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THE CONSTITUTION OF THE GRIGNARD REAGENT VI. THE DEGREE OF ASSOCIATION OF ETHYLMAGNESIUM COMPOUNDS IN 1-ETHOXY-2-METHYLBUTANE

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SUMMARY

The degrees of association of EtMgBr (prepared from ethylbromide and magnesium), Et_2Mg and of a mixture of Et_2Mg and $MgBr_2$ in 1-ethoxy-2-methylbutane are measured at concentrations up to 30 millimolar at 27.3°.

The following conclusions are drawn:

1. Both EtMgBr and Et_2Mg are present in monomer/dimer equilibria, (1) and (2), with $K_1 = 19.1 \pm 1.3$ l/mole and $K_2 = 64.8 \pm 6.3$ l/mole, respectively.
2. $MgBr_2$ reacts with Et_2Mg with formation of EtMgBr.
3. When $MgBr_2$ is added to an excess Et_2Mg, the two species in the solution, *viz.* Et_2Mg and EtMgBr, also complex with each other with formation of (EtMgBr)·(Et_2Mg), constituting an equilibrium, (3), with K_3 about 50 l/mole.

INTRODUCTION

The constitution of organomagnesium compounds in solution depends on the concentration, the organic group, the halogen, and on the solvent[1]. The role of the solvent in Grignard chemistry is in our field of interest, and we have previously measured association numbers of ethylmagnesium compounds in diethyl ether[2] and in tetrahydrofuran[3] at low concentrations (up to 30 millimolar). To obtain more information on the role of the ether in the complexing of organomagnesium compounds the use of (+)(*S*)-1-ethoxy-2-methylbutane would probably be fruitful, since the specific optical activity of the ether is considerably enhanced by complexation[4], but information had first to be obtained on the degree of association of ethylmagnesium bromide and of diethylmagnesium in 1-ethoxy-2-methylbutane. Magnesium bromide appears to be almost insoluble in this ether.

EXPERIMENTAL

All experiments are carried out in a fully closed glass apparatus under extreme exclusion of oxygen and moisture, using the same technique as described previously[2,3].

EtMgBr is prepared from ethyl bromide and sublimed magnesium crystals in 1-ethoxy-2-methylbutane in the manner described previously[2], where diethyl ether was used as the solvent. Beside ethylmagnesium bromide, 7 mole% magnesium bromide is present in solution, as deduced from the determination of the amount of basic and total magnesium in a sample by titration with standard acid and Complexon III.

Et_2Mg is prepared from ethylmagnesium bromide in diethyl ether, by adding 1.25 equivalents of dioxane. The clear solution of diethylmagnesium is decanted from the white precipitate, and the solvent evaporated, after which the remaining white solid material is heated at 150° for six hours in high vacuum (obtained by cooling part of the apparatus with liquid nitrogen) to free the diethylmagnesium from residual solvent. It is then dissolved in 1-ethoxy-2-methylbutane. This solution also contains 1–3 mole% of magnesium bromide.

$MgBr_2$ is prepared from sublimed magnesium crystals and 1,2-dibromoethane in diethyl ether. Magnesium bromide was freed from solvent in the way described for diethylmagnesium.

The *association numbers* are determined by measuring the rate of quasi-isothermal distillation of pure 1-ethoxy-2-methylbutane to a solution of ethylmagnesium compounds in the same solvent, using an apparatus developed in this laboratory[5]: A silver wire gauze evaporator, suspended on a thin quartz fibre spiral is wetted with the pure solvent. Distillation of the solvent from the evaporator to the solution causes loss of weight of the evaporator. The apparent rate of the rise of the evaporator, S_a (in mm/hour), which is measured with a cathetometer, depends on the number of particles present in solution. The standard rate S_s (in mm/hour/mmole/litre) is obtained by calibrating the apparatus for this solvent with triphenylmethane as the solute, which is assumed to be monomeric in the concentration range used. The theoretical rate of the rise of the evaporator S_{th} (in mm/hour) is then given by S_s multiplied with the theoretical concentration of monomeric particles (Et_2Mg or EtMgBr). The association number i is given by S_{th}/S_a. All measurement are carried out at 27.3°.

