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Electron Transfer in the Reactions of Geminal Dihalides with Ph_2P^-. Evidence for the Formation of a Carbene Intermediate from a Radical Precursor

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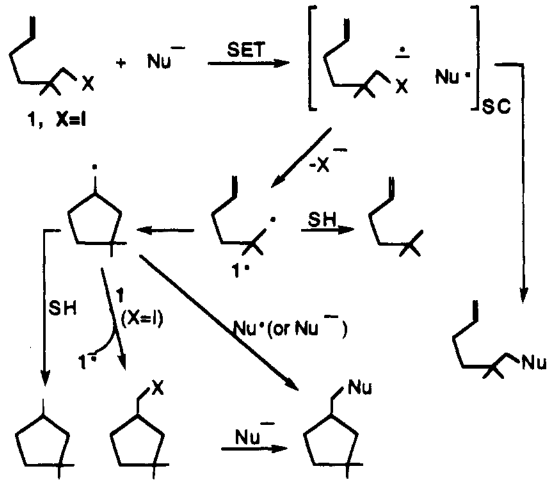
The reactions of two sterically hindered geminal dihalides, 6,6-dichloro-5,5-dimethyl-1-hexene (**5a**) and 6,6-diiodo-5,5-dimethyl-1-hexene (**5b**), with Ph_2P^- have been found to involve a single electron transfer (SET) pathway. Since the corresponding monochloride reacts with Ph_2P^- by a S_N2 pathway, it is clear that adding a second chlorine atom on a carbon atom produces a more favorable reduction potential resulting in a change in mechanism from S_N2 to SET. Evidence is also presented that shows that the geminal dihalides produce carbene-derived products and that the carbene was derived from a haloalkyl radical precursor.

Introduction

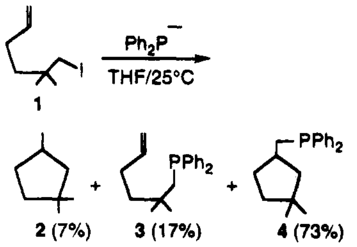
The most commonly encountered organophosphide anions are diphenylphosphide and dimethylphosphide, and they are considered to be powerful nucleophiles. In their reactions with alkyl halides, these anions lead to substitution products in high yields, primarily by a S_N2 pathway.[1,2] A considerable amount of work has been carried out, especially by Rossi and co-workers, on the photostimulated reactions of the diphenylphosphide anion with a variety of alkyl halides, and evidence for electron transfer has been obtained for the systems studied.[3-8] Wreford reported[9] the involvement of free radicals in the nonphotostimulated reactions of certain alkyl halides with dialkylphosphides using ^{31}P CIDNP and product analysis as means of supporting radical involvement. He has shown that alkyl, allyl, and benzyl iodides and bromides react, to a certain extent, by a radical pathway, with dialkylphosphides, whereas alkyl chlorides react by the S_N2 pathway. However, he did not obtain evidence for a radical mechanism in reactions of alkyl halides with diphenylphosphide.

The probe **1** has been used successfully over a number of years by this group to study SET in nucleophilic aliphatic substitution reactions. Scheme 1 shows the general mechanistic pathway that has been observed.[10-13] We have recently reported that SET is involved in the reaction of **1** with the diphenylphosphide anion under nonphotostimulated conditions (eq 1).[14] SET was established on the basis of the formation of the cyclized substitution product **4** in 73% yield and a significant increase in the yield of the cyclized hydrocarbon product **2** from 7% to 61% in the presence of the radical trap, dicyclohexylphosphine (DCPH). Also, when the above reaction was carried out using THF-d_8 as a solvent, **2** was found to have 12% deuterium incorporation.

Scheme 1



(SC=solvent cage)



(1)

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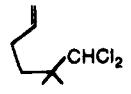
Realizing that Ph_2P^- is a good one-electron donor toward alkyl halides, and based on evidence obtained for the involvement of free radicals in the reaction of Ph_2P^- with certain alkyl halides, it was decided to study the reactions of this nucleophile with cyclizable aliphatic geminal dihalides of the type **5**.

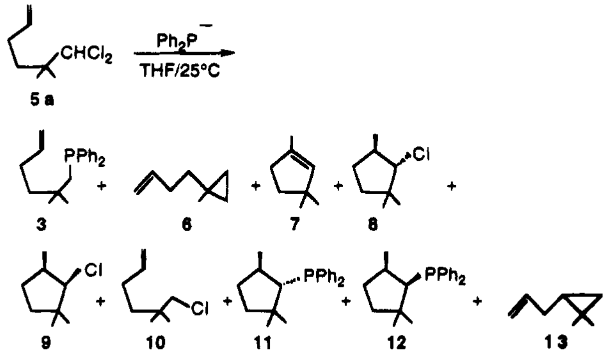


5, **5a**: X=Cl
5b: X=I

The main objective of this proposed study was to explore mechanistically the reactions of Ph_2P^- with the geminal dihalides **5a** and **5b** in the absence of photostimulation 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 seemed worthwhile to determine how this change would affect the mechanistic features of its reactions with Ph_2P^-. Considering the fact that alkyl monochlorides do not have a very favorable reduction potential and hence to not appear to react via electron transfer (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 **5a** with Ph_2P^- might involve a significant electron transfer pathway.

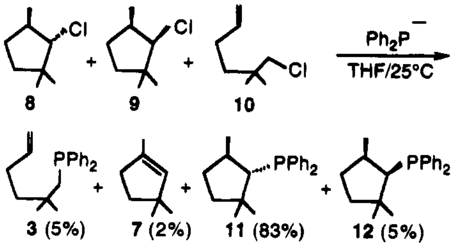
Results and Discussion

Reaction of 6,6-Dichloro-5,5-dimethyl-1-hexene (5a) with NaPPh₂. The reaction of 6,6-dichloro-5,5-dimethyl-1-hexene (**5a**) with $NaPPh_2$ was studied at a molar ratio **5a**:$NaPPh_2$ of 1:5. The reaction, in THF at 25 °C, required slightly over 1 h for complete conversion of **5a** to the products (eq 2, Table 1).



