The Mechanism of Reaction of Geminal Dihalides with Sodium Trimethyltin. Evidence for a Single Electron Transfer Initiated Reaction Which Produces Both Radical and Carbene Intermediates

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The reactions of two geminal dihalides, 6,6-dichloro-5,5-dimethyl-1-hexene (**2a**) and 6,6-diiodo-5,5-dimethyl-1-hexene (**2b**) with sodium trimethyltin ($NaSnMe_3$), a known one-electron donor toward alkyl halides, have been studied. Evidence for a single electron transfer (SET) pathway has been obtained for both reactions. Although the monochloro analog of **2a**, namely **7**, was inert toward $NaSnMe_3$, **2a** afforded 11 products. The nature of the products clearly indicates that the presence of two chlorine atoms on the same carbon atom results in a more favorable reduction potential than when just one chlorine atom is present. Both **2a** and **2b** on reaction with $NaSnMe_3$ also produced carbene-derived products, and evidence is presented that establishes that the carbene intermediate was in fact preceded by a radical intermediate. In addition, trimethyltin-substituted products (open chain as well as cyclized) were also obtained from both substrates and were found to be derived from radical intermediates.

Introduction

Tetraalkyltin compounds can be synthesized quite readily and in good yields by reacting an alkyl halide with an alkali metal trialkyltin compound (eq 1). At first

$$R_3SnNa + R'X \rightarrow R_3SnR' + NaX \qquad (1)$$

glance, the reaction appears to be a simple S_N2 substitution process; however, extensive studies by Kuivila and others have revealed that depending on the nature of the alkyl halide, the reaction can actually proceed by a single electron transfer (SET) pathway (eq 2).[1,2,3b,4-8] In addi-

$$R_3Sn^- + R'X \rightarrow R'X^{\bullet -} \rightarrow R'^{\bullet} + R_3Sn^{\bullet} \qquad (2)$$

$$R'^{\bullet} + R_3Sn^- \rightarrow R_3SnR'^{\bullet -} \rightarrow R_3SnR' + R'X^{\bullet -}$$

$$R'^{\bullet} + R_3Sn^{\bullet} \rightarrow R_3SnR'$$

tion, a halogen–metal exchange (HME) pathway has also been suggested to occur in reactions of aryl (as well as alkyl) halides with an alkali metal organotin compound (eq 3).[2]

$$R_3Sn^- + ArX \rightarrow ArSnR_3 + X^- \qquad (3)$$

Experimental evidence to support the S_N2 pathway for the reaction of R_3Sn^- with alkyl halides has been reported by a number of workers,[1,2,9-17] mainly based on stereochemical studies. By the use of cyclizable radical probes and radical traps, an electron transfer pathway has been established in reactions of R_3Sn^- with alkyl halides.[1-8] The HME pathway has been established on the basis of anion-trapping studies (using *tert*-butylamine as an anion trap).[3,4,18]

The trimethyltin anion has been proven to be an excellent one-electron donor toward alkyl halides.[1-8] Observation of cyclized products in the reaction of a cyclizable alkyl halide with the trimethyltin anion has served to support radical involvement in the reaction. For example, the reaction between 6-bromo-1-heptene and sodium trimethyltin in THF at 0 °C yields the cyclized trimethyltin-substituted product (as a mixture of *cis* and *trans* isomers) in 88% yield.[6] Further strong evidence that supports the intermediacy of radicals involves the trapping of the radicals formed in the reaction by the radical trap, dicyclohexylphosphine (DCPH).[2,6-8] The radical trapping resulted in a significant increase in the yield of the hydrocarbon products with a simultaneous decrease in the yield of the trialkyltin substitution products. The mechanism that has been proposed[6] for the reaction of 6-bromo-1-heptene with Me_3Sn^- is shown in Scheme 1.

One useful approach to detect SET in the reaction of a primary alkyl halide with a nucleophile is to use a

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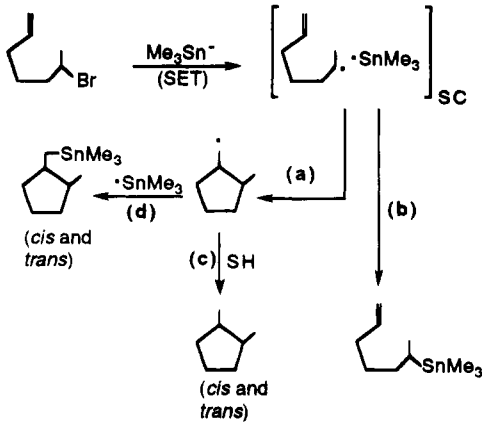
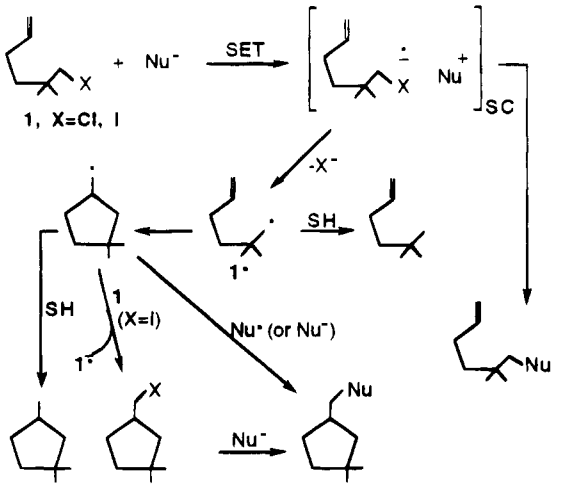
Scheme 1

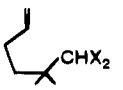


Scheme 2



neopentyl halide system **1**. Work carried out by this group has shown that in reactions of **1** with a variety of nucleophiles, products are formed from radical intermediates (Scheme 2).[19-22] Compound **1** is a neopentyl type halide which is a special case in that the rate of reaction via the S_N2 pathway should be very slow, dehydrohalogenation is not possible, and an S_N1 process would also be prohibitively slow, so that if SET is at all a possible pathway, it should be observed in reactions of **1**, provided the reaction takes place at an appreciable rate. Indeed, the reaction is very rapid. Kuivila has reported,[2] on the basis of his studies of the reaction of sodium trimethyltin with neopentyl halides, that there is 90% S_N2 and 5% ET for the chloride, 58% S_N2 and 32% ET for the bromide, and 22% S_N2, 0% ET, and 77% HME for the iodide.

