

BIFUNCTIONAL AND CYCLIC ORGANOMAGNESIUM COMPOUNDS I. PENTAMETHYLENEBIS(MAGNESIUM BROMIDE) AND MAGNESIA-CYCLOHEXANE

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SUMMARY

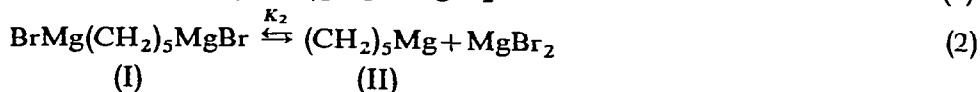
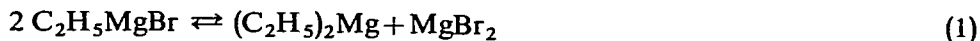
Magnesiacyclohexane, the first example of a magnesiacycloalkane, has been prepared from the corresponding mercury derivative. Association measurements on solutions of magnesiacyclohexane and of mixtures of magnesiacyclohexane and magnesium bromide, in tetrahydrofuran at concentrations up to about 0.03 *M* at 28.25° and 48.50° lead to the following conclusions:

- (1). Magnesiacyclohexane is present in a monomer/dimer equilibrium, with $K(28.25^\circ) = 531 \pm 81$ l/mole and $K(48.50^\circ) = 223 \pm 41$ l/mole.
- (2). In mixtures of magnesiacyclohexane and magnesium bromide a second equilibrium, $(\text{CH}_2)_5\text{Mg} + \text{MgBr}_2 \rightleftharpoons \text{BrMg}(\text{CH}_2)_5\text{MgBr}$, is also established, with $K(28.25^\circ) = 299 \pm 30$ l/mole and $K(48.50^\circ) = 361 \pm 50$ l/mole.
- (3). In tetrahydrofuran the association number, *i*, of an equimolar mixture of magnesiacyclohexane and magnesium bromide is the same as that of the "di-Grignard" reagent prepared from 1,5-dibromopentane and magnesium. This strongly indicates that both solutions are identical. In diethyl ether the "di-Grignard" reagent has the structure of pentamethylenebis(magnesium bromide).

INTRODUCTION

As part of our work on the elucidation of the structure of Grignard reagents¹ we have begun the investigation of bifunctional and cyclic organomagnesium compounds in tetrahydrofuran.

Bifunctional Grignard reagents have often been referred to as intermediates in synthesis², especially of bifunctional and cyclic organometallics (for a recent example see ref. 3). Although the existence of cyclic organomagnesium compounds in reaction mixtures has been suggested by several authors⁴, such compounds have not been thoroughly investigated. By analogy with the Schlenk equilibrium (1) for the Grignard reagent $\text{C}_2\text{H}_5\text{MgBr}$ in tetrahydrofuran⁵, we expected to find equilibrium (2) for the bifunctional Grignard reagent $\text{BrMg}(\text{CH}_2)_5\text{MgBr}$ (I):

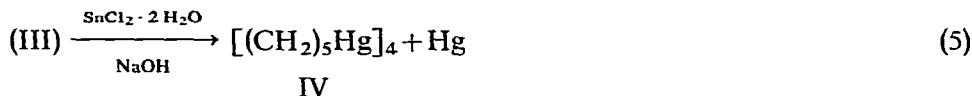
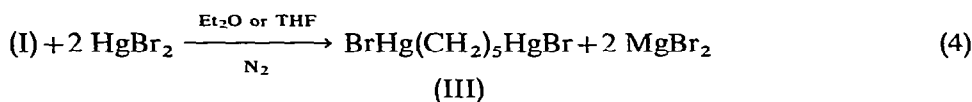
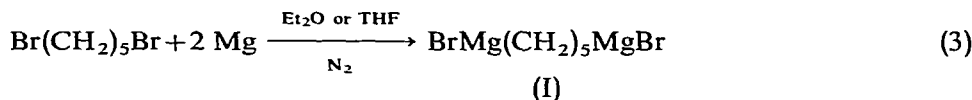


The change in the number of particles in eqn. (2) offers the possibility, not present with (1), of determining the occurrence and position of this equilibrium by association measurements.

