

## INSERTION REACTIONS OF DIETHYLALUMINIUM DERIVATIVES III. REACTIONS OF DIETHYLALUMINIUM DIMETHYLAMIDE, ETHANETHIOLATE AND ETHANOLATE WITH LACTONES OR ACID ANHYDRIDES

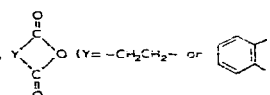

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### SUMMARY

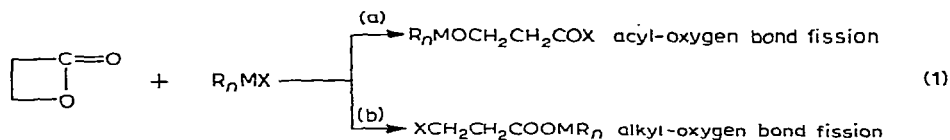
Diethylaluminium derivatives,  $\text{Et}_2\text{AlX}$  ( $\text{X} = \text{NMe}_2$  or  $\text{OEt}$ ) were found to react with  $\beta$ -propiolactone by Al-X bond cleavage of the  $\text{Et}_2\text{AlX}$  and acyl-oxygen bond fission of the lactone to give selectively the corresponding diethylaluminium (2-aminocarbonyl)ethanolate or (2-alkoxycarbonyl)ethanolate  $\text{Et}_2\text{AlOCH}_2\text{CH}_2\text{COX}$ . In the case of  $\text{Et}_2\text{AlSEt}$ , the products were the mixture of  $\text{Et}_2\text{AlOCH}_2\text{CH}_2\text{COSEt}$  and  $\text{EtSCH}_2\text{CH}_2\text{COOAlEt}_2$ . The reactions of  $\text{Et}_2\text{AlNMe}_2$  with  $\gamma$ -butyrolactone or phthalide occurred with acyl-oxygen bond fission.

Acid anhydrides,  (Y =  $-\text{CH}_2\text{CH}_2-$  or ) react with one molar proportion of

$\text{Et}_2\text{AlNMe}_2$  to give mainly  $\text{Me}_2\text{NCOYCOOAlEt}_2$  and with two molar proportions to give the diamide.

### INTRODUCTION

Cationic polymerization and copolymerizations of  $\beta$ -propiolactone with  $\text{Et}_3\text{Al}^1$ ,  $\text{Et}_3\text{Al}/0.5 \text{H}_2\text{O}^{1,2}$  or organozinc compounds<sup>3</sup> as catalysts has been described. We have been interested in the stoichiometric reactions of  $\beta$ -propiolactone with organometallic compounds,  $\text{R}_n\text{MX}$  ( $\text{X} = \text{NR}_2$ ,  $\text{PR}_2$ ,  $\text{OR}$ ,  $\text{SR}$  and  $\text{M}$  a Group IIB IIIA or IVA metal), since the selectivity between two types of ring-opening reaction of  $\beta$ -propiolactone would depend on the natures of both metal  $\text{M}$  and group  $\text{X}$ .



Recently, Itoh *et al.* showed that in the reactions between  $\beta$ -propiolactone and Group IVA metal amides,  $\text{Me}_3\text{SiNR}_2^4$  and  $\text{Me}_3\text{GeNR}_2^5$  gave only alkyl-oxygen bond fission products while  $\text{Me}_3\text{SnNMe}_2^5$  gave acyl-oxygen fission, and Noltes *et al.*<sup>7</sup> showed that the reaction of  $\beta$ -propiolactone with  $\text{EtZnOMe}$  and  $\text{EtZnNPh}_2$  also involves acyl-oxygen fission.

The reaction between equimolar amounts of  $\beta$ -propiolactone and  $\text{R}_2\text{AlX}$  have not previously been studied, though the reactions of  $\text{Et}_2\text{AlX}$  ( $\text{X} = \text{NMe}_2$ ,  $\text{SEt}$  and  $\text{OEt}$ ) with the unsaturated bonds of isocyanates or nitriles, involving  $\text{Al-X}$  bond cleavage, have been described<sup>7,8</sup>. In this paper we describe the reactions of  $\text{Et}_2\text{AlX}$  with lactones, and acid anhydrides.

