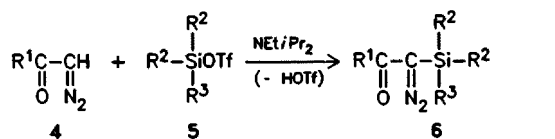


cleavage. Such a mechanism is also operating in the acid-catalyzed hydrolysis of α -silyldiazoacetic esters^{13a)}.

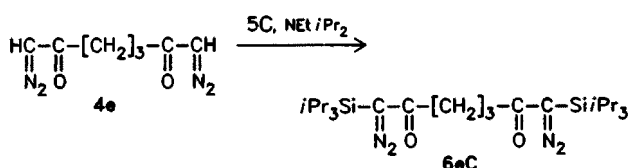
The silylated diazo ketones **6a–d** are characterized by a $\nu(\text{CN}_2)$ IR vibration at $2058\text{--}2064\text{ cm}^{-1}$, whereas the α -diazo ketones **4a–d** absorb at $2100\text{--}2110\text{ cm}^{-1}$. The bis-(diazo ketone) **6eC** shows the diazo stretching vibration at 2045 cm^{-1} , this value being about 75 cm^{-1} lower than in the nonsilylated diazo ketone **4e**. This shift to lower wavenumbers is a general phenomenon of α -silylated diazocarbonyl compounds^{13b)}.



4	a	b	c	d	5	A	B	C
R ¹	Me	tBu	nBu	Ph[CH ₂] ₃ -	R ²	Et	Me	iPr
					R ³	Et	tBu	iPr

6	aA	aB	aC	bA	bB	bC	cB	dC
R ¹	Me	Me	Me	tBu	tBu	tBu	nBu	Ph[CH ₂] ₃ -
R ²	Et	Me	iPr	Et	Me	iPr	Me	iPr
R ³	Et	tBu	iPr	Et	tBu	iPr	tBu	iPr
Yield [%]	a)	b)	76	87	81	68	b)	85

a) Not determined. - b) Not obtained purely.

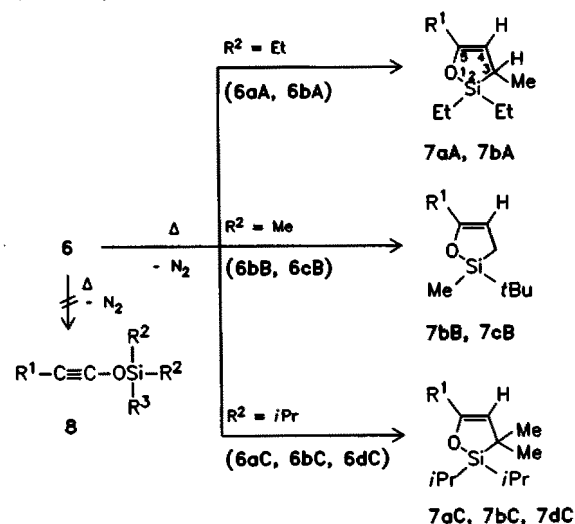


Thermolysis of α -Diazo- α -(trialkylsilyl)alkanones **6**

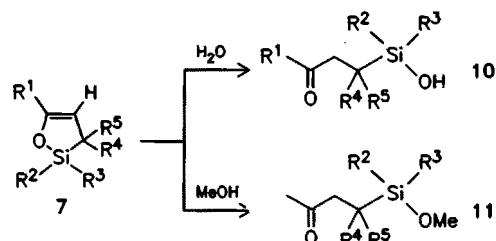
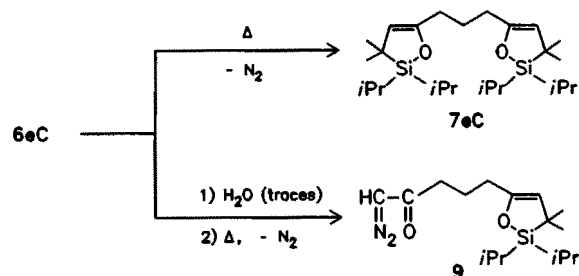
Contrary to (aryldiazomethyl)silanes **1c** ($\text{R} = \text{aryl}$) which are slowly transformed into siloxyalkynes **3** already at room temperature⁴⁾, the (alkanoyldiazomethyl)silanes **6** are thermally stable under these conditions. When heated in refluxing benzene, however, they split off dinitrogen as well; 1-oxa-2-sila-4-cyclopentenes **7** are isolated as the sole reaction products. Diazo ketone **6aB** made an exception, since it suffered hydrolysis by traces of moisture faster than thermolysis, so that only 1,3-di-*tert*-butyl-1,1,3,3-tetra-methyldisiloxane was obtained. Similarly, bis(diazo ketone) **6eC** underwent partial hydrolysis at one $\text{C}(\text{N}_2)\text{---Si}$ bond; thermal reaction then occurred only at the silylated diazocarbonyl unit to give compound **9**. Siloxyacetylenes **8** were not found even in trace amounts; because of the generally very strong $\nu(\text{C}\equiv\text{C})$ absorption of this class of compounds^{4,14)}, their presence in the reaction mixtures would have been detected by IR spectroscopy.

