142. Photochemical Reactions

148th Communication[1])

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

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The syntheses, photolyses, and thermolyses of the α,β-unsaturated silyl ketones (*E*/*Z*)-**7**, (*E*)-**8**, and (*E*)-**9** are described. On n,π*-excitation ($\lambda > 347$ mm), the aforementioned compounds undergo (*E*/*Z*)-isomerization followed by γ-H abstraction. The intermediate enols are trapped intermolecularly by siloxycarbenes leading to the dimeric acetals **27A** + **B**, **30A** + **B**, and **31A** + **B**. In addition, the acylsilanes (*E*/*Z*)-**7** undergo photoisomerization by δ-H abstraction furnishing the acylsilanes **29A** + **B**. Flash vacuum thermolyses (FVT) of (*E*/*Z*)-**7**, (*E*/*Z*)-**8**, and (*E*)-**9** give rise to intramolecular reactions of the siloxycarbene intermediates. Thus, FVT (520°) of (*E*)- and (*Z*)-**7** selectively leads to the enol silyl ethers **32** and (*E*)-**33**, respectively, arising from carbene insertion into an allylic C–H bond. FVT of (*E*/*Z*)-**8** (560°) and (*E*)-**9** (600°) affords the trienol silyl ethers **34A** + **B** and the cyclic silyl ethers **37A** + **B**, respectively, which are formed by CH insertion of the siloxycarbenes. As further products of (*E*)-**8** and (*E*)-**9**, the bicyclic enol ethers **35** and **36** are formed, presumably *via* siloxycarbene addition to the cyclohexene C=C bond.

1. Introduction. – Recently, we reported on the photochemistry of the acylsilane **1** [3]. It was found that the major photochemical processes are *Norrish* type-II fragmentation (leading to the diene **2** and the enol **3**) and rearrangement to the siloxycarbene **a** (*Scheme 1*). The latter reacts by *intermolecular* insertion of the carbene center into the O–H bond of **3** (furnishing the enol acetal **4**) and by *intramolecular* addition of the carbene center to the methylidene group or insertion into an adjacent C–H bond (leading to compounds **5** and **6**, respectively, as minor products).

As part of our studies of the intramolecular trapping of siloxycarbenes by reaction with various neighboring groups, we describe here the photolyses and thermolyses of the α,β-unsaturated acylsilanes (*E*/*Z*)-**7**, (*E*)-**8**, and (*E*)-**9** (*Scheme 2*). They were considered as suitable models to delineate the reactivity of the expected siloxycarbene intermediate with a neighboring double bond. It was of particular interest to find out, whether or not the siloxycarbene intermediate would undergo ring closure to a cyclopropene, as observed in vinyl carbenes [4].

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[1]) 147th Communication: [1].

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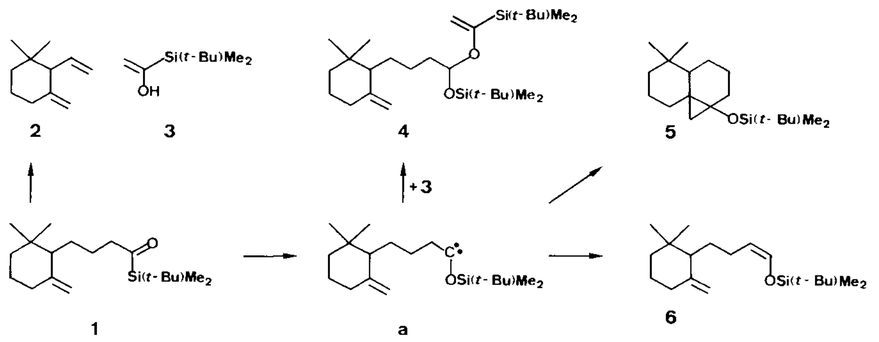
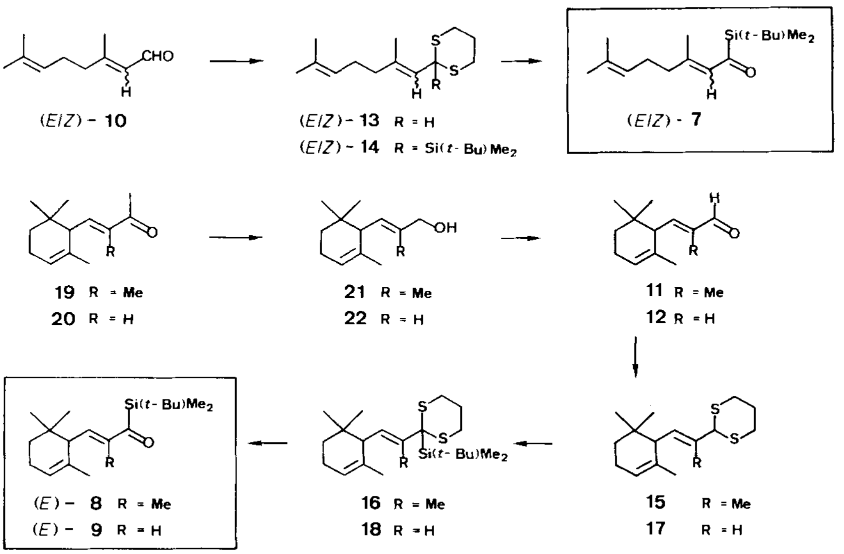
Scheme 1



2. Preparation of the Acylsilanes (*E*/*Z*)-7, (*E*)-8, and (*E*)-9. – The compounds (*E*/*Z*)-**7**, (*E*)-**8**, and (*E*)-**9** were synthesized *via* the dithiane route[5]) starting from the aldehydes (*E*/*Z*)-**10**, **11**, and **12**, respectively. Thus, thioacetalization of citral (*E*/*Z*)-**10** (*ca.* 2:1) with propanedithiol ($BF_3 \cdot Et_2O$, CH_2Cl_2) furnished the 1,3-dithianes (*E*/*Z*)-**13** [6] (*ca.* 3:2; 91%), which were transformed to (*E*/*Z*)-**14** (*ca.* 3:2; 98%) by reaction with BuLi and (*t*-Bu)Me_2SiCl. Dethioacetalization with $Tl(NO_3)_3 \cdot 3H_2O$ [7] led to the acylsilanes (*E*/*Z*)-**7** (*ca.* 2:1; 50%; overall yield 45%)[6]).

Scheme 2



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[5]) After completion of this work [2], a further practical and efficient synthesis of α,β-unsaturated acylsilanes involving silyl-*Wittig* rearrangement and *Swern* oxidation was published by *Danheiser et al.* [5].

[6]) Dethioacetalization of pure (*E*)- or (*Z*)-**14** under the same conditions also led to a *ca.* 2:1 mixture of (*E*)/(*Z*)-**7**.

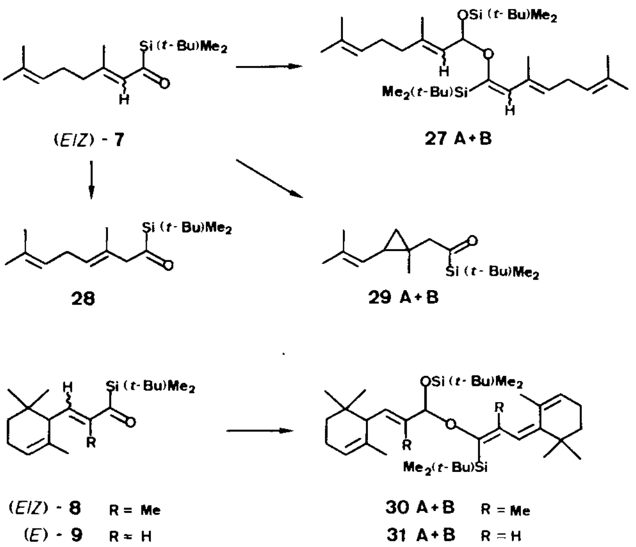
Analogously, the acylsilanes (*E*)-**8** and (*E*)-**9** were obtained from the aldehydes **11** (*via* **15** and **16**) and **12** [8] (*via* **17** and **18**), respectively. Compounds **11** and **12** were prepared by degradation of 8-methyl-α-ionone (**19**) and α-ionone (**20**), respectively, (a) I_2/pyridine, b) $LiAlH_4$) and subsequent oxidation of the alcohols **21** and **22** [9] with MnO_2.

It is noteworthy that dethioacetalization of **16** and **18** did not cause ($E \rightarrow Z$) isomerization as was observed for (*E*)-**14**. Furthermore, using $HgO/HgCl_2$ [10] instead of $Tl(NO_3)_3 \cdot 3H_2O$ for the cleavage of the dithiane **16**, the yield of the acylsilane (*E*)-**8** improved from 45% to 93%[7]).

3. Photolyses of (*E*/*Z*)-7, (*E*)-8, and (*E*)-9. – 3.1. *Irradiation* of (*E*)-**7** (0.010M soln. in MeCN; $\lambda > 347$ nm; 100% conversion) afforded: **27A** + **B**[8]) (*ca.* 1:1; 22%), **28** (12%), **29A** + **B** (*ca.* 1:1; 10%; *Scheme 4*), and (*E*/*Z*)-**10** (17%; *Scheme 2*).

3.2. *Irradiation* of (*Z*)-**7** (0.015M soln. in MeCN; $\lambda > 347$ nm; 83% conversion) gave **27A** + **B** (*ca.* 1:1; 24%), **28** (19%), **29A** + **B** (*ca.* 1:1; 14%), and (*E*/*Z*)-**10** (16%).

Scheme 4



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[7]) An analogous improvement was observed on dethioacetalization of the dithianes **23** and **24** [2] (*Scheme 3*). With $Tl(NO_3)_3 \cdot 3\ H_2O$, the acylsilanes **25** and **26** were produced in only *ca.* 25% yield, whereas the reaction with $HgO/HgCl_2$ led to the yields of 86 and 88%, respectively. On dethioacetalization of (*E*/*Z*)-**14**→(*E*/*Z*)-**7** with $HgO/HgCl_2$ instead of $Tl(NO_3)_3 \cdot 3\ H_2O$, however, the yield could be increased only slightly from 50 to 56%.

Scheme 3

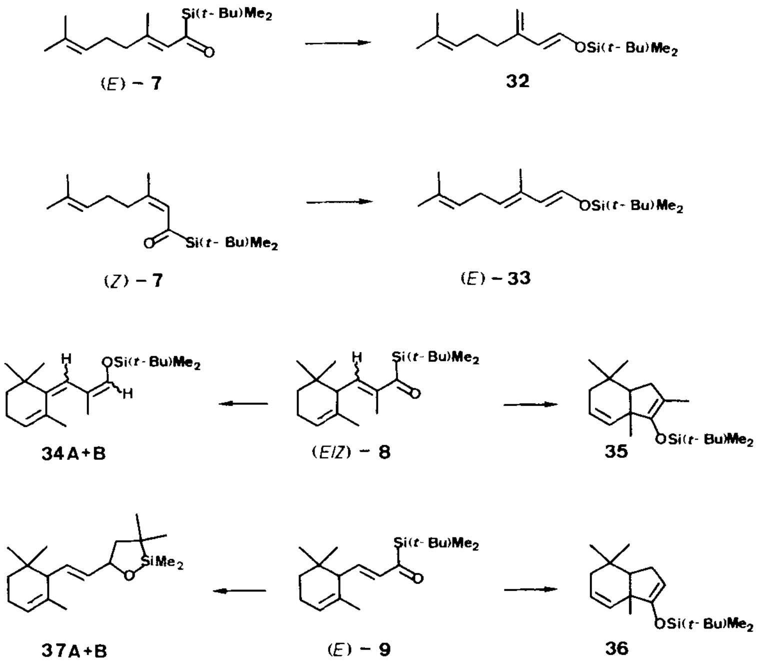
[8]) The terms **A** and **B** are used for the description of diastereoisomers whose configurations were not assigned conclusively.

3.3. *Irradiation* of (*E*)-**8** (0.012M soln. in MeCN; λ > 347 nm; 98% conversion) gave (*Z*)-**8** (21%), **30A** (4%), and **30B** (3%; *Scheme 4*). Irradiation of (*E*)-**8** in THF under the same conditions afforded (*Z*)-**8** (22%), **30A** (6%), and **30B** (4%).

3.4. *Irradiation* of (*E*)-**9** (λ > 347 nm) in MeCN or THF led to mixtures containing *ca.* 30% of the acetals **31A** + **B** which, however, decomposed on chromatography on SiO_2.

4. Thermolyses of (*E*/*Z*)-7, (*E*/*Z*)-8, and (*E*)-9. – 4.1. *Flash Vacuum Thermolysis* (*FVT* [11]) of (*E*)-**7** and (*Z*)-**7** (520°) afforded the dienol ethers **32** (42%) and (*E*)-**33** (46%), respectively (*Scheme 5*).

Scheme 5



4.2. *FVT* of (*E*)- and (*Z*)-**8** (560°[9]) furnished the trienol ethers **34A** (17 and 15%, respectively) and **34B** (5%), and the enol ether **35** (30%; *Scheme 5*).

4.3. *FVT* of (*E*)-**9** (600°[9]) gave compounds **36** (25%), and **37A** + **B** (*ca.* 1:1; 39%; *Scheme 5*).