## EXPERIMENTAL

### General

Diethylaluminium derivatives  $\text{Et}_2\text{AlX}$  [ $\text{X} = \text{NMe}_2$  (Ia) b.p.  $71-73^\circ/0.15$  mm,  $\text{SEt}$  (Ib) b.p.  $84-85^\circ/0.05$  mm,  $\text{OEt}$  (Ic) b.p.  $61-63^\circ/0.3$  mm) were prepared<sup>8</sup> from  $\text{Et}_3\text{Al}$  and the corresponding bases  $\text{HX}$ , and purified by distillation. Commercial lactones and acid anhydrides were redistilled or recrystallized. Hydrocarbon solvents were dried with  $\text{Na}$  wire and  $\text{CaH}_2$ . All procedures, including the treatment of products, were carried out under dry nitrogen as previously described<sup>7</sup>.

### Reaction of diethylaluminium dimethylamide (Ia) with $\beta$ -propiolactone (IIa)

A solution of compound (Ia) 1.707 g (13.23 mmole) in 10 ml of benzene was frozen at  $-78^\circ$  and (IIa) 0.960 g (13.34 mmole) was added at once with a syringe. The temp. was slowly raised to room temp. The reaction tube was stoppered tightly and kept at  $70^\circ$  for 8 h. Benzene and unreacted lactone were removed under reduced pressure and the solid residue was washed several times with benzene/*n*-hexane 1/9. A white crystalline product, diethylaluminium 2-[(dimethylamino)carbonyl]ethano-

TABLE I

NMR CHARACTERISTICS OF  $\text{Et}_2\text{AlOX-CONMe}_2$  AND  $-\text{COOEt}$  IN BENZENE<sup>a</sup>

Compounds		Assignment of chemical shifts $\tau$					
		$\text{Et}_2\text{Al-}$	$-\text{OCH}_2-$	$-\text{CH}_2-$	$-\text{CH}_2\text{CO-}$	$-\text{NMe}_2$	$-\text{OEt}$
$\text{Et}_2\text{AlO}(\text{CH}_2)_2\text{CONMe}_2$	(IIIa)	9.63 (q) 8.39 (t)	6.12 (t)		7.98 (t)	8.09 (s) 7.50 (s)	
$\text{Et}_2\text{AlO}(\text{CH}_2)_2\text{COOEt}$	(IIIb)	9.97 (q) 8.82 (t)	6.43 (t)		7.95 (t)		8.89 (t) 6.19 (q)
$\text{Et}_2\text{AlO}(\text{CH}_2)_3\text{CONMe}_2$	(IIIc)	9.75 (q) 8.60 (t)	6.35 (t)	8.26 (q) <sup>b</sup>	7.75 (t)	7.62 (s) 7.33 (s)	
$\text{Et}_2\text{AlOCH}_2\text{C}_6\text{H}_4\text{CONMe}_2$	(IIIc)	9.70 (q) 8.55 (t)	5.32 (q)			7.50 (s) 7.13 (s)	
$\text{Et}_2\text{AlOCOC}_6\text{H}_4\text{CONMe}_2$	(VIa)	9.75 (q) 8.64 (t)				7.42 (s) 7.20 (s)	

<sup>a</sup> Starting materials:  $\text{Et}_2\text{AlNMe}_2$  [ $\tau$  9.94, quartet (q), 8.87, triplet (t), 7.89, singlet (s)],  $\text{Et}_2\text{AlSEt}$  [ $\tau$  9.80 (q), 8.90 (t), 9.04 (t), 7.70 (q)],  $\text{Et}_2\text{AlOEt}$  [ $\tau$  9.87 (q), 8.73 (t), 8.91 (t), 6.45 (q)],  $\beta$ -propiolactone [ $\tau$  6.27 (t), 6.99 (t),  $J = 5.4$  Hz]. <sup>b</sup> quintuplet.

late (IIIa), (nc), m.p.  $> 122^\circ$  (decomp.) was obtained in 99% yield. (Found: C, 53.36; H, 9.63; Al, 14.07; N, 6.36; active ethyl groups 1.69.  $C_9H_{20}AlNO_2$  calcd.: C, 53.71; H, 10.02; Al, 13.41; N, 6.96%; active ethyl groups 2.00/mole.) NMR and IR data of (IIIa) are shown in Table 1 and Table 3, respectively.

