

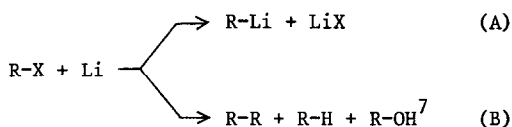
CAGE STRUCTURE ORGANOMETALLIC COMPOUNDS: 1-DIAMANTYL, 1-TWISTYL, 1-TRIPTYCYL  
AND 2-ADAMANTYL LITHIUM COMPOUNDS. SYNTHESIS AND REACTIVITY.

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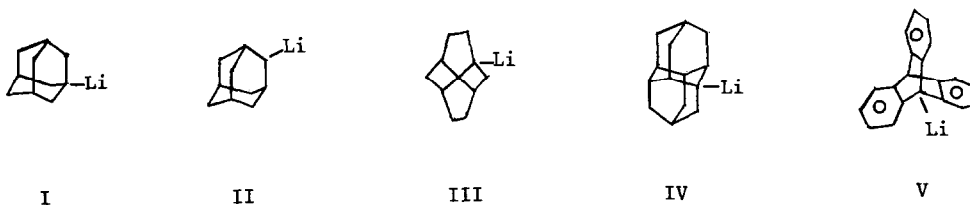
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As showed previously,<sup>1</sup> the failures encountered in attempts at direct synthesis of 1-adamantyl lithium (I),  $RX + Li \rightarrow RLi + LiX$ ,<sup>2,3</sup> are due to two main factors: the condition of the metal surface and the nature of the halide. However, the difficulties involved in synthesizing this type of lithium compound might also arise from the volume and geometry of the "cage" radical. In order to verify this assumption, we have sought to extend the synthesis method implemented for (I) to other "cage" structures where formation of the organolithium compound has either never been attempted or has never been achieved other than by an exchange reaction.<sup>4-6</sup>

The working method is the same as that used for 1-adamantyl lithium.<sup>1</sup> Twenty m.moles of the halide placed in 100 ml of anhydrous pentane react under solvent reflux on 280 mg. atoms of a 2% sodium-lithium alloy. The ratio  $[Li]/[RX]$  has been increased from 2.7 to 14, because we have ascertained that this modification brings about an increase in the rate of formation of the lithium compound (A) and a decrease in the quantity of side reactions (B). Thus:



For 2-adamantyl (II), 1-twistyl (III), 1-diamantyl (IV) and 1-triptycyl (V) lithium compounds, the best results are obtained when using alkyl chlorides and a 2% sodium-lithium alloy whose surface is scoured throughout the entire reaction.



Under these conditions, II and V, previously synthesized by an exchange reaction,<sup>4-6</sup> are obtained for the first time by direct synthesis, with respective yields of 85 and 93%. Furthermore, compounds III and IV, never before synthesized, are obtained with respective yields of 90 and 76% (Table I).

TABLE I

Product Yields<sup>a</sup> from the Reaction of Alkyl Chloride on Lithium

R-Cl	R-Li	R-H	R-R	R-OH
1-adamantyl chloride	82%	4%	2%	12%
2-adamantyl chloride	85%	6%	3%	6%
1-twistyl chloride	90%	7%		3%
1-diamantyl chloride	76%	18%	2%	4%
1-triptycyl chloride	93%	4%		3%

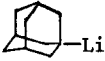
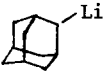


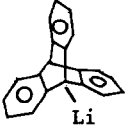

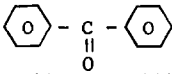
a) Yields are expressed with respect to the halide and were determined by mass spectrometry and vapor-phase chromatography.



A 90% yield of tertibutyl lithium itself is obtained by this method. Organolithium compounds II, III and IV were prepared in pentane, where they are stable but not very soluble:  $< 2 \cdot 10^{-3}M$  for II and IV, and  $12 \cdot 10^{-3}M$  for III. However, the formation of V occurs very slowly in this solvent because of the very weak solubility of the halide. After 30 hrs. of reflux stirring, 8% of the organolithium compound has formed, whereas 90% of the halide has not reacted. Nevertheless, unlike I, II, III and IV, which react on ether at room temperature, a 93% yield of V can be obtained over a 2 hr. reflux of diethyl ether, a solvent in which this lithium compound is stable at the reflux temperature.

In order to test the reactivity of these organolithium compounds, each one of them has been condensed on three non-enolizable ketones of increasing steric hindrance: adamantanone, benzophenone and hexamethylacetone. Except in the case of V which has been synthesized in





diethyl ether, the weak solubility of these lithium compounds in pentane led us to use pentane-ether or pentane-THF solutions for the condensations on these ketones.<sup>8</sup> The yields obtained are shown in Table II.

