Synthesis and ring enlargement of 2-ethoxycarbonyl-1-silacyclobutanes

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2-Ethoxycarbonyl-1-silacyclobutanes were synthesized by intramolecular C–H insertion of carbenes generated photochemically from α-(di-*tert*-butylsilyl)-α-diazoacetates; they undergo smooth thermal ring-expansion by a 1,3(C → O) silyl shift to form 6-ethoxy-1-oxa-2-silacyclohex-5-enes.

Silacyclobutanes are useful precursors for other organosilicon compounds (*e.g.* larger silaheterocycles by ring expansion,[1,2] silaethenes by cycloreversion,[3] organosilicon polymers by ring opening[4]) and can be employed in C–C bond forming processes, such as the aldol reaction,[5] allylation of carbonyl compounds,[1,6] and metal-catalyzed cross-coupling reactions.[7] Much of this chemistry has been carried out with silacyclobutanes functionalized only at the silicon atom, and the synthesis of these compounds begins typically with a Wurtz-type cylisation reaction of γ-halopropyl(chloro)silanes.[8] Silacyclobutanes bearing functional groups at the ring carbon atoms appear to be rare; some notable exceptions are 3-alkenylsilacyclobutanes[9] and 3-(alkoxycarbonyl)methyl-1-silacyclobutanes.[10]

During our investigations into the chemistry of silicon-substituted carbenes,[11] it occured to us that the intramolecular 1,4-C,H insertion of these reactive intermediates might offer a novel route to silacyclobutanes. While the 1,5-C,H insertion of silylcarbenes or silylcarbenoids under thermal,[12] photochemical,[13] and transition-metal catalyzed[14] conditions is well documented, the formation of a 1-oxa-2-silacyclobutane from trimethoxysilylcarbene in an argon matrix[15] represents so far the only reported 1,4-C,H insertion involving a silicon-attached substituent in a silylcarbene.

We report now that photolysis of α-(di-*tert*-butylsilyl)-α-diazoacetates **1** provides convenient access to 2-alkoxycarbonyl-1-silacyclobutanes **2**. When solutions of **1a**–**d**[16] in toluene were irradiated with 300 nm light, silacyclobutanes **2a**–**d** were formed (Scheme 1).† From the photolysis of **1a** and **1c**, silacyclobutanes **2a** and **2c**, respectively, were obtained as the only produts and in high yield. In both cases, only one diastereomer was detected by NMR. In the absence of spectroscopic evidence for its configuration (irradiation into the Bu^t resonance did not provide a NOE effect with the ring-CH proton), a *trans*-relationship between the Bu^t and ester groups is assumed for steric reasons. Photolysis of **1b**,**d** led to an unseparable mixture of the expected silacyclobutanes **2b**,**d**, formed again as single diastereomers, and the isomeric 1-oxa-2-silacyclohex-5-enes **3b**,**d**. We reasoned that the latter compounds are ring-expansion products of **2**, and in fact, conversion of **2** into **3** was achieved when these product mixtures as well as the isolated silacyclobutanes **2a**,**c** were heated at *ca.* 85 °C in toluene.‡ The constitution of the cyclic *O*-silylketene acetals **3** was indicated by some characteristic NMR signals [δ(=CH) 3.70–3.81; δ(C$_{\text{olefin}}$) 154.4 ± 0.3 and 72.0 ± 0.3] as well as by strong IR absorptions at 1650–1680 cm^{-1} which are assigned to the C=C stretching mode (Table 1).

The 4 → 6 ring expansion of silacyclobutanes **2** proceeds by a 1,3(C → O) silyl shift. Monitoring of the isomerisation **2c** → **3c** by ^{1}H NMR spectroscopy indicated a first-order reaction with $k = 1.25 \times 10^{-4}$ s^{-1} at 70 °C in [D$_6$]benzene, corresponding to a half-life time of 92.7 min. Compounds **3** constitute cyclic *O*-silyl ketene acetals, and it should be recalled that acyclic compounds of this type undergo reverse thermal isomerisation, *i.e.* they rearrange to form α-silylcarboxylates.[17] Certainly, the smooth ring-expansion of silacyclobutane-2-carboxylates is due largely to the relief of ring-strain[18] for this four-membered ring.

