The Composition of Grignard Compounds. VII. The Composition of Methyl- and *tert*-Butylmagnesium Halides and Their Dialkylmagnesium Analogs in Diethyl Ether and Tetrahydrofuran as Inferred from Nuclear Magnetic Resonance Spectroscopy[1]

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Abstract: Variable-temperature, 100-MHz nuclear magnetic resonance spectroscopy has been employed in the study of methyl- and *tert*-butylmagnesium halides and their dialkylmagnesium analogs in diethyl ether and tetrahydrofuran. For the first time it has been possible to observe directly RMgX and R_2Mg species individually in an ether solution of these Grignard reagents. The results of these studies are entirely consistent with our earlier representation of the composition of Grignard reagents by the Schlenk equilibrium ($R_2Mg + MgX_2 \rightleftarrows 2RMgX$). The results are also consistent with the earlier view of ourselves and others that the composition of Grignard reagents varies with the nature of the solvent, the organic group, and the halide. The present results also reveal that the composition varies as well with the temperature and the concentration of the solution. The solvent is the single most important factor in determining the position of the Schlenk equilibrium for alkyl Grignard reagents, the RMgX species being favored in diethyl ether and a statistical equilibrium resulting in tetrahydrofuran. On the other hand, the rate of alkyl group exchange is primarily determined by the structure of the alkyl group and only secondarily affected by the nature of the solvent. For example, methyl group exchange is much faster than *tert*-butyl group exchange under similar conditions and alkyl groups exchange faster in diethyl ether than in tetrahydrofuran. The purity of magnesium used in the preparation of the reagents seems to have little if any effect upon the position or dynamics of the equilibrium. An interpretation of the nature of exchange phenomena is presented.

The composition of Grignard compounds in ether solvents has been the subject of considerable interest since the discovery of Grignard reagents in 1900. In the past few years a very simple picture has emerged in which the composition is pictured as an equilibrium involving RMgX, R_2Mg, and MgX_2 species.[3] It has

$$R_2Mg + MgX_2 \overset{K}{\rightleftharpoons} 2RMgX \qquad (1)$$

been found that the nature of this equilibrium changes depending on the nature of R, X, and solvent. Thus, the composition of Grignard compounds in hydrocarbon,[4] diethyl ether,[5] tetrahydrofuran,[5b,6] and triethylamine,[7] although represented by the Schlenk equilibrium, varies to the extent that the equilibrium constant (*K*) is extremely small in hydrocarbon, ~4 in tetrahydrofuran, moderately large (480 for ethylmagnesium bromide) in diethyl ether, and very large in triethylamine for primary alkylmagnesium chlorides and bromides.

Although the ideal method for studying such an equilibrium is by spectroscopic means such as ir and nmr, these methods have met with limited success. Mosher and coworkers[6b] were able to determine the value of *K* for methyl bromide and chloride Grignard reagents in tetrahydrofuran by infrared spectroscopy; however, the same method failed when diethyl ether was the solvent. It was not possible to distinguish diethyl ether or tetrahydrofuran solutions of ethylmagnesium bromide and diethylmagnesium by infrared analysis.

Several reports have appeared concerning nmr investigations of Grignard reagents and related dialkyl- or arylmagnesium compounds in ether solvents. Evans and Maher[8] showed that the proton resonance signal for methyl, ethyl, and *n*-propyl Grignard reagents and the corresponding dialkylmagnesium compounds were remarkably similar and therefore concluded that the Grignard reagents in solution were mixtures of R_2Mg and MgX_2. Evans and Khan[9] succeeded in observing two species in an ether solution of pentafluorophenyl bromide Grignard reagent which they considered to be C_6F_5MgBr and $(C_6H_5)_2Mg$ in statistical equilibrium at room temperature, although the composition was shown to be temperature dependent. Roberts and coworkers[10] have used nmr to demonstrate that inversion of configuration at the carbon–magnesium bond of primary alkyl Grignard compounds and dialkylmagnesium compounds is rapid, but they did not study the compositions of these systems. More recently House and Whitesides[11] have studied Grignard reagents and dial-

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[1] We are indebted to the National Science Foundation (Grant No. GP-14795) for partial support of this work.

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[3] (a) E. C. Ashby, *Quart. Rev., Chem. Soc.*, 21, 259 (1967); (b) B. J. Wakefield, *Organometal. Chem. Rev.*, 1, 131 (1966).

[4] (a) E. C. Ashby and R. Reed, *J. Org. Chem.*, 31, 971 (1966); (b) L. I. Zakharkin, O. Yu. Okhlobystin, and B. N. Strunin, *Tetrahedron Lett.*, 631 (1962).

[5] (a) E. C. Ashby and M. B. Smith, *J. Amer. Chem. Soc.*, 86, 4363 (1964); (b) F. Walker and E. C. Ashby, *ibid.*, 91, 3845 (1969); (c) R. E. Dessy, S. Green, and R. M. Salinger, *Tetrahedron Lett.*, 1369 (1964).

[6] (a) E. C. Ashby and W. E.Becker, *J. Amer. Chem. Soc.*, 85, 118 (1963); (b) R. M. Salinger and H. S. Mosher, *ibid.*, 86, 1782 (1964); (c) M. B. Smith and W. E. Becker, *Tetrahedron Lett.*, 3843 (1965); (d) M. B. Smith and W. E. Becker, *Tetrahedron*, 22, 3027 (1966).

[7] (a) E. C. Ashby and F. Walker, *J. Org. Chem.*, 33, 3821 (1968); (b) J. Toney and G. D. Stucky, *Chem. Commun.*, 22, 1168 (1967).

[8] D. F. Evans and J. P. Maher, *J. Chem. Soc.*, 5125 (1962).

[9] D. F. Evans and M. S. Khan, *Chem. Commun.*, 67 (1966).

[10] G. M. Whitesides, F. Kaplan, and J. D. Roberts, *J. Amer. Chem. Soc.*, 85, 2167 (1963).

