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Mechanism of Reaction of Geminal Dihalides with Magnesium. Evidence for the Formation of Carbenes from Radical Precursors. The Similarity in Reactions of Geminal Dihalides with Magnesium and LiAlH$_4$

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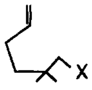
Two geminal dihalides, 6,6-dichloro-5,5-dimethyl-1-hexene (**2a**) and 6,6-diiodo-5,5-dimethyl-1-hexene (**2b**) were allowed to react with Rieke activated magnesium (Mg*) in THF at 25 °C. Both radical and carbene intermediates were identified by product analyses, by radical trapping experiments using DCPH and THF-d_8, and by selective experiments in which isolated intermediates were shown to form the predicted products. Although carbene products predominated over radical products when the dichloride was allowed to react with Mg*, radical products predominated when the diiodide was allowed to react with Mg*. Evidence is presented that indicates that the carbene intermediate arises from a radical precursor. A mechanistic scheme (Scheme 5) is presented that is consistent with all of the observed data. A comparison of the reactions of **2b** with Mg* and **2b** with LiAlH$_4$ shows that most of the products are common in both reactions thereby providing further evidence for LiAlH$_4$ as a one-electron donor, as is the known behavior of Mg*.

Introduction

One of the most extensively employed reactions in synthetic organic chemistry involves the use of Grignard reagents which are prepared by the reaction of an organic halide with magnesium metal.[1−10] Having realized the potential of these organomagnesium compounds as very useful reagents, workers have concentrated their attention on the mechanistic features underlying the formation of Grignard reagents. In this connection, convincing evidence for the involvement of free radical intermediates has been obtained[1,2,11−19] and the results of these studies clearly show that magnesium metal can act as a one-electron donor in its reactions with alkyl halides. The involvement of free radicals in the reactions of alkyl halides with magnesium has been established mainly due to the early studies by Walborsky involving chiral halides.[11] In addition, studies involving cyclizable radical probes and trapping experiments with the radical trap, dicyclohexylphosphine (DCPH), have served as supporting evidence for the formation of radical intermediates during Grignard reagent formation.[19] Work carried out by this group concerning the mechanism of Grignard reagent formation has involved the cyclizable halide probe **1**.



1, 1a: X=Cl, 1b: X=I
1c: X=Br

Although a great deal of work has been carried out utilizing aliphatic monohalides as substrates in reactions involving Grignard reagent formation, relatively few reports have appeared concerning the use of dihalides, especially geminal dihalides, as substrates. With respect to the preparation of di-Grignard reagents, Tissier and Grignard attempted the synthesis of a di-Grignard

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[1] Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice-Hall: New York, 1954.

[2] Ashby, E. C. *Q. Rev. Chem. Soc.* **1967**, *21*, 259.

[3] Millar, I. T.; Heaney, H. *Q. Rev. Chem. Soc.* **1957**, *11*, 110.

[4] Heaney, H. *Organomet. Chem. Rev.* **1966**, *1*, 27.

[5] Gaylord, N.; Becker, E. I. *Chem Rev.* **1951**, *49*, 413.

[6] Bruylants, A. *Bull. Soc. Chim. Fr.* **1958**, 1291.

[7] Benkeser, R. A. *Synthesis* **1971**, 347.

[8] Villieras, *J. Organomet. Chem. Rev.* **1971**, *A7*, 81.

[9] Ashby, E. C. *Bull Soc. Chim. Fr.* **1972**, 2133.

[10] Noltes, J. G. *Bull. Soc. Chim. Fr.* **1972**, 2151.

[11] (a) Walborsky, H. M.; Young, A. E. *J. Am. Chem. Soc.* **1961**, *83*, 2595. (b) Walborsky, H. M. *Rec. Chem. Prog.* **1962**, *23*, 75. (c) Walborsky, H. M.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3288. (d) Walborsky, H. M.; Aronoff, M. S. *J. Organomet. Chem.* **1973**, *51*, 33. (e) Walborsky, H. M.; Banks, R. B. *Bull. Soc. Chim. Belg.* **1980**, *89*, 849. (f) Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625. (g) Boche, G.; Walborsky, H. M. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley & Sons, Ltd.: London, 1987; Chapter 12. (h) Walborsky, H. M.; Rachon, J. *J. Am. Chem. Soc.* **1989**, *111*, 1896. (i) Walborsky, H. M.; Rachon, J. *Tetrahedron Lett.* **1989**, *30*, 7345. (j) Boche, G.; Walborsky, H. M. *Cyclopropane Derived Reactive Intermediates*; John Wiley & Sons: London, 1990. (k) Walborsky, H. M. *Acc. Chem. Res.* **1990**, *23*, 286. (l) Walborsky, H. M. *Chem. Unserer Zeit* **1991**, *25*, 108.

[12] (a) Garst, J. F.; Deutch, J. M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 2490. (b) Garst, J. F.; Swift, B. L.; Smith, D. W. *J. Am. Chem. Soc.* **1989**, *111*, 234. (c) Garst, J. F.; Swift, B. L. *J. Am. Chem. Soc.* **1989**, *111*, 241.

[13] Gomberg, M.; Bachman, W. E. *J. Am. Chem. Soc.* **1927**, *49*, 236.

[14] Blomberg, C. *Bull. Chim. Soc. Fr.* **1972**, 2143.

[15] (a) Rogers, H. R.; Hill, C. L.; Fugiwara, Y.; Rogers, R. J.; Mitchell, H. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 217. (b) Rogers, H. R.; Rogers, R. J.; Mitchell, H. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 231. (c) Barber, J. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 239. (d) Root, K. S.; Deutch, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 5475. (e) Root, K. S.; Lawrence, L. M.; Hill, C. S.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 5405. (f) Vogler, E. A.; Stein, R. L.; Hayes, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 3163.

[16] (a) Schaart, B. J.; Blomberg, C.; Akkerman, O. S.; Bickelhaupt, F. *Can. J. Chem.* **1990**, *58*, 932. (b) Bodewitz, H. W. H. J.; Schaart, B. J.; Van der Neit, J. D.; Blomberg, C.; Bickelhaupt, F.; der Hollander, J. A. *Tetrahedron* **1978**, *34*, 2523. (c) Bodewitz, H. W. H. J.; Blomberg, C.; Bickelhaupt, F. *Tetrahedron Lett.* **1972**, 251. (d) Bodewitz, H. W. H. J.; Blomberg, C.; Bickelhaupt, F. *Tetrahedron* **1973**, *29*, 719. (e) Bodewitz, H. W. H. J.; Blomberg, C.; Bickelhaupt, F. *Tetrahedron* **1975**, *31*, 1053.

[17] (a) Dubois, J. E.; Molle, G.; Tourillon, G.; Bauer, P. *Tetrahedron Lett.* **1979**, 5069. (b) Dubois, J. E.; Molle, G.; Bauer, P. *J. Org. Chem.* **1982**, *47*, 4120.

[18] (a) Yurchenko, A. G.; Fedorenko, T. V.; Rodionov, U. N. *Zh. Org. Khim.* **1985**, *21*, 1673. (b) Lamb, R. C.; Ayers, P. W.; Toney, M. K.; Garst, J. F. *J. Am. Chem. Soc.* **1966**, *88*, 4261.

[19] Ashby, E. C.; Oswald, J. *J. Org. Chem.* **1988**, *53*, 6068.

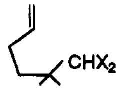
0022-3263/94/1959-6223$04.50/0

reagent from 1,2-dibromoethane and 1,3-dibromopropane.[20] The syntheses failed and resulted in the formation of ethylene and cyclopropane, respectively (magnesium bromide being the other product). Later, Grignard and Vignon reported the synthesis of the di-Grignard reagent from 1,5-dibromopentane.[21,22]

In order to successfully synthesize di-Grignard reagents, it has been determined that the two halogen atoms of the dihalide must be separated by at least four carbon atoms.[23] This restriction suggests that the synthesis of geminal di-Grignard reagents is unlikely, although a few such syntheses have been reported by Emschwiller[24] and later by Cainelli et al.[25] who used magnesium amalgam instead of magnesium metal. Bickelhaupt et al. have reported the synthesis of the geminal di-Grignard reagent from dibromomethane using Mg/Hg and isopropyl ether as the solvent. The yield of the di-Grignard was 80% (eq 1).[26] One serious complication in the isolation of the di-Grignard reagent is the rapid α-elimination of MgX_2 from the intermediate mono-Grignard carbenoid that eventually leads to the formation of hydrocarbon products.

$$CH_2Br_2 \xrightarrow[i\text{-}Pr_2O]{Mg/Hg} CH_2(MgBr)_2 \quad (1)$$

Based on the well established fact that reactions of alkyl halides with magnesium involve free radical intermediates, and that the reaction of magnesium with geminal dihalides leads to products derived from a carbenoid intermediate, it was decided to undertake a study of the mechanistic features of the reaction of geminal dihalides **2** with magnesium.



