Trimeric n-Butylmagnesium Isopropoxide. An Improved One-step Synthesis of Alkylmagnesium Alkoxides from Alkyl Chlorides

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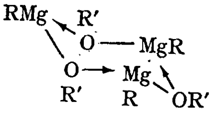
PREPARATIONS and properties of various alkylmagnesium alkoxides have been previously reported.[1] The degrees of association and the tendency to form etherates have not hitherto been definitely known although Vreugdenhil and Blomberg have inferred from a study of the oxidation of diethylmagnesium that ethylmagnesium ethoxide is trimeric in ether.[2] In the accompanying Communication, Coates and Ridley have prepared several ether-free alkylmagnesium alkoxides by reactions of the corresponding dialkylmagnesium diethyl etherates with the appropriate alcohol, and have reported them to be tetramers and higher oligomers, depending on the natures of the groups.[3]

We have prepared unsolvated n-butylmagnesium isopropoxide by the procedure given below and have found it to be trimeric (f.p. depression of benzene) over the concentration range 0·12—0·47 molal (based on the hypothetical monomer), the value being invariant over a period of three days. Apart from the inference in ref. 2, no trimeric organomagnesium species have hitherto been recognised. Organomercury alkoxides exist as trimers.[4] Organo-zinc, -cadmium, and -beryllium alkoxides are usually tetra- or di-meric,[5] but one trimeric alkylzinc alkoxide [$(EtZnOCHPh_2)_3$] is known.[5b] Comparison of the present results with those reported in the accompanying Communication[3] suggests that the degree of association of alkylmagnesium alkoxides is very sensitive to the nature of the organic groups and/or the method of preparation.

We have also found that the addition of diethyl ether to a benzene solution of n-butylmagnesium isopropoxide, followed by removal of solvents below 20° under reduced pressure, gave a product which produced less than 10 mol. % of ether on hydrolysis. The tendency for solvation with diethyl ether is therefore very slight.

At first sight, $(\mathrm{RMgOR'})_3$ might be expected to have the structure illustrated which is based on *sp*^{3}-hybridised orbitals on O and Mg. This structure, which contains three-co-ordinate magnesium, fails to account adequately for the weakness of the acceptor properties. We therefore suggest that there may be some additional Mg–O π-bonding which could be considered to arise from overlap of the *p*π-component of the occupied *n*-orbital on oxygen with a vacant orbital on adjacent magnesium. Such π-bonding would be expected to lead to a slightly flattened version of the above "chair" structure or its "boat" isomer.



The following simple procedure is recommended for the preparation of solutions of organomagnesium alkoxides.

A mixture of a primary alkyl or aryl chloride (2 mol.) and the appropriate alcohol (1 mol.) is added over 1 hr. to fresh magnesium powder[6] (2·5 g. atom) stirred in refluxing methylcyclohexane under nitrogen: an iodine crystal initiates the reaction (no stirring). Heating under reflux is continued until the solution is chloride-free (usually 3 hr.). The following organomagnesium alkoxides have been prepared by this procedure (yields in parentheses): $\mathrm{Bu^nMgOEt}$ (98%), $\mathrm{Bu^nMgOPr^n}$ (98%), $\mathrm{Bu^nMgOPr^i}$ (80%), $\mathrm{Bu^nMgOBu^s}$ (90%), n-$\mathrm{C_6H_{13}MgOPr^i}$ (50%), PhMgOEt (50%). The lower alkylmagnesium lower alkoxides are only sparingly soluble in methylcyclohexane. They are better prepared in an aromatic solvent such as toluene, although it is then more difficult to obtain products which are completely chloride-free.

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