Mechanism of Reaction of Geminal Dihalides with Lithium Naphthalenide (LiNp·−): Evidence for an Electron Transfer Mechanism. Similarities to the Mechanism of Reaction of Geminal Dihalides with Certain Nucleophiles and Other One-Electron Donors

E. C. Ashby* and Abhay K. Deshpande

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

The reactions of the sterically hindered geminal dihalides 6,6-dichloro-5,5-dimethyl-1-hexene (**1a**) and 6,6-diiodo-5,5-dimethyl-1-hexene (**1b**) with lithium naphthalenide (LiNp·−) in THF were investigated in an attempt to compare the results of reactions involving a known one-electron donor (LiNp·−) with those involving nucleophiles believed to be one-electron donors. On the basis of radical-trapping studies, deuterium tracer studies, and product studies using cyclizable radical probes, it can be concluded that the reactions studied are very similar to those reported by us earlier involving magnesium metal, LiAlH₄, and other nucleophiles. In addition to radical-derived products, the reaction of **1a** with LiNp·− afforded hydrocarbons, in high yields, that were derived from a carbene intermediate. On the other hand, **1b**, on reaction with LiNp·−, did not yield any carbene-derived hydrocarbons. These results show that the formation of a carbene intermediate, derived from a radical, depends on the nature of the halogen present. It was also found that naphthalene can behave as a hydrogen atom donor toward a radical in the presence of known hydrogen atom donors, such as THF.

Introduction

The naphthalene radical anion has been shown to react with alkyl monohalides in 1,2-dimethoxyethane (DME) leading to both reduction and alkylation products, by an electron transfer pathway.[1–5] The general mechanism for the reaction of the naphthalene radical anion with an alkyl halide is depicted in Scheme 1.[1] In addition to alkyl monohalides, studies have also been carried out with α,ω-dihaloalkanes as substrates;[1] however, geminal dihalides have not been employed in such studies so far.

The reactions of the two geminal dihalides, 6,6-dichloro-5,5-dimethyl-1-hexene (**1a**) and 6,6-diiodo-5,5-dimethyl-1-hexene (**1b**), with lithium naphthalenide (LiNp·−) were studied because LiNp·− is a well-known one-electron donor (toward alkyl halides[1–5]) and therefore, both compounds were expected to react by an electron transfer mechanism. The results of these studies were then compared with those obtained earlier in their reactions with Mg* (magnesium activated by the Rieke procedure)[6] and LiAlH₄,[7] as well as other one-electron donors.[8] As will be discussed, the similarities in the nature of products formed in the reactions of **1a** and **1b** with LiNp·− compared to their reactions reported earlier[6–8] further support SET as a major reaction pathway describing all of these reactions.

Results and Discussion

Reaction of 6,6-Dichloro-5,5-dimethyl-1-hexene (1a) with LiNp·−. Effect of Stoichiometry. When the

Scheme 1
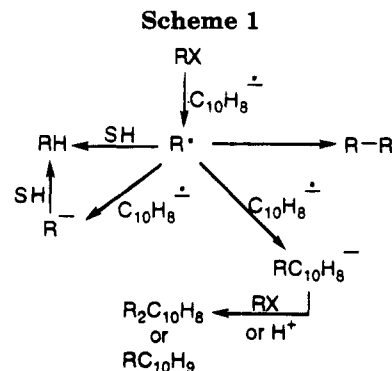
reaction of **1a** with LiNp·− was carried out, in THF at 25 °C, at a molar ratio of 1:2, product formation was instantaneous; however, 60% of **1a** was recovered unreacted. Eleven products (eq 1) were obtained in the
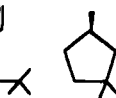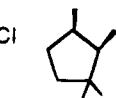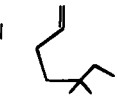

$$\tag{1}$$
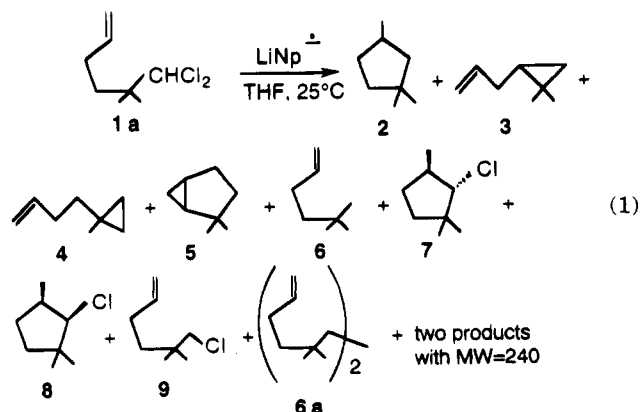
reaction (Table 1, experiment 1). No change in product composition was observed on stirring the reaction mix-

