

having a larger dipole moment than II) increases as the dielectric constant of the solvent increases. At infinite dilution, $N_I = 0.09 \pm 0.04$ as determined by n.m.r. spectroscopy employing both proton spin coupling (eq. 1) and chemical shift (eq. 2) parameters is in fair agreement with $N_I = 0.15$ (in heptane) as determined by dipole moment measurement.^{4b} Although there appears to be good agreement between the results employing eq. 1 and 2 (Table II), there exists a possibility that model compounds used to obtain values of δ_I and δ_{II} (no. 1 and 5 in Table I) are not totally satisfactory because of long range shielding effects arising from the *t*-butyl group.^{2b,c,9} Eliel and co-workers¹⁰ have tabulated empirical corrections for the shielding effects of alkyl groups on the α -carbinol protons of alkylated cyclohexanols. From their results, a correction of $+0.03$ p.p.m. for the δ_{II} values and no correction for the δ_I values (Fig. 2) can be estimated. Using the "corrected" δ_{II} values, new values of N_I were derived from eq. 2 and these are shown as parenthetical entries in Table II. It is difficult to justify

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(10) E. L. Eliel, M. H. Gianni, Th. H. Williams, and J. B. Stothers, *Tetrahedron Letters*, 741 (1962).

the need for these corrections in this instance, since agreement between the uncorrected values of N_I (Table II) obtained from eq. 1 and 2 appears satisfactory.

Experimental

cis- and *trans*-2-bromo-4-*t*-butylcyclohexanones,¹¹ 2-bromocyclohexanone,^{4b} and *trans*-2,6-dibromocyclohexanone¹² were prepared according to reported procedures. Freshly distilled or crystallized materials were used for all n.m.r. spectra which were determined using Varian DP-56.4 and DP-40 spectrometers. Chemical shifts and coupling constants represent averages of at least four sweeps (both directions) and are reproducible to 0.01 p.p.m. and 0.1–0.2 c.p.s., respectively.

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(11) N. L. Allinger and J. Allinger, *J. Am. Chem. Soc.*, **80**, 5476 (1958).

(12) E. J. Corey, *ibid.*, **75**, 3297 (1953). The procedure used for the synthesis of both *cis*- and *trans*-2,6-dibromocyclohexanones was that described by R. Metzger and P. Schreiber, *Chem. Ber.*, **89**, 2470 (1956).

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Infrared Spectral Studies of Grignard Solutions

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The infrared spectra of the Grignard and dialkyl- or diphenylmagnesium reagents prepared from methyl, ethyl, and phenyl halides in ethyl ether and in tetrahydrofuran have been investigated. The R–Mg absorption shows as a rather wide band between 500 and 535 cm^{-1} for R = Me or Et and between 365 and 383 cm^{-1} for R = Ph. The spectra of the Grignard solutions prepared in THF from methyl chloride, methyl bromide, ethyl chloride, ethyl bromide, and phenyl bromide and the corresponding dialkylmagnesium solutions in THF are noticeably different and can be interpreted in terms of the equilibrium, $\text{R}_2\text{Mg} + \text{MgX}_2 \rightleftharpoons 2\text{RMgX}$, where the species may be in part ionized. The infrared spectra of ether solutions of the same reagents, in contrast to those of the THF solutions, are not definitive and do not warrant such a conclusion. In every case the infrared spectrum of an equimolecular mixture of dialkylmagnesium (or diphenylmagnesium) and magnesium halide was identical with that of the corresponding solution of Grignard reagent. Reactions of alkyl iodides with magnesium in THF gave heterogeneous mixtures, the solutions from which were rich in dialkylmagnesium and contained but little iodide. It is evident from these data that conclusions drawn concerning the nature of any one Grignard reagent cannot be safely extrapolated to other such reagents because of the varying effects of R, X, and solvent on the Grignard system.

