Silicon-Oxygen Heterocycles from Thermal, Photochemical, and Transition-Metal-Catalyzed Decomposition of α-(Alkoxysilyl and Alkenyloxysilyl)-α-diazoacetates

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Photolysis of (ethoxy)silyl-, (propyloxy)silyl-, and (isopropyloxy)silyl-substituted diazoacetates **1a–c** leads to tetrahydro-1,2-oxasiloles **2a–c** by intramolecular C–H insertion of a carbene intermediate. Photochemical or catalytic decomposition of (allyloxysilyl)diazoacetates **3a–e** results in intramolecular cyclopropanation which provides 3-oxa-2-silabicyclo[3.1.0]hexane systems **5a–e**. In contrast, the thermal reaction of **3b–d** gives rise to 2,5-dihydro-1,2-oxasiloles **4b–d**, which are likely to be formed on a pyrazoline rather than a carbene route. For (3-butenyloxysilyl)diazoacetate **3f**, all modes of decomposition generate the 3-oxa-2-silabicyclo[4.1.0]heptane system **7**. Fluoride-induced cleavage of the bicyclic systems **5b–d** provides *trans*-2-hydroxyalkyl-1-cyclopropanecarboxylates **9** diastereospecifically.

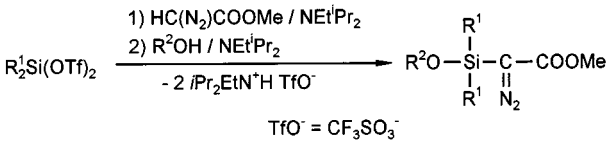
Introduction

Intramolecular reactions of carbenes or carbenoids are among the most important and versatile strategies for the construction of cyclic molecules.[1] Particularly useful in this respect is the transition-metal-catalyzed decomposition of diazo compounds which are structurally suited for carbenoid reactions such as C−H or X−H insertion, cyclopropanation, or ylide formation.[2][3] While copper catalysts dominated this application in earlier times,[4] rhodium carboxylates and amidates have emerged recently as more powerful and versatile catalysts,[5] since ligand variation appears to provide a better control of chemoselectivity,[6] diastereoselectivity,[7] and even enantioselectivity[8] for the cyclization reactions. In a program directed towards the synthesis of sila heterocycles from carbenes or carbenoids derived from silyldiazo compounds, we became interested in a strategy where the reactive intermediate would react by intramolecular C−H insertion or alkene cyclopropanation at a silicon-attached substituent. Only a few intramolecular reactions of silylcarbenes leading to sila heterocycles have been reported.[9] (Alkyldimethylsilyl)carbenes, generated from alkyl(chloromethyl)dimethylsilanes and sodium, were found to undergo both 1,3- and 1,5-C−H insertion,[10] and similarly generated (ω-alkenyl)dimethylsilylcarbenes underwent both intramolecular 1,5-C−H insertion and cyclopropanation in low yields.[11] While 1,3-C−H insertions have been invoked in several cases,[9][10] a stable silirane has never been isolated from these reactions. On the other hand, short-wavelength irradiation of matrix-isolated (trimethoxysilyl)carbene, generated from (trimethoxysilyl)diazomethane, resulted in a clean 1,4-C−H insertion to form a 1,2-silaoxetane.[12]

In this paper, we report that α-(alkoxysilyl and alkenyloxysilyl)-α-diazoacetates are suitable precursors for carbenes or carbenoids which react intramolecularly with C−H and C=C bonds to form five- and six-membered 1-oxa-2-sila heterocycles, generally in preparatively useful yields. In the thermal reaction mode, however, it appears that instead of a carbene route, intramolecular [3+2] cycloaddition of the diazo dipole to a C=C bond, followed by elimination of N_2, accounts in most cases for the sila heterocycles obtained.

Results and Discussion

Silicon-functionalized α-silyl-α-diazoacetates are easily available by successive treatment of a silyl bis(triflate) with an alkyl diazoacetate and a nucleophile in the presence of a tertiary amine.[13] Among others, the nucleophile may be an aliphatic, allyl, or homoallyl alcohol as well as an enolizable ketone, and the synthesis of most α-(alkoxysilyl- and alkenyloxysilyl)-α-diazoacetates used in this study (**1a−c**, **3a−d**, **3f**) has been described already.[13] Compund **3e** was newly prepared by this method [R^2OH = methyl (*E*)-4-hydroxy-2-butenoate].



Scheme 1. Synthesis of α-oxysilyl-α-diazoacetates

Decomposition of (Alkoxysilyl)diazoacetates 1a−c

Photochemical extrusion of N_2 from (ethoxy)silyl-, (propyloxy)silyl- and (isopropyloxy)silyl-substituted diazoace-

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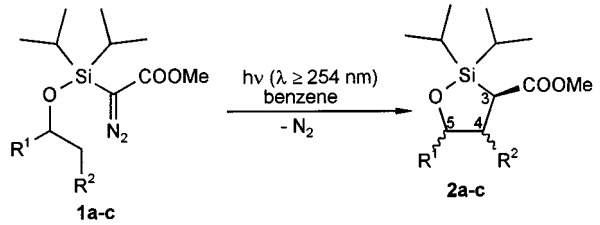
tates **1a**−**c** in pentane solution led to tetrahydro-1,2-oxasiloles **2a**−**c** (Scheme 2). The yields were better with 254-nm light than at $\lambda \geq 300$ nm, and it was also necessary to keep the stationary concentration of **1** as low as possible which was achieved by slow addition of the diazo compound to the reaction vessel by means of an infusion pump. For example, irradiation of a 0.03 M solution of **1b** in pentane for 10 h furnished **2b** in only about 10% yield and the ketazine derived from a diazo + carbene reaction appeared to be the major product; in contrast, the yield of **2b** rose to 62% under high-dilution conditions.



1,2	a	b	c
R^1	H	H	Me
R^2	H	Me	H
yield, %	39	62[a]	51[b]

