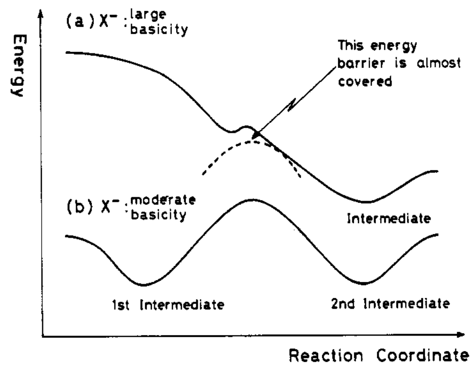

Figure 5. Double-well potential curves.

destabilization in separating the second intermediate into Cl^- and CH_3COX is the common feature in the gas-phase ion-molecule reaction.

The reactivity of trifluoro substrate CF_3COCl is compared to that of CH_3COCl. This substitution lowers the lumo and (lu + 1)mo and accordingly is expected to enlarge the rate constant of the nucleophilic displacement. In fact, $k = 1.77 \times 10^{-10}$ cm^3 mol^{-1} s^{-1} for $^{37}Cl^- + CF_3CO-^{35}Cl$, whereas $k = 1.19 \times 10^{-10}$ cm^3 mol^{-1} s^{-1} for $^{37}Cl^- + CH_3CO-^{35}Cl$.[2]

The stable tetrahedral intermediate has not been found in our calculation. In the gas phase, its possibility is determined by the criterion of whether the low-lying σ^* MO [(lu + 1)mo] is available to the $\sigma^*-\pi^*$ mixing or not. For $H^- + H_2C{=}O$,[3] CH_3O^- may be formed, because the σ^*_{C-H} level is very high and accordingly the mixing is unlikely. The stable intermediate is merely the solvation adduct, $X^- \cdots CH_3COCl$ or $Cl^- \cdots CH_3COX$. The bond interchange shown in Figure 2 is similar to the mechanism of the S_N2 reaction where the C=O bond length is kept almost constant. Like Walden inversion, the approach of X^- pushes out Cl^- in a concerted fashion.

Acknowledgment. We thank Institute for Molecular Science for the allotment of the CPU time of the HITAC M-200H computer.

Registry No. CH_3COCl, 75-36-5.

High-Yield Direct Synthesis of a New Class of Tertiary Organolithium Derivatives of Polycyclic Hydrocarbons

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For the first time, 1- and 2-adamantyllithium, 1-diamantyllithium, 3,5,7-trimethyl-1-adamantyllithium, 1-twistyllithium, 3-methyl-7-noradamantyllithium, 1-triptycyllithium, and 3-homoadamantyllithium have been directly synthesized from the reaction of an organic halide and lithium metal. By use of certain experimental parameters, the phenomena at the metal-solution interface are controlled, thereby resulting in exceptionally high yields of this new class of organometallic compounds (>75%, except in the case of 3-homoadamantyllithium). Competition between formation of the organometallic compound and formation of solvent-attack byproducts is determined by the degree of adsorption of the transient species (anion radical $RX^{-\cdot}$ or radical pair $R\cdot\cdot Li$) generated at the metal surface during attack by the halogenated derivative.

Unlike adamantane derivatives, which have many technological and pharmacological applications, homologous cage-structure compounds (twistane, homoadamantane, diamantane, ...) have received scant attention. One of the difficulties encountered with the latter has been the impossibility to obtain their corresponding organometallic compounds by direct synthesis.

In preceding articles,[1-3] we have shown that the failures encountered in synthesizing adamantyl organomagnesium compounds stemmed from poor knowledge about the phenomena occurring at the metal-solution interface during attack of the metal by the halogenated derivative. Light shed on these phenomena has enabled us to develop original methods whereby 60% yields of adamantyl organomagnesium compounds could be obtained.

Our own tests on the adamantyl organomagnesium compounds previously obtained by our methods[3] give limited yields of condensation products, because condensation is sensitive to steric hindrance of the reagent. We believed this restraint could be surmounted by using more reactive organometallic compounds.

Actually, all previous attempts at the direct synthesis of organolithium compounds[4,5] had failed, and only the exchange R′X + RLi → R′Li + RX had resulted in a few cage-structure organolithium compounds, the first of which was 1-triptycyllithium.[6] In previous attempts at direct syntheses using secondary or tertiary adamantyl halides and methyl or *tert*-butyllithium, tertiary[7-10] and secondary[10,11] adamantyl organolithium compounds could be obtained *only when an excess of tert-butyllithium is used.*[12] Extending this technique to 3-iodonor-

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(12) When no excess of *tert*-butyllithium was used, only dimerization hydrocarbons were obtained.[4,8,13]

Table I. Stability of Ia Solutions in Pentane at 25 °C

	time, h					
	1/2	17	24	48	72	144
[Ia], M	0.16	0.15	0.14	0.12	0.115	0.095

Table II. Role of the Solvent and of the Halide in the Synthesis[a] of Ia

solvent	RX[b]	% RLi	% RH	% RR	% ROH[d]
pentane,[c] 35 °C	Ib	82	13	2	3
	Ic	18	51	26	5
Et_2O,[c] −45 °C	Ib	76	20.5	1	2.5
	Ic	76	19	1.5	3.5

[a] Yields are expressed in comparison to the starting halide and are determined after deuterolysis by mass spectrometry and GLC. [b] [Ib] = [Ic] = 0.1 M. [c] Solvents are distilled and stored under argon to avoid the formation of alkoxy derivatives during synthesis. [d] This alcohol results from the presence of traces of oxygen in the solvent.

adamantane[14] had also yielded the corresponding organometallic compound. But, in all cases, the presence of an excess of *tert*-butyllithium needed for the shift in equilibrium has resulted in high amounts of byproducts (*tert*-butyl derivatives) in subsequent condensations.

