

Rate of Formation and Characterization of Magnesium Anthracene

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^1H and ^{13}C NMR studies on magnesium anthracene $\cdot 3$ THF (**2a**), which can be recrystallized from THF, indicate that magnesium has the strongest interaction with the 9,10-positions of anthracene. While the rate of formation of **2a** from magnesium and anthracene in THF at 60°C is proportional to both anthracene concentration and magnesium surface area, at 25°C it is proportional only to magnesium surface area. Magnesium, anthracene and THF exist in a temperature dependent, reversible equilibrium with **2a** (eq. 6), the formation of **2a** being favoured at lower temperatures. At higher temperatures **2a** reacts with the solvent to produce ring opening of THF and insertion of butyleneoxy units in the Mg–C bonds, so that on hydrolysis the alcohols **6** and **7** are obtained.

Bildungsgeschwindigkeit und Charakterisierung von Magnesiumanthracen

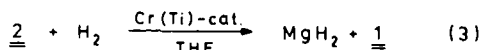
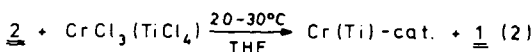
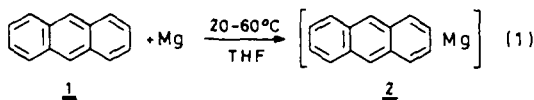
Aufgrund kernresonanzspektroskopischer Untersuchungen (^1H - und ^{13}C -NMR) ist Magnesium im aus THF kristallisierbaren Magnesiumanthracen $\cdot 3$ THF (**2a**) an den 9,10-Positionen des Anthracens gebunden. Die Bildungsgeschwindigkeit von **2a** aus Magnesium und Anthracen ist in THF bei 60°C sowohl zur Anthracenkonzentration als auch zur Magnesiumoberfläche, bei 25°C nur zur Magnesiumoberfläche proportional. Magnesium, Anthracen und THF stehen mit **2a** in einem temperaturabhängigen, reversiblen Gleichgewicht (Gl. 6), wobei tiefe Temperaturen die Bildung von **2a** begünstigen. Bei erhöhten Temperaturen reagiert **2a** mit dem Lösungsmittel unter Ringöffnung von THF und Einschlebung von Butylenoxy-Einheiten in die Mg–C-Bindungen, so daß nach Hydrolyse die Alkohole **6** bzw. **7** erhalten werden.

We recently reported that homogeneous catalysis by transition metals can be used to hydrogenate magnesium under mild conditions to yield magnesium hydride of high reactivity that is highly efficient as a hydrogen storage medium¹⁾. Particularly active catalysts for the hydrogenation of magnesium are obtained by the reaction of magnesium anthracene with chromium, titanium or iron halides in tetrahydrofuran (THF).

The following experimentally verified reactions have been proposed as individual steps in the homogeneously catalyzed magnesium hydrogenation using the magnesium anthracene- CrCl_3 or $-\text{TiCl}_4$ catalyst in THF^{1a)}: (i) reaction of metallic magnesium with anthracene (**1**) in THF to give magnesium anthracene (**2**) [eq. (1)]; (ii) reaction of **2** with CrCl_3 or TiCl_4 in THF to form the catalytically active species as well as free anthracene (**1**) [eq. (2)]; (iii) hydrogenation of **2** in the

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presence of the dissolved chromium or titanium catalyst to give magnesium hydride with the liberation of anthracene (**1**) [eq. (3)] (only small amounts of 9,10-dihydroanthracene are formed as by-product). The reaction sequence of eq. (1) and (3) constitutes a catalytic cycle for magnesium hydrogenation *via* magnesium anthracene (**2**) as a reactive intermediate.

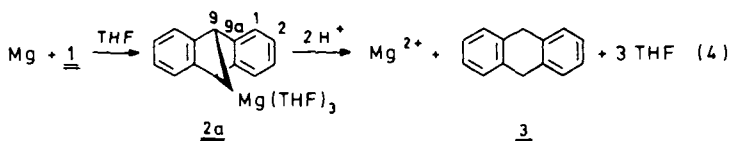


Since the formation of magnesium anthracene [eq. (1)] appears to be one of the key steps in the homogeneous hydrogenation of magnesium and in the synthesis of organo-transition metal complexes using anthracene-activated magnesium²⁾, we report here studies of the rate of formation and some chemical properties of magnesium anthracene as well as its characterization by NMR spectroscopy.

The Chemical and NMR Spectroscopic Characterization of Magnesium Anthracene

The reaction of magnesium with anthracene in THF to form an orange, sparingly soluble 1:1 adduct and the reaction of this with dibutyltin dichloride were described in 1965 in a patent by *Ramsden*³⁾, but no further data about the compound have since appeared in the literature^{4)*)}.

According to our investigations, the orange crystalline 1:1 adduct (**2a**) which can be prepared from magnesium and anthracene in THF at ambient temperature contains 3 mols THF/mol adduct, on the basis of its protolysis to magnesium ions, 9,10-dihydroanthracene (**3**) and THF in the molar ratio of 1:1:3 [eq. (4)]. The amount of 3



formed on protolysis was used throughout this work as a quantitative measure of **2a** present in a sample. Probably as a result of the reversibility of its formation (s. p. 1385), it is difficult to prepare **2a** completely free from traces of **1** and from elemental magnesium; the amount of the latter was determined by measuring the quantity of hydrogen liberated on protolysis of a sample of **2a**. The compound can be recrystallized from a large volume of THF to give orange needles of approximately the same composition: the solubility of **2a** ($\text{C}_{14}\text{H}_{10}\text{Mg} \cdot 3\text{THF}$) in THF is 3 g/l at 23°C and 5.5–6 g/l at

*) After completion of this manuscript the preparation of "magnesium anthracene dianion" from sodium anthracene and MgBr_2 or from magnesium and anthracene in the presence of MgBr_2 in THF has been reported by *P. K. Freeman* and *L. L. Hutchinson* [J. Org. Chem. **48**, 879 (1983)], obviously not knowing of the work of *Ramsden*³⁾.

