

THE STRUCTURE OF 1,4-BISORGANOMAGNESIUM COMPOUNDS IN SOLUTION: 1,4-BIS(BROMOMAGNESIO)BUTANE AND (DIMERIC) MAGNESACYCLOPENTANE

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Summary

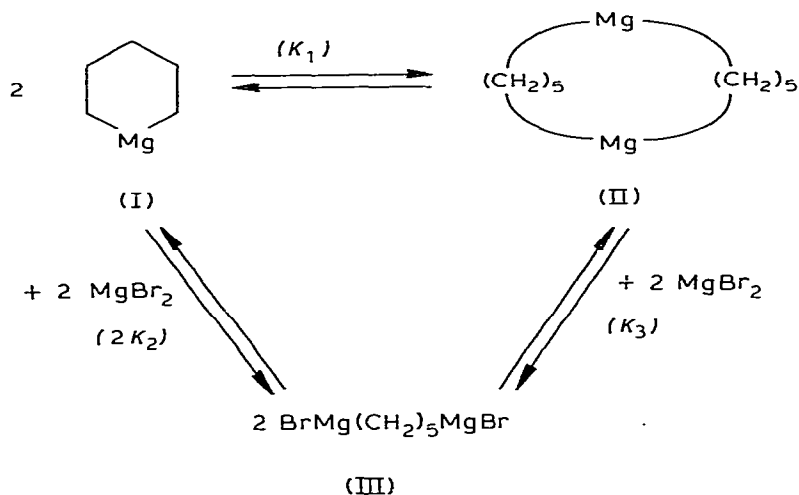
1,4-Bis(bromomagnesio)butane (VI) and magnesacyclopentane (IV) were prepared and investigated as such and in combination with $MgBr_2$ by measuring the degree of association in THF solution at three temperatures. It was established that IV does not exist as such, but is completely dimerized to 1,6-dimagnesacyclodecane (V). A Schlenk equilibrium is established between V and VI with $K_4(28.17^\circ) = 100 \pm 50$, $K_4(39.75^\circ) = 250 \pm 100$ and $K_4(48.84^\circ) = 500 \pm 200$ and the thermodynamic parameters $\Delta H_4 = 15 \text{ kcal mol}^{-1}$ and $\Delta S_4 = 59 \text{ e.u.}$. These values are very close to those of the higher homologue, 1,5-bis(bromomagnesio)pentane (III) and of ethylmagnesium bromide. It is concluded that these di-Grignard reagents behave essentially like the normal monovalent Grignard reagents.

Introduction

For some time, we have been interested in the preparation, structure and application of bifunctional organomagnesium [1] and organozinc compounds [2]. In particular, we have reported [1a, 1c] on a detailed investigation of the structure of magnesacyclohexane (I) which is dimeric in the crystalline state (1,7-dimagnesacyclododecane (II)) and which exists as a monomer-dimer equilibrium in THF solution; the dimer is highly favoured ($K_1(28.25^\circ) = 609 \pm 35 \text{ l mol}^{-1}$; $K_1(48.50^\circ) = 182 \pm 9 \text{ l mol}^{-1}$; $\Delta H = -11.5 \pm 0.8 \text{ kcal mol}^{-1}$; $\Delta S_1 = -25 \pm 3 \text{ e.u.}$) (Scheme 1).

The corresponding Grignard reagent, 1,5-bis(bromomagnesio)pentane (III) is wholly monomeric in diethyl ether, and gives no indications of a Schlenk equilibrium $I + MgBr_2 \rightleftharpoons III$, but in THF this equilibrium is established ($K_2(28.25^\circ) = 300 \pm 30 \text{ l mol}^{-1}$; $K_2(48.50^\circ) = 370 \pm 50 \text{ l mol}^{-1}$; $\Delta H_2 \approx 2 \text{ kcal mol}^{-1}$; $\Delta S_2 \approx 18 \text{ e.u.}$).

We now report our results with the lower homologue of I, magnesacyclopentane (IV), its dimer 1,6-dimagnesacyclodecane (V) and the corresponding Grignard reagent 1,4-bis(bromomagnesio)butane (VI).

