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## The Crystal and Molecular Structure of $Mg_4Br_6O \cdot 4C_4H_{10}O$ , a Grignard Reagent Oxidation Product<sup>1</sup>

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$Mg_4Br_6O \cdot 4C_4H_{10}O$  is readily formed by contaminating the Grignard reagent with small amounts of oxygen. X-Ray analysis showed  $Mg_4Br_6O \cdot 4C_4H_{10}O$  crystals consist of polyhedra of  $Mg_4Br_6O$  surrounded by ether molecules. The oxygen atom in each polyhedron is tetrahedrally coordinated to four magnesium atoms lying on the alternate faces of an octahedron described by the bromine atoms. The four ether molecules are coordinated to the magnesium atoms with a MgO distance of about 2.11 Å.

### Introduction

A preliminary study of phenylmagnesium bromide in diethyl ether revealed the occasional formation of crystals at room temperature (*ca.* 27°). Chemical and initial structural analyses showed that this compound does not possess a carbon-metal bond (see below), but is formed as the result of air contamination of the phenylmagnesium bromide solution. Some of the physical properties of this material, which is here proved to be  $Mg_4Br_6O \cdot 4C_4H_{10}O$ , were determined as part of an investigation of the particular Grignard system, phenylmagnesium bromide in diethyl ether.<sup>3</sup>

### Preparation and Properties of the Crystals

Large polyhedral transparent crystals were obtained from a 1.5 *N* solution of phenylmagnesium bromide in diethyl ether by (1) allowing the ether to evaporate directly into the atmosphere through a small orifice, or (2) exposing the solution to commercial oxygen which had been passed through phosphorus pentoxide. Similar crystals have been described previously by Holyrod,<sup>4</sup> who passed acetylene dried with phosphorus pentoxide over a solution of phenylmagnesium bromide in diethyl ether, and by Nesmeyanow,<sup>5</sup> who used air free of CO<sub>2</sub>. From the different methods of preparation, it is clear that the exclusion of oxygen well enough to prevent formation of this compound is difficult. Both Holyrod and Nesmeyanow decided the crystals were  $Mg_2Br_3OH \cdot 2C_4H_{10}O$ , and that the principal reaction was between phenylmagnesium bromide and water.

By increasing the temperature of the ether solution to 60° and slowly evaporating the diethyl ether, well-formed tetragonal needle crystals (class  $\bar{4}2m$ ) grew both independently and as outgrowths of the polyhedral crystals. Single crystal X-ray diffraction patterns of the two different forms of crystals were identical.

Crystals of  $Mg_4Br_6O \cdot 4C_4H_{10}O$ , mol. wt. 889.26, were found to be soft and very hygroscopic, and to decompose rapidly in air with the evolution of heat and diethyl ether. The crystals gave a negative chemical test for a carbon-metal bond.<sup>6</sup> The bromine/magnesium ratio was approximately 1.5; however, carbon and hydrogen analysis did not distinguish between the formulas  $Mg_2Br_3OH \cdot 2(C_4H_{10}O)$  and  $Mg_4Br_6O \cdot 4(C_4H_{10}O)$ . After the

crystals were allowed to react with the moisture in the atmosphere, the carbon content vanished while the bromine/magnesium ratio remained 1.5. The crystals decomposed in an inert atmosphere above 39.5°. In the presence of moisture, the crystals gained weight below this temperature, presumably indicating an increase of coordination number of the magnesium ion by binding water. Infrared spectra of the Grignard oxidation product and of several hydrated oxides and hydroxides of magnesium were compared, but these were of little aid in arriving at the composition of the oxidation product. The final molecular composition  $Mg_4Br_6O \cdot 4C_4H_{10}O$  was determined by the detailed X-ray structure analysis described here.

Several crystals were transferred to Lindemann capillaries in a dry argon atmosphere for single crystal X-ray study. A thin coating of petroleum jelly, applied immediately upon the removal of the crystals from the Grignard solution, was sufficient to preserve the crystals for this brief transfer within a drybox. Crystals protected in this manner were stable for a period of at least 2 to 3 months.

