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Preliminary communication

Silicon–carbon unsaturated compounds

XXXIX *. Photolysis of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene

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Abstract

Photolysis of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene gives a silene which can be trapped by t-butyl alcohol and acetone in high yields.

Recently, we demonstrated that thermolysis of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (**1**) at 250°C produces 1,2-bis(diethylsilylene)cyclohexa-3,5-diene, *o*-quinodisilane, (**2a**) as a reactive intermediate [1]. We now report that photolysis of **1** affords a different silene from **2a**: 1-ethyl-1-(2-diethylsilylphenyl)-1-silapropene (**2b**). Photolysis of **1** using a low-pressure mercury lamp (254 nm) in the presence of t-butyl alcohol in a hexane solution gave 1-(t-butoxydiethylsilyl)-2-(diethylsilyl)benzene, whose spectral data were identical with those obtained from thermolysis of **1** at 250°C with t-butyl alcohol [1].

Interestingly, irradiation of **1** in the presence of t-butyl alcohol-d_1 gave 1-[t-butoxy(1-deuterioethyl)ethylsilyl]-2-(diethylsilyl)benzene ** (**3b**) in 94% yield (Scheme 1).

No product involving a deuterium atom on the silicon at the C_2 position of the phenylene ring was detected by spectroscopic analysis. The formation of **3b** may be best understood by the addition of t-butyl alcohol-d_1 to silene **2b**, arising from

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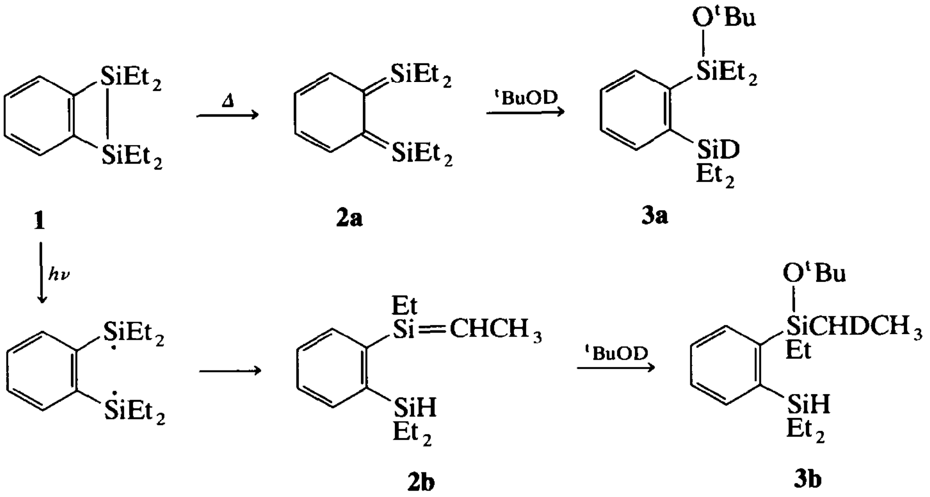
** Compound **3b**: Mass spectra: m/z 294 ($M^+ - \mathrm{Et}$). IR: 2144 cm^{-1} (ν(Si–H)); ^{1}H NMR ($CDCl_3$): δ 0.79–1.02 (m, 19H, EtSi), 1.30 (s, 9H, ^{t}Bu), 4.60 (quint, 1H, HSi, $J = 3.3$ Hz), 7.25–7.73 (m, 4H, phenylene ring protons). ^{2}H NMR (ppm in C_6D_6) 0.96 ($CDHCH_3$); ^{13}C NMR: ($CDCl_3$): δ 4.56, 7.10, 7.19, 8.34, 8.47 (t, J(C–D) = 18.3 Hz), 8.84 (EtSi), 32.1 (Me_3C), 72.9 (C–O), 127.6, 127.7, 134.8, 135.2, 142.3, 144.9 (phenylene ring carbons). ^{29}Si NMR ($CDCl_3$): δ −9.59, 0.73.