Introduction

The problem of the precise nature of the Grignard reagent has attracted renewed interest since the definitive experiments of Dessy, *et al.*¹ demonstrated that there was essentially no magnesium exchange between diethylmagnesium in ether solvent and radioactive magnesium bromide. Recently Ashby and Becker² showed that in tetrahydrofuran (THF), monomeric species predominate in some simple Grignard reagents, in contrast to the dimeric species existing in ethyl ether. Vreugdenhil and Blomberg³ reported that *dilute* solutions (*ca.* 0.01 *M*) of ethylmagnesium bromide in ethyl ether or in THF contain only monomeric species. Stucky and Rundle,⁴ by X-ray studies, found that phenylmagnesium bromide etherate crystals con-

tain $\text{PhMgBr} \cdot 2\text{Et}_2\text{O}$ units. Nuclear magnetic resonance studies⁵ have been very revealing but not definitive concerning the species RMgX vs. $\text{R}_2\text{Mg} \cdot \text{MgX}_2$. The demonstration by Walborsky⁶ of the stereochemical stability of the Grignard reagent from 1-bromo-1-methyl-2,2-diphenylcyclopropane establishes the integrity of the carbon–magnesium bond in this specific case. This body of diverse and partially conflicting data suggests that the nature of the Grignard reagent may be very dependent upon the variables of solvent, R group, and halide, and that a comparative study of several reagents by some suitable physical method should be made. It should be emphasized that physical methods may reveal the composition of the Grignard solution but may reveal little or nothing concerning the reactive species of the Grignard reagent.

Infrared spectroscopy should serve as a useful tool,

(1) R. E. Dessy, J. H. Wotiz, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **79**, 3476 (1957).

(2) E. C. Ashby and W. E. Becker, *ibid.*, **85**, 118 (1963).

(3) A. D. Vreugdenhil and C. Blomberg, *Rec. trav. chim.*, **82**, 453, 461 (1963).

(4) G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 1002 (1963).

(5) G. M. Whitesides, F. Kaplan, and J. D. Roberts, *ibid.*, **85**, 2167 (1963), and papers cited therein.

(6) H. M. Walborsky and A. E. Young, *Record Chem. Progr.*, **23**, 75 (1962).

but previous studies have not been too fruitful. Plum⁷ studied the infrared spectra of ethyl- and phenylmagnesium bromide in ethyl ether, but could make no definite assignments. Zeil⁸ examined the 1–13- μ region and assigned bands at 780 and 900 cm^{-1} to Mg–Br stretching modes. More recently Hamelin and Hayes⁹ studied spectra of organomagnesium compounds and magnesium halides in ethyl ether and in THF, and showed that the bands reported by Zeil were in reality bands due to the C–O–C group in ether, which were shifted by the coordination with magnesium halide or organomagnesium species. We are unaware of any other study which has established the position of the carbon–magnesium absorption frequency in the infrared spectra of Grignard reagents and dialkylmagnesium compounds.

The infrared spectra of other group II dimethylmetal compounds have been studied by Gutowsky.^{10,11} Table I lists his values for the C–M–C asymmetric stretching frequency as well as values calculated using Gordy's¹² approximation which makes use of molecular parameters to calculate force constants and hence the absorption frequency. By use of this formula, the C–Mg stretching frequency was estimated to be *ca.* 490 cm^{-1} . We have studied this accessible region of the spectrum using a Perkin–Elmer Model 421 spectrometer equipped with mid-infrared grating interchange.

