Journal of Organometallic Chemistry, 55 (1973) 57–63

THE CONSTITUTION OF THE GRIGNARD REAGENT

VIII. THE STRUCTURE OF COMPLEXES BETWEEN ETHYLMAGNESIUM BROMIDE AND 1-ETHOXY-2-METHYLBUTANE*

P. VINK**, C. BLOMBERG and F. BICKELHAUPT
Chemical Laboratory of the Vrije Universiteit, De Lairessestraat 174, Amsterdam (The Netherlands)
(Received October 30th, 1972)

SUMMARY

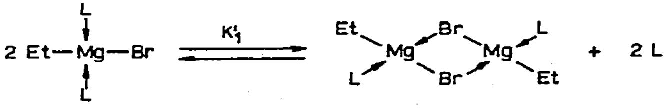
From measurements of the degree of association and of the optical rotation of solutions of ethylmagnesium bromide in (+)(*S*)-1-ethoxy-2-methylbutane [(+)-(*S*)-L] and benzene it is concluded that these solutions contain the species $EtMgBr \cdot 2L$ (I), $(EtMgBr)_2 \cdot 3L$ (III) and $(EtMgBr \cdot L)_2$ (II) which have molecular rotations $[M]_D^{25}$ of 3.79°, 5.92° and 4.26° respectively. Equilibrium constants of 103 mole/l and 1.41 mole/l at 25°C were calculated for the equilibria between these species.

INTRODUCTION

In a previous communication[2] it was demonstrated that in 1-ethoxy-2-methylbutane (L) as solvent ethylmagnesium bromide exists in a monomer–dimer equilibrium (1) with $K_1 = 19.1 \pm 1.3$ l/mole.

$$2\ EtMgBr \overset{K_1}{\rightleftarrows} (EtMgBr)_2 \qquad (1)$$

Assuming the coordination number of magnesium to be four and taking bromine as the bridging atom in the dimer, equilibrium (1) can be extended to



(I) (II)

(1′)

of which equilibrium the constant K'_1 is:

$$K'_1 = K_1 \times [L]^2 \qquad (2)$$

At the low concentrations of our measurements (less than 30 m*M*) [L] has a mean

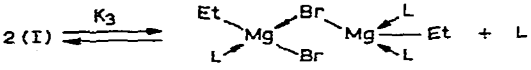
---

* Part of the Ph.D. thesis of P. Vink (ref. 1), which is available on request.

** Present address: Centraal Laboratorium TNO, P.O. Box 217, Delft, The Netherlands.

value of 6.545 mole/l, which leads to $K'_1 = 818.2$ mole/l. In order to investigate the different types of complexes and equilibria present in the solution at higher concentrations (up to 4 *M*) we have carried out experiments using optically active L. It has been shown[3] that the specific rotation of complexed (+)(*S*)-L is considerably higher than the specific rotation of uncomplexed (+)(*S*)-L. It was hoped that from measurements of the optical rotations of solutions of ethylmagnesium bromide complexed with optically active L more information on the complexes in solution might be obtained.

From the results of these measurements no consistent values for the molecular rotation of the complexes involved in equilibrium (1') could be calculated. Therefore the existence of more than one dimeric species had to be considered. On the basis of association measurements mentioned above this possibility could not be excluded[2]. The most plausible structure for another dimeric species is a tri-etherated dimeric Grignard compound (III) participating in equilibria (3) and (4).



(III)

(3)

$$\text{(III)} \overset{K_4}{\rightleftharpoons} \text{(II)} + \text{L} \tag{4}$$

The relation between the equilibrium constants K_1, K_3 and K_4 is given by:

$$K_1 = K_3 \frac{([\mathrm{L}] + K_4)}{[\mathrm{L}]^2} \tag{5}$$

or with $[\mathrm{L}] = 6.545$ mole/l:

$$K_3 \cdot (6.545 + K_4) = 818.2 \text{ mole/l} \tag{6}$$

As will be shown in the following, on the basis of the above-mentioned assumption, interpretation of the results obtained from the measurements of the optical rotation was possible. The values for K_3 and K_4 indicate that compound (III) actually is a major constituent of the solution of ethylmagnesium bromide in L.