* Abstract published in *Advance ACS Abstracts,* June 15, 1995.
(1) Garst, J. F. *Acc. Chem. Res.* **1971,** *4,* 400.
(2) Garst, J. F.; Barbas, J. T. *J. Am. Chem. Soc.* **1974,** *96,* 3239.
(3) Garst, J. F.; Pacifici, J. A.; Singleton, V. D.; Ezzel, M. F.; Morris, J. I. *J. Am. Chem. Soc.* **1975,** *97,* 5242.
(4) Garst, J. F.; Roberts, R. D.; Abels, B. N. *J. Am. Chem. Soc.* **1975,** *97,* 4925.
(5) Garst, J. F.; Barton, F. E., II. *Tetrahedron Lett.* **1969,** *7,* 587 and references therein.
(6) Ashby, E. C.; Deshpande, A. K.; Doctorovich, F. *J. Org. Chem.* **1994,** *59,* 6223.

(7) Ashby, E. C.; Deshpande, A. K. *J. Org. Chem.* **1994,** *59,* 3798.
(8) Ashby, E. C.; Deshpande, A. K. *J. Org. Chem.* **1994,** *59,* 7358.

Table 1. Reaction of 6,6-Dichloro-5,5-dimethyl-1-hexene (1a) with LiNp·⁻ in THF at 25 °C

expt no.	ratio of 1a: LiNp·⁻	% of unreacted 1a	% yields of products							
			2	3	4	5	6	7	8	9
1	1:2	60	5	3	10	1	1	2	2	4
2[a]	1:6	0	25	11	35	5	6	0	0	0
3[b]	1:6	0	25	11	35	5	6	0	0	0

[a] In addition, A and B each with a molecular of 240 (total 6%) and the dimer 6a (trace) were also detected. [b] The reaction employed 10 equiv of DCPH.

Scheme 2

Scheme 3
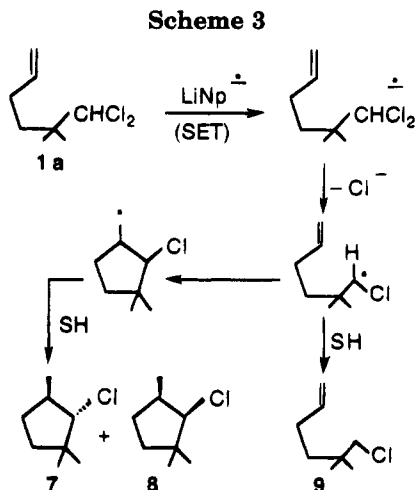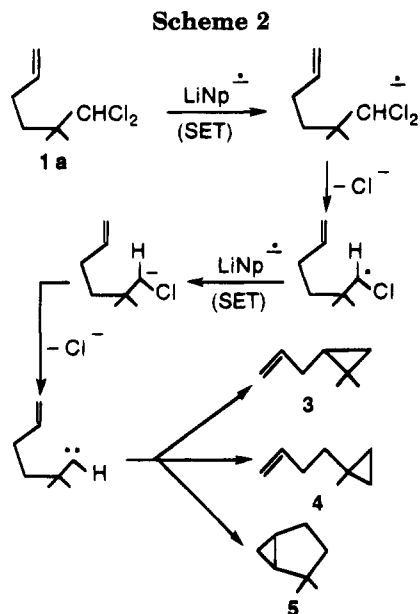
ture for 3 h. When the reaction was carried out at a higher ratio of 1:6 (1a:LiNp·⁻), no unreacted 1a was recovered (expt 2), and the product mixture consisted of eight products (2–6), 6a (<1%), and two products with a molecular weight of 240 each (total yield of 6%). At both ratios employed, it was observed that the major product of the reaction of 1a with LiNp·⁻ was the carbene-derived hydrocarbon, 4. In addition, the other carbene-derived hydrocarbons, 3 and 5, were also formed but in smaller yields at both reactant ratios. The formation of products 2, 6, and 7–9 is an indication that a radical pathway was involved in the reaction of 1a with LiNp·⁻.

The mechanisms of formation of 3–5 most likely involve a precursor carbene which, in turn, can arise from an initially generated chloro radical (by electron transfer from LiNp·⁻ to 1a). On receiving an electron from LiNp·⁻, this radical is converted to a chloro carbanion, which then loses Cl⁻ to form the carbene (Scheme 2). This scheme is the same as that proposed earlier for the reaction of 1a with Mg*[6] and LiAlH₄.[7]

Of the three carbene products, the yield of 5 was the lowest (expts 1 and 2), and this is as expected considering the fact that the carbene shown in Scheme 2 should preferentially undergo C–H insertion to afford 3 and 4 rather than addition across the C=C bond to yield 5. Such high yields of 3 (11%) and 4 (35%) indicate that once the chloro radical (Scheme 2) was formed from 1a, it was further reduced by LiNp·⁻ rapidly.