X-Ray intensity data from  $Mg_4Br_6O \cdot 4C_4H_{10}O$  exhibit the systematic absences:  $\{hhl\}$ ,  $l$  odd;  $\{h00\}$ ,  $h$  odd. The space group, confirmed by the final structure, is  $P\bar{4}2_1c$ , with  $a = b = 10.68 \pm 0.03$ ,  $c = 15.34 \pm 0.03$  Å. The absorption coefficients are 104.02 cm<sup>-1</sup> for Cu K $\alpha$  and 75.70 cm<sup>-1</sup> for Mo K $\alpha$  radiation. The calculated density is 1.69 g./cm.<sup>3</sup>; the observed density of the crystals at 27°, determined by the flotation method with a mixture of isopropyl and *n*-propyl iodides, is 1.72 g./cm.<sup>3</sup>.

### Collection of Intensity Data

The crystals were sensitive to X-rays, changing to a pale yellow color with a decrease in the single crystal integrated intensities at a rate of approximately 20% for every 100 hr. of exposure to Mo K $\alpha$  radiation. The (400) and (006) reflections were measured every 6 hr. as standard intensities for internal reference.

Two sets of three-dimensional intensity data from two different crystals were taken with a General Electric XRD-5 diffractometer, using Mo K $\alpha$  radiation. The two sets of data were redundant with respect to each other and each set was collected in less than 95 hr. The maximum and minimum dimensions (radii) of the two crystals were 0.25 and 0.10, and 0.20 and 0.09 mm. Ten and nine crystal faces, respectively, defined the two polyhedra. The equations of the bounding planes of the crystals were determined from measurements made with a micrometer-equipped microscope, and these equations were then used to calculate the absorp-

(1) Contribution No. 1387; work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) (a) Chemistry Department, University of Illinois, Urbana, Ill.; (b) deceased, Oct. 9, 1963.

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

(4) G. Holyrod, *Proc. Chem. Soc.*, **20**, 38 (1904).

(5) A. N. Nesmeyanow, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **988** (1955).

(6) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

tion correction for each reflection.<sup>7</sup> The accuracy of the absorption calculations was assessed by a plot of the absorption corrected intensities *vs.* the rotation angle of the crystal about a diffraction vector and indicated a maximum error in intensity of less than 10%. Allowances for errors in intensities due to the presence of white radiation were made using eq. 1<sup>8</sup> where  $I^n$  is

$$I^n(\text{streak, corrected}) = I^n(\text{uncorrected}) - \sum_m I_m^n \quad (1)$$

the integrated intensity from the  $n$ th reflection and  $I_m^n$  is the contribution to  $I^n$  from the white radiation from the  $m$ th reflection from the same lattice row line including the origin.  $I_m^n$  includes dispersion and  $L_p$  corrections. The "streak" curve from the (305) reflection was used as a "standard streak" in applying the correction. The form factors used for refinement were obtained from Vol. 3 of "International Tables for X-ray Crystallography," pp. 202 to 207. Bromine form factors were corrected for anomalous dispersion effects.<sup>9</sup> Nine hundred and two Bragg reflections, out to  $\sin \theta/\lambda = 0.616$ , were measured ( $h \geq k$ ) with a 200-sec.  $2\theta$  scan and a 100-sec. background scan for each reflection.

### Structure Determination and Discussion

An initial inspection of the intensities revealed that the reflections  $\{h0l\}$ , with  $h + l = 2n + 1$ , were weak or missing, indicating that (010) and (100) are pseudo- $n$ -glide planes. This condition is satisfied by assuming that bromine atoms in the eightfold general positions of  $P\bar{4}2_1c$  have  $z$ -parameters of 0 or  $1/2$  and that the remaining four bromine atoms are in special positions with no less than twofold symmetry. A three-dimensional Patterson function was calculated using the gradient Patterson function described by Jacobson, *et al.*,<sup>10</sup> and gave initial fourfold bromine parameters,  $x = 0.0$ ,  $y = 0.0$ ,  $z = 0.21$ , and eightfold bromine positions,  $x = 0.29$ ,  $y = 0.06$ ,  $z = 0.0$ . The bromine atoms therefore form octahedra centered about the origin and  $1/2, 1/2, 1/2$ . The magnesium, oxygen at the origin, and ether oxygen positions were also derived from the three-dimensional Patterson. The remarkably compact polyhedron formed by these atoms is shown in Fig. 1.