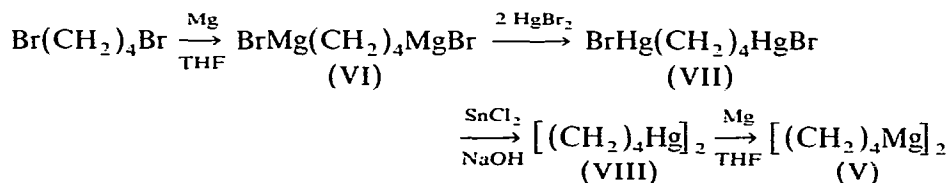


SCHEME 1

Results and discussion

Dialkylmagnesiums can be prepared by several methods. For practical purposes, precipitation of MgBr_2 from the Grignard reagent by dioxane is most convenient; this may, however, be less satisfactory if very pure products are required. In the case of VI, for instance, the solution of IV thus obtained still contained ca. 5% of MgBr_2 . In an alternative attempt, removal of MgBr_2 by crystallisation from THF solutions of VI led (with considerable loss of organomagnesium derivatives in the precipitate) to solutions of IV which still contained 20–35% of MgBr_2 . Therefore, in analogy to I [1a], IV was prepared from VI via the organomercury derivatives VII and VIII (Scheme 2).

SCHEME 2



Compound VIII has been described by Sawatsky and Wright as being dimeric [4]. It decomposes with formation of metallic mercury and is only slightly soluble in THF; nevertheless, on shaking with excess magnesium [5] in THF for several days a clear and colourless solution of V was obtained in practically quantitative yield. In diethyl ether, V is nearly insoluble.

Association measurements were performed in a completely sealed high vacuum system by the method of stationary isothermal distillation [6] as previously described [1a]. It turned out that monomeric IV does not exist as such in THF solution; instead its dimer V is exclusively present at all concentrations and temperatures measured (Table 1); the average degree of association of all measurements was $i = 2.000$. As both II [1c] and V [7] are known to possess a twelve-membered or ten-membered ring structure, respectively, in the crystalline state, and evidence has been presented for a similar structure of II in solution [1c], we assume that V also

TABLE I
ASSOCIATION OF MAGNESACYCLOPENTANE IN THF^a

$T(^{\circ}\text{C})$	$[\text{Mg}]_f^b$	S_a^c	S_{th}^d	i^e
28.17	2.858	0.060	0.122	2.020
	5.717	0.119	0.244	2.042
	8.576	0.189	0.365	1.930
	11.435	0.241	0.487	2.019
	14.294	0.303	0.609	2.008
38.75	2.804	0.074	0.148	2.011
	5.609	0.148	0.296	2.004
	8.414	0.224	0.443	1.984
	11.219	0.295	0.591	2.008
	14.023	0.370	0.739	2.000
48.84	2.794	0.093	0.180	1.934
	5.588	0.175	0.359	2.054
	8.383	0.270	0.539	1.997
	11.177	0.361	0.719	1.991
	13.971	0.449	0.898	2.001