RESULTS AND DISCUSSION

A. The association number of ethylmagnesium bromide in 1-ethoxy-2-methylbutane

To 1-ethoxy-2-methylbutane are added six equivalent portions of ethylmagnesium bromide. After the addition of each portion S_a (see *Experimental*) is determined. The results, listed in Table 1, indicate, that at low concentrations a considerable number of particles containing more than one magnesium atom is present in

TABLE 1

Concn. EtMgBr (mmol/l)	S_a	S_{th}	i	x	K_1
4.65	0.354	0.380	1.07	0.137	19.7
9.30	0.679	0.761	1.12	0.215	18.8
13.95	0.994	1.141	1.15	0.258	16.8
18.60	1.277	1.522	1.19	0.322	18.8
23.25	1.549	1.902	1.22	0.371	20.2
27.90	1.823	2.283	1.25	0.402	20.3

solution. The data can be interpreted by assuming the equilibrium (1):

$$\underset{c(1-x)}{2\,EtMgBr} \overset{K_1}{\leftrightarrows} \underset{\frac{1}{2}\cdot c\cdot x}{(EtMgBr)_2} \tag{1}$$

At each concentration, $x=2(S_{th}-S_a)/S_{th}$ and $K_1=1000\cdot x/2\cdot c\cdot(1-x)^2$ (c in millimoles/litre), thus at each concentration x and K_1 can be calculated, giving a mean value for K_1 of 19.1 ± 1.3 l/mole (see Table 1)*.

These data are not consistent with an assumption that trimeric EtMgBr is present in solution along with monomeric and dimeric species. However they do not exclude the existence of two dimeric species containing a different number of ether molecules in the complex**.

The existence of equilibria in which $MgBr_2$ is present, *e.g.*:

$$Et_2Mg + MgBr_2 \leftrightarrows Et_2Mg\cdot MgBr_2$$

is very unlikely, since magnesium bromide is almost insoluble in this solvent. The results can thus be interpreted as evidence for the existence of EtMgBr in this ether. In the light of evidence for the existence of EtMgBr in other solvents[6] this conclusion is not surprising.

The high degree of association of ethylmagnesium bromide in this ether, as compared with, *e.g.*, diethyl ether and tetrahydrofuran, can be related to the lower basicity of this ether: in a complex of a molecule of EtMgBr with one or more 1-ethoxy-2-methylbutane molecules the ether can be replaced more easily by another molecule of EtMgBr (under formation of a dimer) than is the case when diethyl ether or THF is used as the solvent.

B. The association number of Et_2Mg in 1-ethoxy-2-methylbutane

The association number for diethylmagnesium was determined as described under *A*. For the equilibrium (2) x and K_2 can be calculated (see Table 2*A*), giving a mean value for K_2 of 64.8 ± 6.3 l/mole.

$$2\,Et_2Mg \overset{K_2}{\leftrightarrows} (Et_2Mg)_2 \tag{2}$$

From a duplicate experiment, using diethylmagnesium from another batch, the result was K_2 (mean) $=64.6 \pm 3.8$ l/mole (see Table 2*B*).

It is remarkable that the degree of association of diethylmagnesium is higher than that of ethylmagnesium bromide. Since halogen is thought to be a better bridging group than ethyl, the contrary was expected, and has been shown to be the case with diethyl ether as the solvent[7].

The present results indicate that the degree of association of organomagnesium

* Since the measurements are carried out at very low concentrations the concentration of the ether can be assumed to be constant, and is neglected.

** In this case two equibria will be present in solution:

$$2\,M \overset{K'}{\leftrightarrows} D' \overset{K''}{\longleftrightarrows} D''$$

with $K_1 = K'\cdot(1+K'')$. K' and K'' cannot be calculated separately.

TABLE 2

Concn. Et_2Mg (mmol/l)	S_a	S_{th}	i	x	K_2
A					
2.37	0.178	0.200	1.12	0.220	76.2
4.75	0.342	0.399	1.16	0.286	59.0
7.12	0.488	0.599	1.23	0.371	65.7
9.49	0.635	0.798	1.25	0.409	61.5
11.87	0.777	0.998	1.29	0.443	60.1
14.24	0.904	1.197	1.32	0.490	66.0
B					
5.16	0.370	0.428	1.16	0.271	49.4
10.32	0.671	0.856	1.28	0.432	65.0
15.47	0.962	1.284	1.33	0.502	65.2
20.63	1.258	1.712	1.36	0.530	58.3
25.79	1.513	2.140	1.41	0.586	66.3
30.95	1.774	2.567	1.45	0.618	68.4

compounds is influenced not only by the nature of the organic group and of the halogen which influences the electropositivity of the magnesium atom, but also by the electronic and steric requirements of the ether.