2a: X=Cl, **2b**: X=I

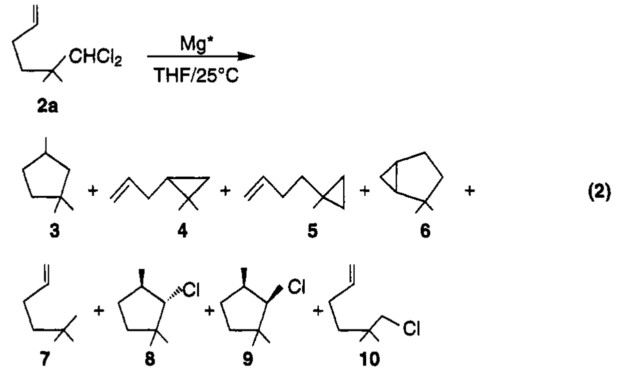
A substrate such as **2** was expected to be very useful in furnishing evidence to support the intermediacy of both carbene and radical intermediates on reaction with magnesium. Indeed, a geminal dihalide should yield products derived from a carbene intermediate and, having a "cyclizable skeleton", any involvement of free radicals would afford cyclized products. It was also of great interest to us to compare the reactivity of **2a** with that of **2b** in order to determine the effect of the halogen on the mechanistic aspects (carbene and/or radical intermediacy) of the reaction as well as comparing the reactivities of geminal dihalides with those of the corresponding monohalides which have already been well studied.

Not all types of magnesium metal react with organic halides to yield the corresponding Grignard reagents. In a previous study we were able to react **2b** with magnesium, but not **2a**.[27] However, Rieke has reported significant success in accomplishing the syntheses of Grignard reagents from relatively inert halides by using a "highly reactive" form of magnesium referred to as Rieke magnesium (henceforth designated as Mg*).[28,29] The synthesis of this type of magnesium involves either a reaction between an anhydrous magnesium halide and an alkali metal or a reaction between lithium naphthalenide and an anhydrous magnesium halide. On having determined that **2a** was very inert toward commercial magnesium shavings, it was decided to study the reactions of **2a** and **2b** with the highly reactive form of magnesium (Mg*) that was synthesized according to Rieke's procedure.

An equally important reason for this study was to compare the products of the reaction of **2b** with magnesium metal (a known one electron donor) with the products of the reaction of **2b** with $LiAlH_4$. If $LiAlH_4$ is functioning as a one electron donor, then the products of the reactions should be similar. Indeed, five of the products formed in the reaction of **2b** with magnesium metal are also formed as the major products in the reaction of **2b** with $LiAlH_4$.

Results and Discussion

Reaction of 6,6-Dichloro-5,5-dimethyl-1-hexene (2a) with Mg*. The reaction of 6,6-dichloro-5,5-dimethyl-1-hexene (**2a**) with Mg* was very sluggish, even at a molar ratio of 1:10 (**2a**:Mg*) under ultrasonic activation conditions at 25 °C. Typically, the complete consumption of **2a** required 5−6 h, and eight products were formed (eq 2). The yields of all the products in eq 2 are listed in Table 1 (exp 1).



The main product of the reaction of **2a** with Mg* was the hydrocarbon **5** (35%), a carbene-derived product. Two other carbene-derived products, **4** and **6**, were detected in 13 and 10% yield, respectively. Formation of products **3**, **7−10**, suggests involvement of radical intermediates.

It is known that during the synthesis of geminal di-Grignard reagents, a rapid α-elimination of a molecule of MgX_2 from the intermediate mono-Grignard takes place resulting in carbene-derived hydrocarbon products.[26] It would, therefore, not be unreasonable to expect the formation of a mono-Grignard intermediate in the reaction of **2a** with Mg* (Scheme 1). The carbene that produces **4−6** is likely to be formed as a result of an α-elimination of a molecule of $MgCl_2$ from the mono-

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[20] Tissier, L.; Grignard, V. *C. R. Hebd. Seances Acad. Sci.* **1901**, *132*, 835.

[21] Grignard, V.; Vignon, G. *C. R. Hebd. Seances Acad. Sci.* **1907**, *144*, 1358.

[22] The preparation of the 1,9-di-Grignard reagent of n-nonane has been claimed earlier by Blaise, E. E.; Houillon, E. *Bull. Soc. Chim. Fr.* **1904**, *31* (3), 960.

[23] Bickelhaupt, F. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 990.

[24] Emschwiller, G. *C. R. Hebd. Seances Acad. Sci.* **1926**, *183*, 665.

[25] Bertini, F.; Grasselli, P.; Zubiani, G.; Cainelli, G. *Tetrahedron* **1970**, *26*, 1281.

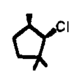
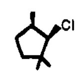
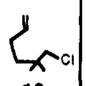
[26] Van de Heisteeg, B. J. J. Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1986**, *308*, 1.

[27] Doctorovich, F.; Deshpande, A. K.; Ashby, E. C. *Tetrahedron* **1994**, *50*, 5945.

[28] Rieke, R. D.; Burns, T. P. *J. Org. Chem* **1987**, *52*, 3674.

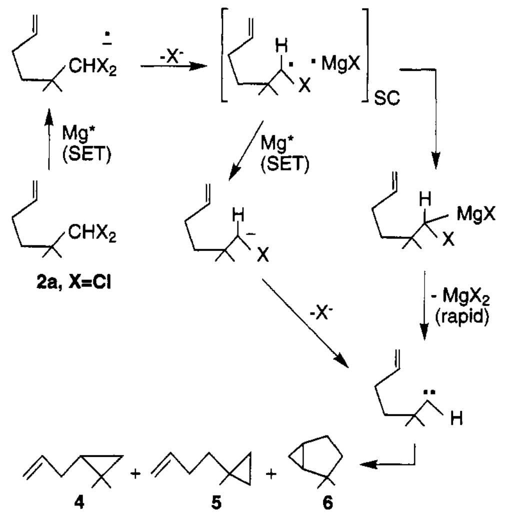
[29] Rieke, R. D.; Burns, T. P.; Li, P. Tzu-Jung; Uhm, S. T. *J. Org. Chem.* **1981**, *46*, 4323.

Table 1. Reaction of 6,6-Dichloro-5,5-dimethyl-1-hexene (2a) with Mg* in THF at 25 °C[a]

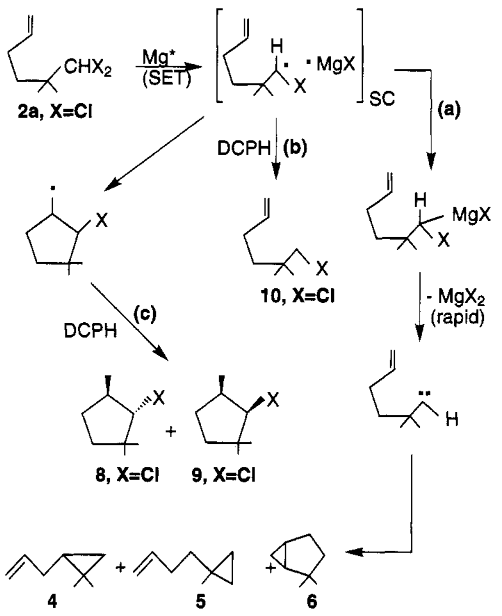
			% Yield of Products							
										
Exp. No.	2a : Mg*	Additive	3	4	5	6	7	8	9	10
1[b]	1 : 10	none	15	13	35	10	5	6	6	3
2	1 : 10	10 equiv. DCPH	17	7	18	6	8	11	12	12

[a] The reactions were carried out under ultrasonic activation conditions. [b] The dimer **7a** was also detected in 2% yield in exp 1.