5. 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 chemical transformations which confirmed the assigned structures. Full data and the assignment of the NMR data are presented in the *Exper. Part.*

*α,β-Unsaturated Silyl Ketones (*E/Z*)-*7*, (*E/Z*)-*8* and (*E*)-*9*.* In particular, these compounds show IR bands shifted to long wavelengths: 1625–1630 cm^{-1} and 1560–1595 cm^{-1}. In the UV spectra, apart from the strong π,π* bands between 225–260 nm (ε ≈ 10000), the characteristic structured n,π* bands in the region of 400–490 nm (ε ≈ 100) are observed. Furthermore, in the ^{13}C-NMR spectra, the C=O groups are evidenced by the low-field shifted signals at *ca.* 235 ppm.

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[9] This temperature was necessary to convert 75–80% of the starting material.

Enol Acetals **27A** + **B**, **30A** + **B**, *and* **31A** + **B** *(Scheme 4)*. The UV maximum of **27A** + **B** at 233 nm (ε = 7600) indicates the dienolether moiety. Characteristic ^{1}H-NMR signals are at 2.70 ppm (*tm*) of the double allylic 2H–C(4), at *ca.* 5.35 ppm (*dm*, *J* = 7 Hz) of H–C(11), and at *ca.* 5.80 ppm (*d*, *J* = 7 Hz) of the acetal H–C(10). In the ^{13}C-NMR spectrum, a *d* at 93 and a *s* at 158 ppm are characteristic of the acetal C(10) and the enol-ether C(8), respectively. Conclusive evidence for the structure of **27A** + **B** was obtained on hydrolysis (2M HCl/Et_2O) leading to the acylsilanes (*E*/*Z*)-**7** and **28**, and to the aldehydes (*E*/*Z*)-**10** *(Scheme 2)*. The enol acetals **30A** and **30B**, which were separated by column chromatography, show spectroscopic data similar to those of **27A** + **B** (see *Exper. Part*). Hydrolysis of **30A** and **30B** (aq. HCl/Et_2O) afforded the acylsilane (*Z*)-**8** and the aldehyde (*E*)-**11** *(Scheme 2)*.

Hydrolysis of **31A** + **B** (THF/5% aq. HCl) gave the aldehyde **12** as the only product. On treatment of the acylsilanes (*E*)-**8** and (*E*)-**9** under the same conditions, it was shown that (*E*)-**8** was stable, whereas (*E*)-**9** was transformed to the aldehyde **12**.

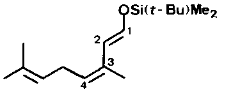
Acylsilanes **28** *and* **29A** + **B** *(Scheme 4)*. These compounds show spectral data characteristic of acylsilanes (see *Exper. Part*). Furthermore, the structure was assigned by comparison of their spectral data with those of the related methyl and phenyl ketones [12].

The *Dienol Silyl Ethers* **32** and (*E*)-**33** show strong IR bands (1635 and 1640 cm^{-1}, respectively) and UV maxima at *ca.* 240 nm ($\varepsilon \approx$ 20000), which are characteristic of the dienol-ether moieties. In the ^{1}H-NMR spectra, the coupling constants *J* = 12.5 Hz of the *AB* systems at *ca.* 6.4 ppm indicate the (*E*)-configuration around the C(1)=C(2) bond. The (*E*)-configuration around the C(3)=C(4) bond of (*E*)-**33** was assigned by an NOE experiment: on irradiation at 2.84 ppm (2H–C(5)), the signals of CH_3–C(3) and CH_3–C(7) showed a positive, and the *AB* system of H–C(1) and H–C(2) a negative NOE [13]. As structure proof, the dienol ethers **32** and (*E*)-**33** were obtained together with their isomer (*Z*)-**33** (see below) by reaction of (*E*/*Z*)-**10** with (*t*-Bu)Me_2SiCl and Et_3N (92% combined yield). The (*Z*)-configuration around the C(3)=C(4) bond of (*Z*)-**33** was again assigned by an NOE experiment. Thus, irradiation at 2.88 ppm (2H–C(5)) caused a positive NOE of the signals of CH_3–C(7) and H–C(2).

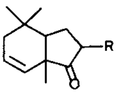
Trienol Silyl Ethers **34A** *and* **34B** *(Scheme 5)*. The trienol-silyl-ether moiety is evidenced by the UV maxima at 221 nm (ε = 9390) and 267 nm (ε = 9555) of **34A**, by the IR bands at 1645 cm^{-1} as well as by the ^{1}H- and ^{13}C-NMR-signals of the olefinic H- and C-atoms, respectively (see *Exper. Part*).

Bicyclic Enol Ethers **35** *and* **36** *(Scheme 5)*. The assigned structures were confirmed by hydrolysis (5% aq. HCl/THF) leading to the bicyclic compounds **38** and **39** (see below) with a cyclopentanone moiety (IR: 1730 cm^{-1}). For the NMR data, see *Exper. Part.*

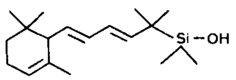
Cyclic Silyl Ethers **37A** + **B** *(Scheme 5)*. On treatment of **37A** + **B** with 5% aq. HCl in THF, the silanol **40** incorporating a conjugated diene system was formed by hydrolysis and subsequent H_2O elimination.



(*Z*)-**33**



38 R = Me
39 R = H



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6. Discussion. – 6.1. *Photolyses.* n,π^* Excitation (λ > 347 nm) of the acylsilane (*E*)- or (*Z*)-**7** causes rapid (*E*/*Z*)-isomerization. Thus, after a short time of irradiation, a photostationary equilibrium of (*E*/*Z*)-**7** (ratio *ca.* 2:1) was obtained. As further main process, γ-H abstraction in (*Z*)-**7** leads – *via* the diradical **b** – to the enol **41** *(Scheme 6)*, which tautomerizes either to (*Z*)-**7** or to the deconjugated acylsilane **28** *(Scheme 4)*. The alternative deconjugated ketone **42**, which would be formed by photoenolization from (*E*)-**7** ($\rightarrow$ **c** $\rightarrow$ **43**; *Scheme 6*), was not detected. In contrast to the dienol **41**, **43** can presumably more readily adopt the conformation necessary for a [1,5] sigmatropic H shift. Thus, reketonization to (*E*)-**7** occurs instead of deconjugation to **42**[10]).

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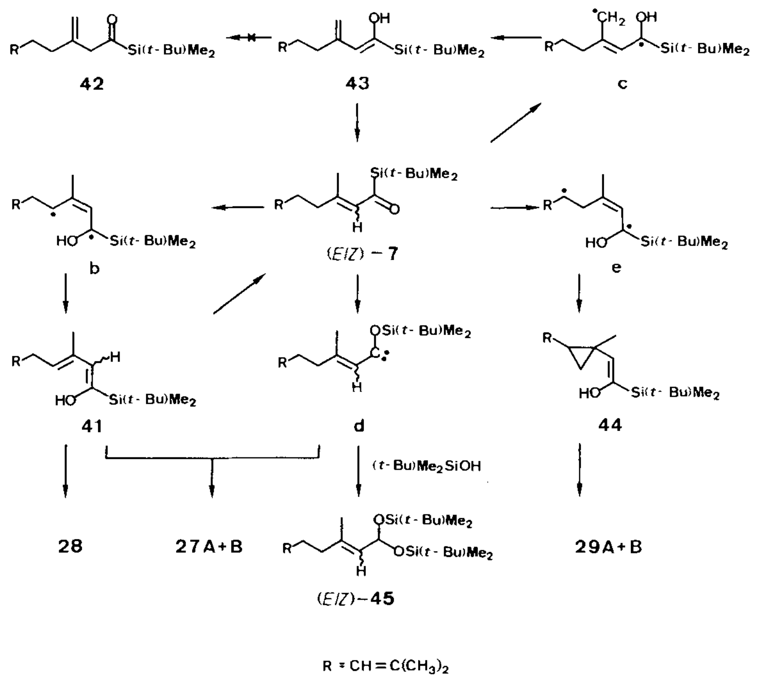
[10]) For a recent investigation of the mechanisms of the photochemical enolization of α,β-unsaturated ketones, see [14].

Scheme 6



The siloxycarbene **d** is formed from (*E*/*Z*)-**7** *via* a second photoprocess, typical of acylsilanes [15]. Analogously to **a** + **3** → **4** *(Scheme 1)*, the siloxycarbene **d** reacts with the dienol **41** leading to **27A** + **B**[11]. It was observed, however, that the formation and trapping of the siloxycarbene **d** is not as efficient as that of **a**. On photolysis of (*E*/*Z*)-**7** in the presence of (t-Bu)Me$_2$SiOH (1.5 equiv.), the acetals (*E*/*Z*)-**45** (24%) are obtained together with **28** (13%) and **29A** + **B** (8%). On the other hand, on photolysis of **1** in the presence of (t-Bu)Me$_2$SiOH (1 equiv.), the acetal corresponding to (*E*/*Z*)-**45** is formed as the only product [3].

The cyclopropyl-acylsilanes **29A** + **B** are most likely formed by δ-H abstraction ((*Z*)-**7** → **e**) followed by cyclization and ketonization (**e** → **44** → **29A** + **B**; *Scheme 6*).

Comparison of the photoproducts of the n,π* excitation of the silyl ketones (*E*/*Z*)-**7** with those of the corresponding methyl ketones (*E*/*Z*)-**46** [12] *(Scheme 7)* shows only the cyclopropyl compounds **29A** + **B** and **47A** + **B** as common product types. Thus, it is noteworthy that the methyl ketones (*E*/*Z*)-**46** do not undergo photodeconjugation to **48**, whereas related methyl ketones [16] with different substitution patterns as well as the phenyl ketone corresponding to (*E*/*Z*)-**46** do show such a process [12]. On the other hand, the methyl ketones (*E*/*Z*)-**46** undergo [2 + 2] cycloaddition and photo-ene reaction furnishing compounds **49** and **50** in high yield *(Scheme 7)*, whereas an analogous photoprocess is not observed with the silyl ketones (*E*/*Z*)-**7**. This different behaviour may be explained by different reactivities of the excited states of silyl and methyl ketones.

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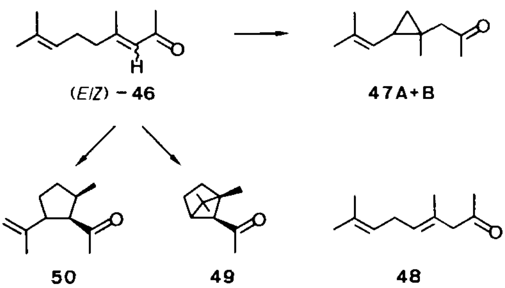
[11] Products analogous to **27A** + **B**, arising from reaction of **d** with **43** or **44**, were not detected.

Scheme 7

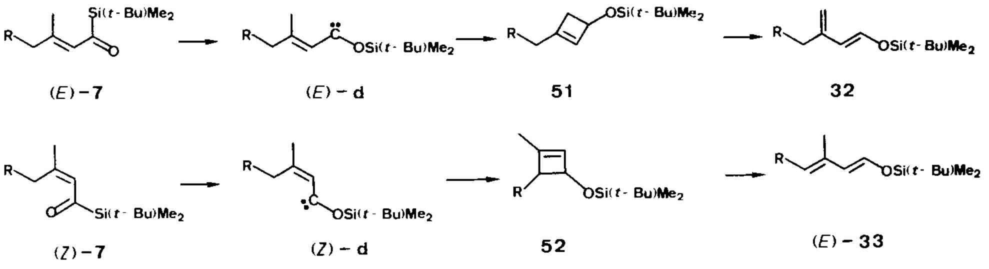


Previously, it was shown that the cyclization products **49** and **50** are formed *via* the ^{3}n,π^{*} excited state of (*E*/*Z*)-**46** [12]. On the other hand, it was disclosed that the ^{3}n,π^{*} state of acylsilanes leads to siloxycarbene formation [17].

An analogous difference is also observed between the photolysis of the acylsilane (*E*)-**8** and that of the corresponding methyl ketone **19** *(Scheme 2)* [18]. Analogously to (*E*/*Z*)-**7**, (*E*)-**8** undergoes rapid (*E*/*Z*)-isomerization as well as γ-H abstraction and siloxycarbene formation leading to the enol acetals **30A** + **B** *(Scheme 4)*. n,π^{*} Excitation of **19**, however, gives rise to the formation of several cyclized products [18].

6.2. *Thermolysis* (520°) of (*E*)- and (*Z*)-**7** selectively leads to the enol ethers **32** and (*E*)-**33**, respectively *(Scheme 5)*. This transformation presumably involves siloxycarbene formation, without preceding (*E*/*Z*)-isomerization, followed by insertion of the carbene center into the allylic C–H bond ((*E*)-**d** → **51**, (*Z*)-**d** → **52**; *Scheme 8*)[12]. Although the cyclobutenes **51** and **52** are plausible intermediates, it may not be ruled out that **32** and (*E*)-**33** are directly formed from the siloxycarbenes (*E*)- and (*Z*)-**d**. The fact that compounds **32** and (*E*)-**33** are not formed by photolysis of (*E*/*Z*)-**7** confirms our previous observation on comparison of the thermal and photochemical behaviour of the acylsilane

Scheme 8



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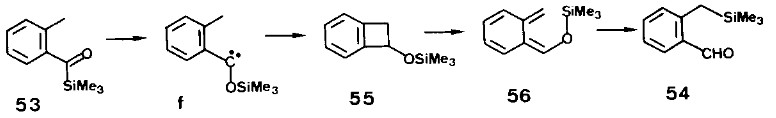
[12] A similar reaction was previously found by *Shih* and *Swenton* [19]. Thermolysis of the acylsilane **53** afforded the aldehyde **54**. The authors assumed that the siloxycarbene **f** undergoes insertion into the C–H bond leading to the benzocyclobutene **55**, which undergoes further thermal rearrangements *via* **56**.