The formation of products 7 and 8 can be proposed as shown in Scheme 3, where the cyclized chloro radical generated from 1a (following electron transfer from LiNp·⁻) abstracts a hydrogen atom to produce the iso-

meric monochloro compounds. This scheme is also the same as that proposed earlier for the reaction of 1a with Mg*[6] and LiAlH₄.[7]

At both ratios, among the products formed, the yield of the cyclized hydrocarbon 2 was greatest, next only to that of product 4. It was thought that the formation of 2 is probably the result of the reaction of the monochloro compounds, 7 and 8 (and possibly even 9) with LiNp·⁻. Since no monochloro compound was detected in the product mixture at the higher ratio (expt 2), it is very likely that these compounds reacted with excess LiNp·⁻ to form the hydrocarbon products, 2 and 6. To confirm this, a mixture of 7, 8, and 9 (in a ratio of 1:1:0.5) was reacted with excess LiNp·⁻ at 25 °C in THF. Indeed, 2 and 6 were formed in a ratio of 10:1 (eq 2), with no

(2)
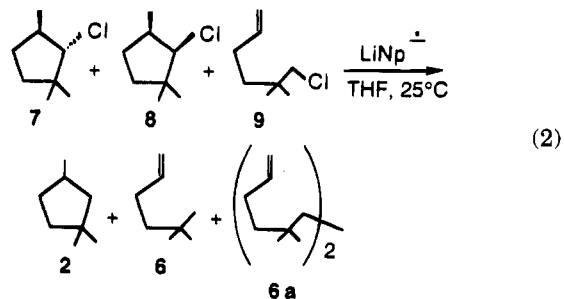
monochloro compound being recovered. A trace amount of 6a was also detected. These results suggest that most of 2 was produced by the reaction of 7 and 8 with LiNp·⁻, and a small portion was formed by the reaction of 9 with LiNp·⁻. Also, all of 6 and 6a must have been produced by the reaction of 9 with LiNp·⁻. These results clearly establish that, in the reaction of 1a with LiNp·⁻ (at a molar ratio of 1:6), 2, 6, and 6a are products of the reactions of 7–9 with excess LiNp·⁻.

Scheme 4
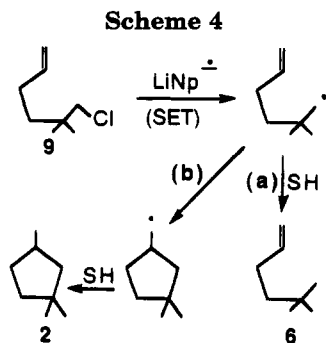
Effect of a Radical Trap. When the reaction of **1a** with LiNp$^{\cdot-}$ (molar ratio 1:6) was carried out in the presence of 10 equiv of the radical trap dicyclohexylphosphine (DCPH) (Table 1, expt 3), it was expected that there would be an increase in the yields of the suspected radical-derived products, **7–9** (DCPH was stirred in a solution of LiNp$^{\cdot-}$ in THF at 25 °C for 1 h and was found by GLC analysis not to react). The initially formed chloro radical (see Scheme 3) was expected to be trapped by DCPH to produce **9**, and the cyclized radical was expected to be trapped by DCPH to produce **7** and **8**. However, despite having employed a large excess of DCPH, none of the three monochloro products was detected (Table 1, expt 3). Additionally, there was no change in the product yields compared to those of the reaction that did not employ DCPH. These observations suggest that however much **7–9** may have been formed in the reaction as a result of "effective" trapping by DCPH, these compounds reacted with the excess LiNp$^{\cdot-}$ at a rapid rate to form products **2** and **6**. Also, the yields of **3–5** (the carbene-derived products) did not change in the reaction that employed DCPH (Table 1, expt 3). The carbene is also believed to be derived from the open chain chloro radical (from **1a**), as shown in Scheme 2. This result could mean that LiNp$^{\cdot-}$ transfers an electron to the open chain chloro radical, to produce a chloro carbanion, at a rate much faster than the rate at which the radical abstracts a hydrogen atom from DCPH. Therefore, it appears that once the open chain chloro radical is formed, the formation of the cyclized chloro radical (Scheme 3) competes with the formation of the chloro carbanion (Scheme 2); however, the reaction of the open chain *or* cyclized chloro radical with DCPH is *not* competitive with either process.

Detection of Organolithium Intermediates. On quenching a reaction between **1a** and LiNp$^{\cdot-}$ with D$_2$O, in order to establish the intermediacy of stable organolithium intermediates, neither **2** nor **6** showed any deuterium incorporation. This rules out the possible involvement of any organolithium products as stable intermediates.

