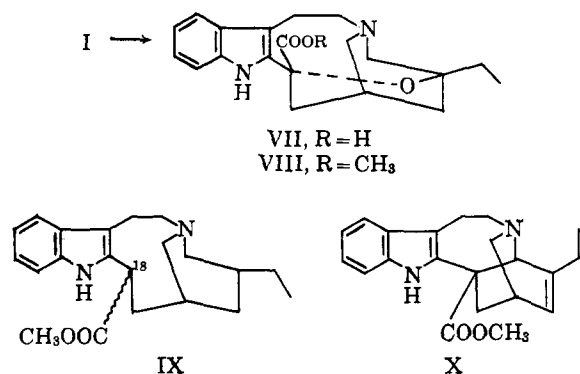The formation of the ether VIII from VLB suggests that the C-4' ethyl group in VLB is β-oriented, and therefore the OH on the same carbon is *trans* to N_b of the indole moiety.

VII, R = H
VIII, R = CH$_3$

IX   X

The stereochemistry at C-3, 4, and 18' is as yet uncertain. Our data are in agreement with structure I for VLB, and the known relationship[3] between VLB and VCR requires the latter to be II. Another example of this type of alkaloid is provided by voacamine[10] derived from *Voacanga* species (*Apocynaceae*).

(10) G. Büchi, R. E. Manning, and S. A. Monti, *J. Am. Chem. Soc.*, **85**, 1893 (1963).

LILLY RESEARCH LABORATORIES   NORBERT NEUSS
ELI LILLY AND COMPANY   MARVIN GORMAN
INDIANAPOLIS 6, INDIANA   WILLIAM HARGROVE
    NANCY J. CONE
DEPARTMENT OF CHEMISTRY   K. BIEMANN
MASSACHUSETTS INSTITUTE OF TECHNOLOGY   G. BÜCHI
CAMBRIDGE 39, MASSACHUSETTS   R. E. MANNING

## Silacyclopropanes[1]

Sir:

No successful synthesis of a three-ring compound with ring silicon has been reported.[2,3] We have not succeeded in the isolation of a silacyclopropane. However, we have strong evidence that it was synthesized and that its thermal instability pre-empted success in isolation.

Silacyclopropanes appear to undergo rearrangement to vinylsilanes, analogous to the rearrangement of cyclopropane to propylene. The several routes employed for the synthesis of a silacyclopropane have
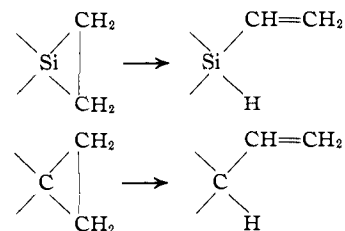

yielded vinylsilanes.[4]

All reactions were carried out by sweeping into an alkali metal vapor atmosphere (Na–K) a helium stream

(1) This work was supported by the National Science Foundation.
(2) F. Johnson and R. S. Gohlke, *Tetrahedron Letters*, 1291 (1962).
(3) R. West and R. E. Bailey, *J. Am. Chem. Soc.*, **85**, 2871 (1963).
(4) The assistance of Dr. A. Lee Smith, Dow Corning Corp., Midland, Mich., in providing authentic samples and infrared spectra for identification of the products isolated in this work is acknowledged with gratitude.

(200 mm.) carrying the organic halogen compound. Reaction temperatures of 260–280° were employed.

(1)[5]

(2)

(3)
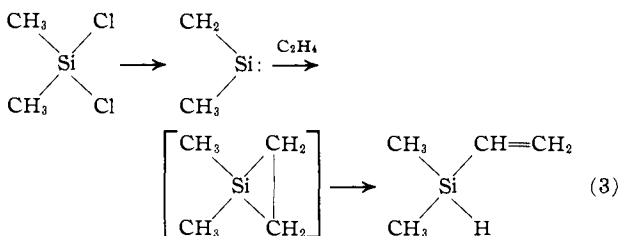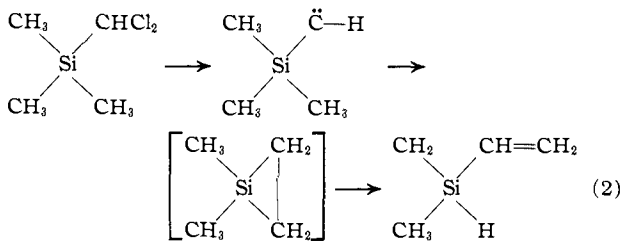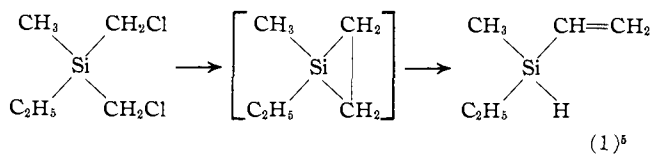
The first two reactions involve skeletal rearrangements which we can best rationalize by the assumption of a silacyclopropane intermediate. Although the third reaction can be rationalized as a dimethylsilene insertion on vinyl C–H, we prefer the mechanism as it is described above.