Scheme 1



Scheme 2



Grignard intermediate. The formation of the mono-Grignard intermediate is likely due to coupling of the chloro radical generated from **2a** with MgCl•. The carbene could also be formed as a result of an electron transfer to the initially generated chloro radical, followed by the loss of Cl^- from the chloro carbanion. The main driving force for the formation of a chloro carbanion (apart from possibly a favorable reduction potential of the chloro radical) is the stabilization that such a carbanion would receive due to an electron-withdrawing chlorine atom.

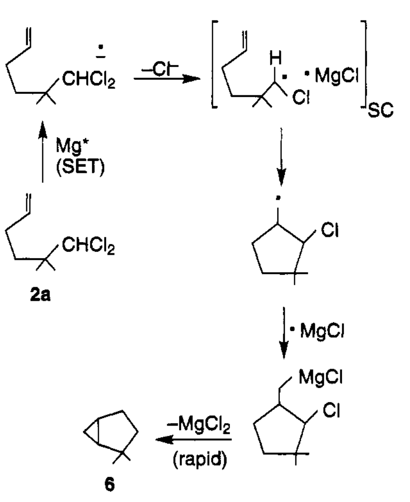
An attempt was made to verify the formation of the proposed mono-Grignard by quenching the reaction between **2a** and Mg* with D_2O. The purpose was to try to hydrolyze the intermediate mono-Grignard to produce deuterated **10**; however, the resulting product was completely devoid of deuterium. This result cannot be interpreted as eliminating the possibility of formation of a mono-Grignard intermediate, since such an intermediate would be expected to eliminate $MgCl_2$ rapidly after its formation, to produce the carbene. In order to test for the possible involvement of any other stable organomagnesium compounds as intermediates, the reaction mixture of **2a** with Mg* was quenched with D_2O and the resulting deuterium incoporation determined in all the products. The fact that no deuterium was incorporated in any of these products indicated that no stable organomagnesium compound remained after the reaction was complete, although intermediate Grignard compounds are possible.

As shown in Scheme 1, if SET were involved, the open chain chloro radical (from **2a**) could act as a precursor to the carbene intermediate and the subsequent products **4**−**6**, as well as provide a route to the radical products **3**, **7**−**10**. In order to substantiate a radical pathway, it was decided to study the reaction of **2a** with Mg* in the presence of the radical trap, dicyclohexylphosphine (DCPH). The product composition and yields are shown in Table 1 (exp 2).

Effect of a Radical Trap. The reaction of **2a** with Mg* was carried out in the presence of 10 equiv of DCPH. Two important observations were made (i) a considerable reduction in the yields of the carbene-derived products **4**−**6**, and (ii) an enhancement in the yields of the radical derived products **3**, **7**−**10**. The increase in the yield of **10** from 3% in exp 1 to 12% in exp 2 is an indication that **10** was formed from a radical precursor. As shown in Scheme 2 (pathway b) the radical was trapped by DCPH to afford an increased yield of **10**. Cyclization of the radical, followed by hydrogen atom abstraction from DCPH (pathway c), would produce **8** and **9**. The fact that the yields of the carbene-derived products (**4**−**6**) were lowered in the presence of DCPH indicates that the carbene was preceded by a radical. Since the chloro radical was trapped by DCPH (pathway b), the possibility of the generation of the mono-Grignard intermediate (pathway a) was lowered.

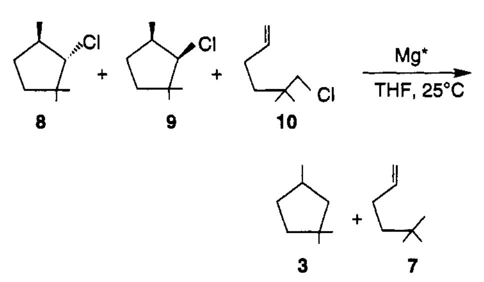
On comparing the yields of the three carbene-derived hydrocarbons (**4**−**6**), it is seen that in the absence, as well as the presence of DCPH, their ratio is approximately the same (1.3:3.5:1.0 vs 1.2:3.0:1.0). Considering the fact that the carbene suggested in Scheme 1 would be expected to undergo intramolecular insertion into C−H bonds preferentially over intramolecular addition across the C=C bond, the formation of **6** should be less favorable

Scheme 3



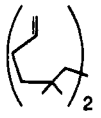
than that of **4** and **5** (*it has been shown*[30a] *that for the carbenes of the type shown in Scheme 2, the main C—H insertion product is derived from insertion into the methyl C—H bond and the other insertion product is that following insertion into the γ-C—H bond of the chain. Therefore,* **5** *would be expected to be formed predominantly, followed by* **4**. *It has also been established*[30b] *that intramolecular addition across a C═C bond constitutes a relatively minor pathway in the case of carbenes with the C═C bond being separated from the carbene center by two or more carbon atoms in the chain*). However, in both experiments, the yield of **6** (10 and 6%) is only slightly less than that of **4** (13 and 7%). It is unlikely, given the pattern of reactivity of the proposed carbene, that both **4** and **6** would be formed in nearly identical yields. This suggests that **6** may also be derived from a precursor other than the carbene. A possible mode of formation of **6** involves a coupling between the cyclized radical (after the chloro radical cyclizes) and the MgCl• radical, followed by a rapid elimination of $MgCl_2$ (Scheme 3). Syntheses of cyclopropanes from 1,3-dihalides using magnesium (as well as zinc and alkali metals) is a common synthetic transformation.[20] In the presence of DCPH, the yields of the cyclized monochloro compounds, **8** (11%) and **9** (12%), were found to be twice their respective yields in the absence of DCPH. This was expected since the cyclized radical precursor to **8** and **9** was trapped by DCPH (pathway c, Scheme 2) at a rate faster than that at which it can couple with the MgCl• radical to eventually form **6** as shown in Scheme 3. The reduction in the yield of **6** could be due to the fact that the amount of the carbene intermediate (pathway a, Scheme 2) that produces **6** was lower in the presence of DCPH. Thus, there is evidence that **6** is probably produced by both a radical and a carbene intermediate.

Hydrocarbon **3** is likely to be the product of the reaction of the cyclized monochloro compounds **8** and **9**, with Mg*, and **7** could be formed by a reaction of the open chain monochloro compound **10**, with Mg*. When a mixture of **8, 9**, and **10** (in a ratio of 1:1:0.5) was allowed to react with excess Mg* in THF at 25 °C, under ultrasonic activation conditions for 5 h, **3** and **7** were formed in a ratio of 8:1 (eq 3). Additionally, 11% of **8**, 7% of **9**, and 2% of **10** remained unreacted.



(3)

When the reaction mixture was quenched with D_2O, no deuterium was detected in the resulting hydrocarbons **3** and **7**. This result suggests that the reaction shown in eq 3 probably did not involve organomagnesium intermediates as precursors to the observed hydrocarbon products, since the corresponding Grignard reagents would be expected to be stable (*the observed lack of formation of Grignard reagents from* **8–10** *can be explained with the help of the proposed "D" model for the mechanism of formation of Grignard reagents from alkyl halides.*[31] *Based on the model, it is very likely that once the radicals were formed from* **8–10**, *following SET from Mg*, they rapidly diffused into solution from the magnesium surface. This diffusion could have been accelerated under ultrasonic activation conditions. Formation of Grignard reagents could have occurred if the radicals were to couple with the MgCl• radical on the surface of the magnesium*). Based on these results, it appears that in the reaction of **2a** with Mg*, a portion of **3** in the product mixture can be formed from **10**, most likely by a SET pathway. One basis for such an assumption was the detection of a product with a molecular weight of 222 in a 2% yield in exp 1 (in the absence of DCPH). This compound possesses the dimeric structure **7a**, concluded on the basis of MS data. In the presence of DCPH, this dimer was not detected supporting the notion that **3**, **7**, and **7a** (produced from **10**) have radical precursors. Scheme 4 shows the proposed pathway.



