

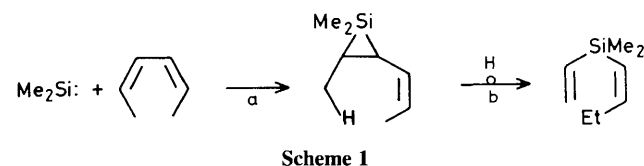
Addition of Dimethylsilanediyl (Dimethylsilylene) to *cis,cis*-Hexa-2,4,-diene: Evidence for a Concerted Vinylsilacyclopropane Rearrangement

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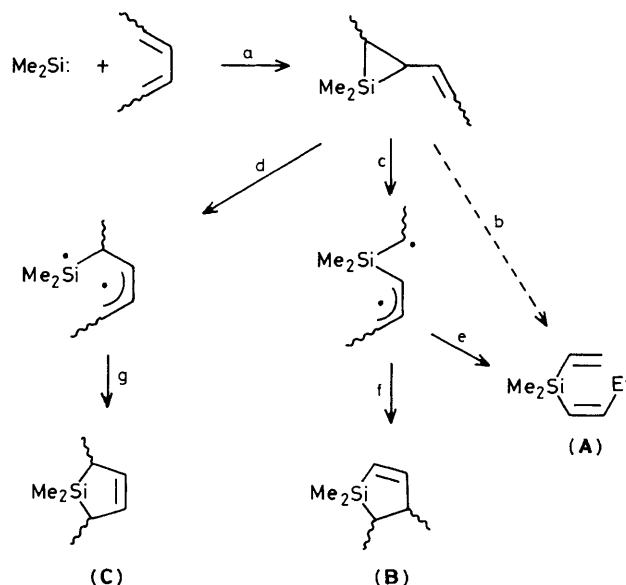
The formation of *cis*-3,3-dimethyl-3-silahepta-1,4-diene as the major product from addition of dimethylsilanediyl (dimethylsilylene) to *cis,cis*-hexa-2,4-diene is believed to result from a concerted 1,5-sigmatropic hydrogen shift in the rearrangement of the vinylsilacyclopropane intermediate formed by concerted 1,2-*cis*-addition of the silanediyl.

It is the purpose of this communication to record a new reaction of vinylsilacyclopropanes, a 1,5-sigmatropic shift of a hydrogen atom in a transient intermediate formed from the reaction of dimethylsilanediyl, $\text{Me}_2\text{Si}:$, with *cis,cis*-hexa-2,4-diene (Scheme 1). Recognition of this process lends support to, but also requires amendment of, the proposed mechanism for the addition of silanediyls to substituted buta-1,3-dienes. The pathway for this reaction had been illuminated by study of the addition of $\text{Me}_2\text{Si}:$ to *cis,trans*- and *trans,trans*-hexa-2,4-diene.¹ The previous results suggested that vinylsilirane intermediates are formed by concerted 1,2-addition of a silanediyl to one of the diene π -bonds (step a of Schemes 1 and 2), and that ring-opening of these siliranes occurs by both C–C and C–Si bond cleavage (steps c and d of Scheme 2). The nonstereospecific formation of silacyclopent-2-enes and -3-enes [products (B) and (C) in Scheme 2] was attributed to the cyclization of diradicals formed by cleavage of the silacyclopropane ring (steps c and d in Scheme 2). The acyclic product (A) was earlier obtained in lower relative yields and was thought to result chiefly from intramolecular disproportiona-




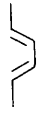

tion (step e of Scheme 2) of the diradical whose ring closure (step f of Scheme 2) leads to product (B).²

In Table 1 are given the yields of the products from gas-phase copyrolysis of the dimethylsilanediyl precursor 1,2-dimethoxytetramethyldisilane and an excess of each of the diene substrates under identical conditions in a throttled



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Table 1. Product yields (% absolute) from addition of Me₂Si: to hexa-2,4-dienes.^a

	Me ₂ Si	Me ₂ Si	Me ₂ Si	Me ₂ Si	Me ₂ Si
	1.2	1.3	12.7	8.3	50.5
	7.5	1.8	27.3	18.4	20.4
	2.3	2.3	24.6	21.4	35.1

^a All copolyolyses of MeOSiMe₂SiMe₂OMe with excess of hexa-2,4-dienes (ratio of diene to MeOSiMe₂SiMe₂OMe 15:1) were carried out at 400 °C and 2 Torr total pressure. Spectroscopic data for all products are given in ref. 1.

vacuum flow system. Residence times of *ca.* 0.01 s in the 400 °C hot zone led to a *ca.* 30% decomposition of the silanediyl precursor, and the products were unaffected by repassage under the reaction conditions.‡

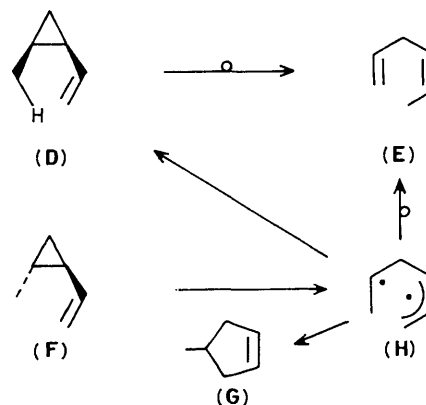
It is now clear from the high yield of *cis*-3,3-dimethyl-3-silahepta-1,4-diene (A) obtained from *cis,cis*-hexa-2,4-diene (68.2% of the total volatile products, 50.5% absolute) that the tendency to form this product is enhanced by the *cis*-relationship of the C-methyl and the propenyl substituents on the alkenylsilirane intermediate shown in Scheme 1. This *cis*-relationship allows the concerted rearrangement depicted in Scheme 1 to occur.§

