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THE CONSTITUTION OF THE GRIGNARD REAGENT

VII. THE DEGREE OF ASSOCIATION OF ETHYLMAGNESIUM COMPOUNDS IN DIISOPROPYL ETHER

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SUMMARY

The degrees of association of ethylmagnesium bromide, diethylmagnesium and of a mixture of diethylmagnesium and magnesium bromide in the weakly basic solvent diisopropyl ether have been measured at concentrations up to 0.040 *M* at 27.7°. It is concluded that: (1), ethylmagnesium bromide is present as a dimer, (2), diethylmagnesium is present in a dimer–tetramer equilibrium with $K_1 = 24.9$ l/mol, and (3), when magnesium bromide is added to an excess of diethylmagnesium it reacts to form ethylmagnesium bromide. Diethylmagnesium and ethylmagnesium bromide are also in equilibrium with ($EtMgBr \cdot Et_2Mg$), with K_3 approximately 2.5.

INTRODUCTION

In Grignard chemistry strongly basic solvents have attracted much attention because of their solvating power, which has a marked influence on the physical and chemical properties of the organomagnesium compounds*. There are few reports, however, on the physical properties of organomagnesium compounds in weakly basic solvents. In a previous report from this laboratory[1] it was demonstrated that the degree of association of ethylmagnesium compounds in the weakly basic 1-ethoxy-2-methylbutane was considerable even at concentrations as low as 0.030 *M*. Furthermore it was found that diethylmagnesium had a higher degree of association than ethylmagnesium bromide in the same ether, which is rather surprising, because the bromine atom is considered to be a better bridging group than the ethyl group.

We show below that in the even more weakly basic solvent diisopropyl ether[2], ethylmagnesium bromide is still less associated than diethylmagnesium.

EXPERIMENTAL

All experiments were carried out in a fully closed glass apparatus, with rigorous exclusion of oxygen and moisture, using the same technique as described previously[3,4].

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* The term "basic" and "basicity" refer to coordination with Lewis acids.

Ethylmagnesium bromide

Ethylmagnesium bromide was prepared from ethyl bromide and sublimed magnesium crystals (Specpure^R from Johnson Matthey Chemicals Ltd., London) in the manner described previously for diethyl ether solutions[3]. The solubility of ethylmagnesium bromide in diisopropyl ether at 25° was approximately 0.7 *M*; the solution contained a slight excess of diethylmagnesium, as was demonstrated by titration of a hydrolysed aliquot of the solution with hydrochloric acid, followed by titration with EDTA[5]. On standing, magnesium bromide crystallised out of the saturated solution of ethylmagnesium bromide, but the crystals readily redissolved on warming.

Diethylmagnesium

Diethylmagnesium was prepared from diethylmercury (GLC pure on an SE 30/Chromosorb W 80–100 column) on heating with magnesium crystals at 90° overnight[6]. The dry material was extracted with diisopropyl ether in which solvent diethylmagnesium is soluble up to about 0.070 *M* at 25°. Qualitative analysis of a residue of such a solution with the aid of dithizone proved the absence of any mercury compound.

Magnesium bromide

Magnesium bromide was prepared from sublimed magnesium crystals and 1,2-dibromoethane in tetrahydrofuran, and was freed from the solvent by heating at 150° during 24 h in vacuum. Magnesium bromide is insoluble in diisopropyl ether.

Association numbers

The association numbers were determined in an apparatus in which the rate of quasi-isothermal distillation of diisopropyl ether to a solution of an organomagnesium compound in the same solvent is measured[7]; S_a (in mm/h), S_s (in mm/h/mmole/l) and S_{th} (in mm/h) are respectively the apparent rate, the standard rate and the theoretical rate of the evaporator. The association number i is given by S_{th}/S_a; all measurements were carried out at 27.7°.

RESULTS AND DISCUSSION

A. The association number of ethylmagnesium bromide in diisopropyl ether

S_a was measured at five different concentrations between 0.0091 *M* and 0.0456 *M* (formal concentrations): at each measurement S_a was about half the value of S_{th} leading to $i=2.00\pm0.02$. So in this concentration range ethylmagnesium bromide is essentially dimeric in diisopropyl ether.