The reaction of an isolated mixture of the monochloro isomers **7**, **8**, and **9** with excess LiNp$^{\cdot-}$, which resulted in an instantaneous formation of **2** and **6** (eq 2), was also quenched with D$_2$O. Once again, neither **2** nor **6** was found to have any deuterium content, thereby ruling out the formation of organolithium products as stable intermediates. A plausible pathway that leads to **2** and **6** from **9** is shown in Scheme 4, and a pathway that forms **2** from **7** and **8** is shown in Scheme 5.

Attempts to Establish the Intermediacy of Radicals by Deuterium-Labeling Studies. In order to determine if radicals were indeed involved in the reaction of **1a** with LiNp$^{\cdot-}$, the reaction of **1a** with LiNp$^{\cdot-}$ (1:6) was carried out first in THF-d_8 (Table 2, expt 4) and later

**Scheme 5**
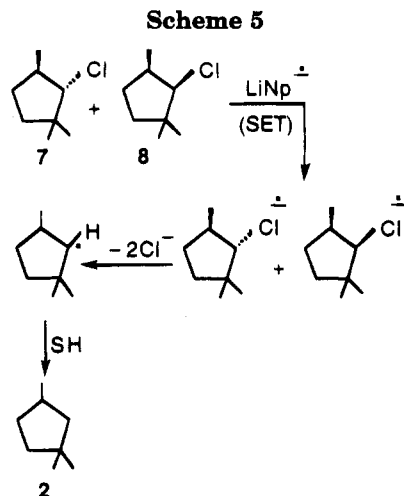
Table 2. Reaction of 1a with LiNp$^{\cdot-}$ and the Reaction of 1a-d_1 with LiNp$^{\cdot-}$ in THF-d_8 at 25 °C^a

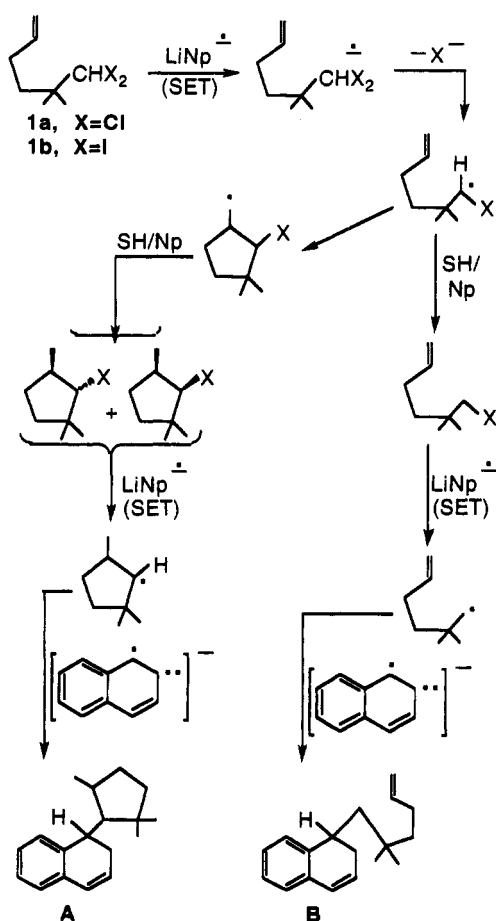|		% deuterium in products^{b,c}			
expt no.	conditions	**2**	**6**	**7**	**8**
4^d	THF-d_8	26 (d_1)	15 (d_1)	n/a	n/a
		1 (d_2)	0 (d_2)	n/a	n/a
5^d	THF-d_8/Np-d_8	48 (d_1)	27 (d_1)	n/a	n/a
		16 (d_2)	0 (d_2)	n/a	n/a
6^d	THF-d_8/Np-d_8	39 (d_2)	41 (d_2)	n/a	n/a
		52 (d_3)	50 (d_3)	n/a	n/a

^{a} The ratio between **1a/1a-1d_1** and LiNp$^{\cdot-}$ was 1:6. ^{b} The % D incorporation was analyzed in products that were suspected to be derived from radical intermediates. ^{c} Compounds **7** and **8** were not detected at this ratio. ^{d} Experiments 4 and 5 employed **1a** as the substrate and expt 6 employed **1a-d_1** as the substrate.

using naphthalene-d_8 for the synthesis of LiNp$^{\cdot-}$, in THF-d_8 (Table 2, expt 5). The deuterium content in **2** and **6**, which were the suspected radical-derived products, was determined. The results (depicted in Table 2) clearly show that radicals are involved. However, as was the case with the reaction of **1a** and Mg*,[6] in addition to THF and naphthalene, there was another source of hydrogen atoms in the reaction system; the most likely source being **1a**. In order to confirm the hypothesis that **1a** could act as a hydrogen atom donor to the radicals formed during the reaction of **1a** with LiNp$^{\cdot-}$, the monodeuteriated compound **1a-d_1** was synthesized and reacted with