Realizing that Me_3Sn^- is an excellent one-electron donor toward alkyl halides, and based on evidence obtained for the involvement of free radicals in the reactions of Me_3Sn^- with certain alkyl halides, it was decided to study the reactions of Me_3Sn^- with the cyclizable aliphatic geminal dihalides of the type **2**.

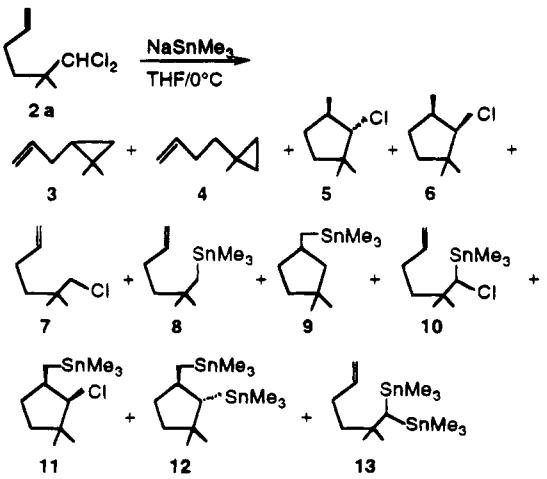


2a: X=Cl, 2b: X=I

The main objective of this proposed study was to explore mechanistically the reactions of Me_3Sn^- with the geminal dihalides **2a** and **2b** and to compare their reactivity to that of the already studied monohalides. The introduction of two halogen atoms on one carbon atom was expected to affect the reduction potential of the molecule, and it was considered important to determine how this change would affect the mechanistic features of the reactions. Considering the fact that alkyl monochlorides do not have a very favorable reduction potential and hence do not appear to react via ET, it was of considerable interest to determine if placing a second chlorine atom on the same carbon holding the first chlorine atom would change the reduction potential enough that the reaction of the dichloride, **2a**, with Me_3Sn^- might involve a significant electron transfer pathway.

Results and Discussion

Reaction of 6,6-Dichloro-5,5-dimethyl-1-hexene (2a) with $NaSnMe_3$: Effect of Stoichiometry and Radical Trap. When 6,6-dichloro-5,5-dimethyl-1-hexene (**2a**) was allowed to react with sodium trimethyltin at 0 °C, in THF, the reaction proceeded rapidly affording 11 products as shown in eq 4. The reaction was carried



(4)

out at two different stoichiometries and, as shown in Table 1, at the lower ratio of 1:1 (**2a**:$NaSnMe_3$), 20% of **2a** was recovered (experiment 1) after 8 h. The products formed were the same at the higher ratio of 1:3 (experiment 2), but in different yields, and no unreacted **2a** remained after 8 h at the higher ratio. On both occasions, initial product formation was instantaneous. No change in product composition was observed on allowing the reaction (at both ratios) to stir further for a period of 8 h at 0 °C.

The formation of products **5**-**13** suggests the involvement of radical intermediates in the mechanistic pathway of the reaction of **2a** with $NaSnMe_3$. In order to substantiate radical intermediacy, experiment 2 was repeated in the presence of 10 equiv of the radical trap dicyclohexylphosphine (Table 1, experiment 3). The same products were formed; however, there was a significant change in the product composition and also product yields. The monochloro compounds **5**-**7** were formed in

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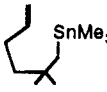
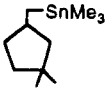
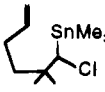
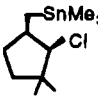
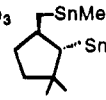
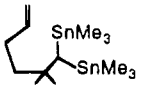
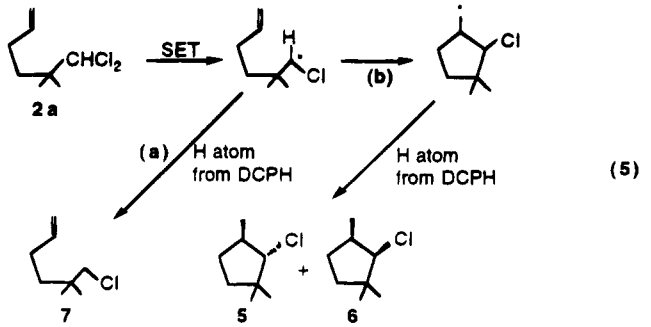
Table 1. Reaction of 6,6-Dichloro-5,5-dimethyl-1-hexene (2a) with $NaSnMe_3$ in THF at 0 °C

EXP. No.	% Yields of Products										
	 3	 4	 5	 6	 7	 8	 9	 10	 11	 12	 13
1[a]	2	8	1	1	4	1	1	17	15	5	10
2[b]	3	9	2	2	5	5	3	10	12	10	28
3[c]	0	0	6	6	30	5	6	14	6	3	5

[a] Ratio of **2a** to $NaSnMe_3$ was 1:1, and 20% of **2a** was recovered after 8 hours. [b] Ratio of **2a** to $NaSnMe_3$ was 1:3, and the reaction was carried out for 8 h. No unreacted **2a** was recovered. [c] The ratio was again 1:3, the reaction employed 10 equiv of DCPH, and was carried out for 8 h.

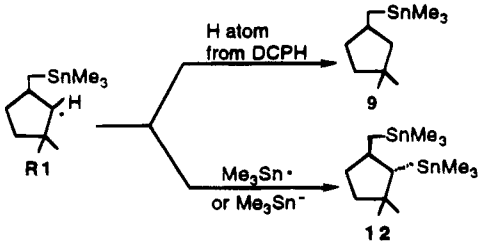
yields of 6%, 6%, and 30%, respectively, in the presence of DCPH, compared to their yields of 2%, 2%, and 5%, respectively, in the absence of DCPH. These significant differences in the yields of the monochloro products can be considered as evidence supporting involvement of radicals that were trapped by DCPH and, hence, did not form substitution products (eq 5). In the absence of



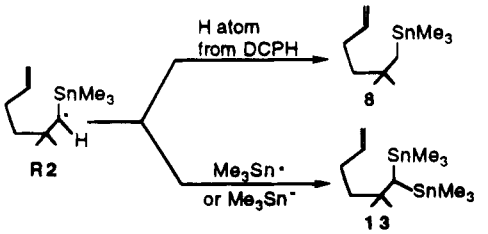
(5)

DCPH, an initially formed open chain chloro radical (if formed) can cyclize, abstract a hydrogen atom from solvent (THF), and also possibly undergo geminate coupling with a trimethyltin radical. However, with 10 equiv of DCPH, which is a very good hydrogen atom donor for radicals,[2] the chlororadical preferentially forms the open chain product (**7**) by hydrogen atom abstraction from the radical trap (eq 5, pathway a). Also, when this radical cyclizes in the presence of DCPH (eq 5, pathway b), the possibility of the cyclized radical abstracting a hydrogen atom from DCPH is greater, and this results in higher yields of **5** and **6** in experiment 3 compared to experiment 2 (Table 1). It is clear from the data that the rate of radical trapping of DCPH is greater than THF and faster than the rate of cyclization of the open chain mono chloro radical.

