

INSERTION REACTIONS OF DIETHYLALUMINIUM DERIVATIVES I. REACTION OF DIETHYLALUMINIUM ETHANETHIOLATE AND DI- ETHYLALUMINIUM DIMETHYLAMIDE WITH ISOCYANATES OR ISO- THIOCYANATES

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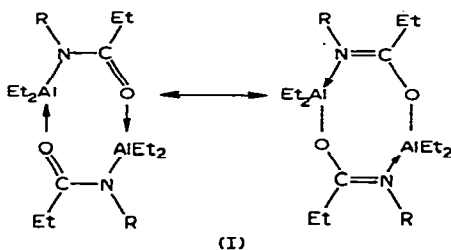
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SUMMARY

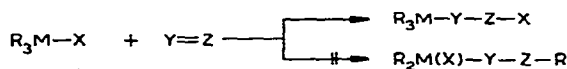
Diethylaluminium ethanethiolate and dimethylamide, Et_2AlX ($\text{X}=\text{SEt}$ and NMe_2), were found to react with equimolar amounts of isocyanate or isothiocyanate, RNCY ($\text{R}=\text{Me}$, Ph , tert-Bu , cyclohexyl ; $\text{Y}=\text{O}$ and S). The occurrence of Al-S or Al-N bond cleavage was confirmed by elemental analysis and by infrared and proton magnetic resonance spectra of the 1/1 adduct obtained. Infrared spectra and cryoscopic molecular weight determinations suggested the existence of an equilibrium between the monomer and a dimer formed through the bridging of heteroatoms by aluminium. Hydrolysis of the adducts gave the corresponding *S*-ethyl thiocarbamate and substituted urea or thiourea derivatives. Formation as by-products of allophanate derivatives and cyclic trimers of the isocyanate indicated the occurrence of successive insertion reactions.

INTRODUCTION

Recent studies on the reactions of trialkylaluminium, especially triethylaluminium, with isocyanate^{1,2} or *N*-substituted propionamide^{3,4} have shown that the adduct formed exist as dimers with mesomeric structures such as (I).

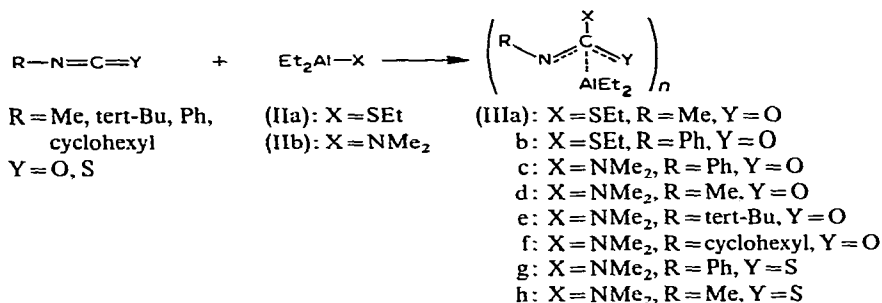


Trimethyl Group IVB metal thiolates⁵ and amides⁶ undergo cleavage selectively at the metal-heteroatom bond, M-X in reaction with various unsaturated dipolar compounds, $\text{Y}=\text{Z}$.



$X = SR', NR'_2$;
 $M = \text{IVb metal}$;
 $R = \text{alkyl or aryl}$

Diethylaluminium ethanethiolate, Et_2AlSEt (IIa), and dimethylamide, Et_2AlNMe_2 (IIb), are known to be polymerization catalysts of ethylene⁷ or butadiene⁸, but no study of the cleavage reactions of Et_2AlX compounds ($X = SR', NR'_2$) has been previously reported. We now describe insertion reactions between (IIa) or (IIb) and isocyanates or isothiocyanates.



The isolation of only 1/1 adducts (III), indicates that there is selective Al-X cleavage. There is no evidence of Al-C cleavage, such as occurs in the corresponding reaction involving diethylaluminium chloride, Et_2AlCl ^{1,2,9}.

