

Intramolecular Carbene and Carbenoid Reactions of α -(Vinyloxy)silyl- α -diazooacetates

Birgit Daucher, Volker Gettwert, Ruth Striegler, and Gerhard Maas

Abteilung Organische Chemie I, Universität Ulm, Albert-Einstein-Allee 11, D-89081 Ulm, Germany

Reprint requests to Prof. Dr. G. Maas. Fax: +49(731)5022803.

E-mail: gerhard.maas@chemie.uni-ulm.de

Z. Naturforsch. **59b**, 1444 – 1450 (2004); received August 24, 2004

Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

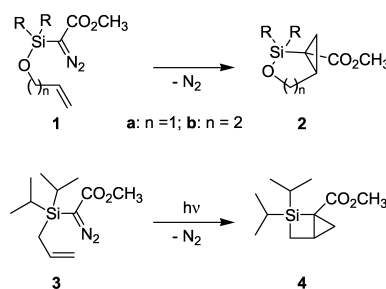
Thermolysis of α -[diisopropyl-1-(methylvinyl)oxysilyl]- α -diazooacetate **5a** at 160 °C yields mainly 2,5-dihydro-1,2-oxasilole-3-carboxylate **6a** and 3-[diisopropyl(methoxy)silyl]-2(5*H*)-furan-2-one **7**. From the thermolysis reaction of α -[diisopropyl-1-(phenylvinyl)oxysilyl]- α -diazooacetate **5b**, only 1-oxa-2-sila-3-cyclopentene-3-carboxylate **6b** could be isolated in low yield. UV-irradiation of **5a,b** generates **6a,b** as the main products. The $\text{Rh}_2(\text{C}_3\text{F}_7\text{COO})_4$ -catalyzed decomposition of **5a** provides primarily the ketene 2-[diisopropyl(methoxy)silyl]-pent-1-ene-1,4-dione (**9**) in high yield. After work-up, 3-[diisopropyl(methoxy)silyl]-2(3*H*)-furan-2-one **10a** and 2(5*H*)-furanone **7** are obtained in relative amounts that depend on work-up conditions. Mechanistic pathways leading to the various products are proposed.

Key words: Carbenes, Diazoacetates, Dihydro-1,2-oxasiloles, Rhodium-Catalyzed Carbenoid Reactions, Silaheterocycles

Introduction

Intramolecular reactions of heteroatom-substituted carbenes and short-lived metal-carbene complexes provide an access to a wide range of often non-classical heterocyclic compounds [1]. In this context, readily available silicon-functionalized α -silyl- α -diazoketones and α -silyl- α -diazooacetates can serve as precursors for a range of diverse silaheterocycles [2]. Starting from appropriately functionalized α -silyl- α -diazooacetates, we have used carbene and carbenoid pathways to generate, *e.g.*, 1-oxa-2-silacyclopentanes [3], 1-oxa-2-sila-3-cyclopentenones [3], 3-oxa-2-silabicyclo[3.1.0]hexanes and -bicyclo[4.1.0]heptanes [3], 2*H*-1,2-oxasilines [4], silacyclobutanes [5], and a 2-silabicyclo[2.1.0]pentane [6].

Two findings of our former studies, related to the subject of this work, are shown in Scheme 1: (Allyloxysilyl)-diazooacetates **1a** as well as [(3-butenyl)oxysilyl]-diazooacetates **1b** are converted, by irradiation with UV light or under transition-metal catalysis (copper(I) triflate, rhodium(II) perfluorobutyrate), into 3-oxa-2-silabicyclo[n.1.0]alkanes **2a** and **2b**, respectively [3]. Similarly, a photochemically induced intramolecular cyclopropanation re-



Scheme 1. Intramolecular cyclopropanation reactions of unsaturated α -silyl- α -diazooacetates **1** and **3**.

action transforms (allylsilyl)-diazooacetate **3** into 2-silabicyclo[2.1.0]pentane **4** [6]. The reaction conditions are important: While the transformation **1b** \rightarrow **2b** was achieved under thermal conditions as well, thermolysis of compounds **1a** led to 1-oxa-2-sila-3-cyclopentenones rather than to bicyclic compounds **2a**, and the thermal or rhodium-catalyzed decomposition of **3** turned out to be unspecific.

We report now on intramolecular carbene and carbenoid reactions of two α -(vinyloxy)silyl- α -diazooacetates which represent oxygen analogues of (allylsilyl)-diazooacetates **3** and lower homologues of (allyloxy)silyl-diazooacetates **1a**. It will be seen that the

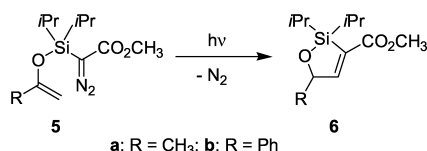
products are structurally different from those obtained from the latter two classes of unsaturated diazo compounds [7].

Results and Discussion

The α -(vinylxy)silyl- α -diazoacetates **5a,b** were prepared as described [8] by successive treatment of diisopropylsilyl bis(triflate) with methyl diazoacetate and acetone (or acetophenone) in the presence of triethylamine.

