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SYNTHESIS AND PROPERTIES OF MONOPHENOXYALUMUNIUM COMPOUNDS

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SUMMARY

Dimethylphenoxyaluminium, methylphenoxychloroaluminium and phenoxydichloroaluminium have been prepared. Their molecular weights have been determined and their IR spectra analysed. The NMR spectrum of methylphenoxychloroaluminium has been investigated.

At room temperature in a hydrocarbon solution the trimer is the stable associated form, but at higher temperatures the formation of the dimer is increasingly favoured. The occurrence of mixed oxygen–chloride bridges in fairly stable transitional forms of trimeric methylphenoxychloroaluminium and phenoxydichloroaluminium is proposed.

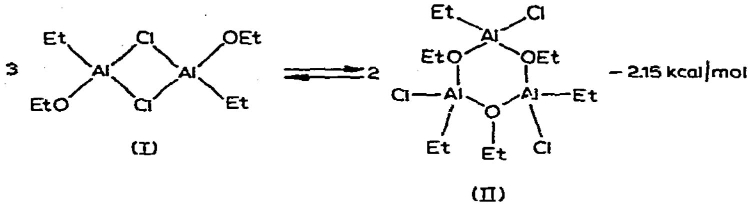
INTRODUCTION

Organoaluminium compounds with one phenoxy substituent have until now not been thoroughly investigated. Thus, Lehmkuhl[1], while studying the complexing ability of organoaluminium compounds with alkaline metal halides, stated that diethylphenoxyaluminium is a slightly weaker Lewis acid than triethylaluminium, and monophenoxyaluminium compounds have been obtained as a result of heating organoaluminium compounds with anisole[2,3]. Mardykin *et al.*[4] have also obtained alkylphenoxyaluminium compounds in the reaction of an aluminium–magnesium alloy with ethyl bromide in anisole at a temperature of 130°.

Mole *et al.*[5] have carried out structural investigations of dimethylphenoxyaluminium, obtained from trimethylaluminium and phenol. On the basis of NMR spectra and ebulliometric molecular weight measurements, they stated that a freshly distilled compound has dimeric structure. In a hydrocarbon solution an equilibrium is set up between a dimer and a trimer of dimethylphenoxyaluminium. Reaction (1), leading to the forming of the trimer from the dimer, is only weakly exothermic.

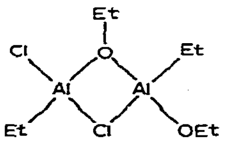
$$3\,(\text{dimer}) \rightleftarrows 2\,(\text{trimer}) \qquad (1)$$

A similar exothermic effect for the reassociation reaction of ethylethoxychloroaluminium resulting in the formation of a trimer from the dimer has been reported by Scherer and Seydel[6] on the basis of IR spectra and molecular weight



(2)

measurements. (Eqn. 2). High temperature favours the reverse of the reassociation reaction, with the trimer being converted back to the dimer. A similar behaviour has been observed for Et(EtO)AlX, where X=Cl, Br or I, by Takeda and Tarao[7] while investigating the IR spectra of these compounds. In their analysis of the IR spectra, Scherer and Seydel have proposed structure (I) for the dimer of ethylethoxychloroaluminium in which chlorine bridges exist. In contrast, Mole[8] has suggested structures (III) or (IV) for the same dimer, stating that partial or complete ethoxy bridging should provide greater stability than structure (I).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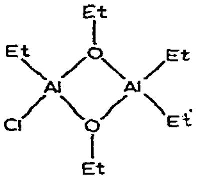
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In this paper the results of further studies of the reactions of organoaluminium compounds with anisole are presented. The solid reaction mixture obtained in this reaction was found to be mainly composed of phenoxy derivatives of organoaluminium compounds. Qualitative and quantitative determinations of these products were however difficult, and for this reason it was decided to obtain pure monophenoxyaluminium compounds and to investigate their chemical and physicochemical properties.

