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INSERTION REACTIONS OF DIETHYLALUMINIUM DERIVATIVES

IX. REACTIONS OF DIETHYLALUMINIUM DIMETHYLAMIDE AND ETHANETHIOLATE WITH KETENIMINE

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Summary

The addition reactions of diethylaluminium dimethylamide, $Et_2Al—NMe_2$ (Ia) and ethanethiolate, $Et_2Al—SEt$ (Ib) with dimethylketene-*N*-arylimine, $Me_2C=C=N—Ar$ [Ar = Ph (IIa) and *p*-tolyl(IIb)] have been studied.

In the reactions of ketenimines with (Ib), both 1/1 and 1/2 adducts were obtained, while the reaction of (Ia) gave the corresponding 1/2 adduct exclusively. Hydrolysis of the isolated 1/2 adducts afforded the corresponding amidine derivatives, (III'a—d). In the case of (Ib), the imidothioethyl ester derivatives (IV'c,d), formed from 1/1 adducts, were found in the hydrolysis products.

Introduction

Most addition reactions of organoaluminium compounds with imines [1,2], nitriles [3 - 6] and isocyanates [7,8] give the corresponding 1/1 adducts, as expected, but in some cases successive insertions of acceptor molecules were observed, such as the formation of cyclic trimers of isocyanates and the polymerization of olefins.

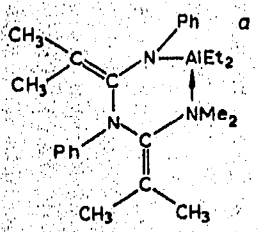
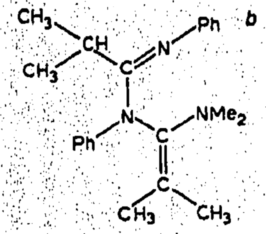
Hirabayashi et al. [9] investigated in detail the reaction of Al—O bond with phenyl isocyanate, and concluded that the intermediate 1/2 adduct was relatively unstable compared with the 1/1 adduct or cyclic trimer. In Ziegler olefin dimerization catalysed by aluminium hydride, the 1/2 adduct was definitely involved as the intermediate [10], in combination with important transition metal catalysis.

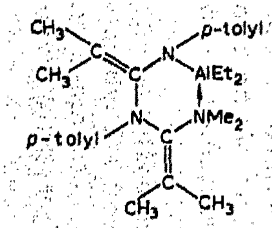
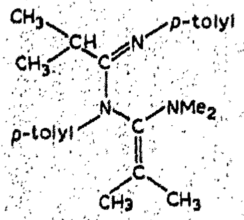
In this paper we describe the specific formation of the stable 1/2 adducts through successive insertion of two molecules of ketenimine into Al—S or Al—N bond. Little was known about the interaction of ketenimine with organometallic compounds [11]: Otsuka et al. [12] have shown that diphenylketene-*N*-phenylimine acts as a ligand towards some iron or cobalt carbonyls,

(Continued on p. 232)

TABLE 1

IR AND NMR DATA FOR (IIIa, b) AND (III'a, b)

Compounds	IR(cm^{-1})			Chemical shift (τ ppm, JHz)					
	ν(C=C)	ν(C=N)	Other absorptions	$AlCH_2$	$AlCH_2C\underline{H}_3$	$N(CH_3)_2$	$(CH_3)_2C$=	$(C\underline{H}_3)_2CH$	$(CH_3)_2C\underline{H}$
 (IIIa)	1590vs		1536s, 1427s 1381m, 1312s 1210s, 1100m 1060m, 751s	9.71q (*J* 8.3)	8.91t (*J* 8.3)	8.16s	8.45s 8.38s		
 (III'a)	1610vs	1667m	1593s, 1488s 1390m, 1365m 1098s, 700s	[also 2.40—3.70m due to two phenyl rings]		7.34s	8.50s	8.96d (*J* 7.2)	7.12septet (*J* 7.2)

 (III b)[a]	1605vs		1502s, 1310s 1213s, 1100m 1060m, 828m 811m	9.63q (J 8.3)	8.80t (J 8.3)	8.20s	8.53s 8.48s 8.38s		
				[also 7.96s and 7.70s due to two CH_3 in aryl rings]					
 (III′b)[b]	1611s	1667m	1585s, 1509s 1480s, 1386m 1237s, 1222s 830s			7.30s	8.51s	8.90d (J 6.0)	7.25septet (J 6.0)
				[also 7.75s and 7.69s due to two CH_3 in aryl rings, 3.03(AB quartet, J7.5) and 2.93(AB quartet, J 7.5) due to two aryl rings]					

