

## Formation of Carbenes from Halo Carbon Radicals

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**Summary:** The reactions of geminal alkyl dihalides with  $\text{Me}_3\text{Sn}^-$ ,  $\text{Ph}_2\text{P}^-$ , and  $\text{Mg}^*$  have been carried out and have been shown to produce carbene products that originate from halo carbon radical intermediates.

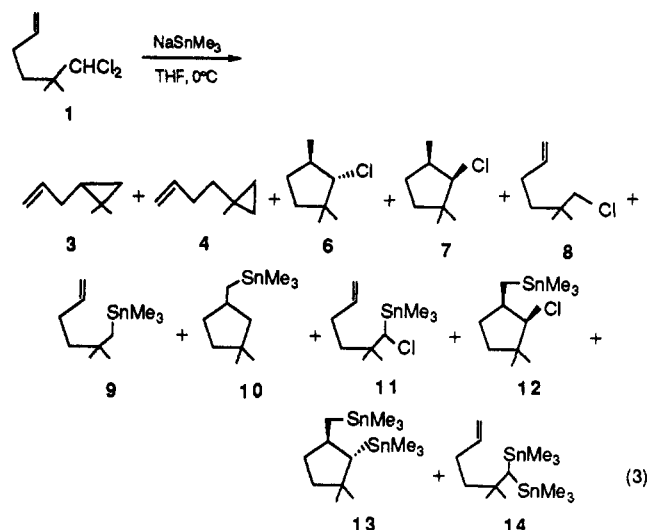
The reaction of an alkyl halide with a one-electron donor (e.g.,  $\text{Me}_3\text{Sn}^-$ ,  $\text{Mg}^*$ ,<sup>1</sup> or naphthalene radical anion) produces an alkyl radical<sup>2,3</sup> which can abstract a hydrogen atom to produce a hydrocarbon (eq 1). If the alkyl radical receives



another electron from the electron donor, an alkyl carbanion is generated,<sup>3</sup> which can then abstract a proton to afford the same hydrocarbon product (eq 2).

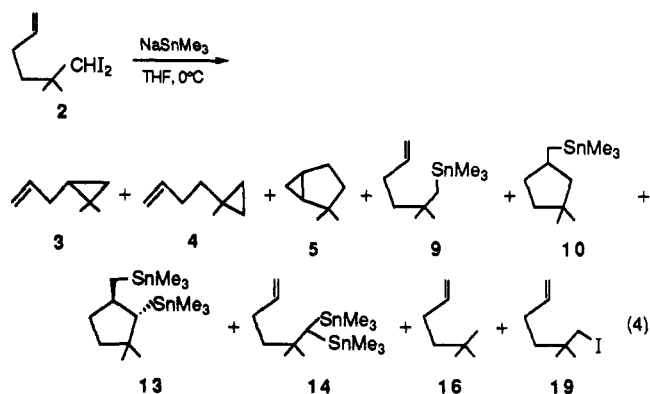
When we investigated the reactions of geminal alkyl dihalides as the substrates with several electron donors, an additional feature was found to be introduced in the mechanistic pathway. This feature is the formation of a halo radical that forms a carbene intermediate. The two geminal dihalides that were selected for this study are 6,6-dichloro-5,5-dimethyl-1-hexene (1) and 6,6-diiodo-5,5-dimethyl-1-hexene (2).<sup>4</sup>

When 1 was allowed to react with  $\text{NaSnMe}_3$  in THF at 0 °C in a 1:3 molar ratio, 11 products<sup>5</sup> were formed (eq 3). Among the products, hydrocarbons 3 and 4 were formed in yields of 3 and 9%, respectively.<sup>9</sup> On the basis of earlier work by this group, where it was shown that 3 and 4 are derived from a carbene,<sup>10a</sup> it is reasonable to assume that in eq 3 products 3 and 4 were preceded by a carbene. When this reaction was carried out in the presence of the radical trap dicyclohexylphosphine (DCPH), neither 3 nor 4 was detected. At the same time, the yield of the reduction product, 8, was found to increase from 5% in the absence



