

THE COMPOSITION OF GRIGNARD COMPOUNDS VIII. ALKYL MAGNESIUM FLUORIDES

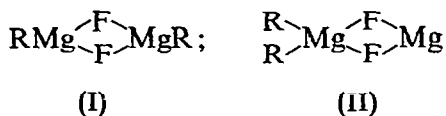
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SUMMARY

Although alkylmagnesium chlorides, bromides and iodides are monomeric in tetrahydrofuran over a wide concentration range, ebullioscopic studies reported herein show that alkylmagnesium fluorides are dimeric in diethyl ether and tetrahydrofuran over the same concentration range. Low temperature NMR, IR, fractional crystallization and dioxane precipitation studies indicate that the mobile Schlenk equilibrium used to describe organomagnesium chlorides, bromides and iodides does not exist in the case of alkylmagnesium fluorides due to the unusual stability of Mg-F-Mg bridge bonds. Instead, the composition of alkylmagnesium fluorides in both diethyl ether and tetrahydrofuran is best described by the dimeric units (I) or (II), or (I) and (II).



Some evidence is presented to support a mixed bridge system (I) for those cases where the RMgF compounds were prepared in the presence of by-product R₂Mg compounds. Alkylmagnesium fluorides react with H₂O, O₂, CO₂, PhCN and Ph₂CO in a manner similar to, but significantly different from, the corresponding alkylmagnesium bromides.

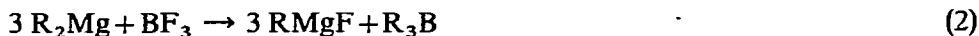
INTRODUCTION

Prior to 1970, all attempts to prepare and isolate organomagnesium fluorides were unsuccessful¹⁻⁴. Recently we have described two routes to this class of compounds. In one report methyl-, ethyl- and hexylmagnesium fluorides were successfully prepared in ether solvents by reaction of the corresponding alkyl fluoride with magnesium in the presence of an appropriate catalyst (I₂, Br₂, BrCH₂CH₂Br, C₂H₅Br and CoCl₂)^{5,6}.



In a second study, alkyl- and arylmagnesium fluorides were prepared by reac-

tion of a dialkyl- or diarylmagnesium compound with a metal or metalloidal fluoride (e.g., BF_3)⁷. Because alkylmagnesium fluorides undoubtedly will be evaluated as



alkylating agents, it would be important to know as much about this new class of compounds as possible. Since fluorine is considered, because of its size and electronegativity, to be a considerably stronger bridging group than chlorine, bromine or iodine, it was not clear to us that the composition of alkylmagnesium fluorides in solution would be similar to that reported for alkylmagnesium chlorides, bromides and iodides. Thus we have sought to learn as much as possible about the nature of alkylmagnesium fluorides in solution with the aim of achieving a useful understanding of the chemistry of this class of compounds. To this end, we have carried out molecular association, crystallization and selective precipitation studies with dioxane as well as IR and NMR spectroscopic studies of the compounds prepared.

EXPERIMENTAL

Alkylmagnesium fluorides were prepared by the reaction of alkyl fluorides with magnesium in THF using iodine as a catalyst^{5,6}. All infrared spectra were obtained using a Perkin-Elmer 621 high resolution grating spectrophotometer equipped with cesium or potassium iodide cells. Room temperature proton magnetic resonance spectra were obtained using a Varian A-60 magnetic resonance spectrometer. Low temperature NMR studies of methylmagnesium fluoride were carried out using a Jeolco 100 MHz magnetic resonance spectrometer.

