CHEMISTRY LETTERS, pp. 1675-1678, 1993.

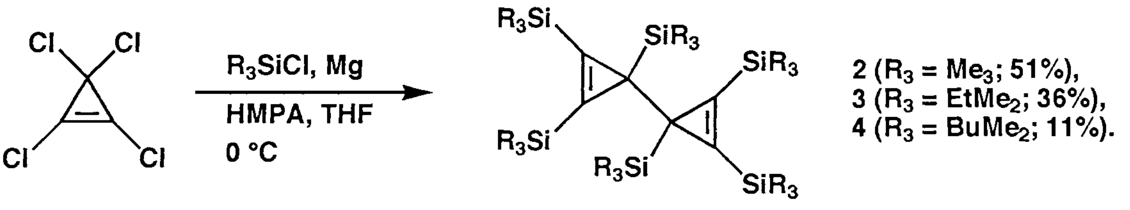
Synthesis, Properties, and Reactions of Hexasilyl-3,3'-bicyclopropenyls and Related Compounds[1)]

Kenkichi SAKAMOTO, Takuya SAEKI, and Hideki SAKURAI
Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980

Silylation of tetrachlorocyclopropene with trialkylchlorosilanes and magnesium in the presence of HMPA gave hexasilyl-3,3'-bicyclopropenyls or conjugated polymers containing both silylcyclopropene and silylallene moieties. Some reactions of these compounds were described.

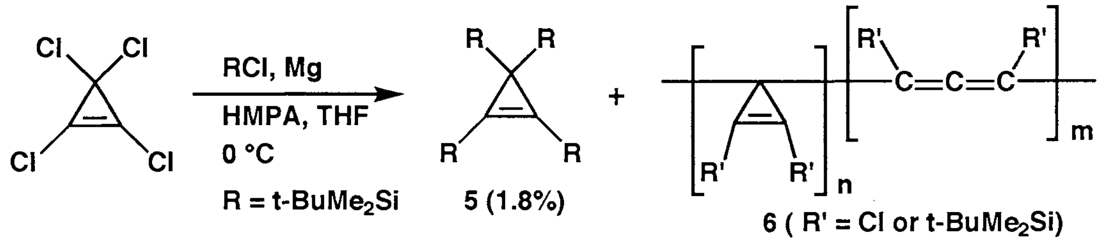
Recently, we have reported preparation and some reactions of hexakis(trimethylsilyl)benzene (**1**) as a member of the fully silylated π-electron systems.[2)] Since silyl groups perturb π-electron systems strongly by both electronic and steric effects, **1** exhibits quite unique properties. For example, the benzene ring of **1** was highly distorted into a chair form and **1** undergoes facile photochemical isomerization to the corresponding Dewar-benzene.[2a)] Moreover, pyrolysis of **1** resulted in the formation of products arising from the rupture of the benzene ring.[2c)] We report herein synthesis and reactions of hexakis(trimethylsilyl)-3,3'-bicyclopropenyl (**2**) which should be the most strained valence isomer of **1**[3-5)] and hence the reaction of **2** should be very much interesting.

The reaction of tetrachlorocyclopropene with trimethylchlorosilane and magnesium in a mixed solvent of THF and HMPA (THF/HMPA = 3/1) at 0 °C gave **2** in 51% yield in addition to a small amount of tetrasilylallene (eq. 1).[6)] The structure of **2** was determined by spectroscopic data.[7)] In the ^{13}C NMR spectrum of **2**, characteristic signals of quaternary and vinyl carbons appeared at 28.36 and 142.15 ppm, respectively. The mass spectrum of **2** showed the molecular ion peak (M^+) at m/z 510 and a substantially strong peak at m/z 255 assignable to the tris(trimethylsilyl)cyclopropenium 2π-aromatic cation.