60 °C. In the recrystallized product, apart from traces of **1** and Mg, a small amount of "1-magnesia-2-oxa-cyclohexane", the product of the THF-cleavage by Mg⁵⁾, was detected *via* its hydrolysis product *n*-butanol. On the basis of the NMR evidence (see below) and of the protolysis to **3** [eq. (4)], **2a** has a structure, with the strongest interaction of magnesium with hydrocarbon residue at the 9,10-positions.

2a exhibits in the ¹H NMR spectrum (saturated solution in [D₈]THF) three signals with the intensity ratio of 2:2:1. The multiplets at $\delta = 5.95$ and 6.01 can be assigned to aromatic protons and the singlet at $\delta = 3.51$ to the protons of the magnesium-bearing carbon atoms.

In the ¹³C NMR spectrum of **2a** examined in [D₈]THF at 40 °C there were in addition to the solvent and 9,10-dihydroanthracene just four signals observed at 145.9, 118.1, 114.1 and 57.7 ppm (see table 1). A further small signal at 129.0 ppm was assigned to impurity since its relative intensity varied significantly from sample to sample. The number of signals, their approximate relative intensities and their multiplicities in the proton coupled spectrum are consistent with the anthracene framework being retained in the magnesium compound. Information from a proton-coupled ¹³C NMR spectrum allows the signals to be assigned; the quaternary ring junction carbon C-9a gives a singlet, while the two doublets of equal intensity at 118.1 and 114.1 ppm can be distinguished by their fine structure arising from vicinal C – H coupling; C-1 (114.1) also couples with 3-H, 9-H and 10-H, giving a quartet-like fine structure, but C-2 has a doublet fine structure due to coupling only with 4-H.

Table 1. ¹³C NMR data for magnesium anthracene (**2a**) and related compounds

	δ_C	C-1 $^1J_{CH}$	C-2 δ_C	$^1J_{CH}$	C-9 δ_C	$^1J_{CH}$	C-9a δ_C	Ref.
Anthracene (1)	128.13	161.6	125.32	160.5	126.20	158.8	131.68	6)
Li ₂ [anthracene] (Li ₂ -a) in ether	102.8	147.0	115.7	147.9	76.4	a)	151.7	7)
in THF	102.4	147.5	115.6	147.5	76.4	145.0	151.4	7)
in THF	101.1	b)	114.2	b)	75.1	b)	150.0	8)
2a ^{c)}	114.1	148.6	118.1	153.4	57.7	138.0	145.9	This work
$\Delta\delta_n$ {Li ₂ -a} ^{d)}	-25.7		-9.7		-49.8		+19.7	
$\Delta\delta_n$ { 2a } ^{e)}	-14.0		-7.2		-68.5		+14.2	
9,10-dihydro- anthracene (3)	127.9		126.7		36.7		137.7	

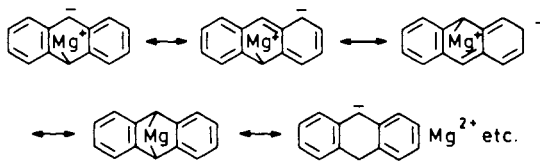
a) Obscured by solvent. – b) Not reported. – c) δ_C using [D₈]THF as reference and converted using factor $\delta_C(\beta\text{-CD}_2) = 25.3$ rel. TMS. – d) $\Delta\delta\{\text{Li}_2\text{-a}\} = \delta_n(\text{Li}_2\text{-a}) - \delta_n(\text{1})$. – e) $\Delta\delta\{\mathbf{2a}\} = \delta_n(\mathbf{2a}) - \delta_n(\mathbf{1})$.

The ¹³C NMR data of the dianion of Li₂[anthracene], anthracene (**1**) and dihydroanthracene (**3**) are collected in table 1 and provide a basis for the discussion of the structure of **2a**. The ¹³C NMR spectrum of the corresponding anthracene dianion (table 1) has been analysed by Müllen⁸⁾ and by Mamatyuk and Koptyug⁷⁾. They showed that the chemical shifts are related to the excess electronic charge on the carbon

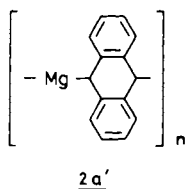
atoms and they compared the experimental data with MO calculations. *Mamatyuk* and *Koptuyug* also took into account the effect of the anisotropy of the magnetic susceptibility of the π -System upon the nuclear shielding and correlated the spin-spin coupling constants $^1J(^{13}\text{C}-^1\text{H})$ with the electronic charges.

An ionic structure for **2a** can be ruled out since its NMR data differ significantly from those of the dianion of $\text{Li}_2[\text{anthracene}]$, although the trends of δ_{C} and $^1J(^{13}\text{C}-^1\text{H})$ are similar. Thus the resonances of C-1 and C-2 are shifted by 14.0 and 7.2 ppm, respectively, to higher field relative to the corresponding signals of anthracene. This indicates that the π -electron density at these carbons is considerably greater in **2a** than in anthracene but not as great as in the dianion, for which these signals are shifted to higher field by 25.7 and 9.7 ppm, respectively. Similarly, the coupling constants $^1J(^{13}\text{C}-^1\text{H})$ and $^1J(^{13}\text{C}-^2\text{H})$ are reduced from their values in **1** but not as much as in the dianion. By way of contrast, δ C-9 lies to higher field in **2a** than in the dianion and $^1J(^{13}\text{C}-^1\text{H})$ is reduced to only 138 Hz. While these observations could be interpreted as due to the π -electron density at C-9 in **2a** being even higher than in the dianion, we regard this as unlikely and interpret these findings as indicating a change in hybridization of C-9 towards sp^3 with the strongest interaction of Mg with anthracene at C-9, C-10. On the other hand, if there were purely covalent bonding of Mg to C-9, C-10 it would be expected that δ C-9 would probably be found to higher field than in 9,10-dihydroanthracene and this is also inconsistent with the highly polar nature of the compound.

