹), 2960-2840 ν (C-H); 1470, 1435, 1380 δ (C-H), 1120 ν (ring C₆H₅), 1070 ν (Si-O-Al); 830 ν
283 (Al-O-Al); 740, 720, 700 (Si-Ph); 670 ν (Al-C); 520, 480; Anal. Calculated for C₂₈H₄₆Al₂Si₂O₂: M_n, 496;
284 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.

285 [^tBuPhSiO)₂(Ph₂Si(OH)O)₂(Al₂O₂)] (3). Yield: 86.3 %; ¹H-NMR (60 MHz, C₆D₆): 1.05 ppm, d, J=6
286 Hz, CH₃ (^tBu-Si); 1.4 ppm d, J=6 Hz, CH₂ (^tBu-Si); IR (cm⁻¹), 3300 ν (O-H); 2980-2860 ν (C-H); 1470,
287 1380 δ (C-H); 1120 ν (ring C₆H₅); 1070 ν (Si-O-Al); 1030 ν (Si-O) 820 ν (Al-O-Al); 720, 700 (Si-Ph); 520,
288 480; Anal. Calculated for C₄₄H₅₄Al₃Si₄O₈: M_n, 872; C, 60.55; H, 6.19; Al, 6.19; Si, 12.84; OH, 3.90, Found:
289 M_n, 920; C, 60.22; H, 6.36; Al, 6.50; Si, 12.90; OH, 4.20.

290 [^tBuPhSiO)₂(Ph₂SiO₂)₄(Ph₂Si(OH)O)₂(^tBuAl₂O)₂(Al₂O₂)] (4). Yield: 99.6 %; ¹H-NMR (60 MHz,
291 C₆D₆): 1.05 ppm, d, J=6 Hz, CH₃ (^tBu-Al); 1.8 ppm m, CH₃ (^tBu-Si); IR (cm⁻¹), 3350 ν (O-H); 2970-2860
292 ν (C-H); 1460, 1375 δ (C-H); 1120 ν (ring C₆H₅); 1070-1020 ν (Si-O-Al); 810 ν (Al-O-Al); 710, 690 (Si-Ph);
293 670 ν (Al-C); 520, 480; Anal. Calculated for C₁₀₀H₁₀₈Al₈Si₈O₂₀: M_n, 2068; C, 58.03; H, 5.22; Al, 10.44; Si,
294 10.83; OH, 1.40, Found: M_n, 2100; C, 57.83; H, 5.17; Al, 10.10; Si, 10.47, OH, 1.64.

295 [^tBuPhSiO)₂(Ph₂SiO₂)₂(^tBu₂Al₂O)₂(^tBu₂Al₂O)₂] (5). Yield: 99.5 %; ¹H-NMR (60 MHz, C₆D₆): 1.1
296 ppm, d, J=6 Hz, CH₃ (^tBu-Al); 1.35 ppm d, J=7 Hz, CH₃ (^tBu-Si); 2.3 ppm, m, CH₃ (^tBu-Al); IR (cm⁻¹),
297 2980-2860 ν (C-H); 1470, 1380 δ (C-H); 1130 ν (ring C₆H₅); 1070-1030 ν (Si-O-Al); 805 ν (Al-O-Al); 720,
298 700 (Si-Ph); 670 ν (Al-C); 520, 480; Anal. Calculated for C₇₆H₁₂₀Al₈Si₄O₁₂: M_n, 1552; C, 58.76; H, 7.73;
299 Al, 13.92; Si, 7.22, Found: M_n, 1520; C, 58.13; H, 7.96; Al, 14.19; Si, 7.62.

300 1-(Diisobutylalumoxymethyl)-3-(hydroxymethyl)-1,1,3,3-tetramethyldisiloxane (6). Yield: 74.0 %; IR
301 (cm⁻¹), 3400 ν (O-H); 2980, 2860 ν (C-H); 1470, 1395, 1370 δ (C-H); 1260 ν (Si-CH₃); 1060-1015
302 ν (Si-O-Si); ν (C-O-Al); 860, 800 ν (O-Si-(CH₃)₂); 665 ν (Al-C); Anal. Calculated for C₁₄H₃₅AlSi₂O₃: M_n,
303 334; 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,
304 OH, 5.20.

305 1,3-Bis(diisobutylalumoxymethyl)-1,1,3,3-tetramethyldisiloxane (7). Yield: 95.5 %; ¹H-NMR (60 MHz,
306 C₆D₆): 0.4 ppm, s, ((CH₃)₂Si, α-diol); 0.5 ppm, broad m, (CH₂,ⁱBu, olyg); 1.05 ppm, d, J=6 Hz, CH₃
307 (ⁱBu–Al); 1.5 ppm, broad m, CH(ⁱBu–Al, olyg); 3.7 ppm, s, (CH₂O–α-diol); IR (cm⁻¹), 2980, 2860 ν(C–H);
308 1465, 1395, 1360 δ(C–H); 1260 ν(Si–CH₃); 1060-1015 ν(Si–O–Si); ν(C–O–Al); 860, 800 (O–Si–(CH₃)₂);
309 665 ν(Al–C); Anal. Calculated for C₂₂H₅₂Al₂Si₂O₃: M_n, 474; C, 55.70; H, 10.97; Al, 11.39; Si, 11.81, Found:
310 M_n, 480; C, 55.42; H, 10.34; Al, 11.10; Si, 11.40.