The disubstituted trimethyltin compounds **12** and **13** were formed in yields of 10% and 28%, respectively, in the abeence of DCPH, whereas their yields in the presence of DCPH dropped to 3% and 5%, respectively. These differences in the yields of **12** and **13** can be rationalized by considering the fate of their respective precursor radicals **R1** and **R2** (if these were to be formed) in the presence of DCPH as shown in eqs 6 and 7. As predicted, the yield of **9** increased and that of **12** decreased. Also, it was predicted that the yield of **13** would decrease, and it did, from 28% to 5%, in the presence of DCPH.

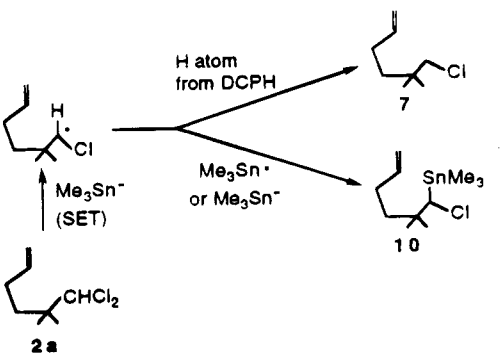


(6)



(7)

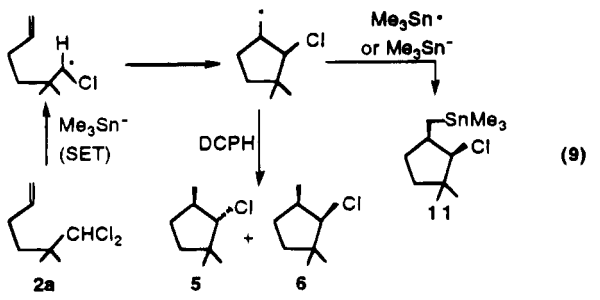
Another very interesting comparison of yield data that helps further to substantiate the involvement of radicals is that of product **7** compared to product **10**. In the absence of DCPH (Table 1, experiment 2), **7** was formed in a 5% yield, with the yield of **10** being twice as much; however, when DCPH was employed in the reaction (experiment 3), the yield of **7** increased 6-fold to 30% and that of **10** increased only marginally to 14%. Once again, these results can be explained by considering the fate of the initially formed open chain chloro radical, from **2a**, as shown in eq 8. DCPH would be expected to increase the yield of **7** relative to **10**.



(8)

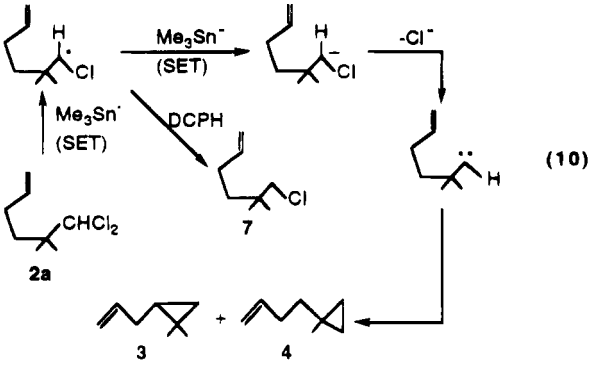
The cyclized monochloro compounds **5** and **6** were formed in much lower yields (2% each) than that of the

cyclized product **11** (12%) in the absence of DCPH; however, in the presence of DCPH, the yields of **5**, **6**, and **11** were the same (6%). These data can be explained by considering the fate of the cyclized chloro radical in the presence of DCPH, as shown in eq 9.



(9)

There was a significant difference in the product distribution of the carbene-derived products, **3** and **4** in experiments 2 and 3 (Table 1). These two products were detected in yields of 3% and 9%, respectively, in the absence of DCPH (experiment 2); however, they were not detected when the reaction was carried out in the presence of DCPH (experiment 3). The most likely pathway that could account for the formation of a carbene involves ET from Me_3Sn^- to the open chain chloro radical, followed by loss of a Cl^- ion from the subsequently formed chloro carbanion (eq 10). However, in the presence of 10

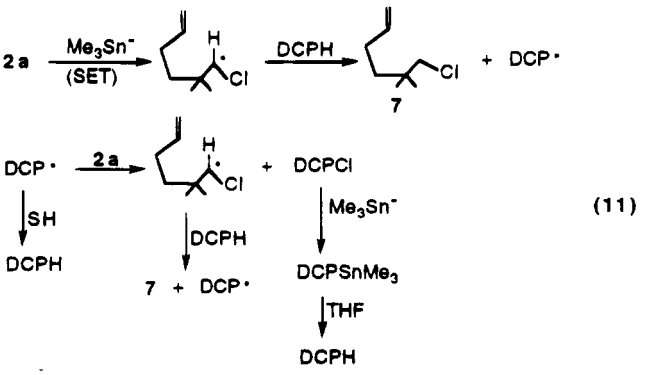


(10)

equiv of DCPH, the intermediate monochloro radical should be intercepted at a much faster rate, thereby precluding the formation of **3** and **4**. Indeed, the yield of **7** increased dramatically at the expense of the formation of **3** and **4**.

The role of DCPH as a radical trap must be considered from yet another perspective. Not only is it a very good H atom donor to trap radicals, but it is also possible that it can influence the mechanism of the reaction. The reason for this is that once DCPH donates a hydrogen atom, the DCP• that is generated can then abstract a halogen atom from the starting material (**2a**), thereby initiating a radical chain mechanism (eq 11).[6] However, analysis of the reaction mixture (by GC–MS) did not reveal any DCPCl or $DCPSnMe_3$ in the mixture of products. In fact, almost all of the DCPH originally introduced into the reaction system was recovered (as determined by GLC analysis). It is possible that once the DCPCl is formed it can react with Me_3Sn^- to form a strong base[23] which can then cleave THF to regenerate the DCPH.

