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ADDITION OF DIMETHYLSILYLENE TO SUBSTITUTED 1,3-BUTADIENES; EVIDENCE FOR CONCERTED 1,2-ADDITION FOLLOWED BY NONCONCERTED REARRANGEMENTS VIA DIRADICAL INTERMEDIATES *

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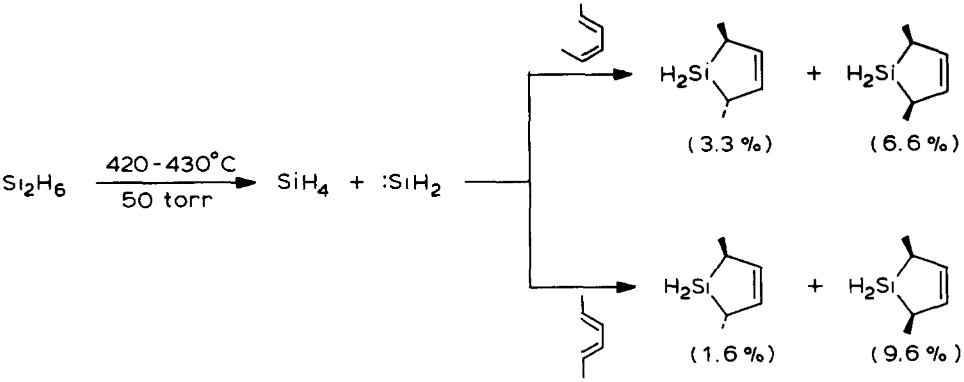
Summary

The mechanism for addition of dimethylsilylene to substituted 1,3-butadienes has been established as consisting of a concerted 1,2-addition followed by ring-opening of vinylsilacyclopropane intermediates to diradicals that can cyclize or disproportionate. The substrates studied were *cis*- and *trans*-piperylene, isoprene, 2,3-dimethylbutadiene, *cis,trans*- and *trans,trans*-2,4-hexadiene, and *trans*-1,3-hexadiene.

Cis,trans- and *trans,trans*-2,4-hexadiene were chosen as the substrates for the first attempt to study the stereochemistry of a silylene addition reaction a decade ago [1]. It was originally reported that the products of formal 1,4-addition, *cis*- and *trans*-



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* This work is dedicated to Professor Makoto Kumada, who has provided inspiration and leadership to chemists the world over by his dedication to science, his intellectual contributions, and by his warm and friendly encouragement to colleagues near and far, known and unknown.

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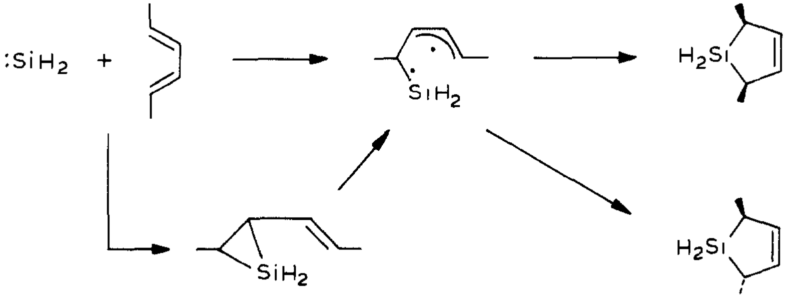
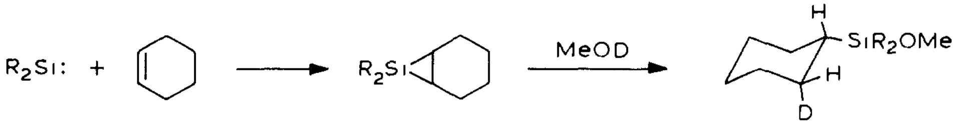
2,5-dimethyl-1-silacyclopent-3-ene were obtained in equal yields, but it was later found that the stereoisomeric dimethylsilacyclopentenes are formed with a *cis/trans* ratio of 2/1 from the *cis,trans*-2,4-hexadiene, and in 6/1 ratio from the *trans,trans*-diene [2,3,4].

