4. Photochemical Reactions

153th Communication[1])

Photochemistry of Acylsilanes: Photolyses and Thermolyses of α,β-Epoxy Silyl Ketones

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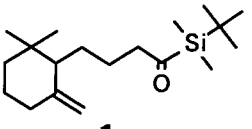
Dedicated to Prof. Dr. *O. Jeger*

The photolyses and thermolyses of the α,β-epoxy silyl ketones **5** and **6** are described. On n,π*-excitation, the silyl ketones **5** and **6** were transformed to the ketone **7** and the ketene **8** in quantitative yield. The formation of **8** may be explained by initial cleavage of the C(α)–O bond and subsequent C(1)→C(2) migration of the (*t*-Bu)Me_2Si group. In contrast to the acylsilanes **5** and **6**, the photolyses of the analogous methyl ketones **11** and **12** gave a very complex mixture of products. On thermolysis, **5** and **6** yielded the ketone **7** and the acetylenic compound **9**, which were probably formed *via* a siloxycarbene intermediate. In addition, the 1,3-dioxole **10** was formed *via* an initial C(α)–C(β) bond cleavage leading to the ylide **g** and subsequent intramolecular addition of the carbonyl group. The analogous 1,3-dioxole **13** was obtained on pyrolysis of the methyl ketones **11** and **12**.

1. Introduction. – In our studies on the intramolecular trapping of siloxycarbenes by reaction with various neighboring groups, we investigated the syntheses, the photolyses, and the thermolyses of several acylsilanes [1] [2]. Thus, it was found that the acylsilanes **1**, (*E*/*Z*)-**2**, **3**, and **4** undergo γ-H abstraction or rearrangement to siloxycarbenes and intramolecular addition to a carbonyl group [1] [3] [4].



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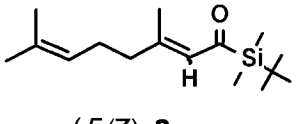
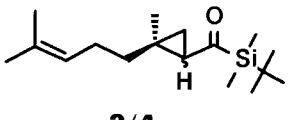


(*E*/*Z*)-**2**



3/**4**

Continuing our studies of the influence of neighboring groups on the reactivity of siloxycarbenes, we were particularly interested in the effects of an epoxy group. Thus, the α,β-epoxy silyl ketones **5** and **6** (*Scheme 1*) [5] were prepared as new model compounds. So far, there is nothing known about the reactivity of epoxy-acylsilanes [6]. Here, we

[1]) 152nd communication, see [1].

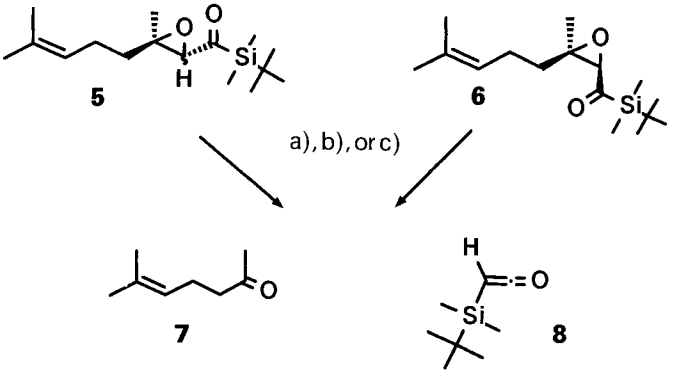
[2]) Taken in part from the Ph. D. thesis of *M. E. S.*, Diss. ETHZ No. 7896, 1985 [2].

[3]) New address: *Ciba-Geigy Ltd.*, Additives Division, CH–4336 Kaisten.

[4]) New address: *Ciba-Geigy Ltd.*, Agricultural Division, CH–4333 Münchwilen.

[5]) Presented in part by *B. F.* at the 'Herbstversammlung der Schweizerischen Chemischen Gesellschaft', Oktober 18, 1985, Bern.

Scheme 1



a) *hv*, MeCN. b) *hv*, MeOH. c) *hv*, Bu_3SnH.

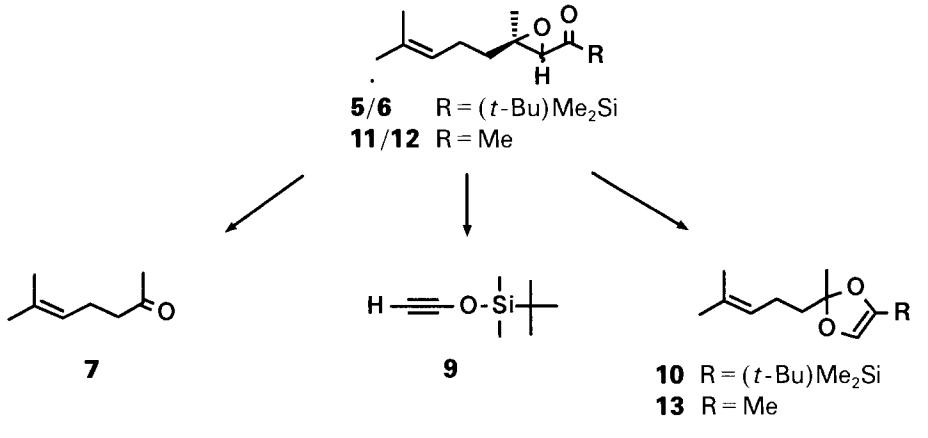
describe the photolyses and thermolyses of **5** and **6** as two representatives of this interesting new class of compounds.

2. Photolysis Experiments. – 2.1. *Irradiation of the acylsilane* **5** *in abs. MeCN* ($\lambda > 347$ nm, 100% conversion) afforded a 1:1 mixture of the ketone **7** and the ketene **8** (93% yield; *Scheme 1*).

2.2. *Irradiation of the acylsilane* **6** *in abs. MeCN* ($\lambda > 347$ nm, 100% conversion) afforded a 1:1 mixture **7**/**8** in quantitative yield (*Scheme 1*).

3. Thermolysis Experiments (see *Scheme 2*). – 3.1. *Flash vacuum thermolysis* (FVT) *of the acylsilane* **5** (420°, conversion 100%) afforded a 1:1 mixture of the ketone **7** and the acetylene **9** (27%[6]) as well as the dioxole **10** (19%)[6].

Scheme 2



3.2. *FVT of the acylsilane* **6** (420°, conversion 100%) afforded a 1.5:1 mixture **7**/**9** and **10**[6]).

[6]) The low yields are due to the high volatility of **7** and **9** as well as to the hydrolysis of **10**.

3.3. *FVT of a mixture of the methyl ketones* **11**[7]) and **12**[7]) (500°, conversion 55%) afforded the dioxole **13** (57%).