TABLE I

ABSORPTION FREQUENCIES OF DIMETHYLMETAL COMPOUNDS

Compound	Me ₂ Zn	Me ₂ Cd	Me ₂ Hg	Me ₂ Mg
C–M–C freq., cm^{-1}	615 ^a	538 ^a	550 ^a	535, ^b 525 ^c
Estimated freq. ^d	565 ^e	535 ^e	530 ^e	490 ^f

^a Vapor phase, data from ref. 10 and 11. ^b THF solution, present study. ^c Ethyl ether solution, present study. ^d Using Gordy's¹² formula; covalent radii from R. T. Sanderson ["Chemical Periodicity," Reinhold Publ. Corp., New York, N. Y., 1960, p. 26]. ^e Using electronegativities from M. A. Fineman and R. Daignault [*J. Inorg. Nucl. Chem.*, **10**, 205 (1959)]. ^f Using orbital electronegativities for tetrahedral magnesium according to C. Hinze and H. H. Jaffé [*J. Am. Chem. Soc.*, **84**, 540 (1962)].

Experimental

Solvents.—Ethyl ether, tetrahydrofuran (THF), and dioxane were freshly redistilled from lithium aluminum hydride before use.

Reagents.—Chloromethane and bromomethane were used as supplied by the Matheson Co. with a specified purity of 99.5% min. Chloroethane was used as supplied by Eastman, b.p. 12.5–13° reported. Bromoethane and iodoethane were Eastman reagent grade, redistilled before use. Iodomethane, 2-iodopropane, chlorobenzene, bromobenzene, iodobenzene, 1,2-dichloroethane, and 1,2-dibromoethane were Matheson, Coleman and Bell reagent grade and redistilled before use. 1,2-Diiodoethane was used as supplied by Aldrich Chemical Co. Triple sublimed magnesium metal¹³ was used in the form of fresh turnings.

Organomagnesium Compound and Magnesium Halides. General Preparative Procedure.—Magnesium turnings (11 g., 0.45 g.-atom) were placed in a three-neck, 500-ml., round-bottom flask fitted with an addition funnel equipped with a pressure-

equalizing by-pass, stirrer, and condenser with a nitrogen inlet at the top. The apparatus was flame-dried and allowed to cool under nitrogen (Matheson prepurified, minimum purity 99.998%). Solvent, 50 ml., was added to the flask and another 80 ml. of solvent mixed with 0.3 g. equiv. of halide (alkyl or aryl halide for the preparation of organomagnesium compounds, 1,2-dihaloethane for magnesium halides) in the addition funnel. Approximately 10 ml. of the halide solution was added to the vigorously stirred reaction mixture. After the reaction had started (slight heating was required in a few cases, but iodine or other initiator was never used) the remaining halide solution was added dropwise. The reaction mixture was stirred for 4 hr. after all the halide was added and allowed to stand overnight. The clear supernatant solution was forced under nitrogen through a glass wool plug into a storage flask, which was then closed with a Teflon stopcock and rubber serum stopper to permit access with a hypodermic syringe. The solutions were essentially colorless with the exception of phenylmagnesium chloride noted below. Grignard solutions from the following halides were prepared by this procedure: in ethyl ether: methyl iodide, ethyl bromide, ethyl chloride, ethyl iodide, phenyl bromide, and phenyl iodide; in THF: ethyl chloride, ethyl bromide, and phenyl bromide. Solutions of magnesium bromide in ether and THF were made by using 1,2-dibromoethane as the halide. Solutions of magnesium chloride and iodide in THF were made by using the corresponding 1,2-dihaloethane.

Exceptions to the General Procedure.—To prepare the Grignard solution from methyl bromide and methyl chloride all the solvent was placed in the reaction flask initially, and a measured volume of liquefied halide allowed to vaporize slowly into the reaction mixture. The brown Grignard solution from phenyl chloride in THF was prepared by stirring at reflux a mixture of phenyl chloride, magnesium, and 0.5 ml. of 1,2-dichloroethane in THF for 15 hr. Magnesium iodide in ether was prepared using iodine instead of diiodoethane in the general procedure. The reactions of alkyl and phenyl iodides with magnesium in THF gave a thick slurry which was stirred with an equal volume of THF and allowed to settle overnight. The supernatant was then removed under nitrogen by means of a hypodermic syringe.

