REACTIONS OF TETRAALKYLALUMINOXANES WITH AMINES

A. PIOTROWSKI, A. KUNICKI and S. PASYNKIEWICZ

Institute of Organic Chemistry and Technology of Warsaw Technical University (Politechnika), Koszykowa, 75, 00-662 Warszawa (Poland)

Summary

A complex of tetraalkylaluminoxane with benzylamine and the complexes of tetraethylaluminoxane with benzylamine and methylamine were synthesized. Investigated complexes decomposed thermically forming alkane and an organoaluminium amide. The structure of the latter was postulated on the basis of ^1H NMR, ^{13}C NMR and IR spectroscopic studies, and cryoscopic molecular weight measurements.

Introduction

Aluminoxanes are known to be catalysts for the polymerization of olefin oxides, vinyl monomers, lactones and acetic aldehyde [1—3]. There are many reports in the literature on the synthesis of aluminoxanes [4—9], their structure [5,10] and structures of their complexes [1,8,11,12]. There are however, few reports on the reactions of aluminoxanes with electron donors. The present work is concerned with the reactions of tetraethylaluminoxane with benzylamine and methylamine, and of tetramethylaluminoxane with benzylamine.

Results

Amines ($MeNH_2$, $PhCH_2NH_2$) react with tetraalkylaluminoxanes R_4Al_2O ($R = Me$, Et) forming complexes I, II, III.

$$Et_4Al_2O + PhCH_2NH_2 \rightarrow Et_4Al_2O \cdot PhCH_2NH_2$$
$$(I)$$

$$Et_4Al_2O + MeNH_2 \rightarrow Et_4Al_2O \cdot MeNH_2$$
$$(II)$$

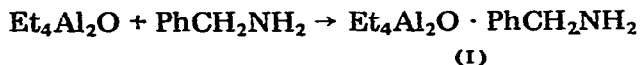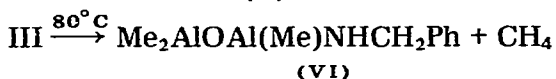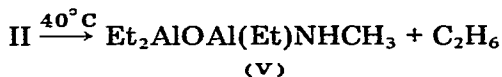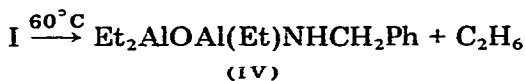$$Me_4Al_2O + PhCH_2NH_2 \rightarrow Me_4Al_2O \cdot PhCH_2NH_2$$
$$(III)$$
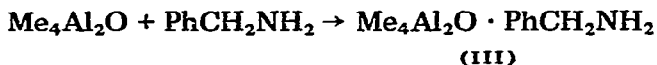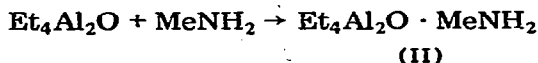
TABLE 1

SPECTRAL DATA FOR THE ADDUCTS I, II, III (The NMR spectra were recorded in 25 wt% CH_2Cl_2 solution)

Compound	ν(a-NH) ν(e-NH) (cm^{-1})	ν(Al—O—Al) (cm^{-1})	τ(NH) (ppm)	τ(AlCH$_2$CH$_3$) (ppm)	τ(AlCH$_2$CH$_3$) (ppm)	$\Delta\tau$(CH$_3$) — τ(CH$_2$) (ppm)
I	3310m 3268m	790vs	6.97	8.80	10.08	1.28
II	3300m 3250m	798vs	5.0 [b]	8.99	10.22	1.23
III [a]	3305m 3255m	780vs	6.97	10.70 [c]		

[a] In the presence of Et_2O. [b] Shielded by solvent signal. [c] Chemical shift of CH_3—Al group.