4. Structure of the Products. – The structures of all new compounds were deduced from the spectral data, of which only the most relevant are discussed herein together with the decisive chemical transformations which confirmed the assigned structures. Full data and the assignments of the NMR data are presented in the *Exper. Part.*

Ketone **7** (*Scheme 1*). The data of **7** were compared with those of an authentical sample (*Fluka AG*, Buchs, SG).

Ketene **8** (*Scheme 1*). Compound **8** shows in the IR spectrum two characteristic absorption bands at 3350 cm^{-1} and 2100 cm^{-1}. *Shchukovskaya et al.* [8] discussed the possibilities of an equilibrium between a ketene and the analogous acetylene compound. However, they demonstrated that the absorption band at 3350 cm^{-1} is due to a combination of the C=C (1270 cm^{-1}) and C=O (2112 cm^{-1}) stretchbond frequency. In the ^{13}C-NMR spectrum, the *s* of the carbonyl C-atom (179.0 ppm) and the *d* (−4.5 ppm) for the extremly high-field shifted C(2). These findings are consistent with the spectral data of the Me_2Si analog [9], synthesized from the corresponding acetylene compound. The ^{29}Si-NMR spectrum shows a *s* at 7.66 ppm (relative to TMS) in contrast to the starting material **5** with a *s* at −1.96 ppm.

Acetylene **9** (*Scheme 2*). The IR absorptions at 3420*w*, 3325*s*, and 2150*s* are typical for the acetylene moiety. In the ^{1}H-NMR spectrum, the *s* for the two Me groups (0.22 ppm) is low-field shifted compared to the ketene **8** (0.09 ppm), and the acetylenic H-atom shows a *s* at 1.07 ppm. Good evidence for the proposed structure is provided by the ^{13}C-NMR spectrum, showing a *d* at 20.2 ppm for C(2) and another *d* (!) for C(1), which also couples with H–C(2). This coupling is typical for acetylene compounds, which are showing coupling constants of 40–70 Hz over the acetylene bond to the adjacent H-atom. The ^{29}Si-NMR spectrum shows a *s* at 35.4 ppm (relative to TMS), which is strongly shifted to low field in comparison with **8** (7.66 ppm) and the starting material **5** (−1.96 ppm).

Dioxoles **10** *and* **13** (*Schemes 2* and *3*). Consistent with the structure is the enol-ether IR absorption at 1595 cm^{-1}, as well as the *s* at 6.14 ppm and the *m* at 5.75 ppm, respectively, in the ^{1}H-NMR spectrum. In the ^{13}C-NMR spectrum, the dioxole group is characterized by a *s* at 115.8 ppm and 114.8 ppm, respectively, and a *d* at 124.0 ppm and 124.5 ppm[9]), respectively. The 4-methyldioxole **13** has similar spectroscopic data similar to those of **10**.

5. Discussion. – 5.1. *Photolyses.* n,π^* Excitation ($\lambda > 347$ nm) of the acylsilanes **5** and **6** leads exclusively to two products: the ketone **7** and the ketene **8**. For the formation of these two compounds, several possible pathways may be discussed.

5.1.1. Via *a γ-H Abstraction.* On photolyses of the acylsilanes **1**, (*E*/*Z*)-**2**, **3**, and **4**, γ-H abstraction and silyloxy-carbene formation were observed [1] [3]. γ-H Abstraction is also a known process on photolyses of α,β-epoxy methyl ketones [10] [11], and may be responsible for the formation of **7** and **8**. Starting from **5** and **6**, the 1,4-diradicals **a** and **b**, respectively, (*Scheme 4*) would be generated, followed by a C(α)–C(β) bond cleavage furnishing the enols **17** and **18**, tautomers of the acylsilanes **19** and **20**, respectively. To obtain the products **7** and **8**, the (*t*-Bu)Me_2Si group in **17** and **18** would have to undergo a

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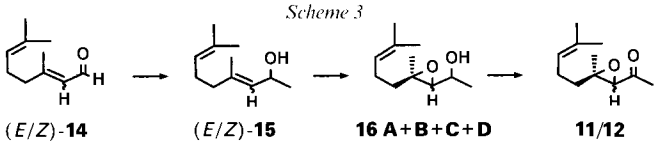
[7]) The methyl ketones **11** and **12** can be easily synthesized (*Scheme 3*) starting from citral (a 1:1 mixture of geranial (*E*-**14**) and neral (*Z*-**14**)) *via* methylation (MeMgBr, 93%) → (*E*/*Z*)-**15**, followed by a *Sharpless* epoxidation [7] (VO{acac}$_2$, *t*-BuOOH, 94%) → **16A** + **B** + **C** + **D**[8]) and finally with a *Collins* oxidation (CrO_3, 72%) → **11** and **12** (for further details, see [2]).

Scheme 3

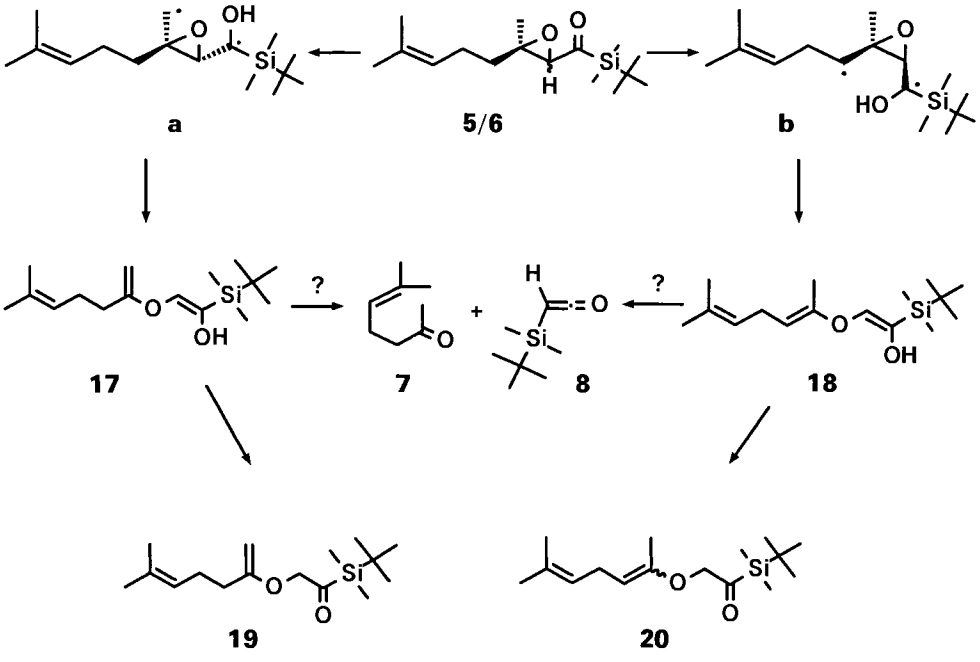


(*E*/*Z*)-**14** (*E*/*Z*)-**15** **16 A+B+C+D** **11/12**

[8]) The letters **A**, **B**, **C**, and **D** are used for the description of diastereoisomers whose configurations were not assigned conclusively.