EXPERIMENTAL

General remarks

Triethylaluminium and diethylaluminium chloride were pure commercial reagents, and were used without further purification. Dimethylamine was distilled from 40% aqueous solution and dried with caustic soda. Ethanethiol and the isocyanates were purified by distillation. Hydrocarbon solvents were dried over sodium wire.

All the following reactions and measurement of physical constants were carried out under dry nitrogen or argon atmosphere.

Measurement of physical constants

Molecular weight in benzene solution was determined cryoscopically under nitrogen. IR spectra in benzene solution on KCl or polyethylene film were obtained using Japan Electron Optics model DS-402G spectrometer. NMR spectra were recorded on a Japan Electron Optics C-60 spectrometer 60 MHz using TMS as an internal standard. Elemental analyses of organoaluminium adducts were by Alfred Bernhardt Mikroanalytisches Laboratorium.

Preparation of diethylaluminium ethanethiolate (IIa)

Ethanethiol (6.20 g, 0.10 mole) in 20 ml cyclohexane solution was carefully

TABLE 1
NMR DATA OF (IIa), (IIIa), (IIIb), (IVa) AND (IVb) IN 15% BENZENE SOLUTION

Compounds	Assignment (τ)				
	AlCH ₂	AlCCH ₃	SCCH ₃	SCH ₂	Other signal
Et ₂ AlSEt (IIa)	9.75(q)	8.90(t)	9.03(t)	7.70(q)	
MeNCOSEt (IIIa) AlEt ₂	9.76(q)	8.63(t)	8.95(t)	7.20(q)	7.21(s) (NCH ₃)
MeNHCOSEt (IVa)			8.80(t)	7.07(q)	7.45(s)
PhNCOSEt (IIIb) AlEt ₂	9.67(q)	8.57(t)	9.01(t)	7.19(q)	^a
PhNHCOSEt (IVb)			8.75(t)	6.92(q)	^a

^aThe absorption from the phenyl protons overlapped with that of solvent.

dropped into triethylaluminium (11.4 g, 0.10 mole) in 20 ml cyclohexane solution at -78° . Ethane gas evolved as the temperature was gradually raised to 40° . Diethylaluminium ethanethiolate (IIa), b.p. $84-85^\circ$ (0.05 mm) [lit. b.p. $160-162^\circ$ (12 mm)⁷, b.p. $100-101^\circ$ (1 mm)¹⁰], 12.4 g (85% yield based on triethylaluminium), was obtained

TABLE 2
NMR DATA OF (IIb), (IIIc, d, e), AND (IVc, d, e) IN 15% BENZENE SOLUTION

Compounds	Assignment (τ)			
	NCH ₃		AlCCH ₃	AlCH ₂
Et ₂ AlNMe ₂ (IIb)	7.89 (s, 6H)		8.87 (t, 6H)	9.94 (q, 4H)
PhNCONMe ₂ (IIIc) AlEt ₂	7.67 (s, 3H)	7.80 (s, 3H)	8.69 (t, 6H)	9.80 (q, 4H)
PhNHCONMe ₂ (IVc) ^a	6.93 (s)			
MeNCONMe ₂ (IIId) AlEt ₂	7.48 7.74 (9H, about 1/2)		8.71 (t, 6H)	9.84 (q, 4H)
MeNHCONMe ₂ (IVd) ^a	7.20 (3H)	7.36 (6H, broad)		
tert-BuNCONMe ₂ (IIIe) ^b AlEt ₂	7.59 (6H)		8.76 (t, 6H)	9.87 (q, 4H)
tert-BuNHCONMe ₂ (IVe) ^{a,b}	7.25			

^a NH protons' signal could not be detected well because it merged into the base line. ^btert-Bu protons gave a singlet at τ 8.64 in (IIIe) and at 8.57 ppm in (IVe).

by distillation at reduced pressure. (Found: Al, 18.84; active ethyl groups, 2.04: mol.wt. cryoscop., 287. $C_6H_{15}AlS$ calcd.: Al, 18.49%; active ethyl groups, 2.00 per mole; mol.wt. dimer, 292.) NMR and IR data are summarized in Tables 1 and 3, respectively.

