

Preliminary communication

1,1-DIMETHYLSILOLE

GARY T. BURNS and T.J. BARTON*

Department of Chemistry, Iowa State University, Ames, Iowa 50011 (U.S.A.)

(Received November 26th, 1980)

Summary

Flash vacuum pyrolysis of 5-benzoyloxy-3,3-dimethyl-3-silacyclopentene afforded 5,5-dimethyl-5-silacyclopentadiene (1,1-dimethylsilole). Although the silole dimerizes at or below room temperature, it could be both trapped with maleic anhydride, and characterized by low-temperature NMR. The silole could also be generated from a thermally-induced retro Diels—Alder reaction of its dimer.

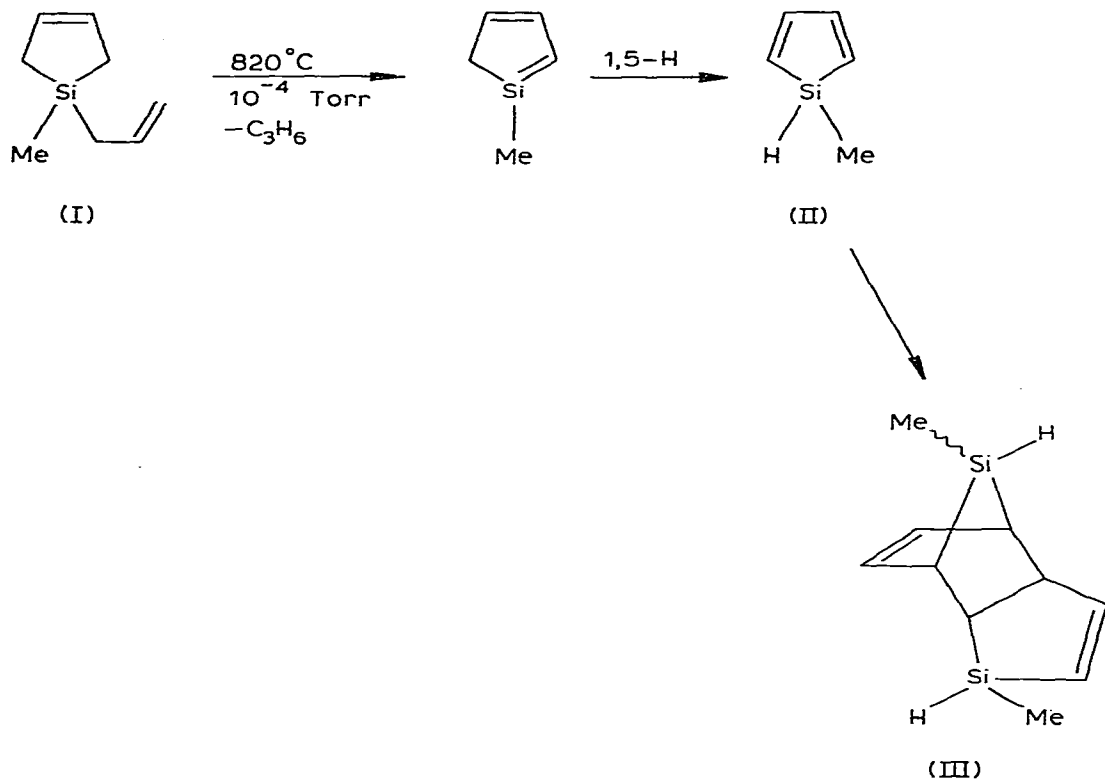
Results and discussion

Recently we reported [1] the generation of 5-methyl-5-silacyclopentadiene (II) from flash vacuum pyrolysis of 4-allyl-4-methyl-4-silacyclopentene (I). Although II was never isolated or observed it could be trapped from the retrograde Diels—Alder decomposition of its dimer, III.

This facile dimerization of II stands in contrast with the literature reports of the isolation of siloles without substitution on the ring carbons [2,3,4]*. However, since the synthesis and characterization of II had never before been claimed, the possibility that it was uniquely reactive could not be dismissed. Thus, we undertook the synthesis of 1,1-dimethylsilole (VI), a molecule whose synthesis and isolation had been reported without a mention of any tendency toward dimerization [2,3].