[9]) The hydrolyses (oxalic acid, dioxane, H_2O, room temperature) of **10** and **13** led to the same ketone **7** in 80% and 85% yield, respectively.

Scheme 4



C(1)→C(2) migration. However, neither the **19** and **20**, nor cyclobutanols, resulting from a possible recombination of the 1,4-diradicals **a** and **b**, were detected. Furthermore, on photolyses of **5** in presence of Bu_3SnH, products of trapping a diradical intermediate could not be detected. Thus, it seems reasonable to exclude a γ-H abstraction as primary photochemical step in the formation of **7** and **8**.

5.1.2. Via *Silyloxy-carbene*. Another possible reaction mechanism is an initial silyloxy-carbene formation leading to **c** (*Scheme 5*). The silyloxy-carbene **c** could react to the oxetene **21** *via* an insertion into the oxirane ring. A [2 + 2] cycloreversion would finally lead to **7** and **9** (*Scheme 5*). However, according to [12], we would expect **21** to undergo ring opening to the ester **22**, which could not be detected. As an alternative, the silyloxy-carbene **c** may undergo an *Eschenmoser* fragmentation [13] leading – *via* the intermediate **d** – to **7** and **9**. Both pathways would lead to **9**, but not to the isolated ketene **8**. A thermal transformation of **9** to **8** would be an endothermic reaction and can be excluded [8]. Even at −30°, only **8** was isolated from the photolysis of the acylsilanes **5** and **6**, respectively. Furthermore, photolysis reactions carried out in the presence of 1 equiv. (*t*-Bu)Me_2SiOH, CCl_4, or even in MeOH[10]) gave none of the expected addition products, but only the **7** and **8**. Therefore, a reaction mechanism *via* a silyloxy-carbene intermediate must also be excluded.

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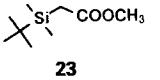
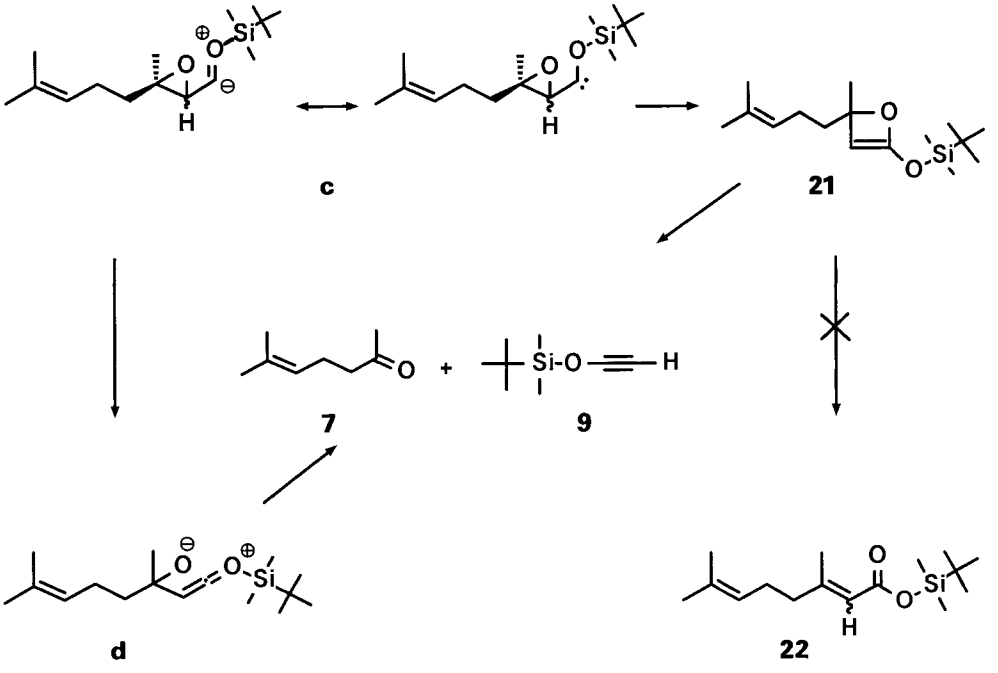
[10]) After photolyses of **5** and **6** in MeOH, when the solution was heated to reflux, the ester **23** was isolated. The analogous reaction occurred already at −15° with the corresponding Me_3Si compound [8].



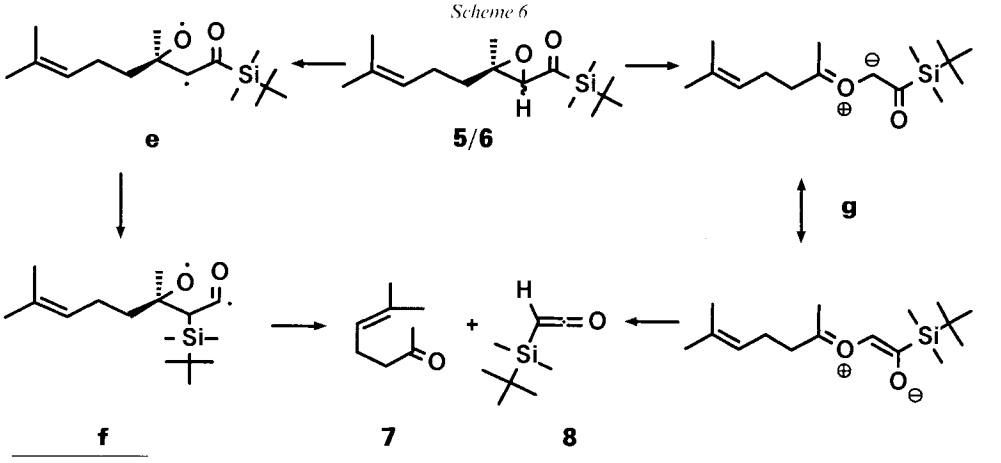
23

Scheme 5



5.1.3. Via *C(α)–O or C(α)–C(β) Bond Cleavage.* A third mechanism, involving a C(α)–O bond cleavage, which is well known on photolyses of expoxy methyl ketones [14], may be taken into consideration. On irradiation of the expoxy-acylsilane chromophore, ring opening to the diradical **e** (*Scheme 6*) may occur, followed by a [1,2] migration[11]) of the (*t*-Bu)Me_2Si group leading to the 1,4-diradical **f**, which would then

Scheme 6



[11]) The [1,2] migration of silyl groups to a neighboring radical center is known to be fast [15].