No vectors could be interpreted in terms of satisfactory carbon positions. The results obtained from the three-dimensional Patterson were confirmed by successive three-dimensional Fourier and difference Fourier calculations. Because both sets of bromine atoms were in centrosymmetric positions, a three-dimensional Fourier calculated using only the signs of the bromine structure factors showed all acentric atoms in the structure in sixteenfold centrosymmetric positions at both  $x, y, z$  and  $x, y, -z$  with only one-half the expected electron density. The inclusion of acentric sets of coordinates for the ether oxygen atom and the magnesium atom gave absolute electron density peak densities of 51, 18, 9, and 5 electrons/Å.<sup>3</sup> of bromine, magnesium, origin oxygen, and ether oxygen atoms, respectively. The opposite number of the centric set (at  $-z$ ) vanished on this Fourier. Least-squares anal-

ysis of the data using an IBM 704 least-squares computer program ORXLS<sup>11</sup> gave an error index,  $R$ , of 0.231 at this point. Temperature factors used were isotropic and had not been varied. A three-dimensional difference Fourier showed a large anisotropy of the bromine position, and structure factor calculations for the bromine, magnesium, and oxygen atoms were accordingly made using anisotropic temperature factors. Subsequent three-dimensional Fourier and difference Fourier maps, however, still gave no indication of the location of the ether ethyl groups.

At this point calculations were made in order to determine the possible steric configurations of the ether molecule with respect to the bromine polyhedron. Since the oxygen-magnesium-ether oxygen bond is a pseudo-threefold axis, there should be three equivalent ways to pack an ether molecule against the alternate faces of the bromine octahedra (*e.g.*, Fig. 2). A disordered structure was also implied by the observation that it was possible to account for the unit cell volume if the ethyl groups were thermally disordered, but that otherwise the packing was very inefficient. Three additional considerations were used to determine the possible ethyl carbon positions: (1) the methylene group-bromine van der Waals distance was assumed to be  $2.0 \pm 0.2$  Å,<sup>12</sup> (2) the methyl group-bromine van der Waals distance was assumed to be  $2.0 \pm 0.2$  Å, and (3) the most stable configuration of the ether molecule was taken as that determined by electron diffraction.<sup>13</sup> Using the above criteria, three equivalent sets of positions for the ethyl carbon atoms were found with the ether molecule trigonally coordinated to the magnesium atom. Least-squares refinement was first carried out with carbon atoms in one set of these positions (ordered model). The final error factors for this model were  $R_w = 0.094$  (all data),  $R = 0.086$  (observed data), where

$$R = \frac{\sum ||F_o| - |F_c||}{\sum F_o}$$

and

$$R_w = \frac{\sum_w ||F_o| - |F_c||^2}{\sum_w |F_o|^2}$$

Some of the atomic parameters, structure factors, and bond angles and bond distances obtained from this model are listed in Tables I-III and Fig. 1 and 3, respectively. Attempts were then made to include more than one set of ether carbons with the carbon atoms weighted accordingly; however, there was no significant improvement with either the observed and calculated structure factor agreement or the refined carbon positional and thermal parameters. Final difference Fourier maps showed no electron densities above background.

In spite of good intensity agreement, this structure determination leaves the positions of the ethyl groups of the ethers in an unsatisfactory state. The very high temperature factors which eliminate data at high angles, the soft character of the crystals, and the low decomposition temperature are in keeping with a disordered structure and with considerable freedom of motion of