[a] 2 diastereomers, *trans* / *cis* = 1.3
[b] 2 diastereomers, d.r. = 1.5

Scheme 2. Photochemical C−H insertion of (alkoxysilyl)diazoacetates **1**

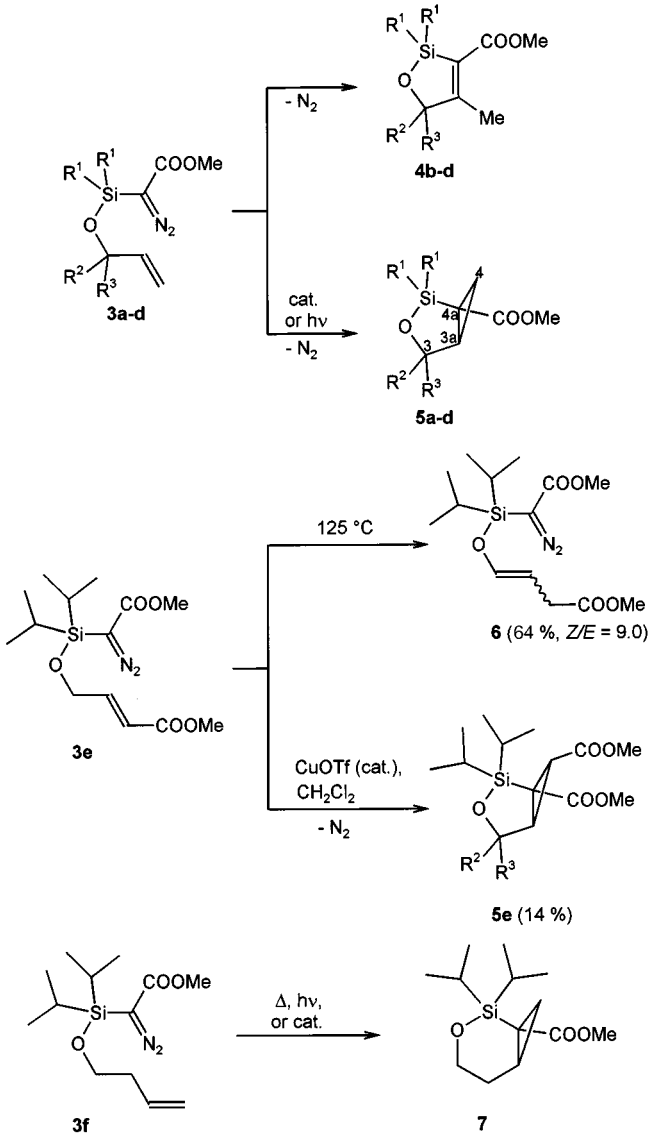
Obviously, silaheterocycles **2a**−**c** are the result of a 1,5-C−H insertion of the carbene intermediate. If one takes the yields of isolated products (39, 62, 51%) as an (admittedly not very reliable) measure, one realizes that, in line with earlier observations,[14] carbene insertion at a methylene group (formation of **2b**) occurs more easily than at a methyl group (**2a**,**c**); a preference of 3.0±0.6:1 for methylene insertion is calculated from the yields after correction for the number of C−H bonds. Notably, there was no indication of a 1,3- or 1,4-insertion into an Si−*i*Pr C−H bond nor a 1,4- or 1,6-insertion at the alkoxy chain. As expected, **2b** and **2c** were obtained as a mixture of two diastereomers at a ratio of 1.3 and 1.5, respectively. In the case of **2b**, the *trans* configuration at the C-3−C-4 bond was assigned to the major diastereomer based on the larger coupling constant ^3J(3-H,4-H) (11.9 vs. 6.9 Hz). No stereochemical assignment was made for the diastereomers of **2c**.

Nowadays, dirhodium carboxylates and carboxamides are the catalysts of choice for effective intramolecular carbenoid C−H insertion reactions.[3a,5a,7b] They are superior to copper catalysts[15] and with sterically unbiased diazocarbonyl compounds normally give rise to formation of five-membered rings.[15][16] In contrast to the photochemical reactions, however, transition-metal-catalyzed decomposition of **2a**−**c** did not provide useful results. With $Rh_2(OAc)_4$ in boiling benzene or copper(I) triflate (CuOTf) (pentane, 20°C), unseparable multi-component mixtures were formed, while rhodium(II) perfluorobutyrate [$Rh_2(OOCC_3F_7)_4$, $Rh_2(pfb)_4$] was deactivated either by the diazo compound or a reaction product. These observations were unexpected since (*trialkyl*silyl)diazoacetates usually react with the same catalysts to give cleanly one or two carbene-derived products.[17] Furthermore, we note a difference between silyldiazoacetates **1a**−**c** and 2-diazo-3-oxoalkanoates, for which the intramolecular 1,5-C−H insertion can be achieved under Rh^{II} catalysis but not with the photochemically generated singlet or triplet carbenes.[18] Only recently, Marsden and co-workers[19] reported that diazo compounds closely related to **1**, but with cyclohexyloxy instead of alkyloxy substitution, are able indeed to undergo carbenoid 1,5-C−H insertion when treated with a catalytic amount of rhodium(II) octanoate dimer.

Decomposition of (Allyloxy)silyl- and [(3-Butenyl)oxysilyl]-diazoacetates 3a−f

The carbenes generated photochemically from (allyloxy)-silyldiazoacetates **3a**,**b** and [(3-butenyl)oxysilyl]diazoacetate **3f** underwent intramolecular cyclopropanation to form the 3-oxa-2-silabicyclo[3.1.0]hexane systems **5a**,**b** and the 3-oxa-2-silabicyclo[4.1.0]heptane derivative **7**, respectively (Scheme 3 and Table 1). Products derived from a reaction of the carbene with the solvent did not seem to be formed at a significant amount. Similarly, catalytic decomposition of diazocompounds **3a**−**d** led to **5a**−**d**, and **3f** gave **7**. Highly electrophilic catalysts such as CuOTf or $Rh_2(pfb)_4$ were required to achieve the decomposition, and copper(I) triflate gave better yields of **5a**−**d** consistently. In part, this fact may be attributed to the difficulty to remove the highly soluble $Rh_2(pfb)_4$ from the reaction mixture, thus requiring additional material-consuming chromatographic purification steps. In earlier work, we had already identified these two catalysts as the most suitable ones for decomposition of other silyldiazoacetates bearing bulky silyl groups.[17] $Rh_2(OAc)_4$, on the other hand, did not even decompose **3d** after 22 h in boiling benzene. Cyclopropa[*c*][1,2]oxasilole derivative **5c** was obtained as a mixture of C-3 epimers. The *exo*-Me diastereomer, which in contrast to the *endo* isomer showed no coupling between 3-H and 3a-H in the ^{1}H-NMR spectrum, was formed with a much higher diasteroselectivity under catalysis by CuOTf than with $Rh_2(pfb)_4$.

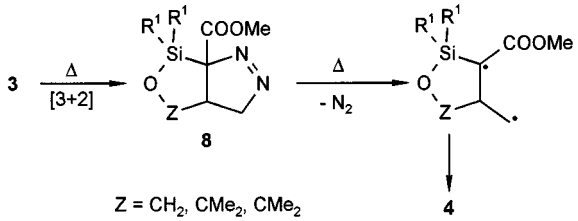
The thermal extrusion of N_2 from **3a**−**d** required temperatures of ≥ 140°C. While unspecific decomposition occurred in the case of **3a**, 2,5-dihydro-1,2-oxasiloles **4b**−**d** were formed besides traces of the cyclopropanation products (**5b**,**c**) and additional unidentified products and were isolated in moderate yields. Control experiments showed that **4b**−**d** did not result from thermal isomerization of **5b**−**d** under the conditions of thermolysis. Rather, intramolecular [3+2] cycloaddition to form bicyclic pyrazolines **8** is likely to occur under the thermal conditions (Scheme 4). Subsequent elimination of N_2 from **8** and isomerization of the resulting 1,3-diradical explains the formation of the monocyclic systems **4**, while the 1,3-cyclization leading to cyclopropanes **5** is obviously less favorable. The fact, that **3b** was transformed into **4b** whereas **3a** decomposed un-



Scheme 3. For conditions and yields, see Table 1

specifically, would be in agreement with this reaction pathway, since the action of a Thorpe-Ingold effect[20] ($SiiPr_2$ vs. $SiMe_2$) should facilitate the intramolecular 1,3-dipolar cycloaddition step.

