dried over anhydrous $MgSO_4$, the crude product was chromatographed (column) by eluting with ethyl acetate/cyclohexane (1:2) to give the monochloride **2** as white crystals: mp 61–62 °C; 1.0 g (95%); MS *m/e* 220 $[M^+(^{37}Cl), 37]$, 218 $[M^+(^{35}Cl), \mathit{100}]$, 183 ($M^+ - Cl$, 19); IR (CsI) 1560, 1425, 1375, 1245 cm^{-1}.

6-(Chloromethyl)-2,2′-bipyridine (3). A mixture of 6-methyl-2,2′-bipyridine[21] (1.0 g, 5.9 mmol), *N*-chlorosuccinimide (770 mg, 5.9 mmol), and benzoyl peroxide (50 mg) in CCl_4 (50 mL) was refluxed under nitrogen for 24 h. After the mixture cooled to 0 °C, the succinimide was filtered. The solvent was removed to give a yellow oil, which was chromatographed (ThLC) on silica gel by eluting with ethyl acetate/cyclohexane (1:3) to give two major fractions.

Fraction A gives 6-(chloromethyl)-2,2′-bipyridine as an oil: 720 mg (60%); R_f 0.28; MS, *m/e* 206 $[M^+(^{37}Cl), 25]$, 204 $[M^+(^{35}Cl), \mathit{100}]$, 169 ($M^+ - Cl$, 31); IR (neat) 1560, 1430, 1080 cm^{-1}.

Fraction B affords 6-(dichloromethyl)-2,2′-bipyridine (**16**) as an oil: 350 mg (25%); R_f 0.34; MS, *m/e* 242 $[M^+(^{37}Cl, ^{37}Cl), 4]$, 240 $[M^+(^{37}Cl, ^{35}Cl), 36]$, 238 $[M^+(^{35}Cl, ^{35}Cl), 47]$, 203 ($M^+ - Cl$, *100*); IR (neat) 1730, 1580, 1555, 1430 cm^{-1}.

N-Oxidation of 6-Methyl-2,2′-bipyridine. To a stirred ice-cold (0 °C) solution of **15** (170 mg, 1 mmol) in $CHCl_3$ (10 mL) was added a $CHCl_3$ (25 mL) solution of *m*-chloroperbenzoic acid (173 mg, 1 mmol) over a period of 3 h. The mixture was stirred for 1 h at 25 °C and washed with a saturated $NaHCO_3$ solution and then water. The combined $CHCl_3$ extract was dried over anhydrous Na_2SO_4, concentrated in vacuo, and chromatographed (ThLC) by eluting with ethyl acetate/methanol (7:1) to give two fractions:

Fraction A was shown to be a single component, 6-methyl-2,2′-dipyridine *N*-oxide (**18**), as an oil: 100 mg (54%); R_f 0.18; MS, *m/e* 186 (M^+, 86), 169 ($M^+ - OH$, 21), 157 ($M^+ - CHO$, *100*); IR (neat) 1600, 1445, 1215 cm^{-1}.

Fraction B was spectrally assigned to the isomeric *N*-oxide **17**: 65 mg (35%); R_f 0.19; MS, *m/e* 186 (M^+, *100*), 169 ($M^+ - OH$, 45), 157 ($M^+ - CHO$, 30); IR (neat) 1585, 1445, 1375, 1225 cm^{-1}.

A mixture of mono-*N*-oxides (**17** and **18**) was dissolved in distilled acetic anhydride (5 mL) and then refluxed for 15 min. The reaction workup was as described for **9**, except that the resultant oil was chromatographed (ThLC) by eluting with ethyl acetate/cyclohexane (1:3) to afford two major components:

Fraction 1 was shown to be 6-(acetoxymethyl)-2,2′-bipyridine (**19**): an oil; 96 mg (42%); R_f 0.15; MS, *m/e* 228 (M^+, 7), 185 ($M^+ - COCH_3$, *100*), 155 ($M^+ - CH_2OAc$, 11); IR (neat) 1740 (C=O), 1580, 1565, 1230 cm^{-1}.

Fraction 2 was spectrally assigned to 6-methyl-6′-acetoxy-2,2′-bipyridine (**20**): an oil; 60 mg (26%); R_f 0.20; MS, *m/e* 228 (M^+, 7), 186 ($M^+ - COCH_2$, *100*), 158 ($M^+ - C_3H_2O_2$, 44), 155 ($M^+ - CH_2OAc$, 11); IR (neat) 1725 (C=O), 1640, 1600, 1525 cm^{-1}.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for partial support of this work and to Reilly Tar and the Ethyl Corp. for generous samples of 2-amino-6-picoline and bromine, respectively.

Registry No. **1**, 74065-64-8; **2**, 82740-64-5; **3**, 82740-65-6; **6**, 74065-63-7; **7**, 4411-80-7; **8**, 82740-66-7; **9**, 82740-67-8; **10**, 82740-68-9; **11**, 82740-69-0; **12**, 82740-70-3; **13**, 82740-71-4; **14**, 366-18-7; **15**, 56100-22-2; **16**, 82740-72-5; **17**, 82740-73-6; **18**, 82740-74-7; **19**, 82740-75-8; **20**, 82740-76-9; 2-bromo-6-picoline, 5315-25-3.

Supplementary Material Available: Analytical data for all new compounds are given. All values, cited therein, are within acceptable limits (1 page). Ordering information is given on any current masthead page.

Formation of Cage-Structure Organomagnesium Compounds. Influence of the Degree of Adsorption of the Transient Species at the Metal Surface

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Secondary and tertiary adamantyl organomagnesium compounds have been synthesized with yields of ca. 60% by means of an original static procedure. By condensing Grignard reagents of adamantane over benzaldehyde, 70% and 72% yields of alcohol are obtained; the 1- and 2-adamantanecarboxylic acid chlorides give 40% and 50% yields of 1,1- and 2,2-diadamantyl ketone, respectively. Competition between the various reactions occurring either at the metal–solution interface (formation of the organomagnesium compound and of the dimerization hydrocarbon) or in the medium (formation of the solvent-attack products) is studied in terms of the stirring, the nature of the halogen, the basicity of the solvent, and the ratio of the magnesium surface to the halide. The kinetic study of the formation of these organomagnesium compounds demonstrates the essential role of the anion radical $R\dot{-}X$) and of radical pair (R··MgX), whose degrees of adsorption at the metal surface, i.e., electrostatic interaction between the transient species at the metal surface, after the single electron transfer (SET), determine the competition between the various reaction pathways. These degrees of adsorption are highly dependant on the nature of the cage structure of the radical. An XPS analysis at different depths of the deposit at the metal surface provides invaluable information on the phenomena occurring at the metal–solution interface when 1-bromoadamantane attacks the magnesium. This makes it possible to retrace the history of the reaction in its initial phase.

Studies on 1-chloro-2-methyl-2-phenylpropane,[1] on 1-bromo-1-methyl-2-diphenylcyclopropane,[2] and, more recently, on neophyl chloride[3] with magnesium indicate that the formation of organomagnesium compounds is of a radical nature. Walborsky et al.[2] suggest the existence of tight-pair radicals and of loose-pair radicals leading to the formation of organomagnesium products. On the basis of

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[1] C. Ruchardt and H. Trautwein, *Chem. Ber.*, **95**, 1197 (1962).

[2] (a) H. M. Walborsky and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3288 (1964); (b) H. M. Walborsky and M. A. S. Aronoff, *J. Organomet. Chem.*, **51**, 31 (1973).

