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INSERTION REACTIONS OF DIETHYLALUMINUM DERIVATIVES

X. SYNTHESIS AND PROPERTIES OF ETHYLALUMINUM SULFIDE, THE INITIAL PRODUCT IN THE REACTION OF TRIETHYLALUMINUM WITH HYDROGEN SULFIDE

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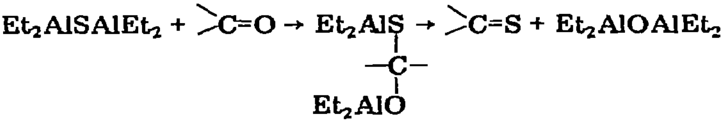
Summary

Ethylaluminum sulfide, $(EtAlS)_n$, was found to be the initial product of the reaction of triethylaluminum with hydrogen sulfide. When heated with an equimolar amount of triethylaluminum, this sulfide gave bis(diethylaluminum) sulfide, $(Et_2Al)_2S$.

$(EtAlS)_n$ reacted with pyridine or vinylpyridines to form $(EtAlS)_2 \cdot 2(Donor)$ type adducts and with *N*,*N*-dimethylamides, $RCONMe_2$ ($R = H, Me, Ph$), to give the corresponding thioamides in good yield.

Introduction

The formation of bis(diethylaluminum) sulfide, $Et_2AlSAlEt_2$, by the reaction of hydrogen sulfide with two molar equivalents of triethylaluminum has been demonstrated [1, 2]. This sulfide is useful for the thiocarbonylation of carbonyl compounds (eqn. 1). In the case of methyl esters, however, distillable *ortho* ester-type 1/1 adducts were obtained.



$$\mathrm{Et_2AlSAlEt_2} + {>}\mathrm{C{=}O} \rightarrow \begin{array}{c}\mathrm{Et_2AlS}\\ | \\ -\mathrm{C}- \\ | \\ \mathrm{Et_2AlO}\end{array} \rightarrow {>}\mathrm{C{=}S} + \mathrm{Et_2AlOAlEt_2} \qquad (1)$$

Recently, Pasynkiewicz et al. [3] prepared $Me_2AlSAlMe_2$, described its stability in several organic solvents and compared its Lewis acidity with that of other organoaluminum compounds. However, a detailed mechanism of formation of $(Et_2Al)_2S$ has not yet been elucidated.

We have found that ethylaluminum sulfide, $(EtAlS)_n$, is the initial product formed in the reaction of H_2S with Et_3Al and that $(Et_2Al)_2S$ is formed in the reaction of $(EtAlS)_n$ with an equimolar quantity of Et_3Al. Preparation and characterization of several new complexes of $(EtAlS)_n$ with donor molecules, as well as its use in the thiocarbonylation of some *N,N*-dimethylamides are reported.

Results and discussion

Products of the reaction of hydrogen sulfide with triethylaluminum

In our previous work on the reaction of H_2S with two molar equivalents of Et_3Al, we obtained $(Et_2Al)_2S$ (I) by evaporating the solvent at 50°C and proposed reaction sequence 2 on the basis of the observation that two moles of ethane were evolved for each mole of H_2S used [1].

$$\begin{aligned} &Et_3Al + H_2S \rightarrow Et_2AlSH + C_2H_6 \\ &Et_3Al + Et_2AlSH \rightarrow (Et_2Al)_2S + C_2H_6 \end{aligned} \qquad (2)$$

On further study, however, we isolated $(EtAlS)_n$ (II) from the same reaction mixture by filtering the white precipitate and found that, although two moles of ethane were still evolved, one mole of Et_3Al remained unreacted in the filtrate. When II was heated at 60°C with one equivalent of Et_3Al, I was indeed formed.

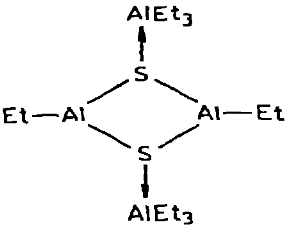
Consequently, we propose an alternative reaction sequence 3 in which II is initially formed and reacts with a second Et_3Al molecule when the mixture is heated to evaporate the solvent. The opposite reaction of the last step has

$$\begin{aligned} &Et_3Al + H_2S \rightarrow Et_2AlSH + C_2H_6 \\ &Et_2AlSH \rightarrow 1/n\ \underset{(II)}{(EtAlS)_n} + C_2H_6 \\ &Et_3Al + 1/n\ (EtAlS)_n \rightleftharpoons \underset{(I)}{(Et_2Al)_2S} \end{aligned} \qquad (3)$$

already been reported [1] as a disproportionation reaction of I at higher temperature. Such a reaction has often been described in the literature for $(R_2Al)_2O$ [4, 5].

