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INSERTION REACTIONS OF DIALKYLALUMINIUM DERIVATIVES

VIII. THE FORMATION OF ORGANOALUMINIUM CHELATES WITH DIKETENE.

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SUMMARY

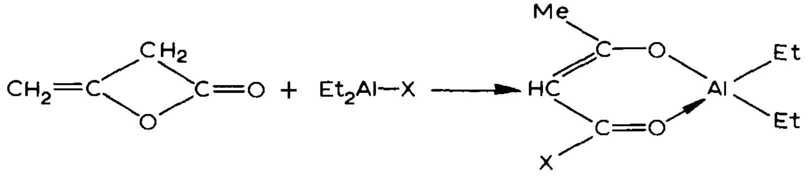
Diethylaluminium dimethylamide and diethylaluminium ethanethiolate, $Et_2Al{-}X$ ($X = NMe_2$ and SEt) reacted with diketene by acyl–oxygen bond cleavage followed by a 1,3-hydrogen shift to give the corresponding diethylaluminium acetoacetic acid dimethylamide (Ia) or acetothioloacetic ethyl acid ester (Ib). Both products have chelate structures.

INTRODUCTION

Diethylaluminium derivatives, $Et_2Al{-}X$ ($X = NMe_2$, OR and SEt) have been shown to react with various acceptor molecules, such as isocyanates[1], nitriles[2], β-lactone and cyclic acid anhydrides[3], by selective cleavage of Al–X bonds. In this paper we describe the formation of monomeric diethylaluminium chelates by the reactions of diethylaluminium dimethylamide and ethanethiolate with diketene.

RESULTS AND DISCUSSION

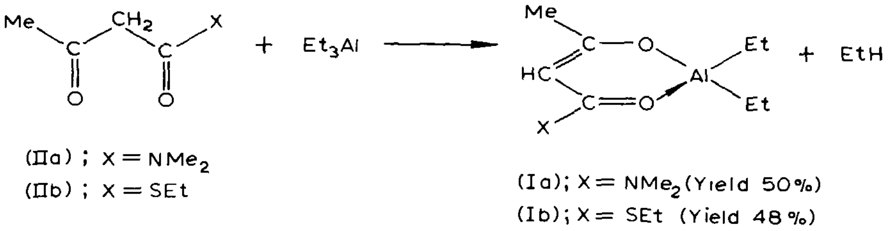
The reaction of diethylaluminium dimethylamide or ethanethiolate with diketene proceeded smoothly under rather mild conditions. The isolated products were monomeric 1/1 adducts, and spectroscopic evidence discussed below, favoured the chelate structures, (Ia) and (Ib) (eqn. 1).


(1)

(Ia); $X = NMe_2$ (Yield 52%)

(Ib); $X = SEt$ (Yield 30%)

These diethylaluminium chelates, (Ia) and (Ib), were also prepared by the reaction of triethylaluminium with acetoacetic acid dimethylamide(IIa) or acetothioloacetic acid ethyl ester (IIb) as shown in eqn. (2).



(2)

(IIa) ; $X = NMe_2$
(IIb) ; $X = SEt$

(Ia); $X = NMe_2$ (Yield 50%)
(Ib); $X = SEt$ (Yield 48%)

This method of obtaining dialkylaluminium acetylacetonate compounds had been used in the case of acetylacetonate chelates[4,5].

The infrared and NMR spectroscopic data of (Ia), (Ib), (IIa) and (IIb) are summarized in Table 1 and 2. In the infrared spectra, strong absorptions due to the carbonyl group were observed at 1570 cm^{-1} (Ia) and 1580 cm^{-1} (Ib). These frequencies indicate that the carbonyl oxygen must be coordinated strongly to the aluminium atom.

The characteristic NMR methyl proton signals at τ 8.19 s (Ia) and τ 8.45 s (Ib), as well as the olefinic proton signals at τ 5.38 s (Ia) and 4.70 s (Ib) are fully consistent with the formulations as shown in eqns. (1) and (2).