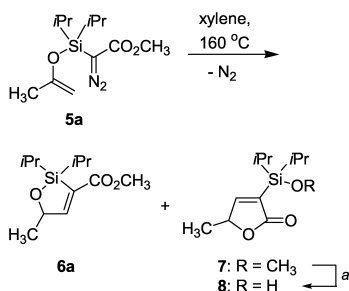
Photolysis and thermolysis of **5a,b**

UV irradiation ($\lambda \geq 300$ nm) of **5a,b** generated product mixtures which contained 2,5-dihydro-1,2-oxasilole-3-carboxylates **6a,b** as the major constituents according to ^1H NMR spectra (Scheme 2). However, these hydrolytically labile compounds could be isolated only in low yield after the necessary purification by column chromatography and distillation (**6a**: 19%; **6b**: 12%).



Scheme 2. Photolysis of (vinylxy)silyl-diazoacetates **5a,b**.

Similar to the photochemical reaction, thermolysis of **5b** (toluene, 160 °C, thick-walled Schlenk tube) gave a product mixture from which **6b** could be isolated as the only identified compound in low yield (24% after work-up). From the thermolysis reaction of **5a** (xylene, 160 °C), 1-oxa-2-sila-3-cyclopentene **6a** (25%), 3-[diisopropyl(methoxy)silyl]-2(5*H*)-furanone **7** (24%), and the related silanol **8** (4%) were isolated after careful chromatographic work-up (Scheme 3). Silanol **8** obviously results from partial hydrolysis of methoxysilane **7** during column chromatography; in fact, it was found that complete transformation of **7**



Scheme 3. Thermolysis of (1-methylvinyl)oxysilyl-diazoacetate **5a**; a: hydrolysis.

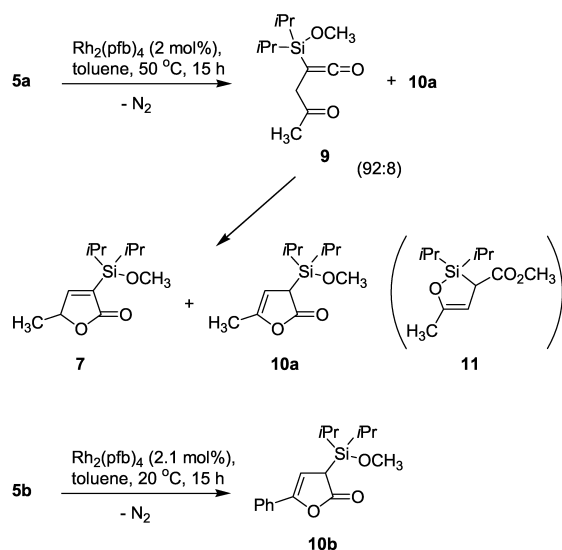
into **8** occurred on prolonged standing in CDCl_3 solution in an NMR tube.

Rhodium-catalyzed dediazonation of **5a,b**

We have found earlier that transition-metal catalyzed decomposition of silyl-diazoacetates in general and of those with bulky substituents on silicon in particular requires highly electrophilic copper and rhodium catalysts [3, 4, 9]. Remarkably, copper(I) triflate failed to decompose **5a,b**, but elimination of N_2 could be achieved with dirhodium tetrakis(perfluorobutyrate) $[\text{Rh}_2(\text{pfb})_4]$, $\text{pfb} = \text{C}_3\text{F}_7\text{COO}$. Unfortunately, the notorious difficulty to remove this catalyst from the product mixture made the work-up procedure cumbersome and led to product losses during the required chromatographic purification. Furthermore, a careful examination of the catalytic decomposition of **5a** (toluene, 50 °C, 12 h) showed that the result depends on the work-up conditions (Scheme 4). At the end of the reaction, ^1H and ^{13}C NMR spectra indicated the almost quantitative formation of [diisopropyl(methoxy)silyl]ketene **9** and of a compound **10a** (vide infra) in a 92:8 ratio. Although the ketene could not be fully purified due to the presence of $\text{Rh}_2(\text{pfb})_4$ and gradual further transformation, its constitution follows without doubt from its spectroscopic data [IR: $\nu(\text{C}=\text{C}=\text{O}) = 2088\text{ cm}^{-1}$; ^1H NMR: $\delta = 2.23$ (CH_3), 3.17 (CH_2), 3.52 (SiOCH_3); ^{13}C : $\delta = 4.19$ ($\text{C}=\text{C}=\text{O}$), 179.38 ($\text{C}=\text{C}=\text{O}$)]. Immediate chromatography of the crude product over neutral alumina and then over silica gel provided 2(5*H*)-furanone **7** in 62% yield. However, when the crude product consisting mostly of ketene **9** and still containing $\text{Rh}_2(\text{pfb})_4$ was kept for 1–2 days before chromatography on silanized silica gel, the yields of isolated products **7** and **10a** were $\leq 7\%$ and 37%, respectively.

For compound **10a**, the constitution of a 3-[diisopropyl(methoxy)silyl]-2(3*H*)-furanone is proposed based on the spectroscopic data and the observation, that in methanol solution 2(5*H*)-furanone **7** is converted in less than a day into a mixture of products which according to ^1H NMR integration contains at least 25–30% of 2(3*H*)-furanone **10a**. This constitutes rather strong evidence against the isomeric structure of a 2,3-dihydro-1,2-oxasilole-3-carboxylate **11** for which NMR data quite similar to **10a** would be expected.