The synthesis of VI was initiated by the allylic oxidation of 4,4-dimethyl-4-silacyclopentene (IV) with *t*-butyl peroxybenzoate in the presence of cuprous bromide [5]. The resulting 5-benzoyloxy-3,3-dimethyl-3-silacyclopentene (V) was isolated in 60% yield after chromatography on silica gel (9/1, hexane/ethylacetate): NMR (CCl₄): δ (ppm) 0.21 (s, 3H), 0.28 (s, 3H), 0.82 (d of d, 1H, J_{AB} 15 Hz, J_{AC} 6 Hz), 1.57 (d of d, 1H, J_{BC} 9 Hz), 5.90 (m, 1H), 6.14

*See ref. 1 for a discussion of these claims.

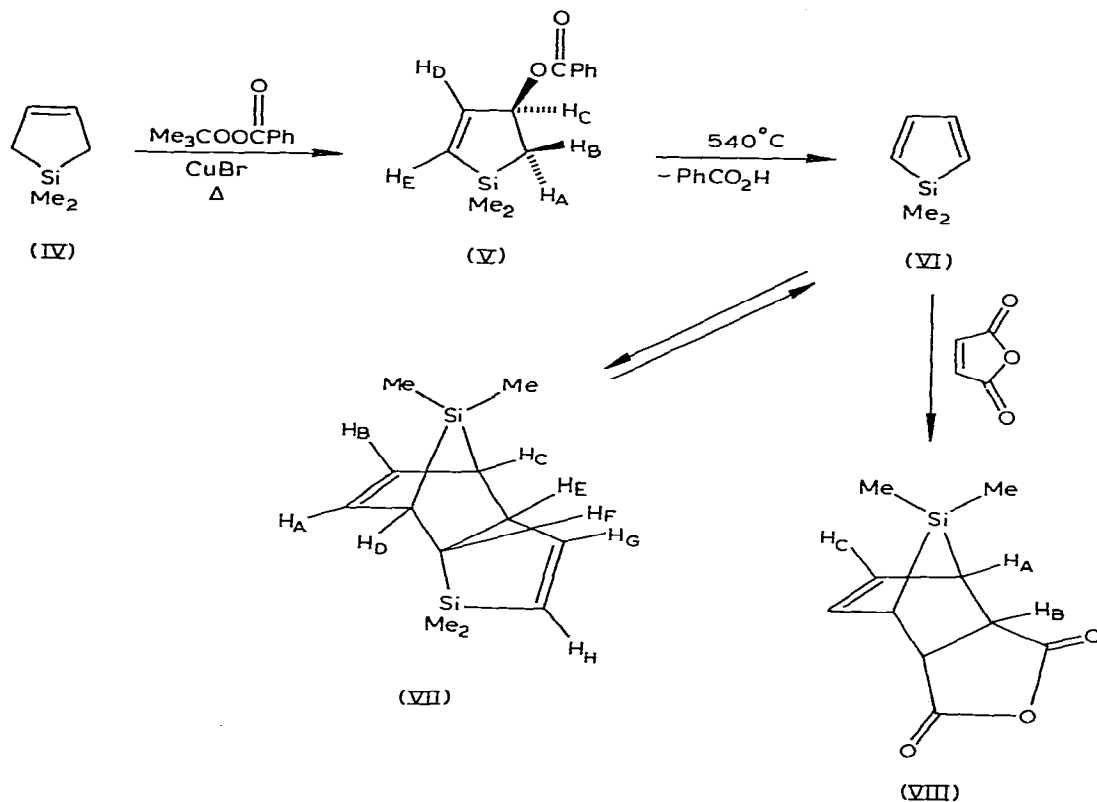


(d of d, 1H, J_{DE} 10 Hz, J_{EC} 2 Hz), 6.75 (d of d, 1H, J_{DC} 3 Hz), 7.28–8.21 (m, 5H); IR (neat), C=O (1720 cm^{-1}); calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{Si}$, 208.09196, measured m/e 208.09133.

