Pericyclynosilanes: Synthesis of a New Class of Cyclic Organosilicon Compounds

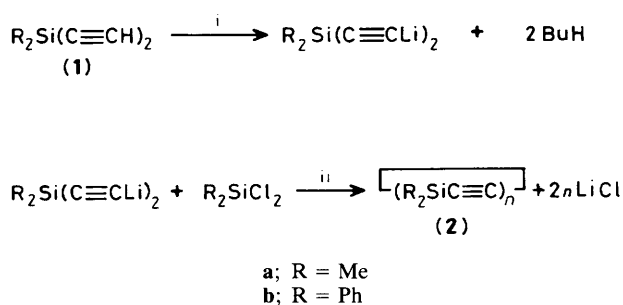**Roberto Bortolin,* Bhukan Parbhoo,* and Scott S. D. Brown**

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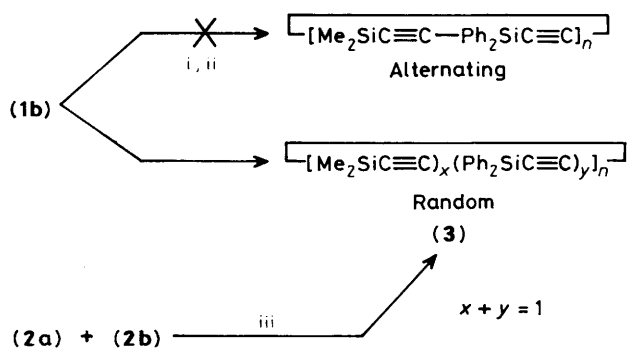
The pericyclynosilanes, systematically known as cyclopoly(silapropynylenes), $(R_2SiC\equiv C)_n$ (where R = Me or Ph, $n \geqslant 5$) have been synthesised, in high yield, by the reaction of the dilithium derivatives of diorganodiethynylsilanes with the corresponding diorganodichlorosilanes, and the dodecamethyl ($n = 6$) and dodecaphenyl ($n = 6$) derivatives have been isolated and fully characterised; when the organic substituents present in the diorganodiethynylsilane differ from those of the diorganodichlorosilane, a redistribution reaction is observed, leading to a product in which the organosilicon units are randomly distributed.

Cyclic species containing alternating acetylenic units have recently been the subject of much attention, because of both their unusual orbital interactions[1] and their potential co-ordination chemistry.[2] Pericyclynes, macrocyclic molecules with alternating Me_2C and $C\equiv C$ units, have been reported.[3]

Herein, we report the synthesis of an analogous class of cyclic compounds containing $R_2SiC\equiv C$ units, the pericyclynosilanes (2). Although compound (2; R = Me, $n = 3$) has been synthesised by the extrusion of dimethylsilylene at high temperature,[4] higher homologues of this class of compounds

$$R_2Si(C\equiv CH)_2 \xrightarrow{\ i\ } R_2Si(C\equiv CLi)_2 + 2\,BuH$$
$$(1)$$

$$R_2Si(C\equiv CLi)_2 + R_2SiCl_2 \xrightarrow{\ ii\ } \overline{[(R_2SiC\equiv C)_n]} + 2n\,LiCl$$
$$(2)$$

a; R = Me
b; R = Ph

Scheme 1. *Reagents:* i, BuLi (2 equiv.) in thf, room temp., 3 h; ii, thf, room temp., 8 h; (**2a**) and (**2b**) are mixtures of cyclic species with different values of *n*, and can be purified by precipitation in MeOH (95 and 93% yield, respectively).

(**1b**) →[i, ii] $\overline{[Me_2SiC\equiv C-Ph_2SiC\equiv C]_n}$
Alternating

(**1b**) → $\overline{[Me_2SiC\equiv C)_x(Ph_2SiC\equiv C)_y]_n}$
Random
(**3**)

(**2a**) + (**2b**) ──[iii]──→ $x + y = 1$

Scheme 2. *Reagents:* i, BuLi (2 equiv.) in thf, room temp., 3 h; ii, Me$_2$SiCl$_2$ in thf, room temp., 8 h; iii, trace amount of the dilithium derivative of (**1a**) or (**1b**) in thf, room temp., 8 h; the mixture of cyclic species (**3**) may be purified by precipitation in MeOH (96% yield).

have not been reported. Our synthetic route is a room temperature reaction that leads to compounds (**2**) with various alkyl or aryl substituents (Scheme 1). Addition of BuLi (2 equiv.) to a tetrahydrofuran (thf) solution of the diorgano-diethynylsilane[5] (**1**) followed by the addition of the diorgano-dichlorosilane (1 equiv.) affords the desired compound (**2**) in >90% yield. Kruerke[5] reported that the reaction between the diorganodichlorosilane and the dilithium or diGrignard acetylide did not lead to the formation of this type of cyclic compound.