(2)

As can be seen in Table 1, after **5a** had completely reacted, the product mixture consisted of both reduction products (**8**–**10**) as well as diphenylphosphinyl substituted products (**3**, **11**, and **12**). In addition, small amounts of **7** and the carbene-derived hydrocarbons **6** and **13** were also formed. On allowing the reaction mixture to stir further, it was observed that **9** was consumed completely in about 40 h with the simultaneous enhancement in the yield of **11**, **12**, and **7**. After 75 min, all of **5a** had reacted and **9** was produced in 18% yield. At 40 h, the yield of **9** was 0%, and the combined yields of **11**, **12**, and **7** had increased by the same amount that the yield of **9** decreased, namely 18%. These observations suggested that **11**, **12**, and **7** resulted from a reaction between **9** and Ph_2P^-. Very little reaction was observed between **8** and **10** and $NaPPh_2$, even after allowing the reaction mixture to stir for a few hours beyond 40 h. This difference in reactivities between **8**–**10** toward the Ph_2P^- anion was tested by treating a mixture of the three monochloro compounds with excess $NaPPh_2$, in THF at 25 °C. It was observed that all of **9** had reacted after 24 h. The product mixture was comprised predominantly of **11**, with small amounts of **3**, **7** and **12** also being formed. Both **8** and **10** were found to have reacted to a very small extent (eq 3).



(3)

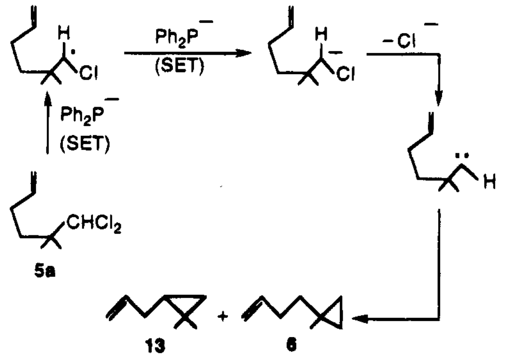
+ unreacted **8** (94%) and **10** (92%)

(yield of **3** based on **10**, yield of **7** based on **9**, yield of **11** based on **9**, and yield of **12** based on **8**)

The results of the reaction shown in eq 3 indicate that the lack of reactivity of **8** and **10**, compared to **9**, toward PPh_2^- is most likely due to steric factors. Whereas the nucleophile attacks the C–Cl bond in **9** probably by S_N2 attack to form the substitution product **11**, such an attack on the C–Cl bond in either **8** (the *trans*-isomer) or **10** is made relatively difficult due to steric hindrance. In fact, we have reported previously that **10** reacts with Ph_2P^- (1:2 ratio) very slowly at 25 °C probably by a S_N2 pathway (98% unreacted **10** after 4 h).[14] The results shown in eq 3 also reveal that the precursors to **3**, **11**, and **12** formed in the reaction of **5a** with $NaPPh_2$ are **10**, **9**, and **8**, respectively. Formation of **7** suggests dehydrohalogenation of **9**, which has the H and Cl anti to each other. On the other hand, such an elimination is made difficult in the case of the *trans* isomer **8**.

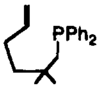
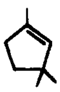
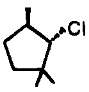
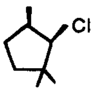
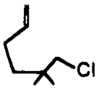
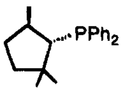
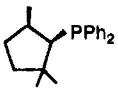
The formation of **6** and **13**, which are carbene-derived hydrocarbons,[11] can be visualized as being preceded by a radical intermediate (Scheme 2). As shown, following SET from Ph_2P^- to **5a**, the open chain chloro radical is formed. On receiving another electron, the radical is converted to a chloro carbanion, which rapidly loses Cl^- to generate the carbene that leads to the formation of **6** and **13** (C–H insertion products).

Scheme 2



All the products formed in the reaction of **5a** with $NaPPh_2$ suggest that the reaction involves radical intermediates. We reported earlier, on the basis of studies

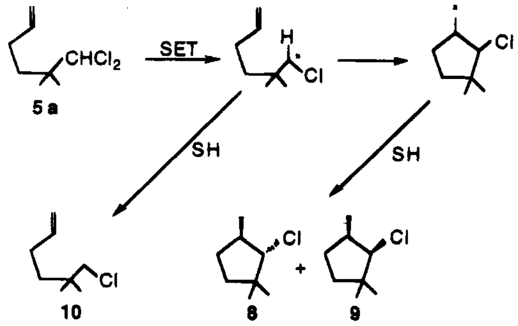
Table 1. Rate Profile Study of the Reaction of 6,6-Dichloro-5,5-dimethyl-1-hexene (5a) with $NaPPh_2$ at a 1:5 Ratio in THF at 25 °C[a]

Time after adding **5a** to $NaPPh_2$	% **5a** Recovered	% Yields of Products[b]							
		 **3**	 **6**	 **7**	 **8**	 **9**	 **10**	 **11**	 **12**
1 min.	51	2	0	1	10	8	5	5	3
30 min.	37	3	2	2	14	11	7	7	4
75 min.	0	5	2	3	23	18	12	12	9
12 hrs.	0	7	2	4	22	9	10	18	10
26 hrs.	0	8	2	6	21	3	9	22	11
40 hrs.	0	8	2	7	21	0	9	24	11

[a] The reaction was also carried out at a molar ratio of 1 : 3. At this ratio, after 45 min., about 60% of **5a** was recovered and products **8**, **9**, and **10** were formed in very small amounts as the major products. [b] In addition to all the products shown, **13** was also formed (except after 1 min.) in 0.7% yield in this reaction.