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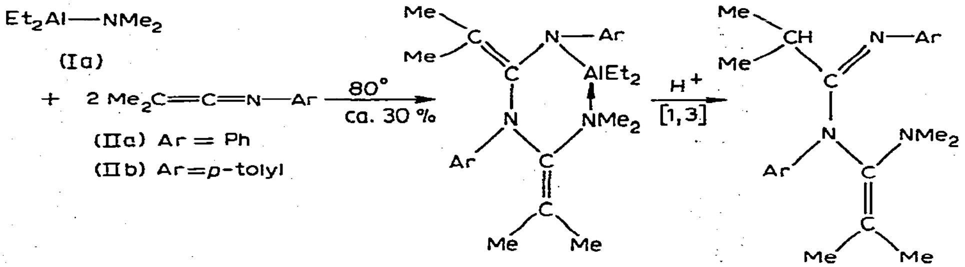
[a] In benzene. [b] In CCl_4.

but insertion reactions of ketenimines with main group organometallic compounds had not been examined. Consequently dimethylketen-*N*-arylimines were used as new acceptors for insertions of $Et_2Al—NMe_2$ (Ia) and $Et_2Al—SEt$ (Ib).

Results and discussion

The reactions between (Ia) and (IIa) or (IIb) proceeded slowly even at the reflux temperature of benzene. It took over one week for the characteristic absorption of ketenimine [2000 cm^{-1}; ν(C=C=N).] to disappear completely. The crystalline products (IIIa)(Ar = Ph) and (IIIb)(Ar = *p*-tolyl), were shown to be 1/2 adducts on the basis of their elemental analyses, cryoscopic molecular weights, and infrared and NMR spectra and those of the hydrolysis products (III'a) and (III'b) (see Table 1).

Surprisingly, no 1/1 adducts could be detected by spectroscopy, or by isolation of them or of their hydrolysis products [eqn. (1)].



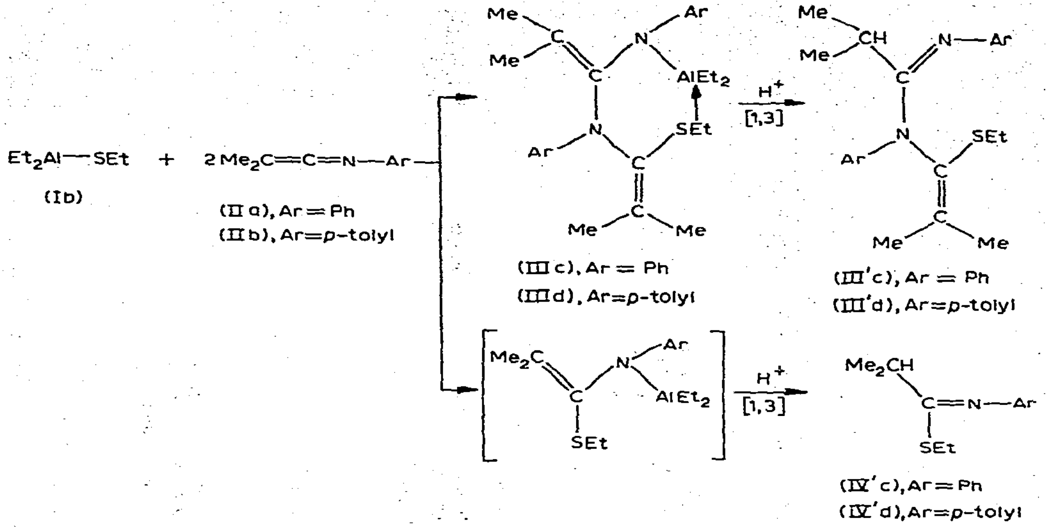
(1)