Preparation of diethylaluminium dimethylamide (IIb)

Diethylaluminium chloride (10.8 g, 0.09 mole) in 10 ml of petroleum ether was added dropwisely to lithium dimethylamide (0.09 mole) previously prepared at -5° from *n*-butyllithium and dimethylamine in petroleum ether. After removal of lithium chloride and solvent, diethylaluminium dimethylamide (IIb), b.p. $67-69^\circ$ (0.12 mm) [lit.⁷ b.p. $69-70^\circ$ (0.15 mm)], 8.00 g (yield 68%), was obtained. (Found: Al, 20.50; active ethyl groups, 2.05; mol.wt. cryoscop. in benzene, 257. $C_6H_{16}AlN$ calcd.: Al, 20.93%; active ethyl groups, 2.00 per mole; mol.wt. dimer, 258.) The NMR

TABLE 3
IR DATA OF (II), (III) AND (IV)

Compound	Assignment of main absorptions (cm^{-1})			
	$\nu(NH)$	$\nu(C=O)$	$\nu(N=C=O)$	Other absorptions ^a
Et_2AlSEt (IIa)				1255 (s), 980 (vs)
Et_2AlNMe_2 (IIb)				1055 (s), 665 (s), 560 (w), 520 (w)
$MeNCOSEt$ (IIIa) $AlEt_2$		1690(w)	1555(vs, br)	1190, 1070(s), 875
$PhNCOSEt$ (IIIb) $AlEt_2$		1695(w)	1545(vs, br)	1205(vs), 935
$PhNCONMe_2$ (IIIc) $AlEt_2$		1680(w)	1540 (s, br)	1060(m), 980, 900, 625(s), 570
$MeNCONMe_2$ (IIId) $AlEt_2$		1675(w)	1550 (s, br)	1145, 895, 630(s), 575
<i>tert</i> - $BuNCONMe_2$ (IIIe) $AlEt_2$		1705(m), 1680(w), 1615(w)	1555 (s, br)	1190, 1020, 630(s), 575
$MeNHCOSSEt$ (IVa)	3420(m)	1690(vs)		1190(vs), 860, 810
$PhNHCOSSEt$ (IVb)	3395(w)	1695(vs)		1305, 1225, 1140(vs), 875, 755
$PhNHCONMe_2$ (IVc)	3405(w)	1680(vs)		1340, 1240, 1160
$MeNHCONMe_2$ (IVd)	3435(w)	1695(vs)		1320, 1240, 1155
<i>tert</i> - $BuNHCONMe_2$ (IVe)	3425(w)	1675(vs)		1360, 1240, 1185
$C_6H_{11}NHCONMe_2$ (IVf)	3410(m)	1675(vs)		1190(vs)

^a $\nu(C-N)$, $\nu(C-S)$, $\nu(Al-N)$, $\nu(Al-S)$, etc.

and IR data are included in Tables 2 and 3. The residue probably contains links such as N-Al-N, etc.

Reaction of methyl isocyanate with (IIa), and hydrolysis of the product, (IIIa)

Methyl isocyanate (0.88 g, 0.0152 mole) was added dropwise to an equimolar amount of (IIa) (2.21 g, 0.0153 mole) cooled at -78° and the mixture was gradually warmed, with stirring, to room temperature over a period of more than 6 h. The product was distilled under reduced pressure, to give the liquid adduct $\text{Me}(\text{Et}_2\text{Al})\text{NCOSEt}$ (IIIa), b.p. $120\text{--}123^{\circ}$ (0.3 mm), in 75% yield. (Found: C, 47.17; H, 9.08; Al, 13.02; active ethyl groups, 1.98; mol. wt. cryoscop. in benzene, 321. $\text{C}_8\text{H}_{18}\text{AlNOS}$ calcd.: C, 47.27; H, 8.92; Al, 13.17%; active ethyl groups, 2.00 per mole; mol. wt., 203; $n=1.58$).

