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Photochemical Reactions of Polysilacycloalka-1,2-dienes: Synthesis of Polysila 1,3-Bridged Cyclopropenes

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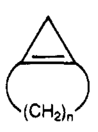
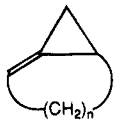
Summary: The photochemical reaction of the hexasilacyclonona-1,2-diene **6** *provides the hexasilabicyclo[6.1.0]non-1(9)-ene* **7** *together with the corresponding ring-contracted derivatives pentasilacycloocta-1,2-diene* **8** *and pentasilabicyclo[5.1.0]oct-1(8)-ene* **9**. *Similarly, the photolysis of the tetrasilacyclohepta-1,2-diene* **10** *yields the tetrasilabicyclo[4.1.0]hept-1(7)-ene* **11**; *however, no ring-contracted compounds are observed in this case.*

In recent years the chemistry of strained unsaturated cyclic compounds has been focused on molecules exhibiting unusual structures and reactivities;[1] e.g., the isolation of strained polysilacycloalkynes[2] and polysilacyclic allenes[3] has been reported. Bicyclo[*n*.1.0]alkenes **1**–**3**, as representatives of highly strained olefins, are of considerable interest.[4] In the series of 1,2-bridged cyclopropenes (**1**), bicyclo[4.1.0]heptene derivatives (*n* = 4) are the smallest representatives which have been isolated so far.[4,5] Previously we observed that such bicyclic systems can be effectively stabilized by introduction of suitable heteroatoms which enable us to isolate several heteroatom-substituted bicyclo[4.1.0]hept-1(6)-enes.[2c,6] Bicyclo[4.1.0]hept-1(2)-ene derivatives (**2**; *n* = 4)[4,7] and 1,3-bridged cyclopropene derivatives (**3**) such as bicyclo[6.1.0]nonene (*n* = 6) could be isolated.[4] Nevertheless, up to now the isolation of smaller ring system has not been reported. Herewith, we wish to report the synthesis of polysila 1,3-bridged cyclopropenes by photochemical transformations of the corresponding polysilacyclic allenes.



1



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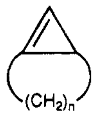

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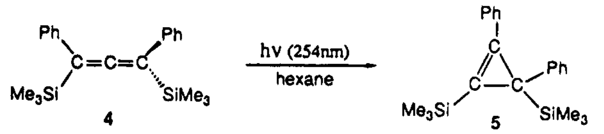
Scheme 1



As an example of an acyclic silyl-substituted allene, the conversion of 1,3-diphenyl-1,3-bis(trimethylsilyl)-propadiene (**4**)[8] was studied. Irradiation of a solution of **4** in hexane with a low-pressure mercury lamp afforded 1,3-diphenyl-2,3-bis(trimethylsilyl)cyclopropene (**5**)[9] in 91% yield. Similarly, after photolysis of the hexasilacyclonona-1,2-diene **6**[3a] under identical conditions the corresponding hexasilabicyclo[6.1.0]non-1(9)-ene **7**[10] was obtained in 59% yield; additionally, the ring-contracted allene **8**[11] and pentasilabicyclo[5.1.0]oct-1(8)-ene **9**[12] were isolated in yields of 14% and 23%, respectively. On the other hand, irradiation of the tetrasilacyclohepta-1,2-diene **10**[3a] gave the tetrasilabi-

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[1] (a) Special issue on strained organic compounds: *Chem. Rev.* **1989,** *89.* (b) Greenberg, A.; Liebman, J. F. *Strained Organic Compounds*; Academic Press: New York, 1978.

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[6] (a) Ando, W.; Hanyu, Y.; Takata, T.; Ueno, K. *J. Am. Chem. Soc.* **1982,** *104,* 4981. (b) Ando, W.; Hanyu, Y.; Takata, T.; Ueno, K. *J. Am. Chem. Soc.* **1984,** *106,* 2216.

[7] Baumann, M.; Köbrich, G. *Tetrahedron Lett.* **1974,** 1217.