Scheme 9

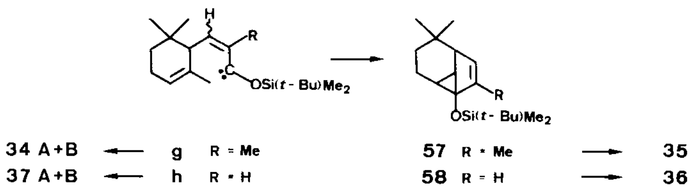


1 [13] *(Scheme 1)*. Consequently, the photochemically generated siloxycarbenes **a** as well as **d** react preferentially by intermolecular insertion into an O–H bond rather than by an intramolecular insertion into a C–H bond or by addition to a C=C bond[13]). Furthermore, it is noteworthy that, on thermolysis of (*E*)- and (*Z*)-**7**, the β,γ-unsaturated acylsilane **28** could not be detected, whereas the thermolysis of citral (*E*/*Z*)-**10**, the aldehyde related to (*E*/*Z*)-**7**, led to two β,γ-unsaturated aldehydes [20].

Thermolysis of the acylsilane (*E*)-**8** gives rise to (*E*/*Z*)-isomerization followed by carbene insertion into the C(γ)–H bond furnishing the enol ethers **34A** + **B**[14]). As additional product, the bicyclic enol ether **35** was obtained. Its formation can be explained by an intramolecular addition of the carbene center to the cyclohexene double bond (**g** → **57**)[15]). The tricyclic compound **57**, incorporating a vinylcyclopropane moiety, is assumed to be thermally unstable undergoing a [1,5]-homosigmatropic H shift [21] to **35**.

On thermolysis of (*E*)-**9**, in addition to the bicyclic enol ether **36** (formed *via* **h** → **58**), the cyclic silyl ethers **37A** + **B** were obtained. The latters are obviously formed by siloxycarbene insertion into the C–H bond of the *t*-Bu group *(Scheme 10)*[16]).

Scheme 10



7. Conclusion. – On n,π* excitation, the α,β-unsaturated silyl ketones (*E*/*Z*)-**7**, (*E*)-**8**, and (*E*)-**9** show as main processes (*E*/*Z*)-isomerization, γ-H-abstraction, and formation of siloxycarbenes. The siloxycarbenes rapidly react with the enol intermediates (arising from γ-H abstraction) leading to dimeric acetals (see **27A** + **B**, **30A** + **B**, and **31A** + **B**; *Scheme 4*). Products of *intramolecular* reactions of the *photochemically generated siloxycarbenes* were, however, not detected. On the other hand, the *thermally formed siloxycarbenes* react by insertion into C–H bonds or by addition to a C=C bond, thus showing reactivity typical of carbenes. In particular, these types of processes are also observed in vinyl carbenes [4]. As further reactions, vinyl carbenes undergo ring closure to cyclopropenes as well as insertion into adjacent olefinic C–H bonds leading to allenes [4]. Compounds of this type were, however, not detected as products of the unsaturated siloxycarbenes **d**, **g**, and **h**. On the basis of the aforementioned findings, it may be concluded that the unsaturated siloxycarbenes differ from vinyl carbenes. Furthermore, it may be suggested that the photochemically and the thermally generated siloxycarbenes are two differently reactive species.

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[13]) *Shih* and *Swenton* [19] found that the acylsilane **53** was photochemically quite stable. Therefore, they assumed that, if the carbene **f** is generated photochemically, it apparently has insufficient thermal energy to insert into the benzylic C–H bond.

[14]) In the thermolysis mixture of (*E*)-**8** (80% conversion), (*Z*)-**8** could not be detected, however, thermolysis of (*Z*)-**8** gave the same product distribution.

[15]) An intramolecular addition of a thermally generated siloxycarbene to an electron-rich double bond was previously observed on FVT of the acylsilane **1** (**a**→**5**; *Scheme 1*).

[16]) An analogous reaction was observed previously on thermolysis of pivaloyltrimethylsilane [22].

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Experimental Part

General. See [3]. ^{1}H-NMR spectra were taken in $CDCl_3$ solns. or, exceptionally (as indicated below), in C_6D_6 solns. on a *Bruker WP-80 CW* (80 MHz) or on a *Bruker WM 300* (300 MHz) instrument. *Filter A* 12. *Lamp B:* Hg medium-pressure lamp (125 W). Thermolyses were carried out in a quartz tube (30 cm × 1.7 cm), which was generally filled with quartz rings, and which was previously silylated by evaporation of bis(trimethylsilyl)-acetamide, at 0.5 Torr under N_2. For a detailed description of the thermolysis apparatus and procedure, see [11].

1. Preparations of (*E*/*Z*)-7, (*E*)-8, and (*E*)-9. – 1.1. *Acylsilanes (*E/Z*)-***7**. 1.1.1. *Thioacetalization of (*E/Z*)-***10**. To a soln. of (*E*/*Z*)-**10** (11.76 g, 77.25 mmol) in abs. CH_2Cl_2 (138 ml) and AcOH (*Fluka*, 138 ml) was added a soln. of propanedithiol (9.2 ml, 91.5 mmol) in AcOH (46 ml) and $BF_3 \cdot Et_2O$ (6.9 ml, 54.9 mmol) at 0° during 15 min. After stirring for 3 h at r.t., the mixture was worked up in CH_2Cl_2 (1000 ml) by the addition of ice and extraction with 2N aq. NaOH, 0.5N aq. $NaHCO_3$ and sat. aq. NaCl soln. Distillation (165°/0.1 Torr) afforded (*E*/*Z*)-**13** [6] (17.1 g, 91%; 3:2 mixture).

*(*E*)-2-(2',6'-Dimethyl-1',5'-heptadienyl)-1,3-dithiane* ((*E*)-**13**). B.p. 165°/0.1 Torr. UV (1.731 mg in 20 ml): 235 (1350), 244 (sh), (1260), end absorption to 330. IR: 2970*s*, 2930*s*, 2890*s*, 2850*s*, 2825*m* (sh), 1655*m*, 1440*m*, 1430*m*, 1420*m*, 1410*m*, 1380*m*, 1375*m*, 1270*s*, 1240*w*, 1170*m*, 1165*m*, 1110*w*, 1050*w*, 1040*w*, 910*m*, 860*m*. ^{1}H-NMR (300 MHz): 1.59, 1,68, 1.75 (3*d*, $J = 0.3, 1, 1.3$, CH_3–C(2'), CH_3–C(6'), 3 H–C(7')); 1.77–2.20 (*m*, 2 H–C(5), 2 H–C(3'), 2 H–C(4')); 2.75–2.86, 2.88–3.00 (2*m*, split into *dddd*, $J = 14.5, 12, 3, 2.5$, 2 H–C(4), 2 H–C(6)); 4.87 (*d*, $J = 10$, H–C(2)); 5.06 (*tm*, $J = 6$, $w_{1/2} = 5$, H–C(5')); 5.14 (*dm*, $J = 9.5$, $w_{1/2} = 4$, H–C(1')). ^{13}C-NMR: 16.8, 17.7, 25.7 (3*q*, CH_3–C(2'), CH_3–C(6'), C(7')); 25.1, 26.3, 39.3 (3*t*, C(5), C(3'), C(4')); 30.6 (*t*, C(4), C(6)); 44.4 (*d*, C(2)); 121.2, 123.6 (2*d*, C(1'), C(5')); 131.7, 140.8 (2*s*, C(2'), C(6')). MS: 242 (20, $M^{+\cdot}$, $C_{13}H_{22}S_2$), 195 (13), 173 (54), 136 (14), 135 (55), 134 (12), 125 (19), 121 (16), 119 (21), 111 (11), 106 (13), 99 (46), 98 (13), 97 (14), 93 (34), 91 (11), 85 (10), 79 (11), 73 (10), 69 (97), 67 (25), 65 (13), 55 (13), 53 (14), 45 (21), 43 (16), *41* (100). Anal. calc. for $C_{13}H_{22}S_2$ (242.44): C 64.40, H 9.15; found: C 64.45, H 9.16.

*(*Z*)-2-(2',6'-Dimethyl-1',5'-heptadienyl)-1,3-dithiane* ((*Z*)-**13**). B.p. 165°/0.1 Torr. UV (0.136 mg in 2 ml): 235 (1120), 246 (960). IR: 2950*s*, 2920*s*, 2870*s*, 2850*s*, 1655*w*, 1465*s* (sh), 1455*s*, 1420*m*, 1410*m*, 1375*s*, 1275*m*, 1240*w*, 1170*w*, 1030*w*, 910*m*, 860*m*. ^{1}H-NMR (300 MHz): 1.63, 1.70, (2*m*, $w_{1/2} = 3$) and 1.75 (*d*, $J = 1.5$, CH_3–C(2'), CH_3–C(6'), 3 H–C(7')); 1.76–1.89, 2.04–2.14 (2*m*, 2 H–C(5), 2 H–C(3'), 2 H–C(4')); 2.75–2.86, 2.88–3.00 (2*m*, split into *dddd*, $J = 15, 12, 3, 2.5$, 2 H–C(4), 2 H–C(6)); 4.87 (*d*, $J = 10$, H–C(2)); 5.16 (*dm*, overlapping with *m*, $J = 10$, H–C(1'), H–C(5')). ^{13}C-NMR (75 MHz): 17.7, 23.4, 25.7 (3*q*, CH_3–C(2'), CH_3–C(6'), C(7')); 25.0, 26.8, 32.7 (3*t*, C(5), C(3'), C(4')); 30.6 (*t*, C(4), C(6)); 44.2 (*d*, C(2)); 121.7, 123.8 (2*d*, C(1'), C(5')); 132.0, 141.2 (2*s*, C(2'), C(6')). MS: 242 (24, $M^{+\cdot}$, $C_{13}H_{22}S_2$), 195 (17), 173 (52), 136 (16), 135 (67), 134 (15), 125 (18), 121 (20), 119 (43), 111 (13), 107 (12), 106 (14), 99 (49), 98 (14), 97 (15), 93 (44), 91 (13), 85 (10), 79 (13), 77 (11), 73 (11), 69 (90), 67 (25), 65 (15), 55 (14), 53 (15), 47 (10), 45 (23), 43 (20), *41* (100). Anal. calc. for $C_{13}H_{22}S_2$ (242.44): C 64.40, H 9.15; found: C 64.38, H 9.24.

1.1.2. *Transformation of (*E/Z*)-***13** *to (*E/Z*)-***14**. To a soln. of (*E*/*Z*)-**13** (9.31 g, 38.4 mmol, 3:2 mixture) in abs. THF (220 ml) and abs. HMPT (8 ml) was added a soln. of BuLi (28.9 ml, 1.6M in hexane, 46.2 mmol) at – 78°. After stirring the mixture for 1 h at – 30°, it was again cooled to – 78°, and a soln. of (*t*-Bu)Me_2SiCl (6.97 g, 46.2 mmol) in abs. THF (42 ml) was added. The mixture was allowed to warm to r.t., stirred for 2 h, and worked up affording (*E*/*Z*)-**14** (13.44 g, 98%; 3:2 mixture).

*(*E*)-2-[(*tert*-Butyl)dimethylsilyl]-2-(2',6'-dimethyl-1,5-heptadienyl)-1,3-dithiane* ((*E*)-**14**). B.p. 150°/0.07 Torr. UV (2.300 mg in 20 ml): 257 (730). IR: 2960*s*, 2930*s*, 2900*s*, 2850*s*, 1465*m*, 1460*m*, 1455*m*, 1440*m* (br.), 1430*m*, 1420*m*, 1405*m*, 1390*m*, 1380*m*, 1370*m*, 1360*m*, 1270*m*, 1255*s*, 1245*s*, 1190*w*, 1170*w*, 1150*w*, 1105*w*, 1070*w*, 1005*w*, 930*w*, 920*m*, 890*w*, 880*w*, 870*w*. ^{1}H-NMR (300 MHz): 0.16 (*s*, 2 CH_3Si); 1.03 (*s*, 3 CH_3CSi); 1.62, 1.68 (2*m*, $w_{1/2} = 4$, CH_3–C(6'), 3 H–C(7')); 1.99 (*d*, $J = 1.2$, CH_3–C(2')); 1.94–2.03, 2.06–2.18, 2.41–2.48, 3.02–3.12 (4*m*, 2 H–C(4), 2 H–C(5), 2 H–C(6), 2 H–C(3'), 2 H–C(4')); 5.13 (*tm*, $J = 7$, $w_{1/2} = 4$, H–C(5')); 5.57 (*m*, $w_{1/2} = 5$,

H–C(1')). ^{13}C-NMR (75 MHz): – 6.8 (*q*, 2 CH_3Si), 15.2, 17.9, 26.0[17] (3*q*, *C*H_3–C(2'), *C*H_3–C(6'), C(7')); 28.4 (*q*, 3 *C*H_3CSi); 25.8, 26.0[17], 26.8, 42.7, (5*t*, C(4), C(5), C(6), C(3'), C(4')); 124.6, 128.0 (2*d*, C(1'), C(5')); 19.8 (*s*, CSi); 45.7 (*s*, C(2)); 131.5, 137.0 (*s*, C(2'), C(6')). MS: 356 (3, $M^{+\cdot}$, $C_{19}H_{36}S_2Si$), 223 (21), 193 (12), 191 (29), 149 (28), 115 (14), 106 (12), 91 (18), 74 (13), *73* (100), 69 (42), 59 (34), 44 (20), 41 (42). Anal. calc. for $C_{19}H_{36}S_2Si$ (356.71): C 63.98, H 10.17; found: C 64.17, H 10.06.

