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THE CHEMISTRY AND THE STEREOCHEMISTRY OF POLY(*N*-ALKYLIMINOALANES)

VI. A NOVEL SYNTHESIS OF POLY(*N*-ALKYLIMINOALANES) BY REACTION OF ALKALI METAL ALANATES WITH PRIMARY AMINES

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Summary

A novel synthesis of poly(*N*-alkyliminoalanes) (PIA) is reported. This involves the reaction in hydrocarbon solvents of $LiAlH_4$ or $NaAlH_4$ with primary amines having a nitrogen with α- or β- secondary carbon atoms or with tert-butylamine. Complexes of iminoalanes with alkali metal hydrides are obtained from linear amines. The same reaction carried out in polar solvents always gives complexes of PIA with LiH or NaH and the solvent. This new synthesis is simpler and convenient for producing soluble and well characterized PIA, some of which are not obtainable by other methods.

Introduction

Several routes for the syntheses of poly(*N*-alkyliminoalanes) (PIA) are known which involve the reaction of aluminum hydride with primary amines [1,2], nitriles, ethylenimine or of $LiAlH_4$ with amine hydrochloride [2]. Aluminum alkylamides [3] can be used satisfactorily with $LiAlH_4$ or with complexes of AlH_3 with Lewis bases for synthesis of PIA.

More recently, a detailed structural characterization carried out in our laboratories on the products obtained from different routes has shown that PIA are oligomers derived from the combination of —AlHNR— units forming three-dimensional cages with four or six membered rings [4,5]. The structure of the PIA is influenced not only by the nature of the amine employed, but also by the method of synthesis. In view of this, the reactions of sodium or lithium alanates with primary amines have been investigated as a simpler route to PIA. This paper describes these new routes, and shows how the

TABLE 1

THE REACTION OF $NaAlH_4$ WITH PRIMARY AMINES IN HYDROCARBON MEDIA[a]

Example	Amine	Solvent	Reaction time (h)	Product[b]		Chemical composition found (calcd.)				Mol. wt.[d]	n in $(HAlNR)_n$	X-ray analysis[e]	ν(Al—H) (cm^{-1})[f]	Physico-chemical data suggest·
				Nature	%	Al (%)	N (%)	Na (%)	$H_{act.}$[c]					
1/1	$C_2H_5NH_2$	Benzene	95	I	100	27.03	12.83	24.71	23.90			A		
1/2	n-$C_3H_7NH_2$	Benzene	100	I	100	24.25	12.35	19.19	20.02			A		
1/3	iso-$C_3H_7NH_2$	Benzene	35	S	93	29.81 (31.71)	16.10 (16.46)	0.31	11.21 (11.75)	455	5.3	XX	1850	hexamer
1/4	iso-$C_3H_7NH_2$	Heptane	50	S	85	31.05 (31.71)	16.38 (16.46)	0.06	11.41 (11.75)			XX	1850	hexamer
1/5	n-$C_4H_9NH_2$	Benzene	40	I	100	22.00	10.51	15.50	17.53			A		
1/6	sec-$C_4H_9NH_2$	Benzene	80	S	95	26.01 (27.22)	13.35 (14.13)	0.27	10.00 (10.09)	573	5.8	XX	1850	essentially hexamer and products with higher mol. wt.
1/7[g]	iso-$C_4H_9NH_2$	Benzene	150	S	40	23.90 (27.22)	13.15 (14.13)	1.35	8.45 (10.09)			XX	1850	predominately hexamer
1/8	tert-$C_4H_9NH_2$	Benzene	100	S	80	26.20 (27.22)	13.55 (14.13)		9.52 (10.09)	382	3.8	XX	1850	tetramer
1/9	$C_6H_{11}NH_2$	Benzene	140	S	45	20.31 (21.56)	10.35 (11.19)	0.56	7.44 (7.99)	675	5.4	XX	1850	predominately hexamer