TABLE 2

NMR CHARACTERISTICS OF PROTONOLYSIS PRODUCTS IN BENZENE

Compounds	Assignment of chemical shifts $\tau$	Assignment of chemical shifts $\tau$						
		HO-	-OCH <sub>2</sub> -	-CH <sub>2</sub> -	-CH <sub>2</sub> CO-	-NMe <sub>2</sub>	-SEt	-OEt
HO(CH <sub>2</sub> ) <sub>2</sub> CONMe <sub>2</sub> (IVa)	6.90 (t)	6.10 (t)		7.76 (t)	7.61 (s) 7.35 (s)			
HO(CH <sub>2</sub> ) <sub>2</sub> COSEt (IVd)	6.85 (s)	6.28 (t)		7.48 (t)		8.98 (t) 7.27 (q)		
EtS(CH <sub>2</sub> ) <sub>2</sub> COOH (IVe)	-1.8 br	7.60 (t) (SCH <sub>2</sub> )		7.51 (t)		8.99 (t) 7.74 (q)		
HO(CH <sub>2</sub> ) <sub>2</sub> COOEt (IVf)	6.22 (s)	6.12 (t)		7.55 (t)			8.96 (t) 5.93 (q)	
HO(CH <sub>2</sub> ) <sub>3</sub> CONMe <sub>2</sub> (IVb)	6.35 (s)	6.10 (t)	8.03 (q)	7.53 (t)	7.05 (s) 6.89 (s)			

TABLE 3

IR CHARACTERISTICS OF THE ADDUCTS FROM REACTIONS OF LACTONES OR ACID ANHYDRIDES WITH Et<sub>2</sub>AlX IN BENZENE

Compounds		$\nu(C=O)$ (cm <sup>-1</sup> )	Other characteristic absorptions (cm <sup>-1</sup> )
Et <sub>2</sub> AlO(CH <sub>2</sub> ) <sub>2</sub> CONMe <sub>2</sub> (IIIa)		1626	1400, 1160, 1100, 1060, 945, 895, 620
Et <sub>2</sub> AlO(CH <sub>2</sub> ) <sub>3</sub> CONMe <sub>2</sub> (IIIb)		1630	1495, 1460, 1405, 1220, 1150, 1025
Et <sub>2</sub> AlOCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CONMe <sub>2</sub> (IIIc)		1626	1445, 1404, 1270, 1190, 1035, 825, 740
Et <sub>2</sub> AlOCOC <sub>6</sub> H <sub>4</sub> CONMe <sub>2</sub> (VIb)		1645	1600, 1495, 1425, 1260, 1060, 1005, 805
		1570	
Et <sub>2</sub> AlO(CH <sub>2</sub> ) <sub>2</sub> COSEt/ } EtS(CH <sub>2</sub> ) <sub>2</sub> COOAlEt <sub>2</sub> }	(III d)	1680 1635 <sup>a</sup> 1585	1458, 1385, 1265, 1095, 990, 815, 635
Et <sub>2</sub> AlO(CH <sub>2</sub> ) <sub>2</sub> COOEt (III f)		1730	1450, 1405, 1380, 1350, 1190, 1060, 900

<sup>a</sup> Reaction conditions: 70° for 24 h; the band at 1635 cm<sup>-1</sup> appeared under other conditions, for example at 0° after 10 h.

*Protonolysis of diethylaluminium 2-[(dimethylamino)carbonyl]ethanolate (IIIa)*

Compound (IIIa), 1.69 g was treated at 0° with 18 ml of 50% aq. ethanol containing ten drops of conc. HCl. When the gas evolution ceased, the pH of the mixture was adjusted to 6.4–6.8 by addition of aq. ammonia. The oily product which separated was distilled to give  $\beta$ -hydroxy-*N,N*-dimethylpropionamide (IVa), b.p. 55–57°/0.06 mm, 0.70 g (71%), (lit.<sup>57</sup> b.p. 71–74°/0.17 mm) as a colourless liquid. The distillation residue was polyacrylamide. NMR and IR data of (IVa) are summarized in Table 2 and Table 4, respectively.