[8] Compound **4**: mp 55–56 °C; colorless crystals. Anal. Calcd for $C_{21}H_{28}Si_2$: C, 74.91; H, 8.38. Found: C, 74.51; H, 8.16. HRMS (EI, 20 eV): *m/e* calcd for $C_{21}H_{28}SI_2$ 336.1730, found 336.1725. LRMS (EI, 70 eV): *m/e* 336 (M^+), 263, 248 (100%). ^{1}H NMR (C_6D_6, 90 MHz): δ 0.28 (s, 18H), 6.9–7.8 (m, 10H). ^{13}C NMR (C_6D_6, 22.5 MHz): δ 0.02 (q), 95.1 (s), 125.9 (d), 127.6 (d), 128.6 (d), 137.2 (s), 209.5 (s). ^{29}Si NMR (C_6D_6, 17.6 MHz): δ −4.1. IR (KBr): 1889 (C=C=C), 1595, 1493, 1251, 917 cm^{-1}. UV (hexane): λ_{max} (ϵ) 259 nm (13 000).

[9] Compound **5**: colorless oil. Anal. Calcd for $C_{21}H_{28}Si_2$: C, 74.91; H, 8.38. Found: C, 76.62; H, 8.04. HRMS (EI, 20 eV): *m/e* calcd for $C_{21}H_{28}SI_2$ 336.1730, found 336.1743. LRMS (EI, 70 eV): *m/e* 336 (M^+), 263, 248 (100%). ^{1}H NMR (C_6D_6, 90 MHz): δ 0.21 (s, 9H), 0.23 (s, 9H), 7.0–7.8 (m, 10H). ^{13}C NMR (C_6D_6, 100 MHz): δ −0.6 (q), −0.5 (q), 24.6 (s), 118.7 (s), 125.5 (d), 126.8 (d), 128.4 (d), 128.8 (d), 129.5 (d), 130.1 (d), 130.9 (s), 135.2 (s), 149.8 (s). ^{29}Si NMR (C_6D_6, 17.6 MHz): δ −10.5, 0.9. IR (neat): 1596, 1493, 1250 cm^{-1}.

[10] Compound **7**: colorless oil. Anal. Calcd for $C_{27}H_{46}Si_6$: C, 60.15; H, 8.60. Found: C, 59.99; H, 8.42. HRMS (EI, 20 eV): *m/e* calcd for $C_{27}H_{46}SI_6$ 538.2215, found 538.2201. LRMS (EI, 70 eV): *m/e* 538 (M^+), 465, 392 (100%). ^{1}H NMR (C_6D_6, 400 MHz): δ 0.14 (s, 3H), 0.261 (s, 3H), 0.264 (s, 6H), 0.29 (s, 6H), 0.31 (s, 3H), 0.32 (s, 3H), 0.35 (s, 3H), 0.43 (s, 3H), 0.58 (s, 3H), 0.70 (s, 3H), 7.111 (t, *J* = 7.2 Hz, 1H), 7.116 (t, *J* = 7.2 Hz, 1H), 7.220 (t, *J* = 7.2 Hz, 2H), 7.223 (t, *J* = 7.2 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (C_6D_6, 100 MHz): δ −5.01 (q), −4.95 (q), −4.8 (q), −4.7 (2 × q), −4.6 (q), −4.3 (q), −3.8 (q), −2.1 (q), −0.7 (q), −0.3 (q), 0.8 (q), 24.6 (s), 119.3 (s), 125.7 (d), 128.3 (d), 128.5 (d), 128.6 (d), 129.5 (d), 130.2 (d), 130.7 (s), 136.6 (s), 149.8 (s). ^{29}Si NMR (C_6D_6, 79 MHz): δ −45.2, −41.8, −41.2, −38.2, −25.8, −8.5. IR (neat): 1597, 1489, 1446, 1402, 1249 cm^{-1}. UV (cyclohexane): λ_{max} (ϵ) 301 (12 300), 323 (12 800).