The constitution of the heterocycles **7** and **9** follows from spectroscopic data. The IR spectrum is void of an absorption in the $\nu(\text{C}=\text{O})$ region; instead a medium-strong absorption at $1617\text{--}1645\text{ cm}^{-1}$ is observed which is assigned to the $\nu(\text{C}=\text{C})$ vibration of the cyclic enol ether moiety. Another characteristic

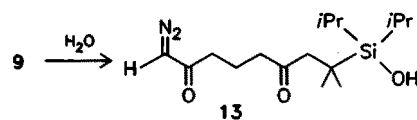
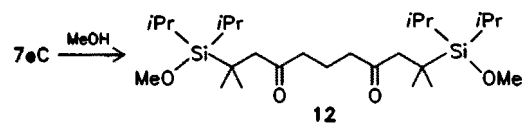
feature is a strong band at 1079 ± 6 (**7aA, bB, cB, dC**), 1121 ± 1 (**7aC, dC, eC, 9**), or 1140 cm^{-1} (**7aA**) which is not present in the precursors **6**. This absorption may be tentatively assigned to the Si---O---C vibration^{3,15)}.



(R¹ as for **4**)



	R ¹	R ²	R ³	R ⁴	R ⁵
7aA, 10a	Me	Et	Et	Me	H
7aC, 10b	Me	iPr	iPr	Me	Me
7bC, 10c	tBu	iPr	iPr	Me	Me
7dC, 10d	Ph[CH ₂] ₃ -	iPr	iPr	Me	Me
7bB, 11	tBu	Me	tBu	H	H



In the $^1\text{H-NMR}$ spectrum, the presence of one vinylic proton ($\delta = 4.40\text{--}4.74$) and of additional signals in the aliphatic region (as compared to diazo ketones **6**) corroborate the structural assignment of the heterocycles. $^{13}\text{C-NMR}$ signals in the olefinic range constitute another hint to the silyl enol ether moiety [**7aC**: $\delta(\text{C-4}) = 114.41$, $\delta(\text{C-5}) = 152.12$]. Finally, the mass spectrum of **7bC** contains a fragment which corresponds to a loss of $\text{OSi}(\text{CHMe}_2)_2$ from the molecule.

All cyclic silyl enol ethers **7** and **9** are readily cleaved by protic nucleophiles. The hydrolysis products **10a–d** and **13** as well as the methoxysilanes **11** and **12** resulting from solvolysis by methanol have been synthesized in preparative runs. They were fully characterized by their spectroscopic data (see Experimental), which need no further discussion here.

Mechanism of the Transformation **6** \rightarrow **7**

Two pathways may be conceived for the formation of sila-heterocycles **7** (Scheme 1). Pathway A corresponds to the usual reactivity of α -diazo ketones which split off dinitrogen on thermal impact, thereby yielding a keto carbene **14**. Formation of **7** from **14** would require $\beta\text{-C/H}$ insertion¹⁶⁾ yielding acylsilylirane **15** which would furnish **7** by ring expansion.

This mechanistic proposal has at least two weak points. Firstly, according to the experience with α -silyl diazo esters **1a**^{10,17)} and disilanyldiazomethyl ketones **1b**¹¹⁾, all of which are rather stable thermally, it is not expected that silylated diazo ketones **6** will furnish keto carbenes by thermal loss of N_2 under the conditions chosen in this study (80°C , 3 h). We have used this argument already in the case of (aroyl-diazomethyl)silanes **1c**, some of which decompose with loss of N_2 even at room temperature⁴⁾. Secondly, Wolff rearrangement is expected to be the preferred reaction mode of keto carbenes **14**. Even in simple keto carbenes, a $\beta\text{-C/H}$ insertion into a Si-C-H bond seems to occur rarely or not at all^{17,18)}. In fact, Wolff rearrangement to the corresponding (trialkylsilyl)ketene is the dominating process if diazo ketones **6** are decomposed either photochemically or by transition-metal catalysis¹⁹⁾. This leads to the conclusion that keto carbenes are not involved in the thermal decomposition of diazo ketones **6**²⁰⁾.