311 2-Isobutyl-7,7,9,9-tetramethyl-1,3,8-trioxa-7,9-disila-2-alumacyclododecane (8). Yield: 85.0 %; IR
312 (cm⁻¹), 2980, 2860 ν(C–H); 1465, 1380, 1360, 1320 δ(C–H); 1255 ν(Si–CH₃); 1060-1010 ν(Si–O–Si);
313 ν(C–O–Al); 860, 800 ν(O–Si–(CH₃)₂); 670 ν(Al–C); Anal. Calculated for C₁₄H₃₃AlSi₂O₃: M_n, 332; C,
314 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.

315 1,3-Bis(diisobutylalumoxypropyl)-1,1,3,3-tetramethyldisiloxane (9). Yield: 93.4 %; ¹H-NMR (60 MHz,
316 C₆D₆): 0.3 ppm, s, ((CH₃)₂Si, γ-diol); 0.5 ppm, broad m, (CH₂,ⁱBu, olyg); 1.05 ppm, d, J=6 Hz, CH₃
317 (ⁱBu–Al); 1.4 ppm, broad m, (α-CH₂, γ-diol); 2 ppm, broad m, (β-CH₂, γ-diol); 3.7 ppm, broad m, (γ-
318 CH₂, γ-diol); IR (cm⁻¹), 2980, 2860 ν(C–H); 1465, 1400, 1365, 1320 δ(C–H); 1255 ν(Si–CH₃); 1060-1020
319 ν(Si–O–Si); ν(C–O–Al); 840, 800 ν(O–Si–(CH₃)₂); 670 ν(Al–C); Anal. Calculated for C₂₆H₆₀Al₂Si₂O₃: M_n,
320 530; 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.

321 {[Me₄(O)Si₂(CH₂)₂O₂]₄(ⁱBu₂Al)₂(ⁱBuAl)₂(ⁱBuAl₂O₂)₂} (10). Yield: 99.9 %; IR (cm⁻¹), 2980, 2860 ν(C–H);
322 1460, 1395, 1360 δ(C–H); 1255 ν(Si–CH₃); 1060-1020 ν(Si–O–Si); ν(C–O–Al); 860, 800 (O–Si–(CH₃)₂);
323 750 ν(Al–O–Al); 660 ν(Al–C); Anal. Calculated for C₅₆H₁₃₆Al₈Si₈O₁₆: M_n, 1504; C, 44.68; H, 9.04; Al,
324 14.36; Si, 14.89, Found: M_n, 1490; C, 44.34; H, 9.23; Al, 14.70; Si, 15.10.

325 {[Me₄(O)Si₂(CH₂CH₂CH₂)₂O₂]₄(ⁱBu₂Al)₂(ⁱBuAl)₂(ⁱBuAl₂O₂)₂} (11). Yield: 99.3 %; IR (cm⁻¹), 2980, 2860
326 ν(C–H); 1465, 1380, 1360, 1320 δ(C–H); 1260 ν(Si–CH₃); 1065-1015 ν(Si–O–Si); ν(C–O–Al); 840, 800,
327 770 (O–Si–(CH₃)₂), ν(Al–O–Al); 670 ν(Al–C); Anal. Calculated for C₇₂H₁₆₈Al₈Si₈O₁₆: M_n, 1728; C, 50.00;
328 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.

329 4. Conclusion

330 Triisobutylaluminium interaction with diphenylsilanediol results in oligomer products only at
331 the equimolar ratio of the starting Al(ⁱBu)₃ and Ph₂Si(OH)₂. During the reaction, the isobutyl and
332 phenyl groups at aluminium and silicon may migrate. In the interaction of alkylalumoxanes with
333 diphenylsilane diol, the increase in molecular weight occurs not due to chain growth, but only due
334 to the replacement of alkyl radicals by diphenylsilanol groups. When Al(ⁱBu)₃ interacts with α- and
335 γ-diols no oligomer compounds are produced. Tetraisobutylalumoxane reaction with α- and γ-diols
336 results in oligomer compounds, and yet, as in the case of diphenylsilanediol, the increase in the
337 molecular weight is due only to the replacement of isobutyl radicals by oxyorganosiloxane
338 groupings.

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417 **Sample Availability:** Samples of the compounds are not available from the authors.

418