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Synthesis of N-Alkyliminoalanes in Tetrahydrofuran

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The synthesis of N-alkyliminoalanes in tetrahydrofuran (THF) has been performed in order to identify the nature of the possible intermediates of the final product poly(N-alkyliminoalanes) (PIA), starting from aluminium hydride and primary amines.

The use of THF gives sufficient stability to intermediates, such as $HAl(N\text{-}isoC_3H_7\text{-}AlH_2)_2\cdot 2THF$, $H_2Al\text{-}(N\text{-}isoC_3H_7)AlH_2\cdot 2THF$, $H_2Al(N\text{-}isoC_3H_7)AlH_2\cdot LiH\cdot THF$, $Al(N\text{-}n\text{-}C_4H_9\text{-}AlH_2)_3\cdot LiH\cdot THF$, *which have been isolated and identified.*

The reactions between AlH_3 *and primary amines have also been followed conductimetrically and a relationship between the conductimetric curves and composition of intermediates has been found.*

Introduction

Reaction (1) has been recently investigated

$$AlH_3\cdot NMe_3 + RNH_2 \xrightarrow{Et_2O} \frac{1}{n}(HAlNR)_n + 2H_2 + NMe_3 \quad (1)$$

in order to characterize the poly(N-alkyliminoalane) (PIA), $(HAlNR)_n$, obtained from different amines.

In this investigation, it has been shown that the structure of PIA is connected with the nature of the alkyl group bonded to nitrogen of the primary amine[1,2].

Nevertheless, the study of reaction (1) in tetrahydrofuran (THF) starting from the complex of AlH_3 with THF has been continued in order to attempt the isolation and characterization of the N-alkyliminoalane derivatives, which can be regarded as possible intermediates in the PIA synthesis, by taking advantage of their supposed higher stability in THF.

The reaction leading to PIA has been followed conductimetrically and shows a relationship between the conductimetric curve and the composition of intermediates.

Results and Discussion

In a previous paper[3], an unsuccessful attempt to obtain complexes of N-n-butyliminodialane (I) in Et_2O:

$$\underset{\text{(I)}}{H_2Al\text{–}N(C_4H_9)\text{–}AlH_2}$$

by reaction (2) was reported:

$$Cl_2Al\text{–}N(C_4H_9)\text{–}AlCl_2 \xrightarrow[-LiCl]{+LiH} H_2Al\text{–}N(C_4H_9)\text{–}AlH_2\cdot LiH \quad (2)$$

However, because of a disproportionation, reaction (3) occurs leading to PIA and $LiAlH_4$:

$$H_2Al\text{–}N(C_4H_9)\text{–}AlH_2\cdot LiH \rightarrow LiAlH_4 + \frac{1}{n}(HAlNC_4H_9)_n \quad (3)$$

Later, in an attempt to reproduce Ehrlich's reaction (4):

$$2\,AlH_3\cdot NR_3 \cdot CH_3CN \rightarrow H_2Al\text{–}N(C_2H_5)\text{–}AlH_2\cdot NR_3 + NR_3 \quad (4)$$

evidence[5] was obtained in favour of a mixture of aluminum hydride complexed with NR_3 and PIA instead of the expected N-alkyliminodialane, which is probably due to the following disproportionation reaction:

$$H_2Al\text{–}N(C_2H_5)\text{–}AlH_2\cdot NR_3 \rightarrow AlH_3\cdot NR_3 + \frac{1}{n}(HAlNC_2H_5)_n \quad (5)$$

In an attempt to stabilize the possible intermediates, the more basic THF was used in this work instead of Et_2O.

Most of the work has been done with isopropylamine since this has the advantage of a rapid reaction with AlH_3, and that of giving as a final product, a pure cage structure having the formula $(HAlNi\text{–}Pr)_6$[1,2].