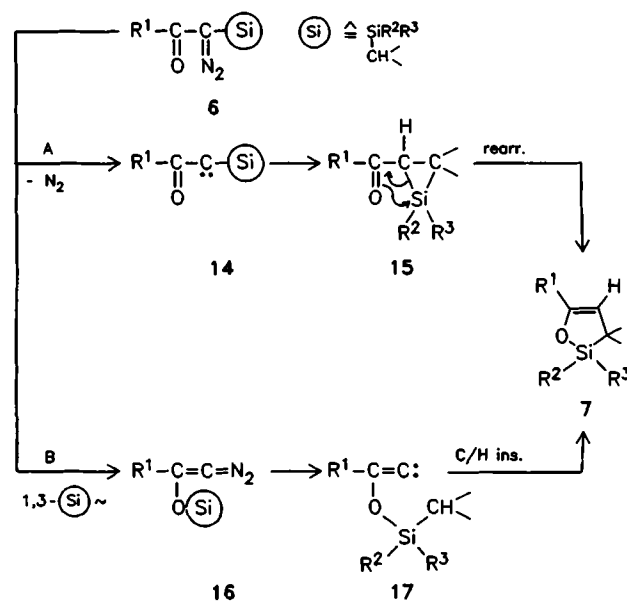
In this context, it should be mentioned that for the transformation **6aA** \rightarrow **7aA** in the presence of copper powder in boiling cyclohexane, the mechanistic pathway A has been proposed, and it has been assumed that the keto carbene in this case was generated by copper catalysis³⁾. We challenge this proposal, since we have shown that this transformation occurs under purely thermal conditions (i.e. in the absence of copper powder) and that the copper(I) triflate-catalyzed decomposition of **6aA** at room temperature produces methyl(triethylsilyl)ketene rather than **7aA**¹⁹⁾.

We propose to describe the transformation **6** \rightarrow **7** by pathway B (Scheme 1). The reaction sequence is opened by a thermally induced 1,3-C \rightarrow O silyl shift which yields diazoethene **16**. Such silyl group migrations usually occur at temperatures above 150°C in (acylmethyl)silanes²¹⁾. The enhanced tendency of silylated diazo ketones **6** to undergo this rearrangement is certainly due to the contribution of a diazonium enolate resonance structure to the bond state of **6**,

creating a higher electron density on the carbonyl oxygen than in ordinary (acylmethyl)silanes.

Diazoethenes have not been isolated up to now. Despite of two successful trapping experiments by intermolecular [3 + 2] cycloaddition reactions²²⁾, they must be regarded as thermally extremely unstable compounds which furnish alkylidenecarbenes by loss of N_2 (**16** \rightarrow **17**)^{7d,7e,23)}. Cyclization of carbene **17** to a five-membered ring by C/H insertion has ample precedent in alkylidenecarbenes with an all-carbon chain^{7b,24,25)}; also, a few such cyclizations by insertion into an XC-H bond ($\text{X} = \text{O}$ ^{26,27)}, N ^{26,28)}) have been realized. Our results constitute the first example for intramolecular alkylidenecarbene insertion into a SiC-H bond which can be a primary, secondary, or tertiary one.

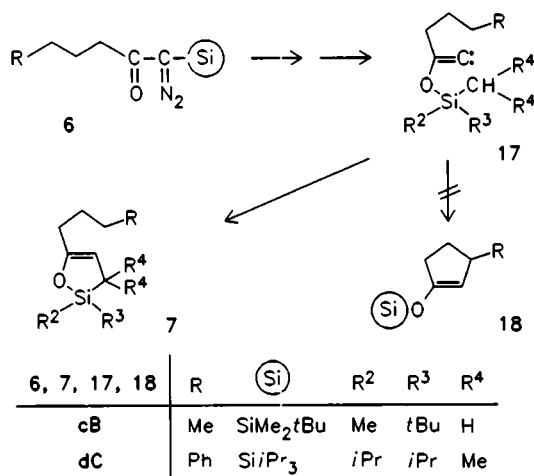
Scheme 1



The selectivity of C/H insertion by alkylidenecarbenes was found to be $1^\circ < 2^\circ$ aliphatic $< 2^\circ$ benzylic $< 3^\circ$ ^{24a,25b,29)}. Concerning the insertion process **17** \rightarrow **7**, the substitution pattern on silicon (SiEt_3 , Si^iPr_3 , SiMe_2tBu) does not allow to verify such a reactivity ranking. However, the possibility of competing C/H insertion pathways is given in the carbene intermediates **17cB** and **17dC** (Scheme 2): Insertion into a C-H bond of the alkyl chain would yield cyclopentenes **18**, but such products were not detected. This means that in alkylidenecarbenes **17** insertion into a secondary C-H bond cannot compete with insertion into a primary SiC-H bond (**17cB**), and the same holds true for benzylic C-H vs. tertiary SiC-H bond (**17dC**). Gilbert has argued that heteroatom activation favors carbene insertion into a XC-H bond because of reduced bond dissociation energies of such bonds²⁸⁾; this correlation uses the assumption that the transition state is radical-like. Whereas the argument seems justified for OC-H and NC-H bonds, which have bond dissociation energies about $9\text{--}10\text{ kcal/mol}^{-1}$ lower than alkyl C-H bonds²⁸⁾, is not so evident in the case of the SiC-H bond. The only known bond dissociation energy of such a

bond appears to be that of tetramethylsilane which turned out to be only 0.5 kcal mol⁻¹ lower than that of a C–H bond in neopentane³⁰. With respect to these data, a truly competitive situation could have been expected in the case of **17cB** (CH₂ vs. SiCH₃) and **17dC** (PhCH₂ vs. SiCH₃). The fact that this was not the case points to a dominating influence of entropy factors on the energy of the transition state. The greater bond lengths of Si–O and Si–C as compared to C–C as well as the greater variability of the C–O–C angle as compared to the tetrahedral angle of C–C–C may contribute to the relief of steric strain in the cyclic transition state of the C–H insertion process.

