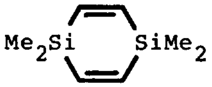
Tetrahedron Letters,Vol.23,No.5,pp 543-546,1982 0040-4039/82/050543-04$03.00/0
Printed in Great Britain

POLYSPIRO DISILACYCLOHEXADIENES
A NOVEL SERIES OF COMPOUNDS SHOWING SPIROCONJUGATION[1]

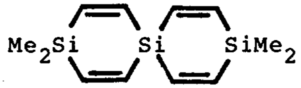
Hideki Sakurai, Takeshi Koyama, Mitsuo Kira, Akira Hosomi and Yasuhiro Nakadaira
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980 Japan

Summary: Three novel unsaturated spirocompounds with silicon as spiro atom(s) have been prepared. These constitute the first series of "polyspirene" and show interesting spectral properties.

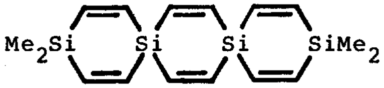
A number of spiroconjugated compounds has been prepared since the idea of spiroconjugation was introduced.[2,3] However, there has been no series of compounds corresponding to "polyspirene". We now report the first series of compounds in which polyspiroconjugation may be expected. Unsaturated spirocompounds with silicon as spiro atoms are of special interest, since the inclusion of 3d orbitals can cause a considerable increase of the spiro LUMO splitting.[4]



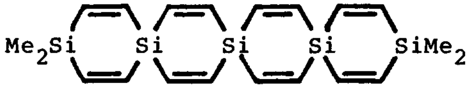
1



2



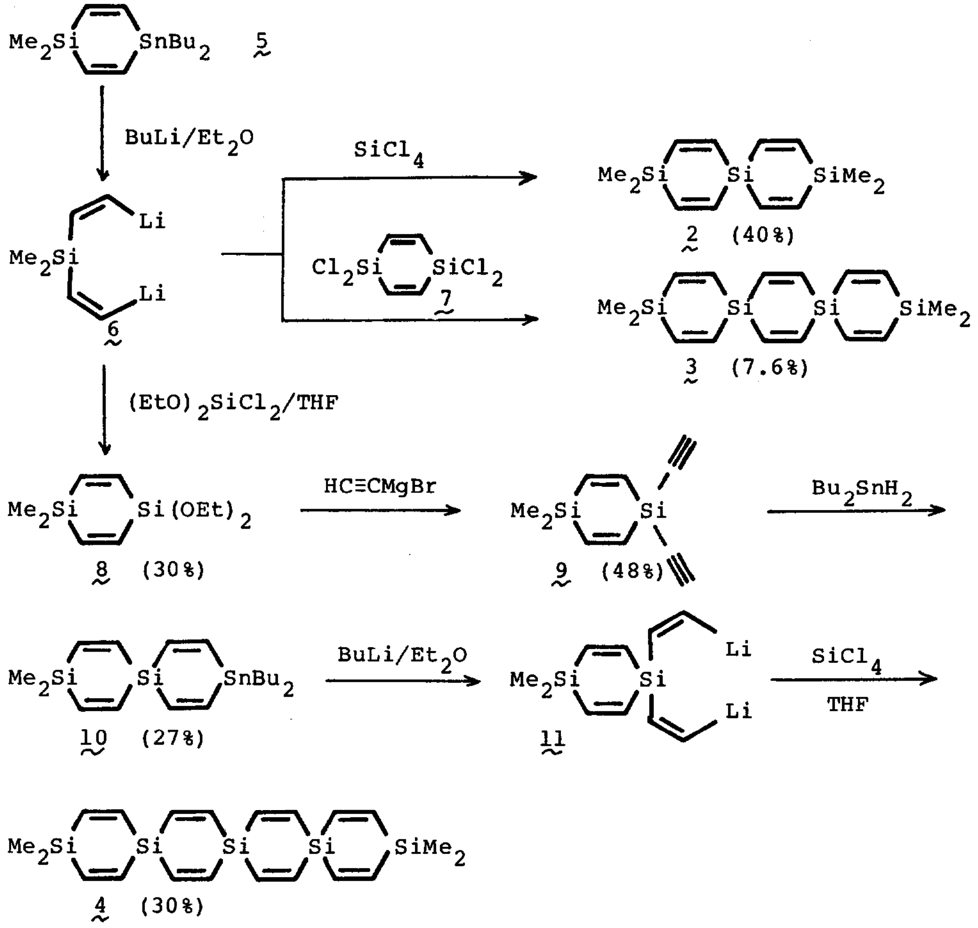
3



4

The synthetic route to these compounds is depicted in Scheme 1. The key intermediate, bis(2-lithioethenyl)dimethylsilane (**6**), was prepared by the Sn/Li transmetallation reaction from 3,3-dimethyl-6,6-dibutyl-3-sila-6-stanna-1,4-cyclohexadiene (**5**).[5] The reaction of **6** with tetrachlorosilane and 3,3,6,6-tetra-chloro-3,6-disila-1,4-hexadiene (**7**)[6] gave **2** and **3**, respectively. The reaction of **6** with dichlorodiethoxysilane gave **8**, the precursor of 3,3-dimethyl-6,6-diethynyl-3,6-disilacyclohexadiene (**9**).[7,8] Hydrostannylation of **9** with

Scheme 1



dibutylstannane catalyzed by 2,2'-dicyano-2,2'-azopropane (AIBN) gave a spiro-compound (10),[9] which was converted to 4 by transmetallation followed by the reaction with tetrachlorosilane. All new compounds gave satisfactory elemental analyses and/or high resolution mass spectra. Some representative physical data of 2, 3 and 4 are summarized in Table 1.

