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THE PREPARATION OF ORGANOMAGNESIUM FLUORIDES BY ORGANOMETALLIC EXCHANGE REACTIONS

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Summary

The preparation of alkyl- and aryl-magnesium fluorides by the reaction of dialkyl- and diaryl-magnesium compounds with fluorinating agents, such as BF_3 etherate, SiF_4, Bu_3SnF, Ph_3SiF and Et_2AlF in tetrahydrofuran were studied. Methyl-, ethyl-, and phenyl-magnesium fluoride were prepared in high yield by the reactions of dimethyl-, diethyl-, and diphenyl-magnesium with boron trifluoride diethyl etherate in tetrahydrofuran. Methylmagnesium fluoride was prepared in quantitative yield by the reaction of dimethylmagnesium with silicon tetrafluoride in tetrahydrofuran and butylmagnesium fluoride was prepared in quantitative yield by the reaction of tributyltin fluoride in THF with dibutylmagnesium. Other combinations of R_2Mg compounds and fluorinating agents resulted in the formation of less pure products.

Introduction

For many years chemists have been interested in the preparation of organomagnesium fluorides, but all attempts to synthesize this class of Grignard reagents failed. In 1921 Swarts [1] reported the first attempt to prepare an organomagnesium fluoride by the reaction of amyl fluoride and iodine-activated magnesium in diethyl ether. Decane and magnesium fluoride were produced after one hundred hours of reflux. Schiemann and Pillarsky [2] reported in 1931 that phenylmagnesium fluorides could not be prepared by the reaction of magnesium with fluorobenzene or its *o*-methyl or *p*-nitro derivatives. During the same year Gilman and Heck reported [3] that a small quantity of biphenyl was formed when fluorobenzene and magnesium were allowed to react without solvent in a sealed tube at 300° for 200 hours. Gilman in 1930 reported the sealed tube reaction of fluorobenzene with an activated magnesium—copper alloy in diethyl ether at room temperature. After six months, no active organomagnesium compound was formed, but after 18 months the color test for an active reagent was positive [4]. Several pathways directed toward the preparation of benzylmagnesium fluoride were investigated by Bernstein and coworkers [5]. They found that benzyl fluoride and magnesium did not react in refluxing diethyl ether solvent and that the reaction was not activated by the addition of phenylmagnesium bromide or iodine crystals. The use of dibutyl ether and more vigorous reaction conditions resulted in polymerization of the benzyl fluoride. It was also observed that the reaction between benzyl fluoride and activated magnesium in an autoclave at 100° for ten days resulted in a coupling reaction producing bibenzyl. In 1969 Respess and Tamborski [6] reported a series of reactions which suggested the intermediacy of perfluoroarylmagnesium fluorides. These workers examined the reaction of perfluoraryl compounds with two molar equivalents of ethylmagnesium bromide in tetrahydrofuran with a catalytic amount of certain transition metal halides. They also allowed hexafluorobenzene in THF and in diethyl ether to react with magnesium and an equimolar quantity of ethylene bromide. The hydrolysis of the reaction product produced pentafluorobenzene which can be accounted for by assuming the intermediate formation of perfluorophenylmagnesium fluoride, but the formation of this intermediate product was not established.

Before the report by Respess and Tamborski, we had prepared several organomagnesium fluorides in high yield by the reaction of alkyl fluorides with magnesium in ether solvents employing certain catalysts [7—9]. Since this time we have investigated the scope of this reaction in more detail [8, 9] and have found some serious limitations. First, fluorobenzene does not react with magnesium under the conditions found successful for the preparation of primary alkyl fluoro Grignard compounds. Secondly, secondary and tertiary alkyl fluorides are very difficult to synthesize and there is serious question as to the extent of dehydrohalogenation that might be experienced under the more forcing conditions required to prepare the fluoro Grignard compounds. For this reason we have studied the preparation of fluoro Grignard compounds by the redistribution of dialkyl- and diaryl-magnesium compounds with metal and metalloid fluorides such as SiF_4, Et_2AlF, SnF_4, BF_3, Bu_3SnF and Ph_3SiF [10]. Since the more electronegative fluorine atoms would be expected to reside on the more electropositive metal, the reaction should proceed as shown in eqn. 1. Furthermore, this method should provide an alternative route to fluoro Grignard compounds and especially those compounds difficult to prepare by the direct route (e.g., secondary and tertiary alkyl- and aryl-fluoro Grignard compounds). An important feature of the new route (eqn. 1) is that the MR_4 by-

$$4R_2Mg + MF_4 \rightarrow 4RMgF + MR_4 \qquad (1)$$

product should be soluble in hydrocarbon solvent whereas the RMgF compound would not. Thus, separation of the fluoro Grignard compound could be achieved by running the reaction in an ether solvent, removing the solvent after reaction, extracting the MR_4 by-product with hydrocarbon, followed by redissolution of the RMgF compound in ether solvent.