TABLE II  
Alcohol Yields<sup>a</sup> Obtained by Condensation

Ketones	R-Li					
						
	34% <sup>b</sup> 42% <sup>c</sup>	75% <sup>b</sup> 85% <sup>c</sup>	85% <sup>b</sup> 93% <sup>c</sup>	57% <sup>b</sup> 78% <sup>c</sup>	80% <sup>d</sup>	
 e	47% <sup>b</sup> 30% <sup>c</sup>	69% <sup>b</sup> 44% <sup>c</sup>	48% <sup>b</sup> 16% <sup>c</sup>	0% <sup>b</sup> 0% <sup>c</sup>	90% <sup>d</sup>	
tBu - C(=O) - tBu f	30% <sup>b</sup> 40% <sup>c</sup>	45% <sup>b</sup> 65% <sup>c</sup>	65% <sup>b</sup> 41% <sup>c</sup>	4% <sup>b</sup> 0% <sup>c</sup>	0% <sup>d</sup>	

- a) Yields are calculated with respect to the organolithium compound. All the alcohols were isolated and characterized by their mass NMR and IR spectra and by centesimal analysis.  
 b) Pentane-ether solution (10/2 volume ratio).  
 c) Pentane-THF solution (10/2 volume ratio).  
 d) As V is synthesized in diethyl ether, condensations are carried out in this solvent.  
 e) The ketone R--CO- and its reduction alcohol are obtained by condensation of I, II and III on benzophenone, with respective yields of 15, 6 and 49% in solution b, and 39, 23 and 78% in solution c.  
 f) For the condensation of I, II and III on hexamethylacetone in solution c, fragmentation ketone R-CO-tBu is respectively observed in 15, 12 and 17% amounts. This product is absent for condensations in solution b.

With adamantanone, the substitution of ether by THF in the pentane medium increases the yield of condensation alcohol, which, for compounds II, III and IV, is between 78 and 93%.

Condensations with benzophenone and hexamethylacetone are more sensitive to steric hindrance, since, in particular for IV, no condensation product is obtained. For compounds II and III, as in the case of compound I,<sup>1</sup> aside from the condensation alcohol, by products are observed: products derived from 1,6 addition on benzophenone (R--CO- and R--CHOH-) , and fragmentary ketones (R-CO-tBu) on hexamethylacetone. All of these products are more abundant in the pentane-THF medium than in the pentane-ether medium.

For triptycyl lithium, V, the condensations carried out in pure ether on adamantanone and benzophenone, the respective yields are 80 and 90%. In contrast, the reaction with hexamethylacetone is in all likelihood inhibited by the steric effect.

During formation of the lithium compound, the formation of duplication products R-R and of hydrocarbons R-H (Table I) confirms the radical nature of the mechanism.<sup>9</sup> Since these lithium compounds are stable in pentane, the R-H hydrocarbon can only be due to the attack of the radical on the solvent. If, as in the case of organomagnesium compounds,<sup>10</sup> the formation of these lithium compounds occurs at the metal surface, the stability of the radical should influence the competition between these different reactions. The great stability of the R' radical, enhances its diffusion in the solvent and hence increases the formation of R-R and R-H hydrocarbons and probably hinders the formation of these lithium compounds. Indeed, comparison of the yields of I, II, III, IV and V with the relative stabilities of the corresponding "cage" radicals (1-diamantyl > 1-adamantyl > 2-adamantyl > 1-twistyl > 1-triptycyl)<sup>11</sup> shows that the percentages of organolithium compound formation decrease as the stability of the radicals increases.

Acknowledgments: We wish to thank Mrs. S. Briand and Mr. M. Pellas for their technical assistance.

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6. In the case of these  $RX + R'Li \rightleftharpoons RLi + R'X$  exchange reactions, it is necessary to work under an excess of R'Li which increases the quantity and number of by-products during condensation.
7. The alcohols formed during this reaction are never deuterated after deuterolysis of the reaction medium. In all likelihood they result from the attack on the solvent by the alcoxides formed in the medium by the residual oxygen.
8. The use of a mixed solvent, particularly pentane-THF (10/2), brings about side reactions whereby the lithium compound attacks the oxygenated solvent. For example, in a pentane-THF (10/2) solution, I is completely destroyed in 15 mins., whereas in the same time period in pentane-ether (10/2) solution, the attack is very weak. When steric hindrance hampers condensation, the attack on the oxygenated solvent prevails and the resulting hydrocarbon can be obtained almost quantitatively (96% diamantane during the condensation of IV on hexamethylacetone). In contrast, in the case of V, where no attack on the solvent is observed, condensation yields are very high.
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(Received in UK 9 June 1978; accepted for publication 22 June 1978)