

# Reactions of trialkylaluminium with sterically hindered diols<sup>1</sup>

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## Abstract

The reactions of trialkylaluminium  $R_3Al$  ( $R = Me, Et$ ) with 2,4-pentandiol [(CH<sub>3</sub>)<sub>2</sub>(OH)CCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>OH (**A**)], [(CH<sub>3</sub>)<sub>2</sub>(OH)CCH<sub>2</sub>CH(OH)CH<sub>3</sub> (**B**)] and 2,5-dimethyl-2,5-hexanediol (**C**) were studied. Sterically hindered 2,4-pentandiol (**A**, **B**) react with alkylaluminium compounds to form mainly cyclic compounds **1–3** of a formula  $R_5Al_3[diol(-2H)]_2$  possessing one central five-coordinated aluminium atom and two terminal four-coordinated aluminium atoms. All the compounds were characterised by means of NMR spectra, elemental analysis and molecular weight determination. The molecular structure of the solid  $Me_5Al_3[O(CH_3)_2CCH_2C(CH_3)_2O]_2$  **1** was determined by X-ray diffraction analysis. Substituted at terminal carbon atoms 2,5-dimethyl-2,5-hexanediol (**C**) forms organoaluminium oligomers exclusively. The influence of the diol carbonchain lengths and its substituents on the yield of the cyclic complexes and organoaluminium oligomers are discussed. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Trialkylaluminium; Sterically hindered diols; Cyclic compounds

## 1. Introduction

We have previously found that *cis*-isomers of unsaturated diols form with alkylaluminium compounds complexes of the type shown on Fig. 1 with high yield [1–3].

Aliphatic diols without rigid structure such as 1,3-propanediol and its derivatives and 1,4-butanediol also have formed similar cyclic compounds in the reactions with  $AlMe_3$ . The yield of these complexes depends on the lengths of the diol carbon chain and on its substituents [4]. Ethylene glycol does not form the cyclic compound but only oligomeric organoaluminium products. 1,3-Propanediol and 2,2-dimethyl-1,3-propanediol produce complexes with low yield (7–8%). On the other hand 1,4-butanediol formed the cyclic complex with

47% yield (Table 1).

The purpose of this work was to find out the influence of the diol carbonchain lengths and its substituents on the yield of the complexes **3** and to determine their crystal and molecular structure.

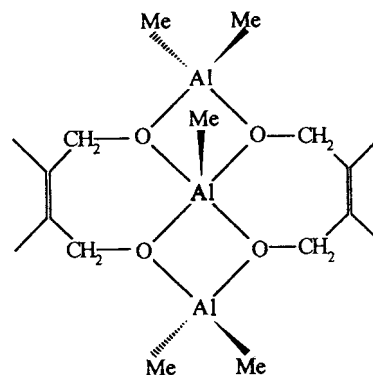


Fig. 1. The structure of the products formed in the reaction of  $AlMe_3$  with unsaturated diols.

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<sup>1</sup> Dedicated to Prof. R. Bruce King on the occasion of his 60th birthday in recognition of his outstanding contribution to organometallic chemistry.

Table 1  
The reactions of diols with  $\text{AlMe}_3$  and the yield of the cyclic products<sup>a</sup>

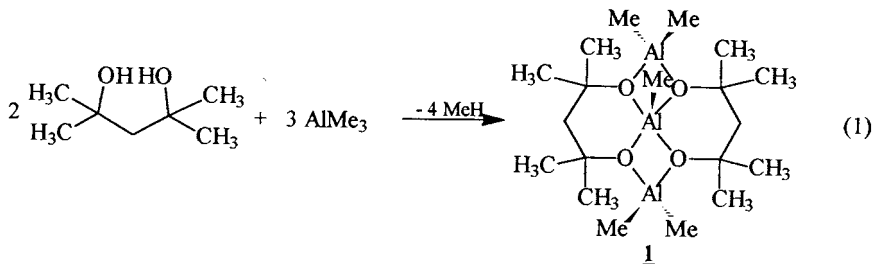
Entry	Diols	Conformers of diols		Isolated yield of cyclic products	Ref.
		a	b		
1.	2,4-dimethyl-2,4-pentanediol <u>A</u>			82.5%	this work
2.	2-methyl-2,4-pentanediol <u>B</u>			87.0%	this work
3.	2,5-dimethyl-2,5-hexanediol <u>C</u>			0%	this work
4.	1,3-propanediol <u>D</u>			8.5%	[4]
5.	2,2-dimethyl-1,3-propanediol <u>E</u>			7.2%	[4]
6.	2,4-butanediol <u>F</u>			17.5%	[4]
7.	1,4-butanediol <u>G</u>			47.0%	[4]
8.	ethanediol			0%	

<sup>a</sup> Molar ratio of diol: $\text{AlMe}_3 = 2:3$ .

## 2. Results and discussion

The reactions of trimethyl- and triethylaluminium with substituted 1,3-propanediol and 1,4-butanediol were studied. The diols were substituted with three or four methyl groups at terminal carbon atoms.

2,4-Dimethyl-2,4-pentanediol (**A**) reacts with trimethylaluminium to form crystalline compound **1** with a high yield 82.5% (Eq. 1).