Since we were interested to know whether a more electron-deficient C=C bond would favor the intramolecular [3+2] cycloaddition, we synthesized diazoacetate **3e**. After heating it at 125°C, only the rearranged diazoacetate **6** could be isolated, but no products associated with the accompanying extrusion of N_2. The constitution of **6** follows from comparison of the olefinic ^{13}C chemical shifts with other (vinyloxy)silyldiazoacetates,[13] and the (*Z*) configuration of the major isomer was indicated by the smaller coupling constant of the olefinic protons [^3J = 5.6 Hz vs. 12.0 Hz for the (*E*) isomer]. Photolysis and $Rh_2(pfb)_4$-catalyzed decomposition of **3e** led to mixtures of unidentifiable products, while catalysis with copper(I) triflate furnished the bicyclo[3.1.0]hexane system **5e** (14%). Since the carbene or metal-carbene intermediates, derived from diazo compounds **3**, are electrophilic species, it is not surprising that the attack at the rather electron-deficient C=C bond in **3e** is not a favorable process. The *exo* position of the methoxycarbonyl group at the three-membered ring is indicated by the small value of the coupling constant for the two cyclopropane protons ($^3J_{trans}$ = 4.1 Hz) and is in agreement with the expected[7] stereospecific cyclopropanation of the C=C bond.



Scheme 4. Pyrazoline pathway for the transformation **3** → **4**

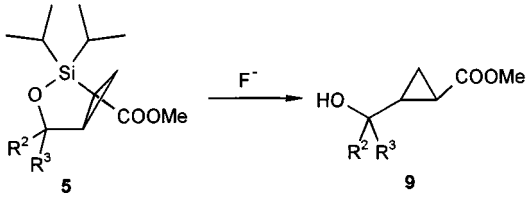
In contrast to **3a**–**d**, the [(3-butenyl)oxysilyl]diazoacetate **3f** yielded the bicyclo[4.1.0]heptane system **7** no matter whether the reaction was carried out thermally, photochemically or with transition-metal catalysis. Although the isolated yields were only moderate, other products could not be identified nor isolated.

Intramolecular 1,3-dipolar cycloaddition reactions of unsaturated diazo compounds are known,[21] and the resulting bicyclic pyrazolines have been isolated in a few cases.[22] Among the reported examples, allyl and homoallyl (diazomethyl)phosphinates[23] are structurally most closely related to **3a**–**f** [(P(=O)Ph instead of SiR_2]. They undergo the intramolecular [3+2] cycloaddition already at room temperature to form isolable bicyclic pyrazolines which yield products structurally similar to **4** and **5** after photolysis or thermolysis (140°C).

Desilylation of 3-Oxa-2-silabicyclo[3.1.0]hexanes 5b–d

Silabicyclic compounds **5** can be considered as silicon-tethered *trans*-2-hydroxymethyl-1-cyclopropanecarboxylates. We were therefore pleased to find that fluoride ion induced desilylation of **5b**–**d** leads indeed to monocyclic cyclopropanes **9a**–**c** (Scheme 7). Although the silicon atom is significantly shielded by the two *i*Pr groups and the cyclopropyl substituent, this transformation could be achieved with cesium fluoride in wet THF for **5b**,**c**, but potassium hydrogen fluoride in DMF[30] was required for **5d**. Other methods, such as KF/18-crown-6 or Bu_4NF in THF, were unsuccessful. Cyclopropanes **9a**–**c** were formed with complete retention of the stereochemistry at the three-membered ring, the *trans* substitution being indicated by a rather small vicinal coupling constant [^3J(1-H, 2-H) = 4.1–4.6 Hz].

With the reaction sequence **3** → **5** → **9**, we have demonstrated a new application of the synthetic strategy to use silicon as a temporary tether,[31] namely to achieve intramolecular cyclopropanation reactions of carbenes or carbenoids. Diastereomerically pure *trans*-cyclopropane **9a** and



Compound	R^2	R^3	Conditions	Product (yield, %)
5b	H	H	CsF, THF, H_2O, 40 °C	**9a** (74)
5c	H	Me	CsF, THF, H_2O, 40 °C	**9b** (79)
5d	Me	Me	KHF_2, DMF, 70 °C	**9c** (63)

Scheme 5. Desilylation of sila heterocycles **5**

related carboxy derivatives have been synthesized before by oxidation or reduction of appropriate *trans*-1,2-difunctionalized cyclopropanes (e.g. ref.[32]) or from glutamic acid in five steps.[33] Cyclopropane **9c** has been prepared from dimethyl cyclopropane-1,2-dicarboxylate with MeMgI, but no spectroscopic data were given.[34] On the other hand, direct copper- or rhodium-catalyzed cyclopropanation of allylic alcohol with an alkoxycarbonylcarbene is unproductive since O−H insertion is the favored process.[35] For the photolysis of ethyl diazoacetate in the presence of an allylic alcohol, cyclopropanation is somewhat more favorable than the O−H insertion but still is a rather low-yielding process.[36]

Conclusion

We have demonstrated that intramolecular carbene and carbenoid reactions of silicon-functionalized α-silyl-α-diazoacetates provide rapid access to sila heterocycles with an Si−O bond. In this work, we have focused on 1,5-cyclization by carbene insertion into an unactivated C−H bond and on intramolecular cyclopropanation of an olefinic C=C bond. Other carbene reactions, such as 1,2 (Si → C) substituent migration with formation of silenes[17] or C−H insertion at the Si−*i*Pr groups, could not be observed. Also, the intermediate carbenes or carbene complexes did not seem to react to a significant extent with solvent molecules (benzene, toluene, xylene).

The sila heterocycles so obtained can be used for further transformations, which was demonstrated by fluoride-induced ring opening and desilylation of bicyclic systems **5b**−**d**, from which *trans*-2-(1-hydroxyalkyl)-1-cyclopropanecarboxylates **9** were obtained. Considering the whole synthetic sequence, the silicon atom serves as a temporary tether which prepares the stage for the intramolecular cyclopropanation reaction.

Another aspect is also worth mentioning. In spite of the impressive progress in transition-metal-catalyzed diazo decomposition reactions, catalytic N_2 extrusion from compounds where the diazo carbon atom is rather electron-poor and/or sterically shielded still constitutes a problem. The α-silyl-α-diazoacetates used in this study certainly belong to this category, and we have shown that only highly electrophilic catalysts such as CuOTf or $Rh_2(pfb)_4$ serve the purpose. However, the ridge between success and failure can be narrow, and we have met several cases where these catalysts were deactivated by some functional group in the diazo compound itself. Therefore, the search for powerful and versatile diazo decomposition catalysts must go on.

Experimental Section

General Remarks: All reactions were carried out in oven-dried glassware and under argon. 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 LiChroprep columns, Si 60, particle size 40−63 μm; two columns (240 × 10 mm and 310 × 25 mm) connected; gradient pump Merck-Hitachi L6200]. − NMR: Bruker AMX 500 (^{1}H: 500.14 MHz; ^{13}C: 125.76 MHz, ^{29}Si: 99.36 MHz), Bruker AMX 400 (^{1}H: 400.1 MHz; ^{13}C: 100.6 MHz), and Bruker AC 200 (^{1}H: 200.13 MHz; ^{13}C: 50.32 MHz); $CDCl_3$ was used as solvent. As the internal reference, Me_4Si was used for the ^{1}H and ^{29}Si spectra, and the solvent signal for the ^{13}C-NMR spectra [$\delta(CDCl_3) = 77.0$]. 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, IR 397, Beckman Acculab IR 20A. − MS: Finnigan MAT SSQ 7000 (EI, CI). − Microanalyses: Perkin−Elmer EA 240 and EA 2400. − α-Silyl-α-diazoacetates **1a**−**d**,**f**,[13] the copper(I) triflate − benzene complex [$Cu(O_3SCF_3) \cdot 0.5\ C_6H_6$],[37] and dirhodium tetrakis(tetrafluorobutyrate)[38] were prepared by literature methods.