TABLE 4

THE  $\nu(\text{C}=\text{O})$  ABSORPTION BAND IN THE STARTING MATERIAL AND IN THE PROTONOLYZED CARBONYL COMPOUNDS IN BENZENE

Starting compounds		$\nu(\text{C}=\text{O})$ ( $\text{cm}^{-1}$ )	Hydrolyzed compounds		$\nu(\text{C}=\text{O})$ ( $\text{cm}^{-1}$ )
$\beta$ -propiolactone	(IIa)	1843	$\text{HO}(\text{CH}_2)_2\text{CONMe}_2$	(IVa)	1630
		1830	$\text{HO}(\text{CH}_2)_3\text{CONMe}_2$	(IVb)	1631
$\gamma$ -butyrolactone	(IIb)	1780	$\text{HO}(\text{CH}_2)_2\text{COSEt}$	(IVd)	1685
phthalide <sup>a</sup>	(IIc)	1770	$\text{EtS}(\text{CH}_2)_2\text{COOH}$	(IVe)	1714
succinic anhydride <sup>a</sup>	(Va)	1860	$\text{HO}(\text{CH}_2)_2\text{COOEt}$	(IVf)	1735
		1780			
phthalic anhydride <sup>a</sup>	(Vb)	1850	$\text{HOCO}(\text{CH}_2)_2\text{CONMe}_2$	(VIIa)	1728, 1653
		1765	$\text{Me}_2\text{NCO}(\text{CH}_2)_2\text{CONMe}_2$	(VIII)	1648
			$\text{HOCOC}_6\text{H}_4\text{CONMe}_2$	(VIIb)	1715, 1640

<sup>a</sup> By KBr tablet method.*Reaction of triethylaluminium with  $\beta$ -hydroxy-*N,N*-dimethylpropionamide (IVa) and *N,N*-dimethyl- $\beta$ -alanine*

$\text{Et}_3\text{Al}$ , 0.825 g (8.11 mmole) in 5 ml of benzene was added dropwise to (IVa) (prepared as described in ref. 10), 0.955 g (8.16 mmole) in 15 ml of benzene cooled at  $0^\circ$ . Ethane evolution was violent and quantitative. Removal of the benzene gave compound (IIIa).

The equimolar reaction between  $\text{Et}_3\text{Al}$  and  $\beta$ -(dimethylamino)alanine, m.p.  $141\text{--}143^\circ$ , (4.20 mmole) in 10 ml of benzene gave a 91% yield of ethane, but the product remained as a viscous yellow liquid even after evaporation of the benzene under vacuum.

*Reaction of diethylaluminium ethanethiolate (Ib) with (IIa)*

The reaction of equimolar amounts of (Ib) and (IIa) gave the transparent yellow solid (IIIId-A) in 96% yield under the conditions used for (Ia) and (IIa). The IR spectrum in benzene showed absorptions at 1680 and  $1585\text{ cm}^{-1}$ . A slow decomposition occurred in the broad temp. range ( $110\text{--}140^\circ$ ).

When the reaction was carried out at  $0^\circ$  without freezing and with dropwise addition bringing the final temp. up to  $20^\circ$ , the yellow liquid mixtures (IIIId-B) obtained showed the two carbonyl absorptions along with a band at  $1635\text{ cm}^{-1}$  assignable to some other species. Elemental analyses of both (IIIId-A) and (IIIId-B) were nearly consistent with a 1/1 adduct. (IIIId-B) was converted into (IIIId-A) after retreatment at  $70^\circ$  for 20 h. We could not separate both compounds from (IIIId-A) or (IIIId-B).

*Protonolysis of the mixture (IIIId-A, B)*

Protonolysis of (IIIId-A) was carried out as with (IIIa). Extraction with ether, chloroform and benzene, was followed by distillation to give mainly *S*-ethyl  $\beta$ -hydroxypropionethiolate (IVd) (44%), b.p.  $44\text{--}45^\circ/0.15\text{ mm}$ . Attempts to isolate organic compounds from the aq. layer were unsuccessful. Protonolysis of (IIIId-B) was carried out with 20 ml ether saturated with HCl gas. After the aluminium hydroxide had been filtered off, large amounts of ether were added and then extracted with small amounts

of water. The product from the ether soluble part was (IVd), and the fraction boiling at 80–95°/0.7–1.0 mm from the aq. part was mainly  $\beta$ -ethylthiopropionic acid (IVe) along with small amounts of (IVd).

*Reaction of Et<sub>3</sub>Al with  $\beta$ -ethylthiopropionic acid (IVe)*

Equimolar amounts of Et<sub>3</sub>Al and (IVe), b.p. 97–98°/1.0 mm (see ref. 10) reacted with quantitative evolution of ethane and gave the brown solid, diethylaluminium  $\beta$ -ethylthiopropionate (IIIe), m.p. 242–245°, which had only one IR absorption band at 1580 cm<sup>-1</sup> in the carbonyl region. (IIIe) underwent no change on heating at 70° for 20 h.