[a] Usually 110 mmol of $NaAlH_4$ were treated with 105 mmol of amine in 150 ml of solvent. For the linear amines a stoichiometric amount of amine with respect to $NaAlH_4$ was used. [b] I = insoluble; S = soluble. The yield is calculated with respect to the initial amine. [c] $H_{act.}$ = hydridic hydrogen content indicated as meq/g. The calcd. values are referred to $(HAlNR)_n$. [d] By ebulliometry in diethyl ether. [e] As shown by the X-ray powder pattern, with reference to the formation of imino derivatives. A = amorphous, XX = crystalline. [f] In nujol mull. [g] An excess of $NaAlH_4$ was added during the reaction

structures of the PIA depend on the nature of the amine, the type of alanate, and the solvent used. The advantages of a synthesis according to eqn. 1 over the conventional methods based on the AlH_3-H_2NR or $LiAlH_4-H_2NR \cdot HCl$ reactions are clear. Moreover, taking into account that the metal hydride is completely recovered from reaction 1, and can be employed again for the synthesis of $MAlH_4$ [6] (reaction 2), the combination of the two reactions corresponds to a direct synthesis of PIA (reaction 3).

$$MAlH_4 + RNH_2 \rightarrow \frac{1}{n}(HAlNR)_n + MH + 2H_2 \qquad (1)$$

$$MH + Al + \frac{3}{2}H_2 \rightarrow MAlH_4 \qquad (2)$$

$$Al + RNH_2 \rightarrow \frac{1}{n}(HAlNR)_n + \frac{1}{2}H_2 \qquad (3)$$

Research work is now in progress in our laboratories on this direct method.

Results and discussion

The reaction between lithium or sodium alanate and primary amines leads to soluble PIA or to insoluble complexes of PIA with alkali metal hydrides, depending on the nature of the amine and the solvent.

$$\begin{tikzcd} & \frac{1}{n}(HAlNR)_n + MH + 2H_2 \quad (1a) \\ & (I) \\ MAlH_4 + RNH_2 \arrow[uur] \arrow[dr] & \\ & \frac{1}{n}(HAlNR)_n \cdot (MH)_x + 2H_2 \quad (1b) \\ & (II) \end{tikzcd}$$

The addition of the amine to the stirred suspension of the alanate usually causes a vigorous reaction with hydrogen evolution at room temperature; the reaction is completed at higher temperature, the necessary reaction time varying with the amine employed. An excess of alanate is necessary in some cases.

The soluble products of type I were easily identified [4] by means of ^1H NMR, mass spectrometry and X-ray analysis. The products II obtained from reaction 1b cannot always be satisfactorily characterized by physico-chemical techniques because of their low volatility and insolubility in hydrocarbon solvents. On the basis of their chemical analyses, they are suggested to be complexes of PIA with the alkali metal hydride.

The dependence of the nature of the products on the nature of the amine, of the alkali metal alanate and of the solvent is considered in detail below.

The influence of the amine

The nature of the hydrocarbon radical of the amine was recently shown to affect the structure of PIA obtained from $AlH_3 \cdot NR_3$ or $AlH_3 \cdot THF$ with primary amines [4,7]. Such a dependence is also found in the reactions starting from $NaAlH_4$ and various amines in hydrocarbon medium; in particular (see Table 1):