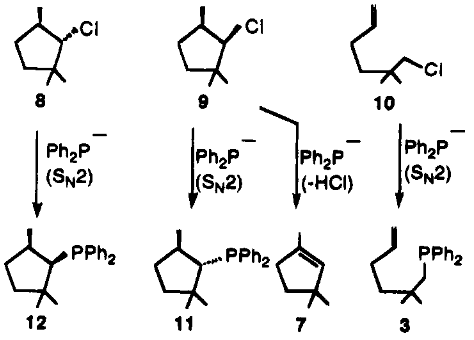
involving the reaction of the monochloro compound **10** with $NaPPh_2$, that no evidence for SET was found for this reaction.[14] So, the observation of **8**, **9**, and **10**, which are the reduction products, in the reaction of the geminal dichloride **5a** with $NaPPh_2$, is evidence supporting a SET pathway in the reaction. The formation of the three monochloro compounds can be proposed as shown in Scheme 3.

Scheme 3

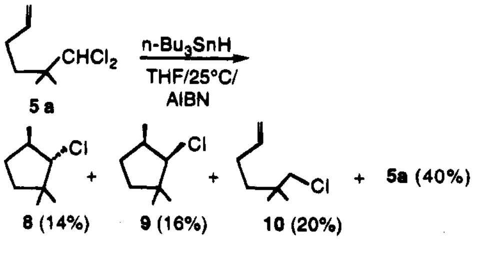


Products **3**, **7**, **11**, and **12** were found to be derived from the three monochloro compounds (see eq 3). On the basis of these results, and on the results of a study reported by this group[14] concerning the reaction of **10** with Ph_2P^-, the modes of formation of **3**, **7**, **11**, and **12** can be proposed as outlined in Scheme 4.

Scheme 4



In order to determine whether or not the cyclized monochloro isomers **8** and **9** were actually formed via radical cyclization, it was decided to analyze the *cis*:*trans* ratio of the two isomers. However, it is important to realize that both **8** and **9** underwent further reaction with excess Ph_2P^- (especially **9**) to afford the two cyclized substitution products **12** and **11**, respectively. In addition, **9** also produced **7**. Therefore, the actual ratio **9** (*cis*):**8** (*trans*) would be obtained by adding the yields of **8** and **12** and comparing this total yield with the total yield of **9**, **11**, and **7**. By doing so, the ratio **9**:**8** (*cis*:*trans*) in the first three entries in Table 1 is found to be 1.1 (in subsequent entries, **9** reacted completely to afford **7** and **11**, but **8** reacted to a limited extent). In order to determine if this ratio represented the actual ratio of the *cis* and *trans* isomers from a radical cyclization, **5a** was allowed to react with $n\text{-}Bu_3SnH$, in the presence of AIBN in THF, at 25 °C. Results of the reaction are shown in eq 4. It can be seen from eq 4 that the ratio **9**:**8** is 1.1.



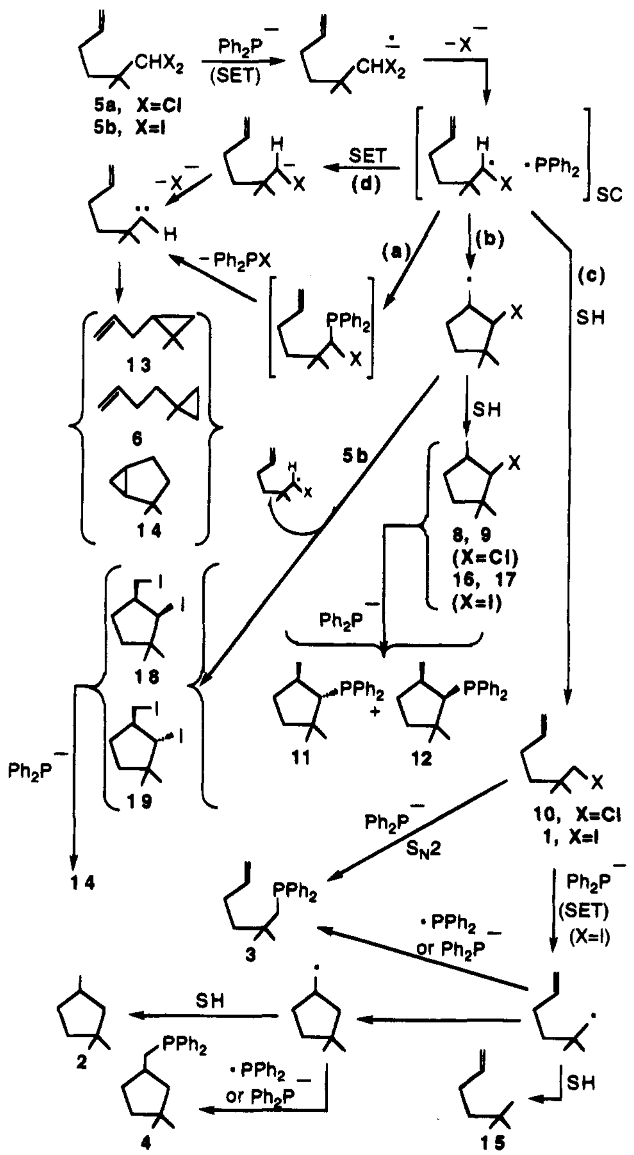
(4)

(**5a** : $n\text{-}Bu_3SnH$ = 1 : 10)

This value, obtained from a reaction that is known to proceed via a radical mechanism, compared with the *cis*:*trans* ratio obtained in the reaction of **5a** with $NaPPh_2$, strongly supports a radical mechanism that leads to the formation of **8** and **9**.