The study described herein was conducted to determine whether the phenomena observed previously at the magnesium surface during the synthesis of cage-structure Grignard reagents could also be the source of failure to synthesize cage-structure organolithium compounds.

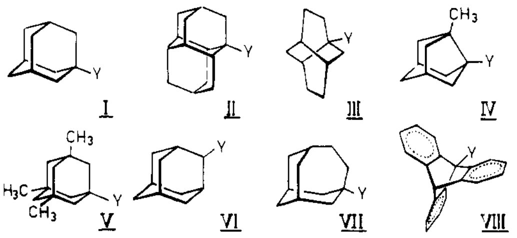
Results

Extension of the previously described method used for magnesium compounds[3] to organolithium compounds was unsuccessful because of the well-known fact that most tertiary organolithium compounds attack diethyl ether[15] at a temperature above −30 °C, and because, in the absence of stirring, lithium chloride slowly coats the metal with a film which very quickly inhibits attack by the halogenated derivative. So we chose a method that would simultaneously permit scouring the metal surface during synthesis while limiting the adverse role of stirring observed in the synthesis of cage-structure organomagnesium compounds.[3] We also chose an apolar solvent (pentane) to limit solvent-attack side reactions and used a 2% sodium lithium alloy.[15]

Under these conditions, 1-adamantyllithium (Ia) has been obtained for the first time[16] with a yield greater than 80%. Since the instability of Ia has been mentioned in the literature[17] as an explanation for failure in its synthesis, sampling of the lithium solution were taken at various points in time, subjected to deuterolysis, and analyzed by mass spectrometry (Table I). The small decrease in concentration indicates that this organolithium compound has good stability in pentane.

To determine the influence of parameters such as the nature of the halogen or of the solvent, we undertook the synthesis of Ia from chloro- and bromoadamantane (Ib and Ic) in pentane at 35 °C and in diethyl ether at −45 °C

Chart I[a]



[a] a, Y = Li; b, Y = Cl; c, Y = Br.

Table III. Yields[a] of Cage-Structure Organolithium Compounds Formed in Pentane at 35 °C

starting[b] halide	% RLi	% RH	% RR	% ROH[c]
Ib	82	13	2	3
IIb	76	17.5	2.5	4
IIIb	90	7		3
IVb	91	8		1
Vb	85	6		9
VIb	85	6	3	6
VIIb	0	42	55	3
VIIIb				

[a] Yields are expressed in comparison to the starting halide and are determined after deuterolysis by mass spectrometry and GLC. [b] [Starting halide] = 0.2 M. [c] This alcohol comes from the residual oxygen in the reaction medium.

Table IV. Evolvement of Overall Yields of VIIa during Formation

time of samplings	% RLi[a]	% RH[b]	% RR[b]	% ROH[b]
$^2/_5$ addition	13.5	34.5	49	3
$^3/_4$ addition	10.5	37.5	50	2
end of addition	9	40	48	3
15 min after addition	7	43.5	47	2.5

[a] Determined by deuterolysis and analysis by mass spectrometry. [b] Determined by GLC.

(Table II). It is seen that in pentane the yield drops from 82% to 18% when chloride is replaced by bromide. In contrast, in ether at −45 °C, the yield of organolithium from Ib and Ic is 76%.

The nature of the alloy also plays a major role in the synthesis of 1-adamantyllithium, as attested by the drop in yield from 82% to 57% when the sodium content of the alloy went from 2% to 1%. Previous tests, carried out with *tert*-butyllithium, also showed a large drop in yield, from 88% to 20%, when the sodium content of the alloy went from 2% to 1%.

Extension to the Synthesis of Homologous Adamantane Organolithium Compounds. We extended the conditions used in synthesizing 1-adamantyllithium to the synthesis of other alicyclic structures, in pentane at 35 °C as well as in ether at −45 °C.

In Pentane at 35 °C. For the first time, 1-diamantyllithium (IIa, Chart I), 1-twistyllithium (IIIa), 3-methyl-7-noradamantyllithium (IVa), and 3,5,7-trimethyl-1-adamantyllithium (Va) have been prepared in yields above 75%, whereas 2-adamantyllithium (VIa), previously synthesized by exchange, was directly synthesized with an 85% yield (Table III).