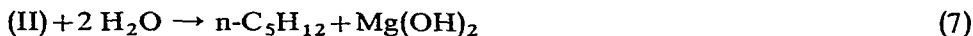
RESULTS AND DISCUSSION

Magnesiacyclohexane

Before investigating equilibrium (2) we decided to study one of its components, *i.e.* magnesiacyclohexane, (II), in more detail. For the preparation of such a dialkylmagnesium compound several different routes are possible. As we wanted to be sure that no trace of magnesium bromide was contaminating the cyclic compound we chose to make it from the corresponding mercurial and magnesium metal, rather than by more usual methods, such as elimination of magnesium bromide from the di-Grignard reagent by crystallization⁶ or by precipitation with dioxane⁷. The sequence of reactions leading to magnesiacyclohexane is summarized in the reaction scheme below. Reactions (3)⁸ and (4)⁸, have been described in the literature; reaction (5) was carried out by analogy with the preparation of mercuracyclopentane⁹.



Because of the extreme susceptibility of all organomagnesium compounds to oxygen and moisture, reaction (6) was carried out in a fully closed and evacuated glass apparatus without stopcocks and ground joints^{6,10}. (IV) turned out to be unstable (mercury was formed on standing) and was therefore subjected to reaction (6) without delay. (IV) has a very low solubility in tetrahydrofuran, but it reacted with an excess of magnesium crystals and disappeared in the course of a few days. Acid-base¹¹ and complexon-III¹² titration of a hydrolyzed aliquot of the clear solution gave a ratio for basic and total magnesium of 1/1, as required for a dialkylmagnesium compound. Evaporation of another aliquot gave a crystalline residue which could be redissolved in tetrahydrofuran. On treatment with water it yielded 100% of n-pentane according to eqn. (7):



We can thus conclude that (II) (or a polymer hereof) was obtained. In order to verify that the monomeric form of (II) was present in solution, we carried out associa-

tion measurements in tetrahydrofuran in the Van Vulpen apparatus¹³ at different concentrations and at two temperatures (for a short explanation see the *Experimental* part). The results, listed in Table 1, can be interpreted by assuming that equilibrium (8) is established.



At each concentration the association constant α and the equilibrium constant K_1 can be calculated from $\alpha = 2(S_{\text{th}} - S_a)/S_{\text{th}}$ and $K_1 = 1000\alpha/2c \cdot (1 - \alpha)^2$ (c in mmole/l). The mean value for K_1 at 28.25° is 531 ± 81 l/mole; at 48.50° it is 223 ± 41 l/mole.

With the aid of the equation $-2.303 RT \cdot \log K = \Delta H - T \cdot \Delta S$, the enthalpy and entropy of dimerization have been calculated: $\Delta H = -8$ kcal/mole ± 3 and $\Delta S = -15$ e.u. ± 9 . These values must be regarded with reserve, because the measurements have been carried out at two temperatures only and the K_1 values have a rather broad range of uncertainty error. Nevertheless, we may conclude that dimerization is exothermic and is accompanied by a negative change of entropy.

TABLE 1

ASSOCIATION MEASUREMENT OF MAGNESIACYCLOHEXANE^a

Concn. total Mg ^{b,c}	Temp.	S_a^d	S_{th}^e	i^f	α	K_1
3.512	28.25°	0.106	0.149	1.41	0.577	459
	48.50°	1.163	0.216	1.33	0.491	270
7.024	28.25°	0.195	0.297	1.52	0.687	499
	48.50°	0.301	0.432	1.44	0.606	278
10.536	28.25°	0.278	0.446	1.60	0.753	586
	48.50°	0.452	0.648	1.43	0.605	184
14.048	28.25°	0.359	0.594	1.65	0.791	645
	48.50°	0.583	0.864	1.48	0.650	189
17.560	28.25°	0.446	0.743	1.67	0.799	563
	48.50°	0.710	1.080	1.52	0.685	197
21.072	28.25°	0.538	0.891	1.66	0.792	434
	48.50°	0.828	1.296	1.57	0.722	222

^a For details see *experimental part*. ^b Concentration in mmoles/litre (this is the theoretical concentration if all particles are monomeric, i.e. contain one magnesium atom). ^c In this case conc. total Mg = conc. basic Mg. ^d S_a = apparent rate in mm/hour. ^e S_{th} (in mm/hour) = conc. $\times S_5/S_5$ (in mm/hour/mmmole/litre) is the standard rate found by calibration of the apparatus with triphenylmethane; $S_5(28.25^\circ) = 0.0423$ $S_5(48.50^\circ) = 0.0615$. ^f Association number $i = S_{\text{th}}/S_a$.