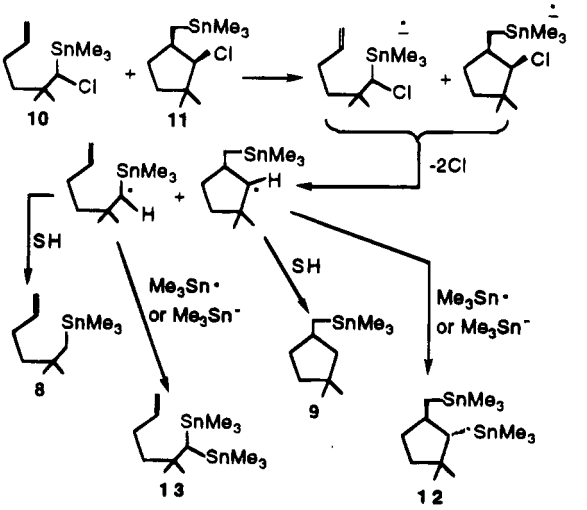
(23) Maier, L. *Organic Phosphorus Compounds;* Wiley: New York, 1972; Vol. I.



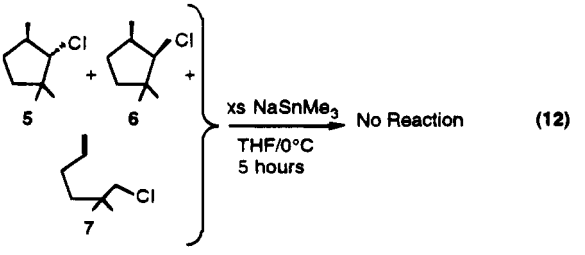
(11)

Examination of the product yields in experiments 1 and 2 suggests that the formation of products **12** and **13** is very likely a result of the reaction of **11** and **10** with excess trimethyltin anion (Scheme 3). As can be seen in Table 1, an increase in the amount of Me_3Sn^- resulted in an increase in the yield of **12** with a reduction in the yield of **11** and also an increase in the yield of **13** with a simultaneous redution in the yield of **10**. An increase in the yields of **8** and **9** in experiment 2 with a lowering of the yields of **10** and **11** shows that **8** and **9** could also arise from **10** and **11**, respectively (Scheme 3).

Scheme 3



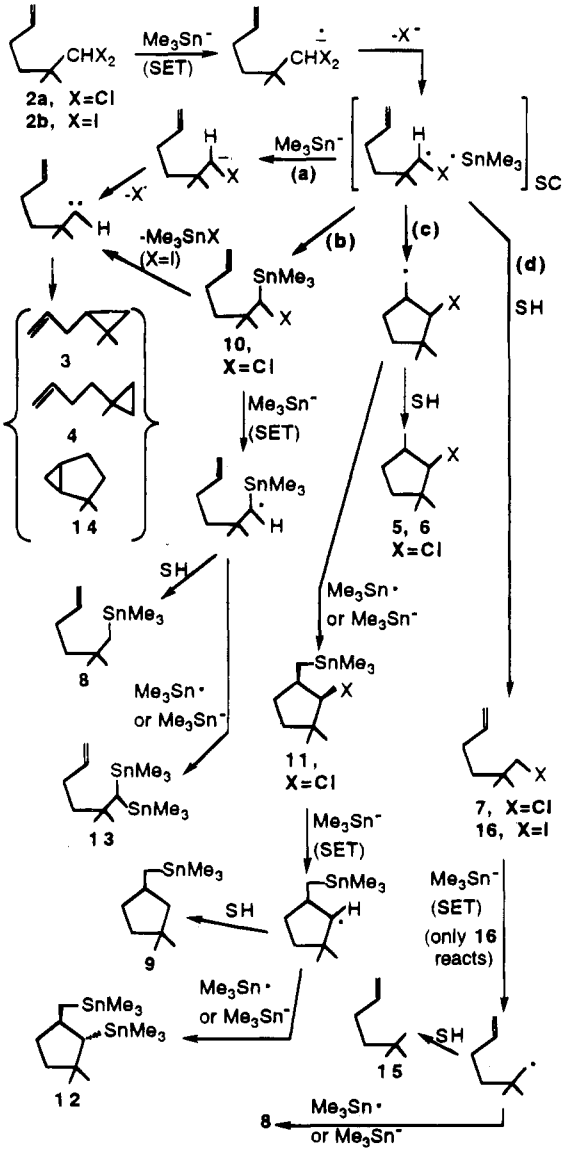
It could be argued that the open chain monosubstituted product **8** could be formed by the reaction of **7** with excess Me_3Sn^-. On allowing a mixture of the three monochloro compounds **5**–**7** to react with excess $NaSnMe_3$, no reaction was detected, even after 5 h (eq 12).



(12)

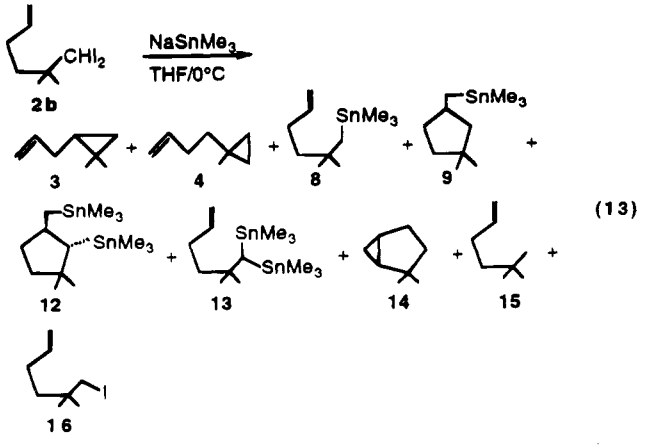
The results of the reactions of **2a** with $NaSnMe_3$ at different ratios and in the presence and absence of DCPH provide evidence for initiation of the reaction by SET followed by the formation of both radical and carbene intermediates which then become the precursors to all

Scheme 4



of the observed products. A general mechanism that is consistent with the data is shown in Scheme 4.