The experimental findings suggest that ketene **9** undergoes cyclization to form lactone **7** in a reaction cat-



Scheme 4. $\text{Rh}_2(\text{pfb})_4$ -catalyzed decomposition of (vinyl-oxy)silyl-diazoacetates **5a,b**.

alyzed by silica gel, while the cyclization $9 \rightarrow 10\text{a}$ occurs on standing of the neat liquid compound in the presence of $\text{Rh}_2(\text{pfb})_4$. In contrast to the isomerization $7 \rightarrow 10\text{a}$ taking place in methanol solution, we did not observe this to happen with purified liquid **7**. Typically, α,β -unsaturated butenolides are thermodynamically more stable than the isomeric β,γ -unsaturated butenolides (for a discussion, see lit. [10]). The isomerization $7 \rightarrow 10\text{a}$ suggests, however, that the non-conjugated isomer **10a** is more stable than the conjugated one. This may be due to the presence of the bulky silyl substituent which causes more destabilizing steric interactions with the adjacent carbonyl group in **7** than in **10a** where the torsion angle Si–C–C–O is larger.

From the $\text{Rh}_2(\text{pfb})_4$ -catalyzed decomposition of diazoacetate **5b**, 1-oxa-2-sila-4-cyclopentene **10b** was isolated as the sole product in about 82% yield after column chromatography.

Structural assignments

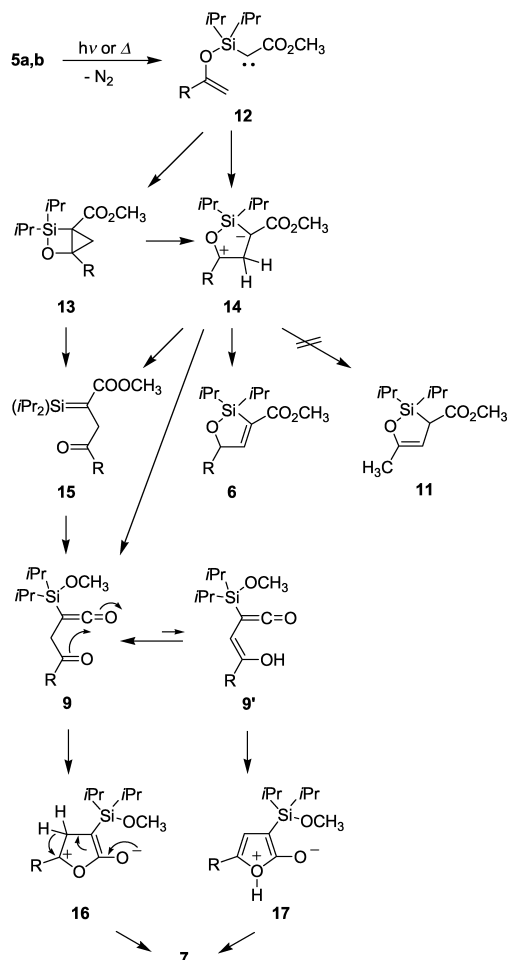
2,5-Dihydro-1,2-oxasiloles have been synthesized along various routes [3, 4, 11–13]. The constitution of the 2,5-dihydro-1,2-oxasilole-3-carboxylates **6a,b** is established by the ^1H and ^{13}C NMR data (see Experimental Section) and their comparison with close relatives prepared independently [3]. The ^{29}Si NMR resonance of **6a** is found at $\delta = 32.29$ ppm in CDCl_3 solution.

The proposed constitution of 2(5*H*)-furanone **7** is also in accord with the NMR and IR data. In particular, the absence of a C,H correlation peak between the carbonyl carbon and the methoxy hydrogen atoms in the HMBC spectrum suggests that the ester function is no longer intact, and the ^{29}Si resonance at $\delta = 4.42$ ppm indicates a different environment for silicon compared to **6a**. The IR absorption at 1745 cm^{-1} is in the expected range for α,β -unsaturated five-membered lactones. Furthermore, the relevant ^1H and ^{13}C NMR data are in close agreement with those reported for 5-methyl-3-trimethylsilyl-2,5-dihydro-2-furanone [14].

The structural assignment of compounds **10a,b** is more difficult. Although the ^1H and ^{13}C NMR data clearly indicate the presence of an enolether moiety (OC(R)=CH : $\delta_{\text{H}} = 5.18$ (**10a**), 5.89 (**10b**); $\delta_{\text{CH}} = 101.28$ (**10a**), 100.61 (**10b**)), they do not allow to distinguish unequivocally between lactone **10a** and 2,3-dihydro-1,2-oxasilole-3-carboxylate **11** for which very similar chemical shifts and coupling constants should be expected. The absence of a heteronuclear coupling between carbonyl-C and methoxy-H also supports the presence of a SiOCH₃ moiety in **10a**. Furthermore, the IR absorption at 1776 cm^{-1} is at a frequency too high for simple methyl esters, but it is closer to the typical range (close to 1800 cm^{-1} [15]) of β,γ -unsaturated five-membered lactones (*i.e.*, cyclic vinyl esters). It should also be mentioned that the ^1H and ^{13}C chemical shifts of **10a** agree well with those of 5-methyl-2(3*H*)-furanone (α -angelica lactone) and its 3- and 4-methyl derivatives [10, 16]. The values of the long-range H,H coupling constants in **10a** are identical with those that we have observed for α -angelica lactone [^1H NMR (400.13 MHz, CDCl_3): $\delta = 2.00$ (dt, 3 H, CH₃), 3.17 (mc, 2H, 3-H₂), 5.13 (mc, 1H, 4-H); $^4J(5\text{-CH}_3, 4\text{-H}) = 1.52\text{ Hz}$, $^5J(5\text{-CH}_3, 3\text{-H}_2) = 2.52\text{ Hz}$].

