

INSERTION REACTIONS OF DIETHYLALUMINIUM DERIVATIVES

VI. REACTIONS OF BIS(DIETHYLALUMINIUM) SULFIDE AND DIETHYLALUMINIUM THIOLATE OR AMIDE WITH ESTERS

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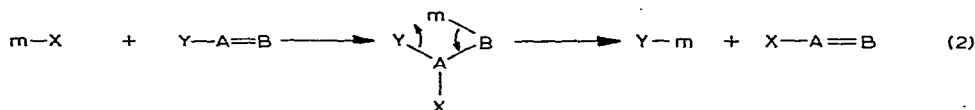
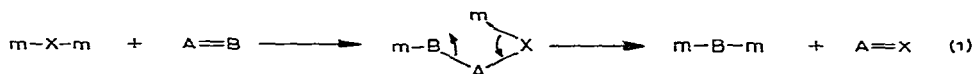
SUMMARY

The reactions of bis(diethylaluminium) sulfide with organic esters gave stable 1/1 adducts. Elimination of diethylaluminium alcoholate was observed when large alkyl substituents were present in the esters.

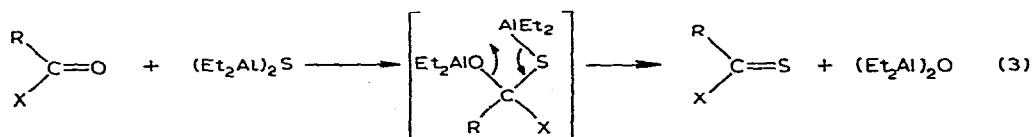
Similar elimination of diethylaluminium alcoholate occurred in the reactions of diethylaluminium thiolate or amide, Et_2AlX ($\text{X}=\text{SEt}$ or NMe_2), with esters to give the corresponding thioesters or amides.

INTRODUCTION

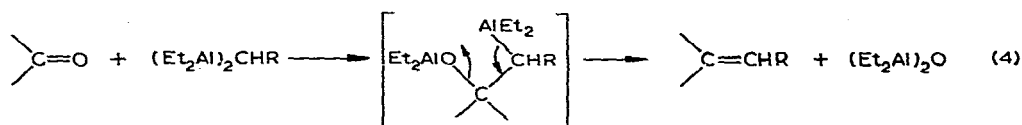
Many addition-elimination reactions of Group IV organometallic compounds have been investigated¹. The reactions can be generally represented by the following equations:



Some of these addition-elimination reactions have been useful in organic syntheses. Thus, in our previous paper², it was shown that bis(diethylaluminium) sulfide can be used as a thiocarbonylation agent with various carbonyl compounds (eqn. 3).



In this connection, the following pseudo-Wittig reactions of organoaluminium compounds^{3,4} (eqn. 4) can also be included in the addition-elimination reactions represented by eqn. (1).



The ready occurrence of these thiocarbonylation and pseudo-Wittig reactions in organoaluminium chemistry depends on the strong tendency for the formation of the stable Al-O-Al linkage.

In the course of extensive studies on the chemical behaviour of bis(diethylaluminium) sulfide, unexpected results were obtained by the reaction with esters. In this paper, we first describe the isolation of the stable 1/1 adducts and the occurrence of the addition-elimination reaction via eqn. (2). Secondly we discuss the interaction of diethylaluminium thiolate or amide with esters in addition-elimination reactions of the type shown in eqn. (2).

RESULTS AND DISCUSSION

In thiocarbonylation with bis(diethylaluminium) sulfide, the stability of thiocarbonyl compounds produced and the ease of the isolation procedures are important². Initially we expected that the easy conversion of esters into the corresponding thio esters would occur in the reaction of eqn. (5), which corresponds to eqn. (3). However the distillates obtained from the equimolar reactions with various esters had sharp boiling points, and the analyses agreed well with 1/1 adducts (Table 1). These adducts were thermally stable, but extremely sensitive to air and moisture.