Experimental

All operations were carried out either in a Kewaunee nitrogen-filled glove box equipped with a recirculating system to remove oxygen and moisture, or at the bench using typical Schlenk tube and syringe techniques [11]. All glassware was heated to dryness and flushed with nitrogen prior to use.

Analyses

Active alkyl groups were analyzed by hydrolyzing samples with aqueous HCl on a high vacuum line. The volume of evolved gas was determined by transferring the gas to a calibrated bulb via a Toepler pump. Active phenyl groups were determined by hydrolysis of the phenyl magnesium compound in hexane followed by GLC analysis of the resulting hydrocarbon solution. Further analysis of active C—Mg bonds was carried out by addition of a known amount of acid to the C—Mg compound followed by back titration with standard base using methyl red as an indicator. The same sample was then analyzed for total magnesium by a conventional EDTA complexometric titration at pH 10 with Eriochrome Black T indicator. Magnesium in the presence of aluminum was determined by EDTA titration (aluminum complexed by triethanolamine). In order to analyze solutions containing both aluminum and fluoride, the analyses were preceded by a Willard—Winter distillation in which fluoride was separated as fluorosilicic acid by steam distillation from perchloric acid [12]. The distillation was performed in the recommended distillation apparatus. Fluoride was analyzed by the precipitation of PbClF followed by a Volhard chloride determination or potentiometric titration [13].

Chemicals

Magnesium (Grignard grade turnings) was washed with ether and dried prior to use. Ethyl bromide, isopropyl chloride, butyl chloride, hexyl bromide and bromobenzene were washed with a sodium bicarbonate solution, dried over magnesium sulfate and distilled from 4-A molecular sieves through a packed column. Boron trifluoride diethyl etherate was distilled under vacuum. A lecture bottle of diethylaluminum fluoride in heptane (Texas Alkyls) was taken into the dry-box, emptied into a round-bottom flask and used without further purification. Silicon tetrafluoride (Matheson) was used without further purification. Tributyltin fluoride (Alfa Inorganics), triphenylfluorosilane (Peninsular Chem. Research) and tin tetrafluoride (Peninsular Chem. Research) were dried by subjecting to vacuum prior to use. Tetrahydrofuran, 1,4-dioxane and benzene were distilled from $NaAlH_4$. Hexane was stirred with concentrated sulfuric acid, washed with an aqueous solution of sodium bicarbonate followed by distilled water, dried over magnesium sulfate and then distilled from $NaAlH_4$ through a packed column. Dimethylmercury (Orgmet) was used without further purification. Diethyl ether was distilled from $LiAlH_4$.

Preparation of dialkyl and diarylmagnesium compounds

Dimethylmagnesium was prepared by the reaction of dimethylmercury with magnesium turnings at room temperature in the absence of solvent [14]. On completion of the reaction the dimethylmagnesium was extracted with THF and filtered. The active methyl to magnesium ratio was 2.02/1.00.

Except for dimethylmagnesium, the dialkylmagnesium compounds and diphenylmagnesium were prepared by the reaction of the corresponding alkyl or aryl halide with magnesium in ether followed by precipitation of the magnesium halide by addition of dioxane [15]. When the magnesium halide byproduct settled, the solution was filtered and then analyzed (active alkyl/magnesium/halide = 2/1/0). The dioxane was removed under vacuum at 80—100° overnight. The residual solid was redissolved in tetrahydrofuran and the solution restandardized.

The following examples are indicative of the procedures carried out for the reaction of R_2Mg compounds with metal and metalloid fluorides for the purpose of preparing alkyl and aryl fluoro Grignard compounds.