RESULTS AND DISCUSSION

Dimethylphenoxyaluminium, methylphenoxychloroaluminium and phenoxydichloroaluminium were obtained by the reaction of phenol with the respective organoaluminium compound.

$$\mathrm{Me}_n\mathrm{AlCl}_{3-n}+\mathrm{PhOH} \rightarrow \mathrm{Me}_{n-1}(\mathrm{PhO})\mathrm{AlCl}_{3-n}+\mathrm{MeH} \quad (3)$$

$$n=1, 2, \text{ or } 3$$

After removal of the solvent, cryoscopic measurements indicated that both dimethylphenoxyaluminium and phenoxydichloroaluminium have trimeric structures, and it was found that methylphenoxychloroaluminium was a mixture of the dimer and the trimer. In three successive syntheses compounds of molecular weights 436, 481 and 423 were respectively obtained. The values of these molecular weights were found to be influenced by a variety of factors including temperature, time of

TABLE 1

THE MOLECULAR WEIGHTS OF MONOPHENOXYALUMINIUM COMPOUNDS AS DETERMINED CRYOSCOPICALLY IN BENZENE

Compound	Molecular weight						
	Calcd. for		Found after about[a] (h)				
	Dimer	Trimer	½	3	5	24	48
$Me_2(OPh)Al$	300	450					
Not distilled			441			441	
Distilled			320			390	445
$Me(PhO)AlCl$	341	511.5					
Not distilled			436			510	
Distilled			348	394	471	508	508
$(PhO)AlCl_2$	382	573					
Not distilled			571			571	
Distilled			516			570	

[a] Time calculated from the moment of solution. The mean values of at least 4 measurements are given in the Table. Measurement error 4%.

synthesis, speed of removal of the solvent from the reaction mixture, etc. Although strict control of these factors was not employed, nevertheless the reactant concentration has no apparent influence on the degree of association of the resultant methylphenoxychloroaluminium.

Dimethylphenoxyaluminium, freshly distilled at a temperature of about 110° under a pressure of 10^{-2} mm, was found to be dimeric, and the same was also true for methylphenoxychloroaluminium distilled at a temperature of about 140° under a pressure of 10^{-2} mm. When distilled at a temperature of about 170° under a pressure of 10^{-3} mm, phenoxydichloroaluminium was found to be a mixture of a dimer and a trimer, the latter being the main constituent. These products were all crystalline substances.

In 2% benzene solution at a temperature of about 5° all the products obtained after distillation reassociated to trimers. After 48 h all the investigated compounds were trimeric and no further increase in molecular weight was observed (Table 1).

On the basis of these data it appears that the trimer is the stable form of the above compounds when these are present in solution. If elevated temperatures are used during the distillation process, the equilibrium depicted in Eqn. (1) is shifted to the left, which results in an increase in the dimer concentration in the system.

The IR spectra of the above compounds have been investigated over the spectral range 400–1400 cm^{-1}. The characteristic bands, ascribed to the stretching frequencies of C–O–Al bonds, are presented in Table 2.

The IR spectrum of dimethylphenoxyaluminium contains a single very strong and broad band corresponding to C–O–Al at 1225 cm^{-1}. Since both the dimer and the trimer of dimethylphenoxyaluminium involve only coordination via oxygen atoms and since terminal phenoxy groups are apparently absent from their structures,

TABLE 2

IR STRETCHING FREQUENCY BANDS[a] (C–O–Al) OF PHENOXYALUMINIUM COMPOUNDS IN 3% BENZENE SOLUTIONS

Compound	Time from dissolving (h)	ν(C–O–Al) terminal (cm^{-1})	ν(C–O–Al) bridging (cm^{-1})[b]
Me_2AlOPh			
Not distilled	0.5		1223 vs (br)
Distilled	0.5		1223 vs (br)
	24		1227 vs (br)
Me(PhO)AlCl			
Not distilled	0.5	1160 m	1206 s
Distilled	0.5	1160 s	1212 ms
	24	1160 w	1206 s
	48		1205 vs
$(PhO)AlCl_2$			
Not distilled	0.5	1140 s	1192 ms
	48	1140 m	1192 s
	140		1192 vs

[a] Intensity signs: v very; s strong; m medium; w weak; (br) broad. [b] A medium strong band corresponding to $\delta(CH_3)$ exists for dimethylaluminium phenoxide and methylphenoxychloroaluminium in the same spectral range.

TABLE 3

CHEMICAL SHIFTS (ppm) OF Al–CH_3, PROTONS OF PURE Me(PhO)AlCl UPFIELD RELATIVE TO THE CH_3 PROTONS OF TOLUENE

Peak intensity is given in brackets as the percentage of its area to the total area of the group of CH_3Al peaks.