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TABLE I

FINAL VALUES OF THE PARAMETERS AND THEIR STANDARD DEVIATIONS<sup>a</sup>

Atom	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Br <sub>1</sub>	0.0000	0.0000	0.2065	0.0138	0.0163	0.0039	0.0039	0.0000	0.0000
$\delta$	0.0000	0.0000	0.0002	0.0008	0.0008	0.0001	0.0007	0.0000	0.0000
Br <sub>2</sub>	0.2930	0.0586	-0.0054	0.0088	0.0180	0.0091	-0.0022	-0.0009	0.0026
$\delta$	0.0002	0.0002	0.0004	0.0003	0.0004	0.0002	0.0002	0.0004	0.0004
Mg	0.1262	-0.0821	0.0722	0.0086	0.0091	0.0048	-0.0004	-0.0022	0.0001
$\delta$	0.0007	0.0007	0.0005	0.0009	0.0009	0.0003	0.0007	0.0006	0.0006
O <sub>1</sub>	0.2627	-0.1701	0.150	0.020	0.014	0.006	0.003	-0.006	0.002
$\delta$	0.002	0.002	0.001	0.003	0.002	0.001	0.002	0.002	0.001
C <sub>1</sub>	0.157	0.241	0.373	0.039	0.060	0.102	-0.019	0.053	-0.014
$\delta$	0.006	0.008	0.011	0.011	0.014	0.019	0.011	0.014	0.012
C <sub>2</sub>	0.099	0.273	0.364	0.011	0.053	0.056	-0.004	-0.020	-0.024
$\delta$	0.003	0.007	0.007	0.005	0.011	0.009	0.006	0.006	0.006
C <sub>3</sub>	0.277	0.239	0.286	0.053	0.055	0.009	-0.017	-0.007	-0.005
$\delta$	0.007	0.006	0.002	0.013	0.015	0.005	0.012	0.007	0.008
C <sub>4</sub>	0.141	0.431	0.293	0.068	0.067	0.018	-0.025	0.017	-0.013
$\delta$	0.006	0.007	0.004	0.013	0.015	0.005	0.012	0.007	0.008
O <sub>2</sub>	0.0000	0.0000	0.0000	0.0088	0.0088	0.0025	0.0000	0.0000	0.0000
$\delta$	0.0000	0.0000	0.0000	0.002	0.002	0.001	0.0000	0.0000	0.0000

<sup>a</sup> The form of the temperature factor is  $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$ .

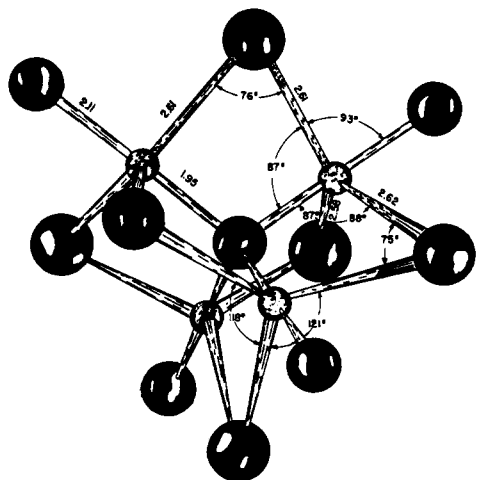


Fig. 1.—Structure of magnesium, bromine, and oxygen atoms in crystals of  $\text{Mg}_4\text{Br}_6\text{O} \cdot 4\text{C}_4\text{H}_{10}\text{O}$ : spheres represent bromine, oxygen, and magnesium atoms in order of decreasing size.

the ethyl group. The very rigid inorganic polyhedra are held in a very soft organic matrix. Low temperature studies might yield good ether parameters, but since the nature of the oxidation product is established without it, we do not contemplate such a study.

The bromine–magnesium distances (2.58–2.62 Å.) compare with that expected for ionic bonding (2.60 Å.).<sup>12</sup> The bromine atoms are not packed closest with each other, but with the origin oxygen (3.18 Å.) and the ether groups. The close approach of the bromine atoms to the origin oxygen and ionic considerations preclude the possibility of the compound being  $\text{Mg}_2\text{Br}_3\text{OH} \cdot 2\text{C}_4\text{H}_{10}\text{O}$  as described by Nesmeyanow and Holyrod (twice as many  $\text{OH}^-$  as  $\text{O}^{2-}$  would be required). The magnesium–origin oxygen distance falls short (1.95 Å.) of the predicted covalent or ionic bond distance (2.05 Å.) and is apparently a strong bond, shorter than in  $\text{MgO}$  (2.1 Å.). The fact that the usual sixfold coordination of the magnesium atom has been reduced to five is consistent with the decrease in the  $\text{Mg}-\text{O}$  bond length and the large steric requirements of ethers. The magnesium–ether oxygen distance (2.11 Å.) is of the expected magnitude for a solvated  $\text{Mg}-\text{O}$  distance, comparing well with the distance in the di-