Hydrolysis of (IIIa) with aqueous ethanol gave *S*-ethyl methylthiocarbamate, MeNHCOSSEt (IVa), yield 85% based on (IIIa), b.p. $61\text{--}62.5^{\circ}$ (20 mm) [lit.¹¹ b.p. $63\text{--}65^{\circ}$ (20 mm)]. These adducts and carbamates were identified by the NMR and IR spectra which are shown in Tables 1 and 3.

Reaction of phenyl isocyanate with (IIa) and hydrolysis of the product (IIIb)

In an analogous manner, the reaction between phenyl isocyanate (3.51 g, 0.0295 mole) and (IIa) (4.25 g, 0.0291 mole) gave the white crystalline adduct $\text{Ph}(\text{Et}_2\text{Al})\text{NCOSEt}$ (IIIb) in quantitative yield during the 6 h gradual temperature increase, and this was recrystallized from benzene, m.p. $95\text{--}100^{\circ}$ (decompn.). (Found: C, 60.02; H, 7.77; Al, 10.46; active ethyl groups, 2.09. $\text{C}_{13}\text{H}_{18}\text{AlNOS}$ calcd.: C, 58.84; H, 7.60; Al, 10.55%; active ethyl groups, 2.00 per mole.) Molecular weight measurement of (IIIb) was difficult because of the lack of suitable solvent.

Hydrolysis of (IIIb) gave *S*-ethyl phenylthiocarbamate, PhNHCOSSEt (IVb), m.p. $68\text{--}69^{\circ}$. The NMR and IR data are shown in Tables 1 and 3, respectively.

Reaction of phenyl isocyanate with (IIb)

Method A. Phenyl isocyanate (1.44 g, 0.0121 mole) in 10 ml benzene solution was added slowly at -5° , with stirring, to diethylaluminium dimethylamide (IIb) (1.57 g, 0.0122 mole) in 10 ml benzene. After few minutes, a white crystalline product began to precipitate. The temperature was raised to the reflux temperature of benzene during 6 h.

The precipitate was recrystallized from aqueous ethanol, and identified as triphenyl isocyanurate (Vc) which is a cyclic trimer of the isocyanate, m.p. $287\text{--}289^{\circ}$ (lit.¹² 291°), 0.86 g (yield 60% based on phenyl isocyanate). (Found: C, 70.42; H, 4.31. $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}_3$ calcd.: C, 70.59; H, 4.21%.) The IR spectrum of (Vc) showed absorptions at 3026 cm^{-1} [$\nu(\text{=CH})$], 1710 cm^{-1} [$\nu(\text{C=O})$] and 1421 cm^{-1} [$\nu(\text{N-C})$], and only phenyl protons were detected in the NMR spectrum.

Distillation of the filtrate gave recovered (IIb) [0.34 g, 22% based on starting (IIb)], the liquid 1/1 adduct, $\text{Et}_2\text{AlN}(\text{Ph})\text{CONMe}_2$ (IIIc), b.p. $112\text{--}115^{\circ}$ (0.07 mm), 0.079 g [yield 5% based on starting (IIb)] and residue 0.51 g (17%). [(IIIc) found: C, 62.13; H, 9.03; Al, 11.08; active ethyl groups, 2.01; mol. wt., 390. $\text{C}_{13}\text{H}_{21}\text{AlN}_2\text{O}$ calcd.: C, 62.87; H, 8.59; Al, 10.89%; active ethyl groups, 2.00 per mole; mol. wt., 248; n , 1.57.] The NMR and IR data of (IIIc) are summarized in Tables 2 and 3, respectively. The red-brown viscous residue contained active ethyl groups.