7a

In the presence of DCPH, the yield of **3** was only slightly higher (17%) than that in the absence of DCPH (15%). However, the yields of the three precursors to **3**, namely, **8–10**, increased significantly in the presence of DCPH. Based on the results of eq 3, it appears that a reasonable portion of the total amount of **3** comes from **10** (in exps 1 and 2). In the presence of DCPH, the open chain radical produced from **10** is trapped, thereby precluding the formation of **3**, and this results in only a marginal increase in the yield of **3** in exp 2 where most of **3** probably comes from **8** and **9**. As mentioned earlier, the absence of the dimer **7a** indicates that the precursor radical that forms **7a** was trapped by DCPH. In fact, this is reflected by the marginal enhancement in the yield of **7** in exp 2 (8%) compared to that in exp 1 (5%).

Attempts to Determine the Source of Hydrogen Atoms That Trapped the Radicals. It was of interest to determine whether or not, in the absence of the radical trap, DCPH, the radicals shown in Scheme 2 abstracted hydrogen atoms from the THF solvent. In order to do

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[30] (a) Kirmse, W.; Schladetsch, H. J.; Bucking, H. W. *Chem. Ber.* **1966**, *99*, 2579. (b) Kirmse, W.; Grassman, D. *Chem. Ber.* **1966**, *99*, 1746.

[31] Garst, J. F. *Acc. Chem. Res.* **1991**, *24*, 95.

Scheme 4

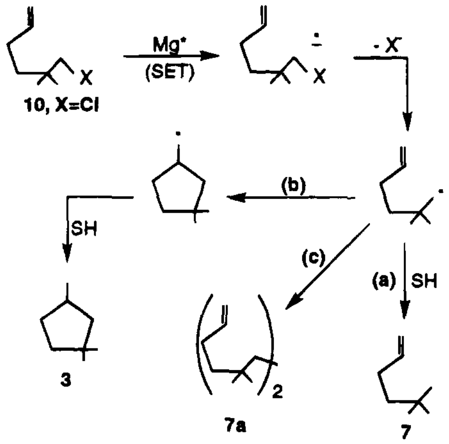
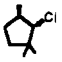
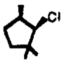
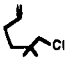


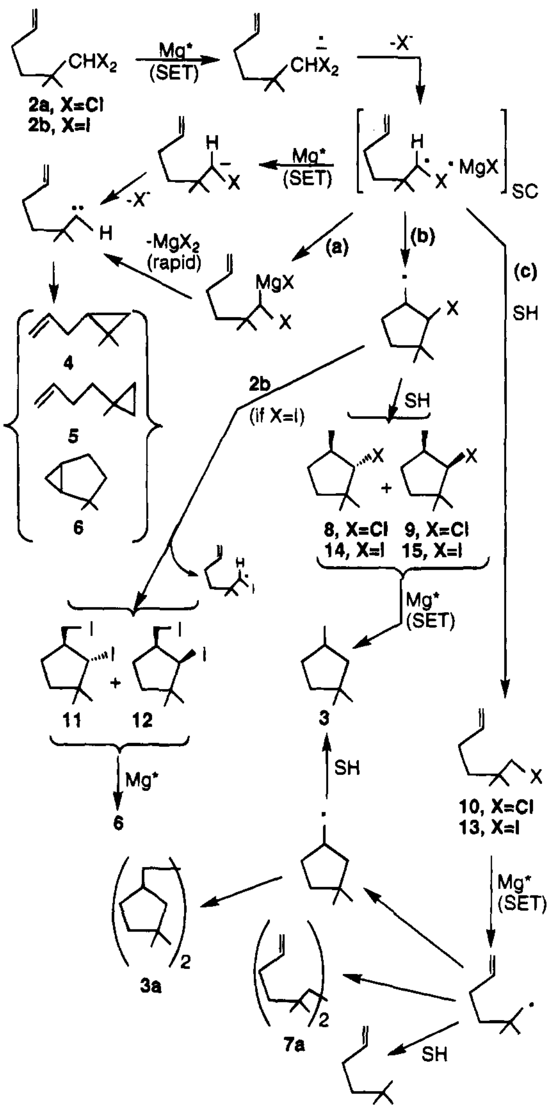
Table 2. Reaction of 2a with Mg* in THF-d_8[a]

		% Deuterium in Products[b]				
Exp. No.	Conditions	 3	 7	 8	 9	 10
3	THF-d_8	16 (d_1) 1 (d_2)	19 (d_1) 2 (d_2)	7 (d_1) 0 (d_2)	8 (d_1) 0 (d_2)	3 (d_1) 0 (d_2)
4	THF-d_8/ Naph-d_8	46 (d_1) 15 (d_2)	45 (d_1) 11 (d_2)	28 (d_1) 0 (d_2)	31 (d_1) 0 (d_2)	28 (d_1) 0 (d_2)

[a] The reactions were carried out under ultrasonic activation conditions. [b] The percent deuterium incorporation was analyzed in products that were suspected to be derived from radical intermediates.

so, a reaction of **2a** with Mg* was carried out in THF-d_8 at 25 °C, and the deuterium contents of the products that were categorized as being radical-derived (**3**, **7**–**10**) were analyzed (Table 2, exp 3). The low deuterium incorporation in the radical-derived hydrocarbons **3** and **7** (16% d_1 and 19% d_1, respectively) and in the radical-derived monochloro compounds **8**–**10** (7, 8, and 3%, respectively) suggests that in addition to THF there is another source of hydrogen atoms. The most likely source that could be capable of donating hydrogen atoms is suspected to be naphthalene (present as an impurity in the Rieke magnesium). To test this hypothesis, a reaction of **2a** with Mg*, that had been prepared from lithium naphthalene-d_8 radical anion (in THF-d_8), was carried out at 25 °C in THF-d_8 (exp 4). The deuterium incorporation in **3** increased to 46% d_1 and 15% d_2, and that in **7** increased to 45% d_1 and 11% d_2. The deuterium incorporation in **8**–**10** increased to 28, 31, and 28%, respectively. These data show that, in addition to THF, naphthalene is a significant source of hydrogen atoms. These data also imply that there is yet another source of hydrogen atoms in the reaction system. A possible source could be the starting material **2a**. Although no attempts to prove this hypothesis were made, there is reason to believe that *radicals do abstract hydrogen atoms from* **2a** (primarily the hydrogen attached to the carbon bearing the two chlorine atoms), since we have found evidence to support this hypothesis in a study of reaction of **2a** with lithium naphthalenide.[32] In any event, the higher deuterium incorporation observed in exp 4 clearly indicates the intermediacy of radicals in the reaction of the geminal dichloride **2a**, with Mg*.

Scheme 5



On the basis of all of the results obtained in the reaction of **2a** with Mg* in the presence of DCPH and THF-d_8, and having analyzed the reaction for the involvement of organomagnesium intermediates, it appears that the reaction proceeds predominantly by an electron transfer mechanism as shown in Scheme 5.

Reaction of 6,6-Diiodo-5,5-dimethyl-1-hexene (2b) with Mg*: Effect of Stoichiometry. Contrary to the slow reaction between the dichloro derivative **2a** and Mg*, the reaction of 6,6-diiodo-5,5-dimethyl-1-hexene (**2b**) with Mg* was relatively rapid, even at a ratio of 1:1 (**2b**:Mg*), in THF at 25 °C. Although product formation was detected soon after mixing the reactants, still there was some unreacted **2b** even after 8 h. A total of eight products were formed (Table 3, exp 5). When the ratio was increased to 1:3, no unreacted **2b** remained and the product distribution and yields differed from those at the lower ratio (exp 6). The overall reaction of **2b** with Mg* is represented by eq 4.

Perhaps the most noticeable feature of the reaction of **2b** with Mg*, at both the molar ratios employed, was the formation of compound **6** as the major product (15% at 1:1, and 25% at 1:3). The formation of **6** could be attributed to an intramolecular addition across a C=C bond by a carbene intermediate which could also be the precursor to both **4** and **5**. The formation of a carbene

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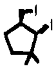
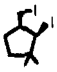
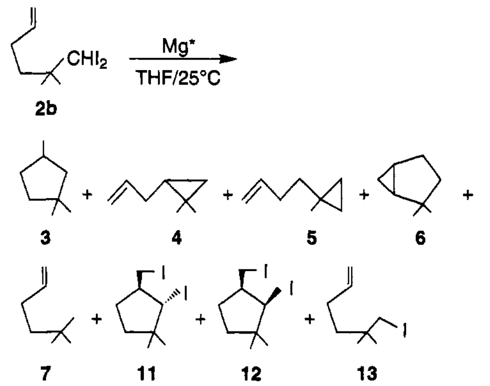
(32) Ashby, E. C., to be reported at a later time.