<sup>1</sup>H-NMR spectrum of **1** revealed three singlets of protons of methyl groups bonded to aluminium at  $-0.37$ ,  $-0.38$  and  $-0.41$  ppm with the integration ratio 2:2:1. The integration ratio allowed to assign the singlet at  $-0.41$  ppm to the methyl group bonded to the central five-coordinated aluminium atom. The signals at  $-0.37$  and  $-0.38$  ppm corresponded to four methyl groups bonded to two four-coordinated aluminium atoms.

The  $-\text{CH}_2-$  groups appeared in the <sup>13</sup>C-NMR spectrum as one singlet at 51.45 ppm which is consistent with the proposed structure of **1**.

The following signals were present in <sup>27</sup>Al-NMR spectrum: broad 155 ppm in the region characteristic

for four-coordinated aluminium and more narrow at 65 ppm in the region characteristic for five-coordinated aluminium.

The molecular weight of **1** determined cryoscopically was 450 (calc. 416) which indicated an association degree of 1.08.

The crystal structure of the compound **1** was determined by X-ray diffraction study. A perspective view of the molecule with the atom numbering system is shown on Fig. 2. The X-ray crystal structure analysis revealed an example of a central aluminium atom with a square-based pyramid coordination geometry, where four oxy-

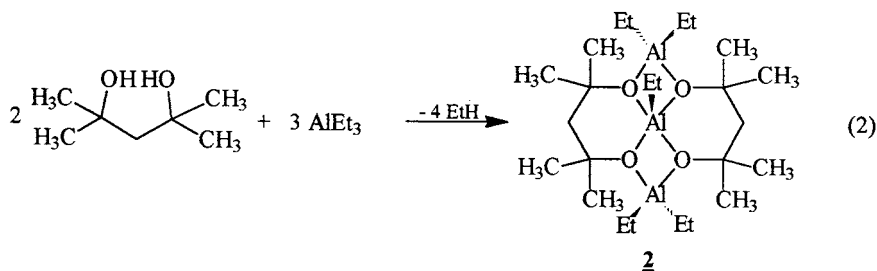
gen atoms occupy the basal sites. Atomic coordinates are in Table 2 and bond lengths and angles in Tables 3 and 4. The structure shows the five-coordinated aluminium atom is displaced of 0.623 Å from the O<sub>4</sub> plane. Four oxygen atoms form a distorted rectangle with angles of O(3), O(1), O(2) 93.6 (1)°, O(1), O(2), O(4) 85.0 (1)°, O(3), O(4), O(2) 93.9 (1)° and O(4), O(3), O(1) 85.0 (1)°. The distances between O(1)–O(2), O(3)–O(4), O(1)–O(3) and O(2)–O(4) are 2.665(1), 2.660(1),

2.350(1) and 2.345(1) Å, respectively. The two four-membered rings Al<sub>2</sub>O<sub>2</sub> are almost flat; the rms deviations of the ring atoms from mean least-square planes are 0.02 and 0.03 Å.

The similar structure of [RAl(OCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>(AlR<sub>2</sub>)<sub>2</sub>]<sub>2</sub>, where R = CH(SiMe<sub>3</sub>)<sub>2</sub> was described by Uhl et al. [5].

The solid product [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Al<sub>3</sub>B<sub>4</sub>Cl<sub>5</sub>O<sub>6</sub>] obtained in the reaction of tribenzene boroxine (C<sub>6</sub>H<sub>5</sub>BO)<sub>3</sub> with aluminium trichloride possesses also similar structure with two (AlOBOBO)-rings bonded through one penta-coordinated aluminium atom [6].

Triethylaluminium reacts with 2,4-dimethyl-2,4-pentanediol (**A**) similarly to trimethylaluminium to form a product **2** with 83.0% yield (Eq. 2).



The <sup>1</sup>H-NMR spectrum of **2** showed the complex signals of ethyl groups bonded to aluminium. The analysis of the structure of **2** indicated that there were three different kinds of ethyl groups. We observed the multiplet of CH<sub>3</sub>CH<sub>2</sub>Al protons consisting of two triplets at 1.36 and 1.34 ppm.

The signals of CH<sub>3</sub>CH<sub>2</sub>Al protons were the multiplet consisted of three quartets at 0.21, 0.16 and 0.13 ppm. The first two of these signals were assigned to four CH<sub>3</sub>CH<sub>2</sub>Al groups bonded to two terminal aluminium atoms and a signal at 0.13 ppm corresponded to one CH<sub>3</sub>CH<sub>2</sub>Al group bonded to central aluminium atom.