Method B. The compound (IIb) (2.17 g, 0.0168 mole) in 10 ml *n*-hexane and

phenyl isocyanate (1.90 g, 0.0160 mole) in 10 ml n-hexane were mixed at -78° , and the mixture was very slowly warmed to room temperature. After 2 h refluxing, the mixture was cooled to room temperature, the precipitate, (Vc), was filtered off and recrystallized from ethanol, 0.323 g [yield 17% based on starting (IIb)]. The filtrate gave: recovered (IIb), 0.174 g (8%); (IIIc), 1.03 g [25% based on starting (IIb)]; and a residue 1.24 g (30% based on starting materials).

Hydrolysis of (IIIc) gave a quantitative yield of *N,N*-dimethyl-*N'*-phenylurea, PhNHCONMe_2 , (IVc), m.p. $132\text{--}134^{\circ}$ (lit.¹³ 134°). (Found: C, 65.60; H, 7.09. $\text{C}_9\text{H}_{12}\text{N}_2\text{O}$ calcd.: C, 65.85; H, 7.32%.) Spectroscopic data are given in Tables 2 and 3.

Reaction of methyl isocyanate with (IIb)

Methyl isocyanate (0.62 g, 0.0108 mole) in 10 ml of cold benzene was added to (IIb) (1.39 g, 0.0109 mole) in 10 ml benzene at -5° , and the mixture was gradually raised to the reflux temperature during 6 h. The formed precipitate, (Vd), 0.030 g (5%) was filtered off, and identified as trimethyl isocyanurate, m.p. $171\text{--}173^{\circ}$ (lit.¹⁴ $172\text{--}174^{\circ}$). (Found: C, 42.27; H, 5.20. $\text{C}_6\text{H}_9\text{N}_3\text{O}_3$ calcd.: C, 42.10; H, 5.29%.) There was an IR absorption at 1705 cm^{-1} [$\nu(\text{C}=\text{O})$] and the NMR spectrum showed only a singlet signal at τ 6.85 ppm. The filtrate was distilled to give: recovered (IIb), 0.095 g (7%); the adduct, $\text{Me}(\text{Et}_2\text{Al})\text{NCOMe}_2$ (IIIId), b.p. $102\text{--}104^{\circ}$ (0.15 mm), 1.37 g [yield 68% based on (IIb)]; and residue. [(IIIId) found: C, 53.05; H, 10.15; Al, 14.77; active ethyl groups, 2.10; mol. wt. cryoscop., 270. $\text{C}_8\text{H}_{19}\text{AlN}_2\text{O}$ calcd.: C, 51.60; H, 10.29; Al, 14.48%; active ethyl groups, 2.00 per mole; mol. wt., 166; n , 1.45.] NMR and IR data are summarized in Tables 2 and 3. Hydrolysis of (IIIId) gave trimethylurea, MeNHCONMe_2 (IVd), m.p. $71\text{--}72^{\circ}$ (lit.¹⁵ $72\text{--}73^{\circ}$). (Found: C, 48.98; H, 9.97. $\text{C}_4\text{H}_{10}\text{N}_2\text{O}$ calcd.: C, 48.98; H, 10.21%.) NMR and IR data of (IVd) are given in Tables 2 and 3, also. A trace of *N,N'*-dimethyl urea was detected in the hydrolysis products; it was probably formed from unrecovered methyl isocyanate.

Reaction of cyclohexyl isocyanate and tert-butyl isocyanate with (IIb)

Isocyanate (0.0060 mole; cyclohexyl, 0.75 g; tert-butyl 0.60 g) in 10 ml benzene solution was added to (IIb) (0.77 g, 0.0060 mole) in 10 ml benzene at -5° . The reaction was carried out with methyl isocyanate. Hydrolysis of the adduct gave the corresponding substituted urea, [*N,N*-dimethyl-*N'*-cyclohexylurea, $\text{C}_6\text{H}_{11}\text{NHCONMe}_2$ (IVf), m.p. $160\text{--}161^{\circ}$, 0.32 g (31%) (Found: C, 63.49; H, 10.80; N, 16.45. $\text{C}_9\text{H}_{18}\text{N}_2\text{O}$ calcd.: C, 63.48; H, 10.77; N, 16.24%); and *N,N*-dimethyl-*N'*-tert-butyl urea, tert-BuNHCONMe₂ (IVe), m.p. $85\text{--}86^{\circ}$, 0.53 g (61%), (Found: C, 58.07; H, 11.04. $\text{C}_7\text{H}_{16}\text{N}_2\text{O}$ calcd.: C, 58.33; H, 11.19%.)]