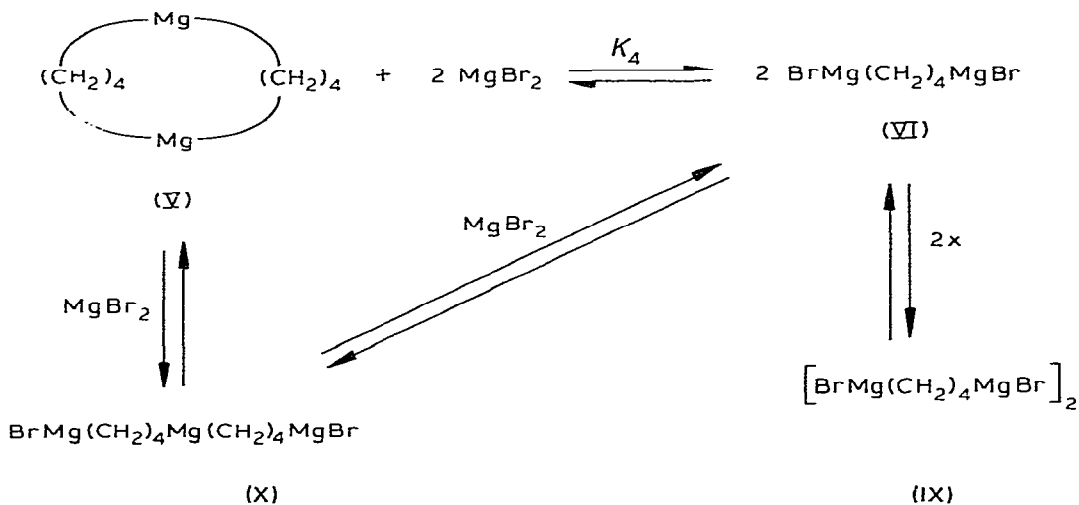
^a For details of the experimental technique and apparatus see ref. 1a. ^b $[\text{Mg}]_f$ = formal concentration of Mg in mgat l^{-1} (i.e. concentration if all particles were monomeric containing one Mg atom). ^c S_a = apparent rate of the evaporation in mm h^{-1} . ^d S_{th} = theoretical rate of evaporation (in mm h^{-1}) = $[\text{Mg}]_f \cdot S_s$, where S_s (in $\text{mm h}^{-1} \text{mmol}^{-1}$) is the standard rate of evaporation found by calibration of the apparatus with triphenylmethane: $S_s(28.17^{\circ}) = 0.0426$, $S_s(38.75^{\circ}) = 0.0527$, $S_s(48.84^{\circ}) = 0.0643$. ^e Degree of association $i = S_{th}/S_a$.

has a ten-membered ring structure in THF solution. These results in THF are at variance with those of Fauvarque and coworkers [8], who for IV found degrees of association $i = 1.35$ in dioxane and $i = 1.17$ in hexamethylphosphoric triamide (HMPT), which indicates considerable dissociation of V to IV. It is unclear whether this difference is due only to the difference in solvents; the authors reported some instability of IV in dioxane and apparently did not investigate the concentration dependence of i .

As discussed previously [1c], the strong tendency of IV to dimerize can be accounted for in terms of the typically large C–Mg–C bond angles (e.g. 128° in crystalline V [7]). Such large angles cannot be incorporated into the six-membered ring of I without strain; the strain in the five-membered ring of IV would even be higher.

The degree of association of magnesacyclopentane being established as two, i.e. pure V is present in THF solution, we were able to attack the problem of the behaviour of VI in THF. In principle, the situation outlined in Scheme 3 might apply; besides the expected Schlenk equilibrium ($\text{V} + 2 \text{MgBr}_2 \rightleftharpoons 2 \text{VI}$; K_4), the dimer IX of VI and the intermediate mixed species X might be involved.

The presence of IX and X can be excluded on the following grounds. In the first place, dialkylmagnesiums and Grignard reagents are usually monomeric in dilute THF solution [9], so that the formation of IX is highly unlikely. This was corroborated by association measurements on VI in diethyl ether where, contrary to the situation of THF, the Schlenk equilibrium strongly favours the Grignard reagent.



Compound VI is only slightly soluble in diethyl ether ($c \leq 5 \text{ mmol l}^{-1}$; while V is hardly soluble at all, *vide supra*), and so the measurements were not very accurate, but i was found to be approximately 1. When VI is monomeric in diethyl ether, a monomeric structure is even more likely in the more basic solvent THF.

The absence of significant amounts of X cannot be so easily established. Undoubtedly, X is a real intermediate in the conversion of V to VI. However, its concentration in THF solution must be negligible, as calculations based on the exclusive involvement of V and VI gave reasonable, constant values for K_4 (Scheme 3; *vide infra*), while the inclusion of IX led to varying, sometimes negative "equilibrium constants". The conclusion that IX and X are not present in significant amounts is further supported by our previous demonstration [1c] that their pentamethylene analogues do not participate in the corresponding equilibria of I, II and III.