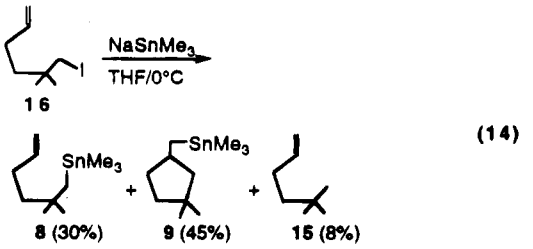
Reaction of 6,6-Diiodo-5,5-dimethyl-1-hexene (2b) with $NaSnMe_3$: Effect of Stoichiometry. When 6,6-diiodo-5,5-dimethyl-1-hexene (**2b**) was allowed to react with $NaSnMe_3$ in THF, at 0 °C, nine products were obtained (eq 13). The reaction was studied at two



(13)

different molar ratios (**2b**:Me_3Sn^- = 1:0.5 and 1:3) and the results are shown in Table 2. At the lower ratio (experiment 4), 40% of **2b** was recovered after 8 h whereas at the higher ratio (experiment 5), all of **2b** had reacted. In both cases, formation of products was complete in less than 1 min. On allowing the reaction at the 1:0.5 ratio to stir further for 8 h at 0 °C, no change in the product composition was observed.

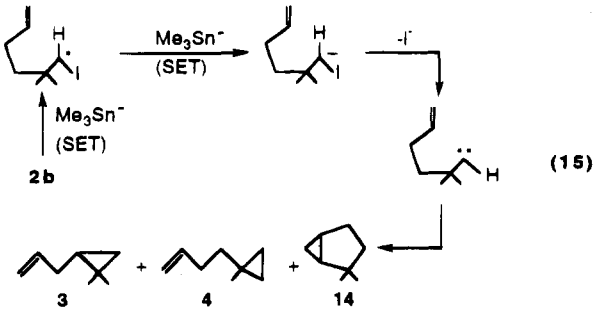
On comparing the product distribution of the two experiments, it can be seen that the yields of all the products were influenced by the molar ratio of **2b** to Me_3Sn^-. At the lower ratio of 1:0.5, 10% of **16** was formed; however, **16** was not detected at the higher ratio of 1:3, as expected. Also, whereas **15** was not detected at the lower ratio, it was formed in 5% yield at the higher ratio. This suggests that **15** may have been the result of a reaction between **16** and excess Me_3Sn^-. In addition, the yields of the monosubstituted products **8** and **9** increased significantly at the higher ratio employed. Once again, these two products could be derived from **16**. In order to confirm this possibility, **16** was treated with excess $NaSnMe_3$ (**16** was completely consumed in 10 min) in THF at 0 °C, and it was found that **8**, **9**, and **15** were the sole products (eq 14). These data support the proposal



(14)

that at a higher ratio of **2b**:Me_3Sn^-, the amount of **16** would be expected to decrease and the amounts of **8**, **9**, and **15** would be expected to increase.

An important feature of the product mixture in the reaction of **2b** with $NaSnMe_3$ is the formation of products **3** and **4** in high yields, especially in experiment 5 (Table 2), where they were formed in yields of 21% and 23%, respectively. This observation suggests the involvement of a carbene intermediate. Once again, as was discussed earlier in the case of **2a**, the carbene intermediate could be formed as a result of ET from Me_3Sn^- to an initially formed iodo radical followed by loss I^- from the subsequently formed iodo carbanion (eq 15). Alternatively, the



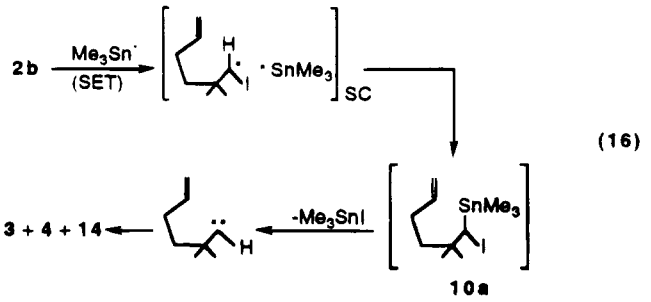
(15)

carbene could be formed as a result of a rapid elimination of a molecule of Me_3SnI from an intermediate compound that can be formed by geminate coupling of the open chain iodo radical with $Me_3Sn^{\bullet}$ inside the solvent cage, as shown in eq 16. However, unlike the reaction of **2a** with $NaSnMe_3$, the iodo analog of **10** (**10a** in eq 16) was not detected in the reaction of **2b** with $NaSnMe_3$. This lack of formation of **10a** could mean that once it was

Table 2. Reaction of 6,6-Diiodo-5,5-dimethyl-1-hexene (2b) with $NaSnMe_3$ in THF at 0 °C[a]

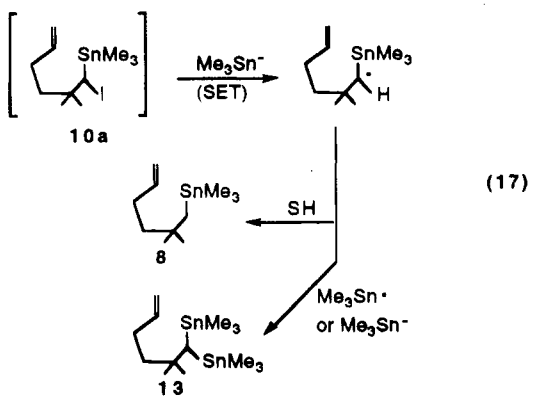
Exp. No.	Ratio 2b : Me_3Sn^-	% Yields of Products[b] 3	4	8	9	12	13	14	15	16
4[c]	1 : 0.5	7	12	1	1	1	5	5	0	10
5[d]	1 : 3.0	21	23	10	12	2	10	10	5	0
6[e]	1 : 3.0	0	0	14	7	0	0	10	40	0

[a] The reactions were carried out for 8 h. [b] In experiment 4, products **17** and **18** were also formed in yields of 2% and 6%, respectively. Neither **17** nor **18** was formed in experiment 5. [c] In experiment 4, 40% of **2b** was recovered after 8 h. [d] No unreacted **2b** remained in experiment 5. [e] The reaction employed 10 equiv of DCPH.



(16)

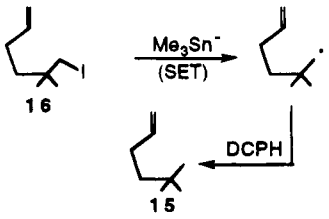
formed, it underwent α-elimination of Me_3SnI very rapidly. Further support for the intermediate compound **10a** is based on the premise that **10a** is very likely to be the precursor to the bis(trimethyltin)-substituted open chain compound **13** (eq 17). It is reasonable that **10a**



(17)

reacted rapidly with excess Me_3Sn^- to form both **8** and **13**, as shown in eq 17.