[3] E. Grovenstein, A. B. Cottingham, and L. T. Gelbaum, *J. Org. Chem.*, **43**, 3332 (1978).

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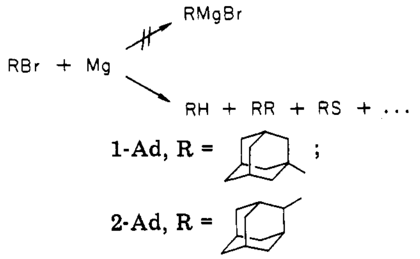
^1H NMR studies, Blomberg et al.[4] demonstrated the existence of CIDNP effects in the organomagnesium formation products; only the coupling of free radicals in solution or the formation of free radicals at the surface of the magnesium can account for these effects. Stereochemical studies on the reaction of cyclopropane,[2] benzonorbornadiene,[5] or vinyl chloride derivatives[6] with magnesium, as well as various kinetic studies[7,8] on the reaction rates of certain alkyl halides with magnesium, seem to indicate that the rate-determining step of the formation mechanism of the Grignard reagents involves the transfer of a single electron from the metal to the halogenated derivative.

Nevertheless, none of these many studies provides an explanation for the systematic failures encountered in attempts at synthesizing cage-structure organomagnesium compounds.[9-13] Thus, at no time does 1- or 2-adamantyl bromide yield an organometallic compound (eq 1), whereas



(1)

secondary or tertiary halides such as isopropyl chloride, *tert*-butyl chloride, and 3-chloro-3-ethylpentane give excellent yields of organomagnesium compounds. Therefore, we have attempted to determine and understand the factors governing these wild differences in behavior.

After many unsuccessful attempts at synthesizing 1-adamantylmagnesium bromide we finally achieved an initial result with 1-AdBr and magnesium. Indeed, by eliminating all stirring of the medium during the reaction, a low yield (20%) of this organometallic compound was obtained. A very adherent deposit on the metal surface was also observed at the end of the reaction. This led us to conceive the likelihood of a surface state conducive to the formation of cage-structure radicals that disappears when the medium is stirred. The study on the formation of cage-structure organomagnesium compounds reported herein was undertaken to test this hypothesis and to gain a better understanding of the phenomena occurring at the metal–solution interface.

Table I. Product Yields from the Attack of of Mg by 1- and 2-AdBr

	yield,[d] %			
RBr[a]	RMgBr[b]	RH[c]	RR[c]	others[c]
1-AdBr	58 (59)	17.5 (21)	12.5 (11)	12 (7,9)
2-AdBr	60 (61)	2 (4)	35 (33)	3 (2)

[a] Halide, 0.25 M in Et_2O; $BrCH_2CH_2Br$, 0.1 mL. [b] Determined by acid-base titration and mass spectrometry after hydrolysis; after 3 days of refluxing in ether, there is no change. [c] Determined by GLC. [d] Yields in parentheses are obtained with 0.5 mL of dibromoethane. With 2 mL of dibromoethane the product yields from attack by 1-AdBr become 59.5%, 26%, 5%, and 5%, respectively.

Table II. Role of the Ratio F = [Mg]/[RX] on the Formation of 1-AdMgBr

		% yield			
runs	F[a]	1-AdMgBr	Ad-Ad	AdH	others
1	5	37	<0.5	53	9.5
2	10	54	2.5	36	7.5
3	15	58	6.5	29	6.5
4	30	59	11	20	10

[a] The concentration of AdBr is constant (25 mmol in 25 mL of ether). The stoichiometry of the reaction is 1/1.

Results

When 1-adamantylmagnesium bromide was synthesized by using a highly reactive magnesium obtained in situ by the standard method of Rieke,[14] no trace of organomagnesium compound was detected, but a 60% yield of adamantane and a 30% yield of 1,1′-biadamantane were isolated. In contrast, when stirring was halted in the course of halide addition, an acid–base titration conducted 2 h after addition indicated the presence of a small amount (20%) of adamantylmagnesium bromide.

This initial result led us to develop a so-called "static" method whereby the entire reaction is conducted without any stirring whatsoever of the reaction medium. This resulted in a 58% yield of 1-adamantylmagnesium bromide.[15a] When this process was extended to 2-AdBr, the yield of 2-adamantylmagnesium bromide was 60% (Table I).[15b] In this latter case, unlike what was observed for 1-adamantylmagnesium bromide, the most abundant product was 2,2′-biadamantane.

To test the reactivity and confirm the formation of these compounds, we attempted the synthesis of the symmetrical diadamantyl ketones via the organometallic pathways only. By introducing a slow stream of previously dried carbon dioxide into the magnesium solutions, we were able to synthesize equal yields (90%) of the secondary and tertiary carboxylic acids which, after being treated with thionyl chloride, gave the corresponding acid chlorides (eq 2a).

$$\mathrm{RMgBr} \xrightarrow[2.\ \mathrm{H_2O}]{1.\ \mathrm{CO_2}} \mathrm{RCOOH} \xrightarrow{\mathrm{SOCl_2}} \mathrm{RCOCl} \qquad (2a)$$

$$\mathrm{RMgBr} + \mathrm{RCOCl} \xrightarrow{\mathrm{CuBr}} \mathrm{R_2C{=}O} \qquad (2b)$$

$$\mathrm{R} = \text{1-Ad or 2-Ad}$$

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Table III. Influence of the Halide on Organomagnesium Compound Formation[a]

	% yield				
AdX	1-AdMgX	AdH	AdAd	others	$t_{1/2}$, min
1-AdCl	60	14	17	9	370
1-AdBr	56	29	7	8	180
1-AdI	13	69.5	5.5	12	45

[a] [AdX] = 1.0 M, [Mg]/[RX] = 15, solvent Et_2O, θ = 35 °C, Mg with 2000 ppm of impurities.

Then, by a method developed here at the Institute,[16] which consists of slowly adding the organomagnesium compound at 0 °C to the acid chloride in the presence of copper salts, we obtained a 45% yield of 1,1-diadamantyl ketone and a 50% yield of 2,2-diadamantyl ketone based on starting RMgBr (eq 2b). At the same time, we condensed these magnesium compounds over benzaldehyde and got 70% and 72% yields of (1- and 2-adamantyl)phenylcarbinol, respectively. The similarity between these yields seems to indicate that the reactivity of these two organomagnesium compounds is comparable and, above all, that it is conditioned by the steric hindrance which is practically the same in both cases.

The success in synthesizing this type of organomagnesium compound by the "static" method led us to surmise that the phenomena occurring at the metal–solution interface play a major role and that the area of the metal surface open to attack by the halide must be one of the major factors in achieving this synthesis.

In view of the difficulty in assessing the surface of the Mg turnings, we worked from the premise that the molar ratio F = [Mg]/[halide] was proportional to the surface/[halide] ratio, and we were thereby able to study the influence of this ratio on the yields of the various products formed during synthesis. Thus, Table II shows that (i) as the surface of the Mg increases, the yield of organomagnesium compounds and of dimerization products increases, whereas that of adamantane quickly decreases and that (ii) the yield of organomagnesium compound is highest for values of F equal to or greater than 15. No difference in yield is observed when the magnesium contains 5, 2000, or 20 000 ppm of impurities (mainly ferric); however, the purer the metal, the harder it is to initiate a reaction between the adamantyl halide and the magnesium.

Table III shows that the surface area and the degree of purity of the metal are not the only factors governing the outcome of the reaction. Indeed, as shown by the use of 1-adamantyl bromide, chloride, or iodide, the nature of the halogen also affects the reaction rate and the percentage yield of organometallic compound. Although 1-AdCl and 1-AdBr result in similar yields of magnesium compound, the reaction is twice as fast in the latter case. Although the reaction rate increases with the iodide derivative, the yield drops to 13%.

