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Thermal behaviour of 1,1-dimethyl-6-[1,1-dimethyl-2-(trimethylsilyl)ethyl]-4-(pentamethyldisilanyl)silepin

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Abstract

Thermolysis of 1,1-dimethyl-6-[1,1-dimethyl-2-(trimethylsilyl)ethyl]-4-(pentamethyldisilanyl)silepin in a degassed sealed tube at 250 °C for 10 h gave 1,1,3,3-tetramethyl-6-(pentamethyldisilanyl)-1-silaindane and 4-(isobutyldimethylsilyl)-1-(pentamethyldisilanyl)-5-(trimethylsilyl)benzene. 3-(Isobutyldimethylsilyl)-1-(pentamethyldisilanyl)-4-(trimethylsilyl)benzene was isolated from the mixture after thermolysis of 1,1-dimethyl-6-[1,1-dimethyl-2-(trimethylsilyl)ethyl)]-3-(pentamethyldisilanyl)silepin.

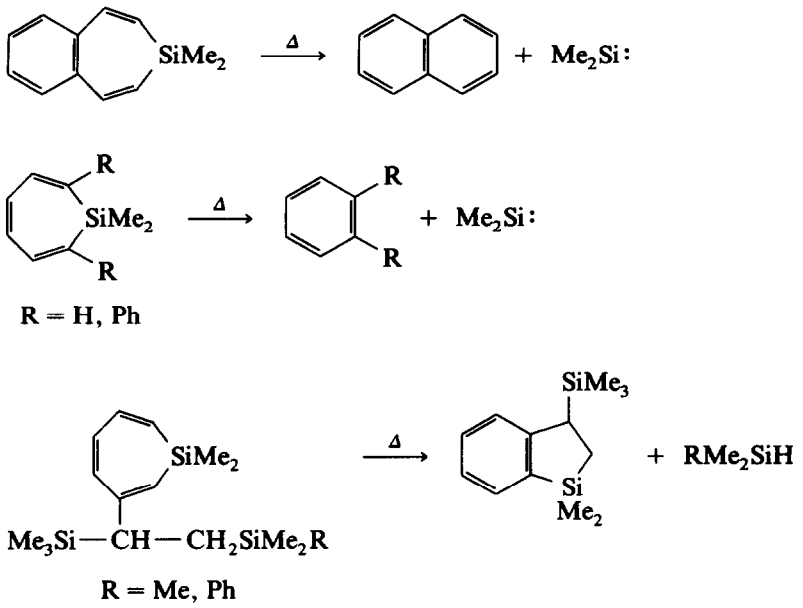
Introduction

Although several types of silepins have been synthesized to date [1–11], the information concerning their chemical behaviour is limited. To our knowledge, two different types of reactions for thermolysis of the silepins have been reported. One involves the formation of arene derivatives with extrusion of silylene species, and the other, which we found, comprises the production of a silaindane with loss of hydrosilanes (Scheme 1).

Previously, we found that nonannulated silepins can readily be obtained by the photolysis of pentamethylphenyldisilane and pentamethyl(*p*-tolyl)disilane in the presence of a vinylsilane [9,10]. We have also demonstrated that the photolysis of 1,3- and 1,4-bis(pentamethyldisilanyl)benzene affords 4,6- and 3,6-di-substituted silepsins, which can readily be separated by preparative GLC from ene adducts [12]. In this paper we report the thermal behaviour of the 4,6- and 3,6-di-substituted silepsins.

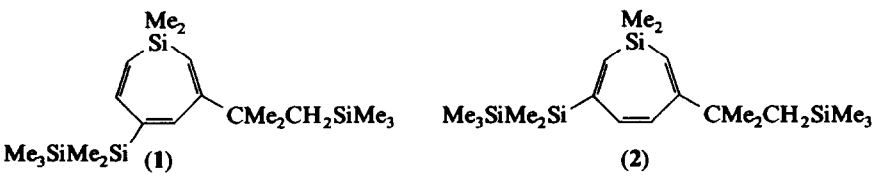
Results and discussion

1,1-Dimethyl-6-[1,1-dimethyl-2-(trimethylsilyl)ethyl]-4-(pentamethyldisilanyl)-silepin (**1**) and 1,1-dimethyl-6-[1,1-dimethyl-2-(trimethylsilyl)ethyl]-3-(pentamethyldisilanyl)silepin (**2**) were obtained by the photolysis of 1,3- and 1,4-bis(pentamethyldi-