Reaction of dimethylmagnesium and boron trifluoride diethyl etherate

To 130.1 ml of 0.384 *M* dimethylmagnesium (49.96 mmoles) in tetrahydrofuran was added 108 ml of 0.149 *M* boron trifluoride diethyl etherate (16.10 mmoles) in tetrahydrofuran. The boron trifluoride was added slowly through a dropping funnel and a white solid precipitated from solution after the addition of approximately 60% of the boron trifluoride. The solution was stirred for 24 h and filtered. The ether solvent and trimethylborane byproduct were removed under vacuum and the resultant solid washed with hexane to ensure complete removal of the boron product. The solid was redissolved in tetrahydrofuran, and a boron flame test indicated the absence of boron. An absorption band at 530 cm^{-1} was observed in the IR spectrum, and a singlet at 11.71 τ in the NMR spectrum. Analysis of the solution indicated an active methyl/magnesium/fluoride ratio of 1.0/1.1/1.0; the yield was 80%.

Reaction of diphenylmagnesium and boron trifluoride diethyl etherate

To 58.5 ml of 0.500 *M* diphenylmagnesium (29.25 mmoles) in tetrahydrofuran was added 1.23 ml of neat boron trifluoride diethyl etherate (9.75 mmoles) Solid precipitated during the addition and was filtered from the solution. The infrared spectrum of the solution exhibited a C—Mg absorption at 300 cm^{-1}, and the NMR spectrum contained a complex aromatic multiplet with the absorption of highest intensity centered at 3.21 τ. The solution gave a negative boron flame test. Analysis of the solution gave an active phenyl/magnesium/fluoride ratio of 1.00/1.03/0.763, indicating 100% completion of reaction and a 74% yield of phenylmagnesium fluoride.

Reaction of dimethylmagnesium with silicon tetrafluoride

All reactions involving silicon tetrafluoride were carried out in a hood. An apparatus consisting of a calibrated buret filled with mercury and attached to mercury equalizing bulbs was used to measure the volume of silicon tetrafluoride to be added in the reaction. The apparatus was directly attached to a gas diffusion tube (fritted disc) allowing for a slow diffusion of gas into the dialkylmagnesium solution. The entire apparatus (except for the section containing mercury) was heated with a flame, then purged with nitrogen gas, and finally purged with silicon tetrafluoride prior to begiining the reaction. The three-neck round bottom flask containing the dialkylmagnesium solution was equipped with a three-way stopcock and dry-ice condensor. To 80 ml of 1.530 *M* dimethylmagnesium (122.3 mmoles) was added 768 ml of silicon tetrafluoride (30.6 mmoles). The NMR spectrum of the reaction solution showed the formation of tetramethylsilane and methylmagnesium fluoride. The silane by-product was removed by gently warming the solution. No solid formation occurred and analysis of the solution indicated an active methyl/magnesium ratio of 1.07/ 1.00, indicating a 100% completion of reaction and a 100% yield of methylmagnesium fluoride.

Reaction of dibutylmagnesium and tributyltin fluoride

Tributyltin fluoride (29.965 g, 97 mmoles) was added in the dry box to 77.3 ml of 1.255 *M* dibutylmagnesium (97 mmoles) in tetrahydrofuran. The solid tributyltin fluoride, which is insoluble in tetrahydrofuran, dissolved immediately and the reaction was stirred overnight at room temperature. No precipitate formed in the reaction and the infrared spectrum of the solution showed an absorption band at 520 cm^{-1} characteristic of a C—Mg bond, and two bands at 500 and 580 cm^{-1} characteristic of tetrabutyltin. The solvent was removed under vacuum resulting in a semi-solid and a colorless liquid which were washed with hexane repeatedly to remove the tetrabutyltin product. The semi-solid was then dried and redissolved in tetrahydrofuran. The infrared spectrum of the solution exhibited a band at 520 cm^{-1} characteristic of a C—Mg bond, and no absorptions characteristic of tetrabutyltin. Analysis of the solution indicated an active butyl/magnesium/fluoride ratio of 1.00/1.18/1.35. The yield of butylmagnesium fluoride was 55%.

Results and discussion

The reactions of dialkyl- and diaryl-magnesium compounds with readily available metal and metalloid fluorides were investigated in an attempt to develop a route to fluoro Grignard compounds. Tetrahydrofuran was chosen as the solvent for carrying out the exploratory reactions since preliminary work indicated that organomagnesium fluorides could be prepared and are stable in this solvent. Identification of the prepared organomagnesium fluorides involved elemental analyses (C—Mg/Mg/F = 1/1/1), observation of infrared absorption bands in the C—Mg stretching region [9, 16] and in some cases comparison of the NMR spectrum of the reaction product with the appropriate fluoro Grignard compound prepared by the direct synthetic method [8, 9].