In all three cases, at the start of the reaction, a temporary coloring which changes with the nature of the halogen is observed: light pink for AdCl, violet for AdBr, and blue for AdI. No coloring is observed if drastic measures are taken to avoid any trace of oxygen (solvents distilled under an argon stream; magnesium priorly degassed at 200 °C). Moreover, the presence of 1-adamantanol is detected in hydrolysis products only when coloring has been observed. These observations indicate that the coloring might be due to oxidation of the organomagnesium compound which leads to the formation of AdO–OMgX peralkoxides which then give rise to AdOMgX alkoxides.

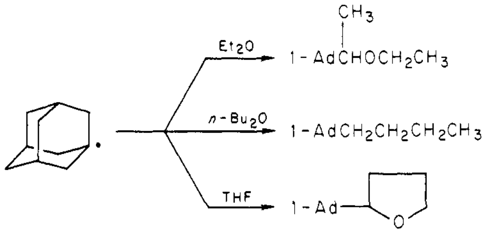
Table IV. Influence of the Solvent (S) on the Formation of 1-AdMgBr[a]

	% yield			
solvent	AdMgBr	AdH	AdAd	AdS
Et_2O	58	17.5	12.5	4.5
n-Bu_2O	60	20.5	8	6
THF	25	34	26	7.3

[a] [AdX] = 0.25 M, F = 15, and Mg with 2000 ppm of impurities.

A study of the formation of 1-adamantylmagnesium bromide in different solvents (Table IV) also indicates that although the yield of organomagnesium compound is practically the same in dibutyl and diethyl ether, it drops in THF. Attempts to prepare Grignard reagents in HMPA and benzylic ether (aprotic solvents) and in heptane (apolar solvent) were unsuccessful. Indeed, regardless of the amount of dibromoethane added, the reaction could not be initiated.

Among the reaction products, there are solvent-attack byproducts (AdS) whose presence was heretofore undetected and which we were able to identify by mass spectrometry. Thus, depending on the solvent used, we obtained (1-adamantyl)ethyl ethyl ether, n-butyladamantane, and 2-(adamant-1-yl)tetrahydrofuran (eq 3). These products probably result from the solvent trapping the adamantyl radical which, in all likelihood, is generated when 1-AdBr attacks the metal. When 1-AdBr reacts with Mg, it is also probably this same radical which dimerizes to yield biadamantane and which attacks the hydrogen atoms of the solvent to yield adamantane.



(3a)

(3b)

(3c)

Unfortunately, probably because of the difficulties encountered in studying this type of heterogeneous reaction, there are only a few studies on the formation of organomagnesium compounds[7,8] which deal with the first-order kinetics in the halide.

Kinetic Study. Our static method is more suitable for kinetic studies than the standard method, because the surface state of the magnesium is not affected by mechanical stirring. To conduct such studies under satisfactory conditions, we designed a measurement cell (described in the Experimental Section).

The kinetic studies conducted for the molar ratio F = [Mg]/[RX] = 10 for 1-AdMgBr (Figure 1) and for 2-AdMgBr (Figure 2) show that (i) the disappearance of 1- and 2-AdBr, the formation of organomagnesium compounds, and the formation of solvent attack products, are governed by zero-order kinetics and that (ii) the kinetics are faster with the secondary adamantane derivative than with the tertiary one; moreover, in the second case the initiation period is undetectable whereas in the first one most of the biadamantane dissolves during this period.

The zero-order kinetics for the formation, reduction, and disappearance of the halide indicates that these reactions indeed have in common a kinetic rate-determining step occurring at the metal surface. When F equals 4 (Figure 3), the rate of attack by the halide clearly diminishes ($t_{1/2}$ = 400 instead of 240 min). However, the formation of the

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[16] M. Boussu, Thèse d'Université, Université Paris VII, 1973.

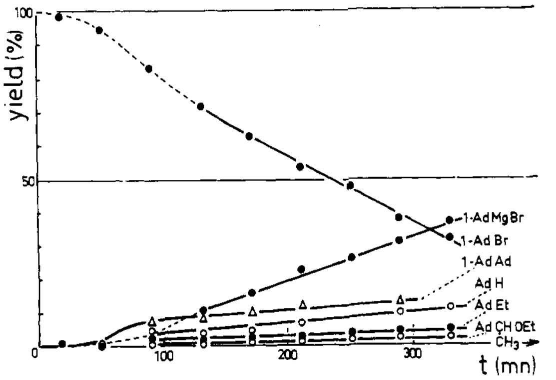

Figure 1. Formation of 1-AdMgBr in ether at 35 °C when F = 10.

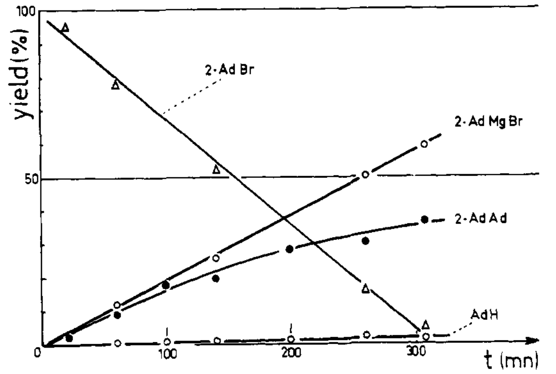

Figure 2. Formation of 2-AdMgBr in ether at 35 °C when F = 10.

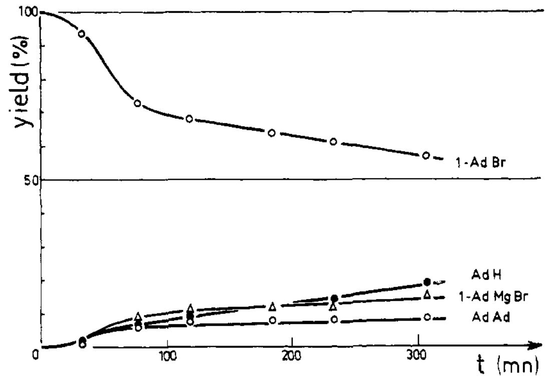

Figure 3. Formation of 1-AdMgBr in ether at 35 °C when F = 4.

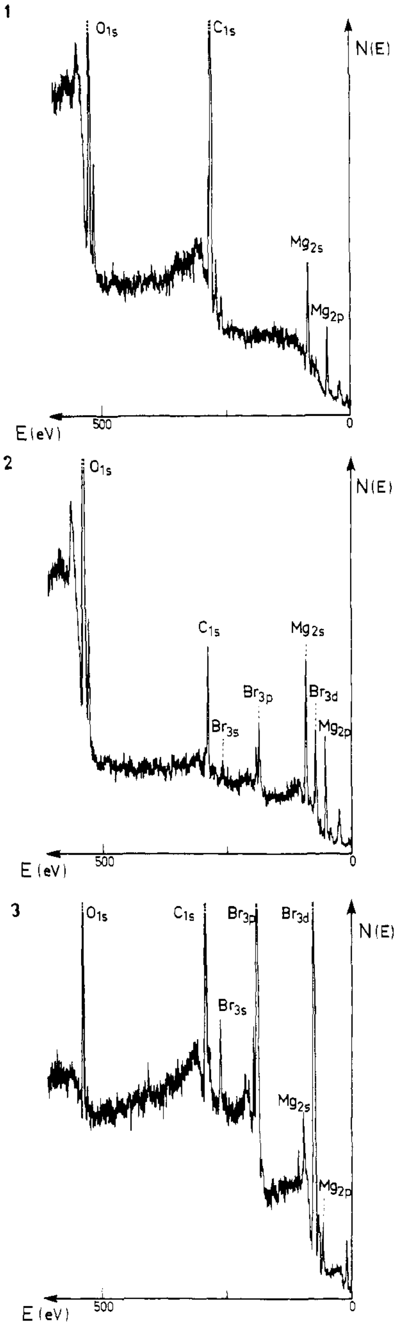

Figure 4. XPS spectra of Mg turnings: (1) Mg before reaction, (2) Mg after initiating the reaction with dibromoethane, (3) Mg after the reaction with 1-AdBr.

different products is indeed governed by zero-order kinetics. Moreover, this study confirms the percentage yields of organomagnesium compounds when F decreases.