A possible structure III in place of I was not considered because of the unsatisfied coordination of the aluminum atom. The reaction product IV from this compound and ethyl acetate also supports the structure I, since the structure III cannot directly supply two Et_2Al groups in this reaction under rather mild conditions.

While I is sparingly soluble in benzene and decomposes rapidly in air, II is practically insoluble in both aliphatic and aromatic hydrocarbon solvents and fairly stable in air. These facts suggest that II has an enhanced inorganic



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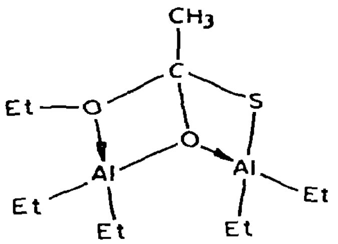
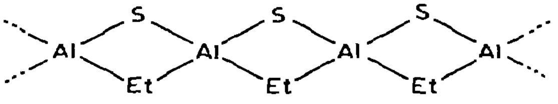


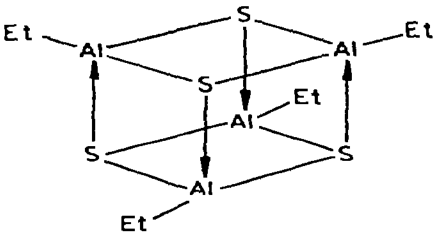
(IV)

character and associates to form a polymeric species V or an oligomer. Among oligomeric structures, a cubic tetramer VI is most probable since analogous



(V)

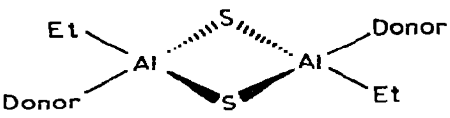
structures have been established for the compounds $(PhAlNPh)_4$ [6] and $(EtZnX)_4$ (X = OMe [7] or halogen [8]) on the basis of X-ray analyses. Unfortunately, the molecular weight of II could not be determined because of its lack of solubility.



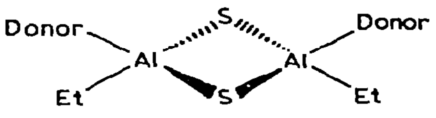
(VI)

Reaction of sulfide II with some donor compounds

Sulfide II dissolved readily in pyridine and white crystals of $(EtAlS)_2 \cdot 2(C_5H_5N)$ precipitated on addition of a large amount of petroleum ether. This product may have structure VIIa or VIIb and showed in its NMR spectrum in pyridine an internal shift, i.e. $\delta(CH_3{-}C{-}Al) - \delta(CH_2{-}Al)$, of 49 Hz which suggests that II is a weaker Lewis acid than Et_3Al (64 Hz for $Et_3Al \cdot C_5H_5N$). Similar products were obtained from 2- and 4-vinylpyridine but not from acetonitrile.



(VIIa)



(VIIb)

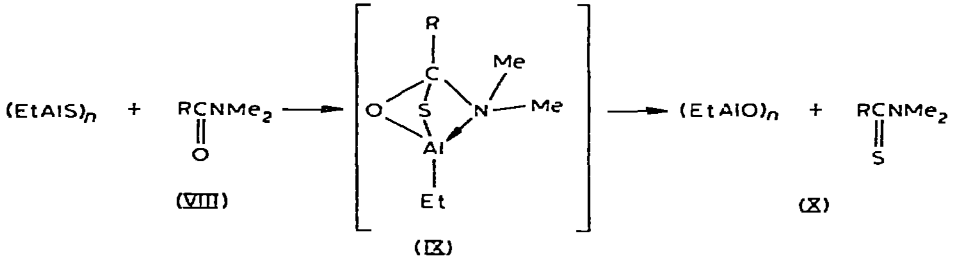
Donor = Pyridine, 2-vinylpyridine and 4-vinylpyridine

TABLE 1

REACTION OF *N,N*-DIMETHYLAMIDES, $RCONMe_2$ (VIII), WITH SULFIDE II

	R	Conditions		Thioamides (X)		
		Temp.	Time (h)	m.p. (°C)	b.p. (°C/Torr)	Yield (%)
VIIIa	CH_3	r.t.	3	74-75		71.5
VIIIb	H	r.t.	3		51-53/1	80.2
VIIIc	C_6H_5	60°C	5		78-81/0.15	68.2