Ebullioscopic determination of molecular association

A complete description of the apparatus and its operation has been presented elsewhere^{8,9}. The association studies were carried out in Et_2O and THF at a pressure of 740.0 mm. The results are calculated in terms of solute association expressed as an i value. The relationship employed is shown by eqn. 3:

$$i = \frac{W_2 \cdot M_1}{W_1 \cdot M_2} \cdot \left(\frac{1}{e^{-\Delta T_B \cdot M_1 / 1000 K_B} - 1} \right) \quad (3)$$

ΔT_B , boiling point elevation constant (2.01 for Et_2O and 2.20 for THF at 740 mm); W_1 , grams of solvent; W_2 grams of solute; M_1 , molecular weight of solvent and M_2 , the calculated formula weight of solute. Since analytical results indicate that the R/Mg/F ratio is not exactly 1/1/1 in the solutions used (a typical ratio is 1.1/1.0/0.9, although some compounds exhibited a slightly better or worse ratio), the formula weight of solute was calculated according to the analyses in terms of a mixture of R_2Mg and MgF_2^* . For reasons given before⁹, the monosolvated formula weight of the solute was chosen for the computation of i values.

* For example $\text{C}_6\text{H}_{13}\text{MgF}$ in Et_2O was calculated according to $M_2 = 54.3\% \text{R}_2\text{Mg} + 45.7\% \text{MgF}_2 + \text{Et}_2\text{O}$.

Fractional crystallization and dioxane precipitation studies

An Et₂O solution of hexylmagnesium fluoride (Found*: Mg_B, 1.514 F; Mg_T, 1.316 F; Mg_B/Mg_T, 1.15) was cooled slowly in a dry ice/acetone bath by the periodic addition of dry ice. An appreciable amount of needle-like crystals was formed. Analysis of the supernatant solution: found: Mg_B, 1.644 F; Mg_T, 1.502 F; Mg_B/Mg_T, 1.09 (higher concentration of the solution after crystallization was due to the increase of the density of solvent at low temperature).

A THF solution of hexylmagnesium fluoride (Found: Mg_B, 1.051 F; Mg_T, 1.044 F; Mg_B/Mg_T, 1.01) did not deposit crystals when cooled to -78°. Unfortunately, no appreciable amount of crystal formation took place before the freezing of solvent when the solution was cooled in liquid nitrogen. The frozen solution was partially melted at -78°, and the supernatant layer analyzed. (Found: Mg_B, 1.077 F; Mg_T, 1.04 F; Mg_B/Mg_T, 1.04.)

When 2 ml of dioxane (23.2 mmole) was mixed with 2 ml of hexylmagnesium fluoride THF solution (2.1 mmole), a fine white precipitate was formed slowly. Analysis of the supernatant after standing overnight: found: Mg_B, 0.4579 F; Mg_T, 0.4532 F; Mg_B/Mg_T, 1.01. When 0.5 ml of dioxane (5.8 mmole) was mixed with 4 ml of hexylmagnesium fluoride THF solution (4.2 mmole), only a very small amount of precipitate was formed. (Found: Mg_B, 0.9781 F; Mg_T, 0.9600 F; Mg_B/Mg_T, 1.02.)

Preparation of magnesium fluoride

Anhydrous hydrogen fluoride was bubbled into a polyethylene bottle (with magnetic stirring) which contained 2 g of magnesium in 250 ml of THF. Even after the addition of 0.5 ml of water, analysis of the solution showed a negligible concentration of soluble magnesium. Then anhydrous hydrogen fluoride bubbled through 66 ml of THF solution of dimethylmagnesium (9.6 mmol) for 15 min. (Found: Mg_B, 0.296 F; Mg_T, 0.148 F; Mg_B/Mg_T, 1.99.)

Another attempt to prepare anhydrous magnesium fluoride was made by treating mercuric fluoride (4.1 g, 17 mmol) (Alfa Inorganics) with magnesium (2.5 g, 102 mmol) in 60 ml of THF at reflux. After 4 days, analysis showed negligible reaction. These reagents also did not react in 50 ml of 1,2-dimethoxyethane during a 3 day reflux period.

Distilled boron trifluoride etherate (4.4 ml, 33 mmol) (Eastman purified) was first dissolved in 20 ml of Et₂O and added dropwise into a reaction flask containing 100 ml of 0.5 M (50 mmol) dimethylmagnesium in diethyl ether solution. A white solid precipitate was observed after the addition of a few drops of the BF₃·OEt₂ solution and the reaction was exothermic. The addition was completed in three minutes and the reaction mixture was stirred overnight. Analysis of the solution showed negligible amounts of magnesium and boron to be present, and the solid after filtration and washing with Et₂O showed a ^aF/Mg_T ratio of 2.11.