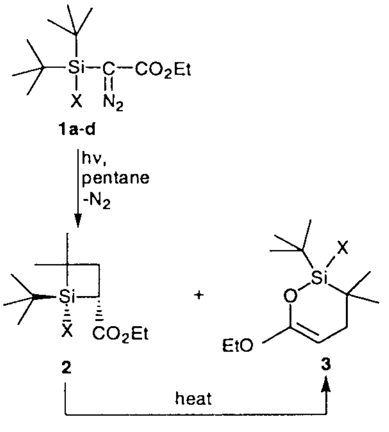
The cyclic ketene acetals **3** appear not to be storable for a long time, and signs of decomposition were detected by ^{1}H NMR after just a few days. Nevertheless, the different functional groups in these molecules should allow some useful transformations. As an example, we treated **3a**,**d** with an excess of LiAlH$_4$ and obtained 3-(hydroxybutyl)silane **4** in yields of 39 and 61% (Scheme 2).§ The IR absorptions at ν_{max} 2110, 922 and 848 cm^{-1} are in the ranges expected for dialkylsilanes.[19]

In summary, we have reported a novel synthesis of silacyclobutanes, namely by intramolecular 1,4-insertion of a carbene center into the C–H bond of a Si–Bu^t group. It appears that the presence of a SiBu$^t_2$X group in (silyl)diazoacetates **1** is

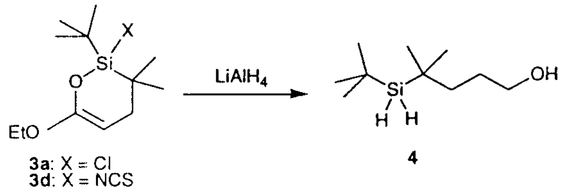
Table 1 UV-irradiation of diazoacetates **1a**–**d** in toluene and conversion of silacyclobutanes **2** into 1-oxa-2-silacyclohex-5-enes **3**

Diazoacetate	X	Product(s) and relative Yields[a] (%)	Yield of **3**[b] (%)
1a	Cl	**2a** (100)	36
1b	N$_3$	**2b** (46), **3b** (54)	45
1c	N=C=O	**2c** (100)	39
1d	N=C=S	**2d** (26), **3d** (74)	67

[a] According to ^{1}H NMR spectra, product formation was nearly quantitative (90–95%). [b] The yield after thermal isomerization is given and is based on diazoacetate **1**.



Scheme 1



Scheme 2

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a favorable case for this type of C,H insertion which has not been reported so far for closely related α-silyl-α-diazoacetates with a β-C–H bond in the silyl group. For example, UV irradiation of the SiEt$_3$ and SiPr$^i_3$ substituted diazoacetates in benzene was unspecific while their copper- or rhodium-catalysed decomposition gave products derived from other carbene-type reactions.[20] α-Alkoxy(diisopropyl)silyl-α-diazoacetates, on the other hand, underwent a photochemical 1,5-C–H insertion of the carbene at the alkoxy chain but no 1,4-C,H insertion at the isopropyl substituents.[13] In spite of these apparent structural limitations, it is obvious that the transformation **1** $\longrightarrow$ **2** represents an easy entry to silacyclobutanes with functionalities at both the silicon and the α-position of the ring which offer opportunities for further synthetic transformations.