*(Z)-2-[(*tert*-Butyl)dimethylsilyl]-2-(2',6'-dimethyl-1',5'-heptadienyl)-1,3-dithiane* ((*Z*)-**14**). B.p. 150°/0.07 Torr. UV (2.247 mg in 20 ml): 257 (sh), (710). IR: 2960*s*, 2920*s*, 2900*s*, 2850*s*, 1725*w*, 1465*m*, 1455*m*, 1440*m*, 1415*m*, 1405*m*, 1385*m*, 1370*m*, 1360*m*, 1285*w*, 1270*m*, 1250*m* (sh), 1245*s*, 1190*w*, 1160*w*, 1140*w*, 1105*w*, 1070*w*, 1000*w*, 930*w*, 910*m*, 905*w*, 890*w*. ^{1}H-NMR (300 MHz): 0.18 (*s*, 2 CH_3Si); 1.00 (*s*, 3 CH_3CSi); 1.60, 1.68 (2*m*, $w_{1/2}$ = 4), 3 H–C(7'), CH_3–C(6')); 1.82 (*d*, *J* = 1.2, CH_3–C(2')); 1.90–2.03 (*m*, 2 H–C(4')); 2.03–2.13 (*m*, 2 H–C(3')); 2.42–2.49, 2.51–2.61, 3.07–3.19 (3*m*, 2 H–C(4), 2 H–C(5), 2 H–C(6)); 5.13 (*tm*, *J* = 7, $w_{1/2}$ = 4, H–C(5')); 5.60 (*m*, $w_{1/2}$ = 4, H–C(1')). ^{13}C-NMR (75 MHz; *ca.* 80% pure): – 6.4 (*q*, 2 CH_3Si); 17.8, 25.2[17] (3*q*, *C*H_3–C(2'), *C*H_3–C(6'), C(7')); 28.5 (*q*, 3 *C*H_3CSi); 25.9[17], 26.4, 30.6 (5*t*, C(4), C(5), C(6), C(3'), C(4')); 124.8, 128.5 (2*d*, C(1'), C(5')); 19.8 (*s*, CSi); 45.2 (*s*, C(2)); 131.3, 137.4 (2*s*, C(2'), C(6')). MS: 356 (2, $M^{+\cdot}$, $C_{19}H_{36}S_2Si$), 221 (12), 167 (16), 135 (10), 133 (12), 125 (11), 115 (13), 91 (11), *73* (100), 69 (49), 59 (13), 41 (39). Anal. calc. for $C_{19}H_{36}S_2Si$ (356.71): C 63.98, H 10.17; found: C 64.23, H 10.20.

1.1.3. *Dethioacetalization of (*E/Z*)-***14**. 1.1.3.1. *With* $Tl(NO_3)_3 \cdot 3\ H_2O$. To a soln. of (*E/Z*)-**14** (2.50 g, 7.01 mmol; 3:2 mixture) in THF (50 ml) and H_2O (70 drops) was added rapidly, at 0°, a soln. of $Tl(NO_3)_3 \cdot 3\ H_2O$ (3.00 g, 7.68 mmol) in MeOH (*Fluka,* 40 ml). After stirring for 5 min at r.t., the mixture was diluted with hexane, filtered through *Celite,* washed with aq. sat. NaCl, and dried ($MgSO_4$). CC (pentane/Et_2O 25:1) afforded (*E*)-**7** (608 mg, 33%), and (*Z*)-**7** (323 mg, 17%).

*(*E*)-1-[(*tert*-Butyl)dimethylsilyl]-3,7-dimethyl-2,6-octadien-1-one* ((*E*)-**7**). B.p. 118–120°/0.07 Torr. UV (0.212 mg in 20 ml): 254 (13830). UV (1.644 mg in 2 ml): 441 (145), 461 (135), 490 (60). IR: 2940*s*, 2920*s*, 2880*s*, 2850*s*, 1625*s*, 1560*s* (br.), 1460*m* (sh), 1455*m*, 1440*m*, 1410*m*, 1380*m*, 1360*m*, 1320*w*, 1245*s*, 1190*w*, 1100*w*, 1070*w*, 1000*w*, 935*w*. ^{1}H-NMR (300 MHz, C_6D_6): 0.16 (*s*, 2 CH_3Si): 0.97 (*s*, 3 CH_3CSi); 1.48, 1.63 (2*m*, $w_{1/2}$ = 4, CH_3–C(7), 3 H–C(8)); 1.94–1.96, 2.04–2.08 (2*m*, 2 H–C(4), 2 H–C(5)); 2.12 (*d*, *J* = 1, CH_3–C(3)); 5.06 (*tm*, *J* = 7.5, $w_{1/2}$ = 4, H–C(6)); 6.58 (*q*, *J* = 1, H–C(2)). ^{13}C-NMR (75 MHz, C_6D_6): – 6.9 (*q*, 2 CH_3Si); 17.8, 19.6, 25.8 (3*q*, *C*H_3–C(3), *C*H_3–C(7), C(8)); 26.8 (*q*, 3 *C*H_3CSi); 26.4, 41.1 (2*t*, C(4), C(5)); 123.8, 127.9 (2*d*, C(2), C(6)); 16.9 (*s*, CSi); 131.9, 150.9 (2*s*, C(3), C(7)); 234.7 (*s*, C(1)). MS: 266 (1, $M^{+\cdot}$, $C_{16}H_{30}OSi$), 251 (6), 209 (4), 141 (20), 127 (13), 75 (46), *73* (100), 69 (29), 59 (11), 41 (20).

*(Z)-1-[(*tert*-Butyl)dimethylsilyl]-3,7-dimethyl-2,6-octadien-1-one* ((*Z*)-**7**). B.p. 118–120°/0.07 Torr. UV (0.489 mg in 20 ml): 256 (8200). UV (1.864 mg in 2 ml): 443 (95), 461 (90), 490 (45). IR: 2945*s*, 2920*s*, 2895*s* (sh), 2880*s*, 2850*s*, 1685*w*, 1625*s*, 1565*s* (sh), 1560*s*, 1555*s* (sh), 1455*m*, 1440*m*, 1405*w*, 1385*m*, 1370*m*, 1360*m*, 1320*w*, 1290*w*, 1245*s*, 1225*m*, 1155*w*, 1150*w*, 1080*w*, 1000*w*, 935*w*. ^{1}H-NMR (300 MHz, C_6D_6): 0.15 (*s*, 2 CH_3Si); 0.96 (*s*, 3 CH_3CSi); 1.60 (*d*, *J* = 1.5, CH_3–C(3)); 1.63, 1.65 (2*m*, $w_{1/2}$ = 4, CH_3–C(7), 3 H–C(8)); 2.24 (*ddd*, $J_1 = J_2 = J_3 =$ *ca.* 8, 2 H–C(5)); 2.65 (*dd*, *J* = 8, 8, 2 H–C(4)); 5.27 (*tm*, *J* = 7.5, $w_{1/2}$ = 4, H–C(6)); 6.54 (*m*, $w_{1/2}$ = 4, H–C(2)). ^{13}C-NMR (75 MHz, C_6D_6): – 6.8 (*q*, 2 CH_3Si); 17.8, 25.4, 25.9 (3*q*, *C*H_3–C(3), *C*H_3–C(7), C(8)); 26.8 (*q*, 3 CH_3CSi); 27.7, 34.7 (2*t*, C(4), C(5)); 124.5, 128.7 (2*d*, C(2), C(6)); 17.0 (*s*, CSi); 131.8, 152.4 (2*s*, C(3), C(7)); 234.7 (*s*, C(1)). MS. 266 (1, $M^{+\cdot}$, $C_{16}H_{30}OSi$), 251 (8), 209 (4), 141 (12), 115 (17), 75 (76), *73* (100), 69 (28), 59 (11), 41 (20).

1.1.3.2. *With* $HgCl_2/HgO$. To a soln. of (*E/Z*)-**14** (2.52 g, 7.06 mmol; *ca.* 2:1 mixture) in MeOH (*Fluka,* 38 ml) $HgCl_2$ (5.03 g, 18.5 mmol) and HgO (2.23 g, 10.3 mmol) was added. The mixture was heated at reflux temp. for 30 min, filtered through *Celite*, and worked up in Et_2O. CC (hexane/Et_2O 30:1) afforded (*E/Z*)-**7** (1.06 g, 56%).

1.2. *Acylsilane (*E*)-***8**. 1.2.1. *Transformation of* **19** *to* **21**. To a soln. of I_2 (28 g, 110 mmol) in pyridine (42 ml) was added **19** (21 g, 102 mmol) at r.t. The mixture was stirred at 100° for 1 h, concentrated under reduced pressure, stirred with 2N NaOH (330 ml) at 100° overnight, cooled to 0°, acidified with 10% aq. HCl, and extracted with Et_2O. The org. phase was extracted with 2N aq. Na_2CO_3, and the aq. phase was acidified again with 10% HCl and extracted with Et_2O. After washing with 20% aq. $Na_2S_2O_3$, this org. phase was worked up affording (*E*)-2-methyl-3-(2,5,5-trimethyl-2-cyclohexenyl)acrylic acid (15.8 g, 74%). This material was dissolved in abs. Et_2O (100 ml) and added dropwise over 10 min to a suspension of $LiAlH_4$ (3.67 g, 96.6 mmol) in abs. Et_2O (450 ml). After stirring for 30 min at r.t., the mixture was worked up by adding *Celite,* sat. aq. NH_4Cl, and $MgSO_4$. Distillation (80°/0.07 Torr) afforded **21** (9.38 g, 65%).

1.2.2. *Oxidation of* **21** *to* **11**. A soln. of **11** (9.38 g, 48.4 mmol) in hexane (900 ml) was stirred with MnO_2 (61 g, 70.1 mmol) overnight under Ar. The mixture was filtered through *Celite* and evaporated under reduced pressure affording crude **11** (8.1 g, 87%).

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[17] Two signals overlapping.

1.2.3. *Transformation of* **11** *into* **15**. A soln. of 1,3-propanedithiol (5 ml, 49.8 mmol) and $BF_3 \cdot OEt_2$ (3.7 ml, 29.5 mmol) in AcOH (24 ml, *Merck*) was added dropwise to a soln. of **11** (8.1 g, 42.2 mmol) in AcOH (*Merck*, 80 ml) and abs. CH_2Cl_2 (80 ml) at 0°. The mixture was stirred for 45 min at 0° and for 3 h at r.t. After the addition of ice (150 g), it was diluted with Et_2O, washed with 2N NaOH (twice), 0.5N $NaHCO_3$ (twice), and sat. NaCl, and dried ($MgSO_4$). CC (SiO_2, hexane/Et_2O 50:1) gave **15** (8.9 g, 75%).

2-[1'-Methyl-2'-(2",6",6"-trimethyl-2"-cyclohexenyl)vinyl]-1,3-dithiane (**15**). IR: 3010*w* (sh), 2950*s*, 2890*s*, 2850*s* (sh), 1440*m*, 1425*m*, 1415*m*, 1375*m*, 1355*m*, 1270*m*, 1170*m*, 1115*w* (br.), 1070*w*, 1005*w* (br.), 960*w*, 910*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 0.83, 0.90 (2*s*, 2 CH_3–C(6")); 1.08–1.75 (*m*, 2 H–C(5), H–C(5")); 1.55 (*m*, $w_{1/2}$ = 4, CH_3–C(1')); 1.80–2.18 (*m*, 2 H–C(4"), H–C(5")); 1.88 (*s*, CH_3–C(2')); 2.45 (*d*, *J* = 11, H–C(1")); 2.75–3.05 (*m*, 2 H–C(4), 2 H–C(6)); 4.58 (*s*, H–C(2)); 5.25–5.43 (*m*, $w_{1/2}$ = 8, H–C(3")); 5.43 (*d*, *J* = 11, H–C(2')). MS: 282 (73, $M^{+\cdot}$, $C_{16}H_{26}S_2$), 226 (10), 176 (10), 175 (24), 161 (20), 159 (14), 152 (32), 151 (43), 137 (46), 125 (12), 121 (10), 120 (47), *119* (100), 111 (11), 107 (23), 106 (38), 105 (29), 91 (21), 79 (12), 77 (13), 55 (12), 53 (11), 45 (11), 41 (29).

1.2.4. *Transformation of* **15** *into* **16**. To a soln. of **15** (8.9 g, 31.6 mmol) in abs. THF (150 ml) and abs. HMPA (5.9 ml) was added under Ar at – 78° BuLi (1.6M in hexane, 24 ml, 38.4 mmol). The mixture was stirred for 1 h, a soln. of (*t*-Bu)Me_2SiCl (5.6 g, 37.2 mmol) in abs. THF (30 ml) was added dropwise, and the mixture was allowed to warm to r.t. slowly. After stirring for 1 h, the mixture was worked up with Et_2O, and CC (hexane:Et_2O 50:1) gave **16** (9.5 g, 76%).