Reaction of dialkyl- and diaryl-magnesium compounds with boron trifluoride diethyl etherate

In order to determine the usefulness of boron trifluoride etherate as a fluorinating agent, reactions between boron trifluoride etherate and dimethyl-, diethyl-, dihexyl- and diphenyl-magnesium were examined. The anticipated reaction course is described by eqn. 2. The priciple of the reaction is that the

$$3R_2Mg + BF_3 \xrightarrow{THF} 3RMgF + R_3B \qquad (2)$$

borane by-product is hydrocarbon-soluble and can be removed from the hydrocarbon-insoluble organomagnesium fluoride. Methyl-, ethyl- and phenyl-magnesium fluoride were successfully prepared by this route. Although hexylmagnesium fluoride has been prepared in diethyl ether and in tetrahydrofuran by the reaction of hexylfluoride and magnesium, borane-free hexylmagnesium fluoride was produced only in low yield by the reaction of dihexylmagnesium and BF_3 etherate.

During the addition of boron trifluoride etherate in tetrahydrofuran to dimethylmagnesium, a precipitate formed which was filtered from the solution. The precipitate appeared to be a complex of CH_3MgF and $(CH_3)_3B$, possibly $FMgB(CH_3)_4$ since the product contained a substantial amount of boron. The THF solvent was then removed at room temperature and under vacuum, a process which also removes the last traces of trimethylborane. Redissolving the resulting solid in THF produced a boron-free solution that exhibited an active methyl/magnesium/fluoride ratio of 1.0/1.1/1.0. The NMR spectrum of the solution exhibited a singlet at 11.71 τ (dimethylmagnesium in tetrahydrofuran exhibits a singlet at 11.76 τ). An infrared spectrum of the solution exhibited a band at 530 cm^{-1} which is characteristic of the C—Mg stretching frequency exhibited by alkyl Grignard compounds. The yield of methylmagnesium fluoride was 80%.

Ethylmagnesium fluoride was also prepared by the above method and in quantitative yield. No solid formation occurred during the reaction and the borane product was readily removed by hydrocarbon extraction. Elemental analysis indicated an active ethyl/magnesium/fluoride ratio of 1.11/1.00/1.24. The NMR spectrum showed a quartet at 10.65 τ and the infrared spectrum exhibited a C—Mg absorption band at 480 cm^{-1}.

The direct preparative route (fluorobenzene and magnesium) proved to be unsuccessful for the preparation of phenylmagnesium fluoride, but phenylmagnesium fluoride was prepared in 74% yield by the reaction of boron trifluoride etherate in tetrahydrofuran with diphenylmagnesium. A white solid formed during the reaction which was removed by filtration, resulting in a boron-free solution with an active phenyl/magnesium/fluoride ratio of 1.0/1.0/0.76. The NMR spectrum of the solution exhibited a complex, aromatic multiplet with the absorption of highest intensity being centered at 3.21 τ (3.02 τ for the signal of highest intensity for diphenylmagnesium). The course of this reaction is best described by eqns. 3 and 4.

$$3Ph_2Mg + BF_3 \rightarrow 3PhMgF + Ph_3B \qquad (3)$$
$$3PhMgF + Ph_3B \rightarrow Ph_4BMgF + 2PhMgF \qquad (4)$$

Reaction of dimethylmagnesium and diisopropylmagnesium with silicon tetrafluoride

Silicon tetrafluoride is a readily available and inexpensive fluorinating agent and is easily handled in a hood. Methylmagnesium fluoride was easily prepared by reacting dimethylmagnesium with SiF_4 in tetrahydrofuran (eqn. 5).

$$4Me_2Mg + SiF_4 \rightarrow 4MeMgF + Me_4Si \qquad (5)$$

The reaction has the inherent advantage of producing four moles of the fluoro Grignard to one mole of tetramethylsilane and thus the amount of by-product to be removed is small relative to the desired product. In addition $(CH_3)_4Si$ is low boiling (34°) and therefore easy to remove from the reaction mixture. The formation of tetramethylsilane was established by NMR analysis after it was removed from the reaction mixture by gentle heating. Methylmagnesium fluoride was produced in 100% yield by this method.