1a-d_1
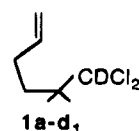
LiNp$^{\cdot-}$ prepared from naphthalene-d_8, and the reaction carried out in THF-d_8 as the solvent. The deuterium contents of products **2** and **6** were determined. The results are also shown in Table 2 (expt 6). The fact that the deuterium incorporation in **2** changed from 48% d_1 and 16% d_2 in expt 5 (involving the protio substrate **1a** (C$_8$H$_{14}$Cl$_2$)), to 39% d_2 and 52% d_3 in expt 6, which employed **1a-d_1** as the substrate (C$_8$H$_{13}$DCl$_2$), very clearly indicates that once the radicals are formed in the reaction of **1a** with LiNp$^{\cdot-}$, in addition to THF and naphthalene, the radicals also abstract hydrogen atoms from **1a**.

Scheme 6

Scheme 7

Similarly, the deuterium incorporation in **6** changed from 27% d_1 and 0% d_2 in expt 5, to 41% d_2 and 50% d_3 in expt 6. These results also support the hypothesis that **1a** can provide hydrogen atoms to the radicals produced in its reaction with LiNp$^{\cdot-}$. The hydrogen atom that is being abstracted from **1a** is the one attached to the carbon atom bearing the two chlorine atoms ($pK_a = 31$).[9] It is possible that, in addition to this hydrogen atom, the hydrogen atom from the allylic site in **1a** ($pK_a = 35.5$) can also be abstracted by the radicals.

MS data of the products with molecular weights of 240 (total yield, 6%) indicate[1] that these compounds could be derived from coupling of an alkyl radical with Np$^{\cdot-}$. Possible structures (**A** and **B**), with their modes of formation, are shown in Scheme 6.

With all the evidence that could be obtained from the reaction of **1a** with LiNp$^{\cdot-}$ at various ratios, by quenching with D$_2$O, and by carrying out deuterium-labeling experiments, it appears that 6,6-dichloro-5,5-dimethyl-1-hexene reacts with LiNp$^{\cdot-}$, a known one-electron donor, to form products via a SET mechanistic pathway (Scheme 7). The mechanistic pathways outlined in the scheme are very similar to those that were outlined for the reaction of **1a** with Mg*.[6] and LiAlH$_4$.[7] Observation of the same radical-derived and carbene-derived products in the reactions of **1a** with LiNp$^{\cdot-}$ (Table 1), Mg* (Table 3) and LiAlH$_4$ (Table 4), can be considered as being consistent with similar mechanistic pathways in operation for the three reactions, i. e., SET.

Reaction of 6,6-Diiodo-5,5-dimethyl-1-hexene (1b) with LiNp$^{\cdot-}$. The reaction of 6,6-diiodo-5,5-dimethyl-

(9) Ashby, E. C.; Deshpande, A. K.; Patil, G. S. *J. Org. Chem.* **1995**, *60*, 663.
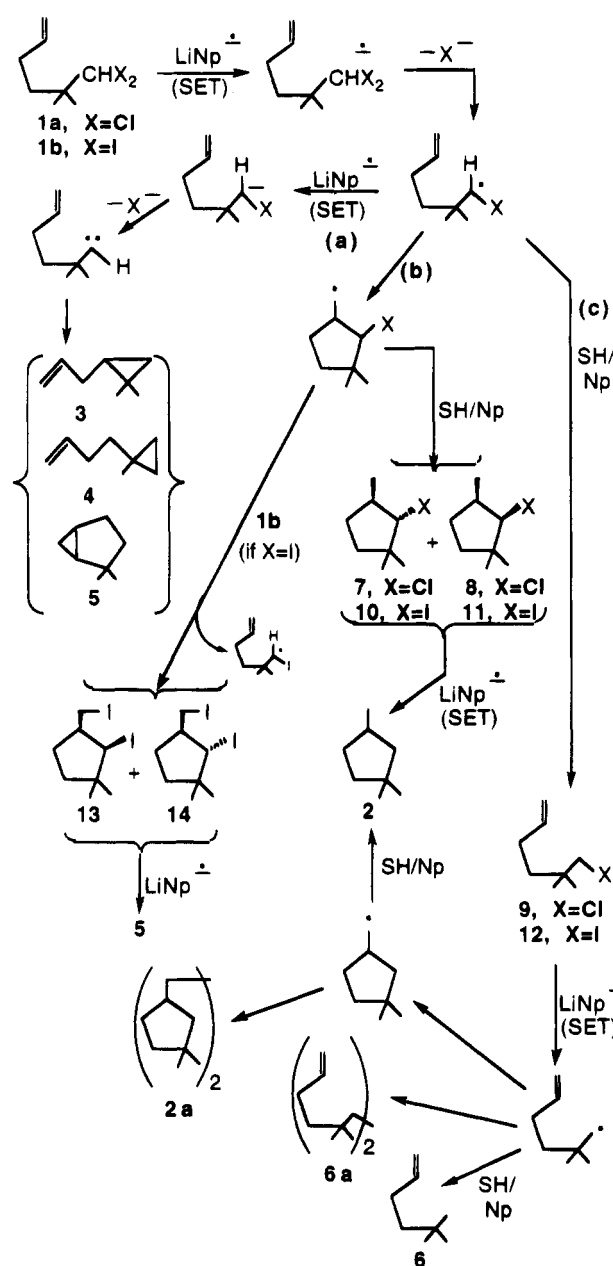
1-hexene (**1b**) with LiNp$^{\cdot-}$ at a molar ratio of 1:3 in THF at 25 °C, is shown in eq 3. No **1b** was recovered, and