The NMR data are thus consistent with neither a purely ionic or covalent structure but with **2a** being an ion pair with a strong interaction at C-9, C-10 or a covalent compound with a large polar contribution representable by the canonical forms.



The crystal structure of the related $\text{Mg}(\text{THF})_3$ -(*s-cis*-1,4-diphenyl-1,3-butadiene) with a trigonal bipyramidal geometry around the magnesium atom has been recently reported⁹. For **2a** a monomeric structure (shown in eq. 4) analogous to that of the butadiene derivative above mentioned can be proposed, the possibility of oligomeric forms (**2a'**) however cannot be excluded. An X-ray crystallographic investigation of



magnesium (9,10-dihydro-9,10-anthrylene)diethylhydrido aluminate, prepared from **2a** and diethylaluminium hydride, showed that Al and Mg occupy axial positions in a 9,10-dihydro-9,10-anthrylene system¹⁰.

Rate of Magnesium Anthracene Formation

Kinetic measurements on the formation of magnesium anthracene (**2a**) proved somewhat difficult to carry out. The reaction rate is extremely sensitive to the traces of moisture or oxygen in the THF¹¹) and these must be rigorously excluded. Nevertheless the experimental error is probably fairly large and average values from several parallel experiments (s. exp. part) were used in the most cases.

The experiments to determine the kinetics and equilibria (s. next section) were performed by removal of samples from the reaction mixture at intervals, quenching them with ethanol and determining in the protolyzed samples the concentration of **1** with respect to a standard (method *a*) and percentage of **1** and **3** (method *b*) by gas chromatography. The accuracy of the latter method depends in part upon the homogeneity of the fine suspension of **2a** in THF during removal of samples. A comparison of the two sets of data obtained using the methods *a* and *b* is given in the table 3a, exp. part. In most cases a satisfactory agreement between the two methods of evaluation was found, but method *a* should in general give more reliable data.

Magnesium does not react readily with **1** in THF unless it is *activated*, for instance with a small amount of ethyl bromide³). Since we observed that the rate of reaction of magnesium with **1** is increased significantly when the time over which it has been treated with ethyl bromide is prolonged, in the experiments described below magnesium was stirred with ethyl bromide for 20–22 h before anthracene was added.

The influence of the *rate of stirring* on the rate of formation of **2a** was investigated at 25 °C using stirring rates of 200, 350 and 1100 min⁻¹, but (fig. 1) no significant influence upon the reaction rate was found. We used a stirring rate of 1100 min⁻¹ in the kinetic experiments described below.

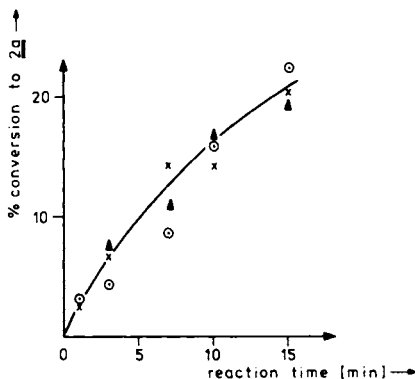


Fig. 1. Influence of the stirring rate on the rate of formation of **2a** at 25 °C in THF; initial concentration of **1** 0.1 mol/l, molar ratio Mg: **1** = 10:1; ○ ○ ○, stirring rate 200 min⁻¹; × × ×, stirring rate 350 min⁻¹; ▲ ▲ ▲, stirring rate 1100 min⁻¹

Influence of Anthracene Concentration, Magnesium Surface Area and Temperature on the Rate of Formation of Magnesium Anthracene

The influence of anthracene concentration on the formation rate of **2a** was studied at 25° and 60°C by allowing **1** at initial concentrations of 0.02, 0.05 and 0.1 mol/l to react with a constant amount of magnesium powder (50 mesh) in large excess (Mg: **1** = 50:1, 20:1 and 10:1, respectively). The decrease of anthracene concentration with time for the experiments at 25° and 60°C is shown in the fig. 2. From the fig. 2 (right) it can be

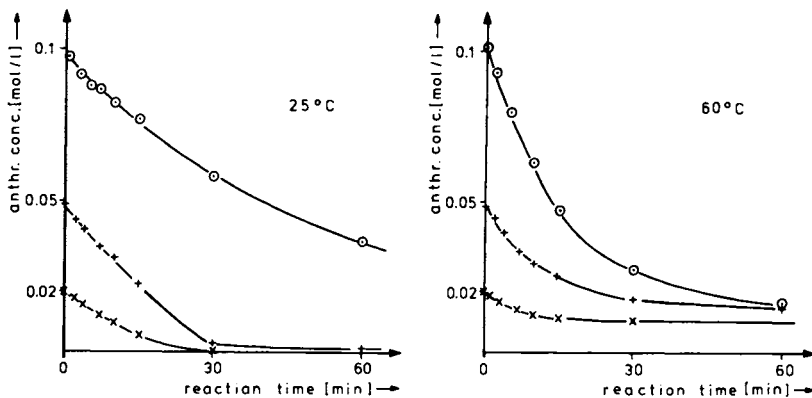


Fig. 2. Influence of anthracene concentration on the rate of formation of **2a** at 25°C (left) and 60°C (right) in THF, for the initial anthracene concentrations of 0.02 (— × —), 0.05 (— + —) and 0.1 mol/l (— ○ —); Mg powder (50 mesh) 1 mol/l THF

seen that the initial reaction rates at 60°C are roughly proportional to the initial anthracene concentrations, indicating a pseudo first-order reaction. Since the reaction is reversible, no further net conversion of magnesium to **2a** occurs at 60°C once the anthracene concentration has dropped to the equilibrium value of ca. 0.01 mol/l. For a pseudo first-order reversible reaction eq. (6), *i. e. assuming that the surface area of magnesium does not change appreciably during the reaction*¹²⁾, the relationship