These ureas were identified from their melting points and by comparison of spectra with those of authentic samples. In another run the adduct, tert-BuN-(Et₂Al)CONMe₂ (IIIe), b.p. $75\text{--}78^{\circ}$ (0.04 mm), was isolated by distillation and identified by its NMR spectrum as shown in Table 2.

Reaction of phenyl and methyl isothiocyanate with (IIb)

Precooled (IIb) (1.05 g, 0.0082 mole) and phenyl isothiocyanate (1.11 g, 0.0082 mole) or methyl isothiocyanate (0.59 g, 0.0080 mole) were mixed in an ampoule at -78° under a current of argon. The ampoule was closed and kept at 85° for 20 h. In the case of methyl isothiocyanate, the reaction product contained a large quantity of unreacted isothiocyanate (0.43 g, 74%). Hydrolysis of the reaction product afforded:

corresponding thiourea derivative, MeNHCSNMe_2 (IVg), m.p. 87–88° (lit.¹⁶ m.p. 87–88°), 0.135 g (14%) (Found: C, 40.18; H, 8.65; N, 23.42. $\text{C}_4\text{H}_{10}\text{N}_2\text{S}$ calcd.: C, 40.65; H, 8.53; N, 23.70%); and cyclic trimer, trimethyl isothiocyanurate (Vg), m.p. 130–140° (lit.¹⁷ m.p. 140°), 0.035 g (6%) (Found: C, 33.06; H, 4.58; N, 19.08. $\text{C}_6\text{H}_9\text{N}_3\text{S}_3$ calcd.: C, 32.85; H, 4.22; N, 19.11%), which was characterized by IR absorption at 1390 and 1090 cm^{-1} .

In the case of the phenyl compound, no reaction had taken place after 20 h at 85°, but after 80 h hydrolysis of the mixture gave 5% of *N,N*-dimethyl-*N'*-phenylthiourea, PhNHCSNMe_2 , (IVh), m.p. 131–133° (lit.¹⁸ m.p. 133–134°), 0.072 g. When the reaction was carried out at 170° for 20 h, the absorption at 2140 cm^{-1} [$\nu(\text{N}=\text{C}=\text{S})$] entirely disappeared, and the product was mostly resinous polymer, but on hydrolysis the thiourea derivative (IVh), 0.245 g (17%), was produced. The IR spectrum of (IVh) showed characteristic absorptions at 3445, 1545 and 1328 cm^{-1} .

Reaction of phenyl isocyanate with (IIa) in 2/1 and 3/1 molar ratio

Under the conditions used in the equimolar reaction, PhNCO (0.894 g, 0.00751 mole) and (IIa) (0.548 g, 0.00375 mole) were brought into reaction at –5 to 80° over 6 h (2/1 reaction). The hydrolysis products contained three crystalline compounds, namely: (VIb), m.p. 118–119°, 0.618 g (55%); (Vc), m.p. 289–290°, 0.045 g (5%); (VIIb), m.p. 235–240° (trace); and also a yellowish oily product which could not be identified.