Method of Preparation				
Not distilled		Distilled		Residue
½ h[a] 25°	1 h 100°	½ h 25°	48 h 25°	½ h 25°
2.47(12)	2.49(42)	2.48(77)[b]	2.47(14)	2.47(15)
2.61(12)	2.66(18)		2.61(10)	2.59(22)
2.74(44)	2.81(15)	2.74(14)	2.71(48)	2.71(37)
2.96(7)	2.98(7)	2.91(5)	2.93(8)	2.92(10)
3.04(20)	3.09(7)	3.04(4)	3.03(21)	3.03(16)

[a] Period of time between dissolution and measurement. [b] Shoulder at 2.52 ppm.

the 1225 cm^{-1} band has been ascribed to the stretching frequency of the bridging C–O–Al bonds (Fig. 1a). The dimer and trimer of methylphenoxychloroaluminium can, however, involve coordination by chlorine as well as by oxygen atoms, and the spectrum of this compound after distillation exhibits two characteristic bands at 1160 and 1212 cm^{-1}, ascribed to the stretching frequency of C–O–Al bonds (Fig. 1b). When conversion from dimer to trimer occurs in the system a corresponding decrease of intensity of the 1160 cm^{-1} band is observed (Fig. 1c). Since coordination via the

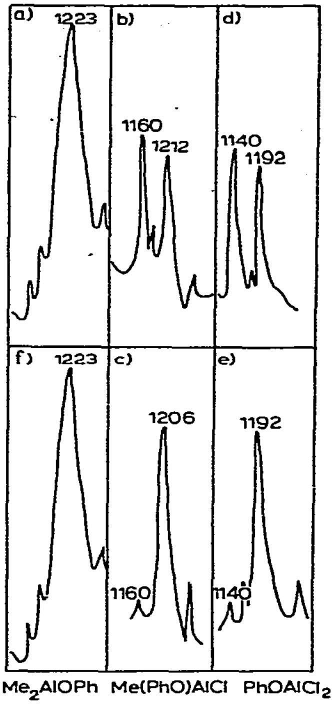


Fig. 1. The IR spectra of monophenoxyaluminium compounds in the 1100–1300 cm^{-1} region. Solution in benzene. (Fig. a,b,d: after solution for 0.5 h; Fig. c,e,f: after solution for 2 days.)

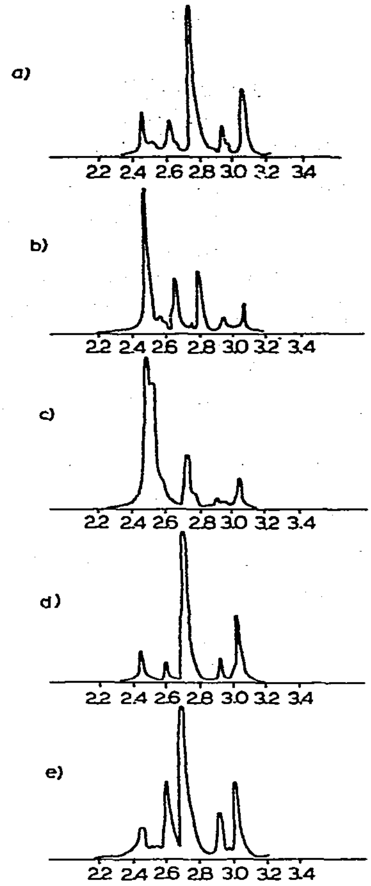


Fig. 2. 60 MHz NMR spectra of methylphenoxyaluminium chloride in benzene. Internal standard CH$_3$ of toluene. Only the CH$_3$Al resonances are shown. (a), Compound after synthesis, spectrum recorded at room temperature after solution for 0.5 h; (b), the same spectrum at a temperature of 100° after heating the compound in toluene for 0.5 h; (c), distilled compound, spectrum recorded at room temperature after solution for 0.5 h; (d), the same spectrum taken after solution for 24 h; (e), residue after distillation, spectrum recorded at room temperature after solution for 0.5 h.

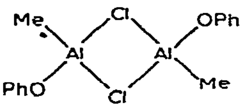
oxygen atom is more energetically advantageous in the trimer[6,7] it is probable that the 1212 cm^{-1} band is related to the bridging phenoxy groups and the 1160 cm^{-1} band to terminal groups of OPh. Since the observed decrease of the band intensity at 1160 cm^{-1} is slower than the change of molecular weight (the spectrum of the trimeric compound still contains this particular band) the conversion from a dimer to a trimer which occurs in a hydrocarbon solution of methylphenoxychloroaluminium must proceed via a fairly stable trimer structure containing mixed bridges [structure (VIb)].