(IIIa), Ar=Ph
(IIIb), Ar=*p*-tolyl

(III'a), Ar = Ph
(III'b), Ar=*p*-tolyl

The evidence for the structure of the isolated 1/2 adducts (IIIa,b) was as follows: (*i*) the monomeric molecular weight indicated by cryoscopic measurements; (*ii*) the strong ν(C=C) absorptions around 1600 cm^{-1} [1590 for (IIIa) and 1605 cm^{-1} for (IIIb)], as present in enamines [13]. The hydrolysis products (III'a) and (III'b), both showed ν(C=N) at 1667 cm^{-1} and ν(C=C) at 1610(III'a) and 1611(III'b) cm^{-1}, respectively. (*iii*) The NMR spectrum of (IIIb) (Fig. 1) can be interpreted as follows. Two methyl protons H_4 and H_5 appear at τ8.38 ppm, but this signal is absent in the hydrolysis product (III'b), because $H_{4,5}$ are now present in an isopropyl group following a rapid hydrogen shift during hydrolysis. The other two methyl protons (H_6 and H_7) at τ8.48 and 8.53 ppm retain their positions (τ8.51 ppm) upon hydrolysis. The considerable change in the $N—CH_3$ proton signals in the 1/2 adduct (IIIb) at τ8.16 ppm and the hydrolysis product (III'b) at τ7.34 ppm can be ascribed to coordination of dimethylamide group to aluminium atom. The one of the two $p\text{-}CH_3C_6H_4$-protons (H_2 at τ7.96 ppm) close to the organoaluminium group underwent a low field shift to τ7.75 ppm upon hydrolytic demetallation.

In contrast, $Et_2Al—SEt$ (Ib) reacted with ketenimines (IIa) and (IIb) rapidly at room temperature or below 0° to give both 1/2 (IIIc,d) and 1/1 adducts (IVc,d). The structure of the crystalline 1/2 adducts was determined in the same manner as (IIIa,b); their spectroscopic features and those of hydroly-



(2)

sis products(III'c,d) are summarized in Table 2. The 1/1 adducts could not be isolated but were identified as the imidothioethyl esters (IV'c,d), by hydrolytic demetallation [eqn. (2)].

Clearly the rates of addition were quite different for $Et_2Al{-}NMe_2$ [(Ia); 80° over a week] and $Et_2Al{-}SEt$[(Ib); 25° for 12h]. (A corresponding differ-

(Continued on p. 236)

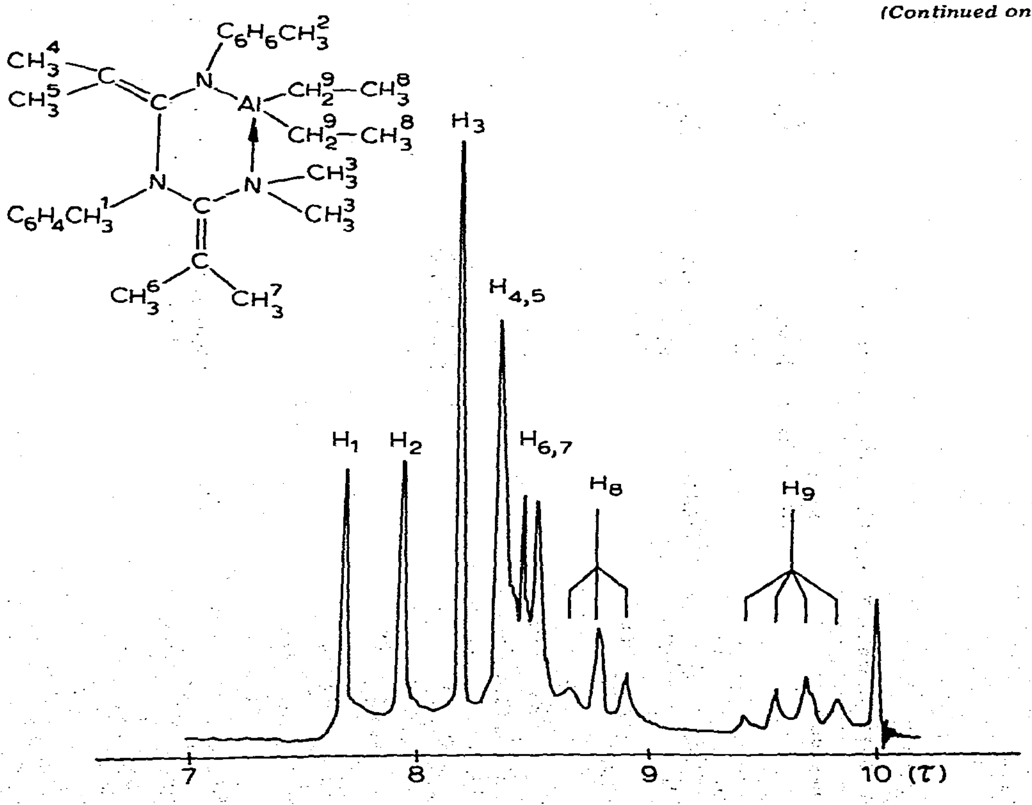
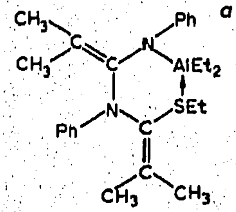
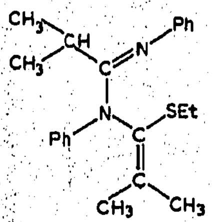
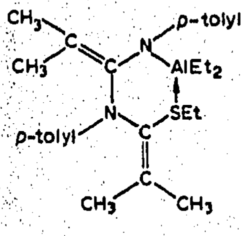
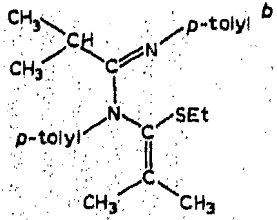
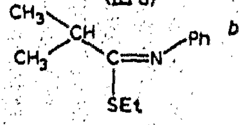
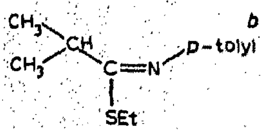