Silicon tetrafluoride was also added to a tetrahydrofuran solution of diisopropylmagnesium. A reaction stoichiometry of 3/1 was employed since it is difficult to replace the fourth fluorine atom in silicon tetrafluoride with a secondary alkyl group (eqn. 6). The uptake of the gas occurred very readily by the diisopropylmagnesium solution. The clear solution was worked up by the

$$3\,\text{i-Pr}_2\text{Mg} + \text{SiF}_4 \rightarrow 3\,\text{i-PrMgF} + \text{i-Pr}_3\text{SiF} \qquad (6)$$

removal of solvent at room temperature followed by the washing of the reaction mixture with hydrocarbon. After this procedure the residual product redissolved in tetrahydrofuran; however, on standing a precipitate appeared rapidly. Analysis of the solution indicated an active isopropyl/magnesium ratio of 1.45/1.00. Only 30% of the theoretical amount of magnesium remained in solution. The reaction was repeated using the same stoichiometry and after the workup, the reaction mixture only partially redissolved. The active isopropyl/magnesium ratio of the solution was 1.39/1.00. This time only 24% of the theoretical amount of magnesium remained in solution. These reactions indicate that either isopropylmagnesium fluoride disproportionates or that incomplete alkyl—fluorine exchange is taking place. However it was found in another experiment that the addition of SiF_4 beyond the stoichiometry of 3/1 resulted in a greater loss of active alkyl groups in solution indicating that the results are not due to incomplete reaction.

Reaction of dibutylmagnesium and diphenylmagnesium with tributyltin fluoride

Tributyltin fluoride was allowed to react with dibutyl- and diphenyl-magnesium according to eqn. 7. The fluorine atom was shown to be the only readily

$$\text{R}_2\text{Mg} + \text{n-Bu}_3\text{SnF} \rightarrow \text{RMgF} + \text{n-Bu}_3\text{SnR} \qquad (7)$$

exchangeable group in tributyltin fluoride, therefore allowing the compound to act only as a fluorinating agent. Butylmagnesium fluoride was readily formed by this method and phenylmagnesium fluoride formed in 50% yield.

Tributyltin fluoride which is insoluble in tetrahydrofuran dissolved immediately in the presence of dibutylmagnesium. The infrared spectrum showed a strong absorption band at 570 cm^{-1} characteristic of the C—Mg bond and two strong absorption bands at 500 and 586 cm^{-1} characteristic of tetrabutyltin. Solvent removal under vacuum resulted in the isolation of a semi-solid and colorless liquid. The mixture was extracted with hexane and redissolved in tetrahydrofuran. The infrared spectrum of the resulting solution did not exhibit absorption bands characteristic of tetrabutyltin; however, weak absorption bands characteristic of butylmagnesium fluoride were observed. The theoretical yield of butylmagnesium fluoride was 55% as determined in tetrahydrofuran solution indicating that butylmagnesium fluoride THF etherate must have some solubility in hexane. Analysis of the solution showed an active butyl/magnesium/fluoride ratio of 1/1.18/1.35. Distillation of a separate reaction mixture at 1—2 mm was attempted in order to remove the tin product without loss of the n-butylmagnesium fluoride. Tetrabutyltin distilled quantitatively at 101.5—108° (IR of distillate identical to IR of tetrabutyltin) but the Grignard solution would not redissolve in tetrahydrofuran.

Tributyltin fluoride did not compeltely dissolve in the presence of diphenylmagnesium even after refluxing in tetrahydrofuran for four days. Elemental analysis indicated that the reaction proceeded to 50% completion and that the active phenyl/magnesium/fluoride ratio was 1.52/1.00/0.79.

Reactions of dibutylmagnesium and diphenylmagnesium with triphenylsilicon fluoride

Dibutylmagnesium and triphenylsilicon fluoride were allowed to react in 1/1 ratio. Analysis after 24 h indicated little reaction. The solution was then refluxed for three days after which time analysis indicated 60% reaction (active butyl/magnesium/fluoride = 1.3/1/0.78).