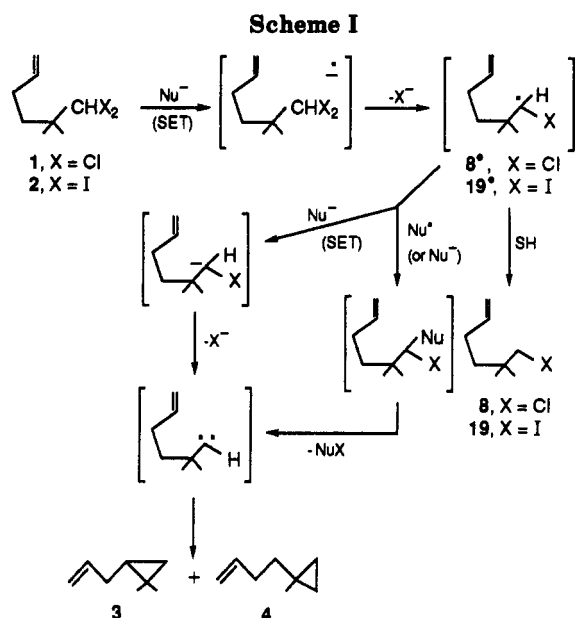
of DCPH to 30% in the presence of DCPH. By use of THF-*d*<sub>3</sub> it was established that a radical (8<sup>•</sup>) is the precursor to 8 (Scheme I). Therefore, the more efficient trapping of 8<sup>•</sup> by DCPH, compared to THF, inhibited the further reduction of 8<sup>•</sup> to the anion and eventually to the carbene that produced 3 and 4 (by intramolecular carbene C-H insertion process<sup>10a</sup>).

The reaction of 6,6-diiodo-5,5-dimethyl-1-hexene (2) with  $\text{NaSnMe}_3$  in THF at 0 °C in a 1:3 molar ratio is shown in eq 4.<sup>8</sup> The yields of 3, 4, and 5 were 21, 23, and

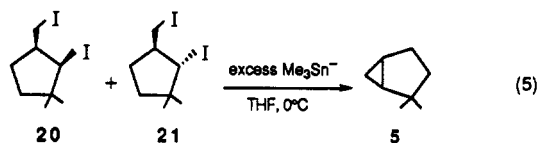


10%, respectively. In the presence of DCPH, 3 and 4 were not detected. The yield of 5 was unchanged, and the yield of 16 was 40%, compared to 5% in the absence of DCPH. These data indicate that the formation of the carbene that produces 3 and 4 takes place following the formation of iodo radical 19<sup>•</sup>. The fact that the yield of 5 remained unchanged indicates that 5 is formed predominantly from a precursor other than the carbene (by an intramolecular addition across the C=C bond<sup>10a</sup>) shown in Scheme I (although 5 is reported to be derived from the carbene,<sup>10a</sup> the main product obtained from this carbene has been shown to be the C-H insertion product, 4.<sup>10a</sup> It has been established that for carbenes similar to the one

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 (2) (a) Kuivila, H. G.; Smith, G. F.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* 1981, 103, 833. (b) Ashby, E. C.; DePriest, R. N.; Su, W.-Y. *Organometallics* 1984, 3, 1718. (c) Ashby, E. C.; Oswald, J. *J. Org. Chem.* 1988, 53, 6068.  
 (3) Garat, J. F.; Barton, F. E., II *Tetrahedron Lett.* 1969, 587.  
 (4) The substrates 1 and 2 were synthesized from 2,2-dimethyl-5-hexene-1-ol<sup>6</sup> by employing standard procedures for preparation of gem-dichlorides<sup>6</sup> and gem-diiodides.<sup>7</sup>  
 (5) House, H. O.; Liang, W. C.; Weeks, P. D. *J. Org. Chem.* 1974, 39, 3102.  
 (6) King, W. H.; Smith, H. A. *J. Am. Chem. Soc.* 1950, 72, 3459.  
 (7) Pross, A.; Sternhell, S. *Aust. J. Chem.* 1970, 23, 989.  
 (8) The following products were identified by matching their respective MS data with those reported in the literature: 3-5, 15;<sup>10a</sup> 8, 19;<sup>10b</sup> 16.<sup>10c</sup> All the other products were isolated from product mixtures by preparative GLC or flash column chromatography and characterized by MS, high-resolution MS, and <sup>1</sup>H NMR.  
 (9) The product yields reported in all the reactions discussed are absolute yields determined by GLC.  
 (10) (a) Ashby, E. C.; Park, B.; Patil, G. S.; Gadru, K.; Gurumurthy, R. G. *J. Org. Chem.* 1993, 58, 424. (b) Ashby, E. C.; DePriest, R. N.; Goel, A. B.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* 1984, 49, 3545. (c) House, H. O.; Weeks, P. D. *J. Am. Chem. Soc.* 1975, 97, 2778.