Photolysis of Diazoacetates 1a−c

General Procedure: A photolysis vessel (quartz glass) was charged with benzene (240 mL). Under irradiation with UV light (high-pressure mercury lamp, Heraeus TQ 150), a solution of diazoacetate **1a**−**c** (15 mmol) in benzene (60 mL) was added continuously during 12 h via a syringe pump (Bioblock Scientific, model A-99). When the addition was complete, irradiation was continued for 30 min. The solvent was removed by distillation at 40 °C/236 mbar. Bulb-to-bulb distillation of the pale-yellow oil thus obtained furnished 2,5-dihydro-1,2-oxasiloles **2a**−**c**.

Methyl 2,2-Diisopropyl-tetrahydro-1,2-oxasilole-3-carboxylate (2a): Obtained from **1a**; bulb-to-bulb distillation at 62 °C/0.001 mbar, colorless oil; yield: 0.89 g (39%). − IR (film): $\tilde{\nu}$ = 1715 (C=O), 1645, 1455, 1335, 1285, 1230, 1210, 1155 cm^{-1}. − ^{1}H NMR (400.1 MHz): δ = 0.98−1.20 (m, 12 H, CH*Me*$_2$), 1.21−1.24 (m, 2 H, SiCH), 2.06 (m_c, 1 H, 4-H^1), 2.35 (m_c, 1 H, 4-H^2), 2.46 (dd, 1 H, 3-H), 3.66 (s, 3 H, OMe), 3.82 (m_c, 1 H, 5-H^1), 4.06 (m_c, 1 H, 5-H^2). − ^{13}C NMR (100.6 MHz): δ = 12.30, 12.36 (both Si−CH), 16.50, 16.75, 16.86, 16.88 (all CH*Me*), 29.45 (C-4), 29.73 (C-3), 50.99 (OMe), 66.87 (C-5), 174.82 (C=O). − $C_{11}H_{22}O_3Si$ (230.4): calcd. C 57.35, H 9.62; found C 57.3, H 9.5.

Methyl 2,2-Diisopropyl-4-methyl-tetrahydro-1,2-oxasilole-3-carboxylate (2b): Obtained from **1b**; bulb-to-bulb distillation at 63 °C/0.10 mbar, colorless oil; yield: 1.52 g (62%), mixture of diastereomers, *trans*/*cis* = 1.3:1.− IR (film): $\tilde{\nu}$ = 1715 (C=O), 1455, 1425, 1340, 1280 cm^{-1}. − ^{1}H NMR (400.1 MHz): *trans*-**2b**: δ = 0.90−1.05 (m, 12 H, CH*Me*$_2$), 1.07 (m, 2 H, SiCH), 1.52 (d, 3 H, 4-Me), 2.03 (d, ^3J = 11.9 Hz, 1 H, 3-H), 2.61 (m_c, 1 H, 4-H), 3.59

(s, 3 H, OMe), 3.62 (dd, J = 8.8, 5.1 Hz, 1 H, 5-H^1), 3.79 (dd, J = 11.0, 8.8 Hz, 1 H, 5-H^2); *cis*-**2b**: δ = 0.85 (d, 3 H, 4-Me), 0.90−1.05 (m, 12 H, CHMe_2). 1.07 (m, 2 H, SiCH), 2.24 (m_c, 1 H, 4-H), 2.37 (d, ^3J = 6.9 Hz, 1 H, 3-H), 3.24 (dd, J = 11.3, 9.3 Hz, 1 H, 5-H^1), 3.56 (s, 3 H, OMe), 4.02 (dd, J = 9.3, 6.9 Hz, 1 H, 5-H^2). − ^{13}C NMR (100.6 MHz): *trans*/*cis* diastereomers: δ = 12.07, 12.33, 12.46, 12.61 (all Si−CH, both diastereomers), 16.46, 16.64, 16.73, 16.91, 17.27, 17.49 (all CHMe_2), 25.90/24.79 (4-CH_3), 36.92/34.95 (C-3), 38.54/37.19 (C-4), 51.03/50.55 (OCH_3), 73.08/72.55 (C-5), 173.71/174.15 (C=O). − $C_{12}H_{24}O_3Si$ (244.4): calcd. C 58.97, H 9.90, found C 59.2, H 9.9.

Methyl 2,2-Diisopropyl-5-methyl-tetrahydro-1,2-oxasilole-3-carboxylate (2c): Obtained from **1c**; bulb-to-bulb distillation at 63°C/0.02 mbar, colorless oil; yield: 1.25 g (51%), mixture of diastereomers, 1.5:1. − IR (film): ṽ = 1720 (C=O), 1460, 1380, 1340 cm^{-1}. − ^{1}H NMR (400.1 MHz): Major diastereomer: δ = 1.01−1.07 (m, 12 H, CHMe_2) 1.18 (m_c, 2 H, SiCH), 1.31 (d, 3 H, 5-Me), 1.93 (m_c, 1 H, 4-H^1), 2.16 (ddd, J = 13.0, 8.0, 7.0 Hz, 1 H, 4-H^2), 2.53 (dd, J = 8.0, 7.0 Hz, 1 H, 3-H), 3.64 (s, 3 H, OMe), 3.98 (m_c, 1 H, 5-H); minor diastereomer: δ = 1.23 (d, 3 H, 5-Me), 1.56 (m_c, 1 H, 4-H^1), 2.43 (m_c, 1 H, 4-H^2), 2.50 (dd, J = 8.0, 5.0 Hz, 3-H), 4.36 (m_c, 1 H, 5-H), all other signals coinicide with those of major diastereomer. − ^{13}C NMR (100.6 MHz): Major/minor diastereomer: δ = 12.06, 12.26, 12.47, 12.59 (all SiCH), 16.50, 16.60, 16.82, 16.89, 17.11, 17.22, 17.32 (all CHMe_2), 22.81/23.12 (5-Me), 31.15/29.45 (C-3), 37.10/36.46 (C-4), 50.97 (OMe), 73.67/73.82 (C-5), 174.52/175.30 (C=O). − $C_{12}H_{24}O_3Si$ (244.4): calcd. C 58.97, H 9.90; found C 58.7, H 9.8.

Decomposition of Diazoacetates 3a−f

Thermal Decomposition (Method A): The diazoacetate (2−3 mmol) was heated, either neat in a thick-walled Schlenk tube (volume: 10 mL) or dissolved in xylene (20 mL); for temperatures and reaction times, see Table 1. If necessary, the solvent was evaporated, and the product was isolated by column chromatography [silica gel, 15 g, eluant petroleum ether/diethyl ether (9:1)] and was purified further by bulb-to-bulb distillation.

