Some Alkylmagnesium Alkoxides and Reaction Products from Grignard Reagents and Carbonyl Compounds

By **G. E. Coates, J. A. Heslop, M. E. Redwood,** and **D. Ridley,** Department of Chemistry, Durham University, South Road, Durham

Several alkylmagnesium alkoxides have been prepared by alcoholysis of the dialkyls in diethyl ether, and can be obtained free from ether. In benzene, $EtMgOPr^n$, Pr^iMgOMe, and Pr^iMgOEt are oligomers (degrees of association *ca.* 8), but those alkoxides we have studied in which there is chain-branching α to oxygen are tetramers, $(EtMgOPr^i)_4$, $(EtMgOBu^t)_4$, and $(Pr^iMgOPr^i)_4$. The 3-ethyl-pentan-3-ol derivative, from $Et_2Mg + Et_2CO$or $Et_2Mg + Et_3COH$, crystallises as an ether complex ($EtMgOCEt_3,Et_2O$) which loses ether very readily: the tetrahydrofuran adduct is dimeric in benzene $(EtMgOCEt_3,THF)_2$. Some alkylmagnesium alkoxides are tetramers in diethyl ether, $(EtMgOEt)_4$, $(MeMgOBu^t)_4$, and $(EtMgOBu^t)_4$, but two are dimers, $(EtMgOCMeEt_2)_2$ and $(EtMgOCEt_3)_2$. Methylmagnesium t-butoxide disproportionates in dilute solution in benzene. Both dimethylmagnesium and ethylmagnesium ethoxide crystallise from diethyl ether at room temperature without solvent of crystallisation.

The diethyl ether complex of t-butoxymagnesium bromide crystallises from the solution obtained when acetone is added to methylmagnesium bromide in ether. It is a dimer, $(Bu^tOMgBr,Et_2O)_2$, both in benzene and in ether and in the crystalline state. Several analogous products have been obtained by other similar reactions, and all those whose molecular weights were measured were also dimeric (solvent given) examples are $(Bu^tOMgBr,THF)_2$ (benzene), $(Et_3COMgBr,THF)_2$ (benzene), $(Et_2MeCOMgBr,Et_2O)_2$ (ether), $(Et_2MeCOMgI,Et_2O)_2$ (ether), $(Me_2Pr^nCOMgI,Et_2O)_2$ (ether). t-Butoxymagnesium bromide-diethyl ether complex has also been prepared from magnesium bromide and both $Mg(OBu^t)_2$ and $MeMgOBu^t$. The ^1H n.m.r. spectra of several of the compounds described are anomalous in unexplained ways.

ALKYLMAGNESIUM alkoxides have been mentioned in various connections, and are discussed in a review.[1] Two of them have been found to be trimeric, $(EtMgOEt)_3$ in diethyl ether,[2] and $(Bu^nMgOPr^i)_3$ in benzene.[3] Recently,[4] methylmagnesium 3-methyl-pentyl-3-oxide has been found to have an apparent degree of association of 2·8 in 0·112M (calculated as monomer) solution in diethyl ether at 40°.

Since alkylmagnesium alkoxides feature in the most reasonable mechanisms for reactions between Grignard reagents and carbonyl compounds,[5] information bearing on their constitution both in hydrocarbon and ether solvents is desirable. Tetramers appear to be the commonest form in which alkyl alkoxides of second group metals are found. Most alkylberyllium alkoxides [6] are

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[1] B. J. Wakefield, *Organometallic Chem. Rev.*, 1966, **1**, 131.

[2] A. D. Vreugdenhil and C. Blomberg, *Rec. Trav. chim.*, 1965, **84**, 39.

[3] D. Bryce-Smith and I. F. Graham, *Chem. Comm.*, 1966, 561.

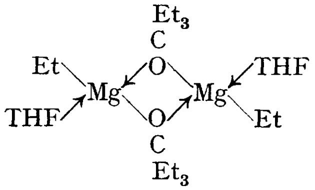
[4] H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, 1967, **32**, 2481.

[5] E. C. Ashby, *Quart. Rev.*, 1967, **21**, 259.

[6] G. E. Coates and A. H. Fishwick, *J. Chem. Soc.* (*A*), 1968, 477.

tetramers, dimers occurring when the groups bound to metal or oxygen are large, and only one trimer is known so far: $(EtBeOCEt_3)_3$. The alkyl alkoxides of zinc are similar,[7] though there are in some instances complications due to disproportionation,[8] and only one trimer [9] is known, $(EtZnOCHPh_2)_3$. Few cadmium analogues have been described, and these are dimers or tetramers,[10] but mercury [11] gives rise to some trimers $(R^1HgOR^2)_3$. The crystal structure of only two second group alkyl alkoxides have been determined: $(MeZnOMe)_4$ has a near-cubic Zn_4O_4 arrangement and $(MeZnOBu^t)_4$ is similar though the structure is disordered.[12]

We have prepared ten alkylmagnesium alkoxides by the reaction, preferably at low temperature, between the magnesium dialkyl in diethyl ether and one mol. of the appropriate alcohol. As the products are all very soluble in ether, most of them were isolated by evaporation of ether (finally under reduced pressure) followed by crystallisation from a hydrocarbon solvent. In two instances, alkoxides were crystallised from diethyl ether. Ethylmagnesium ethoxide, prepared from diethylmagnesium and magnesium ethoxide, crystallised from ether without solvent of crystallisation and had an i.r. spectrum identical to that of ethylmagnesium ethoxide, from diethylmagnesium and one mol. of ethanol, which had been purified by sublimation. Ethylmagnesium 3-ethylpentyl-3-oxide, from diethylmagnesium and either 3-ethylpentan-3-ol or pentan-3-one, crystallised from ether as an ether complex, $EtMgOCEt_3,Et_2O$. This complex loses ether very readily when warmed, or under reduced pressure, and its apparent molecular weight in benzene is *ca.* 1·1—1·2 times the formula weight consistent with some dissociation into free ether and associated species such as $(EtMgOCEt_3)_4$. Ether can be detected (by its ^1H n.m.r. spectrum) in solvent evaporated from solutions of the ether complex in benzene, and, though we did not measure the dissociation pressure of the solid complex, this was greater than 30 mm. at room temperature. We also prepared the tetrahydrofuran complex, and found, as expected, that it dissolved in benzene as a dimer (I) which is likely to have alkoxy-bridges.