Two strong bands at 1140 and 1192 cm^{-1} have also been observed in the spectrum of trimeric phenoxydichloroaluminium (Fig. 1d), and these have been ascribed respectively to the C–O–Al stretching frequencies of the terminal and bridging phenoxy groups. The intensity of these bands also gradually decreased in a similar fashion to that described above for the 1160 and 1212 cm^{-1} bands of methylphenoxychloroaluminium. Complete disappearance of the 1140 cm^{-1} band, however, only occurred after 5 days. When the molecular weight of the compound approximates to that of a trimer, the IR spectrum of the latter contains an intense band at 1140 cm^{-1}, thus confirming the suggestion that trimeric phenoxydichloroaluminium has a structure containing mixed bridges similar to that shown in (VIb).

The NMR spectrum of methylphenoxychloroaluminium consists of five peaks with chemical shifts of the magnitude expected for CH_3–Al protons. These chemical shifts and their intensities are shown in Table 3 and Fig. 2.

The intensity of the CH_3–Al peaks in the NMR spectra of methylphenoxychloroaluminium depends on the method of preparation of the compound and of the temperature of measurement, (the slight positional change of these peaks is well within the limits of errors for these measurements).

According to Mole[9], the internal or intermolecular change of methyl groups is very slow in organoaluminium compounds containing oxygen atoms. For this reason it was, therefore, concluded that the presence of a large number of peaks in the spectrum may be connected with the occurrence of various dimer and trimer isomers in the system. Thus, for methylphenoxychloroaluminium, even excluding structural isomers the possibility of geometric and even conformational isomers cannot be ignored.



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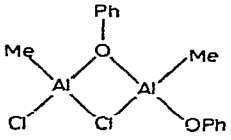
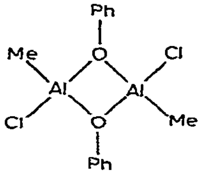
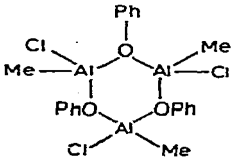


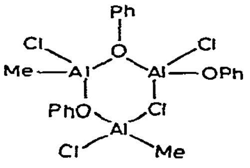
(Vb)



(Vc)



(VIa)



(VIb)

The spectrum of the 1/1 complex of Me(PhO)AlCl with picoline[10] contains only one, fairly wide peak corresponding to CH_3–Al protons, with a chemical shift 2.24 ppm upfield relative to that of the toluene methyl resonance. This observation confirms the assumption that methylphenoxychloroaluminium is present in solution as a mixture of isomers.

In the spectrum of the undistilled compound at elevated temperature the peak intensity at 2.48 ppm increases from 12 to 42% (Fig. 2b). Again, according to Mole[5] the equilibrium depicted in Eqn. (1) shifts to the left when the temperature is raised. The spectrum of the distilled compound which contains a large amount of dimer possesses a very strong peak at 2.48 ppm (77%) (Fig. 2c), the intensity of which decreases after 48 h (Fig. 2d). Over the same period of time the intensities of two peaks at 2.74 and 3.04 ppm increases (the intensity ratio of these two peaks in all spectra was found to be ca. 2/1). From these data the peak at 2.48 ppm may be related to the presence of the dimer of Me(PhO)AlCl, whilst the peaks at 2.74 and 3.04 ppm are related to the trimer.

EXPERIMENTAL

(I). Compounds of $Me_n(PhO)AlCl_{2-n}$ type with $n=0, 1, 2$ were obtained by adding a 30% solution of phenol in benzene to an equimolar quantity of the organoaluminium compound in heptane (concentration 20%). The reaction was carried out below −10°. After reaction, immediate removal of solvent resulted in the formation of a white crystalline solid.

(II). Me(PhO)AlCl was obtained as above in a 4% solution of Me_2AlCl in heptane at a temperature of −20°. No changes in the degree of association of the products were observed. (Analysis of Me(PhO)AlCl: Found: Al, 15.7; Cl, 20.7. C_7H_8AlClO calcd.: Al, 15.8; Cl, 20.8%. Analysis of $(PhO)AlCl_2$: Found: Al, 14.2; Cl, 37.2. $C_6H_5AlCl_2$ calcd.: Al, 14.0; Cl, 37.1%).

The NMR spectra were recorded on a JEOL-INM-C-60H spectrometer. The spectra were recorded for 10% solutions of the compounds in a hydrocarbon mixture (10% toluene+90% benzene).

The IR spectra of 3% benzene solutions of the compounds were recorded within the range 400–1400 cm^{-1} on a Zeiss-UR-10 spectrophotometer, using a liquid cell of 0.15 mm thickness.

Molecular weights were measured cryoscopically in benzene using a standard freezing point depression apparatus modified so as to enable the measurements to be made in an atmosphere of nitrogen.

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