Journal of Organometallic Chemistry, 52 (1973) 269–274

STRUCTURAL INVESTIGATIONS OF 2,6-DIMETHYLPHENOXYALUMINIUM COMPOUNDS*

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(Received September 19th, 1972)

SUMMARY

Dimethyl-(2,6-dimethylphenoxy)aluminium, methyl-(2,6-dimethylphenoxy)-chloroaluminium, (2,6-dimethylphenoxy)dichloroaluminium, methyl-(2,6-dimethylphenoxy)bromoaluminium and methyl-(2,6-dimethylphenoxy)iodoaluminium have been prepared, their molecular weights determined and their IR and NMR spectra recorded and analysed. These data have been used as a basis for determining the chemical constitution of these compounds in benzene solution.

All these compounds exist as dimers in benzene solution. Those compounds which include a halogen in addition to the 2,6-dimethylphenoxy group in their structure coordinate solely via the halogen atoms.

On the basis of the NMR spectra, it was found that at room temperature and in benzene solution methyl-(2,6-dimethylphenoxy)chloroaluminium exists as a mixture of *cis* and *trans* isomers.

INTRODUCTION

Monoalkoxyaluminium compounds exist as dimers or trimers. Thus, Davidson and Brown[1] whilst examining dimethylmethoxyaluminium found it to be trimeric while Mole[2] attributed a dimeric structure to Me_2AlOBu-t.

We have previously investigated methylphenoxyaluminium compounds[3]. In benzene solution at room temperature, these compounds exist as oxygen-bonded trimers but during distillation these trimeric molecules dissociate to form dimers. The structure of dimeric dimethylphenoxyaluminium involves coordination via the oxygen atoms of the phenoxy groups. Dimeric methylphenoxychloroaluminium and phenoxydichloroaluminium, on the other hand, involve coordination via oxygen and chlorine atoms.

The present work extends our previous investigations and attempts to determine the effect of the constitution of the phenoxy group upon the bridge-type structure of the compounds studied.

RESULTS AND DISCUSSION

Dimethyl-(2,6-dimethylphenoxy)aluminium (I), methyl-(2,6-dimethylphe-

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* This investigation was supported by the Polish Academy of Sciences.

noxy)chloroaluminium (II), 2,6-dimethylphenoxydichloroaluminium (III), methyl-(2,6-dimethylphenoxy)bromoaluminium (IV) and methyl-(2,6-dimethylphenoxy)-iodoaluminium (V) were obtained by treating 2,6-dimethylphenol with the relevant organoaluminium compounds. After the solvents had been distilled off, each compound was sublimed in vacuo at 10^{-4} mmHg.

Cryoscopic molecular weights indicated that all the compounds exist as dimers in benzene solution (Table 1). The molecular weights of these compounds did not change with time and this indicates that no reassociation to the trimer takes place in solution.

TABLE 1

MOLECULAR WEIGHTS OF MONO-2,6-DIMETHYLPHENOXYALUMINIUM COMPOUNDS DETERMINED CRYOSCOPICALLY IN BENZENE

Compound	*Molecular weight*		
	Found after[a]		*Calculated for dimer*
	1 h	*8 days*	
$(CH_3)_2AlOC_6H_3(CH_3)_2$	354	360	356
$CH_3[(CH_3)_2C_6H_3O]AlCl$	402	411	397
$[(CH_3)_2C_6H_3O]AlCl_2$	430	428	438
$CH_3[(CH_3)_2C_6H_3O]AlBr$	502		492
$CH_3[(CH_3)_2C_6H_3O]AlI$	602		580

[a] Time calculated from the instant of solution. The mean values of at least four measurements are given in the table.

The IR spectra of the 2,6-dimethylphenoxyaluminium compounds were studied in an attempt to elucidate their structures. Some of the spectral bands observed within the 200–1400 cm^{-1} range are presented in Table 2. For purposes of comparison, the corresponding bands of the dimeric monophenoxyaluminium compounds referred to previously[3] are also included in Table 2.