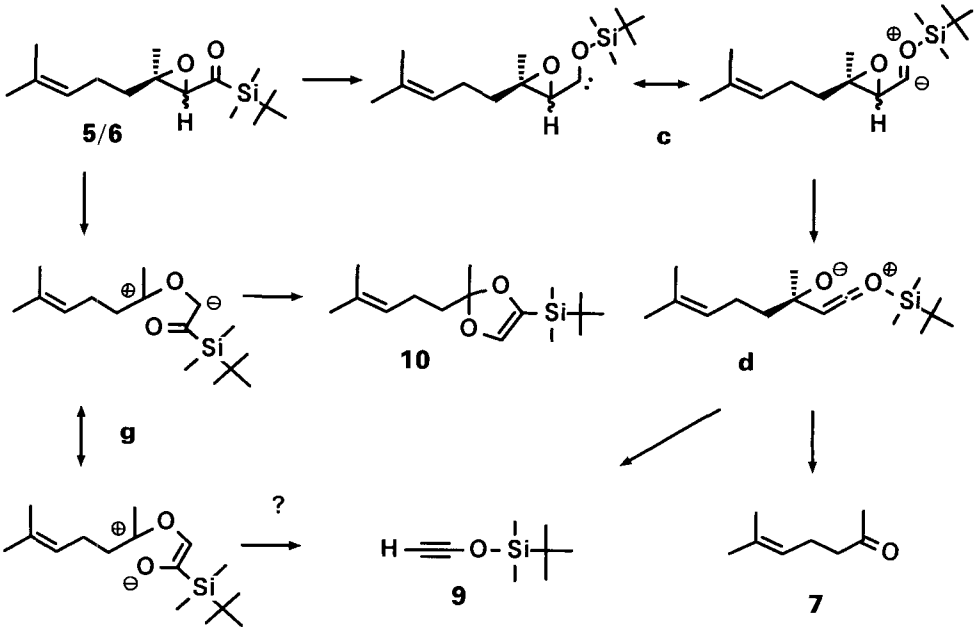
undergo fragmentation to **7** and **8**. As a key step, a C(1)→C(2) migration of the (*t*-Bu)Me_2Si group is assumed to occur. Although C(1)→O migration of the (*t*-Bu)Me_2Si group in **e** would be expected to be more likely (see *Brook* rearrangement [16]), it must be ruled out, as it would lead to the acetylene **9**.

On photolysis of epoxy methyl ketones, in addition to C(α)–O bond cleavage, cleavage of the C(α)–C(β) bond is well known [14]. In the case of **5** and **6**, it would lead to the ylide **g**. For the formation of **7** and **8**, again a C(1)→C(2) migration of the (*t*-Bu)Me_2Si group would have to occur, which seems to be very unlikely as discussed above [16].

Therefore, of the aforementioned reaction mechanisms, the one involving a C(α)–O bond cleavage, seems to be the most reasonable one to explain the transformation of the acylsilanes **5** and **6** to the ketone **7** and the ketene **8**.

5.2. On thermolysis, α,β-epoxy methyl ketones have been reported [17] to undergo a thermal ring opening *via* a C–O or a C–C bond cleavage leading to a diradical or an ylide intermediate, respectively, or *via* a [1,5] homosigmatropic H-shift. Comparing the products of the photolyses of **5** and **6** with those of the thermolyses, it is quite obvious that they arise from different intermediates. On photolysis only the ketone **7** and the ketene **8** were isolated, whereas on thermolyses the ketone **7** and, as new types of compounds, the acetylene **9** and the dioxole **10** were obtained (*Scheme 7*). While, on photolysis of **5** and **6**, it seems to be reasonable to exclude the carbene **c** as an intermediate, on thermolyses, **c** might well be the reactive intermediate. Thus, it may induce cleavage of the oxirane ring to the zwitterionic intermediate **d**, which may fragment to **7** and **9** *via* an *Eschenmoser* fragmentation [13] (*Scheme 5*). To exclude the possibility of thermal rearrangement of **8** to **9**, it was treated under the thermolysis conditions and could be recovered quantitatively.

Scheme 7



The formation of the dioxole **10** may be explained *via* a primary C–C bond cleavage, forming the ylide **g** (*Scheme 7*), which is intramolecularly trapped by the C=O group. The same type of compound, **13**, was found on thermolyses of the methyl ketones **11** and **12** (*Scheme 2*).

The formation of the acetylene **9** *via* the ylide **g** may also be discussed. Thus, in competition to the electrocyclic reaction, the C(1)→O migration of the (*t*-Bu)Me_2Si group is reasonable, followed by a fragmentation yielding **7** and **9**.

6. Conclusion. – This investigation of the photolyses and thermolyses of the α,β-epoxy silyl ketones **5** and **6** concludes a series of our systematic studies of the influence of neighboring groups on the reactivity of silyloxy-carbene intermediates.

Of the investigated acyl silanes, the α,β-epoxy silyl ketones **5** and **6** show a distinguished behavior. Thus, the photolysis of compounds **1**, (*E*/*Z*)-**2**, and **3** give rise to product formation *via* γ-H abstraction and silyloxy-carbene intermediates often leading to complex mixtures. In all cases, the photochemically generated silyloxy-carbene reacts preferentially by an intermolecular insertion into an O–H bond, rather than by an intramolecular addition to a C=C bond or by an insertion into a neighboring C–H or C–C bond. On the other hand, on photolyses of **5** and **6**, **7** and **8** are obtained as the only products. Most likely, they are formed *via* initial C(α)–O bond cleavage of the oxirane, rather than *via* γ-H-abstraction or *via* a silyloxy-carbene intermediate.

On thermolysis, **1**, (*E*/*Z*)-**2**, **3**, **5**, and **6** undergo rearrangement *via* silyloxy-carbene intermediates. In addition, the cyclopropyl silyl ketones **3** and the α,β-epoxy silyl ketones **5** and **6** show product formation *via* a [1,5] sigmatropic H-shift and *via* a carbonyl ylide, respectively.

In conclusion, it may be noted, that, on both photolysis and thermolysis of the investigated acylsilanes, product formation is not only dependent on the neighboring group, but also on the substituents in γ-position (γ-H abstraction).