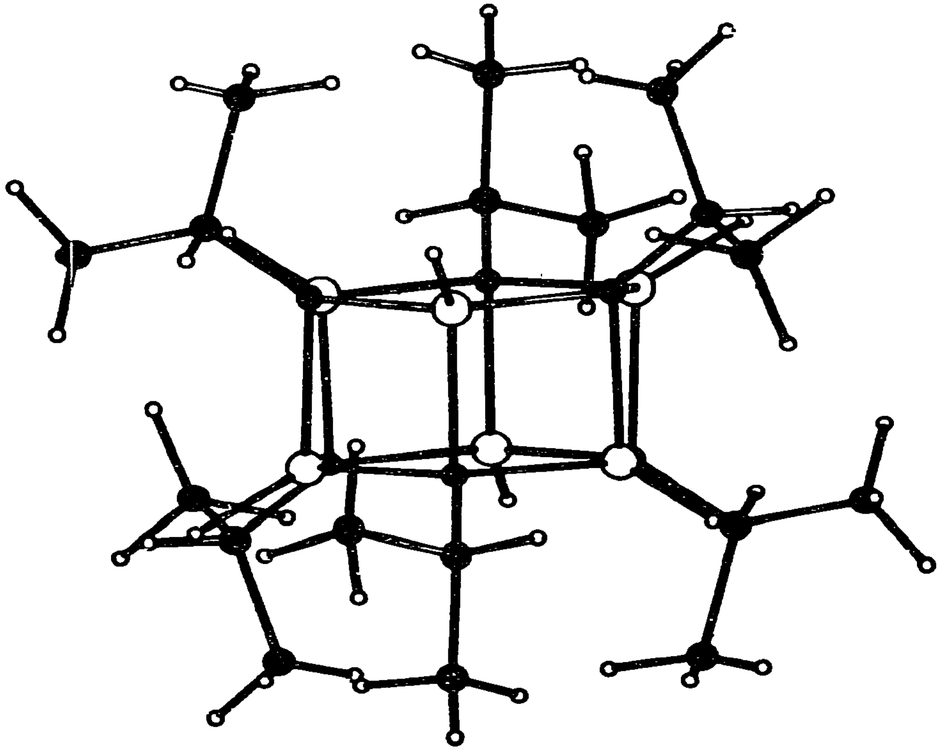
(i) Soluble PIA (eqn. 1a) are obtained from amines bearing an α- or β-secondary carbon atom on the nitrogen atom e.g. iso-$C_3H_7NH_2$, sec-$C_4H_9NH_2$,

$C_6H_{11}NH_2$, iso-$C_4H_9NH_2$ or a tertiary carbon atom in an α position, such as tert-$C_4H_9NH_2$.

In the reactions with complexes of AlH_3 with organic bases [4,7] amines containing a nitrogen with α- or β-secondary carbon atoms give hexakis(*N*-alkyliminoalanes), and tert-butylamine gives tetrakis(*N*-tert-butyliminoalane).

(ii) Insoluble products (eqn. 1b) are obtained from amines having —CH_2— groups α or β to the nitrogen, e.g. $C_2H_5NH_2$, n-$C_3H_7NH_2$, n-$C_4H_9NH_2$. In the reactions with AlH_3 complexes [4,7] these amines give a mixture of PIA oligomers.

When iso-$C_3H_7NH_2$ is treated with $NaAlH_4$ in benzene a quantitative yield of hexa-(*N*-isopropyliminoalane), (HAlN-iso-C_3H_7)$_6$ is obtained, the product has the characteristic cage structure (III) previously reported [5]. The same reaction carried out in n-heptane gives a PIA which has a slightly different crystalline structure, now under investigation, but its ^1H NMR spectrum is similar to that already reported [4].



(III)

PIA hexamers are also formed from sec-$C_4H_9NH_2$ and iso-$C_4H_9NH_2$ in quantitative yield. $C_6H_{11}NH_2$ also gives soluble ($HAlNC_6H_{11}$)$_6$; its yield is lower because of the low solubility of this compound in both diethyl ether [4] and hydrocarbon solvents.

For (HAlN-sec-C_4H_9)$_6$ and (HAlN-iso-C_4H_9)$_6$, the X-ray powder pattern shows the same structural features as the compounds obtained from $AlH_3 \cdot NR_3$ and amine [4]; some different features were found for ($HAlNC_6H_{11}$)$_6$.

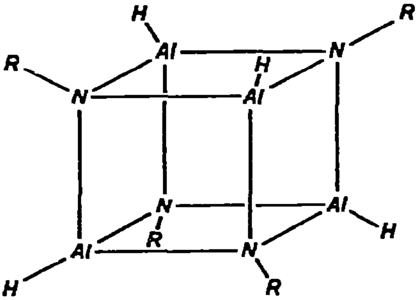
The reaction between $NaAlH_4$ and tert-$C_4H_9NH_2$ gives a closed tetramer (HAlN-tert-C_4H_9)$_4$ for which a cubic structure has been previously suggested [4]. Linear primary amines such as $C_2H_5NH_2$, n-$C_3H_7NH_2$ and n-$C_4H_9NH_2$ in non polar solvents always give a quantitative yield of insoluble products. On the basis of the experimental information available at present, the formation of complexes of imino derivatives with NaH (eqn. 1b) is suggested. The presence of $NaAlH_4$ or Na_3AlH_6, evidenced by X-ray powder analysis, also suggests the presence of derivatives with three aluminum—nitrogen bonds.