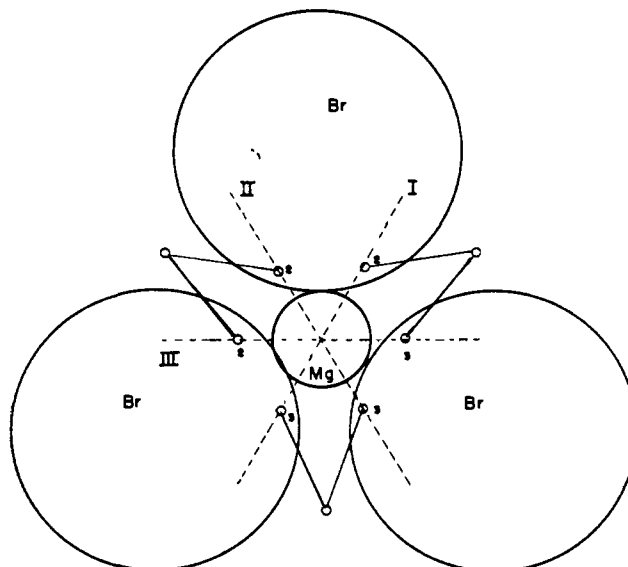


Fig. 2.—Projection along pseudo-threefold axis through an octahedral face of  $\text{Mg}_4\text{Br}_6\text{O} \cdot 4\text{C}_4\text{H}_{10}\text{O}$ : dashed lines indicate planes for optimum packing of a linear (excluding hydrogens) ether molecule trigonally coordinated to the magnesium atom.

etherate of phenylmagnesium bromide (2.06 Å.), where the coordination number of magnesium is only four.<sup>3</sup> As indicated in Table III, the  $\text{O}-\text{Mg}-\text{O}$  vector is linear within experimental error.

The greatest thermal displacements of the bromine atoms with twofold symmetry ( $0, 0, z$ ; etc.) are parallel to the (001) plane. The thermal ellipsoids of the bromine atoms in the general positions are intersected by the respective planes  $z = 0$  and  $z = 1/2$ .

A mechanism for the formation of  $\text{Mg}_4\text{Br}_6\text{O} \cdot 4\text{C}_4\text{H}_{10}\text{O}$  is difficult to propose because of the large number of by-products which may be formed by the contamination of the Grignard solution. Past mechanisms described by various workers<sup>14</sup> for the oxidation of diethyl ether Grignard solutions have postulated the existence of species of the type  $\text{ROMgX}$ ,  $\text{ROOMgX}$ ,  $\text{MgX}_2$ ,  $(\text{MgX})_2\text{O}$ ,  $\text{MgO}$ , and various other organic perox-

(14) See M. H. Wuyts, *Compt. rend.*, **148**, 930 (1909); C. W. Porter and C. Steel, *J. Am. Chem. Soc.*, **42**, 2650 (1920); H. Gilman and A. Wood, *ibid.*, **48**, 806 (1926); and J. Meisenheimer, *Ber. deut. chem. Ges.*, **61**, 708 (1928).

TABLE II  
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Mg<sub>4</sub>Br<sub>2</sub>O 4C<sub>4</sub>H<sub>10</sub>O<sup>a</sup>