In both cases (F = 4 and 10) a black deposit forms at the metal surface.[17] However, for F = 4 the reaction has stopped after 24 h, whereas 20% of the 1-AdBr still remains. This highly surprising result indicates that in the latter case, counter to our initial hypothesis, the black deposit acts as a screen when it reaches a certain thickness.

XPS Study. In attempting to understand this observation, we extracted some of the metal turnings coated with the black deposit from the medium and then washed them in ether in an argon atmosphere before placing them in the ethereal 1-AdBr solution. Under these conditions, the organometallic compound formed immediately without any need to initiate the reaction with dibromoethane. So in this particular case the deposit seems to enhance the start of the reaction. Because of these seemingly conflicting results, we subjected the black deposit to XPS analysis to determine its chemical structure and its homogeneous or heterogeneous nature;[18] we also subjected it to scouring by ion bombardment[19] so as to reconstitute the phenomena involved in the surface change and in the synthesis of the organometallic compounds.

XPS recordings of the metal were taken (1) before reaction, (2) after the reaction was initiated with dibromoethane, and (3) at the end of the reaction when the metal was coated with the black deposit.

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[17] In the formation of 2-AdMgBr, no deposit is visible on the metal at the end of the reaction.

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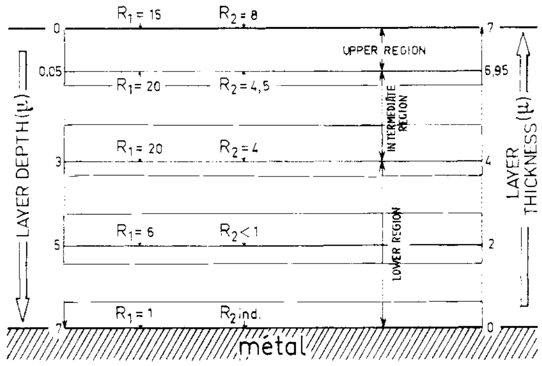

Figure 5. History of the reaction by XPS analysis of the components in the deposit at different depths ($R_1 = [C_{1s}]/[Mg_{2s}]$ and $R_2 = [Br_{3d}]/[Mg_{2s}]$).

(1) The XPS spectrum of the metal before reaction (spectrum 1, Figure 4) indicates surface contamination by oxides (O_{1s}, 720 eV), aliphatic carbons (C_{1s}, 285 eV), and carbonate or acid carbons (C_{1s}, 289 eV). The values found for the oxidized magnesium[20] are 90.1 eV for Mg_{2s} (lit.[21] 89.5–89.95 eV) and 51.3 eV for Mg_{2p} (lit.[21] 50.9–51 eV).

(2) The XPS spectrum recorded immediately after the addition of dibromoethane to the medium (spectrum 2, Figure 4) depicts a strong decrease in the intensity of the peak of the contaminat carbon and the appearance of low-intensity peaks due to the 3s, 3p, and 3d electrons of the bromine. Scouring a commercial Mg turning by ion bombardment also shows a marked decrease in the contaminating carbon peak. The signal-intensity ratio R_1 of the C_{1s} and Mg_{2s} electrons ($=C_{1s}/Mg_{2s}$) is always <1.[22]

(3) The XPS spectrum of the Mg turning coated with a black deposit (spectrum 3, Figure 4) indicates that the signal intensity ratio R_1 is 15, whereas the signal intensity ratio R_2 for the Br_{3d} and Mg_{2s} electrons ($=Br_{3d}/Mg_{2s}$) is 8.

XPS spectra of this Mg turning recorded at different times after ion bombardment (1 µA at 1000 eV) show that, in the first 500 Å of the layer, the ratio R_1 increases, while the ratio R_2 decreases. Both ratios then become constant up to a depth of 3 µm and then gradually decrease until they reach zero at 7 µm, when the metal surface is reached. The XPS spectrum recorded after reaching the surface is identical with that of a scoured Mg turning.

The same results are observed whether scouring is by ion bombardment or is mechanical. In particular, the different ratios are identical in value, thereby implying that the changes in ratio are due to the changing chemical composition of the deposit at different depths and not to decomposition phenomena during ion bombardment.

An additional XPS analysis of the magnesium bromide indicates that the ratio of the peaks for the Br_{3d} and Mg_{2s} electrons lies between 8 and 10, which is consistent with the theoretical value of 8.[23]

When this bromide is subjected to ion bombardment, the ratio decreases slightly but then remains constant during scouring. This indicates that for a homogeneous substance such as $MgBr_2$, there is no significant chemical decomposition at the ion-beam intensity used and that the Br_{3d} and Mg_{2s} electron emission is constant whatever the duration of the scouring.

Table V. Influence of Dilution on the Composition of the Grignard Solutions

[AdBr],[a] mol/L	% yield			
	AdAd[b]	AdH	1-AdS	others
1.00	6.5	86	2	5.5
0.50	10	80	4	6
0.25	12.5	77	5	5.5
0.10	17	65	9	9

[a] The [Mg]/[halide] ratio is held constant at 15. [b] Percent in the solution.

The 4-µm-thick lower region of the deposit (Figure 5) is heterogeneous, as indicated by the increase in R_1 and R_2; the bromide content is low, and the main constituents are Mg and organic compounds detected by the C_{1s} electron signals. The heterogeneous character of the deposit in the lower region can be explained by the fact that, as the layer spreads, the magnesium detected by analysis tends to be only Mg^0 from the radical complex, without any trace of the subjacent magnesium from the turning (thereby explaining the increase in R_1 and R_2). Above 4 µm, in the intermediate region, the two ratios are constant, thereby indicating that the deposit is homogeneous and made up of the same components.

In the upper region which is 500 Å, R_2 increases and reaches a value very near that obtained by XPS analysis of a magnesium bromide sample. This upper region is mostly composed of this salt and probably results from evaporation of the ether film containing this salt when the turning to be analyzed is extracted from the medium. Indeed, rinsing the black layer coated Mg sample with ether causes the R_2 ratio in the upper layer to drop from 8 to 1.5 [this can be explained by the very high solubility of this salt in this solvent (50 g/L)].

Silver nitrate titration shows that almost all the bromide ions are in solution. Thus, the XPS study indicates that the lower and intermediate regions of the black deposit are composed of Mg^0 and 1,1′-biadamantane.

To confirm the absence of MgH_2 in this deposit, we rinsed the coated Mg turnings with ether before adding benzophenone; no benzopinacol or benzhydrol which would have resulted from the presence of magnesium hydride was detected.

