

G for two cyclopropane hydrogens in 6^- is observed. In 7 and 8 couplings for both H_a' and H_b' are obtained and are quite large in 7, 1.07 and ~ 0.5 G, respectively. Possibly the semidione π -system is interacting differently with the cyclopropane Walsh orbitals.¹⁷ The decrease in hyperfine splitting of H_v and H_b in the sequence 3^- , 6^- , and 5^- is likely the result of changes in geometry rather than an electronic effect of the cyclopropyl and isopropylidene groups. Both spin polarization^{2b,4c} and spin delocalization^{13b} mechanisms appear to be involved in these couplings.

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(17) W. D. Walsh, *Nature (London)*, **159**, 167 (1947).

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Stereochemistry of a Silylene Addition Reaction

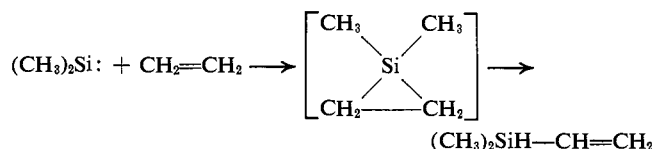
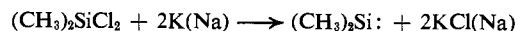
Sir:

While the stereochemistry of carbene addition reactions has provided data useful for the construction of mechanistic models¹ and for the diagnosis of the electronic states of reacting carbenes,² this communication is the first report of the stereochemistry of a silylene addition reaction.

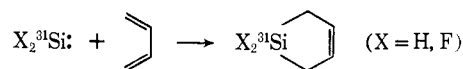
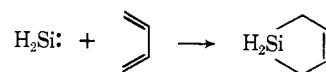
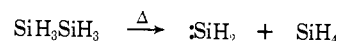
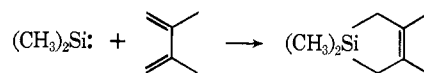
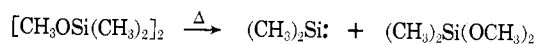
(1) For a review and references see D. Bethell, "Organic Reactive Intermediates," S. P. McManus, Ed., Academic Press, New York N. Y., 1973, Chapter 2.

(2) For a review and references see P. P. Gaspar and G. S. Hammond, "Carbenes," Vol. II, M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, N. Y., in press.

The scarcity of stereochemical information is due to the reluctance of divalent silicon species to form stable adducts with structures such that they would reveal the stereochemistry of addition.³ The addition of dimethylsilylene to ethylene, for instance, leads to vinyl dimethylsilane as the only product isolated, although the intermediacy of the silacyclopentane was inferred.^{4,5}



There is, however, a reaction which is capable of revealing the stereochemistry of silylene addition. The reaction of dimethylsilylene and 2,3-dimethylbuta-1,3-diene produces 1,1,3,4-tetramethyl-1-silacyclopent-3-ene in 15% yield,⁶ and the addition of silylene to buta-1,3-diene gives the unsubstituted 1-silacyclopent-3-ene in 40% yield.⁷ Nucleogenic $^{31}\text{SiF}_2$ and $^{31}\text{SiH}_2$ also undergo addition to butadiene.⁷⁻⁹



We have studied the gas-phase addition of silylene to *trans*-2-*trans*-4-hexadiene, a substrate capable of yielding stereoisomeric products. Pyrolysis of disilane was the method chosen to generate silylene.^{3,10} Rather than employing a recirculating flow system¹⁰ a single-pass system was utilized in order to minimize the risk of pyrolyzing the silylene addition products. A 1:5 mixture of disilane and the diene was passed once through an 8 mm i.d. Pyrex tube with a 12 cm-long hot zone maintained at 420°. The pressure in the reaction zone was *ca.* 50 Torr and the contact time in the hot zone was *ca.* 1 sec.

Reaction products were trapped at 77°K. Vapor-chromatographic analysis revealed two major products each formed in 10% yield based on the initial amount

(3) For a review and references see P. P. Gaspar and B. Jerosch Herold, "Carbene Chemistry," 2nd ed, W. Kirmse, Ed., Academic Press, New York, N. Y., 1971, Chapter 13.