An initial test run on 3-homoadamantyllithium (VIIa), from a sampling taken 1 h after addition of VIIb, shows only reduction and dimerization hydrocarbons. In contrast, for a sampling taken as soon as the halide has been added, the presence of a small amount of the expected lithium compound is detected. Therefore, several tests in

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Table V. Yield[a] of Cage-Structure Organolithium Compounds Formed in Ether at –45 °C

starting halides	% RLi	% RH	% RR	% RS[b]	% ROH
Ic	76	18.5	1.5	0.5	3.5
IIc	55	33		5	7
IIIc	80	13	1.5	1	4.5
IVc	81	13	1	0.5	4.5
Vc	80	5	6	1	8
VIc	80	4	4		12
VIIc	0	40	60		
	8[c]	32[c]	60[c]		

[a] Yields are expressed in comparison to the starting halide and are determined after deuterolysis by mass spectrometry and GLC. [b] RS is the solvent-attack byproduct $CH_3C(R)HOEt$. [c] % yield at –65 °C.

pentane were required to confirm the presence of this organolithium compound (Table IV). Thus, samplings taken during the addition of VIIb indicate that it is possible to synthesize VIIa but that VIIa attacks the solvent at 35 °C and yields the reduction hydrocarbon.[18]

For 1-triptycyllithium (VIIIa), previously synthesized by exchange, formation is very slow in pentane, probably because of the low solubility of the halide. After reflux with stirring for 30 h, only 8% of the organolithium compound had formed, and over 90% of the 1-chlorotriptycene had not reacted. In contrast, when the reaction occurs in refluxing diethyl ether in 2 h, it affords a 93% yield of VIIIa which displays surprising stability in this solvent, unlike most tertiary organolithium compounds which attack ether as soon as the temperature rises above –30 °C. If chloride is replaced by bromide, yields drop from 93% to 60%, whereas the yield of triptycene rises from 4% to 39%.

With the concentrations used (0.2 M), the solubility of these lithium compounds, except for Va, in pentane is very low: 2×10^{-3} mol L^{-1} for Ia, IIa, and VIa; ca. 12 to 2×10^{-3} mol L^{-1} for IIIa and IVa.

In Diethyl Ether at -45 °C. All syntheses of these cage-structure organolithium compounds were repeated in ether at –45 °C, with the exception of VIIIa, because of the insolubility of halides VIIIb and VIIIC. Results obtained with these bromide derivatives are given in Table V.

It is seen that yields are slightly lower in ether than in pentane and that the amounts of dimerization hydrocarbons are practically negligible, except in the case of VIIc for which there is a 40% yield of reduction hydrocarbon and a 60% yield of dimerization hydrocarbon. However, when the temperature is lowered to –65 °C, an 8% yield of this organolithium compound can be obtained. At this temperature, samplings taken at various points in time from the lithium solution display no alteration as time elapses, since 1 h after the sampling has been taken the lithium content is still 8%.

Discussion

The formation mechanism of organolithium compounds has been studied previously, but to a lesser extent than the synthesis of Grignard reagents. Studies on different cyclopropane halogenated derivatives[19,20] and neophyl chloride[21] indicate that, like for analogous Grignard reagents,[22] a radical mechanism occurs at the metal surface via two processes: single electron transfer (SET) from the metal to the halogenated derivative, thereby forming a highly adsorbed tight radical ion pair (pathway 1), and

$$RX + M \rightarrow R^{-}{\cdot}X^{-}, M^{+} \qquad (1)$$

halogen abstraction by the metal, forming a barely adsorbed loose radical pair, in which case, the rate-determining step is the breaking of the C–X bond (pathway 2).

$$RX + M \rightarrow R\cdot + \cdot MX \qquad (2)$$

It should be recalled that the past and present methods for the direct synthesis of adamantyl organometallic compounds at our institute are based on (i) *the suppression of mechanical stirring*, resulting in a 60% yield of *organomagnesium compound*,[1-3] and (ii) *very vigorous stirring* that scours, resulting in an 82% yield of *organolithium compound*.[16] Stirring or its suppression plays a basic role in the synthesis of organolithium and organomagnesium compound, respectively.

Our work in the synthesis of adamantyl organomagnesium compounds[1-3] has indicated that formation of all the products stems from transient species generated at the metal surface when the halide derivative attacks the magnesium.

A recent study[3] indicates (i) that competition between adamantyl organomagnesium compound formation and side reactions depends on the degree of adsorption of the transient species at the metal surface (i.e., on electrostatic interaction between these species and the metal) and (ii) that *desorption* of these transient species from the metal surface is the rate-determining step in the synthesis of these organomagnesium compounds.

When the rate of desorption of the transient species is low, their lifetime at the metal surface is long and these species have the time to interact and yield the adamantyl organomagnesium compound. As the main factor conditioning the lifetime is stirring, *the suppression of stirring* explains the satisfactory (60%) yield of 1-adamantylmagnesium bromide. Conversely, *with stirring*, the rate of desorption of the transient species rises considerably, and their lifetime at the metal surface is short so that these species diffuse in the medium before interacting and only byproducts are obtained.

The nature of the metal might provide an explanation as to why there are good yields of adamantyl organolithium compounds by direct synthesis when vigorous stirring is used. As lithium is more electropositive than magnesium, it should release its electron more easily than magnesium, thereby creating a stronger electrostatic interaction between the lithium metal cation and the radical anion than between the magnesium metal cation and the radical anion. If this hypothesis is valid, then pathway 1 would prevail in the case of the lithium compounds, whereas pathway 2 would prevail in the case of the organomagnesium compounds. Other factors such as the electronegativity of the halogen in RX, the structure of group R, and the basicity of the solvent must also influence the degree of adsorption of the anion radical formed via pathway 1.