^{1}H NMR and IR spectra of I, II, III were recorded. The chemical shifts of the NH$_2$ signals in the ^{1}H NMR spectra of the adducts I, II, III are shifted down-field (Table 1). In the case of I and II an increase of the internal chemical shift difference (δ(CH$_3$) — δ(CH$_2$) in ppm) of the ethyl groups bonded to aluminium was also noticed (Table 1). The NH stretching vibrations of the adducts give sharp bands shifted to lower wave numbers (Table 1). These results conform formation of the complexes I, II, III. Approximate minimum decomposition temperatures of adducts I, II, III are 5, 0, and 35°C respectively. Corresponding deuterated amine (ND$_2$) complexes were obtained. Their decomposition tempe-ratures were at least 10°C higher than in the case of I, II, III. Deuterated adducts I and III were stable enough for their molecular weights to be deter-mined cryoscopically in benzene. It was found that complex I was mainly monomeric $n = 1.20$, and complex III mainly dimeric $n = 2.23$. At elevated temperatures adducts I, II, III form compounds IV, V, VI.

$$\text{I} \xrightarrow{60°C} \text{Et}_2\text{AlOAl(Et)NHCH}_2\text{Ph} + \text{C}_2\text{H}_6$$
$$(\text{IV})$$

$$\text{II} \xrightarrow{40°C} \text{Et}_2\text{AlOAl(Et)NHCH}_3 + \text{C}_2\text{H}_6$$
$$(\text{V})$$

$$\text{III} \xrightarrow{80°C} \text{Me}_2\text{AlOAl(Me)NHCH}_2\text{Ph} + \text{CH}_4$$
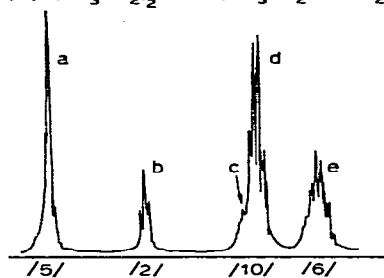$$(\text{VI})$$

These reactions proceed quantitatively. Compounds IV, V and VI were iso-lated and identified by means of elemental analysis (Table 2) and NMR spectra (Fig. 1). The ^{13}C NMR spectrum of IV was also recorded (Fig. 2). The associa-tion degree of IV, V and VI changes in time. Cryoscopic molecular weight mea-surements of IV, V, VI showed that these compounds were exactly trimeric (Table 2) 36 h after completion of the reaction. No further increase of the asso-ciation degree was observed, even after 14 days.

The ^{1}H NMR spectrum of IV (Fig. 1A) contains four groups of signals with a proton ratio of 5/2/10/6. The signal of the NH proton c is overlapped by mul-tiplet d. However, in the low temperature ^{1}H NMR spectrum of IV, signal c is
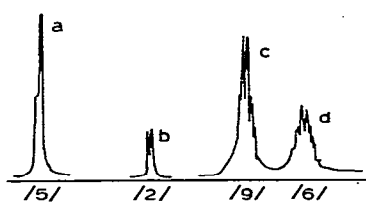
TABLE 2

ANALYTICAL DATA

Compound	(Found (calcd.) (%))			
	Al	R	molecular weight	n
IV	20.53 (20.49)	33.35 (33.11)	783 (263.3)	2.97
V	28.74 (28.83)	45.92 (46.57)	556 (187.2)	2.97
VI	25.00 (24.39)	20.03 (20.39)	667 (221.1)	3.02

Fig. 1. ^{1}H NMR spectra in CH_2Cl_2. Concentration 25 wt.% CH_2Cl_2 as an internal standard —4.70 ppm.

visible as a shoulder on the left side of multiplet d.

In the ^{1}H NMR spectrum, the protons of the benzyl methylene group would be expected to appear as singlet, or as a doublet due to the coupling with NH protons. However, the "triplet" b (Fig. 1A) was observed in the ^{1}H NMR 100 MHz spectrum of IV. The measured distances between the two terminal and the central signal in this "triplet" are not equal (7.1 and 6.9 Hz). In the ^{1}H NMR 30 MHz spectrum of IV, instead of the "triplet" a broad doublet was observed. It appears that the "triplet" d present in the ^{1}H NMR 100 MHz spectrum (Fig. 1A) is composed of two overlapping doublets. In fact, in the ^{1}H NMR 100 MHz spectrum of the deuterated amide IV (N-D, Fig. 1B) two singlets of the benzyl methylene group protons were observed, providing the evidence of two different benzyl groups in this system.