To explain the occurence of nonstereospecific addition we proposed in 1974 a rearrangement of an initially formed vinylsilacyclopropane adduct via cleavage to a diradical [1]. It was recognized that his diradical could also arise by direct nonconcerted addition, as shown in Scheme 1:



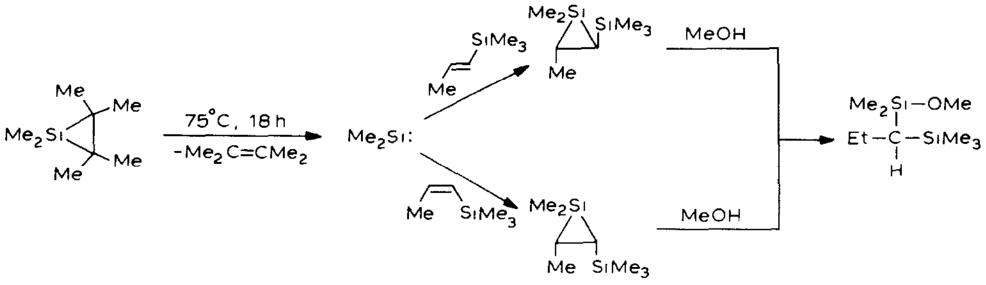
SCHEME 1

Ishikawa and Kumada subsequently found evidence for a vinylsilacyclopropane intermediate, trapping it with methanol in a photochemical experiment [5]. More recently both the Kumada and Jones groups have elegantly demonstrated that dimethylsilylene, diphenylsilylene and phenyl(trimethylsilyl)silylene all undergo stereospecific *cis*-addition to *cis*- and *trans*-2-butene [6,7,8]. That addition and ring-opening by methanol are both *cis*-processes was shown in experiments with cyclopentene and cyclohexene [8]:



(R = Me, Ph)

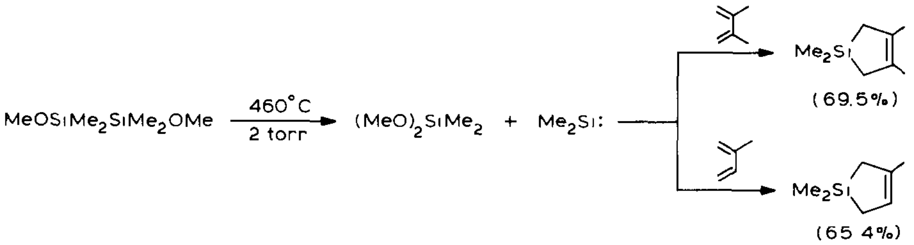
Seyferth and coworkers have directly analyzed the NMR spectra of the dimethylsilylene adducts from *cis*- and *trans*-propenyltrimethylsilane prior to methanolysis and concluded that stereospecific addition had taken place [9]:



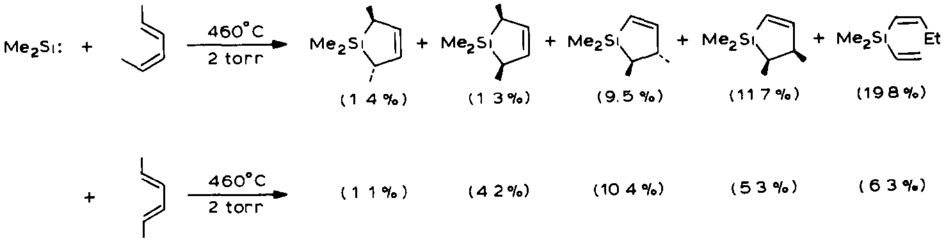
The nonstereospecific formation of 1-silacyclopent-3-enes from reactions of SiH_2 with 1,3-dienes is consistent with the evidence for concerted addition of silylenes to monoolefins if the reaction with a diene consists of a concerted 1,2-addition followed by a nonconcerted vinylsilacyclopropane-to-silacyclopentene rearrangement [10]. It was in order to determine whether this process indeed occurs that the further experiments described here were undertaken.