Role of the Halogen and of the Solvent. Our studies on 1-adamantylmagnesium bromide show that the yield

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[18] Reduction hydrocarbon RH can only be the result of an attack on solvent SH by the radical R·, because cage radicals can not give rise to disproportionation (Bredt's rule). The presence of solvent-attack byproducts RS was demonstrated in a previous paper.[3]

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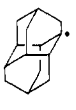
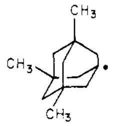
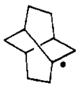
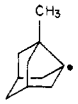
[22] (a) Walborsky, H. M.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3288. (b) Walborsky, H. M.; Aronoff, M. A. S. *J. Organomet. Chem.* **1973**, *51*, 31.

Table VI. Relative Stabilities of Cage Radicals

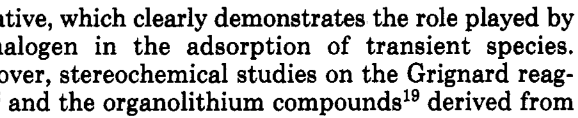
R·						
relative constant k^a	46	6.5	1.0	0.42	3.5×10^{-2}	6.3×10^{-3}
log k	1.66	0.81	0	−0.37	−1.45	−2.20

[a] k correlated with or extrapolated from perester thermolysis scales.[17,30]

of organomagnesium compound drops from 60% for chloride and bromide derivatives to 13% for the iodide derivative, which clearly demonstrates the role played by the halogen in the adsorption of transient species. Moreover, stereochemical studies on the Grignard reagents[22] and the organolithium compounds[19] derived from diphenylcyclopropane highlight the influence of the halogen. Thus, the optical purity of acids increases in the same direction as the strength of the carbon–halogen bonds: Cl > Br > I.

The yield of cage-structure organolithium compounds obtained from bromide and chloride derivatives in ether at −45 °C is the same. In contrast, in pentane at 35 °C, the yield of Ia obtained from Ib and Ic is 82% and 18%, respectively.

Thus, in a weakly solvating apolar solvent such as pentane, the halogen indeed plays a determinant role. The lower yield of organolithium compound in this solvent might be due to (i) the diminishing electronegativity-dependent strength of the C–X bond—thereby reducing the degree of adsorption of the transient species and causing their desorption—or (ii) a weaker C–Br bond as opposed to the C–Cl bond—thereby accelerating pathway 2. In either case, the abstraction of the hydrogen atom from the solvent (reaction 3) would become sizable. In contrast,



$$\mathrm{R^{\cdot} + CH_3CH_2OCH_2CH_3 \rightarrow RH + CH_3\underset{\cdot}{C}HOCH_2CH_3} \qquad (3)$$
$$\mathrm{CH_3\underset{\cdot}{C}HOCH_2CH_3 \xrightarrow{R^{\cdot}} CH_3\underset{\substack{|\\R}}{C}HOCH_2CH_3 + \cdots}$$

in a more highly polar solvent such as ether, this effect is masked by much greater solvation of the transient species. In this case, the solvation phenomena would favor diffusion of the transient species in the medium and result in higher yields of byproducts. Unfortunately, it is impossible to operate in diethyl ether at 35 °C, because at this temperature the organolithium compounds are quickly destroyed. Although this destruction is avoided in ether at −45 °C, reaction 3 is also clearly slowed down under these conditions, and results thereby obtained are hard to compare with those in pentane at 35 °C. Thus, at −45 °C, the yields of organolithium compounds are the same for bromide and chloride derivatives, and there is an increase in the yield of byproducts.[23] If one chooses a stable organolithium compound such as 1-triptycyllithium in ether at 35 °C, these difficulties have been surmounted, and, with the chloride derivative, the yield of organolithium compound reaches 90%, whereas with the bromide derivative it does not exceed 65%, thereby confirming the role played by halogen.

Influence of the Nature of the Metal. While, in the case of magnesium, the purity of the metal has no effect on the yields of Grignard reagents other than reducing the initiation period of the reaction when the amount of impurities increases, this is not the case of lithium, where a certain sodium content is needed for organolithium formation to occur.[24-27] In the first tests on *tert*-butyl-chloride, the 20% yield of organolithium compound obtained with a 1% sodium alloy and the 88% yield obtained with a 2% sodium alloy prepared by us indicate that the sodium content influences the yield of *tert*-butyllithium. For the cage-structure compounds studied, the best alloy is that with a 2% sodium content.

Just as the alloy used can affect the yield of organolithium compound, it can, as shown by Walborsky et al.,[19] also affect the stereochemistry of cyclopropyllithium derivatives. Our own results tend to corroborate this, and, on the basis of semiconductor theory,[28] it would seem that the presence of a sodium atom in the metal lattice of the lithium could modify the position of the Fermi level at the metal surface, thereby conditioning the capacity of the metal surface to adsorb the added halogenated derivative RX. Thus, depending on the alloy used, the transient species formed at the metal surface would be adsorbed to a lesser extent and would diffuse more easily in the medium to give rise to byproducts.