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Experimental Part

General. See [18] except as noted below. Column chromatography (CC) was carried out on silica gel *60 Merck* 0.040–0.063 mm, 230–400 mesh ASTM (SiO_2) according to [19] ('flash chromatography'). Anal. pure samples were obtained, in general, after repeated CC on SiO_2; in some cases further purification was necessary with an HPLC (*Du Pont Instruments*, model *830*, UV detector), using a 25 × 23.6 cm SiO_2 column. In general, ^{1}H-NMR spectra were taken in $CDCl_3$ solns. on a *Bruker WP-80 CW* (80 MHz) on *WM 300* (300 MHz) instrument. For the description of the thermolysis procedures and the silylation of the thermolysis tubes, see [20].

1. Photolyses. – 1.1. *Photolysis of (* tert-*Butyl)dimethylsilyl 3-Methyl-3-(4-methylpent-3-enyl)oxiran-2-yl Ketone* (**5**). 1.1.1. *In MeCN.* A soln. of 256 mg (0.906 mmol) of **5** in abs. MeCN (25 ml) was irradiated (lamp *B*, filter *A* [21]; conversion 100%). After adding pentane (150 ml), the soln. was washed with sat. NaCl soln., dried ($MgSO_4$), and the solvent was removed *via* a *Vigreux* column, yielding a 1:1 mixture **7**/**8** (239 mg, 93%).

2-[(tert-*Butyl)dimethylsilyl]ketene* **8** (1:1 mixture with **7**). B.p. 110°/25 Torr. IR for **8**: 3350*w*, 3030*w*, 2950*s*, 2920*s*, 2880*m* (sh), 2850*m*, 2100*s*, 1710*s*, 1455*m* (sh), 1440*m*, 1405*m*, 1370*m*, 1350*m*, 1335*m* (sh), 1265*m*, 1255*m*, 1250*m*, 1175*w*, 1150*m*, 1110*w*, 1045*w*, 1000*w*, 935*w*, 900*m*. IR for **7**: u.a. 1710. ^{1}H-NMR (300 MHz) for **8**: 0.09 (*s*, 2 CH_3Si); 0.86 (*s*, 3 CH_3CSi); 1.70 (*s*, H–C(2)). ^{1}H-NMR for **7**: 1.58, 1.64 (2*m*, $w_{1/2}$ = 4, CH_3–C(6), 3 H–C(7));

2.09 (*s*, 3 H–C(1)); 2.15–2.25 (*m*, 2 H–C(4)); 2.35–2.45 (*m*, 2 H–C(3)); 5.03 (*tsept.*, $J_1 = 7.2$, $J_2 = 1.5$, H–C(5)). ^{13}C-NMR (75 MHz) for **8**: −4.5 (*q*, 2 CH_3Si); 25.9 (*q*, 3 CH_3CSi); −3.2 (*d*, C(2)); 17.6 (*s*, CSi); 179.0 (*s*, C(1)). ^{13}C-NMR for **7**: 17.6, 25.7, 29.9 (3*q*, C(1), CH_3–C(6), C(7)); 22.6, 43.8 (2*t*, C(3), C(4)); 122.8 (*d*, C(5)); 132.7 (*s*, C(6)); 208.7 (*s*, C(2)). ^{29}Si-NMR (59.6 MHz): 7.66 (Si–C(2)) (*vs.* TMS). MS for **8**: 156 (4, M^+, $C_8H_{16}OSi$), 141 (3), 99 (100), 88 (5), 86 (25), 84 (42). MS for **7**: 126 (6, M^+, $C_8H_{14}O$), 111 (13), 108 (25), 93 (9), 83 (6).

1.1.2. *In the Presence of (*t*-Bu)Me$_2$SiOH.* A soln. of 39 mg (0.139 mmol) of **5** and 18.3 mg (0.139 mmol) of (*t*-Bu)Me_2SiOH in abs. MeCN (12 ml) was irradiated (lamp *B*, filter *A*; conversion 100%, 10 min). After removing the solvent on the rotavapor, a 1:1 mixture (GC, ^{1}H-NMR) **7**/**8** (26 mg, 67%) was obtained.

1.1.3. *In the Presence of MeOH.* A soln. of 22 mg (0.078 mmol) of **5** in abs. MeOH (3 ml) was irradiated (lamp *B*, filter *A*; conversion 100%). After adding pentane (30 ml), MeOH was separated and the solvent removed on the rotavapor: a 1:1 mixture (GC, IR, ^{1}H-NMR) **7**/**8** (18 mg, 82%).

1.1.4. *In the Presence of Bu$_3$SnH.* A soln. of 32 mg (0.112 mmol) of **5** and 165 mg (0.15 ml, 0.566 mmol) Bu_3SnH in abs. MeCN (10 ml) was irradiated (lamp *B*, filter *A*; conversion 100%). Removing the solvent on the rotavapor yielded a 1:1 mixture (TLC, GC, IR, ^{1}H-NMR) **7**/**8**.

1.2. *Photolysis of* **6**. *In MeCN.* A soln. of 24 mg (0.085 mmol) of **6** in abs. MeCN (10 ml) was irradiated (lamp *B*, filter *A*; conversion 100%): a 1:1 mixture (GC, ^{1}H-NMR) **7**/**8**.

2. Thermolyses. – 2.1. *Thermolysis of* **5** (113 mg, 0.400 mmol) at 420° in a silylated *Quartz* tube (conversion 100%). After adding pentane (25 ml), the solvent was removed *via* a *Vigreux* column (100°/25 Torr), yielding a 1:1 mixture **7**/**9** (31 mg, 27%). The residue was purified *via* CC (SiO_2, Et_2O/hexane 1:10) yielding **10** (21 mg, 19%).

*{[(*tert*-Butyl)dimethylsilyl]oxy}acetylene* (**9**) (1:1 mixture with **7**). B.p. 100–110°/25 Torr. IR: 3680*w*, 3420*w*, 3325*s*, 2950*s*, 2920*s*, 2880*s*, 2850*s*, 2150*s*, 2130*m* (sh), 2100*w*, 1710*s*, 1465*m*, 1455*m*, 1440*m*, 1430*m*, 1405*m*, 1385*m*, 1365*m*, 1360*s*, 1350*s* (sh), 1340*m* (sh), 1255*s*, 1250*s*, 1175*m*, 1150*s* (sh), 1140*s*, 1105*w*, 1050*w*, 1000*w*, 935*m*, 885*w*, 840*s*. ^{1}H-NMR (300 MHz) for **9**: 0.22 (*s*, 2 CH_3Si); 0.91 (*s*, 3 CH_3CSi); 1.07 (*s*, H–C(2)). ^{13}C-NMR for **9**: −5.8 (*q*, 2 CH_3Si); 25.3 (*q*, 3 CH_3CSi); 20.2 (*d*, C(2)); 18.4 (*s*, CSi); 87.9 (*d*!, C(1)). ^{29}Si-NMR (59.6 MHz): 35.4 (SiO) (*vs.* TMS).