Unsuccessful efforts were made to trap the silacyclopropane intermediates by limiting residence time in the reaction zone to ~ 1 sec. and elapsed time in transference to the liquid nitrogen-cooled trap to ~ 10 sec. No vinylsilane precursor could be detected. A unimolecular decay of $t_{1/2} \leqslant 0.1$ sec. at 270° requires $E_{act} \leqslant 36$ kcal./mole (assuming $A = 10^{15.2}$ as observed for cyclopropane). This value approximates the E_{act} for a silacyclopropane thermolysis.

The large difference in thermal stability of cyclopropanes ($E_{act} \sim 60$ kcal./mole) and silacyclopropanes is attributed to strain, enhanced in the latter by the large size of the silicon atom, making the C–Si–C angle $\sim 48°$.

(5) The analogous conversion of 1,3-dibromo-2,2-dimethylpropane to 1,1-dimethylcyclopropane occurs in good yield.

DEPARTMENT OF CHEMISTRY   P. S. SKELL
THE PENNSYLVANIA STATE UNIVERSITY   E. J. GOLDSTEIN
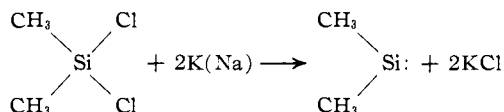UNIVERSITY PARK, PENNSYLVANIA

Dimethylsilene: CH$_3$SiCH$_3$[1]

Sir:

We wish to report the synthesis of dimethylsilene, CH$_3$SiCH$_3$, the silicon analog of a carbene, as a short-lived intermediate.

Dimethylsilene has been generated in the gas phase at temperatures between 260 and 280° by the reaction of sodium–potassium vapor with dimethyldichlorosilane. When the reaction is carried out in a helium atmosphere (200 mm.) most of the product is left in the reaction zone, probably as a polymer. However,

(1) This work was supported by the National Science Foundation.

$$\underset{CH_3}{\overset{CH_3}{\diagdown}}Si\underset{Cl}{\overset{Cl}{\diagup}} + 2K(Na) \longrightarrow \underset{CH_3}{\overset{CH_3}{\diagdown}}Si: + 2KCl$$

if trimethylsilane, $(CH_3)_3SiH$, is added to the helium stream the dimethylsilene inserts into the Si–H bond to produce pentamethyldisilane.[2,3]

$$CH_3\overset{CH_3}{\underset{CH_3}{-Si-H}} + \overset{CH_3}{\underset{CH_2}{Si:}} \longrightarrow CH_3\overset{CH_3}{\underset{CH_3}{-Si-}}\overset{CH_3}{\underset{CH_3}{Si-H}}$$
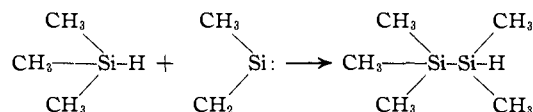
Dimethylsilene was generated from dimethyldichlorosilane (5.9 g.) in the presence of a 10-fold excess of trimethylsilane. The excess trimethylsilane was separated by low temperature distillation and the higher boiling materials by gas chromatography to yield 1.8 g. of pure pentamethyldisilane (30% of theoretical).

The pentamethyldisilane was identified by infrared, proton magnetic resonance, and mass spectra which proved it to be identical with an authentic sample.

Earlier reports claiming dimethylsilene intermediates in condensed systems are considered to be ambiguous.[4,5] To the best of our knowledge no previous experimental chemical observations require a bivalent silicon intermediate.[6]

There do not seem to be satisfactory alternative hypotheses to explain the formation of pentamethyldisilane. A radical chain process involving $(CH_3)_2$-SiCl and $(CH_3)_3Si$ radicals can be eliminated since trimethylsilyl radical generated under comparable conditions couples in good yield to hexamethyldisilane. For example, from either trimethylchlorosilane alone or a mixture of methylene bromide and trimethylsilane, reaction with alkali metal vapor produces hexamethyldisilane. From the reaction of dimethyldichlorosilane-trimethylsilane mixtures, at most a trace of hexamethyldisilane could be detected among the products.

