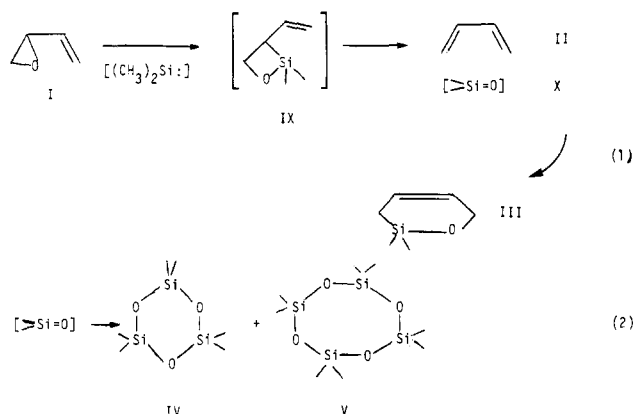


Mechanism of Reaction of Dimethylsilylene with α,β -Unsaturated Epoxides

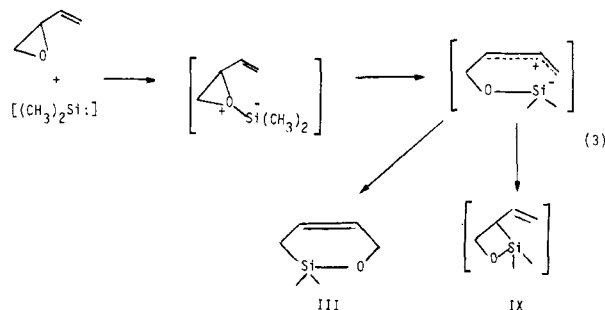
Sir:

We report a novel reaction of dimethylsilylene with α,β -unsaturated epoxides which we believe involves zwitterionic intermediates.¹ For example, dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane² in 3,4-epoxy-1-butene (I) as solvent at 0 °C yields 1,3-butadiene (35%, II), 2,2-dimethyl-1-oxa-2-silacyclohex-4-ene (15%, III), hexamethylcyclotrisiloxane (3%, IV), and octamethylcyclotetrasiloxane (6%, V). Likewise, dimethylsilylene reacts with 3,4-epoxy-2,3-dimethyl-1-butene (VI) to yield 2,3-dimethyl-1,3-butadiene (25%, VII), 2,2,4,5-tetramethyl-1-oxa-2-silacyclohex-4-ene (38%, VIII), IV (3%), and V (4%).

Let us consider the case of reaction of dimethylsilylene with 3,4-epoxy-1-butene. The formation of these products might result from initial insertion of dimethylsilylene into a strained C–O single bond of the epoxide to yield 2,2-dimethyl-1-oxa-2-sila-3-vinylcyclobutane (IX), a silaoxetane intermediate. Silaoxetanes are known to decompose to yield alkenes and silanones ($R_2Si=O$).^{3–5} If IX decomposed in this manner, it would yield II and dimethylsilanone (X). A Diels–Alder reaction between II and X might yield III (eq 1). Cyclooligomerization of X is known to yield IV and V^{3–5} (eq 2).

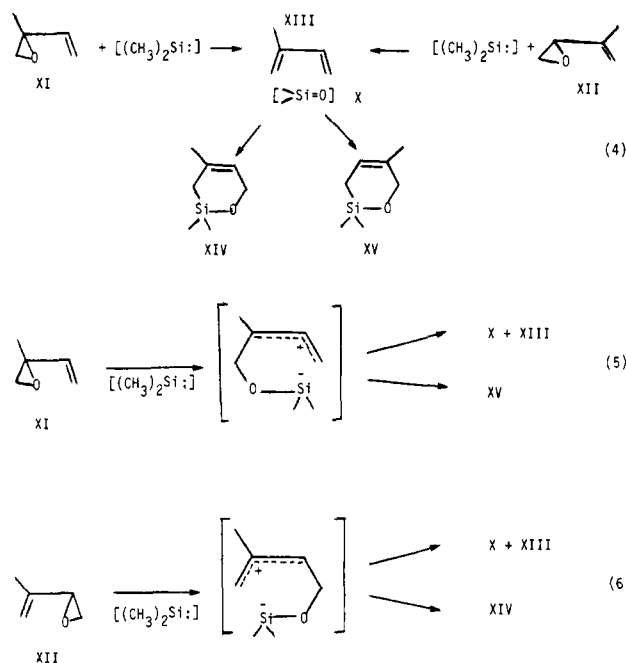


An alternative possibility is that dimethylsilylene initially coordinates to the oxygen of the epoxide to yield a 1,2-zwitterionic intermediate⁶ which opens to yield an allylic carbonium ion–silyl anion pair which recombine to yield III and IX. Decomposition of IX yields II and X (eq 3).



To distinguish between these two possibilities, we have studied the reactions of 3,4-epoxy-3-methyl-1-butene (XI) and 3,4-epoxy-2-methyl-1-butene (XII) with dimethylsilylene. In the case of the first mechanism both XI and XII are expected to react with dimethylsilylene to yield mixtures of isoprene (XIII) and 2,2,4-trimethyl-1-oxa-2-silacyclohex-4-ene (XIV) and 2,2,5-trimethyl-1-oxa-2-silacyclohex-4-ene (XV) (eq 4). On the other hand, the second mechanism predicts that XI will

react with dimethylsilylene to yield only XIII and XV (eq 5) and that XII will react with dimethylsilylene to yield only XIII and XIV (eq 6).



Our experimental results are in complete agreement with eq 5 and 6. The assignment of structure to isomers XIV and XV is largely based on NMR. See paragraph at the end of the paper regarding supplementary material. For this reason, we believe that the reaction of dimethylsilylene with 3,4-epoxy-1-butene involves initial formation of a 1,2-zwitterionic intermediate which opens to yield an allylic carbonium ion–silyl anion pair—which reacts further to yield II and III.

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Supplementary Material Available: Experimental data for compounds II–V, VII, VIII, and XIII–XV (3 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) For a recent review of silylene chemistry, see P. P. Gaspar in "Reactive Intermediates", Vol. I, M. Jones, Jr., and R. A. Moss, Eds., Wiley Interscience, New York, 1978, pp 229–277.
- (2) M. Ishikawa and M. Kumada, *J. Organomet. Chem.*, **42**, 325 (1972).
- (3) D. N. Roark and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 167 (1973).
- (4) T. J. Barton and J. A. Kilgour, *J. Am. Chem. Soc.*, **96**, 2278 (1974).
- (5) P. B. Valkovich and W. P. Weber, *J. Organomet. Chem.*, **99**, 231 (1975).
- (6) T. Y. Gu and W. P. Weber, unpublished work.
- (7) T. Asahara, M. Sano, Y. Shimozato, E. Shima, and M. Otsu, *Nippon Kagaku Zasshi*, 1251 (1972).
- (8) M. N. Sheng and J. G. Zajacek, *J. Org. Chem.*, **35**, 1839 (1970).
- (9) E. J. Reist, I. G. Jung, and B. R. Baker, *J. Org. Chem.*, **25**, 1674 (1960).
- (10) R. West, *Ann. N.Y. Acad. Sci.*, **239**, 262 (1974).
- (11) M. Laguerre, J. Dangles, and R. Calas, *J. Chem. Soc., Chem. Commun.*, 272 (1978).
- (12) XIV and XV are well separated by GLC. A 1% yield of either could be detected.

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