*4-[(*tert*-Butyl)dimethylsilyl]-2-methyl-2-(4′-methylpent-3′-enyl)-1,3-dioxole* (**10**). B.p. 100°/0.06 Torr. IR: 2980*m*, 2950*s*, 2920*s*, 2895*s*, 2880*s*, 2850*s*, 2740*w*, 2710*w*, 1725*w*, 1670*w*, 1595*s*, 1465*m*, 1460*m*, 1445*m*, 1410*w*, 1385*m*, 1370*m*, 1360*m*, 1340*w*, 1300*w*, 1285*w*, 1265*m*, 1250*s*, 1195*m*, 1175*m*, 1160*s*, 1110*m*, 1090*w*, 1070*w*, 1030*m*, 1005*w*, 965*w*, 940*w*, 920*m*, 905*m*. ^{1}H-NMR (300 MHz): 0.08 (*s*, 2 CH_3–Si); 0.94 (*s*, CH_3CSi); 1.41 (*s*, CH_3–C(2)); 1.61, 1.68 (2*m*, $w_{1/2} = 4$, CH_3–C(4′), 3 H–C(5′)); 1.75–1.80 (*m*, 2 H–C(1′)); 2.05–2.15 (*m*, 2 H–C(2′)); 5.10 (*tm*, $J = 7$, $w_{1/2} = 4$, H–C(3′)); 6.14 (*s*, H–C(5)). ^{13}C-NMR (75 MHz): −6.8 (*q*, 2 CH_3Si); 17.7, 23.7, 25.8 (3*q*, CH_3–C(2), CH_3–C(4′), C(5′)); 26.5 (*q*, 3 CH_3CSi); 22.2, 38.9 (2*t*, C(1′), C(2′)); 124.0 (*d*, C(3′)); 135.6 (*d*, C(5)); 16.7 (*s*, CSi); 115.8 (*s*, C(2)); 131.7 (*s*, C(4′)); 137.3 (*s*, C(4)). MS: 282 (20, M^+, $C_{16}H_{30}OSi$); 267 (7), 225 (7), 200 (17), 199 (100), 143 (16), 117 (21), 115 (26), 99 (46), 75 (52), 73 (85), 69 (59), 59 (13), 43 (68), 41 (34).

2.2. *Thermolysis of* **6** (9 mg, 0.03 mmol) at 420° in a silylated Quartz tube (conversion 100%). Workup as in *2.1* yielded a 1:1 mixture (GC, IR, ^{1}H-NMR) **7** + **9**/**10**.

2.3. *Thermolysis of a 1:1 mixture* **7**/**8** (184 mg, 0.65 mmol) at 420° in a silylated *Quartz* tube. Workup as described in *2.1* yielded an unconverted 1:1 mixture (GC, IR, ^{1}H-NMR) **7**/**8** (148 mg, 81%).

2.4. *Thermolysis of* **10** (2 mg, 0.007 mmol) at 420° in a silylated *Quartz* tube yielded only unconverted **10** (GC, IR, ^{1}H-NMR).

2.5. *Thermolysis of a 1:1 mixture* **11**/**12** (*methyl 3-methyl-3-(4-methylpent-3-enyl)oxiran-2-yl ketone*; 234 mg, 1.28 mmol) at 500° in a silylated *Quartz* tube (conversion 55%). Workup as described in *2.1* yielded **11**/**12** (105 mg) and **13** (73 mg, 57%).

2,4-Dimethyl-2-(4′-methylpent-3′-enyl)-1,3-dioxole (**13**). B.p. 125°/0.2 Torr. IR: 3140*w*, 2980*s*, 2970*s*, 2920*s*, 2880*s*, 2855*m*, 2750*w*, 2730*w*, 1695*m* (br.), 1615*w*, 1445*s*, 1435*m*, 1425*s*, 1380*s*, 1370*s*, 1340*m*, 1310*m*, 1280*s*, 1270*s*, 1230*s*, 1200*s*, 1170*m*, 1160*m*, 1130*s*, 1110*s*, 1095*s*, 1055*s*, 1000*m*, 970*w*, 930*m*, 920*m*, 900*w*, 855*m*, 835*m*. ^{1}H-NMR (300 MHz, C_6D_6): 1.45, 1.56 (6 H), 1.64 (3*s*, CH_3–C(2), CH_3–C(4), CH_3–C(4′), 3 H–C(5′)); 1.86–1.94 (*m*, 2 H–C(1)); 2.25–2.40 (*m*, 2 H–C(2′)); 5.21 (*tm*, $J = 7$, $w_{1/2} = 4$, H–C(3′)); 5.73 (*m*, $w_{1/2} = 5$, H–C(5)). ^{13}C-NMR (75 MHz, C_6D_6): 9.6 (*q*, CH_3–C(4)); 17.5, 23.7, 25.7 (3*q*, CH_3–C(2), CH_3–C(4′), C(5′)); 22.4, 39.3 (2*t*, C(1′), C(2′)); 121.6 (*d*, C(3′)); 124.5 (*d*, C(5)); 114.8 (*s*, C(2)); 131.2 (*s*, C(4′)); 135.1 (*s*, C(4)). MS: 182 (4, M^+, $C_{11}H_{18}O_2$), 167 (2), 139 (7), 124 (19), 111 (15), 109 (15), 108 (21), 99 (43), 86 (17), 84 (27), 71 (12), 69 (55), 67 (12), 58 (10), 55 (22), 43 (57), 43 (100), 41 (57).

3. Additional Experiments. – 3.1. *Preparation of* **11** *and* **12**. 3.1.1. *Epoxidation of (*E*/*Z*)-4,8-Dimethylnona-3,7-dien-2-ol* ((*E*/*Z*)-**15**). Compound (*E*/*Z*)-**15** was prepared from citral (1:1 mixture of (*E*/*Z*)-**14**) with MgBrMe in 93% yield [20]. Under Ar, a soln. of (*E*/*Z*)-**15** (4.97 g, 29.53 mmol) in abs. benzene (200 ml, filtered through Al_2O_3

super *B*) was cooled to 4°, until 2/3 of the soln. was frozen. After the addition of $VO(acac)_2$ (124 mg, 0.46 mmol), a soln. of *t*-BuOOH (5.66 g, 80%, 50.26 mmol) in benzene (100 ml) was added during 20 min. After stirring for 20 min, the soln. was worked up by the addition of hexane/Et_2O 1:1 and then filtered through a sintered funnel (5 cm, packed with a 1-cm layer of *Celite* and a 2-cm layer of Si_2O slurry in hexane/Et_2O 1:1 and 1% Et_3N). Further workup with sat. aq. NaCl and $MgSO_4$ afforded a crude product, which was immediately distilled (83°/0.06 Torr) yielding **16A** + **B** + **C** + **D** (5.10 g, 94%).

