$NHBD_3$, NH:ND = 13.3, BH:BD = 0.053; for $(CH_3)_2NDBD_3$, NH:ND = 0.150, BH:BD = 0.053; for $(CH_3)_2NDBH_3$, NH:ND = 0.282, BH:BD = 31.2. Samples prepared from $(CH_3)_2ND$ and B_2H_6 always showed a small amount of B–D bonds, indicating that exchange of isotopes had occurred in the preparation. Once isolated, the amine–boranes were stable to further self-exchange. However, small changes in isotopic composition could be detected when the samples were sublimed.

Isotopic analysis of the molecular hydrogen species was carried out on a Bendix Time-of-Flight mass spectrometer. Sensitivity coefficients for H_2, D_2, and HD were determined on known mixtures and over the pressure range to be used for unknown mixtures. The data for H_2 were corrected, when necessary, for the presence of D^+.

Experiments to Test Exchange Reactions.—(a) Approximately equal amounts of hydrogen and deuterium were heated for 24 hr with mercury in a sealed glass tube. The mass spectrum of the gas showed no evidence of a peak at *m/e* 3, characteristic of HD.

(b) Trimethylamine–borane or dimethylamine–borane was heated at 100° in sealed tubes containing 150 mm of D_2. After 1 hr no HD was found in the gas, nor was there any evidence for B–D bonds in the spectrum of the recovered boranes (1800 cm^{-1}). After 24 hr the trimethylamine–borane sample showed a small amount of B–D, estimated to be less than 5%. The dimethylamine–borane sample apparently produced, in addition to dimethylaminoborane, dimethylaminodiborane, whose absorption spectrum masked the 1800-cm^{-1} region. The B–D deformation around 900 cm^{-1}, however, was exceedingly weak.

(c) Dimethylamine–borane containing 78% N–D bonds and about 97% B–H bonds was heated as above. The remaining material after about 30% reaction contained 85% N–D bonds and more than 92% B–H bonds.

(d) Dimethylamine–borane-d_3 (mol wt 62) and N-deuteriodimethylamine–borane (mol wt 60) in approximately equal proportions were sublimed into a glass tube, and the sealed tube was heated as above. The solid remaining in the reaction was analyzed in the mass spectrometer. No peak at *m/e* 63 was found and the peaks at *m/e* 62 and 61 were at nearly the same intensity as for dimethylamine–borane-d_3. The mass spectrum of $(CH_3)_2NDBD_3$, independently obtained, showed low-intensity but easily detectable peaks at *m/e* 63 and 62 and a very intense peak at *m/e* 61, corresponding to loss of D^+.

Pyrolyses.—Samples of the desired amine–boranes were sublimed *in vacuo* into previously baked-out Pyrex tubes of about 50-ml capacity from tared storage containers. When mixtures were used, the quantities were very closely equimolar, approximately 1 mmol of each component. When small extents of reaction were desired, the sample was heated for 1 hr at 100–102° and quenched. The hydrogen produced was removed with a Toepler pump and measured and then subjected to mass spectroscopic analysis. After longer reaction times, the condensable materials revealed the presence of dimethylaminoborane and dimethylaminodiborane.

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Concerning the Existence of HMgX Compounds

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The preparation of "HMgX" compounds (where X = Cl, Br, and I) by hydrogenolysis and pyrolysis of Grignard compounds in diethyl ether has been previously reported. The authenticity of the "HMgX" product as distinguished from a physical mixture of MgH_2 and MgX_2 was shown by dta–tga analysis, but mainly by X-ray powder pattern data on the basis that the powder patterns for the "HMgX" compounds were different from those of MgH_2 and MgX_2. A repetition of the prior art plus additional work indicates that both hydrogenolysis and pyrolysis of Grignard compounds does *not* produce HMgX compounds, but a physical mixture of MgH_2 and MgX_2. The reason for the discrepancy was the comparison by prior workers of X-ray powder patterns for "HMgX" compounds containing 0.2–0.3 mol of ether of solvation with ether-free MgH_2 and MgX_2 containing 1.0 mol of ether. When comparison of X-ray powder pattern data was made for the "HMgX" compounds and MgH_2 and MgX_2 containing the same amount of ether of solvation, the "HMgX" compounds were found to exhibit the same X-ray powder lines as those found for a physical mixture of MgH_2 and MgX_2.

Introduction

The hydridomagnesium halides ("HMgX"[2] compounds) represent a novel new class of compounds which presumably can function as a selective reducing agent toward organic substrates[3] and as a starting material toward novel complex magnesium hydrides. The first comprehensive report of the preparation of "HMgX" compounds was made by Wiberg and Strebel[4] in 1957. These workers reported the preparation of crystalline soluble compounds of empirical formula $HMgX \cdot 2O(C_2H_5)_2$, where X = Cl, Br, and I, by the reaction of ethyl Grignard reagents and diborane

$$6C_2H_5MgBr + B_2H_6 \longrightarrow 6HMgBr + 2(C_2H_5)_3B \qquad (1)$$

Later we reported[5] that it was not possible to isolate these compounds under the exact conditions described earlier[4] or under a variety of other conditions that might be favorable for forming such compounds. Instead, only chloromagnesium borohydride could be ob-

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(1) To whom all inquiries should be sent.

(2) "HMgX" in quotes will be used to represent the product formed from pyrolysis or hydrogenolysis of Grignard compounds which according to this report is actually a mixture of MgH_2 and MgX_2.

(3) R. A. Firestone, *Tetrahedron Letters*, **27**, 2629 (1967).

(4) E. Wiberg and P. Strebel, *Ann.*, **607**, 9 (1957).