Scheme 2



So far, all our efforts have failed to trap the alkylidene-carbenes **17** intermolecularly. Neither a [2 + 1] cycloaddition to cyclohexene (with **6aC**) or cyclooctene (with **6bC**) nor an insertion into the Si–H bond of triethylsilane (with **6bC**) could be realized, although both reaction modes are well known in alkylidene-carbene chemistry^{6,7}. This is not surprising in view of the fact that favorable intramolecular processes tend to suppress any intermolecular reaction mode. We have found comparable results in such alkylidene-carbenes related to **17**, where appropriate substituents allowed 1,2-aryl migration to the carbenic center⁴ or intramolecular cyclopropanation of an aromatic nucleus³¹.

This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*.

Experimental

Melting points: Mettler FP 5. – Elemental analyses: Perkin-Elmer Analyzer 240. – IR spectra: Perkin-Elmer Spectrometer 397. – NMR spectra: Varian EM 390 (90 MHz, ¹H NMR) and Bruker WP 200 (50.28 MHz, ¹³C NMR), solvent CDCl₃, TMS as internal standard. – Mass spectra: Varian MAT 311.

The following diazo ketones were prepared according to literature procedures: **4a**³², **4b**³³, **4e**³⁵; **4c**³⁴ was obtained by the same recipe as **4b**³³. The trialkylsilyl trifluoromethanesulfonates **5A–C** were purchased from Fluka AG (Neu-Ulm). All syntheses of compounds **6** and **7** were carried out in anhydrous, distilled solvents under argon. Column chromatography was usually carried out on

Lobar columns (Merck, Lichroprep Si 60, 40–63 μm) with anhydrous and distilled solvents. Elemental analyses of compounds **6** and **7**, in some cases, were not fully satisfactory because of their high hydrolytic lability and/or the difficulty to completely purify them.

1-Diazo-5-phenyl-2-pentanone (4d): The solution of 4-phenylbutanoyl chloride (6.40 g, 0.035 mol) in 10 ml of ether is added dropwise at 0 °C to an ethereal solution (400 ml) of diazomethane [prepared from 35 g (0.34 mol) of *N*-methyl-*N*-nitrosourea³⁶]. The mixture is allowed to assume room temperature, stirred for another hour and filtered. After evaporation of the solvent at 14 Torr/25 °C, 5.96 g (90%) of crude **4d** is left as a yellow oil, which decomposes on attempted distillation. – IR (film): 2100 cm⁻¹ (CN₂), 1630 (C=O). – ¹H NMR: δ = 1.95 (m, 2H), 2.30 (t, 2H), 2.65 (t, 2H), 5.13 (s, 1H), 7.06–7.34 (m, 5H).

C₁₁H₁₂N₂O (188.2) Calcd. C 70.19 H 6.43 N 14.88
Found C 69.0 H 6.56 N 14.3

α-Diazo-*α*-(trialkylsilyl)alkanones **6**: General Procedure

The solution of *α*-diazo ketone **4a–d** (10 mmol) and 1.74 ml (10 mmol) of ethyldiisopropylamine in 60 ml of anhydrous ether is chilled to 0 °C under argon, and trialkylsilyl trifluoromethanesulfonate **5A–C** (10 mmol) in 5 ml of ether is added dropwise. The mixture is brought to room temp. and stirred for another 4 h. The precipitated ethyldiisopropylammonium trifluoromethanesulfonate is filtered off with suction and washed with some ether. The combined ethereal solutions are concentrated at 14 Torr/25 °C, and the remaining oil is purified by Lobar chromatography (eluent chloroform/pentane 7:3). Because of their thermal lability, none of diazo ketones **6** was distilled.

1-Diazo-1-(triethylsilyl)-2-propanone (6aA): Red oil, which was not subjected to Lobar chromatography because of its proneness to desilylation. – IR (film): 2062 cm⁻¹ (CN₂), 1638 (C=O) (ref.³¹ 2060, 1650 cm⁻¹). – ¹H NMR: δ = 0.54, 1.10 (m, 15H), 2.23 (s, 3H).

1-(tert-Butyldimethylsilyl)-1-diazo-2-propanone (6aB) was obtained as a red oil which was not analytically pure according to ¹H NMR (impurities in the aliphatic region) and IR (impurity at 1719 cm⁻¹). – IR (film): 2060 cm⁻¹ (CN₂), 1640 (C=O). – ¹H NMR: δ = 0.22 (s, 6H), 0.98 (s, 9H), 2.28 (s, 3H).