Flow pyrolysis (540°C , 0.01 Torr) of V afforded benzoic acid (88%, condensed before the trap) and a yellow liquid which was determined to be VII, the dimer of dimethylsilole: (60% yield based on V); NMR (CDCl_3): δ (ppm), 0.10 (s, 3H), 0.08 (s, 3H), 0.06 (s, 3H), 0.23 (s, 3H), 1.57 (d of d, 1H, J_{CE} 2.2 Hz, J_{CB} 9 Hz), 1.85 (broad d, 1H), 1.99 (broad M, 1H, $h\nu$ at He collapses 1H to d, J_{DF} 6 Hz), 3.60 (d of d of d, 1H), 5.74 (d of d, J_{GE} 2 Hz), 5.80 (overlapped d of d, 1H, J_{AB} 6 Hz), 6.14 (overlapped d of d, 1H), 6.34 (d of d, 1H, J_{HG} 10 Hz, J_{HE} 2.5 Hz); calcd. for $\text{C}_{12}\text{H}_{20}\text{Si}_2$, 220.11036, measured m/e 220.11030.

When maleic anhydride (in DCCl_3) was included in the trap (liquid nitrogen cooled), examination of the resulting solution after pyrolysis revealed that 1,1-dimethylsilole had been trapped as white, crystalline VIII in 66% yield. This same product (VIII) could be quantitatively obtained by heating dimer VII with maleic anhydride at 160°C in a sealed tube for 30 hours. [(VIII): m.p. $89.5\text{--}90.5^\circ \text{C}$; NMR (CDCl_3): δ (ppm) 0.22 (s, 3H), 0.28 (s, 3H), 2.55 (m, 2H, $h\nu$ at H_c collapses to broad singlet), 3.32 (overlapped d of d, 2H, $h\nu$ at H_A collapses to s), 6.28 (overlapped d of d, 2H, $h\nu$ at H_A collapses to s); calcd. for $\text{C}_9\text{H}_9\text{O}_3\text{Si}$ ($P-15$) 193.03210, measured m/e 193.03192.]

Thus, it was obvious that dimer VII was arising from dimerization of 1,1-dimethylsilole in the trap during warming to room temperature. Indeed, direct



observation of monomeric VI was possible by condensing the pyrolysate from V directly into an NMR tube containing DCCl_3 , and cooled to -196°C . PMR spectra recorded at -70°C showed only a singlet at $\delta 0.72$ (6H, SiMe_2) and an AB quartet centered at $\delta 6.40$ (4H, vinyl, $J = 14$ Hz, $\nu_A = 6.78$, $\nu_B = 6.02$). The ^{13}C NMR spectrum at -70°C further confirmed the structure of VI as only the expected two vinyl absorptions ($\delta 131.3$ and 145.6 and a single Si-Me peak ($\delta -5.52$) were observed. On warming the NMR sample in 10° increments to 10°C , the spectrum of dimer VII very slowly appeared. At 37°C dimerization was complete in 15 minutes.

Acknowledgment. The partial support of this work by the Dow Corning Corporation is gratefully acknowledged. A Procter and Gamble Fellowship to G.T.B. is also gratefully acknowledged.

References

- 1 T.J. Barton and G.T. Burns, *J. Organometal. Chem.*, **179** (1979) C17.
- 2 J. Goubeau, T. Kalmar and H. Hofmann, *Ann. Chim. (Paris)*, **659** (1962) 39.
- 3 O.M. Nefedov and M.H. Manakov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1963) 769; *Chem. Abstr.*, **59** (1963) 8780.
- 4 For evidence of the existence, but not isolation of the parent silole see: R.-J. Hwang and P.P. Gaspar, *J. Amer. Chem. Soc.*, **100** (1978) 6626; and E.E. Siefert, K.L. Loh, R.A. Ferrieri and Y.-N. Tang, *ibid.*, **102** (1980) 2285.
- 5 M.S. Kharasch, G. Sosnovsky and N.C. Yang, *J. Amer. Chem. Soc.*, **81** (1959) 5810.