(5) W. E. Becker and E. C. Ashby, *Inorg. Chem.*, **4**, 1816 (1965).

tained, regardless of the stoichiometry of the reaction or the mode of reagent addition. The reaction proceeded according to

$$3C_2H_5MgCl + 2B_2H_6 \longrightarrow 3ClMgBH_4 + (C_2H_5)_3B \qquad (2)$$

Sometime later, Dymova and Eliseeva[6] reported a second route to "HMgX" compounds. This method involved the hydrogenolysis of ethylmagnesium halides (X = Cl, Br, I; R = H)

$$RCH_2CH_2MgX + H_2 \xrightarrow{\Delta} RCH_2CH_3 + HMgX \qquad (3)$$

They found that all of the "HMgX" compounds were insoluble in the usual organic solvents and the products contained a nonstoichiometric amount of ether contrary to the results reported earlier by Wiberg and Strebel. They proposed a polymeric structure for the "HMgX" compounds. Heating and cooling curves as well as gas evolution polytherms for these compounds were reported and discussed. The "HMgX" compounds showed a strong irreversible and endothermic effect at ~125° accompanied by evolution of gas. This transition was assigned to an intramolecular disproportionation of "HMgX" to MgH_2 and MgX_2 accompanied by a loss of ether. All subsequent effects in the thermometric analysis at temperatures higher than 125° were consistent with transitions occurring in either MgH_2 or MgX_2 produced in the thermal disproportionation reaction. Thus the conclusion was that "HMgX" compounds are formed by the hydrogenolysis of Grignard compounds; however, disproportionation to MgH_2 and MgX_2 occurs at 125°.

At about the same time as the Dymova report, we reported[7] that hydrogenolysis of ether solutions of various Grignard reagents led to the formation of MgH_2 and MgX_2 readily and cleanly. The apparent inconsistency between these two latter reports is resolved when it is realized that we washed all products in the work-up procedure with tetrahydrofuran (eq 4)

$$2HMgX \xrightarrow{THF} MgH_2 + MgX_2 \qquad (4)$$

in an attempt to remove the tetrahydrofuran-soluble MgX_2 compounds, while the Russian workers claim that "HMgX" compounds disproportionate in tetrahydrofuran. One discrepancy that was not resolved however is the fact that in the cases of hydrogenolysis of RMgBr and RMgI compounds we found that MgH_2 and MgX_2 were indeed formed before tetrahydrofuran washing of the solid since nearly all of the $MgBr_2$ and MgI_2 were found in the diethyl ether solution immediately after hydrogenolysis and prior to washing of the solid with tetrahydrofuran. On the other hand, Russian workers claimed that $MgBr_2$ and MgI_2 were not found in solution but in the solid phase of the reaction mixture. Since $MgCl_2$ is insoluble in diethyl ether we could not, at the time, say that insoluble HMgCl was not initially formed by hydrogenolysis of the RMgCl compound followed by disproportionation of the HMgCl on washing with tetrahydrofuran.[8]

A third route reported to produce "HMgX" compounds involves the pyrolysis of Grignard compounds at ~200°. Rice, *et al.*,[9] reported the preparation of nonsolvated HMgBr by pyrolysis of ethylmagnesium bromide. The analysis of the product appeared to be unusually good (H:Mg:Br = 1.00:1.00:1.00). These workers cited X-ray powder pattern data (Table V) which were reportedly different from those of MgH_2 and $MgBr_2$. Therefore, it was concluded that HMgBr could not be an equimolar mixture of MgH_2 and $MgBr_2$. Prior to the report by Rice, other workers reported that "HMgX" compounds actually exist as equimolar mixtures of hydride and halide.[10,11] These workers based their conclusion primarily on the rapid rate at which magnesium halide is extracted when these products are stirred with THF or ether. However, since Rice, *et al.*, reported that extraction of "HMgBr" with dry ether led to *disproportionation* to MgH_2 and $MgBr_2$ followed by *extraction* of the magnesium bromide, the earlier reports were discounted.

The controversial points are as follows. Do "HMgX" compounds exist as discrete species differing from equimolar mixtures of magnesium hydride and the corresponding magnesium halide? Does treatment of an "HMgX" compound with tetrahydrofuran or diethyl ether result in simple extraction of magnesium halide from the mixture or is magnesium halide extraction preceded by disproportionation of the "HMgX" to halide and hydride? Furthermore, if HMgX compounds do exist, are they soluble crystalline compounds containing 2 equiv of ether $[HMgX \cdot 2O(C_2H_5)_2]$ as reported by Wiberg or are these compounds insoluble polymeric solids carrying nonstoichiometric amounts of solvent as reported by Dymova? Also, are HMgX compounds subject to thermally induced disproportionation at ~125° as suggested by Dymova or are these species stable when heated to ~200° as suggested by Rice?

Experimental Section

Equipment and Materials.—Manipulation of air-sensitive materials was accomplished by use of standard bench-top techniques and dry nitrogen purge or in a drybox equipped with an atmosphere-purification system for removal of oxygen and moisture.[12] X-Ray powder diffraction data were obtained using a Philips Norelco X-ray unit, using an 11.46-cm diameter camera with Ni-filtered Kα radiation. Exposure times were 6.0 hr for all samples. *d* spacings were evaluated using a precalibrated scale equipped with viewing apparatus. Line intensities were

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(6) T. N. Dymova and N. G. Eliseeva, *Russ. J. Inorg. Chem.*, **8**, 820 (1963).

(7) W. E. Becker and E. C. Ashby, *J. Org. Chem.*, **29**, 954 (1964).

(8) It is, of course, quite possible that disproportionation (or lack of it) could occur depending on the purity of the magnesium used to prepare the Grignard compound. In the present studies triple-sublimed magnesium was used which resulted in the formation of clear and colorless Grignard solutions. Ethylmagnesium bromide prepared from Grignard grade turnings was used. The nature and exact purity of the magnesium used by the Russian workers is not known and therefore could conceivably account for the different observations.

(9) M. J. Rice, Jr., and P. J. Andrellos, Technical Report to the Office of Naval Research, Contract ORN-494 (04), 1956.

(10) E. Wiberg and R. Bauer, *Chem. Ber.*, **85**, 593 (1952).

(11) P. Jolibois, *Compt. Rend.*, **155**, 353 (1912).

(12) T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, **33**, 491 (1962).