[11] Compound **8**: colorless crystals; mp 156–157 °C. Anal. Calcd for $C_{25}H_{40}Si_5$: C, 62.42; H, 8.38. Found: C, 62.09; H, 8.16. HRMS (EI, 20 eV): *m/e* calcd for $C_{25}H_{40}SI_5$ 480.1976, found 480.1970. LRMS (EI, 70 eV): *m/e* 480 (M^+), 407. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.24 (s, 6H), 0.30 (s, 6H), 0.33 (s, 6H), 0.47 (s, 6H), 0.54 (s, 6H), 7.10 (t, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 4H), 7.59 (t, *J* = 7.8 Hz, 4H). ^{13}C NMR (C_6D_6, 100 MHz): δ −5.3 (q), −4.93 (q), −4.88 (q), −1.5 (q), −0.6 (q), 95.2 (s), 126.9 (d), 128.5 (d), 129.3 (d), 137.8 (s), 210.4 (s). ^{29}Si NMR (C_6D_6, 79 MHz): δ −42.5, −42.3, −16.0. IR (KBr): 1888 (C=C=C), 1596, 1490, 1247 cm^{-1}. UV (hexane): λ_{max} (ϵ) 265 nm (22 900).

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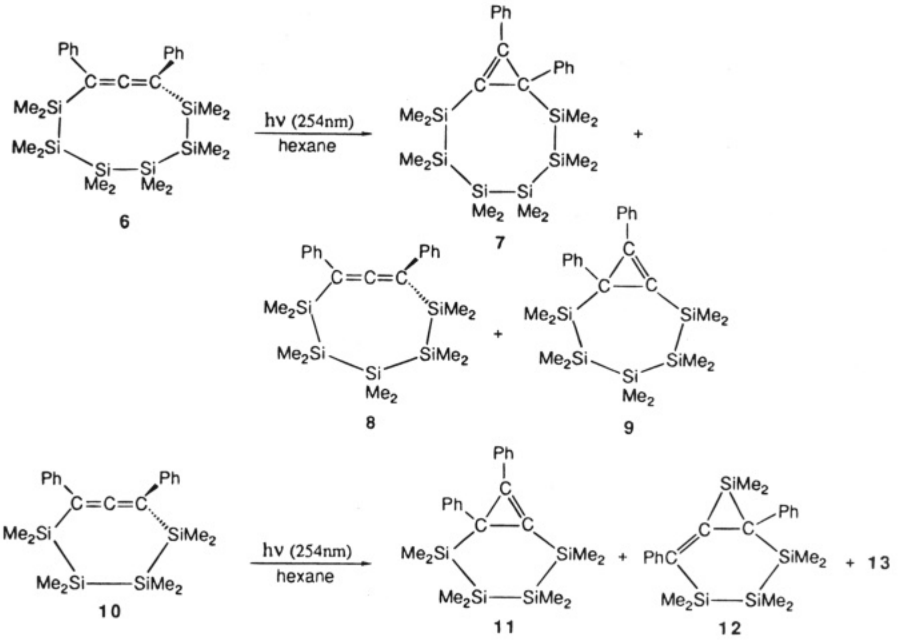
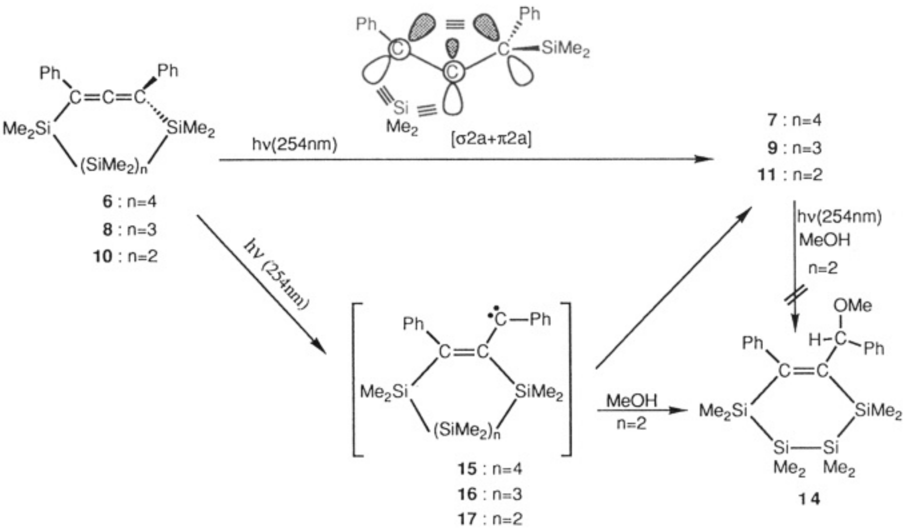
Scheme 2