Fig. 1. The NMR spectrum for the 1/2 adduct (IIIb) in 20% benzene solution.

TABLE 2

IR AND NMR DATA FOR (IIIc, d), (III′c, d) AND (IV′c, d)

Compounds	IR (cm^{-1})			Chemical shift (τ ppm, J Hz)						
	ν(C=C)	ν(C=N)	Other absorptions	$AlCH_2$	$AlCH_2C\underline{H}_3$	SCH_2	$SCH_2C\underline{H}_3$	$(C\underline{H}_3)_2C=$	$(C\underline{H}_3)_2CH$	$(CH_3)_2C\underline{H}$
 (III c) [a]	1595vs		1453s, 1310s 1253s, 993m 752m	9.52q (J 7.5)	8.35t (J 7.5)	7.90q (J 6.8)	8.91t (J 6.8)	8.47s 8.30s 8.23s 8.15s		
 (III′c) [b]	1622s	1670s	1598s, 1488m 1388m, 1105m 973m, 700s			7.88q (J 7.5)	9.06t (J 7.5)	8.49s	8.92d (J 6.8)	7.15septet (J 6.8)
				[also 2.60—3.50m due to two phenyl rings]						
 (III d) [a]	1608s		1500s, 1302s 990m, 811m	9.50q (J 6.8)	8.35t (J 6.8)	7.97q (J 6.8)	8.59t (J 6.8)	8.27s 8.24s		
				[also 8.03s and 7.81s due to two CH_3 in aryl rings]						

 (III'd) [b]	1620s	1672s	1507s, 1464m 1388m, 1240m 1155m, 1110m 990m, 865m	[also 7.99s and 7.73s due to two CH_3 in aryl rings, 3.35(AB quartet, *J* 8.3) and 3.19(AB quartet, *J* 8.3) due to two aryl rings]	7.87q (*J* 7.2)	9.06t (*J* 7.2)	8.53s	8.95d (*J* 6.8)	7.19septet (*J* 6.8)
 (IV'c) [b]		1700m	1614s, 1600s 1486m, 1185m 973m, 703s	[also 2.67—3.61m due to a phenyl ring]	7.19q (*J* 6.8)	8.76t (*J* 6.8)		8.93d (*J* 6.8)	7.12septet (*J* 6.8)
 (IV'd) [b]		1703m	1613s, 1505s 1466m, 1180m 1150m, 967m 885m	[also 7.76s due to a CH_3 in aryl ring, 3.32(AB quartet, *J* 8.3) due to an aryl ring]	7.19q (*J* 6.8)	8.75t (*J* 6.8)		8.93d (*J* 6.8)	7.11septet (*J* 6.8)

