Journal of Organometallic Chemistry, *443* (1993) C3–C5

JOM 23167PC

Preliminary Communication

Silicon-carbon unsaturated compounds

XLII *. Novel dimerization of a silene generated from 1-pentamethyldisilanyl-4-(trimethylsilyl)benzene

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(Received March 13, 1992; in revised form August 29, 1992)

Abstract

The photolysis of 1-pentamethyldisilanyl-4-(trimethylsilyl)benzene in the absence of a trapping agent afforded two isomers derived from head-to-head dimerization of the silene arising from a 1,3-trimethylsilyl shift to the phenylene ring.

The photolysis of benzenoid aromatic disilanes affords the rearranged silenes arising from a 1,3-shift of a terminal silyl group of the disilanyl unit to the *ortho* position of the phenyl ring [1,2]. In the presence of a trapping agent such as alcohols, olefins and carbonyl compounds, the silenes thus formed react with these trapping agents to give addition products, while in the absence of the trapping agent the silenes undergo polymerization to give non-volatile products [3]. We report here the first example of dimerization of the rearranged silene produced photochemically from 1-pentamethyldisilanyl-4-(trimethylsilyl)benzene (**1**).

We first carried out the photolysis of **1** in the presence of an trapping agent, in order to learn whether or not the rearranged silene is produced. Thus, the photolysis of **1** in the presence of an 18-fold excess of isobutene was carried out with a low-pressure mercury lamp bearing a Vycor filter (254 nm) in hexane, and afforded 1-isobutyl-dimethylsilyl-2,4-bis(trimethylsilyl)benzene (**3**) in 65% yield, in addition to a 3% yield of a product whose molecular weight was calculated to be 560, corresponding to a dimer of the starting compound **1**. The structure of **3** could be readily confirmed by spectrometric analysis [MS *m/e* 336 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.36 (s, 9H, Me_3Si), 0.51 (s, 9H, Me_3Si), 0.53 (s, 6H, Me_2Si), 0.96 (d, 2H, CH_2, $J = 6.60$ Hz), 1.02 (d, 6H, CH_3, $J = 6.60$ Hz), 1.90 (nonet, 1H, CH, $J = 6.60$ Hz), 7.60 (dd, 1H, Ph–H, $J = 7.26$, 1.16 Hz), 7.81 (d, 1H, Ph–H, $J = 7.26$ Hz), 8.15 (br s, 1H, Ph–H); ^{13}C NMR (δ in $CDCl_3$) -1.18 (Me_3Si), 1.19 (Me_2Si), 2.29 (Me_3Si), 25.47 (CH_2), 26.49 (CH_3), 28.27 (CH), 133.12, 135.15, 139.21, 140.38, 144.84, 146.38 (ring carbons)], as well as by elemental analysis.

This result clearly shows that the rearranged silene (**2**) is produced in the photolysis of **1** (Scheme 1). In this photolysis, neither the product formed from the reaction of the silene arising from homolytic scission of a silicon–silicon bond, followed by disproportionation of the resulting silyl radicals with isobutene, nor the hydrosilane was detected in the photolysis mixture.

Irradiation of **1** in the absence of isobutene gave the product, which corresponds to a dimer of **1**, in 51% yield, after 84% of **1** was photolyzed. The formation of the dimer is of considerable interest for us, because, according to our knowledge, all of the rearranged silenes produced from the photolysis of benzenoid aromatic disilanes undergo polymerization to give non-volatile substances in the absence of a trapping agent. For example, the photolysis of phenyl- and *p*-tolyl-substituted pentamethyldisilane, and 2- and 3-trimethylsilyl-1-(pentamethyldisilanyl)benzene in the absence of a trapping agent in hexane and benzene afforded no dimerization products, but produced non-volatile polymeric substances. GLC analysis of the resulting photolysis mixture revealed a homogeneous peak for the dimerization product, but recycling GPC showed the presence of two isomers of the dimer. These two isomers could be isolated as crystals and identified as compounds **4** and **5**, respectively.

