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VINYLSILYLENE REARRANGEMENT. A POSSIBLE SILACYCLOPROPANYLIDENE INTERMEDIATE

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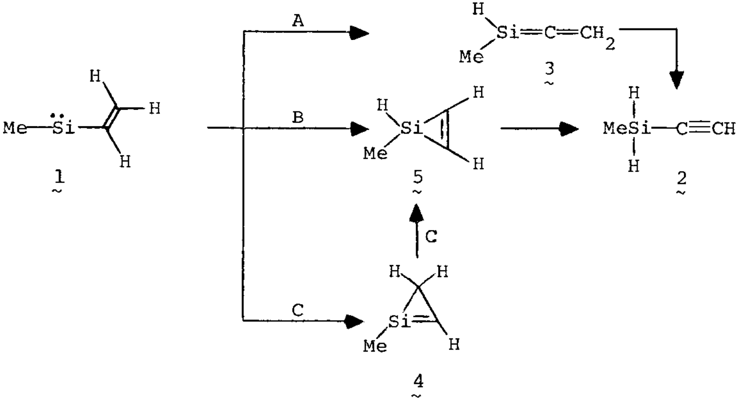
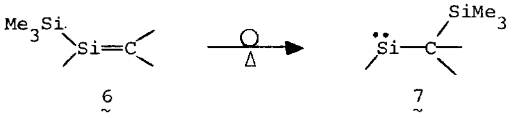
Abstract: It is proposed that trimethylsilylvinylsilylene undergoes sequential rearrangement to a silacyclopropanylidene by silene to silylene isomerization of an intermediate 1-silacyclopropene.

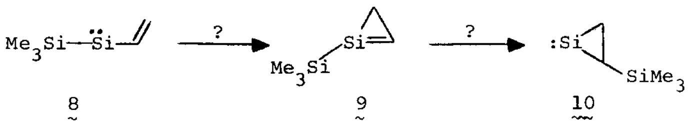
Recently we reported that when methylvinylsilylene 1 was generated in a flash vacuum pyrolysis the major volatile product was its isomer, methylethynylsilane 2.[1] At least three mechanistic routes for the transformation of 1 to 2 must be considered (Scheme 1). Although intramolecular C-H insertion by silylenes is an established process,[2] it has never been observed for vinyl C-H bonds as required for Paths A and B. Thus, since π-addition by silylenes is well known[3], and because of analogy with vinylcarbenes,[4] we favored Path C, involving intramolecular π-addition by 1 to form 1-silacyclopropene 4, hydrogen migration to silicon to produce 3-silacyclopropene 5, from which a second hydrogen migration to silicon affords the product 2.



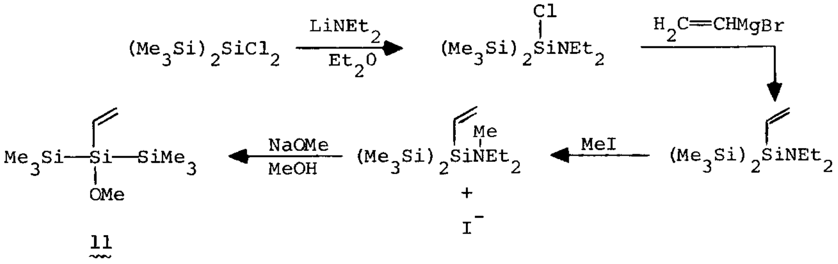
A major objection to Path C is found in the recently reported ab initio calculations of Gordon[5] for the SiC_2H_4 isomers. Indeed, Gordon finds the 1-silacyclopropene (4, Me=H) to be more than 50 kcal/mole above vinylsilylene (1, Me=H), 36 kcal/mole above 1-silaallene (3, Me=H), and 50 kcal/mole above 3-silacyclopropene (5, Me=H). Thus, insofar as these numbers can be quantitatively trusted, the isomerization of 1 to 4 would appear to be a thermodynamically unreasonable suggestion.

Although nontrivial labeling experiments could conceivably be employed to eliminate or confirm Path A, it is not obvious how an experimental distinction between Paths B and C might be made. However, we have recently discovered[6] that silylsilenes (6) will thermally rearrange to β-silylsilylenes (7). Thus, it seemed possible that if trimethylsilylvinylsilylene 8 rearranged to 1-silacyclopropene 9, it might be diverted from Path C by 1,2-silyl migration to produce silacyclopropanylidene 10.