RESULTS

Use was made of (+)(*S*)-L with $[\alpha]_D^{25}$ +0.95° which is 92.5% of the maximal rotation; the impurity was 1-ethoxy-3-methylbutane which is of comparable basicity.

Measurements were performed on two types of solutions: one containing EtMgBr and (+)(*S*)-L in a 1/1 ratio in benzene as the solvent (A) and one containing EtMgBr in pure (+)(*S*)-L as the solvent (B).

(*A*). To a solution of 6.83 mmol of EtMgBr (containing 0.18 mmol Et_2Mg) and 7.30 mmol (+)(*S*)-L in 23.08 ml benzene small portions of (+)(*S*)-L were added and the rotation of the solution was measured. The results are given in Table 1.

By the method of freezing point depression it was found that the solution of a 1/1 mixture of EtMgBr and L in benzene contains almost exclusively dimeric particles (see Experimental part). It was also found that although the specific optical

TABLE 1

OPTICAL ROTATIONS OF BENZENE SOLUTIONS OF ETHYLMAGNESIUM BROMIDE CONTAINING INCREASING AMOUNTS OF (+)(*S*)-1-ETHOXY-2-METHYLBUTANE

Expt. no.	*[EtMgBr]*	*[L]*	*[L]/[EtMgBr]*	$\alpha_D^{25\,a}$
1	0.296	0.316	1.068	1.755
2	0.290	0.442	1.524	1.807
3	0.284	0.565	1.989	1.873
4	0.277	0.713	2.574	1.925
5	0.269	0.892	3.316	1.993
6	0.261	1.059	4.057	2.008
7	0.245	1.389	5.669	2.080
8	0.220	1.912	8.691	2.136

[a] For the rotation of L see text. Length of the polarimeter tube is 2.98 dm.

TABLE 2

THE OPTICAL ROTATIONS OF SOLUTIONS OF ETHYLMAGNESIUM BROMIDE IN (+)(*S*)-1-ETHOXY-2-METHYLBUTANE AT DIFFERENT CONCENTRATIONS

[EtMgBr]	α_D^{25}	*[EtMgBr]*	α_D^{25}	*[EtMgBr]*	$\alpha_D^{25\,a}$
0	0.59	1.223	3.31	2.206	5.38
0.111	0.86	1.298	3.47	2.372	5.71
0.224	1.08	1.397	3.70	2.546	5.90
0.345	1.32	1.429	3.77	2.719	6.27
0.502	1.67	1.586	4.11	2.875	6.54
0.565	1.83	1.722	4.33	3.031	6.66
0.702	2.11	1.770	4.53	3.214	6.95
0.736	2.17	1.847	4.67	3.326	7.05
0.846	2.46	1.938	4.86	3.373	7.03
0.956	2.62	2.011	5.01	3.631	7.35
1.053	2.87	2.077	5.13	3.743	7.45
1.130	3.07	2.189	5.39		

[a] For the purity of L see text. Length of the polarimeter tube is 0.846 dm.

rotation of L in benzene is concentration independent the value of [α] of L dissolved in benzene is lower than [α] for pure L, 0.855° and 0.943° respectively (92.5 % optical purity).

(*B*). The optical rotations of solutions of ethylmagnesium bromide in (+)(*S*)-L were measured at different concentrations. The results are given in Table 2.

DISCUSSION

The equations for the equilibrium constants K_3 and K_4 are given by:

$$K_3 = y\cdot(a-b-x-y)/x^2 \tag{7}$$

$$K_4 = (b-x-2y)\cdot(a-b-x-y)/2y \tag{8}$$

where x and y represent the unknown concentrations of (I) and (II) respectively and

a and b represent the known (formal) concentrations of L and EtMgBr. The relation between K_3 and K_4 is given by eqn. (6).

In order to solve these equations more information is required on the concentrations of each of the ethylmagnesium bromide species (I), (II) and (III). Such information is obtained by measuring the optical rotations of the solutions of ethylmagnesium bromide in benzene in the presence of (+)(*S*)-L (Experiment A); from these rotations it would be possible to calculate x and y if the molecular rotations[4] $[M]_{(I)}$, $[M]_{(II)}$ and $[M]_{(III)}$ of compounds (I), (II) and (III) were known.