TABLE I

HYDROGENOLYSIS OF GRIGNARD REAGENTS

	Experimental conditions					Product analysis, atomic ratio				Halogen recovery from filtrate,
Expt no	RMgX	Concn, M	Pressure, psig	Reaction time, hr	Temp, °C	H	Mg	X	Ether	%
1	C_2H_5MgCl	1.0	1400–2000	4	125	0.83	1.00	1.03	0.26	7
2[a]	C_2H_5MgBr	1.7	2100–2800	3.5	150	0.73	1.00	1.01	0.45	
3	C_2H_5MgBr	1.0	1900–2200	4	150	1.90	1.00	0.07	0.03	
4	C_2H_5MgBr	1.0	1800–2000	4	150	1.88	1.00	0.05	0.02	
5	C_2H_5MgBr	0.5	1600–2000	4	150	1.94	1.00	0.06	0.00	
6	C_2H_5MgBr	1.0	1550–1750	5	125	1.78	1.00	0.10	0.03	
7	C_2H_5MgBr	1.0	2000	16	125	2.02	1.00	0.05	0.07	
8	C_2H_5MgBr	1.0	4000–4500	4	100–125	1.90	1.00	0.07	0.07	
9	C_2H_5MgBr	3.9	1500–3000	5	100	1.62	1.00	0.30	0.15	
10	C_2H_5MgI	1.0	2250	4	125	1.74	1.00	0.13	0.16	88
11	C_2H_5MgI	1.0	2000–2100	4	100	1.30	1.00	0.10	0.22	93
12	i-C_3H_7MgCl	2.0	3600–4700	12	75	0.86	1.00	1.04	0.29	
13	i-C_3H_7MgCl	2.0	2900–3400	12	75	0.84	1.00	1.07	0.36	4
14	i-C_3H_7MgCl	2.0	1900	4	75	0.77	1.00	1.09	0.97	
15	i-C_3H_7MgCl	2.0	1900–2000	4	75	0.72	1.00	1.19	0.68	
16	i-C_3H_7MgBr	2.0	2000	3.5	75	1.89	1.00	0.14	0.12	
17	i-C_3H_7MgBr	2.0	3400–3900	17.5	75	1.88	1.00	0.07	0.03	94
18	i-C_3H_7MgI	1.0	4500–4700	12	75	1.71	1.00	0.11	0.10	98
19	t-C_4H_9MgCl	0.5	3500	5	150	0.96	1.00	1.02	0.05	

[a] Almost all of the ether was gone. No X-ray powder pattern was obtained.

estimated visually. Nuclear magnetic resonance spectra were obtained using a Varian Associates Model A-60 spectrometer (benzene internal standard). Fisher Certified reagent grade ethyl bromide, ethyl iodide, isopropyl chloride, isopropyl bromide, isopropyl iodide, and isobutyl iodide were distilled over P_2O_5 prior to use. Ethyl chloride was distilled over molecular sieve 4A before use. Mallinckrodt anhydrous ether was further purified by distillation over $LiAlH_4$. All Grignard compounds were prepared using Dow triply sublimed magnesium.[13]

Preparation of Grignard Reagents.—Grignard reagents were prepared as described previously.[5] All Grignard reagents were filtered in a dry nitrogen box producing clear, colorless solutions. Magnesium was determined by Versene titration and halogens were determined by the Volhard method. In all cases the magnesium and halogen analyses indicated a magnesium to halogen ratio of 1.0:1.0 to within 2% with the exceptions of i-C_3H_7MgBr, i-C_3H_7MgI, and i-C_4H_7MgI which contained 2–5% excess magnesium halide (Table VII). t-Butylmagnesium chloride–ether which is dimeric in benzene solution[14] was prepared from a solution of t-butylmagnesium chloride in ether into which excess dry benzene had been distilled. Codistillation of the ether left the desired compound in solution. The Mg to Cl ratio was 1:1. The proton magnetic resonance spectrum of this benzene solution revealed three signals at 226 (quartet), 345 (singlet), and 373 (triplet) Hz above the benzene signal of area ratio 3.9, 8.5, and 6.3, respectively. These signals are assigned to ether methylene, t-butyl, and ethyl methyl, respectively.

$C_2H_5MgBr\cdot 2O(C_2H_5)_2$ was isolated by the method reported earlier.[15] Confirmation of this species was obtained from the proton magnetic resonance spectrum which showed ether methylene quartet, ether methyl triplet, $Mg\mathit{CH_2}CH_3$ quartet, and $MgCH_2\mathit{CH_3}$ triplet signals at 230, 370, 481, and 375 Hz above the benzene internal reference. The relative area ratio of the ether methylene and $Mg\mathit{CH_2}CH_3$ signals was 3.98:1.00.

Hydrogenolysis Procedure.—Two different reaction conditions were used based on the previous reports[6,7] (Table I). In one,[7] a 75- or 150-ml aliquot of a 1 M ether solution of ethyl Grignard reagent was charged into a 300-ml Magne-Dash autoclave. The mixture was heated to 100, 125, and 150° for 4–5 hr under 1600–2400 psi of hydrogen. In another procedure,[6] a 50-, 75-, or 150-ml aliquot of a 2 M ether solution of isopropyl Grignard reagent was heated to 75° for 12 hr under 1900–4700 psi of hydrogen. After the reaction mixture had been cooled and vented, it was filtered in the drybox. Both the precipitate, after drying under vacuum at 40° for 2 hr, and the filtrate were analyzed for magnesium and halogen as mentioned above. Analysis for hydridic hydrogen, where applicable, was accomplished by measuring the gas evolved upon hydrolysis of a weighed sample. The presence of ether was confirmed by hydrolyzing a weighed sample in excess benzene diluent using a minimum amount of 10 vol % H_2SO_4. The ether released into the benzene was then analyzed by gas–liquid partition chromatography. Typical hydrogenolysis experiments are as follows.

Ethylmagnesium Chloride.—Ethylmagnesium chloride (0.075 mol in 75 ml of ether) was charged into a 300-ml Magne-Dash autoclave. The mixture was heated at 125° for 4 hr under 1400–2000 psi of hydrogen. After the reaction mixture had been cooled and vented, it was filtered in a drybox. The white voluminous precipitate was dried under vacuum at 45° for 2 hr and analyzed. The H:Mg:Cl:ether ratio of 0.83:1.00:1.03:0.26 shows that this product has the empirical formula $HMgCl[O(C_2H_5)_2]_x$. The filtrate was found to contain some (7%) unreacted ethylmagnesium chloride.