(1)

Hexakis(ethyldimethylsilyl)- and hexakis(butyldimethylsilyl)bicyclopropenyls (**3** and **4**) were also obtained in 36 and 11% yields, respectively, by the similar reactions of tetrachlorocyclopropene with the corresponding R_3SiCl/Mg/HMPA reagents. On the other hand, the similar silylation reaction with *t*-butyldimethylchlorosilane resulted in the formation of tetrakis(*t*-butyldimethylsilyl)cyclopropene (**5**) in 1.8% yield, together with a polymer **6** as a major product of the reaction (eq. 2).[8)]



(2)

By precipitation, the polymer was obtained as black powder soluble in various organic solvents such as hexane. The molecular weight of **6** amounted to over 10^6 as determined by GPC analysis. The structure of **6** was elucidated by the following spectroscopic data. A considerable amount of chlorine was detected by elemental analysis for **6**. In the ^1H NMR spectrum of **6**, only the *t*-butyldimethylsilyl moiety was observed. The IR spectrum of **6** indicated the presence of both cyclopropene and allene moieties. Since three-membered ring compounds can conjugate with double-bonded species, **6** should be a highly conjugated polymer. Actually, the polymer shows broad electronic absorption whose end is longer than 700 nm.

The bicyclopropenyl **2** exhibits an electronic absorption maximum at 263 nm and a discernible shoulder at around 310 nm. The absorption maximum of **5** is located at 305 nm. These low-energy absorptions are explained in terms of a σ(C-Si)-π interaction which results in the destabilization of the HOMO levels of silyl-substituted cyclopropenes as shown in Fig. 2.

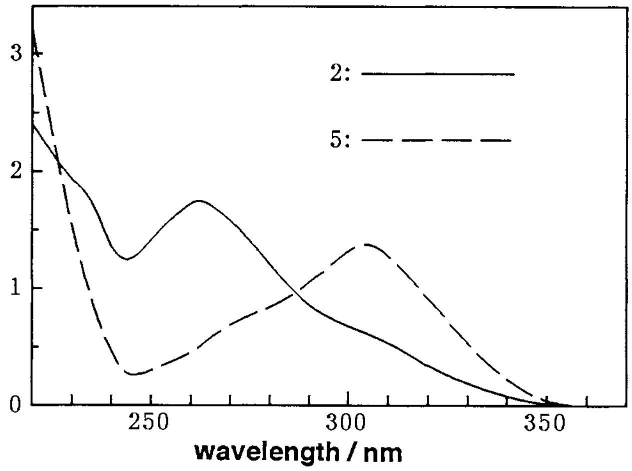


Fig.1. UV spectra of **2** and **5** in hexane.

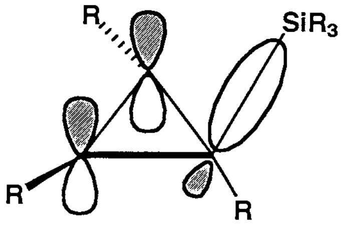
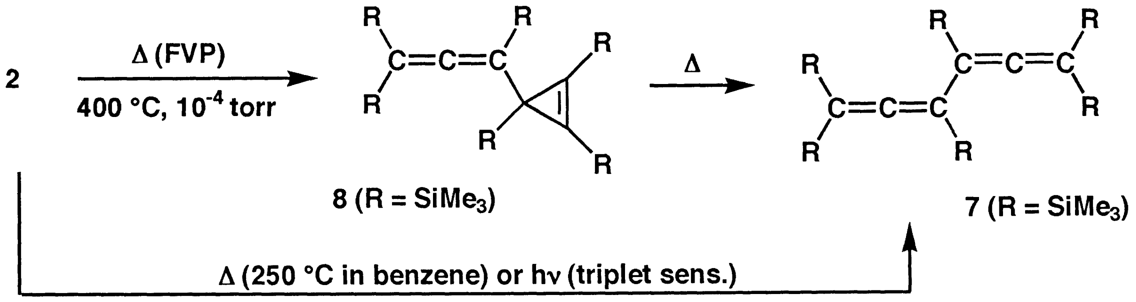


Fig. 2. σ-π interaction in silylcyclopropene.