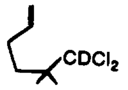
A reaction of **5a** with $NaPPh_2$ was then carried out in THF-d_8 in order to analyze the deuterium content in **8**–**10**. The deuterium content was determined to be 7% in **8**, 7% in **9**, and 6% in **10**. These results indicate that

Scheme 5



radicals are precursors to 8–10 and that they abstract hydrogen atoms from THF and also from a source other than THF. A likely source of hydrogen atoms in the reaction medium, in addition to the solvent THF, is **5a**.

To verify the hypothesis that **5a** can be a hydrogen atom donor, the reaction of the monodeuterated substrate **5a**-d_1 with $NaPPh_2$ in THF-d_8 was carried out, and the deuterium content in **8–10** was determined. It was



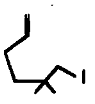
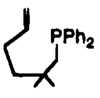
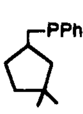
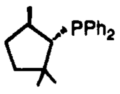
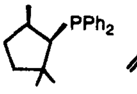
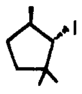
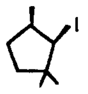
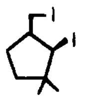
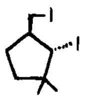
5a-d_1

found that the deuterium incorporated in the three monochloro compounds was 9%, 9%, and 10%, respectively. These values, although low, appear to indicate that **5a** acts as a hydrogen atom donor to the chloro radicals generated in the reaction of **5a** with $NaPPh_2$. The hydrogen that is abstracted ($pK_a = 31$) is the one attached to the carbon atom bearing the two chlorine atoms in **5a**. However, the results of the two experiments carried out, one employing **5a**/THF-d_8 and the other **5a**-d_1/THF-d_8, indicate that the radicals produced in the reaction of **5a** with Ph_2P^- abstract hydrogen atoms from a source other than THF and **5a**. It is possible that the radicals could abstract a hydrogen atom from the allylic site in **5a** ($pK_a = 35.5$).

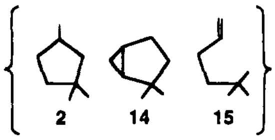
Based on all the results that were obtained from the various experiments described, it appears that the reaction of 6,6-dichloro-5,5-dimethyl-1-hexene with Ph_2P^- involves an electron transfer pathway, and a general mechanism is shown in Scheme 5.

Reaction of 6,6-Diiodo-5,5-dimethyl-1-hexene (5b) with $NaPPh_2$. (a) Effect of Stoichiometry. When 6,6-diiodo-5,5-dimethyl-1-hexene (**5b**) was allowed to react with $NaPPh_2$ in a molar ratio of 1:1, in THF at 25 °C, product formation was instantaneous, and no **5b** was recovered. Nine products were formed in the reaction (Table 2, exp 1), and on allowing the mixture to stir for 2 h at 25 °C, the product composition did not change. On the other hand, when the reaction was carried out at a molar ratio of 1:3 (exp 2), the cyclized mono- and diiodo compounds **16–19** previously detected in exp 1 were absent. In addition, four other products were formed in exp 2 (**3**, **4**, **11**, and **12**) that were not formed in exp 1.

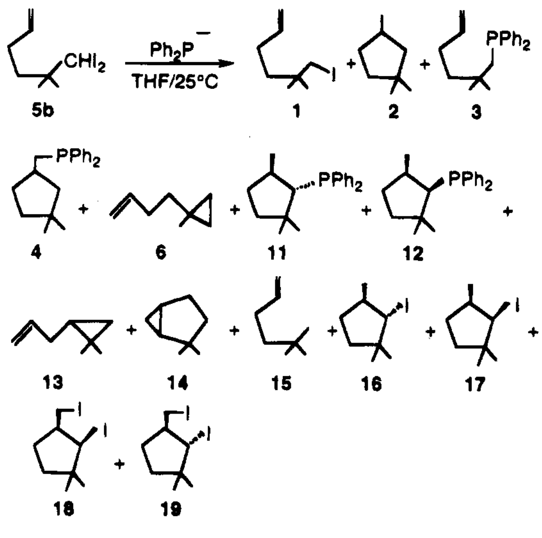
Table 2. Reaction of 6,6-Diiodo-5,5-dimethyl-1-hexene (5b) with $NaPPh_2$ in THF at 25 °C

EXP. No.	% Yields of Products										
	 1	 3	 4	 6	 11	 12	 13	 16	 17	 18	 19
1[a]	35	0	0	2	0	0	1	4	8	15	23
2[b]	13	8	10	27	3	3	16	0	0	0	0

[a] The ratio **5b** : $NaPPh_2$ was 1 : 1. Products **2** and **14** were also detected, each in 1% yield. [b] The ratio was 1 : 3. A trace amount of **15**, 5% of **2** and 5% of **14** were also detected.



Equation 5 shows all of the products formed in the reaction of **5b** with Ph_2P^- at both ratios.

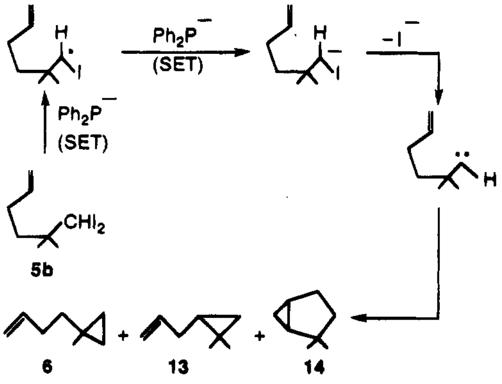


(5)