Attempted preparation of alkylmagnesium fluorides by redistribution of dialkylmagnesium compounds with magnesium fluorides

A solution of diethylmagnesium (1.15 M, 19.5 mmol) in diethyl ether was

* Mg_B (basic magnesium) was determined by acid-base titration and Mg_T (total magnesium) was determined by EDTA titration.

allowed to redistribute with commercially available magnesium fluoride (3.4 g, 55 mmol) (Alfa Inorganics) in 60 ml of THF. After 3 days at reflux, analysis showed no increase in Mg_T in the solution and the ratio of Mg_B to Mg_T corresponded to unreacted dialkylmagnesium.

Magnesium fluoride (2.4 g, 38 mmol), prepared from boron trifluoride and dimethylmagnesium in diethyl ether (above), was allowed to react with dimethylmagnesium (10 mmol) in 50 ml of Et_2O . After it has been stirred overnight, analysis of the solution showed the ratio of Mg_B to Mg_T to be 1.99. Then 25 ml of Et_2O was replaced by THF and more dimethylmagnesium (20 mmol) added. After 2 days of stirring, analysis of the solution also showed the ratio of Mg_B to Mg_T to be 1.99.

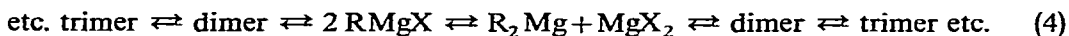
Chemical reactions of hexyl- and ethylmagnesium fluorides

Standard solutions of hexyl- and ethylmagnesium fluorides (0.33 *F* and 0.37 *F*) and bromides (0.49 *F* and 0.78 *F*) in THF were prepared. All reactions were carried out in 15 ml bottles fitted with a rubber septum cap at 25°. Two samples of 0.78 *M* benzonitrile (1.56 mmole) and 0.74 *M* benzophenone (1.48 mmole) solutions were allowed to react with 5 ml of each of the above Grignard reagents for 5 days and 13 h, respectively. VPC analyses* of hydrolyzed samples showed that the alkylmagnesium fluorides and bromides gave the same products.

Oxygen and carbon dioxide were injected via a 50 ml syringe into separate bottles each containing 5 ml of hexylmagnesium fluoride solution. The reactions were exothermic and were stopped when gas absorption ceased. VPC analyses of the hydrolyzed samples showed the reaction of oxygen gave hexanol in quantitative yield and carbon dioxide gave heptanoic acid in 19% yield. No attempt was made to optimize the yield of heptanoic acid or determine the other products produced by carbonation.

RESULTS AND DISCUSSION

The composition of organomagnesium chlorides, bromides and iodides in solution^{10,11} should be considered briefly before discussing the composition of alkylmagnesium fluorides in solution. It is already known that organomagnesium bromides and iodides exist in diethyl ether as monomeric species at low concentration and that the molecular association increases with concentration. Organomagnesium bromides and iodides are best represented by a series of equilibria [eqn. (4)] in diethyl ether in which the association has been shown to exist predominantly through halogen bridge bonds⁹.



On the other hand, alkylmagnesium chlorides are believed to be dimeric over a wide concentration range⁹ in diethyl ether, although some dissociation to monomeric species probably takes place at very low concentration. Whereas organomagnesium chlorides, bromides and iodides are associated in diethyl ether at concentrations >0.1 *m*, the same compounds are monomeric in tetrahydrofuran even at concentrations as high as 2 *m*⁹ [concentrations give in molality (*m*) for association data]. The pronounced difference in association in these two solvents presumably results from a

* Columns were 6-ft., 10% Carbowax 20M.