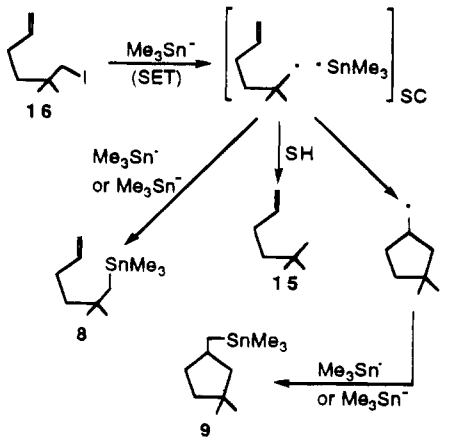
Effect of a Radical Trap. In order to further establish radical intermediacy in the reaction of **2b** with $NaSnMe_3$, the reaction was carried out in the presence of DCPH (Table 2, experiment 6), and the results were compared with experiment 5 (Table 2). A significant difference in the results of the two reactions is reflected in the increase in the amount of **15** (from 5% to 40%) when the reaction employed DCPH. The high yield of **15** indicates a radical precursor. As shown in eq 14, the formation of **15** involves the reaction of **16** with Me_3Sn^-. Although the yield of **15** is lower than both **8** and **9** in the absence of DCPH, in the presence of DCPH, it appears that the initially generated radical is effectively trapped by DCPH (eq 18), since the yield of **15** increased



(18)

from 5 to 40%, while all other products except **8** and **14** decreased in yield.

It was also observed that in the presence of DCPH, the yield of **8** (14%) was twice that of **9** (7%); in the absence of DCPH, the respective yields were 10% and 12%. These results indicate that the formation of **8** and **9** also involved radical precursors. However, it is essential to realize that each one of these two products can be formed from more than one radical precursor. Two pathways could result in the formation of **8** and **9**. One of these involves the reaction of **16** with Me_3Sn^- where the formation of **8** and **9** is due to coupling of the alkyl substrate radical (open chain and cyclized, respectively) with a $Me_3Sn^\cdot$ or Me_3Sn^- as shown in eq 19. The other

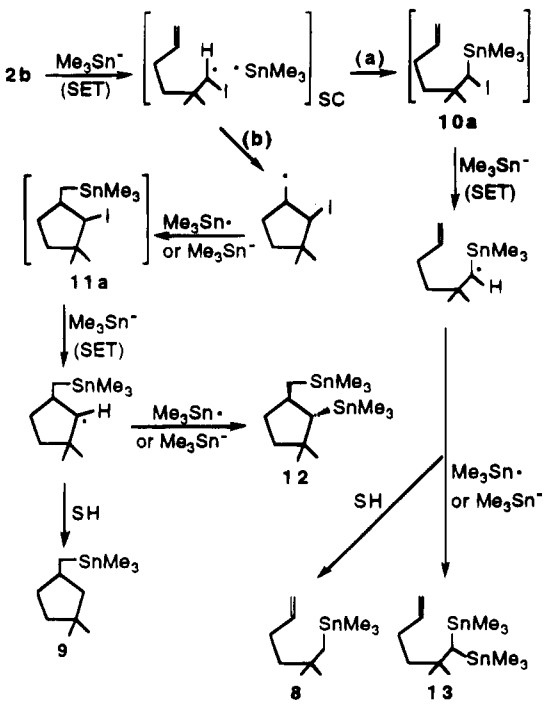


(19)

pathway could involve intermediates **10a**, which leads to **8** and **13**, and **11a** (the iodo analog of **11**) that leads to the formation of **9** and **12**. Neither **10a** nor **11a** was detected in the reaction of **2b** with $NaSnMe_3$. This proposed pathway is shown in Scheme 5.

An important feature of the reaction of **2b** with $NaSnMe_3$ in the presence of DCPH was the lack of formation of the disubstituted products **12** and **13**. This result suggests that the pathway shown in Scheme 5 is

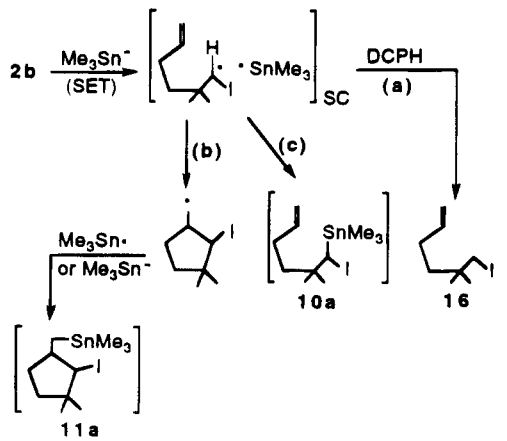
Scheme 5



very likely to be operational. In the presence of DCPH, both the open chain and cyclized trimethyltin-substituted radicals (derived from **10a** and **11a**, respectively) are effectively trapped by DCPH to afford exclusively **8** and **9**, respectively, and this trapping prevents the formation of **12** and **13**.

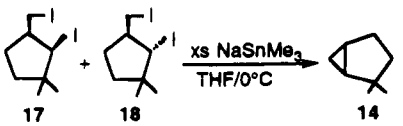
The lack of formation of **12** and **13** is also affected by the role played by DCPH once the open chain iodo radical (derived by ET from Me_3Sn^- to **2b**) is formed. If this radical were to be effectively trapped by DCPH, then the formation of intermediates such as **10a** and **11a** would be prevented. This, in turn, would preclude the formation of both **12** and **13**. As shown in Scheme 6, the presence of DCPH leads to the formation of **16** (pathway a) thereby making pathways b and c less favorable. Compound **16** can then react with $NaSnMe_3$ to afford **8**, **9**, and **15** (see eq 14).

Scheme 6



The detection of carbene-derived products **3** and **4** in high yields in the reaction of **2b** with $NaSnMe_3$ (Table 2, experiment 5) together with their complete absence in the reaction carried out in the presence of DCPH (Table 2, experiment 6), strongly suggests that the formation of the carbene intermediate, most likely, was preceded by a radical intermediate. This radical, in the presence of DCPH, was probably trapped so effectively that all other pathways that were operational in the absence of DCPH were blocked effectively, one of these being the formation of the carbene intermediate. The proposed modes of formation of the carbene in the reaction of **2b** with $NaSnMe_3$ (see eqs 15 and 16) involve the open chain iodo radical (derived by ET from Me_3Sn^- to **2b**) as the precursor to the carbene. It then becomes clear that in the presence of 10 equiv of DCPH, this radical is trapped to form exclusively **16** which subsequently affords **8**, **9**, and **15**. As a result of the trapping by DCPH, the only products that were detected in experiment 6 (except **14**) were products of the reaction of **16** with Me_3Sn^- in the presence of DCPH.