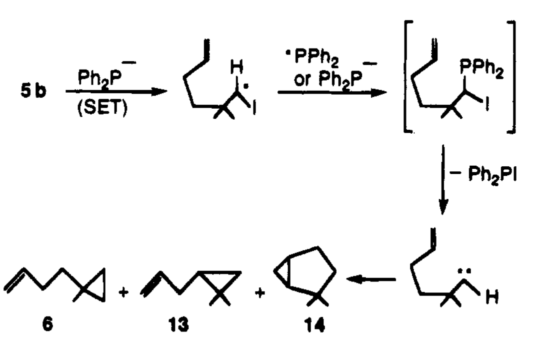
The cyclized products **16**–**19**, formed at the 1:1 ratio (**5b**:Ph_2P^-), disappeared when the amount of Ph_2P^- was increased, as expected, and the diphenylphosphinyl-substituted products (**3**, **4**, **11**, and **12**) which were not observed at the 1:1 ratio, were formed in significant yields at the 1:3 ratio. At the lower ratio of 1:1 (exp 1), the main product of the reaction was **1**, formed in 35% yield. Products **18** and **19** were also formed in significant yields (15% and 23%, respectively) at the lower ratio. At the higher ratio of 1:3 (exp 2), the major products were the carbene-derived hydrocarbons **6** (27%) and **13** (16%). On the other hand, products **6** and **13** were detected in yields of 2% and 1%, respectively, at the 1:1 ratio (exp 1). It is not possible that **6** and **13** could have been derived from any one of the four products **16**–**19**, which were formed at the lower ratio, but were not detected at the higher ratio. This suggests that the mechanistic pathways that account for the products formed in the reaction of **5b** with the Ph_2P^- anion are governed by the amount of the nucleophile present.

At the lower ratio (1:1), the formation of a carbene intermediate is not as favorable as at the higher ratio (1:3). A carbene can only be formed in the reaction of **5b** with $NaPPh_2$ by either of two schemes, Scheme 6 or 7. In Scheme 6, it is suggested that the formation of the iodo radical (by ET from Ph_2P^- to **5b**) is followed by an additional electron transfer to form the iodo carbanion. On losing an iodide ion, the carbanion is converted to a carbene. In Scheme 7, the initially formed iodo radical undergoes geminate coupling with a $Ph_2P^\bullet$ radical (or it reacts with Ph_2P^- in an $S_{RN}1$ fashion) to form an intermediate which on elimination of a molecule of Ph_2PI affords the carbene. On the basis of the yields of **6** and **13** at the two ratios employed, it seems that at higher concentrations of Ph_2P^-, both Scheme 6 and 7 explain the increased yields of **6** and **13** at the expense of **16**–**19**, since these products originate from the open chain iodo radical. Products **18** and **19** are most probably a result of a radical chain mechanism (Scheme 8).

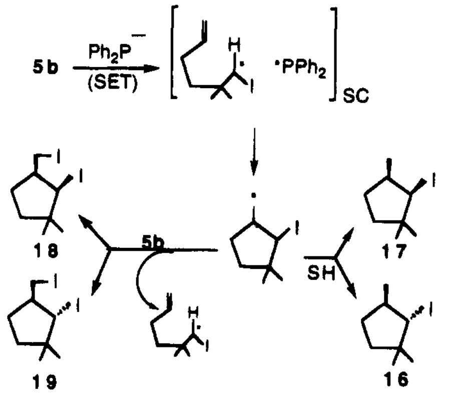
Scheme 6



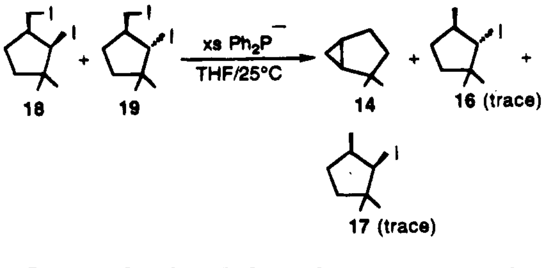
Scheme 7



Scheme 8



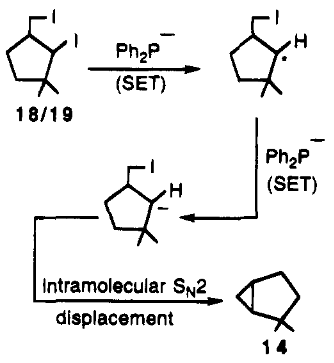
As the ratio **5b**:Ph_2P^- is changed from 1:1 to 1:3, the cyclization of the iodo radical (to form **16**–**19**) competes less favorably with carbene formation as shown in Schemes 6 and 7. On the other hand, if any of these four products (**16**–**19**) were formed at the higher ratio, they would be expected to react further with Ph_2P^-. The formation of **14** (5%), **11** (3%), and **12** (3%) suggests that these compounds could have been produced by the reaction of the iodo compounds (**16**–**19**) with Ph_2P^-. When a mixture of **18** and **19** was allowed to react with excess $NaPPh_2$ in THF at 25 °C, **14** was the main product (formed instantaneously), with trace quantities of **16** and **17** also being detected (eq 6). Formation of **14** from **18** and **19** on reaction with Ph_2P^- can be rationalized by the mechanism proposed in Scheme 9.



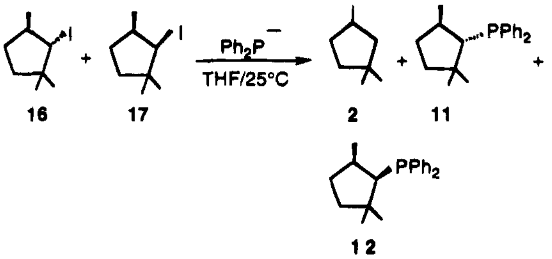
(6)

It was also found that when a mixture of **16** and **17** (1:1 ratio) was allowed to react with excess $NaPPh_2$, **11**,

Scheme 9

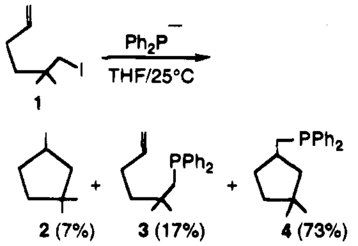


12, and 2 were formed, in a 1:1:2 ratio (eq 7). Complete consumption of **16** and **17** required less than 5 min.



