

**987. Proton Magnetic Resonance Spectra of Grignard Reagents and Related Metal Alkyls.**

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The proton resonance spectra of ethereal solutions of methyl, ethyl, and propyl Grignard reagents closely resemble those of the corresponding dialkyls. The small differences found have been studied in detail for "methylmagnesium iodide" and dimethylmagnesium. These results support other evidence that Grignard reagents are better represented as  $R_2Mg, MgX_2$  than as  $RMgX$ . Proton resonance data are also presented for related mercury, zinc, and cadmium compounds.

GRIGNARD reagents are usually formulated as  $RMgX$ . However, since their discovery by Grignard in 1900, there has been considerable speculation about the species present in solution; a comprehensive review of work up to 1950 has been given by Kharasch and Reinmuth.<sup>1</sup> The addition of dioxan to ethereal Grignard solutions precipitates the magnesium halide and " $RMgX$ " and leaves the dialkylmagnesium in solution, suggesting the presence of an equilibrium mixture:  $2RMgX \rightleftharpoons R_2Mg + MgX_2$ . However, this Schlenk equilibrium<sup>2</sup> seems very much over-simplified.

More recently Dessy and his collaborators<sup>3</sup> measured the dielectric constants and conductivities of Grignard solutions and of the (apparently identical) solutions prepared by mixing compounds  $R_2Mg$  with  $MgX_2$ . They concluded that Grignard reagents were better represented as  $R_2Mg, MgX_2$ . In agreement with this, no exchange was observed between  $^*MgBr_2$  (radioactive magnesium) and diethylmagnesium in ethereal solution,<sup>4</sup> which seems to preclude the Schlenk equilibrium.

The elegant work of Roberts and his collaborators<sup>5</sup> on the proton magnetic resonance spectra of allyl and related Grignard reagents was mainly concerned with the structure of the organic group. However, they noted that "dibutenylmagnesium shows the same chemical shifts as does the ordinary Grignard. This can be taken as an argument against the Grignard formula  $RMgBr$  since the bromine ought to have some influence on the chemical shift of the  $CH_2$  resonance."

In the present work the proton magnetic resonance spectra of Grignard reagents and related compounds has been studied in further detail.

<sup>1</sup> Kharasch and Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice Hall, New York, 1954.

<sup>2</sup> Schlenk and Schlenk (jun.), *Ber.*, 1929, **62**, 920.

<sup>3</sup> Dessy and Jones, *J. Org. Chem.*, 1956, **21**, 1063; Dessy and Handler, *J. Amer. Chem. Soc.*, 1958, **80**, 5824; Dessy, *J. Org. Chem.*, 1960, **25**, 2260.

<sup>4</sup> Wotiz, Hollingsworth, and Dessy, *J. Org. Chem.*, 1956, **21**, 1063.

<sup>5</sup> Norlander, Young, and Roberts, *J. Amer. Chem. Soc.*, 1961, **83**, 494.

## EXPERIMENTAL

Solutions of Grignard reagents and dialkylmagnesiums were prepared *in vacuo* in the apparatus shown in Fig. 1. In the preparation of the Grignard solutions, the alkyl halide and an excess of ether were distilled on to the magnesium turnings (baked *in vacuo* at  $\sim 300^\circ$ ), and the apparatus was sealed off at point C. A rapid reaction occurred on shaking at  $0^\circ$ . The apparatus was again evacuated, through limb A1, the break-seal (B) being broken, and the ether and any excess of alkyl halide were thus removed. A quantity of ether containing a small amount of tetramethylsilane was distilled into the apparatus, which was then sealed at point C1. A small portion of the mixture was filtered through the sinter S, and sealed off (at C2) in the nuclear magnetic resonance tube T. In preliminary experiments, where the Grignard solutions were prepared and transferred under oxygen-free nitrogen, irreproducible nuclear magnetic resonance spectra were obtained.

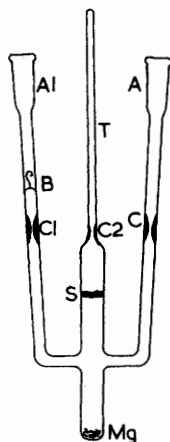


FIG. 1. Apparatus used in preparation of Grignard and dialkylmagnesium solutions.

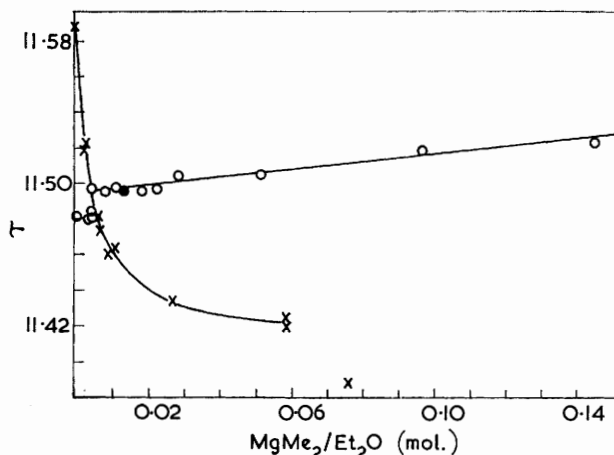


FIG. 2. Concentration-dependence for the chemical shift ( $\tau$ ) of diethyl ether solutions of  $\text{MgMe}_2$  and "MeMgI."