$$\text{(3)}$$

2 (15%) 5 (23%)

6 (7%)   6a   2a

(9%)

+ Two Products with MW=240 (17%)
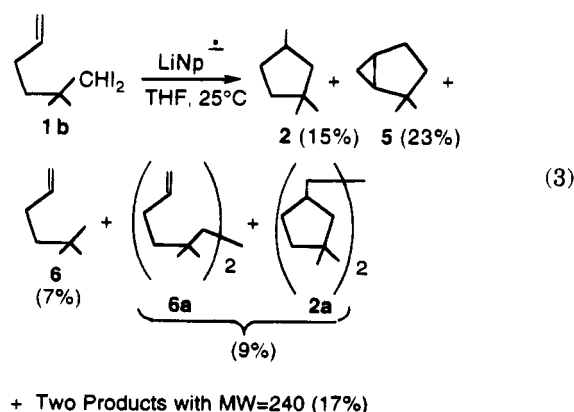
the formation of products was instantaneous. Among the products formed, **5** was formed in 23% yield, followed by **2** in 15%, and **6** in 7% (eq 3). In addition, two dimers

Table 3. Reaction of 6,6-Dichloro-5,5-dimethyl-1-hexene (1a) with Mg* in THF at 25 °C[a]

| | | % yields of products[b] | | | | | | | |
		2	3	4	5	6	7	8	9
ratio of 1a:Mg*	additive								
1:10	none	15	13	35	10	5	6	6	3

[a] This has been reported by us recently (see ref 6). *[b]* The reaction also resulted in the formation of the dimer **6a**.

Table 4. Reaction of 6,6-Dichloro-5,5-dimethyl-1-hexene (1a) with LiAlH₄ in THF at 25 °C[a]

| | | % yields of products | | | | |
		2	4	7	8	9
ratio of 1a:LiAlH₄	additive					
1:7	none	1	3	35	35	4

[a] This has been reported by us recently (see ref 7).

(**2a** and **6a**, on the basis of their MS data), both with a molecular weight of 222, were also formed in about 9% total yield. Two additional products with molecular weights of 240 (discussed earlier) were detected in a total yield of 17%.

The observation that **2** was formed in 15% yield, along with **6** in 7%, suggests that the reaction of **1b** with LiNp·⁻ involves a radical pathway. The most likely mechanism of formati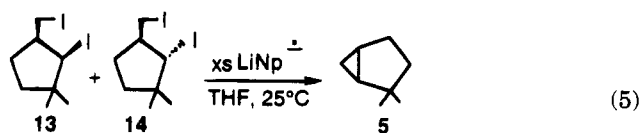on of these two hydrocarbons is the reaction of the intermediate monoiodo compounds (not detected in the reaction of **1b** with LiNp·⁻), **10**, **11**, and **12** with LiNp·⁻ (eq 4). It would be reasonable to assume that

(4)

these monoiodo compounds, although not detected in the reaction, should have been formed, and once formed, reacted very rapidly with LiNp·⁻ to form **2** and **6**. On allowing a mixture of **10**, **11**, and **12** (in a 1:1:2 ratio) to react with excess LiNp·⁻ at 25 °C in THF, it was observed that **2** and **6** in a 5:1 ratio (along with trace quantities of dimers **2a** and **6a**, as shown in eq 4) were formed instantaneously.