Table 3. Reaction of 6,6-Diiodo-5,5-dimethyl-1-hexene (2b) with Mg* in THF at 25 °C[a]

Exp. No.	2b : Mg*	% 2b Recovd.	% Yield of Products							
			 3	 4	 5	 6	 7	 11	 12	 13
5	1 : 1	20	5	2	5	15	1	12	10	10
6	1 : 3[b]	0	10	5	6	25	3	0	0	0
7[c]	1 : 1	20	20	0	0	15	2	0	0	18

[a] The reactions were carried out under ultrasonic activation conditions. [b] Dimers **3a** and **7a** were also detected in a total yield of 9% in exp 6. [c] The reaction employed 10 equivalents of DCPH, and the isomers **14** and **15** were also detected in yields of 6% and 5%, respectively.

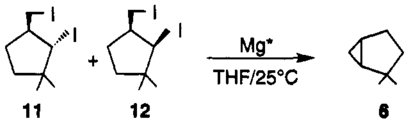


(4)

intermediate in the reaction of **2b** with Mg* is possible in a fashion analogous to that described in Scheme 1 in the case of **2a**. However, ET from Mg* to an open chain iodo radical, formed from **2b** (**X** = **I**) following SET from Mg*, may not be as favorable as to an open chain chloro radical (from **2a**) because the resulting iodo carbanion would not be as stabilized by an iodine atom compared to a chlorine atom. It is therefore possible that the major pathway, shown in Scheme 1, that leads to a carbene intermediate involves initial geminate coupling between an iodo radical and the MgI radical, followed by loss of MgI_2.

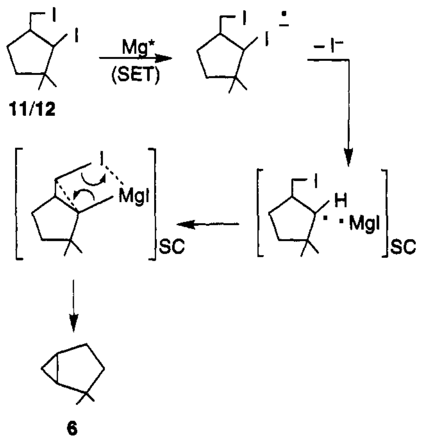
In order to determine if the reaction of **2b** with Mg* involved any stable organomagnesium iodide intermediates, the reaction mixture of **2b** with Mg* was quenched with D_2O and the deuterium content in all hydrocarbon products was analyzed. The results showed no deuterium incorporation in any product, thereby ruling out the possibility of any stable organomagnesium iodide intermediates.

Although **6** can be formed from a carbene as shown in Scheme 1, it is important to realize that among the three carbene-derived products, the C−H insertion products, namely, **4** and **5**, would be expected to be formed in higher yields than **6**. Contrary to this expected result, the yields of **4** and **5** were considerably lower than those of **6** at both molar ratios employed. This result indicates that **6** (as in the case of the reaction of **2a** with Mg*) is probably formed by an additional pathway. The likely candidates that could form **6** are the cyclized diiodo compounds **11** and **12**. These two products were detected in yields of 12 and 10%, respectively at a 1:1 ratio (exp 5), whereas at the higher ratio of 1:3 (exp 6), **11** and **12** were not formed. Lack of detection of **11** and **12** suggests that these two compounds were consumed by excess Mg*. On allowing a mixture of **11** and **12** to react with excess Mg*, in THF at 25 °C, the only product detected was **6** (eq 5). All of compound **11** reacted in less than 30 min; however, about 30% of the unreacted *cis* isomer **12** was recovered after 90 min. This result shows that **6** is formed from **11** and **12**, in addition to being formed from a carbene intermediate, in the reaction of **2b** with Mg*. A possible pathway that can lead to the formation of **6** from **11** and **12** is shown in Scheme 6.



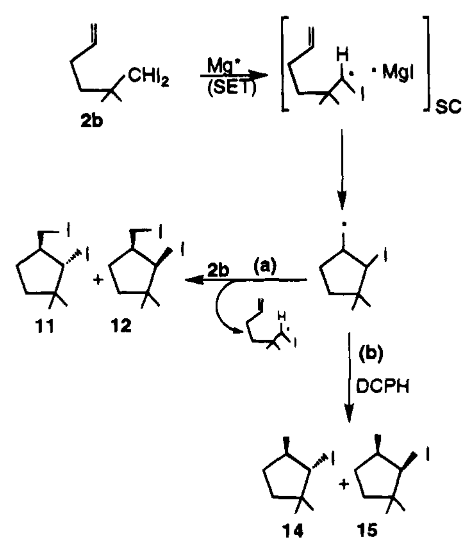
(5)

Scheme 6

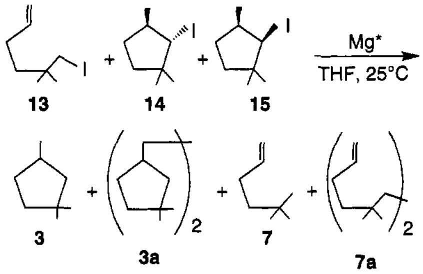


The open chain monoiodo compound **13** was formed in 10% yield at the 1:1 (**2b**:Mg*) ratio (exp 5); however, at a 1:3 ratio, **13** was not detected in the product mixture (exp 6). This suggests that **13** must have reacted with the excess Mg*. If **13** were to react with Mg*, the products that could be formed would be either only **7** (if there is no SET), or **3** and **7** (if there is SET). On comparing the yields of **3** in exp 5 (5%) and exp 6 (10%), and comparing the yields of **7** in exp 5 (1%) and exp 6 (3%), it is clear that their formation was influenced by the amount of Mg* present. With an increased amount of Mg*, more of **3** and **7** were formed, thereby indicating that their precursors should have been monoiodo compounds that on further reaction with Mg* afford hydrocarbon products. Although the cyclized monoiodo compounds **14** and **15** (eq 6) were not detected at both ratios, it is quite possible that if these compounds were formed, they would have rapidly reacted with Mg* to produce **3**. This meant that **3** could be formed from the open chain

Scheme 7



monoiodo compound 13, as well as the cyclized monoiodo compounds (14 and 15). When a mixture of 13–15 (in a ratio 2:1:1) was allowed to react with excess Mg*, in THF at 25 °C, the main products formed were 3 and 7 in 73 and 16% yields, respectively (eq 6). Two dimeric products **3a** and **7a**, whose structures were based on MS data, were also formed in a total yield of 4%. No unreacted iodo compound was recovered. According to eq 6, **7** must have been produced from **13**, and based on the 73% yield of **3**, it can be concluded that some of **3** was produced from **13**. The dimers **3a** and **7a** can also arise from **13** (we have previously reported the formation of both **3a** and **7a** by a radical pathway in the reaction of 6-bromo-5,5-dimethyl-1-hexene with magnesium[19]).



(6)

On quenching the reaction between a mixture of the monoiodo compounds **13**–**15** and excess Mg* with D_2O and analyzing the resulting hydrocarbon products **3** and **7** for any deuterium content, no evidence for an organomagnesium intermediate was obtained.

The results of the reaction shown in eq 6 indicate that in the reaction of **2b** with Mg*, as the amount of Mg* was increased, whatever the amount of **13** that was formed, it reacted further to produce **3** and **7**, and any **14** and **15** generated in the reaction reacted further to form **3**.

The observation that the reaction of **2b** with Mg* affords cyclized products **3**, **11**, and **12** indicates that an electron transfer pathway is involved in the reaction. In order to substantiate this, the reaction of **2b** with Mg* was studied in the presence of DCPH.