$$\ln \frac{[1]_t - [1]_e}{[1]_i - [1]_e} = - (k_1 + k_{-1}) S t \quad (5)$$

should hold¹³⁾; $[1]_i$, $[1]_e$ and $[1]_t$ denote initial, equilibrium and anthracene concentration at a time t respectively and S a constant related to the magnesium surface area. A semi-logarithmic plot of the *effective* anthracene concentration ($[1]_t - [1]_e$) versus time for experiments at 60°C and the approximation of the plots by straight lines give for initial anthracene concentrations of 0.02, 0.05 and 0.1 mol/l values of $(k_1 + k_{-1}) S$ (*i. e.* the slopes of the lines) of 11.4, 6.7 and $6.0 \times 10^{-2} \text{ min}^{-1}$, respectively, which can be taken as a satisfactory evidence of the 1. order dependence of the reaction rate on anthracene concentration, taking into account the large experimental error. A small but significant decrease of the $(k_1 + k_{-1}) S$ -values with increasing initial anthracene concentration probably reflects the fact that the surface area of magnesium is not

constant but is reduced in the course of the reaction. The higher the initial concentration of anthracene the more the surface area will be reduced. (The dependence of the reaction rate on the magnesium surface area is shown below.)

In contrast to the 60°C experiments, at 25°C the reaction rate increases with increasing anthracene concentration (fig. 2, left) by much less than would correspond to a pseudo first-order reaction rate and no simple dependence of the reaction rate on anthracene concentration at this temperature could be derived. Since the equilibrium shifts towards **2a** with decreasing temperature (cf. next section), **1** is almost completely converted to **2a** at 25°C when equilibrium is reached (fig. 2, left and table 3).

The influence of the magnesium surface area on the rate of formation of **2a** has been investigated by reacting anthracene at an initial molar concentration of approx. 0.1 mol/l with magnesium powder (50 mesh) at 25°C in the molar ratio of 1:10, 1:50 and 1:100 and at 60°C in the molar ratio of 1:10 and 1:50. In fig. 3 the decrease of anthracene concentration for the experiments at 25°C (left) and 60°C (right) is plotted against the reaction time. In the fig. 4 the initial reaction rates (slopes of the curves of the fig. 3 at the time $t = 0$) are plotted against the amount of magnesium powder used in the experiments. As it can be seen from the fig. 4, the initial reaction rates for both temperatures are roughly proportional to the amounts of magnesium powder. Since it can be assumed that the magnesium surface area is a linear function of the amount of magnesium powder used¹⁴, the results indicate a first-order dependence of the reaction rate for the formation of **2a** [eq. (6)] upon the magnesium surface area.

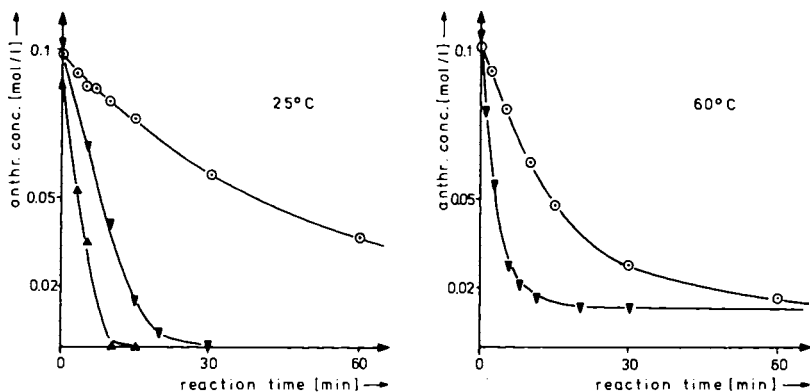


Fig. 3. Influence of magnesium surface area on the rate of formation of **2a** at 25°C (left) and 60°C (right) in THF, for the initial anthracene concentration of ≈ 0.1 mol/l; $-\circ-$, Mg powder (50 mesh) 1 mol/l; $-\triangle-$, Mg powder (50 mesh) 5 mol/l; $-\blacktriangledown-$, Mg powder (50 mesh) 10 mol/l

According to preliminary results (see table 4, exp. part), the particle size (0.08–0.09, 0.15–0.20 and 0.25–0.3 mm) and the origin of magnesium powder (Ventron and Riedel-de Haën) seem to have no significant influence on the rate of **2a** formation at 60°C. Since it has been shown (see above) that the reaction rate is proportional to the surface area of magnesium, it can be concluded that the surface area is determined by

factors other than the particle size; this is the case if the surface area of magnesium is largely determined by the presence of cracks, pores etc. in the outer layer of magnesium particles.

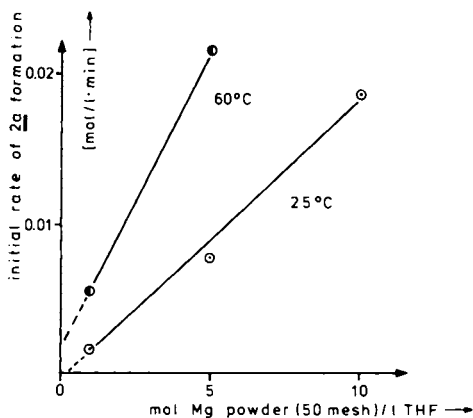


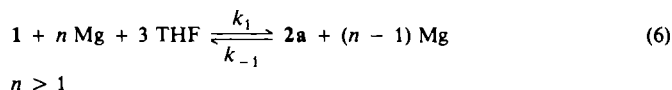
Fig. 4. Dependence of the initial rate of formation of **2a** (in mol/l min) upon the magnesium surface area for the initial anthracene concentration of 0.1 mol/l at 25°C (—○—) and 60°C (—●—)

Additionally, the rate of **2a** formation has been measured at 25°C in THF at a molar ratio Mg: **1** \approx 1:1 and with **1** in a large excess; the data are given in the table 5 (s. exp. part).