Compound (VIb) was recrystallized from aqueous ethanol and identified as *S*-ethyl *N,N'*-diphenyl thioallophanate, PhNHCONPhCOSEt . (Found: C, 64.07; H, 5.31. $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ calcd.: C, 63.86; H, 5.38%.) The IR spectra of (VIb) was similar to that of carbamate (IVb) except for an absorption at 1730 cm^{-1} in place of that at 1691 cm^{-1} for (IVb). Furthermore, the product from 1,3-diphenyl-1,3-diazetidinedione¹⁹ (the four-membered cyclic dimer of phenyl isocyanate) and ethyl mercaptan was identical with (VIb), as was the compound obtained by hydrolysis of the mixture formed from (IIa) and the diazetidinedione. Compound (Vc) was the cyclic trimer of phenyl isocyanate, described above. Compound (VIIb) was shown to be as *N,N'*-diphenyl urea by comparison with an authentic sample prepared from phenyl isocyanate and aniline.

Similarly, the reaction of PhNCO and (IIa) in 3/1 molar ratio gave, after hydrolysis, the thioallophanate derivative (VIb) (45%) and the trimer (Vc) (35%).

Reaction of phenyl isocyanate with (VIb)

Phenyl isocyanate was added at –5 to 40° during 15 h to the (unhydrolyzed) mixture obtained from the 2/1 molar ratio reaction; this mixture contained at least 55% $\text{PhN}(\text{Et}_2\text{Al})\text{CONPhCOSEt}$ along with a small amount of trimer (Vc) and was free of ethanethiol. Hydrolysis gave thioallophanate derivative (VIb) (32%), the cyclic trimer of PhNCO (28%), and *N,N'*-diphenylurea (25%) formed from unreacted isocyanate.

RESULT AND DISCUSSION

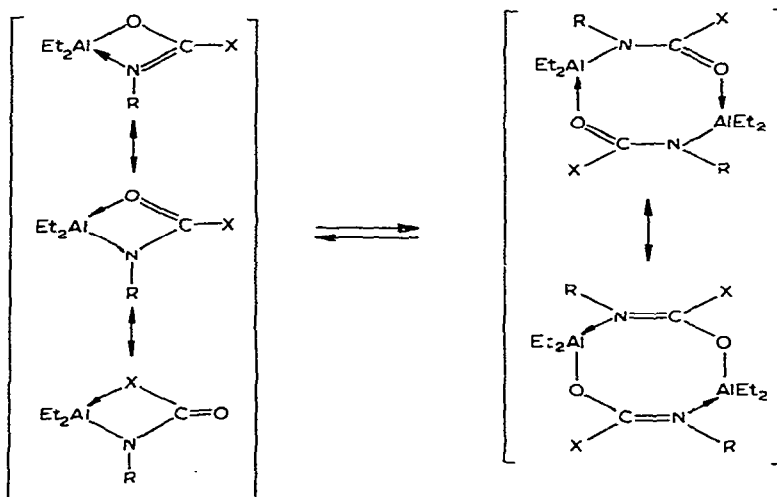
Two modes of insertion of isocyanate into diethylaluminium ethanethiolate and dimethylamide are possible:

TABLE 4

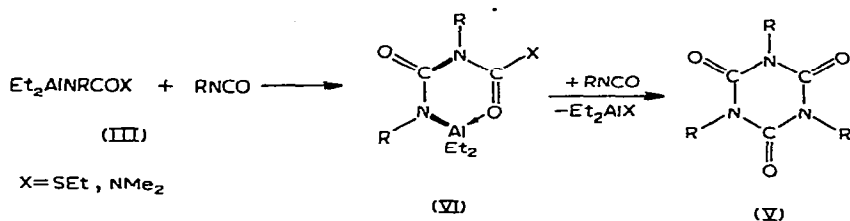
 YIELD OF ADDUCTS (III), $RN(Et_2Al)C(=Y)X$, AND CYCLIC TRIMER (V), $(-NR-CY-)_3$