Effect of a Radical Trap. The results of the reaction of **2b** with Mg* (1:1 ratio) in the presence of 10 equiv of DCPH are shown in Table 3 (exp 7). It can be seen that in the presence of DCPH, the yield of **13** increased from 10%, in exp 5, to 18%. This increase is clearly an indication that a radical intermediate has been trapped. If ET does take place from Mg* to **2b**, then the formation of the radical anion of **2b** would be followed by the generation of the open chain iodo radical. The fact that the yield of **13** was higher in exp 7 suggests that the open chain iodo radical was trapped by DCPH (see Scheme 5).

The two cyclized diiodo compounds **11** and **12** were not detected in the presence of DCPH, but were formed in yields of 12 and 10%, respectively, in its absence (exp 5). At the same time, while the monoiodo compounds, **14** and **15**, were not detected in the absence of DCPH, they were formed in yields of 6 and 5%, respectively, when DCPH was employed (exp 7). In the absence of DCPH, the formation of **11** and **12** from the cyclized radical proceeds uninhibited (Scheme 7, pathway a). However, when DCPH is employed, the cyclized radical gets trapped by DCPH quite effectively (pathway b) to form **14** and **15** and thus making pathway a less favorable to form **11** and **12**.

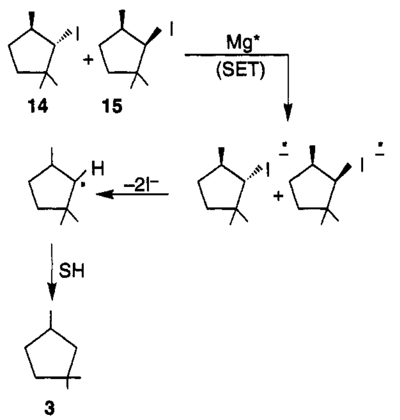
The yield of **6** was found to be the same in the presence and absence of DCPH (15%, in both cases). This result could be explained as follows: In exp 5, at a 1:1 molar ratio (**2b**:Mg*), where more of **11** and **12** were formed compared to exp 7 (where the ratio of **2b** to Mg* was the same, but included 10 equiv of DCPH), a part of the total amount of **11** and **12** formed was converted to **6** (see eq 5), leaving behind "unreacted" **11** and **12** (12 and 10%). But in exp 7, the fact that **11** and **12** were not detected indicates that DCPH trapped the radical that preceded the formation of **11** and **12** (Scheme 7). However, whatever amount of **11** and **12** was formed (probably in a total yield of 15%) in the presence of DCPH (exp 7), it reacted completely to yield **6** (15%).

The lack of formation of carbene-derived hydrocarbons **4** and **5** in the presence of DCPH (exp 7) suggests a radical precursor to the carbene intermediate. This radical, apparently gets trapped by DCPH, thereby producing more of **13**. This trapping, therefore, precludes the formation of the carbene intermediate and hence the formation of **4** and **5**, as shown in Scheme 2. With DCPH present, pathway b becomes the predominant pathway.

When DCPH was employed in the reation of **2b** with Mg*, the major product was the cyclized hydrocarbon **3** (20%, exp 7). This compound can be formed when the cyclized monoiodo compounds **14** and **15** react with Mg* and also when the open chain monoiodo compound **13** reacts with Mg* (see eq 6). Formation of **3** from **13** appears to involve radical intermediates formed by ET from Mg* to **13**, according to the scheme proposed earlier for formation of **3** from **10** (Scheme 4, X = I for **13**). The radical formed, on abstracting a hydrogen atom, would afford the open chain hydrocarbon **7** and on cyclization followed by hydrogen atom abstraction, it would form **3**. That the amount of **13** produced in the presence of DCPH was more than that produced in the absence of DCPH, and that **14** and **15** were also detected in the presence of DCPH, means that **3** would be produced in higher yield in exp 7, merely due to the subsequent reaction of these monoiodo compounds with Mg*. Compound **3** can be formed from **14** and **15** by an ET pathway as shown in Scheme 8.

Attempts to Determine the Source of Hydrogen Atoms. As in the case of the dichloro substrate **2a**, it was decided to identify the source(s) of H atoms in the reaction of **2b** with Mg*. Once again, the deuterium incorporation in the products that were suspected to be

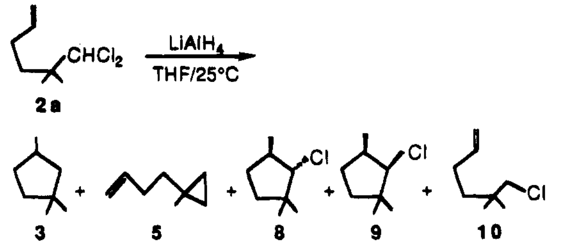
Scheme 8



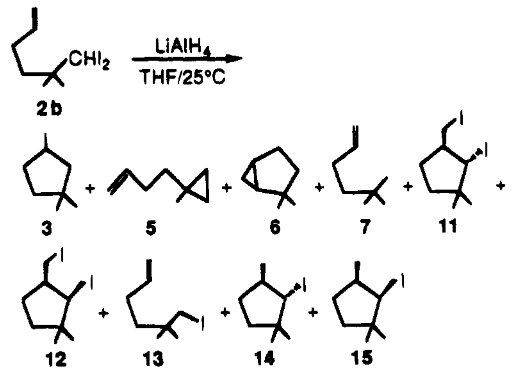
derived from radicals (**3**, **7**, and **13**) was low (11% d_1, 14% d_1, and 9% d_1, respectively) when the reaction of **2b** with Mg* was carried out in THF-d_8. In addition to this, on carrying out the reaction in THF-d_8 in the presence of naphthalene-d_8, the deuterium content in these products increased only slightly, indicating that in addition to THF and naphthalene, there was another source of hydrogen atoms in the reaction system. The most likely source is the starting material **2b** itself. However, no attempts were made to substantiate this hypothesis.

Based on the results of the reaction of **2b** with Mg* at different stoichiometries, in the presence of a radical trap, in the presence of THF-d_8 and by quenching with D_2O, a mechanistic pathway for the reaction of the substrate 6,6-diiodo-5,5-dimethyl-1-hexene with Mg* can be proposed (Scheme 5). As shown in the scheme, ET from Mg* to **2b** (X = I) leads to the formation of the radical anion of **2b**, which loses I^- to form the open chain iodo radical (X = I). The fate of this iodo radical then determines the nature of the products formed in the reaction of **2b** with Mg*.

Comparison of Reactions of 2a and 2b with Mg* and LiAlH$_4$. One of the objectives of this study was to carry out the reactions of **2a** and **2b** with Mg* in order to compare the products formed in these reactions with the corresponding reactions of **2a** and **2b** with $LiAlH_4$. Since Mg* is known to be a one-electron donor toward alkyl halides, and since the one-electron donation ability of $LiAlH_4$ toward alkyl halides has been questioned,[33] it was interesting to find that most of the products formed in the reactions of **2a** and **2b** with $LiAlH_4$ (eqs 7 and 8)[34] were also formed in the reactions of **2a** and **2b** with Mg*. All the products reported in the present study with Mg* as originating from radical precursors are also formed as products in the corresponding reactions with $LiAlH_4$, providing further evidence that the course of the reaction in both cases is similar and that indeed $LiAlH_4$ can function as a one-electron donor.



