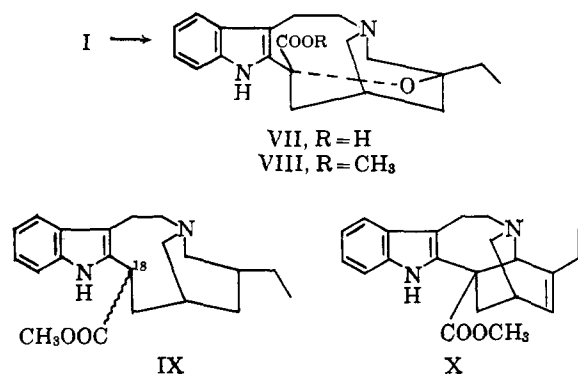


The formation of the ether VIII from VLB suggests that the C-4' ethyl group in VLB is  $\beta$ -oriented, and therefore the OH on the same carbon is *trans* to N<sub>b</sub> of the indole moiety.



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<sup>8</sup> between VLB and VCR requires the latter to be II. Another example of this type of alkaloid is provided by voacamine<sup>10</sup> derived from *Voacanga* species (*Apocynaceae*).

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

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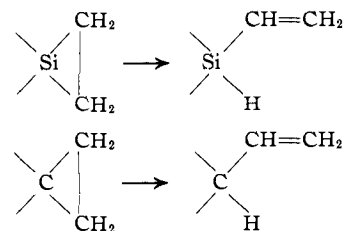
RECEIVED OCTOBER 21, 1963

### Silacyclopropanes<sup>1</sup>

Sir:

No successful synthesis of a three-ring compound with ring silicon has been reported.<sup>2,3</sup> 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

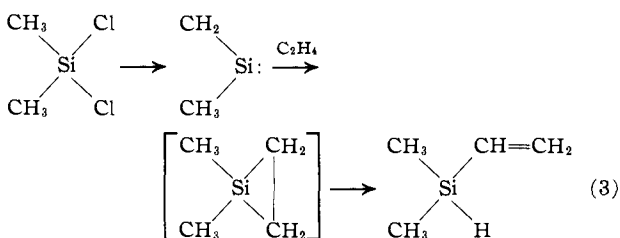
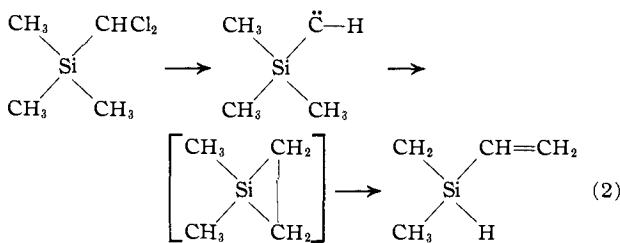
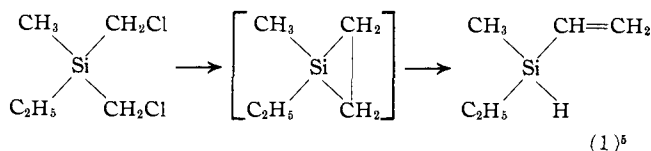


yielded vinylsilanes.<sup>4</sup>

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.



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  $\sim 1$  sec. and elapsed time in transference to the liquid nitrogen-cooled trap to  $\sim 10$  sec. No vinylsilane precursor could be detected. A unimolecular decay of  $t_{1/2} \leq 0.1$  sec. at 270° requires  $E_{\text{act}} \leq 36$  kcal./mole (assuming  $A = 10^{15.2}$  as observed for cyclopropane). This value approximates the  $E_{\text{act}}$  for a silacyclopropane thermolysis.

The large difference in thermal stability of cyclopropanes ( $E_{\text{act}} \sim 60$  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  $\sim 48^\circ$ .

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

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### Dimethylsilene: CH<sub>3</sub>SiCH<sub>3</sub><sup>1</sup>

Sir:

We wish to report the synthesis of dimethylsilene, CH<sub>3</sub>SiCH<sub>3</sub>, 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.