[11] H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, 32, 2481 (1967).

kylmagnesium compounds by nmr and were unable to distinguish RMgX from R_2Mg species in the Grignard reagents. However, they did show that methyl exchange between dimethylmagnesium and cyclopentadienylmethylmagnesium is many times more rapid than inversion of configuration at the carbon–magnesium bond is expected to be. They showed by direct observation of $(CH_3)_3CCH_2CH_2MgC_5H_5$ that the alkyl group exchange is second order and at least 10^3 times faster than inversion. The rate of alkyl group exchange was diminished by addition of better solvating solvents and was greatly enhanced by $MgBr_2$.

Thus, for alkyl Grignard reagents it appears that there is little direct spectroscopic evidence for the Schlenk equilibrium in ether solvents or the mechanisms of alkyl exchange between R_2Mg and RMgX species. In an effort to clarify this situation we undertook the study of methyl and *tert*-butyl Grignard reagents in both diethyl ether and tetrahydrofuran by variable temperature nmr.

Experimental Considerations

It was desirable to observe Grignard compounds which offer both simple nmr spectra and represent a variety of steric requirements. Methyl- and *tert*-butylmagnesium reagents were chosen because they fit both of these criteria well. There was some concern about the purity of magnesium used in these studies because there is evidence that the reactions of these reagents may be quite sensitive to trace impurities.[12] However, we have found that the nmr spectra of methylmagnesium bromide and dimethylmagnesium in diethyl ether prepared from Grignard grade magnesium turnings were not distinguishable from reagents prepared from Dow triply[13] sublimed magnesium or even ultrapure[14] grades of zone refined magnesium. Thus the nmr spectra are apparently relatively insensitive to trace impurities. Even under optimum conditions, there are several problems in studying these systems which make detailed interpretation of the spectra difficult. In these systems labile equilibria exist involving a number of distinct species. Alkyl exchange can be extremely rapid and a variety of mechanisms for such exchange is possible. The solubilities of some of the solute components are low, particularly at low temperature, and preferential precipitation of certain components changes the composition of the solution with respect to temperature and time. Even with 100-MHz nmr the signals of simple methyl and *tert*-butyl alkyl groups bound to different magnesium sites often overlap, and near the freezing point of the solvent additional line broadening due to viscosity is encountered. However, much important information can be obtained at temperatures as low as −105° prior to extreme viscosity problems.

Dimethylmagnesium in Diethyl Ether. We have recently communicated a partial low-temperature profile study of dimethylmagnesium in diethyl ether.[15a]

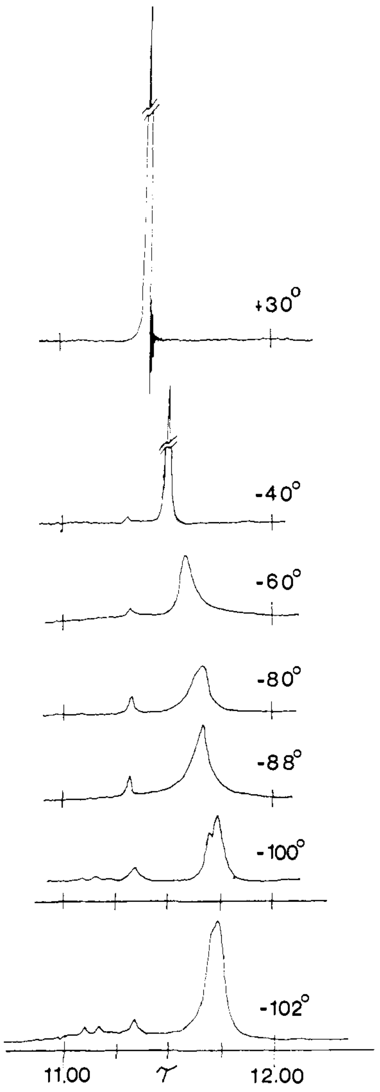

Figure 1. Detailed low-temperature nmr profile of dimethylmagnesium in diethyl ether.

The complete profile is presented in Figure 1 and the corresponding numerical data are to be found in Table I. Spectra of a 0.31 *M* solution were recorded successively at intervals of 10–20 min as the sample was cooled and thermal equilibrium achieved. At +30° a single sharp signal was observed. The signal moved from τ 11.45 to 11.50 as the temperature was lowered from +30 to −40°. At −40° a small signal was observed at τ 11.38 while the large signal moved to 11.51. At −60° the small signal resided at 11.32,[15b] while the large signal was displaced to 11.59. When the −80 to −88° region was reached the high-field signal was still on the move (now at τ 11.69) and had assumed a

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(12) E. C. Ashby, F. W. Walker, and H. M. Neumann, *Chem. Commun.*, 330 (1970).

(13) Kindly provided by Dow Chemical Co.

(14) Kindly provided by Professor Royal W. Stark, University of Chicago.

(15) (a) E. C. Ashby, G. Parris, and F. Walker, *Chem. Commun.*, 1464 (1969); (b) dimethylmagnesium in ether has been observed in this temperature region before,[11] but no signal at τ 11.32 was reported. We, therefore, questioned the origin of this signal with regard to alkoxide impurities which were reported to produce signals in this region. Two experiments were directed toward this problem. A completely new sample of dimethylmagnesium was prepared in a drybox under a stream of prepurified nitrogen. Air and moisture were rigorously excluded. A nmr sample was prepared as described in the Experimental Section of this paper. This sample showed the same 11.32 signal with no loss of relative intensity (sample concentration 0.81 *M*). In a second test, an ether solution of methanol was added to $(CH_3)_2Mg$ in the same solvent in a mole ratio of 1:2. A large amount of solid formed. Methoxy groups could not be detected in the nmr spectrum of the supernatant liquid. Their signals might be hidden by the ether signals. When the supernatant liquid was observed at low temperature, the signal for methyl bound to magnesium rapidly deteriorated at −41° and disappeared with only one signal (at 11.50) ever being observed.