(I)

Ethylmagnesium ethoxide is not sufficiently soluble in benzene to permit measurement of its molecular weight by methods presently available to us. Ethylmagnesium n-propoxide, however, crystallises readily from hexane and dissolves in benzene, in which its degree of association (cryoscopically) appears to be just under seven at 2·8 and 3·3 wt.% concentration. Similar degrees of association, in the range 7—8·4, were observed also for isopropylmagnesium methoxide and isopropylmagnesium ethoxide, both of which were white solids. The solubility of Pr^iMgOMe in benzene is only *ca.* 5 wt.% at room temperature. Of all the alkylmagnesium alkoxides prepared, $EtMgOPr^n$ was obtained as the best-formed crystals. Dr. H. M. M. Shearer and Mr. M. L. Schneider of this department report they are orthorhombic, with unit cell dimensions $a = 15·61$, $b = 18·68$, and $c = 18·55$ Å. The space group is probably *Cmma*, with 32 monomer units. Further study of the crystal structure is in progress.

Three of the alkylmagnesium alkoxides were found to be tetrameric in benzene, and all of these had chain-branching α to oxygen, namely, $(EtMgOPr^i)_4$, $(EtMgOBu^t)_4$, and $(Pr^iMgOPr^i)_4$. These, we believe, are likely to have cubic-type structures similar to that of crystalline methylzinc methoxide. Several of the above results have been reported in a brief communication.[13]

Methylmagnesium t-butoxide would be expected also to be tetrameric in hydrocarbon, but its solutions in benzene (*ca.* 10 wt.%) were very viscous at room temperature suggesting the presence of polymeric material, and dilute solutions decomposed with the formation of a white precipitate. For this reason, its molecular weight in benzene could not be determined.

If, as we believe, both magnesium and oxygen are four-co-ordinate in the tetrameric and the more highly associated alkylmagnesium alkoxides (and this would require the use of both lone pairs of each oxygen), then the question arises whether bases such as ether are able to displace one or even both of the alkoxy lone-pairs. The latter is not very likely to happen, since alkoxy-oxygen is more basic than ether oxygen (as shown, for example, by formation of the alkoxy-bridged dimer, rather than the chelate monomer, when Et_3Al reacts with one mol. of $EtOC_2H_4OH$ [14]). A few instances are known, however, where alkoxy-oxygen does not act as a bridging group in the presence of ether, but these involve beryllium bound to large alkoxy-groups [*e.g.*, $MeBeOCHPh_2(Et_2O)$ is monomeric in benzene [15]]. Alkylberyllium alkoxides,[6] most of which are tetrameric in benzene, are dimeric in dilute (0·004—0·015M, calculated as monomer) solution in diethyl ether, and are formulated with alkoxy-bridges like (I). In more concentrated solution (0·09M, as monomer) methylberyllium t-butoxide has a degree of association of 3·8.

On account of the larger radius of magnesium relative to beryllium we would not expect to find alkylmagnesium

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[7] G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1965, 1870.

[8] G. Allen, J. M. Bruce, D. W. Farren, and F. G. Hutchinson, *J. Chem. Soc.* (*B*), 1966, 799; J. M. Bruce, B. C. Cutsforth, D. W. Farren, F. G. Hutchinson, F. M. Rabagliatti, and D. R. Reed, *ibid.*, p. 1020.

[9] G. E. Coates and D. Ridley, *J. Chem. Soc.* (*A*), 1966, 1064.

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

[11] G. Holan, *Tetrahedron Letters*, 1966, 1985.

[12] H. M. M. Shearer and C. B. Spencer, *Chem. Comm.*, 1966, 194; Y. Matsui, K. Kamiya, M. Mishikawa, and Y. Tomiie, *Bull. Chem. Soc. Japan*, 1966, **39**, 1828.

[13] G. E. Coates and D. Ridley, *Chem. Comm.*, 1966, 560.

[14] E. G. Hoffmann, *Annalen*, 1960, **629**, 104.

[15] N. A. Bell and G. E. Coates, *J. Chem. Soc.* (*A*), 1966, 1069.

alkoxides that are monomeric in diethyl ether. In no case have we observed degrees of association less than two, and in three instances we were surprised to find that tetramers persisted—even in ether. Molecular weights were measured using a differential ebulliometer and a 36-junction copper–Constantan thermocouple. The results for the alkyl alkoxides studied are: EtMgOEt, $n = 4{\cdot}05$ (0·008—0·05M), $MeMgOBu^t$, $n = 4{\cdot}04$ (0·01—0·07M), $EtMgOBu^t$, $n = 3{\cdot}99$ (0·008—0·04M), $n = 3{\cdot}86$ (0·04—0·08M), $EtMgOCEt_3$, $n = 2{\cdot}01$ (0·007—0·05M), $EtMgOCMeEt_2$, $n = 2{\cdot}07$ (0·017—0·041M). Concentrations are given as moles of monomer per litre. The same apparatus was checked by measurement of the degree of association of methylmagnesium bromide [5] (up to 0·017M); this gave $n = 1{\cdot}00$.