Dialkylmagnesium compounds in ether were prepared by dropwise addition of 0.3 mole of dioxane in 100 ml. of ether to a solution of 0.3 g. equiv. of alkylmagnesium bromide in 300 ml. of ether, followed by stirring overnight and settling for 24 hr. The supernatant was forced with prepurified nitrogen through a sintered glass filter, evaporated, and baked for 2 hr. at about 100° *in vacuo*. The residue was allowed to cool and was then dissolved in ether. Dimethyl-, diethyl-, and diphenylmagnesium were prepared in this manner. Dialkylmagnesium compounds in THF were prepared in a similar manner except that 25 ml. of THF was added to the solution prior to evaporation, and the final residue was dissolved in THF; dimethyl-, diethyl-, and diphenylmagnesium were prepared this way.

Analyses.—All organomagnesium solutions were analyzed for basic magnesium by acid titration to phenolphthalein endpoint¹⁴ and for halide by Volhard titration.¹⁵ Magnesium halide solutions were analyzed for halide by Volhard titration.

Spectra.—Infrared spectra were obtained on a Perkin–Elmer 421 spectrometer with the mid-infrared grating interchange. Connecticut Instrument Co. fixed thickness cesium bromide cells were used with Teflon plugs and spacers (0.025–0.2 mm.) and were checked for matching path lengths where necessary. Samples were prepared and cells filled in a nitrogen atmosphere. Spectra were run against a pure solvent reference except where otherwise indicated. Tetrahydrofuran shows no discrete absorption in the 300–600 cm^{-1} region critical to this study; ether shows weak absorption at 375, 440, and 500 cm^{-1} , but this was compensated for successfully by solvent in the reference beam. Ultraviolet spectra were obtained on a Cary Model 14M recording spectrophotometer in matched quartz cells by M. S. Singer.

Results

Typical spectra are shown in Fig. 1. In addition, the following observations were made: (1) Spectra of mixtures of R₂Mg and MgX₂, taken 5 min. after

(14) H. Gilman, E. Zoellner, and J. Dickey, *J. Am. Chem. Soc.*, **51**, 1576 (1929).

(15) J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

(7) W. B. Plum, *J. Chem. Phys.*, **5**, 172 (1937).

(8) W. Zeil, *Z. Elektrochem.*, **56**, 789 (1952).

(9) R. Hamelin and S. Hayes, *Compt. rend.*, **252**, 1616 (1961). See also S. Hayes, Thesis, de L'Université de Paris, 1963.

(10) H. S. Gutowsky, *J. Am. Chem. Soc.*, **71**, 3194 (1949).

(11) H. S. Gutowsky, *J. Chem. Phys.*, **17**, 128 (1949).

(12) W. Gordy, *ibid.*, **14**, 305 (1946).

(13) We acknowledge with gratitude the gift from Dow Chemical Co. of triple sublimed magnesium with the following analysis in p.p.m.: Al, <1; Cu, <1; Fe, <4; Pb, <10; Si, <10; Sn, <10; Zn, <100; Ba, <1; Ca, <18; K, <5; Na, <6; and Sr, <1.