TABLE 1

IR DATA OF (Ia, b) AND (IIa, b)

Compound	*Assignment of main absorptions* (cm^{-1})	
	ν(C=O)	*Other absorptions*
(Ia)[a]	1580 (vs)	1500 (s, br), 1380 (s), 1180 (m), 995 (m), 965 (m), 770 (m)
(Ib)[a]	1570 (vs)	1500 (s, br), 1410 (s, br), 1235 (s), 1135 (s), 970 (m), 850 (s), 760 (m)
(IIa)[b]	1723 (s) 1640 (vs) 1600 (s)	1362 (s), 1250 (m), 1158 (m), 935 (m)
(IIb)[b]	1725 (s) 1680 (s) 1620 (vs) 1590 (s)	1400 (s), 1190 (s), 1093 (s), 838 (s)

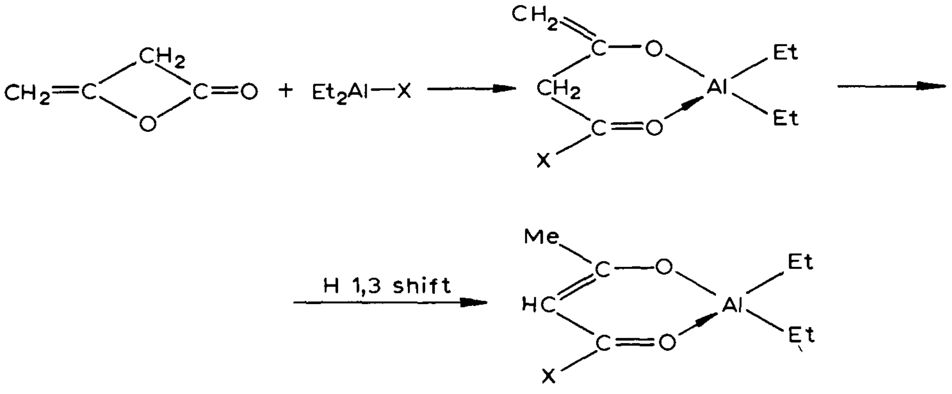
[a] In 2% benzene solution [b] In 2% CCl_4 solution

In the case of (Ia), two N-Me signals at τ 7.93(s) and τ 7.63(s) at 25° (signal distance 18.0 Hz) coalesced to a broad doublet (signal distance 10.5 Hz) upon heating to 70°. Such behaviour is characteristic of acid dimethylamides.

Cryoscopic molecular weight determinations in benzene solution gave no indication of association.

These observations indicated clearly the chelate structures (Ia) and (Ib).

Formation of (Ia) and (Ib) can be explained by the acyl–oxygen bond fission of diketene followed by rapid proton migration (eqn. 3).

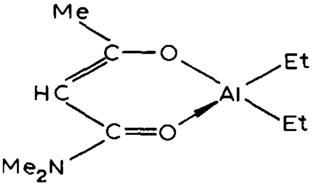
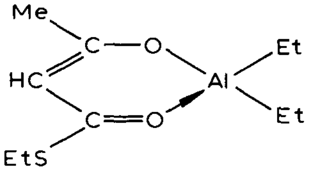


(Ia) ; X=NMe$_2$, (Ib); X=SEt

(3)

TABLE 2

NMR DATA FOR (Ia,b) AND (IIa,b)

Compound		*Assignment* (τ)
	(Ia)[a]	9.68(q, $AlCH_2$, *J* 8.0 Hz), 8 58(t, $AlCCH_3$, *J* 8 0 Hz), 8 19(s, CH_3CO), 7 93(s, NCH_3), 7 63(s, NCH_3), 5 38(s, CH)
	(Ib)[a]	9 75(q, $AlCH_2$, *J* 8 3 Hz), 9 10(t, $SCCH_3$, *J* 7.5 Hz), 8.70(t, $AlCCH_3$, *J* 8 3 Hz), 8 45(s, CH_3CO), 7 46(q, SCH_2, *J* 7 5 Hz), 4 70(s, CH)
$MeCOCH_2CONMe_2$	(IIa)[b]	8.18(s, CH_3CO), 7 92(s, CH_3CO), 7.21(s, NCH_3), 7 15(s, NCH_3), 6 65(s, CH_2), 5.03(s, CH), −3 00 to −6.00(br, enol proton)
$MeCOCH_2COSEt$	(IIb)[b]	8.74(t, $SCCH_3$, *J* 6 8 Hz), 8 09(s, CH_3CO), 7 82(s, CH_3CO), 7 11(q, SCH_2, *J* 6 8 Hz), 6 43(s, CH_2), 4.63(s, CH), −2.45(bs, enol proton)

[a] In 20% benzene solution [b] In 40% CCl_4 solution

The comparative yields of both the 1/1 adducts (Ia, b) and the acetoacetic acid derivatives (IIa, b) reflect the reactivity difference between SEt and NMe_2. The soft nucleophile SEt has a poorer nucleophilicity.