Ethylmagnesium Bromide.—Ethylmagnesium bromide (0.150 mol in 150 ml of ether) was heated at 150° for 4 hr under 1800–2200 psi of hydrogen. The white compact solid contained H, Mg, Br, and ether in the ratio of 1.88:1.00:0.05:0.02. The filtrate showed two layers. Analysis of the lower layer showed an Mg:Br ratio of 1.00:1.64.

Isopropylmagnesium Chloride.—Isopropylmagnesium chloride (0.3 mol in 150 ml of ether) was heated at 75° for 12 hr under 2900–3400 psi of hydrogen. Twenty grams (77%) of the white voluminous precipitate contained an H:Mg:Cl:ether ratio of 0.84:1.00:1.07:0.36. Its X-ray powder pattern is almost exactly the same as that of the hydrogenolysis product of ethylmagnesium chloride. The filtrate contained unreacted (4%) isopropylmagnesium chloride.

Isopropylmagnesium Bromide.—Isopropylmagnesium bromide (0.3 mol in 150 ml of ether) was heated at 75° for 17.5 hr under

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[13] Ethylmagnesium bromide prepared from Grignard grade magnesium turnings was subjected to hydrogenation in one attempt to prepare an authentic HMgBr compound with results analogous in every respect to those reported for hydrogenation of ethylmagnesium bromide prepared from triple-sublimed magnesium. Conclusions reached in this paper are thus valid for Grignard compounds prepared from these two grades of magnesium.

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

[15] L. J. Guggenberger and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 5344 (1964).

TABLE II

PYROLYSIS OF GRIGNARD REAGENTS

	Experimental conditions				Atomic molar ratio			
Expt no.	RMgX	Temp, °C	Reaction time, hr	Pressure, mm	H	Mg	X	Ether[a]
1	$C_2H_5MgBr \cdot 2(O(C_2H_5)_2)_2$	200	2	1	0.88	1.00	1.06	0.08
2	C_2H_5MgBr	195	22	3	0.56	1.00	0.99	0.26
3		195	18	1	0.51	1.00	0.99	0.31
4		195	6	3	0.39	1.00	1.00	0.34
5		150	5	3	0.53	1.00	0.98	0.44
6	i-C_3H_7MgCl	140	4	3	0.74	1.00	1.02	0.15
7		140	2.5	4	0.74	1.00	1.08	0.05
8		140	1	2	0.71	1.00	1.12	0.01
9		140	0.5	4	0.67	1.00	1.05	0.12
10		130	17	3	0.69	1.00	0.95	0.01
11		130	10	5	0.54	1.00	1.20	0.13
12		130	6	3	0.83	1.00	1.07	0.03
13		130	6	5	0.79	1.00	1.04	0.04
14		130	4	3	0.80	1.00	1.03	0.08
15		130	2	2	0.61	1.00	1.09	0.31
16		130	1	4	0.51	1.00	1.05	0.33
17		110	72	3	0.84	1.00	1.05	0.33
18		110	16	5	0.78	1.00	1.04	0.13
19		110	5	5	0.73	1.00	0.99	0.17
20	i-C_3H_7MgBr	160	5.5	1	0.83	1.00	1.07	0.04
21		140	6	1	0.81	1.00	1.09	0.09
22		130	6	3	0.72	1.00	1.08	0.21
23		120	6	1	0.56	1.00	1.07	0.34
24		110	24	3	0.65	1.00	1.07	0.26
25	i-C_4H_9MgI	150–160	$1^1/_3$	0.5	0.49	1.00	1.12	
26		150–160	$2^1/_3$	0.5	0.56	1.00	1.20	
27		160–170	1	1	0.75	1.00	1.08	0.162
28		170	1	1	0.78	1.00	1.06	0.802
29		170	2	1	0.74	1.00	1.06	
30		180	1	1	0.76	1.00	1.05	0.245
31		205	1	1	0.70	1.00	1.06	1.34

[a] Ether by difference.

3400–3800 psi of hydrogen. The white compact precipitate contained an H:Mg:Br:ether ratio of 1.88:1.00:0.07:0.03. The filtrate contained 0.19 g-atom of Mg and 0.28 g-atom of Br.

Dimeric *t*-Butylmagnesium Chloride–Ether in Benzene.—*t*-Butylmagnesium chloride:ether (0.075 mol in 150 ml of benzene) was heated at 150° for 5 hr under 3500 psi of hydrogen. The gray-white precipitate which formed contained an H:Mg:Cl:ether ratio of 0.96:1.0:1.02:0.05.

Pyrolysis Procedure.—A number of experiments were carried out in order to determine the best combination of reaction temperature and time needed to produce a pure HMgX product. Typical results are shown in Table II. A typical procedure for pyrolysis of Grignard reagents follows.

Grignard reagents in ether were charged into a 200-ml round-bottom flask containing a large "egg shape" stirring bar. The ether was removed under vacuum at 50°. The Grignard solution gradually became viscous during the ether solvent removal process until finally the stirrer could not move. At this stage, the stirrer was made to move by occasional shaking of the flask while the temperature was increased to the reaction temperature. Pyrolytic reactions of ethyl- and isopropylmagnesium bromide and isopropylmagnesium chloride were carried out in this way.

In another procedure, the ether was removed under vacuum at 50° until the stirring bar stopped moving. Nujol was added and the mixture was heated to 90° for a prolonged time (120 hr) to ensure complete removal of solvated ether. The temperature was raised gradually to the point where pyrolysis was carried out over a period of 1 hr. Isobutylmagnesium iodide was pyrolyzed in this way. A white product instead of a gray one was obtained.

Extraction Experiments.—A 2.684-g sample of solid produced by the hydrogenolysis of C_2H_5MgCl in diethyl ether (H:Mg:Cl:ether = 0.84:1.00:1.07:0.36) was stirred in 50 ml of dry THF for 3 min. The mixture was filtered quickly and 0.42 g of a white solid was obtained. The solid product and the filtrate were analyzed. The solid contained an H:Mg:Cl ratio of 1.77:1.00:0.10 and its X-ray powder pattern showed lines for only MgH_2. The filtrate contained 99 and 62% of the original amount of Cl and Mg, respectively. Experiments using "HMgCl," "HMgBr," and "HMgI" prepared from pyrolysis reactions gave similar results which are shown in Table III.

