

## Photochemical Reactions of a Silacyclopene with Nitriles Leading to New Organosilicon Ring Systems

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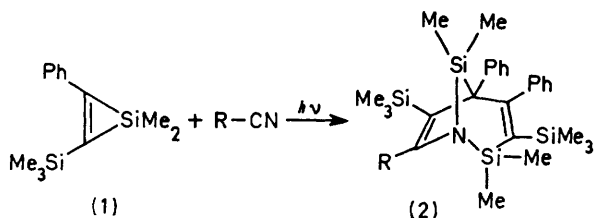
**Summary.** Irradiation of 1,1-dimethyl-2-phenyl-3-trimethylsilylsilacyclopene (**1**) in the presence of RCN (R = Ph, Me, and CH<sub>2</sub>=CHCH<sub>2</sub>) resulted in the formation of aza-2,8-disilabicyclo[3.2.1]octa-3,6-diene derivatives (**2**), whereas the photochemical reaction of (**1**) with acrylonitrile afforded, in addition to (**2**), another new ring system, 1-aza-2,8-disilabicyclo[3.3.0]octa-3,6-diene (**3**).

Four independent groups (Gaspar,<sup>1</sup> Seyferth,<sup>2</sup> Kumada,<sup>3</sup> Sakurai,<sup>4</sup> and their collaborators) have recently reported the preparation of silacycloprenes. Silacycloprenes are thermally stable but quite reactive toward olefins,

acetylenes, and carbonyl compounds under a variety of conditions.<sup>2-4</sup>

We report here a novel reaction of a silacyclopene with nitriles to give new organosilicon ring systems. A solution of the silacyclopene (**1**) (*ca.* 0.15 mmol) and excess of benzonitrile (0.68 mmol) in benzene (0.3 ml) was irradiated under argon with a 450 W high-pressure mercury arc lamp in a quartz n.m.r. tube for 0.5 h. Preparative t.l.c. on silica gel gave the 2:1 addition product (**2a**); 42.6% yield) as white crystals (m.p. 138—139 °C), the structure of which was assigned on the basis of satisfactory elemental analyses and the following spectral data: *m/e* (70 eV) 567 (*M*<sup>+</sup>, 0.3%) and 393 (*M*<sup>+</sup> - PhC≡CSiMe<sub>3</sub>,

100%);  $\lambda_{\max}$  (n-hexane) 256.0 nm ( $\epsilon$  7.800);  $^1\text{H}$  n.m.r. Si-Me singlets at  $\delta$  ( $\text{CCl}_4$ ) -0.92 (9H), -0.32 (3H) -0.16 (9H), 0.14 (3H), and 0.32 (6H), and an aromatic multiplet at 7.0-7.6 (15H). The Si-Me signal at  $\delta$  0.32 splits into two singlets at  $\delta$  0.28 (3H) and 0.32 (3H) in acetone. The occurrence of one  $\text{SiMe}_3$  signal as a singlet at exceptionally high field,  $\delta$  -0.92, indicates the signal to be due to the 6-trimethylsilyl group.

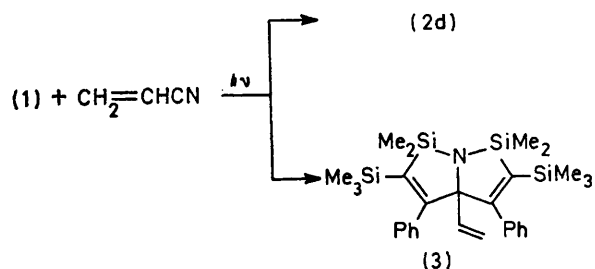


- a, R = Ph  
b, R = Me  
c, R =  $\text{H}_2\text{C}=\text{CHCH}_2$   
d, R =  $\text{H}_2\text{C}=\text{CH}$