Triphenylsilicon fluoride was added to diphenylmagnesium, and a solid precipitated after stirring overnight. Analysis of the solution indicated that the reaction proceeded to 50% completion (active phenyl/magnesium = 1.5/1). The solution was then refluxed for 24 h, and the white solid redissolved on heating and reprecipitated from solution on cooling. All magnesium was in solution and analysis indicated a 100% yield of phenylmagnesium fluoride (active phenyl/magnesium/fluoride = 1.14/1.00/1.06). After filtration of the white solid from the reaction mixture, the resulting solution was found to contain 40% of the tetraphenylsilane by-product. The solution was stripped of solvent resulting in the isolation of a solid product. On stirring, almost all of the solid dissolved in benzene, preventing the separation of the tetraphenylsilane from the fluoro Grignard. A fractional crystallization was then attempted to remove the silicon product since tetraphenylsilane should be less soluble than phenylmagnesium fluoride in tetrahydrofuran. After three fractions had been removed from solution, the infrared spectrum of the resulting filtrate showed an increase in intensity of the 400 cm^{-1} band of phenylmagnesium fluoride relative to the 510 cm^{-1} band of tetraphenylsilane. The infrared spectrum and the elemental analyses indicated that both products were co-precipitating. Phenylmagnesium fluoride appears to crystallize from solution later than tetraphenylsilane, but with each crystallization too much of the Grignard product is lost to make the method attractive. The infrared spectrum of the purest product indicated the presence of 18% tetraphenylsilane.

Reaction of tin tetrafluoride and diphenylmagnesium

Tin tetrafluoride was not found to be a very effective fluorinating agent. After 24 h tin tetrafluoride and diphenylmagnesium showed no reaction in tetrahydrofuran (active phenyl/magnesium = 1.96/1). In addition tin tetrafluoride showed only partial solubility in the reaction solution. Reflux of the reaction mixture for four days resulted in only 24% yield of phenylmagnesium fluoride (active phenyl/magnesium = 1.76/1).

Reaction of diethylmagnesium with diethylaluminum fluoride

Diethylmagnesium and diethylaluminum fluoride (50% in heptane) were allowed to react in tetrahydrofuran, benzene and hexane. Diethylmagnesium is soluble in tetrahydrofuran, but insoluble in benzene and hexane; diethylaluminum fluoride is soluble in all three solvents. The reaction in tetrahydrofuran resulted in solid formation. Both the solution and solid contained aluminum and no aluminum-free ethylmagnesium fluoride could be isolated. The reactions in hydrocarbon were pursued in the hope that the fluoro Grignard compound would precipitate and the aluminum product would stay in solution. Again, sizeable quantities of aluminum were found in both the solid product and in solution. This result could possibly be due to the formation of a complex between triethylaluminum and ethylmagnesium fluoride which would be difficult to separate from the fluoro Grignard product.

$$Et_2Mg + Et_2AlF \rightarrow EtMgF + Et_3Al \quad (8)$$

$$EtMgF + Et_3Al \rightarrow FMgAlEt_4 \text{ or } EtMgAlEt_3F \quad (9)$$

Conclusion

It appears from these studies that dialkyl- and diaryl-magnesium compounds redistribute with metal and metalloid fluorides to form alkyl- or aryl-magnesium fluorides. In some cases the redistribution is very rapid (e.g., BF_3, SiF_4 and Et_2AlF) and in some cases it is very slow (e.g., Bu_3SnF, Ph_3SiF, SnF_4). Some fluorinating agents appear to be far superior to others, for example, BF_3 and SiF_4 were found to react rapidly with Me_2Mg to form MeMgF in quantitative yield whereas with fluorinating agents such as SnF_4 and Bu_3SnF, reaction was very slow, producing RMgF in the presence of R_2Mg. There were also some cases (Ph_3SiF and Et_2AlF) where although reaction took place readily to produce a high yield of fluoro Grignard compound, the by-products (Ph_4Si and $FMgAlEt_3F$) could not be removed from the desired product. In some cases the C—Mg/Mg/F was not 1/1/1 but somewhat higher or lower in fluorine content than expected. These solutions are presumably mixtures of RMgF and R_2Mg or MgF_2.

These studies show that methyl-, ethyl- and phenyl-magnesium fluoride, which are either difficult or impossible to prepare by the reaction of the alkyl or aryl halide with magnesium, are prepared pure and in high yield by the reaction of the appropriate R_2Mg compound with BF_3 etherate in THF. Methylmagnesium fluoride was also prepared pure and in quantitative yield by the reaction of Me_2Mg with SiF_4 in tetrahydrofuran.

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