Compounds (**2a**) and (**2b**) have been characterised by ^{29}Si and ^{13}C n.m.r. spectroscopy† and h.p.l.c. analysis. The data

† *Selected physical and spectroscopic data:* n.m.r. spectra were recorded in CDCl$_3$ using a Bruker WM 360 MHz spectrometer.
  (**2a**): ^{13}C: δ 110.75—110.14 (m, C≡C); ^{29}Si: δ −41.23 to −42.00 (m, SiC≡C).
  (**2a**), *n* = 6: ^{13}C: δ 110.75 (s, C≡C), −0.12 (s, Me); ^{29}Si: δ −41.32 (s); *m/z* 492.1413 (*M*$^+$ calc. 492.1433).
  (**2b**): ^{13}C: δ 111.14—110.42 (m, C≡C); ^{29}Si: δ −47.97 to −50.09 (m, SiC≡C).
  (**2b**), *n* = 6: ^{13}C: δ 134.84 (C^{2}Ph), 131.39 (C^{1}Ph), 130.31 (C^{4}Ph), 127.98 (C^{3}Ph), 110.87 (s, C≡C); ^{29}Si: δ −49.74 (s); *M*(v.p.o.) 1240 (calc. 1236).
  (**3**): ^{13}C: δ 113.90 (m, C≡C), 110.61 (m, C≡C), 107.03 (m, C≡C); ^{29}Si: δ −39.97 to −41.39 (m, Me$_2$Si), −49.58 to −50.53 (m, Ph$_2$Si).
  (**4**): ^{13}C: δ 135.67—127.92 (m, Ph), 95.13 (s, ≡CH), 87.59 (s, Si-C), 26.18—13.61 (q, Bu), −2.90 (s, Me); ^{29}Si: δ −19.02 (s); *m/z* 210 (*M*$^+$).
  (**5**): ^{13}C: δ 134.20—127.77 (m, Ph), 96.44 (s, ≡CH), 86.24 (s, Si-C), −2.46 (s, Me); *m/z* 222 (*M*$^+$).

$$MePhSi(C\equiv CH)_2 \xrightarrow{\ i,\ ii\ } BuMePhSiC\equiv CH + HC\equiv CH$$
$$(4)$$

$$(2b) \xrightarrow{\ iii,\ iv\ } MePh_2SiC\equiv CH$$
$$(5)$$
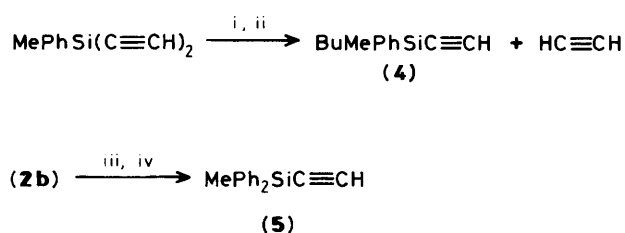
Scheme 3. *Reagents:* i, BuLi (3 equiv.) in thf, room temp., 3 h; ii, H$_2$O/HCl; iii, MeLi (*n* equiv.) in thf, room temp., 3 h; iv, H$_2$O/HCl.

$$\overline{(SiC\equiv C)_m}Li + \overline{(SiC\equiv C)_n}$$
$$(6)\qquad\qquad (7)$$