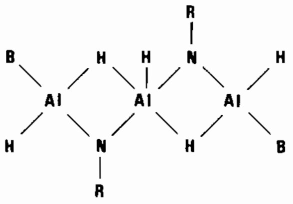
Reaction of Alanes with Isopropylamine

When AlH_3, synthesized by the method reported by Finholt *et al.*[6], is reacted with isopropylamine at a molar ratio 1:0.5 in THF, a mixture of products is obtained which contains the complex, N-isopropyliminodialane (II), expected from the reaction (6), together with bis(N-isopropylimino)trialane (III):

$$2\,AlH_3 + isoC_3H_7NH_2 \xrightarrow{THF} \underset{\text{(II)}}{H_2Al\text{–}N(isoC_3H_7)\text{–}AlH_2} + 2H_2 \quad (6)$$

Lamellar crystals precipitate as the reaction solution is concentrated.

The molecular weight and analytical data of these crystals are given in Table I and together with the two bands in the IR spectrum due to ν(Al–H), which indicate the presence of tetra and pentacoordinated aluminum atoms, are consistent with the suggested structure (III).

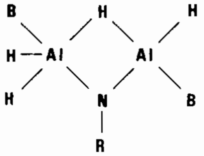


(III) R = isoC_3H_7, B = THF

No direct evidence in favour of (III) is available by ^1H NMR measurements in benzene, because THF exhibits strong signals in the same range of signals due to the hydrocarbon radicals bonded to nitrogen. However the spectrum excludes the presence of poly(N-isopropyliminoalane)[1], which would be a probable disproportionation product from (III). This disproportionation is also excluded by the X-ray powder pattern.

Another crystalline compound precipitates by further concentration and cooling of the reaction mixture.

Analytical and physical properties (Table I) suggest this compound is monomeric in accordance with the proposed structure (IV):

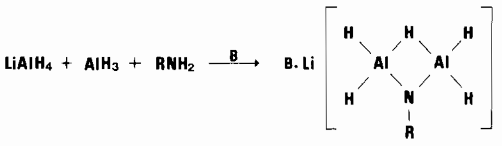


(IV)

R = isoC_3H_7, B = THF

Also in this case ^1H NMR data and X-ray powder pattern do not give evidence of formation of poly(N-isopropyliminoalane), therefore disproportionation reactions such as (3) and (5) can be excluded.

In order to test the generality of the reaction (6) the stabilization of further intermediates was attempted by using an excess of LiH as complexing agent



(7)

R = isoC_3H_7, B = THF (V)

Although crystals did not separate from this reaction mixture, the residue obtained by the evaporation of the solvent has been characterized. Analytical and physico-chemical properties (Table I) suggest the formation of monomeric lithium N-isopropyliminodialanate in accordance with the structure (V).

Starting from $AlH_3 \cdot NMe_3$, $LiAlH_4$ and iso$C_3H_7NH_2$, reaction (7) was attempted in diethyl ether–hexane solution, and complex (V) was not obtained indicating the influences of the solvent and/or the nature of aluminum hydride complex in the synthesis of these iminoalane compounds. In this case, from the reaction mixture, crystals of a complex of poly(N-isopropyliminoalane) with LiH and Et_2O were isolated with a composition corresponding to (VI):

$$H\text{–}(HAlNR)_5\text{–}AlH_2 \cdot LiH \cdot 2Et_2O$$
(VI)

In order to follow the reaction between the alanes and iso$C_3H_7NH_2$ in THF from a conductimetric point of view, the reaction was carried out in a conductimetric cell, equipped with an apparatus for the measurement

TABLE I. Analytical and Physico–Chemical Data of N-Alkyliminoalanes.