In order to determine the position of the Schlenk equilibrium three types of association measurements were performed. In the first place, the establishment of the Schlenk equilibrium was demonstrated in a semi-quantitative fashion by adding increasing amounts of MgBr_2 to V in THF and determining the association (Table 2). For MgBr_2 in THF, $i = 1$ [9]; for V, $i = 2$ (*vide supra*). If MgBr_2 and V did not react at all, i would be expected to decrease rapidly: $i = (2 \times [\text{V}] + [\text{MgBr}_2]) / ([\text{V}] + [\text{MgBr}_2])$; e.g. for $[\text{V}] / [\text{MgBr}_2] = 1/2$, i would be 1.33. On the other hand, if MgBr_2 and V reacted completely to form VI, the value of i would remain unchanged at 2, since, MgBr_2 would be completely consumed and the newly formed VI, like V, has 2 Mg atoms per particle in solution; only when the molar ratio V/ MgBr_2 fell below 1/2 would i be expected to decrease. The experimental values of i (Table 2) lie in between the extremes, which means that the Schlenk equilibrium between V and VI (Scheme 3) is established at an intermediate position (*cf.* also Table 4).

Assuming the absence of IX and X and applying corrections for the "initial rise" of the evaporator as previously described [1c], average values for K_4 can be calculated:

$$K_4 = \frac{[\text{VI}]^2}{[\text{V}][\text{MgBr}_2]^2}$$

TABLE 2
ASSOCIATION OF MIXTURES OF V AND $MgBr_2$ IN THF^a

[Mg] _r	[MgBr ₂]	T 28.17°C			T 38.75°C			T 48.84°C		
		S _a	S _{th}	i	S _a	S _{th}	i	S _a	S _{th}	i
26.272	3.139	0.620	1.119	1.805	0.739	1.385	1.874	0.868	1.689	1.946
29.411	6.278	0.697	1.253	1.798	0.846	1.550	1.832	1.007	1.891	1.878
32.550	9.417	0.792	1.387	1.751	0.958	1.715	1.791	1.144	2.093	1.830
35.689	12.556	0.906	1.520	1.678	1.071	1.881	1.756	1.277	2.295	1.797
38.828	15.695	0.983	1.654	1.683	1.184	2.046	1.728	1.395	2.497	1.790
41.366	18.233	1.073	1.762	1.699	1.267	2.180	1.721	1.510	2.660	1.761

^a For notes see Table 1.

These values ($K_4(28.17^\circ) = 533 \text{ l mol}^{-1}$; $K_4(38.75^\circ) = 757 \text{ l mol}^{-1}$; $K_4(48.84^\circ) = 1214 \text{ l mol}^{-1}$), however, are relatively unreliable as far as their absolute value goes; they are estimated to have an accuracy not better than ca. 50%. Besides errors in titration and variations in the contents of ampoules (assumed to be equal by filling equal volumes on the vacuum line) the main reason for the lesser degree of accuracy is inherent in the experimental approach: the addition of small amounts of MgBr_2 to a large excess of V leads to particularly large systematic errors and standard deviations.

More reliable numbers for i and K_4 could be obtained by two alternative, more direct approaches: we measured the association of a preformed 1/1 mixture of V and MgBr_2 (Table 3) and, approaching the equilibrium from the other side, of authentic VI (Table 4). In order to obtain IV (from 1,4-dibromobutane and magnesium) as pure as possible, side reactions such as Wurtz coupling (which are particularly troublesome for the divalent Grignard reagents under ordinary preparative conditions) were minimised by careful slow addition of the halide to the metal in a high vacuum system: under these conditions, VI contained only 4.5% excess of MgBr_2 , and no other impurities.

By the treatment used for the results of Table 2, the results of Table 3 yield values of $K_4(28.17^\circ) = 111(\pm 5) \text{ l mol}^{-1}$, $K_4(38.75^\circ) = 300(\pm 27) \text{ l mol}^{-1}$ and $K_4(48.84^\circ) = 565(\pm 60) \text{ l mol}^{-1}$; Table 4 gives $K_4(28.24^\circ) = 81(\pm 10) \text{ l mol}^{-1}$ (standard deviations between brackets). These values confirm the temperature dependence revealed by the less reliable values from Table 2; they differ by a factor 2–5, which we consider satisfactory in view of the limitations of the method. As approximate values we assume $K_4(28.17^\circ) = 100 \pm 50 \text{ l mol}^{-1}$, $K_4(38.75^\circ) = 250 \pm 100 \text{ l mol}^{-1}$ and $K_4(48.84^\circ) = 500 \pm 200 \text{ l mol}^{-1}$.