○ Methyl Grignard solution. ×  $\text{MgMe}_2$ . ● Grignard solution containing 4 mol. excess of  $\text{MgI}_2$ .

The dialkylmagnesiums were prepared similarly, from magnesium turnings and an ethereal solution of the appropriate dialkylmercury, which were shaken together at room temperature for about 3 days. For very dilute solutions, a trace of mercury was added to initiate the reaction.

The remaining compounds were prepared and purified by standard procedures. Measurements were made at 56.45 Mc./sec. on a Varian V4311 spectrometer, tetramethylsilane being normally used as an internal reference. The  $\tau$  values are accurate to *ca.*  $\pm 0.01$  p.p.m.

## RESULTS AND DISCUSSION

With mercury, all three species  $\text{R}_2\text{Hg}$ ,  $\text{RHgX}$ , and  $\text{RHg}^+$  can be observed, and the results obtained for these species are presented in Table I. As expected, there are very large changes in the proton resonance spectrum in going from  $\text{R}_2\text{Hg}$  to  $\text{RHgX}$  or  $\text{HgR}^+$ . These changes can be partly attributed to the inductive effect of the electronegative halogen atom or the (formal) positive charge of the cation. However, for the ethylmercuric halides the  $\delta$  values increase slightly in going from the chloride to the iodide, which is the opposite order to that expected from electronegativity considerations. This effect could be explained on the basis of  $\pi$ -bonding between the mercury atom and the halogen atom, but in addition there may well be long-range deshielding caused by the

TABLE 1.

| Compound  | $\tau\text{CH}_3$ | Compound  | $\tau\text{CH}_2$ | $\tau\text{CH}_3$ | $\tau\text{CH}_3 - \tau\text{CH}_2$ ( $\delta$ ) |
|---|-------------------|---|-------------------|-------------------|--|
| HgMe <sub>2</sub> (pure) .....                  | 9.714             | Et <sub>2</sub> Hg (CH <sub>2</sub> Cl <sub>2</sub> ) ..... | 8.996             | 8.706             | -0.291   |
| MeHgCl (CH <sub>2</sub> Cl <sub>2</sub> ) ..... | 8.908             | EtHgCl (CH <sub>2</sub> Cl <sub>2</sub> ) .....             | 8.026             | 8.652             | +0.626   |
| MeHgClO <sub>4</sub> (D <sub>2</sub> O) .....   | 8.79 *            | EtHgBr (CH <sub>2</sub> Cl <sub>2</sub> ) .....             | 7.979             | 8.635             | +0.656   |
|   |                   | EtHgI (CH <sub>2</sub> Cl <sub>2</sub> ) .....              | 7.897             | 8.571             | +0.674   |
|   |                   | EtHgClO <sub>4</sub> (D <sub>2</sub> O) .....               | 7.71 *            | 8.69 *            | +0.878   |

\* Based on  $\tau\text{CMe}_3\text{OH}$  in water = 8.69,<sup>6</sup>  $J(^{199}\text{Hg}-\text{H})$  are: HgMe<sub>2</sub> 102.5, MeHgCl 202.4, and MeHgClO<sub>4</sub> 260.2 c./sec.

magnetically anisotropic Hg-X bonds, which will be largest for ethylmercuric iodide (cf. McConnell,<sup>7</sup> Schneider<sup>8</sup>).

In contrast to these results the proton resonance spectra of methyl, ethyl, and n-propyl Grignard reagents closely resemble those of the corresponding dialkylmagnesiums (see Tables 2 and 3), indicating the absence of appreciable quantities of the species RMgX, but consistent with the formulation R<sub>2</sub>Mg.MgX<sub>2</sub>. Small concentration-dependent differences are observed, however, which were studied for dimethylmagnesium and "MeMgI," and the results are plotted in Fig. 2. The  $\tau$  values for dimethylmagnesium in ether show an appreciable concentration-dependence, especially at high dilutions, which can be attributed plausibly to the dissociation of polymeric species on dilution. The concentration-dependence for the Grignard reagent, on the other hand, is very small over a considerable concentration range. At high dilution an apparent drop in the values was observed, but this may be due to impurities since the reproducibility of the results was less than at higher concentrations. (No comparable effect was observed with dimethylmagnesium which is easier to obtain pure.) This very small concentration-dependence, together with the fact that the curves for dimethylmagnesium and "MeMgI" curves, when extrapolated, do not afford the same  $\tau$  value at infinite dilution, suggests that the complex Me<sub>2</sub>Mg.MgI<sub>2</sub> is stable. In agreement, a solution containing a large excess of magnesium iodide gave a value which, within experimental error, fell on the Grignard curve (Fig. 2), indicating that the equilibrium Me<sub>2</sub>Mg + MgI<sub>2</sub>  $\rightleftharpoons$  Me<sub>2</sub>Mg.MgI<sub>2</sub> lies well to the right.