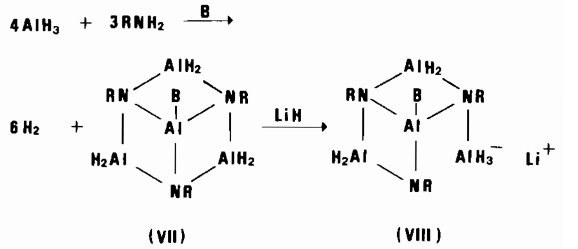
Ref.[a]	Compound	Analysis found (calcd.)				Mol. wt.[b] found (calcd.)	IR bands (cm^{-1})[c] ν(Al–H)
		Al%	Li%	N%	H_{active}/Al		
(III)	$C_{14}H_{35}Al_3N_2O_2$	22.76	–	8.08	1.64	375	1805, 1660
		(23.49)	–	(8.14)	(1.66)	(344.35)	
(IV)	$C_{11}H_{27}Al_2NO_2$	21.74	–	5.48	1.98	260	1795, 1655
		(20.80)	–	(5.39)	(2.00)	(259.26)	
(V)	$C_7H_{20}Al_2LiNO$	28.67	4.01	7.28	2.45	197	1690, 1800÷1750
		(27.64)	(3.56)	(7.17)	(2.50)	(195.11)	shoulder
(VI)	$C_{23}H_{64}Al_6LiN_5O_2$	26.14	1.16	11.57	1.33	n.d.	1835, 1770, 1700
		(26.46)	(1.13)	(11.45)	(1.50)		
(VIII)	$C_{16}H_{42}Al_4LiN_3O$	28.10	1.86	9.96	1.78	420	1800[d]
		(26.49)	(1.70)	(10.32)	(1.75)	(407.38)	

[a] Reference is made to the compounds in the text. [b] Measured ebullioscopically in THF soln. [c] Measured in nujol mulls. [d] Measured in THF soln.

of the hydrogen evolution. An excess of amine with respect to stoichiometric alane was used and its addition was performed slowly in order to approach the equilibrium curve. The conductimetric plots of the reaction between AlH_3 and $isoC_3H_7NH_2$, and of a mixture of $LiAlH_4$–AlH_3 with the same amine, are reported in Fig. 1. From these plots, it should be noted that the conductimetric curves show inflections corresponding to a molar ratio H_2/Al (where H_2 indicates the evolved H_2) at *ca.* 1. A ratio of H_2/Al equal to 1 corresponds to the formation of the products of the reactions (6) and (7) respectively. The higher conductivities observed for the reaction of the $LiAlH_4$–AlH_3 can be attributed to the enhancement of dissociated species due to the increased concentration of LiH complexes. Also in the other reaction, in which AlH_3 obtained by the Finholt method[6] is used, the presence of a small amount of complexed LiH has been confirmed[7]. In the complete absence of LiH, it was not possible to observe any significant change of conductivity greater than the very low value of $\varkappa$ equals *ca.* 10^{-5} Ω^{-1} cm^{-1}.

Reaction of Alanes with Linear Amines

In the case of linear amines, *i.e.* of ethyl or n-butylamine, the conductivity trend of the reactions is rather different (Fig. 2), showing a maximum at H_2/Al at *ca.* 1.5. This maximum can be connected with the formation of (VII) whose dissociation is promoted by the presence of LiH, with the already mentioned effect of increasing the conductivity. The same reaction, per-