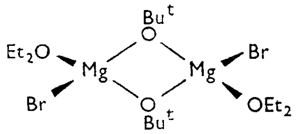
The above results provide additional evidence about the effect of steric factors on the degree of association of alkoxides. In a cubic-type tetramer alkoxy-groups have to take up a *cis*-position relative to each other, whereas a *trans*-arrangement is possible in dimers such as (I). The contrast between tetrameric $EtMgOBu^t$ and dimeric $EtMgOCEt_3$ is of particular interest, and must be due to the greater interference between CEt_3 than between CMe_3 groups. We have had opportunity to study only one of the compounds which is intermediate between the two just mentioned, *viz.* $EtMgOCMeEt_2$, and we found this was just perceptibly more associated than the triethyl compound. After we had completed our experimental work, we were interested to note that $MeMgOCMeEt_2$ had been found [4] to be still more associated, $n = 2{\cdot}8$, at a higher concentration (0·112M) than the highest concentration used for our experiments on the ethylmagnesium analogue.

We examined, in ether solution, only one of the alkoxides, $EtMgOPr^n$, which were 7—8-fold associated in benzene, and this one had a degree of association of *ca.* 6·5 at a concentration of 0·035M in diethyl ether. We make no further comment on this compound while its structure is being studied.

Products from Grignard Reagents and Carbonyl Compounds.—Though an immense number of reactions between Grignard reagents and carbonyl compounds have been carried out, the products formed before hydrolysis have only rarely been isolated. Products which have been isolated and analysed include $PhEtCHOMgBr,OEt_2$ (from EtMgBr + PhCHO, EtMgBr + PhEtCHOH, and PhMgBr + EtCHO), $PhMeEtCOMgBr,OEt_2$ (from EtMgBr + PhMeEtCOH, and from EtMgBr + PhCOMe), and $Ph_2CHOMgBr,OEt_2$ (from $Bu^iMgBr + Ph_2CO$ or Ph_2CHOH). These authors [16] noted that some of their alkoxymagnesium bromides lost ether readily, and that they were sparingly soluble in ether. No molecular weights were reported.

Preliminary experiments soon showed that relatively few alkoxymagnesium halides had solubilities in diethyl ether such as would allow their convenient recrystallisation from that solvent. There were other complications; for example, reaction between equimolar proportions of methylmagnesium bromide and acetaldehyde in ether resulted in the separation of a viscous lower phase from which we could obtain no crystalline material. Though ether could be displaced by tetrahydrofuran to give a crystalline complex ($Me_2CHOMgBr,THF$) this was too sparingly soluble in benzene to allow measurement of its molecular weight. Upon working with methyl- and ethyl-magnesium halides we were not troubled with significant alkane formation. This complication is evidently more pronounced with reactions of higher alkylmagnesium halides and carbonyl compounds.[17]

Fortunately, methylmagnesium bromide and acetone gave a t-butoxy-compound which was soluble enough to crystallise satisfactorily from ether. This product is dimeric both in ether and in benzene, though solutions in the latter very slowly deposited insoluble $(Bu^tOMgBr)_x$ which is very likely to be polymeric, there being at least two vacant co-ordination sites on each magnesium atom (of a hypothetical monomer) and various lone-pairs available (for example two on each oxygen and at least one on each bromine). The crystal structure of $(Bu^tOMgBr,OEt_2)_2$, which will be reported in detail elsewhere, has been determined by Dr. H. M. M. Shearer and Mr. P. T. Moseley, and is represented by (II).



(II)

The presence of bridging butoxy-groups rather than bridging bromine is additional evidence for the strong donor character of alkoxy-oxygen, and hence also for the formulation (I) of dimeric alkylmagnesium alkoxide–ether complexes. This compound (II) may have a similar structure in solution, though the t-butoxy ^1H n.m.r. signal is unexpectedly a doublet. This effect also observed for some other alkoxymagnesium compounds, is mentioned again later.

Ether-free t-butoxymagnesium bromide dissolves slowly in diethyl ether, and crystallisation then gives compound (II) again. Though compound (II) is the final product which crystallises from the solution obtained by the addition of acetone to methylmagnesium bromide, the reaction mechanism best supported by kinetic data would have $MeMgOBu^t$ as the primary product of the step in which the carbonyl group is alkylated.[5] In a subsequent step R^1MgOR^2 reacts with $MgBr_2$ to form R^2OMgBr and R^1MgBr. Such a reaction has been observed in one instance: [5]

$$Ph_2MeCOMgMe + MgBr_2 \longrightarrow Ph_2MeCOMgBr + MeMgBr$$

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[16] A. N. Nesmeyanov and V. A. Sazonova, *Izvest. Akad. Nauk S.S.S.R., Org. Khim. nauk*, **1941**, 499 (translated in 'Selected Works in Organic Chemistry,' A. N. Nesmeyanov, pp. 252—276, Pergamon Press, Oxford, 1963).

[17] Y. Yasuda, N. Kawabata, and T. Tsuruta, *J. Org. Chem.*, 1967, **22**, 1720.

We have found that compound (II) is formed, and crystallises, in the reaction:

$$(\mathrm{MeMgOBu^t})_4 + 4\mathrm{MgBr}_2 \xrightarrow{\mathrm{Et_2O}} 2(\mathrm{Bu^tOMgBr,OEt_2})_2 + 4\mathrm{MeMgBr}$$

The butoxy-bromide (II) is also formed from magnesium di-t-butoxide:

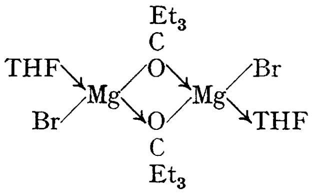
$$\mathrm{Mg(OBu^t)_2} + \mathrm{MgBr_2} \xrightarrow{\mathrm{Et_2O}} (\mathrm{Bu^tOMgBr,OEt_2})_2$$

As expected, tetrahydrofuran displaces diethyl ether from (II), to give $(\mathrm{Bu^tOMgBr,THF})_2$ which is dimeric in benzene and does not, in contrast to compound (II), slowly deposit insoluble $(\mathrm{Bu^tOMgBr})_x$.

