Direct Nuclear Magnetic Resonance Observation of Me_2Mg and MeMgBr in a Diethyl Ether Solution of Methylmagnesium Bromide

By E. C. ASHBY,* GEORGE PARRIS, and FRANK WALKER
(*School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia* 30332)

Summary 100 MHz n.m.r. spectra of dimethylmagnesium, methylmagnesium bromide, and a mixture of dimethylmagnesium and methylmagnesium bromide from +30 to −105° reveal the presence of MeMgBr and Me_2Mg species in diethyl ether solution of the Grignard reagent.

INFORMATION concerning the representation of Grignard compounds in tetrahydrofuran by the Schlenk equilibrium has been obtained by i.r.[1] Unfortunately all previous efforts to obtain comparable information for Grignard compounds in diethyl ether solution by i.r. or n.m.r. have failed,[1-3] since it is not possible to distinguish between the n.m.r. and i.r. signals of many Grignard compounds and those of the corresponding R_2Mg compounds.

We report for the first time the observation of separate signals for RMgX and R_2Mg for a Grignard compound in diethyl ether by 100MHz n.m.r. at low temperature. Structural information has been obtained which supports the representation of the Grignard reagent by the Schlenk equilibrium (Equation 1) and distinguishes both bridging and terminal alkyl groups in the R_2Mg species present.

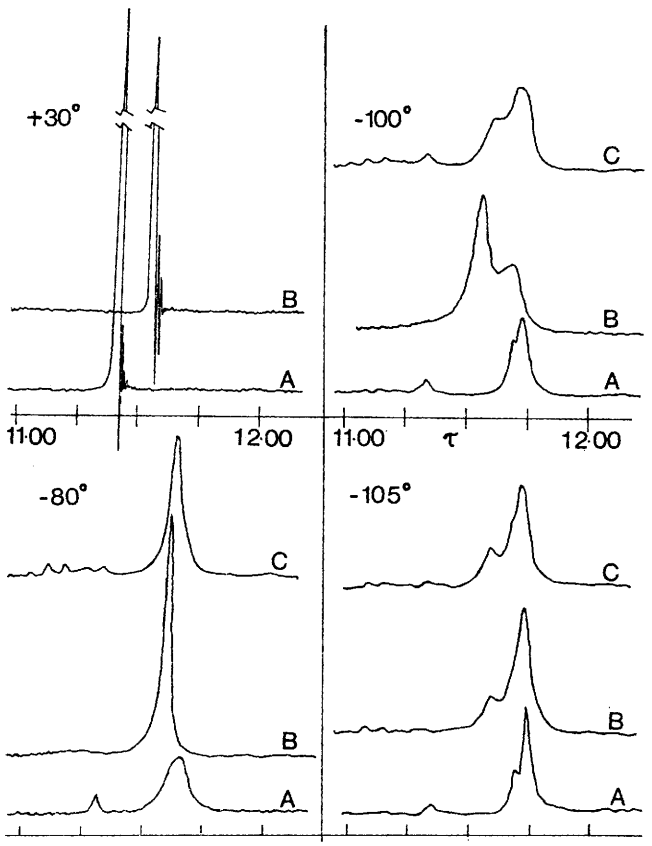

FIGURE. *Low-temperature* 100 *MHz n.m.r. spectra of* A, *dimethylmagnesium*; B, *methylmagnesium bromide*; *and* C, 1 : 1 *mixture of* A *and* B.

$$R_2Mg + MgX_2 \rightleftharpoons 2\ RMgX \qquad (1)$$

In the spectra of Me_2Mg (Figure 1, A), a low field (τ 11·32) signal is resolved at relatively high temperature (−80°) and at lower temperature (−100°) it is possible to resolve the high-field signal into two separate signals (τ 11·69, 11·74). We tentatively assign these three signals to bridging, terminal, and monomer methyl sites, respectively. We have also found similar low-field signals at τ 11·10 and 11·16 when the Me_2Mg solution is cooled rapidly. These signals, which are also observed in the 1 : 1 mixture of Me_2Mg and methylmagnesium bromide (C), are probably characteristic of distinct bridging sites in associated Me_2Mg species. In the pure Grignard solution, bridging methyl signals are not observed, consistent with our earlier report that halogen is the predominant bridging group in diethyl ether solutions of Grignard compounds.[4]

The signal of methylmagnesium bromide (B) unlike Me_2Mg is not resolved until −100°. This spectrum exhibits a signal characteristic of Me_2Mg and a lower-field signal which we assign to MeMgBr. In the spectrum of methylmagnesium bromide (B), the relative intensities of the two signals change drastically with temperature and time. These observations are consistent with the disproportionation of MeMgBr to Me_2Mg and the less soluble $MgBr_2$ which we have shown precipitates to some extent with time at lower temperature. This phenomena is also exhibited in the 1 : 1 mixture (C). At −100° the ratio of Me_2Mg in (C) is greater than MeMgBr (opposite result in B) because of the added Me_2Mg. At −105° the relative ratio of MeMgBr to Me_2Mg is even less due to precipitation of $MgBr_2$.

It was not possible to determine an equilibrium constant for the Schlenk equilibrium under these non-equilibrium conditions since some of the components precipitated from solution. However, it must lie greatly in favour of MeMgBr since the signals for Me_2Mg appear only slowly as $MgBr_2$ precipitates rather than appearing as an independent signal of substantial intensity. This conclusion is consistent with those drawn earlier by ourselves[5] and others[6] on the basis of other experiments.

We thank the National Science Foundation for partial support of this work.

(*Received, October* 13*th*, 1969; *Com.* 1543.)

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