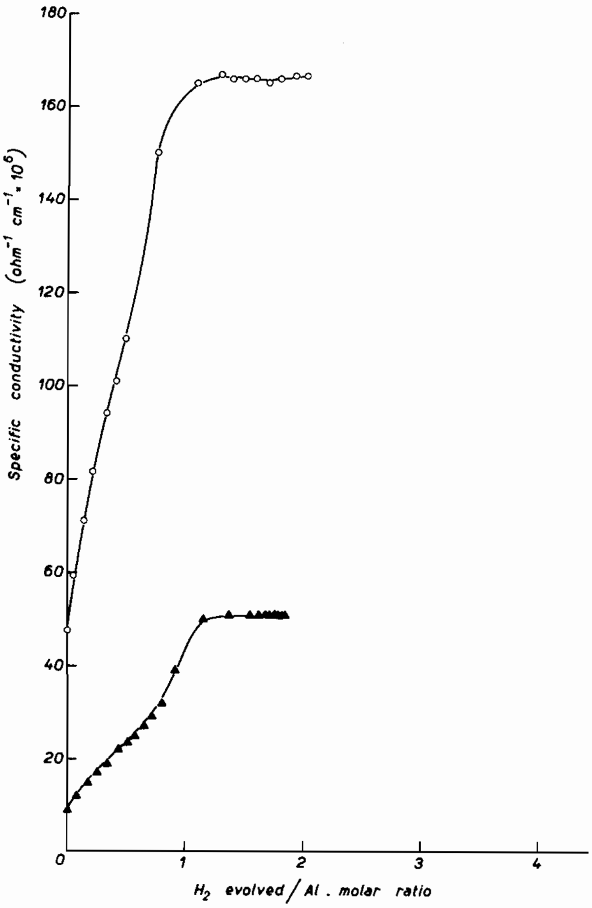


Figure 1. Conductivity curves observed in the reaction of alanes with $isoC_3H_7NH_2$ in THF solution; ▲ AlH_3; ○ $LiAlH_4$–AlH_3 (Li/Al = 0.5). Reaction conditions: a 5 *M* solution of amine was added to an 0.06 *M* solution with respect to aluminum at 20° C; the addition rate was 0.25 ml/10 min.

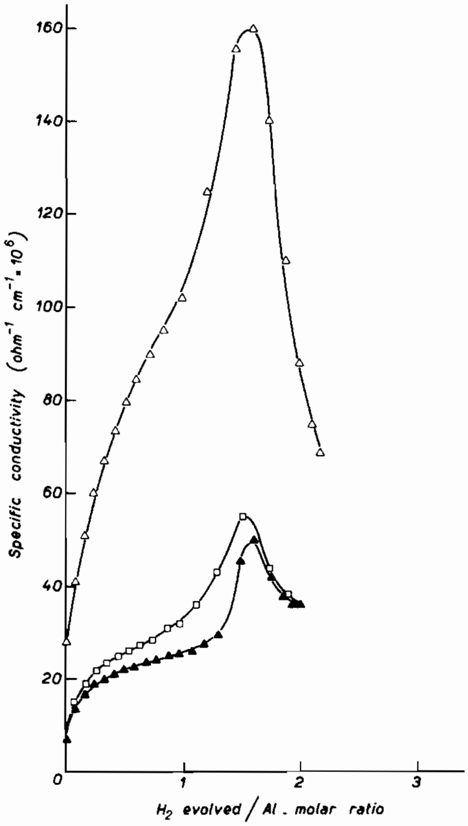


Figure 2. Conductivity curves observed in the reaction of alanes with $C_2H_5NH_2$ or n-$C_4H_9NH_2$ in THF solution; □ AlH_3, $C_2H_5NH_2$- ▲ AlH_3, n-$C_4H_9NH_2$; △ $LiAlH_4$–AlH_3 (Li/Al = 0.25), n-$C_4H_9NH_2$. Reaction conditions: a 5 *M* solution of amine was added to a 0.06 *M* solution with respect to aluminum at 20° C; the addition rate was 0.25 ml/10 min.

formed in presence of $LiAlH_4$ using stoichiometric quantity corresponding to the compound (VIII), *i.e.* with a ratio $LiAlH_4$: AlH_3: n-$C_4H_9NH_2$ = 1:3:3 gave a compound for which chemical and physical data are reported in Table I. These data are in agreement with the formation of lithium aluminum tris(N-n-butyliminoalanate) (VIII). The IR spectrum excludes the presence of soluted, unreacted $LiAlH_4$. Further an agree has been found with the data obtained in attempts to synthesize (VIII) by different methods[3].

