CHEMISTRY LETTERS, pp. 1971-1974, 1982.

NEW [2.2]ORTHOCYCLOPHANES AND [2.2]METACYCLOPHANE HAVING SILICON-SILICON BONDS AS BRIDGING UNITS[1)]

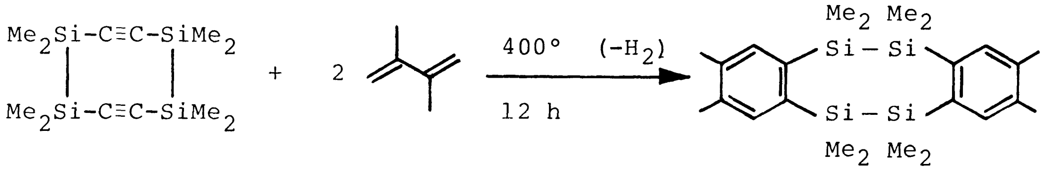
Hideki SAKURAI,* Yasuhiro NAKADAIRA, Akira HOSOMI, and Yuichi ERIYAMA
Department of Chemistry, Tohoku University, Sendai 980

Four new [2.2]cyclophanes having two silicon-silicon bridges were prepared by the Diels-Alder reaction of 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacycloocta-1,5-diyne. These novel cyclophanes and two other related compounds are characterized by various spectra.

Since the first description of di-p-xylene ([2.2]paracyclophane) by Brown and Farthing in 1949,[2,3)] a large number of [2.2]cyclophanes were prepared. Because of the rigid structure with known geometry, these cyclophanes have gathered much attention to studies on physical and chemical properties.[4)]

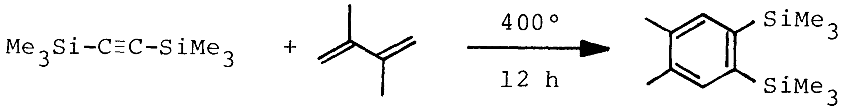
However, no cyclophane having silicon-silicon bond(s) as a bridge, instead of carbon-carbon bonds, has been prepared up to date at least to our knowledge. If such a compound could be prepared, interesting properties would be expected, because a silicon-silicon σ bond can interact efficiently with a directly bound π system due to σ-π conjugation.[5)] In this paper, we describe preparation of several new cyclophane compounds with silicon-silicon bonds as bridging units for the first time.

The reaction of 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacycloocta-1,5-diyne (**1**)[6)] with 2,3-dimethylbutadiene under a forced condition (400°, 12 h) afforded **2** in 56% yield. The Diels-Alder reaction followed by dehydrogenation is a reasonable course to the product. Since the reaction of bis(trimethylsilyl)acetylene with 2,3-dimethylbutadiene under the same condition gave 1,2-dimethyl-1,2-bis(trimethylsilyl)benzene only in 3% yield, the reactivity of the carbon-carbon triple bond of **1** must be enhanced considerably. A possible intermediate, that may be derived by the Diels-Alder reaction of only one triple bond of **1**, must be very reactive due to the internal strain and hence reacts further to give **2**. The compound **2** corresponds to the first 1,2,9,10-tetrasila[2.2]orthocyclophane.



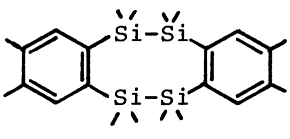
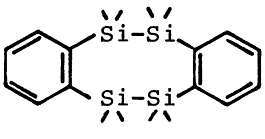
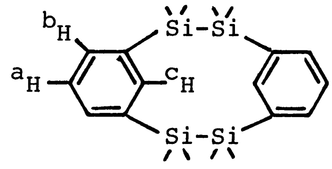
1 **2**

(56%)



(3%)

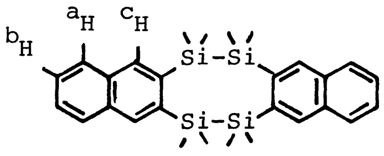
Table 1 Physical Properties of New Compounds[a]