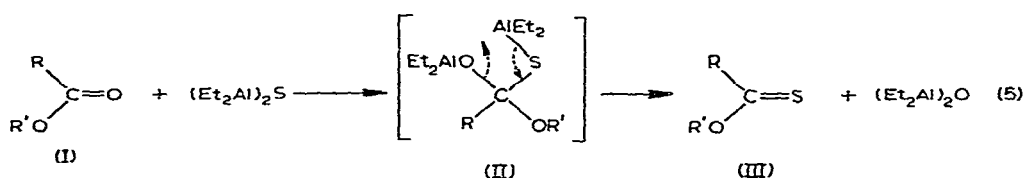


TABLE 1

ANALYTICAL DATA FOR RC(OMe)(OAlEt₂)(SAlEt₂)

R		Analysis, found (calcd.) (%)		
		C	H	Al
Methyl	(IIa)	47.67(47.81)	9.57(9.49)	19.67(19.52)
Cyclopropyl	(IIc)	51.53(51.64)	9.52(9.53)	17.71(17.88)
Phenyl	(IIl)	56.42(56.78)	8.64(8.34)	15.81(15.94)
2-Furyl	(IIg)	51.05(51.21)	7.97(7.98)	16.29(16.45)

TABLE 2

PHYSICAL AND SPECTROSCOPIC DATA FOR RC(OMe)(OAlEt₂)(SAlEt₂)

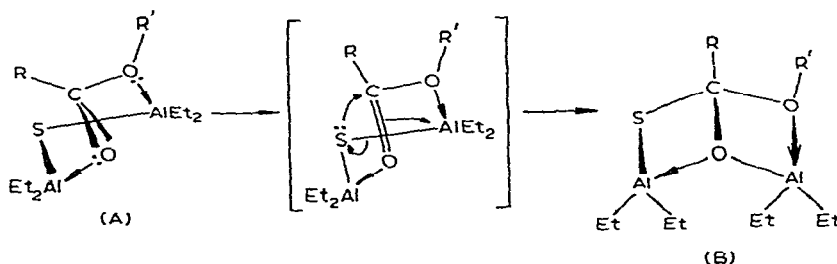
R	No.	B.p. (°C/mmHg)	Yield ^a (%)	NMR (τ) ^b			IR (cm ⁻¹)	
				OCH ₃	AlCCH ₃	AlCH ₂	ν(Al-O-C)	ν(C=O) ^c
Me	(IIa)	65-67/0.15	71	6.75	8.71	9.78	985	1635
i-Pr	(IIb)	66-70/0.1	70	6.80	8.81	9.85	985	1650
	(IIc)	82-83/0.2	83	6.76	8.83	9.90	985	1635
Ph	(IIf)	97-101/0.2	58	6.65	8.69	9.83	980	1640
	(IIg)	92-95/0.3	46	6.78	8.77	9.98	980	1650

^a The yields are based on the amounts actually distilled. There was no lower boiling product such as Et₂AlOMe. ^b The NMR spectra were measured as 15% solutions in benzene. Proton signals of OCH₃ in the starting esters appeared at τ 6.58 (Ia), 6.60 (Ib), 6.65 (Ic), 6.40 (If) and 6.41 (Ig). ^c These values were recorded after 1 h reaction, and correspond to the chelating intermediate (A).

Surprisingly, the isolated 1/1 adducts (II) did not show any characteristic stretching frequencies due to carbonyl or thiocarbonyl groups and must thus be insertion products. All the other spectroscopic data listed in Table 2 can be explained in terms of the *ortho* ester structure, RC(OMe)(OAlEt₂)(SAlEt₂).

Soon after the ester was added to bis(diethylaluminium) sulfide, the carbonyl stretching vibration of the parent esters shifted to lower wave numbers by about 100 cm⁻¹ (see the last column of Table 2), then gradually disappeared. Accordingly, the first step of the addition must be a coordination of esters to (Et₂Al)₂S to give complex (A). Subsequently, the nucleophilic attack of SAlEt₂ group to the coordinated carbonyl carbon atom takes place, with simultaneous σ-bonding between the other aluminium atom and the carbonyl oxygen atom. The process is illustrated in Scheme 1.

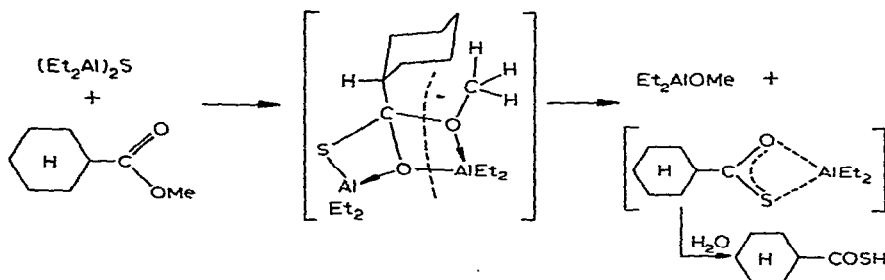
SCHEME 1



The thermal stability of the adducts (II) can be reasonably attributed to the two sets of intramolecular coordinations between oxygen and aluminium atoms, depicted in (B), in which the coordination number of each of the two oxygen atoms is three and that of each aluminium atom is four. The ready isolation of the *ortho* ester adducts (II) is in contrast with the instability of the intermediate adducts such as RR'C(OMe)-(OMgX) formed in the Grignard reaction between RCO₂Me and R'MgX⁵.