(4) P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, **86**, 1442 (1964) (two papers).

(5) Recently silacyclopentanes have been isolated: R. L. Lambert, Jr., and D. Seyferth, *J. Amer. Chem. Soc.*, **94**, 9246 (1972); D. Seyferth, C. K. Haas, and D. C. Annarelli, *J. Organometal. Chem.*, **56**, C7 (1973).

(6) W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968).

(7) P. P. Gaspar, R.-J. Hwang, and W. C. Eckelman, *J. Chem. Soc., Chem. Commun.*, 242 (1974).

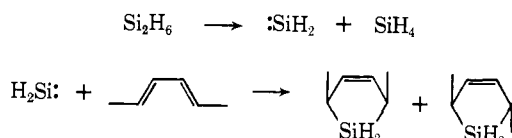
(8) Y.-N. Tang, G. P. Gennaro, and Y.-Y. Su, *J. Amer. Chem. Soc.*, **94**, 4355 (1972).

(9) G. P. Gennaro, Y.-Y. Su, O. F. Zeck, S. H. Daniel, and Y.-N. Tang, *J. Chem. Soc., Chem. Commun.*, 637 (1973).

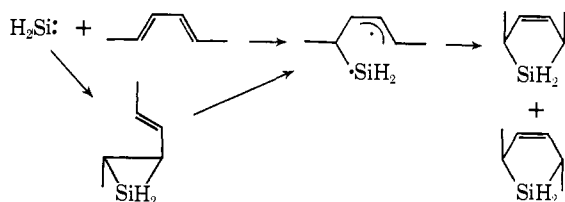
(10) E. M. Tebben and M. A. Ring, *Inorg. Chem.*, **8**, 1787 (1969); P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *ibid.*, **9**, 1068 (1970); M. Bowrey and J. H. Purnell, *Proc. Roy. Soc., Ser. A*, **321**, 341 (1971).

of disilane. Several minor products were formed in ca. 1% yield in addition to a high yield of silane from the disilane pyrolysis. Nuclear magnetic resonance, infrared, and mass spectra of the major products revealed their identity as the *cis* and *trans* isomers of 2,5-dimethyl-1-silacyclopent-3-ene. Characteristic ratios of vinyl-methyl-silyl hydrogens and the doublet splittings of the methyl hydrogens observed in the nmr spectra ensure that the two major products differ only in the *cis-trans* relationship of the methyl groups rather than in the location of the double bond. Each of the isolated products was subjected to pyrolysis under the original reaction conditions. While some decomposition (ca. 20%) occurred, no interconversion of the two isomers was detected. Thus formation of one isomer in a stereospecific reaction followed by rearrangement to the other isomer was excluded. Spectroscopic and chromatographic analysis of the recovered diene indicated that neither geometric isomerization of *trans,trans-* to *cis,trans-* 2,4-hexadiene nor structural isomerization of the reactant diene occurred during pyrolysis of the disilane.

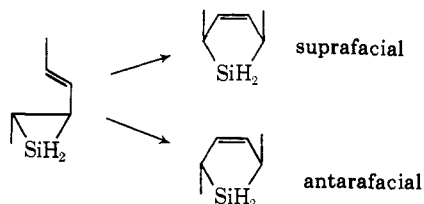
The reaction can be formulated



The formation of both stereoisomers in equal amounts (product ratio 1.0 ± 0.1) rules out a concerted 1,4-addition which would have yielded the *cis* product exclusively. Two reaction mechanisms are consistent with the observed stereochemistry. (1) A diradical is produced along the reaction coordinate either as the primary adduct or from ring opening of a vinylsilacyclopropane.³ (2) A vinylsilacyclopropane is formed in a



concerted addition and subsequently undergoes concerted antarafacial and suprafacial 1,3-sigmatropic rearrangements¹¹ with equal facility.