Reversibility of Magnesium Anthracene Formation

When **1** at an initial concentration of 0.02 mol/l reacts with a large excess of magnesium powder (**1**:Mg = 1:50) in THF at 25°C, 97–99% is converted to **2a** within approx. 30 min (fig. 2, left) and this remains unchanged in the next 22 hours (fig. 5, left). If thereafter the reaction mixture is heated to 60°C, the concentration of **1** increases at the expense of **2a** and after a further 1–2 h the extent of conversion to **2a** has decreased to 60–65% (fig. 5, middle)^{15,16}. On lowering the temperature to 25°C the extent of conversion to **2a** again reaches 97–99% (fig. 5, right).

From the experiment described it follows that the reaction of magnesium with **1** in THF to form **2a** is a temperature dependent equilibrium reaction eq. (6). The formation of **2a** is more favoured at lower temperatures.



The equilibrium constant for the reaction eq. (6), neglecting the influence of THF which is present in large excess, is given by the expression:

$$K = \frac{k_1}{k_{-1}} = \frac{[\mathbf{2a}]}{[\mathbf{1}]} \quad (7)$$

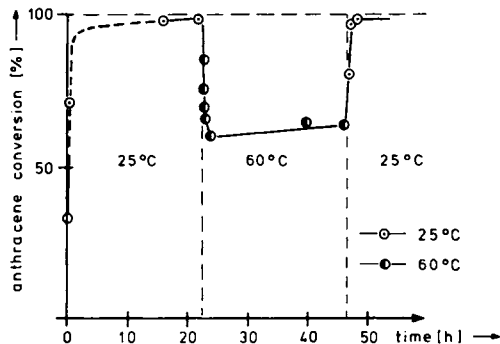


Fig. 5. Change in the percentage conversion of anthracene (**1**) to magnesium anthracene (**2a**) with temperature for the initial anthracene concentration of 0.02 mol/l and the molar ratio Mg:1 = 50:1

From eq. (7) it follows that at a given temperature in a saturated solution of **2a** in THF (the usual case because of the low solubility of **2a** in THF, p. 1379) the equilibrium concentration of anthracene, $[1]_e$, will be constant, independent of the initial anthracene concentration and the amount of **2a** formed.

$[1]_e$ has been measured at 25° and 60°C for different initial anthracene concentrations, $[1]_i$, by allowing anthracene to react with an excess of magnesium powder in THF and by determining the anthracene concentration after 22 h or longer. As it can be seen from table 2, $[1]_e$ at 25° and at 60°C is constant within experimental error when $[1]_i$ is varied within a factor of 5. These results confirm the formulation of the reaction eq. (6) as an equilibrium reaction¹⁷⁾.

Table 2. Reversibility of magnesium anthracene formation: the equilibrium anthracene concentration, $[1]_e$, measured for different initial anthracene concentrations, $[1]_i$, and 1 mol Mg powder^{a)} per 1 THF, at 25°C and 60°C

t [°C]	molar ratio Mg/1	$[1]_i$ [mmol/l]	$[1]_e^{b,c)}$ [mmol/l] (numb. of exp.)	conversion to 2a in %
25	50	20	0.6 (5)	97
25	20	50	0.6 (4)	98.8
25	10	100	1.0 (5)	99
60	50	20	8.4 (7)	58
60	20	50	12.4 (3)	75.2
60	10	100	10.7 (3)	89.3

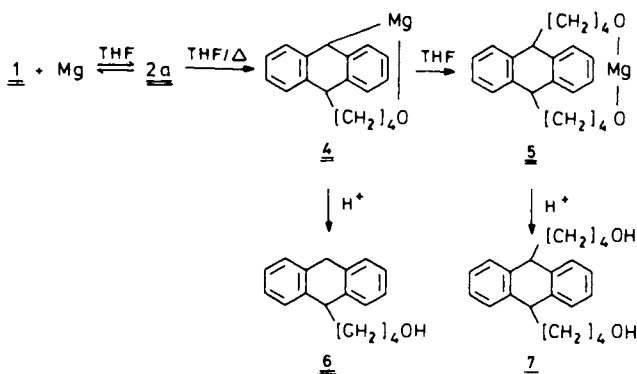
a) 50 mesh. – b) Anthracene concentrations (average values from several experiments, the number of experiments given in brackets) measured after reaction times of 20 h or more. – c) Compare also fig. 2 and 3 and table 3.

Reaction of Magnesium Anthracene with THF

In the course of equilibrium determination experiments described in the last section a novel ring opening of THF by reaction with **2a** was observed. While in such experiments at 60°C, the sum of the mole fractions of **1** and **2a** is approximately 1 after short

reaction times, this is not the case for longer reaction times, thus indicating a side reaction. An investigation of the products obtained on protolysis of a reaction mixture ($[1]_i = 0.05 \text{ mol/l}$, molar ratio $\text{Mg} : 1 = 20 : 1$) after 140 h reaction time at 60°C by GC- and GC-MS-coupled analysis revealed two additional compounds with molecular weights 252 (**6**) and 324 (**7**) (4.4% **6** and 15.8% **7** with respect to **1**) corresponding to mono- and bis(hydroxybutyl)dihydroanthracene, respectively. Since at 60°C and in boiling THF the formation of **6** and **7** from **2a** is extremely slow, in a following experiment a mixture of magnesium powder, **1** and THF (molar ratio $\text{Mg} : 1 : \text{THF} = 1 : 0.82 : 32$) was heated in an autoclave to 120°C for 72 h. The hydrolysis of the precipitate formed during the reaction gave **6** and **7** (1% and 57% yields, respectively, on the basis of **1** reacted; conversion of 1.85%). **7** was isolated from the mixture by column chromatography and by crystallization (m. p. $110 - 111^\circ\text{C}$) and identified on the basis of ^1H and ^{13}C NMR and mass spectra as 9,10-bis(4-hydroxybutyl)-9,10-dihydroanthracene (a single isomer, according to the ^{13}C NMR spectrum, the stereochemistry, *cis* or *trans*, of which has not yet been determined). **6** was shown by GC-chromatography to be identical with 9-(4-hydroxybutyl)-9,10-dihydroanthracene, prepared from lithium, anthracene and THF according to the literature¹⁸⁾.