Table 2  
Data collection and structure analysis parameters

Empirical formula	C <sub>19</sub> H <sub>43</sub> Al <sub>3</sub> O <sub>4</sub>
Crystal size (mm)	0.70 × 0.70 × 0.70
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /n
Unit cell dimensions:	
<i>a</i> (Å)	11.070(2)
<i>b</i> (Å)	12.813(3)
<i>c</i> (Å)	18.120(4)
β (°)	91.38(3)
<i>V</i> (Å <sup>3</sup> )	2569.4(9)
<i>Z</i>	4
Formula weight	416.47
<i>D</i> <sub>calc.</sub> (g cm <sup>-3</sup> )	1.077
<i>D</i> <sub>meas.</sub> (g cm <sup>-3</sup> )	1.09
Temperature (K)	293(2)
Absorption coefficient (cm <sup>-1</sup> )	1.65
<i>F</i> (000)	912
Radiation (Mo–K <sub>α</sub> )	λ = 0.71069 Å, graphite monochromator
2θ range for data collection (°)	4.50–60.10
Scan type	ω–2θ
Index ranges	–15 ≤ <i>h</i> ≤ 15, 0 ≤ <i>k</i> ≤ –17, –25 ≤ <i>l</i> ≤ 25
Reflections collected	3784
Independent reflections	3324 [ <i>R</i> <sub>int</sub> = 0.0220]
Observed reflections	3324
No. of parameters refined	244
Final <i>R</i> indices [ <i>I</i> > 2.5σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0459; <i>wR</i> <sub>2</sub> = 0.1100
GOF on <i>F</i> <sup>2</sup>	1.103
<i>R</i> <sub>1</sub> <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0409
<i>wR</i> <sub>2</sub> <sup>b</sup>	<i>wR</i> <sub>2</sub> = 0.1017
<i>R</i> indices for all data	<i>R</i> <sub>1</sub> = 0.0409, <i>wR</i> <sub>2</sub> = 0.1017
Weighing scheme	σ <sub>w</sub> <sup>-1</sup>
Largest difference peak and hole (e Å <sup>-3</sup> )	0.282 and –0.188

$$^a R_1 = \Sigma(|F_o| - |F_c|) / \Sigma(F_o)$$

$$^b wR_2 = \{ \Sigma[(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2] \}^{1/2}$$

$$^c w^{-1} = [\sigma^2(F_o^2) + (0.0704P)^2 + 0.5162P] \text{ where } P = (F_o^2 + 2F_c^2)/3$$

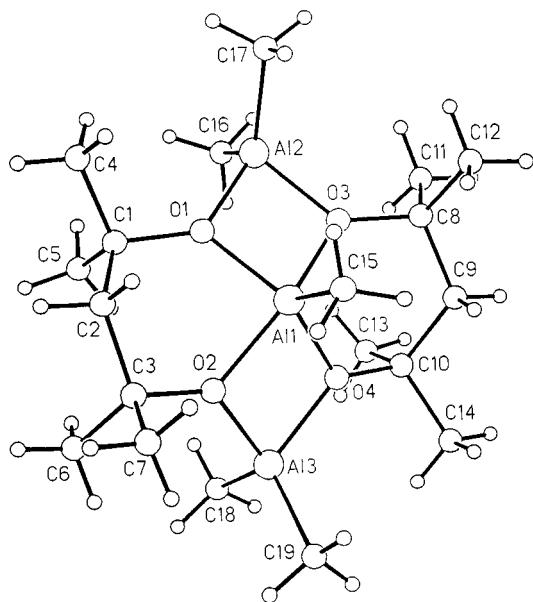


Fig. 2. The molecular structure of **1** with the atom-numbering scheme.

Table 3  
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
Al (1)	0.00475(6)	0.23997(5)	0.22013(4)	0.0363(2)
Al (2)	–0.14660(7)	0.37145(7)	0.30589(4)	0.0482(2)
Al (3)	0.20320(7)	0.28035(6)	0.12593(4)	0.0478(2)
O (1)	–0.1295(1)	0.3265(1)	0.2107(1)	0.0402(4)
O (2)	0.0403(1)	0.2622(1)	0.1194(1)	0.0420(4)
O (3)	–0.0107(1)	0.2924(1)	0.3172(1)	0.0446(4)
O (4)	0.1691(1)	0.2679(1)	0.2240(9)	0.0433(4)
C (1)	–0.1946(2)	0.3560(2)	0.1437(1)	0.0516(6)
C (2)	–0.1715(2)	0.2724(2)	0.0853(1)	0.0530(6)
C (3)	–0.0437(2)	0.2554(2)	0.0571(1)	0.0502(6)
C (4)	–0.3292(2)	0.3544(2)	0.1599(2)	0.0812(11)
C (5)	–0.1535(2)	0.4643(2)	0.1228(2)	0.0846(11)
C (6)	–0.0061(3)	0.3341(3)	–0.0006(2)	0.0720(9)
C (7)	–0.0366(3)	0.1457(3)	0.0245(2)	0.0768(10)
C (8)	0.0636(2)	0.2656(2)	0.3817(1)	0.0554(7)
C (9)	0.1866(2)	0.2288(3)	0.3544(2)	0.0611(7)
C (10)	0.2443(2)	0.2856(3)	0.2893(2)	0.0595(7)
C (11)	0.0700(3)	0.3596(3)	0.4328(2)	0.0766(10)
C (12)	0.0040(3)	0.1754(3)	0.4217(2)	0.0843(11)
C (13)	0.2562(4)	0.4033(3)	0.2991(2)	0.0912(12)
C (14)	0.3669(3)	0.2366(4)	0.2761(2)	0.105(2)
C (15)	–0.0335(3)	0.0917(2)	0.2276(2)	0.0624(8)
C (16)	–0.1169(3)	0.5206(3)	0.3187(2)	0.0860(11)
C (17)	–0.2859(3)	0.3115(4)	0.3539(2)	0.0894(12)
C (18)	0.2587(3)	0.4189(3)	0.0984(2)	0.0894(12)
C (19)	0.2922(3)	0.1631(3)	0.0865(2)	0.0824(11)