B. The association number of diethylmagnesium in diisopropyl ether

S_a was measured at six different concentrations between 0.0052 *M* and 0.0314 *M* (formal concentrations): i values increased from 2.12 to 2.39. K-values were calculated for different possible equilibria; only for equilibrium (1) constant K-values were obtained; the mean value for K_1 is 24.9 ± 1.3 l/mole.

$$2\,(Et_2Mg)_2 \overset{K_1}{\rightleftharpoons} (Et_2Mg)_4 \qquad (1)$$

C. The association number of a mixture of diethylmagnesium and magnesium bromide in diisopropyl ether

Four equivalent portions of magnesium bromide, each leading to a theoretical concentration (magnesium bromide is insoluble in diisopropyl ether) of 0.00495 *M*, were added to a 0.0314 *M* (formal concentration) solution of diethylmagnesium in diisopropyl ether (*i.e.* the final solution obtained in experiment *B*); the corresponding i-values were 2.20, 2.07, 2.02 and 2.00.

The ready disappearance of crystalline magnesium bromide into the solution of diethylmagnesium indicates that the compounds react with each other according to equation (2) (with $n=2$ or 4).

$$(Et_2Mg)_n + n\ MgBr_2 \rightarrow n\,(EtMgBr)_2 \qquad (2)$$

If it is assumed that the remaining dimeric and tetrameric diethylmagnesium does not interact with dimeric ethylmagnesium bromide, formed by reaction (2), the number of particles in the solution, and hence a hypothetical value of S'_a, can be calculated using the value of $K_1=24.9$ l/mole for equilibrium (1); S'_a deviates +2.6, +4.3, +4.7 and +2.7% respectively from the values for S_a, actually measured.

On the other hand, an equilibrium (3), as was found in 1-ethoxy-2-methylbutane[1], can be assumed to exist between diethylmagnesium and ethylmagnesium bromide on the one side and a complex of both on the other side:

$$(Et_2Mg)_2 + (EtMgBr)_2 \overset{K_3}{\rightleftarrows} 2(Et_2Mg\cdot EtMgBr) \qquad (3)$$

Calculations of K_3 gave the values 0.501, 2.367, 3.243 and 10.110 respectively. On the basis of an assumed intermediate value for K_3 of 2.5 a corresponding value for S''_a could be calculated for each point of measurement; the calculated values for S''_a were in close agreement with S_a (deviation +1.6, +0.1, −0.2 and −0.2% respectively). Thus the assumption of an interaction between diethylmagnesium and ethylmagnesium bromide leads to better agreement with experimental data than neglect of such an interaction. Therefore the existence of equilibrium (3) in diisopropyl ether (as in 1-ethoxy-2-methylbutane) appears very likely, although not too much significance can be assigned to the actual value of $K_3=2.5$.

The composition of the solution after the addition of the fourth portion of magnesium bromide {$[MgBr_2]$ (formal) 19.452 mmole/l; $[Mg_{total}]$ 50.580 mmole/l}, calculated with the aid of the known values of K_1 (24.9 l/mole) and K_2 (2.5) is illustrative: $[(Et_2Mg)_2]$ 1.737 mmole/l, $[(Et_2Mg)_4]$ 0.075 mmole/l, $[(EtMgBr\cdot Et_2Mg)]$ 8.171 mmole/l and $[(EtMgBr)_2]$ 15.366 mmole/l. It indicates that there is little uncomplexed $(Et_2Mg)_2$ left in the solution.

CONCLUSION

The observation that the degree of association of organomagnesium compounds is related to the basicity of the complexing solvent[1] has been substantiated; the weaker the basicity of the solvent the more easily it can be replaced in the complex by another organomagnesium compound, leading to the formation of associated species. Obviously a second molecule of organomagnesium compound and the solvent compete to maintain a coordination number of four for magnesium. It is surprising

TABLE 1

DEGREE OF ASSOCIATION, *i*, OF ETHYLMAGNESIUM COMPOUNDS AT 27° IN 0.030 *M* SOLUTIONS IN DIFFERENT ETHERS

	THF[a]	*Et₂O*[b]	1-*Ethoxy-2-methylbutane*[c]	*i-Pr₂O*
Diethylmagnesium	1.00	1.00	1.45	2.38
Ethylmagnesium bromide	1.00	1.00	1.27	2.00

[a] See ref. 4. [b] See ref. 3. [c] See ref. 1.

that the degree of association of diethylmagnesium is influenced more strongly by the solvent than is that of ethylmagnesium bromide (see Table 1). A possible explanation is that the Lewis basicity of diisopropyl ether towards diethylmagnesium is much less than towards ethylmagnesium bromide, because of specific steric interactions. Probably the fact that diethylmagnesium prefers to complex with ethylmagnesium bromide rather than with itself has also to be related to steric hindrance in diethylmagnesium. Further experiments are in progress to prove the validity of this hypothesis.

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