Table I. Nmr Studies of Dimethylmagnesium in Diethyl Ether

Ref	Concn, *M*	Temp, °C	Chemical shift(s) (τ)
		A. Previous Results	
11	0.71	~30	11.39[a]
11	0.18	~30	11.42[a]
11	0.090	~30	11.45[a]
11	0.028	~30	11.50[a]
11	0.84	+33	11.40[a]
11	0.84	−29	11.45[a]
11	<0.84	−54	11.47 (3.6)[a]
		B. Present Study[c,g]	
	0.31	+30	11.45 (1.5)
		−12	11.47 (1.5)
		−20	11.49 (1.5)
		−30	11.38 (−), 11.50 (1.5)
		−40	11.38 (−), 11.51 (3)
		−60	11.32 (3), 11.59 (5)
		−80	11.32 (2), 11.67 (10)[d]
		−88	11.32 (2), 11.69 (8)[d]
		−100	11.32 (3), 11.70 (5),[e] 11.74 (5)[e]
		−105	11.32 (4), 11.69 (4),[e] 11.74 (4)[e]
		−110	11.32 (3), 11.69 (4),[e] 11.74 (4)[e]
		−102	11.10,[f] 11.16,[f] 11.33,[f] 11.70 (sh), 11.74

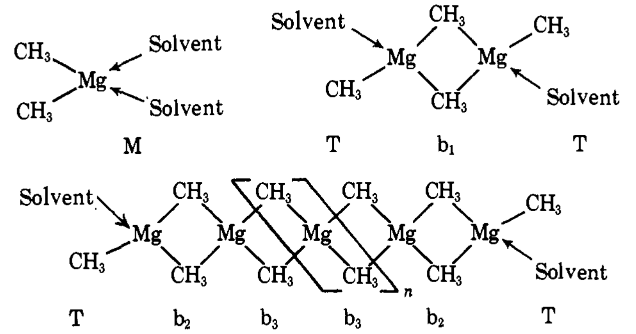
[a] Converted to comparable 100-MHz shifts. [b] Full widths at half-height ($W_{1/2}$) in hertz are given in parentheses. [c] This work. [d] Signal is distinctly asymmetric. [e] Assuming each component is symmetric. [f] These signals rest on a distinct rise in the base line between τ ~11.00 and ~11.50 which is as intense as the signals. [g] Vertical order of chemical shift values indicates sequential cooling.

broadened, asymmetric shape, but the small low-field signal remained at 11.32. It should be noted that by now precipitation has seriously eroded signal intensity so that subtle changes in the spectra were difficult or impossible to observe. Between −100 and −110° the low-field signal (11.32) remained virtually unchanged, but the high-field signal (~11.70) partially resolved into a main peak at 11.74 with a shoulder at 11.69. The relative intensities of these high-field signals varied with time as the lower field signal (11.69) lost intensity. To increase signal strength at low temperature, the sample was brought back to room temperature and was allowed to equilibrate for several days (all solid redissolved). The sample was then frozen solid in ~10 sec by dipping in liquid nitrogen. The solid solution, which was clear, was warmed just to melting, then placed in the nmr probe which had been precooled to −102°. The spectrum of the supersaturated solution obtained immediately showed a considerably increased signal intensity and it was possible to observe not only the small signal at 11.32 but also signals at 11.10 and 11.16, all three of which were superimposed upon a distinct rise in the base line between ~11.00 and ~11.50. The intensity of the low-field shoulder (11.69) on the high-field signal decreased slowly in time relative to the bulk of the signal. The rather large shift in the position of the high-field signals (11.45 → 11.69, 11.74) is much greater than would be expected to result from changes in the overall characteristics of the solvent, but might result from either a specific solvation effect or changes in the composition of an exchange system.

Structural features of the components of the dimethylmagnesium system are most logically inferred from the low-temperature spectra. In the solid state, dimethylmagnesium exists as a long-chain polymer held together by methyl bridge bonds.[16] Dissolution of dimethylmagnesium in diethyl ether or THF is an endothermic process and dimethylmagnesium may be crystallized solvent free from diethyl ether.[17] Based on comparison with other systems, it is reasonable to attribute the lower field signals (~11.00 to ~11.50) to bridging methyl groups in associated dimethylmagnesium and the higher field signals (11.69, 11.74) to terminal methyl groups of associated species as well as methyl groups of solvated monomers.

Evans and Maher[8] have reported a detailed study of the concentration dependence of the position of the nmr signal for dimethylmagnesium at room temperature. They plotted chemical shift *vs.* concentration and extrapolated the curve obtained to infinite dilution. Though the accuracy of this extrapolation is limited by the steep slope of the curve in the low concentration region, the infinite dilution chemical shift can be estimated to be greater than 11.60. In the hypothetical state of infinite dilution, dimethylmagnesium would tend to the limiting (monomeric) degree of association with a small ratio of bridging to terminal (or monomer) sites. The data of Evans and Maher can be taken to infer a monomer and terminal methyl shift greater than 11.60, in reasonable agreement with our general assignments.

It is more difficult, however, to make more precise assignments of the observed signals. Kovar and Morgan[18] have recently discussed the nmr spectrum of dimethylberyllium in dimethyl sulfide. The arguments which were made for the assignment of observed signals to chemical structures in that system are based upon the relative signal intensities and chemical shifts. In addition to the usual argument that methyl groups in terminal sites of polymeric species should absorb at higher field than methyl groups in bridging sites, it was hypothesized that the magnetic environment of a bridging methyl group is determined by its proximity to the solvent molecules coordinated to the polymer at the terminal positions. The application of these arguments to the system of dimethylmagnesium in diethyl ether appears just as reasonable. The assignment scheme which evolves is illustrated below. Clearly, the relative separation of the various signals depends upon the nature of the solvent and metal.