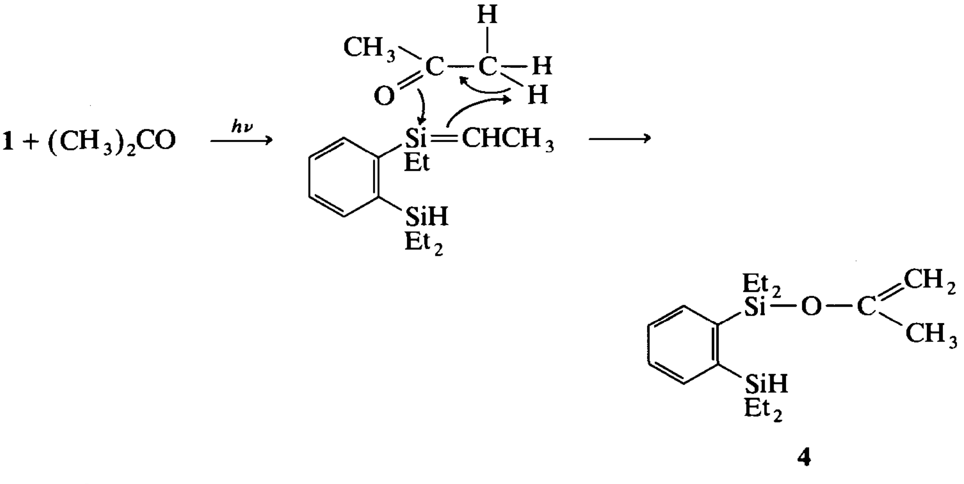


Scheme 1

homolytic scission of a silicon–silicon bond of **1**, followed by intramolecular disproportionation of the resulting silyl radicals.

On the other hand, thermolysis of **1** with t-butyl alcohol-d_1 gave 1-(t-butoxydiethylsilyl)-2-(deuteriodiethylsilyl)benzene [**3a**: Mass spectroscopy: m/z 294 (M^+ – Et). IR: 1568 cm^{-1}, ν(Si–D). ^{2}H NMR ($CDCl_3$): δ(ppm) 4.65 (D–Si)] which is probably produced from 1,4-addition of t-butyl alcohol-d_1 to *o*-quinodisilane **2a** in 39% yield, along with a 59% yield of the dimer 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octaethyl-1,2,3,6-tetrasilacycloocta-4,7-diene [1].

The formation of the silene **2b** can also be demonstrated by the fact that photolysis of **1** in the presence of acetone gives the product formed from the ene reaction. Thus, irradiation of a hexane solution of **1** using a low-pressure mercury lamp in the presence of acetone afforded 2-diethylsilyl-1-[diethyl(isopropenyloxy)-



Scheme 2

silyl]benzene * (**4**), produced from the reaction of the silene **2b** with acetone in 91% yield (Scheme 2).

It is well known that silenes produced photochemically from benzenoid aromatic disilanes undergo the ene reaction with acetone to give isopropenyloxy-substituted silanes, analogous to compound **4** [2–4].

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* Compound **4**: Mass spectra: m/z 277 ($M^+ - \mathrm{Et}$). Ir: 2145 cm^{-1} (ν(Si–H)); ^{1}H NMR ($CDCl_3$): δ 0.75–1.01 (m, 20H, EtSi), 1.84 (s, 3H, Me), 3.94 (s, 1H, $H_aC(H_b)$=), 4.00 (s, 1H, $H_bC(H_a)$=), 4.47 (quint, 1H, HSi, $J = 3.3$ Hz), 7.33–7.70 (m, 4H, phenylene ring protons). ^{13}C NMR ($CDCl_3$): δ 4.46, 6.85, 6.92, 8.28 (EtSi), 30.9 (Me), 90.8 (CH_2=), 127.9, 128.2, 134.9, 135.0, 142.3, 142.9 (phenylene ring carbons), 155.9 (C(O)=); ^{29}Si NMR ($CDCl_3$): δ −8.42, 7.62. Anal. Found: C, 66.57; H, 9.83. $C_{17}H_{30}Si_2O$ calc.: C, 66.60; H, 9.86%.