A diradical pathway seems more likely in view of the cumbersome transition state for concerted antarafacial rearrangement and the demonstrated participation of diradical intermediates in the all-carbon vinylcyclopropane rearrangements.^{12,13}

(11) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Verlag Chemie and Academic Press, Weinheim, 1971, pp 121-122.

(12) M. R. Willcott and V. H. Cargle, *J. Amer. Chem. Soc.*, **89**, 723 (1967); **91**, 4311 (1969).

(13) P. H. Mazzocchi and H. J. Tamburin, *J. Amer. Chem. Soc.*, **92**, 7220 (1970).

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Use of Solid-Gas Reactions to Distinguish between Left- and Right-Handed Single Crystals of an Enantiomeric Pair

Sir:

From the separation by Pasteur of hemihedral crystals of racemic sodium ammonium tartrate,¹ the resolution of optical antipodes has been a continuing challenge to the organic chemist. Although it is now evident that few racemates can be expected to crystallize with hemihedral faces which would permit visual identification of the dextro and levo crystals, it is also generally recognized² that many substances crystallize as "conglomerates" or mixtures of crystals which taken individually are either dextro or levo. Although this phenomenon has been somewhat misleadingly called "spontaneous resolution," there is no practical resolution until the dextro and levo crystals have been identified and separated. A number of methods capable of identification of those crystals with a common chirality have been developed. In addition to the rarely applicable visual method of Pasteur, use has been made of polarimetric measurements of single crystals³ or solutions prepared from them,⁴ anomalous scattering of X-rays,⁵ etching,⁶ nucleation by a single crystal of one enantiomer of a second chiral substance,⁷ microscopic observation of the effect of a single crystal on a nematic liquid crystalline phase,⁸ nmr observation of interaction of the dissolved crystal with a chiral solvent⁹ or a chiral shift reagent,¹⁰ and relative rate of reaction in solution with a chiral reagent.¹¹ These methods, although cumbersome or limited in scope, have been or could be

(1) (a) L. Pasteur, *Ann. Chim. Phys.*, [3] **24**, 442 (1848); see T. Martin Lowry, "Optical Rotatory Power," Dover Publications, New York, N. Y., 1964, p 28 ff; (b) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 4 ff.

(2) See, for example, A. Collet, M.-J. Brienne, and J. Jacques, *Bull. Soc. Chim. Fr.*, 127 (1972); S. H. Wilen, *Top. Stereochem.*, **6**, 107 (1971); R. E. Pincock and K. R. Wilson, *J. Chem. Educ.*, **50**, 455 (1973).

(3) N. H. Hartshorne and A. Stuart, "Crystals and the Polarizing Microscope," Edward Arnold, London, 1960, p 141 ff.

(4) For an example see P.-T. Cheng, C. H. Koo, I. P. Mellor, S. C. Nyburg, and J. M. Young, *Acta Crystallogr., Sect. B*, **26**, 1339 (1970).

(5) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," McMillan, New York, N. Y., 1968, p 425.

(6) See, for example, P. Groth, "Chemische Crystallographie," Vol. 3, Engelmann, Leipzig, 1917, p 304.

(7) For example, chiral single crystals of glycine [Y. Iitaka, *Acta Crystallogr.*, **13**, 35 (1960); *ibid.*, **14**, 1 (1961)] can induce the specific crystallization of D- or L-asparagine; the configuration of the asparagine thus apparently providing a means of identification of the chirality of the glycine crystal used to inoculate the crystallization [R. M. Secor, *Chem. Rev.*, **63**, 306 (1963)].

(8) P. Gaubert, *Bull. Soc. Fr. Mineral.*, **66**, 293 (1943); *Chem. Abstr.*, **39**, 5146⁷ (1943).

(9) W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **91**, 5150 (1969); *ibid.*, **93**, 2817 (1971).

(10) M. D. McCreary, D. W. Lewis, D. L. Wernick, and G. M. Whitesides, *J. Amer. Chem. Soc.*, **96**, 1038 (1974).

(11) See ref 1b, p 65.