*(E)-2-[(*tert*-Butyl)dimethylsilyl]-2-[1'-methyl-2'-(2", 6", 6"-trimethyl-2"-cyclohexenyl)vinyl]-1,3-dithiane* (**16**). M.p. 50–53°. IR: 3020*w* (sh), 2940*s*, 2920*s*, 2890*s*, 2850*s*, 2800*w* (sh), 1430*m* (sh), 1455*m*, 1415*m*, 1405*m*, 1385*m*, 1370*m*, 1355*m*, 1340*w*, 1290*w*, 1265*m*, 1250*s* (sh), 1245*s*, 1120*w* (br.), 1000*m*, 915*m*, 880*m*, 830*s*. ^{1}H-NMR (80 MHz, $CDCl_3$): 0.15 (*s*, 2 CH_3Si); 0.90, 0.95 (2*s*, 2 CH_3–C(6")); 1.06 (*s*, 3 CH_3CSi); 1.20–1.78 (*m*, 2 H–C(5), H–C(5")); 1.63 (*m*, $w_{1/2}$ = 4, CH_3–C(2")); 1.80–2.05 (*m*, 2 H–C(4"), H–C(5")); 1.98 (*s*, CH_3–C(1')); 2.25–3.18 (*m*, 2 H–C(4), 2 H–C(6), H–C(1")); 5.22–5.42 (*m*, $w_{1/2}$ = 8, H–C(3")); 5.84 (*d*, *J* = 11, H–C(2')). MS: 396 (18, $M^{+\cdot}$, $C_{22}H_{40}S_2Si$), 340 (3), 339 (4), 281 (40), 159 (18), 151 (19), 149 (42), 147 (11), 137 (17), 129 (14), 127 (11), 123 (11), 119 (19), 115 (14), 111 (11), 109 (11), 107 (14), 97 (21), 95 (18), 93 (10), 91 (13), 85 (18), 84 (12), 83 (24), 82 (12), 81 (43), *73* (100), 71 (25), 70 (15), 69 (94), 60 (25), 59 (11), 57 (44), 56 (14), 55 (40), 43 (41), 41 (46). Anal. calc. for $C_{22}H_{40}S_2Si$ (396.78): C 60.60, H 10.16, S 16.16; found: C 66.68, H 10.34, S 15.91.

1.2.5. *Dethioacetalization of* **16**. 1.2.5.1. *With* $Tl(NO_3)_3 \cdot 3\,H_2O$. To a soln. of **16** (9.5 g, 24 mmol) in THF (150 ml) and H_2O (50 drops) was added at 0° at once a soln. of $Tl(NO_3)_3 \cdot 3\,H_2O$ (12 g, 27 mmol) in abs. MeOH (*Fluka*, 180 ml). After stirring at r.t. for 5 min, the mixture was diluted with hexane, filtered through *Celite*, washed with sat. aq. NaCl, and dried ($MgSO_4$). CC (pentane/Et_2O 50:1) yielded (*E*)-**8** (3.3 g, 45%).

*(E)-1-[(*tert*-Butyl)dimethylsilyl]-2-methyl-3-(2', 6', 6'-trimethyl-2'-cyclohexenyl)-2-propen-1-one* ((*E*)-**8**). M.p. 56–57°. B.p. 60°/0.07 Torr. UV (0.134 mg in 10 ml): 244 (13960). UV (1.02 mg in 2 ml): 418 (130). IR: 3020*w*, 2950*s*, 2920*s*, 2850*s*, 1630*w* (br.), 1575*s*, 1465*m* (sh), 1375*m*, 1360*m*, 1275*m*, 1245*m*, 1225*w*, 1205*w*, 1170*m*, 1025*w*, 1005*w* (sh), 960*w*, 945*w* (br.), 895*w*, 835*m*. ^{1}H-NMR (300 MHz, C_6D_6): 0.24, 0.25 (2*s*, 2 CH_3Si); 0.83, 0.88 (2*s*, 2 CH_3–C(6')); 0.95 (*s*, 3 CH_3CSi); 1.13–1.20 (*m*, H–C(5')); 1.45–1.53 (*m*, H–C(5')); 1.50 (*m*, $w_{1/2}$ = 4, CH_3–C(2')); 1.82 (*d*, *J* = 1.5, CH_3–C(2)); 1.95–1.99 (*m*, $w_{1/2}$ = 15, 2 H–C(4')); 2.65 (*d*, *J* = 11, H–C(1')); 5.37 (*m*, $w_{1/2}$ = 8, H–C(3')); 6.43 (*dd*, *J* = 11, 1.5, H–C(3)). ^{13}C-NMR (75 MHz, C_6D_6): – 3.9, – 3.5 (2*q*, 2 CH_3Si); 10.8 (*q*, *C*H_3–C(2)); 23.0 (*q*, *C*H_3–C(2')); 27.1 (*q*, 3 *C*H_3CSi, *C*H_3–C(6')); 27.6 (*q*, CH_3–C(6')); 23.4 (*t*, C(5')); 32.2 (*t*, C(4')); 50.7 (*d*, C(1')); 122.0 (*d*, C(3')); 150.0 (*d*, C(3)); 17.2 (*s*, CSi); 33.0 (*s*, C(6')); 133.8 (*s*, C(2')); 146.0 (*s*, C(2)); 233.3 (*s*, C(1)). MS: 306 (1, $M^{+\cdot}$, $C_{19}H_{34}OSi$), 250 (13), 183 (46), 179 (19), *127* (100), 119 (13), 107 (10), 105 (10), 91 (22), 75 (25), 73 (94), 59 (12). Anal. calc. for $C_{19}H_{34}OSi$ (306.38): C 74.44, H 11.18; found: C 74.47, H 11.30.

1.2.5.2. *With* $HgCl_2/HgO$. To a soln. of **16** (191 mg, 0.48 mmol) in MeOH (3.5 mol) was added $HgCl_2$ (452 mg, 1.66 mmol) and HgO (201 mg, 0.93 mmol). The mixture was heated under reflux for 30 min, filtered through *Celite*, and worked up in Et_2O. CC (hexane/Et_2O 10:1) afforded (*E*)-**8** (137 mg, 93%).

1.3. *Acylsilane (E)*-**9**. 1.3.1. *Transformation of* **20** *into* **17**. The reaction sequences analogous to those described in *Sect. 1.2.1* to *1.2.3* gave **17**.

(E)-2-[2'-(2",6",6"-Trimethyl-2"-cyclohexenyl)vinyl]-1,3-dithiane (**17**). B.p. 150°/0.05 Torr. IR: 3030*m*, 2950*s*, 2900*s*, 2850*s*, 2810*w* (sh), 1465*m*, 1445*m*, 1430*m*, 1420*s*, 1415*m*, 1385*m*, 1375*m*, 1365*m*, 1345*w*, 1300*w*, 1275*s*, 1240*w*, 1175*m* (sh), 1170*m*, 1135*w*, 1130*w*, 1075*w*, 975*m*, 965*m*, 960*m* (sh), 930*w* (br.), 910*m*, 880*w*, 865*w*. ^{1}H-NMR (100 MHz, CCl_4): 0.83, 0.88 (2*s*, 2 CH_3–C(6")); 1.00–1.52 (*m*, 2 H–C(5), H–C(5")); 1.58 (*m*, $w_{1/2}$ = 4, CH_3–C(2")); 1.84–2.16 (*m*, 2 H–C(4"), H–C(5"), H–C(1")); 2.68–2.88 (*m*, 2 H–C(4), 2 H–C(6)); 4.50 (*d*, *J* = 7, H–C(2)); 5.35 (*m*, $w_{1/2}$ = 8, H–C(3")); 5.51 (*AB*, *J* = 16, δ_A = 5.40, δ_B = 5.62, split into *d*, *J* = 8, H–C(1'), H–C(2')). MS: *268* (100, $M^{+\cdot}$, $C_{15}H_{24}S_2$), 212 (8), 197 (9), 161 (19), 147 (11), 145 (17), 138 (21), 137 (17), 132 (11), 123 (33), 119 (19), 107 (14), 106 (33), 105 (25), 91 (22), 79 (14), 77 (14), 41 (23). Anal. calc. for $C_{15}H_{24}S_2$ (268.49): C 67.10, H 9.00, S 23.89; found: C 66.96, H 8.74, S 24.16.

1.3.2. *Transformation of* **17** *into* **18**. The reaction of a soln. of **10** (7.0 g, 26.1 mmol) in abs. THF (150 ml) and HMPA (4.7 ml) with BuLi (1.6M in hexane; 19 ml, 30.4 mmol) and (*t*-Bu)Me_2SiCl (4.43 g, 29.4 mmol) in abs. THF (20 ml) as described in *Sect. 1.2.4* yielded **18** (7.34 g, 73%).

*(*E*)-2-[(*tert*-Butyl)dimethylsilyl]-2-[2'-(2",6",6"-trimethyl-2"-cyclohexenyl)vinyl]-1,3-dithiane* (**18**). B.p. 180°/0.05 Torr. IR: 3010*w*, 2960*s*, 2930*s*, 2850*s*, 1465*m*, 1460*m*, 1445*m*, 1430*m*, 1420*m*, 1410*m*, 1390*m*, 1380*m*, 1375*w*, 1345*w*, 1270*m*, 1255*m*, 1245*s*, 1180*w*, 1140*w*, 1075*w*, 1045*w*, 1025*w*, 1005*w*, 980*m*, 940*w* (sh), 930*w*, 920*m*, 890*w*, 865*w*, 830*s*. ^1H-NMR (100 MHz, CCl_4): 0.09 (*s*, 2 CH_3Si); 0.92, 0.94 (2*s*, 2 CH_3–C(6")); 1.02 (*s*, 3 CH_3CSi); 1.12–1.60 (*m*, 2 H–C(5), H–C(5")); 1.66 (*m*, $w_{1/2}$ = 4, CH_3–C(2")); 1.86–2.44 (6 H), 2.74–3.12 (2 H) (2*m*, 2 H–C(4), 2 H–C(6), 2 H–C(4"), H–C(1"), H–C(5")); 5.37 (*m*, $w_{1/2}$ = 8, H–C(3")); 5.57 (*AB*, *J* = 15, δ_A = 5.52, δ_B = 5.62, split into *d*, *J* = 7, H–C(2'), H–C(1')). MS: 382 (24, $M^{+\cdot}$, $C_{21}H_{38}S_2Si$), 267 (38), 259 (48), 235 (28), 211 (17), 179 (14), 161 (12), 145 (69), 137 (17), 119 (14), 115 (19), 113 (48), 105 (22), 91 (28), *73* (100), 59 (22), 41 (20). Anal. calc. for $C_{21}H_{38}S_2Si$ (382.75): C 65.90, H 10.01, S 16.75; found: C 66.01, H 10.02, S 16.60.

1.3.3. *Transformation of* **18** *into* (E)-**9**. The reaction of **18** (7.34 g, 19.2 mmol) in THF (120 ml) with $Tl(NO_3)_3 \cdot 3\ H_2O$ (9.65 g, 21.7 mmol) in MeOH (150 ml) as described in *Sect. 1.2.5* gave (*E*)-**9** (5.0 g, 67%).

*(*E*)-1-[(*tert*-Butyl)dimethylsilyl]-3-(2',6',6'-trimethyl-2'-cyclohexenyl)-2-propen-1-one* ((*E*)-**9**). B.p. 55°/0.07 Torr. UV: (0.18 mg in 10 ml) 225 (12990), (1.195 mg in 2 ml) 412 (120). IR: 3020*w*, 2950*s*, 2920*s*, 2880*m* (sh), 2850*s*, 1635*m*, 1620*m* (sh), 1580*s*, 1555*m* (sh), 1465*m* (sh), 1455*m*, 1430*w*, 1380*w*, 1360*m*, 1285*w* (br.), 1245*s*, 1185*w*, 1155*m*, 980*m*, 935*w*. ^1H-NMR (300 MHz, C_6D_6): 0.19 (*s*, 2 CH_3Si); 0.81, 0.83 (2*s*, 2 CH_3–C(6')); 0.96 (*s*, 3 CH_3CSi); 1.00–1.10, 1.30–1.42 (2*m*, 2 H–C(5')); 1.52 (*m*, $w_{1/2}$ = 5, CH_3–C(2')); 1.89 (*m*, $w_{1/2}$ = 15, 2 H–C(4')); 2.08 (*d*, *J* = 9.5, H–C(1')); 5.36 (*m*, $w_{1/2}$ = 8, H–C(3')); 6.40 (*d*, *J* = 15.5, H–C(2)); 6.60 (*dd*, *J* = 15.5, 9.5, H–C(3)). ^{13}C-NMR (75 MHz, C_6D_6): – 5.64, – 5.58 (2*q*, 2 CH_3Si); 23.0 (*q*, CH_3–C(2')); 26.9 (*q*, 3 CH_3Si, CH_3–C(6')); 27.9 (*q*, CH_3–C(6')); 23.4 (*t*, C(5')); 31.8 (*t*, C(4')); 54.7 (*d*, C(1')); 122.6 (*d*, C(3')); 138.4 (*d*, C(2)); 147.0 (*d*, C(3)); 17.0 (*s*, CSi); 32.6 (*s*, C(6')); 132.5 (*s*, C(2')); 233.2 (*s*, C(1)). MS: 292 (1, $M^{+\cdot}$, $C_{18}H_{32}OSi$), 250 (10), 183 (32), 179 (13), 128 (11), 127 (93), 119 (11), 91 (15), 75 (28), *73* (100), 59 (12). Anal. calc. for $C_{18}H_{32}OSi$ (292.54): C 73.90, H 11.03; found: C 73.88, H 11.08.