h	k	l	F <sub>o</sub>	F <sub>c</sub>	A <sub>o</sub>	A <sub>c</sub>	B <sub>o</sub>	B <sub>c</sub>
0	0	0	100	100	100	100	100	100
1	0	0	100	100	100	100	100	100
2	0	0	100	100	100	100	100	100
3	0	0	100	100	100	100	100	100
4	0	0	100	100	100	100	100	100
5	0	0	100	100	100	100	100	100
6	0	0	100	100	100	100	100	100
7	0	0	100	100	100	100	100	100
8	0	0	100	100	100	100	100	100
9	0	0	100	100	100	100	100	100
10	0	0	100	100	100	100	100	100
11	0	0	100	100	100	100	100	100
12	0	0	100	100	100	100	100	100
13	0	0	100	100	100	100	100	100
14	0	0	100	100	100	100	100	100
15	0	0	100	100	100	100	100	100
16	0	0	100	100	100	100	100	100
17	0	0	100	100	100	100	100	100
18	0	0	100	100	100	100	100	100
19	0	0	100	100	100	100	100	100
20	0	0	100	100	100	100	100	100
21	0	0	100	100	100	100	100	100
22	0	0	100	100	100	100	100	100
23	0	0	100	100	100	100	100	100
24	0	0	100	100	100	100	100	100
25	0	0	100	100	100	100	100	100
26	0	0	100	100	100	100	100	100
27	0	0	100	100	100	100	100	100
28	0	0	100	100	100	100	100	100
29	0	0	100	100	100	100	100	100
30	0	0	100	100	100	100	100	100
31	0	0	100	100	100	100	100	100
32	0	0	100	100	100	100	100	100
33	0	0	100	100	100	100	100	100
34	0	0	100	100	100	100	100	100
35	0	0	100	100	100	100	100	100
36	0	0	100	100	100	100	100	100
37	0	0	100	100	100	100	100	100
38	0	0	100	100	100	100	100	100
39	0	0	100	100	100	100	100	100
40	0	0	100	100	100	100	100	100
41	0	0	100	100	100	100	100	100
42	0	0	100	100	100	100	100	100
43	0	0	100	100	100	100	100	100
44	0	0	100	100	100	100	100	100
45	0	0	100	100	100	100	100	100
46	0	0	100	100	100	100	100	100
47	0	0	100	100	100	100	100	100
48	0	0	100	100	100	100	100	100
49	0	0	100	100	100	100	100	100
50	0	0	100	100	100	100	100	100
51	0	0	100	100	100	100	100	100
52	0	0	100	100	100	100	100	100
53	0	0	100	100	100	100	100	100
54	0	0	100	100	100	100	100	100
55	0	0	100	100	100	100	100	100
56	0	0	100	100	100	100	100	100
57	0	0	100	100	100	100	100	100
58	0	0	100	100	100	100	100	100
59	0	0	100	100	100	100	100	100
60	0	0	100	100	100	100	100	100
61	0	0	100	100	100	100	100	100
62	0	0	100	100	100	100	100	100
63	0	0	100	100	100	100	100	100
64	0	0	100	100	100	100	100	100
65	0	0	100	100	100	100	100	100
66	0	0	100	100	100	100	100	100
67	0	0	100	100	100	100	100	100
68	0	0	100	100	100	100	100	100
69	0	0	100	100	100	100	100	100
70	0	0	100	100	100	100	100	100
71	0	0	100	100	100	100	100	100
72	0	0	100	100	100	100	100	100
73	0	0	100	100	100	100	100	100
74	0	0	100	100	100	100	100	100
75	0	0	100	100	100	100	100	100
76	0	0	100	100	100	100	100	100
77	0	0	100	100	100	100	100	100
78	0	0	100	100	100	100	100	100
79	0	0	100	100	100	100	100	100
80	0	0	100	100	100	100	100	100
81	0	0	100	100	100	100	100	100
82	0	0	100	100	100	100	100	100
83	0	0	100	100	100	100	100	100
84	0	0	100	100	100	100	100	100
85	0	0	100	100	100	100	100	100
86	0	0	100	100	100	100	100	100
87	0	0	100	100	100	100	100	100
88	0	0	100	100	100	100	100	100
89	0	0	100	100	100	100	100	100
90	0	0	100	100	100	100	100	100
91	0	0	100	100	100	100	100	100
92	0	0	100	100	100	100	100	100
93	0	0	100	100	100	100	100	100
94	0	0	100	100	100	100	100	100
95	0	0	100	100	100	100	100	100
96	0	0	100	100	100	100	100	100
97	0	0	100	100	100	100	100	100
98	0	0	100	100	100	100	100	100
99	0	0	100	100	100	100	100	100
100	0	0	100	100	100	100	100	100

<sup>a</sup> Columns are running index,  $I$ ,  $F_{\text{obsd}}$ ,  $F_{\text{calcd}}$ ,  $A_{\text{calcd}}$ , and  $B_{\text{calcd}}$ , respectively. Asterisks indicate unobserved reflections entered as their probable value, using Hamilton's method [(C. V. Hamilton, *Acta Cryst.*, 8, 185 (1955))].

ides and ethers. In addition, Gilman<sup>14</sup> has found that diethyl ether is also oxidized in diethyl ether solutions of arylmagnesium halides and has described the oxidation products formed by this reaction and the subsequent reactions with the ether oxidation products and the Grignard reagent.