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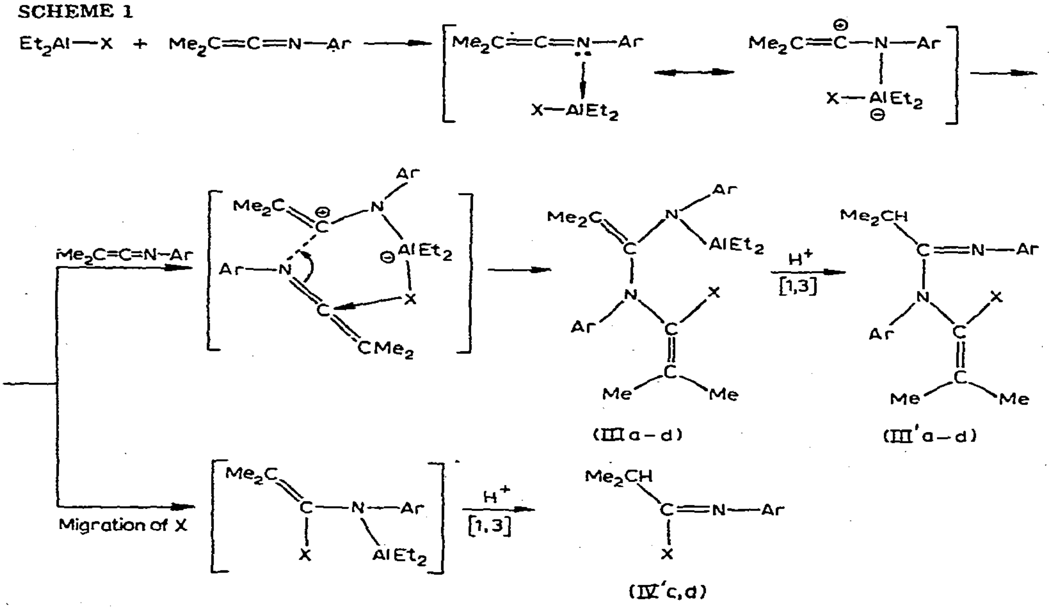
[a] In benzene solution. [b] In CCl_4 solution.

ence was observed in the addition reactions of isocyanates [7].) During the reaction, the colour of the reaction mixture changed gradually from pale yellow (ketenimine itself is greenish yellow) to orange-yellow, red-brown, and finally dark reddish. The insertion reaction of (Ia,b) with nitrile showed a similar change in colour [3], which was ascribed to coordination of the aluminium atom by the lone pair(n-electron) of the nitrile nitrogen atom.

The initial step of the present reaction is thus likely to involve the coordination of the lone pair electrons of ketenimines to the organoaluminium moiety; such coordination to aluminium atom will weaken the original Al—X bond. The extent of this weakening would be larger for the soft SEt than for the hard NMe_2 group. [According to Pearson's views, Al(hard acid) will prefer N(hard base) to S(soft base)]. Thus the reactivity of the Al—S bond should be much higher than that of the Al—N bond. Moreover, the more reactive Al—SEt would attack a carbocation at a rate competitive with that of the second attack of ketenimine. As a result, the insertion products will be a mixture of 1/1 and 1/2 adducts. On the other hand, the NMe_2 group is held tightly to aluminium atom, so that its migration occurs much more slowly than the capture of the second ketenimine by carbocation, and only 1/2 adduct is formed.

A possible reaction mechanism is shown in Scheme 1.

SCHEME 1



Experimental

General

The organoaluminium compounds, Et_2AlNMe_2 (Ia) and Et_2AlSEt (Ib), were prepared as previously described [7]. Dimethylketene-*N*-phenylimine (IIa) and *N*-*p*-tolylimine (IIb) were synthesized by the published method [14]. Hydrocarbon solvents were thoroughly dried over sodium wire. All the reactions and measurements of physical constants of the products were carried out under dry nitrogen or argon. Molecular weights in benzene were determined cryoscopically. Infrared spectra were recorded on a Japan Spectroscopic Co. Model IR—S, and NMR spectra on a Japan Electron Optics Co. Model C-60HL, with TMS as an internal standard. Demetallated organic compounds were identified by GLC analyses. Elemental analyses of organoaluminium compounds were carried out by the Alfred Bernhardt Microanal. Lab., West Germany.