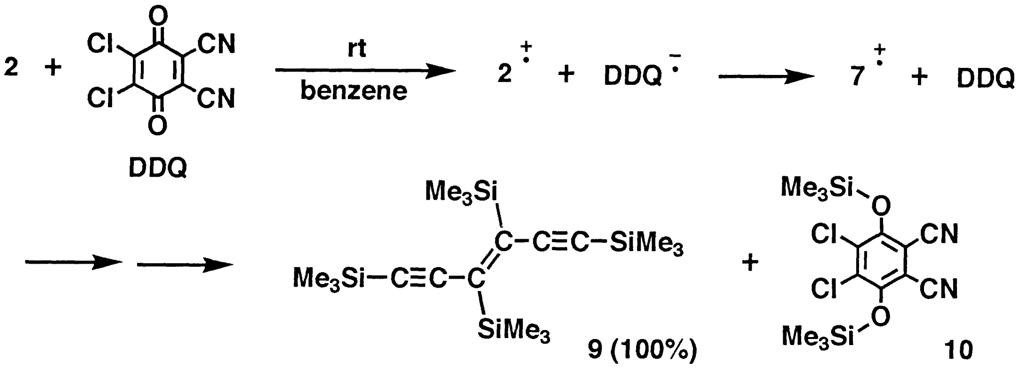
Isomerization of bicyclopropenyls has been widely investigated.[9] Although the most bicyclopropenyls are isomerized to benzene derivatives, pyrolysis of **2** in benzene at 250 °C did not give **1**, but biallene **7** in a quantitative yield.[2c] Since silyl-substituted cyclopropenes were known to isomerize to allene derivatives,[10,11] the isomerization of **2** should proceed in a stepwise manner through the corresponding cyclopropenylallene. Actually, flash vacuum pyrolysis (400 °C, 10^{-4} torr) of **2** gave hexasilylcyclopropenylallene **8**[12] that was isomerized to **7** by further pyrolysis.

Photolysis of **2** in the presence of benzophenone as a triplet sensitizer with a medium-pressure mercury-arc lamp with a Pyrex filter also produced the biallene **7** in 84% yield. Hexasilylbenzene **1** also was converted to biallene **7** under thermochemical conditions.2c) Therefore, **7** should be the most stable compound among the $C_6(SiMe_3)_6$ isomers. The results are summarized in Scheme 1.



Scheme 1.

Oxidation of **2** with dichlorodicyanoquinone (DDQ) gave a desilylated product, tetrakis(trimethylsilyl)-3-hexene-1,5-diyne (**9**) in a quantitative yield;13) the fate of the silyl groups was found in the doubly silylated product of DDQ (**10**) as shown in Scheme 2. In a separate experiment, a catalytic amount of aluminum chloride promoted a quantitative conversion of **2** to biallene **7**. The reaction of **7** with DDQ also gave **9** quantitatively. Therefore, it is possible that the cation radical of **7** is produced as an intermediate in the oxidative transformation of **2** to **9**, since aluminum chloride is well known as a one electron oxidant.14)



Scheme 2.

This work was supported by the Ministry of Education, Science and Culture of Japan (Specially Promoted Research No. 02102004).

References

1) Chemistry of Organosilicon Compound 310.

2) a) H. Sakurai, K. Ebata, C. Kabuto, and A. Sekiguchi, *J. Am. Chem. Soc.*, **112**, 1799 (1990); b) A. Sekiguchi, K. Ebata, C. Kabuto, and H. Sakurai, *ibid.*, **113**, 1464 (1991); c) A. Sekiguchi, K. Ebata,

Y. Terui, and H. Sakurai, *Chem. Lett.*, **1991**, 1417.

3) A. Greenberg and J. F. Liebman, *J. Am. Chem. Soc.*, **103**, 44 (1981).

4) Quite recently, we have found that photolysis of **1** using a low-pressure mercury-lamp gave **2** as a minor product among many isomers of **1**. The details of the reaction will be described elsewhere soon.

5) For unsubstituted 3,3'-bicyclopropenyl, see: W. E. Billups and M. M. Haley, *Angew. Chem., Int. Ed. Engl.*, **28**, 1711 (1989); R. Boese, D. Blaser, R. Gleiter, K.-H. Pfeifer, W. E. Billups, and M. M. Haley, *J. Am. Chem. Soc.*, **115**, 743 (1993).