Experimental

Reagents and Solvents

Lithium hydride (Degussa) and aluminum trichloride (Kuhlman) were used throughout. AlH_3 and $LiAlH_4$ were prepared in diethylether by the method reported by Finholt *et al.*[6]. For their solutions in THF, the diethyl ether was removed *in vacuo* and the residue redissolved in THF; the solvent was again removed and further THF was added. Commercially pure grade amines were dried and distilled from Na. All solvents were purified and dried by the known methods and all operations were carried out under an argon atmosphere.

Conductivity Measurements

For the protection of the reaction solutions against traces of moisture, the hydrogen evolution and the conductivity measurements were carried out using the equipment described in Figure 3. The reactions were carried out by dropping the amine solution from the burette into the stirred solutions of AlH_3 or $LiAlH_4$ –AlH_3 mixtures, after equilibrating the equipment at room pressure. The hydrogen evolved was measured by means of the displacement of an equal volume of water previously saturated with hydrogen. During the experiments, the temperature was maintained constant by means of thermostated liquid circulated around all the equipment components. The conductivities were measured on a Wissenschaftlich–Technische Werkstätten Model LF 39; the cell employed was AMEL model 131/10 with a constant *ca.* 0.1 cm^{-1}, the exact value was measured every time from the measured conductivity of a 0.01 *N* solution of KCl in water. In all experiments, precipitate formation was not observed.

Owing to the low values of conductivity and to the absence of correction for dilution caused by addition of small quantities of amine solution the conductivity values have no absolute significance. However, reproducible results were found within ± 10% range.

A decrease of the addition rate of the amine solution, (0.25 ml/25 min), with respect to the experiments described in Figure 1, did not influence the shape of the curve reported. Therefore, it is reasonable to assume that the experimental curve approaches the equilibrium curve.

Chemical Analyses and Physico–chemical measurements

Chemical analyses were carried out on solutions obtained by decomposition of weighted samples with

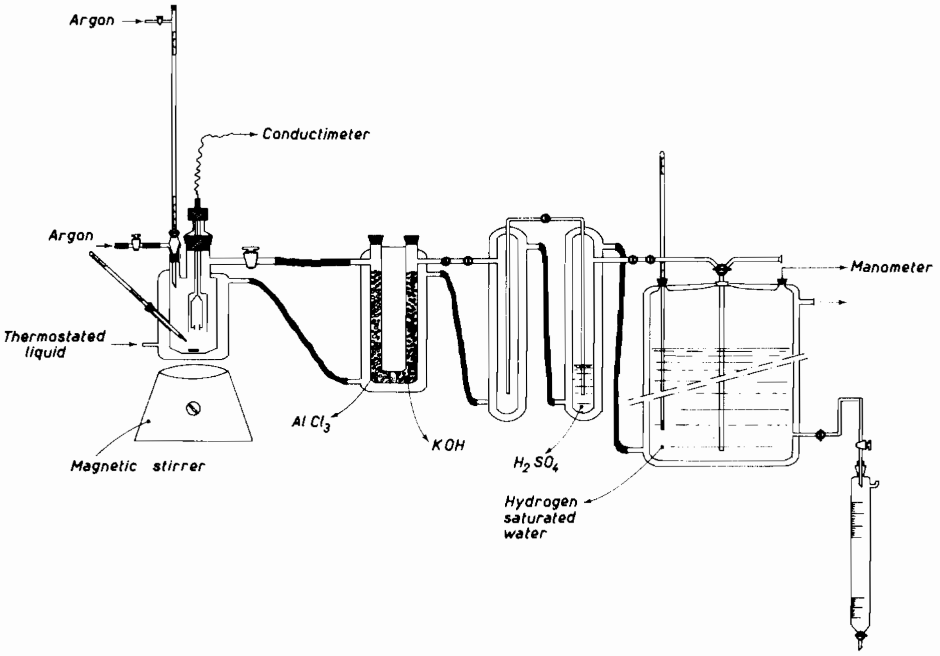


Figure 3. Apparatus used for the measurements of the hydrogen evolution and the conductivity changes.

dilute aqueous acid. The aluminum content was evaluated by the EDTA/$ZnSO_4$ method and the Kjeldahl method was used for nitrogen. IR spectra were recorded on a Perkin–Elmer Model 225 instrument.