The influence of alkali metal hydride

The use of $LiAlH_4$ instead of $NaAlH_4$ (Table 2) leads to considerable structural modifications for the PIA obtained in hydrocarbon media from amines having a nitrogen with a secondary α-C atom.

From iso-$C_3H_7NH_2$, sec-$C_4H_9NH_2$ and $C_6H_{11}NH_2$ the tetrakis(*N*-alkyliminoalane) is formed along with hexakis(*N*-alkyliminoalane). The formation of these novel tetramers has been demonstrated by mass spectrometry, which shows the presence of abundant ions at *m/e* 325, $[M-CH_3]^+$, for (HAlN-iso-C_3H_7)$_4$; at *m/e* 367, $[M-Et]^+$, for (HAlN-sec-C_4H_9); and at *m/e* 500, M^+, for (HAlNC_6H_{11})$_4$.

The ^1H NMR spectrum in benzene of the PIA from $LiAlH_4$ and iso-C_3H_7-NH_2 shows, besides the typical doublet (τ 8.49) and septet (τ 6.29) assigned to (HAlN-iso-C_3H_7)$_6$ [4], a new doublet at τ 8.68 and a new septet at τ 6.70. These new signals are due to the equivalent CH_3 and CH protons of (HAlN-iso-C_3H_7)$_4$, and indicate that this compound has a symmetrical structure. The formation of a cubic structure (IV) is very probable, as was previously shown for (HAlN-tert-C_4H_9)$_4$ [4]. The ^1H NMR spectrum also indicates that the molar ratio hexamer/tetramer in the product is ca. 2/1. The isolation of pure crystals of the tetramer was achieved by sublimation at 3 10^{-3} Torr at room temperature. The determination of the molecular structure by X-ray diffraction on a single crystal is now in progress.



(IV)

In the product from $LiAlH_4$ and sec-$C_4H_9NH_2$, the ^1H NMR shows the known signals of (HAlN-sec-C_4H_9)$_6$ (a triplet due to the CH_3 γ to nitrogen at τ 9.04, a doublet due to the CH_3 β to the nitrogen at τ 8.40, and two multiplets at τ 8.06 and τ 6.54 due to the CH_2 and CH groups respectively) and other signals assignable to equivalent hydrocarbon radicals of (HAlN-sec-C_4H_9)$_4$, i.e., a doublet at τ 8.63 (due to CH_3 β to the nitrogen), a multiplet at τ 8.27 (CH_2 protons), and a multiplet at τ 6.88 (CH protons). The resonance due to the CH_3

TABLE 2

THE REACTION OF $LiAlH_4$ WITH PRIMARY AMINES IN HYDROCARBON MEDIA[a]