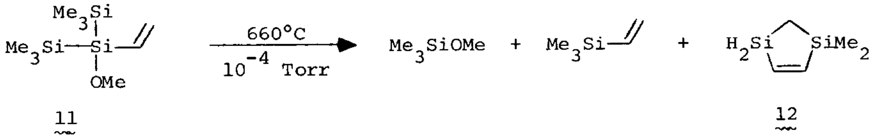




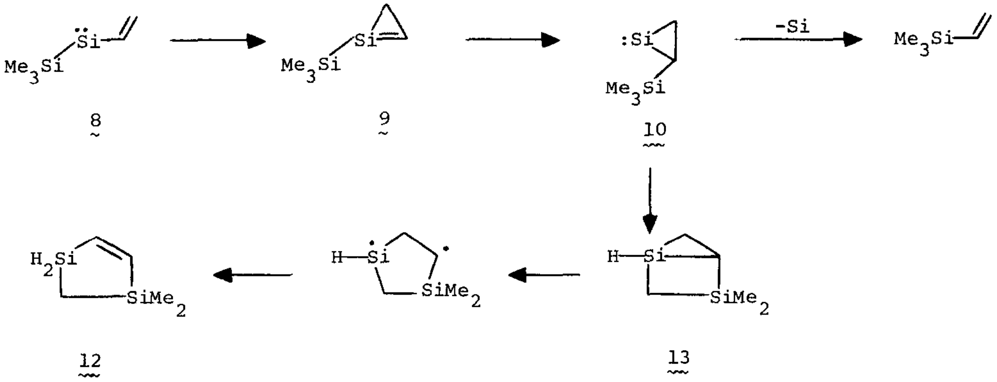
To the end of probing this possibility 2-methoxy-2-vinylhexamethyltrisilane (11)[7] was synthesized in a "one-pot synthesis" by sequential treatment of 2,2-dichlorohexamethyltrisilane with lithium diethylamide (LDA), vinylmagnesium bromide, methyl iodide and sodium methoxide.[8] Preparative gas chromatographic (GC) isolation of 11 was accomplished for an overall 16% yield.



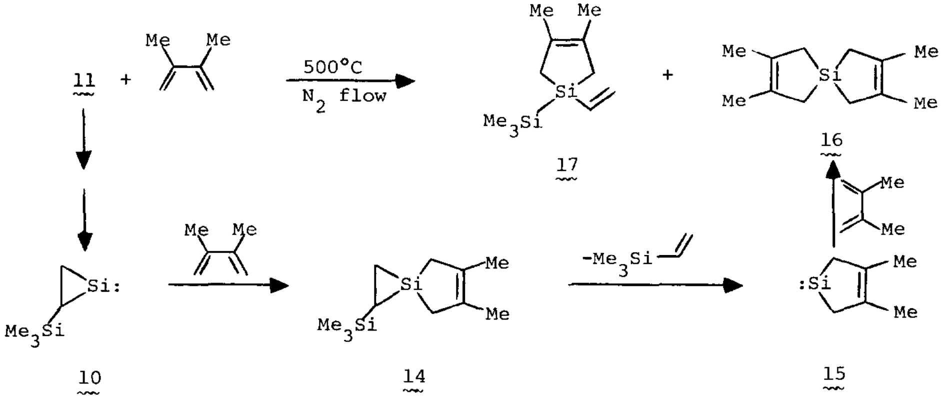
Flash vacuum pyrolysis of 11 was conducted through a horizontal quartz tube packed with quartz chips heated to 660°C (10^{-4} Torr). From the pyrolysate (68% mass recovery) three products were isolated by preparative GC. Trimethylmethoxysilane (69%) and trimethylvinylsilane (12%) were identified by spectral comparison with authentic samples. The third product was 3,3-dimethyl-3,5-disilacyclopentene (12)[9] and was formed in 13% yield (19% based on Me_3SiOMe).



Both the formation of trimethylvinylsilane and of disilacyclopentene 12 are consistent with isomerization of silylene 8 to silirene 9 and subsequent rearrangement to silacyclopropanylidene 10. Extrusion of silicon from 10 would afford trimethylvinylsilane, while C-H insertion to form disilabicyclo[2.1.0]pentene 13 followed by homolysis of the strained internal Si-C bond and hydrogen migration would account for the production of 12.