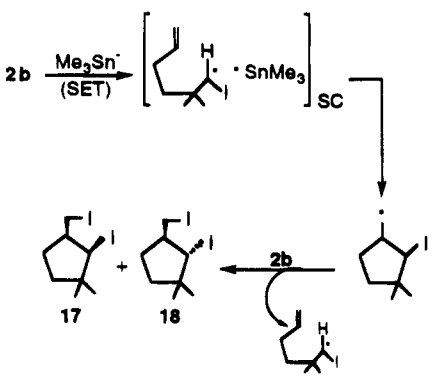
The formation of **14** could be the result of an intramolecular addition of the carbene across a C=C. However, the fact that **14** was detected in 10% yield in experiment 6 (Table 2, employing DCPH) where the other carbene-derived products, **3** and **4**, were not detected at all, indicates that **14** can also be formed by a noncarbene pathway. A possible way of forming **14** is suggested to be in a reaction of the cyclized diiodo isomers **17** and/or **18** (which were formed in 2% and 6% yield, respectively in experiment 4 but not in experiment 5, Table 2) with excess Me_3Sn^- (eq 20). These diiodo compounds could be



(20)

formed as a result of a radical chain mechanism (Scheme 7) wherein the originally formed iodo radical cyclizes, followed by an iodine atom radical chain process to afford the isomeric diiodo products **17** and **18**.

Scheme 7

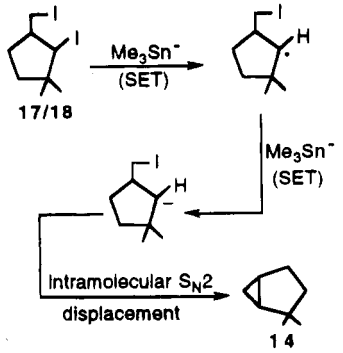


Since neither **17** nor **18** was detected in the reaction of **2b** with $NaSnMe_3$ at the higher ratio of 1:3, it is likely that these compounds reacted rapidly with the excess $NaSnMe_3$ at this ratio. In order to determine whether or not **14** could have been formed from **17** and **18**, a mixture of **17** and **18** was allowed to react with excess $NaSnMe_3$ at 0 °C. The reaction was instantaneous, and **14** was formed in nearly quantitative yield as shown in eq 20.

A plausible mechanistic pathway that can account for the formation of **14** from **17/18** is shown in Scheme 8.

Analysis of the products of the reaction of **2b** and $NaSnMe_3$ in the presence of DCPH did not reveal the formation of any DCPI. This results indicates that

Scheme 8



whatever DCP• (or DCPI) was generated, it probably underwent other fates as suggested in eq 11.

On the basis of all the observations made in the reactions of **2b** with $NaSnMe_3$ at different stoichiometries and in the presence of a radical trap, a general mechanism that is consistent with the data obtained is shown in Scheme 4. An initial electron transfer from Me_3Sn^- to the geminal diiodide **2b** leads to the formation of the iodo radical, which then serves as the precursor to all the observed products in the reaction.

Conclusions

Evidence for SET pathways in the reactions of the two geminal dihalides, **2a** and **2b**, with the known one electron donor, Me_3Sn^-, was obtained. Both **2a** and **2b** were found to react rapidly with the trimethyltin anion at 0 °C. The products formed in their reactions clearly showed the involvement of both radical and carbene intermediates. Mono- and bis(trimethyltin)-substituted products were found to be derived from radicals. In addition to radical-derived hydrocarbons, the reactions of **2a** and **2b** with Me_3Sn^- also afforded, in high yields, carbene-derived hydrocarbons. Evidence for the formation of a carbene intermediate (from a geminal dihalide) that was preceded by a radical intermediate was obtained.

The high reactivity of the geminal dichloride, **2a**, toward the one-electron donor, Me_3Sn^-, is a very clear indication that the presence of two chlorine atoms on the same carbon atom results in a favorable reduction potential for ET to occur. On the basis of the results of the reactions of **2a** and **2b** with the trimethyltin anion, it appears that Me_3Sn^- is a good one-electron donor toward alkyl geminal dichlorides as well as geminal diiodides.

Experimental Section

Materials. Tetrahydrofuran was purchased from Fisher Scientific and distilled from sodium benzophenone ketyl. Sodium metal, as lumps in kerosene, was purchased from Aldrich. Hexamethylditin was purchased from Alfa Products and used as received (99% pure by GLC). DCPH was purchased from Strem Chemicals and was also used as received (97% pure by GLC). All other materials required for the synthesis and purification of the starting materials were the same as described in the literature.[24]

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°/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.

Preparations. 6,6-Dichloro-5,5-dimethyl-1-hexene (2a). The preparative details are described in one of our recent works.[24]

6,6-Diiodo-5,5-dimethyl-1-hexene (2b). The preparative details are described in one of our recent works.[24]

Sodium Trimethyltin. The method adopted to synthesize $NaSnMe_3$ was the one described in the literature.[2] The concentration of the solution of $NaSnMe_3$ was determined by GLC analysis to be typically 0.40–0.50 M. This determination was made by quenching a 1.0 mL aliquot of the freshly prepared solution of sodium trimethyltin in THF with excess *n*-butyl bromide at 0 °C (which leads to a quantitative conversion to *n*-butyltrimethyltin).

Procedure for the Reaction of the Geminal Dihalides with Sodium Trimethyltin and the Subsequent Isolation/Characterization of Products. To a solution of 0.15 mmol of the dihalide, with a measured amount of the internal reference *n*-decane, in 2.00 mL of THF at 0 °C, was added 1.10 mL of a 0.40 M solution of $NaSnMe_3$, dropwise. The volumes specified here correspond to a molar ratio of the dihalide to the nucleophile of 1:3, with a resultant concentration of the dihalide being 0.05 M. The reactions were extremely rapid for both the substrates **2a** and **2b** as established by the GLC analyses of small volumes of the reaction mixtures drawn out less than 30 s following the mixing of reactants. The termination of the reaction was accomplished by simply quenching the reaction mixture with water (at 0 °C) and extracting the products with diethyl ether. When the radical trap DCPH was used (typically 10 equiv) to 1 equiv of the dihalide, it was added to the solution of the substrate in THF prior to addition of $NaSnMe_3$.