The structures of **4** and **5** were verified by spectroscopic analysis [**4**: m.p. 125.0–126.5°C; MS *m/e* 560 (M^+); ^{1}H NMR (δ in C_6D_6) 0.10 (s, 18H, Me_3Si), 0.34 (s, 18H, Me_3Si), 0.28_7 (s, 6H, MeSi), 0.29_4 (s, 6H, MeSi), 2.43 (s, 2H, H_a), 2.57 (s, 2H, H_b), 6.07 (d, 2H, H_c, $J = 4.95$ Hz), 6.49 (d, 2H, H_d, $J = 4.95$ Hz); ^{13}C NMR (δ in C_6D_6) -6.54 (MeSi), -4.76 (MeSi), -0.34 (Me_3Si), 0.62 (Me_3Si), 28.77 (CH_a), 39.92 (CH_b), 129.85 (CH_c), 136.28 (C(Si)=), 137.09 (CH_d), 144.03 (C(Si)=).

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* For Part XLI, see ref. 4.

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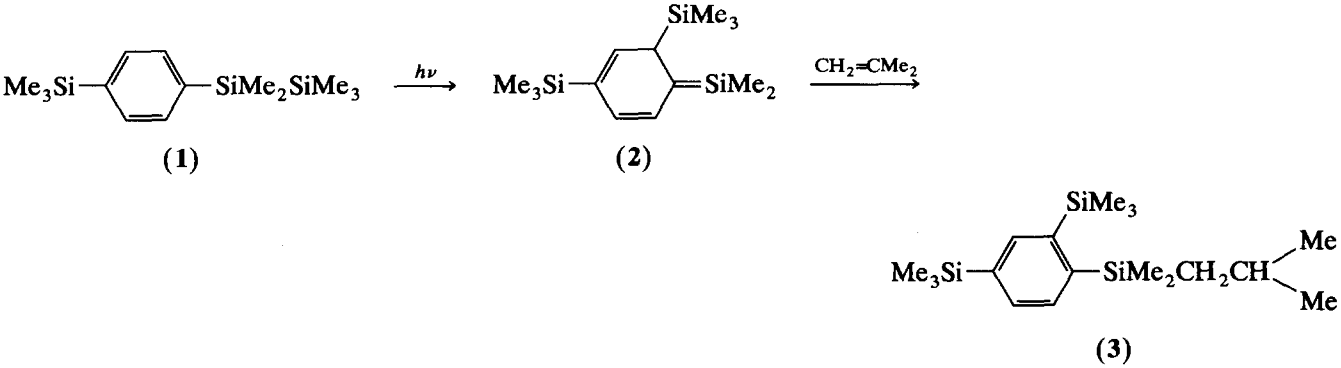


Scheme 1

5: m.p. 111.0–114.0°C; MS m/e 560 (M^+); ^{1}H NMR (δ in C_6D_6) 0.10 (s, 9H, Me_3Si), 0.18 (s, 9H, Me_3Si), 0.20 (s, 3H, MeSi), 0.29 (s, 3H, MeSi), 0.30 (s, 3H, MeSi), 0.31 (s, 9H, Me_3Si), 0.33 (s, 9H, Me_3Si), 0.34 (s, 3H, MeSi), 2.24 (br s, 1H, H_a), 2.62 (t, 1H, H_b, $J = 3.63$ Hz), 2.70 (dd, 1H, H_c, $J = 0.99, 0.66$ Hz), 3.47 (m, 1H, H_d), 5.83 (d, 1H, H_e, $J = 2.64$ Hz), 6.09 (d, 1H, H_f, $J = 4.95$ Hz), 6.36 (dd, 1H, H_g, $J = 3.63, 0.99$ Hz), 6.41 (dd, 1H, H_h, $J = 4.95, 0.99$ Hz); ^{13}C NMR (δ in C_6D_6) −6.05, −5.94, −4.52, −3.14 (MeSi), −2.33, 0.02, 0.26, 0.71 (Me_3Si), 27.80 (CH_a), 36.79 (CH_b), 42.67 (CH_c), 47.93 (CH_d), 129.60 (CH_f), 134.72 (CH_e), 136.43