The formation of **6** and **7** from **2a** and THF can be formulated as shown, with the organomagnesium compound **4** being the intermediate of the reaction of **2a** with THF leading to the magnesium alcoholate **5**:



Whereas the ring opening of THF by reaction with lithium anthracene to give **6** on hydrolysis is known¹⁸⁾ (see above), no double insertion, leading to **7** on hydrolysis, was observed in that case even in the presence of excess lithium. The ring opening of THF by reaction with organomagnesium compounds under cleavage of a C–O bond has been described^{19,20)}.

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Experimental Part

The ^1H NMR spectra were measured at 400 MHz on a Bruker WH-400 spectrometer. – ^{13}C NMR measurements were carried out at 75.4 MHz on a Bruker WM-300 spectrometer. – GC-analysis: 25 m, OV₁ column; temperature: 100/280°C, 8°C/min; carrier gas: H₂ 0.5 bar; FID. – All reactions and operations were carried out under argon.

Starting materials: In all experiments, unless otherwise stated, magnesium powder, 50 mesh, from Ventron GmbH was used and had a magnesium content of 99.3% according to elemental analysis. 99.7% of this powder had a particle size between 0.08 and 0.3 mm, 89.5% between 0.1 and 0.25 mm, as determined by sieving. Anthracene (Rütgerswerke AG, 99% purity) was used without further purification. THF was refluxed for several hours over catalytically prepared MgH₂¹⁾, distilled, refluxed over MgEt₂ and distilled again.

Preparation of 2a: 2.43 g (0.10 mol) of magnesium powder in 0.6 l of THF were stirred with 0.06 ml of C₂H₅Br at ambient temperature for 18 h. 32.21 g (0.18 mol) of **1** were added and the suspension stirred for further 48 h. The orange suspension was filtered, **2a** washed with 3 portions of THF (50 ml) and dried for 24 h at 25°C in high vacuum. 36.21 g (86.5%) of **2a** as orange microcrystalline powder were obtained.

C₂₆H₃₄MgO₃ (418.8) Calcd. C 74.55 H 8.18 Mg 5.80 Found C 74.56 H 7.82 Mg 6.26

0.8818 g of **2a** yielded on protolysis with 2 ml 2-ethyl-1-hexanol and subsequently with 1 ml 5 N H₂SO₄ 4.3 ml H₂ (20°C, 1 bar), according to MS-analysis. This amount of H₂ corresponds to a metallic magnesium content in the sample of 0.49%. The corrected Mg-content: 6.26 – 0.49 = 5.77%.

0.2153 g of **2a** yielded on protolysis with 25.0 ml of a toluene-CH₃OH-mixture (25/1-vol./vol.), containing 8.0855 g of *n*-octane/l and 7.4545 g of *n*-hexadecane/l as internal standards, 94.2 mg of **3**, 0.8 mg of **1** and 110.1 mg of THF, according to GC-analysis. On the basis of these data and of the corrected Mg-content of the sample the molar ratio Mg: **3**: THF was calculated to be 1.00: 1.02: 2.99.

Crystallization of 2a: 9.49 g of raw **2a** were suspended in 1 l of THF, the suspension stirred for 40 min at 60°C on a water bath and the hot suspension filtered through a glass frit with a heated mantle (60°C). The orange filtrate was cooled from 60°C to ambient temperature in a Dewar flask over 48 h and kept for further 4–5 h at +10°C, to yield **2a** in the form of long orange needles. The mother liquor was siphoned off by means of an U-tube with the entry drawn out to a fine capillary, the crystals washed with cold THF and dried in high vacuum at 25°C to a constant weight of 2.76 g.

Found C 75.19 H 8.29 Mg 6.04

0.5965 g of the crystals **2a** yielded on protolysis with 2-ethyl-1-hexanol and 5 N H₂SO₄ as described above 0.7 ml H₂ (20°C, 1 bar) (MS-analysis), corresponding to a content of metallic magnesium of the sample of 0.14%. The corrected Mg-content: 5.90%.

0.2373 g of the crystals **2a** gave on protolysis with the toluene-CH₃OH-mixture as described above 99.9 mg of **3**, 1.8 mg of **1**, 120 mg of THF and 2.0 mg of *n*-butanol, according to GC-analysis. On the basis of these data and of the corrected Mg-content of the sample the calculated molar ratio Mg: **3**: THF is 1.00: 0.96: 2.90.

Determination of solubility of 2a in THF: 10.8 g of non-recrystallized **2a** were suspended in 1.0 l of THF and the suspension stirred at ambient temperature (23°C) for 16 h. The suspension was allowed to settle, 2.0 ml sample of the clear supernatant solution removed by a calibrated pipette and the sample protolyzed with 1.0 ml of a 2-ethyl-1-hexanol-THF mixture (1/50-vol./vol.) containing an analytically weighed amount of *n*-hexadecane as a standard. According to GC-analysis the protolyzed sample contained 3.0 mg of **3**, corresponding to a solubility of **2a** in

THF at 23 °C of 3.5 g/l or 8.4 mmol/l. The **2a**-THF-suspension was subsequently heated under stirring for 1 h at 60 °C, the hot suspension filtered through a glass frit with a heated mantle (60 °C) and a 2.0 ml sample of the filtrate protolyzed and analyzed for **3** as described above. From the amount of **3** in the protolyzed sample (5.2 mg) a solubility of **2a** at 60 °C in THF of 6.1 g/l (14.5 mmol/l) is calculated. In further experiments of the same kind solubilities of 3.1, 3.4, 2.6 and 2.6 g/l at 23 °C and 5.4 and 5.5 g/l at 60 °C have been measured, giving, including the experiment described above, average values for solubility of **2a** in THF at 23 °C of 3.0 g/l (7.2 mmol/l) and 5.7 g/l (13.6 mmol/l) at 60 °C, respectively.