2. Photolyses. – 2.1. *Photolyses of* (E/Z)-**7**. 2.1.1. *Irradiation* (λ > 347 nm; lamp *B*, filter *A*, 100% conversion) of (*E*)-**7** (543 mg, 2.04 mmol) in abs. MeCN (200 ml) followed by CC (hexane/Et_2O 25:1 and 0.1% of Et_3N) of the mixture gave: **27A + B** (*ca.* 1:1; 120 mg, 22%), **28** (67 mg, 12%). **29A + B** (*ca.* 1:1; 74 mg, 10%), and (*E*/*Z*)-**10** (52 mg, 17%).

2.1.2. *Irradiation* of a soln. of (*Z*)-**7** (200 mg, 0.75 mmol) in abs. MeCN (200 ml) as described above (conversion 83%) gave after CC (hexane/Et_2O 40:1 and 0.1% of Et_3N): **27A + B** (*ca.* 1:1; 40 mg, 24%), **28** (33 mg, 19%), **29A + B** (*ca.* 1:1; 23 mg, 14%), and (*E*/*Z*)-**10** (15 mg, 16%).

*(5*E/Z*,7*E/Z*,11*E/Z*)-8-[(*tert*-Butyl)dimethylsilyl]-10-[(*tert*-butyl)dimethylsilyloxy]-2,6,12,16-tetramethyl-9-oxaheptadeca-2,5,7,11,15-pentaene* (**27A + B**). B.p. 132°/0.06 Torr. UV (0.406 mg in 20 ml): 233 (sh) (7600). IR: 3020*w* (sh), 2950*s*, 2930*s*, 2890*s*, 2880*s*, 2850*s*, 2730*w*, 2720*w*, 1665*w*, 1610*w*, 1585*w*, 1470*m*, 1460*m*, 1445*m*, 1410*w*, 1390*w*, 1375*m*, 1360*w*, 1250*s*, 1155*w*, 1140*m* (br.), 1105 *m*, 1095*m*, 1065*m* (sh), 1040*m*, 1025*m*, 1005*m*, 965*m* (br.), 940*m*, 870*w* (sh). ^1H-NMR (300 MHz): 0.006, 0.01, 0.052, 0.057, 0.06, 0.071, 0.074, 0.078 (8*s*, CH_3Si); 0.86, 0.87, 0.88, 0.91 (4*s*, 3 CH_3CSi); 1.52, 1.60, 1.63, 1.67, 1.68, 1.69, 1.71, 1.72, 1.76, 1.77 (10*s*, 3 H–C(1), CH_3–C(2), CH_3–C(6), CH_3–C(12), CH_3–C(16), 3 H–C(17)); 1.95–2.20 (*m*, 2 H–C(13), 2 H–C(14)); 2.70 (*tm*, *J* = 6.5, $w_{1/2}$ = 4, 2 H–C(4)); 5.05–5.25 (*m*, H–C(3), H–C(5), H–C(15)); 5.35, 5.38 (2*dm*, overlapping, *J* = 7, $w_{1/2}$ = 4, H–C(11)); 5.77, 5.80 (2*d*, overlapping, *J* = 7, H–C(10)); 6.18 (*m*, $w_{1/2}$ = 5, H–C(7)). ^{13}C-NMR (75 MHz): – 4.0, – 3.3 (2*q*, CH_3Si); 17.0, 17.7, 17.8, 23.1, 25.8, 26.6, 27.0 (7*q*, C(1), CH_3–C(2), CH_3–C(6), CH_3–C(12), CH_3–C(16), C(17)); 25.9, 27.6 (2*q*, 3 CH_3CSi); 26.2, 32.6, 39.3 (3*t*, C(4), C(13), C(14)); 93.4, 93.9 (2*d*, C(10)); 124.0, 124.1, 124.2, 126.4, 126.6, 126.9 (6*d*, C(3), C(5), C(7), C(11), C(15)); 17.4, 18.1 (2*s*, CSi); 131.4, 131.8, 138.0 (3*s*, C(2), C(6), C(12), C(16)); 158.2, 158.3 (2*s*, C(8)). MS: 532 (< 1, $M^{+\cdot}$, $C_{32}H_{60}O_2Si_2$), 517 (< 1), 475 (< 1), 401 (< 1), 343 (1), 268 (13), 267 (57), 173 (36), 135 (32), 115 (11), 107 (17), 93 (14), 75 (34), *73* (100), 69 (50), 59 (15), 41 (28).

*(*E*)-1-[(*tert*-Butyl)dimethylsilyl]-3,7-dimethyl-3,6-octadien-1-one* (**28**). B.p. 100°/0.08 Torr. UV (2.118 mg in 2 ml): 346 (80), 361 (115), 374 (150), 388 (150). IR: 3020*w*, 2950*s*, 2920*s*, 2880*s*, 2850*s*, 1715*w*, 1640*m*, 1625*s*, 1465*m*, 1460*m*, 1440*m* (sh), 1390*m* (sh), 1380*m*, 1375*m*, 1360*m*, 1295*w*, 1270*w*, 1245*s*, 1180*w* (br.), 1000*w*, 935*w*. ^1H-NMR: 0.2 (*s*, 2 CH_3Si); 0.96 (*s*, 3 CH_3CSi); 1.61, 1.65, 1.71 (3*m*, $w_{1/2}$ = 3, CH_3–C(3), CH_3–C(7), 3 H–C(8)); 2.74 (*tm*, *J* = 6.5, $w_{1/2}$ = 4, 2 H–C(5)); 3.27 (*s*, 2 H–C(2)); 5.00–5.30 (*m*, H–C(6), H–C(4)). ^{13}C-NMR: – 6.5 (*q*, 2 CH_3Si); 16.8, 17.7, 25.6 (3*q*, CH_3–C(3), CH_3–C(7), C(8)); 26.4 (*q*, 3 CH_3CSi); 27.2 (*t*, C(5)); 60.5 (*t*, C(2)); 122.6, 128.7 (2*d*, C(4), C(6)); 16.6 (*s*, CSi); 127.8, 131.7 (2*s*, C(3), C(7)); *ca.* 240 (*s*, C(1)). MS: 266 (< 1, $M^{+\cdot}$, $C_{16}H_{30}OSi$), 251 (1), 238 (1), 209 (1), 143 (8), 115 (52), 75 (10), *73* (100), 59 (8), 41 (7).

*(*tert*-Butyl)dimethylsilyl [1-Methyl-2-(2'-methyl-1'-propenyl)cyclopropyl]methyl Ketone, Isomer A* (**29A**). UV (1.479 mg in 2 ml): 349 (sh) (60), 364 (100), 378 (140), 395 (115). IR: 3060*w*, 3010*m* (sh), 2950*s*, 2930*s*, 2880*s*, 2860*s*, 2740*w*, 2730*w*, 2720*w*, 1710*w*, 1690*w*, 1645*s*, 1470*s*, 1460*s*, 1445*s*, 1400*m* (sh), 1390*m*, 1375*s*, 1360*m*, 1335*m*, 1325*m* (sh), 1275*w*, 1255*s* (sh), 1250*s*, 1170*w*, 1145*w*, 1075*w*, 1030*m*, 1005*m*, 985*w*, 940*m*. ^{1}H-NMR (80 MHz): 0.10–0.40, 0.70–0.90 (2*m*, 2 H–C(3)); 0.20 (*s*, 2 CH_3Si); 0.96 (*s*, 3 CH_3CSi); 1.05–1.40 (*m*, H–C(2)); 1.14 (*s*, CH_3–C(1)); 1.70, 1.73 (2*m*, $w_{1/2} = 3$, CH_3–C(2'), 3 H–C(3')); 2.61 (*AB*, $J = 18$, $\delta_A = 2.49$, $\delta_B = 2.74$, CH_2CO); 4.69 (*dm*, $J = 7$, $w_{1/2} = 4$, H–C(1')). ^{13}C-NMR (75 MHz): – 6.9, – 6.8 (2*q*, 2 CH_3Si); 18.4, 25.3, 25.8 (3*q*, CH_3–C(1), CH_3–C(2'), C(3')); 26.5 (*q*, 3 CH_3CSi); 21.8 (*t*, C(3)); 55.2 (*t*, CH_2CO); 22.8 (*d*, C(2)); 124.4 (*d*, C(1')); 16.7, 18.8 (2*s*, CSi, C(1)); 133.9 (*s*, C(2')); 246.8 (*s*, CO). MS: 266 (< 1, $M^{+\cdot}$, $C_{16}H_{30}OSi$), 251 (1), 225 (< 1), 209 (1), 143 (3), 115 (36), 75 (10), *73* (100), 41 (7).

Isomer B (**29B**). UV (2.174 mg in 2 ml): 350 (sh) (60), 366 (100), 381 (140), 398 (128). IR: 3060*w*, 3010*w* (sh), 2960*s*, 2930*s*, 2900*s*, 2880*s*, 2860*s*, 2740*w*, 2730*w*, 2720*w*, 1700*w* (br.), 1640*s*, 1470*m*, 1460*s*, 1445*m*, 1410*w*, 1390*m*, 1380*m*, 1365*m*, 1335*w*, 1320*w*, 1300*w* (sh), 1255*m* (sh), 1250*s*, 1170*w*, 1140*w*, 1080*w*, 1035*w*, 1025*w*, 1010*w*, 990*w*, 940*m*. ^{1}H-NMR (300 MHz): 0.16 (*s*, 2 CH_3Si); 0.28 (*dd*, $J_1 = J_2 = 5.2$) and 0.70 (*dd*, $J = 8.6, 4.8$, 2 H–C(3)); 0.92 (*s*, 3 CH_3CSi); 1.02 (*s*, CH_3–C(1)); 1.16–1.50 (*m*, H–C(2)); 1.71 (*s*, CH_3–C(2'), 3 H–C(3')); 2.58 (*AB*, $J = 17$, $\delta_A = 2.52$, $\delta_B = 2.64$, CH_2CO); 4.85 (*dm*, $J = 8.1$, $w_{1/2} = 4$, H–C(1')). ^{13}C-NMR (75 MHz): – 6.9 (*q*, 2 CH_3Si); 18.4, 19.2, 25.9 (3*q*, CH_3–C(1), CH_3–C(2'), C(3')); 26.6 (*q*, 3 CH_3CSi); 21.1 (*t*, C(3)); 60.9 (*t*, CH_2CO); 22.3 (*d*, C(2)); 123.9 (*d*, C(1')); 16.8, 18.0 (2*s*, CSi, C(1)); 133.3 (*s*, C(2')); 247.2 (*s*, CO). MS: 266 (< 1, $M^{+\cdot}$, $C_{16}H_{30}OSi$), 251 (< 1), 209 (< 1), 143 (4), 115 (45), 75 (6), *73* (100), 59 (8), 41 (7).

2.1.3. *Photolysis of (*E/Z*)-**7** in the Presence of (*t*-Bu)Me_2SiOH.* A soln. of (*E*/*Z*)-**7** (*ca.* 2:1; 326 mg, 1.22 mmol) and (*t*-Bu)Me_2SiOH (262 mg, 1.98 mmol) in abs. MeCN (100 ml) was irradiated as described above (95% conversion). CC (hexane/Et_2O 50:1) afforded: (*E*/*Z*)-**45** (110 mg, 24%), **28** (40 mg, 13%), **29A** + **B** (*ca.* 1:1; 25 mg, 8%), and (*E*/*Z*)-**10** (43 mg, 24%).

*(*E/Z*)-3,7-Dimethyl-2,6-octadien-1-al-bis[(*tert*-butyl)dimethylsilyl]-acetal* ((*E*/*Z*)-**45**). IR: 2950*s*, 2930*s*, 2890*s*, 2850*s*, 2740*w*, 2710*w*, 1665*w*, 1640*w*, 1470*m*, 1460*s*, 1440*m*, 1405*w*, 1390*m*, 1380*m*, 1360*m*, 1250*s*, 1215*w*, 1185*w*, 1150*m* (sh), 1130*s*, 1105*m*, 1070*s*, 1025*s* (br.), 1000*s*, 940*m*, 890*m*. ^{1}H-NMR (80 MHz): 0.13 (*s*, 2 CH_3Si); 0.91 (*s*, 3 CH_3CSi); 1.65, 1.73 (2*m*, $w_{1/2} = 4$, CH_3–C(3), CH_3–C(7), 3 H–C(8)); 1.95–2.25 (*m*, 2 H–C(4), 2 H–C(5)); 4.95–5.45 (*m*, H–C(2), H–C(6)); 5.75, 5.78 (2*d*, $J = 7$, H–C(1)). MS: 341 (8, $M^{+\cdot} - C_4H_9$), 267 (6), 263 (7), 247 (10), 221 (13), 182 (18), *181* (100), 147 (20), 135 (23), 125 (26), 121 (25), 113 (26), 107 (21), 99 (10), 97 (13), 93 (11), 75 (17), 74 (14), 73 (98), 69 (32), 59 (38), 41 (23).