Dramatic confirmation of the intermediacy of vinylsilacyclopropanes that undergo rearrangement via diradicals has been found in the addition of dimethylsilylene to isomeric hexadienes and pentadienes. Copyrolyses of 1,2-dimethoxytetramethyldisilane and a 5/1 excess of diene substrate were carried out in a vacuum flow system.

When there are no substituents on the terminal carbon atom of the diene, i.e. 2,3-dimethylbutadiene and isoprene, 1,1-dimethyl-1-silacyclopent-3-enes are formed in high yields, and no isomeric products are detected:



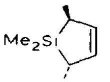
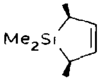
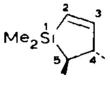
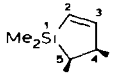
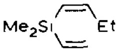
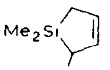
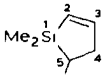
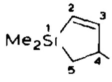
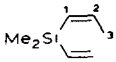
With methyl substituents at the diene termini, yields of the products from formal 1,4-addition decline, and the formation of 1-silacyclopent-3-enes is nonstereospecific from both *cis,trans*- and *trans,trans*-2,4-hexadiene. In both cases the stereoisomer formed in greater yield retains the geometry of the starting diene, but the other stereoisomer is formed in a yield too great to be accounted for by isomerization of the starting diene before reaction or by secondary isomerization of the products [11].



Major products from both of these 2,4-hexadienes have structures that point to a vinylsilacyclopropane intermediate that undergoes cleavage of a carbon–carbon bond giving a diradical that can cyclize to stereoisomeric 1-silacyclopent-2-enes or undergo intramolecular disproportionation [12]. Cleavage of the silicon–carbon bond of the three-membered ring leads to formation of the 1-silacyclopent-3-enes [13]. The proposed mechanism is shown in Scheme 2:

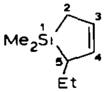
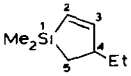
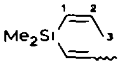
TABLE 1

NMR SPECTRA OF DIMETHYLSILYLENE ADDUCTS FROM *cis,trans*- AND *trans,trans*-2,4-HEXADIENE, *cis*- AND *trans*-PIPERYLENE, AND *trans*-1,3-HEXADIENE[a]