Isolation/Characterization of Products Obtained in the Reactions of 2a and 2b with $NaSnMe_3$. 2-(2-Propenyl)-1,1-dimethylcyclopropane (3). This compound was identified by matching its MS data with that reported in the literature.[25]

1-(3-Butenyl)-1-methylcyclopropane (4). The structure was established by matching the MS data obtained with that reported for an authentic sample.[26]

***trans*-2-Chloro-1,1,3-trimethylcyclopentane (5).** This product was isolated by preparative GLC using a 10% Carbowax column (10 ft × 1/4 in.) under temperature programming conditions of 70–180 °C at 4 °C/min and a helium flow rate of 40 mL/min. **5** was collected after 10 min. NMR: δ 0.95 (s, 3H), 1.05 (s, 3H), 1.10 (d, 3H), 1.20–2.00 (m, 5H), 3.40 (d, J = 10.2 Hz, 1H). 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 146.086 228, obsd 146.085 892.

***cis*-2-Chloro-1,1,3-trimethylcyclopentane (6).** This compound was also isolated by preparative GLC under the same conditions that were employed for the isolation of **5**, and it had a retention time of 14 min. NMR: all H shift values were

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essentially the same as those for the *trans* isomer **5**, 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 146.086 228, obsd 146.085 953.

6-Chloro-5,5-dimethyl-1-hexene (7). This product was identified by matching its MS data with that reported in the literature.[27]

5,5-Dimethyl-6-(trimethylstannyl)-1-hexene (8). This compound was isolated from the product mixture by preparative GLC using a 10% OV-101 column (10 ft × 1/4 in.) at 120−230 °C at 4°/min, with a He flow rate of 40 mL/min. The retention time of this compound was 17 min. NMR: δ 0.05 (s, 9H), 0.84 (s, 2H), 0.87 (s, 6H), 1.20−1.95 (m, 4H), 4.90 (m, 2H), 5.70 (m, 1H). MS m/e (relative intensity): $C_{11}H_{24}Sn$ M^+ 276 (not seen), 261 (47), 165 (100), 149 (46), 135 (23). High-resolution MS (for M − 15 peak) calcd 261.0665 248, obsd 261.067 856.

1,1-Dimethyl-3-[(trimethylstannyl)methyl]cyclopentane (9). The conditions employed to isolate this compound were the same as those mentioned for the isolation of **8**. **9** had a retention time of 18 min. NMR: δ 0.05 (s, 9H), 0.80 (s, 3H), 0.90 (s, 3H), 0.90 (m, 2H), 1.80 (m, 1H), 1.50−2.00 (m, 6H). MS m/e (relative intensity): $C_{11}H_{24}Sn$ M^+ 276 (not seen), 261 (85), 165 (100) 151 (90), 132 (25). High-resolution MS (for M − 15 peak): calcd 261.0665 248, obsd 261.063 721.

6-Chloro-5,5-dimethyl-6-(trimethylstannyl)-1-hexene (10). The isolation of this product was also accomplished under the same GLC conditions as those listed for the isolation of **8**. The retention time of **10** under these conditions was 19 min. NMR: δ 0.20 (s, 9H), 0.96 (s,3H), 0.99 (s, 3H), 1.50−2.00 (m, 4H), 3.60 (s, 1H), 4.90 (m, 2H), 5.80 (m, 1H). MS m/e (relative intensity): $C_{11}H_{23}ClSn$ M^+ 310 (not seen), 295 (5), 259 (5), 185 (96), 165 (36), 110 (40), 95 (100), 81 (42), 69 (63). High-resolution MS (for M − 15 peak): calcd 295.0275 525, obsd 295.032 196.

***cis*-2-Chloro-1,1-dimethyl-3-[(trimethylstannyl)methyl]cyclopentane (11).** This compound was isolated under the same GLC conditions described earlier for the isolation of **8**. The retention time of **11** was 21 min. NMR: δ 0.052 (s, 9H), 0.95 (d, 2H), 1.00 (s, 3H), 1.10 (s, 3H), 1.40−1.90 (m, 4H), 2.50 (m, 1H), 3.80 (d, J = 4.80 Hz, 1H). MS m/e (relative intensity): $C_{11}H_{23}ClSn$ M^+ 310 (not seen), 295 (5) 259 (3), 185 (69), 165 (25), 110 (21), 95 (100). High-resolution MS (for M − 15 peak): calcd 295.0275 525, obsd 295.031 708.

***trans*-1,1-Dimethyl-2-(trimethylstannyl)-3-[(trimethylstannyl)methyl]cyclopentane (12).** The isolation of **12** was accomplished under the same GLC conditions as listed for **8**. The retention time of **12** was 25 min. NMR: δ 0.10 (s, 9H), 0.15 (s, 9H), 1.00 (s, 3H), 1.10 (s, 3H), 1.50 (d, J = 9.0 Hz, 1H). MS m/e (relative intensity): $C_{14}H_{32}Sn_2$ M^+ 438 (not seen), 423 (5), 274 (31), 313 (2), 259 (69), 165 (100), 150 (30), 135 (30) 109 (18). High-resolution MS (for M − 15 peak): calcd 423.0307 318, obsd 423.035 461.

6,6-Bis(trimethylstannyl)-5,5-dimethyl-1-hexene (13). The isolation of the product was performed under the same GLC conditions as those described for the isolation of **8**. It had a retention time of 26 min. NMR: δ 0.05 (s, 18H), 0.94 (br s, 7H), 1.30−1.95 (m, 4H), 4.90 (m, 2H), 5.80 (m, 1H). MS m/e (relative intensity): $C_{14}H_{32}Sn_2$ M^+ 438 (not seen), 423 (20), 313 (10), 274 (20), 259 (46), 165 (100), 150 (35), 135 (49), 109 (12). High-resolution MS (for M − 15 peak): calcd 423.0307 318, obsd 423.033 554.

2,2-Dimethylbicyclo[3.1.0]hexane (14). 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.[20]

5,5-Dimethyl-1-hexene (15). 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.[28]

6-Iodo-5,5-dimethyl-1-hexene (16). This product was identified by matching its MS data with that reported in the literature.[27]

***cis*-2-Iodo-3-(iodomethyl)-1,1-dimethylcyclopentane (17).** This compound was isolated by flash column chromatography, using silica gel with hexane as eluent. NMR: δ 1.15 (s, 3H), 1.25 (s, 3H), 1.55−2.00 (m, 4H), 2.15 (m, 1H), 3.23 (m, 2H), 4.32 (d, J = 4.80 Hz, 1H). 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 (18).** 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 **17**, 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).

Acknowledgment. We gratefully acknowledge that this work was supported by the National Science Foundation, Grant No. CHE 8914309.

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