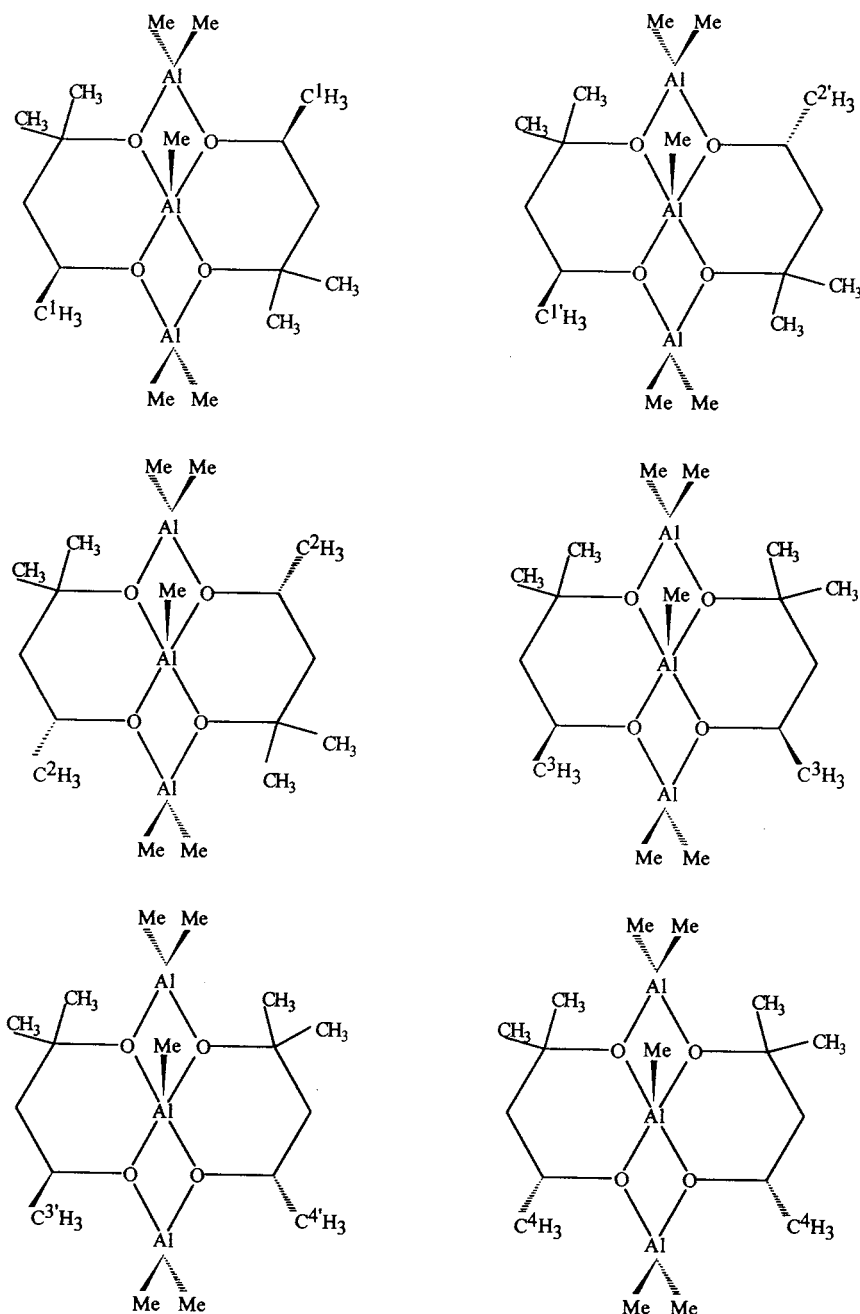
<sup>a</sup>  $U(\text{eq}) = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* a_i a_j$  i.e. one-third of the trace of the orthogonalised  $U_{ij}$  tensor.