The value for $[M]_{(II)}$ follows from Table 1: the rotation of a benzene solution of (II) at a concentration of 0.296/2 mole/l (it was demonstrated that the solution contains largely dimeric particles) is 1.74° (by extrapolation of the given values to a 1/1 ratio [L]/[EtMgBr]). This leads to $[M]_{(II)} = 11.756°$ ($l = 2.98$ dm).

To determine the values for $[M]_{(I)}$ and $[M]_{(III)}$ it is assumed that the increase in molecular rotations, $[M]_c$, of (I) and (III), formed by consecutive complexation of (II) with a molecule of (+)(*S*)-L, is constant for each complexed molecule of L. This can be expressed in the following equations:

$$[M]_{(III)} = [M]_{(II)} + [M]_c = 11.756 + [M]_c \qquad (9)$$

$$[M]_{(I)} = ([M]_{(II)} + 2[M]_c)/2 = (11.756 + 2[M]_c)/2 \qquad (10)$$

If it is assumed that these values for the molecular rotations are constant and concentration independent for each species, the experimentally found optical rotation of the solution, α_{exp} is the result of the contribution of each of the three species (I), (II) and (III) and of L:

$$\alpha_{exp} = (b - x - 2y/2)[M]_{(II)} + y([M]_{(II)} + [M]_c) + x([M]_{(II)} + 2[M]_c)/2$$
$$+ (a - b - x - y)[M]_o \qquad (11)$$

in which $[M]_o$ is the molecular rotation of the uncomplexed solvent (+)(*S*)-L, dissolved in benzene, which value is 0.297° under these conditions ($l = 2.98$ dm; 92.5% rotation) (see Experimental part).

By assuming certain values for one of the constants, *e.g.* for K_3, the other unknown values in eqns. (6)–(8) and (11) (at each α_{exp}) can be evaluated. It is assumed that the value for K_3 that leads to the lowest standard deviation in any of the other constants is the correct one. The results of such calculations indicate that $K_3 = 103$ mole/l with $K_4 = 1.41$ mole/l and $[M]_c = 4.543°$. For standard length of the polarimetertube of 1 dm the following $[M]$-values can be calculated: $[M]_c = 1.525°$, $[M]_{(I)} = 3.50°$, $[M]_{(II)} = 5.47°$ and $[M]_{(III)} = 3.94°$; when corrected for 92.5% optical purity of the (+)(*S*)-L used in these experiments, the values for the optically pure complexes are $[M]_c = 1.65°$, $[M]_{(I)} = 3.79°$, $[M]_{(II)} = 5.92°$ and $[M]_{(III)} = 4.26°$, all at 25°C.

The correctness of the assumptions on which the above mentioned calculations were made, was checked on and proven by the results of experiment B: assuming that EtMgBr forms the same complexes in pure L with the same equilibrium constants, it should be possible to calculate the optical rotation of a solution of EtMgBr in pure (+)(*S*)-L at any given concentration. The results of such calculations are given in Table 3. In Fig. 1 these values are plotted against the concentration; Fig. 1 shows that the calculated curve compares extremely well with the values which were found experimentally for the optical rotations.

TABLE 3

CALCULATED OPTICAL ROTATIONS OF SOLUTIONS OF EtMgBr IN (+)(*S*)-1-ETHOXY-2-METHYLBUTANE (92.5% ROTATION)[a]

[EtMgBr]	α_{calc}	[EtMgBr]	α_{calc}	[EtMgBr]	α_{calc}
0.1	0.85	1.0	2.88	2.6	6.06
0.2	1.09	1.2	3.33	2.8	6.38
0.3	1.33	1.4	3.74	3.0	6.69
0.4	1.55	1.6	4.17	3.2	6.97
0.5	1.78	1.8	4.57	3.4	7.22
0.6	2.01	2.0	4.96	3.6	7.47
0.7	2.23	2.2	5.34	3.8	7.60
0.8	2.45	2.4	5.72	4.0	7.77
0.9	2.67				

[a] In order to make possible a comparison between the calculated rotations and the experimentally found ones (Table 2) it has to be considered that (a) the length of the polarimeter tube was 2.98 dm in experiment A and 0.846 dm in experiment B, and (b) the molecular rotation of L, $[M]_0$, in benzene is 0.297° while this value is 0.326° for pure L. Thus the calculated rotations have been multiplied by $(0.846 \times 0.326)/(2.98 \times 0.297) = 0.310$.