$\tau_{b_3} \lesssim \tau_{b_2} \lesssim \tau_{b_1} << \tau_T \lesssim \tau_M$

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(16) E. Weiss, *J. Organometal. Chem.*, **2**, 314 (1964).

(17) G. E. Coates, D. Ridley, J. A. Heslop, and M. E. Redwood, *J. Chem. Soc. A*, 1118 (1968).

(18) R. A. Kovar and G. L. Morgan, *J. Amer. Chem. Soc.*, **91**, 7269 (1969).

In the dimethylmagnesium–diethyl ether system there is the problem that the signals for terminal sites of associated species and monomer sites are observed at very similar chemical shifts (τ 11.69, 11.74). Assignment of the signals on the basis of chemical shift alone is equivocal, but the time dependence of the intensity of the 11.69 signal parallels the behavior of the bridging signals (*i.e.*, after standing for extended periods at low temperature the intensity of the bridging signals and the 11.69 signal is distinctly eroded), allowing this signal to be attributed to the terminal sites of associated species which are precipitating from solution. The τ 11.74 signal must then represent monomeric dimethylmagnesium. In the dimethylberyllium–dimethyl sulfide system the terminal and monomer signals were more distinctly separated so that not only was their assignment more straightforward but also it was possible to integrate the area under the terminal signal and the bridging signals to aid in the determination of the type of polymers in solution. The lowest ratio of bridging to terminal methyl groups observed by Kovar and Morgan was 2:1 so that it was possible to conclude that the observed bridging signal represented sites of type b_2 in a trimer. While at very low temperatures a bridging signal for sites of type b_3 in extended polymers was observed, no evidence was found for a dimer with sites of type b_1.[19] Unfortunately in the dimethylmagnesium–diethyl ether system, it is not possible to integrate meaningfully the areas under the bridging and terminal signals for comparison. Thus it is impossible to assign unambiguously the observed bridging signals; the τ 11.32 signal is reasonably attributed to the bridging sites in the dimer (b_1) or trimer (b_2).

Considering the uncertainties in the precise assignment of the signals in these spectra, it is difficult to do more than generalize about their temperature dependence. It does seem clear that at room temperature the time average signal represents contributions from both monomeric and associated magnesium species. Also it appears that the shift of this signal to higher field at lower temperature at least in part reflects a situation in which more highly associated species are preferentially precipitated from solution at lower temperature leaving in solution only monomeric dimethylmagnesium. Although no resort to a monosolvate–disolvate equilibrium has been made, such a situation was shown to exist in the case of dimethylberyllium in dimethyl sulfide[18] and could conceivably be invoked in the magnesium system. Considering the affinity of magnesium for oxygen and the larger radius of magnesium (Mg^{2+}, 0.66 Å) compared to beryllium (Be^{2+}, 0.35 Å), such an equilibrium between distinctly different solvates seems unlikely. However, at lower temperatures some form of enhanced solvation of monomeric dimethylmagnesium may account for part of the observed shift to higher field.

Methyl Grignard Reagents in Diethyl Ether. Heretofore nmr spectroscopy has been largely unsuccessful in distinguishing various organomagnesium species in solution. It has been reported that the nmr spectra of solutions of methyl-, ethyl- and *n*-propylmagnesium bromide in diethyl ether are indistinguishable from the corresponding dialkylmagnesium compounds and thus the conclusion was drawn that Grignard compounds in solution consist of mixtures of R_2Mg and MgX_2 with no RMgX species present.[8] We recently reported that CH_3MgBr can be distinguished from $(CH_3)_2Mg$ in a diethyl ether solution of methyl bromide Grignard reagent at low temperature.[15] At $-100°$ (Figure 2), two distinct signals are observed. The lower field signal (τ 11.55) is attributed to CH_3MgBr and the higher field signal ($\sim$11.70) is attributed to dimethylmagnesium (see previous section). Although some precipitation took place at $-100°$, the CH_3MgBr species is still in excess; however, on further standing or at lower temperature more $MgBr_2$ precipitates and hence the ratio of CH_3MgBr to $(CH_3)_2Mg$ decreases as is exhibited in the spectrum at $-105°$. We have demonstrated that the nmr spectra are consistent with the disproportionation of CH_3MgBr to $(CH_3)_2Mg$ and sparingly soluble $MgBr_2$ below $-80°$ by cooling $\sim$0.3 *M* methyl bromide Grignard solution in diethyl ether to $-70°$ for 10 min followed by filtration and analysis of the precipitate. Analysis of the solid phase revealed a ratio of total magnesium to basic magnesium of 1.00:0.86, consistent with the precipitation of halogen-rich species from solution.[20]

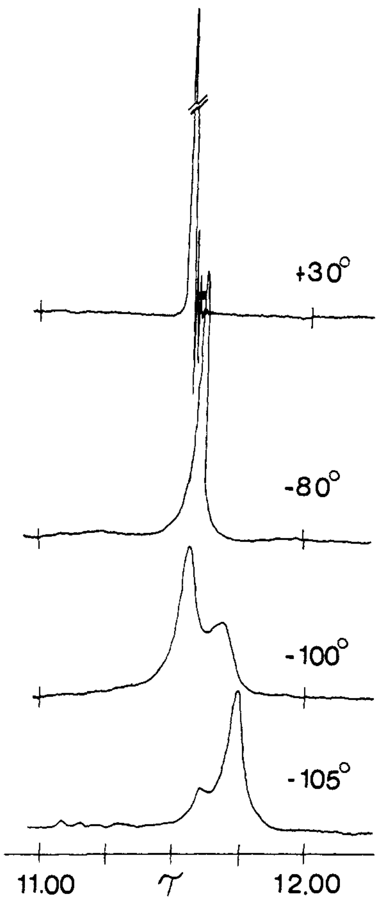

Figure 2. Partial low-temperature nmr profile of methylmagnesium bromide in diethyl ether.