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Notes and references

† *General procedure* for the irradiation of diazoacetates **1**: a solution of **1a–d** (3–6 mmol) in dry pentane (80 ml) was irradiated with a high-pressure mercury lamp ($\lambda \geqslant 300$ nm) until evolution of nitrogen had ceased (2.5–4.5 h). The solvent was evaporated at 0.01 mbar to leave the crude product(s) (**2** or **2**/**3**) which, except for **2c**, could not be purified further. *Selected data* for ethyl 1-*tert*-butyl-1-chloro-4,4-dimethylcyclobutane-2-carboxylate **2a**: δ_H(500 MHz, CDCl$_3$) 1.13 (s, 9H, CMe$_3$), 1.22 (s + t, 6H, 4-Me and CH$_2$*Me*), 1.26 (s, 3H, 4-Me), 1.91 (dd, 1H, *J* 12.7, 9.5 Hz, 3-H^A), 2.41 (dd, 1H, *J* 12.7, 9.9 Hz, 3-H^B), 2.96 (pseudo-t, 1H, 2-H), 4.03–4.21 (m, 2H, OCH$_2$). δ_C(125.77 MHz, CDCl$_3$) 14.46 (CH$_2$*Me*), 23.03 (*C*Me$_3$), 25.44 and 25.51 (C*Me*$_2$), 25.67 (C*Me*$_3$), 32.36 (CH), 32.77 (*C*Me$_2$), 35.74 (CH$_2$-ring), 59.95 (OCH$_2$), 172.11 (C=O). For **2b**: δ_H(400 MHz, CDCl$_3$) 1.08 (s, 9H, CMe$_3$), 1.23 (s, 3H, 4-Me), 1.25 (t, 3H, CH$_2$*Me*), 1.26 (s, 3H, 4-Me), 1.98 (dd, 1H, *J* 12.9, 9.6 Hz, 3-H^A), 2.41 (dd, 1H, *J* 12.9, 9.6 Hz, 3-H^B), 2.86 (t, 1H, 2-H), 4.10 and 4.21 (2q, 2H, OCH$_2$). δ_C(100.61 MHz, CDCl$_3$) 14.3 (CH$_2$*Me*), 21.7 (*C*Me$_3$), 24.7 and 24.9 (C*Me*$_2$), 25.6 (C*Me*$_3$), 31.8 (CH), 32.9 (*C*Me$_2$), 36.4 (CH$_2$-ring), 60.1 (OCH$_2$), 172.7 (C=O). ν_{max}(film)/cm^{-1} 2148 (vs, N$_3$), 1720 (s, C=O). For **2c**: bp. 50 °C/0.01 mbar. δ_H(500 MHz, CDCl$_3$) 1.09 (s, 9H, CMe$_3$), 1.20 and 1.22 (2s, 6H, CMe$_2$), 1.24 (t, 3H, CH$_2$*Me*), 1.93 (dd, 1H, *J* 12.8, 9.5 Hz, 3-H^A), 2.36 (dd, 1H, *J* 12.8, 9.8 Hz, 3-H^B), 2.81 (pseudo-t, 1H, 2-H), 4.05–4.23 (m, 2H, OCH$_2$). δ_C(125.77 MHz, CDCl$_3$) 14.35 (CH$_2$*Me*), 21.07 (*C*Me$_3$), 24.94 and 25.15 (C*Me*$_2$), 25.42 (C*Me*$_3$), 30.95 (*C*Me$_2$), 31.10 (CH), 35.89 (CH$_2$-ring), 60.11 (OCH$_2$), 125.35 (NCO), 172.64 (C=O). ν_{max}(film)/cm^{-1} 2273 (vs, NCO), 1720 (C=O). For **2d**: δ_H(400 MHz, CDCl$_3$) 1.10 (s, 3H, 4-Me), 1.13 (s, 9H, CMe$_3$), 1.16 (s, 3H, 4-Me), 1.23 (t, 3H, CH$_2$*Me*), 1.96 (dd, 1H, *J* 12.7, 9.7 Hz, 3-H^A), 2.39 (dd, 1H, *J* 12.7, 9.7 Hz, 3-H^B), 2.82 (t, 1H, 2-H), 4.01–4.32 (m, 2H, OCH$_2$). ν_{max}(film)/cm^{-1} 2110–1940 (vs, br, NCS), 1725 (C=O).