Synthesis of bis(N-isopropylimino)trialane and N-isopropyliminodialane

A soln. of iso$C_3H_7NH_2$ (53.5 mmol) in THF (50 ml) was added dropwise to a stirred soln. of AlH_3 (107 mmol) in THF (200 ml). The reaction mixture was stirred for 18 h at room temp. The soln. was then concentrated to 200 ml and cooled to –5° C. The separation of lamellar crystals was observed after *ca.* 60 h. These were separated by filtration, washed with cooled THF, and dried *in vacuo* (room temp., 16 h, 10^{-1} mmHg) (Yield: 4.8 g). Analytical and physico–chemical data are given in Table I.

The soln., from which these crystals had been separated, was concentrated to *ca.* 50 ml and cooled to –5° C whereupon further crystals were formed, which after 24 h were separated, washed with cooled THF, and dried *in vacuo* (room temp., 16 h, 10^{-1} mmHg) (Yield 3.8 g).

Synthesis of Lithium N-isopropyliminodialanate

A soln. of iso$C_3H_7NH_2$ (75 mmol) in THF (60 ml) was added dropwise to a stirred soln. of AlH_3 (75 mmol) and $LiAlH_4$ (75 mmol) dissolved in THF (200 ml). The reaction mixture was stirred for 5 h at room temp.

An attempt to separate crystals of the reaction product by concentration and cooling at –10° C failed. The concentrated soln. was then filtered to eliminate traces of an insoluble material and evaporated to dryness, *in vacuo.*

The product is readily soluble in boiling diethyl ether; it is sparingly soluble in benzene or hexane at room temp.

By prolonged benzene extraction (24 h) at room temp. two fractions of different composition: soluble fraction (Al, 24.73; Li, 1.6; N, 8.34%); insoluble fraction (Al, 34.51; Li, 7.15; N, 4.88%), were separated which indicate a disproportionation reaction under these conditions.

Synthesis of $H\text{–}(HAlNisoC_3H_7)_5\text{–}AlH_2 \cdot LiH \cdot 2O(C_2H_5)_2$

A soln. of iso$C_3H_7NH_2$ (100 mmol) in diethyl ether–hexane (250 ml) was added to a stirred suspension of $LiAlH_4$ (100 mmol) and $AlH_3 \cdot NMe_3$ (100 mmol) in diethyl ether (250 ml) – hexane (100 ml) at reflux temperature. This mixture was allowed to react for 3 h, and then filtered from an insoluble product, which resulted to be essentially $LiAlH_4$.

After cooling to –10° C, two layers in the concentrated solution were formed which were readily separable. The lower fraction separated prismatic crystals on standing at –10° C, which were collected and dried *in vacuo.*

The X-ray crystal structure was defined for the complex $H\text{–}(HAlNisoC_3H_7)_5\text{–}AlH_2LiH \cdot Et_2O$ obtained by a different method[8].

Synthesis of Lithium Aluminum tris(N-n-butyliminoalanate)

A soln. of n-$C_4H_9NH_2$ (90 mmol) in THF (100 ml) was added dropwise to a stirred soln. of AlH_3 (90 mmol) and $LiAlH_4$ (30 mmol) dissolved in THF (200 ml). The reaction mixture was stirred for 5 h at room temp. Attempts to separate crystals by concentration and cooling to low temperature were unsuccessful; the reaction solution was then filtered to remove traces of an insoluble material and evaporated to dryness *in vacuo* (10 h, room temp., 10^{-2} mmHg).

At room temp., the product is sparingly soluble in diethylether and benzene, and practically insoluble in hexane.

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