*Reaction of diethylaluminium ethanolate (Ic) with (IIa) and protonolysis of the reaction products*

Equimolar amounts of (Ic) and (IIa) reacted to give a white crystalline product, diethylaluminium 2-(ethoxycarbonyl)ethanolate (IIIf) (96%), m.p. > 120° (decomp.), which showed one carbonyl absorption at 1730 cm<sup>-1</sup> in IR spectra. (Found: C, 52.66; H, 9.46; Al, 13.30; active ethyl groups 1.89. C<sub>9</sub>H<sub>19</sub>AlO<sub>3</sub> calcd.: C, 53.45; H, 9.75; Al, 13.34%; active ethyl groups 2.00/mole). After protonolysis of (IIIf), the product isolated from the aq. layer was ethyl  $\beta$ -hydroxypropionate (IVf) (59%), b.p. 52–53°/0.2 mm, (lit.<sup>11</sup> b.p. 81–83°/13 mm).

*Reaction of (Ia) with  $\gamma$ -butyrolactone (IIb) and protonolysis of the reaction products*

Equimolar amounts of (Ia) and (IIb) were allowed to react at 70° for 30 h and gave diethylaluminium 3-[(dimethylamino)carbonyl]propanolate (IIIb) (nc), m.p. 150–157° (decomp.), in 90% yield. (Found: C, 56.19; H, 9.86; Al, 12.36; active ethyl groups 1.90. C<sub>10</sub>H<sub>22</sub>AlNO<sub>2</sub> calcd.: C, 56.78; H, 10.30; Al, 12.53%; active ethyl groups 2.00/mole.) Protonolysis of (IIIb) produced  $\gamma$ -hydroxy-*N,N*-dimethylbutyramide (IVb), b.p. 74–78°/0.2 mm, in 55% yield.

*Reaction of (Ia) with phthalide\* (IIc) and protonolysis of the reaction product*

The benzene solution of equimolar amounts of (Ia) and (IIc) was heated at 70° for 40 h. Removal of the benzene and washing with benzene/*n*-hexane 1/4 gave the yellowish solid, diethylaluminium *o*-[(dimethylamino)carbonyl]benzylate (IIIc) (nc), m.p. 106–110° (decomp.). (Found: C, 64.40; H, 8.21; Al, 9.87; mol. wt. cryoscopic, 284. C<sub>14</sub>H<sub>22</sub>AlNO<sub>2</sub> calcd.: C, 63.85; H, 8.42; Al, 10.25%; mol. wt. for 1/1 adduct, 263.) The starting material (IIc), m.p. 72–73°, was recovered quantitatively when (IIIc) was acid-hydrolyzed.

*Reaction of (Ia) with succinic anhydride (Va) and protonolysis of the reaction product*

Compound (Va), m.p. 119–120° was added at room temperature to benzene containing an equimolar amount of (Ia) and the mixture was heated at 70° for 7 h. Cooling gave a red-brown ppt. of (VIa) in 83% yield. Protonolysis of (VIa) gave succinic mono(dimethylamide) (VIIa), m.p. 61–62°. Spectral data are shown in Table 4.

In a reaction involving a molar ratio (Va)/(Ia) =  $\frac{1}{2}$ , (VIIa) (11%) was obtained

\*  $\alpha$ -Hydroxy-*o*-toluic acid lactone.

from the aqueous solution and bis(dimethyl)succinamide (VIII) (65%), m.p. 79–81° (lit.<sup>1,2</sup> 80–81°), as plates (CHCl<sub>3</sub>) from the benzene soluble products. The NMR spectra of (VIII) showed peaks at  $\tau$  7.36 (singlet; 4H), 7.08 and 6.95 (singlet; 6H).

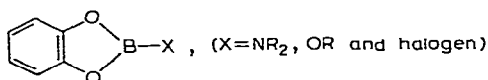
*Reaction of (Ia) with phthalic anhydride (Vb) and protonolysis of the reaction product*

When equimolar amounts of (Vb) and (Ia) were allowed to react in benzene solution at 70° for 30 h, red-tinged white crystals of diethylaluminium *o*-[(dimethylamino)carbonyl]benzoate (VIb), m.p. 152–156° were obtained in 52% yield. (Found: Al, 10.10; active ethyl groups 2.09. C<sub>14</sub>H<sub>20</sub>AlNO<sub>3</sub> calcd.: Al, 9.74%; active ethyl groups 2.00/mole). Protonolysis of (VIb) with H<sub>2</sub>O/Na<sub>2</sub>CO<sub>3</sub> gave phthalic mono-(dimethylamide) (VIIb) in 61% yield.