In view of such uncertainties it seems risky to calculate equilibrium parameters from K_4 ; they are $\Delta H_4 = 15 \text{ kcal mol}^{-1}$ and $\Delta S_4 = 59 \text{ e.u.}$ for the Schienk equilibrium $\text{V} + 2 \text{MgBr}_2 \rightleftharpoons 2 \text{VI}$. However, these parameters are in surprisingly good agreement with those of the higher homologues II and III; from the values reported in the introduction $\Delta H_3 = -\Delta H_1 + 2 \Delta H_2 = 15.5 \text{ kcal mol}^{-1}$ and $\Delta S_3 = -\Delta S_1 + 2 \Delta S_2 = 61 \text{ e.u.}$ are calculated. Thus, in spite of the relatively large uncertainty involved, one may be confident in regarding these thermodynamic parameters as representative for the Schlenk equilibria of di-Grignard reagents of this type.

TABLE 3
ASSOCIATION OF A 1/2 MIXTURE OF V AND MgBr_2 IN THF^a

[Mg] _f	T 28.17°C			T 38.75°C			T 48.84°C		
	S_a	S_{th}	i	S_a	S_{th}	i	S_a	S_{th}	i
4.162	0.132	0.177	1.343	0.164	0.219	1.337	0.198	0.268	1.352
8.324	0.253	0.355	1.402	0.307	0.439	1.429	0.367	0.535	1.458
12.486	0.370	0.532	1.438	0.448	0.658	1.469	0.539	0.803	1.490
16.648	0.481	0.709	1.474	0.583	0.877	1.505	0.690	1.070	1.551
20.810	0.595	0.887	1.490	0.708	1.097	1.649	0.847	1.338	1.580

^a For notes see Table 1.

TABLE 4
ASSOCIATION OF VI IN THF AT 28.24°C^a

[Mg] _f ^b	S _a ^c	S _{th} ^d	i ^e	i ^f	i ^g
4.016	0.118	0.168	1.426	1.957	1.324
8.032	0.228	0.337	1.476	1.957	1.324
12.048	0.336	0.505	1.502	1.957	1.324
16.064	0.448	0.673	1.502	1.957	1.324
20.080	0.565	0.841	1.489	1.957	1.324

^a For details of the experimental technique and apparatus see ref. 1a. ^b [Mg]_f = formal concentration of Mg in mgat l⁻¹; the solution contained 4.5% MgBr₂ in excess of the stoichiometric composition of VI. ^c S_a = apparent rate of the evaporator (in mm h⁻¹). ^d S_{th} = theoretical rate of the evaporator (in mm h⁻¹) = [Mg]_f S_s, where S_s (in mm h⁻¹, mmol⁻¹ l) = 0.0419. ^e Degree of association $i = S_{th}/S_a$. ^f $i^f = i$ in case of no Schlenk equilibrium. ^g $i^g = i$ in case of complete dissociation of VI to V and MgBr₂.

TABLE 5
REACTION PARAMETERS OF SCHLENK EQUILIBRIA IN THF

Reaction	T (°C)	ΔH (kcal mol ⁻¹)	ΔS (e.u.)	ref.
Et ₂ Mg + MgBr ₂ ⇌ 2 EtMgBr	25	6.1	23.7	[10]
$\frac{1}{2}$ II + MgBr ₂ ⇌ III	28.25	7.8	30.5	[1c]
$\frac{1}{2}$ V + MgBr ₂ ⇌ VI	28.17	7.5	29.5	

Interestingly, these parameters are not much different from those of normal, monovalent Grignard reagents. Smith and Becker [10] investigated the system of diethylmagnesium, ethylmagnesium bromide and MgBr₂ in THF by direct thermochemical measurements. Their results are compared with those of the tetramethylene and pentamethylene series in Table 5. The agreement is quite close: in view of the large errors involved in the association measurement approach the difference cannot be considered significant at this stage. In all cases, the formation of the Grignard reagent in the Schlenk equilibrium is endothermic but facilitated by the gain in entropy which is presumably caused by release of THF molecules from MgBr₂ [10].

Obviously, the influence of the second magnesium centre in the molecules on the behaviour of the first one is small; III and VI behave in first approximation like monovalent Grignard reagents. This conclusion is consistent with the rather normal behaviour of III and VI in chemical reactions.

Acknowledgement

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References and Notes

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