In order to confirm the initial formation of silylene 8 from the decomposition of 11, a copyrolysis (500°C) of 11 and excess 2,3-dimethyl-1,3-butadiene was performed in a vertical tube with nitrogen (30 mL/min) as the carrier gas. From the pyrolysate could be isolated two trapping products by preparative GC. The expected adduct of 8 and the butadiene, 4-trimethyl-4-vinyl-4-sila-1,2-dimethylcyclopentene (17),[10] was the major product, but most interesting was the formation of spirosilanonadiene 16 which was identified by spectral comparison with an authentic sample prepared from the copyrolysis of 2,3-dimethyl-1,3-butadiene and bis(trimethylsilyl)dimethoxysilane.[11] Formation of spiracycle 14 would be expected from the trapping of silylene 10 followed by the extrusion[12] of silylene 15 which in turn is trapped by the butadiene.[13,15]



Acknowledgement. We are grateful to the National Science Foundation for generous support of this work.

Notes and References

1) T. J. Barton, G. T. Burns, W. F. Goure and W. D. Wulff, J. Am. Chem. Soc., 104, 1149 (1982).

2) W. D. Wulff, W. F. Goure and T. J. Barton, J. Am. Chem. Soc., 100, 6236 (1978); L. E. Gusel'nikov, E. Lopatnikova, Yu. P. Polyakov and N. S. Nametkin, Dokl. Akad. Nauk SSSR, 253, 1387 (1980).

3) D. Seyferth and D. C. Annarelli, J. Organometal. Chem., 117, C51, 1976.

4) W. Kirmse, "Carbene Chemistry", Academic Press, New York, pp 328-332 (1971).

5) M. S. Gordon and R. D. Koob, J. Am. Chem. Soc., 103, 2939 (1981).

6) T. J. Barton, S. A. Burns and G. T. Burns, Organometallics, 1, 210 (1982).

7) NMR ($DCCl_3$) δ 0.27 (s, 18H), 3.50 (s, 3H), 5.44-6.37 (m, 3H); mass spectrum (70 eV) m/e (% rel. int.) 232 (M^+, 20), 217 (30), 143 (37), 117 (70), 89 (40), 73 (100), 59 (60); calcd for $C_9H_{24}OSi_3$ m/e 232.11351, measured m/e 232.11373 (NMR's are 60 MHz).

8) Details of this general sequence for the synthesis of methoxyalkyl di- and trisilanes from the geminal dichlorides are in press: T. J. Barton and G. T. Burns, Organometallics

9) NMR ($DCCl_3$) δ -0.13 (t, J = 4 Hz, collapses to s with $h\nu$ at δ 4.27, 2H) 0.20 (s, 6H), 4.27 (t, J = 4 Hz, s with $h\nu$ at δ -0.13), 7.00 (d, 1H, J = 16 Hz), 7.20 (d, J = 16H, 1H); m/e (% rel. int.) 128 (M^+, 52), 127 (12), 113 (100), 58 (12); calcd for $C_5H_{12}Si_2$ m/e 128.04776, measured m/e 128.04779.

10) NMR ($DCCl_3$) δ 0.19 (s, 9H), 1.54 (brd. s, 4H), 1.72 (brd. s, 6H), 5.42-6.59 (m, 3H); GCMS m/e (% rel. int.) 210 (33), 195 (17), 168 (21), 125 (35), 124 (70), 123 (22), 113 (35), 111 (16), 110 (48), 109 (61), 97 (20), 96 (11), 95 (54), 85 (30), 83 (22), 73 (100), 69 (23), 59 (83), 55 (33); calcd for $C_{11}H_{22}Si_2$ m/e 210.12601, measured m/e 210.12630.

11) T. J. Barton and S. A. Burns, submitted for publication.

12) D. Seyferth and D. C. Annarelli, J. Am. Chem. Soc., 97, 7162 (1975).

13) An alternative explanation for the formation of 16 is reaction of atomic silicon with dimethylbutadiene. However, a yield of > 1% is incompatible with this as a major route.[14] That spiracycle 16 does not arise from initial reductive elimination of trimethylvinylsilane from 11 and trapping of Me(MeO)Si: by the diene is indicated by the fact that pentamethylvinyldisilane does not decompose under the reaction conditions.

14) P. P. Gaspar, Y. Chen, A. P. Helfer, S. Konieczny, E. C.-L. Ma and S.-H. Mo, J. Am. Chem. Soc., 103, 7344 (1981).

15) With a 3:1 excess of 2,3-dimethylbutadiene the yields of 16 and 17 are 8% and 20%, while an 8:1 ratio affords yields of 8% and 44% respectively.

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