R	Reaction conditions			Yield (%)	
	Temp. (°C) ^a	Time (h) ^b	Solvent	(III)	(V)
<i>X = SEt, Y = O</i>					
Me	-78 to r.t.	6	None	75	
Ph	-78 to r.t.	6	None	98	
<i>X = NMe₂, Y = O</i>					
Ph	-5 to 85	6	Benzene	5	60
Ph	-78 to r.t.	6	n-Hexane	25	17
Me	-5 to 85	6	Benzene	68	5
tert-Bu	-5 to 85	6	Benzene	61 ^c	
C ₆ H ₁₁	-5 to 85	6	Benzene	31 ^c	
<i>X = NMe₂, Y = S</i>					
Me	-78 to 85	20	None	14 ^c	6
Ph	-78 to 85	80	None	5 ^c	
Ph	-78 to 170	20	None	17 ^c	

^a Reaction temperature was described as first contact temperature ~ final temperature. ^b Total reaction time from the contact instant to the reaction stop. ^c From hydrolysis product *i.e.*, corresponding urea or thiourea.



was added to the 1/1 adduct (IIIb), the thioallophanate derivative (VI) was obtained along with the cyclic trimer. This indicated that stepwise insertions can occur. In the case of the amide (IIb), the amount of cyclic trimer of the isocyanate produced depended on the conditions, even in the 1/1 molar ratio reaction. The reaction sequence may be as follows:



The first step might involve the active monomer of (III)²⁰.

Comparative yields of 1/1 adducts and trimers are summarized in Table 4. The reactions with isothiocyanates occurred analogously, but less readily than those with isocyanates.

REFERENCES

- 1 H. REINHECKEL, D. JANKE AND G. KRETZSCHMAN, *Chem. Ber.*, 99 (1966) 11.
- 2 M. F. LAPPERT AND J. R. HORDEN, *J. Chem. Soc. A*, (1968) 2004.
- 3 E. V. MITROFANOVA AND L. P. STEPOVIK, *Zh. Obshch. Khim.*, 36 (1966) 1488.
- 4 K. WADE, B. K. WYATT AND J. R. JENNINGS, *J. Chem. Soc., A*, (1968) 2535.
- 5 K. ITOH, K. MATSUZAKI AND Y. ISHII, *J. Chem. Soc., C*, (1968) 2709.
- 6 A. G. DAVIES AND A. J. BLOODWORTH, *J. Chem. Soc.*, (1965) 5238.
- 7 K. ZIEGLER, *Brit. Patent* 799,823 (1955).
- 8 G. LONGIAVE AND R. CASTELLI, *J. Polymer Sci., Part C*, 4 (1966) 387.
- 9 H. REINHECKEL, K. HAAGE AND R. GENSKE, *Angew. Chem.*, 77 (1965) 810; 78 (1966) 491; *J. Organometal. Chem.*, 10 (1967) P28, P29.
- 10 L. I. ZAKHARKIN AND V. V. GAVRILENKO, *Izv. Akad. Nauk SSSR., Otd. Khim. Nauk*, (1960) 1391.
- 11 O. BILLEFER, *Chem. Ber.*, 43 (1910) 1853.
- 12 J. R. BALLEY AND A. T. MCPHERSON, *J. Amer. Chem. Soc.*, 39 (1917) 1322.
- 13 R. STOLLE, *J. Prakt. Chem.*, [2] 117 (1927) 201.
- 14 E. BILLMANN AND J. BJERRUM, *Chem. Ber.*, 50 (1917) 503.
- 15 FRANCHIMONT, *Rec. Trav. Chim. Pays-Bas*, 3 (1888) 226.
- 16 H. LECHER AND F. GRAF, *Chem. Ber.*, 56 (1923) 1327.
- 17 PALAZZO AND SCELSI, *Gazz. Chim. Ital.*, [1] 38 (1908) 672.
- 18 R. F. HUNTER AND E. R. STYLES, *J. Chem. Soc.*, (1927) 1209.
- 19 E. W. ABEL AND I. H. SABHERWAL, *J. Chem. Soc., A*, (1968) 1105.
- 20 E. C. ASHBY AND J. T. LAEMMLE, *J. Org. Chem.*, 33 (1968) 3398.

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