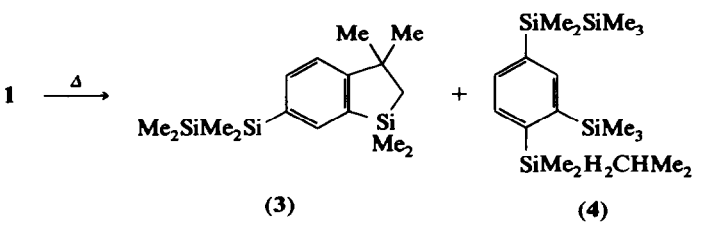


Scheme 1

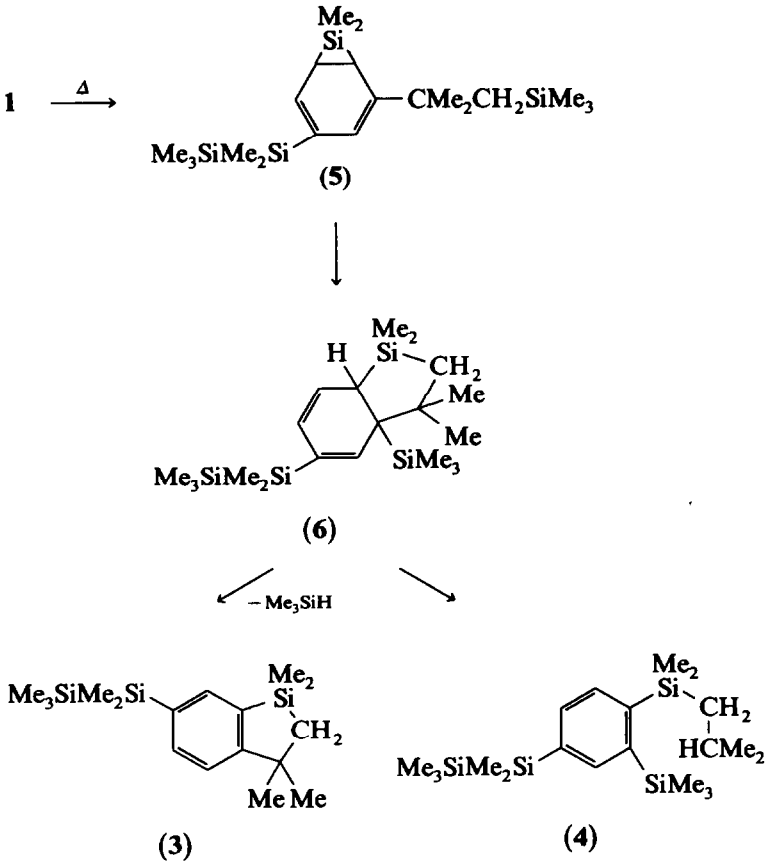
silanyl)benzene, respectively, in the presence of isobutene as reported previously [12].



Thermolysis of compound **1** proceeded cleanly to give two products. Thus, when **1** was heated in a degassed sealed tube at 250 °C for 10 h, 1,1,3,3-tetramethyl-6-(pentamethyldisilanyl)-1-silaindane (**3**) was obtained in 55% yield. To our surprise, 4-(isobutyldimethylsilyl)-1-(pentamethyldisilanyl)-5-(trimethylsilyl)benzene (**4**), which was the major product in the synthesis of the silepin **2** by the photolysis with isobutene of 1,4-bis(pentamethyldisilanyl)benzene (but not of the 1,3-isomer) was also produced in 12% yield. In this thermolysis, trace amounts of two other unidentified products were detected by GLC analysis (less than 7% combined yield).



The structure of compound **3** was verified by mass, IR, ^{1}H and ^{13}C NMR spectrometric analyses. The ^{1}H NMR spectrum revealed resonances at δ 0.05, 0.30,



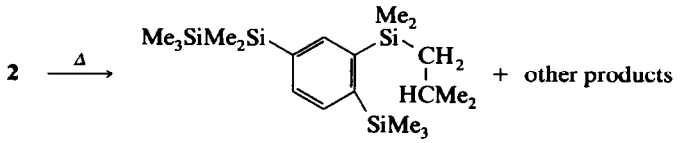
Scheme 2

0.31 and 1.32 ppm, attributed to Me_3Si protons, two different Me_2Si protons and Me_2C protons, respectively, and resonances at 0.97, 7.25, 7.43 and 7.55, due to CH_2 protons and three protons on the aromatic ring. The ^{13}C NMR spectrum was also consistent with the proposed structure (see Experimental). The location of substituents on the silaindanyl ring was established by NOE-FID difference experiments at 200 MHz. Thus, saturation of the dimethylsilyl protons at 0.30 ppm produced a positive NOE of protons at the C-2 and C-7 positions, while irradiation of the resonance of the trimethylsilyl protons led to the strong enhancement of protons at the C-5 and C-7 positions of the silaindanyl ring. Saturation of methyl protons on the ring carbon caused a positive NOE representing a proton at the C-4 position as well as protons at the C-2 position. These results are wholly consistent with the proposed structure.

All spectral data obtained for compound **4** were identical with those of the authentic sample prepared from the photolysis of 1,4-bis(pentamethyldisilanyl)benzene in the presence of isobutene [12].

Scheme 2 illustrates a possible mechanistic interpretation of the observed reaction course. The mechanism leading to the products **3** and **4** involves formation of a

silanorcaradiene intermediate (**5**), followed by ring enlargement to a five-membered system with a 1,3-trimethylsilyl shift from the methylene carbon to the juncture carbon atom giving a bicyclic compound (**6**). Finally, a 1,2-shift of a pentamethyldisilanyl group and elimination of trimethylsilane from the bicyclic compound **6** would produce compound **3**. The formation of compound **4** can be understood in terms of scission of the carbon–carbon bond in the five-membered ring of **6**, accompanied by a 1,3-hydrogen shift from the juncture carbon.