RESULTS AND DISCUSSION

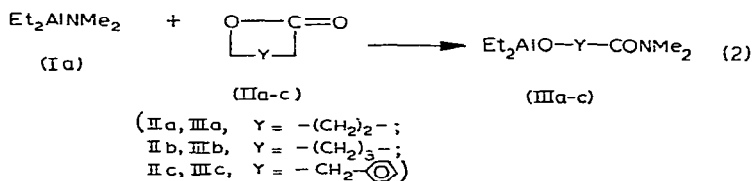
*Reactions with lactones*

Reactions of  $\beta$ -propiolactone with a variety of reagents<sup>13</sup> are known to involve two modes of ring-opening, as represented in eqn. 1. As mentioned in the introduction, the mode of ring-opening of  $\beta$ -propiolactone in the reaction with Group IVA organometal amides, ethylzinc methanolate or diphenylamide depends upon the natures of both the metal atom and the heteroatom. With Group IIIA organometallic compounds, Lappert and Horder<sup>14</sup> found that the reaction of diketone with equimolar amounts of organoboron compounds, took place through the acyl–oxygen fission, with a reactivity

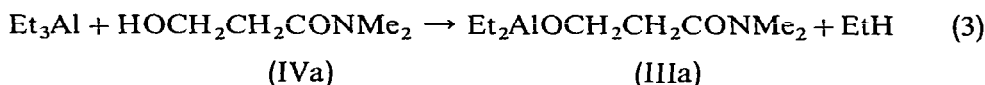


order of halogen > NR<sub>2</sub> > OR. On the other hand, alkyl–oxygen bond fission was shown by Lundeen<sup>15</sup> to take place in the reaction of Et<sub>3</sub>Al with  $\beta,\beta$ -dimethylpropiolactone.

We have now found that the insertion reactions of Et<sub>2</sub>AlNMe<sub>2</sub> into lactones take place with the acyl–oxygen bond fission to give diethylaluminium  $\omega$ -[(dimethylamino)carbonyl]alcoholates [eqn. (2)].



The products were identified by (1) the single absorption band in the IR spectra in the carbonyl region at 1625–1630 cm<sup>-1</sup> [ $\nu$ (C=O) of acid amides], (2) the appearance of two singlet peaks for the N–Me protons in the NMR spectra, in contrast with the singlet peak for N–Me in Et<sub>2</sub>AlNMe<sub>2</sub> and (3) the identity of the adduct formed from  $\beta$ -propiolactone coincided with the product obtained from  $\beta$ -hydroxy-*N,N*-dimethylpropionamide and Et<sub>3</sub>Al [eqn. (3)].



In the IR spectra of the products, strong absorptions at 1020–1100  $\text{cm}^{-1}$  (attributable to the Al–O–C linkage) were also present in all cases.

The reaction product (IIIc) formed from  $\text{Et}_2\text{AlNMe}_2$  and phthalide showed an interesting NMR spectrum, the methylene quartet peak of the AB type at  $\tau$  5.32 in Fig. 1 is rather similar to the peak for the non-equivalent methylene protons in the  $\text{PhCH}_2\text{--O--Al}$  system<sup>16</sup>. The adduct (IIIc) was found to be monomeric (degree of association = 1.07), and thus the coordination of the O atom of the amide group to an Al atom must be intramolecular. The anisotropy of methylene protons can be explained by reference to the molecular structure illustrated in Fig. 1 involving an Al–O bond distance of ca. 1.8 Å<sup>17</sup>. Intramolecular (or intermolecular) coordination in which the coordination of the carbonyl oxygen atom to an Al atom caused restricted rotation, ( $\text{N}=\text{C}=\text{O}\cdots\text{Al--O}$ ) would be expected to a greater or lesser degree in all the products.

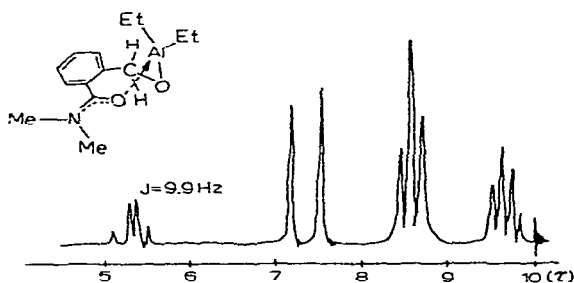


Fig. 1. The NMR spectrum of diethylaluminum *o*-[(dimethylamino)carbonyl]benzylate.