Similar reactions of (1) with acetonitrile and allyl cyanide gave white crystals of (2b) and (2c) in 22 and 15% yields, respectively; (2b), m.p. 125-126 °C;  $m/e$  (70 eV) 505 ( $M^+$ , 20.4% and 331 ( $M^+$  -  $\text{PhC}=\text{CSiMe}_3$ , 100%);  $^1\text{H}$  n.m.r. Si-Me singlets at  $\delta$  ( $\text{CCl}_4$ ) -0.56 (9H), -0.26 (9H), 0.04 (3H), 0.23 (3H), 0.30 (3H), 0.35 (3H), and 1.64 (3H); aromatic multiplet at 6.9-7.3 (10H); (2c) m.p. 59-60 °C;  $m/e$  (70 eV) 531 ( $M^+$ , 9.6%) and 73 (100%);  $^1\text{H}$  n.m.r. Si-Me singlets at  $\delta$  ( $\text{CCl}_4$ ) -0.56 (9H), -0.30 (9H), -0.02 (3H), 0.20 (3H), 0.27 (3H), 0.37 (3H), and signals at  $\delta$  2.34 (1H, dd,  $J$  5.0 and 15.0 Hz, =CH-CH), 3.04 (1H, dd,  $J$  5.0 and 15.0 Hz, =CH-CH-), 4.70-5.80 (3H, m, -CH=CH<sub>2</sub>), and 6.80-7.30 (10H, m, Ph).

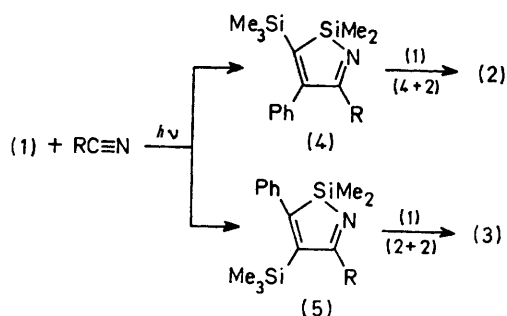
The photochemical reactions of (1) with acrylonitrile gave a somewhat different result. Thus, in addition to (2d) (28% yield); white crystals; m.p. 141-143 °C;  $m/e$  (70 eV) 517 ( $M^+$ , 57.4%) and 342 (100%);  $^1\text{H}$  n.m.r. Si-Me singlets at  $\delta$  ( $\text{CCl}_4$ ) -0.62 (9H) -0.28 (9H), 0.05 (3H), 0.17 (3H), 0.22 (3H), and 0.33 (3H), and signals at  $\delta$  4.70 (1H, dd,  $J$  3.0 and 9.0 Hz, =CH), 5.26 (1H, dd,  $J$  3.0 and 17.0 Hz, =CH), 6.14 (1H, dd,  $J$  9.0 and 17.0 Hz, -CH=), and 6.7-7.2 (10H, m, Ph), compound (3) was obtained (20% yield); white crystals; m.p. 137-138 °C;  $m/e$  (70 eV) 517 ( $M^+$ , 50.8%) and 343 (100%);  $^1\text{H}$  n.m.r. SiMe singlets at  $\delta$  ( $\text{CCl}_4$ ) -0.34 (18H), 0.22 (6H), and 0.35 (6H), and signals at  $\delta$  5.00 (1H, dd,  $J$  3.0 and 10.0 Hz, =CH), 5.30 (1H, dd,  $J$

3.0 and 16.0 Hz, =CH), and 6.4-6.9 (11H, m, -CH= and Ph), was obtained.



Interestingly, these compounds are fairly stable towards protic solvents despite the known instability of the Si-N bond to solvolysis; all the new compounds can be recrystallized from ethanol.

The mechanism of the reaction is not fully elucidated, but it is reasonable to assume the initial formation of (2 + 2) adducts, (4) and/or (5), which give (2) and (3) by (4 + 2) and (2 + 2) processes, respectively (Scheme.)



SCHEME

Addition products similar to (4) and (5) have been reported for acetylenes,<sup>4</sup> but isolation of (4) and (5) in the present reactions failed; apparently they are very reactive and give the final products immediately after their formation.

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<sup>2</sup> D. Seyferth, D. C. Annarelli, and S. C. Vick, *J. Amer. Chem. Soc.*, 1976, **98**, 6382; D. Seyferth, D. P. Duncan, and S. C. Vick, *J. Organometallic Chem.*, 1977, **125**, C5; D. Seyferth, S. C. Vick, M. L. Shannon, T. F. O. Lim, and D. P. Duncan, *ibid.*, 1977, **135**, C37.

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