↓

$$\left[\begin{array}{c} \overline{(Si-C\equiv C)_n} \\ \overline{(SiC\equiv C)_m}Li \end{array} \right]$$

$$\overline{(SiC\equiv C)_{m+x}} + Li\overline{(C\equiv CSi)_y} \qquad \overline{(SiC\equiv C)_{m+n}}Li$$
$$(8)\qquad\qquad\qquad (9)\qquad\qquad\qquad\qquad\qquad (10)$$
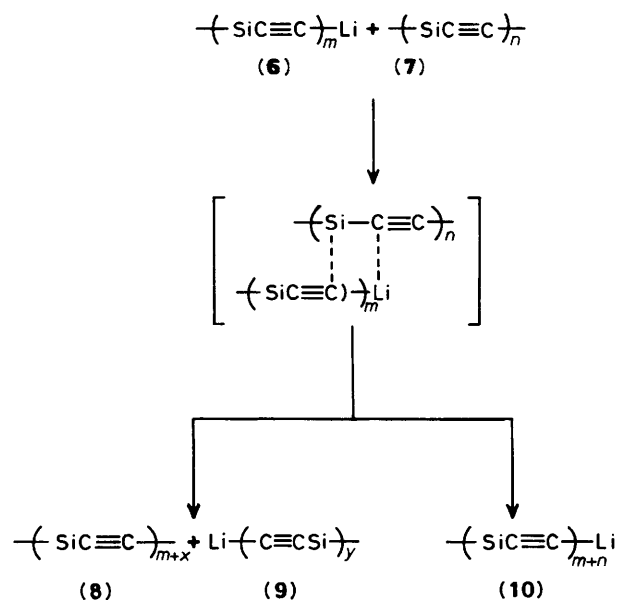
Scheme 4

show that the products obtained are a mixture (4 ≤ *n* ≤ 25) of cyclic species consisting of alternating R$_2$Si and C≡C units. Furthermore, signals due to end groups in non-cyclic species were not observed.

Compound (**2**; R = Me, *n* = 6) (structure confirmed by mass spectral and n.m.r. data†), can be isolated from the mixture (**2a**) by sublimation and subsequent recrystallisation from toluene. H.p.l.c. analysis shows that this compound constitutes *ca.* 65% of (**2a**).

Compound (**2**; R = Ph, *n* = 6), confirmed by v.p.o. measurements and n.m.r. data, can be isolated by fractional precipitation from MeOH–thf (1:1). H.p.l.c. analysis shows that this compound constitutes *ca.* 50% of (**2b**).

Diphenyldiethynylsilane (**1b**) reacts, *via* its dilithium derivative, with dimethyldichlorosilane to yield (**3**) (Scheme 2). The ^{29}Si and ^{13}C n.m.r. spectra† of (**3**) show that the product obtained is a mixture of cyclic species with randomly distributed Me$_2$SiC≡C and Ph$_2$SiC≡C units,[6] whereas a regular alternating pattern might have been expected (Schemes 1 and 2). The mixture of cyclic species (**3**) is also obtained when the mixtures (**2a**) and (**2b**) are equilibrated, the reaction being catalysed by dilithium derivatives of (**1a**) or (**1b**) (Scheme 2). The randomisation occurring by condensation and by equilibration to yield (**3**) suggests that the lithium derivatives of the

diorganodiethynylsilanes are responsible for the redistribution reactions. The redistribution process is further supported by the detection of $(2; R = Me, n = 5)$ in the mixture $(2a)$ by mass spectrometry† because only cyclic species with n being an even number would be formed in the absence of any such process (Schemes 1 and 2).

We have found that BuLi reacts with methylphenyl-diethynylsilane and MeLi with $(2b)$, displacing one ethynyl group, to produce quantitatively (4) and (5), respectively (Scheme 3). Similar reactions for cyclosiloxanes and cyclosilanes with MeLi have also been reported.[7] The redistribution reactions observed in the synthesis of pericyclynosilanes can be interpreted as the nucleophilic attack of the silylethynyl-lithium species (6) at the silicon atom of the rings or growing chains (7) leading to (8) and (9) if (7) is an intermediate open chain, and (10) if (7) is a ring (Scheme 4). The repetition of the redistribution process allows the random exchange of R_2Si groups among chains and the formation of cyclic species with n being an odd number. Rings can also be formed by 'back-biting' of lithium-terminated chains. The stocheiometric amounts of (1) and R_2SiCl_2 which give (2) and (3) drive the redistribution process towards termination by $\alpha-\omega$ elimination of LiCl. We are currently assessing the molecular orbital 'picture' of these cyclic species by photoelectron spectroscopy and theoretical calculations, investigating their co-ordination chemistry, and using the route to pericyclynosilanes as a general method for the synthesis of cyclic acetylenic species containing heteroelements.

References

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