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# A Bridged Spiro[6.6]silatridecane via Double 7-endo Radical Cyclisation

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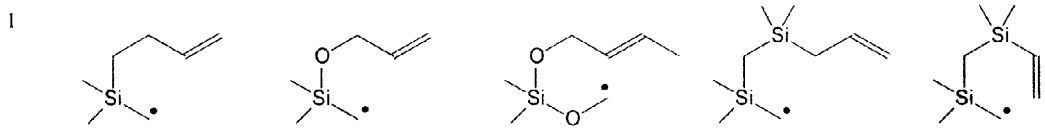
**Abstract**

The double intramolecular radical induced reaction of **5** gives in a highly regioselective reaction via a 7-endo mode the tricyclic silaalkane **7** in 42% yield. In addition. The bicyclic trisilane **8** also formed by a 7-endo cyclisation, is obtained in 33% yield. The structure of **7** has been confirmed by X-ray structure analysis.


*Key words*: Radical cyclisations, Si-heterocylces, Silacyclopentadiene, Disilacycloheptanes

The regioselectivity in the cyclisation of hex-5-enyl and hept-6-enyl radicals depends on the kinetic or thermodynamic control under which these reactions are run [1]-[4]. In addition substituents effects as well as heteroatoms in the chain connecting the double bond and the carbon centered radical exert a strong influence on the size of the ring to be formed [5][6]. Whereas hex-5-enyl radicals lead in a 5-exo mode to cyclopentyl radicals under kinetic control, 2-silahex-5-enyl radicals **I** lead to a mixture of cyclopentane and cyclohexane derivatives [7]. Similarly, five- and six-membered ring compounds are obtained from 2-sila-3-oxa-hex-5-enyl radicals **II** [8]-[10]. The intramolecular cyclisations of radicals with a silaketal group in the chain like **III** proceed preferentially by an endo mode and give predominantly sevenmembered ring compounds [11][12].



I II III IV V

In the course of the preparation of spiro- and polycylic silaalkanes we investigated the cyclisation of radicals like **IV** and **V** containing 2 Si atoms. The required siloles **5** and **6a** were prepared via the siloles **3** and **4** by reductive cyclisation of the bis(phenylethynyl)-silanes **1**

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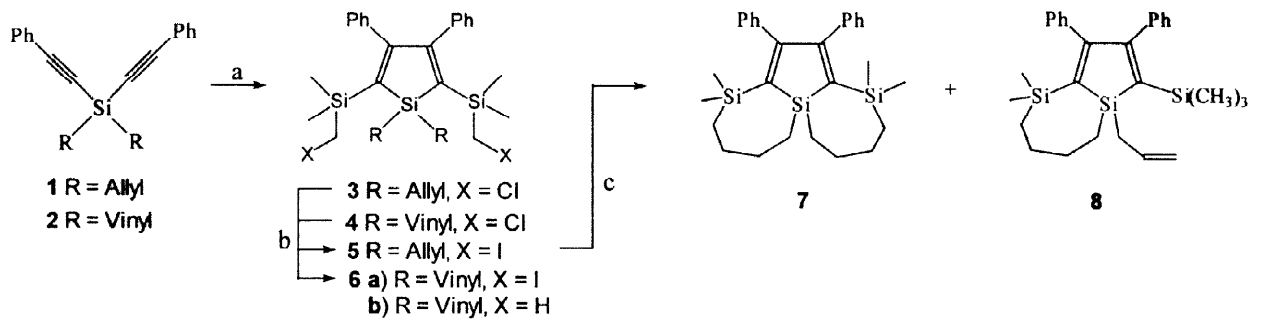
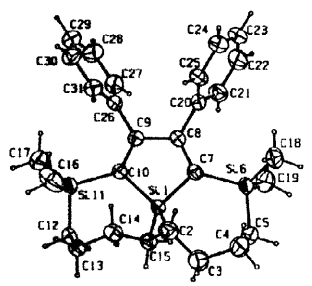
and **2** in overall yields of 23% and 20% respectively (Scheme) [13]. It is worth mentioning that no siloles could be obtained when the dianions, formed in the reaction of **1** or **2** with Li-naphthalene [14], were treated with $BrCH_2(CH_3)_2SiCl$. The siloles **5** and **6a** were readily obtained by reaction of **3** and **4** by $S_N2$ reactions with $I^-$ ions [15].

Scheme




a) $LiC_{10}H_8$, THF, r.t., 3h; **1** or **2** added at -70°C, 15min; $ClCH_2Me_2SiCl$ added at -70°C, then to r.t.[13][14] b) NaI / butanone, reflux, 24h [15]; c) $Bu_3SnH$, AIBN, $C_6H_6$.

