Alkylmagnesium Alkoxides and Related Compounds

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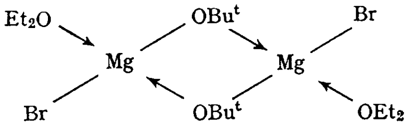
ALKYLMETAL ALKOXIDES are not only of interest in connection with the addition of metal alkyls to carbonyl compounds, but also on account of the structural consequences of the common use of both of the oxygen lone pairs when the metal belongs to Group II. For example, the alkyl-zinc,[1] -cadmium,[2] and -beryllium[3] alkoxides are tetramers unless the organic groups are relatively bulky, the alkoxides then being dimers containing three-co-ordinate metal.

Alkylmagnesium alkoxides, which can be prepared by several methods,[4] differ from this pattern and we have obtained tetramers only when there is chain-branching at the carbon α to oxygen. Examples are $(EtMgOPr^i)_4$, $(EtMgOBu^t)_4$, and $(Pr^iMgOPr^i)_4$ which are all tetrameric (cryoscopically in benzene) and are likely to have cubane-type structures like that of $(MeZnOMe)_4$.[5] In contrast, $EtMgOPr^n$, Pr^iMgOMe, and Pr^iMgOEt are oligomers under similar conditions, all having degrees of association in the range 7—8·4, whilst EtMgOEt[6] is too sparingly soluble in benzene to permit molecular-weight measurement. It is probable that the last four alkoxides are polymeric in the crystalline state. All the alkoxides mentioned above were prepared from the dialkylmagnesium diethyl etherate and the appropriate alcohol and with subsequent removal of all the ether.

We cannot yet exclude the possibility that a sufficient degree of steric hindrance would result in the formation of dimeric alkoxides, and in this connection it may be noted that secondary aminomagnesium alkyls are dimeric in benzene, and have to be formulated with three-co-ordinate magnesium when the amine is sterically hindered. Examples are $(Pr^iMgNPr^i)_2$ and $(EtMgNEtCH_2Ph)_2$, the latter being formed from diethylmagnesium and benzalanil.

Crystalline alkylmagnesium alkoxide ether complexes can in some instances be formed by the addition of R_2Mg to a carbonyl group, *e.g.*, $EtMgOCEt_3,OEt_2$ (m.p. 63—64°) from Et_2Mg and Et_2CO. This resembles the formation of ether complexes of methylberyllium alkoxides, *e.g.*, $MeBeOCHPh_2,OEt_2$, when the alkoxy-group is relatively bulky.[7]

The product of the reaction between methylmagnesium bromide and acetone crystallises from ether as a complex also containing one ether molecule for each magnesium. Being dimeric in benzene (cryoscopically), it is at present formulated as an alkoxide (I), and a crystallographic study of this compound is in progress.



(I)

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[1] G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1965, 1870; *J. Chem. Soc.* (*A*), 1966, in the press.

[2] G. E. Coates and A. Lauder, *J. Chem. Soc.* (*A*), 1966, 264.

[3] G. E. Coates and A. H. Fishwick, unpublished results.

[4] D. Bryce-Smith and B. J. Wakefield, *Proc. Chem. Soc.*, 1963, 376; B. J. Wakefield, *Organometallic Chem. Rev.*, 1966, **1**, 131.

[5] H. M. M. Shearer and C. B. Spencer, *Chem. Comm.*, 1966, 194.

[6] W. H. Birnkraut, *Inorg. Chem.*, 1963, **2**, 1074.

[7] N. A. Bell and G. E. Coates, *J. Chem. Soc.* (*A*), 1966, in the press.