¹H and ¹³C NMR spectra of **2a**: 6.7 mg of **1** and 6.3 mg of an "active magnesium"²¹⁾ were stirred in 2.0 ml of [D₈]THF (dried over NaAlEt₄ and condensed directly in the reaction flask) for 2 h. The suspension of **2a** was allowed to settle, the clear yellow supernatant liquid transferred into the NMR tube using a pipette and the tube sealed under argon. ¹H NMR spectrum of **2a** (400 MHz; ca. 0.3 wt.%; 25 °C): δ = 6.01 (m; 2-H), 5.95 (m; 1-H), 3.51 (s; 9-H). The spectrum shows additionally the presence of **3** (δ = 7.25 m, 7.11 m, 3.90 s). - ¹³C NMR spectrum of **2a**, see p. 1380 and table 1.

Kinetic and equilibrium measurements: Optimal results were obtained using the THF solvent from the same run which had been freshly dried and distilled. In a typical experiment 2.43 g (0.10 mol) of magnesium powder were suspended in 100 ml of THF, 0.06 ml of C₂H₅Br added and the mixture stirred for 22 h at ambient temperature in order to ensure the activation of the magnesium surface. The run was then brought to the desired temperature and 0.3565 g (2.00 mmol) of **1** were added at once to the stirred suspension. The experiments with varied amounts of Mg and/or **1** have been performed analogously. During the reaction the suspension was stirred magnetically at a rate of 1100 min⁻¹, if not otherwise stated, and the temperature kept constant (+ 0.1 °C) by means of a thermostat. At defined intervals 2.0 ml of the solution were removed (after allowing the suspension to settle for a few seconds) by means of a pipette, the samples injected into 2.0 ml of an air-free ethanol-THF mixture (1/5-vol./vol.) which contained an analytically weighed amount (ca. 10 g/l) of *n*-hexadecane as reference. Mg(OEt)₂ formed was left to precipitate and the clear solution analyzed for **1** relative to the reference by gas chromatography (method *a*).

From the GC data the concentration of **1** (in mmol/l) was calculated according to [1] = $1000 \frac{P \cdot 1\%}{178.2 \cdot C_{16}H_{34}\%}$, where *P* = gram of C₁₆H₃₄ per l of the standard solution.

In the method *b* the 2.0 ml samples of the stirred suspension were taken, worked up as in the method *a* and the percentage of **1** and **3** in the sample determined by gas chromatography. The concentration of **1** (in mmol/l) was calculated according to [1] = $\frac{1\%}{1\% + 3\% \cdot 178.2/180.2} [1]_i$, where [1]_{*i*} = initial anthracene concentration (in mmol/l).

The data from the measurements of the rate of **2a** formation are collected in tables 3, 3a, 4 and 5 and those from equilibrium measurements in table 2.

6 and 7 from 2a and THF: To a suspension of 3.28 g (135 mmol) magnesium powder in 200 ml of THF were added 0.1 ml of C₂H₅Br and the mixture stirred at ambient temperature for 18 h. After addition of 20.00 g (111 mmol) of **1** and stirring for further 2 h (during which time the formation of **2a** took place) 150 ml of THF were added and the mixture transferred into a 0.5 l stainless steel autoclave equipped with a magnetic stirring device. The mixture was heated in the autoclave to 120 °C under stirring for 72 h. After the autoclave was cooled and opened, the suspension was filtered and the solid (Mg-alcoholates and Mg) washed with THF and dried in vacuum (0.2 bar). The mother liquor contained 16.6 mmol of **1** and 2.3 mmol of **3**. The solid (53.4 g) was suspended in 250 ml of diisopropyl ether and hydrolyzed by addition of 50 ml of H₂O

Table 3. Decrease of anthracene concentration as a function of time for the reaction of anthracene (1) with Mg in large excess in THF at 25° and 60°C

<i>t</i> [°C]	Mg powder ^{a)} [mol/l]	molar ratio Mg/1	initial conc. of 1 [mmol/l]	conc. of 1 [mmol/l]						
				reaction time [min]						
25	1.0	50	20.1	17.6	15.7	12.0	9.4	4.8	0.3	0.3 ^{b)}
				2	4	7	10	15	30	240
25	1.0	20	49.0	44.0	41.0	35.0	31.4	22.5	2.0	1.1 ^{c)}
				2	4	7	10	15	30	60
25	1.0	10	98.4	92.2	88.3	87.2	82.5	77.3	58.0	37.0 ^{b,d)}
				3	5	7	10	15	30	60
25	5.0	50	100.5	82.5	67.8	41.5	15.3	4.0	0.9 ^{e)}	
				2	5	10	15	20	30	
25	10.0	100	87.7	52.3	34.2	0.4	0.5	0.4		
				3	5	10	15	30		
60	1.0	50	19.7	19.1	16.9	14.6	12.4	11.5	10.4 ^{c)}	
				1	3	7	10	15	30	
60	1.0	20	48.0	44.9	39.5	33.4	30.0	25.9	18.4	15.5 ^{c)}
				2	4	7	10	15	32	60
60	1.0	10	101.5	92.9	79.8	62.9	47.8	28.0	16.9	15.7
				2	5	10	15	30	60	120
60	5.0	50	104.0	80.0	55.0	28.0	21.5	17.0	13.5	13.4
				1	3	6	8	11	20	30

a) 50 mesh. — b) Averaged values from 4 experiments. — c) Averaged values from 3 experiments. — d) Anthr. conc. after 120 and 240 min reaction time were 2.6 and 1.5 mmol/l, respectively. — e) Averaged values from 2 experiments.