Tetrahydrofuran can be used as a solvent instead of diethyl ether to obtain an oxy salt from the phenylmagnesium bromide system. Initial space group and

lattice constant determinations have been made for these crystals; however, they are not isomorphous with the diethyl ether salt. One can speculate that the stronger electron-donor properties of the oxygen atom in tetrahydrofuran do not readily permit the formation of halogen bridges so that one has a higher solvent/bromine ratio. The lower density of these crystals, about 1.5 g./cm.<sup>3</sup>, supports this conclusion.

It is noteworthy that scrupulous exclusion of oxygen

TABLE III  
BOND ANGLES AND INTERATOMIC DISTANCES  
 $Mg_4Br_6O \cdot 4C_4H_{10}O^a$

Atoms	Distance, Å.	Atoms	Angle, deg.
Br <sub>1</sub> -Br <sub>2</sub>	4.555 ± 0.005	O <sub>2</sub> -Mg-Br <sub>2</sub>	87.36 ± 0.3
Br <sub>1</sub> -Br <sub>2</sub> (II)	4.438 ± 0.005	O <sub>2</sub> -Mg-Br <sub>2</sub> (III)	88.48 ± 0.3
Br <sub>2</sub> -Br <sub>2</sub> (II)	4.516 ± 0.003	O <sub>2</sub> -Mg-Br <sub>1</sub>	86.61 ± 0.3
Br <sub>1</sub> -Mg	2.613 ± 0.009	O <sub>2</sub> -Mg-O <sub>1</sub>	179.80 ± 0.7
Br <sub>2</sub> -Mg	2.617 ± 0.008	Br <sub>1</sub> -Mg-Br <sub>2</sub>	121.14 ± 0.3
Br <sub>1</sub> -Mg (II)	2.578 ± 0.008	Br <sub>1</sub> -Mg-Br <sub>2</sub> (III)	117.53 ± 0.3
Br <sub>1</sub> -O <sub>2</sub>	3.192 ± 0.002	Mg-Br <sub>1</sub> -Mg (I)	75.93 ± 0.4
Br <sub>1</sub> -O <sub>2</sub>	3.168 ± 0.003	Mg-Br <sub>2</sub> -Mg (III)	75.33 ± 0.3
Br <sub>1</sub> -O <sub>1</sub>	3.45 ± 0.02	Mg-O <sub>1</sub> -C <sub>1</sub>	127.85 ± 6.04
Br <sub>2</sub> -O <sub>1</sub>	3.43 ± 0.02	Mg-O <sub>1</sub> -C <sub>3</sub>	118.85 ± 2.9
Br <sub>2</sub> -O <sub>1</sub> (II)	3.38 ± 0.02	Mg-O <sub>1</sub> -C <sub>2</sub>	136.44 ± 3.6
Mg-O <sub>1</sub>	2.11 ± 0.02	Mg-O <sub>1</sub> -C <sub>4</sub>	114.82 ± 2.4
Mg-O <sub>2</sub>	1.952 ± 0.008		
O <sub>1</sub> -C <sub>1</sub>	1.33 ± 0.09		
O <sub>1</sub> -C <sub>3</sub>	1.44 ± 0.05		

<sup>a</sup> Subscripts correspond to Table I. Roman numeral suffix denotes the subscripted atom has been operated on by the following: (I)  $\bar{x}\bar{y}\bar{z}$ ; (II)  $\bar{y}\bar{x}\bar{z}$ ; (III)  $\bar{y}\bar{x}\bar{z}$ .

from the ethyl Grignard solution produces a reagent in which there is but one magnesium atom per molecule,<sup>15</sup> in contrast to most previous work which has suggested dimers or polymers. Oxidation products such as the one reported here, or perhaps their precursor, are likely

(15) A. C. Vrengdenhal and C. Blomberg, *Rec. trav. chim.*, **82**, 453 (1963).