Thermolysis of crude **6aB** (refluxing benzene, 3 h) followed by Kugelrohr distillation gave 1,3-di-tert-butyl-1,1,3,3-tetramethyldisiloxane as a colorless liquid, b.p. 100 °C/0.01 Torr, in a 64% yield based on **4a**. – IR (film): 1465/1458 cm⁻¹ (m), 1250 (s), 1075–1045 (br, s). – ¹H NMR: δ = 0.02 (s, 12H), 0.82 (s, 18H).

C₁₂H₃₀OSi₂ (246.5) Calcd. C 58.46 H 12.27
Found C 58.4 H 12.18

1-Diazo-1-(triisopropylsilyl)-2-propanone (6aC): Yellow oil, 76% yield. – IR (film): 2060 cm⁻¹ (CN₂), 1632 (C=O). – ¹H NMR: δ = 1.00–1.42 (m, 21H), 2.27 (s, 3H).

C₁₂H₂₄N₂OSi (240.4) Calcd. C 59.95 H 10.06 N 11.65
Found C 60.2 H 10.08 N 11.4

1-Diazo-3,3-dimethyl-1-(triethylsilyl)-2-butanone (6bA): Yellow oil, 87% yield. – IR (film): 2060 cm⁻¹ (CN₂), 1623/1613 (C=O). – ¹H NMR: δ = 0.49–1.12 (m, 15H), 1.24 (s, 9H). The compound contains traces of the parent diazo ketone **4b**.

1-(tert-Butyldimethylsilyl)-1-diazo-3,3-dimethyl-2-butanone (6bB): Yellow oil, 81% yield. – IR (film): 2058 cm⁻¹ (CN₂), 1622 (C=O). – ¹H NMR: δ = 0.22 (s, 6H), 0.91 (s, 9H), 1.25 (s, 9H).

C₁₂H₂₄N₂OSi (240.4) Calcd. C 59.95 H 10.06 N 11.65
Found C 59.8 H 9.95 N 11.4

1-Diazo-3,3-dimethyl-1-(triisopropylsilyl)-2-butanone (6bC): Yellow oil, 68% yield. — IR (film): 2059 cm^{-1} (CN_2), 1623 ($\text{C}=\text{O}$). — $^1\text{H NMR}$: $\delta = \text{ca. } 1.0\text{--}1.2$ (m, 21 H, *i*Pr), 1.29 (s, 9 H, *t*Bu).

$\text{C}_{15}\text{H}_{30}\text{N}_2\text{OSi}$ (282.5) Calcd. C 63.78 H 10.70 N 9.92
Found C 63.9 H 10.69 N 10.0

1-(tert-Butyldimethylsilyl)-1-diazo-2-hexanone (6cB): Red oil (2.05 g), which could not be purified completely. — IR (film): 2060 cm^{-1} (CN_2), 1635/1626 ($\text{C}=\text{O}$). — $^1\text{H NMR}$: $\delta = 0.21$ (s, 6H), 0.91 (s, 9H), 1.18–1.82 (m, $\text{CH}_3\text{CH}_2\text{CH}_2$), 2.55 (t, COCH_2). $^1\text{H NMR}$ signals of impurity at $\delta = 0.86$ (intensity 33% of *t*Bu signal of 6cB) and $\delta = 3.96$.

1-Diazo-5-phenyl-1-(triisopropylsilyl)-2-pentanone (6dC): Yellow oil, 85% yield. — IR (film): 2058 cm^{-1} (CN_2), 1622 ($\text{C}=\text{O}$). — $^1\text{H NMR}$: $\delta = 1.01\text{--}1.40$ (m, 21H, *i*Pr), 2.00 (q, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.53 (t, 2H), 2.64 (t, 2H), 7.25 (m, 5H). The compound contains traces of parent diazo ketone 4d.

1,7-Bis(diazo)-1,7-bis(triisopropylsilyl)-2,6-heptanedione (6eC): The mixture of 1.80 g (10 mmol) of 4e and 3.50 ml (20 mmol) of ethyldiisopropylamine in 80 ml of anhydrous ether is chilled to 0°C under argon, and the solution of 5.38 ml (20 mmol) of triisopropylsilyl trifluoromethanesulfonate (5C) in 10 ml of ether is added dropwise. Stirring is continued for 2 h at room temp., and the precipitated ammonium salt is filtered off with suction. After evaporation of the solvent, an orange-red oil is left which crystallizes on standing. After recrystallization from pentane at -78°C , 2.32 g (47%) of light-yellow 6eC is obtained, m. p. 54–55°C. — IR (KBr): 2045 cm^{-1} (CN_2), 1630 ($\text{C}=\text{O}$). — $^1\text{H NMR}$: $\delta = 1.05\text{--}1.62$ (m, 42H, 1.98 (m, 2H), 2.64 (t, 4H, COCH_2).

$\text{C}_{25}\text{H}_{48}\text{N}_4\text{O}_2\text{Si}_2$ (492.9) Calcd. C 60.93 H 9.82 N 11.37
Found C 60.5 H 9.68 N 11.4

1-Oxa-2-sila-4-cyclopentenes 7

General Procedure: A solution of a diazo ketone 6 in 60 ml of anhydrous benzene is heated at reflux temperature for a time interval specified below. The solvent is evaporated and the residue is subjected to Kugelrohr distillation (oven temperatures are given below).