(7)



(8)

Experimental Section

Materials. Ethyl isobutyrate and diisopropylamine were purchased from Aldrich and distilled over calcium hydride prior to use. Pyridinium chlorochromate, phosphorus pentachloride, triethylamine, hydrazine hydrate, and THF-d_8 were purchased from Aldrich and used as received. Methyllithium, as a 1.6 M solution in diethyl ether, was purchased from Aldrich and titrated before use. 4-Bromo-1-butene was purchased from Wiley Organics and distilled over calcium hydride prior to use. Tetrahydrofuran and diethyl ether were purchased from Fisher Scientific and distilled from sodium benzophenone ketyl. Methylene chloride was also purchased from Fisher and distilled over calcium hydride just prior to use. HPLC grade hexane, from Fisher, was used as received. Neutral Alumina (Brockman activity I, 60–325 mesh) was purchased from Fisher Scientific and silica gel (200–400 mesh, 60 Å) was purchased from Aldrich. THF-d_8 was purchased from Aldrich and used as received. Ultrahigh purity magnesium chloride was purchased from Alfa Products. Lithium rod (165 × 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. All reactions were carried out in a nitrogen or argon inert atmosphere in glassware that was dried in an oven for at least 2 h at 150 °C. Solutions and solvents were transferred by means of syringes, or at times cannulas, under a stream of inert gas. GLC analyses were performed using a Varian 3700 gas chromatograph equipped with a flame ionization detector and a 30 m fused silica DB-5 column (0.32 mm i.d.). All GLC analyses were conducted with n-decane as an internal reference. A typical procedure employed a He flow rate of 1 mL/min, and temperature programming from 50 °C (held for 5 min) to 250 °C or 270 °C (held for 15 min), at 15 °C/min. The injection port was maintained at 250 °C with the detector at 280 °C. All product yields were obtained by GLC. NMR spectra were recorded in $CDCl_3$ solution with tetramethylsilane as the reference (δ 0.0), using a 300 MHz Varian Gemini spectrometer. Mass spectra were recorded using a VG 70-SE instrument equipped with a double sector magnetic analyzer. The percent deuterium incorporation in products, where applicable, was calculated on the basis of MS data. Preparative GLC was performed using a Varian 1400 Series dual column gas chromatograph equipped with a thermal conductivity detector. For isolation of compounds, the columns used were (A) 10% OV-101, 10 ft × $^1/_4$ in., (B) 10% Carbowax, 10 ft × $^1/_4$ in., and (C) 10% SE-30, 6 ft × $^1/_4$ in. The reactions of **2a** and **2b** with Mg* were carried out under ultrasonic activation conditions at 25 °C using a Branson ultrasonic cleaner.

Preparations. Ethyl 2,2-Dimethylhex-5-enoate (16). This compound was prepared according to the method described by Beckwith and Lawrence.[35] The spectral data of the product matched with those reported in the literature.[35]

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[33] Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206.

[34] Ashby, E. C.; Deshpande, A. K. *J. Org. Chem.* **1994**, *59*, 3798–3805.

[35] Beckwith, A. L. J.; Lawrence, T. *J. Chem. Soc. Perkin Trans.* **1979**, *2*, 1535.

2,2-Dimethylhex-5-en-1-ol (17). An amount of 15.0 g (0.09 mol) of ester **16** was added dropwise to a suspension of 7.40 g (0.19 mol) of $LiAlH_4$ in 350 mL of anhydrous diethyl ether at 0 °C, with vigorous stirring. The mixture was then allowed to warm to 25 °C and stirred for a period of 18 h. The excess $LiAlH_4$ was then destroyed by sequential addition of 7.40 mL of water, 7.50 mL of 15% NaOH solution, and finally, 22.5 mL of water. Next, the supernatant was decanted and the ether was removed using a rotary evaporator. The residual liquid was then distilled under reduced pressure to afford 9.60 g of the alcohol (bp 85 °C at 10 mmHg); the yield was 83% based on the ester. The spectroscopic data of this alcohol were the same as those reported in the literature.[35]

2,2-Dimethylhex-5-en-1-al (18). This aldehyde was prepared from alcohol **17** using the general procedure described for the synthesis of aldehydes by Corey and Suggs.[36] Accordingly, 8.00 g (0.06 mol) of alcohol **17** dissolved in 12.0 mL of dry methylene chloride was added, in one portion, to a suspension of 20.0 g (0.09 mol) of pyridinium chlorochromate in 120 mL of dry methylene chloride, with vigorous stirring, at 25 °C. The reaction mixture was then stirred at 25 °C for about 2 h, after which it was diluted with 120 mL of diethyl ether. The supernatant was decanted and the residue was washed with three 30.0 mL portions of diethyl ether. The combined organic layer was passed through a pad of Fluorisil, repeatedly, in order to obtain a clear solution. The solvent was then removed on a rotary evaporator. On analyzing the residual liquid by GLC, it was found that the product was 97% pure. The NMR data obtained for the product matched those reported for compound **18** in the literature.[37] This aldehyde was used in subsequent syntheses without any further purification.

6,6-Dichloro-5,5-dimethyl-1-hexene (2a). To a suspension of 6.70 g (0.032 mol) of PCl_5 in 25.0 mL of HPLC grade hexane was added, dropwise, 4.0 g of aldehyde **18** in 25.0 mL of hexane, with vigorous stirring at 25 °C. Following the addition of the aldehyde, the contents were then stirred at 25 °C for 24 h. The reaction flask was then cooled to 0 °C and the reaction was quenched with a saturated solution of Na_2CO_3. The lower layer was discarded and the hexane layer was washed with 10% HCl, after which it was dried over anhydrous K_2CO_3. The hexane was then removed on a rotary evaporator and the dark residual liquid that was obtained was passed through a short column of neutral alumina, using hexane as the eluent, to obtain a clear liquid. The pure geminal dichloride was finally obtained by preparative GLC using a 10% Carbowax column (10 ft × $^1/_4$ in.). Employing isothermal conditions (110 °C) and a He flow rate of 40.0 mL/min, the pure product was collected after 16.0 min. The geminal dichloride **2a** exhibited the following characteristics. NMR: the following peak assignments were made by comparing the NMR data reported for the corresponding protons of **16**:[35] δ 1.10 (6H, s, 2 × CH_3), 1.50–2.20 (4H, m, CH_2CH_2), 4.90–5.20 (2H, m, $=CH_2$), 5.70–6.10 (1H, m, $=CH$), and the following assignment was made on the basis of calculated values reported:[38] 5.65 (1H, s, $CHCl_2$); MS, *m/e* (relative intensity): 180 (2), 145 (2), 109 (10), 97 (68), 81 (29), 69 (45), 55 (100), 41 (32); high resolution mass spectrum $C_8H_{14}Cl_2$ calcd 180.047256, obsd 180.046722.

6,6-Diiodo-5,5-dimethyl-1-hexene (2b). This compound was synthesized from aldehyde **18**, via the corresponding hydrazone **19**. The hydrazone was prepared according to the general procedure described by Pross and Sternhell.[39] The aldehyde (2.0 g) in 15.0 mL of absolute ethanol was added slowly to 4.0 g of hydrazine hydrate, with vigorous stirring. The resulting mixture was then allowed to reflux on a steam bath for 1 h. The contents were then cooled and extracted with chloroform. The chloroform layer was washed with water and dried over anhydrous K_2CO_3. Removal of the solvent, using a rotary evaporator, afforded hydrazone **19** as a colorless viscous liquid. Its formation was confirmed by MS and NMR data. The hydrazone was then used in the subsequent synthesis of the geminal diiodide without any further purification.

The crude hydrazone (2.0 g) was added dropwise with stirring to a solution of 7.0 g of iodine in 25.0 mL of diethyl ether. Following the addition of the hydrazone, triethylamine was added very slowly until the evolution of nitrogen ceased. The contents were then diluted with 25.0 mL of diethyl ether and the resulting organic layer washed with 5% $Na_2S_2O_3$, followed by 3 N HCl and finally, a 5% solution of Na_2CO_3 in water. The organic layer was then dried over anhydrous K_2CO_3 and the solvent (and any excess triethylamine) removed under vacuum. The residual oil that was obtained was passed through a short silica gel column, with hexane as the eluent. The product that was obtained showed a single peak on GLC analysis. The MS and NMR data of this product confirmed that it was the desired geminal diiodide **2b**. Its approximate yield based on aldehyde **18** was found to be 28%. NMR: the following peak assignments were made by comparing the NMR data reported for the corresponding protons of **16**:[35] δ 1.15 (6H, s, 2 × CH_3), 1.50–2.10 (4H, m, CH_2CH_2), 4.90–5.10 (2H, m, $=CH_2$), 5.70–6.00 (1H, m, $=CH$), and the following assignment was made by comparing with a reported value for a geminal diiodide:[40] 5.25 (1H, s, CHI_2); MS, *m/e* (relative intensity) 364 (3), 239 (20), 183 (15), 127 (10), 109 (100), 69 (97), 55 (90), 41 (71); high resolution mass spectrum $C_8H_{14}I_2$ calcd 363.918504, obsd 363.918640.