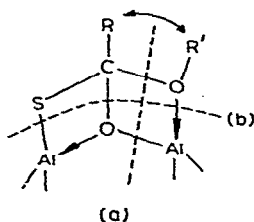
The stability of the 1/1 adducts (II) should decrease when the steric repulsion between mutually *cis*-located alkyl groups R and R', becomes significant [see structure (B) in Scheme 1]. Selective elimination of diethylaluminium methanolate (b.p. 43–45°/0.3 mmHg) was, in fact, observed in the reaction of bis(diethylaluminium) sulfide with methyl cyclohexanecarboxylate (R=cyclohexyl, R'=methyl). Hydrolysis of the distillation residue gave thiocyclohexanecarboxylic acid [$\nu(\text{C}=\text{O})$, 1690 and $\nu(\text{S}-\text{H})$, 2680 cm^{-1}] as the other fragment. Thus this addition–elimination process seems to involve the processes shown in Scheme 2.

SCHEME 2

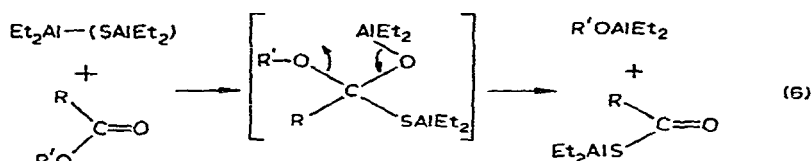


Similar elimination of diethylaluminium methoxide was observed in the case of methyl pivalate (R=tert-butyl, R'=methyl). The steric effect on the stability of adduct for the methyl ester series appears between R=tert-butyl and isopropyl, giving a 1/1 adduct, as shown in Table 2. The reaction of isopropyl isobutyrate (R=R'=i-Pr) with bis(diethylaluminium) sulfide was thus examined to clarify the borderline region. Although it was difficult to separate the products in a pure form because of the closeness of their boiling points, the distillate was a mixture of nearly equal amounts of the adduct, i-PrC(O-i-Pr)(OAlEt₂)(SAlEt₂), and one of the elimination fragments, (Et₂AlO-i-Pr)₂. The amounts of these two components were estimated from the NMR peak intensities of two different OCH(CH₃)₂ signals (see Experimental section).

The elimination of diethylaluminium alcoholate, Et₂AlOR', (path a) is preferred to elimination of (Et₂Al)₂O, giving thiocarbonylation as represented in eqn. (1) (path b), probably because of the larger release of steric strain.



If the elimination of aluminium alcoholate is rewritten as in eqn. (6), this addition–elimination reaction can reasonably be classed with the processes generally represented by eqn. (2).



In view of the above results, it seemed of interest to examine the reaction of esters with Et_2AlX ($\text{X}=\text{SEt}$, NMe_2). The expected adducts could have only one aluminium atom, and the stabilization by formation of a rigid structure of type (B) would be impossible. The reaction of diethylaluminium ethanethiolate with various esters in fact gave diethylaluminium methanolate and the corresponding *S*-ethyl thio esters. Similarly, diethylaluminium dimethylamide gave the corresponding acid amides according to eqn. (7), but the reactivity was lower than that of the ethanethiolate. The results are summarized in Table 3.