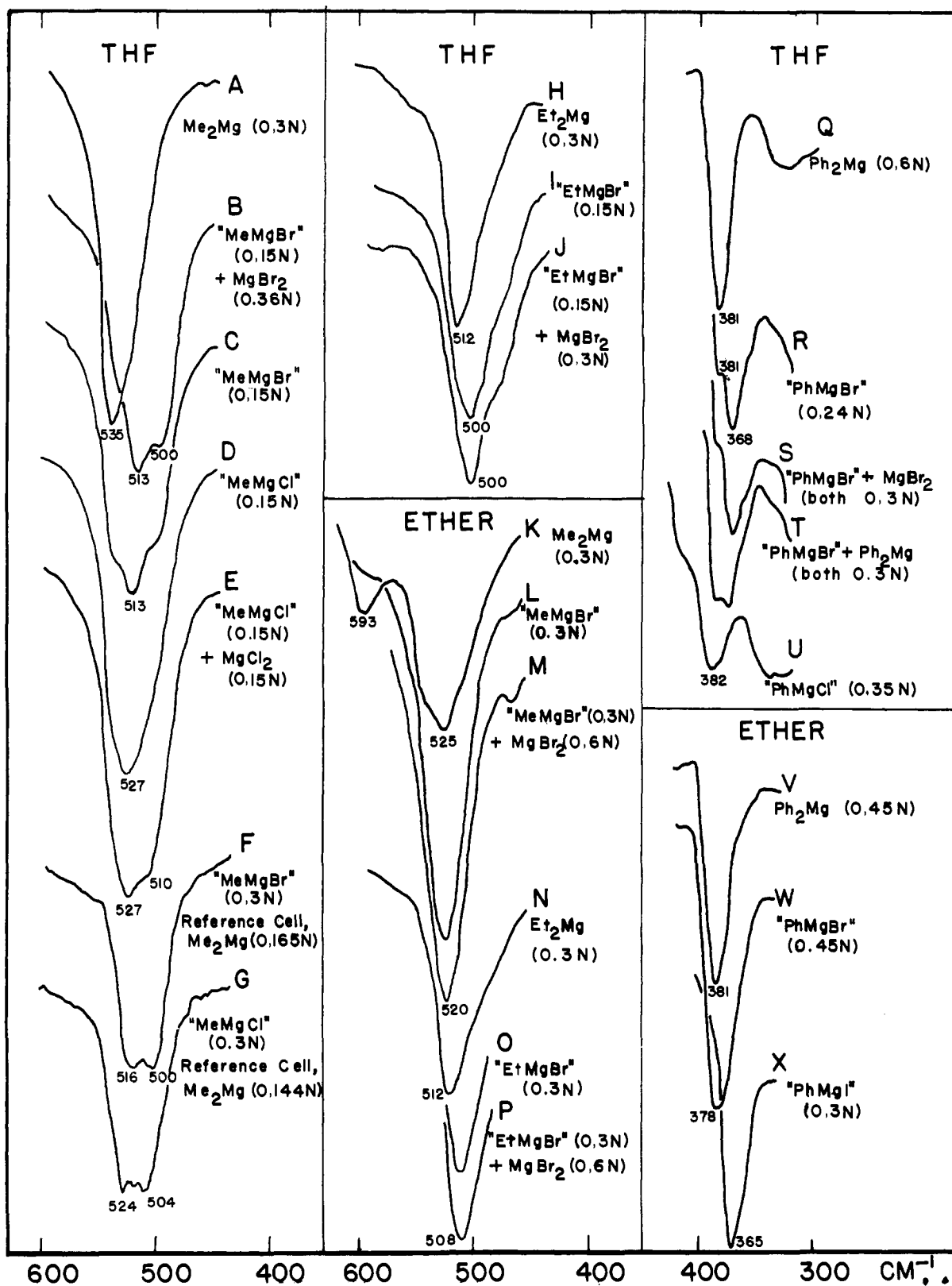


Fig. 1.—Infrared spectra of Grignard and dialkylmagnesium solutions. "RMgX" denotes the Grignard reagent prepared from RX and is not necessarily intended to represent the actual structure of the reagent. THF refers to tetrahydrofuran. Frequencies are accurate to $\pm 2 \text{ cm}^{-1}$.

mixing, were identical with those of the Grignard reagent, "RMgX," prepared from the corresponding halide where $R = \text{Me, Et, Ph}$, and $X = \text{Br, Cl}$, in THF, and where $R = \text{Me, Et, Ph}$, and $X = \text{Br, I}$, in ether. (2) Spectra of "MeMgI" and "MeMgBr" in ether were essentially the same in this region;

"MeMgCl" spectra were not studied since the ether solutions slowly precipitated MgCl_2 on standing at room temperature for a long time. Spectra of "EtMgCl" and "EtMgI" in ether were essentially similar to those of "EtMgBr." The "EtMgCl" spectra in THF were similar to those of "EtMgBr"

(Fig. 1, I and J). (3) No appreciable changes in the nature of any of the spectra with changes in concentration over a four- to eightfold range were observed. (4) Attempted preparations of Grignard solutions from alkyl and phenyl iodides in THF did not result in the usual reagent, but instead gave solutions rich in organomagnesium compound with but little iodide present and a precipitate containing the remaining halide. Analyses of the supernatant solutions are given in Table II.