3,4-Epoxy-4,8-dimethylnon-7-en-2-ol (**16A** + **B** + **C** + **D**; 4 diastereoisomeres). B.p. 83°/0.06 Torr. IR: 3600*w*, 3450*m* (br.), 2960*s*, 2920*s*, 2850*s*, 2720*w*, 1460*m*, 1445*s*, 1375*s*, 1180 (sh), 1245*m*, 1165*w*, 1140*w*, 1105*m*, 1055*s*, 1035*m*, 985*w*, 945*w*, 915*w*, 900*m*, 875*s*. ^{1}H-NMR (80 MHz): 1.18, 1.22 (2*d*, J = 3, H–C(1)); 1.28, 1.31 (2*s*, CH_3–C(4)); 1.25–1.85 (*m*, 2 H–C(5)); 1.61, 1.69 (2*s*, CH_3–C(8), 3 H–C(9)); 1.85–2.30 (*m*, 2 H–C(6)); 2.69 (*d*, J = 8, H–C(3)); 3.25 (br. *s*, OH); 3.65 (*dq*, J_1 = 8, J_2 = 3, H–C(2)); 5.10 (*tm*, J = 7, $w_{1/2}$ = 4, H–C(7)). MS: 184 (< 1, M^+, $C_{11}H_{20}O_2$), 166 (1), 139 (3), 110 (25), 109 (45), 95 (28), 93 (13), 85 (10), 84 (13), 83 (16), 82 (65), 81 (23), 71 (43), 70 (28), 69 (100), 68 (14), 67 (42), 59 (23), 57 (33), 55 (38), 53 (15), 45 (25), 43 (79), 41 (98).

3.1.2. *Oxidation of* **16A** + **B** + **C** + **D**. To a soln. of pyridine (4 ml) in abs. CH_2Cl_2 at 0°, CrO_3 (2.0 g, 20 mmol) was added carefully and the mixture stirred for 15 min. A soln. of **16A** + **B** + **C** + **D** (630 mg, 3.42 mmol) in CH_2Cl_2 (6 ml) was added in one portion, and after stirring for *ca.* 1 h at r.t. (TLC control), the mixture was worked up by adding Et_2O (400 ml). CC (SiO_2, dimethoxyethane/hexane 1:9) afforded **11** and **12** (447 mg, 72%). An anal. sample was separated by HPLC (SiO_2, p = 45 bar, flow = 33 ml/min, λ_{Det} = 281 nm, Et_2O/hexane 1:10) to obtain pure **11** and **12**.

*(3*RS,*4*SR*)-3,4-Epoxy-4,8-dimethylnon-7-en-2-one* (**11**). B.p. 125°/0.1 Torr. UV (3.574 mg in 2 ml): 295 (30). IR: 3430*w*, 3400*w*, 2970*s*, 2930*s*, 2915*s*, 2880*m*, 2860*s*, 1725*s*, 1705*s*, 1670*w*, 1455*w* (sh), 1450*s*, 1440*s*, 1435*m*, 1400*s*, 1380*s*, 1355*s*, 1240*s*, 1185*m*, 1145*w*, 1110*w*, 1075*m*, 1040*w*, 980*w*, 940*w*, 925*w*, 910*w*, 890*w*, 875*w*. ^{1}H-NMR (80 MHz): 1.14 (*s*, CH_3–C(4)); 1.10–1.75, 1.80–2.40 (*m*, 2 H–C(5), 2 H–C(6)); 1.51, 1.60 (2*m*, $w_{1/2}$ = 4, CH_3–C(8), 3 H–C(9)); 2.09 (*s*, 3 H–C(1)); 3.31 (*s*, H–C(3)); 5.03 (*tm*, J = 7, $w_{1/2}$ = 4, H–C(7)). ^{13}C-NMR: 16.2, 17.7, 25.7, 27.9 (4*q*, C(1), CH_3–C(4), CH_3–C(8), C(9)); 23.7, 38.2 (2*t*, C(5), C(6)); 64.9 (*d*, C(3)); 122.9 (*d*, C(7)); 63.3 (*s*, C(4)); 132.6 (*s*, C(8)); 204.3 (*s*, C(2)). MS: 182 (< 1, M^+, $C_{11}H_{18}O_2$), 164 (1), 139 (4), 121 (5), 109 (31), 99 (20), 82 (47), 81 (14), 74 (10), 71 (18), 70 (10), 69 (72), 67 (24), 59 (11), 55 (21), 53 (11), 43 (100), 41 (89). Anal. calc. for $C_{11}H_{18}O_2$ (182.12): C 72.46, H 9.95; found: C 72.46, H 10.02.

*(3*RS,*4*RS*)-3,4-Epoxy-4,8-dimethylnon-7-en-2-one* (**12**). B.p. 125°/0.1 Torr. UV (3.489 mg in 2 ml): 287 (30). IR: 3430*w*, 3400*w*, 2970*s*, 2930*s*, 2910*s*, 2865*s* (sh), 2860*s*, 2730*w*, 1730*s*, 1705*s*, 1455*m*, 1450*s*, 1435*s*, 1430*m* (sh), 1420*m* (sh), 1405*s*, 1375*s*, 1355*s*, 1290*w*, 1250*m* (sh), 1235*m*, 1180*m*, 1145*w*, 1110*w*, 1075*m*, 1060*m*, 1045*m*, 1020*w*, 985*w*, 965*w*, 940*w*, 925*m*. ^{1}H-NMR (80 MHz): 1.33 (*s*, CH_3–C(4)); 1.00–1.75 (*m*, 2 H–C(5)); 1.50, 1.58 (2*m*, $w_{1/2}$ = 4, CH_3–C(8), 3 H–C(9)); 1.75–2.30 (*m*, 2 H–C(6)); 2.14 (*s*, 3 H–C(1)); 3.28 (*s*, H–C(3)); 4.95 (*tm*, J = 7, $w_{1/2}$ = 4, H–C(6)). ^{13}C-NMR: 17.5, 22.1, 25.7, 28.2 (4*q*, C(1), CH_3–C(4), CH_3–C(8), C(9)); 24.1, 32.4 (2*t*, C(5), C(6)); 65.8 (*d*, C(3)); 122.8 (*d*, C(7)); 63.8 (*s*, C(4)); 132.6 (*s*, C(8)); 204.3 (*s*, C(2)). MS: 182 (< 1, M^+, $C_{11}H_{18}O_2$), 164 (2), 149 (5), 139 (3), 121 (7), 109 (44), 99 (17), 83 (11), 82 (73), 81 (21), 74 (11), 71 (14), 70 (10), 69 (66), 67 (40), 59 (13), 55 (26), 53 (14), 43 (100), 41 (86). Anal. calc. for $C_{11}H_{18}O_2$ (182.12): C 72.49, H 9.95; found: C 72.47, H 10.03.