Example	Amine	Solvent	Reaction time (h)	Product[b]		Chemical composition found (calcd.)				Mol. wt.[d]	n in $(HAlNR)_n$	X-ray analysis[e]	ν(Al—H) (cm^{-1})[f]	Physico-chemical data suggest:
				Nature	%	Al (%)	N (%)	Li (%)	$H_{act.}$[c]					
2/1	$C_2H_5NH_2$	Benzene	80	I	100	28.01	14.75	7.48	20.71			XX		
2/2	n-$C_3H_7NH_2$	Benzene	90	I	100	26.35	14.10	7.38	20.30			A		
2/3	iso-$C_3H_7NH_2$	Benzene	18	S	97	30.10	16.17	0.001	12.95	400	4.7	XX	1850	tetramer, hexamer
						(31.71)	(16.46)		(11.75)[g]					
2/4	iso-C_3H_7NH-	Heptane	25	S	97	30.52	16.17	0.003	12.03			XX	1850	tetramer, hexamer
						(31.71)	(16.46)		(11.75)[g]					
2/5	n-$C_4H_9NH_2$	Benzene	45	S	61	24.30	12.75	1.41	9.60	1045		A	1820-	hexamer, heptamer,
						(26.69)	(13.85)	(1.71)	(12.36)[h]				1850	octamer and products
													1600-	with higher
													1700	mol. wt.
2/6	sec-$C_4H_9NH_2$	Benzene	75	S	96	26.51	13.41	0.20	10.15				1850	essentially hexamer,
						(27.22)	(14.13)		(10.09)[g]					tetramer, products
														with higher mol. wt.
2/7[i]	iso-$C_4H_9NH_2$	Benzene	100	S	80	27.15	13.79	0.28	10.35	652	6.6	XX	1850	predominately hexamer
						(27.22)	(14.13)		(10.09)[g]					hexamer
2/8	tert-$C_4H_9NH_2$	Benzene	90	S	85	26.65	13.60	0.25	10.35			XX	1850	tetramer
						(27.22)	(14.13)		(10.09)[g]					
2/9	$C_6H_{11}NH_2$	Benzene	90	S	48	20.60	10.27	0.20	7.95	510	4.1	XX	1850	tetramer, hexamer
						(21.56)	(11.19)		(7.99)[g]					
2/10	$C_6H_5NH_2$	Benzene	40	I	100	21.21	11.42	5.50	15.85			A		
						(21.22)	(11.03)	(5.47)	(15.75)[j]					

[a] Usually 110 mmol of $LiAlH_4$ were treated with 105 mmol of amine in 150 ml of solvent. For the linear amines a stoichiometric amount of amine with respect to $LiAlH_4$ was used. [b] I = insoluble; S = soluble. The yield is calculated with respect to the initial amine. [c] $H_{act.}$ = hydridic hydrogen content indicated as meq/g. [d] By ebulliometry in diethyl ether. [e] As shown by the powder X-ray pattern, with reference to the formation of imino derivatives. A = amorphous, XX = crystalline. [f] In nujol mull. [g] Calcd. for $(HAlNR)_n$. [h] Calcd. for $1/n(HAlNR)_n \cdot 0.25\,LiH$. [i] During the reaction an excess of $LiAlH_4$ was added. [j] Calcd. for $1/n(HAlNPh)_n \cdot LiH$.

γ to the nitrogen is not influenced by the structural modification of the PIA; the corresponding signal occurs at τ 9.04 for the tetramer also. In this case a cubic structure (IV) is also very probable. It has not been possible to separate pure tetramer from the reaction product by sublimation or by crystallization; on crystallization in diethyl ether, pure crystals of hexamer are the first to separate.

Because of the broad signals in its ^{1}H NMR spectrum [4], no detailed discussion is possible for the PIA obtained from $C_6H_{11}NH_2$. In this case pure crystals of $(HAlNC_6H_{11})_4$ have been separated by crystallization in benzene from its mixture with hexamer.

As far as the reaction of $LiAlH_4$ with linear amines is concerned, insoluble imino derivatives have also been obtained from $C_2H_5NH_2$ and n-$C_3H_7NH_2$. However, the product from n-$C_4H_9NH_2$ is soluble. The physical evidence is in favour of the formation of complexes of poly(*N*-n-butyliminoalane) with LiH. The mass spectrum exhibits the typical fragments of a mixture of oligomers of the corresponding PIA [4], probably derived from decomposition of these complexes. The formation of PIA species is also indicated by the ^{1}H NMR spectrum.

Finally, $LiAlH_4$ reacts with aniline to give an insoluble product for which the formula $\frac{1}{n}(HAlNPh)_n \cdot LiH$ is suggested in view of the increased acidity of the aluminum resulting from the electron withdrawal by the aniline group.

Reactions in polar solvents

With diethyl ether or tetrahydrofuran as the reaction medium, the course of the reaction between alkali metal alanate and a primary amine is more complex (Table 3). For example, the reaction between $LiAlH_4$ and iso-$C_3H_7NH_2$ in diethyl ether gives a mixture of soluble PIA consisting of tetramer, hexamer, traces of heptamer and some products of higher molecular weight whose chemical analyses show them to contain complexed LiH and $(C_2H_5)_2O$. Mass spectrometry shows the presence of ions corresponding to the heptamer at *m/e* 580, $[M{-}CH_3]^+$, together with ions characteristic of tetramer and hexamer [4]. These ions would arise from thermal decomposition of the complexes.

