Journal of Organometallic Chemistry, 125 (1977) C11- C17

Preliminary communication

THE PREPARATION OF A 1,2-DISILACYCLOBUTANE AND A 1,2-DISILACYCLOBUT-3-ENE BY DIMETHYLSILYLENE INSERTION INTO THE SILACYCLOPROPANE AND SILACYCLOPROPENE RING SYSTEMS. NEW SILACYCLOPROPENES.

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(Received November 26, 1976)

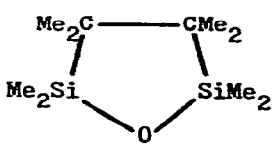
Summary

The thermolysis of hexamethylsilacyclopropane in the presence of 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacyclopropene resulted in formation of octamethyl-1,2-disilacyclobutane and 1,1,2,2-tetramethyl-3,4-bis(trimethylsilyl)-1,2-disilacyclobut-3-ene via Me_2Si insertion into the silacyclopropane and silacyclopropene rings. Thermolysis of hexamethylsilacyclopropane alone in benzene at 70° gave the former compound in 40% yield. Oxidation of these compounds with O_2 gave the respective 1,3-disila-2-oxa-cyclopentane and 1,3-disila-2-oxa-cyclopent-4-ene compounds. Four new silacyclopropenes (VIIIa-d) have been prepared and characterized.

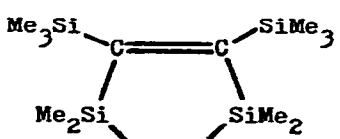
In 1973, Atwell and Uhlmann[1] reported that vapor phase pyrolysis of 1,2-dimethoxytetramethyldisilane at 400° in the presence of 2-butyne produces 1,1,2,2,3,4-hexamethyl-1,2-disilacyclobut-3-ene. The reasonable suggestion was made that this product was formed by a sequence of dimethylsilylene addition to the acetylene

(s, 18H, Me_3Si) and 0.46 ppm (s, 12H, Me_2Si); ^{13}C FT NMR (proton-decoupled): δ_C 200.8 (ring C)*, 1.4 ($Si(CH_3)_3$) and -0.6 ppm ($Si(CH_3)_2$); ^{29}Si FT NMR (proton-coupled): δ_{Si} 12.5 (3 of the expected 7 lines, Me_2Si) and -10.2 ppm (8 of the 10 expected lines, Me_3Si). The mass spectrum of V showed the expected molecular ion and the $Me_4Si_2^+$ fragment. Both products are very stable thermally. Both were unaffected by a heating period of 20 hr at 175° and IV was decomposed only to the extent of about 2% after it had been heated at 250° for 20 hr.

The products, IV and V, account for 51% of the hexamethylsilirane charged. It would appear that dimethylsilylene insertion into the very strained and highly reactive silacyclopropane and silacyclopropene rings is a very favorable process. Thermolysis of hexamethylsilirane alone in benzene at 70° for 18 hr gave IV in 40% yield. In another experiment, a mixture of 5.12 mmol of hexamethylsilirane and 2.99 mmol of I (R = Me_3Si) in benzene was heated at 70° as before. After 18 hr, oxygen was bubbled slowly into the reaction mixture at room temperature. An immediate exotherm resulted and a transient blue color was formed which faded to pale green. The oxidation products of IV and V, the cyclic siloxanes VI (a liquid, $n^{25}D$ 1.4526) and VII (a solid, mp 62-64°), could be isolated from the reaction mixture by GLC. Both were



VI



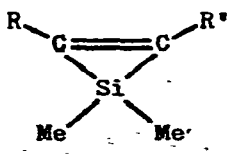
VII

* Due to the long relaxation time of the ring carbon atoms, a

characterized spectroscopically and by combustion analysis and mass spectrometry. The Si-O-Si frequencies in the IR spectra of these compounds (922 cm^{-1} for VI, 920 cm^{-1} for VII) are characteristic of the Si-O-Si linkage in a 1,3-disila-2-oxacyclopentene ring.[1]

It would appear that the eq. 2,3 route to II (R = CH_3) is an entirely feasible one. 1,2-Disilacyclobut-3-enes are rather rare.[6] In addition to II (R = CH_3), only some 1,1,2,2-tetrafluoro-1,2-disilacyclobut-3-enes, prepared by reaction of acetylenes with the SiF_4 + Si reaction product (SiF_2 or Si_2F_4), are known.[7] 1,2-Disilacyclobutanes are equally rare,[8] and their chemistry is completely unexplored. The reaction of the SiF_4 + Si reaction product with ethylene has been claimed to give 1,1,2,2-tetrafluoro-1,2-disilacyclobutane,[9] and more recently, Brook and Harris[10] described a route to 1,2-disilacyclobutanes highly substituted with bulky groups on silicon and carbon which proceeds <u>via</u> Si=C intermediates. The reactions which we report in this communication should be applicable to other silacyclopropane and silacyclopropene systems and thus should prove to be a useful new synthetic method in organosilicon chemistry.

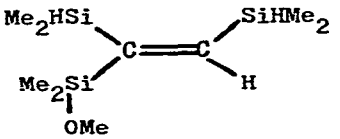
The 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacyclopropene used in this study was prepared by thermolysis of hexamethylsilirane in the presence of bis(trimethylsilyl)acetylene at 70° for 18 hr.[4] In further work, we have extended this procedure to the synthesis of four new silacyclopropenes, VIIIa-d. Two of



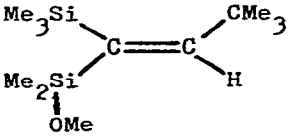
VIII (a) R = R' = Me_2HSi
(b) R = Me_3Si; R' = Me_3C
(c) R = Me_3Si; R' = CH_3
(d) R = Me_3C; R' = CH_3

these, VIIIa and VIIIb, have been isolated by GLC (3 ft. x 0.25

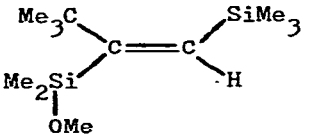
and 125°, respectively) as highly air-sensitive liquids. Both are thermally stable and were characterized by ^{1}H and ^{29}Si NMR, IR and mass spectroscopy, combustion analysis and reaction with methanol to give the appropriate ring-opened products, IX and a 70/30 mixture of Xa and Xb, respectively. Silacyclopropenes



IX

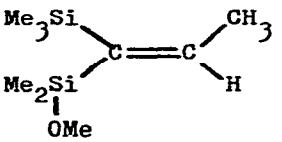


Xa



Xb

VIIIc and VIIId also appear to be thermally stable but thus far have been characterized only by their ^{29}Si NMR spectra and VIIIc additionally by its methanolysis reaction which gave XI. Like the



XI

^{29}Si NMR resonance of the ring silicon atom of I (R = Me_3Si) (106.2 ppm upfield from tetramethylsilane, TMS), those of VIIIa-d also are far upfield from TMS: VIIIa,-102.1 ppm; VIIIb,-91.9 ppm; VIIIc,-88.6 ppm; VIIId,-87.0 ppm. A ^{29}Si signal in the range 85-110 ppm upfield from TMS thus may be considered indicative of the presence of a silacyclopropene.

Acknowledgments. The authors are grateful to the U.S. Air force Office of Scientific Research (NC)-AFSC (Grant AF-AFOSR-76-2917) for generous support of this research, to Mara O. Nestle and Joseph S. Merola for obtaining the ^{13}C and ^{29}Si NMR spectra, and

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