Table 1. Thermal, photochemical, and transition-metal-catalyzed decomposition of diazo compounds **3a−d**,**f**

3	R^1	R^2	R^3	Method[a]	Product (yield,%)
a	Me	H	H	190°C, 3 h, xylene	[b]
				hv, 3 h	**5a** (34)
				CuOTf (4), 4 h	**5a** (63)
				$Rh_2(pfb)_4$ (3), 4 h	**5a** (50)
b	*i*Pr	H	H	142°C, 3 h, neat	**4b** (57), **5b** (≤ 2)
				hv, 4 h	**5b** (55)
				CuOTf (3), 21 h	**5b** (95)
c	*i*Pr	Me	H	142°C, 3 h, xylene	**4c** (21), **5c** (≤ 2)
				CuOTf (10), 15 h, CH_2Cl_2	**5c** (73)[c]
				$Rh_2(pfb)_4$ (3), 7 h	**5c** (25)[d]
d	*i*Pr	Me	Me	142°C, 3 h, xylene	**4d** (63)
				CuOTf (10), 24 h, CH_2Cl_2	**5d** (73)
f				195°C, 75 min, neat	**7** (58)
				hv, 2.5 h	**7** (32)
				CuOTf (3), 20 h	**7** (28)

[a] The solvent was benzene if not stated otherwise. Thermolyses were carried out in thick-walled Schlenk tubes. Photolyses (λ ≥ 300 nm) and catalytic decompositions were done at 20°C. For the catalytic decompositions, the mol-% of catalyst are given in parentheses; $Rh_2(pfb)_4$ = $Rh_2(OOCC_3F_7)_4$. − [b] Unspecific decomposition. − [c] *exo*-Me/*endo*-Me = 97.5:2.5 (by GC-MS). −[d] *exo*-Me/*endo*-Me = 85:15 (by ^{1}H NMR).

Photochemical Decomposition (Method B): A solution of the diazoacetate (ca. 3−4 mmol) in benzene (50 mL) was irradiated with a high-pressure mercury lamp (Philips HPK 125 W, λ ≥ 300 nm) until evolution of N_2 had ceased (ca. 3−4 h). The solvent was evaporated at 20°C/0.01 mbar, and the residue was subjected to bulb-to-bulb distillation. Further purification is described below; for products and yields, see Table 1.

Copper-Catalyzed Decomposition (Method C): A solution of the diazo compound (2−4 mmol) in dichloromethane (10 mL) was added gradually during 3 h to a solution of copper(I) triflate−benzene complex (3 or 10 mol-%) in dichloromethane (15 mL). After complete addition, the reaction was allowed to continue for 1 h. For **2a**, the catalyst was removed by addition of charcoal (11 g), stirring for 2 h, and filtration through Na_2SO_4 (8 g). The filtered-off solid was washed with diethyl ether (2 × 10 mL), the combined filtrates were concentrated, and the residue was purified by bulb-to-bulb (kugelrohr) distillation. For **2b**,**c**, the reaction mixture was separated by column chromatography [silica gel, 15 g, eluant petroleum ether/diethyl ether (9:1)].

Rhodium-catalyzed decomposition (Method D): A solution of the diazo compound (ca. 3−4 mmol) in benzene (10 mL) was added during 3 h to a solution of dirhodium tetrakis(perfluorobutyrate) (3 mol-%) in benzene. After an additional hour, the solvent was evaporated at 20°C/0.01 mbar, and the residue was purified by bulb-to-bulb distillation; for products and yields, see Table 1.

Methyl 2,2-Diisopropyl-4-methyl-2,5-dihydro-1,2-oxasilole-3-carboxylate (4b): Obtained from **3b** (811 mg, 3.0 mmol) by method A; yield: 414 mg (57%); colorless oil, bp. 95°C/0.028 mbar (kugelrohr). − IR (film): ṽ = 1720 (C=O), 1614, 1463, 1434, 1366, 1286, 1243, 1217, 1075 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 0.99 (d, 6 H, CHMe_2), 1.02 (d, 6 H, CHMe_2), 1.17 (sept, 2 H, SiCH), 2.17 (s, 3 H, =CMe), 3.72 (s, 3 H, OMe), 4.55 (s, 2 H, OCH_2). − ^{13}C NMR (125.76 MHz): 13.04 (SiCH), 14.92 (=C*Me*), 16.77 (CH*Me*), 16.91 (CH*Me*), 50.83 (OMe), 77.07 (OCH_2), 122.22 (SiC=), 167.84 (C=O), 171.58 (=*C*CH_3). − ^{29}Si{^{1}H} NMR: δ = 36.74. − MS (EI, 70 eV); *m*/*z* (%): 242 (11) [M^+], 211 (7), 199 (100) [M^+ − *i*Pr], 171 (35), 139 (9), 129 (28). − $C_{12}H_{22}O_3Si$ (242.4): calcd. C 59.46, H 9.15; found C 59.10, H 9.10.

Methyl 2,2-Diisopropyl-4,5-dimethyl-2,5-dihydro-1,2-oxasilole-3-carboxylate (4c): Obtained from **3c** (853 mg, 3.0 mmol) by method A; yield: 162 mg (21%), colorless oil, b.p. 96°C/0.024 mbar (kugelrohr). − IR (film): ṽ = 1719 (C=O), 1609, 1463, 1434, 1277, 1240, 1231, 1109, 1082, 1043 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 0.97 (d, 3 H, SiCH*Me*), 1.00 (d, 3 H, SiCH*Me*), 1.01 (d, 3 H, SiCH*Me*), 1.03 (d, SiCH*Me*), 1.10−1.15 (m, 2 H, SiCH), 1.34 (d, ^3J = 6.5 Hz, 3 H, OCH*Me*), 2.14 (s, 3 H, =CMe), 3.71 (s, 3 H, OMe), 4.66 (q, ^3J = 6.5 Hz, 1 H, OCH). − ^{13}C NMR (125.76 MHz): δ = 12.37 (SiCH), 13.23 (SiCH), 15.63 (OC*Me*), 16.86 (SiC*Me*), 17.00 (SiC*Me*), 17.13 (SiC*Me*), 17.30 (SiC*Me*), 21.76 (=C*Me*), 50.89 (OMe), 82.22 (OCH), 122.38 (SiC=), 168.27 (C=O), 174.82 (=*C*Me). − ^{29}Si{^{1}H} NMR: δ = 33.15. − $C_{13}H_{24}O_3Si$ (256.8): calcd. C 60.89, H, 9.43; found C 59.81 (value could not be improved), H 9.60.

Methyl 2,2-Diisopropyl-4,5,5-trimethyl-2,5-dihydro-1,2-oxasilole-3-carboxylate (4d): Obtained from **2d** (895 mg, 3.0 mmol) by method A; yield: 511 mg (63%); colorless oil; bp. 75°C/0.016 mbar (kugelrohr). − IR (film) ṽ = 1720 (C=O), 1604, 1463, 1433, 1381, 1359, 1300, 1235, 1191, 1172, 1144, 1064, 1017 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 0.99 (d, 6 H, CHCH_3), 1.03 (d, 6 H, CHCH_3), 1.11 (sept, 2 H, SiCH), 1.37 (s, 6 H, CMe_2), 2.17 (s, 3 H, =CMe), 3.71 (s, 3 H, OMe). − ^{13}C NMR (125.76 MHz): δ = 12.74 (SiCH), 15.45 (=C*C*H_3), 17.26 (CH*C*H_3), 17.52 (CH*C*H_3), 28.25 (CMe_2),

50.89 (OMe), 85.90 (O*C*Me), 121.78 (SiC=), 168.59 (C=O), 177.65 (=*C*Me). − ^{29}Si{^{1}H} NMR: δ = 29.56. − $C_{14}H_{24}O_3Si$ (270.4): calcd. C 62.18, H 9.68; found C 62.3, H 9.5.