In the spectrum of compound (I) a very strong band is observed at 1178 cm^{-1}, this band shifting towards 1290 cm^{-1} in the 1/1 complex of this compound with β-picoline. Compound (I) may well involve coordination via oxygen atoms only and for this reason the 1178 cm^{-1} band has been ascribed to the stretching frequency of the C–O bonds in the 2,6-dimethylphenoxy bridging group. The 495 cm^{-1} band is absent from the spectrum of the 1/1 complex of compound (I) with β-picoline but, in contrast, is present in the spectra of dimeric dimethylphenoxyaluminium, methylphenoxychloroaluminium and phenoxydichloroaluminium which have previously been shown[3] to involve coordination via both the chlorine and the oxygen atoms. For this reason, the 495 cm^{-1} band is considered as being related to the presence of the $\mathrm{Al{-}\overset{|}{O}{-}Al}$ bridging group.

With compounds (II), (IV) and (V), bands were observed at 1160, 1157 and 1155 cm^{-1} corresponding to the C–O bond stretching frequencies, but, in addition with compound (II) a band was also found at 455 cm^{-1}. The absence of such a band in the spectra of compounds (IV) and (V) indicates that it is probably related to the

TABLE 2

PRINCIPAL BANDS IN THE IR SPECTRA OF DIMERIC MONOPHENOXYALUMINIUM AND 2,6-DIMETHYLPHENOXYALUMINIUM COMPOUNDS

Compound	$\nu(Al-X)$ *bridging* (cm^{-1})	$\nu(Al-\overset{\mid}{O}-Al)$ (cm^{-1})	$\nu(C-O)$ *terminal* (cm^{-1})	$\nu(C-O)$ *bridging* (cm^{-1})
$[(CH_3)_2AlOPh]_2$	—[a]	497 m	—	1223vs(br)[b]
$[CH_3(PhO)AlCl]_2$	465 m	502 s	1160 s[b]	1212 ms[b]
$[PhOAlCl_2]_2$	430 m	500 s(br)	1140 s[b]	1192 ms[b]
(I)	—	495 m	—	1178 s
(II)	455 m	—	1160 s	—
(III)	435 m	—	1140 s	—
(IV)	380 (sh)	—	1157 s	—
(V)	315 m	—	1155 s	—
$CH_3[(CH_3)_2C_6H_3O]AlCl\cdot Me_3Al$	?	500 w	—	1172 s

[a] v, very; s, strong; m, medium; w, weak; (br), broad. [b] Earlier data[3].

stretching frequency of the Al–Cl bond. In the spectra of compounds (IV) and (V), however, bands were observed at 388 and 315 cm^{-1} respectively, and these were ascribed to the stretching frequency of Al–X.

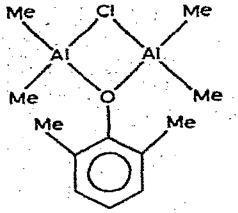
Bands at about 460 and 1160 cm^{-1} were also observed in the spectrum of dimeric Me(PhO)AlCl. The 1160 cm^{-1} band has previously[3] been attributed to the stretching frequency of the C–O bond associated with the terminal phenoxy group in the $[Me(PhO)AlCl]_2$ dimer. Disappearance of the 1160 cm^{-1} band is accompanied by the simultaneous disappearance of the band at 465 cm^{-1} and for this reason this latter band was therefore ascribed to the Al–Cl stretching frequency in the bridge.

The constant position of the ν(C–O) band at 1160 cm^{-1} and the close affinity of the ν(Al–Cl) band in $[Me(PhO)AlCl]_2$ and (II), together with the concurrent absence of a band at 500 cm^{-1} in (II), indicate that in compound (II) coordination only occurs via chlorine atoms.

The similar appearance of a ν(C–O) band in (IV) and (V) at the same frequency as the ν(C–O) terminal position in (II) indicates that compounds (IV) and (V) are also halogen bonded. This suggestion is also supported by the absence of the 500 cm^{-1} band.

The IR spectrum of compound (III) exhibits bands corresponding to ν(C–O) and ν(Al–Cl) at 1140 and 435 cm^{-1}, respectively, in a similar fashion to the spectra of dimeric $[(PhO)AlCl_2]_2$. The 1140 cm^{-1} band has been ascribed to the C–O stretching frequencies of the terminal phenoxy groups. Conversion of the dimer $[PhOAlCl_2]_2$ into the trimer leads to the disappearance of these bands and for this reason it is supposed that the 430 cm^{-1} band in the spectrum of $[PhOAlCl_2]_2$ is related to the Al–Cl stretching frequencies in the bridge. From these data it may also be concluded that compound (III) is chlorine bonded. This is once more supported by the absence of the 500 cm^{-1} band associated with the bridging effect brought about by the presence of oxygen atoms.