2.2. *Photolyses of (*E*)-**8**.* 2.2.1. *In THF.* A soln. of (*E*)-**8** (522 mg, 1.7 mmol) in abs. THF (140 ml) was irradiated ($\lambda > 347$ nm, lamp *B*, filter *A*, *ca.* 100% conversion) under Ar. Evaporation of the solvent and CC (SiO_2, hexane/Et_2O gradient, O→2.5% Et_2O) of the residue gave (*Z*)-**8** (115 mg, 22%), **30A** (30 mg, 6%), and **30B** (23 mg, 4%).

2.2.2. *In MeCN.* A soln. of (*E*)-**8** (460 mg, 1.5 mmol) in abs. MeCN (130 ml) was irradiated as described in *Sect. 2.1.1* (98% conversion). CC of the mixture afforded (*Z*)-**8** (97 mg, 21%), **30A** (20 mg, 4%), and **30B** (3%).

*(*Z*)-1-[(*tert*-Butyl)dimethylsilyl]-2-methyl-3-(2',6',6'-trimethyl-2'-cyclohexenyl)-2-propen-1-one* ((*Z*)-**8**). UV (0.132 mg in 10 ml): 263 (5100). UV (1.243 mg in 2 ml): 402 (130), 418 (130). IR: 3020*w* (sh), 2950*s*, 2920*s*, 2850*s*, 1625*m*, 1595*m*, 1460*m* (sh), 1455*s*, 1445*s*, 1430*s*, 1405*w*, 1380*m*, 1370*m*, 1360*m*, 1300*w*, 1245*s*, 1195*w*, 1185*w*, 1130*w*, 1080*w*, 1035*w* (br.), 1000*w* (sh), 980*m*, 935*w*, 900*w* (sh), 870*w*, 830*s*. ^{1}H-NMR (80 MHz, C_6D_6): 0.25 (*s*, 2 CH_3Si); 1.04 (3 H), 1.08 (12 H) (2*s*, 3 CH_3CSi, 2 CH_3–C(6')); 1.15–1.72 (*m*, 2 H–C(5')); 1.81 (*d*, $J = 1.5$, CH_3–C(2)); 1.90 (*m*, $w_{1/2} = 4$, CH_3–C(2')); 2.25 (*m*, $w_{1/2} = 16$, 2 H–C(4')); 2.90 (*d*, $J = 11$, H–C(1')); 5.15 (*dm*, $J = 11$, $w_{1/2} = 4$, H–C(3)); 5.44 (*m*, $w_{1/2} = 6$, H–C(3')). MS: 306 (21, $M^{+\cdot}$, $C_{19}H_{34}OSi$), 291 (27), 235 (18), 193 (16), 179 (41), 175 (33), 173 (16), 159 (38), 127 (11), 119 (31), 115 (12), 105 (12), 91 (19), 75 (90), 74 (15), *73* (100), 59 (19), 41 (14).

*5-[(*tert*-Butyl)dimethylsilyl]-3-[(*tert*-butyl)dimethylsilyloxy]-2,6-dimethyl-1-(2',6',6'-trimethyl-2'-cyclohexenyl)-7-(2",6",6"-trimethyl-2"-cyclohexenyliden)-4-oxa-1,5-heptadiene, Isomer A* (**30A**). UV (0.134 mg in 10 ml): 205 (31 650), 245 (14 680). IR: 3020*w*, 2950*s*, 2920*s*, 2850*s*, 1465*m* (sh), 1455*m*, 1380*m*, 1370*m*, 1355*m*, 1325*m*, 1245*s*, 1220*w* (br.), 1170*w*, 1100*m*, 1075*m*, 1030*m* (sh), 1020*s*, 1000*m* (sh), 965*m*, 935*w*, 890*s*, 870*m*, 830*s*. ^{1}H-NMR (300 MHz, C_6D_6): 0.20, 0.23, 0.39, 0.50 (4*s*, 4 CH_3Si); 0.97, 1.00 (2*s*, 2 CH_3–C(6')); 1.05, 1.18 (2*s*, 6 CH_3CSi); 1.10–1.26, 1.47–1.60 (2*m*, 2 H–C(5'), 2 H–C(5")); 1.34, 1.43 (2*s*, 2 CH_3–C(6")); 1.95, 1.97 (2*d*, $J \approx 1$, CH_3–C(2), CH_3–C(6)); 2.03–2.16 (*m*, 2 H–C(4'), 2 H–C(4")); 2.06 (*m*, $w_{1/2} = 5$, CH_3–C(2")); 2.49 (*d*, $J = 9$, H–C(1')); 5.20 (*d*, $J = 9$, H–C(1)); 5.35 (*m*, $w_{1/2} = 9$, H–C(3')); 5.70 (*m*, $w_{1/2} = 9$, H–C(3")); 5.96 (*s*, H–C(3)); 6.07 (*s*, H–C(7)). ^{13}C-NMR (75 MHz, C_6D_6): –3.7, –3.3, –2.8, –2.6 (4*q*, 4 CH_3Si); 11.6 (*q*, CH_3–C(2)); 21.9, 22.9, 23.8, 27.3, 27.4, 29.2, 29.5 (7*q*, CH_3–C(2'), 2 CH_3–C(6'), CH_3–C(2"), 2 CH_3–(6")); 26.6, 27.9 (2*q*, 2 (3 CH_3CSi)); 24.1 (2*t*, overlapping, C(5'), C(5")); 31.7 (*t*, C(4')); 40.1 (*t*, C(4")); 49.2 (*d*, C(1')); 101.2 (*d*, C(3)); 121.1 (*d*, C(3')); 125.3 (*d*, C(3")); 128.0, 129.5 (2*d*, C(1), C(7)); 18.9, 19.7 (2*s*, 2 CSi); 32.9, 35.7 (2*s*, C(6'), C(6")); 133.4, 135.9, 137.0, 137.6, 143.3 (5*s*, 1 *s* is hidden or overlapped by *d* at 121.1, 125.3 or 128.0, C(2), C(5), C(6), C(2′), C(1″), C(2″)). MS: 612 (1, $M^{+\cdot}$, $C_{38}H_{68}O_2Si_2$), 535 (1), 481 (3), 309 (15), 308 (57), *307* (100), 251 (22), 186 (11), 185 (70), 175 (47), 147 (11), 119 (28), 115 (18), 105 (18), 75 (41), 74 (27), 73 (99), 69 (11), 59 (20). Anal. calc. for $C_{38}H_{68}O_2Si_2$ (613.14): C 74.44, H 11.18; found: C 74.36, H 11.24.

Isomer B (**30B**), 80% pure. UV (0.122 mg in 10 ml): 206 (24100), 244 (13600). IR: 3010*w*, 2950*s*, 2920*s*, 2850*s*, 1465*m* (sh), 1455*m*, 1445*m* (sh), 1435*m* (sh), 1380*m*, 1355*m*, 1325*m*, 1245*s*, 1220*w*, 1170*w*, 1100*m*, 1075*m*, 1015*s*, 1000*m*, 970*s*, 935*w*, 890*m*, 865*m*, 830*s*. ^{1}H-NMR (300 MHz, C_6D_6): 0.19, 0.22, 0.41, 0.49 (4*s*, 4 CH_3Si); 0.99, 1.00 (2*s*, 2 CH_3–C(6′)); 1.05, 1.18 (2*s*, 6 CH_3CSi); 1.24–1.28, 1.52–1.59 (2*m*, 2 H–C(5′), 2 H–C(5″)); 1.43 (*s*, 2 CH_3–C(6″)); 1.73 (*m*, $w_{1/2} \approx 3$, CH_3–C(2′)); 1.96, 1.98 (2*d*, $J \approx 1$, CH_3–C(2), CH_3–C(6)); 2.02–2.15 (*m*, 2 H–C(4′), 2 H–C(4″)); 2.07 (*m*, $w_{1/2} = 6$, CH_3–C(2″)); 2.57 (*d*, $J = 11$, H–C(1′)); 5.30 (*dm*, $J = 11$, $w_{1/2} \approx 4$, H–C(1)); 5.42 (*m*, $w_{1/2} = 9$, H–C(3′)); 5.71 (*m*, $w_{1/2} = 9$, H–C(3″)); 5.84 (*s*, H–C(3)); 6.15 (*s*, H–C(7)). ^{13}C-NMR (75 MHz, C_6D_6): –4.0, –3.8, –2.9, –2.6 (4*q*, 4 CH_3Si); 11.3 (*q*, CH_3–C(2)); 21.7, 22.6, 27.0, 27.3, 27.4, 28.6 (6*q*, 1*q* presumably overlapping with *s* at 27.6, CH_3–C(6), CH_3–C(2′), 2 CH_3–C(6′), CH_3–C(2″), 2 CH_3–C(6″)); 26.2, 27.6 (2*q*, 6 CH_3CSi); 23.6 (2*t*, overlapping, C(5′), C(5″)); 33.3 (*t*, C(4′)); 39.6 (*t*, C(4″)); 48.8 (*d*, C(1′)); 101.1 (*d*, C(3)); 120.8 (*d*, C(3′)); 125.6, 127.0, 129.3 (3*d*, C(1), C(7), C(3″)); 18.5, 19.4 (2*s*, 2 CSi); 33.2, 35.3 (2*s*, C(6′), C(6″)); 121.1, 129.2, 133.3, 135.4, 138.0, 142.7 (6*s*, C(2), C(5), C(6), C(2′), C(1″), C(2″)). MS: 612 (< 1, $M^{+\cdot}$, $C_{38}H_{68}O_2Si_2$), 555 (1), 481 (> 1), 309 (20), 308 (73), 307 (98), 305 (10), 251 (31), 249 (17), 186 (14), 185 (83), 175 (52), 159 (10), 147 (14), 127 (14), 119 (29), 115 (19), 105 (19), 75 (48), 74 (26), *73* (100), 69 (14), 59 (21). Anal. calc. for $C_{38}H_{68}O_2Si_2$ (613.14): C 74.44, H 11.18; found: C 74.50, H 11.36.

2.3. *Photolyses of* (*E*)-**9**. 2.3.1. *In THF.* A soln. of (*E*)-**9** (720 mg, 2.47 mmol) in abs. THF (150 ml) was irradiated ($\lambda > 347$ nm, lamp *B*, filter *A*, *ca.* 100% conversion) under Ar for 3 h. CC (SiO_2; hexane/Et_2O 100:1) gave a mixture of dimers **31A + B** (199 mg, 28%) and intractable material.

2.3.2. *In MeCN.* A soln. of (*E*)-**9** (1.045 g, 3.58 mmol) in abs. MeCN (170 ml) was irradiated as described above for 2.5 h (92% conversion). CC gave a mixture of dimers **31A + B** (260 mg, 27%), and intractable material. Further purification of **31A + B** by CC led to decomposition.

3. Thermolyses. – 3.1. *Thermolyses of* (E)- *and* (Z)-**7**. 3.1.1. *Thermolysis of* (E)-**7**. a) *FVT* (520°) of (*E*)-**7** (187 mg, 0.702 mmol) in a silylated quartz tube without packing (100% conversion) afforded **32** (79 mg, 42%). b) *FVT* (350°) of (*E*)-**7** (180 mg, 0.675 mmol) afforded **32** (44 mg, 32%) and (*E*/*Z*)-**7** (*ca.* 5:1; 44 mg; 76% conversion).

(E)-*1-[(*tert*-Butyl)dimethylsilyloxy]-7-methyl-3-methyliden-1,6-octadiene* (**32**). B.p. 100°/0.07 Torr. UV (0.158 mg in 20 ml): 240 (20300). IR: 3070*w*, 3030*w*, 2950*s*, 2920*s*, 2890*s*, 2850*s*, 1750*w*, 1635*s*, 1600*m*, 1465*m* (sh), 1460*m*, 1445*m*, 1415*w*, 1385*w*, 1370*m*, 1360*m*, 1330*w*, 1250*s*, 1185*s*, 1165*s* (br.), 1100*w*, 1000*w*, 920*s*, 895*m*, 870*s*. ^{1}H-NMR (300 MHz, C_6D_6): 0.07 (*s*, 2 CH_3Si); 0.93 (*s*, 3 CH_3CSi); 1.54, 1.65 (2*m*, $w_{1/2} = 4$, CH_3–C(7), 3 H–C(8)); 2.21–2.34 (*m*, 2 H–C(4), 2 H–C(5)); 4.81, 4.91 (2*d*, $J_1 = 1.3, 0.9$, CH_2=C(3)); 5.23 (*m*, $w_{1/2} = 9$, H–C(6)); 6.45 (*AB*, $J = 12$, $\delta_A = 6.13$, $\delta_B = 6.77$, H–C(1), H–C(2)). ^{13}C-NMR (75 MHz, C_6D_6): –5.1 (*q*, 2 CH_3Si); 17.8, 25.9 (2*q*, CH_3–C(7), C(8)); 25.8 (*q*, 3 CH_3CSi); 27.6, 33.5 (2*t*, C(5), C(4)); 111.0 (*t*, CH_2=C(3)); 116.1 (*d*, C(2)); 124.8 (*d*, C(6)); 141.8 (*d*, C(1)); 18.5 (*s*, CSi); 131.3 (*s*, C(7)); 144.0 (*s*, C(3)). MS: 266 (11, $M^{+\cdot}$, $C_{16}H_{30}OSi$), 224 (15), 223 (77), 209 (17), 186 (14), 150 (12), 141 (35), 135 (24), 129 (10), 107 (14), 75 (91), *73* (100), 69 (96), 59 (17), 43 (11), 41 (52).