The methylene groups CH<sub>2</sub> appeared in <sup>13</sup>C-NMR spectrum as one signal at 51.48 ppm. Two broad signals at 3.40 and 2.63 ppm were assigned to the carbons of CH<sub>3</sub>CH<sub>2</sub>Al groups bonded to four- and five-coordinated aluminium atoms, respectively. Two signals at 154 and 65 ppm were present in the <sup>27</sup>Al-NMR spectrum of **2** which confirmed the existence of two kinds of aluminium atoms (four- and five-coordinated). The as-

Table 4  
Bond lengths (Å) between non-hydrogen atoms in **1**<sup>a</sup>

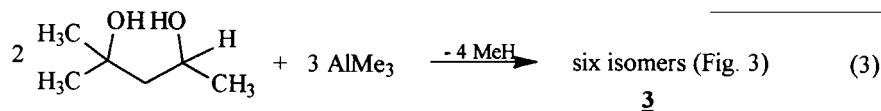
Al(1)–Al(2)	2.861(1)	O(1)–C(1)	1.448(3)
Al(1)–Al(3)	2.861(1)	O(2)–C(3)	1.448(3)
Al(1)–O(1)	1.859(2)	O(3)–C(8)	1.454(3)
Al(1)–O(2)	1.898(2)	O(4)–C(10)	1.449(3)
Al(1)–O(3)	1.894(2)	C(1)–C(2)	1.532(4)
Al(1)–O(4)	1.854(2)	C(1)–C(4)	1.526(3)
Al(1)–C(15)	1.952(3)	C(1)–C(5)	1.511(4)
Al(2)–O(1)	1.832(2)	C(2)–C(3)	1.531(4)
Al(2)–O(3)	1.821(2)	C(3)–C(6)	1.518(4)
Al(2)–C(16)	1.952(3)	C(3)–C(7)	1.526(4)
Al(2)–C(17)	1.946(3)	C(8)–C(9)	1.534(4)
Al(3)–O(2)	1.819(2)	C(8)–C(11)	1.520(4)
Al(3)–O(4)	1.832(2)	C(8)–C(12)	1.523(4)
Al(3)–C(18)	1.947(3)	C(9)–C(10)	1.538(4)
Al(3)–C(19)	1.942(3)	C(10)–C(13)	1.523(5)
		C(10)–C(14)	1.519(4)

<sup>a</sup> Estimated standard deviations in parentheses.

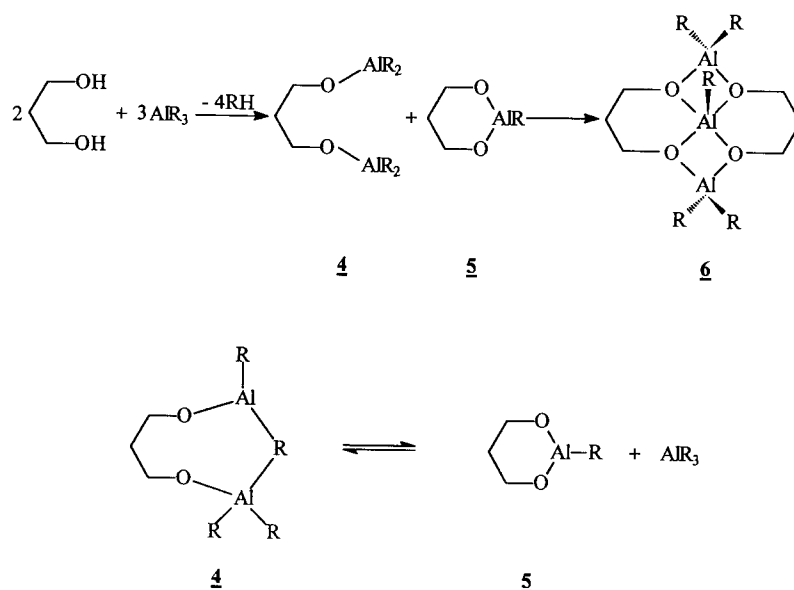
Fig. 3. Six isomers of **3**.

sociation degree of **2** calculated on the basis of the molecular weight determination was 0.93.

Less sterically hindered 2-methyl-2,4-pentandiol **B** reacted with  $\text{AlMe}_3$  to form a product **3** with 87% yield (Eq. 3). The product was a mixture of six isomers (Fig. 3) analogously to the previously studied reaction of another asymmetric diol 2,4-butanediol [4].



The mixture of isomers was isolated by distillation ( $T = 150^\circ\text{C}$ ,  $p = 1 \times 10^{-3}$  Torr) as a colourless viscous liquid. Its NMR spectra, molecular weight and elemental analysis were measured. The structure of isomers was determined on the bases of NMR spectra analysis. The signals in the  $^1\text{H}$ -NMR spectrum appeared as three complex multiplets (about 4.00 ppm  $-\underline{\text{CH}}(\text{CH}_3)\text{O}$ ;



Scheme 1.

0.81–1.6 ppm ( $\text{CH}_3$ )<sub>2</sub>CO, ( $\text{CH}_3$ )HCO,  $\text{CH}_2$  and about  $-0.44$  ppm  $\text{AlCH}_3$ ) because of the number of isomers present in the mixture. The integration ratio of two multiplets  $\text{CH}(\text{CH}_3)\text{O}:\text{AlCH}_3$  (2:15) was consistent with the proposed structure **3**.

<sup>13</sup>C-NMR spectrum revealed five groups of sharp signals (see Section 3) and one very broad (from  $-5.3$  to  $-7.4$  ppm) of methyl groups bonded to aluminium.