The reaction of **1b** with LiNp·⁻ did not afford the carbene-derived products, **3** and **4**. This means that **5** could originate from a precursor other than a carbene. The most likely source(s) of **5** are the cyclized diiodo compounds, **13** and **14** (not detected in the reaction of **1b** with LiNp·⁻) which are produced by the iodine atom radical chain process as shown in Scheme 7. It was found that on treating a mixture of the cyclized diiodo compounds, **13** and **14**, with LiNp·⁻, **5** was the only product formed, instantaneously (eq 5). This result shows why neither **13** nor **14** was observed in the reaction of **1b** with LiNp·⁻. A possible mode of formation of **5** from **13** and **14** is shown in Scheme 8.
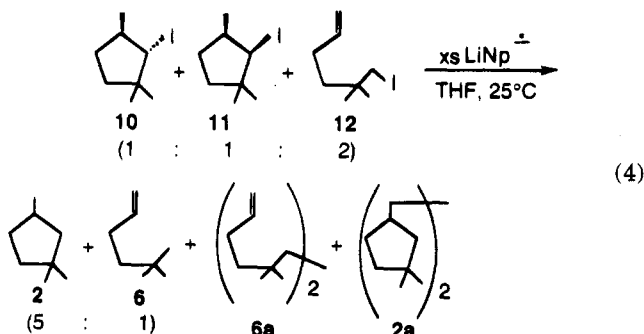
(5)

The lack of formation of the carbene-derived products **3** and **4** can be explained as follows: the initially formed iodo radical (from **1b**) could be further reduced by LiNp·⁻ to form the iodo carbanion (Scheme 9). Loss of an iodide ion from this carbanion would result in a carbene (which could produce **5**). However, the formation of a carbene was prevented in the reaction (as suggested by the absence of **3** and **4**). The possible reason why a carbene was not formed in the reaction of **1b** with LiNp·⁻, whereas it was formed quite readily in the reaction involving the geminal dichloro substrate, **1a**, is that the carbanion that is generated after the initial open chain halo radical receives an electron from LiNp·⁻ is better stabilized by a chlorine atom than by an iodine atom. This difference in the stabilities of the resulting carbanions accounts for the observation that the major product in the reaction of **1a** with LiNp·⁻ was **4**, whereas neither **3** nor **4** was detected in the reaction of **1b** with LiNp·⁻.

The formation of dimeric products in the reaction of **1b** with LiNp·⁻ also suggests radical intermediacy. The two dimers, **2a** and **6a** (formed in 4% and 5% yields, respectively) mentioned in eq 3 were identified by their MS data. These dimers can be formed when **12** reacts with the excess LiNp·⁻ (see eq 4) by geminate coupling of the open chain and cyclized radical precursors.

The two products with molecular weights of 240 each, which were formed in a total yield of 17% appeared to be naphthalene-derived products. Possible structures (on the basis of MS data) for these compounds (**A** and **B**) with molecular weights of 240 each are shown in Scheme 6. It is suggested that the formation of these two products is due to coupling between an alkyl radical, that is generated from a monoiodo compound (formed from **1b**), and the naphthalene radical anion,[1] as shown in Scheme 6.
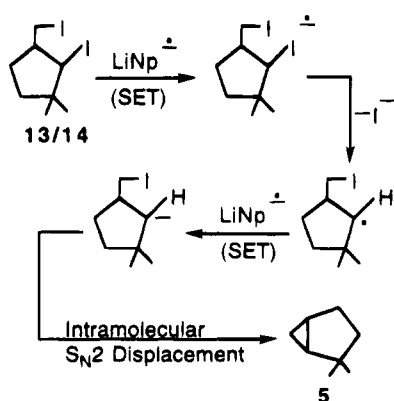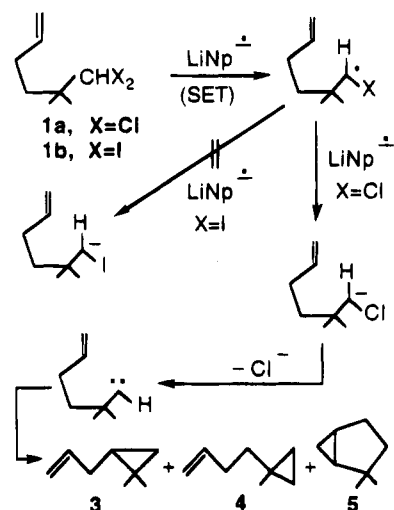
No deuterium was found incorporated in any product when the reaction mixture of **1b** with LiNp·⁻ was quenched with D₂O. This result suggests that no stable organolithium product was formed. Also, when the reaction of a mixture of **10**, **11**, and **12** with LiNp·⁻ (eq

Scheme 8

Scheme 9

4) was quenched with D₂O, no deuterium was found incorporated in **2** and **6**, thereby suggesting that a stable organolithium compound was not likely to have been formed in the reaction.

The results of the experiments that were carried out employing deuteriated solvent and reagent in the reaction of the dichloro substrate, **1a** and LiNp⁻ (expts 4 and 5), indicate the ability of naphthalene to act as a hydrogen atom donor toward halo radicals. In order to substantiate this further, the reaction of the diiodo compound, **1b**, was carried out with LiNp⁻ that was prepared from naphthalene-d_8, in protio THF. It was found that the deuterium contents in **2** and **6** were 24% d_1 and 15% d_1, respectively, thereby indicating that naphthalene *can* provide hydrogen atoms to the halo radicals even when in competition with protio THF.