Systems containing -MgBr

With data available for equilibrium (8), it was possible to return to the problem of the Schlenk equilibrium (2) and the determination of its equilibrium constant K_2 . Two experiments were carried out for this purpose. First we measured the association of a solution of (I) prepared from 1,5-dibromopentane and magnesium in tetrahydro-

furan. From the results, listed in Table 2, it is seen that the association number i is between 1.28 and 1.58 in the concentration range used (i is based on the concentration of magnesium atoms in the solution; on this basis a monomeric species with the structure of pentamethylenebis(magnesium bromide) would have $i=2$). This means that dissociation of (I) occurs and that equilibrium (2) does exist. As the monomeric cyclic species (II) resulting from this dissociation can be assumed to be in equilibrium with dimeric species according to equation (8), $K_2 = [I]/[II] \cdot [MgBr_2]$ can be calculated (where $[II]$ is concentration of monomeric magnesiacyclohexane). The mean values from Table 2 are $K_2(28.25^\circ) = 250 \pm 65$ l/mole and $K_2(48.53^\circ) = 300 \pm 92$ l/mole.

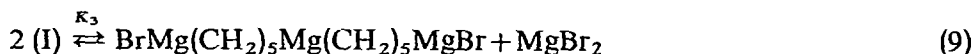
TABLE 2

ASSOCIATION MEASUREMENT OF PENTAMETHYLENEBIS(MAGNESIUM BROMIDE)

For notes see Table 1.

Conc. total Mg ^b	Conc. basic Mg ^b	Temp.	S_a^d	S_{th}^e	i^f	K_2
9.947	4.945	28.25°	0.322	0.421	1.31	213
		48.53°	0.480	0.612	1.28	188
19.894	9.890	28.25°	0.617	0.842	1.36	188
		48.53°	0.877	1.223	1.39	255
29.841	14.835	28.25°	0.888	1.262	1.42	221
		48.53°	1.255	1.835	1.46	291
39.788	19.780	28.25°	1.137	1.683	1.48	283
		48.53°	1.614	2.447	1.52	335
49.735	24.725	28.25°	1.376	2.104	1.53	347
		48.53°	1.940	3.059	1.58	434

Obviously there are in principle other possibilities in this system, notably equilibrium (9), but calculations based on the assumption of the occurrence of (9) are



not consistent with the observed results. Furthermore, we feel that equilibrium (10) can be excluded in tetrahydrofuran because it is not found to be important in diethyl ether (see later).



In a second experiment we added solvent-free magnesium bromide⁶, up to a final concentration of 29.544 mmoles/l in six equivalent portions to a solution of 21.072 mmoles/l of (II) in tetrahydrofuran and measured the association as before (Table 3). Comparison of Tables 2 and 3 shows that the association number i of an equimolar mixture of (II) and magnesium bromide is equal to that of "(I)". In Table 3 this point is reached for 42.144 mg-atoms/l of total Mg; interpolation gives $i=1.49$ at 28.25° and $i=1.53$ at 48.50° for both experiments. We take this as a strong indication

that the two solutions are identical, which means that equilibrium (2) is established from both sides. This conclusion allows the calculation of equilibrium constants from Table 3: $K_2(28.25^\circ) = 299 \pm 30$ l/mole and $K_2(48.50^\circ) = 361 \pm 50$ l/mole. Because of the smaller error limits we slightly prefer the K values of Table 3.

TABLE 3

ASSOCIATION MEASUREMENT OF MIXTURES OF MAGNESIACYCLOHEXANE AND MAGNESIUM BROMIDE
Concentration of basic Mg^b is 21.072 mg-atom/l. For notes see Table 1.

Concn. MgBr ₂ ^b	Concn. total Mg ^b	Temp.	S _a ^d	S _{th} ^e	i ^f	K ₂
4.924	25.996	28.25°	0.680	1.100	1.62	277
		48.50°	1.014	1.599	1.58	364
9.848	30.920	28.25°	0.822	1.308	1.59	343
		48.50°	1.195	1.902	1.59	432
14.772	35.844	28.25°	0.979	1.516	1.55	326
		48.50°	1.401	2.204	1.57	399
19.696	40.768	28.25°	1.148	1.724	1.50	295
		48.50°	1.631	2.507	1.54	350
24.620	45.692	28.25°	1.326	1.933	1.46	265
		48.50°	1.868	2.810	1.50	331
29.544	50.616	28.25°	1.488	2.141	1.44	289
		48.50°	2.131	3.113	1.46	292

It is hardly justifiable to derive thermodynamic parameters from these rather uncertain equilibrium constants (ΔH is approximately +2 kcal/mole, ΔS is approximately +17 e.u. in both cases), but the reaction of magnesium bromide with magnesia-cyclohexane seems to be an endothermic process, a conclusion which is in agreement with the results of Smith and Becker for the system consisting of magnesium bromide and diethylmagnesium in tetrahydrofuran⁵.