stronger coordination of the magnesium atom by tetrahydrofuran as compared to diethyl ether, thus preventing association through halogen bridge bonds. The association of organomagnesium compounds in tetrahydrofuran has been reported recently for alkylmagnesium alkoxides¹⁴, thio-¹⁵ and aminomagnesium alkyls¹⁶. The association in tetrahydrofuran is explained on the basis of available electron pairs on oxygen, sulphur and nitrogen interacting with the vacant orbitals of magnesium. Presumably the competition involves stability due to bridge bond formation versus solvate formation. Weak bridge bonds (*e.g.* CH₃, Br) are not formed in tetrahydrofuran

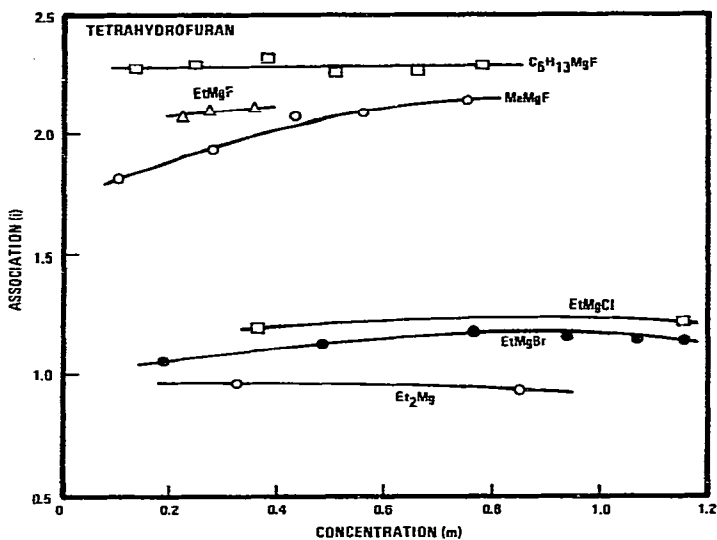


Fig. 1. Association of Grignard compounds in tetrahydrofuran.

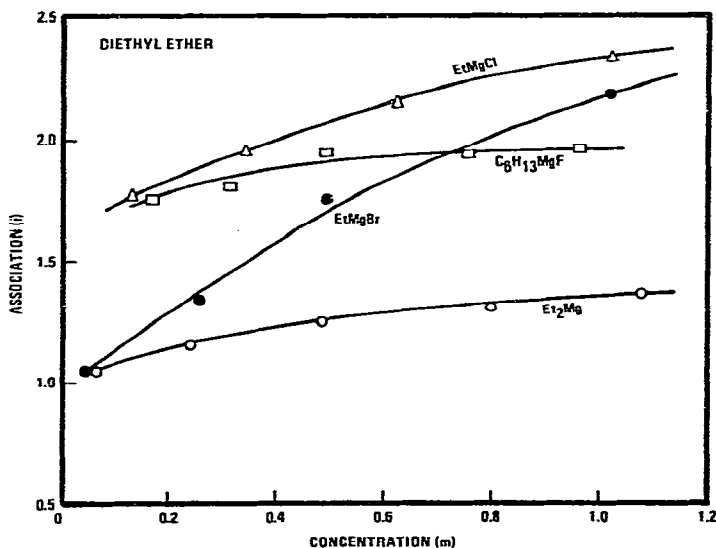


Fig. 2. Association of Grignard compounds in diethyl ether.

due to the greater heat of solvation on reaction a Grignard species with THF as compared to the ΔH of bridge bonding. However, stronger bridge bonds are apparently formed as the electronegativity of the bridging atom increases. From this consideration, fluorine should be an even stronger bridging atom. Therefore in tetrahydrofuran it is not too surprising that alkylmagnesium fluorides associate through stable Mg-F-Mg bridge bonds.