TABLE 2.

| MgEt <sub>2</sub> /Et <sub>2</sub> O<br>(mol.) | $\tau\text{CH}_3$     | $\tau\text{CH}_2$ | MgEt <sub>2</sub> /Et <sub>2</sub> O<br>(mol.) | $\tau\text{CH}_3$ | $\tau\text{CH}_2$ |
|--|-----------------------|-------------------|--|-------------------|-------------------|
|  | For MgEt <sub>2</sub> |                   |  | For "EtMgBr"      |                   |
| 0.376  | 8.793                 | 10.620            | 0.148  | 8.849             | 10.674            |
| 0.103  | 8.801                 | 10.640            | 0.085  | 8.836             | 10.665            |
| 0.016  | 8.747                 | 10.674            | 0.020  | 8.806             | 10.626            |
| Satd.*   | 8.840                 | 10.84             |  |                   |                   |

\* In dioxan.

TABLE 3.

| MgPr <sup>n</sup> /Et <sub>2</sub> O<br>(mol.) | $\tau\text{CH}_2$     | $\tau\text{CH}_2$ | $\tau\text{CH}_3$ | MgPr <sup>n</sup> /Et <sub>2</sub> O<br>(mol.) | $\tau\text{CH}_2$ | $\tau\text{CH}_2$ | $\tau\text{CH}_3$ |
|--|-----------------------|-------------------|-------------------|--|-------------------|-------------------|-------------------|
|  | For MgPr <sup>n</sup> |                   |                   |  |                   |                   |                   |
| 0.111  | 10.566                | 8.500             | 9.087             | "Pr <sup>n</sup> MgCl"                         | 0.172             | 10.464            | 8.362             |
| <0.04  | 10.595                | 8.495             | 9.100             | "Pr <sup>n</sup> MgBr"                         | 0.081             | 10.507            | 8.498             |
| Satd.*   | 10.665                | 8.536             | 9.113             | "Pr <sup>n</sup> MgI"                          | 0.041             | 10.483            | —                 |

\* In dioxan.

Although the present results are in agreement with previous evidence that Grignard reagents (in solution) should be formulated as R<sub>2</sub>Mg.MgX<sub>2</sub> rather than RMgX, it may be noted that they do not provide information about numerous finer details of Grignard

<sup>6</sup> Green, McCleverty, Pratt, and Wilkinson, *J.*, 1961, 4854.

<sup>7</sup> McConnell, *J. Chem. Phys.*, 1957, **27**, 226.

<sup>8</sup> Spiesscke and Schneider, *J. Chem. Phys.*, 1961, **35**, 722.

TABLE 4.

| Solvent                               | EtZnI                  |                        | ZnEt <sub>2</sub>      |                        | CdEt <sub>2</sub>      |                        |
|---------------------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
|                                       | $\tau$ CH <sub>2</sub> | $\tau$ CH <sub>3</sub> | $\tau$ CH <sub>2</sub> | $\tau$ CH <sub>3</sub> | $\tau$ CH <sub>2</sub> | $\tau$ CH <sub>3</sub> |
| None .....                            | —                      | —                      | 9.698                  | 8.854                  | 9.471                  | 8.716                  |
| Et <sub>2</sub> O .....               | 9.651                  | ~8.78                  | 9.778                  | 8.874                  | 9.317                  | 8.736                  |
| Dioxan .....                          | 9.740                  | 8.897                  | —                      | —                      | 9.688                  | 8.760                  |
| CH <sub>2</sub> Cl <sub>2</sub> ..... | —                      | —                      | 9.744                  | 8.87                   | 9.528                  | 8.728                  |
| C <sub>6</sub> H <sub>6</sub> .....   | —                      | —                      | 9.851                  | 9.064                  | —                      | —                      |

solutions, such as the extent of solvation by the ether, the bonding between R<sub>2</sub>Mg and MgX<sub>2</sub>, the degree of polymerisation of the species, and the nature of the ions present.

The proton resonance spectrum of ethylzinc iodide in ether is very similar to that of diethylzinc in ether, indicating that, in solution, this reagent should similarly be formulated as Et<sub>2</sub>Zn, ZnI<sub>2</sub>. The results obtained, together with those for dilute solutions of diethylzinc and -cadmium in various solvents are presented in Table 4.

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