Some of the more important spectra obtained from a low-temperature nmr study of methylmagnesium bromide in diethyl ether are shown in Figure 2. Unfortunately it is not possible to determine equilibrium con-

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(19) The assignments in the dimethylberyllium–dimethyl sulfide system as given by Kovar and Morgan are $\tau_{b_3} = 10.31$, $\tau_{b_2} = 10.41$, $\tau_T = 10.80$, τ_M(monosolvate) = 10.77, τ_M(disolvate) = 11.30, with τ_{b_1} unobserved or coincident with τ_{b_2}.[18]

(20) E. C. Ashby and W. E. Becker, *J. Amer. Chem. Soc.*, **85**, 118 (1963).

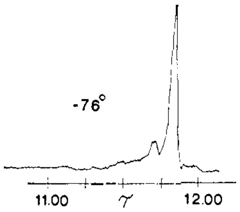

Figure 3. Nmr spectra of dimethylmagnesium in tetrahydrofuran at −76°.

stants describing the nature of the Schlenk equilibrium due to the fact that precipitation slowly takes place during the cooling process. However, since the Schlenk equilibrium lies far in favor of CH_3MgBr at room temperature,[6c,d] it seems likely that the τ 11.55 signal at room temperature is due primarily to CH_3MgBr. It is only during the cooling process and precipitation of $MgBr_2$ that a significant upfield shift (τ 11.55 → 11.70) takes place due to the generation of $(CH_3)_2Mg$.

The study of this system was expanded in two experiments. First, a 1:1 mixture of dimethylmagnesium and methyl bromide Grignard reagent was observed under the same conditions as the pure Grignard reagent. The results were that the signals assigned to dimethylmagnesium were more predominant at all temperatures. In the last experiment "synthetic" methyl bromide Grignard and 1:1 methyl bromide Grignard–dimethylmagnesium were prepared by mixing solutions of dimethylmagnesium and magnesium bromide in 1:1 and 2:1 ratios, respectively. The spectra of these mixtures were in every way consistent with those of the "authentic" methyl bromide Grignard and 1:1 Grignard–dimethylmagnesium mixture.

To complete the survey of methyl Grignard reagents in diethyl ether, a solution of methyl iodide Grignard (~0.5 *M*) was observed at temperatures between +20 and −40°. Attempts to obtain data at lower temperatures were inhibited by virtually total precipitation of the reagent. At room temperature, a single signal was observed at τ 11.49. At −41° the main signal was at 11.51 with two very small signals at 11.28 and 11.34. The low-field signals are probably due to bridging methyl sites. The high-field signal is an average exchange signal for CH_3MgI and $(CH_3)_2Mg$. Methyl chloride Grignard reagent is known to disproportionate in ether solution at room temperature depositing magnesium chloride; therefore it was not studied

Dimethylmagnesium in Tetrahydrofuran. Surprisingly little nmr data are available for tetrahydrofuran (THF) solutions of alkylmagnesium compounds. Although dimethylmagnesium is associated in diethyl ether at concentrations >0.1 *m*, it is monomeric in tetrahydrofuran over a wide concentration range.[21] We observed the nmr spectra of dimethylmagnesium in THF between +20 and −76°. At +20° a single signal is observed at 11.76 (0.86 *M*) which shifts to higher field with decreasing temperature as shown in Table II. Consistent with the proposed monomeric constitution, the shift is only 7 cps as compared to 29 cps for the same compound in diethyl ether. At −76° the major signal at 11.83 is attributed to $(CH_3)_2Mg$ monomer and a small signal at 11.70 is attributed to terminal sites in an associated species. The assignment of the weak 11.70 signal to associated $(CH_3)_2Mg$ at −76° is reasonable on the basis that the monomeric nature of $(CH_3)_2Mg$ at the concentration used in these studies was determined at a considerably higher temperature (~+35°). The low signal to noise ratio apparently obscures the assumed bridging signal which is expected to be broad in any event. This spectrum is shown in Figure 3.

Table II. Low-Temperature Nmr Profile of Methylmagnesium Reagents in Tetrahydrofuran

Temp,[a] °C	Chemical shift (τ) $(CH_3)_2Mg$	CH_3MgBr	CH_3MgCl
+20	11.76	11.70	11.72
−20		11.77	
−40		11.78	11.77
−60	11.81	11.80	
−76	11.70, 11.83		
−90		11.84	11.82
−100		11.85	11.83

[a] These are convenient comparison temperatures. The chemical shifts cited are for the observed temperature ±3° of that listed.

Methyl Grignard Reagents in Tetrahydrofuran. The methyl bromide and methyl chloride Grignard reagents were observed in THF (methyl iodide Grignard reagent is not stable in THF) where they have been reported to be essentially statistical mixtures of $(CH_3)_2Mg$ and CH_3MgX.[3,6d] Unlike the solutions of methyl bromide Grignard in diethyl ether, the chemical shifts of these reagents are very temperature dependent, moving to higher field with lower temperature until at −100° the major signals are observed at τ ~11.85. These results are summarized in Table II. At no time was it possible to observe distinct signals for $(CH_3)_2Mg$ and CH_3MgX as was done in diethyl ether.[15a] From the data it appears that the Schlenk equilibrium at low temperature in THF shifts in favor of $(CH_3)_2Mg + MgBr_2$ since the spectrum of the methyl chloride and methyl bromide Grignard approaches that of $(CH_3)_2Mg$ at −76° (Table II). It is also possible that MgX_2 precipitates from the Grignard solution thus producing a low-temperature spectrum similar to $(CH_3)_2Mg$. To determine if magnesium halide precipitated from solution under the conditions of the nmr experiment, a sample of 0.68 *M* methyl bromide Grignard was cooled to −70° for 20 min. Analysis of the solid phase showed the Mg:Br ratio to be 1.0:1.2, while the liquid phase ratio was 1.0:0.44, indicating that indeed some magnesium bromide did precipitate under the conditions of the experiment. Since all of the $MgBr_2$ did not precipitate it appears that the resemblance of the nmr spectra of the methyl bromide and methyl chloride Grignard reagents in THF to the spectrum of dimethylmagnesium is due in part to the precipitation of $MgBr_2$ and in part to the shifting of the Schlenk equilibrium at low temperature.