Figs. 1 and 2 show the association of a number of alkylmagnesium compounds in diethyl ether and tetrahydrofuran expressed as an i value (observed mol.wt./calculated mol.wt.) plotted against the monoetherate solute concentration (molality). It is very interesting to note that the i value curves representing hexylmagnesium fluoride in diethyl ether and tetrahydrofuran, as well as methyl- and ethylmagnesium fluorides in tetrahydrofuran, are clustered around the dimer value ($i=2$) and display a very small concentration dependence. On the other hand, alkylmagnesium chlorides and bromides in tetrahydrofuran show an $i \cong 1$, indicating only monomeric species whereas in diethyl ether association is observed as a function of concentration. The lack of significant curvature in the line plots describing alkylmagnesium fluorides argues against an equilibrium-type association [eqn. (4)] since the i values would be expected to increase with an increase in concentration. For these kinds of association data, the most obvious interpretation⁹ is that alkylmagnesium fluorides are essentially dimeric over a wide concentration range in both tetrahydrofuran and diethyl ether and that the slight curvature observed for the i value curves is due to a deviation of the solutions from ideal behavior, impurities and experimental error. These unusual association data in tetrahydrofuran is the first evidence showing association of organomagnesium halides in this solvent.

Infrared spectral data for the alkylmagnesium fluorides and related organomagnesium compounds are shown in Table 1.

From previous high-resolution infrared studies¹⁷, the absorption band

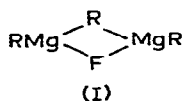
TABLE 1

COMPARISON OF INFRARED SPECTRA OF ALKYL-MAGNESIUM FLUORIDES, CHLORIDES, BROMIDES AND DIALKYL-MAGNESIUM COMPOUNDS^{a,b}

Grignard Compound RMgX		$\nu(\text{C-Mg}) (\text{cm}^{-1})$	
R	X	Et ₂ O	THF
CH ₃	F		535
	Cl		527
	Br	520	513
	CH ₃	525 (593)	535
C ₂ H ₅	F		505 (560)
	Br	508	500
	C ₂ H ₅	512	512
n-C ₆ H ₁₃	F	501 (550)	500 (548)
	n-C ₆ H ₁₃	501 (551)	

^a Except for the alkylmagnesium fluorides and dihexylmagnesium, all spectra are from Ref. 17. ^b Bands as shoulders are given in parentheses.

between 500 and 535 cm^{-1} has been assigned to the C-Mg stretching frequency for alkylmagnesium compounds in diethyl ether and tetrahydrofuran respectively. The infrared spectrum of $(\text{CH}_3)_2\text{Mg}$ in diethyl ether exhibits a shoulder on the high frequency side of the C-Mg stretching band which is ascribed to Mg-CH₃-Mg bridge bonds. Since Grignard compounds are monomeric in tetrahydrofuran and organomagnesium halides are associated through the halogen in diethyl ether, a shoulder is not observed in these cases. Examination of Table I reveals that all alkylmagnesium fluorides exhibit C-Mg stretching at a frequency between 500-535 cm^{-1} . However the alkylmagnesium fluorides, except methylmagnesium fluoride which contained no excess dimethylmagnesium, exhibit a shoulder even in tetrahydrofuran of the type previously observed for dimethyl- and dihexylmagnesium in diethyl ether. Furthermore, the intensity of the shoulder is a function of the $\text{R}_2\text{Mg}/\text{RMgF}$ ratio. One possible explanation for the shoulder observed in the spectra of ethyl- and hexylmagnesium fluoride is that it is due to a mixed alkyl-halogen bridged species (I) in solution. The ethyl- and hexylmagnesium fluoride prepared from the corresponding alkyl fluoride and magnesium contains some of the corresponding dialkylmagnesium (see ref. 6). It is not unreasonable that a stable mixed bridge system such as (I) exists even in tetrahydrofuran when one considers the strong bridging capability of RMgF compounds.