The most interesting and striking fact found in the series of compounds is red shift in the uv spectra from 2 to 3 and from 3 to 4. Since the parent compound 1 shows only end absorption at 190 nm (ε = 7,000), this fact indicates that silicon atoms can relay spiroconjugation effectively.

Both monospiro and dispiro compounds (2 and 3) gave anion radicals on contact with potassium metal in dimethoxyethane (DME) at -90°. The experimental spectrum of $2^{\bar{\cdot}}$ was satisfactorily computer-simulated with two hfcc values, 1.68G (4H) and 1.40G (4H), indicating delocalization of the spin into two rings.

Table 1 Properties of New Compounds

Compound	mp[a] (°C)	^{1}H NMR[b] (δ ppm)	^{13}C NMR[c] (δ ppm)	^{29}Si NMR[d] (δ ppm)	UV (ε)[e] (nm)
2	77 - 78	0.21 (s, $SiCH_3$)	- 1.44	-57.67	197 (44,000)
		6.79 (d, J=20.1 Hz)	146.41		
		6.90 (d, J=20.1 Hz)	152.03		
3	164.5-165.5	0.20 (s, $SiCH_3$)	- 1.40	-57.50	213 (64,000)
		6.79 (d, J=18.9 Hz)	146.50	-26.60	
		6.87 (s)	148.99		
		7.01 (d, J=18.9 Hz)	152.62		
4	195 - 196	0.16 (s, $SiCH_3$)	-1.37	-58.2	216 (72,000)
		7.00 (brs, 4H)	146.94	-57.9	
		7.03 (brs, 4H)	149.22	-27.5	
		7.06 (brs, 8H)	149.94		
			152.94		

[a] Uncorrected. [b] In CCl_4 with CH_2Cl_2 (δ=5.43 ppm) as a standard. [c] In $CDCl_3$, $\delta(CDCl_3)$=76.96 ppm. [d] In $CDCl_3$. Chemical shirts are relative to Me_4Si. [e] In n-hexane.

No significant temperature effect was observed. In strong contrast, however, Gerson et al. have reported that esr spectra of spiro[5.5]undeca-1,4,6,9-tetraene-3,8-dione indicate an essential localization of the spin population on one dienone moiety.[10]

A broad quintet with hfcc of 2.90G was obtained for **3**$^{\overline{\cdot}}$, apparently indicating that the spin resided mostly in the central ring. However, since the anion radical of **1** in the same condition revealed a larger hfcc (3.17G) for vinyl protons,[11] the spin also delocalized into outer rings of **3** in some extent.

Further studies are in progress on this new interesting system.

Acknowledgement: This work was supported in part by a grant-in aid (No. 543007) of the Ministry of Education. We also thank Toshiba Silicone Co., Ltd., for a gift of chlorosilanes.

References and Notes

(1) Chemistry of Organosilicon Compounds 154.

(2) (a) H. E. Simmons and T. Fukunaga, J. Am. Chem. Soc., **89**, 5208 (1967). (b) M. D. Gordon, T. Fukunaga and H. E. Simmons, ibid., **98**, 8401(1976).

(3) M. F. Hoffmann, A. Imamura and G. D. Zeiss, J. Am. Chem. Soc., **89**, 5215 (1967).

(4) M. C. Böhn and R. Gleiter, J. C. S. Perkin II, 443 (1979).

(5) G. Märkl, H. B. Baier and R. Lieble, Synth., **12**, 842 (1977).

(6) E. A. Chernyshev, N. G. Komalenkova and S. A. Bashkirova, Zh. Obsh. Khim., **41**, 1175 (1971).

(7) **8**: an oil; bp 76-77°C/2 mmHg; MS *m/e*(%) M$^+$ 228(1), 213(15), 175(100); ^{1}HNMR δ (CCl$_4$) 0.17(s, 6H, SiMe), 1.23(t, J=8Hz, 6H, CH$_3$), 3.27(q, J=8Hz, 4H, -CH$_2$-), 6.83(d, J=20Hz, 2H, =-H), 7.02(d, J=20Hz, 2H, =-H).

(8) **9**: mp. 87°C; MS *m/e*(%) M$^+$ 188(6), 173(100); ^{1}HNMR δ (CCl$_4$) 0.16(s, 6H, SiMe), 2.52(s, 2H, ≡CH), 6.88(d, J=20Hz, 2H, =-H), 7.68(d, J=20Hz, 2H, =-H).

(9) **10**: an oil; MS *m/e*(%) M$^+$ 424(5), 365(68), 78(100); ^{1}HNMR δ (CCl$_4$) 0.13 (s, 6H, SiMe), 0.70-1.76(m, 18H, n-Bu), 6.90(d, J=20Hz, 2H, =-H), 7.43(d, J=20Hz, 2H, =-H), 7.03(d, J=20Hz, 2H, =-H), 7.02(d, J=20Hz, 2H, =-H).

(10) F. Gerson, R. Gleiter, G. Moshuk and A. S. Dreiding, J. Am. Chem. Soc., **94**, (1972).

(11) E. G. Janzen, J. B. Pickett and W. H. Atwell, J. Am. Chem. Soc., **90**,2719 (1968), reported the first esr spectra of **1**$^{\overline{\cdot}}$ with hfcc values of 3.04G and 0.24G. However, the reported spectra was not free from coupling with potassium. Our hfcc values of **1**$^{\overline{\cdot}}$ are in G: 3.17 (vinyl H), 0.25 (CH$_3$) and 6.85 (^{29}Si).

(Received in Japan 23 October 1981)