Synthesis and Stepwise Desolvation of $MgCl_2$, $MgBr_2$, and MgI_2.—$MgCl_2 \cdot O(C_2H_5)_2$ was prepared from the reaction of isopropylmagnesium chloride and HCl in diethyl ether. Dropwise addition of a stoichiometric quantity of HCl to the stirred Grignard solution under nitrogen purge resulted in precipitation of the halide containing an Mg:Cl:ether ratio of 1.00:1.98:1.02. Stepwise desolvation was accomplished by heating this material under vacuum for different periods of time and at different temperatures. Heating for 1 hr at room temperature produced a material with a Mg to ether ratio of 1.00:0.77. This ratio was found to be 1.00:0.5, 1.00:0.28, 1.00:0.09, and 1.00:0.01 when this material was heated for 1-hr periods at 50, 75, 100, and 125°, respectively. The ratio of magnesium to chlorine was found to be 1:1.98 in the completely desolvated material. Magnesium bromide–ether and magnesium iodide–2-ether were prepared by the reaction of the appropriate mercuric halide with triply sublimed magnesium metal in ether solution.[16] Magnesium to halide ratios were found to be 1:1.98 and 1:1.97, respectively. Stepwise desolvation was accomplished as above for magnesium chloride.

Preparation of MgH_2. A. Reaction of $LiAlH_4$ with Diethyl-

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[16] E. C. Ashby and R. C. Arnott, *J. Organometal. Chem.* (Amsterdam), **14**, 1 (1968).

TABLE III

RESULTS OF EXTRACTION OF "HMgX" PRODUCTS

Compound	Solvent	Atomic ratio of original compound			Analysis of residue, atomic ratio			Analysis of soln, %	
		H	Mg	X	H	Mg	X	Mg	X
Hydrogenolysis HMgCl[a]	THF	0.84	1.00	1.07	1.77	1.00	0.10	62	99
Pyrolysis HMgCl[a]	THF	0.79	1.00	1.09	1.02	1.00	0.73	49	60
Pyrolysis HMgBr[a]	Ether	0.83	1.00	1.07	1.68	1.00	0.13	43	78
Pyrolysis HMgI	Ether	0.73	1.00	1.09	1.43	1.00	0.07		

[a] X-Ray powder pattern of residues of these cases show lines only for MgH_2.

magnesium.[17]—Diethylmagnesium (0.1 mol) in diethyl ether from 0.1 mol of diethylmercury and excess magnesium[16] was allowed to react with 0.45 mol of $LiAlH_4$ in diethyl ether. Precipitation of MgH_2 was noted with addition of the first drops of hydride. The mixture was stirred for 3 days after completion of the addition and then filtered in the drybox. The precipitate was washed three times with diethyl ether to remove any excess diethylmagnesium followed by vacuum drying at room temperature for 1 hr. The magnesium to hydrogen ratio was found to be 1.00:1.92.

B. Reduction of Diethylmagnesium with Hydrogen at Elevated Temperatures.—Diethylmagnesium (0.1 mol in 150 ml of ether) was charged into an autoclave and heated under 2000 psi of hydrogen at 75° for 10 hr. The precipitate which had formed was filtered in the drybox and washed three times with diethyl ether. The magnesium to hydrogen ratio was found to be 1.00:1.91.

C. Pyrolysis of Diethylmagnesium.—Diethylmagnesium (0.05 mol) was heated for 2-hr periods at 100, 150, 200, and 220°. Infrared analysis (Nujol mull) of these materials indicated only partial pyrolysis after heating at 200° for 2 hr. All of the diethylmagnesium had been pyrolyzed by heating for 2 hr at 220°. The yield was 0.98 g of a yellow-brown material violently explosive upon exposure to the atmosphere. The magnesium to hydrogen ratio was found to be 1.00:1.94.

Results and Discussion

Our evaluation of the reaction of ethyl Grignard compounds with diborane as a route to HMgX compounds was reported earlier.[5] We were not able to prepare HMgX compounds by this method under any conditions including the exact conditions stated by Wiberg and Strebel in their earlier report. It was clearly demonstrated that the products of this reaction in tetrahydrofuran under a variety of conditions are the halogenomagnesium borohydride ($XMgBH_4$) and triethylborane (eq 2).

The two other methods reported for the preparation of HMgX compounds involve hydrogenolysis and pyrolysis of Grignard compounds. Dymova, *et al.*,[6] claimed to have prepared HMgCl, HMgBr, and HMgI containing 0.1–0.9 mol of solvated ether by the hydrogenolysis of ethyl Grignard compounds in diethyl ether. Rice, *et al.*,[9] claimed to have prepared HMgBr by the pyrolysis of ethyl- and *t*-butylmagnesium bromides at 190 and 200°, respectively. Since the "HMgX" compounds were stated by the Russian workers to disproportionate in tetrahydrofuran,[6] it was clear that this solvent was to be avoided especially in the hydrogenolysis experiments in which the Grignard compounds are allowed to react with hydrogen in solution. It also appeared clear that the Russian work[6] had to be repeated since the hydrogenolysis experiments were performed in diethyl ether whereas earlier Rice reported that "HMgX" compounds disproportionate in diethyl ether.[9] Furthermore the pyrolysis studies of Rice[9] had to be repeated since the Russian workers claimed that "HMgX" compounds disproportionate on heating to 125°[6] and Rice reported the preparation of "HMgX" compounds by pyrolysis of Grignard compounds at 200°.[9] As a starting material for hydrogenolysis and pyrolysis reactions, ethyl-, isopropyl-, and isobutylmagnesium halides were chosen. Isopropyl compounds were chosen because earlier we had shown that isopropylmagnesium chloride reacts with hydrogen at a faster rate than any other Grignard compounds investigated at the time.[7] Thus lower reaction temperatures could be used to effect hydrogenolysis of the isopropyl Grignard reagent which presumably would lead to a purer product. Isobutyl compounds were investigated since triisobutylaluminum is known to undergo hydrogenolysis and pyrolysis readily compared to other aluminum alkyls. The ethyl Grignard compounds were investigated because previous workers used these compounds for both hydrogenolysis and pyrolysis studies and it was considered necessary to repeat this work.