For the soluble product obtained in the reaction between $NaAlH_4$ and iso-$C_3H_7NH_2$ in diethyl ether, there is some indication of the formation of a complex of hexameric PIA with NaH and $(C_2H_5)_2O$, and mass spectroscopic analysis shows the presence of a hexamer.

A complex of hexameric PIA with NaH and THF is also formed from $NaAlH_4$ and $C_6H_{11}NH_2$. Starting from linear primary amines, insoluble products are formed in diethyl ether, while soluble complexes are obtained in tetrahydrofuran. The low active hydrogen content in PIA obtained in THF may be due to the cleavage of C—O bonds of the solvent by the hydridic hydrogens.

Hypothesis on the reaction mechanism

The reaction between $LiAlH_4$ or $NaAlH_4$ and iso-$C_3H_7NH_2$ in hydrocarbon solvents has been studied in more detail. The results are shown in Table 4. The addition of the amine to a stirred suspension of $NaAlH_4$ at room temperature gives an insoluble product containing practically all the amine. The mass spectrum of this solid shows the formation of tetrameric and hexameric PIA, while X-ray powder analysis suggests the presence of unreacted $NaAlH_4$ and does not show the presence of crystalline PIA. We think it likely that the formation of

(continued on p. 266)

TABLE 3

THE REACTION OF $NaAlH_4$ OR $LiAlH_4$ WITH PRIMARY AMINES IN POLAR SOLVENTS[a]

Example	Amine	$MAlH_4$	Solvent	Reaction time (h)	Product[b]		Chemical composition found (calcd.)				Mol. wt.[d]	X-ray analysis[c]	$\nu(Al-H)$[f] (cm^{-1})	Mass spectrometry suggests:
					Nature	%	Al (%)	N (%)	M (%)	$H_{act.}$[c]				
3/1	$n-C_3H_7NH_2$	$NaAlH_4$	Et_2O	50	I	100	21.20	10.91	17.45	16.15		A		
3/2	$n-C_3H_7NH_2$	$NaAlH_4$	THF	20	I	8.5	0.20	3.75	52.20	26.51				
					S	91.5	25.12	12.85	6.60	8.86		A	1650-1750	
							(23.10)	(12.00)	(6.50)	(11.40)[g]				
3/3	$iso-C_3H_7NH_2$	$LiAlH_4$	Et_2O	5	S	80	28.10	15.00	2.01	15.21		A	1600-1850	essentially tetramer and hexamer, heptamer and products with higher mol. wt.
							(26.48)	(13.75)	(1.70)	(12.29)[h]				
3/4	$iso-C_3H_7NH_2$	$NaAlH_4$	Et_2O	35	S	88	26.72	14.20	4.08	12.75	637	XX	1850;	hexamer
							(25.77)	(13.38)	(4.39)	(11.46)[i]			1700-1770	
3/5	$n-C_4H_9NH_2$	$NaAlH_4$	THF	8	S	100	22.50	11.15	2.65	10.00	560	XX	1600-1800	
							(21.69)	(11.26)	(2.77)	(9.25)[k]				
3/6	$C_6H_{11}NH_2$	$NaAlH_4$	Et_2O	18	S	25	16.25	8.76	3.60	7.20		A		
							(18.02)	(9.36)	(3.84)	(8.35)[l]		A		
3/7	$C_6H_{11}NH_2$	$NaAlH_4$	THF	15	S	95	17.65	9.02	4.45	8.05		A	1050-1850	hexamer
							(18.08)	(9.39)	(3.85)	(8.38)[l]				

[a] In all cases 110 mmol of $MAlH_4$ were treated with a stoichiometric amount of amine in 150 ml of solvent. [b] I = insoluble; S = soluble. [c] $H_{act.}$ = hydridic hydrogen content indicated as meq/g; [d] By ebulliometry in diethyl ether. [c] As shown by the powder X-ray pattern with reference to the formation of imino derivatives. A = amorphous, XX = crystalline. [f] In nujol mull. [g] Calcd. for $1/n(HAlNR)_n \cdot 0.33NaH \cdot 0.33THF$. [h] Calcd. for $1/n(HAlNR)_n$. $0.25LiH \cdot 0.20Et_2O$. [i] Calcd. for $1/n(HAlNR)_n \cdot 0.20NaH \cdot 0.20Et_2O$. [k] Calcd. for $1/n(HAlNR)_n \cdot 0.15NaH \cdot 0.30THF$. [l] Calcd. for $1/n(HAlNR)_n$. $0.25NaH \cdot 0.25B$ ($B = Et_2O$; THF).