‡ Diazoacetates **1a–d** were photolyzed as described above. The solvent was replaced by dry toluene (10 ml) and the solution was heated at 85 °C (**2c**: 82 °C, 2.5 h). The solvent was evaporated, and the residue was fractionated by bulb-to-bulb distillation. *Selected data* for **3a**: bp 70-80 °C (oven temp.)/0.01 mbar. δ_H(500 MHz, CDCl$_3$) 1.10 (s, 3H, 3-Me), 1.14 (s, 9H, CMe$_3$), 1.18 (s, 3H, 3-Me), 1.29 (t, 3H, CH$_2$*Me*), 1.63 (dd, *J* 16.2, 6.2 Hz, 1H, 4-H^A), 2.34 (dd, *J* 16.2, 2.6 Hz, 1H, 4-H^B), 3.74 (dd, 1H, 5-H), 3.79 (q, 2H, OCH$_2$). δ_C(125.77 MHz, CDCl$_3$) 14.47 (CH$_2$*Me*), 20.81 (*C*Me$_2$), 21.60 (*C*Me$_3$), 24.11 and 25.29 (C*Me*$_2$), 26.30 (C*Me*$_3$), 37.07 (CH$_2$-ring), 63.21 (OCH$_2$), 72.32 (=CH), 154.14 (C-6). ν_{max}(film)/cm^{-1} 1758, 1738, 1681, 1665, 1467, 1395, 1385, 1368, 1332, 1229. For **3b**: bp 90–100 °C/0.04 mbar. δ_H(500 MHz, CDCl$_3$) 1.10 (s, 3H, 3-Me), 1.11 (s, 9H, CMe$_3$), 1.12 (s, 3H, 3-Me), 1.31 (t, 3H, CH$_2$*Me*), 1.78 (dd, *J* 16.3, 6.0 Hz, 1H, 4-H^A), 2.23 (dd, *J* 16.3, 3.1 Hz, 1H, 4-H^B), 3.73 (dd, 1H, 5-H), 3.81 (q, 2H, OCH$_2$). δ_C(125.77 MHz, CDCl$_3$) 14.45 (CH$_2$*Me*), 20.00 (*C*Me$_2$), 20.48(*C*Me$_3$), 24.34 and 24.87 (C*Me*$_2$), 26.10 (C*Me*$_3$), 37.00 (CH$_2$-ring), 63.26 (OCH$_2$), 71.88 (=CH), 154.66 (C-6). ν_{max}(film)/cm^{-1} 2152 (N$_3$), 1678, 1662, 1466, 1368, 1330, 1229. For **3c**: bp 80–90 °C/0.02 mbar. δ_H(500 MHz, CDCl$_3$) 1.08 (s, 3H, 3-Me), 1.09 (s, 9H, CMe$_3$), 1.11 (s, 3H, 3-Me), 1.30 (t, 3H, CH$_2$*Me*), 1.75 (dd, *J* 16.3, 6.0 Hz, 1H, 4-H^A), 2.19 (dd, *J* 16.3, 3.1 Hz, 1H, 4-H^B), 3.70 (dd, 1H, 5-H), 3.78 (q, 2H, OCH$_2$). δ_C(125.77 MHz, CDCl$_3$) 14.46 (CH$_2$*Me*), 18.94 (*C*Me$_2$), 19.61 (*C*Me$_3$), 23.81 and 25.14 (C*Me*$_2$), 26.04 (C*Me*$_3$), 36.92 (CH$_2$-ring), 63.20 (OCH$_2$), 71.62 (=CH), 123.00 (NCO), 154.56 (C-6). ν_{max}(film)/cm^{-1} 2287 (NCO), 1679, 1664, 1469, 1368, 1337, 1230. For **3d**: bp 70–80 °C/0.01 mbar. δ_H(400 MHz, CDCl$_3$) 1.12 (s, 9H, CMe$_3$), 1.12 and 1.13 (2s, 6H, 3-Me), 1.30 (t, 3H, CH$_2$*Me*), 1.63 (dd, *J* 16.2, 6.2 Hz, 1H, 4-H^A), 2.34 (dd, *J* 16.2, 2.6 Hz, 1H, 4-H^B), 3.74 (dd, 1H, 5-H), 3.79 (q, 2H, OCH$_2$). δ_C(100.6 MHz, CDCl$_3$) 14.4 (CH$_2$*Me*), 19.2 (*C*Me$_2$), 19.9 (*C*Me$_3$), 24.9 and 25.7 (C*Me*$_2$), 25.9 (C*Me*$_3$), 36.8 (CH$_2$-ring), 63.3 (OCH$_2$), 71.9 (=CH), 144.3 (NCS), 154.4 (C-6). ν_{max}(film)/cm^{-1} 2115–1917 (vs, br, NCS), 1730, 1652, 1458, 1358, 1324, 1225, 1141, 1087, 1006.

§ Compound **2d** (547 mg, 1.91 mmol) in diethyl ether (10 ml) was added to a suspension of LiAlH$_4$ (593 mg, 15.6 mmol) in diethyl ether (30 ml) and the suspension was heated at reflux for 3 h. Work-up by addition of ice-water and extraction with diethyl ether yielded 220 mg (61%) of *tert*-butyl(1,1-dimethyl-4-hydroxybutyl)silane **4**. *Selected data*: δ_H(200 MHz, CDCl$_3$) 1.05 (s, 15H, CMe$_3$ and CMe$_2$), 1.33–1.72 (m, 4H, SiC*H*$_2$C*H*$_2$), 3.45 (s, 2H, SiH), 3.62 (t, 2H, OCH$_2$). δ_C(100.61 MHz, CDCl$_3$) 17.6 (*C*Me$_2$), 21.0 (*C*Me$_3$), 26.1 (C*Me*$_2$), 28.0 (CH$_2$), 28.9 (C*Me*$_3$), 37.7 (CH$_2$), 63.5 (OCH$_2$). ν_{max}(film)/cm^{-1} 3300 (br, OH), 2110 (Si–H), 922, 848. Anal. Calc. for $C_{10}H_{24}OSi$ (188.4): C, 63.76; H, 12.84. Found: C, 63.50; H, 12.10%.

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