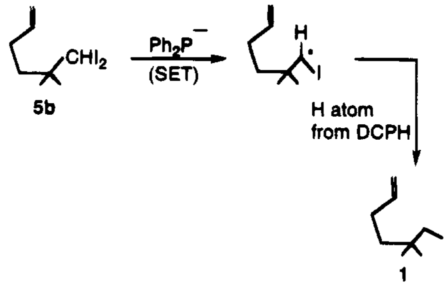
(7)

In exp 2 (ratio **5b**:Ph_2P^- was 1:3), the two other diphenylphosphinyl-substituted products formed were **3** and **4**. The fact that they were not detected when the reaction was carried out at the lower ratio indicates that they could be products of a reaction of **1** with $NaPPh_2$. Earlier work by this group[14] has shown that the reaction of **1** with the Ph_2P^- anion (carried out for 30 min) produces **2**–**4** (eq 8) and that this reaction involves SET. Therefore, it is not unreasonable to assume that products **2**–**4** formed in the reaction of **5b** with $NaPPh_2$ were, in fact, products derived from **1**, after it reacted with excess Ph_2P^-.

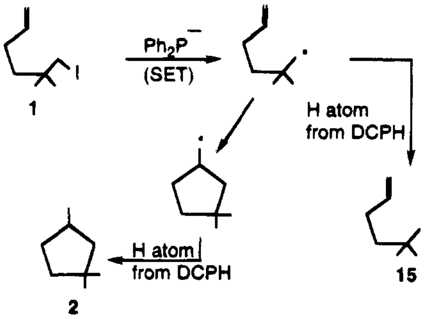


(8)

(b) Effect of a Radical Trap. The observation of products **16**–**19**, **1**, **3**, **4**, **11**, and **12** in the reaction of **5b** with $NaPPh_2$ strongly suggests that the reaction involves radical intermediates. In order to provide further evidence of a radical pathway, the reaction of **5b** with $NaPPh_2$ was carried out in the presence of DCPH. The results of the reaction in the presence of DCPH are shown in Table 3 (exp 3), and these results were compared with the results obtained in the absence of DCPH (exp 2). It was observed that 65% of the product mixture of the reaction in the presence of 10 equiv of DCPH was comprised of **2** (25%), **1** (35%), and **15** (5%), whereas in the absence of DCPH, **2**, **1**, and **15** were formed in 5%, 13%, and trace amount, respectively. These results indicate that the reaction of **5b** with $NaPPh_2$ involves a radical pathway. The high yield of **1** in the presence of DCPH can be explained with the help of eq 9. Once the open chain iodo radical is formed, it is very effectively trapped by DCPH. This results in a high yield of **1**. Thus, the formation of **2** (25%), and also **15** (5%), can be explained by invoking a radical intermediate. Once formed, **1** can further react with Ph_2P^- to produce **2** and **15** in much higher yields than observed in the absence of DCPH (exp 2). Further evidence for a SET pathway for the reaction of **1** with Ph_2P^- has recently been reported by this group.[14] Once the open chain radical is formed from **1**, in the presence of DCPH, it is trapped to produce **15** (eq 10). The radical that cyclizes is then trapped by DCPH to form **2**. The fact that **2** was formed in a yield five times that of **15** means that the radical cyclized at a rate that was faster than the rate at which it was trapped by DCPH.

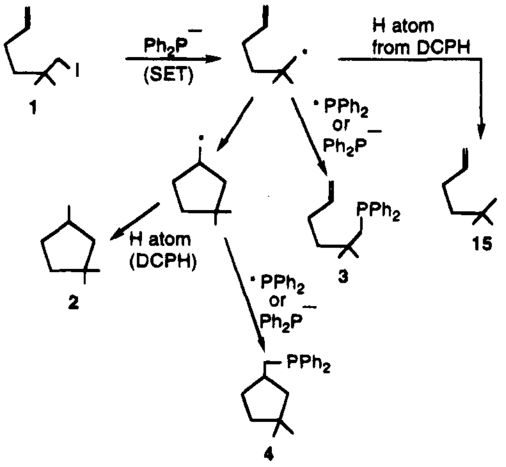


(9)



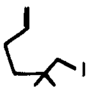
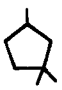
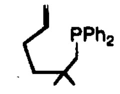
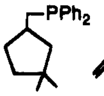
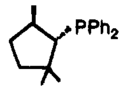
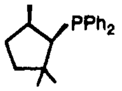
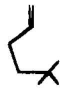
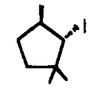
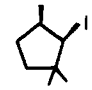
(10)

In the presence of DCPH, the yields of **3** and **4** were found to be 5% and 3%, respectively; however, in the absence of DCPH, these products were formed in yields of 8% and 10%, respectively. These results can be rationalized by considering the fate of the precursor radicals to **3** and **4** in the presence of DCPH (eq 11). As shown, the open chain radical, generated from **1**, is trapped by DCPH to form **15** and this lowers the possibility of reaction between the radical and $Ph_2P^\bullet$ or

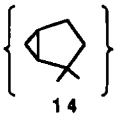


(11)

Table 3. Reaction of 6,6-Diiodo-5,5-dimethyl-1-hexene (5b) with $NaPPh_2$ in THF at 25 °C in the Pesence of DCPH

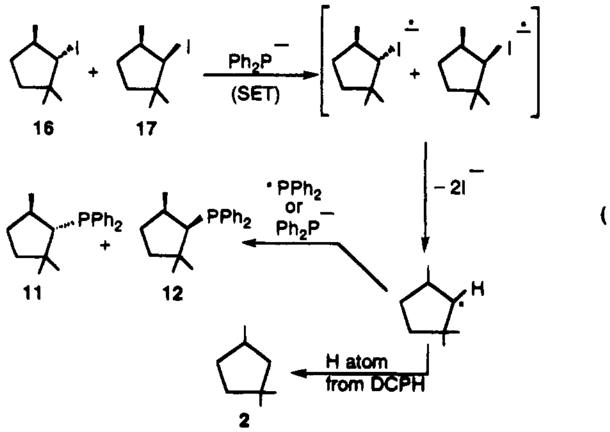
EXP. NO.	% Yields of Products										
	 1	 2	 3	 4	 6	 11	 12	 13	 15	 16	 17
2[a]	13	5	8	10	27	3	3	16	<1	0	0
3[b]	35	25	5	3	2	2	2	1	5	0	0

[a] Ratio of 5b to $NaPPh_2$ was 1 : 3. Also, 5% of 14 was fromed in exp. 2. [b] The ratio was the same, but this reaction employed 10 equivalents of DCPH. Also among the products was 5% of 14.