2,2-Diethyl-3,5-dimethyl-1-oxa-2-sila-4-cyclopentene (7aA): The crude diazo ketone 6aA, obtained from 0.84 g (10 mmol) of 4a by silylation with 5A (see above), was used without purification. Reaction time 2.5 h, b. p. 50°C/0.2 Torr, yield 0.62 g (37%, based on 4a). The compound is very labile to hydrolysis. — IR and $^1\text{H-NMR}$ data correspond to literature data³.

5-tert-Butyl-2,2-diethyl-3-methyl-1-oxa-2-sila-4-cyclopentene (7bA): From 1.20 g (5.00 mmol) of 6bA, 3 h, b. p. 55°C/0.03 Torr. Yield: 0.59 g (56%). — IR (film): 3042 cm^{-1} ($=\text{CH}$), 1621 ($\text{C}=\text{C}$), 1083. — $^1\text{H NMR}$: $\delta = \text{ca. } 0.5\text{--}1.25$ (m, Et and CHMe), 1.06 (s, *t*Bu), 1.60–1.88 (m, CHMe), 4.65 (m, 4-H).

$\text{C}_{12}\text{H}_{24}\text{OSi}$ (212.4) Calcd. C 67.86 H 11.39
Found C 66.6 H 11.36

2,5-Di-tert-butyl-2-methyl-1-oxa-2-sila-4-cyclopentene (7bB): From 1.20 g (5.00 mmol) of 6bB, 3 h, b. p. 60°C/0.03 Torr. Yield: 0.61 g (58%). — IR (film): 3058 cm^{-1} ($=\text{CH}$), 1621 ($\text{C}=\text{C}$), 1073. — $^1\text{H NMR}$: $\delta = 0.21$ (s, SiMe), 0.91 (s, Si*t*Bu), 1.08 (s, 5-*t*Bu), 1.24 and 1.33 (AB part of ABX system), 4.73 (X part of ABX, $^3J_{\text{AX}} = ^3J_{\text{BX}} = 3$ Hz, 4-H).

$\text{C}_{12}\text{H}_{24}\text{OSi}$ (212.4) Calcd. C 67.86 H 11.39
Found C 66.7 H 11.46

5-Butyl-2-tert-butyl-2-methyl-1-oxa-2-sila-4-cyclopentene (7cB): Diazo ketone 6cB was synthesized from 10 mmol of 4c (see above)

and thermolyzed without purification for 6 h. Kugelrohr distillation at 80°C/0.1 Torr gave 0.74 g (28%) of 7cB. — IR (film): 3030 cm^{-1} ($=\text{CH}$), 1616 ($\text{C}=\text{C}$), 1985–1055. — $^1\text{H NMR}$: $\delta = 0.28$ (s, SiMe), 0.95–1.00 (m, 12H, Si*t*Bu, $[\text{CH}_2]_3\text{Me}$), 1.28–1.68 (m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Me}$ and 2 3-H), 1.99–2.38 (m, 5- CH_2), 4.74 (t, $^3J = 3.5$ Hz, 4-H).

$\text{C}_{12}\text{H}_{24}\text{OSi}$ (212.4) Calcd. C 67.86 H 11.39
Found C 66.6 H 11.22

2,2-Diisopropyl-3,3,5-trimethyl-1-oxa-2-sila-4-cyclopentene (7aC): From 1.40 g (5.8 mmol) of 6aC, 4 h, b. p. 60°C/0.08 Torr. Yield: 0.74 g (60%). — IR (film): 3010 cm^{-1} ($=\text{CH}$), 1641 ($\text{C}=\text{C}$), 1122, 1079. — $^1\text{H NMR}$: $\delta = 0.99\text{--}1.21$ (m, *i*Pr, 3-Me), 1.78 (s, 5-Me), 4.41 (s, 4-H). — $^{13}\text{C NMR}$: $\delta = 12.13$ (Si– CHMe_2), 17.60 and 17.67 (diastereotopic, Si CHMe_2), 17.88 (5-Me), 25.89 (3-Me), 57.18 (C-3), 114.41 (C-4), 152.12 (C-5).

