

SHORT COMMUNICATIONS

ORGANOALUMINIUM COMPOUNDS*

VI.† FORMATION AND STABILITY OF THE METHYLALUMINIUM CHLORIDES IN ETHER

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Von Grosse and Mavity¹ showed that compounds of the types $R_4Al_2X_2$ and $R_2Al_2X_4$, where R = alkyl or phenyl and X = halogen, can be formed by fusion together of two appropriate aluminium compounds (e.g. $2Et_3Al_2Cl_3 + Al_2Cl_6 \rightarrow 3Et_2Al_2Cl_4$; $2Et_3Al_2Cl_3 + Et_6Al_2 \rightarrow 3Et_4Al_2Cl_2$). The bromides and chlorides so prepared did not disproportionate readily and in many cases could be distilled at temperatures around 100°.

The rapid exchange of methyl groups for chloride groups has been established for methylaluminium chlorides in cyclohexane,² but there appears to be no information about the exchange of alkyl groups for halogeno groups in coordinating solvents. This situation differs from that examined by von Grosse and Mavity, firstly in that the alkylaluminium halides exist in these solutions not as dimers but as complexes ($R_nAlX_{3-n} \cdot B$, where $n = 1, 2$ and B represents the coordinating base), and secondly in that a much lower rate of exchange would be expected in the coordinating solvent than in the absence of the solvent.^{3,4}

The purpose of this note is to describe an examination by proton magnetic resonance spectrometry of the system $Me_3Al/Me_2AlCl/MeAlCl_2/AlCl_3$ in ether. Mixtures of any two of these compounds show peaks at one or two of the positions, -0.92 , -0.73 , and -0.51 p.p.m., measured with respect to tetramethylsilane as internal standard, but never at intermediate positions. The peak at -0.92 p.p.m. is due to trimethylaluminium, which in ether shows its aluminium-methyl peak at this position. The variation of relative intensities of peaks with composition of the mixture leaves no doubt that the -0.73 p.p.m. and -0.51 p.p.m. peaks must be due to dimethylaluminium chloride and methylaluminium dichloride, rather than vice versa.

From the fact that distinct resonances at a spacing of the order of 10 c/s are obtained for the above methylaluminium compounds it follows that neither exchange of a methyl group for a chloride group nor of a methyl group of one species for a methyl group of another species can occur with a half-life less than 10^{-1} sec. The spectrum

* Manuscript received March 12, 1964.

† Part V, *Aust. J. Chem.*, 1964, **17**, 961.

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¹ Von Grosse, A. V., and Mavity, J. M., *J. Org. Chem.*, 1940, **5**, 106.

² Brownstein, S., Smith, B. C., Ehrlich, G., and Laubengayer, A. W., *J. Amer. Chem. Soc.*, 1960, **82**, 1000.

³ Mole, T., and Surtees, J. R., *Aust. J. Chem.*, 1964, **17**, 310.

⁴ Mole, T., and Surtees, J. R., *Aust. J. Chem.*, 1964, **17**, 961.

observed from any mixture is invariant with time beyond the period of about 2 min required to prepare the mixture and scan the relevant part of the spectrum. It is, however, not simply the spectrum of the reactants, but includes up to two peaks to be expected from products of exchange of methyl groups for chloro groups. The half-life for this exchange must therefore lie in the range 10^{-1} to 10^2 sec. Furthermore, it is clear from the results obtained that mixtures of stoichiometry Me_2AlCl and MeAlCl_2 exist almost entirely as the respective single etherates, rather than as mixtures formed by disproportionation.

An attempt to carry out a similar study of the methylaluminium bromides in ether was frustrated because resonances could be observed only at two positions, -0.61 and -0.92 p.p.m. The latter position, which is that to be expected for trimethylaluminium, appears also to represent the resonance of dimethylaluminium bromide, and the -0.61 p.p.m. peak is thought to represent methylaluminium dibromide. When aluminium bromide was added to trimethylaluminium in ether, the -0.61 peak appeared in less than 2 min alongside the -0.92 peak. Thus an exchange of methyl group for bromide group occurs with a half-life less than 10^2 sec.

The simple picture here obtained for the composition of the methylaluminium chlorides in ether contrasts strongly with the present uncertainty about the structures of Grignard reagents (see for example Ashby and Becker⁵).

Experimental

Organoaluminium compounds were handled by procedures previously described.^{3,4,6} Proton magnetic resonance spectra were measured using a Varian A60 spectrometer operating at 60° . The sample tubes were closed by serum caps so as to allow rapid additions by syringe to the sample and re-measurement of the spectrum. Methylaluminium chloride was prepared by fusing together trimethylaluminium and the appropriate quantity of aluminium chloride.

Methylaluminium dichloride (0.4 mmole) in ether (4 ml) showed a single proton magnetic resonance peak at -0.51 p.p.m. with respect to tetramethylsilane as internal standard. The gradual addition of an approximately molar solution of trimethylaluminium in ether led to diminution of the -0.51 p.p.m. peak and the appearance and growth of a second singlet at -0.73 p.p.m. On further addition, a third peak at -0.92 p.p.m. appeared only when the -0.51 peak had virtually disappeared; this -0.92 p.p.m. peak proceeded to grow at the expense of the -0.73 p.p.m. peak as addition was continued.

A solution of trimethylaluminium (0.4 mmole) in ether (0.4 ml) showed a single proton magnetic resonance peak at -0.92 p.p.m. The addition of aluminium chloride (c. 0.1 mmole) in ether led to the rapid (complete in less than 2 min) appearance of a peak at -0.73 p.p.m.

⁵ Ashby, E. C., and Becker, W. E., *J. Amer. Chem. Soc.*, 1963, **85**, 118.

⁶ Mole, T., *Aust. J. Chem.*, 1963, **16**, 794.