Salinger and Mosher[3] have used infrared data to describe methyl bromide and methyl chloride Grignard reagents in THF as virtually statistical mixtures of CH_3MgX and $(CH_3)_2Mg$. These results are quite compatible with the thermometric observations of Smith and Becker.[6d] Statistical distribution of methyl groups in the Schlenk equilibrium gives an equilibrium constant of 4. Although we could not make a direct ob-

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(21) F. W. Walker and E. C. Ashby, *J. Amer. Chem. Soc.*, **91**, 3845 (1969).

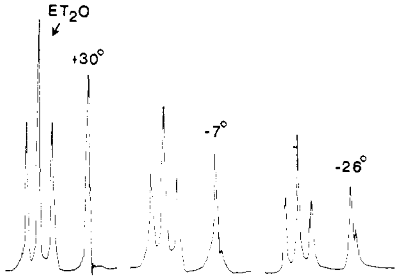

Figure 4. Low-temperature nmr profile of *tert*-butylmagnesium chloride in diethyl ether.

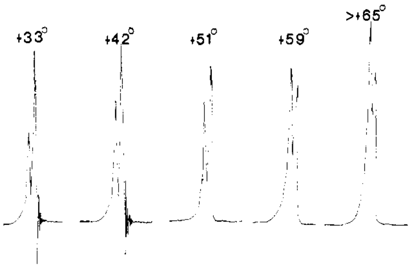

Figure 5. High-temperature nmr profile of *tert*-butylmagnesium chloride in tetrahydrofuran.

servation of $(CH_3)_2Mg$ and CH_3MgX species in THF, it is possible to calculate an equilibrium constant relating these two species from the data at hand. The approach is *via* application of eq 2 and 3, where N_i is the mole

$$\delta_{Av} = \sum_i N_i \delta_i \qquad (2)$$

$$1 = \sum_i N_i \qquad (3)$$

fraction of the *i*th component and δ_i is the chemical shift of the *i*th component. It is easy enough to obtain the chemical shift of dimethylmagnesium in THF at room temperature. While the shift observed at room temperature represents predominantly monomeric dimethylmagnesium, it is reasonable to assume that its behavior is essentially the same in the Grignard mixture and the contribution to the observed Grignard signal should be τ 11.76. On the other hand, it is impossible to observe CH_3MgX in THF without interference from $(CH_3)_2Mg$. An analogous problem exists in the interpretation of the ir spectra by Salinger and Mosher.[3] In that case Salinger and Mosher estimated the shape of an ir band characteristic of CH_3MgX in the presence of $(CH_3)_2Mg$. In an attempt to determine the nmr chemical shift of pure CH_3MgX in THF, small amounts of the methyl bromide Grignard solution were added to samples of 0.2 *M* magnesium bromide in the same solvent. The lowest observed chemical shift was τ 11.66. This is at considerably higher field than observed in diethyl ether (τ 11.55), but is not unreasonable since the signal for monomeric dimethylmagnesium is shifted from τ 11.74 to 11.83 (9 cps) in going from diethyl ether to THF. Thus, allowing for some contribution from $(CH_3)_2Mg$ even in the presence of excess magnesium bromide, a chemical shift for pure CH_3MgBr in THF of $\sim$11.64 may be calculated. The problem may be analyzed mathematically as

$$K = \frac{[RMgX]^2}{[R_2Mg][MgX_2]} = \frac{[RMgX]^2}{[R_2Mg]^2} \qquad (4)$$

Since methyl groups rather than magnesium atoms are represented by the observed signals

$$K = \left(\frac{N_{RX}}{{}^1/_2 N_{RR}}\right)^2 = 4\left(\frac{N_{RX}}{N_{RR}}\right)^2 \qquad (5)$$

From eq 2 and 3

$$N_{RR} = \frac{\delta_{Av} - \delta_{RX}}{\delta_{RR} - \delta_{RX}} \qquad (6)$$

Letting $N_{RR} = X$ for computational purposes

$$K = 4\left(\frac{1 - X}{X}\right)^2 \pm 8\left(\frac{1 - X}{X^3}\right)dx \qquad (7)$$

where the error term is simply

$$dK = \sqrt{(f'(x)dx)^2} \qquad (8)$$

and the uncertainty in "X," dx, is estimated to be 0.08 corresponding to an error of 0.1 cps in the measured chemical shift. The room temperature chemical shifts observed for methyl bromide Grignard and methyl chloride Grignard in THF are τ 11.70 and 11.72, respectively, which lead to equilibrium constants of 4 ± 2.6 and 1 ± 0.72, respectively, in good agreement with previous reports.[6b,d]

tert-Butylmagnesium Compounds in Diethyl Ether and Tetrahydrofuran.[6b,d] There has been little nmr investigation of *tert*-butylmagnesium compounds. Coates and Heslop[22] have reported that a disolvated dimer of *tert*-butylmagnesium chloride is precipitated from diethyl ether and that when dissolved in benzene the compound exhibits a single *tert*-butyl signal at 6.02 ppm upfield from benzene at room temperature. We observed the nmr spectra of *tert*-butyl chloride Grignard reagent in diethyl ether between +30 and −26°. The results are shown in Figure 4. At room temperature only a time average signal is observed (9.09), but at −26° this signal is resolved into two signals (9.09, 9.11). These signals are assigned to *tert*-butylmagnesium chloride and di-*tert*-butylmagnesium, respectively. It should be noted that since the protons on the β-carbon relative to the carbon–metal bond are being observed the sensitivity to changes in the carbon–metal bond is greatly reduced (less than 2 cps) compared to the sensitivity observed in the case of the corresponding methyl compounds (19 cps). From these spectra, it is observed that, as in the methyl case, *tert*-butylmagnesium chloride is in considerably higher concentration than di-*tert*-butylmagnesium at room temperature in diethyl ether, but that at lower temperatures the Schlenk equilibrium moves toward the dialkyl compound. Another observation is that *tert*-butyl exchange is much slower than methyl exchange under similar conditions.