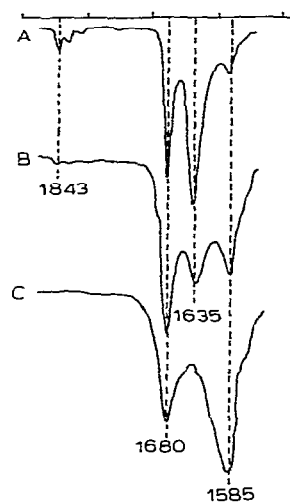
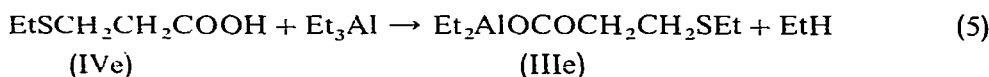
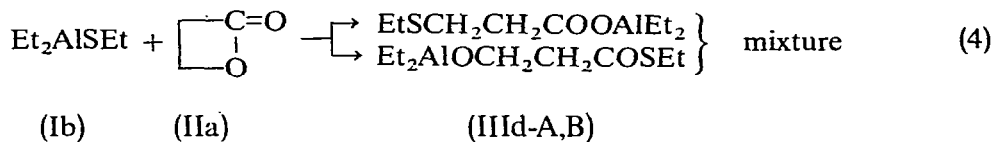


Fig. 2. IR spectra of a mixture of  $\text{Et}_2\text{AlEt}$  and  $\beta$ -propiolactone. A: after 1 h at 20°; B: after 32 h at 20° and C: after the same mixture had been kept at 70° for 24 h.

Protonolysis of the adducts (IIIa, b) gave the corresponding  $\omega$ -hydroxyacid amides (IVa, b) in fairly good yield. It was surprising that in the case of phthalide (IIc) starting material was recovered instead of *o*-hydroxymethyl benzamide, but this does not mean that the reaction did not occur, for it is well known<sup>18</sup> that cyclization occurs readily with such compounds in the presence of small amounts of water (especially under acidic conditions).

The reaction of  $\beta$ -propiolactone with  $\text{Et}_2\text{AlOEt}$  (Ic) occurred selectively via acyl–oxygen fission, as shown by the presence of only one absorption band, at 1730  $\text{cm}^{-1}$ , in the carbonyl region and a strong absorption band at 1180  $\text{cm}^{-1}$  [ $\nu(\text{C--O})$  of an ester] in the IR spectrum of the product (IIIf).

On the other hand, two products were obtained from the reaction of  $\text{Et}_2\text{AlSEt}$  (Ib) with  $\beta$ -propiolactone at  $70^\circ$ , and the IR spectrum of the products (III d-A) showed two carbonyl absorption bands, at  $1680$  and  $1585\text{ cm}^{-1}$  (relative intensity ca. 4/6). The adsorption band at  $1680\text{ cm}^{-1}$  is assignable to thiolester ( $\text{RCOSEt}$ ) and that at  $1585\text{ cm}^{-1}$  to aluminium carboxylate ( $\text{RCOOAlEt}_2$ ), which was also identified as the compound giving rise to a single carbonyl frequency in the products from  $\text{Et}_3\text{Al}$  with  $\beta$ -ethylthiopropionic acid [eqn. (5)]. The ratio of the products varied with the



reaction conditions. When the reaction temp. was held below  $20^\circ$ , a viscous liquid was obtained after removal of the solvent, and the IR absorptions of the mixture (III d-B) appeared at  $1685$ ,  $1635$  and  $1585\text{ cm}^{-1}$  (intensities about 4/5/1). The absorption at  $1635\text{ cm}^{-1}$  decreased gradually with the time, but the intensity ratio became finally constant (at  $20^\circ$ , ca. 5/3/3), as long as the temp. was kept constant. The same absorption bands appeared at higher temps. ( $35$ – $60^\circ$ ), and the higher the temp., the weaker was the absorption at  $1635\text{ cm}^{-1}$ . When an equilibrated mixture was heated up to  $70^\circ$ , two species, *i.e.* thiolester and carboxylate, were found to be present (Fig. 2). It is difficult to interpret these variations of IR spectra quantitatively, and also to assign the band at  $1635\text{ cm}^{-1}$ . There may be an interconversion between two or three structures, and we are studying this interconversion further.