TABLE 4

CHEMICAL COMPOSITION OF INTERMEDIATE PRODUCTS IN THE REACTION OF $NaAlH_4$ OR $LiAlH_4$ WITH iso-$C_3H_7NH_2$ IN HYDROCARBON MEDIA

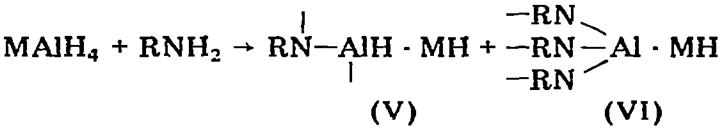
$MAlH_4$	Solvent	Temperature	Reaction time (h)	Soluble fraction			Insoluble fraction		
				N/Al	M/Al	$H_{act.}$/Al	N/Al	M/Al	$H_{act.}$/Al
$NaAlH_4$[b]	Benzene	Room temp.	3				0.81	0.99	2.50
		Boiling temp.	4[a]	1.48	0.10	0.61	0.07	2.70	4.50
		Boiling temp.	8[a]	1.41	0.05	0.76	0.09	2.80	4.75
		Boiling temp.	12[a]	1.35	0.05	0.87	0.15	2.96	4.59
		Boiling temp.	20[a]	1.23	0.05	0.95	0.21	3.60	5.98
		Boiling temp.	35[a]	1.03	0.03	1.05	0.42	6.2	7.90
$LiAlH_4$[c]	n-Heptane	Room temp.	3				0.82	1.08	2.59
		Boiling temp.	7[a]	1.07	0.03	1.17	0.85	8.1	9.65
		Boiling temp.	25[a]	1.02		1.08	0.22	6.7	8.6

[a] The time was calculated from the onset of boiling. [b] 355 mmol of amine were added to 365 mmol of $NaAlH_4$ in 250 ml of benzene. [c] 200 mmol of iso-$C_3H_7NH_2$ were added to an equimolar amount of $LiAlH_4$ in 250 ml of heptane.

the PIA revealed by mass spectrometry is due to a thermal decomposition of more complex products. On heating the reaction mixture to its boiling point, some compounds having an atomic ratio N/Al equal to ca. 1.5 go into solution; they contain only very small amount of sodium. The mass spectrum of this soluble species shows ions at *m/e* 338, 395, 452, 509 and 568 (i.e. at intervals of 57 mass units, involving loss of a NR radical) together with the typical ions of the hexameric PIA. These ions show the intermediate formation of a tetrameric compound $(\text{iso-}C_3H_7NH{-}AlN\text{-iso-}C_3H_7)_4$ (mol. wt. 568) probably with a structure of type IV in which hydridic hydrogens are substituted by NHR groups. The ^1H NMR spectrum of the reaction solution exhibits signals due to tetra- and hexakis(*N*-isopropyliminoalane) together with other unidentified signals. The presence of $NaAlH_4$ and of small amounts of Na_3AlH_6 in the insoluble species are suggested by X-ray analysis.

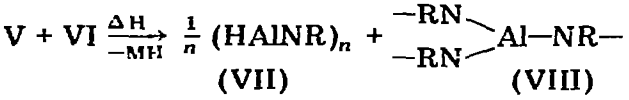
Physico-chemical measurements showed that as the reaction proceeds, there is progressive formation of the PIA hexamer (the molar ratio N/Al decreases in solution), and at the end of the reaction this is the sole product. The insoluble material becames gradually richer in NaH. Similar behaviour has been found for the reaction of $LiAlH_4$ and $\text{iso-}C_3H_7NH_2$, except that a mixture of tetramer and hexamer is the final product.