This interpretation gains support from consideration of the analogous rearrangement of *cis*- and *trans*-1-methyl-2-vinylcyclopropane shown in Scheme 3.^{3,3-7} The *cis*-cyclopropane (D) gives exclusively *cis*-hexa-1,4-diene (E) upon pyrolysis, and the low pre-exponential factor and activation energy were interpreted as indicating a concerted rearrangement.^{3,4} The *trans*-cyclopropane (F) gives both *cis*-hexa-1,4-diene (E) and 4-methylcyclopentene (G).¶ Both Frey and Roth have argued persuasively that the geometry of *trans*-1-methyl-2-vinylcyclopropane (F) precludes a concerted rearrangement to its major pyrolysis product, *cis*-hexa-1,4-diene (E). Thus the higher values observed for the Arrhenius parameters for rearrangement of (F) can be interpreted in terms of cleavage to diradical (H). This can cyclize to 4-methylcyclopentene (G), disproportionate intramolecularly

‡ When *cis,cis*-hexa-2,4-diene (initial purity >99%) is passed through the hot zone under the reaction conditions the recovered material consists of 85% *cis,cis*-, 8% *cis,trans*-, and 4% *trans,trans*-hexa-2,4-dienes and 3% hexa-1,3-dienes.

§ That the concerted rearrangement, step b of Schemes 1 and 2 has the lowest barrier is suggested by the observation that the yield of acyclic product (A) decreases relative to that of the silacyclopentenes (B) and (C) when the addition of Me₂Si: to *cis,cis*-hexa-2,4-diene is carried out at higher temperatures.

¶ Ellis and Frey (ref. 4) reported that 3- rather than 4-methylcyclopentene was formed, but this was due to a numbering error (personal communication from H. M. Frey and R. Walsh).

**Scheme 3**

to *cis*-hexa-1,4-diene (E), or reclose to *cis*-1-methyl-2-vinylcyclopropane (D) that undergoes concerted rearrangement to (E).

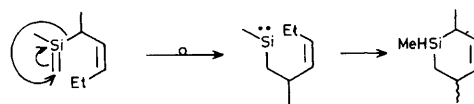
If the high temperature addition of dimethylsilanediyl to *cis,cis*-hexa-2,4-diene involved *only* the process shown in Scheme 1, whose second step parallels the rearrangement of *cis*-1-methyl-2-vinylcyclopropane (D) to *cis*-hexa-1,4-diene (E) in Scheme 3, the exclusive product would be *cis*-3,3-dimethyl-3-silahepta-1,4-diene (A). As revealed by Table 1, there are other products, silacyclopentenes (B) and (C), but the sum of their yields is less than half that of (A). It seems clear that the silirane intermediate in the addition of Me₂Si: to *cis,cis*-hexa-2,4-diene does undergo some of the radical cleavages shown in Scheme 2 that are more prevalent in the additions to *cis,trans*- and *trans,trans*-hexa-2,4-dienes reported previously.¹ The silacyclopropanes of Scheme 2 seem more prone to radical reactions than the corresponding cyclopropanes of Scheme 3, probably because of the greater ring strain in the siliranes. The predominance of product (A) in the silanediyl addition to *cis,cis*-hexa-2,4-diene is in accord with a sequence consisting of a concerted *cis*-1,2-addition of the silanediyl, followed by a concerted 1,5-hydrogen shift leading to (A) as shown in Scheme 1.

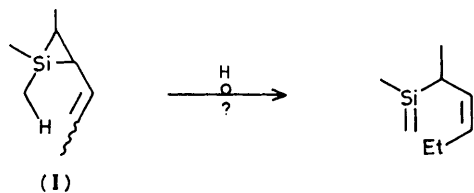
It is thus necessary to add step b to the mechanism of Scheme 2 to encompass the reactions of all three hexa-2,4-diene isomers. The present results suggest that when the methyl and alkenyl groups of the silirane intermediate formed in step a of Scheme 2 are in a *cis*-orientation, the concerted rearrangement step b is preferred over the cleavages c and d leading to diradicals.

The open-chain siladiene product (A) is likely to have a *higher* heat of formation than the silacyclopentene products (B) and (C). Therefore, the formation of these latter products, even from *cis,cis*-hexa-2,4-diene, may speak for the *reversibility* of path b of Schemes 1 and 2 under the reaction conditions. This would lead to enhancement of the consumption of the silirane intermediate in Scheme 2 via pathways c and d.

While it is obvious that path b of Scheme 2 is closed to *trans*-1,1,2-trimethyl-3-(1-prop-1-enyl)-1-silacyclopropane (I) in Scheme 4, it is of interest that *no* evidence has yet been found for participation of a methyl group on silicon in a 1,5-hydrogen shift analogous to step b of Scheme 1.||

|| The resulting allylsilene could rearrange to stable products by several pathways. The most likely may be the following, for which precedent exists:





Scheme 4

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