Previous workers employed elemental analysis but particularly powder diffraction and dta–tga analysis of reaction products in order to determine whether the product was a single compound, HMgX, or a mixture of MgH_2 and MgX_2. Powder diffraction and dta–tga analytical evaluation of the product are crucial since the reported "HMgX" compounds are insoluble in diethyl ether and are said to disproportionate in tetrahydrofuran. It was by evaluation of both X-ray powder diffraction and dta–tga data that both Russian and American workers decided that the products of hydrogenolysis and pyrolysis of Grignard compounds produced "HMgX" compounds and not mixtures of MgH_2 and MgX_2.

Pyrolysis of Grignard reagents yielded materials which contain hydridic hydrogen, magnesium, halide, and ether in the approximate ratio 1:1:1:n, where $n << 1$. As can be seen from Table II the hydrogen content of the product was usually low presumably due to decomposition of the product during heating. The pyrolytic reactions were not markedly temperature or time dependent; however, as expected, pyrolysis was effected under much milder conditions and with shorter reaction times when the alkyl group was isopropyl or isobutyl. The nature of the pyrolytic product was independent of the alkyl group as demonstrated

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[17] G. Barbaras, C. Dillard, A. Finholt, T. Wartik, K. Wilzbach, and H. Schlesinger, *J. Am. Chem. Soc.*, **73**, 4585 (1951).

TABLE IV

X-RAY POWDER PATTERN *d*-SPACING DATA. HYDROGENOLYSIS AND PYROLYSIS OF GRIGNARD COMPOUNDS

"HMgCl" (hydrogenolysis)	"HMgCl" (hydrogenolysis, heated at 120° for 2 hr)	"HMgCl" (pyrolysis)	"HMgBr" (pyrolysis)	"HMgI" (pyrolysis)
12.3 m	5.9 s	6.0 s	6.3 m	3.6 vw
9.3 s	2.92 s	3.2 vw	3.28 w	3.4 m
7.2 m	2.76 s	3.1 vw	3.10 m	3.15 s
6.3 vw	2.60 s	2.98 s	2.90 s	2.48 m
5.5 vw	2.50 vw	2.79 w	2.68 w	2.08 m
4.75 vw	1.80 s	2.60 s	2.49 vw	1.93 m
3.19 w	1.73 w	2.52 w	2.26 m	1.78 m
2.76 vw	1.67 vw	2.43 vw	1.90 s	1.74 w
2.50 vw		2.27 vw	1.82 vw	1.72 w
2.35 vw		2.02 vw	1.76 w	1.60 vw
2.13 vw		1.83 s	1.66 vw	1.56 vw
1.82 vw		1.75 w	1.62 m	1.42 vw
1.67 vw		1.69 w	1.59 w	1.34 w
		1.56 w	1.56 w	1.33 w
		1.49 w	1.225 m	1.29 vw
			1.20 m	1.27 vw
				1.20 vw
				1.17 vw
				1.13 vw
				1.10 vw

by the fact that the powder diffraction patterns obtained from the products of pyrolysis of ethylmagnesium bromide and isopropylmagnesium bromide were identical. Analogous results were obtained for the chloro and iodo Grignard compounds. Furthermore, the X-ray powder diffraction pattern obtained from the pyrolysis product of the bromo Grignard compounds contains almost all of the lines reported earlier (Tables IV and V) for the pyrolysis of ethylmagnesium bromide,[9] indicating identical products.

In order to determine whether the "HMgX" products exist as an authentic single compound or as equimolar mixtures of hydride and halide, the X-ray powder diffraction patterns of these products were compared with the powder diffraction patterns for magnesium hydride and MgX_2 (X = Cl, Br, and I). Powder diffraction data for MgH_2 synthesized by different routes (see Experimental Section) was compiled since the reactivity of each MgH_2 is sensitive to the synthetic route and it was felt that differences in reactivity might be due to differences in structure, although a contrary explanation to this phenomenon has appeared.[18] Powder diffraction patterns for MgH_2 produced from the various different synthetic routes were found to be identical with the exception that in the case of the reduction of a dialkylmagnesium compound with $LiAlH_4$ or with hydrogen at elevated temperature the lines were broader and more diffuse than for MgH_2 produced in the other reactions. A representative MgH_2 spectrum is recorded in Table V. X-Ray powder diffraction data were compiled for solvated MgX_2, MgX_2 of intermediate solvation, and desolvated MgX_2, since the diffraction patterns are expected to be sensitive to changes in coordination about magnesium. It was initially thought most meaningful to compare the diffraction data for the pyrolytic "HMgX" products which contain relatively small amounts of coordinated ether with the diffraction patterns of the magnesium halides which contain little or no coordinated ether. Powder diffraction patterns for the magnesium halides were markedly sensitive to the degree of coordination and are summarized in Table VI.

TABLE V

X-RAY POWDER PATTERN *d*-SPACING DATA. MgH_2 AND "HMgX" COMPOUNDS

MgH_2	"HMgCl" (hydrogenolysis of (t-$C_4H_9MgCl\cdot O(C_2H_5)_2)_2$	"HMgBr" (pyrolytic product of C_2H_5MgBr by Rice[9])
3.19 vs	6.0 s	5.51
2.76 vw	3.18 m	3.30
2.495 vs	3.05 m	2.94 s
2.24 m	2.94 s	2.12
1.67 s	2.75 m	1.91 s
1.59 m	2.55 vs	1.65
1.50 w	2.48 m	1.61
1.42 w	2.24 m	1.22
1.36 w	1.97 m	1.10
1.335 w	1.80 s	
1.246 w	1.72 m	
1.15 w	1.66 m	
1.125 w	1.59 w	
	1.54 m	
	1.45 m	
	1.42 w	
	1.36 w	
	1.34 w	
	1.28 w	
	1.25 w	
	1.17 w	
	1.14 m	
	1.04 m	