Attempts at the preparation of chloro-analogues of (II) were not successful. Reaction between methylmagnesium chloride, in ether, with acetone gave a precipitate in which the ratio Mg : Cl was 1 : 1·44, and which was not significantly soluble in ether, tetrahydrofuran, benzene, or toluene. Precipitates of no simple composition were also obtained from ethylmagnesium chloride and both butan-2-one and pentan-2-one. However, reaction with 6-methylheptan-3-one gave a precipitate in which the magnesium : chlorine ratio was 1 : 1, and corresponded to the ether-free alkoxy-chloride $\mathrm{Me_2CHC_2H_4Et_2COMgCl}$. Studies on the molecular weights of Grignard reagents in ether indicate that chlorine has stronger bridging character towards magnesium than bromine or iodine, thus alkoxymagnesium chlorides are more likely to separate solvent-free from ether than the other halides.

Three alkoxymagnesium iodide–diethyl ether complexes have been prepared. The t-butoxy-compound $(\mathrm{Bu^tOMgI,Et_2O})$, from methylmagnesium iodide and acetone, is sparingly soluble both in ether and in benzene (less than 1 wt.%), and we did not measure its molecular weight. The solubilities in ether of the t-butoxy-series are Br > I > Cl, though the last is complicated probably by disproportionation processes. Reactions between methylmagnesium iodide and both pentan-3-one and pentan-2-one gave the crystalline ether complexes $(\mathrm{Et_2MeCOMgI,Et_2O})_2$ and $(\mathrm{Me_2Pr^nCOMgI,Et_2O})_2$, both dimeric in ether. The second of these was extremely soluble in ether and could be crystallised only from ether–hexane mixtures. The product $(\mathrm{Et_2MeCOMgI,Et_2O})_2$ is less soluble in ether than the corresponding bromide.

Though the products from alkylmagnesium bromides were, in general, easier to prepare, their relatively high dissociation pressures made it difficult to isolate the ether complexes in a pure state. To our surprise, the product $(\mathrm{Et_3COMgBr,Et_2O})$ from ethylmagnesium bromide and pentan-3-one is only slightly soluble in ether, and is much less soluble than the t-butoxy-complex (II). It loses ether readily, and when heated in a sealed capillary under nitrogen it softens at *ca.* 55° and becomes dry by 95° due to loss of ether. Its insolubility in benzene, in contrast to compound (II), may be ascribed to its ready loss of ether to give polymeric $(\mathrm{Et_3COMgBr})_x$. Naturally, ether is displaced by tetrahydrofuran and the product dissolves in benzene without the deposition of insoluble matter. The degree of association (1·72 and 1·79 at 1·67 and 2·50 wt.% concentration) of this complex suggests that the solution consists largely of compound (III) together with some free tetrahydrofuran and some benzene-soluble species more associated than dimeric. This is also likely to be true for the t-butoxy-analogue of (III), the observed degrees of association of which in benzene (see Experimental section) were also rather less than two.



(III)

The product $(\mathrm{Et_2MeCOMgBr,Et_2O})$, from methylmagnesium bromide and pentan-3-one, separates from ether as very large crystals, which can only be preserved in an atmosphere containing much ether. Attempts at the measurement of dissociation pressures were hindered by the very slow rate at which equilibrium was attained, but in this one instance measurements were continued until the pressure was constant for many hours. The dissociation pressure is 20·6 mm. at 20·0°. The ether-free material, easily obtained by warming compound (III) to 55° for 2 hr. under reduced pressure, is insoluble in benzene and is no doubt a co-ordination polymer $(\mathrm{Et_2MeCOMgBr})_x$. The ether complex is insoluble in benzene because it at once decomposes to ether and the polymer. In diethyl ether, however, it is dimeric, the observed degree of association being 2·03 over the concentration range 0·0019 to 0·012 moles per litre (of monomer), a structure similar to compound (II) being indicated.

^{1}H *N.m.r. Spectra*.—The spectra of some of the alkylmagnesium alkoxides contain unexpected splitting of certain resonances. For example, that of methylmagnesium t-butoxide in benzene consists of two broad resonances (the solution is viscous) at 8·06 (MeMg) and 5·94 ($\mathrm{Bu^tO}$) p.p.m. to the high field from benzene. When the temperature was raised to 100° a decrease in viscosity occurred and the t-butoxy-resonance was split into two unequal components, 4·2 c./sec. apart, that at low field being the more intense. The methylmagnesium resonance becomes a sharp singlet.

Each resonance in the spectrum of ethylmagnesium t-butoxide in benzene (*ca.* 20 wt.%) is split into a close doublet 1—2 cycles apart. The t-butoxy-resonance is a doublet at +5·86 and +5·89 p.p.m. from benzene, the former being somewhat bigger. Likewise, each member of the Mg–$\mathrm{CH_2}$ quartet is split: +7·11, 7·16; 7·24, 7·30; 7·41, 7·45 and 7·52, and 7·57, and each member of the $\mathrm{MgCH_2C}H_3$ triplet, 5·49, 5·54; 5·64, 5·69 and 5·77, and 5·81. The spectrum of Pr^iMgOPr^i (in benzene) is normal except that the three strongest components of the $MgCHMe_2$ septet are split by *ca.* 1·5 cycles. Both Pr^iMgOPr^i and $EtMgOBu^t$, which are tetrameric in benzene, and $MeMgOBu^t$ which is tetrameric even in ether, are evidently more complicated, at least in solution, than would be indicated by a simple structural analogue of crystalline $(MeZnOMe)_4$. In contrast, the spectrum of the other tetramer, $(EtMgOPr^i)_4$, contains no unexplained splitting, as it consists (benzene solution) of a doublet at +6·03 (*J* 6 c./sec.) and a septulet at +3·30 (*J* 6) due to OPr^i, and a triplet at +5·64 (*J* 7·8) with a quartet at +7·36 (*J* 8·4) due to EtMg, resonances being expressed as p.p.m. from benzene.