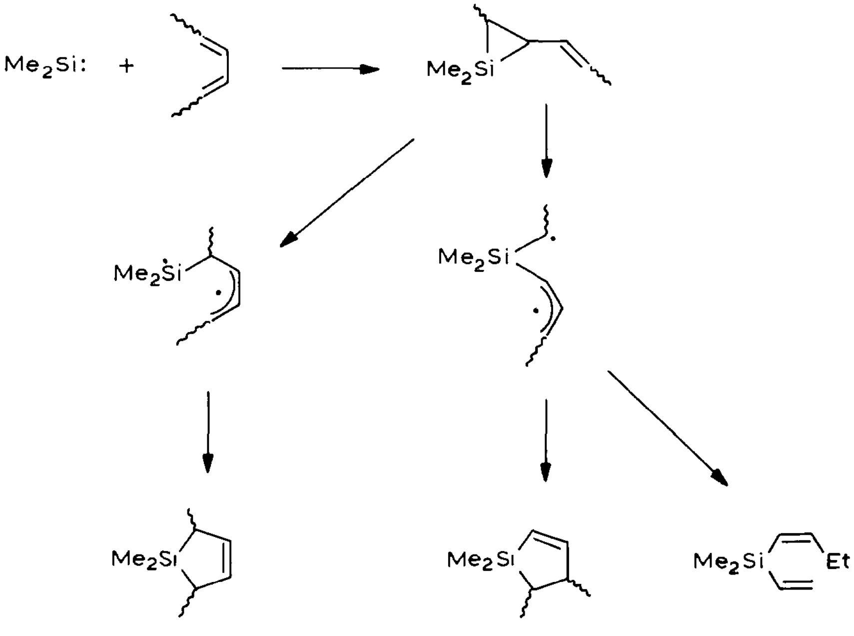
Compound	Nucleus observed	δ (ppm)
	^{1}H	0.012(s, 6H, Si–CH$_3$), 1.02(d, 6H, J 7.3, C–CH$_3$), 1.67(m, 2H, CHMe), 5 75(broad. s, 2H, CH=CH)
	^{1}H	−0.027(s, 3H, Si–CH$_3$), 0.055(s, 3H, Si–CH$_3$), 1.06 (d, 6H, J 7.4, C–CH$_3$), 1 50(m, 2H, CHMe), 5.75 (broad s, 2H, CH=CH)
	^{1}H	0.046(s, 3H, Si–CH$_3$), 0.12(s, 3H, Si–CH$_3$), 0.59 (m, 1H, C(5)–H), 1.03(d, 3H, J 7.3, C(5)–CH$_3$), 1.05 (d, 3H, J 7.1, C(4)–CH$_3$), 2.15(m, 1H, C(4)–H), 5.89 (dd, 1H, J_{23} 10.3, J_{24} 2.2, C(2)–H), 6.58 (dd, 1H, J_{32} 10.3, J_{34} 2.1, C(3)–H)
	^{13}C	−4.42(q, Si–CH$_3$), −0.76(q, Si–CH$_3$), 14.20(q, C(4)–CH$_3$) 21.69(q, C(5)–CH$_3$), 26.93(d, C(4)), 48.46(d, C(5)), 129.82(d, C(3)), 157,97(d, C(2))
	^{1}H	0.080(s, 3H, Si–CH$_3$), 0.10(s, 3H, Si–CH$_3$), 0.91 (d, 3H, J 7.2, C(5)–CH$_3$), 0.95(d, 3H, J 7.6, C(4)–CH$_3$), 1.05(m, 1H, C(5)–H), 2.65(m, 1H, C(4)–H), 5.95 (dd, 1H, J_{23} 10.5, J_{24} 1.4, C(2)–H), 6.70 (dd, 1H, J_{32} 10.5, J_{34} 2.9, C(3)–H)
	^{1}H	0.19(s, 6H, Si–CH$_3$), 0.89(t, 3H, J 7.3, C–CH$_3$) 2.08(m, 2H, CH$_2$), 5.44–6.48(m, 5H, olefinic H)
	^{13}C	−1.25(q, Si–CH$_3$), 14.25(q, C–CH$_3$), 27.36(t, CH$_2$) 128.97(d, =*C*HMe), 131.69(t, =CH$_2$), 139.55(d, Si–*C*H=CH$_2$), 152.08(d, Si–*C*H=CHEt)
	^{1}H	−0 12(s, 3H, Si–CH$_3$), −0.051(s, 3H, Si–CH$_3$), 0.82(d, 3H, J 7.3, C–CH$_3$), 1.10(m, 2H, CH$_2$), 1.32(m, 1H, CHMe), 5.54(m, 2H, CH=CH)
	^{1}H	0.064(s, 3H, Si–CH$_3$), 0.098(s, 3H, Si–CH$_3$), 1.00(m, 4H, CHCH$_3$), 1.96(m, 1H J_{gem} 15.6, C(4)–H), 2.62(m, 1H, J_{gem} 15.6, C(4)–H′), 5.97(dt, 1H, J_{23} 10.5, J_{24} 2.2, C(2)–H), 6.70(dt, 1H, J_{32} 10.5, J_{34} 2.7, C(3)–H)
	^{1}H	0.10(s, 3H, Si–CH$_3$), 0.15(s, 3H, Si–CH$_3$), 0.89(d, 2H, J 8.3, CH$_2$), 1.03(d, 3H, J 7.1, C–CH$_3$), 2.57(m, 1H, C(4)–H), 5.92(dd, 1H, J_{23} 10.1, J_{24} 2.0, C(2)–H), 6.65(dd, 1H, J_{32} 10.1, J_{34} 2.2, C(3)–H)
	^{1}H	0.00(s, 6H, Si–CH$_3$), 1.58(dd, 3H, J_{23} 6.8, J_{13} 1.5, CH$_3$), 5.23–6.10(m, 4H, olefinic H),