Influence of the Structure of the Cage Radical. Kinetic studies on the formation of secondary and tertiary adamantane organomagnesium compounds[3] unambiguously indicate that the transient species generated at the metal surface are the precursors of all the products formed. So it is indeed at the level of the anion radical or pair of radicals that predominance of one of the competing pathways is determined. If we assume that the same mechanism is also involved in the formation of organolithium compounds (an assumption in complete agreement with results reported in the literature), then the degree of adsorption of the transient species, obtained after the single electron transfer from the metal to the halogenated derivative, should be highly affected by the nature of the cage radical constituting these species. In this case, as already observed for our organomagnesium compounds and for the Barbier reaction,[29] there should be evidence for outright dependence between the yield of organolithium compound and cage radical stability.

Results from different studies on the stability of cage radicals, measured from the thermolysis of peresters[17,30] or from the thermolysis of diazoic compounds,[31] and from aldehyde decarbonylation,[32] have been compared with

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[23] This result was also observed with adamantyl Grignard reagents as there was a 60% yield of organomagnesium compound in ether and only a 13% yield in THF, which is more polar than ether.

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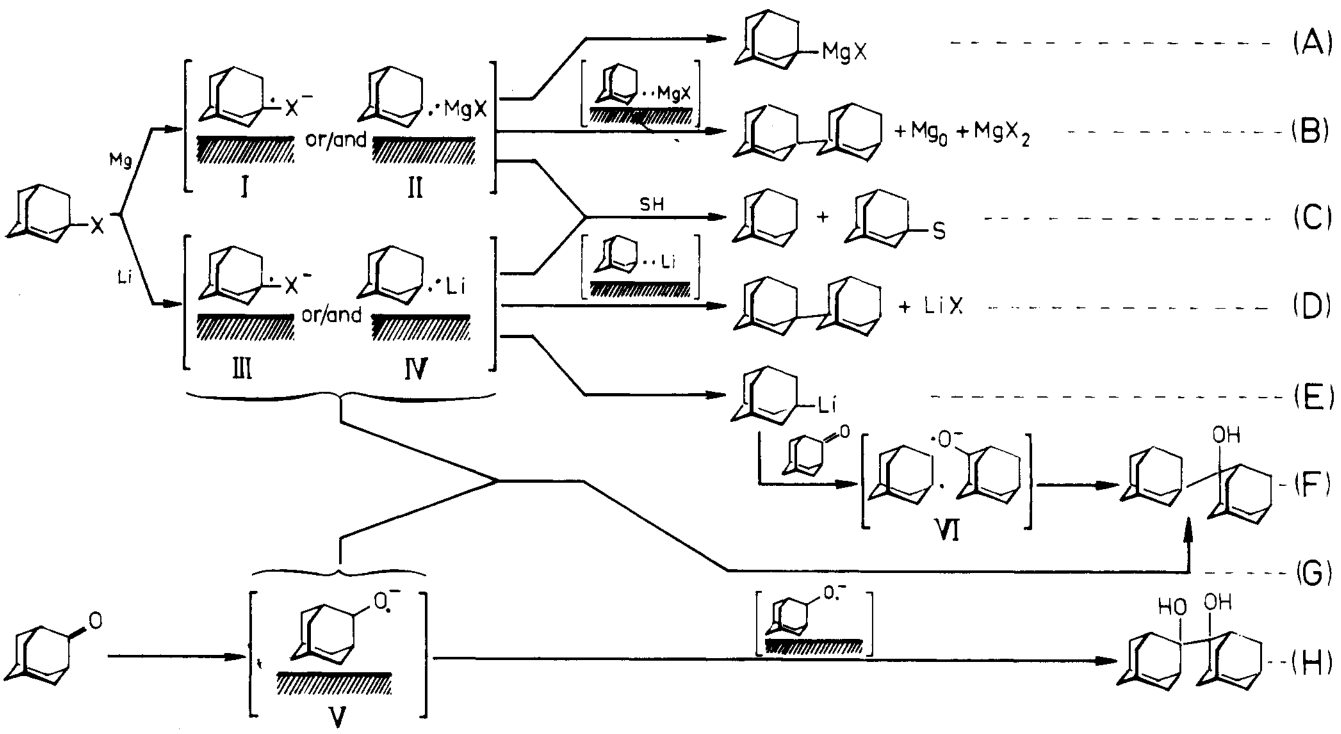
Scheme I



results from the solvolysis[33] of carbocations. The very good correlation shown by certain authors[34] to exist between these radical and carbocation scales has allowed us to extrapolate perester thermolysis rate constants, missing in the literature, from known solvolysis rate constants (Table VI).

The plot of the yields of organolithium formation vs. the colog of the perester thermolysis rate constants (Figure 1) shows that the evolvement of the yields as a function of the stability of the cage radicals is similar whether in pentane or in ether. In both cases, *the yield of organolithium compound increases as the stability of the radical decreases.* Conversely, when the stability of the radical increases, the yield of byproducts increases. This very important result confirms the role of the structure of group R in the formation of cage-structure compounds and its influence on the competition between reaction pathways at the metal surface.

It should be noted that in a previous study on the Barbier reaction[29] between cage-structure halogenated derivatives and various ketones, we showed that the in situ formation of the organometallic compound was not necessary to obtain the expected alcohol. This might be explained by the presence of a purely radical pathway between the ketyl radical of the ketone and the transient species ($R^-\cdot X^-$ or $R\cdot\cdot Li$) formed at the lithium surface by attack of the halogenated derivative before the transient species can generate the organometallic compound. Competition between the radical and organometallic pathways would thus depend on the degree of adsorption of these transient species. When the species formed at the metal surface are highly adsorbed, the organometallic pathway would predominate (twistane, methylnoradamantane), whereas when they are slightly adsorbed, we show[29] that the stability of the radical is greater and that these species have time to react with the ketyl radical of the ketone (diamantane, adamantane) and directly yield the alcohol.