Reaction of (Ia) with dimethylketene-N-phenylimine (IIa), and hydrolysis of the product

A benzene (10 ml) solution of (IIa) (0.93 g, 6.4 mmol) was added dropwise to a half molar proportion of (Ia) (0.41 g, 3.2 mmol) in benzene (10 ml) at room temperature. The mixture was stirred at room temperature for 24 h, then heated to reflux. An absorption band at 2000 cm^{-1} [ν(C=C=N)] in the IR spectrum of the mixture disappeared after 152 h, and a dark reddish solution was formed. Removal of the solvent under reduced pressure and recrystallization of the residue from petroleum ether gave reddish crystals (IIIa), m.p. 154 - 157°, 0.40 g [yield 30% based on used (Ia)]. [Found: C, 74.18; H, 8.93; Al, 6.29; active ethyl groups 1.81; mol.wt. (cryoscop. in benzene), 440. $C_{26}H_{38}N_3Al$ calcd.; C, 74.43; H, 9.13; Al, 6.44%; active ethyl groups, 2.00 per mol.; mol. wt., 420.] After demetallation of (IIIa) (0.38 g) with dilute hydrochloric acid followed by treatment with aqueous alkali, the organic substances were extracted with chloroform. After drying of the extract (Na_2SO_4) and removal of the solvent, the amidine derivative (III'a) was obtained as an oil, 0.19 g [yield 63% based on (IIIa)]. (Found: C, 78.78; H, 8.61; N, 12.60. $C_{22}H_{29}N_3$ calcd.; C, 78.96; H, 8.71; N, 12.53%). Similar hydrolysis of the dark reddish residue (0.85 g) gave an oil (0.55 g), which was shown by GLC also to be compound (III'a). NMR and IR data are shown in Table 1.

Reaction of (Ia) with dimethylketene-N-p-tolylimine (IIb) and hydrolysis of the product

The reaction between (Ia) (0.502 g, 3.9 mmol) in 10 ml benzene and (IIb) (1.25 g, 7.8 mmol) in 10 ml benzene at reflux temperature gave a dark reddish solution after 168 h. Recrystallization gave reddish yellow crystals (IIIb), m.p. 121 - 124°, 0.44 g [yield 25% based on used (Ia)]. [Found: C, 74.83; H, 9.20; Al, 6.85; active ethyl groups 2.16; mol. wt. (cryoscop. in benzene), 466. $C_{28}H_{42}N_3Al$ calcd.; C, 75.13; H, 9.46; Al, 6.03%; active ethyl groups, 2.00 per mol.; mol. wt. 448.]. Hydrolysis of (IIIb) (0.40 g) in an analogous manner gave an amidine derivative (III'b), oil, 0.22 g [yield 69% based on (IIIb)]. [Found: C, 79.72; H, 9.28; N, 11.00. $C_{24}H_{33}N_3$ calcd.; C, 79.29; H, 9.15; N, 11.56%.]. Hydrolysis of the reddish residue (1.10 g) as before gave an oil (0.63 g), which was also identified as (III'b) by GLC. NMR and IR data are shown in Table 1.

Reaction of (Ib) with dimethylketene-N-phenylimine (IIa) and hydrolysis of the product

The petroleum ether (10 ml) solution of (Ib) (0.55 g, 3.8 mmol) was cooled to —78°, and (IIa) (1.10 g, 7.6 mmol) was added dropwise. The mixture was allowed to warm slowly to room temperature, and after few hours the absorption band in the IR spectrum at 2000 cm^{-1} [ν(C=C=N)] had disappeared. The mixture was stirred for 12 h more then removal of the solvent under reduced pressure and recrystallization of the residue from petroleum ether gave pale yellow crystals (IIIc), m.p. 80 - 85°, 0.53 g [yield 32% based on used (Ib)]. [Found: C, 71.14; H, 8.34; Al, 6.58; active ethyl groups 2.09; mol. wt. (cryoscop. in benzene), 418. $C_{26}H_{37}N_2SAl$ calcd.; C, 71.52; H, 8.54; Al, 16.18%; active ethyl groups 2.00 per mol., mol. wt. 437.] Demetallation of (IIIc) (0.53 g) with dilute hydrochloric acid and extraction with chloroform, drying (Na_2SO_4), and removal of the solvent gave the amidine derivative, (III'c) as an oil (0.20 g) [yield 52% based on (IIIc)]. (Found: C, 75.41; H, 7.94; N. 7.56. $C_{22}H_{28}N_2S$ calcd.; C, 74.95; H, 8.01; N, 7.95%.) The hydrolysis of the reddish residue (1.10 g) gave an oil (0.58 g). GLC analysis of this oil showed the presence of three components, isobutyl-*N*-phenyl-imidothioethyl ester (IV'a) [45%], (III'c) [43%] and its isomer (III''c) [6%]. The first compound (IV'a) was identical with an authentic sample prepared from equimolar amounts of ketenimine and ethanethiol [15]. (Found: C, 69.55; H, 8.09; N, 6.89. $C_{12}H_{17}NS$ calcd.; C, 69.51; H, 8.26; N, 6.76%.) NMR and IR data are shown in Table 2.