TABLE II

REACTION OF ALKYL IODIDES WITH MAGNESIUM IN THF

Halide	Basic Mg concn., <i>N</i>	Iodide concn., <i>N</i>
MeI	0.185	0.011
EtI	.023	.015
<i>i</i> -PrI	.98	.025
PhI	1.5	.017
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A benzophenone-magnesium bromide-THF solution was colorless and had an ultraviolet spectrum identical with that of benzophenone in THF alone in the 343- μ region. On brief exposure to air, a yellow color appeared in the benzophenone-magnesium bromide-THF solution and the absorption at 343 μ was greatly enhanced. A benzophenone-"MeMgBr"-THF solution had a spectrum similar to that of benzophenone-THF except for a small decrease in intensity of the 343 μ band due to reaction which had occurred by the time the spectrum was obtained (*ca.* 3 min. after mixing).

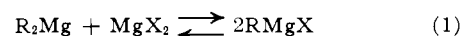
Discussion

The spectra of alkyl Grignard reagents and dialkylmagnesium compounds in ether and in THF show absorption occurring between 500 and 535 cm^{-1} (Fig. 1, A-P). Because of the proximity of the position of this band to that found for the C-metal frequency in Me_2Zn , Me_2Cd , and Me_2Hg compounds by Gutowsky (see Table I), because of its agreement with the frequency predicted using Gordy's approximation,¹² and because of its variation with change in the alkyl group of the organomagnesium compounds, it is assigned to the C-Mg stretching frequency. The C-Mg band in the phenylmagnesium compounds appears at lower frequencies, between 365 and 383 cm^{-1} (Fig. 1, Q-X). In this region there is also a band at 440 cm^{-1} due to the phenyl ring, and in ether solutions, a band near 500 cm^{-1} due to a shift in the ethyl ether absorption resulting from interaction with the organomagnesium compounds. The 500- cm^{-1} band is absent in phenyl Grignard reagents in THF since this solvent, in contrast to ether, does not have an absorption band in this region. We conclude therefore that the band between 365 and 383 cm^{-1} is due to the C-Mg bond in phenylmagnesium compounds.

Dimethylmagnesium solutions in ether show two bands, at 593 and at 525 cm^{-1} (Fig. 1, K). The latter is the normal band, but the former, which is not observed in THF, disappears upon admixture of magnesium halide. This band becomes somewhat more intense as the concentration is increased from 0.15 to 0.9 *N*, which suggests that it may be due to a dimeric or polymeric form of dimethylmagnesium in ether.

The identity of the spectra of $\text{R}_2\text{Mg} + \text{MgX}_2$ mixtures with Grignard solutions prepared in the classical manner is direct evidence compatible with the conclusion that the same species exist in both solutions. Reaction between R_2Mg and MgX_2 to give the Grignard reagent, whatever its composition, is therefore relatively rapid, being complete in the 5- to 10-min. interval between the time the solutions were mixed and the spectra obtained. This equivalence of $\text{R}_2\text{Mg} + \text{MgX}_2$ mixtures with classically prepared Grignard reagents has been demonstrated previously for "ethylmagnesium bromide" in ether by Dessy¹⁶ (with respect to dielectric constant), and for "ethylmagnesium chloride" in THF by Ashby² (with respect to conductance, dipole moment, and infrared spectrum). In view of the present results it appears that this equivalency may be generalized to most cases.