Methyl 1,1-Dimethyltetrahydro-1*H*-cyclopropa[*c*][1,2]oxasilole-4a-carboxylate (5a): Obtained from **3a** by methods B, C, D in yields of 34, 63, and 50%, respectively; pale-yellow oil, bp. 95°C/0.1 mbar (kugelrohr). − IR (film): ṽ = 1715 (C=O), 1435, 1260, 1145, 1100, 1045, 1010 cm^{-1}. − ^{1}H NMR (400.1 MHz): δ = 0.26 (s, 3 H, SiMe), 0.32 (s, 3 H, SiMe), 0.94 (dd, ^2J = 3.9 Hz, ^3J = 5.5 Hz, 1 H, 4-H^{endo}), 1.48 (dd, ^2J = 3.9 Hz, ^3J = 8.2 Hz, 1 H, 4-H^{exo}), 2.07 (m_c, 1 H, 3a-H), 3.66 (s, 3 H, OMe), 3.90 (d, ^2J = 9.8 Hz, 2 H, 3-H^{endo}), 4.08 (dd, ^2J = 9.8 Hz, ^3J = 3.3 Hz, 1 H, 3-H^{exo}). − ^{13}C NMR (100.6 MHz): δ = −3.71 (SiMe), −1.31 (SiMe), 16.3 (C-4), 17.2 (C-4a), 28.2 (C-3a), 51.8 (OMe), 65.2 (C-3), 174.4 (C=O). − $C_8H_{14}O_3Si$ (186.3): calcd. C 51.58, H 7.58; found C 50.9, H 7.1.

Methyl 1,1-Diisopropyl-tetrahydro-1*H*-cyclopropa[*c*][1,2]oxasilole-4a-carboxylate (5b): Obtained from **3b**; method B: The product resulting from bulb-to-bulb distillation was purified further by column chromatography [silica gel, 15 g, petroleum ether/diethyl ether (8:2)]; yield: 55%. Method C: yield 95%; colorless oil. − IR (film): ṽ = 1726, 1266, 1105 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 1.05 (d, ^2J = 3.8 Hz, 1 H, 4-H^{endo}), 1.05 (d, 3 H, CH*Me*), 1.08 (d, 3 H, CH*Me*), 1.09 (d, 3 H, CH*Me*), 1.14 (d, 3 H, CH*Me*), 1.15 (sept, 1 H, SiCH), 1.28 (sept, 1 H, SiCH), 1.47 (dd, ^3J = 8.4 Hz, ^2J = 3.8 Hz, 1 H, 4-H^{exo}), 2.09 (m_c, 1 H, 3a-H), 3.67 (s, 3 H, OMe), 3.91 (d, ^2J = 9.7 Hz, 1 H, 3-H^{endo}), 4.14 (dd, 1 H, ^2J = 9.7 Hz, ^3J = 3.7 Hz, 3-H^{exo}). − ^{13}C NMR (125.76 MHz): δ = 11.86 (SiCH), 13.36 (SiCH), 15.41 (C-4a), 16.89 (CH*Me*), 17.29 (C-4), 17.50 (2 × CH*Me*), 17.60 (CH*Me*), 27.12 (C-3a), 51.17 (OMe), 66.73 (OCH_2), 174.52 (C=O). − ^{29}Si{^{1}H} NMR: δ = 27.45. − $C_{12}H_{22}O_3Si$ (242.4): calcd. C 59.46, H 9.15; found C 59.6, H 9.0.

Methyl 1,1-Diisopropyl-3-(*exo*- and *endo*-)methyl-tetrahydro-1*H*-cyclopropa[*c*][1,2]oxasilole-4a-carboxylate (5c): Decomposition of **3c** (568 mg, 2.0 mmol) according to method C gave 374 mg (73%) of **5c**, *exo*-Me/*endo*-Me = 97.5:2.5 (by GC-MS); colorless oil; bp. 105°C/0.028 mbar (kugelrohr). Decomposition of **3c** (486 mg, 1.71 mmol) according to method D gave a multi-component product mixture, which was fractionated by column chromatography [silica gel, 25 g, petroleum ether/diethyl ether (8:2)]; bulb-to-bulb distillation of fractions 7 and 8 gave **5c** as a mixture of diastereomers (110 mg, 25%), *exo*-Me/*endo*-Me = 85:15 (by ^{1}H NMR). − IR (film): ṽ = 1723 (C=O), 1465, 1435, 1374, 1261, 1137, 1113, 1034 cm^{-1}. − ^{1}H NMR (500.14 MHz): Major diastereomer: δ = 1.02 (dd, ^3J = 5.4 Hz, ^2J = 3.8 Hz, 1 H, 4-H^{endo}), 1.07−1.19 [m, 14 H, Si(C*HMe*$_2$)$_2$], 1.34 (d, ^3J = 6.5 Hz, 3 H, 3-Me) 1.44 (dd, ^3J = 8.4 Hz, ^2J = 3.8 Hz, 1 H, 4-H^{exo}), 1.92 (dd, 1 H, *J* = 8.4, 5.3 Hz, 1 H, 3a-H), 3.66 (s, 3 H, OMe), 4.13 (q, ^3J = 6.5 Hz, 1 H, OCH); additional signals of the minor diastereomer in the *exo*-Me/*endo*-Me mixture: 4-H^{endo} signal covered by signal at δ = 1.07−1.19; 1.20 (d, 3 H, 3-Me), 1.32 (dd, 1 H, 4-H^{exo}), 2.08 (ddd, 1 H, 3a-H), 3.65 (s, 3 H, OMe), 4.48 (dq, 1 H, OCH). − ^{13}C NMR (125.76 MHz): δ = 12.33, 13.92 (both SiCH), 17.35 (C-4a), 17.38, 17.77, 17.81, 18.01 (all SiCH*Me*), 18.57 (C-4), 24.67 (3-Me), 32.89 (C-3a), 51.65 (OMe), 73.91 (OCH). − ^{29}Si{^{1}H} NMR: δ = 26.12. − MS (CI, CH_4, 100 eV); *m*/*z*: 297 (4) [M + Allyl$^+$], 285 (13) [M + Et$^+$], 257 (18) [MH$^+$], 241 (5), 225 (7), 213 (100). − MS (EI, 70 eV); *m*/*z* (%): 225 (5) [M$^+$ − OMe], 213 (100) [M$^+$ − *i*Pr], 181 (9), 171 (13). − $C_{13}H_{24}O_3Si$ (256.4): calcd. C 60.89, H, 9.43; found C 60.72, H 9.47.