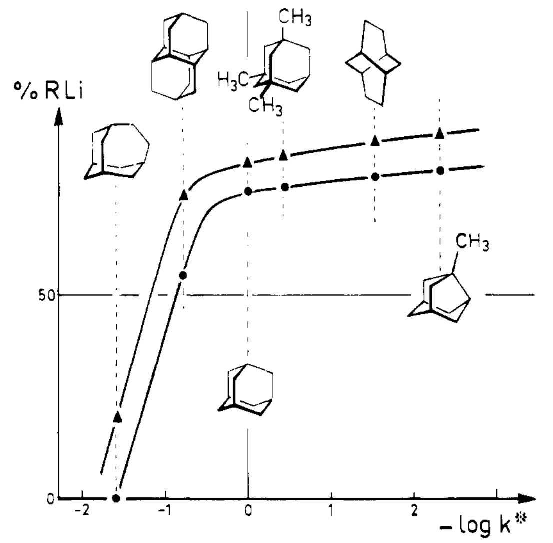


Figure 1. Yield of cage-structure organolithium compounds vs. perester thermolysis rate constant $-\log k$: (▲) with RCl in pentane at 35 °C (●) with RBr in Et_2O at -45 °C.

Conclusion

The formation of cage-structure organolithium and organomagnesium compounds could occur via multistep mechanism (cf. Scheme I) in which the first step is a single electron transfer from the metal surface to the halogenated derivative, leading to an anion radical (I, III), or abstraction of the halogen by the metal, leading to a radical pair (II, IV). The transient species generated during this first step would lead to three main reactions: (1) formation of the organometallic compound (paths A and E), (2) formation of the dimerization hydrocarbon (paths B and D), (3) formation of the reduction hydrocarbon (path C).

Our results indicate that the prevalence of one reaction or another depends on the degree of adsorption of the transient species generated at the metal surface. This

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degree of adsorption varies according to various parameters such as the nature of the metal, the electronegativity of the halogen, the basicity of the solvent, and, primarily, the structure of the cage radical. Moreover, the evolvement of yields of cage-structure lithium compounds seems closely related to the stability of the radicals generated at the metal surface. Actually, counter to generally accepted theory regarding this reaction, a previous study[29] indicates that the Barbier reaction can occur via a purely radical pathway (path G) without the in situ formation of an organolithium compound. Product formation via this pathway would result from condensation of the ketyl radical (V) (formed by single electron transfer between the metal and the ketone) with the transient species generated at the metal surface (III and IV) (also formed by SET between the halogenated derivative and the metal).

However, with certain cage-structure halogenated derivatives, there can be competition between radical pathway G and organometallic pathway F. Once again, the stability of the cage radical formed during the step common to both pathways is one of the determinant facts in this competition. Our overall results indicate that, in the formation of cage-structure organometallic compounds as well as in the Barbier reaction, competition between these essentially surface reactions (paths A, B, D, E, G, and H) and the reactions occurring partly in the medium (paths C and F) is mainly determined by the degree of adsorption of transient species I–IV (which rises as the stability of the radicals decreases).

Experimental Section

Melting points were determined with a Mettler FP5 apparatus. Infrared spectra were recorded on a Perkin-Elmer Model 225 infrared spectrophotometer. Nuclear magnetic resonance 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 Gas 20 K GLO and a JEOL mass data system computer. Gas chromatographic analyses were performed on an Intersmat IGC 12 DFL instrument fitted with a Carbowax 20M or an SE-30 gas chromatography column at different temperatures. Merck alumina (neutral grade II) was used for liquid column chromatography; petroleum ether (bp 30–60 °C), CCl_4, and diethyl ether were used for product purification.

Three types of lithium alloys were used to study the influence of the sodium content: a lithium ingot with 1% sodium (Merck); a lithium powder with 2% sodium (Alfa), degreased by soxhlet extraction with pentane; and a lithium wire with 2% sodium, which we prepared in the following manner.

Lithium (98 g) and sodium (2 g) were placed in a nickel crucible with a three-holed lid—a hole for an argon inlet, a hole for a thermometer, and a hole for a stirrer. Under high argon flushing, the crucible was slowly heated until the medium was completely liquified (ca. 190 °C). After homogenization, the medium was then quickly poured into a crystallizing dish containing Vaseline oil dried over sodium by heating at 160 °C for 1 h. This yielded irregularly shaped morsels, which, before use, were made into wires by a sodium press with a pot warmed by a heating wire.

Diethyl ether (Prolabo) and THF (Merck) were dried over calcium chloride, distilled under an argon stream over potassium hydroxide, and then stored away from light over sodium wire. Pentane (Merck) was also distilled under argon before being placed over sodium. 1-Bromoadamantane, 1-chloroadamantane, 1-bromodiamantane, 1-bromotwistane, 3-bromohomoadamantane, and 7-methyl-3-bromonoradamantane were prepared by previously described methods.[29] 2-Bromoadamantane was an Aldrich product.