Of the alkoxides which were more associated (*n*, *ca.* 7—8 in benzene), $EtMgOPr^n$ shows no abnormality in its ^1H n.m.r. spectrum, but this is not true for Pr^iMgOMe and Pr^iMgOEt. The methoxy-compound was not sufficiently soluble in benzene to allow the observation of details of the $MgCHMe_2$ septet, but the methoxy-resonance is an unequal doublet at +3·80 (stronger) and +3·86 p.p.m. from benzene. The ethoxide, Pr^iMgOEt, is more soluble in benzene, and each component of its spectrum is split into unequal doublets 1·5—2·5 c./sec. apart. We cannot offer any satisfactory explanation for these effects, nor have we been able to explore the influence of concentration and temperature.

Still less have the ^1H n.m.r. spectra of the alkoxymagnesium halides been studied, although one of these shows anomalies of the type reported above. The spectrum of $(Bu^tOMgBr,Et_2O)_2$ in benzene (*ca.* 5 wt.%) consists of a quartet at +3·58 (*J* 6·6, but the peaks are not sharp), and a sharp triplet at +6·16 (*J* 7·2) due to ethyl groups, and a nearly equal doublet at +5·79 and +5·84 p.p.m. from benzene due to t-butoxy-groups. The splitting of the t-butoxy-resonance may possibly be due to the presence of an isomer of compound (II) in which the bromine atoms have a *cis*-rather than the *trans*-configuration found for the crystal. Effects due to possible *cis–trans* isomerism of t-butyl groups about the Mg_2O_2 ring are not likely to be significant since the skeleton consisting of the Mg_2O_2 ring and the two tertiary carbon atoms are all in one plane (in the crystal). The resonance due to t-butoxy-groups in the tetrahyrofuran complex (in benzene) is single. An identical ether-free product is obtained when a solution of dimethylmagnesium in diethyl ether crystallises at room temperature.

EXPERIMENTAL

All compounds described are very sensitive to air and were at all times handled *in vacuo*, or under nitrogen. They were analysed by hydrolysis in apparatus attached to a ' vacuum line ', followed by determination of magnesium (E.D.T.A.) and (when appropriate) halide and hydrolysable alkyl. Dimethyl- and diethyl-magnesium were prepared both from magnesium and the mercury dialkyl,[18] and by the dioxan precipitation method.[19] Di-isopropylmagnesium was made by the latter method.

Crystallisation of Dimethylmagnesium.—Colourless needles separated when a solution of dimethylmagnesium in ether (*ca.* 0·4 moles/l.) was cooled to −78°. These were separated but were not dried under reduced pressure. As they warmed to room temperature the transparent needles became white and powdery. A specimen of the white product was sealed in a capillary and its diffraction pattern was obtained using Cu-K_α radiation. The *d*-values (Å) are listed, those obtained for a product which had been thoroughly separated from ether *in vacuo*, and which was shown analytically to be ether-free dimethylmagnesium, being given in parentheses: 5·79 (5·76), 5·33 (5·34), $3{\cdot}30_4$ ($3{\cdot}30_2$), $2{\cdot}65_2$ ($2{\cdot}66_6$), $2{\cdot}42_5$ ($2{\cdot}43_0$), $2{\cdot}07_4$ ($2{\cdot}07_4$), $2{\cdot}01_4$ ($2{\cdot}01_7$), $1{\cdot}96_9$ ($1{\cdot}97_1$), and $1{\cdot}90_0$ ($1{\cdot}90_3$). An identical ether-free product is obtained when a solution of dimethylmagnesium in diethyl ether crystallises at room temperature.

Alkylmagnesium Alkoxides

Methylmagnesium t-Butoxide.—Addition of t-butyl alcohol (0·736 g., 0·0099 mole) to be a vigorously stirred solution of dimethylmagnesium (0·01 mole) in ether (32 c.c.) at −96°, resulted in evolution of methane when the mixture had warmed to *ca.* −70°. Removal of solvent left a white residue which was soluble in pentane and hexane but could not be crystallised. Solvent was removed from the solution in pentane by evaporation, finally at 50° for 2 hr. under reduced pressure. The *product* decomposed at *ca.* 270° when heated under nitrogen, but slowly sublimed *in vacuo* at 200° (Found: Mg, 21·59; hydrolysable methyl, 13·50. $C_5H_{12}MgO$ requires Mg, 21·62; hydrolysable methyl, 13·36%).

Ethylmagnesium Ethoxide.—Magnesium ethoxide was prepared by addition of ethanol (0·01 mole) in ether (10 c.c.) to diethylmagnesium (0·005 mole) in ether (17·5 c.c.) at −78°. Solvent was evaporated at room temperature and the residue was heated at 100° for 30 min. Addition of diethylmagnesium (0·005 mole) in ether (17·5 c.c.) to the magnesium ethoxide resulted in solution of nearly all the latter when the mixture was vigorously stirred. The solution was filtered, and the ethoxide crystallised when the filtrate was cooled (Found: Mg, 24·6; hydrolysable ethyl, 30·0. Calc. for $C_4H_{10}MgO$: Mg, 24·7; hydrolysable ethyl 29·5%). The i.r. spectrum of the product was identical to that of ethylmagnesium ethoxide prepared from equimolar proportions of diethylmagnesium and ethanol, and purified by sublimation.[20] It is almost insoluble both in hexane and toluene.

Ethylmagnesium n-Propoxide.—Addition of n-propanol (0·78 g., 0·013 mole) in ether (10 c.c.) to diethylmagnesium (0·0128 mole) in ether (20 c.c.) at −70° resulted in formation of a gelatinous precipitate, which dissolved with gas evolution as the mixture reached room temperature. The reaction was completed by boiling for 10 min. Ether was evaporated and the *alkoxide* was recrystallised from hexane (−20°), m.p. 260—290° (decomp.) [Found: Mg, 21·6; hydrolysable ethyl, 25·6%; *M* (cryoscopically, 2·80,

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[18] R. E. Dessy, F. Kaplan, G. Coe, and R. M. Salinger, *J. Amer. Chem. Soc.*, 1963, **85**, 1191; D. Cowan and H. Mosher, *J. Org. Chem.*, 1962, **27**, 1.