EXPERIMENTAL

General remarks

Diethylaluminium dimethylamide (IIIa), Et_2AlNMe_2, and diethylaluminium ethanethiolate (IIIb), Et_2AlSEt, were prepared as previously described[1]. Diketene (IV) was purified by distillation. Hydrocarbon solvents were dried with sodium wire. All the reactions and all measurements of the physical constants of the products were carried out under dry nitrogen or argon. Molecular weights were determined cryoscopically in benzene. 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. Elemental analyses of the organoaluminium compounds were carried out by Alfred Bernhardt Mikroanal. Lab. in West Germany.

Preparations of acetoacetic acid derivatives(IIa) and (IIb)

The preparations of the acetoacetic acid derivatives, $MeCOCH_2CONMe_2$ (IIa) and $MeCOCH_2COSEt$ (IIb), were carried out as previously described[6] with slight modifications. Their IR and NMR data are summarised in Table 1 and 2, respectively. (IIa), b.p. 122–124° (18 mm), was obtained in 70 % yield (Found: C, 55.91; H, 8.52; N, 10.79. $C_6H_{11}NO_2$ calcd.: C, 55.80; H, 8.58; N, 10.84%.), and (IIb), b.p. 95–100° (15 mm) in 30% yield (Found: C, 49.22; H, 6.89: $C_6H_{10}O_2S$ calcd.: C, 49.29; H, 6.96%.).

Reaction of Et_2AlNMe_2 (IIIa) with diketene (IV)

Diketene (IV), (1.1 g, 0.012 mole) in 10 ml benzene was added to Et_2AlNMe_2 (IIIa), (1.6 g, 0.012 mole) in 10 ml benzene at −78°, and the mixture was allowed to rise to room temperature with stirring during 6 h. It was then refluxed for 7 h. After removal of solvent, the product was distilled under reduced pressure to give the liquid adduct, (Ia), b.p. 80° (0.12 mm), 1.4 g (yield 52 %) (Found: C, 56.16; H, 9.31; Al, 12.67; active ethyl groups, 2.06; mol. wt. (cryoscop. in benzene), 220. $C_{10}H_{20}AlNO_2$ calcd.: C, 56.36; H, 9.39; Al, 12.65 %; active ethyl groups, 2.00 per mol.; mol. wt., 213.). NMR and IR data are summarized in Table 1 and 2, respectively.

Reaction of Et_2AlSEt (IIIb) with diketene (IV)

In an analogous manner, the reaction between Et_2AlSEt (IIIb), (2.5 g, 0.017 mole) in 10 ml benzene and diketene (IV), (1.4 g, 0.017 mole) in 10 ml benzene gave the liquid adduct, (Ib), b.p. 80° (0.2 mm) 1.1 g (yield 30%). (Found: C, 51.96; H, 8.18; Al, 11.73; active ethyl groups, 1.94; mol. wt. (cryoscop. in benzene), 224. $C_{10}H_{19}AlO_2S$ calcd.: C, 52.15; H, 8.31; Al, 11.71%; active ethyl groups, 2.00 per mol.; mol. wt., 230.). NMR and IR data are summarized in Table 1 and 2, respectively.

Reaction of Et_3Al with (IIa)

(IIa), (1.6 g, 0.012 mole) in 10 ml benzene was added dropwise to Et_3Al, (1.4 g, 0.012 mole) in 10 ml benzene at 0°, during the addition evolution of gas was observed.

After the gas evolution ceased completely, the solvent was removed and the product was distilled under reduced pressure to give the liquid adduct, (Ia) b p. 75° (0 07 mm), 1.3 g (yield 50 %). NMR and IR data were identical with those of the product obtained from the interaction of (IV) and (IIIa).

Reaction of Et_3Al with (IIb)

Analogously, the reaction of (IIb), (2.2 g, 0.015 mole) in 10 ml benzene with Et_3Al, (1.7 g, 0.015 mole) in 10 ml benzene gave the liquid adduct (Ib), b.p 70–71° (0.2 mm), 1.6 g (yield 48 %). The NMR and IR spectra were identical with those of the product obtained from (IV) and (IIIb).

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