Reaction mechanisms

Carbenes **12** are expected as the primary products of the photochemical or thermal nitrogen elimination from **5a,b**. By analogy to the carbene reactions shown in Scheme 1, intramolecular cyclopropanation leading to oxasilabicyclo[2.1.0]pentane **13** may occur. In contrast to the carbon analogue **4** [6], however, compound **13** was not observed. This may be due to the fact that **13** is more strained than **4** because the Si–O ring bond is significantly shorter than the corresponding Si–C bond in **4**. Furthermore, **13** constitutes a 1,2-donor-acceptor substituted cyclopropane, and this class of



Scheme 5. Possible mechanistic pathways in the photolysis and thermolysis of diazoacetates **5**; R = CH₃, Ph.

compounds is prone to undergo more or less facile (often Lewis acid assisted) heterolytic ring opening to form 1,3-dipolar species [17]. Thus, heterolytic cleavage of the 1,4-bond in **4** would generate the monocyclic betaine **14** with considerable release of ring strain. Transformations of **14** into (methoxycarbonyl)silene **15** (by heterolytic Si-O bond cleavage) and into 2,5-dihydro-1,2-oxasilole **6** (by a C-4 \rightarrow C-5 hydride shift) appear reasonable. The latter hydride shift may be preferred for electronic reasons over a proton migration converting **14** into dihydrooxasilole **11** which was not found.

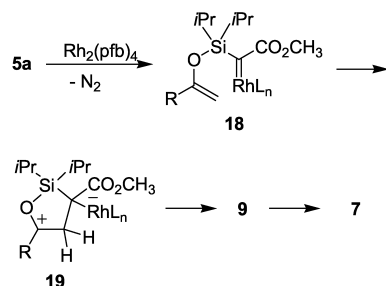
Silene **15**, like other short-lived acyl-silenes [9, 18], is expected to rearrange rapidly into (methoxysilyl)ketene **9** by a 1,3(C \rightarrow Si) migration of the methoxy group. The conversion of **9** into **7** may occur either

from the keto form **9** or from the enol form **9'** via intermediates **16** and **17**, respectively. Although the ¹H NMR spectrum of **9** did not indicate the simultaneous presence of enol **9'**, this does not exclude the participation of **9'** in the cyclization event. The situation is similar to the lactone formation from 4-oxopentanoic acid (levulinic acid) [19] or 4-oxo-carboxamides [10] which is also thought to involve the corresponding enol tautomers.

Silene **15** could also result from a thermally induced [2+2] cycloreversion occurring in the strained bicyclopentane **13**. In fact, we have found evidence for such a reaction in the thermolysis (150 °C) of photochemically generated 2-silabicyclopentane **4** from which the allyl-silyl-ketene analogous to **9** was isolated in low yield [6]. The finding that lactone **7**, resulting from ketene **9** (see Scheme 4), was isolated from the thermolysis of **5a** at 160 °C, but not from the photolysis at 20 °C, is in line with the photochemical and thermal behavior of **4** and lends support to the hypothesis of a thermally induced [2+2] cycloreversion of **13**. It cannot be excluded, however, that betaine **14** rearranges directly, without intervention of silene **15**, into silylketene **9** by a 1,3(C \rightarrow Si) migration of the MeO⁻ group accompanied by Si-O_{ring} cleavage (*i. e.*, intramolecular nucleophilic substitution at silicon).

Evidently, the preceding discussion could only suggest some reasonable pathways and intermediates. The proper pathways, including the reversibility of some steps (*e. g.*, **13** \rightarrow **14**, **14** \leftarrow **13**), are not known at present, and additional pathways cannot be excluded. For example, as silyl-substituted diazoacetates are known to be exceptionally stable towards thermally induced elimination of N₂, thermal impact on **5a,b** may induce an intramolecular [3+2] cycloaddition reaction [3, 20], and subsequent N₂ elimination from the formed bicyclic pyrazolines may yield product **6** via diradical intermediates. Also, the proposed cleavage of the internal cyclopropane bond in silabicyclopentane **13** may occur in a homolytic rather than a heterolytic manner under both thermal and photochemical conditions.

For the Rh₂(pfb)₄-catalyzed reaction of alkyl α -silyl- α -diazoacetates, formation of (alkoxysilyl)ketenes appears to be typical, and possible mechanistic details have been discussed [9]. The transformation includes a substituent migration from silicon to the adjacent carbenoid carbon atom. The formation of ketene **9** offers a novel aspect, because this rearrangement includes a heteroallylic rearrangement



Scheme 6. Mechanistic proposal for the formation of ketene **9** in the $\text{Rh}_2(\text{pfb})_4$ -catalyzed reaction of **5a**.

of the migrating vinyloxy group. While such a rearrangement is conceivable already for the free carbene intermediate **12** (Scheme 5) due to its electrophilic character and the nucleophilic enolether double bond, it is even more likely in the case of metal carbene intermediate **18** which is believed to have a strong resonance contribution from a rhodium-stabilized carbocation structure [9 and lit. cit.] (Scheme 6). Thus, we suggest that the $\text{Rh}_2(\text{pfb})_4$ -catalyzed reaction of **5a** proceeds *via* the rhodium-containing betaine **19** which yields mainly ketene **9**, either directly (MeO migration to silicon and Si–O_{ring} cleavage, see above) or *via* (methoxycarbonyl)silene **15**.