Unlike the shoulder observed for dimethylmagnesium in diethyl ether, the relative intensity of the shoulder absorption for hexylmagnesium fluoride in tetrahydrofuran is not affected on dilution from 0.4 to 0.08 *F*. This is additional evidence in favor of a stable dimeric structure (I) to represent the shoulder band observed in solutions of RMgF compounds containing a small amount of R_2Mg compound and against a Schlenk equilibrium involving different associated species. Unfortunately, direct observation of the mixed bridge structure by low temperature NMR using the optimum system, $(\text{CH}_3)_2\text{Mg}/\text{CH}_3\text{MgF}$, was not possible due to the similar proton resonance bands observed for $(\text{CH}_3)_2\text{Mg}$ and CH_3MgF in THF at low temperature. NMR observations of other $\text{R}_2\text{Mg}/\text{RMgF}$ systems would not be as satisfactory on the basis of the multiplet absorptions of the higher alkyl groups and the similarity of the absorption positions of the multiplets expected for R_2Mg and RMgF compounds.

The NMR spectra of alkylmagnesium fluorides are summarized in Table 2. The NMR spectra of all the alkylmagnesium fluorides studied exhibit α -proton resonance signals upfield from TMS as do all other alkyl Grignard compounds¹⁸.

Low temperature NMR profiles of several methylmagnesium compounds in tetrahydrofuran are shown in Table 3.

The α -proton resonance signal for dimethylmagnesium shifts from 11.76 τ at 20° to 11.83 τ at -76° with a small signal at 11.70 τ attributed to terminal sites in an associated species¹⁹. The signals of methylmagnesium bromide and chloride are observed at 11.70 τ and 11.72 τ respectively at 20° and approach that of dimethylmagnesium at -100° due to precipitation of the corresponding magnesium halide at low temperature. No distinct signals for dimethylmagnesium and methylmagnesium

TABLE 2
NMR SPECTRA OF ALKYL MAGNESIUM FLUORIDES^a

RMgF	Solvent	Chemical shift (τ) ^{b,c}
CH ₃ MgF	THF	11.76 (0, s)
C ₂ H ₅ MgF	THF	11.01 (8.2, q)
C ₆ H ₁₃ MgF	THF	10.55 (7.5, t)
C ₆ H ₁₃ MgF	Et ₂ O	10.93 (7.4, t)
C ₆ H ₁₃ MgF	DME	11.03 (7.5, t)

^a For protons on α -carbon attached to the magnesium atom. ^b Except methylmagnesium fluoride, all the signals refer to external TMS. ^c Coupling constants are given in Hz and the multiplicities (s=singlet, t=triplet and q=quartet) are given in parentheses.

TABLE 3
LOW TEMPERATURE NMR PROFILE OF METHYL MAGNESIUM COMPOUNDS IN TETRAHYDROFURAN^{a,b}

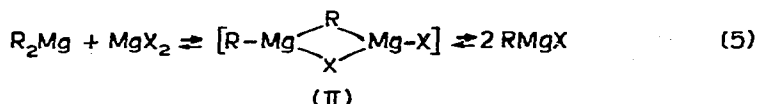
Temp. (°C)	Chemical shift (τ)			
	(CH ₃) ₂ Mg (0.86 F)	CH ₃ MgBr (0.68 F)	CH ₃ MgCl (0.49 F)	CH ₃ MgF (2.24 F)
+20	11.76	11.70	11.72	11.76
-20		11.77		11.76
-40		11.78	11.77	
-60	11.81	11.80		11.77
-76	11.70, 11.83			
-100		11.85	11.83	11.82

^a Except for methylmagnesium fluoride, all data from ref. 19. ^b All signals refer to internal TMS.

halide are observed in tetrahydrofuran as in diethyl ether¹⁹. Methylmagnesium fluoride has the same chemical shift as dimethylmagnesium at 20°. At -100° only a single signal is observed and at a position similar to that of dimethylmagnesium and methylmagnesium chloride and bromide. However, unlike methylmagnesium chloride and bromide, the similarity in chemical shift of methylmagnesium fluoride to that of dimethylmagnesium at low temperature is probably not due to the precipitation of the corresponding magnesium halide. If it were, then the 11.82 τ signal for methylmagnesium fluoride should occur at a higher temperature than that for methylmagnesium bromide and chloride, since magnesium fluoride is less soluble than magnesium chloride or bromide. Furthermore if MgF₂ precipitated from solution, it would not redissolve since we have shown that dimethylmagnesium and MgF₂ do not redistribute and MgF₂ is very insoluble in THF.