Methyl 1,1-Diisopropyl-3,3-dimethyl-tetrahydro-1*H*-cyclopropa[*c*][1,2]oxasilole-4a-carboxylate (5d): Obtained from **3d** (498 mg, 1.7 mmol) by method C as a colorless oil; yield: 363 mg (73%). − IR (film): ṽ = 1720 (C=O), 1460, 1430, 1360, 1270, 1195, 1140 cm^{-1}. − ^{1}H NMR (400.1 MHz): δ = 1.02−1.21 (m, 15 H, CH*Me*$_2$, C*H*Me$_2$, 4-H^{endo}), 1.23 (s, 3 H, 3-Me^A), 1.33 (dd, ^2J = 4.1 Hz, ^3J = 8.4 Hz, 1 H, 4-H^{exo}), 1.41 (s, 3 H, 3-Me^B), 1.99 (dd, ^3J = 8.4, 5.5 Hz, 1 H, 3a-H), 3.65 (s, 3 H, OMe). − ^{13}C NMR (100.6 MHz): δ = 12.19 (SiCH), 14.57 (SiCH), 16.57, 17.59, 18.01, 18.05, 18.31, 18.36 (all SiCH*Me*, C-4a, C-4), 28.4 (3-Me^A), 31.3 (3-Me^B), 37.5 (C-3a), 51.7 (OMe), 77.2 (C-3), 174.5 (C=O). − $C_{14}H_{26}O_3Si$ (270. 5): calcd. C 62.18, H 9.69; found C 61.9, H 9.3.

Methyl 1,1-Diisopropyl-perhydrocyclopropa[*c*][1,2]oxasiline-5a-carboxylate (7): Obtained from **3f** by methods A (195°C, neat), B, and C. In each case, a single bulb-to-bulb distillation of the product mixture did not give a pure product. A second distillation at 84°C/0.003 mbar, in which the first 30% cut was discarded, afforded spectroscopically and analytically pure **7**; yields: 58% (A), 28% (B), 32% (C). − IR (film): ṽ = 1715 (C=O), 1355, 1265, 1245, 1150, 1130, 1090 cm^{-1}. − ^{1}H NMR (400.1 MHz): δ = 1.05 (d, 6 H, CH*Me*$_2$), 1.06 (d, 6 H, CH*Me*$_2$), 1.20 (sept, 2 H, C*H*Me$_2$), 1.28 (m_c, 1 H, 5-H^{endo}), 1.43 (m_c, 1 H, 5-H^{exo}), 1.78 (m_c, 1 H, 4-H), 1.91−1.94 (m, 1 H, 4-H), 2.14−2.22 (m, 1 H, 4a-H), 3.64 (s, 3 H, OMe), 3.69 (m_c, 1 H, 3-H), 3.77−3.82 (m, 1 H, 3-H). − ^{13}C NMR (100.6 MHz): δ = 10.78 (C-5a), 13.05 (SiCH), 14.44 (SiCH), 15.77 (C-5), 16.93, 17.24, 17.42, 17.52 (all SiCH*Me*), 22.0 (C-4a), 26.3 (C-4), 51.4 (OMe), 59.6 (C-3), 175.9 (C=O). − $C_{13}H_{24}O_3Si$ (256.4): calcd. C 60.89, H 9.43; found C 60.9; H 9.3.

Methyl (*E*)-4-{[(1-Diazo-1-methoxycarbonylmethyl)diisopropylsilyl]oxy}-2-butenoate (3e): The compound was synthesized by analogy to a literature procedure[13] from diisopropylsilyl bis(trifluoromethanesulfonate), methyl diazoacetate, and methyl (*E*)-4-hydroxy-2-butenoate.[39] The product was purified by twofold column chromatography at −40°C [silica gel, 40 g, petroleum ether/diethyl ether (7:3)]; yield: 61%; yellow oil. − IR (film): ṽ = 2093 (C=N$_2$), 1727 (C=O), 1693 (C=O), 1435, 1265, 1200, 1167, 1131, 1081, 1021 cm^{-1}. − ^{1}H NMR (200.1 MHz): δ = 1.09 (d, 6 H, SiCH*Me*), 1.10 (d, 6 H, SiCH*Me*), 1.33 (sept, 2 H, SiCH), 3.73 (s, 3 H, OMe), 3.75 (s, 3 H, OMe), 4.48 (dd, ^3J = 3.4 Hz, ^4J = 2.3 Hz, OCH_2), 6.11 [dt, ^3J = 15.4 Hz, ^4J = 2.3 Hz, C(O)CH=], 6.99 (dt, 1 H, ^3J = 15.4 Hz, ^3J = 3.4 Hz, =C*H*CH$_2$). − ^{13}C NMR (50.32 MHz): δ = 12.68 (SiCH), 16.95 (CH*Me*), 17.06 (CH*Me*), 42.75 (CN_2), 51.53 (OMe), 51.86 (OMe), 62.84 (OCH_2), 119.37 [C(O)*C*H=], 146.44 (=*C*HCH$_2$), 166.88 (C=O), 169.31 (C=O). − ^{29}Si{^{1}H} NMR: δ = 6.36. − $C_{14}H_{24}N_2O_5Si$ (328.4): calcd. C 51.20, H 7.37, N 8.53; found C 51.62, H 7.63, N 8.46.

Methyl 4-{[(1-Diazo-1-methoxycarbonylmethyl)diisopropylsilyl]oxy}-3-butenoate (6): Diazoacetate **3e** (4.50 g, 13.7 mmol) was subjected to bulb-to-bulb distillation at 125°C/0.02 mbar. Under these conditions, isomerization to **6** and partial decomposition occurred. Diazo compound **6** was obtained as a yellow oil; yield: 2.88 g (64%); mixture of diastereomers, (*Z*)/(*E*) = 90:10. − IR (film): ṽ = 2098 (C=N$_2$), 1743 (C=O), 1694 (C=O), 1267 cm^{-1}. − ^{1}H NMR (200.13 MHz): (*Z*)-**6a**: δ = 1.06 (d, 6 H, CH*Me*), 1.07 (d, 6 H, CH*Me*), 1.31 (sept, 2 H, SiCH), 3.12 (dd, ^3J = 7.0 Hz, ^4J = 1.7 Hz, CH_2), 3.65 (s, 3 H, OMe), 3.71 (s, 3 H, OMe), 4.73 (dt, ^3J = 7.0, 5.6 Hz, 1 H, =C*H*CH$_2$), 6.39 (dt, ^3J = 5.6 Hz, ^4J = 1.7 Hz, 1 H, OCH=); diagnostic signals of (*E*)-**6a**: δ = 2.91 (dd, ^3J = 7.6 Hz, ^4J = 1.3 Hz, CH_2, 2 H), 5.16 (dt, ^3J = 12.0, 7.6 Hz, 1 H, = C*H*CH$_2$), 6.42 (dt, ^3J = 12.0 Hz, ^4J = 1.3 Hz, 1 H, OCH=). − ^{13}C NMR (50.32 MHz): (*Z*)-**6a**: δ = 12.68 (SiCH), 16.64 (CH*Me*), 16.77 (CH*Me*), 29.17 (CH_2), 42.66 (CN_2), 51.66 (OMe), 51.84 (OMe), 102.78 (CH$_2$*C*H=), 140.03 (OCH), 168.86 (C=O), 172.38 (C=O). − ^{29}Si{^{1}H} NMR: δ = 7.34. − $C_{14}H_{24}N_2O_5Si$ (328.4): calcd. C 51.20, H 7.37, N 8.53; found C 51.69, H 7.60, N 8.69.