The following mechanism can be proposed: *1st step*



$$MAlH_4 + RNH_2 \rightarrow \underset{(V)}{\overset{|}{R N}-\underset{|}{Al}H \cdot MH} + \underset{(VI)}{\begin{matrix}-RN\\-RN\\-RN\end{matrix}\!\!>\!Al \cdot MH} \qquad (4)$$

In this step insoluble products, which are likely to be complexes of PIA and amide derivatives with MH, are formed. This step would be independent of the nature of the amine. *2nd step*



$$V + VI \xrightarrow[-MH]{\Delta H} \underset{(VII)}{\frac{1}{n}(HAlNR)_n} + \underset{(VIII)}{\begin{matrix}-RN\\-RN\end{matrix}\!\!>\!Al{-}NR{-}} \qquad (5)$$

In this step the complexes of type V and VI slowly decompose on heating with formation of soluble products, viz. PIA and compounds containing amido groups (VIII).

3rd step.

$$VIII + MAlH_4 \rightarrow MH + \frac{1}{n}(HAlNR)_n \qquad (6)$$

In this step the amide intermediates react with the remaining $MAlH_4$ giving soluble PIA. With linear primary amines the higher stability of the initial complexes with MH would prevent the final formation of free PIA.

Experimental

Reagents and solvents

Commercially pure $LiAlH_4$ and $NaAlH_4$ (both Metalgesellschaft) were used. Commercial samples of pure amines were dried by distillation from Na or KOH. All solvents were purified and dried by standard methods and all syntheses were carried out under nitrogen.

Chemical analyses and physico-chemical measurements

These measurements were carried as previously described [4].

Reaction conditions

Typical reactions are the following:

(a) Reaction between $LiAlH_4$ and iso-$C_3H_7NH_2$ in heptane. A solution of isopropylamine (105 mmol) in heptane (30 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (115 mmol) in heptane (120 ml), maintained at 0°. Hydrogen evolution took place immediately. The mixture was stirred at its boiling point and the N/Al atomic ratio in the solution was monitored. When this ratio reached a value of 1, the mixture was filtered and the filtrate evaporated to near dryness in vacuo at room temperature. The white solid residue was further dried (10 h, room temperature, 5 10^{-3} Torr) and analyzed (found: Al, 30.52; Li, 0.003; N, 16.17%; H_{active}/Al, 1.06.$(HAlNC_3H_7)_n$ calcd.: Al, 31.71; N, 16.46%; H_{active}/Al, 1). The yield was ca. 9 g. Additional information is reported in Table 2.

(b) Reaction between $NaAlH_4$ and iso-$C_3H_7NH_2$ in diethyl ether. A solution of isopropylamine (110 mmol) in diethyl ether (50 ml) was added slowly to a stirred suspension of $NaAlH_4$ (110 mmol) in diethyl ether (100 ml) maintained at -10°. The mixture was stirred at its boiling point until the atomic ratio N/Al in the solution was ca. 1. The mixture was then filtered and the filtrate was evaporated in vacuo. The white solid residue was dried (10 h, 5 10^{-3} Torr, room temperature) and analyzed (found: Al, 26.72; N, 14.20; Na, 4.08%; H_{active}/Al 1.29. $(HAlNC_3H_7) \cdot 0.2\ NaH \cdot 0.2\ (C_2H_5)_2O$ calcd.: Al, 25.91; N, 13.45; Na, 4.40%; H_{active}/Al 1.2). Further information is reported in Table 3.

(c) Reaction between $LiAlH_4$ and n-$C_3H_7NH_2$ in benzene. A solution of n-propylamine (105 mmol) in benzene (50 ml) was added dropwise to a suspension of $LiAlH_4$ (105 mmol) in benzene (100 ml) at 10°. The mixture was stirred at its boiling point for 80 h, after which nitrogen, aluminum and lithium were practically absent in the solution. The insoluble product was recovered by filtration, dried (10 h, 10^{-3} Torr, room temperature) and analyzed (found: Al, 26.35; Li, 7.38; N, 14.10%; H_{active}/Al, 2.07).

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