3.2. *Methanolyses of* **8**. A soln. of a 1:1 mixture **7**/**8** (148 mg, 0.52 mmol) in MeOH (3 ml) was stirred overnight at reflux temp. After removing the solvent at the rotavapor, a bulb-to-bulb distillation (125°/50 Torr) afforded a 1:1 mixture **7**/**23** (156 mg, 95%).

*Methyl 2-[(*tert*-Butyl)dimethylsilyl]acetate* (**23**) (1:1 mixture with **7**). B.p. 125°/30 Torr. IR: 2940*s*, 2920*s*, 2890*s*, 2875*s*, 2850*s*, 2820*w*, 1715*s*, 1455*m*, 1430*s*, 1400*m*, 1385*m*, 1370*m*, 1360*m*, 1350*m*, 1340*w*, 1245*s*, 1170*w* (br.), 1150*m*, 1135*s*, 1095*s*, 1070*m*, 1050*m*, 1015*w*, 1005*w*, 980*w*, 935*w*, 875*s*. ^{1}H-NMR (80 MHz): 0.00 (*s*, 2 CH_3Si); 0.84 (*s*, 3 CH_3CSi); 1.83 (*s*, 2 H–C(2)); 3.55 (*s*, CH_3O). ^{13}C-NMR: –6.1 (*q*, 2 CH_3Si); 26.0 (*q*, 3 CH_3CSi); 50.9 (*q*, CH_3O); 22.4 (*t*, C(2)); 16.6 (*s*, CSi); 173.6 (*s*, C=O). MS: 157 (3, $[M - OCH_3]^+$), 131 (24), 108 (15), 89 (100), 73 (18), 69 (21), 59 (22), 58 (12), 55 (21), 43 (58), 41 (37).

3.3. *Hydrolyses*. 3.3.1. *Hydrolysis of* **10**. A soln. of **10** (11 mg, 0.04 mmol) oxalylic acid (19 mg, 0.21 mmol), and H_2O (0.7 ml) was stirred overnight at r.t. After adding Et_2O (30 ml), the usual workup afforded only **7** (4.3 mg, 85%).

3.3.2. *Hydroylsis of* **13**. A soln. of **13** (14.4 mg, 0.079 mmol), aq. HCl soln. (1 ml, 2M) was stirred for 24 h. After adding Et_2O (20 ml), the solvent was removed at the rotavapor: only **7** was detected (8 mg, 80%).

REFERENCES

[1] M. E. Scheller, B. Frei, *Helv. Chim. Acta* **1990,** *73,* 923.
[2] M. E. Scheller, Dissertation, ETHZ No. 7897, 1985.
[3] M. E. Scheller, B. Frei, *Helv. Chim. Acta* **1984,** *67,* 1734.
[4] M. E. Scheller, G. Iwasaki, B. Frei, *Helv. Chim. Acta* **1986,** *69,* 1378.
[5] M. E. Scheller, W. B. Schweizer, B. Frei, *Helv. Chim. Acta* **1989,** *72,* 264.
[6] A. Ricci, A. Degl'Innocenti, *Synthesis* **1989,** 647.
[7] A. O. Chong, K. B. Sharpless, *J. Org. Chem.* **1977,** *42,* 1589.
[8] a) L. L. Shchukovskaya, R. I. Pal'chik, A. N. Lazarev, *Dokl. Akad. Nauk SSSR* **1965,** *164,* 357; b) L. L. Shchukovskaya, A. I. Kol'tsov, A. N. Lazarev, R. I. Pal'chik, *ibid.* **1968,** *179,* 892.
[9] Y. K. Gishin, S. V. Ponomarev, S. A. Levedev, *J. Org. Chem. USSR* **1974,** *10,* 402.
[10] E. P. Müller, O. Jeger, *Helv. Chim. Acta* **1975,** *58,* 2273.
[11] R. Phaff, N. Bischofberger, P. Mathies, W. Petter, B. Frei, O. Jeger, *Helv. Chim. Acta* **1985,** *68,* 1214.
[12] L. E. Friedrich, J. D. Bower, *J. Am. Chem. Soc.* **1973,** *95,* 6869.
[13] D. Felix, R. K. Müller, U. Horn, R. Joos, J. Schreiber, A. Eschenmoser, *Helv. Chim. Acta* **1972,** *55,* 1276.
[14] a) O. Jeger, K. Schaffner, H. Wehrli, *Pure Appl. Chem.* **1964,** *9,* 555; b) A. Pawda, *Org. Photochem.* **1967,** *1,* 91; c) N. R. Bertonier, G. W. Griffin, *ibid.* **1973,** *3,* 115.
[15] a) H. Sakurai, A. Hosomi, M. Kumada, *Tetrahedron Lett.* **1968,** 2469; b) A. J. Ashe, III, *J. Am. Chem. Soc.* **1973,** *95,* 819.
[16] a) A. G. Brook, *Acc. Chem. Res.* **1974,** *7,* 77; b) A. G. Brook, A. R. Bassindale, 'Molecular Rearrangements of Organosilicon Compounds', Essay 9 in 'Rearrangements in Ground and Excited States', Ed. P. de Mayo, Academic Press, New York, 1980; c) E. Colvin, 'Silicon in Organic Synthesis', 'Monographs in chemistry and chemical engineering', Butterworths, London, 1981.
[17] a) S. Braslavsky, J. Heicklen, *Chem. Rev.* **1977,** *77,* 473; b) R. F. C. Brown, 'Pyrolytic Methods in Organic Chemistry', Academic Press, New York, 1980, pp. 302.
[18] A. P. Alder, H. R. Wolf, O. Jeger, *Helv. Chim. Acta* **1980,** *63,* 1833.
[19] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978,** *43,* 2923.
[20] A. O'Sullivan, N. Bischofberger, B. Frei, O. Jeger, *Helv. Chim. Acta* **1985,** *68,* 1089.
[21] M. Yoshika, K. Ishii, H. R. Wolf, *Helv. Chim. Acta* **1980,** *63,* 571.