TABLE VI

X-RAY POWDER PATTERN *d*-SPACING DATA. MgX_2 COMPOUNDS

$MgCl_2(O(C_2H_5)_2)_n$			$MgBr_2$-$(O(C_2H_5)_2)$	$MgBr_2$	MgI-$(O(C_2H_5)_2)_2$	MgI_2
n = 1	n = 0.27	n = 0				
10.6 vs	12.4 s	5.8 s	8.0 s	6.2 m	8.0 m	3.5 w
9.5 vw	9.2 s	3.05 w	7.3 s	3.27 w	6.90 m	3.38 m
7.8 vw	7.2 m	2.94 s	5.7 vw	3.10 m	6.10 w	3.13 s
6.3 w	6.2 w	2.75 m	5.3 w	2.89 s	5.80 vw	2.46 m
6.0 w		2.55 s	4.40 vw	2.68 w	5.20 m	2.05 m
5.6 w	5.5 w	2.45 w	3.95 vw	2.26 m	4.30 w	1.92 m
2.9 w	4.8 w	2.32 w	3.55 s	1.90 s	3.94 vw	1.76 m
2.5 w	2.75 w	2.13 m	3.92 vw	1.82 w	3.88 vw	1.73 m
2.56 w	2.30 w	1.95 w	3.24 m	1.76 w	3.80 w	1.70 m
1.80	2.10 w	1.80 s	3.18 vw	1.63 m	3.66 w	1.58 w
	1.80 w	1.72 m	2.98 m	1.59 w	3.43 m	1.53 vw
		1.65 w	2.86 vw	1.56 w	3.31 w	1.405 vw
		1.54 m	2.75 vw	1.46 vw	3.20 w	1.325 m
		1.51 w	2.62 vw	1.30 vw	3.05 w	1.315 m
		1.47 m	2.51 w	1.225 m	2.86 vw	1.275 vw
		1.43 w	2.39 w	1.205 m	2.75 vw	1.255 w
		1.37 w	2.29 vw	1.16 w	2.64 vw	1.195 w
		1.33 w	2.13 vw	1.10 w	2.48 w	1.165 w
		1.27 w	2.07 vw		2.38 vw	1.125 w
		1.14 m	1.90 w		2.33 vw	1.085 w
		1.04 m	1.84 vw		2.26 vw	1.035 w
		0.98 m	1.73 vw		2.20 vw	
		0.905 w	1.61 vw		2.13 vw	
			1.58 vw		2.09 vw	
					2.06 vw	
					1.83 vw	

From comparison of the data listed in Tables IV and VI it can be concluded that all of the lines present in the spectra of the desolvated magnesium halides are present in the spectra of the corresponding pyrolytic "HMgX" product. The spectrum of "HMgI" contains

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(18) K. M. Mackay, "Hydrogen Compounds of the Elements," Wilmer Bros. Ltd., Birkenhead, Cheshire, England, 1966, p 41.

only the lines present in desolvated MgI_2 while the spectra of "HMgCl" and "HMgBr" contain lines present in desolvated $MgCl_2$ and $MgBr_2$, respectively, and additional relatively weak lines which correspond exactly to the strongest lines present in a pure sample of MgH_2. These are the results expected for an equimolar mixture of MgH_2 and MgX_2 since equimolar mixtures of hydride and halide contain a relatively low weight percentage of hydride owing to the relatively low molecular weight of this component. Furthermore, the weight percentage of MgH_2 present in equimolar mixtures of hydride and halide is expected to decrease in the series where halide = Cl, Br, and I, and lines due to HgH_2 might be impossible to detect in an equimolar mixture of MgH_2 and MgI_2. This was confirmed from analysis of the powder diffraction spectrum of an authentic 1:1 molar mixture of MgH_2 and MgI_2, while weak lines due to MgH_2 could be detected in authentic 1:1 molar mixtures of MgH_2 and MgX_2 (X = Cl and Br). The X-ray powder patterns for the authentic 1:1 molar mixtures of MgH_2 and MgX_2 (X = Cl, Br, and I) were identical with the corresponding pyrolytic HMgX product, and thus it must be concluded that these materials exist as equimolar mixtures.

Essentially all of the $MgCl_2$ was extracted into solution when pyrolytic "HMgCl" was stirred with excess, dry THF for 3 min (Table III), while $MgBr_2$ and MgI_2 were readily extracted when pyrolytic "HMgBr" and "HMgI," respectively, were stirred with excess, dry diethyl ether for a period of 3 min. X-Ray powder patterns of the undissolved solids were identical with that of MgH_2.