14

Ph_2P^- to form **3**. When the radical cyclizes, the cyclized radical is trapped by DCPH to form **2**, while the coupling of this cyclized radical with $Ph_2P^\bullet$ or Ph_2P^- to form **4** becomes a minor pathway.

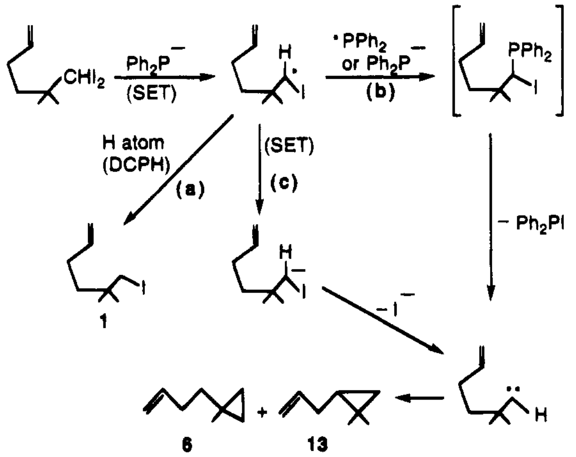
The yields of the cyclized diphenylphosphinyl-substituted isomers **11** and **12** were found to be 2% each in the presence of DCPH, and 3% each in the absence of DCPH. Not only can both **11** and **12** arise from **16** and **17** (see eq 7), but also compound **2**. It therefore appears that when **16** and **17** react with excess $NaPPh_2$, the cyclized radical that is generated can be trapped by THF or DCPH to produce **2**, and the radical that couples with $Ph_2P^\bullet$ (or Ph_2P^-) produces **11** or **12** (eq 12).



(12)

A very interesting observation, as far as the product composition of the reaction carried out in the presence of DCPH is concerned, is the formation of carbene-derived products **13** and **6** in yields of 1% and 2%, respectively. The yields of these two hydrocarbons in the absence of DCPH were 16% and 27%, respectively. Such a drastic reduction in the yields of the two carbene-derived products serves as a good indication that the carbene intermediate was preceded by a radical intermediate, as proposed in Schemes 6 and 7, and that in the presence of DCPH, the radical was trapped quite effectively (Scheme 10). With DCPH present in the reaction medium, pathway a becomes the major pathway leading to high yields of **1**. At the same time, formation of the carbene by pathways b and/or c is made less likely, which results in lower yields of **13** and **6** in exp 3 compared to their respective yields in exp 2.

Scheme 10



On the basis of the results that were obtained by carrying out the reaction of **5b** with Ph_2P^- at different stoichiometries, and in the presence of the radical trap DCPH, it is clear that the reaction involves a radical pathway. The mechanistic pathways consistent with all the data gathered in the reaction of 6,6-diiodo-5,5-dimethyl-1-hexene with $NaPPh_2$ are shown in Scheme 5.

As shown, the first step constitutes the transfer of an electron from Ph_2P^- to **5b** which produces the radical anion of **5b** (X = I). Loss of an iodide ion from the radical anion generates the open chain iodo radical (X = I). The iodo radical then becomes the precursor to all the observed products in the reaction.

Experimental Section

Materials. The procedures employed in the syntheses of the two geminal dihalides **5a** and **5b** were the same as described by us earlier.[15] Sodium metal, as lumps in kerosene, was purchased from Aldrich. DCPH was purchased from Strem Chemicals and was used as received (97% pure by GLC). Tetrahydrofuran was distilled from sodium benzophenone ketyl. Diphenylphosphine was purchased from Alfa products.

General Procedures. The general procedures that were followed to carry out reactions, and the procedures for GLC and spectroscopic analyses were the same as those described in our earlier work.[15]

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

Preparations. 6-Deutero-6,6-dichloro-5,5-dimethyl-1-hexene (5a-d_1). The synthesis of this compound was carried out following the same sequence that was employed for the synthesis of **5a**,[15] except that ethyl 2,2-dimethylhex-5-eneoate was reduced by $LiAlD_4$ to afford the deuterated alcohol, 2,2-dimethyl-1,1-dideuterohex-5-en-1-ol. Oxidation of this alcohol by pyridinium chlorochromate gave the deuterated aldehyde, 2,2-dimethyl-1-deuterohex-5-en-1-al. This aldehyde was then converted to **5a**-d_1 using PCl_5. Purification of the product was accomplished by preparative GLC. NMR and MS data indicated 100% d_1 incorporation in the product.

Sodium Diphenylphosphide. To 0.276 g (12.0 mmol) of sodium metal, cut into very small pieces, was added freshly distilled THF at 25 °C under nitrogen. Next, 1.86 g (10.0 mmol) of diphenylphosphine was added dropwise while the contents were stirred vigorously. In a few minutes, the solution had acquired an orange-red color. The stirring was maintained, for a period of 8 h, at 25 °C, after which the synthesis of $NaPPh_2$ was complete. The phosphide was analyzed by ^{31}P NMR and showed a chemical shift value (at 25 °C in THF) of δ −19 (lit.[1c] δ −24.4). The concentration of the resulting diphenylphosphide solution was determined by quenching an aliquot with water and titrating the NaOH produced with standardized HCl. Normally, the concentration had a value in the range of 0.20−0.30 M.