The radical reactions were performed under standard conditions by heating a mixture of **5**, 2 molequiv. $Bu_3SnH$ and AIBN in $C_6H_6$ and gave the tricyclic silaalkane **7** with two seven membered rings and the bicyclic silaalkane **8** with one sevenmembered ring in 42% and 33% yield. No 6-exo products have been detected. The X-ray structure analysis of **7** clearly shows the arrangement of the two seven membered rings (Figure)[16]. The bond angle $CH_2$- Si(1)$CH_2$ (C(2)-Si(1)-C(15)) is slightly larger than that in the $(CH_3)_2Si$ groups C(16)-Si(11)-C(17).



Selected bond distances (Å) and bond angles (°)

Si(1)-C(7) 1.867(2), Si(1)-C(2) 1.875

Si(6)-C(7) 1.860(3), Si((6)-C(5) 1.887

C(7)-Si(1)-C(10) 93.72(11), C(2)-Si(1)-C(15) 112.71(15)

Si(6)-C(7)-Si(1) 121.25(13), C(16)-Si(11)-C(17) 110.3(2)

Figure. Molecular structure of **7** (thermal ellipsoids at 50% probability level)

When **6a** was submitted to the same reaction conditions, only reduction of the $CH_2$-I groups was observed to give **6b** in 80% yield. No bi- or tricyclic product is formed under these conditions. Our results might suggest, that the intramolecular cyclisation of a radical of type IV has a high propensity for a 7-endo- rather than a 6-exo reaction, whereas a type V radical leads to reduction rather than a 6-endo mode cylisation.

## Experimental

**General.** For experimental details and analytical instrumentation see [13].

The siloles **3 or 4** were prepared as described with $ClCH_2(CH_3)_2SiCl$ as trapping agent [13][14]. **3**: 68%. $R_f$ (hexane:$Et_2O$=50:1): 0.32. IR: 1205(s);$^1$H NMR: 0.087(s, 12H); 2.06(d, J=7.7Hz, 4H); 2.39(s, 4H); 4.92-5.06(m, 4H); 5.77-5.91(m, 2H); 6.81-6.84(m, 4H); 7.06-7.08(m, 6H). $^{13}$C NMR: -2.27(q); 20.15(t); 31.15(t); 114.41(t); 126.79(d); 127.19(d); 128.46(d); 133.01(d); 138.50(s); 141.94(s); 172.84(s). $^{29}$Si NMR: -8.108; 20.213. MS: 526($M^+$, 1); 485(14); 443(18); 407(16); 343(22); 277(89); 173(72); 159(45); 145(100); 129(51).

**4**: 67%. $R_f$ (hexane:$Et_2O$=50:1): 0.15. IR: 3000(s); 1252(s); 1005(s);$^1$H NMR: -0.016(s, 12H); 2.42(s, 4H); 6.12(dd, J=19.1Hz, 5.1Hz, 2H); 6.25(dd, J=14.3Hz, 4.8Hz, 2H); 6.35(dd, J=18.7Hz, 14.3Hz, 2H); 6.86-6.89(m, 4H); 7.07-7.09(m, 6H). $^{13}$C NMR: -2.47(q); 31.29(t); 126.81(d); 127.27(d); 128.31(d); 131.77(d); 136.30(t); 139.78(s); 141.90(s); 172.63(s).$^{29}$Si NMR: -7.379; 2.129. MS: 500($M+2^+$, 50); 498($M^+$, 56); 451(52); 449(100); 421(40); 413(74); 405(84); 391(46); 356(59); 327(36); 290(82); 275(35); 200(34); 183(34); 145(32). HR-MS: 498.1173 (calc. $C_{26}H_{32}Si_3Cl_2^+$ 498.1189). The siloles **5 or 6** were prepared according to [15] with butanone as solvent. **5**: 81%. $R_f$ (hexane:$Et_2O$=50:1): 0.39. IR: 1000(s); 995(s);$^1$H NMR: 0.15(s, 12H); 1.63(s, 4H); 2.06(d, J=8.1Hz, 4H); 4.96-5.07(m, 4H); 5.81-5.95(m, 2H); 6.84-6.87(m, 4H); 7.05-7.07(m, 6H). $^{13}$C NMR: -11.43(t); -0.40(q); 20.18(t); 114.44(t); 126.72(d); 127.12(d); 128.37(d); 133.12(d); 138.60(s); 141.87(s); 172.52(s).$^{29}$Si NMR: -7.061; 19.914. MS: 710($M^+$, 12); 669(100); 627(18); 583(12); 541(42); 499(22); 413(12); 385(13); 369(15). HR-MS: 710.0111 (calc. $C_{28}H_{36}Si_3I_2^+$ 710.0214).