We were not able to isolate HMgX compounds (where X = Br and I) by hydrogenolysis of Grignard compounds in diethyl ether. Twelve hydrogenolysis experiments were carried out in which several Grignard compounds were allowed to react under a variety of conditions (varying the temperature, pressure, and concentration), including those specified by the Russian workers.[6] Under all conditions, when the Grignard compound was a bromide or iodide, a white solid was formed which was shown by both elemental and X-ray powder analysis to be predominantly MgH_2. The filtrate contained almost all of the initial halide (Table I). Hydrogenolysis of both ethyl- and isopropylmagnesium chlorides in ether produced a white, insoluble product which contained hydrogen, magnesium, chlorine, and ether in the approximate ratio of 1:1:1:n (where $n < 1$). This result is to be expected since $MgCl_2$ is insoluble in diethyl ether. Thus the solid product could be HMgX or a mixture of MgH_2 and MgX_2. The results in Table I show that the hydrogen content of the product was always slightly low and the chlorine content slightly high. The X-ray powder pattern of the product from ethyl- and isopropylmagnesium chlorides showed similar lines, indicating that the same product is formed from hydrogenolysis of these Grignard compounds. Very few of these lines were in common with the X-ray powder patterns of $MgCl_2 \cdot O(C_2H_5)_2$ and desolvated $MgCl_2$ indicating either an authentic HMgCl compound or an intermediate degree of coordination on $MgCl_2$ (Tables IV and VI). Several lines are present, however, which can be assigned to MgH_2 (Table V). Two experiments were conducted in order to decide between these possibilities. A sample of the hydrogenolysis "HMgCl" was heated under vacuum at 120° for a period of 2 hr to remove coordinated ether. None of the characteristic ether bands was present in the infrared spectrum of this heated material and the X-ray powder pattern (Table IV) showed strong lines identical with those in desolvated $MgCl_2$ and weak lines identical with the lines in X-ray powder spectra of pure MgH_2, indicating an equimolar mixture of MgH_2 and $MgCl_2$. Desolvation of HMgCl at 120°, however, could have been accompanied by an intramolecular disproportionation to MgH_2 and $MgCl_2$ suggested earlier by Dymova, *et al.*[6] We therefore compared the X-ray powder patterns of hydrogenolysis "$HMgCl \cdot (O(C_2H_5)_2)_n$" (where $n = 0.9$–0.3) with powder diffraction data for $MgCl_2 \cdot (O(C_2H_5)_2)_n$ (where $n = 0.9$–0.3). We found that spectra obtained for $MgCl_2$ of intermediate solvation were very similar to spectra of hydrogenolysis "HMgCl" (compare, for example, the spectra of hydrogenolysis "HMgCl" and of $MgCl_2$ containing 27 mol % $O(C_2H_5)_2$, Tables IV and VI) with the exception that lines attributable to MgH_2, present in the latter spectrum, are not present in the former spectra. We, therefore, conclude that the hydrogenolysis "HMgCl" consists of an equimolar mixture of MgH_2 and $MgCl_2$. Essentially all of the chloride goes into solution when this material is stirred with excess, dry THF for 3 min. During this period the composition of the solid changed markedly. X-Ray and elemental analyses indicated that the insoluble residue is MgH_2 (Table III).

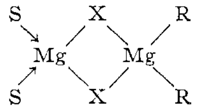
TABLE VII
ANALYSES OF GRIGNARD SOLUTION

Grignard	Concn, *M*: Mg	Concn, *M*: X	Mg:X	% MgX_2
C_2H_5MgBr	1.74	1.70	1.000:0.977	2
i-C_3H_7MgCl	0.361	0.365	1.000:1.011	1
i-C_3H_7MgCl	2.55	2.61	1.000:1.024	2
C_2H_5MgBr	3.88	3.85	1.000:0.992	1
C_2H_5MgBr	3.64	3.65	1.000:0.997	1
i-C_3H_7MgCl	2.48	2.50	1.000:1.000	0
i-C_3H_7MgCl	1.99	2.09	1.000:1.050	5
i-C_3H_7MgBr	1.92	2.04	1.000:1.062	6
C_2H_5MgCl	3.58	3.60	1.000:1.009	1
C_2H_5MgI	3.54	3.44	1.000:0.972	2
i-C_3H_7MgI	1.07	1.26	1.000:1.178	18
i-C_3H_7MgI	1.001	1.125	1.000:1.118	12
i-C_3H_7MgI	0.894	1.07	1.000:1.200	20
i-C_3H_7MgI	0.206	0.251	1.000:1.218	21
i-C_3H_7MgCl	1.714	1.724	1.000:1.007	1
i-C_3H_7MgBr	0.812	0.823	1.000:1.014	1
i-C_4H_9MgI	0.594	0.629	1.000:1.059	6

It was of some concern that the nature of the product formed in the hydrogenolysis or pyrolysis of Grignard compounds would depend to a large extent on the composition of the Grignard compound in solution (Table VII) (hydrogenolysis) or the solid-state structure (pyrolysis). For example RMgX species would be expected to form HMgX, and $R_2Mg{-}MgX_2$ species would be expected to form a mixture of MgH_2 and MgX_2

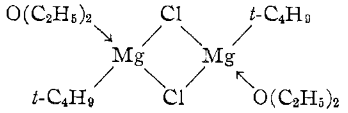
$$2RMgX \longrightarrow HMgX$$
$$R_2Mg + MgX_2 \longrightarrow MgH_2 + MgX_2$$

Therefore it seemed worthwhile to pyrolyze a Grignard compound that was known to possess the RMgX solid-state structure. In this connection the bis(diethyl ether) adduct of ethylmagnesium bromide was isolated prior to pyrolysis since earlier[19] it had been demonstrated that this species exists as an RMgX compound with each magnesium atom bonded to one bromine and one alkyl group. It had also been suggested that simple removal of solvent from a Grignard compound, as in vacuum distillation, results in precipitation of a material containing unsymmetrically bridged alkyl and halogen groups which should result on pyrolysis in the formation of a mixture of MgH_2 and MgX_2.



A material containing hydrogen, magnesium, and bromine in the ratio 0.88:1.00:1.06 (Table II) was obtained when the bis(diethyl ether) adduct of ethylmagnesium bromide was heated at 200° for 2 hr. The X-ray powder pattern of this material was identical with the patterns obtained from pyrolysis of other bromo Grignard compounds indicating that a mixture of MgH_2 and $MgBr_2$ was again obtained.

The 1:1 etherate adduct of *t*-butylmagnesium chloride, which is dimeric in benzene, was hydrogenated since earlier[14] it had been suggested that this compound exists in benzene solution as the symmetrically bridged dimer



Hydrogenolysis of this Grignard compound resulted in precipitation of a gray, white solid containing very little ether (essentially all of the diethyl ether is present in the benzene) and hydrogen, magnesium, and chloride in a ratio of 0.91:1.00:1.02. The X-ray powder pattern of this material (Table V) is identical with the pattern obtained for an authentic 1:1 molar mixture of MgH_2 and $MgCl_2$ and, therefore, this material also exists as a mixture.

In conclusion, we were not able to prepare HMgX compounds (X = Cl, Br, or I) from either pyrolysis or hydrogenolysis of Grignard reagents under a variety of reaction conditions. In contrast to earlier reports by Russian, German, and American workers, the products of these reactions were shown, by careful comparison of appropriate X-ray powder diffraction data, to consist of mixtures of MgH_2 and the corresponding MgX_2. Reduction of an RMgX compound to HMgX by the reactions described in this study must necessarily follow immediately with formation of mixtures of hydride and halide.

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[19] L. J. Guggenberger and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 5344 (1964).