[19] G. O. Johnson and A. Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 1943; W. Strohmeier and F. Seifert, *Chem. Ber.*, 1961, **94**, 2356.

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

2·30 wt.% in benzene), 783, 802. $C_5H_{12}MgO$ requires Mg, 21·6; hydrolysable ethyl, 25·8%; *M*, 112].

Ethylmagnesium Isopropoxide.—This was similarly prepared, but the gelatinous precipitate decomposed more slowly and the mixture had to be warmed to 30° for several minutes before all of the ethane was evolved and a clear solution was obtained. After evaporation of ether the residue was crystallised from hexane as small *needles*, m.p. 230—270° (decomp.) [Found: Mg, 21·4; hydrolysable ethyl, 25·5%; *M* (cryoscopically, 1·73, 2·05 wt.% in benzene), 458, 470. $C_{20}H_{48}Mg_4O_4$ requires Mg, 21·6; hydrolysable ethyl, 25·8%; *M*, 449].

Ethylmagnesium t-Butoxide.—Reaction in this instance was completed by warming at 35° for 10 min. The solution was filtered free from a small amount of insoluble matter, and ether was then removed, finally at 70° (10^{-2} mm.) for 30 min. Nearly all the residue dissolved in hexane, and the *butoxide* crystallised at −70°, decomp. 200° [Found: Mg, 19·1; hydrolysable ethyl, 23·0%; *M* (cryoscopically, 1·84, 2·25 wt.% in benzene) 490, 498. $C_{24}H_{56}Mg_4O_4$ requires Mg, 19·2; hydrolysable ethyl, 23·0%; *M*, 505].

Isopropylmagnesium Methoxide.—Similarly prepared, from di-isopropylmagnesium and methanol, the *methoxide* left, after removal of ether, was crystallised from warm toluene–hexane, decomp. 210—250° [Found: Mg, 24·5; hydrolysable propyl, 43·4%; *M* (cryoscopically, 1·25, 1·40, 4·06 wt.% in benzene) 682, 722, 818. $C_4H_{10}MgO$ requires Mg, 24·7; hydrolysable propyl, 43·7%; *M*, 98].

Isopropylmagnesium Ethoxide.—Addition of ethanol (0·46 g., 0·010 mole) in ether (15 c.c.) to di-isopropylmagnesium (0·0095 mole) in ether (50 c.c.) at −30° resulted in formation of a white precipitate of amorphous appearance. The mixture slowly evolved gas at room temperature and the solution became clear after 30 min., apart from a trace of white solid, probably $Mg(OPr^n)_2$. Ether was removed from the filtrate and the residue was extracted with boiling hexane. The *ethoxide* crystallised at *ca.* −50° [Found: Mg, 21·5; hydrolysable propyl, 38·0%; *M* (cryoscopically, 1·31, 1·70 wt.% in benzene) 840, 910. $C_5H_{12}MgO$ requires Mg, 21·6; hydrolysable propyl, 38·3%; *M*, 112].

Isopropylmagnesium Isopropoxide.—Reaction between isopropyl alcohol (0·010 mole) in ether (15 c.c.) and di-isopropylmagnesium (0·0097 mole) in ether (50 c.c.) produced an adduct which slowly evolved gas at room temperature, but left a white solid in suspension. Evaporation of ether gave a residue of gelatinous appearance which became dry and friable after 1 hr. *in vacuo*. This product dissolved in hexane (20 c.c.) and crystallised (−20°) as *needles*, decomp. 230° without melting [Found: Mg, 19·0; hydrolysable propyl, 34·0%; *M* (cryoscopically, 2·0, 3·1 wt.% in benzene) 520, 530. $C_{24}H_{56}Mg_4O_4$ requires Mg, 19·2; hydrolysable propyl, 34·0%; *M*, 505].

Ethylmagnesium 3-Ethylpentyl-3-oxide.—Pentan-3-one (0·91 g., 0·0106 mole) in ether (10 c.c.) was added to a stirred solution of diethylmagnesium (0·0106 mole) in ether (15 c.c.) at −70°, to give a pale yellow solution. The colour disappeared as the solution warmed to *ca.* −30°. After the mixture had been stirred for a few minutes at room temperature, it was cooled to −70° when crystals of the *ether complex* separated [Found: Mg, 10·2; hydrolysable ethyl, 12·15; diethyl ether, 30·0%; *M* (cryoscopically, 1·12, 2·69 wt.% in benzene) 255, 295. $C_{13}H_{30}MgO_2$ requires Mg, 10·0, hydrolysable ethyl, 11·95; diethyl ether, 30·5%; *M*, 242]. This complex loses ether very easily. When heated under nitrogen in a sealed capillary tube it softens with the appearance of melting at 63—64°, then becomes dry, and finally melts at 247—248°, the last m.p. also being the m.p. of the ether-free material. The same complex (with the same i.r. spectrum and behaviour on heating) was obtained from diethylmagnesium and 3-ethylpentan-3-ol in ether; it also crystallised at −70° (Found: Mg, 10·0; hydrolysable ethyl, 12·0%).

The ether-free alkoxide was obtained by heating the ether complex at 55° under reduced pressure, m.p. 247—248° (Found: Mg, 14·4; hydrolysable ethyl, 17·1. $C_9H_{20}MgO$ requires Mg, 14·5; hydrolysable ethyl, 17·2%). It is insoluble in benzene.

The tetrahydrofuran complex, $EtMgOCEt_3(C_4H_8O)$, crystallised when a solution of the ether complex in tetrahydrofuran was cooled to −78°, m.p. 161—162° [Found: Mg, 10·0; hydrolysable ethyl, 11·6%; *M* (cryoscopically, 1·0, 1·5 wt.% in benzene) 502, 535. $C_{26}H_{56}Mg_2O_4$ requires Mg, 10·1; hydrolysable ethyl, 12·0%; *M*, 480].