On the basis of all the results obtained in these studies, a general mechanism for the reaction of 6,6-diiodo-5,5-dimethyl-1-hexene (**1b**) with LiNp⁻ is proposed in Scheme 7. As shown, electron transfer from LiNp⁻ to **1b** results in the formation of the open chain halo radical which then serves as the precursor to all the products of the reaction. The entire mechanistic scheme is very similar, if not identical, to the schemes reported earlier for the reaction of **1b** with Mg*[6] and LiAlH₄.[7]

Experimental Section

Materials. The reagents and solvents that were employed in the syntheses of the two compounds **1a** and **1b** were the same as described earlier.[7] Tetrahydrofuran, from Fisher, was distilled from sodium benzophenone ketyl prior to use. THF-

d_8 was purchased from Aldrich and used as received. Naphthalene was purchased from Alfa Products. Lithium rod (165 mm × 12.7 mm), packaged in mineral oil, was purchased from Alfa Products. Naphthalene-d_8 was purchased from Aldrich. Dicyclohexylphosphine (DCPH) was purchased from Strem Chemicals and used as received.

General Procedures. The general procedures that were followed to carry out all the reactions and the procedures for GLC and spectroscopic analyses were the same as those described earlier.[7]

Preparations. Lithium Naphthalenide. A solution of lithium naphthalenide in THF was prepared by combining equimolar amounts of lithium (freshly cut pieces) and naphthalene in dry THF and stirring the mixture at 25 °C, under argon, for about 1 h. The resulting solution was clear (no unreacted lithium metal pieces remained in the solution), and had an olive-green color which is characteristic of alkali metal naphthalenides.

6-Deutero-6,6-dichloro-5,5-dimethyl-1-hexene (1a-d_1). The synthesis of this compound was carried out following the same sequence that was employed for the synthesis of **1a**,[7] except that ethyl-2,2-dimethylhex-5-eneoate was reduced by LiAlD₄ to afford the deuteriated alcohol, 2,2-dimethyl-1,1-dideuteriohex-5-en-1-ol. Oxidation of this alcohol by pyridinium chlorochromate gave the deuteriated aldehyde, 2,2-dimethyl-1-deuteriohex-5-en-1-al. This aldehyde was then converted to **1a-d_1** using PCl₅. Purification of the product was accomplished by preparative GLC. NMR and MS data indicated 100% d_1 incorporation in the product.

Compounds **10**–**14** were synthesized by reaction of **1b** with LiAlH₄ and were isolated and characterized as described earlier.[7]

Procedure for the Reaction of the Geminal Dihalides with Lithium Naphthalenide and the Characterization of Products. Following the synthesis of lithium naphthalenide (LiNp⁻) in THF, as described earlier, a solution of the dihalide (with an appropriate amount of n-decane as the internal reference) in THF was added dropwise, at 25 °C, with vigorous stirring under an argon atmosphere. The molar ratio of **1a** to LiNp⁻ was 1:2 or higher whereas that of **1b** to LiNp⁻ was 1:3. The status of the reaction was checked by quenching a small volume of the reaction mixture with water and analyzing the organic layer by GLC. Termination of the reaction was carried out by quenching with water which was, followed by extraction of the products with a small volume of anhydrous diethyl ether.

The reaction of 6,6-dichloro-5,5-dimethyl-1-hexene (**1a**) with LiNp⁻ afforded the following products and these products, were identified by matching their respective MS data and GLC retention times with those of authentic samples (references are cited after each compound): 1,1,3-trimethylcyclopentane (**2**),[6] 2-(2-propenyl)-1,1-dimethylcyclopropane (**3**),[10] 1-(3-butenyl)-1-methylcyclopropane (**4**),[6] 2,2-dimethylbicyclo [3.1.0] hexane (**5**),[11] 5,5-dimethyl-1-hexene (**6**),[12] trans-2-chloro-1,1,3-trimethylcyclopentane (**7**),[7] cis-2-chloro-1,1,3-trimethylcyclopentane (**8**),[7] and 6-chloro-5,5-dimethyl-1-hexene (**9**).[13]

The reaction of 6,6-diiodo-5,5-dimethyl-1-hexene (**1b**) with LiNp⁻ gave the following three products, which were easily identified by matching their MS data and GLC retention times with those of the authentic compounds (as described above): 1,1,3-trimethylcyclopentane (**2**), 2,2-dimethylbicyclo[3.1.0]-hexane (**5**), and 5,5-dimethyl-1-hexene (**6**).

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