Grignard solutions from methyl bromide and methyl chloride in THF are concluded to exist as equilibrium mixtures, containing the species represented in eq. 1 with a possible but unknown contribution from the ionic counterparts ($\text{RMgX}_2^- + \text{RMg}^+$).



Addition of excess MgX_2 to these solutions alters the shape of the absorption band (Fig. 1, B and E) in the manner expected for an increase in the concentration of RMgX and a decrease in the concentration of R_2Mg , such as would result from a shift of equilibrium 1 to the right. Since there is no change in shape of the peak as the concentration of the Grignard reagent is varied from 0.15 to 1.2 *N*, the data are incompatible with an appreciable contribution from the equilibrium represented by eq. 2, whose position is concentration



dependent, but are in accord with the equilibrium represented by eq. 1, whose position would be concentration independent. Assuming the validity of equilibrium 1, its position may be estimated. When the concentration of Me_2Mg in the reference cell equals the concentration of Me_2Mg in the Grignard solution in the sample cell, the contribution of Me_2Mg to the observed spectrum should be eliminated and the resulting spectrum should be that for MeMgX alone. The subtractive procedure requires one to estimate what the appearance of the spectrum of a pure RMgX species in THF would be. If the spectra represented by curves F and G in Fig. 1 are in reality those of the MeMgX species,¹⁷ then the concentration of Me_2Mg in "MeMgBr" and "MeMgCl" solutions in THF is such as to give values of $K_{\text{eq}} = 3.5$ and 4.5, respectively, for equilibrium 1. These values indicate that the MeMgX , Me_2Mg , and MgX_2 species are approximately distributed in a statistical manner ($K = 4$) in these solutions. Assuming a >0.8 *N* THF solution of the Grignard reagent from an alkyl bromide in which RMgBr , R_2Mg , and MgBr_2 are statistically distributed

(16) R. E. Dessy, *J. Org. Chem.*, **25**, 2260 (1960).

(17) This conclusion is drawn from the relative shapes of spectra A, B, and C in Fig. 1. Spectrum C apparently results from a mixture containing a species absorbing at *ca.* 513 and 500 cm^{-1} and another (Me_2Mg) absorbing at 535 cm^{-1} . Addition of excess MgBr_2 results (spectrum B) in the intensification of the absorption near 513 and 500 cm^{-1} and a decrease in the relative intensity of the absorption at 535 cm^{-1} (Me_2Mg). This is interpreted in terms of a shift of equilibrium 1 and a spectrum of MeMgBr alone absorbing at 516 and 500 cm^{-1} .

according to eq. 1, then the magnesium bromide must be at higher concentration than its solubility in pure THF alone. This enhanced solubility may be due to the higher dielectric constant of the Grignard system, or to some more specific interaction; but the concentration independence rules out substantial contribution of specific association represented by eq. 2.

Solutions of "EtMgBr," "EtMgCl," and "PhMgBr" in THF show approximately the same spectral characteristics, and can also be represented by equilibrium 1. However, no estimate of the value of K_{eq} could be obtained for these compounds because of the width and proximity of the bands. Owing to the absorption of magnesium chloride near the Ph-Mg band in THF, the spectra of "PhMgCl" in THF could not be readily interpreted with any degree of certainty.

The ultraviolet spectra of benzophenone-magnesium bromide-THF and benzophenone-"MeMgBr"-THF solutions do not preclude the existence of appreciable amounts of magnesium bromide in "MeMgBr" solutions in THF. This observation is contrary to Bikales and Becker's recent report¹⁸ of the existence of a colored complex between magnesium bromide and benzophenone in THF; this complex was reported to be absent in "MeMgBr"-benzophenone mixtures, leading to their conclusion that no appreciable amounts of magnesium bromide could exist in "MeMgBr" solutions in THF.