Reactive Magnesium (Mg*). The synthesis of Mg* was carried out according to an established procedure.[29] In a typical synthesis, 4.00 mL of dry THF was added to a flask containing 25.0 mg (3.57 mmol) of freshly cut lithium (which had been rinsed in dry hexane repeatedly after having been cut under mineral oil), 46.0 mg (0.359 mmol) of naphthalene, and 171.0 mg (1.80 mmol) of anhydrous $MgCl_2$ in an argon filled glove box. The mixture was then stirred vigorously, and within a few minutes the solution had acquired a characteristic green color. Stirring was then continued at 25 °C, for 24 h. At the end of this period the solution had acquired a black color. After allowing the solution to stand, the Mg* settled as a fine black powder leaving a very clear solution. A volume of THF was syringed out from the flask (to remove as much undesired naphthalene as possible) such that there was enough THF to cover the Mg*. An equal volume of fresh, dry THF was then added to the flask.

Procedure for the Reaction of the Geminal Dihalides with Mg* and the Subsequent Characterization of Products. Following the synthesis of Mg*, the reaction flask was then placed in an ultrasonic cleaner containing water at 25 °C. A steady stream of nitrogen was maintained in the flask. A solution of the appropriate dihalide, with a specific amount of the internal reference n-decane, in THF, was syringed into the reaction flask. The typical molar ratio of **2a** to Mg* was 1:10 while that of **2b** to Mg* was 1:3 or less. The molar concentration of the dihalide in the final reaction mixture was maintained around 0.05 M. Immediately following the addition of the substrate, the reaction mixture was activated ultrasonically. The status of the reaction was periodically checked by drawing out small volumes of the reaction mixture, quenching with 10% HCl, and analyzing the products in the organic layer by GLC. The reaction of **2a** with Mg* was quite slow and required 6–8 h at 25 °C for complete consumption of **2a**. On the other hand, **2b** reacted with Mg* at a much faster rate. When a radical trap DCPH was used, a solution of the dihalide containing the trap (10.0 equiv), and n-decane, was prepared in THF. Reactions that were performed in THF-d_8 involved the synthesis of Mg* in THF-d_8 with the solution of the dihalide also being prepared in THF-d_8.

Product Isolation and/or Characterization. 1,1,3-Trimethylcyclopentane (3). The MS data of this product matched the MS data obtained for an authentic sample bought from Wiley Organics. Also, the GLC retention time of **3** was the same as that of the commercial sample.

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(36) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, *16*, 2647.

(37) House, H. O.; Liang, W. C.; Weeks, P. D. *J. Org. Chem.* **1974**, *39*, 3102.

(38) Patai, S., Ed. *The Chemistry of the Carbon-Halogen Bond*; John Wiley and Sons: New York, 1973; Part I.

(39) Pross, A.; Sternhell, S. *Aust. J. Chem.* **1970**, *23*, 989.

(40) Kropp, P. J.; Pienta, N. J. *J. Org. Chem.* **1983**, *48*, 2084.

2-(2-Propenyl)-1,1-dimethylcyclopropane (4). This compound was identified by matching its MS data with that reported in the literature.[41]

1-(3-Butenyl)-1-methylcyclopropane (5). The structure was established by matching the MS data obtained with that reported for an authentic sample.[42]

2,2-Dimethylbicyclo[3.1.0]hexane (6). The structure was assigned on the basis of matching MS data with that reported for an authentic sample of 2,2-dimethylbicyclo [3.1.0] hexane prepared in earlier work carried out by this group.[43]

5,5-Dimethyl-1-hexene (7). The structure was assigned on the basis of the MS data that matched with that reported in the literature for 5,5-dimethyl-1-hexene.[44]

***trans*-2-Chloro-1,1,3-trimethylcyclopentane (8).** This product was isolated by preparative GLC using a 10% Carbowax column (10 ft × $^1/_4$ in.) under temperature programming conditions of 70 °C to 180 °C at 4 °C/min and a helium flow rate of 40 mL/min. **8** was collected after 10 min. NMR: the following peak assignments were made by comparing the NMR data reported for the corresponding protons of **3**:[35] δ 0.95 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.10 (d, 3H, CH_3), 1.20−2.00 (m, 5H, ring CH and CH_2CH_2), and the following assignment was made on the basis of calculated values reported:[38] 3.40 (d, J = 10.2 Hz, 1H, CHCl); MS, *m/e* (relative intensity) 146 (30), 110 (22), 95 (42), 69 (100), 56 (40), 55 (50); high resolution MS $C_8H_{15}Cl$ calcd 146.086228, obsd 146.085892.

***cis*-2-Chloro-1,1,3-trimethylcyclopentane (9).** This compound was also isolated by preparative GLC under the same conditions that were employed for the isolation of **8**, and it had a retention of 14 min. NMR: all H shift values were essentially the same as those for the *trans* isomer **8**, except for the CHCl unit at δ 4.00 (d, J = 5.10 Hz, 1H); MS, *m/e* (relative intensity) 146 (26), 110 (22), 95 (45), 69 (100), 56 (61), 55 (59); high resolution MS $C_8H_{15}Cl$ calcd 146.086228, obsd 146.085953.

6-Chloro-5,5-dimethyl-1-hexene (10). This product was identified by matching its MS data with that reported in the literature.[45]

***cis*-2-Iodo-3-(iodomethyl)-1,1-dimethylcyclopentane (12).** This compound was isolated by flash column chromatography, using silica gel with hexane as eluent. NMR: the following peak assignments were made by comparing the NMR data reported for the corresponding protons of **3**:[35] δ 1.15 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.55−2.00 (m, 4H, 2 × ring CH_2), 2.15 (m, 1H, CH), and the following assignments were made on the basis of calculated values reported:[38] 3.23 (m, 2H, CH_2I), 4.32 (d, J = 4.80 Hz, 1H, CHI); MS, *m/e* (relative intensity) 364 (85), 254 (40), 237 (40), 109 (95), 67 (90), 55 (70).

***trans*-2-Iodo-3-(iodomethyl)-1,1-dimethylcyclopentane (11).** This compound was also isolated by flash column chromatography using silica gel with hexane as the eluent. NMR: all the chemical shift values for the protons in this molecule were the same as those in **12**, except for the CHI unit at δ 3.62 (d, 1H, J = 10.5 Hz); MS, *m/e* (relative intensity) 364 (85), 254 (25), 237 (100), 109 (95), 127 (10), 69 (75), 55 (50).

6-Iodo-5,5-dimethyl-1-hexene (13). This product was identified by matching its MS data with that reported in the literature.[45]

***trans*-2-Iodo-1,1,3-trimethylcyclopentane (14).** This compound was isolated by preparative GLC using a 10 ft × $^1/_4$ in. 10% OV-101 column, with a He flow rate of 40 mL/min. NMR: the following peak assignments were made by comparing the NMR data reported for the corresponding protons of **3**:[35] δ 0.97 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.07 (d, 3H, CH_3), 1.40−2.00 (m, 4H, 2 × ring CH_2), 2.27 (m, 1H, CH), and the following assignment was made on the basis of calculated values reported:[38] 3.49 (d, J = 11.1 Hz, 1H, CHI); MS, *m/e* (relative intensity): 238 (<2), 127 (5), 111 (80), 69 (100), 55 (50), 41 (35).

***cis*-2-Iodo-1,1,3-trimethylcyclopentane (15).** This compound showed the following spectroscopic characteristics. NMR: all values of the chemical shifts for all protons in the molecule were the same as that listed for **14** above except for the value pertaining to the CHI proton at δ 4.27 (d, J = 6.0 Hz, 1H); MS, *m/e* (relative intensity) 238 (<2), 127 (5), 111 (100), 69 (95), 55 (60), 41 (35).

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(41) Kropp, P. J.; Manning, T. D. R. *J. Am. Chem. Soc.* **1981**, *103*, 889.

(42) Ph. D. Dissertation of B. Park, Georgia Institute of Technology, Atlanta, GA, 1988.

(43) Ashby, E. C.; Park, B.; Patil, G. S.; Gadru, K.; Gurumurthy, R. *J. Org. Chem.* **1993**, *58*, 424.

(44) House, H. O.; Weeks, P. D. *J. Am. Chem. Soc.* **1975**, *97*, 2778.

(45) Ashby, E. C.; DePriest, R. N.; Goel, A. B.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* **1984**, *49*, 3545.