Ethylmagnesium 3-Methylpentyl-3-oxide.—This was not isolated but was prepared from diethylmagnesium and 3-methylpentan-3-ol in diethyl ether as described for the corresponding methylmagnesium compound.[4] It was used only for molecular weight measurement in ether solution.

Alkoxymagnesium Halides

t-Butoxymagnesium Bromide.—(a) *Diethyl ether complex*. Acetone (0·63 g., 0·0108 mole) in ether (15 c.c.) was added to a stirred solution of methylmagnesium bromide (0·0108 mole) in ether (25 c.c.) at −70°. As the mixture warmed to *ca.* −20° crystals appeared. The *product* was separated and recrystallised from ether (3 × 50 c.c.). It did not melt when heated, but the crystals shrank at 90° and softened at 200°. Care is necessary to avoid loss of ether during the usual separation processes, and the product takes on a chalky appearance due to loss of ether unless it is kept in an atmosphere containing ether [Found: Br, 31·8; Mg, 9·50; diethyl ether, 29·0%; *M* (cryoscopically, 1·62, 2·82 wt.% in benzene) 437, 475, (ebullioscopically 0·006—0·018M, with respect to monomer, in ether) 510. $C_{16}H_{38}Br_2Mg_2O_4$ requires Br, 31·8; Mg, 9·7; diethyl ether, 29·5%, *M*, 502].

(b) *Ether-free*. A clear solution of the diethyl ether complex (1 g.) in benzene (20 c.c.) was stirred at room temperature. A white precipitate appeared after 20 min., and the precipitation was completed by warming to 50° for 30 min. Solvent was then removed under reduced pressure, benzene (20 c.c.) was added, and the precipitated *butoxide* was filtered off and washed with warm (60°) benzene (2 × 20 c.c.). It did not melt, but appeared to decompose at *ca.* 200° (Found: Br, 43·5; Mg, 13·5. C_4H_9BrMgO requires Br, 45·1; Mg, 13·7%). t-Butoxymagnesium bromide very slowly dissolves when stirred with diethyl ether. It was insoluble in all the hydrocarbons tried.

(c) *Tetrahydrofuran complex*. The diethyl ether complex (1 g.) was dissolved in tetrahydrofuran (10 c.c.). After 1 hr., solvent was removed by evaporation, finally at 55° for 50 min. The residue was dissolved in benzene and crystallised as long thin *plates*. The product decomposed (*ca.* 190°) without melting when it was heated under nitrogen [Found: Br, 32·9; Mg, 9·8%; *M* (cryoscopically, 1·06, 2·12 wt.% in benzene) 434, 446. $C_{16}H_{34}Br_2Mg_2O_4$ requires Br, 32·1; Mg, 9·7%; *M*, 498].

(d) *Preparation of compound* (II) *from methylmagnesium t-butoxide and magnesium bromide.* Magnesium bromide (0·005 mole, prepared from magnesium and bromine in ether at low temperature) in ether (50 c.c.) was added to a solution (at room temperature) of methylmagnesium t-butoxide (0·005 mole) prepared by the addition of t-butyl alcohol (0·376 g., 0·005 mole) in ether (15 c.c.) to dimethylmagnesium (0·005 mole) in ether (16·6 c.c.) at −78°. The initially clear solution became cloudy after *ca.* 10 min. and stirring was continued for 1½ hr. The solution volume was then reduced to *ca.* 15 c.c. and the product which separated after cooling to −78° was found to be compound (II) (identical i.r. spectrum). The filtrate was analysed and contained 0·0047 mole of hydrolysable methyl, 0·00685 mole of magnesium, and 0·00696 mole of bromide, consistent with its being a mixture of MeMgBr (0·0047 mole) and Bu^{t}OMgBr (0·00215 mole).

(e) *Preparation of compound* (II) *from magnesium t-butoxide and magnesium bromide.* t-Butyl alcohol (0·010 mole) in ether (10 c.c.) was added to diethylmagnesium (0·005 mole) in ether (14·8 c.c.) at −78°. Ethane evolution was not immediate but a white precipitate, which did not dissolve at room temperature, was formed at *ca.* −60°. Magnesium bromide (0·005 mole) in ether (50 c.c.) was added, and resulted in the precipitate of magnesium t-butoxide taking on a more voluminous appearance. Most, but not all, of the precipitate dissolved when the mixture was boiled, and compound (II) crystallised when the mixture had been filtered, concentrated to half its original volume, and cooled. It had identical i.r. and ^{1}H n.m.r. spectra to the product from acetone and methylmagnesium bromide.

3-*Ethyl-pentan*-3-*oxymagnesium Bromide*.—(a) *Diethyl ether complex.* Pentan-3-one (0·97 c.c., 0·0092 mole) in diethyl ether (10 c.c.) was slowly added to ethylmagnesium bromide (0·0092 mole) in ether (30 c.c.). The mixture, which was clear and colourless, was allowed to warm and it deposited a precipitate at *ca.* −10°. After the mixture had been stirred for 30 min. at room temperature it was heated to boiling point and filtered. A little of the *ether complex*, which is sparingly soluble in ether, separated as the filtrate cooled. Further amounts were obtained by extraction with warm ether. The product was stored under an atmosphere rich in ether vapour. When heated under nitrogen it appears to soften and moisten at 54°, has a dry appearance (loss of ether) by 95°, and decomposes above 200° without melting (Found: Br, 27·5; Mg, 8·3; diethyl ether, 24·7. $C_{11}H_{25}BrMgO_2$ requires Br, 27·2; Mg, 8·3; diethyl ether, 25·2%).

(b) *Tetrahydrofuran complex.* This was obtained by dissolving the diethyl ether complex in tetrahydrofuran, and concentrating the solution until the *complex* crystallised. When heated, the product became opaque at *ca.* 150° [Found: Br, 27·0; Mg, 8·2%; *M* (cryoscopically, 1·67, 2·50 wt.% in benzene) 500, 520. $C_{22}H_{46}Br_2Mg_2O_4$ requires Br, 27·4; Mg, 8·3%; *M*, 582].

