

Preparation and Characterization of Alkylmagnesium Hydrides

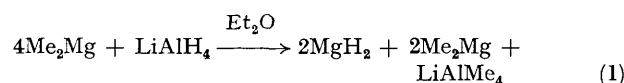
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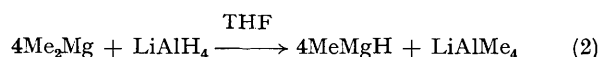
Summary Pure RMgH compounds have been prepared, as stable tetrahydrofuran solutions at room temperature, by the reaction of the corresponding R_2Mg compound with an active form of MgH_2 in THF; in this way MeMgH, EtMgH, PrⁱMgH, and CpMgH have been prepared and characterized (Cp = cyclopentadienyl).

THE existence of compounds of the type RMgH has been the subject of interest and speculation for many years as these compounds are analogues of Grignard reagents. Rice and his co-workers¹ reported in 1956 the formation of PhMgH in the reaction of PhMgBr with $LiAlH_4$ (4:1) in ether. Later we showed² that the products of this reaction were not the same as reported by Rice. In 1962, Bauer³ reported the preparation of EtMgH in the reaction of silane with Me_2Mg in ether, but characterization data were not given. The formation of EtMgH as an intermediate in the reaction of Et_2Mg and $NaBEt_3H$ was reported,⁴ but the compound was stable only at $-78^\circ C$ and disproportionated at $-20^\circ C$ to give MgH_2 and Et_2Mg . Our earlier attempts⁵ to prepare EtMgH by the reaction of $LiAlH_4$ with Et_2Mg (1:4) and of MgH_2 with Et_2Mg in ether were not successful in that MgH_2 was recovered in both cases. We report here for the first time, the preparation of tetrahydrofuran (THF) soluble RMgH compounds.

When $LiAlH_4$ in THF was treated with a THF solution of Me_2Mg (1:4), a clear solution resulted. Since MgH_2 is very insoluble in THF, the reaction course observed in ether [equation(1)] is undoubtedly not involved here. An



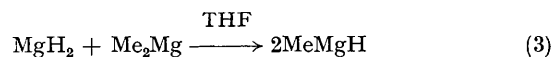
i.r. spectrum of the reaction mixture showed bands at 530 and 695 cm^{-1} characteristic of Mg–Me⁶ and $LiAlMe_4$, respectively, and no bands characteristic of Al–H stretching in the 1700 cm^{-1} region. This supports the reaction shown in equation (2).



¹H N.m.r. spectra of the reaction solution showed a sharp singlet at τ 11.74 (3.53 p.p.m. upfield from the THF multiplet) which was almost at the position of Me_2Mg , and

six closely spaced singlets corresponding to signals due to $LiAlMe_4$.⁷ The 1:1 ratio of the upfield singlet to the six singlets suggests that the number of methyl groups attached to magnesium are the same as those attached to aluminium, supporting the proposed reaction [equation (2)]. $MeMgH$ could not be isolated from the reaction mixture in a pure state.

Pure MeMgH was prepared by the reaction of Me_2Mg with an active† form of MgH_2 in THF at room temperature [equation (3)]. The MgH_2 readily dissolved in the THF



solution of Me_2Mg producing a clear solution in a few minutes. The Me:Mg:H ratio of the reaction product was 1.00:0.98:1.02 and the solution was stable at room temperature for several days. An i.r. spectrum of the solution showed bands at 2800m, 1400w, 1375w, 1290 (bridging Mg–H),[†] 1025s, 860s, 690br, and 525s (Mg–Me) cm^{-1} ,[†] and the ¹H n.m.r. spectrum in THF showed a singlet at τ 11.71 (3.50 p.p.m. upfield from THF multiplet) corresponding to the singlet observed in reaction (2). Unfortunately, the Mg–H signal was not observed in the n.m.r. spectrum probably owing to its masking by the THF solvent. Molecular association studies in THF show MeMgH to be dimeric at low concentrations (0.04); association increases with increase in concentration.

Several other RMgH compounds (where R = Et, Prⁱ, and cyclopentadienyl) have also been prepared by the reaction of the corresponding R_2Mg compound with active MgH_2 in THF. Clear solutions formed in each case that were stable to cleavage by THF, except in the case of EtMgH.

When Me_2Mg was added to active MgH_2 (1:3) in THF ca. 90% of the initial MgH_2 dissolved. I.r. and n.m.r. spectra indicated the formation of $MeMg_2H_3$ [equation (4)].⁸



The RMgH and RMg_2H_3 compounds react with ketones to produce both alkylation and reduction products.

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† The active form of MgH_2 was prepared by the reaction of $LiAlH_4$ with Et_2Mg (1:1) in ether.

‡ Coates (N. A. Bell and G. E. Coates, *J. Chem. Soc.*, 1965, 692) has shown by i.r. studies of RBeH compounds that the strong band at 1330 cm^{-1} is the bridging beryllium hydrogen stretching (BeH_2Be) since the band shifted to 970 cm^{-1} in the RBeD compound. We prepared MeMgD in THF by the reaction of Me_2Mg with MgD_2 and compared its i.r. spectrum with that of MgH_2 . We found that the band at 1290 cm^{-1} (in MeMgH) was shifted to 930 cm^{-1} in the MeMgD solution. By analogy to RBeH compounds, it is suggested that the broad band present at 1290 cm^{-1} in MeMgH is due to bridging magnesium–hydrogen (MgH_2Mg) stretching.

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