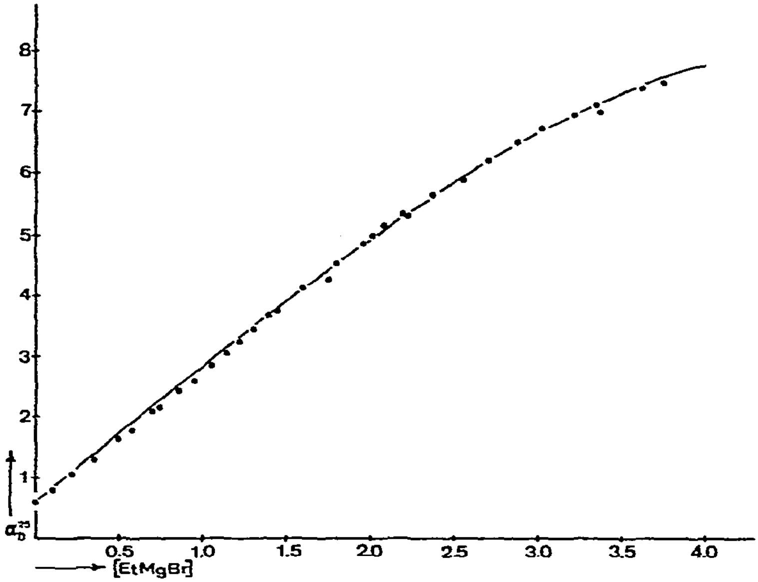


Fig. 1. Plot of optical rotations *versus* the concentration of ethylmagnesium bromide in (+)(*S*)-1-ethoxy-2-methylbutane; dots indicate rotations observed, the solid line indicates calculated rotations.

In the same way as that elaborated for the equilibria containing two different dimeric species, calculations were performed for equilibrium (1′) with $K'_1 = 818.2$. No consistent results were obtained.

CONCLUSION

The present investigation proves that, at least in the weakly basic solvent 1-

ethoxy-2-methylbutane, there is stepwise solvation of a dimer, containing two solvent molecules (II), via a dimer, containing three solvent molecules (III) to a monomer with two solvent molecules (I), as represented by eqns. (3) and (4). This process appears to be kinetically fairly straightforward, and there is no reason why it should not hold for all monomer–dimer equilibria of organomagnesium compounds in basic solvents. However, it is a different question whether the trisolvated dimer of type (III) is a transient intermediate with a low steady state concentration or an important component of the equilibrium mixture.

In the light of the results of Ducom, who, in an investigation of dialkylmagnesium compounds in strongly basic solvents by an NMR technique[5], could not find evidence for the presence of trisolvated dimers analogous to (III), it might be concluded that in these cases the strongly basic solvent competes so efficiently for magnesium with the alkyl bridge that any (III) formed from (II) immediately dissociates to (I).

In the case of a solvent, such as L, which is weakly basic for steric reasons, the Lewis basicity of the bridging group is dominating which results not only in a high dimer–monomer ratio, even at low concentrations, but also in the occurrence of a considerable amount of singly bridged, trisolvated dimer (III).

EXPERIMENTAL

The preparation of solutions of ethylmagnesium compounds was carried out in a fully closed glass apparatus under rigorous exclusion of oxygen and moisture, using the techniques and the starting materials described previously[6].

The solution of ethylmagnesium bromide in benzene and 1 molar equivalent of (+)(*S*)-L used in Experiment A was prepared by the reaction of 10 mmol EtBr with sublimed magnesium crystals in 24.8 ml benzene and about 10 mmol (+)(*S*)-L ($[\alpha]_D^{25} = 0.95°$, for the preparation see ref. 7). After removal of the gaseous side-products and formation of a white flocculated precipitate on standing, the clear supernatant solution was decanted.