$\text{C}_{12}\text{H}_{24}\text{OSi}$ (212.4) Calcd. C 67.86 H 11.39
Found C 67.8 H 11.20

5-tert-Butyl-2,2-diisopropyl-3,3-dimethyl-1-oxa-2-sila-4-cyclopentene (7bC): From 2.00 g (7.1 mmol) 6bC, 5 h, b. p. 100°C/0.005 Torr. Yield: 1.02 g (57%). — IR (film): 3030 cm^{-1} ($=\text{CH}$), 1623 ($\text{C}=\text{C}$), 1076. — $^1\text{H NMR}$: $\delta = 1.03\text{--}1.13$ (m, *i*Pr), 1.10 (s, *t*Bu), 4.40 (s, 4-H). — $^{13}\text{C NMR}$: $\delta = 12.13$ (Si– CHMe_2), 17.66 and 17.75 (Si– CHMe_2), 26.27 (3-Me), 27.90 (CMe_3), 34.14 (CMe_3), 50.7 (C-3), 109.96 (C-4), 128.34 (C-5). — MS (70 eV): m/z (%) = 254 (12, M^+), 239 (100, $\text{M} - \text{CH}_3$), 197 (9, $\text{M} - \text{C}_4\text{H}_9$), 169 (12, $\text{M} - 2\text{C}_3\text{H}_7$), 153 (9), 141 [7, $\text{M} - \text{SiO}(\text{C}_3\text{H}_7)_2$].

$\text{C}_{15}\text{H}_{30}\text{OSi}$ (254.5) Calcd. C 70.79 H 11.88
Found C 70.3 H 11.75

2,2-Diisopropyl-3,3-dimethyl-5-(3-phenylpropyl)-1-oxa-2-sila-4-cyclopentene (7dC): From 3.44 g (10.0 mmol) of 6dC, 12 h, b. p. 170°C/0.15 Torr. Yield: 2.08 g (65%) of a very moisture-sensitive colorless oil which was only characterized spectroscopically: IR (film): 3015 cm^{-1} ($=\text{CH}$), 1632 ($\text{C}=\text{C}$), 1118, 1005. — $^1\text{H NMR}$: $\delta = 1.02\text{--}1.15$ (m, Si*i*Pr, 3-Me), 1.78–1.98 (m, 2H), 2.02–2.20 (m, 2H), 2.53–2.70 (t, 2H), 4.48 (s, 4-H), 7.12–7.30 (m, 5H). Further characterization of 7dC is given by its hydrolysis (see below).

5,5'-(1,3-Propanediyl)bis(2,2-diisopropyl-3,3-dimethyl-1-oxa-2-sila-4-cyclopentene) (7eC) and 1-Diazo-5-(2,2-diisopropyl-3,3-dimethyl-1-oxa-2-sila-4-cyclopentene-5-yl)-2-pentanone (9): The solution of 1.72 g (3.5 mmol) of 6eC in 50 ml of anhydrous benzene is refluxed for 15 h. The brownish-red oil which remains after evaporation of the solvent is fractionated by column chromatography with chloroform/ether (1:1):

a) 1.21 g (79%) of 7eC as a colorless oil. — IR (film): 3010 cm^{-1} ($=\text{CH}$), 1635 ($\text{C}=\text{C}$), 1120, 1008. — $^1\text{H NMR}$: $\delta = 0.95\text{--}1.23$ (m, *i*Pr, Me), 1.70–2.20 (m, $[\text{CH}_2]_3$), 4.43 (s, 4-H).

$\text{C}_{25}\text{H}_{48}\text{O}_2\text{Si}_2$ (436.8) Calcd. C 68.74 H 11.08
Found C 68.9 H 11.21

b) 20 mg (2%) of 9 as a yellow oil. — IR (film): 2098 cm^{-1} (CN_2), 1630 ($\text{C}=\text{O}/\text{C}=\text{C}$), 1120, 1005. — $^1\text{H NMR}$: $\delta = 1.03\text{--}1.27$ (m, *i*Pr, Me), 1.87 (m, 2H), 2.06 (m, 2H), 2.35 (t, 2H), 4.50 (s, 4-H), 5.20 (s, HCN_2). The compound was further characterized by its hydrolysis (see below).

In a second run, 65% of 7eC and 10% of 9 were obtained.

Solvolyses of 1-Oxa-2-sila-4-cyclopentenes 7

4-(Diethylhydroxysilyl)-2-pentanone (10a): The solution of 0.21 g (1.2 mmol) of 7aA in acetonitrile (20 ml) and water (1 ml) is refluxed for 1 h. After cooling, chloroform (60 ml) is added and the mixture is freed from water by stirring over MgSO_4 . After filtering, the solvent is evaporated and the residual oil is subjected to Kugelrohr

distillation. At 180°C (oven temperature)/0.4 Torr 0.14 g (62%) of **10a** is collected. — IR (film): 3420 cm⁻¹ (SiO—H), 1705 (C=O), 1070, 1015. — ¹H NMR: δ = 0.63 (t, CH₂CH₃), 0.94 (q, CH₂CH₃), ca. 1.13–1.47 (m, CH), 2.15 (s, COMe), 2.57 („t“, diastereotopic >C—CH₂), 2.83 (broad s, OH).