(**7**)

In contrast to the silepin **1**, the thermolysis of the silepin **2** under the same conditions gave a complicated reaction mixture. GLC analysis of the resulting mixture showed the presence of at least nine products. The yields of these products were calculated to be in the range 3–16%. One compound whose yield was calculated to be 15% was separated from the mixture by preparative GLC and identified as 3-(isobutyldimethylsilyl)-1-(pentamethyldisilanyl)-4-(trimethylsilyl)benzene (**7**). All spectral data obtained for compound **7** were identical with those of the authentic sample prepared from the photolysis of 1,3-bis(pentamethyldisilanyl)benzene in the presence of isobutene [12].

Experimental

General procedure. Silepins **1** and **2** were prepared by the photolysis of 1,3- and 1,4-bis(pentamethyldisilanyl)benzene in the presence of isobutene as reported previously [12]. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL Model JNM FX-90A spectrometer. NOE-FID difference spectra were determined with a Varian Model VXR-200 spectrometer. IR spectra were measured on a Perking–Elmer 1600 FT infrared spectrometer. Mass spectra were determined with a Shimadzu Model QP-1000 spectrometer.

Thermolysis of 1. In a 6 cm × 6 mm glass tube was placed 0.0706 g (0.179 mmol) of **1** and 0.0070 g (0.0225 mmol) of docosane as an internal standard. The glass tube was sealed under reduced pressure and heated at 250 °C for 10 h. The mixture was distilled under reduced pressure to give volatile products. The distillate was analyzed by GLC as being **3** (55% yield) and **4** (12% yield). Pure **3** and **4** were separated by preparative GLC. For **3**: IR 1581, 1456, 1404, 1380, 1360, 1246 cm^{-1}. ^{1}H NMR (δ in $CDCl_3$): 0.05 (9H, s, Me_3Si); 0.30 (6H, s, Me_2Si); 0.31 (6H, s, Me_2Si); 0.97 (2H, s, CH_2); 1.32 (6H, s, Me_2C); 7.25 (1H, br d, $J_{ortho} = 7.9$ Hz, aromatic ring proton); 7.43 (1H, dd, $J_{ortho} = 7.9$ Hz, $J_{meta} = 1.4$ Hz, aromatic ring proton); 7.55 (1H, br s, aromatic ring proton). ^{13}C NMR (δ in $CDCl_3$): −3.74 (Me_2Si); −2.18 (Me_3Si); −0.62 (Me_2Si); 29.51 (CH_2); 33.70 (Me_2C); 43.46 (CMe_2); 122.7, 135.2, 135.9, 137.6, 138.1, 161.7 (aromatic ring carbons). Exact mass: Found: 320.1838. $C_{17}H_{32}Si_3$ calcd.: 320.1813. All spectral data obtained for compound **4** were identical with those of an authentic sample [12].

Thermolysis of 2. A mixture of 0.0630 g (0.160 mmol) of **2** and 0.0087 g (0.028 mmol) of docosane as an internal standard was heated in a sealed tube at 250 °C for

10 h. The reaction mixture was analyzed by GLC as being 7 (15% yield). Pure 7 was isolated by preparative GLC. All spectral data obtained for compound 7 were identical with those of an authentic sample [12].

Acknowledgements

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References

1 L. Birkofer and H. Haddad, Chem. Ber., 102 (1969) 432 and 105 (1972) 2101.
2 L. Birkofer, H. Haddad and H. Zamarlik, J. Organomet. Chem., 25 (1971) 167.
3 J.Y. Corey, M. Deuber and B. Bichmeir, J. Organomet. Chem., 26 (1971) 167.
4 F.K. Cartledge and P.D. Mollere, J. Organomet. Chem., 26 (1971) 175.
5 T.J. Barton, W.E. Volg and J.L. Johnson, J. Org. Chem., 36 (1971) 3365.
6 K.A. Andrianov, L.M. Volkova, N.V. Delazari and N.A. Chumachskii, Khim. Geterotskil. Soedin., (1967) 435.
7 J.Y. Corey and E.R. Corey, Tetrahedron Lett., (1972) 4669.
8 T.J. Barton, R.C. Kippenhan, Jr. and A.J. Nelson, J. Am. Chem. Soc., 96 (1974) 2272.
9 M. Ishikawa, T. Fuchikami and M. Kumada, Tetrahedron Lett., (1976) 1299.
10 M. Ishikawa, T. Fuchikami and M. Kumada, J. Organomet. Chem., 162 (1978) 223.
11 Y. Nakadaira, in H. Sakurai (Ed.), Organosilicon and Bioorganosilicon Chemistry, Proceedings of the Seventh International Symposium on Organosilicon Chemistry, Kyoto, Japan, 1984, Ellis Horwood Ltd., Chichester, UK.
12 M. Ishikawa, H. Sakamoto, F. Kanetani and A. Minato, Organometallics, 8 (1989) 2767.