The analysis of the structure of isomers indicated that there were eight different kinds of methyl groups in the six isomers. These methyl groups appear in the <sup>13</sup>C-NMR spectrum as four signals at 49.78, 49.66, 48.24 and 47.96 ppm. This is most probably caused by overlapping of the signals, because chemical shifts of the carbons of methyl groups numbered  $\text{C}^1\text{H}_3$  and  $\text{C}^1\text{H}_3$ ,  $\text{C}^2\text{H}_3$  and  $\text{C}^2\text{H}_3$ ,  $\text{C}^3\text{H}_3$  and  $\text{C}^3\text{H}_3$ ,  $\text{C}^4\text{H}_3$  and  $\text{C}^4\text{H}_3$  are the same or very close to each other.

In <sup>1</sup>H-NMR spectrum the signals of these methyl groups and the signals of  $\text{C}(\text{CH}_3)_2$ ,  $\text{CH}_2$  groups overlapped and appeared as complicated multiplet.

There were two signals at 156 and 67 ppm present in the <sup>27</sup>Al-NMR spectrum of mixture of isomers **3** which indicated the presence of four- and five-coordinated aluminium. The molecular weight of **3** determined cryoscopically was 409 (calc. 388), which indicated an association degree of 1.05. The percentage of aluminium and methyl groups bonded to aluminium were very close to their theoretical values (see Section 3) which confirmed the proposed structure of **3**.

The above data show that sterically hindered 2,4-pentanediols (**A**, **B**) react with alkylaluminium compounds to form mainly cyclic compounds **1–3**.

Sterically hindered derivative of 1,4-butandiol (i.e. 2,5-dimethyl-2,5-hexanediol **C**) reacts with trimethylaluminium to form only organoaluminium oligomers as an

amorphous solid insoluble in common organic solvents.

The course of the reaction is presented on Scheme 1, based on present and previously published [1–4] results. For the molar ratio of reactants diol: $\text{AlR}_3 = 2:3$ , both hydroxyl groups of diol can react with two molecules of  $\text{AlR}_3$  to form compound **4** or with one molecule of  $\text{AlR}_3$  to form compound **5**. Compounds **4** and **5** exist in an equilibrium (Scheme 1). The aluminium atoms in compound **4** as well as in **5** are tri-coordinated and tend to achieve higher coordination number what happens in the compound **6**. An excess of trialkylaluminium (diol: $\text{AlR}_3 < 2:3$ ) does not influence on the products and remains in the post-reaction mixture unchanged.

An excess of diol (diol: $\text{AlR}_3 > 2:3$ ) causes its reaction with compounds **4** and **5**. This leads to the formation of oligomers and decreasing the yield or even making the formation of **6** impossible [2].

The data in the Table 1 show that the factor deciding on the yield of complexes **6** is the distance between reacting hydroxyl groups. Both compounds **4** and **5** in conformations shown on Scheme 1 can be formed only if the hydroxyl groups are situated close to each other as in conformations **A<sub>b</sub>–G<sub>b</sub>** (Table 1). Substituents have the decisive influence on the possibility of a rotation around C–C bonds causing steric hindrances and preventing the proper location of hydroxyl groups, e.g. steric hindrance in 2,5-dimethyl-2,5-hexanediol (**C**) makes the formation of the conformer **C<sub>b</sub>** impossible and therefore compounds **4** and **5** cannot be formed. Instead of this the reaction leading to the formation of oligomers proceeds. Steric hindrances in 2,4-dimethyl-2,4-pentanediol cause that diol **A** exists mainly in the form of the conformer **A<sub>b</sub>** with OH groups situated close to each other and it has the decisive influence on the high yield of the complex **1**.

Triethylaluminium reacts with the studied diols as trimethylaluminium to form cyclic complexes with similar yield.

### 3. Experimental section

All manipulations were carried out using standard Schlenk techniques in anhydrous solvents under an inert gas atmosphere.

$^1\text{H-NMR}$  spectra were recorded with a Varian VXR 300 spectrometer, at 299.9 MHz. Chemical shifts were referenced to the residual proton signal of  $\text{C}_6\text{D}_6$  (7.15 ppm).  $^{13}\text{C-NMR}$  spectra were run on the same instrument at 75.4 MHz (standard: benzene  $^{13}\text{CC}_5\text{D}_6 = 128$  ppm).  $^{27}\text{Al}$  spectra were run at 78.2 MHz (standard  $\text{Al}(\text{acac})_3 = 0.0$  ppm). Molecular weight of the complexes was determined by the cryoscopy in benzene.

#### 3.1. Reactions of 2,4-dimethyl-2,4-pentanediol (**A**) with $\text{AlMe}_3$ (2:3)

A sample (1.512 g, 21 mmol) of  $\text{AlMe}_3$  in 30  $\text{cm}^3$  of diethylether was placed in 250  $\text{cm}^3$  two-necked flask and cooled to  $-78^\circ\text{C}$ . The solution of 1.848 g (14 mmol) of diol **A** in 20  $\text{cm}^3$  of diethylether was then added drop by drop within 0.5 h. The reaction mixture was allowed to warm to room temperature within 2 h. Evolution of gases was observed during the course of the reaction. The solvent was distilled off and the remaining white solid was sublimed ( $T = 120^\circ\text{C}$ ,  $p = 1 \times 10^{-3}$  Torr) yielding 2.402 g (82.5%) of **1**.