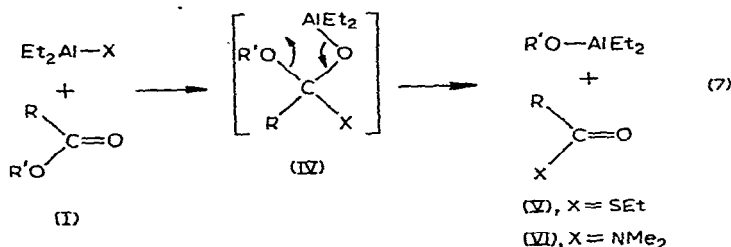


TABLE 3

 PHYSICAL AND SPECTROSCOPIC DATA FOR $\text{RC}(=\text{O})\text{X}$

X	R	No.	B.p. (°C/mmHg)	Yield (%)	NMR (τ) ^a			IR (cm^{-1}) $\nu(\text{C}=\text{O})$
					R	SEt	NMe ₂	
SEt	Me	(Va)	57-60/130	66	8.02 (s)	7.30 (q) 8.95 (t)		1692
	i-Pr	(Vb)	47-48/20	73	8.85 (d) 7.66 (h)	7.33 (q) 8.97 (t)		1685
	t-Bu	(Vd)	57-58/20	79	8.90 (s)	7.28 (q) 8.93 (t)		1675
	H	(Ve)	73-75/5	63	8.2 (m) 8.7 (m)	7.29 (q) 8.93 (t)		1688
	Me	(VIa)	m.p. 66-67	22	8.85 (s)		7.70 (s) 7.35 (s)	1658
NMe ₂	t-Bu	(VIId)	41-42/3	53	8.29 (s)		7.35 (s)	1630

^a In benzene 15% solution at 20°.

These reactions can be considered essentially analogous to the acid-catalyzed ester replacement reactions of organic chemistry; in other words, Et_2AlSEt can be regarded as an active ethylmercaptan containing an acid catalytic site within the molecule. The procedure seems likely to be useful for synthesis of thio esters.

In the unstable intermediate (IV), the elimination of $\text{Et}_2\text{AlOR}'$ ($\text{R}' = \text{Me}$) should occur without the need for any steric assistance. In agreement with this, the change from $\text{R} = \text{Me}$ to cyclohexyl was found not to affect the mode of reaction.

EXPERIMENTAL

General remarks and materials

All the reactions were carried out under argon in dry benzene. IR and NMR spectra were recorded with a Japan Spectroscopic Co. Model IR-S and a Japan Electron Optics Co. Model C-60HL, respectively. Elemental analyses of organo-aluminium adducts were carried out by Alfred Bernhardt Mikroanal. Lab.

$(\text{Et}_2\text{Al})_2\text{S}$, Et_2AlSEt and $\text{Et}_2\text{AlNMe}_2$ were prepared as described in our previous papers^{2,6}.

Reactions of $(\text{Et}_2\text{Al})_2\text{S}$ with methyl acetate (Ia), isobutyrate (Ib), cyclopropylcarboxylate (Ic), benzoate (If) and furoate (Ig)

A typical reaction was carried out as follows. Methyl acetate (Ia) 0.501 g (6.77 mmole) in 2 ml benzene solution was added dropwise at room temperature to a 5 ml benzene suspension of $(\text{Et}_2\text{Al})_2\text{S}$, 1.36 g (6.73 mmole), and the temperature was subsequently kept at 50° . The IR spectral change of the mixture was observed: an absorption at 1740 cm^{-1} [$\nu(\text{C}=\text{O})$ in (Ia)] decreased as a new absorption at 1635 cm^{-1} increased; the latter also disappeared completely after 5 h. The mixture became yellow. After the removal of benzene under reduced pressure, the yellow liquid residue, $\text{MeC(OMe)(OAlEt}_2\text{)(SAlEt}_2\text{)}$ (IIa), was distilled at b.p. $65\text{--}67^\circ/0.15\text{ mmHg}$, in 71% yield. Physical data and elemental analyses data are summarized in Tables 2 and 1, respectively, which include the products from other esters.

Other esters (Ib, c, f, g) (6–9 mmole) also were reacted with equimolar amounts of $(\text{Et}_2\text{Al})_2\text{S}$ under the same conditions to give the corresponding distillable adducts, (IIb, c) (yellow) and (IIf, g) (red), respectively.

Reactions of $(\text{Et}_2\text{Al})_2\text{S}$ with methyl cyclohexanecarboxylate (Ie) and methyl pivalate (Id)

Methyl cyclohexanecarboxylate (Ie), 1.01 g (6.90 mmole) was allowed to react with $(\text{Et}_2\text{Al})_2\text{S}$, 1.40 g (6.93 mmole) in the manner described above. The carbonyl absorption of the ester disappeared completely after 5 h at 50° . Removal of the benzene followed by distillation under reduced pressure gave a colorless liquid; b.p. $43\text{--}45^\circ/0.3\text{ mmHg}$ 0.684 g (78%). This fraction showed only three NMR signals (in benzene) at τ 6.75 (s) (OCH_3), 8.28 (t) and 9.98 (q) (AlCH_2CH_3), and its properties were consistent with those of authentic Et_2AlOMe ⁷.