Reaction of (Ib) with dimethylketene-N-p-tolylimine (IIb) and hydrolysis of the product

The reaction between (Ib) (0.44 g, 3 mmol) in 10 ml petroleum ether and (IIb) (0.96 g, 6 mmol) in 10 ml petroleum ether at room temperature gave a reddish solution after 12 h. Recrystallization gave yellow crystals (IIId), m.p. 105 - 110°, 0.42 g [yield 30% based on used (Ib)]. [Found: C, 72.12; H, 9.05; Al, 5.86; active ethyl groups 1.78; mol. wt. (cryoscop. in benzene), 442. $C_{28}H_{41}N_2SAl$ calcd.; C, 72.37; H, 8.89; Al, 5.80%; active ethyl groups 2.00 per mol.; mol. wt. 465.] Demetallation of (IIId) [0.25 g] gave the brown solid amidine derivative (III'd), m.p. 108 - 110°, 0.10 g [yield 50% based on (IIId)]. (Found: C, 75.91; H, 8.34; N, 7.32. $C_{24}H_{33}N_2S$ calcd.; C, 75.74; H, 8.47; N, 7.36%.) Hydrolysis of the reddish residue (0.92 g) gave an oil (0.50 g) in which 3 components were found by GLC, isobutyl-*N*-*p*-tolylimidothioethyl ester (IV'd) [32%], (III'd) [50%] and its isomer (III''d) [18%]. The first compound was identical with an authentic sample prepared from equimolar amounts of ketenimine and ethanethiol. (Found: C, 70.46; H, 8.70; N, 6.36. $C_{13}H_{19}NS$ calcd.; C, 70.54; H, 8.56; N, 6.33%.) NMR and IR data are shown in Table 2.

Reaction of (Ia) with (IIa) in equimolar ratio

Under the conditions used for the 1/2 molar ratio reactions, (Ia) (0.8 g, 6.2 mmol) in 10 ml benzene and (IIa) (0.9 g, 6.2 mmol) in 10 ml benzene were brought into reaction at room temperature and the mixture then refluxed. The absorption at 2000 cm^{-1} disappeared after 110 h. Recrystallization from petroleum ether gave 1/2 adduct (IIIa), 0.43 g [yield 32% based on used (IIa)]. Distillation of the dark reddish residue at reduced pressure gave a liquid (Ia), b.p. 68 - 70° (0.15 mm) [(Ia) b.p. 69 - 70° (0.15 mm)], 0.32 g [40% recovered as (Ia)]. The black distillation residue also contained an aluminium compound but it could not be identified.

Reaction of (Ib) with (IIa) in an equimolar ratio

Under the conditions used for the 1/2 molar ratio reactions, (Ib) (1.3 g, 8.9 mmol) in 10 ml petroleum ether and (IIa) (1.3 g, 8.9 mmol) in 10 ml petroleum ether were mixed at −78° and allowed to warm to room temperature during 12 h. Recrystallization gave the 1/2 adduct (IIIc), 0.90 g [yield 45% based on used (IIa)]. Distillation of the reddish residue at reduced pressure gave a liquid (Ib), (b.p. 100°/1.0 mm) [(Ib); b.p. 100 - 101°/1.0 mm], 0.60 g [46% recovered as (Ib)]. The dark reddish residue also contained an Al-compound, but could not be identified.

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