Preliminary measurements were carried out on the degree of association of solutions of (I) and of (II) in diethyl ether, which were not free of magnesium bromide. The results were corrected for the known association of magnesium bromide⁶ and indicated that equilibrium (8) exists in the solutions of (II) in diethyl ether as it does in tetrahydrofuran. However, the association number of (I) was found to be about $i=2$. This shows that (I) is present as monomer, and that the Schlenk equilibrium (2) is not established or lies completely over the left in diethyl ether. In this case equilibrium (9) cannot be excluded on the basis of association measurements alone but since it has been shown not to occur in tetrahydrofuran we expect that it is unlikely to be important in diethyl ether.

EXPERIMENTAL

General techniques

The organomagnesium compounds were prepared in a fully closed glass apparatus with rigorous exclusion of oxygen and moisture^{6,10}. Measurements of

association numbers were carried out in the "Van Vulpen apparatus" developed in our laboratory¹³. The rate of quasi-isothermal distillation of pure tetrahydrofuran from a silver wire gauze evaporator to a solution of the organomagnesium compound in the same solvent depends on the number of particles present in solution. This is expressed by the apparent rise of the evaporator, S_a (in mm/hour), which is measured with a cathetometer. The apparatus is calibrated for tetrahydrofuran with triphenylmethane. The calibration leads to the standard rate, S_s (in mm/hour/mole/litre). The theoretical rate of the rise of the evaporator, S_{th} (in mm/hour) is given by S_s multiplied with the theoretical concentration of monomeric particles containing one magnesium atom $[(CH_2)_5Mg$ or $MgBr_2]$. The association number i is then given by S_{th}/S_a . The measurements are carried out at two temperatures.

The concentration of the organomagnesium compounds was determined by acid-base¹¹ and complexon-III¹² titration of an aliquot of the solution and expressed in mg-atoms of magnesium.

Materials

For the preparation of the organomagnesium compounds high purity sublimed magnesium crystals (Johnson, Matthey and Co, Ltd, London) were used. Tetrahydrofuran was purified and degassed in a special glass apparatus⁶. Magnesium bromide was prepared from magnesium crystals and 1,2-dibromoethane in diethyl ether, transferred to ampoules, and freed from solvent by heating the ampoules at 140° for 6 h⁶.

Pentamethylenebis(magnesium bromide), $BrMg(CH_2)_5MgBr$ (I)

1,5-Dibromopentane (11.04 g) was added from an internal dropping-nozzle dropwise to 5.23 g magnesium in 200 ml THF over a 6 h period, while the solution was stirred magnetically. Stirring was continued for 24 h. In addition to the di-Grignard reagent, 8 percent of magnesiumbromide was formed, as revealed by titration. By careful cooling, the excess of magnesium bromide was removed until the ratio of basic Mg to total Mg was 1/2. Hydrolysis of a solution thus obtained gave 98.3% of n-pentane and less than 0.1% of n-decane. This solution was transferred to ampoules and the solvent was evaporated by cooling of the storage vessel. The ampoules were used for the association measurements of the di-Grignard reagent.

Magnesiacyclohexane, $[(CH_2)_5Mg]_n$ (II)

A mixture of mercuracyclohexane (4.5 g), magnesium crystals (4.5 g) and THF (50 ml) was shaken for three days with gentle heating. The insoluble mercuracyclohexane disappeared gradually and a clear solution resulted. This was decanted from magnesium amalgam, and a dithizone-test confirmed the absence of mercury. Titration (acid-base and complexon-III) gave a ratio 1/1 for basic Mg to total Mg. The yield of the magnesium compound, as given by such titration, was quantitative.

Solvent was removed from a sample of the solution and the residual white solid was brought into contact with water vapour. The product, identified by GLC, IR, and NMR as n-pentane, was dried over P_2O_5 and weighed. The yield was 100% as revealed by titration.

Pentamethylenebis(mercury bromide), BrHg(CH₂)₅HgBr (III)

(III) was prepared in 55% yield by Hilpert and Grüttner's method⁸, and after crystallization from toluene, had a melting point of 147–149°. (Found: C, 9.64; H, 1.71; Br, 25.21; Hg, 63.47. C₅H₁₀Br₂Hg₂ calcd.: C, 9.51; H, 1.60; Br, 25.32; Hg, 63.57%.)

Mercuracyclohexane, [(CH₂)₅Hg]₄ (IV)

This compound, m.p. 42°, was obtained as the tetramer in 86% yield by the method of Sawatzky and Wright used for mercuracyclopentane⁹. (Found: C, 22.79; H, 3.48; Hg, 72.59. C₅H₁₀Hg calcd.: C, 22.18; H, 3.72; Hg, 74.0%.) Br was shown to be absent.

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