1-Bromo-3,5,7-trimethyladamantane. 3,5,7-Trimethyladamantanol (20 g) (Aldrich, Gold Label) was treated with a mixture of anhydrous CBr_4 (150 mL) and freshly distilled thionyl bromide (20 mL); the overall contents were then refluxed for 3 h. After the solution was diluted with water, it was extracted with pentane. The organic phase was then washed in water, dried, and evaporated to dryness to yield, after recrystallization in CH_3OH, 26 g (92% yield) of white product, mp 101 °C (lit.[35a] mp 101–102 °C).

1-Chloro-3,5,7-trimethyladamantane. 1-Hydroxy-3,5,7-trimethyladamantane (25 g) was treated with a mixture of CCl_4 (100 mL) and thionyl chloride (25 mL). The yellowish product obtained after drying and evaporation was recrystallized in methanol and yielded 27 g (96% yield) of 1-chloro-3,5,7-trimethyladamantane, mp 88 °C (lit.[35b] mp 90–91 °C).

1-Hydroxydiamantane. 1-Bromodiamantane[29] (50 g) in 0.7 N HCl (75 mL) and DMF (65 mL) were stirred for 1 h at 105 °C. After dilution with water and filtration, the white precipitate was abundantly washed with water (3 × 300 mL). The resulting product 37.8 g (99% yield) was 99.5% pure, mp 293 °C (lit.[36,37] mp 291–292 °C, 292.5–294 °C).

1-Chlorodiamantane. 1-Hydroxydiamantane (5 g) in CCl_4 (40 mL) was treated with thionyl chloride (15 mL) under reflux for 5 h. The resulting crude product was purified by liquid column chromatography on alumina. Elution with pentane yielded 1-chlorodiamantane 4.9 g (98% yield) with 99.8% GLC purity, mp 251 °C (lit.[37] mp 250.5–252.5 °C).

1-Chlorotwistane. 1-Twistanol (3 g), prepared by the method of Deslongchamps,[38] was treated with freshly distilled thionyl chloride (10 mL). The resulting crude product was purified by liquid column chromatography with alumina, thereby yielding 3.1 g of pure 1-chlorotwistane (95%), mp 147 °C (lit.[38b] 147–148 °C).

3-Chlorohomoadamantane. 3-Homoadamantanol (8.15 g), prepared by the method of Stetter,[39] was treated with thionyl chloride (25 mL) under reflux for 3 h. After evaporation of the thionyl chloride, the crude product was recrystallized in methanol, thereby yielding 7 g (77% yield) of pure 1-chlorohomoadamantane, mp 163 °C (lit.[39] mp 160–161 °C).

1-Bromotriptycene. 9-Bromoanthracene (39 g) (Aldrich) was introduced into a 2-L, three-necked flask containing 480 mL of dichloroethane and 30 mL of secondary amylic nitrite. Under vigorous stirring and reflux, 24 g of anthranilic acid in 150 mL of THF were added dropwise. A further addition of secondary amylic nitrite followed by dropwise addition of anthranilic acid raised the yield of 1-bromotriptycene to 65%, in comparison to the 43% yield reported in the literature[40] when only a single addition is carried out. Maleic anhydride (50 g) and toluene (400 mL) were added to this solution, and the solvents lighter than toluene were removed by distillation. The solution was left under toluene reflux with 2 g of animal carbon for 30 min. Then, 400 mL of CH_2Cl_2 were added to the solution, which was then filtered. The filtrate was washed several times with a 15% KOH solution, then washed with 10% HCl solution, and neutralized with a 10% $NaHCO_3$ solution. After drying over sodium sulfate, the organic phase was evaporated under vacuum until dry (bath temperature 90 °C to remove the secondary amylic alcohol formed during the reaction). Recrystallization in warm methanol yielded 25 g (49.5%) of 1-bromotriptycene with 97% GLC purity, mp 254 °C (lit.[41] mp 250–254 °C).

1-Chlorotriptycene. Subjecting 9-chloroanthracene (21 g) to the above treatment yielded 10 g (35%) of 1-chlorotriptycene, mp 257 °C (lit.[42] mp 250–254 °C).

3-Chloro-7-methylnoradamantane. 7-Methyl-3-noradamantanol (4 g) was treated with freshly distilled thionyl chloride (15 mL) under reflux for 2 h. After purification on an alumina column, 4.4 g (98% yield) of pure 3-chloro-7-methyl-

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noradamantane were obtained: mp 155–156 °C; ^{1}H NMR (CCl_4) δ 1.18 (s, 3 H, Me), 1.56 (s, 2 H), 1.72 (s, 4 H), 2.18 (s, 6 H); mass spectrum (75 eV), *m/e* (relative intensity) 172 (5.2, M^+), 170 (13, M^+), 135 (11.5), 93 (100). Anal. ($C_{10}H_{15}Cl$) C, H, Cl.

2-Chloroadamantane. 2-Adamantanol (25 g) (Aldrich) was treated with PCl_5 (50 g) in 300 mL of diethyl ether under reflux for 30 min. The resulting crude product was recrystallized in methanol, and yielded 21 g (75%) of pure 2-chloroadamantane, mp 190–191 °C (lit.[43] mp 186–188 °C, 190–191.8 °C).