3-*Methylpentan*-3-*oxymagnesium Bromide–Diethyl Ether Complex*.—Pentan-3-one (1·57 c.c., 0·0149 mole) in diethyl ether (10 c.c.) was added to methylmagnesium bromide (0·0149 mole) in ether (10 c.c.) at −78°. A precipitate formed as the mixture warmed to room temperature and dissolved to a clear colourless solution at 35°. Very large crystals of the *ether complex* were formed when the filtrate cooled. These were washed once with cold ether, and dried very briefly in dry nitrogen. When heated under nitrogen the product softens at 66° and gradually decomposes from 200—300° without melting (Found: Br, 28·3; Mg, 8·7; diethyl ether, 26·4. $C_{10}H_{23}BrMgO_2$ requires Br, 28·6; Mg, 8·7; diethyl ether (26·4%). The organic hydrolysis product was identified as 3-methylpentan-3-ol by its b.p. and i.r. spectrum.

The *ether-free* alkoxy-bromide was obtained by heating the ether complex at 55° for 2 hr. *in vacuo*. It is insoluble in benzene and, when heated, decomposes from 200° without melting (Found: Br, 39·8; Mg, 11·9. $C_5H_{13}BrMgO$ requires Br, 38·9; Mg, 11·9%).

2-*Methylbutan*-2-*oxymagnesium Bromide-Diethyl Ether Complex*.—Acetone (1·34 c.c., 0·0182 mole) in ether (10 c.c.) was added to ethylmagnesium bromide (0·0182 mole) in ether (20 c.c.) at −78°. The *product* was separated, as described for the product from pentan-3-one and methylmagnesium bromide, and gave large crystals (Found: Mg, 9·2. $C_9H_{21}BrMgO_2$ requires Mg, 9·2%).

2-*Methylpropan*-2-*oxymagnesium Bromide–Tetrahydrofuran Complex*.—Acetaldehyde (1·02 c.c., 0·0180 mole) in ether (10 c.c.) was added to methylmagnesium bromide (0·0180 mole) in ether (20 c.c.) at −78°. Two liquid layers were formed when the mixture had reached room temperature and had been concentrated. Solvent was removed under reduced pressure at 30° and the residue was dissolved in tetrahydrofuran (10 c.c.). The *tetrahydrofuran complex* crystallised when the solution was concentrated. It softens at 74° and decomposes from *ca.* 150° (Found: Br, 34·2; Mg, 10·6. $C_7H_{15}BrMgO_2$ requires Br, 33·9; Mg, 10·3%). The complex is not appreciably soluble in benzene at room temperature.

t-Butoxymagnesium Iodide–Diethyl Ether Complex.—Addition of acetone (0·0091 mole) in ether (20 c.c.) to methylmagnesium iodide (0·0091 mole) in ether (20 c.c.) at −78° gave a white precipitate immediately. After it had been stirred 20 min. at room temperature, the mixture was heated to boiling point and filtered hot. Colourless crystals of the *ether complex* separated as the filtrate cooled. They were separated, washed twice with cold ether, dried briefly in dry nitrogen, and stored under a nitrogen–ether atmosphere (Found: I, 42·6; Mg, 8·5; diethyl ether, 26·8. $C_8H_{19}IMgO_2$ requires I, 44·0; Mg, 8·4; diethyl ether, 27·4%). The iodide is less soluble than the corresponding bromide, both in ether and in benzene.

3-*Methyl-pentan*-3-*oxymagnesium Iodide–Diethyl Ether Complex*.—Addition of pentan-3-one (0·0104 mole) in ether (10 c.c.) to methylmagnesium iodide (0·0104 mole) in ether (20 c.c.) at −78° resulted in the formation of a precipitate only as the mixture warmed to room temperature. The mixture was heated to boiling, more ether (20 c.c.) was added, and most of the precipitate dissolved. The filtrate deposited large crystals of the *ether complex*, which were washed twice with cold ether, and stored in a nitrogen–ether atmosphere [Found: I, 38·3; Mg, 7·4; diethyl ether, 21·6%; *M* (ebullioscopically, 0·002—0·0075M with respect to monomer, in ether) 716 (*n* = 2·2). $C_{20}H_{46}I_2Mg_2O_4$ requires Mg, 7·4; I, 38·9; diethyl ether, 22·6%; *M*, 652]. It is less soluble in ether than the analogous bromide.

2-*Methylpentan*-2-*oxymagnesium Iodide–Diethyl Ether Complex*.—Pentan-2-one (0·0104 mole) in ether (10 c.c.) was added to methylmagnesium iodide (0·0104 mole) in ether (20 c.c.) at −78°. No precipitate appeared at that temperature or when the mixture was boiled. The *ether complex* crystallised when the mixture had been cooled to −78°. It is very soluble in ether, and was recrystallised from an ether–hexane mixture [Found: I, 39·5; Mg, 7·4; diethyl ether, 22·6%; M (ebullioscopically, 0·0128—0·24M in ether, with respect to monomer) 683 ($n = 2·1$). $C_{20}H_{46}I_2Mg_2O_4$ requires I, 38·9; Mg, 7·4; diethyl ether, 22·6%; M, 652].

3-*Ethyl*-6-*methylheptan*-3-*oxymagnesium Chloride*.—Addition of 6-methylheptan-3-one (2·10 c.c., 0·0136 mole) in ether (20 c.c.) to ethylmagnesium chloride (0·0136 mole) in ether (10 c.c.) at −78° resulted in a pale yellow colour, which faded as the mixture warmed. A small amount of precipitate was present at room temperature, and this was filtered off. The filtrate gradually deposited a white *precipitate*, which did not dissolve on heating, and was separated (Found: Cl, 15·9; Mg, 11·1. $C_{10}H_{21}ClMgO$ requires Cl, 16·3; Mg, 11·2%).

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