Obviously more information concerning the composition of alkylmagnesium fluorides in ether solvents might be obtained from ¹⁹F resonance spectra. Our initial efforts in this area were not successful in locating ¹⁹F-¹H coupling or ¹⁹F splitting patterns, however we are continuing our efforts in this area.

The Schlenk equilibrium [eqn. (5)] is generally accepted as an adequate description of the basic composition of Grignard compounds in diethyl ether and tetrahydrofuran⁹⁻¹².



The existence of this equilibrium has been established by association²⁰, IR¹⁶ and NMR¹⁹ studies, in addition to dioxane precipitation and fractional crystallization studies. The interconversion among the species is suggested to proceed via a mixed alkyl-halogen bridge intermediate (II)²⁰. In triethylamine, redistribution of dialkylmagnesium compounds with magnesium halides takes place; however, fractional crystallization studies have shown that in the case of primary alkylmagnesium chlorides and bromides in triethylamine, RMgX and not MgX₂ species crystallize from solution. Thus, it is considered that the Schlenk equilibrium is inhibited simply by changing the nature of the solvent. Since the fluorine atom is a remarkably strong bridging agent in alkylmagnesium fluorides, it would be interesting to know whether or not the Schlenk equilibrium would also be affected by the nature of the bridging agent. Both fractional crystallization and dioxane precipitation studies on hexylmagnesium fluoride demonstrate that precipitation of C₆H₁₃MgF occurs instead of insoluble magnesium fluoride. Because of the insolubility and stronger Lewis acid character of magnesium fluoride, precipitation would be expected either on cooling or on addition of dioxane if a Schlenk equilibrium is operable. Furthermore the association, IR and R₂Mg/MgF₂ redistribution studies also argue against an equilibrium-type association.

Chemical properties

The chemical properties of alkylmagnesium fluorides have also been studied. These Grignard compounds give the same products as the corresponding alkylmagnesium bromides in their reactions with water, oxygen, CO₂, benzonitrile and benzophenone in comparable yields, except for the reaction with carbon dioxide. Since it has already been shown that the physical properties of alkylmagnesium fluorides are different from that of alkylmagnesium chlorides, bromides and iodides, it was speculated that some differences in the reactions of alkylmagnesium fluorides with organic substrates may be noted. Examination of Table 4 reveals that the nature of the halogen in the Grignard compound has a strong influence on the course of the reaction with benzophenone. It has been reported that the ratio of addition to reduction is proportional to the Grignard reagent/ketone ratio and independent of their concentration²¹.

TABLE 4

REACTION OF GRIGNARD COMPOUNDS WITH BENZOPHENONE IN TETRAHYDROFURAN

Grignard reagent	RMgX/ketone	Reaction (%)	Addition/Reduction
n-C ₆ H ₁₃ MgF	1.09	67	0.23
n-C ₆ H ₁₃ MgBr	1.66	61	0.09
C ₂ H ₅ MgF	1.26	91	0.28
C ₂ H ₅ MgBr	2.64	96	0.18

Although the ratio of Grignard reagent to ketone is lower for the alkylmagnesium fluorides than the alkylmagnesium bromides, the addition/reduction ratio is greater. The present result is compatible with previous reports that reactions of diisopropyl ketone with n-propylmagnesium halides in diethyl ether²² and benzaldehyde with ethyl- and sec-butylmagnesium halides in triethylamine¹³ give more addition and less reduction as the halide is changed from iodide to bromide to chloride. By comparison of reaction rates for hexylmagnesium compounds, it was found that the alkylmagnesium fluoride is more reactive than the alkylmagnesium bromide. This result is also consistent with the previous report that the rate of reaction between butylmagnesium compounds and acetone decreases from chloride to bromide to iodide²³. All results are consistent with the fact that the rate and the ratio of addition to reduction are not only a function of the nature of the halide but also a function of the positive character of the metal, *i.e.*, Li > Mg > Al.

ACKNOWLEDGEMENT

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