It is clear that,  $\text{Et}_2\text{AlSEt}$  can attack not only a carbonyl ( $sp^2$ ) but also an alkyl ( $sp^3$ ) carbon atom. In contrast with the preponderant acyl–oxygen fission of  $\beta$ -propiolactone found with Al–N and Al–O compounds, Al–S compounds cleave  $\beta$ -propiolactone in two ways. This can be attributed to (1) the relatively weak nucleophilicity of the –SEt group towards carbonyl carbon and (2) the higher degree of freedom of bonding associated with the nature of the *d*-orbital of the sulphur atom.

### Reactions with acid anhydrides

Some investigations of the reactions of acid anhydride with equimolar amounts of organoaluminium compounds have been described. Thus Reinheckel obtained the product  $\text{EtCOCH}_2\text{CH}_2\text{COOH}$  from the reaction of  $\text{Et}_3\text{Al}_2\text{Cl}_3$  with succinic anhydride<sup>19</sup> and recycled  $\gamma$ , $\gamma$ -diethyl- $\gamma$ -butyrolactone from the reaction involving an excess of the organoaluminium compound<sup>20</sup>. Baba obtained phthalide in the reaction of  $\text{Et}_3\text{Al}$  with phthalic anhydride<sup>21</sup>.

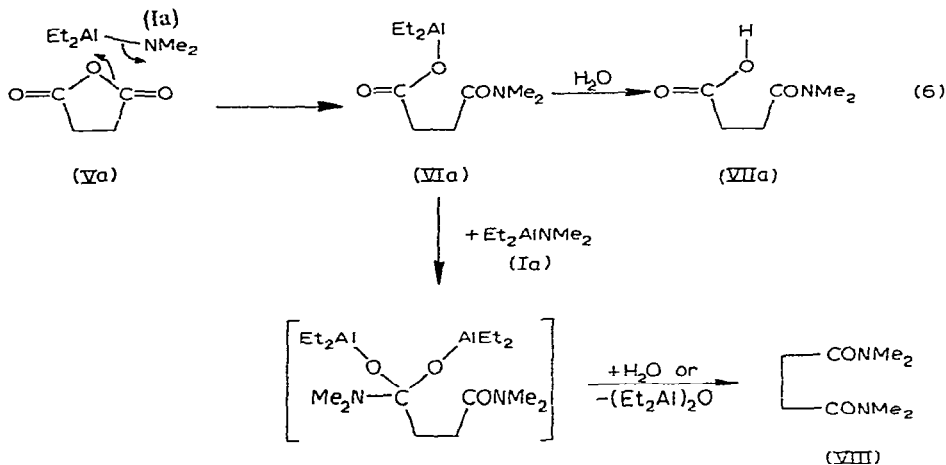
We found that  $\text{Et}_2\text{AlNMe}_2$  (Ia) reacted with an equimolar amount of succinic anhydride to give the ring-opened product (VIa) (analogous to the product obtained by the acyl–oxygen fission of lactones). This was confirmed by the IR spectrum of the protonolysis product (VIIa), which showed the characteristic carboxylic acid absorption at  $3400$ – $2650\text{ cm}^{-1}$  and two carbonyl absorptions at  $1728$  and  $1653\text{ cm}^{-1}$ .

A similar result was obtained with phthalic anhydride, which gave the ring-



opened adduct (VIb). Elemental analysis and the spectral data for this adduct (VIb) and its protonolysis product (VIIb) were consistent with the structures assigned.

When two molar proportions of  $\text{Et}_2\text{AlNMe}_2$  are used, the  $\text{Et}_2\text{AlNMe}_2$  attacks the carbonyl group of the ring-opened adduct. Thus in the reaction of  $\text{Et}_2\text{AlNMe}_2$  with succinic anhydride in molar ratio 2/1, the excess  $\text{Et}_2\text{AlNMe}_2$  attacked the carboxylate group. Only one compound was isolated from the benzene soluble product. This gave an absorption band at  $1648\text{ cm}^{-1}$  in the IR spectrum, and NMR peaks at  $\tau$  7.36 (4H), 6.95, and 7.08 (6H), and was identified as the succinic diamide derivative (VIII). The reaction scheme can be represented as in eqn. (6).



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