The spectrum of deuterated amide IV contains four groups of signals with a proton ratio 5/2/9/6, which indicates that the multiplet 10 in spectrum A (Fig. 1) contains amine proton signal imbedded in the signal of 9 protons of 3 methyl groups d. Two different benzyl groups in IV were also observed in the ^{13}C NMR spectrum.

The ^{13}C NMR spectrum of IV (Fig. 2) contains eleven signals. Signals a of chemical shifts 141.68, 129.33, 128.64, 127.45, 127.13, 126.80 and 126.69 ppm correspond to aromatic carbon atoms and can be attributed to two different phenyl rings. Despite this, only one signal b of the benzyl methylene group carbon atom at 46.76 ppm was present. Signals at 8.76 and 8.63 ppm correspond to the methyl group carbons, c, and the broad signal d between 0.73 and 1.48 ppm corresponds to methylene carbon atoms of ethyl groups bonded to
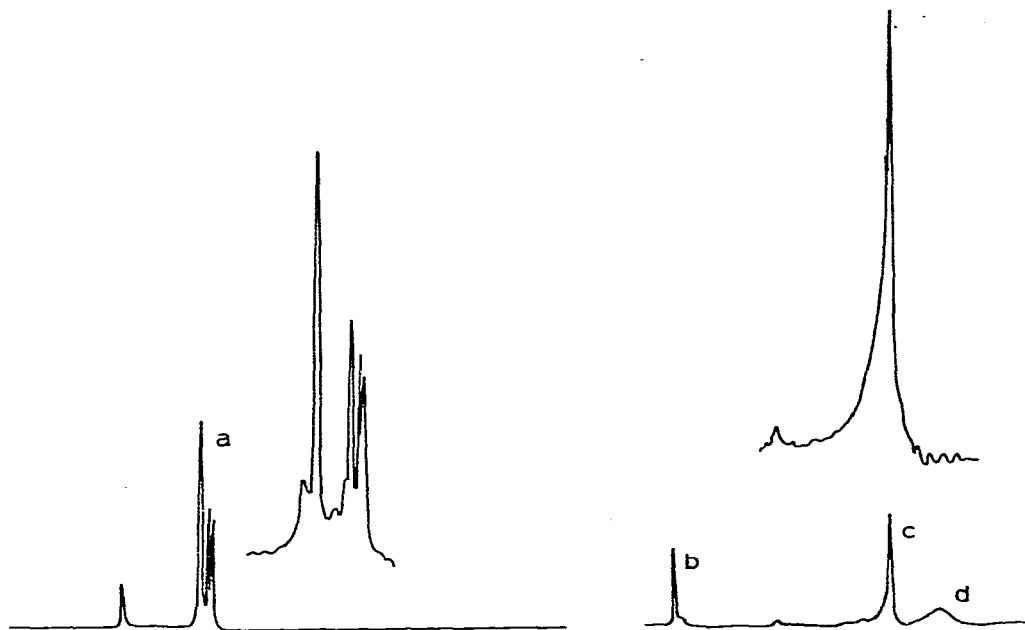

Fig. 2. The ^{13}C NMR of amide IV in CH_2Cl_2. Conc. 30% mol. Lock signal D_2O. At 1.023 sec, PW. 8 s, DP 8192. PD 1.5 sec. Reference line CH_2Cl_2 0 Hz.

aluminium. Signals d is broadened due to the presence of the aluminium atom.

The ^{1}H NMR spectrum of V (Fig. 1C) also contains four groups of signals with a proton ratio 3/9/1/6. The signal of the NH proton c is partly overlapped by multiplet b, so it is difficult to say anything definite about its multiplicity. Two different N—CH$_3$ groups are also observed, corresponding to the different two benzyl groups in IV (Fig. 1D, a). The coupling with NH leads to the formation of two doublets (Fig. 1C, a) with J(NH,CH$_3$) 6.25 Hz. The spectrum of deuterated amide V contains only three groups of signals, with the proton ratio 3/9/6. This indicates that multiplet c in spectrum C (Fig. 1) contains amine proton signal.