C₉H₂₀O₂Si (188.3) Calcd. C 57.39 H 10.70
Found C 57.1 H 10.52

4-(Hydroxydiisopropylsilyl)-4-methyl-2-pentanone (10b): From **7aC** (0.35 g, 1.65 mmol) by a procedure analogous to the synthesis of **10a**; reaction time 3.5 h. Yield: 0.24 g (63%), b.p. 90°C (oven temp.)/0.1 Torr. — IR (film): 3440 cm⁻¹ (SiO—H), 1695 (C=O), 1010. — ¹H NMR: δ = 0.95–1.07 (m, 20H), 2.10 (s, COMe), 2.56 (s, CH₂). — MS (70 eV): *m/z* (%) = 230 (0.8, M⁺), 215 (22, M—Me), 187 (100, M—C₃H₇ or CH₃CO), 173 (4, M—CH₃COCH₂), 145 (13), 131 (13, SiPr₂OH).

C₁₂H₂₆O₂Si (230.4) Calcd. C 62.55 H 11.37
Found C 62.8 H 11.30

5-(Hydroxydiisopropylsilyl)-2,2,5-trimethyl-3-hexanone (10c): From **7bC** (0.42 g, 1.65 mmol) by a procedure analogous to the synthesis of **10a**. Yield: 0.31 g (69%), b.p. 90°C (oven temp.)/0.02 Torr. — IR (film): 3460 cm⁻¹ (SiO—H), 1695 (C=O), 1065, 1010. — ¹H NMR: δ = 1.02–1.23 (29H, tBu, iPr, Me), 2.60 (s, CH₂).

C₁₅H₃₂O₂Si (272.5) Calcd. C 66.11 H 11.84
Found C 65.3 H 11.65

2-(Hydroxydiisopropylsilyl)-2-methyl-7-phenyl-4-heptanone (10d): From **7dC** (1.00 g, 3.2 mmol) by a procedure analogous to the synthesis of **10a**. The product obtained after Kugelrohr distillation at 120°C/0.01 Torr was further purified by Lobar column chromatography with chloroform as eluent; yield: 0.40 g (38%). — IR (film): 3440 cm⁻¹ (SiO—H), 1690 (C=O), 1010/1005. — ¹H NMR: δ = 0.98–1.06 (m, iPr and CMe₂), 1.86 (q, 2H), 2.29–2.69 (m, 4H), 2.50 (s, Si—C—CH₂), 3.70 (broad, OH), 7.08–7.20 (m, 5H).

C₂₀H₃₄O₂Si (334.6) Calcd. C 71.80 H 10.24
Found C 71.1 H 10.03

1-(tert-Butylmethoxymethylsilyl)-4,4-dimethyl-3-pentanone (11): Compound **7bB** (0.21 g, 1.0 mmol) is dissolved in 15 ml of methanol. After 3 h, the solvent is evaporated and the residual oil is subjected to Kugelrohr distillation. At 80°C (oven temp.)/0.05 Torr, 0.17 g (69%) of **11** is obtained as a colorless oil. — IR (film): 1702 cm⁻¹ (C=O), 1095 (SiO—C). — ¹H NMR: δ = 0.09 (s, SiMe), 0.82–ca. 0.90 (m, SiCH₂), 0.90 (s, Si tBu), 1.10 (s, CO tBu), 2.52 (m, COCH₂), 3.46 (s, OMe).

C₁₃H₂₈O₂Si (244.4) Calcd. C 63.87 H 11.54
Found C 63.6 H 11.52

2,10-Bis(diisopropylmethoxysilyl)-2,10-dimethyl-4,8-undecanedione (12): The solution of 1.20 g (2.7 mmol) of **7eC** in 5 ml of anhydrous methanol is refluxed for 2.5 h. After evaporation of the solvent, a yellow oil is obtained which is subjected to Kugelrohr distillation: 0.86 g (64%) of **12**, yellow oil, b.p. 240°C (oven temp.)/0.03 Torr. — IR (film): 1695 cm⁻¹ (C=O), 1097 (SiO—C). — ¹H NMR: δ = 1.0–1.3 (m, 40H, iPr and Me), 1.80 (m, 2H), 2.10 (m, 2H), 2.37–2.56 (m, 2H), 2.47 (s, Si—C—CH₂), 3.57 (s, OMe).

C₂₇H₅₆O₄Si₂ (500.9) Calcd. C 64.73 H 11.27
Found C 64.8 H 11.17

1-Diazo-8-(hydroxydiisopropylsilyl)-8-methyl-2,6-nonanedione (13): The solution of crude diazo ketone **9** (0.14 g, 0.50 mmol) in wet chloroform is stirred for 2 h. The solvent is evaporated and the residue is chromatographed on silica gel with chloroform (400 ml) as eluent. 0.10 g (60%) of **13** is obtained as a yellow oil. — IR (film): 3460 cm⁻¹ (SiO—H), 2098 (CN₂), 1690 [C(=O)], 1640

[C(2)=O]. — ¹H NMR: δ = 1.0–1.3 (m, 20H, iPr and Me), 1.86 (t, 2H), 2.16–ca. 2.50 (m, 4H), 2.57 (s, Si—C—CH₂), ca. 3.65 (br, OH), 5.20 (s, HCN₂).

C₁₆H₃₀N₂O₃Si (326.5) Calcd. C 58.86 H 9.26 N 8.58
Found C 58.4 H 9.27 N 7.8

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