In addition the IR spectrum of compound (II) when mixed with Me_3Al in a ratio of 1/1 has been investigated. In this case the benzene solution was kept for about 4 h at a temperature of 70°. The resulting spectrum contained no band at 455 cm^{-1}, while the ν(C–O) band was shifted from 1160 to 1172 cm^{-1} together with the simultaneous appearance of a band at approx. 500 cm^{-1}. Accordingly, the following molecular structure is proposed for the compound formed:



NMR spectra were recorded for $[(CH_3)_2AlOC_6H_3(CH_3)_2]_2$ and $\{CH_3[(CH_3)_2C_6H_3O]AlX\}_2$ in toluene solution, where X = Cl, Br and I, the corresponding chemical shifts of the protons in the CH_3–Al and CH_3–C groups respectively being recorded in Table 3.

Two peaks exhibiting an intensity ratio of 1/1 are present in the spectrum of $[(CH_3)_2AlOC_6H_3(CH_3)_2]_2$, the respective chemical shifts being −0.29 and 2.57 ppm upfield relative to the proton peak of the toluene methyl group. The first of these peaks belongs to the CH_3–C protons, while the other is related to the CH_3–Al protons. The spectrum of the compound is unchanged by time or temperature down to −80°. This demonstrates the absence of any coordination involving the CH_3 groups and is similar to the situation in trimethylaluminium.

The spectrum of compound (II) at room temperature exhibits two peaks associated with the CH_3–Al protons with chemical shifts of 2.47 and 2.60 ppm respectively and an intensity ratio of approx. 2/1. On replacing chlorine with bromine as in compound (IV), a similar spectrum was obtained.

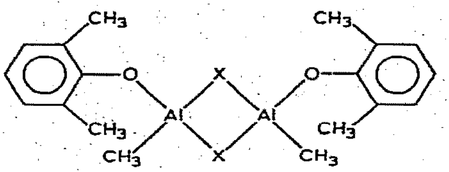
The existence of two CH_3–Al peaks in the spectra of $\{CH_3[(CH_3)_2C_6H_3O]AlX\}_2$ where X = Cl or Br suggests the presence of *cis* and *trans* isomers of these compounds.

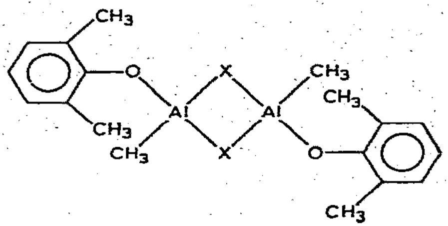
TABLE 3

CHEMICAL SHIFTS OF THE METHYL PROTONS ASSOCIATED WITH THE PHENOXY GROUP AND OF THE PROTONS OF THE CH_3–Al GROUP IN METHYL-(2,6-DIMETHYLPHENOXY)ALUMINIUM COMPOUNDS. SPECTRA PREPARED UNDER ROOM TEMPERATURE CONDITIONS (Internal Standard: CH_3 protons of the toluene solvent).

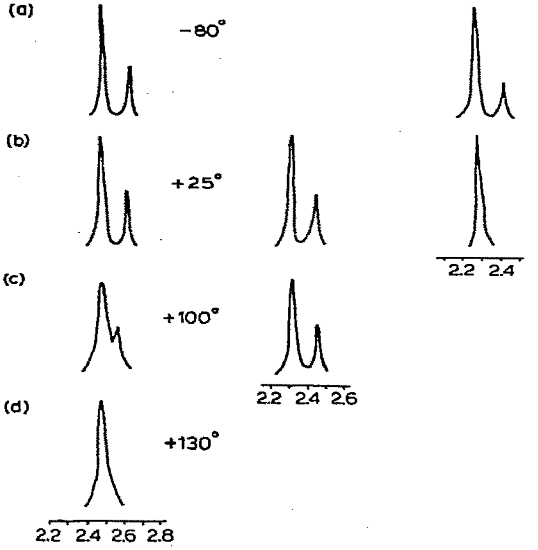
Compound	*CH_3–C (ppm)*	*CH_3–Al (ppm)*
$[(CH_3)_2AlOC_6H_3(CH_3)_2]_2$	−0.29	2.57
$\{CH_3[(CH_3)_2C_6H_3O]AlCl\}_2$	−0.38	2.47 2.60
$\{CH_3[(CH_3)_2C_6H_3O]AlBr\}_2$	−0.42	2.31 2.45
$\{CH_3[(CH_3)_2C_6H_3O]AlI\}_2$	−0.50	2.16[a]