Conclusion

This study has shown that the intramolecular carbene and carbenoid reactions of (vinyloxy)silyl-diazoacetates **5** lead to other results than those of (allyloxy)silyl-diazoacetates **1a** and (allylsilyl)-diazoacetates **3**. Starting with **5**, products of an intramolecular cyclopropanation reaction were neither isolated nor observed. However, their intermediate participation cannot be excluded. The monocyclic betaine **15** and the rhodium-substituted analogue **19**, respectively, are considered as key intermediates leading to ketene **9** and 2,5-dihydro-1,2-oxasilole **6**.

Experimental Section

General methods: All reactions were carried out in oven-dried glassware and under an argon atmosphere. Solvents were dried by standard procedures. The petroleum ether used had a boiling range of 40–60 °C. Column chromatography was performed under hydrostatic conditions (silica gel Si 60, 0.063–0.2 mm, Macherey-Nagel; silica gel Si 60 silanized, 0.063–0.2 mm, Merck; neutral aluminum oxide 90, activity I, Merck) and under medium-pressure conditions (Merck Lobar columns, LiChroprep Si 60, particle size 40–63 μm ; size 310 \times 25 mm; gradient pump Merck-Hitachi L6200) For bulb-to-bulb distillations, oven temperatures are

given. – NMR: Bruker AMX 500 (^1H : 500.14 MHz; ^{13}C : 125.76 MHz, ^{29}Si : 99.36 MHz), Bruker AMX 400 (^1H : 400.13 MHz; ^{13}C : 100.63 MHz), and Bruker AC 200 (^1H : 200.13 MHz; ^{13}C : 50.32 MHz); CDCl_3 was used as solvent if not stated otherwise. As the internal reference, Me_4Si was used for the ^1H and ^{29}Si spectra, and the solvent signal for the ^{13}C NMR spectra [$\delta(\text{CDCl}_3) = 77.0$ ppm]. Assignments of ^{13}C chemical shifts are based on proton-coupled spectra, C,H correlation spectra, and HMBC spectra. – IR: Perkin-Elmer IR 883, IR 1310, Beckmann Acculab IR 20A. – MS: Finnigan MAT SSQ 7000 (EI, CI). – α -Silyl- α -diazoacetates **5a,b** [8], and dirhodium tetrakis(perfluorobutyrate) [21] were prepared by literature methods.

Photolysis of diazoacetates **5a,b**

A solution of **5a** (1.32 g, 4.9 mmol) in anhydrous benzene (50 ml) was irradiated with a high-pressure mercury lamp (Philips HPK 125 W, $\lambda \geq 300$ nm) until evolution of N_2 had ceased (4 h). The solvent was evaporated, and the residue was subjected to column chromatography (1. flash chromatography, silica gel (20 g), ether; 2. medium-pressure column chromatography, Merck LiChroprep Si 60, eluent ether/petroleum ether (3:7)). *Methyl 2,2-diisopropyl-5-methyl-2,5-dihydro-1,2-oxasilole-3-carboxylate* (**6a**) was isolated as a colorless oil after bulb-to-bulb distillation at 120 °C/0.01 mbar; yield: 0.22 g (19%). – ^1H NMR (400.13 MHz): $\delta = 0.99$, 1.01, 1.02, 1.04 (4 d, $^3J = 7.5$ Hz, 12 H, SiCHMe), 1.10–1.19 (m, 2 H, CHMe), 1.34 (d, $J = 6.9$ Hz, 5-Me), 3.75 (s, COOMe), 4.90 (dq, $J = 6.9$ and 1.0 Hz, 5-H), 7.67 (d, $J = 1.0$ Hz, =CH). – ^{13}C NMR (100.63 MHz): $\delta = 12.3$ (SiCHMe), 13.1 (SiCHMe), 16.84, 16.93, 17.09, 17.21 (4 SiCHMe), 22.1 (5-Me), 51.5 (COOMe), 78.2 (C-5), 130.8 (C-3), 164.4 (C-4), 167.3 (C=O). – ^{29}Si NMR (99.37 MHz): $\delta = 32.3$. – IR (film): $\nu = 2945$ (s), 2865 (s), 1724 (s, C=O), 1712 (s), 1595 (m), 1243 (s) cm^{-1} . – MS (EI, 70 eV): m/z (%) = 242 (9) [M^+], 211 (7) [$\text{M}^+ - \text{OMe}$], 199 (100) [$\text{M}^+ - i\text{Pr}$], 171 (38), 129 (31), 113 (8), 99 (8). – $\text{C}_{12}\text{H}_{22}\text{O}_3\text{Si}$ (242.39): calcd. C 59.46, H 9.15; found C 59.6, H 9.02.