tert-Butyl chloride Grignard was also studied in THF. In this case at room temperature, two signals (τ 9.13, 9.15) were observed as shown in Figure 5. These signals were assigned to *tert*-butylmagnesium chloride and di-*tert*-butylmagnesium, respectively. These signals did not coalesce at +65°, the boiling point of THF. In the *tert*-butyl case as in the methyl case, the Schlenk equilibrium is roughly statistical at ambient temperatures. This effect may be due to better solvation of magnesium chloride in THF relative to ether. Also it is interesting to note here that ex-

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[22] G. E. Coates and J. A. Heslop, *J. Chem. Soc. A*, 514 (1968).

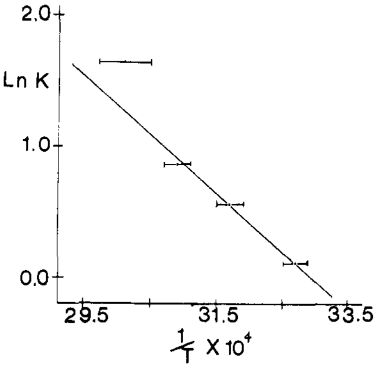


Figure 6. Plot of ln K_{eq} *vs.* $1/T$ for the reaction $(tert\text{-Bu})_2Mg + MgCl_2 \rightleftarrows 2tert\text{-BuMgCl}$.

change of alkyl groups in THF is slower than under similar conditions in diethyl ether.

The equilibrium constant at each temperature as well as an estimate of the rate of exchange of *tert*-butyl groups was obtained by calculating trial spectra using the DNMR computer program. This technique is of little use in evaluating activation parameters for *tert*-butyl exchange since the line broadening is so small. However, it is estimated that the preexchange lifetime of a *tert*-butyl group is approximately 4 sec at +42°. It should be noted that this lifetime refers to exchange from R_2Mg to RMgX or MgX_2 while alkyl exchange from RMgX to MgX_2 may be somewhat more rapid. Quantitative results were obtained concerning the position of the equilibrium at each temperature. These results are presented in Table III and Figure 6. The enthalpy of the reaction represented by eq 1 for the *tert*-butyl chloride Grignard system was calculated to be 9.0 kcal/mol while at +42° the entropy is 15 eu. In the equation, we have not included solvent; however, the endothermic nature of the reaction probably reflects loss of solvation energy from the magnesium halide solvate. The entropy effect is also consistent with a net loss of solvation. The errors indicated for the low-temperature points in Figure 6 correspond to the estimated precision of ±2° in the temperature measurements below +59°. The temperature control was unstable at +59° and a larger estimate of precision has been applied. The equilibrium constant of 7.54 was obtained in a qualitative high-temperature run and is intended to strengthen the qualitative arguments rather than for use in the thermodynamic experiments.

Table III. Thermodynamic Parameters for the Reaction $(tert\text{-Bu})_2Mg + MgCl_2 \rightleftarrows 2tert\text{-BuMgCl}$

Temp, °C	K	ln K	$1/T$
>+65	7.54	2.02	<0.00296
~+59	5.00	1.62	~0.00301
+51	2.36	0.859	0.00309
+42	1.74	0.554	0.00317
+33	1.12	0.109	0.00327

It is easy to see from the spectra in Figure 5 that the Schlenk equilibrium is both mobile and nearly statistical in THF (0.60 *M*). As usual, high temperature favors RMgX over R_2Mg, while the reverse is true at low temperature.

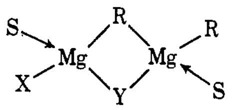
It was of interest to study the effects of concentration on the position of the Schlenk equilibrium. Samples were prepared in the concentration range of 0.12 *M* to saturation. At concentrations below 3.1 *M*, no detectable change in the position of the Schlenk equilibrium occurred at room temperature. In the more concentrated solutions there may be a tendency to favor the RMgX component. The two signals were not resolved but the peak of the signal which was observed was more nearly the chemical shift (relative to TMS) of RMgX than R_2Mg. A slight downfield shift was noted for the solvent high-field signal (relative to TMS), at these high concentrations, accompanied by loss of resolution resulting from viscosity or exchange. The low-field THF signal was used as a lock and not observed.

In the course of these studies it was observed that air oxidation of samples of *tert*-butylmagnesium chloride in THF resulted in signals in the region of τ 8.80 as expected for the *tert*-butoxy group. It was found that in solution containing these alkoxide impurities coalescence of the signals for RMgX and R_2Mg could be achieved at ~+40° whereas pure solutions were not observed to coalesce at +65°. Thus the alkoxide impurities seemed to catalyze the exchange of alkyl groups between R_2Mg and RMgX.

General Conclusions. The composition of a Grignard reagent depends upon the nature of the organic group, the halide, and the solvent, as well as the temperature and concentration of the solution. The effect of solvent seems to play the dominant role in deciding the position of the Schlenk equilibrium and this effect is probably due to the ability to solvate the magnesium halide component of this equilibrium. In general, the alkyl group has very little effect upon the position of the equilibrium. Undue extrapolation to significantly different organic groups should not be made since Evans and Kahn[5] have shown that the pentafluorophenyl bromide Grignard reagent in diethyl ether is essentially a statistical mixture of ArMgX and Ar_2Mg whereas alkyl Grignard reagents are almost entirely composed of RMgX species in this solvent. The distinction between alkyl and aryl Grignard compounds may or may not be general. Our data give little information about the effect of the halide on the position of equilibrium, but as long as the solvent complex of the MgX_2 component is soluble (*e.g.*, $MgI_2 \cdot n$-THF is not)[3] the equilibrium constant seems to be affected only slightly by changes in the nature of the halide.