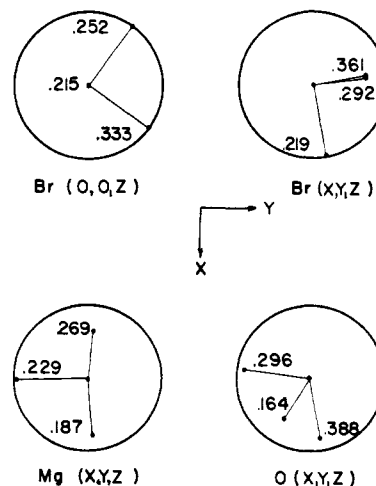


Fig. 3.—Stereograms of anisotropic thermal ellipsoids of Br, Mg, and O atoms on [001]: the magnitudes of the displacements along the axes of the ellipsoids are given in Ångstrom units.

suspects for occluding work on the nature of Grignard reagents, especially in determining their degree of polymerization. Further structural investigations of organomagnesium and organomagnesium halide systems are being made.

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

## The Constitution of the Grignard Reagent, Phenylmagnesium Bromide Dietherate<sup>1</sup>

By G. STUCKY AND R. E. RUNDLE<sup>2</sup>

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In the crystalline state  $C_6H_5MgBr \cdot 2C_4H_{10}O$  consists of a magnesium atom tetrahedrally coordinated to two diethyl ether molecules, a phenyl group, and a bromide atom. There is no evidence of intermolecular interactions between molecules. Some structural properties of crystalline diphenylmagnesium dietherate are briefly discussed.

### Introduction

In an earlier note<sup>3</sup> the partial structure of the Grignard reagent,  $C_6H_5MgBr \cdot 2C_4H_{10}O$ , and evidence suggesting the existence of the same species or possibly a higher etherate in solution were presented. The purpose of this paper is to present in greater detail the structural properties of the Grignard system,  $C_6H_5MgBr$  in diethyl ether.

### Experimental

A 1.5 N solution of  $C_6H_5MgBr$  was prepared by the conventional method of slowly adding a mixture of bromobenzene and diethyl ether to an excess of magnesium. All operations were carried out in previously vacuum- and infrared-dried apparatus under a dry, oxygen-free atmosphere of nitrogen or argon. The procedure used to purify the phenylmagnesium bromide was that described by Strohmeier for diphenylmagnesium dietherate.<sup>4</sup>

The Grignard reagent was transferred under an argon atmosphere to one side of an L-shaped container. Crystallization of the reagent was obtained by cooling the solution to Dry Ice temperature and then allowing the temperature to increase slowly. The excess mother liquid was then decanted to the other side of the L-tube, and pure ether was thermally distilled from

the mother liquor back to the crystals. The crystals were allowed to melt (m.p. 15–20°), and the recrystallization process was repeated several times. By using a partial vacuum and liquid nitrogen to freeze the excess ether and impurities in one side of the L-tube, the liquid reagent was poured into capillaries, n.m.r. tubes, or other suitable containers attached directly to the L-tube. Three samples gave an average Br/Mg ratio of  $1.02 \pm 0.02$ . A positive chemical test was obtained for a metal-carbon bond.<sup>5</sup> Because of the volatility of the diethyl ether and entrainment of the ether in the microcrystals, some excess diethyl ether remained in the melt; however, proton magnetic resonance measurements showed that the diethyl ether to phenyl ratio was no greater than 2.17. An ether content lower than 2 moles/mole of phenylmagnesium bromide gave a sirupy substance in which crystallization could not be induced.

Single crystals for X-ray investigation were grown inside a soft glass, thin-walled capillary by cooling with a cold nitrogen gas stream. The transparent crystals were dendritic and thermally distilled inside the capillary. To minimize the distillation, the crystals were grown with the long crystal axis at a right angle to the nitrogen stream; the dimensions of the crystals still changed with time, however, so that the quality of the X-ray was affected.

An ether/methyl ratio of 2.08 to 1 has been found for a similar low temperature crystalline complex of methylmagnesium bromide in diethyl ether. The crystal structure of the related unsolvated derivative,  $[(CH_3)_2Mg]_n$ , has been independently obtained by one of the authors (G. S.) and by E. Weiss of Cyanamid Research in Geneva. This compound has an orthorhombic cell with  $a = 5.96$ ,  $b = 11.44$ ,  $c = 5.44$  Å. (parameters of G. S.),

(1) Contribution No. 1409; work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) (a) Chemistry Department, University of Illinois, Urbana, Ill.; (b) deceased, Oct. 9, 1963.

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

(4) W. Strohmeier, *Ber.*, **88**, 1218 (1955).

(5) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).