Dimethyl 1,1-Diisopropyl-tetrahydro-1*H*-cyclopropa[*c*][1,2]oxasilole-4,4a-dicarboxylate (5e): A solution of **3e** (1.0 g, 3.0 mmol) in dichloromethane (10 mL) was added gradually during 3 h to a solution of copper(I) triflate−benzene complex (0.06 g, 8 mol-%) in dichloromethane (20 mL). After 12 h, the solvent was evaporated, and the residue was dissolved in petroleum ether/diethyl ether (9:1) and filtered through aluminum oxide (10 g) to remove the catalyst. Product **5e** was obtained as a colorless oil (123 mg, 14%) after bulb-to-bulb distillation at 120°C/0.018 mbar; it contained trace amounts of impurities (^{1}H, ^{13}C: signals in the olefinic region). − IR (film): $\tilde{\nu}$ = 1738 (C=O), 1439, 1325, 1260, 1201, 1167, 1081 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 1.06, 1.07, 1.15, 1.17 (4 × d, 3 H, CH*Me*), 2.00 (d, *J* = 4.1 Hz, 1 H, 4-H), 2.50 (dd, *J* = 4.1, 3.4 Hz, 1 H, 3a-H), 3.68 (s, 3 H, OMe), 3.69 (s, 3 H, OMe), 4.01 (d, $|^2J|$ = 10.3 Hz, 3-H^1), 4.21 (dd, $|^2J|$ = 10.3 Hz, ^3J = 3.4 Hz, 3-H^2). − ^{13}C NMR (125.76 MHz): δ = 12.04 (SiCH), 13.18 (SiCH), 16.64, 16.89, 17.37, 17.51 (all CH*Me*), 25.80 (C-4), 27.78 (C-4a), 30.73 (C-3a), 51.95 (OMe), 52.00 (OMe), 67.07 (CH_2), 170.33 (C=O), 170.84 (C=O). − ^{29}Si{^{1}H} NMR: δ = 28.18. − $C_{14}H_{24}O_5Si$ (300.4): calcd. C 55.97, H 8.05; found C 54.04 (value could not be improved), H 7.79.

Desilylation of 5b−d

Methyl *trans*-2-(Hydroxymethyl)cyclopropane-1-carboxylate (9a): Compound **5b** (242 mg, 1.0 mmol) was dissolved in THF (5 mL), and a solution of cesium fluoride in THF (10 mL) and water (0.4 mL) was added. The mixture was stirred at 40°C for 4 h and at room temp. for 8 h. The solvent was replaced by diethyl ether (30 mL), and the solution was dried (Na_2SO_4). The residue obtained after evaporation of the solvent was subjected to column chromatography [silanized silica gel, 6 g, eluant petroleum ether/diethyl ether (9:1)] to obtain **9a** as a colorless oil; yield: 96 mg (74%). − IR (film): $\tilde{\nu}$ = 3426 (OH), 1720, 1439, 1210, 1174, 1095, 1043, 1024 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 0.88 (ddd, $|^2J|$ = 4.6 Hz, ^3J = 8.4, 6.2 Hz, 1 H, 3-H), 1.22 (ddd, $|^2J|$ = 4.6 Hz, ^3J = 9.1, 4.7 Hz, 1 H, 3-H), 1.58 (ddd, ^3J = 8.4, 4.7, 4.1 Hz, 1 H, CHCO), 1.72 (m_c, 1 H, 2-H), 2.24 (br., 1 H, OH), 3.46 (dd, ^3J = 6.8 Hz, $|^2J|$ = 11.5 Hz, 1 H, OCH_2), 3.63 (dd, ^3J = 6.0 Hz, $|^2J|$ = 11.5 Hz, 1 H, OCH_2), 3.68 (s, 3 H, OMe). − ^{13}C NMR ($CDCl_3$, 125.76 MHz): δ = 12.62 (C-3), 18.05 (C-1), 24.24 (C-2), 51.74 (OMe), 64.28 (OCH_2), 174.33 (C=O). − The NMR data agree reasonably well with those in ref.[32][33]. − $C_6H_{10}O_3$ (130.1): calcd. C 55.37, H 7.74; found C 55.08, H 7.34.

Methyl *trans*-2-(1-Hydroxyethyl)cyclopropane-1-carboxylate (9b): The compound was obtained from **5c** (256 mg, 1.0 mmol, 97.5:2.5 mixture of C-3 epimers) as described above for **5b**; yield: 114 mg (79%); colorless oil. − IR (film): $\tilde{\nu}$ = 3434 (OH), 1720 (C=O), 1438, 1268, 1205, 1176, 1085 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 0.88 (ddd, $|^2J|$ = 4.3, ^3J = 8.4, 6.4 Hz, 1 H, 3-H), 1.18 (ddd, $|^2J|$ = 4.3 Hz, ^3J = 9.2, 4.5 Hz, 1 H, 3-H), 1.28 (d, ^3J = 6.3 Hz, 3 H, CH_3), 1.54 (m_c, 1 H, 2-H), 1.62 (ddd, ^3J = 8.4, 4.5, 4.3, 1 H, 1-H), 2.33 (s, br., 1 H, OH), 3.33 (dq, ^3J = 7.0, 6.3 Hz, 1 H, OCH), 3.67 (s, 3 H, OMe). − ^{13}C NMR (50.32 MHz): δ = 12.28 (C-3), 17.93 (C-1), 22.50 (C*Me*), 29.85 (C-2), 51.69 (O*Me*), 69.55 (OCH), 174.39 (C=O). − The presence of the C-1′ epimer (ca 2%) is suggested by small satellites of most ^{13}C signals. − MS (CI, CH_4, 100 eV); *m*/*z* (%): 173 (11) [M + Allyl$^+$], 145 (2) [MH$^+$], 127 (100) [MH$^+$ − H_2O]. − MS (EI, 70 eV); *m*/*z* (%): 129 (7) [M$^+$ − CH_3], 113 (21) [M$^+$ − OCH_3], 97 (32), 84 (56). − $C_6H_{10}O_3$ (144.2): calcd. C 58.32, H 8.39; found C 57.34, H 8.32.

Methyl *trans*-(1-Hydroxy-1-methylethyl)cyclopropane-1-carboxylate (9c): To a solution of **5d** (270 mg, 1.0 mmol) in DMF (10 mL) was added potassium hydrogen fluoride (KHF_2, 86 mg, 1.1 mmol). After heating at 70°C for 16 h, the solvent was distilled off and diethyl ether (5 mL) was added. After separation by centrifugation, the supernatant solution was pipetted off and concentrated. The residue was subjected to column chromatography [silanized silica gel (6 g), eluant petroleum ether/diethyl ether (9:1)]; yield of **9c**: 98 mg (63%); colorless oil. − IR (film): $\tilde{\nu}$ = 3465 (OH), 1712 (C=O), 1440, 1323, 1211, 1174, 1114, 1088 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 1.00 (ddd, ^3J = 8.5, 6.7 Hz, $|^2J|$ = 4.4 Hz, 1 H, 3-H), 1.09 (ddd, ^2J = 4.4 Hz, ^3J = 9.3, 4.5 Hz, 1 H, 3-H), 1.25 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 1.42 (br., 1 H, OH), 1.56 (ddd, ^3J = 9.3, 6.7, 4.7 Hz, 1 H, 2-H), 1.68 (ddd, *J* = 8.5, 4.7, 4.5 Hz, 1 H, 1-H). − ^{13}C NMR (50.32 MHz): δ = 11.28 (C-3), 16.27 (C-1), 29.01 (Me), 29.32 (Me), 33.07 (C-2), 51.67 (OMe), 68.32 (*C*Me$_2$), 174.39 (C=O). − $C_6H_{10}O_3$ (144.2): calcd. C 60.74, H 8.92; found C 60.66, H 8.90.

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