A solution of **5b** (0.62 g, 1.9 mmol) in anhydrous benzene (50 ml) was irradiated with a high-pressure mercury lamp (Philips HPK 125 W, $\lambda \geq 300$ nm) until evolution of N_2 had ceased (4 h). The solvent was evaporated at 0.01 mbar, and the residue was separated by bulb-to-bulb distillation at 150 °C/0.005 mbar followed by medium-pressure column chromatography (Merck LiChroprep Si 60, eluent ether/petroleum ether (1:9)). *Methyl 2,2-diisopropyl-5-phenyl-2,5-dihydro-1,2-oxasilole-3-carboxylate* (**6b**) was obtained as a colorless oil; yield: 0.064 g (12%). – ^1H NMR (200.1 MHz): $\delta = 1.06$, 1.08, 1.09, 1.10 (4 d, 12 H, SiCHMe), 1.14–1.29 (m, 2 H, SiCHMe₂), 3.76 (s, 3 H, COOMe), 5.80 (d, $^3J = 1.6$ Hz, 5-H), 7.28–7.37 (m, 5 H,

Ph), 7.80 (d, $^3J = 1.6$ Hz, =CH). – ^{13}C NMR (50.32 MHz): $\delta = 12.90$ (CHMe₂), 13.22 (CHMe₂), 16.94, 17.04, 17.21, 17.44 (4 SiCHMe), 51.69 (OMe), 83.62 (C-5), 126.22 (2 C), 127.88, 128.60 (2 C), 131.74, 140.35 (C-3), 162.61 (C-4), 167.22 (C=O). – IR (film): $\nu = 1710$ (s, br, C=O), 1590 (m), 1545 (m) cm^{-1} . – C₁₇H₂₄O₃Si (304.46): calcd. C 67.07, H 7.94; found C 68.1, H 8.0.

Thermal decomposition of **5a**

A solution of **5a** (0.500 g, 1.85 mmol) in anhydrous xylene (10 ml) was heated at 160 °C for 8 h. The solvent was evaporated at reduced pressure. Bulb-to-bulb distillation at 125 °C/0.02 mbar of the residue furnished a mixture of products which was separated by column chromatography (Merck LiChroprep Si 60). Elution with ether/petroleum ether (5:95) at a flow rate of 1 ml/min yielded first 0.111 g (25%) of **6a**, then 0.108 g (24%) of **7**. Further elution with ether gave silanol **8** which was purified by additional chromatography over silanized silica gel; yield: 17 mg (4%).

3-[Diisopropyl(methoxy)silyl]-5-methyl-2,5-dihydro-2-furanone (7): Colorless oil. – ^1H NMR (200.13 MHz): $\delta = 1.05$ – 1.07 (4 d, 12 H, 4 CHMe), 1.28 (2 sept, 2 H, SiCH), 1.43 (d, $^3J = 6.9$ Hz, 3 H, 5-Me), 3.61 (s, 3 H, OMe), 5.11 (dq, $^3J = 6.9$ and 1.3 Hz, 1 H, OCH), 7.71 (d, $^3J = 1.3$ Hz, 1 H, =CH). – ^{13}C NMR (50.32 MHz): $\delta = 11.81$ (SiCH), 16.95 (CHMe), 17.12 (CHMe), 19.07 (5-Me), 52.06 (OMe), 80.13 (C-5), 129.89 (C-3), 168.67 (C-4), 175.64 (C=O). – ^{29}Si NMR (C₆D₆, 99.37 MHz): $\delta = 4.42$. – IR (film): $\nu = 2945$ (s), 1745 (vs, C=O), 1593 (w), 1158 (s), 1092 (s) cm^{-1} . – MS (EI, 70 eV): m/z (%) = 242 (0.1) [M⁺], 199 (100) [M⁺ – iPr], 167 (4), 157 (4), 127 (8), 119 (29), 91 (39). – C₁₂H₂₂O₃Si (242.39): calcd. C 59.46, H 9.15; found C 59.71, H 9.55.

3-[Diisopropyl(hydroxy)silyl]-5-methyl-2(5H)-furanone (8): Colorless oil. – ^1H NMR (200.13 MHz): $\delta = 1.03$ (pseudo-t, 12 H, CHMe), 1.15 (sept, 2 H, SiCH), 1.45 (d, $^3J = 6.9$ Hz, 3 H, 5-CH₃), 2.30 (s, 1 H, OH), 5.12 (dq, 1 H, $^3J = 6.9$ and 1.5 Hz, 1 H, 5-H), 7.60 (d, $^3J = 1.5$ Hz, 1 H, =CH). – ^{13}C NMR (50.32 MHz): $\delta = 12.68$ (SiCH), 16.63 (CHMe), 16.86 (CHMe), 18.96 (OCHMe), 80.53 (OCH), 129.70 (C-3), 166.60 (=CH), 177.12 (C=O). – ^{29}Si NMR (C₆D₆, 99.37 MHz): $\delta = 3.65$. – IR (film): $\nu = 3436$ (br, s, OH), 2944 (s), 1739 (m), 1720 (s, C=O), 1591 (w), 1493 (m), 1164 (m), 1089 (m) cm^{-1} . – MS (CI, 100 eV): m/z (%) = 269 (4) [(M+allyl)⁺], 257 (20) [(M+Et)⁺], 229 (100) [MH⁺], 211 (14) [MH⁺ – H₂O], 185 (33) [M⁺ – iPr]. – C₁₁H₂₀O₃Si (228.36): calcd. C 57.86, H 8.83; found C 57.26, H 8.94.

