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REACTION OF ISOPROPYLIMINOALANE WITH ϵ-CAPROLACTAM AND TRIETHYLALUMINIUM IN AROMATIC HYDROCARBONS

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Summary

Isopropyliminoalane (IMA) reacts with ϵ-caprolactam (KL) in the same way as triethylaluminium, the ligands on the aluminium atom being successively replaced by caprolactam ligands. The reaction gives a quantitative amount of aluminium caprolactamate (AKL) even with a minimum excess of caprolactam. The dependence on composition of the molecular weights, IR spectra and ^1H NMR spectra of the intermediate products and AKL have been studied.

Introduction

Isopropyliminoalane (IMA), $(HAlN\text{-}i\text{-}C_3H_7)_6$, was prepared by Mazzei et al. [1] as an active polymerization cocatalyst, and those authors [2] have also determined its structure. IMA is reactive, and may be used as a reducing agent in organic chemistry [3] or as drying agent for organic solvents [4], and can be cheaply and easily prepared by direct synthesis [5]. It occurred to us that it might react with ϵ-caprolactam (KL) to give aluminium caprolactamate (AKL), which can be used for the synthesis of sodium tetracaprolactamatoaluminate, as initiator for anionic polymerization of lactams [6]. AKL was prepared previously by Komoni and Tani [7] from triethylaluminium and KL, but they did not isolate it nor study its properties, and so we have scanned more fully the reaction between triethylaluminium and KL.

Results and discussion

When IMA reacts with KL at room temperature the hydride hydrogen is first replaced by the caprolactam ligand and the $N\text{-}i\text{-}C_3H_7$ group is then replaced. The reaction gives AKL only at elevated temperatures, and elevated temperatures are also required for the final step of the reaction of triethylaluminium

TABLE 1

RESULTS OF THE REACTION OF IMA WITH KL

Compound	$R(1)$ [a]		Chemical composition (%)				$R(2)$ [b]			n [c]
	KL	IMA	Al	N(total)	N(amin)	H	Al	KL	N-i-C_3H_7	
I	0.51	1	19.61	13.63	10.39	0.36	1	0.54	1.02	
II	1.00	1	13.88	14.24	7.64	—	1	0.94	1.06	4.0
III	1.39	1	11.75	13.10	4.88	—	1	1.35	0.80	3.5
IV	1.98	1	10.00	12.26	2.87		1	1.81	0.55	3.0
V	2.47	1	8.37	10.32	1.30		1	2.38	0.30	2.7
VI	3.00	1	6.32	9.80	0.16		1	2.94	0.05	1.5

[a] $R(1)$ = molar ratio KL/IMA in reaction. [b] $R(2)$ = molar ratio Al/KL/N-i-C_3H_7 in product. [c] Degree of association as determined by cryoscopy in benzene (±0.15 in the concentration range 1.5—12 wt%).

TABLE 2

RESULTS OF REACTION OF $(C_2H_5)_3Al$ WITH KL

Compound	$R(1)$ [a]		Chemical composition (%)			$R(2)$ [b]			n [c]
	KL	$(C_2H_5)_3Al$	Al	N	Et	Al	KL	Et	
VII [d]	0.90	1	15.89	5.24	[e]	1	0.64	[e]	2.0
VIII	0.90	1	14.06	6.34	30.86	1	0.87	2.04	
IX	1.50	1	11.34	8.29	18.67	1	1.41	1.53	2.3
X	2.60	1	7.78	10.28	[e]	1	2.55	[e]	1.6
XI	3.10	1	7.11	11.16	0.0	1	3.03	0	1.5

[a] $R(1)$ = molar ratio KL/$(C_2H_5)_3Al$ in reaction. [b] $R(2)$ = molar ratio Al/KL/(C_2H_5) in product. [c] Degree of association as determined by cryoscopy in benzene

with KL. Tables 1 and 2 show the products obtained with various ratios of KL to IMA or $(C_2H_5)_3Al$.

From the dependence of the association degree of compounds I—VI (numbered as in Table 1) derived formally from AKL by means of replacing caprolactam ligand by isopropylimine groups, is evident that even the replacement of hydride hydrogen in IMA by a caprolactam ligand (II) destroys the hexameric cage which is the basic unit in the structure of IMA [2], and the product is approximately tetrameric. Also tetrameric, involving a cubic cage structure, are the compounds $(C_2H_5AlN\text{-}i\text{-}C_3H_7)_4$ and $(CH_3AlN\text{-}i\text{-}C_3H_7)_4$ prepared by treatment of $(C_2H_5)_3Al$ or $(CH_3)_3Al$ with $H_2N\text{-}i\text{-}C_3H_7$, though the reaction of IMA with $(CH_3)_3Al$ leads to hexameric $(CH_3AlN\text{-}i\text{-}C_3H_7)_6$ [8]. Further replacement of isopropylimine groups by lactam causes a further decrease in the degree of association, and finally there is an equilibrium between the monomer and dimer in the solution of AKL. In the case of the products of the reaction of $(C_2H_5)_3Al$ with KL, the degree of association does not change much. The molecular weight of AKL prepared in this way is practically the same as that prepared from IMA.