Scheme 3



cyclo[4.1.0]hept-1(7)-ene **11**[13] in 45% yield and the tetrasilabicyclo[4.1.0]hept-1(2)-ene **12**[14] in 20% yield.[15]

Stierman and Johnson et al. studied several photorearrangements of carbocyclic allenes giving the bicyclo[6.1.0] systems.[16] In the photoreactions of **4**, **6**, and **10**, the pathway is considered to be via a vinylcarbene intermediate or to be a concerted process. To clarify the reaction mechanism, a methanol solution of the

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[12] Compound **9**: colorless oil. Anal. Calcd for $C_{25}H_{40}Si_5$: C, 62.42; H, 8.38. Found: C, 62.20; H. 8.14. HRMS (EI, 20 eV): *m/e* calcd for $C_{25}H_{40}SI_5$ 480.1976, found 480.2007. LRMS (EI, 70 eV): *m/e* 480 (M^+), 407, 392 (100%). ^1H NMR (C_6D_6, 400 MHz): δ 0.12 (s, 3H), 0.277 (s, 3H), 0.282 (s, 3H), 0.285 (s, 3H), 0.31 (s, 3H), 0.33 (s, 3H), 0.34 (s, 3H), 0.42 (s, 3H), 0.60 (s, 3H), 0.63 (s, 3H), 7.10 (t, J = 8.2 Hz, 1H), 7.11 (t, J = 8.2 Hz, 1H), 7.22 (t, J = 8.2 Hz, 2H), 7.26 (t, J = 8.2 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H). ^{13}C NMR (C_6D_6, 100 MHz): δ −6.0 (q), −5.9 (q), −5.3 (q), −4.9 (q), −4.8 (q), −4.7 (q), −1.9 (q), −1.7 (q), −0.7 (q), −0.4 (q), 24.6 (s), 118.4 (s), 125.6 (d), 128.3 (d), 128.9 (d), 129.4 (d), 129.5 (d), 130.0 (d), 130.6 (s), 136.3 (s), 149.8 (s). ^{29}Si NMR (C_6D_6, 79 MHz): δ −44.5, −42.9, −38.0, −25.5, −7.9. IR (neat): 1490, 1445, 1447 cm^{-1}. UV (hexane): λ_{max} (ϵ) 303 (13 000), 318 nm (12 700).

[13] Compound **11**: colorless crystals; mp 59−61 °C. Anal. Calcd for $C_{23}H_{34}Si_4$: C, 65.32; H, 8.11. Found: C, 65.53; H, 8.14. HRMS (EI, 20 eV): *m/e* calcd for $C_{23}H_{34}SI_4$ 422.1738, found 422.1740. LRMS (EI, 70 eV): *m/e* 422 (M^+). ^1H NMR (C_6D_6, 400 MHz): δ 0.10 (s, 3H), 0.27 (s, 3H), 0.30 (s, 3H), 0.31 (s, 3H), 0.36 (s, 3H), 0.38 (s, 3H), 0.48 (s, 3H), 0.58 (s, 3H), 7.0−7.8 (m, 10H). ^{13}C NMR (C_6D_6, 100 MHz): δ −6.0 (q), −5.9 (q), −5.6 (q), −5.5 (q), −2.2 (q), −1.9 (q), −0.9 (q), −0.8 (q), 24.9 (s), 119.1 (s), 125.5 (d), 126.8 (d), 128.5 (d), 128.7 (d), 129.4 (d), 129.8 (d), 131.2 (s), 136.3 (s), 149.8 (s). ^{29}Si NMR (C_6D_6, 79 MHz): δ −46.5, −44.9, −26.6, −11.1 IR (KBr): 1491, 1447 cm^{-1}. UV (hexane): λ_{max} (ϵ) 310 nm (12 000).