Thermal decomposition of **5b**

A solution of **5b** (0.734 g, 2.21 mmol) in anhydrous toluene (10 ml) was heated for 7 h at 160 °C in a thick-walled Schlenk tube (volume 15 ml). The solvent was evap-

orated at 0.01 mbar, and the residue was fractionated first by flash chromatography (silica gel (20 g), eluent ether), then by column chromatography (Merck LiChroprep Si 60, eluent ether/petroleum ether (3:7)). Further purification by the same type of chromatography, but with ether/petroleum ether (5:95) as the eluent, gave 0.163 g (24%) of **6b**.

Rh₂(pfb)₄-catalyzed transformation of **5a**

A solution of dirhodium(II) tetrakis(perfluorobutyrate) (61 mg, 0.06 mmol) in anhydrous toluene (20 ml) was warmed at 50 °C, and a solution of diazoacetate **5a** (0.800 g, 2.95 mmol) in anhydrous toluene (20 ml) was gradually added during 1 h. The mixture was kept with stirring at 50 °C for 15 h. At this point, almost complete transformation into 2-[diisopropyl(methoxy)silyl]-pent-1-ene-1,4-dione (**9**) and compound **10a** (ratio: 92:8) had occurred. The ketene could not be purified due to its instability. After removal of the solvent, but not of the rhodium catalyst, it was characterized by the following spectroscopic data: ^1H NMR (200.13 MHz): $\delta = 1.02$ – 1.16 (14 H, Si(CHMe)₂), 2.23 (s, 3 H, C(O)Me), 3.17 (d, 2 H, C(O)CH₂), 3.52 (s, SiOMe). – ^{13}C NMR (50.32 MHz): $\delta = 4.19$ (SiC=C=O), 12.94 (SiCH), 17.27 (CHMe₂), 28.21 (C(O)Me), 38.46 (C(O)CH₂), 51.41 (SiOMe), 179.38 (C=C=O), 204.87 (MeC=O). – ^{29}Si NMR (C₆D₆, 99.37 MHz): $\delta = 10.77$. – IR (film): $\nu = 2088$ (s, C=C=O), 1720 (s, C=O) cm^{-1} .

The crude reaction solution consisting mostly of ketene **9** was processed as follows.

a) The solvent was evaporated and the residue was dissolved in ether/petroleum ether (1:9) (20 ml) and filtered through a pad of neutral alumina (5 g). The resulting brown oil, obtained after evaporation of the solvent, was submitted to bulb-to-bulb distillation at 125 °C/0.02 mbar followed by column chromatography (Merck LiChroprep Si 60, ether/petroleum ether (5:95)) to give dihydrofuranone **7** (0.443 g, 62%). Small amounts of **10a** were detected by TLC but not isolated.

b) The solvent was evaporated and the oily residue was kept for 1–2 days at 20 °C until a ^1H NMR spectrum indicated the disappearance of **9**. Column chromatography (silanized silica gel (30 g), petroleum ether) yielded 0.264 g (37%) of **10a**. Several reaction runs were carried out; for some of them, the presence of 2(5H)-furanone **7** (after standing for 1–2 days) was indicated by the ^1H NMR spectra. This product could be isolated by column chromatography (silanized silica gel, ether/petroleum ether (20:80)) in yields up to 7%.

3-[Diisopropyl(methoxy)silyl]-5-methyl-2(3H)-furanone (10a): Colorless oil, b.p. 85 °C/0.035 mbar (bulb-to-bulb distillation). – ^1H NMR (500.14 MHz): $\delta = 1.07$, 1.09, 1.09, 1.12 (4 d, $^3J = 7.5$ Hz, 4 SiCHMe), 1.26 (sept, $^3J = 7.5$ Hz, 2 H, 2 SiCHMe), 2.01 (dd, $^5J = 2.5$ Hz,

$^4J = 1.5$ Hz, 3 H, 5-Me), 3.25 (quin, $^3J = ^5J = 2.5$ Hz, 1 H, 3-H), 3.59 (s, 3 H, OMe), 5.18 (centered m, 1 H, 4-H). – ^{13}C NMR (50.32 MHz): $\delta = 12.08$ (SiCH), 12.37 (SiCH), 13.93 (5-Me), 17.15/17.15/17.25/17.38 (SiCHMe), 36.93 (C-3), 52.03 (COOMe), 101.28 (C-4), 150.20 (C-5), 178.60 (C=O). – ^{29}Si NMR (99.37 MHz): $\delta = 8.94$ ppm. – IR (film): $\nu = 2958$ (s), 2867 (s), 1776 (s), 1672 (w), 1628 (w), 1099 (vs) cm^{-1} . – $\text{C}_{12}\text{H}_{22}\text{O}_3\text{Si}$ (242.39): calcd. C 59.46, 9.15; found C 59.71, H 8.80.