Table 3 lists absorption maxima bands of IR spectra in the range of stretching vibration of caprolactam ligand amide groups of $Al(KL)_x(N\text{-}i\text{-}C_3H_7)_{(3-x)/2}$ (I—VI), and includes for comparison the bands for $Al(KL)_x(C_2H_5)_{3-x}$ (VII—XI) in the same range. In both cases the band around 1560 cm^{-1} predominates at a relatively low value of x in the spectrum; the band around 1600 cm^{-1} predominates in the spectrum at x 1.5. In compounds VII—X we assume (cf. refs. 9—11) that in the presence of an ethyl group the bridge between two aluminium atoms is formed only by the caprolactam ligand. The band at 1580—1585 cm^{-1} in the compounds I—XI probably corresponds to the bridging caprolactam and that at approx. 1600 cm^{-1} to the terminal caprolactam.

Details of the ^1H NMR resonances from the caprolactam methylenes of products of the reaction of KL with IMA or $(C_2H_5)_3Al$ are shown in Table 4. When the ethyl group of dimeric triethylaluminium is gradually replaced by caprolac-

TABLE 3

IR ABSORPTION BANDS OF $Al(KL)_x(N\text{-}i\text{-}C_3H_7)_{(3-x)/2}$(II—VI) [a] AND $Al(KL)_x(C_2H_5)_{3-x}$ (VII—XI) [b] IN BENZENE IN THE RANGE 1500—1650 cm^{-1}

Compound	R [c]	ν(OCN)	
I [a, d]	0.45	1568s [e],	1586vs
II [a]	0.94	1568(sh) [e],	1580vs, 1598s
III [a]	1.35		1580s, 1603s
IV [a]	1.81		1578s, 1598vs, 1609(sh)
V [a]	2.28		1599vs, 1614s
VI [a]	3.00		1582(sh), 1598vs, 1612(sh)
VII [b]	0.64		1584vs
VIII [b]	0.84		1583vs
IX [b]	1.41		1579s, 1604m
X [b]	2.55		1575(sh), 1592s, 1609(sh)
XI [b]	3.03		1582(sh), 1597s, 1610(sh)

[a] Numbers as in Table 1. [b] Numbers as in Table 2. [c] R = molar ratio KL/Al. [d] I corresponds to formula $Al(KL)_{0.45}H_{0.55}(N\text{-}i\text{-}C_3H_7)$. [e] Band corresponding to $=N\text{-}i\text{-}C_3H_7$ group.

TABLE 4

^{1}H NMR SPECTRA OF BENZENE SOLUTIONS OF $Al(KL)_x(N\text{-}i\text{-}C_3H_7)_{(3-x)/2}$ (II—VI) [a] AND $Al(KL)_x(C_2H_5)_{3-x}$ (VII—XI) [b]

(Chemical shifts in ppm, δ-scale [c])

Compound	R [d]	ε-CH_2	α-CH_2	β-δ-CH_2 [e]
I [a, f]	0.45	3.27(bs) 3.57(bs) 3.37(bs)	2.12(bs)	1.15—1.65(m) 1.65—1.95(m)
II [a]	0.94	3.27(bs)	2.30(bs)	1.2—1.7(m)
III [a]	1.35	3.30(bs)	2.33(s)	1.25—1.65(m) 1.85(s)
IV [a]	1.81	3.35(bs) 3.17(bs)	2.36(s)	1.52(bs)
V [a]	2.28	3.34(s) 3.10(s)	2.38(s)	1.56(s) 1.44(s)
VI [a]	3.00	3.34(s) 3.10(s)	2.38(s)	1.56(s) 1.44(s)
VII [b]	0.64	2.74(s)	1.97(s)	1.0—1.45(m)
VIII [b]	0.84	2.79(bs) 3.17(bs) 2.96(bs)	2.02(bs)	1.0—1.7(m)
IX [b]	1.41	3.21(bs) 2.98(bs)	2.24(bs)	1.0—1.7(m)
X [b]	2.55	3.31(s) 3.10(s)	2.33(s)	1.51(bs) 1.43(bs)
XI [b]	3.03	3.33(s) 3.11(s)	2.36(s)	1.56(s) 1.45(s)
$HAlN\text{-}i\text{-}C_3H_7$ [g]		1.51(d); 3.71(sp); 5.57(s) [h]		
$Al(C_2H_5)_3$ [i]		1.11(t); 3.38(q) [j]		