In the ^{1}H NMR spectrum of VI (Fig. 1E) four groups of signals are observed with the proton ratio of 5/2/1/9. Here, signals of both substituents at the nitrogen atom (Fig. 1E) N—CH$_2$—Ph b and N—H c are readily observable. Again signals of two different benzyl CH$_2$ groups are observed as two doublets (Fig. 1E, b). The NH proton is observed as two triplets (Fig. 1E, c) due to the coupling of two magnetically different protons NH with the N—CH$_2$—Ph methylene protons J(NH,CH$_2$) 8.4 Hz.

Discussion

The similar character of the ^{1}H NMR spectra of all the compounds, and the fact that they are all trimeric suggest that they have similar structure.

It was found that strong donor—acceptor bonds were present in the compounds IV, V and VI, and all the aluminium atoms were four-coordinated. When benzonitrile was introduced into solutions of IV, V or VI no complex formation was observed. In the IR spectrum of such mixtures C≡N stretching vibrations were not shifted to higher frequencies. The 2230 cm^{-1} band of the C≡N group of free benzonitrile was observed. It was also found that the trimeric form was the most stable in the solution. The molecular weights of the compounds IV, V and VI change during storage; after reaching the value of 3 the degree of association does not change further. In the IR spectra of the compounds IV, V and VI there is a very intensive band at ca. 800 cm^{-1}, which is characteristic of the Al—O—Al bridge. Such a bridge must be present in all trimers under investigation. As the trimer has 6 Al atoms 3 N atoms and 3 O atoms, all Al atoms must be four coordinated in order to give agreement with the above mentioned facts.

The structure presented in Fig. 3 is the most consistent with the above discussion. It is constructed from three four-membered rings VIIa and VIIb,

VIIa   VIIb
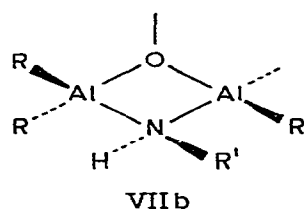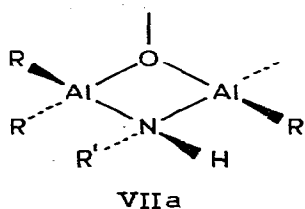
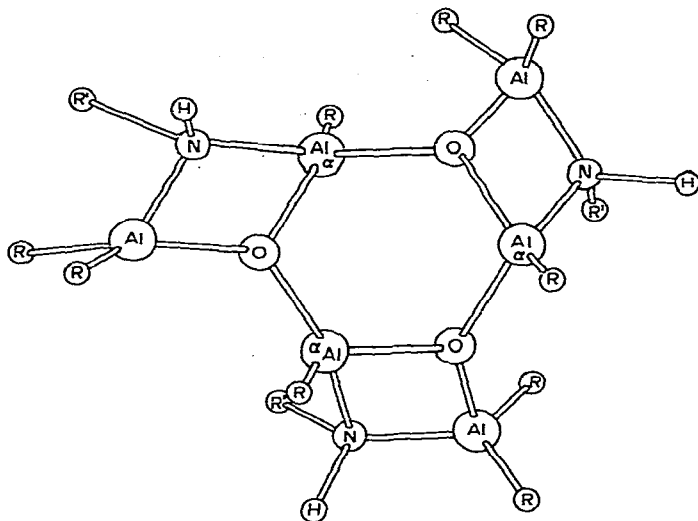which are connected by donor—acceptor bonds between the oxygen atoms and

Fig. 3. The structure of the aluminium amide derivative.

aluminium atoms Al. The Al—O donor acceptor bonds form a six-membered ring.

Differences between the R' substituents in the NMR spectra are probably due to the existance of *cis*-VIIa or *trans*-VIIb isomers. The presence of many signals from the alkyl group R in the ^{1}H NMR spectra is due to various possible arrangements of these groups. It seems that compounds IV, V and VI consist of a mixture of different isomeric trimers as in Fig. 3.

Experimental

The alkylaluminiums and their derivatives are extremely air-reactive and were handled under dry nitrogen or in a conventional vacuum line.