(continued)

TABLE 1 (continued)

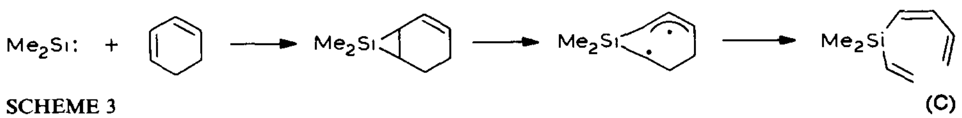
Compound	Nucleus observed	δ (ppm)
	^1H	0.036(s, 3H, Si–CH_3), 0.18(s, 3H, Si–CH_3), 0.93(t, 3H, *J* 6.6, CH_3), 1.26(m, 2H, C(2)–H) 1.45(m, 3H, C(5)–H, CH_2Me), 5.86 (broad s, 2H, CH=CH)
	^1H	0.12(s, 3H, Si–CH_3), 0.16(s, 3H, Si–CH_3), 0.89(m, 5H, Si–CH_2, C–CH_3), 1.35(m, 2H, C–CH_2), 2.52(m, 1H, C(4)–H), 6.01(dd, 1H, J_{23} 10.0, J_{24} 2.2, C(2)–H), 6.69(dd, 1H, J_{32} 10.0, J_{34} 2.2, C(3)–H)
	^1H	0.23(s, 6H, Si–CH_3), 1.69(dd, 6H, J_{23} 6.8, J_{13} 1.5, CH_3), 5.23–6.10(m, 4H, olefinic H), 6.25(sextet, 1H, J_{23} 6.8, J_{12} 6.6, $\overset{H}{\diagdown}C{=}C\genfrac{}{}{0pt}{}{H}{Me}$)

[a] C_6D_6 was used as solvent in all cases.



SCHEME 2

While cleavage of the C–C bond of a silacyclopropane in preference to breaking an Si–C bond may appear unusual, it is neither unprecedented nor unexpected. A similar sequence was suggested to explain the formation of *trans*-3,3-dimethyl-3-sila-1,4,6-heptatriene from the addition of dimethylsilylene to 1,3-cyclohexadiene [14]:



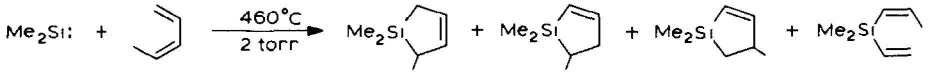
SCHEME 3

The formation of products **A** and **B** of Scheme 2 and **C** of Scheme 3 demands the intervention of a vinylsilacyclopropane. This was recognized previously, but in the addition to cyclohexadiene a concerted rearrangement of the bicyclic intermediate in Scheme 3 was possible [14]. The diradical mechanism shown in Scheme 3 was preferred because of the behavior of analogous hydrocarbons. The formation of products **A** and **B** of Scheme 2 offers compelling evidence for a diradical intermediate, since concerted rearrangements of the vinylsilacyclopropanes offer less attractive routes to the products, especially from the *trans,trans*-starting diene [12].

It was previously suggested that an extremely strained carbon–carbon bond might allow C–C bond cleavage in a silacyclopropane to compete with rupture of a C–Si bond [14]. Recently Sakurai, in reporting the first case of carbon–carbon bond-breaking in a monocyclic silacyclopropane, suggested that in the absence of extra ring strain, stabilization of the resulting diradical by conjugation with π-electron systems could provide the driving force for C–C bond-cleavage [15]. Walsh's estimates of carbon–silicon versus carbon–carbon bond strengths suggest however that competetive cleavage of the two bonds involves only small energy differences [16].