$^1\text{H-NMR}$  (benzene- $d^6$ ):  $\delta$  1.75 (d, 2H,  $\text{CH}_2$ ), 0.96 (d, 2H,  $\text{CH}_3$ ), 1.26 (s, 12H,  $(\text{CH}_3)_2\text{C}$ ), 1.16 (s, 12H,  $(\text{CH}_3)_2\text{C}$ ),  $-0.37$  (s, 6H,  $\text{CH}_3\text{Al}$ ),  $-0.38$  (s, 6H,  $\text{CH}_3\text{Al}$ ),  $-0.41$  (s, 3H,  $\text{CH}_3\text{Al}$ ) ppm.

$^{13}\text{C-NMR}$  (benzene- $d^6$ ):  $\delta$  74.50 ( $(\text{CH}_3)_2\text{C-O}$ ), 51.45 ( $-\text{CH}_2-$ ), 33.65, 30.83 ( $\text{CH}_3$ ),  $-5.40$ ,  $-6.40$  ( $\text{Al-CH}_3$ ) ppm.

$^{27}\text{Al-NMR}$  (benzene- $d^6$ ):  $\delta$  155 (four-coord. Al), 65 (five-coord. Al) ppm.

Molecular weight. Found: 450. Calc.: 416.

Elemental anal. Found: Al, 19.10; hydrolysable methyl groups, 17.55; Calc.: Al, 19.47; Me, 18.03 wt%.

#### 3.2. Reaction of 2,4-dimethyl-2,4-pentanediol (**A**) with $\text{AlEt}_3$ (2:3)

The reaction was carried out as described above using 1.848 g (14 mmol) of diol **A** and 2.394 g (21 mmol) of  $\text{AlEt}_3$ . A total of 2.820 g (83%) of thick liquid compound **2** was obtained by distillation ( $T = 120^\circ\text{C}$ ,  $p = 1 \times 10^{-3}$  Torr) from the post-reaction mixture.

$^1\text{H-NMR}$  (benzene- $d^6$ ):  $\delta$  1.78 (d, 2H,  $\text{CH}_2$ ), 1.36, 1.34 (two triplets, 15H,  $\text{CH}_3\text{CH}_2\text{Al}$ ), 1.30 (s, 12H,  $(\text{CH}_3)_2\text{C}$ ), 1.19 (s, 12H,  $(\text{CH}_3)_2\text{C}$ ), 1.02 (d, 2H,  $\text{CH}_2$ ),

0.21, 0.16, 0.13 (three quartets, 10H,  $\text{CH}_3\text{CH}_2\text{Al}$ ) ppm.

$^{13}\text{C-NMR}$  (benzene- $d^6$ ):  $\delta$  74.29 ( $(\text{CH}_3)_2\text{C-O}$ ), 51.48 ( $\text{CH}_2$ ), 33.54, 30.85 ( $(\text{CH}_3)_2\text{C}$ ), 9.92, 9.55, 9.52 ( $\text{CH}_3\text{CH}_2\text{Al}$ ), 3.40, 3.65 ( $\text{CH}_3\text{CH}_2\text{Al}$ , broad) ppm.

$^{27}\text{Al-NMR}$  (benzene- $d^6$ ):  $\delta$  154 (four-coord. Al), 65 (five-coord. Al) ppm.

Molecular weight. Found: 450. Calc.: 486.

Elemental anal. Found: Al, 16.38; hydrolysable ethyl groups, 30.1; Calc.: Al, 16.67; Et, 29.8 wt%.

#### 3.3. Reaction of 2-methyl-2,4-pentanediol (**B**) with $\text{AlMe}_3$ (2:3)

The reaction was carried out as described in Section 3.1 using 1.180 g (10 mmol) of diol **B** and 1.080 g (15 mmol) of  $\text{AlMe}_3$ . A total of 1.688 g (87%) of liquid compound of **3** was obtained by distillation ( $T = 100^\circ\text{C}$ ,  $p = 1 \times 10^{-3}$  Torr) from the post-reaction mixture.

$^1\text{H-NMR}$  (benzene- $d^6$ ):  $\delta$  about  $-4.00$  (m, 2H,  $\text{CH}(\text{CH}_3)\text{O}$ ), 0.8–1.6 (m, 22H,  $(\text{CH}_2)\text{CO}$ ,  $(\text{CH}_3\text{HCO}$ ,  $\text{CH}_2$ ), about  $-0.44$  (m, 15H,  $\text{AlCH}_3$ ).

$^{13}\text{C-NMR}$  (benzene- $d^6$ ):  $\delta$  74.45, 74.36, 74.27, 74.12, 74.05, 73.95 ( $(\text{CH}_3)_2\text{C-O}$ ), 66.37, 66.19, 66.15, 65.87, 65.72 ( $\text{H}(\text{CH}_3)\text{C-O}$ ), 49.78, 49.66, 48.24, 47.96 ( $\text{H}(\text{CH}_3)\text{C-O}$ ), 32.70, 32.57, 32.51, 32.35 ( $\text{CH}_2$ ), 28.44, 28.40, 27.98, 27.66, 27.56, 27.50, 27.37, 27.33, 24.68, 24.59, 24.54, 24.05, 23.89, 23.81 ( $(\text{CH}_3)_2\text{C-O}$ ), from  $-5.3$  to  $-7.4$  broad ( $\text{CH}_3\text{Al}$ ) ppm.