Experimental Procedure Used in Organolithium Synthesis. In Pentane. Pentane (25 mL) and finely cut lithium wire with 2% sodium (280 mmol) were added under an argon stream to a three-necked Morton flask containing 15 g of coarsely crushed glass and equipped with a carbon dioxide ice condensor and a Hershberg stirrer. The solution was vigorously stirred for 20 min under pentane reflux. Then, while continuing vigorous stirring under a slight argon stream, 20 mmol of halogenated derivative (RCl) in 75 mL of pentane was slowly added. The presence of crushed glass, together with vigorous stirring, allowed the metal surface to be scoured while generating lithium sand, and, later, enabled removal of the lithium chloride adsorbed at the metal surface. After the disappearance of the RCl, a sample was subjected to deuterolysis and analyzed by GLC and mass spectrometry to determine the organolithium concentration.

In Ether. A 125-mL, three-necked Morton flask equipped with a Hershberg stirrer and containing 15 g of coarsely crushed glass was cooled to −50 °C under a heavy argon stream. Once cooled to this temperature, the argon stream was diminished and 0.024 mol of lithium powder and 10 mL of anhydrous diethyl ether were introduced into this flask. After 10 min of vigorous stirring, 0.004 mol of halide (RBr) dissolved in 10 mL of dry ether were added dropwise for 30 min, during which vigorous stirring was continued. Fifteen minutes after this addition, a deuterolysis sample was removed and analyzed by GLC and mass spectrometry to determine the yield of lithium compound.

Acknowledgment. We express our gratitude to S. Briand for her invaluable collaboration.

Registry No. I (Y = H), 281-23-2; Ia, 3732-30-7; Ib, 935-56-8; Ic, 768-90-1; II (Y = OH), 30545-19-8; II (Y = H), 2292-79-7; IIa, 69261-61-6; IIb, 32401-16-4; IIc, 30545-17-6; III (Y = OH), 22635-86-5; IIIa, 69261-60-5; IIIb, 22650-12-0; IIIc, 31297-35-5; IV (Y = OH), 1905-16-4; IVa, 86550-17-6; IVb, 66117-95-1; IVc, 61898-33-7; V (Y = OH), 13987-76-3; Va, 86550-18-7; Vb, 17768-27-3; Vc, 53398-55-3; VI (Y = OH), 700-57-2; VIa, 38256-03-0; VIb, 7346-41-0; VIc, 7314-85-4; VII (Y = H), 281-46-9; VII (Y = 3-homoadamantyl), 32621-99-1; VIIa, 86550-19-8; VIIb, 27011-47-8; VIIc, 14504-84-8; VIII (Y = OH), 14504-80-4; VIIIa, 59239-90-6; VIIIb, 793-40-8; VIIIc, 15364-55-3; PCl_5, 10026-13-8; Et_2O, 60-29-7; thionyl bromide, 507-16-4; thionyl chloride, 7719-09-7; 9-bromoanthracene, 1564-64-3; anthranilic acid, 118-92-3; 9-chloroanthracene, 716-53-0; pentane, 109-66-0.

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Photochemical Additions of Alkenes to Phthalimides. Mechanistic Investigations on the Stereochemistry of Alkene Additions and the Effect of Aryl Substituents on the Regiochemistry of Alkene Additions

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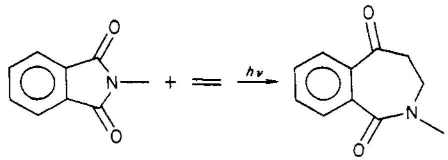
The mechanism of the photochemical addition of alkenes to phthalimides was investigated by determining the stereochemistry of the addition and the effect of aryl substituents on the regiochemistry. Intra- and intermolecular examples were examined. The stereochemistry of the addition of *cis*- and *trans*-2-butene to *N*-methylphthalimide to give 2,3,4-trimethyl-2-benzazepine-1,5-dione was studied. It was found that both alkenes added stereospecifically, each giving the corresponding *cis*- or *trans*-2,3,4-trimethyl-2-benzazepine-1,5-dione with >95% stereospecificity. The mechanistic implication of this result is either that the photochemical addition is a concerted (2 + 2) addition or that any intermediate biradical closes faster than rotation around the C–C bond which would result in loss of stereochemistry. A second approach to this problem employed the directive effects of aryl substituents. The proposed biradical intermediate is similar in structure to the phthalimide radical anion. The directive effects of aryl substituents have been experimentally determined in this system and are consistent with theoretical predictions. Theoretical predictions for aryl-substituent directive effects in the alternative concerted (2 + 2) process are opposite to those for the biradical case, which predicts that donors will direct meta and acceptors para. Irradiation of 4-methoxy- and 4-carbomethoxy-*N*-methylphthalimide in the presence of 1-hexene afforded the benzazepinedione addition products that resulted from addition to the para and meta C(O)–N bonds, respectively. These results are entirely consistent with a concerted process.

Over a period of years several groups have been working on the photochemistry of the phthalimide system. These molecules have exhibited diverse photochemical behavior,[1] including electron-transfer reactions,[2] photoreduction reactions,[3] Paterno–Büchi reactions,[4] and the addition of alkenes to form benzazepinediones (eq 1, NMP = *N*-methylphthalimide), which we reported in 1977.[5] The



(1)

1 (NMP)

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