We have begun to explore the factors that govern the competition between carbon–carbon and carbon–silicon bond cleavage of the silacyclopropane intermediates in these reactions by studying the addition of dimethylsilylene to monosubstituted butadienes.

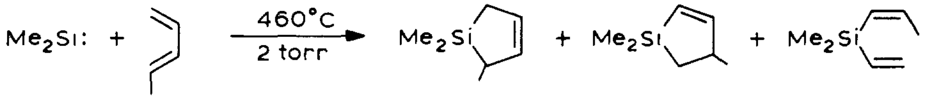
It was reported above that the only detectable silylene adduct of isoprene is the 1-silacyclopent-3-ene, formed in high yield. *cis*-Piperylene, however, yields about the same amounts of stereoisomeric 1-silacyclopent-2-enes (**E** and **F** below) as -3-ene (**D** below), and the product formed in highest yield is an acyclic diene (**G** below) that is believed to result largely from an intramolecular disproportionation similar to that shown in Scheme 2 [17].



(D, 11.4%) (E, 9.5%) (F, 2.0%) (G, 14.2%)

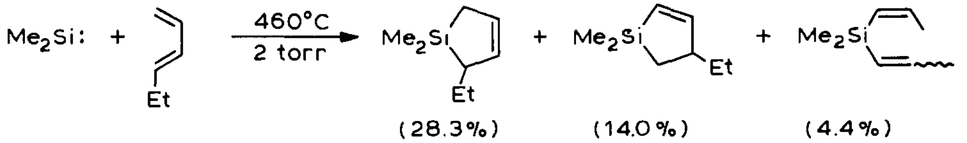
These results are instructive. Formation of products **E** and **G** requires addition of the silylene to the more substituted double bond. Thus it is clear that the methyl group does not significantly hinder addition by a steric effect, and may indeed promote addition via electron release [18].

Carbon–carbon bond cleavage in silacyclopropane intermediates does not make as important a contribution to the formation of products from *trans*-piperylene:



(D, 34.8%) (F, 11%) (G, 4.8%)

The extent to which the more substituted double bond is attacked by the silylene is apparently less in *trans*- than in *cis*-piperylene. This may be a consequence of steric hindrance, which may also be responsible for the similar pattern of products obtained from *trans*-1,3-hexadiene:



In summary we feel that the present results contribute to the understanding of the silylene-diene addition reaction by establishing beyond cavil that the mechanism consists of a concerted 1,2-addition followed by ring-opening of the vinylsilacyclopropane intermediate to diradicals that can cyclize or disproportionate. The intervention of silacyclopropane intermediates is assured by the finding of products whose formation requires carbon–carbon bond cleavage of such vinylsilacyclopropane intermediates. Formation of these vinylsilacyclopropane intermediates by concerted 1,2-addition of the dimethylsilylene, a reaction previously established for monoolefins, is suggested by the large difference between the ratios of cyclization and disproportionation products from carbon–carbon bond cleavage of the silacyclopropane intermediates form *cis*- and *trans*-piperylene. The present results strongly imply that carbon–carbon bond cleavage of a vinylsilacyclopropane can occur without special factors such as extra bond strain or extended delocalization in the resulting diradical.

These results also point to an important distinction between silylenes and germylenes. We reported previously that addition of dimethylgermylene Me_2Ge to stereoisomeric 2,4-hexadienes is stereospecific [20]. This implies that the germylene addition is mechanistically as well as formally a 1,4-process, while silylenes, like carbenes, attack dienes in a 1,2-fashion.

Acknowledgement

We thank Professors Thomas J. Barton and Robert T. Conlin for valuable discussions and invaluable friendship. We are grateful to the United States Department of Energy for financial support of this research. This is DOE technical report COO-1713-130.