With the remaining turnings, a Soxhlet apparatus was used to extract the biadamantane and thereby to detach and recover a powdery deposit. When 1-AdBr was added to the deposit, the adamantane present after hydrolysis indicates that the halide attacked the powder.[24]

This confirmation of the presence of Mg^0 in the deposit indicates that it forms at the metal surface. For this to be so, as soon as the barely soluble 1,1′-biadamantane begins to form it must constitute a compact deposit which protects the Mg^0 from attack by 1-AdBr. A series of analyses on the dilution dependence of the composition of the magnesium solutions bears out the validity of this assumption (Table V). The amount of 1,1′-biadamantane increases with the dilution, and for dilute solutions ([1-AdBr] = 0.1 M) the black deposit has practically disappeared. EDTA titration and GLC analysis of this solution show the Mg^{2+} deficit to be equal to half the sum of the concentration of reduction and dimerization products.

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(20) It is very hard to record XPS spectra of alkaline or alkaline earth metals because they very quickly combine with the residual oxygen in the analysis chamber to yield the corresponding oxides. Studies[18] have shown that vacuums of 5×10^{-10}–10^{-11} torr are needed to obtain magnesium in its metallic form after ion bombardment.

(21) J. C. Fuggle, L. M. Watson, D. J. Fabian, and S. Afarssman, *J. Phys. F.*, **5**, 375 (1975).

(22) It is not certain whether the C_{1s} residual signal comes from the contaminating carbon of our twice-sublimated magnesium. It might come from inevitable contamination of the measuring chamber.

(23) B. Barbaray, Thèse de 3ème cycle, Université Paris VII, 1977.

(24) Because analysis of the various products was done by GLC, it was necessary to use halides yielding nongaseous and nonvolatile hydrocarbons.

Discussion

The direct synthesis of adamantyl organomagnesium compounds was made possible by a method based on the suppression of mechanical stirring and on the presence of an excess of magnesium.

Without mechanical stirring, the yield of 1-AdMgBr is 60%, whereas with stirring no trace of organomagnesium compound is detected, even though 1-AdBr attacks the magnesium, as attested by the formation of the reduction and dimerization products (adamantane and biadamantane, respectively).

The fundamental role played by stirring is highlighted by our kinetic results and those of Whitesides et al.[8] The latter authors have clearly shown that the reaction of various halogenated derivatives (including 1- and 2-AdBr) with magnesium is governed by a first-order kinetic law with respect to RBr and by a pseudo-zero-order law with respect to the magnesium surface. Our own results indicate that with their method 1-AdMgBr does not form. However, our kinetic study on the formation of secondary and tertiary adamantyl organomagnesium compounds (Figures 1 and 2) unambiguously shows that disappearance of the halide and the appearance of the organometallic compound and its secondary derivatives (except diadamantane) are zero-order reactions. It follows therefrom that the rate-determining step of the mechanism is the formation, at the metal surface, of one or several transient species which are precursors of all the products.

Depending on whether or not there is stirring, the final yields of products, like the kinetic rate laws, change.

How can these divergent results be explained?

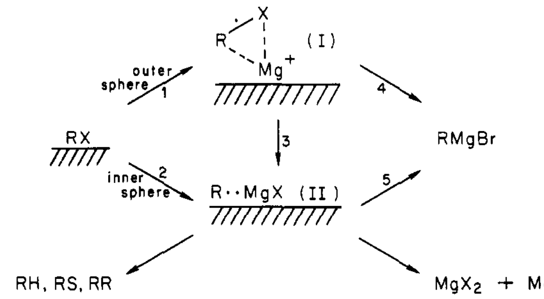
Whitesides et al.[8] have shown that when 1- or 2-AdBr is stirred in ether at 0 °C, the rate at which it disappears *is not diffusion controlled* and should *therefore* vary with stirring. However, instead of yielding organomagnesium compound, this method gives a 70% yield of solvent-attack products and a 30% yield of biadamantane. This result might be explained by a rise in desorption of the transient species at the metal surface brought about by stirring before the transient species can give the organomagnesium compound; diffusion of the transient species in the medium would explain the different byproducts.

Actually, the rate of the reaction between an alkyl halide and a metal can be expressed by $V = k[\mathrm{RX}]S_{\mathrm{Mg}}$ (S_{Mg} is the metal surface area). However, the fact that *our reactions* are governed by zero-order kinetics indicates that the factor $[\mathrm{RX}]S_{\mathrm{Mg}}$ is constant. By analogy with heterogeneous and enzymatic catalysis with zero-order kinetics, it is inferred that this factor is constant when the active surface of the metal is completely covered by adsorbed species. Thus, the rate law would be only dependent of the concentration of the species adsorbed on the metal surface. It would seem reasonable to assume that, like many heterogeneous and enzymatic catalyses, the rate-determining step is the rate of desorption of the transient species formed at the metal surface.

With stirring, this rate of desorption should increase, and, as the organomagnesium compound would not have the time to form, only byproducts would be obtained. The first-order kinetics observed by Whitesides could be explained by diffusion-controlled mass transport or by a single electron transfer (SET). Whitesides has shown that the rate-limiting step is not diffusion controlled, so it must be an SET.

In contrast, in the absence of stirring, (i) the rate of desorption should decrease considerably, and (ii) the organomagnesium compound should form because the transient species would have the time to interact. Formation of the organomagnesium compound with zero-order kinetics, consistent with the coat of adsorbed species on the active surface of the magnesium, actually does occur.

Scheme I



The source of the adsorbed species would have to be the reaction between the halogenated derivative and the magnesium to explain the formation of all the products with zero-order kinetics. These species would also have to be of a radical nature to explain hydrogen atom withdrawal from the solvent and the formation of reduction and dimerization hydrocarbons.

Studies by Walborsky et al.[2] on the stereochemistry of Grignard reagents indicate that retention of the configuration would be due to a tight-pair radical, I, whereas racemization of the reaction products would be dependent on a loose-pair radical, II (Scheme I). Depending on the metal surface and the nature of the halogen in RX, they obtained either one or both of these pathways.[25] Vogler[7] has shown that the absence of isotopic effects when $\mathrm{CH_3I}$ reacts with magnesium is due to pathway 1, while Blomberg et al.,[4] by many studies on CIDNP effects, conclude that a loose-pair radical is present.

Whitesides et al.[8] in a far-ranging kinetic study, could not decide between an outer-sphere SET (creation of the radical anion) and an inner-sphere SET (halogen withdrawal by the magnesium).

All these results lead us to consider that the formation of organomagnesium compounds might be a typical surface reaction, whereas the side reactions would occur in the medium, and competition between these two reaction pathways would depend on the degree of adsorption of the transient species at the metal surface; the degree of adsorption would be dependent on the electrostatic interactions between the transient species and the metal, after the SET. If this is so, the degree of adsorption, and therefore the reaction rates and competition between the pathways, should be influenced by the nature of the halogenated derivatives, of group R, and of the solvent and by the area of the metal surface.

Our results with adamantyl chloride, bromide, and iodide show that the yield of organomagnesium compound decreases from 60% to 56% to 13%, respectively, while the corresponding reaction rate increases. This assessment of the role played by the electronegativity of the halogen is consistent with the findings reported by Walborsky et al.[2] and by Buske et al.[5] When Walborsky detects an increase in racemization in passing from chloride to iodide, we detect an increase in the reactions in the medium.