Rh₂(pfb)₄-catalyzed transformation of 5b

A solution of diazoacetate **5b** (0.850 g, 2.56 mmol) in toluene (20 ml) was gradually added during 1 h to a solution of dirhodium(II) tetrakis(perfluorobutyrate) (57 mg, 2.1 mol-%) in toluene (20 ml). After stirring for 15 h, the solution was submitted to flash chromatography over a column with silica gel (20 g) followed by elution of the column with ether (50 ml). The combined elutes were concentrated, and the product was obtained after column chromatography (Merck LiChroprep Si 60, eluent ether/petroleum ether (1:1)). *Methyl 2,2-diisopropyl-5-*

phenyl-2,3-dihydro-1,2-oxasilole-3-carboxylate (10b) was obtained as a hygroscopic solid which was not completely pure (^1H NMR) but could not be purified further. Mp. 59 °C; yield: 0.639 g (82%). – ^1H NMR (200.13 MHz): $\delta = 1.08 - 1.17$ (m, 12 H, SiCHMe), 1.19–1.33 (m, 2 H, 2 \times SiCHMe), 3.54 (d, $^3J = 2.6$ Hz, 1 H, 3-H), 3.63 (s, 3 H, OMe), 5.89 (d, $^3J = 2.6$ Hz, 1 H, 4-H), 7.26–7.62 (m, 5 H, Ph); traces of impurities are found around $\delta = 1.0$ and 3.6 and in the aromatic region. – ^{13}C NMR (100.63 MHz): $\delta = 12.22$ (SiCHMe), 12.44 (SiCHMe), 17.17, 17.27, 17.40 (SiCHMe), 38.26 (C-3), 52.17 (OMe), 100.61 (C-4), 124.36 (CH), 128.63 (CH), 128.79 (CH), 128.95 (C_q), 151.35 (C-5), 178.05 (C=O). – $\text{C}_{17}\text{H}_{24}\text{O}_3\text{Si}$ (304.46): calcd. C 67.07, H 7.95; found C 65.7, H 8.0.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank the staff of the Analytical Laboratories of the University of Ulm and the University of Kaiserslautern for the elemental analyses.

- [1] a) Y. Cheng, O. Meth-Cohn, *Chem. Rev.* **104**, 2507 (2004); b) A. F. Khlebnikov, M. S. Novikov, R. R. Kostikov, *Adv. Heterocycl. Chem.* **65**, 93 (1996).
- [2] G. Maas, in Z. Rappoport, Y. Apeloig (eds): *The chemistry of organic silicon compounds*, Vol. 2, Part 1, Chapter 13, John Wiley & Sons, Chichester (1998).
- [3] G. Maas, F. Krebs, T. Werle, V. Gettwert, R. Striegler, *Eur. J. Org. Chem.* 1939 (1999).
- [4] V. Gettwert, F. Krebs, G. Maas, *Eur. J. Org. Chem.* 1213 (1999).
- [5] G. Maas, S. Bender, *Chem. Commun.* 437 (2000).
- [6] G. Maas, B. Daucher, A. Maier, V. Gettwert, *Chem. Commun.* 238 (2004).
- [7] These results are taken in part from the Ph.D. Thesis of B. Daucher, University of Kaiserslautern (1996).
- [8] A. Fronda, F. Krebs, B. Daucher, T. Werle, G. Maas, *J. Organomet. Chem.* **424**, 253 (1992).
- [9] G. Maas, M. Gimmy, M. Alt, *Organometallics* **11**, 3813 (1992).
- [10] A. Blaschette, K. Linoh, D. Koch, L. Ernst, *Z. Naturforsch.* **44b**, 465 (1989).
- [11] S. C. Shim, S. T. Lee, *J. Chem. Soc. Perkin Trans. 2*, 1979 (1994); b) M. Ishikawa, H. Sugisawa, T. Fuchikami, M. Kumada, T. Yamabe, H. Kawakami, K. Fukui, Y. Ueki, H. Shizuka, *J. Am. Chem. Soc.* **104**, 2872 (1982); c) D. Seyferth, S. C. Vick, M. L. Shannon, *Organometallics* **3**, 1897 (1984).
- [12] a) H. Oda, M. Sato, Y. Morizawa, K. Oshima, *Tetrahedron* **41**, 3257 (1985); b) Y. L. Chen, T. J. Barton, *Organometallics* **6**, 2590 (1987); c) K. K. Murthi, R. G. Salomon, *Tetrahedron Lett.* **35**, 517 (1994).
- [13] T. E. Krafft, J. D. Rich, T. B. Burnell, US 5,124,468 (June 23, 1992); *Chem. Abstr.* **117**, 151148q (1992).
- [14] a) I. Minami, K. Takahashi, I. Shimizu, T. Kimura; J. Tsuji, *Tetrahedron* **42**, 2971 (1986); b) T. Ito, S. Okamoto, F. Sato, *Tetrahedron Lett.* **44**, 6399 (1990).
- [15] L. J. Bellamy, *Ultrarot-Spektrum und chemische Konstitution*, 2nd ed., Steinkopff, Darmstadt (1966).
- [16] E. Guntrum, W. Kuhn, W. Spönllein, V. Jäger, *Synthesis* 921 (1986).
- [17] H.-U. Reissig, *Top. Curr. Chem.* **144**, 73 (1988).
- [18] W. Ando, A. Sekiguchi, T. Sato, *J. Am. Chem. Soc.* **103**, 5573 (1981).
- [19] Y. S. Rao, *Chem. Rev.* **64**, 353 (1964).
- [20] G. Maas, V. Gettwert, *Tetrahedron* **56**, 4139 (2000).
- [21] R. S. Drago, J. R. Long, R. Cosmano, *Inorg. Chem.* **21**, 2196 (1982).