[a] Compound dissolved in a mixture of benzene and 5% toluene.





The occurrence of the *cis* and *trans* configurations at room temperature may be related either to the free intermolecular exchange of the CH_3–Al groups or to the high energy needed to cleave the chlorine or bromine bridge thus making rotation about the Al–X bond more difficult. A choice between these two possibilities may be made by investigating the NMR spectra at higher temperature (Fig. 1). At 100°, the CH_3–Al peaks of compound (II) broaden and finally merge at a temperature of 130°.



$\{CH_3[(CH_3)_2C_6H_3O]AlCl\}_2$ $\{CH_3[(CH_3)_2C_6H_3O]AlI\}_2$

$\{CH_3[(CH_3)_2C_6H_3O]AlBr\}_2$

Fig. 1. Chemical shifts of CH_3–Al protons in methyl-(2,6-dimethylphenoxy)aluminium compounds. (a) Spectra obtained in toluene solution, (b)–(d) spectra obtained in *p*-xylene solution. Internal standard CH_3 group protons of the respective solvents.

In the spectrum of compound (V), which contains an iodine bridge, only one peak attributable to the CH_3–Al protons is observed at room temperature. When the temperature is lowered to −80° this peak splits into two with respective chemical shifts of 2.24 and 2.41 ppm (Fig. 1). This indicates that at room temperature the iodine bridge in the compound is very easily cleaved. This, in turn, allows rotation about the Al–I bond thus leading to the disappearance of the *cis* and *trans* isomers.

EXPERIMENTAL

Compounds of the type $(CH_3)_n[(CH_3)_2C_6H_3O]AlX_{2-n}$ where $n=0, 1, 2$, were obtained by reaction of a 30% solution of 2,6-dimethylphenol in benzene with an equimolar amount of an organoaluminium compound in n-heptane as solvent. The reaction was carried out at a temperature of −20° to enable the correct route to be followed.

After removal of the solvents by distillation, the resulting compound was sublimed at a temperature of 170–180° under a pressure of the order of 10^{-4} mmHg.

TABLE 4

Analysis	*Brutto formula*	*Found* (*calcd.*)	
		Al	*X*
$(CH_3)_2AlOC_6H_3(CH_3)_2$	$C_{10}H_{15}AlO$	15.2	
		(15.15)	
$CH_3[(CH_3)_2C_6H_3O]AlCl$	$C_9H_{12}AlClO$	13.2	Cl, 17.3
		(13.57)	Cl, (17.86)
$[(CH_3)_2C_6H_3O]AlCl_2$	$C_8H_9AlCl_2O$	12.5	Cl, 31.6
		(12.31)	Cl, (32.4)
$CH_3[(CH_3)_2C_6H_3O]AlBr$	$C_9H_{12}AlBrO$	11.5	Br, 32.3
		(11.1)	Br, (32.9)
$CH_3[(CH_3)_2C_6H_3O]AlI$	$C_9H_{12}AlIO$	9.08	I, 43.8
		(9.31)	I, (43.8)

NMR spectra were measured on a JEOL 100MHz spectrometer using 5% solutions in toluene and *p*-xylene. IR spectra were studied over the range 400–1400 cm^{-1} using a ZEISS UR-10 instrument, sample path length 0.12 mm, with 5% solutions in benzene and on a Perkin–Elmer 225 spectrophotometer over the range 200–450 cm^{-1} using Nujol mulls.

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

The analytical data for aluminium and halogens of the compounds are given in Table 4.

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