6) R. Calas, *J. Organomet. Chem.*, **200**, 11 (1980).

7) **2**: Colorless crystals, mp 228–229 °C; ^{1}H NMR ($CDCl_3$, δ) -0.07 (s, 18 H), 0.18 (s, 36 H); ^{13}C NMR ($CDCl_3$, δ) 1.09, 1.15, 28.36, 142.15; ^{29}Si NMR ($CDCl_3$, δ) -10.34, -0.66; MS (70 eV) m/z (%) 510 (M^+, 8.2), 255 (85), 73 (100); HRMS Found: *m/z* 510.2839. Calcd for $C_{24}H_{54}Si_6$: M, 510.2841; UV (hexane) λ_{max}/nm (logε) 263 (3.4), 310 (sh. 2.8); IR (KBr) ν/cm^{-1} 1246, 1678, 2902, 2956.

8) **5**: Colorless crystals, mp 84.5 °C; ^{1}H NMR ($CDCl_3$, δ) -0.06 (s, 12 H), 0.24 (s, 12 H), 0.96 (s, 18 H), 0.99 (s, 18 H); ^{13}C NMR ($CDCl_3$, δ) -2.60, -0.81, 18.56, 19.33, 27.88, 28.17, 29.19, 139.01; ^{29}Si NMR ($CDCl_3$, δ) -1.46, 10.58; MS (70 eV) m/z (%) 496 (M^+, 0.1), 381 (100); HRMS Found: *m/z* 496.3762. Calcd for $C_{27}H_{60}Si_4$: M, 496.3772; UV (hexane) λ_{max}/nm (logε) 305 (3.3); IR (KBr) ν/cm^{-1} 1687. **6**: Black powder, ^{1}H NMR (C_6D_6, δ) -0.1 - 0.7 (bs, 6 H), 0.7 - 1.5 (bs, 9H); IR (CCl_4) ν/cm^{-1} 1713, 1861; Anal. Found: C, 61.87; H, 7.90; Cl, 6.15%. On the basis of an empirical formula determined by the elemental analysis, the yield of the polymer was estimated to be 13%.

9) R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Am. Chem. Soc.*, **87**, 5139 (1965).

10) F. Gruger and G. Szeimies, *Tetrahedron Lett.*, **27**, 1563 (1986); A. Padwa, K. E. Krumpe, L. W. Terry, and M. W. Wannamaker, *J. Org. Chem.*, **54**, 1635 (1989).

11) Both pyrolysis and photolysis of **5** resulted in the quantitative formation of tetrakis(*t*-butyldimethylsilyl)allene.

12) **8**: Colorless crystals, mp 144–147 °C; ^{1}H NMR ($CDCl_3$, δ) -0.07 (s, 9 H), 0.05 (s, 9 H), 0.11 (s, 18 H), 0.21 (s, 18 H); ^{13}C NMR ($CDCl_3$, δ) 0.37, 0.64, 1.00, 1.67, 18.91, 79.85, 85.67, 144.67, 209.28; ^{29}Si NMR ($CDCl_3$, δ) -10.13, -4.45, -4.43, 2.14; MS (70 eV) m/z (%) 510 (M^+, 11), 364 (19), 261 (20), 155 (21), 73 (100); HRMS Found: *m/z* 510.2839. Calcd for $C_{24}H_{54}Si_6$ 510.2841.

13) **9**: ^{1}H NMR (C_6D_6, δ) 0.18 (s, 18 H), 0.26 (s, 18 H); ^{13}C NMR ($CDCl_3$, δ) -1.1, -0.3, 108.2, 110.7, 149.8; ^{29}Si NMR ($CDCl_3$, δ) -18.7, -4.8; HRMS Found: *m/z* 364.1893. Calcd for $C_{18}H_{36}Si_4$: M, 364.1894.

14) H. Bock and U. Lechner-Knoblauch, *J. Organomet. Chem.*, **294**, 295 (1985).

(Received June 29, 1993)