C. The association number of a mixture of Et_2Mg and $MgBr_2$ in 1-ethoxy-2-methylbutane

Solvent-free magnesium bromide, to a final concentration of 15.04 mmoles/litre, was added in six equivalent portions to a solution of diethylmagnesium in 1-ethoxy-2-methylbutane in a concentration of 14.24 mmoles/litre. After each addition S_a was determined (see Table 3*A*). For the solution finally obtained, containing 29.28 mg-atom Mg/litre, S_a (which is 1.945 mm/h) has almost the same value as S_a for a comparable solution of ethylmagnesium bromide (see Table 1, after extrapolation: 1.90

TABLE 3

Concn. $MgBr_2$ added (mmol/l)	S_a	S_{th}	i	K_3
A				
0	0.904	1.197	1.32	
3.01	1.133	1.450	1.28	61.2
6.02	1.376	1.703	1.24	39.4
9.02	1.572	1.956	1.24	52.2
12.03	1.762	2.209	1.25	82.4
15.04	1.945	2.462	1.27	
B				
0	1.774	2.567	1.45	
3.23	2.025	2.835	1.40	48.5
6.46	2.240	3.103	1.38	55.2
9.68	2.498	3.371	1.35	37.7

mm/h). Thus measurements of the degree of association reveal no difference between a Grignard reagent prepared from ethylbromide and magnesium and that made from a 1 : 1 mixture of diethylmagnesium and magnesium bromide in this solvent. Furthermore it should be emphasized that magnesium bromide is only soluble in this solvent when diethylmagnesium is present. The most reasonable explanation is that magnesium bromide reacts completely with an equivalent amount of diethylmagnesium with formation of ethylmagnesium bromide (EtMgBr). When the amount of added $MgBr_2$ is smaller than 14.24 mmoles/litre, two species are present in solution, Et_2Mg and EtMgBr. However it is not possible to interprete the results listed in Table 3*A* on the basis of the existence of the two independent monomer/dimer equilibria (1) and (2), with $K_1 = 19.1$ l/mole and $K_2 = 64.8$ l/mole. Complexing between Et_2Mg and EtMgBr must also be postulated and thus three equilibria (1), (2), and (3), have to be considered in dilute solution.

$$2\ \mathrm{EtMgBr} \overset{K_1}{\rightleftharpoons} (\mathrm{EtMgBr})_2 \tag{1}$$

$$2\ \mathrm{Et_2Mg} \overset{K_2}{\rightleftharpoons} (\mathrm{Et_2Mg})_2 \tag{2}$$

$$\mathrm{Et_2Mg} + \mathrm{EtMgBr} \overset{K_3}{\rightleftharpoons} (\mathrm{EtMgBr})\cdot(\mathrm{Et_2Mg}) \tag{3}$$

Since K_1 and K_2 are known, K_3 can be calculated (see Table 3*A*), giving a mean value for K_3 of 58.8 l/mole.

From the results of a duplicate experiment, in which magnesium bromide is added to a solution containing 30.95 mmoles/litre diethylmagnesium, the mean value for K_3 is calculated to be 47.1 l/mole (see Table 3*B*), which is fair agreement in view of the indirect way in which K_3 is obtained.

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REFERENCES

1 B. J. WAKEFIELD, *Organometal. Chem. Rev.*, 1 (1966) 131.
2 A. D. VREUGDENHIL AND C. BLOMBERG, *Rec. Trav. Chim. Pays-Bas*, 82 (1963) 453.
3 A. D. VREUGDENHIL AND C. BLOMBERG, *Rec. Trav. Chim. Pays-Bas*, 82 (1963) 461.
4 P. VINK, C. BLOMBERG, A. D. VREUGDENHIL AND F. BICKELHAUPT, *Tetrahedron Lett.*, (1966) 6419.
5 (a) V. VAN VULPEN AND J. COOPS, *Rec. Trav. Chim. Pays-Bas*, 85 (1966) 203;
(b) A. VAN VULPEN, Thesis, Vrije Universiteit, Amsterdam, 1967.
6 (a) M. B. SMITH AND W. E. BECKER, *Tetrahedron*, 22 (1966) 3027;
(b) T. HOLM, *Acta Chem. Scand.*, 19 (1965) 1819;
(c) for further literature see ref. 1.
7 E. C. ASHBY AND F. WALKER, *J. Organometal. Chem.*, 7 (1967) P17.