Table 3a. Decrease in anthracene concentration with time for the reaction of anthracene (1) with Mg in large excess in THF at 60°C: a comparison of the two sets of data obtained using the evaluation methods *a* and *b*

Mg powder ^{a)} [mol/l]	molar ratio Mg/1	initial conc. of 1 [mmol/l]	conc. of 1 [mmol/l], method <i>a</i>					conc. of 1 [mmol/l], method <i>b</i>				
			reaction time [min]									
1	20	45.2	33.2	23.2	18.4	15.5	13.2					
			32.7	24.0	18.4	13.9	13.4					
			7	15	32	60	1120					
1	10	96.0	73.5	56.7	29.4	15.7	11.3	13.9				
			69.1	52.2	32.9	13.8	11.7	11.4				
			5	10	17	32	60	150				

a) 50 mesh.

and of 2 N HCl until the aqueous layer was acid. The two layers were separated and the diisopropyl ether layer dried over Na₂SO₄. The diisopropyl ether was removed in vacuum and the solid residue dried in high vacuum (25°C). The composition of the solid (28.20 g) according to GC-analysis: 61.7% of 7 (gaschromatographic factor 1.3), 1% of 6, rest unknown compounds.

Table 4. Influence of the particle size and of the origin of Mg powder on the rate of formation of **2a** in THF at 60°C; initial concentration of anthracene (**1**) 20.0 mmol/l; Mg: **1** = 50

origin	Mg powder particle size [mm] ^{a)}	conc. of 1 [mmol/l] reaction time [min]					
		Ventron	0.08–0.3	19.1 1	16.9 3	14.6 7	12.4 10
Ventron	0.25–0.3	15.7 3	12.2 6	9.7 10	9.5 15	8.6 25	
Riedel de Haën	0.15–0.2	16.4 3	13.2 6	10.9 10	10.3 16	9.8 25	
Riedel de Haën	0.08–0.09	19.3 1	16.2 3	13.2 6	10.6 10	9.2 15	8.5 26

^{a)} As determined by sieving. – ^{b)} Data from table 3 (averaged values from 2 experiments).

Table 5. Rate of formation of **2a** in THF at 25°C at a molar ratio Mg: **1** ≈ 1:1 and with **1** in a large excess

mol of 1 per l THF	molar ratio Mg/1	% conversion to 2a ^{a)} reaction time [h]						
		0.83 ^{b)}	1/1.08	18.5 2	81 24	98 ^{c)} 48	100 ^{c)} 72	
0.32 ^{b)}	1/6.56	5.5 0.5	11 1	22 3	37 5	86 24	96 48	97 79

^{a)} Evaluation based on the amount of **3** formed on protolysis of samples on the *stirred* suspension with respect to the *n*-hexadecane standard, if not otherwise stated. – ^{b)} **1** not completely dissolved in THF. – ^{c)} Evaluation method *a* used.

4.00 g of the total 28.20 g of the mixture were chromatographed on a silicagel column (Merck 60, elution with pentane and subsequently with pentane-acetic ester 10/1–1/1 vol./vol. mixture). the fractions containing 92–98% of **7** (GC-analysis) were combined, the solvents removed in vacuum, the residue suspended in ether, the ether suspension filtered and **7** dried in vacuum (0.2 mbar). 1.70 g of a sample containing 98.6% of **7** (GC-analysis; m. p. 110–111°C) were obtained. By means of GC-MS-coupled analysis, a 0.6% impurity in the sample with a molecular weight 322, probably 9,10-bis(4-hydroxybutyl)anthracene, was detected. – MS (70 eV) of **7**: *m/e* = 324 [M^+], 306 [$M^+ - H_2O$], 251 [$M^+ - [CH_2]_4OH$], 233 [$M^+ - [CH_2]_4OH - H_2O$], 191, 55. – ¹H NMR spectrum of **7** (400 MHz, 1.5 wt% in [D₆]acetone): δ = 7.31 (m; 1-H), 7.20 (m; 2-H), 3.92 (t; 9-H), 1.77 (m; 1'-H), 1.55 (m; 2',3'-H), 3.53 (quart; 4'-H), 3.41 (t; OH); *J*_{9-H,1'-H} = 7.5 Hz, *J*_{3-H,4'-H} = 6.1 Hz, *J*_{4'-H,OH} = 5.2 Hz. – ¹³C NMR spectrum of **7** (10% in [D₈]THF, 25°C, rel. int. TMS): δ = 129.39 (d; C-1; ¹*J*_{CH} = 154), 126.41 (d; C-2; ¹*J*_{CH} = 160), 141.04 (s; 11-C), 47.55 (d; 9-C; ¹*J*_{CH} = 128), 43.45 (t; 1'-C; ¹*J*_{CH} = 126), 25.81 (t; 2'-C; ¹*J*_{CH} = 126), 34.06 (t; 3'-C; ¹*J*_{CH} = 125), 62.43 (t; 4'-C; ¹*J*_{CH} = 139). – UV-spectrum of **7** (C₂H₅OH): λ_{max} = 270 (ε = 1.11 · 10³) and 264 nm (ε = 1.06 · 10³).

1.56 g of the total 28.2 g of the mixture were crystallized once from ethanol and once from boiling acetone to yield 0.50 g of microcrystalline powder of m. p. 110–111°C.

C₂₂H₂₈O₂ (324.4) Calcd. C 81.44 H 8.70 O 9.86 Found C 81.84 H 8.70 O 9.54

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- 12) Similar approach has been used to study the kinetics of the formation of Grignard reagents: H. R. Rogers, C. L. Hill, Y. Fujiware, R. J. Rogers, H. L. Mitchell, and G. M. Whitesides, *J. Am. Chem. Soc.* **102**, 217 (1980); H. R. Rogers, J. Deutch, and G. M. Whitesides, *ibid.* **102**, 226 (1980); H. R. Rogers, R. J. Rogers, H. L. Mitchell, and G. M. Whitesides, *ibid.* **102**, 231 (1980); J. J. Barber and G. M. Whitesides, *ibid.* **102**, 239 (1980).
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- 15) The conversion to **2a** of 60–65% is attained directly by performing the experiment at 60°C (fig. 2, right).
- 16) It is of interest to note that the decomposition of **2a** in such experiments on raising the temperature takes place readily only in the presence of Mg powder; when a sample of pure **2a** is heated to 60°C in THF only a partial decomposition to **1** and Mg with respect to the equilibrium occurs. Obviously the presence of the free Mg surface is essential both for the formation and decomposition of **2a**.
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