The Crystal Structure of the Addition Product of a Grignard Reagent with a Ketone

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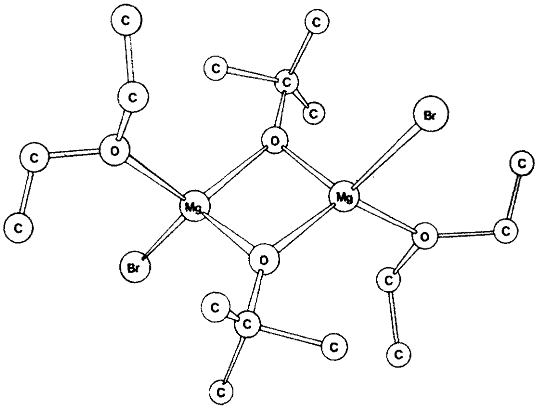
THOUGH much effort has been devoted to the study not only of the constitution of Grignard reagents but also to the kinetics of their reactions with carbonyl compounds,[1] there is little information about the nature of the products of these reactions that are present before the usual hydrolysis is carried out.

Many of these reaction products have inconvenient solubility properties in diethyl ether, but a few, including $Et_2MeCOMgBrOEt_2$, $Et_2MeCOMgIOEt_2$, and $Me_2Pr^nCOMgIOEt_2$, have been crystallised and found to be dimeric in ether.[2] One of them, the t-butoxymagnesium bromide ether complex, is dimeric both in ether and in benzene.[3] The structure and the nature of the association of such compounds is clearly relevant to studies on reactions between Grignard reagents and carbonyl compounds.

The product of the reaction between methylmagnesium bromide and acetone crystallises from diethyl ether in a monoclinic cell with $a = 9{\cdot}68$, $b = 11{\cdot}10$, $c = 15{\cdot}10$ Å, $\beta = 129°8'$, space group $P2_1/c$. The unit cell contains two units of $[Bu^tOMgBrOEt_2]_2$. The structure was solved by the heavy-atom method and was refined by the least-squares method. The reliability index for the 672 independent non-zero reflections is 0·10.

The molecule is a dimer, as in solution, and contains a four-membered Mg–O ring, as shown in the Figure. From the space group requirements, the molecular symmetry is $\bar{1}$. The ring angle at magnesium (83·3°) is smaller than that at oxygen (96·7°) and hence the other angles at magnesium are greater than the tetrahedral value.

Of interest is that all the oxygen atoms are three-co-ordinate, each oxygen and its three attached atoms being co-planar within the limits of experimental error. The ring oxygen atoms, the magnesiums, and the tertiary carbon atoms of the t-butyl groups all deviate by less than 0·01 Å from their mean plane and the situation with respect to the oxygen and α-carbon atoms of the ether molecule and to the magnesiums is scarcely less precise. A similar environment at the ether oxygens was found in EtMgBr(OEt$_2$)$_2$,[4] where the trigonal configuration was thought to be more characteristic of ionic bonding.



FIGURE

A second feature, which may be related to the first, is the occurrence of two different Mg–O distances. While the Mg–O length (2·01 Å) involving the ether oxygen atoms compares well with those measured in the crystalline Grignard reagents,[4,5] the Mg–O distances (1·91 and 1·91Å) in the ring are significantly shorter than any of these values. Though magnesium 3*d* orbitals are normally regarded as relatively diffuse and of high energy, some appreciable $d\pi$–$p\pi$ interaction as suggested in connection with the (Bu^{n}MgOPr^i)$_3$ trimer,[6] would be facilitated by the presence of electronegative atoms bonded to magnesium and may possibly cause this bond shortening in the Mg$_2$O$_2$ ring.

The existence of alkoxy-bridges in the t-butoxymagnesium bromide ether complex makes it likely that the alkoxides EtMgOCMeEt$_2$ and EtMgOCEt$_3$, which also are dimeric in diethyl ether, have alkoxy-bridges. Surprisingly, MeMgOBu^t, EtMgOBu^t, and EtMgOEt are found to be tetrameric, even in diethyl ether (0·008—0·05 g. atom Mg per litre, ebullioscopically),[2] and in these cases each alkoxy-oxygen is likely to use both its lone-pairs giving a cubane-type structure as in (MeZnOMe)$_4$.[7]

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