The distillation residue was hydrolyzed and then extracted with ether to give small amounts of a yellow oil, 0.165 g (15%), having IR absorptions at 2660 and 1690 cm^{-1} , which was identified as $\text{C}_6\text{H}_{11}\text{C(=O)SH}$.

From the reaction of methyl pivalate (Id), Et_2AlOMe (51%) was obtained by distillation of the mixture and $t\text{-BuC(=O)SH}$ (ca. 10%) after hydrolysis of the residue.

Reaction of $(\text{Et}_2\text{Al})_2\text{S}$ with isopropyl isobutyrate (Ih)

$(\text{Et}_2\text{Al})_2\text{S}$, 2.14 g (10.6 mmole) was allowed to react with equimolar amounts of

(Ih), 1.37 g in benzene at 50°. The band at 1728 cm⁻¹ disappeared and a new absorption appeared at 1625 cm⁻¹, probably attributable to aluminium thiocarboxylate. After stirring for 15 h, removal of the benzene followed by distillation of the residue gave one fraction with a wide boiling point range (50–70°/0.1 mmHg), 1.80 g. The nature of the NMR spectrum, and the absence of any absorption at 1625 cm⁻¹, showed that this fraction consisted of *i*-PrC(O-*i*-Pr)(OAlEt₂)(SAlEt₂) (IIh) and *i*-PrOAlEt₂; the NMR assignments were as follows: adduct: τ 8.97 (d), 7.65 (h) (CH₃CHC) and 8.88 (d), 6.02 (h) (CH₃CHO); *i*-PrOAlEt₂: 8.90 (d), 6.04 (h) (CH₃CHO).

The residue was found to contain mainly (*i*-PrCOSAIEt₂)_n, as indicated by the NMR [8.97 (d), 7.62 (h)] and IR [ν (C=O) 1615 cm⁻¹] spectra. The overall ratio of the products, estimated from the NMR intensity of peaks in the original reaction mixture, corresponded to 57% of adduct formation and 43% of elimination.

Reactions of Et₂AlSEt with esters

A typical procedure was as follows. (Ia) (0.845 g, 11.4 mmole) in 3 ml of benzene was added dropwise to 4 ml of a benzene solution of Et₂AlSEt, 1.65 g (11.3 mmole). A new absorption at 1692 cm⁻¹ in the IR spectra increased gradually as the band 1740 cm⁻¹ decreased. After stirring for 15 h at 50°, the latter absorption had disappeared. Benzene was removed, and the residue distilled to give *S*-ethyl thioacetate (Va), 0.896 g (66%), b.p. 57–60°/130 mmHg (lit.⁸ b.p. 116°). NMR data for the thioesters (V) are shown in Table 3. From the NMR spectrum, the residue was shown to be Et₂-AlOMe, b.p. 40–42°/0.3 mmHg, 0.91 g (70%).

Similarly, methyl isobutyrate (Ib), pivalate (Id), or cyclohexanecarboxylate (Ie) was allowed to react with Et₂AlSEt to give the corresponding *S*-ethyl thioesters: (Vb), b.p. 47–48°/20 mmHg (lit.⁹ 156–158°), (Vd), b.p. 57–58°/20 mmHg (lit.¹⁰ 105°/100 mmHg); (Ve), b.p. 73–75°/5 mmHg (lit.¹¹ 81–82°/6 mmHg), respectively. Under lower pressures, Et₂AlOMe was also obtained in each case.

Reactions of Et₂AlNMe₂ with esters

The reaction was carried out in the same manner as described for Et₂AlSEt, but under more severe conditions. After 40 h refluxing, the absorption at 1740 cm⁻¹ due to ester disappeared completely, and the band at 1685 cm⁻¹ due to amide was enhanced. Removal of benzene followed by distillation gave *N,N*-dimethylacetamide (VIa), b.p. 82–83°/30 mmHg (lit.¹² 135°/758 mmHg), 0.314 g (22%). The low yield is a result of purification difficulties arising from the higher m.p. (66–67°) of the product.

Methyl pivalate (Id) was also converted into *N,N*-dimethylpivalamide (VI_d), b.p. 41–42°/3 mmHg (lit.¹³ 43°/3 mmHg) in 53% yield. The NMR data for (VI) are summarized in Table 3.

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