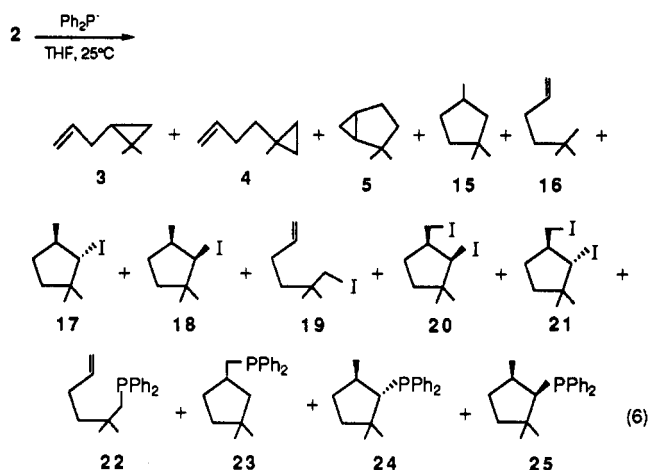


shown in Scheme I the main C-H insertion product is derived by insertion into the methyl C-H bond and the other insertion product is that following insertion into the  $\gamma$ -C-H bond of the chain.<sup>11</sup> Thus, 4 is formed predominantly, followed by 3, from the carbene in Scheme I. Intramolecular addition of the carbene 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.<sup>12</sup> This could be the reason why 5 was not detected in eq 3). It was found that the reaction of the two cyclized diiodo compounds, 20 and 21 (resulting from a radical chain mechanism),<sup>8</sup> with excess  $\text{Me}_3\text{Sn}^-$  produced 5 as the sole product (eq 5). These cyclic isomers were formed, and



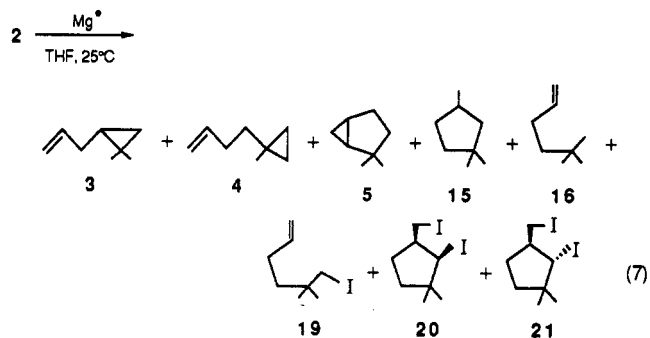
isolated, at a reactant ratio of 1:0.5 (2-NaSnMe<sub>3</sub>) but were not detected in the product mixture at 1:3, indicating that they reacted further with excess NaSnMe<sub>3</sub>. This explains why the yield of 5 remained the same in the absence as well as presence of DCPH.

In the reaction of 2 with NaPPh<sub>2</sub> in THF at 25 °C in a 1:3 ratio, 14 products<sup>8</sup> were formed (eq 6). Products 3, 4, and 5 were detected in yields of 16, 27, and 5%, respectively. In the presence of DCPH, the corresponding yields were 1, 2, and 5% (once again, 5 was confirmed as being derived from 20 and 21, on reaction with excess NaPPh<sub>2</sub>). At the same time, the yield of 19 increased from 13% in the absence of DCPH to 35% in the presence



of DCPH. These observations establish that an iodo radical is the precursor to the carbene intermediate.

The reaction of 2 with  $\text{Mg}^*$  was then investigated, since magnesium is known to react with alkyl halides by SET.<sup>2c,13</sup> When 2 was allowed to react with  $\text{Mg}^*$  in THF at 25 °C in a 1:1 ratio (eq 7), 3, 4, and 5 were formed in 2, 5, and



15% yields, respectively. In the presence of 10 equiv of DCPH, 3 and 4 were not detected, whereas the yield of 5 remained unchanged. As before, 5 was shown to be produced from 20 and 21, on reaction with excess  $\text{Mg}^*$ . In addition, the yield of 19 which was 10% in the absence of DCPH increased to 18% in the presence of DCPH.

The observations made in the reactions of 1 and 2 with  $\text{Me}_3\text{Sn}^-$ ,  $\text{Ph}_2\text{P}^-$ , and  $\text{Mg}^*$  establish that the corresponding halo radical is the precursor to the carbene. On comparing Scheme I with the transformations shown in eqs 1 and 2 (for a monohalide), it is clear that the nature of the steps involved for reaction of a *gem*-dihalide is similar to those steps involving a monohalide substrate; however, following the second ET to the initially generated radical (eq 2), the difference in the fate of the resulting carbanion determines the type of product formed. With an alkyl carbanion (eq 2), abstraction of a proton produces a hydrocarbon; however, with a chloro or iodo carbanion, formation of a carbene (Scheme I) takes place, which leads to 3 and 4.

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