Procedure for the Reaction of the Geminal Dihalides with Sodium Diphenylphosphide and the Subsequent Isolation/Characterization of Products. The general procedure consisted of addition of a solution of the geminal dihalide (with a specific amount of *n*-decane used as an internal reference) in THF to a calculated amount of a solution of sodium diphenylphosphide (also in THF), with vigorous stirring at 25 °C, under nitrogen. Typically, the ratio of the dihalide to the diphenylphosphide ranged from 1:1 (or 1:3) in the case of the diiodide to 1:5 in the case of the dichloride. The concentration of the dihalide was usually maintained around 0.05 M, and that of $NaPPh_2$ was 0.05 M at 1:1, 0.015 M at 1:3, and 0.025 M at 1:5 reactant ratio. When the radical trap DCPH was used, it was added to the halide solution before the addition of the halide solution to the diphenylphosphide. The reactions were monitored by drawing out small volumes of the reaction mixture at specific intervals, quenching them with water, and analyzing the organic layer by GLC. Termination of the reactions (at 25 °C) was accomplished by quenching the reactions with water and extracting the contents with diethyl ether.

Products of Reaction of 6,6-Dichloro-5,5-dimethyl-1-hexene (5a) with Ph_2P^-. *trans*-2-Chloro-1,1,3-trimethylcyclopentane (**8**), *cis*-2-chloro-1,1,3-trimethylcyclopentane (**9**), 6-chloro-5,5-dimethyl-1-hexene (**10**), and 5,5-dimethyl-6-diphenylphosphino-1-hexene (**3**), all of which were identified by matching the respective MS data with those obtained for the corresponding authentic samples (for **8**, **9**, and **10** the relevant data were obtained from our earlier work,[15] and the data for **3** were obtained as described subsequently in this section), 1,3,3-trimethylcyclopentene (**7**), the structure of which was assigned on the basis of matching MS data with that reported in the literature,[16] and 1-(3-butenyl)-1-methylcyclopropane (**6**), the structure being assigned by matching MS data with that reported earlier.[11]

***trans*-2-(Diphenylphosphino)-1,1,3-trimethylcyclopentane (11).** This product was obtained (as the phosphine oxide) by flash column chromatography, using silica gel and a 90:10 mixture of EtOAc and MeOH as eluent. ^1H NMR: δ 0.55 (d, 3H), 0.95/1.10 (s, 3H), 0.95/1.10 (s, 3H), 1.50−2.00 (m, 5H), 2.30 (d, J = 12 Hz, 1H, $CHP(O)Ph_2$), 7.40 (m, 5H), 7.80 (m, 5H). MS (of the authentic product and not the oxide), *m/e* (relative intensity): $C_{20}H_{25}P$; 296 (M^+, 100), 281 (25), 241 (9), 227 (44), 201 (38), 186 (92), 108 (55), 91 (10), 77 (16), 69 (18), 55 (17). High resolution mass spectrum: calculated, 296.169389; observed, 296.169998.

***cis*-2-(Diphenylphosphino)-1,1,3-trimethylcyclopentane (12).** This product was also isolated as the corresponding phosphine oxide by flash column chromatography, using silica gel and a 90:10 mixture of EtOAc and MeOH as the eluent. The product obtained was 85% pure (by GLC). ^1H NMR (of **12**): δ 1.10 (d, 3H), 0.70/1.30 (s, 3H), 0.70/1.30 (s, 3H), 1.50−2.00 (m, 5H), 2.48 (d, J = 6.3 Hz, 1H, $CHP(O)Ph_2$), 7.40 (m, 5H), 7.80 (m, 5H). MS (of the authentic product and not the oxide), *m/e* (relative intensity): $C_{20}H_{25}P$; 296 (M^+, 100), 281 (27), 241 (30), 227 (43), 201 (28), 186 (87), 108 (60), 91 (13), 77 (14), 69 (35), 55 (30). High resolution mass spectrum: calculated, 296.169389; observed, 296.169418.

Products of Reaction of 6,6-Diiodo-5,5-dimethyl-1-hexene (5b) with Ph_2P^-: 1,1,3-Trimethylcyclopentane (**2**), 2-(2-propenyl)-1,1-dimethylcyclopropane (**13**), 1-(3-butenyl)-1-methylcyclopropane (**6**), 2,2-dimethylbicyclo[3.1.0]hexane (**14**), 5,5-dimethyl-1-hexene (**15**), and 6-iodo-5,5-dimethyl-1-hexene (**1**), which were all identified by matching their respective MS data with those of the authentic compounds as described in our earlier work.[15] *trans*-2-Iodo-1,1,3-trimethylcyclopentane (**16**), *cis*-2-iodo-1,1,3-trimethylcyclopentane (**17**), *cis*-2-iodo-3-(iodomethyl)-1,1-dimethylcyclopentane (**18**), and *trans*-2-iodo-3-(iodomethyl)-1,1-dimethylcyclopentane (**19**) were identified by matching their respective MS data and GLC retention times with those of the authentic samples that were isolated and characterized as described earlier.[15] 5,5-Dimethyl-6-(diphenylphosphino)-1-hexene (**3**) and 1,1-dimethyl-3-[(diphenylphosphino)methyl]cyclopentane (**4**) were identified by matching their corresponding MS data with those reported in earlier work by this group.[14] *trans*-2-(Diphenylphosphino)-1,1,3-trimethylcyclopentane (**11**) and *cis*-2-(diphenylphosphino)-1,1,3-trimethylcyclopentane (**12**) were identified by matching their respective GLC retention times and MS data with those obtained for the authentic products (as described earlier in this section).

Acknowledgment. We acknowledge support from the National Science Foundation, Grant No. CHE 8914306.

JO951121Y

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[16] Wolinsky, J.; Clark, G. W.; Thorstenson, P. C. *J. Org. Chem.* **1976**, *41*, 745.