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 $\mathrm{R_2Mg}$ compound with an active form of $\mathrm{MgH_2}$ in THF; in this way MeMgH, EtMgH, $\mathrm{Pr^iMgH}$, 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-workers[1] reported in 1956 the formation of PhMgH in the reaction of PhMgBr with $\mathrm{LiAlH_4}$ (4: 1) in ether. Later we showed[2] that the products of this reaction were not the same as reported by Rice. In 1962, Bauer[3] reported the preparation of EtMgH in the reaction of silane with $\mathrm{Me_2Mg}$ in ether, but characterization data were not given. The formation of EtMgH as an intermediate in the reaction of $\mathrm{Et_2Mg}$ and $\mathrm{NaBEt_3H}$ was reported,[4] but the compound was stable only at −78 °C and disproportionated at −20 °C to give $\mathrm{MgH_2}$ and $\mathrm{Et_2Mg}$. Our earlier attempts[5] to prepare EtMgH by the reaction of $\mathrm{LiAlH_4}$ with $\mathrm{Et_2Mg}$ (1: 4) and of $\mathrm{MgH_2}$ with $\mathrm{Et_2Mg}$ in ether were not successful in that $\mathrm{MgH_2}$ was recovered in both cases. We report here for the first time, the preparation of tetrahydrofuran (THF) soluble RMgH compounds.

When $\mathrm{LiAlH_4}$ in THF was treated with a THF solution of $\mathrm{Me_2Mg}$ (1: 4), a clear solution resulted. Since $\mathrm{MgH_2}$ 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 $\mathrm{cm^{-1}}$ characteristic of Mg–Me[6] and $\mathrm{LiAlMe_4}$, respectively, and no bands characteristic of Al–H stretching in the 1700 $\mathrm{cm^{-1}}$ region. This supports the reaction shown in equation (2).

$$\mathrm{4Me_2Mg + LiAlH_4 \xrightarrow{Et_2O} 2MgH_2 + 2Me_2Mg + LiAlMe_4} \qquad (1)$$

$$\mathrm{4Me_2Mg + LiAlH_4 \xrightarrow{THF} 4MeMgH + LiAlMe_4} \qquad (2)$$

$\mathrm{^1H}$ 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 $\mathrm{Me_2Mg}$, and six closely spaced singlets corresponding to signals due to $\mathrm{LiAlMe_4}$.[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 $\mathrm{Me_2Mg}$ with an active† form of $\mathrm{MgH_2}$ in THF at room temperature [equation (3)]. The $\mathrm{MgH_2}$ readily dissolved in the THF solution of $\mathrm{Me_2Mg}$ 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) $\mathrm{cm^{-1}}$,‡ and the $\mathrm{^1H}$ 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.

$$\mathrm{MgH_2 + Me_2Mg \xrightarrow{THF} 2MeMgH} \qquad (3)$$

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

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

$$\mathrm{Me_2Mg + 3MgH_2 \longrightarrow MeMg_2H_3} \qquad (4)$$

The RMgH and $\mathrm{RMg_2H_3}$ compounds react with ketones to produce both alkylation and reduction products.

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† The active form of $\mathrm{MgH_2}$ was prepared by the reaction of $\mathrm{LiAlH_4}$ with $\mathrm{Et_2Mg}$ (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 $\mathrm{cm^{-1}}$ is the bridging beryllium hydrogen stretching ($\mathrm{BeH_2Be}$) since the band shifted to 970 $\mathrm{cm^{-1}}$ in the RBeD compound. We prepared MeMgD in THF by the reaction of $\mathrm{Me_2Mg}$ with $\mathrm{MgD_2}$ and compared its i.r. spectrum with that of $\mathrm{MgH_2}$. We found that the band at 1290 $\mathrm{cm^{-1}}$ (in MeMgH) was shifted to 930 $\mathrm{cm^{-1}}$ in the MeMgD solution. By analogy to RBeH compounds, it is suggested that the broad band present at 1290 $\mathrm{cm^{-1}}$ in MeMgH is due to bridging magnesium–hydrogen ($\mathrm{MgH_2Mg}$) stretching.

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