References and notes

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2 R.J. Hwang, doctoral dissertation, Washington University, December, 1976.
3 P.P. Gaspar, Reactive Intermediates, (Wiley) 1 (1978) 229.
4 The original experiments were flawed by the misidentification of 2-ethyl-1-silacyclopent-3-ene as one of the stereoisomeric 2,5-dimethylsilacyclopent-3-enes. The ethyl compound is formed in ca. 10% yield from the addition of SiH_2 to 1,3-hexadiene, formed by rearrangement of the 2,4-hexadienes under the reaction conditions.
5 M. Ishikawa, F. Ohi and M. Kumada, J. Organomet. Chem., 86 (1975) C23.
6 M. Ishikawa, K.-I. Nakagawa and M. Kumada, J. Organomet. Chem., 178 (1979) 105.
7 V.J. Tortorelli and M. Jones, Jr., J. Am. Chem. Soc., 102 (1980) 1425.
8 V.J. Tortorelli, M. Jones, Jr., S.-H. Wu and Z.H. Li, Organometallics, 2 (1983) 759.
9 D. Seyferth, D.C. Annarelli and D.P. Duncan, Organometallics, 1 (1982) 1288.
10 Competing suprafacial and antarafacial 1,3-sigmatropic shifts had previously [1] been considered, and rejected on stereochemical grounds, as the mechanism for a concerted rearrangement of a vinylsilacyclopropane to a 1-silacyclopent-3-ene.
11 *trans,trans*-2,4-Hexadiene, originally greater than 99% pure, when recovered after pyrolysis contains 7.6% *cis,trans*-2,4-hexadiene and 1.9% *trans*-1,3-hexadiene. Recovered *cis,trans*-2,4-hexadiene contains

5.7% *trans,trans*-2,4-hexadiene and 18.6% *trans*-1,3-hexadiene. The dimethylsilylene addition products have been subjected to the pyrolysis conditions, and no isomerization was found.

12 The higher yield of *cis*-3,3-dimethyl-3-silahepta-1,4-diene obtained from *cis,trans*-2,4-hexadiene may be due in part to some concerted rearrangement of the vinylsilacyclopropane formed as an intermediate from addition of dimethylsilylene to the *cis*-substituted double bond. This process is geometrically disfavored for the *trans*-substituted silacyclopropane intermediate from *trans,trans*-2,4-hexadiene.

13 None of the evidence presented here or elsewhere excludes a small contribution to the formation of 1-silacyclopent-3-enes from concerted 1,4-addition of a silylene to an *S*-*cis*-1,3-butadiene. That this contribution to the overall addition cannot be large for terminally substituted butadienes is clear from the preponderance of products whose structures demand the intermediacy of vinylsilacyclopropanes in their formation.

14 R.-J. Hwang, R.T. Conlin and P.P. Gaspar, J. Organomet. Chem., 94 (1975) C38.

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16 R. Walsh, Accts. Chem. Res., 14 (1981) 246.

17 The higher yield of product **G** from *cis*- versus *trans*-piperylene may however indicate that the *cis*-substituted vinylsilacyclopropane can undergo concerted rearrangement to **G**.

18 While the product ratio (**E** + **G**)/(**D** + **F**) suggests a reactivity ratio for the double bonds of *cis*-piperylene $k_{\text{subst.}}/k_{\text{unsubst}} \geqslant 1.7$, this ratio could be as low as 0.36 if all of **D** plus all of the silylene not accounted for among the products were associated with addition to the less substituted π-bond of the diene. On the other hand the ratio could be greater than 1.7 if some of product **D** arises from addition of the silylene to the more highly substituted double bond. The upper limit is 50 if only product **F** arises from attack on the less substituted double bond.

19 It is of course true that the *S*-*cis* conformation of the starting diene is much less unfavorable for *trans*- than for *cis*-piperylene. Thus any contribution from direct 1,4-addition would also be favored for *trans*-piperylene.

20 E.C.-L. Ma, K. Kobayashi, M.W. Barzilai, and P.P. Gaspar, J. Organomet. Chem., 224 (1982) C13.