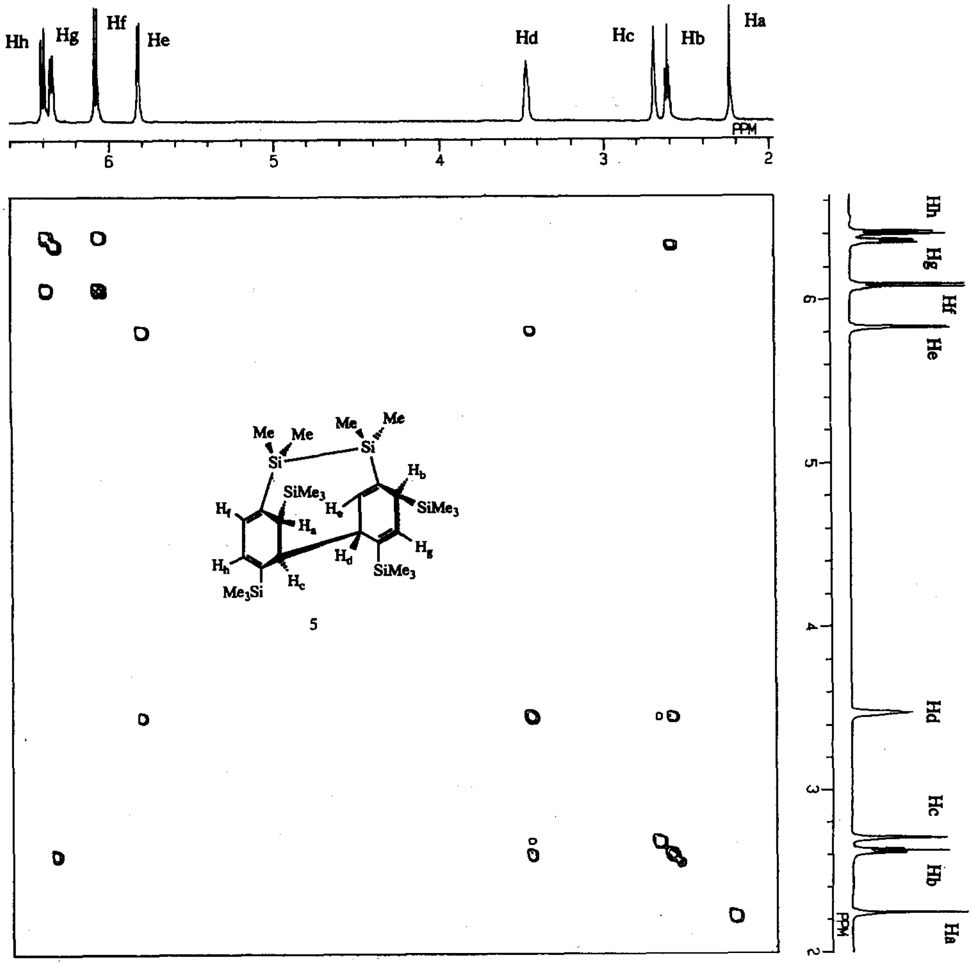
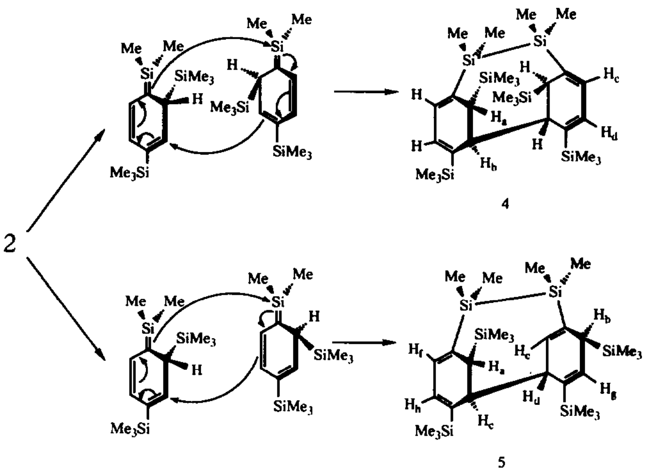


Fig. 1. Two-dimensional COSY experiment for **5** in C_6D_6 at 270 MHz.



Scheme 2

(CH_h), 140.67 (CH_g), 129.47, 133.37, 140.08, 145.81 (C(Si)=)], as well as by elemental analysis. Furthermore, the configuration of the isomers and the location of substituents on ring carbons in both isomers were determined by NOE-FID difference experiments at 270 MHz as well as by $^1H\{^1H\}$ and $^1H\{^{13}C\}$ COSY NMR spectra. The $^1H\{^1H\}$ COSY NMR spectrum in the C–H region, which was obtained for compound **5** is shown in Fig. 1.

The formation of **4** and **5** may be best explained by head-to-head dimerization of silene **2** as shown in Scheme 2.

We are containing to explore this and related systems.

Acknowledgement

This research was supported in part by a Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency from the Ministry of Education, Science and Culture. We also thank Shin-Etsu Chemical Co. Ltd., Nitto Electric Industrial Co. Ltd., Dow Corning Japan Ltd., and Toshiba Silicone Co. Ltd. for financial support.

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