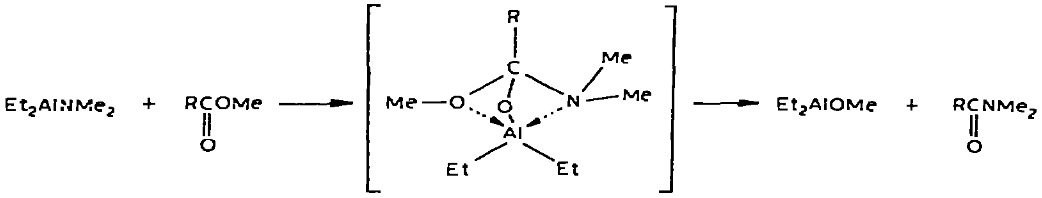
Sulfide II dissolved gradually in an excess of *N,N*-dimethylacetamide (VIIIa) to give a yellowish brown solution. The NMR spectrum of this solution showed absorptions due to *N,N*-dimethylthioacetamide (Xa) and a new Et—Al group, probably of $(EtAlO)_n$. Sublimation at 0.02 Torr gave white needles of Xa in good yield. *N,N*-dimethylformamide (VIIIb) and *N,N*-dimethylbenzamide (VIIIc) underwent similar reactions (Table 1). The thiocarbonylation reactions probably occur as shown in eqn. 4.



(4)

a: R = CH_3
b: R = H
c: R = C_6H_5

A similar reaction sequence has been proposed [2] for the reaction of Et_2AlNMe_2 with organic esters.



(5)

Reactions of II with unsaturated esters at room temperature gave adducts of composition $(EtAlS)_2 \cdot$ (Ester) for methyl α-chloroacrylate and $(EtAlS)_2 \cdot$ 2(Ester) for methyl acrylate and methyl methacrylate as judged from their active Et content. Reactions of II with saturated esters, methyl acetate, ethyl acetate and methyl benzoate, did not occur, in contrast to I, which was found [1, 2] to give distillable 1/1 adducts with these esters.

Experimental

General remarks

All procedures were carried out under dry nitrogen. Petroleum ether (b.p. 60-65°C) or n-hexane, dried over sodium, was used as solvent for reaction. Et_3Al was obtained from Ethyl Corporation Co. Ltd. and distilled immediately before use. Other reagents were purified as usual and dried with extreme care. NMR spectra were recorded with a Hitachi Model R-20B spectrometer.

Ethylaluminum sulfide, $(EtAlS)_n$ (II)

H_2S (1.72 g, 50.7 mmol) was condensed for 1 h with a solution of Et_3Al (12.90 g, 113.2 mmol) in 120 ml of petroleum ether cooled at -78°C. The mixture was gradually warmed to room temperature over 10 h, during which time ethane was evolved continuously and a white powdery solid precipitated. The evolved gas was passed through a conc. aqueous NaOH solution before the measurement of its volume. Ethane evolution ceased at 2158 ml (96.3 mmol) at STP.

The solid was filtered, washed with petroleum ether (50 ml × 4) and dried in vacuo at room temperature. Yield 4.18 g [94% as (EtAlS)]. (Found: Al, 29.90; active ethyl ($Et^\star$), 1.05. C_2H_5AlS calcd.: Al, 30.62%; $Et^\star$, 1.00/mol.)

Bis(diethylaluminum) sulfide, $(Et_2Al)_2S$ (I); reaction of sulfide II with Et_3Al

Et_3Al (2.16 g, 18.9 mmol) was stirred vigorously with II 1.61 g (18.3 mmol) at room temperature. The mixture gradually became greasy and then was warmed at 60°C for 3 h. A white solid again separated. This was dried in vacuo at room temperature. Yield 3.66 g [99.1% as $(Et_2Al)_2S$]. (Found: Al, 26.78; $Et^\star$, 3.98. $C_8H_{20}Al_2S$ calcd.: Al, 26.68%; $Et^\star$, 4.00/mol.)

Reaction of I with ethyl acetate

I (1.01 g, 4.97 mmol) was dissolved in ethyl acetate (0.459 g, 5.21 mmol) to give a red-brown solution. After 5 h at ambient temperature, a 1/1 adduct IV was formed (1.13 g, 78.7% yield) which distilled at 48-49°C/0.04 Torr. The NMR spectrum in benzene showed the following absorptions: τ 6.35 (q, 2H, $COOCH_2$), 7.19 (s, 3H, CH_3CO), ca. 8.8 (broad, t, 15H, $AlOCCH_3$, $AlSCCH_3$ and $COOCCH_3$), and 9.85, 9.90 (two q, 8H, $AlOCH_2$ and $AlSCH_2$).