Likewise, the role played by the solvent in the formation of organomagnesium compounds is far from negligible and is a much-discussed topic.[2,4c] For cage-structure organomagnesium compounds, when solvent basicity increases,

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[25] A recent study on fluoride derivatives of diphenylcyclopropane with lithium indicates that the SET can only occur via pathway 1, because the electron transfers from the metal to the phenyl nucleus and the C–F bond is unchanged in the reaction products [H. M. Walborsky and E. J. Powers, *Isr. J. Chem.*, **29**, 210 (1981)].

the yield of 1-AdMgBr decreases, whereas the yield of solvent-attack products (AdH and AdS) increases (Table IV). This might be explained by a greater solvation of the transient species; as this would lengthen their life-time, it would improve their diffusion in the medium in which these radicals attack the α-hydrogens of the ether to yield the reaction products (eq 4). Blomberg[4c] has clearly shown

$$R\cdot + CH_3CH_2OCH_2CH_3 \rightarrow RH + CH_3\dot{C}H{-}OCH_2CH_3 \quad (4a)$$

$$CH_3\dot{C}H{-}OCH_2CH_3 \xrightarrow{R\cdot} CH_3CHR{-}OCH_2CH_3 + \ldots \quad (4b)$$

that an increase in solvent basicity makes for better cleaning of the metal surface by improving the desorption of the adsorbed species.

With 1-AdBr, the yields of organomagnesium compound and of reduction and dimerization products are 58%, 18%, and 12%, respectively, whereas with 2-AdBr they are 60%, 2%, and 35%,[26] respectively. The similarity in the yields of organomagnesium compounds might be due to the fact that the steric volume of the transient species is the same.

The volume of cage-structure adamantane could have a steric effect on the degree of adsorption of the transient species which would favor reactions in the medium and would thereby explain failures to obtain an organometallic compound with stirring. In contrast, with less hindered molecules, surface reactions would be favored, and the organometallic compound should form. The extent of the role played by the nature of the R group might also explain divergent results, such as those reported in the literature for iodide derivatives; e.g., Vogler[7] suggests an outer-sphere SET with CH_3I, whereas Walborsky suggests the involvement of a loose-pair radical for iodide derivatives of diphenylcyclopropane.

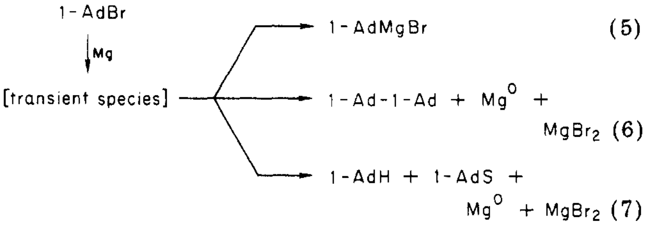
Our overall results indicate that the formation of the various products reveals competition between reactions in the medium and reactions at the metal surface. Stirring apparently favors reactions in the medium; so suppressing stirring and increasing the surface of the magnesium should enable these surface reactions to prevail.

Thus, when the ratio $F = [Mg]/[RX]$ (proportional to $S_{Mg}/[RX]$) increases, (i) the reaction rate increases (for $F = 4$, $t_{1/2} = 400$ min); for $F = 10$, $t_{1/2} = 240$ min; Figures 1–3), (ii) the percentage yield of adamantane (from attack of the solvent by the radical in the medium) decreases (Table II), and (iii) the yields of organomagnesium compound and of dimerization products increase (Table II). This clearly indicates that the ratio F controls the competition between these various reaction pathways.

When F is low, the reaction between 1-AdBr and Mg causes a black deposit to appear on the metal. This deposit can serve as a screen and even halt the reactions. XPS analysis of this deposit shows that its thickness can reach 7 μm. These results and their interpretation indicate that all the components of the deposit result from disproportionation of a radical complex adsorbed at the metal surface.

The lower and intermediate regions of this deposit are indeed made up of highly reactive magnesium (Mg^0) and biadamantane, which seem to have a common origin. Thus, in answer to the question "What becomes of the monovalent magnesium bromide ·MgBr in these reactions?",[27] asked by Blomberg at the Grignard Centennial in Lyons, we are able to reply that it disproportionates and forms Mg^0 and $MgBr_2$ in accordance with reactions 6 and 7 in Scheme II.

Scheme II



Moreover, as confirmed by the titrations, all the reactions which yield no organomagnesium compound generate monovalent magnesium bromide which disproportionates into Mg^0 and $MgBr_2$ (reactions 6 and 7, Scheme II). Therefore, the EDTA titrations of the Mg solutions show a Mg^{2+} deficit equal to half the sum of the concentration of reduction and dimerization products.

As opposed to $MgBr_2$, as soon as the barely soluble 1,1′-biadamantane in the medium begins to form, it constitutes a compact deposit which protects Mg^0 from attack by 1-AdBr.[28] For this reason, only part of the 1,1′-biadamantane passes into the solution, and the kinetic curve for its formation (Figure 1) quickly levels off after the start of the reaction. Furthermore, when dilution increases, the overall concentration of biadamantane in the medium increases and the deposit ceases to form. This deposit reveals that the disproportionation, like dimerization, occurs at the metal surface.

Conclusion

By using an experimental method based on *the absence of mechanical stirring* while preserving the surface state of the magnesium, it is possible to synthesize tertiary and secondary adamantane organomagnesium compounds. A kinetic study conducted during the attack of the magnesium by 1- and 2-AdBr unambiguously shows that all the different products form via the same rate-determining step occurring at the metal surface.

These transient species lead to three main reactions (Scheme II): formation of the organometallic compound (reaction 5), formation of dimerization product (reaction 6), formation of solvent-attack products (reaction 7).

By studying the ratio $F = S_{Mg}/[\text{halide}]$ and by conducting XPS studies of changes in the metal surface during reaction, we have evidence that the formation of solvent-attack products (AdH and AdS) occurs in the medium, whereas the synthesis of the organometallic and dimerization products occurs at the metal–solution interface. We assume that competition between the various pathways in the medium or at the metal surface indeed depends on the degree of adsorption of the transient species ($R^{\cdot-}X$ or $R\cdot\cdot MgX$) formed at the metal surface.

The validity of this hypothesis is borne out by the study of the various parameters which can influence this degree of adsorption. Thus the decreasing electronegativity of the halogen in AdX indeed causes this degree of adsorption to decrease and thereby causes the yield of the organomagnesium to drop. Likewise, when solvent basicity in-

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[26] The fact that with 2-AdBr one obtains mainly 2,2′-biadamantane can be explained by the greater reactivity of the secondary radical of adamantane [I. Tabushi, Y. Aoyana, S. Kojo, J. Hamvro, and Z. Yoshida, *J. Am. Chem. Soc.*, 94, 1177 (1972)] which, as soon as it disorbs, reacts with other radicals before diffusing in the medium.

[27] C. Blomberg, *Bull. Soc. Chim. Fr.*, 2143 (1972); special issue, "Hommage à Victor Grignard".

[28] If no deposit is observed for the formation of 2-AdMgBr, it is because, in ether, 2,2′-biadamantane is much more soluble than 1,1′-biadamantane.

creases, it enhances solvation of the transient species and, as this eases their desorption, increases the reactions in the medium. If the nature of the cage-structure radical, by virtue of the size of its steric volume, decreases the degree of adsorption of the transient species, then one can understand the failures to obtain an organomagnesium compound as reported in the literature.

Our study of all these parameters clearly indicates that the formation of Grignard reagents is mainly influenced by the degree of adsorption of the transient species which determines the competition between side reactions and the reaction yielding the organometallic compound. With stirring, it can be assumed that, when there is a high degree of adsorption of transient species involving an outer-sphere mechanism, there will be a good yield of organomagnesium compound; whereas when there is a small degree of adsorption of transient species involving an inner-sphere mechanism, the yield of organomagnesium compound will be low. Our results indicate that, in the latter case, a good yield of Grignard reagent can be obtained by suppressing stirring and by using a chloride derivative in a low-polarity solvent, in the presence of an excess of magnesium. Such a method can lead to new ways of synthesizing organometallic compounds which were previously impossible to synthesize. An extension of our experiments to other cage-structure compounds such as diamantane and twistane is currently under way and has yielded promising results.