	 (2)	 (3)	 (4)
mp/°C	215-216	122-124	202-203
^{1}H-NMR / δ ppm	0.43 (s, 24H)[b] 2.21 (s, 12H) 7.28 (s, 4H)	0.40 (s, 24H)[c] 7.05-7.50 (m; A_2B_2-type, 8H)	0.26 (s, 24H)[b] 6.43 (d-d, 2H, J_{ac}=0.9, J_{bc}=2.1 Hz, ^{c}H) 7.36 (d-d, 2H, J_{bc}=2.1, J_{ab}=7.5 Hz, ^{b}H) 7.45 (d-d, 4H, J_{ac}=0.9, J_{ab}=7.5 Hz, ^{a}H)
^{13}C-NMR[d] / δ ppm	0.85 (q)[e] 19.52 (q) 136.10 (d)[f] 136.30 (s)[f] 142.11 (s)	0.78 (q)[b] 127.68 (d) 134.21 (d) 145.31 (s)	-5.68 (q)[b] 126.96 (d) 133.04 (d) 135.52 (s) 142.37 (d)
^{29}Si-NMR / δ ppm	-18.34 [e]	-19.25 [b]	-21.73 [b]
MS/ m/e(%)	440 (6.2) 309 (100.0)	384 (28.5) 116 (100.0)	384 (100.0) 369 (62.0)
UV/ λ nm (log ε) in n-hexane	213 (4.72) 241 (sh, 4.45) 284 (sh, 3.04)	239 (sh, 4.24) 282 (sh, 3.26)	239 (4.33) 283 (sh, 2.70)

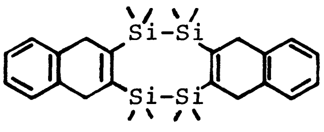
[a] Methyl groups on silicon atoms are omitted from structural formula.
[b] In $CDCl_3$. [c] In CCl_4. [d] Off resonance. [e] In CD_2Cl_2. [f] Measured at 0°C. Signals were not separated at 30°C in CD_2Cl_2. [g] In C_6D_6.

The reaction of 1 with α-pyrone gave unsubstituted [2.2]orthocyclophane (3) in toluene in the presence of triethylamine and [2.2]metacyclophane (4) in bromobenzene in 93 and 22% yield, respectively. It has been reported that a trace amount of acid can catalyze the isomerization of 1,2-bis(trimethylsilyl)benzene to the meta and para isomers.[7] Indeed, prolonged heating of isolated 3 in bromobenzene at 200°C resulted in the isomerization of 3 to 4 in 12% yield. However, the corresponding [2.2]paracyclophane has not been obtained.

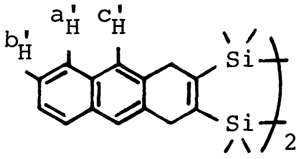
Table 1 (continued)



(5)

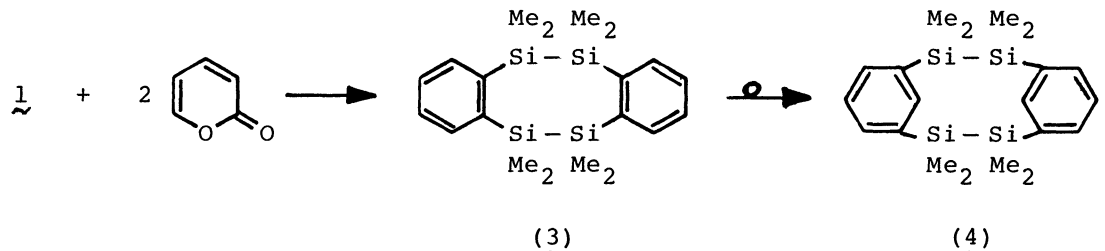


(6)



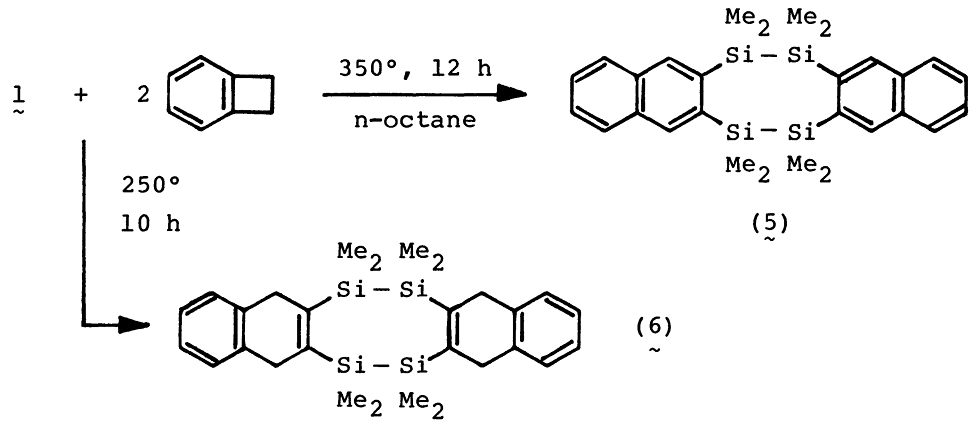
(7)