The solution used in Experiment B, consisting of diethylmagnesium and 0.96 molar equivalents of magnesium bromide in L, was prepared by shaking a solution of Et_2Mg in (+)(*S*)-L (for the preparation see ref. 3) with a known amount of ether-free $MgBr_2$; when an excess of Et_2Mg is present, the $MgBr_2$ dissolves completely. The results of the association measurements indicate that in this solution essentially EtMgBr is present (the slight excess of Et_2Mg is neglected).

Experiment A

A known amount of a solution of ethylmagnesium bromide in (+)(*S*)-L was contained in a closed glass apparatus to which a quartz polarimeter tube of 2.98 dm was connected. The rotation of this solution was measured with a Zeiss Halbschatten polarimeter with an accuracy of ±0.02°, while the whole apparatus was placed in a water-bath, which was kept at 25.0±0.1°. To this apparatus eight small vessels containing a known amount of L were connected. These were separated from the Grignard solution by a thin glass wall. With the aid of a magnet and a breaker consisting of a small piece of iron fused into glass the glass-walls can be broken one by one. The ether was mixed with the Grignard solution and the rotation of the obtained solution was measured. At the end of the experiments the apparatus was opened, the solution hydrolysed and the amount of basic and total Mg determined by titration. Since the ratio EtMgBr/L is known (see below) also the concentration of (+)(*S*)-L in the starting solution is known. Results are listed in Table 1.

In a sample of the solution used in the previous experiment the amount of EtMgBr and Et_2Mg is determined by titration after hydrolysis to be 0.1016 mole/l and 0.0041 mole/l, respectively. The concentration of L is determined by GLC-analysis: a known amount of ethyl propyl ether is added to the sample after hydrolysis. The column used is calibrated with known mixtures of L and ethyl propyl ether. In this manner the amount of L is found to be 0.1057 mole/l. The same ratio EtMgBr/L is also obtained from the NMR-spectrum of this solution by comparing the signal intensities of the two methylene protons of EtMgBr and the four α-methylene protons of L.

The number of particles present in solution is determined by measuring the lowering of the freezing point of benzene. A double-walled glass vessel containing the Grignard solution is cooled until crystals are formed. These crystals are allowed to melt by raising the temperature very moderately, while the solution is stirred. The melting point is measured externally with the aid of a thermistor of about 1000 Ω at 25°, placed in a tube which is in the solution and in which a drop of mercury guarantees a good contact. Its resistance is measured via a Wheatstone bridge. The apparatus is calibrated using triphenylmethane as the solute.

Experiment B

The solution of EtMgBr in (+)(*S*)-L was brought into a glass apparatus, consisting of a calibrated tube and a quartz polarimeter tube of 0.846 dm. Solutions of any desired concentration were obtained in the polarimeter tube compartment by pouring and distillation. At each concentration the rotation of the solution is determined at $25.0 \pm 0.1°$ (see Table 2). Of a sample of the original solution, the weight and the concentration of EtMgBr is determined; from these experimental data the concentration of L can be calculated. From the change of the volume the concentration of L at any other concentration of the EtMgBr solution can be calculated.

ACKNOWLEDGEMENT

The authors wish to express their gratitude to Messrs. L. Vroom and R. Hoogeman for preparing the glass apparatus and to Mr. G. Schat for his assistance in performing the measurements.

REFERENCES

1 P. Vink, Ph.D. thesis, Vrije Universiteit, Amsterdam, 1969.
2 P. Vink, C. Blomberg, A. D. Vreugdenhil and F. Bickelhaupt, *J. Organometal. Chem.*, 15 (1968) 273.
3 P. Vink, C. Blomberg, A. D. Vreugdenhil and F. Bickelhaupt, *Tetrahedron Lett.*, (1966) 6419.
4 S. Kirschner, *Coordin. Chem. Rev.*, 2 (1967) 470, and references cited therein.
5 J. Ducom, *Bull. Soc. Chim. Fr.*, (1971) 3529.
6 A. D. Vreugdenhil and C. Blomberg, *Recl. Trav. Chim. Pays-Bas*, 82 (1963) 453, 461.
7 C. Blomberg and J. Coops, *Recl. Trav. Chim. Pays-Bas*, 83 (1964) 1083.