Experimental Section

Melting points were determined with a Mettler FP5 apparatus. IR spectra were recorded on a Perkin-Elmer Model 225 infrared spectrophotometer. NMR spectra were recorded on a JEOL C-60 HL spectrometer with tetramethylsilane as an internal standard. Mass spectrometric data were obtained with a JEOL JMS 200 spectrometer connected to a JEOL Gaz 20 K gas–liquid chromatograph and a JEOL mass data system computer. XPS data were obtained with an AEI ES 200 X-ray photoelectron spectrometer with an FRR adaptation and a Mg anticathode. GLC analyses were performed on an Intersmatt IGC-12 DFL instrument fitted with a Carbowax 20M or an SE-30 gas chromatography column at different temperatures. Different types of Mg were used: with 5 ppm of impurities, Mattey Johnson; with 2000 ppm of impurities, Aldrich; with 20 000 ppm of impurities, Prolabo.

Diethyl ether was dried over $CaCl_2$ and then distilled over potassium. It was kept away from light and stored over sodium wire. THF and dibutyl ether were very dry Baker products (<150 ppm of H_2O for THF; <40 ppm of H_2O for Bu_2O) containing antioxidants.[29] Pentane, hexane, and heptane were Merck products for UV spectrometry. HMPT (Prolabo) was twice distilled over sodium in an argon atmosphere in order to obtain a dry solvent without amine.

Liquid column chromatography was performed on Merck alumina (neutral, grade II) packed in petroleum ether, followed by elution with petroleum ether/CCl_4 and CCl_4/Et_2O mixtures.

All experiments while studying the various parameters were run at least three times to check reproducibility. Data cited are an average of the results.

1-Bromoadamantane (1-AdBr). Adamantane (244 g; Aldrich, Gold Label) was treated with 310 mL of bromine by the method of Landa or Stetter.[30,31] The resulting crude product was recrystallized from ethyl acetate and yielded 265 g of white solid, mp 119.5 °C (lit. mp 119.5–120,[30] 118 °C[31]).

1-Adamantanol (1-AdOH). 1-AdBr was converted quantitatively to 1-adamantanol [mp 288 °C (lit. mp 288.5–290,[30] 282 °C[32]) by solvolytic methods.[30,32]

1-Chloroadamantane (1-AdCl). 1-AdOH (20 g) was treated with a mixture of thionyl chloride (25 mL) and CCl_4 (60 mL) by using the procedure of Stetter.[32] Recrystallization from methanol yielded 20.5 g of white solid, mp 166 °C (lit.[32] mp 165 °C).

1-Iodoadamantane (1-AdI). 1-AdOH (35 g), 25 mL of hexane, 100 mL of benzene, and 75 mL of hydroiodic acid (d = 1.70) were introduced into an Erlenmeyer flask under argon. The solution was stirred for 10 h before extraction of the organic phase in a separating funnel. This organic solution was washed with water, and the iodine was neutralized by sodium thiosulfate. It was rewashed several times with water and dried over sodium sulfate. After filtration, evaporation under vacuum yielded 36 g of crude AdI. Its recrystallization in methanol yielded 32 g of AdI which was more than 99% pure (55% yield) and had a melting point of 74.7 °C (lit. mp 151–152.5,[30] 75.3–76.4 °C[33]).

2-Bromoadamantane (2-AdBr). Into a 250-mL three-necked flask equipped with a mechanical stirrer, an addition funnel, and a condenser was introduced, under an argon atmosphere, 10.3 g of P_2O_5. With cooling, this was followed by the drop-by-drop addition of 44.7 g of phosphoric acid (26.3 mL) and by the slow addition of 42.3 g of potassium bromide. A white paste formed to which 14.2 g of 2-AdOH (Aldrich) was added. An orange coloring was noticed; this was followed by a rise in temperature up to 120 °C which remained steady for 1.5 h. After the mixture was cooled, 100 mL of H_2O and 50 mL of diethyl ether were added, and the organic phase was removed with a separating funnel and then rewashed in H_2O. The ethereal phase was then dried over calcium chloride and evaporated under vacuum; 16 g of crude product was obtained [75% of this was 2-AdBr (GLC)]. This crude product was recrystallized in methanol and yielded 10 g of 2-AdBr with 99% purity and a melting point of 138 °C (lit. mp 139.1–139.6,[34] 135–136 °C[35]).

1- and 2-AdMgBr. The excess magnesium (9.1 g, i.e., 15 times more than the halide) and 1- or 2-AdBr (5.37 g) were introduced into a two-necked flask under argon. After the addition of diethyl ether and initiation of the reaction with 0.1 mL of dibromoethane, the solution was heated to 35 °C in order to bring it to a very slow boil, permitting the solution to become homogeneous. *No mechanical stirring was used.* After 10 h, the halide was consumed, the Mg became black, and several tests on two fractions of the solution were run: (i) an acid–base titration and a Jolibois[36] titration of the first fraction showed a 58% yield of magnesium compound; (ii) the second fraction was treated with D_2O and analyzed by mass spectroscopy which showed a 60% yield of deuterated adamantane consistent with the preceding result. The stability of this organometallic compound was tested; the solutions remained unaltered over time, since after the ether was refluxed for 3 days, the titrations remained identical. 1- and 2-AdMgBr at the 1 M concentrations used were soluble in diethyl ether.

1- and 2-AdCOOH. The organomagnesium solutions were carbonated by introducing anhydrous CO_2. After hydrolysis and extraction, the secondary and tertiary carboxylic acids were isolated and identified by their melting points: mp 175 °C (lit.[32] mp 181 °C for 1-AdCOOH); mp 144 °C (lit. mp 143–144.6,[34] 143–144 °C[37] for 2-AdCOOH).

1- and 2-AdCOCl. The 1- and 2-carboxylic acids of adamantane were treated with $SOCl_2$ and refluxed for 1 h. The excess $SOCl_2$ (50%) was eliminated by distillation, and the corresponding acid chlorides were purified by distillation or sublimation. Yields were over 90%.

1,1-Diadamantyl Ketone (1-Ad–CO–1-Ad). Into a 100-mL three-necked flask cleaned with an argon stream were introduced 4.2 g of 1-adamantanecarbonyl chloride, 15 mL of anhydrous ether, and 0.35 g of anhydrous copper bromide. This mixture was stirred and held at 0 °C for 15 min. Then a dropper was used for the addition of 47 mL of 1-AdMgBr (0.5 M) at a rate of 1 drop every 3 s over a period of 3 h (stirring and the 0 °C temperature were

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[29] We first checked that the presence of antioxidants did not affect the yields of the different products. However, these antioxidants influence the yield of condensation products obtained when Grignard reagents are added over various substrates.

[30] S. Landa, S. Kriebel, and E. Knobloch, *Chem. Listy*, **48**, 61 (1954).

[31] H. Stetter and C. Wulff, *Ber.*, **93**, 1366 (1960).

[32] H. Stetter, M. Schwarz, and A. Hirshhorn, *Angew. Chem.*, 71, 429 (1959); *Ber.*, **92**, 1629 (1959).

[33] P. v. R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961).

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[35] W. Hoek, J. Strating, and H. Wynberg, *Recl. Trav. Chim. Pays-Bas*, **85**, 1045 (1966).