The dynamics of the Schlenk equilibrium are discussed in the next section, but it is proper to point out here that transition metal impurities seem to have little effect upon the rate of alkyl exchange. This conclusion is based on the observation that there were no fundamental differences in the spectra of methyl bromide Grignard reagents in diethyl ether prepared from all available grades of magnesium.

Comments on the Mechanism of Alkyl Exchange in Organomagnesium Systems. These studies have afforded three qualitative observations which contribute to the understanding of the mechanism of alkyl exchange in Grignard reagents. (1) The structure of the alkyl group has a profound effect upon the rate of exchange. (2) The presence of a good bridging group such as alkoxide catalyzes alkyl exchange. (3) The solvent plays an important though secondary role in the exchange reaction. While our results do not establish the kinetic order or stereochemistry of alkyl exchange, previous studies concerning organomagnesium[10,11] and alkyl mercury halides strongly suggest that alkyl exchange involves a bimolecular process with retention of configuration. Making these assumptions, the key "intermediate" in the exchange reaction is envisaged as the mixed bridge structure I which we initially proposed some time ago.[5a] The stability of this structure is paramount in determining the rate of exchange. It should be pointed out that depending upon R and Y, structure I may be a true intermediate (free energy minimum) or a transition state (free energy maximum). In either case, the observations made can be explained in terms of this structural picture.



R = alkyl
X = halide
S = solvent
Y = halide, alkoxide, etc.

Branching at the α-carbon of the alkyl group (R) undoubtedly inhibits the formation of the bridge bond. This effect seems to be quite general. Quantitative data have been obtained by Hughes and Volger[23] for the exchange of alkyl groups in organomercury systems. Their results show that α branching is much more effective at inhibiting exchange than β branching.

On the other hand, the stability of structure I is also affected by the nature of the second bridging group (Y) which may be an alkyl, halide, or alkoxide group. From the work of Coates and coworkers[24a,b] it is apparent that in typical situations, alkoxide can be a better bridging group than halide in magnesium systems. Thus alkoxide impurities in *tert*-butyl chloride Grignard reagent catalyze the exchange process by stabilizing the mixed bridge system I. We have recently shown that a mixed alkoxy–alkyl organoaluminum bridge structure is quite stable.[24c] Our observation concerning dimethylmagnesium solutions containing alkoxides and those by House and coworkers[11] strongly suggests that the mixed bridge systems play an important role in organomagnesium exchange reactions.

Regarding the effect of solvent upon the rate of exchange, House and coworkers[11] have proposed that the solvent effect in dialkylmagnesium exchange is due to a shift in a rapid preequilibrium between the unreactive disolvated organomagnesium compound and the reactive monosolvate. Thus in the presence of tetramethylethylenediamine or dimethoxyethane alkyl exchange was much slower than in pure diethyl ether or tetrahydrofuran. This explanation is probably equally applicable to solvent effects we observed in the Grignard systems.

Experimental Section

Nmr Techniques. Spectra were obtained on a Jelco 100-MHz nmr spectrometer using the standard variable temperature unit. This unit was calibrated upon installation and was checked by connecting a digital voltmeter across the thermocouple leads and comparing the observed voltages at various temperature settings to those expected from the thermocouple. The accuracy of the temperature readings is estimated to be ±4° with a precision of ±2° at the extremes of the controlled range.

Temperature equilibration in the nmr samples was determined by monitoring the signal feedback meter (Jelco's S meter) which is very sensitive to changes in the gross dielectric properties of the sample which changes with solvent and temperature, concentration, etc. Stabilization of the S meter in the null position was taken as temperature equilibration within the sample. For the determination of chemical shifts in connection with the Schlenk equilibrium study, the digital output of the spin-decoupler unit was used with an estimated accuracy of 0.1 cps. For other experiments, precalibrated chart paper was used.

The computer program DNMR was written by G. Binsch and D. A. Kleier and was obtained through the Quantum Chemistry Program Exchange at Indiana University. Line shapes were calculated for the *tert*-butyl Grignard system in THF by varing populations and rate constants for trial spectra until a good fit with the experimental spectra was obtained. It was impossible to determine populations accurately from ordinary integration of the spectra.

Sample Preparation. For samples which were intended for repeated or extended study, the following technique was used. The material to be studied was taken into the drybox and a sample was transferred by means of a syringe into an nmr tube which had been fitted with a thick-walled adaptor for sealing. TMS was usually added and a three-ring cap used for a temporary seal. Silicone grease was applied around the bottom of the cap before removing the tube from the drybox, freezing in liquid nitrogen, and sealing with a torch. For temporary samples standard nmr tubes were used and they were sealed only by a three-ring cap. These samples were stored in the drybox and run within 24 hr of the time of preparation.

Synthesis. THF and diethyl ether were freshly distilled over sodium aluminum hydride and lithium aluminum hydride, respectively, before use. Bench top techniques with extensive use of Schlenk type apparatus were employed. As noted before, the purity of magnesium used was initially of concern so, even though tests indicated that Grignard grade turnings were usable, Dow triply sublimed magnesium was used to produce clear colorless solutions of organomagnesium reagents in ether. Grignard reagents were prepared from the appropriate alkyl halides and a 50% excess of magnesium in the desired solvent by classical methods. Dimethylmagnesium was prepared by the reaction of magnesium (100% excess) with neat dimethylmercury followed by extraction with the desired solvent. Magnesium halides were prepared by the reaction of magnesium (100% excess) with the appropriate mercury halide in the desired solvent. See ref 5b for the details of typical synthesis. Analysis of the Grignard reagents showed that coupling was less than 1% in the methyl case and less than 4% in the *tert*-butyl case.

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