Reaction of II with pyridine

II (1.76 g, 20.0 mmol) was dissolved in a large excess of pyridine to give a pale yellow solution. After most of the excess pyridine was removed by evaporation, a large amount of petroleum ether was added. A white crystalline product VII began to precipitate on standing. This was filtered and dried in vacuo. Yield 3.27 g [98% as $(EtAlS)_2 \cdot 2(C_5H_5N)$]. (Found: Al, 16.43; $Et^\star$, 2.03. $C_{14}H_{20}Al_2N_2S_2$ calcd.: Al, 16.14%; $Et^\star$, 2.00/mol.)

Reaction of II with 2- or 4-vinylpyridine

Using similar procedures as above, white crystalline products $(EtAlS)_2 \cdot$ 2(2- or 4-vinylpyridine) were obtained in 97 and 98% yields, respectively. (Found:

TABLE 2

PREPARATION OF $(EtAlS)_2 \cdot m(ESTER)$

Ester CH_2=CXCOOMe	$(EtAlS)_n$ (g)	Yield (g)	$Et^{*\,b}$ (ml/g)	m
X = Cl	0.486	0.840 (102.6%)[a]	146.9	1
= H	0.391	0.772 (99.6%)	129.0	2
= CH_3	0.444	0.938 (101.0%)	122.0	2

[a] Based on the adduct with the specified m. [b] Theoretical values are 151.1, 128.2 and 117.2, respectively.

Al, 14.16; Et*, 2.03 for the 2-isomer and Al, 13.99; Et*, 2.01 for the 4-isomer. $C_{18}H_{24}Al_2N_2S_2$ calcd.: Al, 13.96%; Et*, 2.00/mol.)

Reaction of II with N,N-dimethylacetamide, (DMA) (VIIIa)

II (0.808 g, 9.18 mmol) dissolved readily in an excess of VIIIa (10 ml) to give a yellowish brown solution. A viscous liquid (1.59 g) was obtained by a careful evaporation of excess VIIIa under a pressure of > 1 Torr at room temperature. An attempt to isolate the adduct under high vacuum only resulted in the sublimation of *N,N*-dimethylthioacetamide (Xa) (0.676 g, 71.5% yield); white needles, m.p. 74-75°C, (lit. [9] 73-74°C); NMR spectrum in 10% solution of CCl_4, τ 7.39 (s, 3H, CH_3CS), 6.64 (s, 3H, *anti*-NCH_3), 6.54 (s, 3H, *syn*-NCH_3). (Found: C, 46.80; H, 8.60; N, 13.46. C_4H_9NS calcd.: C, 46.58; H, 8.79; N, 13.56%.)

Reaction of II with N,N-dimethylformamide, (DMF) (VIIIb)

II (0.928 g, 10.5 mmol) and an excess of VIIIb (10 ml) were allowed to react at room temperature. The resulting deep green solution was distilled and *N,N*-dimethylthioformamide (Xb) was obtained (0.749 g, 80.2%); b.p. 51-53°C/1 Torr, (lit. [10] 96-97°C/12 Torr); NMR spectrum in 10% solution of CCl_4, τ 6.75 (s, 3H, *anti*-NCH_3), 6.61 (s, 3H, *syn*-NCH_3), and 0.80 (s, 1H, HCO).

Reaction of II with N,N-dimethylbenzamide, (DMB) (VIIIc)

A mixture of II (0.714 g, 8.11 mmol) and VIIIc (1.215 g, 8.15 mmol) was warmed at 60°C for 5 h. It became a homogeneous yellow liquid within 1 h. Distillation gave Xc (0.912 g, 68.2%); b.p. 78-81°C/0.15 Torr, (lit. [11] 180°C/18 Torr); NMR spectrum in 10% solution of CCl_4; τ 6.92 (s, 3H, *anti*-NCH_3), 6.55 (s, 3H, *syn*-NCH_3), and 2.80 (s, 5H, C_6H_5).

Reactions of II with some unsaturated esters

II was dissolved with vigorous stirring in 10-11 molar equivalents of the unsaturated ester at room temperature. Then the excess ester was removed by evaporation. The yellow residue was dried in vacuo to a constant weight. Table 2 summarizes the results.

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