**6**: 65%. $R_f$ (hexane:$Et_2O$=50:1): 0.19. IR: 3000(s); 1252(s); 1009(s).$^1$H NMR: 0.027(s, 12H); 1.65(s, 4H); 6.13(dd, J=19.1Hz, 4.8Hz, 2H); 6.26(dd, J=14.3Hz, 4.8Hz, 2H); 6.37(dd, J=19.1Hz, 14.3Hz, 2H); 6.88-6.91(m, 4H); 7.07-7.09(m, 6H). $^{13}$C NMR: -11.06(t); -0.58(q); 126.75(d); 127.22(d); 128.26(d); 131.88(d); 136.23(t); 139.91(s); 141.90(s); 172.31(s).$^{29}$Si NMR: -6.264; 2.015. MS: 681($M^+$,100); 554(43); 497(22); 483(29); 382(27); 356(32); 255(54); 183(37). HR-MS: 681.9547 (calc. $C_{26}H_{32}Si_3I_2^+$ 681.9901).

*Radical cyclisation*: A mixture of 355mg (0.5mmol)**5**, 290mg (1.0mmol) $Bu_3SnH$ and 8.2mg (0.05mmol) AIBN in 40 ml $C_6H_6$ was degased and refluxed in a preheated oil bath (90°C) for 14h. After replacement of the solvent by 10 ml diethyl ether, 5 ml 10% KF(aq) were added. After stirring for 4 h the precipitate was filtered off and the residue obtained after work up was purified by flash chromatography with hexane. **7**: 42%. $R_f$ (hexane): 0.30. IR: 1005(s). $^1$H NMR: -0.68(s, 6H); 0.14(s, 6H); 0.72-0.91(m, 6H); 1.12-1.21(m, 2H); 1.34-1.45(m, 2H); 1.59-1.72(m, 2H); 1.80-1.93(m, 4H); 6.79-7.07(m, 10H). $^{13}$C NMR: -4.59(q); 1.33(q); 11.09(t); 17.13(t); 24.74(t); 26.49(t); 126.20(d); 126.98(d); 128.62(d); 142.99(s); 148.12(s); 168.89(s). $^{29}$Si NMR: -9.752; 28.059. MS: 458($M^+$, 100); 443(6); 402(8); 385(9); 359(16); 346(9); 284(6); 258(8); 159(12). HR-MS: 458.2274 (calc. $C_{28}H_{38}Si_3^+$ 458.2281).**8**: 33%. $R_f$ (hexane): 0.28. IR: 2900(s); 1470(s); 1245(s); 1020(s); 1005(s).$^1$H NMR: -0.60(s, 3H); -0.13(s, 9H); 0.050(s, 3H); 0.77-0.88(m, 3H); 1.05-1.14(m, 1H); 1.32-1.42(m, 1H); 1.59-1.70(m, 1H); 1.91-2.02(m, 3H);

2.08-2.16(m, 1H); 4.86-5.03(m, 2H), 5.75-5.90(m, 1H); 6.87-7.04(m, 10H). $^{13}$C NMR: -3.71(q); 0.46(q); 0.82(q), 11.88(t); 17.30(t); 20.39(t); 24.63(t); 26.77(t); 113.12(t) 126.09(d); 126.11(d); 126.85(d); 126.95(d); 128.73(d); 128.86(d); 134.06(d); 142.78(s); 142.83(s); 143.51(s); 144.60(s); 170.30(s); 170.57(s). $^{29}$Si NMR: -10.013; -9.789; 24.005. MS: 458($M^+$, 100); 443(13); 417(81); 385(16); 243(17); 220(50); 205(62); 159(25); 145(18); 135(16); 109(12). HR-MS: 458.2269 (calc. $C_{28}H_{38}Si_3^+$ 458.2281).

**6b**: The radical reaction was performed with **6a** as described for **5**; yield: 80%. $R_f$ (hexane): 0.26. IR: 1245(s); 1000(s); 995(s); $^1$H NMR: 0.17(s, 18H); 6.07(dd, J=19.5Hz, 4.0Hz, 2H); 6.19(dd, J=14.7Hz, 4.4Hz, 2H); 6.36(dd, J=19.8Hz, 14.7Hz, 2H); 6.85-6.89(m, 4H); 7.03-7.06(m, 6H). $^{13}$C NMR: 0.79(q); 126.13(d); 126.92(d); 128.68(d); 133.16(d); 135.05(t); 142.27(s); 142.60(s); 171.24(s). $^{29}$Si NMR: -9.060; 2.765. MS: 431($M+1^+$, 42); 430($M^+$, 100); 415(18); 402(27); 330(15); 256(28); 241(24); 228(14). HR-MS: 430.1941 (calc. $C_{26}H_{34}Si_3^+$ 430.1968).

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[16] Crystal data: $C_{28}H_{38}Si_3$, orthorhombic, space group $P2ca_1$, a = 16.939(1), b = 13.780(1), c = 23.608(1) Å, V = 5510.1(6) Å$^3$, Z = 8 (two independent molecules per asymmetric unit), R1 = 0.032, wR2 = 0.059 (7020 obsd, reflections). Stoe Image Plate Diffraction System; Structure solution and refinement: SHELXS & SHELXL (G. Sheldrick, 1997, University of Göttingen). The full data for the X-ray crystal structure have been deposited at the Cambridge Crystallographic Data Centre.