[a] Numbers as in Table 1. [b] Numbers as in Table 2. [c] s singlet, bs broad singlet (line width > 15 Hz), d doublet, t triplet, q quartet, sp septet, m multiplet; the signals in each group are arranged in order of decreasing integral intensity. [d] R = molar ratio KL/Al. [e] The signals of $=NCH(CH_3)_2$ group are present in this region. [f] I corresponds to formula $Al(KL)_{0.45}H_{0.55}(N\text{-}i\text{-}C_3H_7)$. [g] Literature value [2]. [h] Signals due to CH_3, CH and Al—H protons, respectively. [i] Literature value [12]. [j] Signals due to CH_3 and CH_2 protons.

tam ligand, the ε-methylene group first shows up as a signal in the lowest field corresponding to the bridge arrangement Al—N⋯C⋯O—Al, and then as a new signal of the terminal ligand at higher fields, and this dominates in the case of AKL (XI). With compounds I—VI, both peaks of the bridge and terminal capro lactams correspond at higher KL/Al ratio (IV—VI). In compounds I—III, for which the degree of polymerization n is >3, the situation is complicated by the presence of more than one type Al—caprolactam bond. The α-methylene group in compounds I—XI gives only one singlet. The β-δ-methylene group in AKL and in compounds with a relatively high content of KL gives two peaks arising from the terminal and the bridge KL; a sharp multiplet, indicating a rigid arrangement, is present in this region in compounds with a low KL content (I, II, VII, VIII, IX).

It is clear that when caprolactam reacts with dimeric $(C_2H_5)_3Al$ or with hexameric IMA, either ethyl or hydrogen and isopropylamine ligands are successively replaced; in both cases identical samples of aluminium caprolactamate

are obtained, even though it is known that the structure of IMA can vary with the method of synthesis [2]. In the intermediate products, containing less than three KL per one Al atom, it is the caprolactam ligand which provides the bridge between two aluminium atoms.

The compound AKL exists in solution as a monomer and dimer in equilibrium. An eight-membered ring including the Al—N···C···O—Al linkage may be postulated for the dimer by analogy with the adducts formed between amides and isocyanates with alkylaluminium compounds of known structure [9—11]. In accord with this suggestion, in solutions in aromatic hydrocarbon the ϵ-methylene group gives rise to two distinctly separated proton resonances in a ratio of approximately 5/1, evidently corresponding to the terminal and bridge caprolactam ligand, and there is no coalescence even at 100° C. Non-coordinated C=O is either absent in AKL or it is present only to a small extent. The stretching band of free lactam (approx. at 1675 cm^{-1}) completely or almost completely disappears in AKL, and a new very strong band at approx. 1600 cm^{-1} with two shoulders dominates.

Experimental

All reactions and determinations of spectra and molecular weights were carried out under dry argon. Caprolactam was distilled in vacuo before use; isopropyliminoalane contained 96.5% of the theoretical amount of Al (Al/H/N = 1/1.002/1.008) and triethylaluminium after vacuum distillation contained 98.1% of the theoretical amount of Al. Solvents were dried over molcular sieves, and distilled from $NaAlH_2(OCH_2CH_2OCH_3)_2$ solution.

The IR spectra of 2% solutions of compounds I—XI were recorded on a Beckman IR 20 A spectrometer, and the ^1H NMR spectra at 100 MHz on a Varian XL-100-15. AKL was examined at normal temperatures in 5% solutions but at low temperatures in 1% solution since 5% solutions gave very broad signals because of the high viscosity. Tetramethylsilane was used as internal standard. Molecular weights were determined by ebulliometry and cryoscopy as described earlier [13].

Reaction of isopropyliminoalane with ϵ-caprolactam

To a solution of 0.5—0.8 g of IMA in 10 ml of benzene the appropriate amount of a 2.15 *M* benzene solution of KL (Table 1) was added dropwise with stirring during 15 min. When the evolution of hydrogen and of isopropylamine was complete at room temperature, the mixture was heated under reflux for 1 h and benzene was removed by distillation, initially at atmospheric pressure and then in vacuo. The final product was dried for 1 h at 80° C under a pressure of 10 Pa. In all cases a white solid was obtained. The analyses of the products are given in Table 1.

Reaction of triethylaluminium with ϵ-caprolactam

To a solution of 0.4—0.6 g of $(C_2H_2)_3Al$ (98.1%) in 5 ml of benzene the appropriate amount of a 2.15 *M* benzene solution of KL (Table 2) was added dropwise with cooling and stirring. Initially, ethane was vigorously evolved, but later this evolution slowed down even from a hot solution. The reaction was

completed by 2 h heating under reflux. The mixture was then evaporated to dryness to give material for analysis (Table 2), and the solid or liquid residue was stored for 2 h at room temperature at 10 Pa. The product numbered VII was isolated by distillation at 98—120°C at 40 Pa. The analyses for the distilled sample VII and the dried samples VIII—XI are shown in Table 2.

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