These observations not only implicate a dimethylsilene intermediate, but also suggest it is in the singlet state. Spin conservation rules require that a triplet dimethylsilene react with trimethylsilane to produce two monoradicals for which geminate coupling is precluded. Nongeminate coupling should lead to hexamethyldisilane, pentamethyldisilane, and *sym*-tetramethyldisilane in 1:2:1 ratios. The homo-

$$(CH_3)_2Si\uparrow\uparrow + (CH_3)_3SiH \longrightarrow (CH_3)_2\dot{S}iH\uparrow + (CH_3)_3\dot{S}i\uparrow$$
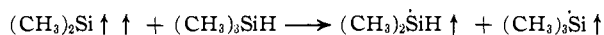
coupling products could not be identified, and all products other than pentamethyldisilane in the ap-

(2) D. Seyferth and J. Burlitch, *J. Am. Chem. Soc.*, **85**, 2667 (1963).

(3) K. Kramer and A. Wright, *Angew. Chem.*, **74**, 468 (1962); *Tetrahedron Letters*, 1095 (1962).

(4) F. Johnson and R. S. Gohlke, *ibid.*, 1291 (1962), and private conversation with Dr. Johnson.

(5) R. West and R. E. Bailey, *J. Am. Chem. Soc.*, **85**, 2871 (1963).

(6) The work reported in ref. 3 and 4 raised doubts about the necessity of postulating a dimethylsilene intermediate in condensed phase reactions of polysilanes, $[(CH_3)_2Si]_x$, or $(CH_3)_2SiCl_2$ + Na, with tolane [M. E. Volpin, Yu. D. Koreshkov, V. G. Dulova, and D. N. Kursanov, *Tetrahedron*, **18**, 107 (1962)]. In private communication, however, Dr. Volpin suggests that the best explanation of their results is essentially as proposed in the 1962 publication, adding to the rationalization a final step in which the silacyclopropene (or the diradical derived from it) undergoes dimerization to a 1,4-disilacyclohexadiene. Analogous rationalizations are made in publications by O. M. Nefedow and co-workers [*Angew. Chem.*, in press; *Bull. Acad. Sci. USSR Div. Chem. Sci.*, 1152 (1962)] describing liquid phase reactions of alkali metals with dichlorosilanes and olefins. See also H. Gilman, *Angew. Chem.*, **74**, 950 (1962).

propriate molecular weight range summed to 4% of the pentamethyldisilane. For this reason dimethylsilene is assigned a singlet state electronic configuration. For kinetic reasons which will be developed elsewhere this is also considered to be the ground state.

The carbon analogs of dimethylsilene, alkylcarbenes, are not generally trapped in bimolecular processes, but instead rearrange to olefinic products.[7] This

$$(CH_3)_2C: \longrightarrow CH_3-CH=CH_2$$

pathway is not favored for dimethylsilene because of the relative instability of the silicon to carbon double bond (no example reported to date). This inability of $(CH_3)_2Si$: to stabilize itself by the above internal rearrangement should increase the probability of bimolecular processes such as insertion into the C–H bonds. However, insertions into the C–H bonds of ethane and trimethylsilane are of low efficiency. These facts suggest that dimethylsilane is much less reactive than singlet CH_2.

(7) R. A. Holroyd and F. E. Blacet, *J. Am. Chem. Soc.*, **79**, 4830 (1957).

DEPARTMENT OF CHEMISTRY   P. S. SKELL
THE PENNSYLVANIA STATE UNIVERSITY   E. J. GOLDSTEIN
UNIVERSITY PARK, PENNSYLVANIA

Number of Particles in Colloidal Suspensions of Silver Bromide

Sir:

In an investigation of the particle size and stability of colloidal aqueous suspensions of silver bromide, suspensions were formed at widely different concentrations of reactants and in the presence of ethanol or of acetone and of complexing agents for silver(I). This communication describes the remarkably simple relation that exists under certain conditions between the number of colloidal particles in suspensions of different ages and the initial supersaturation of the suspension. Light scattering methods[1] were used for measurement of particle diameter from about 2 min. up to several days after mixing the reactants. Since the formation of silver bromide is complete (shown by electrical conductivity) within less than 2 min. after mixing,[2] the concentration of suspended material is known and the number of particles, assumed spherical, can be calculated from the diameter. Deviations from spherical shape and from monodispersity exist[2] but are of minor consequence for the present purpose.

Figure 1 is a plot of $\log n$ vs. $\log \sigma$ where n is the number of particles per ml. of suspension, and σ is the initial supersaturation, equal to the concentration of silver bromide at the instant of mixing divided by the solubility at equilibrium. The sols illustrated in Fig. 1 were prepared by addition over about 30 sec. of a solution of silver nitrate to an equal volume of potassium bromide, the latter being stirred at 900 r.p.m. Other details were similar to those reported before.[2] The concentrations of sol and of bromide, which was always in excess over silver, ranged from 5×10^{-3} to 5×10^{-7} M. Under these conditions dissolved

(1) E. J. Meehan and W. H. Beattie. *J. Phys. Chem.*, **64**, 1006 (1960).

(2) E. J. Meehan and W. H. Beattie. *ibid.*, **65**, 1522 (1961).