[14] Compound **12**: colorless oil. Anal. Calcd for $C_{23}H_{34}Si_4$: C, 65.32; H, 8.11. Found: C, 65.22; H, 8.18. HRMS (EI, 20 eV): *m/e* calcd for $C_{23}H_{34}SI_4$ 422.1738, found 422.1731. LRMS (EI, 70 eV): *m/e* 422 (M^+). ^1H NMR (C_6D_6, 400 MHz): δ −0.14 (s, 3H), −0.07 (s, 3H), 0.09 (s, 3H), 0.13 (s, 3H), 0.30 (s, 3H), 0.45 (s, 3H), 0.56 (s, 3H), 0.72 (s, 3H), 6.9−7.4 (m, 10H). ^{13}C NMR (C_6D_6, 100 MHz): δ −7.6 (q), −5.9 (q), −2.2 (q), −1.2 (2 × q), 0.2 (q), 0.7 (q), 1.4 (q), 45.3 (s), 124.2 (d), 127.3 (d), 127.9 (d), 128.56 (d), 128.63 (d), 128.8 (d), 141.5 (s), 147.8 (s), 168.6 (s), 170.1 (s). ^{29}Si NMR (C_6D_6, 17.6 MHz): δ −46.2, −24.1, −8.6, 12.4. IR (neat): 1597, 1493, 1479, 1247, 1180, 1075 cm^{-1}.

[15] In this reaction the isomer **13** was observed by GCMS (8% GC yield). Although attempts to isolate compound **13** failed, it is most likely another isomeric product, as indicated by the mass spectrum.

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tetrasilacyclohexa-1,2-diene **10** was irradiated with a low-pressure mercury lamp; the methanol-incorporated product **14**[17] was obtained in 54% yield, together with the bicyclo[4.1.0]heptene derivative **11** in 8% yield. The formation of methanol adduct **14** can be explained by the methanol trapping of the vinylcarbene **17**, which was generated by a 1,2-silyl shift. When bicyclo[4.1.0]-heptene derivative **11** was irradiated in methanol, the methanol-incorporated product **14** was not observed. On the other hand, when the hexasilacyclonona-1,2-diene **6** was irradiated in methanol, **7**–**9** were obtained in 81, 6, and 9% yields, respectively, and solvent dependency was not observed in hexane and methanol. Nevertheless, no methanol-incorporated product was found by ^{1}H NMR and GCMS. It is anticipated that there could be two reasons for being unable to trap the vinylcarbene intermediate. One is that the mechanism might be concerted; another may be due to the very short lifetime of the corresponding vinylcarbene intermediates **15** and **16**.[18]

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Supplementary Material Available: Text giving detailed information on the reaction conditions and product isolation (3 pages). Ordering information is given on any current masthead page.

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(17) Compound **14**: colorless oil. HRMS (EI, 20 eV): *m/e* calcd for $C_{24}H_{38}SI_4O$ 454.2000, found 454.2019. LRMS (EI, 70 eV): *m/e* 454 (M^+), 439, 335, 319, 135. ^{1}H NMR (C_6D_6, 90 MHz): δ −0.03 (s, 3H), 0.04 (s, 3H), 0.15 (s, 3 H), 0.29 (s, 3H), 0.336 (s, 3H), 0.342 (s, 3H), 0.39 (s, 3H), 0.69 (s, 3H), 3.28 (s, 3H), 4.03 (s, 1H), 6.9–7.4 (m, 6H), 7.6–7.8 (m, 4H). ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ −8.9 (q), −8.6 (q), −3.0 (q), −2.1 (q), −1.9 (q), −1.6 (q), −1.2 (q), −0.8 (q), 44.8 (d), 50.1 (q), 125.0 (d), 125.3 (d), 127.4 (d), 128.0 (2 × d), 130.6 (d), 141.8 (s), 144.6 (s), 159.5 (s), 160.2 (s). ^{29}Si NMR (C_6D_6, 17.6 MHz): δ −54.1, −15.9, −12.0, 13.6. IR (neat): 2370, 1597, 1251, 1085 cm^{-1}. UV (hexane): λ_{max} (ϵ) 225 (24 300), 264 (3700), 272 nm (3000).

(18) The different lifetimes of vinylcarbene intermediates **15**–**17** are due to easy rearrangements to polysilabicyclo[*n*.1.0]alkenes **7**, **9**, and **11**. Since the tetrasilabicyclo[4.1.0]heptene derivative **11** is a very strained compound, the corresponding vinylcarbene, generated by the photolysis of **10**, has a sufficiently long lifetime to react with methanol. However, since **7** and **9** are less strained than **11**, the corresponding vinylcarbenes of **15** and **16** do not furnish methanol addition products, as the lifetimes of **15** and **16** are too short for reaction with methanol.