In summary, the present evidence indicates that the Grignard solutions prepared in THF from methyl bromide, methyl chloride, ethyl bromide, ethyl chloride, and phenyl bromide are best represented as a mixture of $RMgX$, R_2Mg , and MgX_2 species with an unknown contribution from their ionic counterparts as described by equilibrium 1.

The results of the reactions of alkyl iodides with magnesium in THF may be explained by the extremely low solubility of magnesium iodide (0.003 *N*) in THF. This forces equilibrium 1 far to the left, leaving predominantly R_2Mg in solution. It is seen that the amount of iodide retained in these Grignard solutions in THF exceeds, but only to a small amount, the solubility of pure magnesium iodide in THF alone. These experiments suggest that the reaction of alkyl and aryl iodides with magnesium in THF may be useful for the direct synthesis of solutions containing predominantly R_2Mg species with only slight amounts of iodide present. The utility of this method depends on the nature of the R group, as indicated by the data in Table II.

The Grignard reagent from phenyl iodide in ethyl ether is quite distinct from that prepared from the corresponding phenyl bromide. In the case of the phenyl iodide Grignard reagent in ether there is very little free diphenylmagnesium, as is seen from the position of the C-Mg absorption bands. The position of the absorption of the Grignard solution from phenyl iodide is shifted further from that of the diphenylmagnesium than in the case of other Grignard reagents and their respective R_2Mg solutions in ether. The

magnitude of the shift for "PhMgI" is more nearly that prevalent in THF solutions, and suggests that PhMgI, rather than $Ph_2Mg \cdot MgI_2$ or Ph_2Mg species, predominate. It is thus concluded that the equilibrium, $Ph_2Mg + MgI_2 \rightleftharpoons 2PhMgI$, in ether solution lies far to the right.

With the exception of "PhMgI," all the Grignard reagents studied in *ethyl ether* give spectra showing such a small difference from those of the corresponding dialkylmagnesium compounds that no definite conclusions can be drawn from these data alone.

It must be emphasized that these infrared spectral studies may reveal something concerning the nature of the species present in solution but they cannot *per se* reveal the nature of the reactive species as far as Grignard reactions are concerned. Nevertheless, it may be worthwhile to point out one or two cases where anomalous observations concerning the Grignard reaction can be rationalized on the basis of these findings.

A recent report by Cram and Wilson¹⁹ on the stereoselectivity of various Grignard reagents toward *dl*-3-hydroxy-3-phenyl-2-butanone shows a most interesting reversal in stereoselectivity when the Grignard reagent in ether from phenyl bromide is substituted for that from phenyl iodide. The stereoselectivity in this reaction was interpreted in terms of the relative energies of cyclic and dipolar models for the transition states involved. It was postulated that the cyclic transition state was favored, other variables being equivalent, with the less hindered attacking reagent. Our findings which indicate that the reagent in one case is PhMgI and in the other is possibly $Ph_2Mg \cdot MgBr_2$ are easily accommodated to these findings since the former is most certainly less hindered than the latter.

Stocker and co-workers,²⁰ studying Grignard addition to benzil and to methylbenzoin, also found that the stereochemical outcome of the reaction of "PhMgI" in ether is different from that of "MeMgBr," "MeMgCl," "MeMgI," "PhMgBr," and "PhMgCl" in the same solvent. These observations likewise imply a difference in the nature of the reacting species between "PhMgI" and other Grignard reagents in ethyl ether in accord with the infrared data.

Perhaps one of the most important conclusions to be drawn from this work is that structures of Grignard reagents should not be generalized. The nature of the alkyl or aryl group, the halogen atom, and the solvent all have been shown to have an effect on the structure of the species present in Grignard solutions, and care must be taken when extrapolating data and/or conclusions from one system to another.

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(20) J. H. Stocker, P. Sidisunthorn, B. M. Benjamin, and C. J. Collins, *ibid.*, **82**, 3913 (1960).

(18) N. M. Bikales and E. I. Becker, *Can. J. Chem.*, **41**, 1329 (1963).