	(5)	(6)	(7)
mp/°C	175-176	128-131	203-207
^{1}H-NMR / δ ppm	0.51 (s, 24H)^{b} 7.46 (d-d, 4H, J=2.5, 6.3 Hz, ^{b}H) 7.79 (d-d, 4H, J=2.5, 6.3 Hz, ^{a}H) 8.06 (s, 4H, ^{c}H)	0.28 (s, 24H)^{b} 3.32 (s, 8H) 7.10 (s, 8H)	0.33 (s, 24H)^{b} 3.46 (s, 8H) 7.41 (d-d, 4H, J=3.1, 6.3 Hz, $^{b'}$H) 7.63 (s, 4H, $^{c'}$H) 7.80 (d-d, 4H, J=3.1, 6.3 Hz, $^{a'}$H)
^{13}C-NMR / δ ppm	0.78 (q)^{b} 126.31 (d) 127.55 (d) 132.51 (s) 134.53 (d) 141.52 (s)	-0.07 (q)^{b} 37.01 (t) 125.59 (d) 126.38 (d) 136.82 (s) 148.57 (s)	-0.13 (q)^{b} 37.60 (t) 123.77 (d) 124.87 (d) 127.16 (d) 132.25 (s) 136.62 (s) 149.75 (s)
^{29}Si-NMR / δ ppm	-19.17 ^{b}	-21.73 ^{g}	-21.65 ^{b}
MS/ m/e(%)	484 (8.0) 116 (100.0)	488 (6.4) 116 (100.0)	588 (2.5) 43 (100.0)
UV/ λ nm (log ε) in n-hexane	225(4.93), 247(4.93) 278(4.30), 287(4.17) 299(3.79), 315(2.90) 322(2.90), 330(2.60)	219 (sh, 4.40) 244 (sh, 3.86) 271 (3.23)	230(5.19), 261(4.26) 270(4.25), 281(4.16) 292(3.94), 306(3.51) 315(3.39), 319(3.41)



(3) (4)

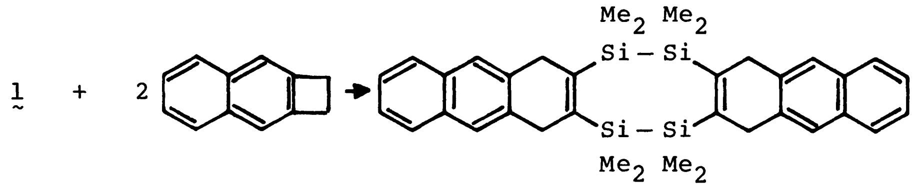
A similar reaction of **1** with benzocyclobutene at 350°C gave an orthocyclonaphtophane (**5**) in 59% yield.



(**5**)

(**6**)

In this case, an intermediate non-aromatic derivative (**6**) was also isolated in 56% yield by heating in octane at 250°C, for 10 h. The reaction of **1** with naphthocyclobutene at 200°C for 5 h resulted in the formation of only non-aromatic derivative (**7**) in 45% yield. Attempted dehydrogenation of **7** by heating at 250°C for 12 h did not yield the aromatized compound.



(**7**)

All the new compounds afforded correct elemental analyses. Table 1 collects physical properties of these compounds which provide firm bases for the structural determination.

References

(1) Chemistry of Organosilicon Compounds 168.

(2) C. J. Brown and A. C. Farthing, *Nature* (London), **164**, 915 (1949).

(3) The first [2.2]metacyclophane and [2.2]orthocyclophane were prepared by M. Pellegrin, *Recl. Trav. Chim. Pays-Bas*, **18**, 458 (1899), and W. Baker, R. Banks, D. R. Lyon, and F. G. Mann, *J. Chem. Soc.*, 27 (1945), respectively.

(4) For reviews, see (a) B. H. Smith, "Bridged Aromatic Compounds", Academic Press, New York, 1964; (b) F. Vogtle and G. Hohner, *Top. Curr. Chem.*, **74**, 1 (1978).

(5) For a review on σ(Si-Si)-π interaction, see H. Sakurai, *J. Organomet. Chem.*, **200**, 261 (1980).

(6) H. Sakurai, Y. Nakadaira, A. Hosomi, and Y. Eriyama, submitted for publication.

(7) D. Seyferth and D. L. White, *J. Organomet. Chem.*, **34**, 119 (1972).

(Received October 25, 1982)