Benzylamine and methylamine were purified by distillation of commercial reagents, and then dried over molecular sieves. Methylamine was further distilled over sodium. Benzylamine was deuterated conventionally. Methylamine was deuterated with D_2O and dried over Na_2O. This procedure was repeated 3 times. The yield of $MeND_2$ exceed 97%. Hydrocarbon solvents were dried over sodium wire, and then distilled over blue ketyl. $Et_2AlOAlEt_2$ was synthesized in the reaction of Et_3Al with water. $Me_2AlOAlMe_2 \cdot Et_2O$ was synthesized in the reaction of $Me_3Al \cdot Et_2O$ with water diluted in Et_2O.

Measurement of physical constants

Molecular weights in benzene solution were determined cryoscopically. IR spectra in a 5 wt-% benzene solutions were recorded on a Perkin—Elmer model 577 spectrometer. ^{1}H NMR spectra were recorded on a JNM-100-H Jeol, Tokyo spectrometer 100 MHz, ^{13}C NMR spectra were recorded on Varian Spectrometer.

Reaction of benzylamine with $Et_2AlOAlEt_2$

$Et_2AlOAlEt_2$ (5.4 mmol) in 4 cm³ of methylcyclohexane was frozen at
—196°C, and an equimolar amount of benzylamine was introduced by distilla-
tion in a vacuum line. The mixture was gradually warmed to the melting point,
and then vigorously stirred by means of a magnetic stirrer for half an hour.
After completion of the reaction methylcyclohexane was distilled off in vacuo.
The tube was then weighed and the yield thus calculated. The reaction of
methylamine with $Et_2AlOAlEt_2$ was carried out analogously.

Reaction of benzylamine with $Me_2AlOAlMe_2$

$Me_2AlOAlMe_2 \cdot Et_2O$ (10.1 mmol) in 10 cm³ of methylcyclohexane was fro-
zen at —196°C, and an equimolar amount of benzylamine was introduced by
distillation in a vacuum line. The mixture was gradually warmed to —70°C, and
then vigorously stirred by means of a magnetic stirrer for half an hour. Et_2O
was then distilled off in vacuo. The reaction tube was warmed to room tempera-
ture and placed in an oil bath for 15 h at 60°C. Further operations were the
same as those for the reaction of tetraethylaluminoxane.

$Et_2AlOAl(Et)NHCH_2Ph$ and $Et_2AlOAl(Et)NHCH_3$ were isolated and purified
by repeated precipitation from n-pentane at low temperature.

$Me_2AlOAl(Me)NHCHPh$ was isolated and purified by repeated precipitation
from the mixture of methylcyclohexane and CH_2Cl_2 (50/1 by weight) at low
temperature.

References

1 N. Ueyama, T. Araki and H. Tami, Inorg. Chem., 12 (1973) 2218.
2 H. Tani, N. Ueyama and T. Araki, Macromolecules, 7 (1974) 153.
3 H. Tani, T. Araki, N. Oguni and N. Ueyama, J. Amer. Chem. Soc., 89 (1967) 173.
4 G.B. Sacharovskaya, N.N. Korneev, A.F. Popov, E.I. Larikov and A.F. Zhigach, Zh. Obsch. Khim.,
   34 (1964) 3435.
5 A. Storr, K. Jones and A.W. Laubengayer, J. Amer. Chem. Soc., 90 (1978) 3173.
6 M. Boleslawski and S. Pasynkiewicz, J. Organometal. Chem., 43 (1972) 81.
7 N. Ueyama, T. Araki and H. Tani, Inorg. Chem., 10 (1973) 2218.
8 M. Boleslawski, S. Pasynkiewicz, K. Jaworski and A. Sadownik, J. Organometal. Chem., 97 (1975) 15.
9 S. Pasynkiewicz, M. Boleslawski and A. Kunicki, PRL Patent 102562, published 1976.
10 M. Boleslawski, S. Patynkiewicz, A. Kunicki and J. Serwatowski, J. Organometal. Chem., 116 (1976)
   285.
11 A. Kunicki, J. Serwatowski, S. Pasynkiewicz and M. Boleslawski, J. Organometal., 128 (1977) 21.
12 M. Boleslawski, S. Pasynkiewicz, A. Minorska and W. Hryniów, J. Organometal. Chem., 65 (1974)
   165.