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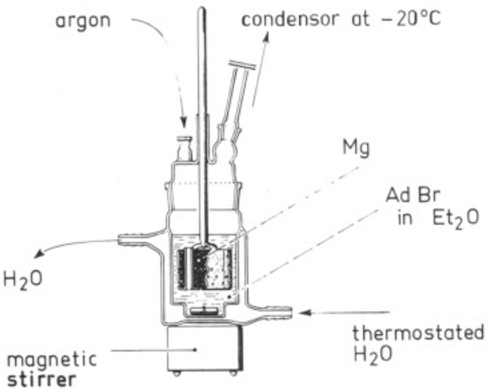

Figure 6. Kinetic cell.

maintained). After the addition, the mixture was stirred again for 1 h and for the duration of its reheating to room temperature. Hydrolysis was conducted directly in the flask with 20 mL of water; acidification was done with a 1 N solution of HCl.

After the aqueous phase was extracted with ether, the ethereal phases were washed with water and neutralized; they were then dried over sodium sulfate. The solution was filtered and then evaporated under vacuum. The crude product obtained was then redissolved in a minimum of CCl_4 and passed over an alumina column. Elution with pentane first eliminated the hydrocarbons and then released the expected ketone for pentane/CCl_4 mixtures. This led to the recovery of 2.85 g of 1,1-diadamantyl ketone with 99% GLC purity (45% yield): mp 185 °C (lit.[38] mp 185 °C); IR (CCl_4) 1670 (CO) cm^{-1}; ^1H NMR (CCl_4) δ 1.75 (m, 12 H), 2 (m, 12 H + 6 H); mass spectrum (75 eV), *m/e* (relative intensity) 298 (3.2, M^+), 163 (1.8, 1-$AdCO^+$), 135 (100, 1-Ad^+). Anal ($C_{21}H_{30}O$) C, H.

2,2-Diadamantyl Ketone (2-Ad–CO–2-Ad). An identical assay was run with 3.6 g ($\simeq$18 mequiv) of 2-adamantanecarbonyl chloride, 2.87 g of CuBr, and 45 mL of 2-AdMgBr (0.47 M). After purification by column chromatography, 2.7 g of 2,2-diadamantyl ketone with 98.5% GLC purity were obtained (50% yield): mp 182 °C (lit.[39] mp 177.5–179.5 °C); IR (CCl_4) 1697 (CO) cm^{-1}; ^1H NMR (CCl_4) δ 1.85 (br, 20 H and 4 H), 2.2 (br, 4 H), 2.6 (br, 2 H); mass spectrum (75 eV), *m/e* (relative intensity) 298 (5, M^+) 163 (3, 2-$AdCO^+$) 135 (100, 2-Ad^+). Anal. ($C_{21}H_{30}O$) C, H.

(2-Adamantyl)phenylcarbinol. Anhydrous (20 mL) ether and 1.45 mL of previously distilled benzaldehyde (15 mg) under an argon stream were added into a 100-mL three-necked flask equipped with a magnetic stirrer. This three-necked flask was placed in an ice bath before the dropwise addition of 20 mL of 2-AdMgBr (0.6 M, (12 mequiv). After the addition, the flask was allowed to reach ambient temperature while stirring was maintained. The aqueous phase was extracted with ether, and the ethereal phases were washed in H_2O, neutralized, and then dried over sodium sulfate. After filtration, the solution was evaporated to dryness. The resulting crude product was redissolved in 30 mL of petroleum ether and poured onto a 90-g alumina column. After elution with pentane, pentane/CCl_4, pure CCl_4, CCl_4/ether, and ether, 2.1 g of pure (2-adamantyl)phenylcarbinol was recovered (72% yield): mp 95.5 °C; IR (CCl_4) 3618 (OH) cm^{-1}; ^1H NMR (CCl_4) δ 1.3–3 (m, 15 H + OH), 4.6–4.8 (s, 1 H), 7.3 (s, 5 H, arom); mass spectrum (75 eV), *m/e* (relative intensity) 242 (3.1, M^+) 224 (2.4, $M^+ - H_2O$) 135 (100, 2-Ad^+) 107 (63.3, $PhCHOH^+$). Anal. ($C_{17}H_{22}O$): C, H.

(1-Adamantyl)phenylcarbinol. (1-Adamantyl)phenylcarbinol (1.75 g, 70%) was obtained from 1-adamantylmagnesium bromide (0.54 M, 19 mL) and benzaldehyde (1.15 g) by a similar procedure: mp 65 °C (lit.[40] mp 66–66.5 °C); IR (CCl_4) 3622 (OH) cm^{-1}; ^1H NMR (CCl_4) δ 1.4–2.1 (m, 15 H, Ad + OH) 4.2 (s, 1 H) 7.27 (s, 5 H, arom); mass spectrum (75 eV), *m/e* (relative intensity) 242 (4.3, M^+) 135 (100, Ad^+) 107 (57.8, $PhCHOH^+$). Anal. ($C_{17}H_{22}O$): C, H.

XPS Spectroscopy. The technique developed by Siegbahn[41] consists of the irradiation of a sample by a monoenergetic photon beam. From XPS measurements it is possible to obtain information about the nature of the elements. This method is particularly well-adapted for the study of thin deposits and is, moreover, an ideal technique for characterization of organic layers since, as opposed to Auger spectroscopy, it is not destructive.

Preparation of Magnesium Turnings before XPS Analysis. Magnesium (99.5%) turnings (6.07 g) and a few turnings as flat as possible (15 × 4 mm) for XPS study were placed in a 100-mL three-necked flask. Then dry, distilled ether (25 mL) was added under argon. The ether was gently boiled for 30 min, and a turning was removed and stored in ether under argon. Then, after the addition of dibromoethane (0.1 mL) and 20 min of reflux, a second sample was removed as before. Finally, 1-bromoadamantane (5.37 g) was introduced, and the mixture was gently boiled for an additional 6 h. All the turnings are covered with the expected black layer. A sample of the solution is deuterolized. GLC shows that the 1-AdBr has reacted and reveals 82% adamantane, 4% 1-AdOH, 5% AdS, and 7% 1-Ad–1-Ad. By mass spectroscopy the yield of organomagnesium is 55%. The turnings are kept in the organomagnesium solution until XPS analysis.

Kinetic Studies. For this work a thermostated cell was designed (Figure 6) so as to homogenize the solution without it being at the boiling point of the solvent. A stirring bar was lodged in the bottom of the cell, and the magnesium was placed in a glass basket with many holes. In this way, stirring homogenizes the solution without destroying the surface state of the Mg turnings necessary for organomagnesium synthesis.

The condenser was cooled by ethanol at −20 °C in order to avoid loss of solvent in the argon stream. Moreover, when the synthesis was complete, it was very easy to raise the basket by sliding its stem in the central socket and to add an organic substrate to the medium without any displacement or decantation. In this case, since the Mg turnings were not in contact with the solution, secondary phenomena were considerably reduced.

Registry No. 1-AdBr, 768-90-1; 1-AdOH, 768-95-6; 1-AdCl, 935-56-8; 1-AdI, 768-93-4; 2-AdBr, 7314-85-4; 1-AdCOOH, 828-51-3; 2-AdCOOH, 15897-81-1; 1-AdCOCl, 2094-72-6; 2-AdCOCl, 40079-92-3; 1-Ad-CO-1-Ad, 38256-01-8; 2-Ad-CO-2-Ad, 82679-52-5; (2-adamantyl)phenylcarbinol, 53140-72-0; (1-adamantyl)phenylcarbinol, 786-08-3.

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