$^{27}\text{Al-NMR}$  (benzene- $d^6$ ):  $\delta$  156 (four-coord. Al), 67 (five-coord. Al) ppm.

Molecular weight. Found: 409. Calc.: 388.

Elemental anal. Found: Al, 21.15; hydrolysable methyl groups, 20.3. Calc.: Al, 20.88; Me, 19.3 wt%.

#### 3.4. Reaction of 2,5-dimethyl-2,5-hexanediol (**C**) with $\text{AlMe}_3$ (2:3)

The reaction was carried out as described in Section 3.1 using 1.460 g (10 mmol) of diol **C** and 1.080 g (15 mmol) of  $\text{AlMe}_3$ . White non-volatile up to  $160^\circ\text{C}$  ( $p = 1 \times 10^{-3}$  Torr) solid insoluble in organic solvents obtained as reaction product.

Elemental anal. of the mixture of organoaluminium oligomers. Found: Al, 19.55; hydrolysable methyl groups, 22.6 wt%.

#### 3.5. Reaction of 2,5-dimethyl-2,5-hexanediol (**C**) with $\text{AlMe}_3$ (2:5)

The reaction was carried out as described in Section 3.1 using 1.460 g (10 mmol) of diol **C** and 1.800 g (25 mmol) of  $\text{AlMe}_3$ . White, non-volatile and insoluble solid was obtained.

Elemental anal. of the mixture of organoaluminium oligomers. Found: Al, 17.65; hydrolysable methyl groups, 22.4 wt%.

Table 5  
Selected bond angles (°) in **1**<sup>a</sup>

O(1)–Al(1)–O(2)	90.4(1)	Al(2)–Al(1)–O(4)	116.9(1)
O(1)–Al(1)–O(3)	77.5(1)	Al(2)–Al(1)–C(15)	113.9(1)
O(1)–Al(1)–O(4)	132.1(1)	Al(3)–Al(1)–O(1)	117.5(1)
O(2)–Al(1)–O(3)	149.9(1)	Al(3)–Al(1)–O(2)	38.7(1)
O(2)–Al(1)–O(4)	77.4(1)	Al(3)–Al(1)–O(3)	125.3(1)
O(3)–Al(1)–O(4)	90.4(1)	Al(3)–Al(1)–O(4)	38.8(1)
O(1)–Al(1)–C(15)	114.4(1)	Al(3)–Al(1)–C(15)	112.9(1)
O(2)–Al(1)–C(15)	105.3(1)	O(1)–Al(2)–O(3)	80.1(1)
O(3)–Al(1)–C(15)	104.8(1)	O(1)–Al(2)–C(16)	113.5(1)
O(4)–Al(1)–C(15)	113.6(1)	O(3)–Al(2)–C(16)	113.3(1)
Al(2)–Al(1)–Al(3)	133.3(1)	O(1)–Al(2)–C(17)	113.4(1)
Al(2)–Al(1)–O(1)	38.8(1)	O(3)–Al(2)–C(17)	113.1(1)
Al(2)–Al(1)–O(2)	124.9(1)	Al(1)–Al(2)–O(3)	40.6(1)
Al(2)–Al(1)–O(3)	38.7(1)	C(16)–Al(2)–C(17)	117.8(2)

<sup>a</sup> Estimated standard deviations in parentheses.

### 3.6. Reaction of 2,5-dimethyl-2,5-hexanediol (**C**) with $AlEt_3$ (2:3)

The reaction was carried out as described in Section 3.1 using 1.460 (10 mmol) of diol **C** and 1.710 g (15 mmol) of  $AlEt_3$ . White non-volatile and insoluble solid was obtained.

Elemental anal. of the mixture of organoaluminium oligomers. Found: Al, 16.76; hydrolysable ethyl groups, 35.3 wt%.

### 3.7. Crystal structure determination

Preliminary Weissenberg photographs showed crystal system, space group and approximate unit-cell dimensions. All measurements were made on a Kuma KM-4 computer-controlled  $\kappa$ -axis diffractometer with graphite-monochromated Mo– $K_\alpha$  radiation. The stability of intensities was monitored by measurement of three standards every 100 reflections. The data were corrected for Lorentz and polarisation effects. No absorption correction was applied. Data collection and

structure analysis parameters are given in Table 2, fractional atomic coordinates in Table 3. Selected bond lengths and bond angles are listed in Tables 4 and 5. The structure was refined by full-matrix least-square methods using SHELXL-93 [7] with anisotropic thermal parameters for non-H atoms. The hydrogen atoms were put in calculated positions and introduced as fixed contributors in the final stage of refinement. Scattering factors were those incorporated in SHELXL-93.

## 4. Supplementary material

Supplementary material, including listings of bond lengths and angles, anisotropic thermal and hydrogen atom parameters, as well as tables of calculated and observed structure factors, is available.

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