3.1.2. *Thermolysis of* (Z)-**7**. *FVT* (520°) of (*Z*)-**7** (87 mg, 0.326 mmol) as described above gave (*E*)-**33** (40 mg, 46%).

(1E,3E)-*1-[(*tert*-Butyl)dimethylsilyloxy]-3,7-dimethyl-1,3,6-octatriene* ((*E*)-**33**). B.p.: 100°/0.07 Torr. UV (0.252 mg in 20 ml): 242 (18800), 282 (2400). IR: 3030*w*, 2950*s*, 2920*s*, 2880*s*, 2850*s*, 1675*w* (br.), 1640*s*, 1615*m*, 1465*m*, 1460*m*, 1440*m*, 1405*w*, 1390*m*, 1375*m*, 1360*m*, 1295*m*, 1250*s*, 1215*m*, 1185*m*, 1170*m*, 1155*s* (sh), 1100*m*, 1055*m*, 1020*w*, 1005*m*, 980*m*, 935*m*, 920*m*, 870*s*. ^{1}H-NMR (300 MHz, C_6D_6): 0.09 (*s*, 2 CH_3Si); 0.96 (*s*, 3 CH_3CSi); 1.55 (*s*, CH_3–C(7)); 1.65 (*s*, 3 H–C(8)); 1.71 (*s*, CH_3–C(3)); 2.84 (*t*, $J = 9$, 2 H–C(5)); 5.20, 5.35 (2*t*, $J = 9$, H–C(4), H–C(6)); 6.35 (*AB*, $J = 12.5$, $\delta_A = 6.08$, $\delta_B = 6.62$, H–C(1), H–C(2)). ^{13}C-NMR (75 MHz, C_6D_6): –5.04 (*q*, 2 CH_3Si); 12.9, 17.8, 25.9 (overlapping with additional *q*) (3*q*, CH_3–C(3), CH_3–C(7), C(8), 3 CH_3CSi); 27.5 (*t*, C(5)); 119.3 (*d*, C(2)); 123.6 (*d*, C(6)); 126.5 (*d*, C(4)); 140.0 (*d*, C(1)); 18.5 (*s*, CSi); 130.9, 131.3 (2*s*, C(3), C(7)). MS: 266 (1, $M^{+\cdot}$, $C_{16}H_{30}OSi$), 251 (1), 223 (1), 209 (7), 186 (10), 135 (7), 103 (18), *75* (100), 73 (26), 69 (19).

3.2. *Thermolyses of* (E)- *and* (Z)-**8**. 3.2.1. *FVT* (560°) of (*E*)-**8** (733 mg, 2.4 mmol) in a silylated quartz tube (81% conversion) followed by CC (hexane) afforded **34A** (124 mg, 17%) and a *ca.* 1:7 mixture (257 mg, 35%) of **34B/35**, which was separated by prep. GC (5% *SE-30*, 185°) affording **34B** (20 mg, 3%) and **35** (130 mg, 18%).

3.2.2. *FVT* of (*Z*)-**8** (40 mg, 0.13 mmol) as described above gave **34A** (6 mg, 15%), and a *ca.* 1:7 mixture (14 mg, 35%) of **34B/35**.

*3-[3'-(*tert*-Butyl)dimethylsilyloxy-2'-methyl-2'-propenylidene]-2,4,4-trimethylcyclohexene, Isomer A* (**34A**). UV (0.186 mg in 10 ml): 221 (9390), 267 (9555). IR: 3010*w*, 2950*s*, 2920*s*, 2850*s*, 1645*m*, 1480*m*, 1435*w* (sh), 1385*w*, 1370*w*, 1355*w*, 1255*m*, 1185*s*, 1170*s*, 1155*s*, 1080*w*, 1000*w*, 935*w*, 895*m*, 865*s*, 835*s*. ^{1}H-NMR (300 MHz, C_6D_6): 0.04 (*s*, 2 CH_3Si); 0.94 (*s*, 3 CH_3CSi); 1.13 (*s*, 2 $CH_3C(4)$); 1.48 (*dd*, $J_1 = J_2 = 6.5$, 2 H–C(5)); 1.89 (*m*, $w_{1/2} = 3$, CH_3–C(2)); 2.04–2.14 (*m*, 2 H–C(6)); 2.07 (*d*, $J = 1.5$, CH_3–C(2')); 5.48 (*m*, $w_{1/2} = 8$, H–C(1)); 5.86 (*m*, $w_{1/2} = 5$, H–C(1')); 6.32 (*dq*, $J = 3, 1.5$, H–C(3')). ^{13}C-NMR (75 MHz, C_6D_6): –4.9 (*q*, 2 CH_3Si); 14.6 (*q*, *C*H–C(2')); 23.1 (*q*, *C*H_3–C(2)); 25.9 (*q*, 3 CH_3CSi); 27.5 (*q*, 2 *C*H_3–C(4)); 24.2 (*t*, C(5)); 37.8 (*t*, C(6)); 121.9 (*d*, C(1)); 127.9 (*d*, C(1')); 138.0 (*d*, C(3')); 18.3 (*s*, CSi); 35.7 (*s*, C(4)); 116.9, 133.0, 145.5 (3*s*, C(2), C(3), (2')). MS: 306 (25, $M^{+\cdot}$, $C_{19}H_{34}OSi$), 291 (25), 235 (11), 175 (24), 173 (13), 159 (30), 119 (25), *75* (100), 73 (99), 59 (13), 41 (12). Anal. calc. for $C_{19}H_{34}OSi$ (306.38): C 74.44, H 11.18; found: C 74.67, H 11.15.

Isomer B (**34B**), contaminated with *ca.* 20% of **35**. IR: 3010*w*, 2950*s*, 2920*s*, 2850*s*, 1645*m*, 1460*m*, 1435*w* (sh), 1385*w*, 1370*w*, 1355*w*, 1255*m*, 1185*s*, 1170*s*, 1155*s*, 1180*w*, 1000*w*, 935*w*, 895*m*, 865*s*, 835*s*. ^{1}H-NMR (300 MHz, C_6D_6): 0.05 (*s*, 2 CH_3Si); 0.95 (*s*, 3 CH_3CSi); 1.17 (*s*, 2 CH_3–C(4)); 1.54 (*dd*, $J_1 = J_2 = 6.5$, 2 H–C(5)); 1.69 (*m*, $w_{1/2} = 3$, CH_3–C(2)); 2.05 (*m*, $w_{1/2} = 4$, CH_3–C(2')); 2.08–2.13 (*m*, $w_{1/2} = 14$, C(6)); 5.45–5.47 (*m*, $w_{1/2} = 8.5$, H–C(1)); 5.82 (*m*, $w_{1/2} = 5$, H–C(1')); 6.01 (*dq*, $J = 3, 1$, H–C(3')). ^{13}C-NMR (75 MHz, C_6D_6): –5.0 (*q*, 2 CH_3Si); 13.4 (*q*, *C*H_3–C(2')); 22.15 (*q*, CH_3–C(2)); 25.7 (*q*, 3 CH_3CSi); 28.0 (2*q*, 2 *C*H_3–C(4)); 24.3 (*t*, C(5)); 37.8 (*t*, C(6)); 119.1 (*d*, C(1)); 126.0 (*d*, C(1')); 135.0 (*d*, C(3')); 18.3 (*s*, CSi); 31.9 (*s*, C(4)); 116.8, 134.1, 146.8 (3*s*, C(2), C(3), C(2')). MS: 306 (23, $M^{+\cdot}$, $C_{19}H_{34}OSi$), 291 (20), 235 (14), 175 (25), 173 (16), 159 (35), 119 (26), *75* (100), 73 (91), 59 (12).

*9-[(*tert*-Butyl)dimethylsilyloxy]-1,5,5,8-tetramethylbicyclo[4.3.0]nona-2,8-diene* (**35**). IR: 3020*w*, 2950*s*, 2920*s*, 2850*s*, 1680*m*, 1465*m* (sh), 1457*m*, 1445*m* (sh), 1380*m*, 1360*m*, 1305*m*, 1280*w* (sh), 1265*s* (sh), 1255*s* (sh), 1245*s*, 1205*s*, 1150*w*, 1175*m*, 1115*m*, 930*w*, 880*s*, 835*s*. ^{1}H-NMR (300 MHz, C_6D_6): 0.18, 0.19 (2*s*, 2 CH_3Si); 0.88, 1.34 (2*s*, 2 CH_3–C(5)); 1.04 (*s*, 3 CH_3CSi); 1.34 (*s*, CH_3–C(1)); 1.52 (*dddd*, $J_1 = 16$, $J_2 = 5.5$, $J_3 = J_4 = 1.5$, H–C(4)); 1.56 (*dd*, $J_1 = J_2 = 1$, CH_3–C(8)); 1.82 (br. *dd*, $J_1 = J_2 = 8.5$, H–C(6)); 1.90–2.12 (*m*, 2 H–C(7), H–C(4)); 5.56 (*ddd*, $J = 10, 5.5, 2.5$, H–C(3)); 5.90 (*dm*, $J = 10$, $w_{1/2} = 6$, H–C(2)). ^{13}C-NMR (75 MHz, C_6D_6): –3.0 (*q*, 2 CH_3Si); 13.4 (*q*, *C*H_3–C(8)); 26.4 (3*q*, 3 *C*H_3CSi); 26.0, 28.0, 29.6 (3*q*, *C*H_3–C(1), 2 *C*H_3–C(6)); 35.3, 35.7 (2*t*, C(4), C(7)); 51.9 (*d*, C(6)); 123.0, 132.6 (2*d*, C(2), C(3)); 19.0 (*s*, CSi); 31.9 (*s*, C(5)); 48.9 (*s*, C(1)); 107.7 (*s*, C(8)); 151.7 (*s*, C(9)). MS: 306 (22, $M^{+\cdot}$, $C_{19}H_{34}OSi$), 292 (25), *291* (100), 249 (12), 175 (12), 159 (10), 75 (37), 73 (92), 59 (16), 57 (11), 43 (10), 41 (18).

3.3. *Thermolysis of (*E*)-9*. *FVT* (600°) of (*E*)-9 (1.073 g, 3.5 mmol) as described in *Sect. 3.2* afforded a mixture (883 mg) of starting material (*E*)-**9** (23%), **36** (30%), and **37A + B** (47%). This mixture was separated by prep. GC (5% *SE-30*, 185°) yielding **36** (55 mg) and **37A + B** (148 mg).

*9-[(*tert*-Butyl)dimethylsilyloxy]-1,5,5-trimethylbicyclo[4.3.0]nona-2,8-diene* (**36**). IR: 3050*w*, 3010*m*, 2940*s* (sh), 2880*s* (sh), 1730*w* (br.), 1640*s*, 1455*s*, 1440*m*, 1380*m*, 1360*s*, 1315*s*, 1295*s*, 1280*s*, 1245*s*, 1230*s*, 1165*m*, 1105*s*, 990*m*, 960*m*, 935*m* (sh), 910*s*, 880*s*, 870*s*. ^{1}H-NMR (300 MHz, C_6D_6): 0.13, 0.15 (2*s*, 2 CH_3Si); 0.88, 0.15 (2*s*, 2 CH_3–C(5)); 0.98 (*s*, 3 CH_3CSi); 1.35 (*s*, CH_3–C(1)); 1.56 (*ddd*, $J_1 = 17$, $J_2 = 5.5$, $J_3 = J_4 = 1.5$, H–C(4)); 1.88 (*dd* br., $J_1 = J_2 = 8.5$, H–C(6)); 1.97 (*ddd*, $J = 17, 2.5, 1.5$, H–C(4)); 2.09 (*ddd*, $J = 15, 8, 2.1$, H–C(7)); 2.15 (*ddd*, $J = 15, 8.5, 2.5$, H–C(7)); 4.41 (*dd*, $J = 2.5, 2.1$, H–C(8)); 5.56 (*ddd*, $J = 10, 5.5, 2.5$, H–C(3)); 5.88 (*ddd*, $J_1 = 10$, $J_2 = J_3 = 1.5$, H–C(2)). ^{13}C-NMR (25.2 MHz, C_6D_6): –4.5 (*q*, 2 CH_3Si); 26.0 (*q*, 3 *C*H_3CSi) and presumably 25.6, 28.2 (3*q*, 2 *C*H_3–C(5), *C*H_3–C(1)); 29.5, 35.6 (2*t*, C(4), C(7)); 53.0 (*d*, C(6)); 97.2 (*d*, C(8)); 123.5, 132.4 (2*d*, C(2), C(3)); 18.4 (*s*, CSi); 31.8 (*s*, C(5)); 48.0 (*s*, C(1)); 159.8 (*s*, C(9)).

*(*E*)-3-[2'-(3",3",4",4"-Tetramethyl-2"-oxa-3"-silacyclopentyl)vinyl]-2,4,4-trimethylcyclohexene* (**37A + B**), *1:1 Mixture*. IR: 3020*w*, 2940*s*, 2900*s*, 2850*s*, 1455*m*, 1430*m* (sh), 1380*m*, 1370*m* (sh), 1360*m*, 1245*s*, 1160*w*, 1070*m* (br.), 1020*s*, 1000*s*, 965*m*, 935*m*, 890*s*, 850*s*. ^{1}H-NMR (300 MHz, C_6D_6): 0.08, 0.09, 0.11 (3*s*, 2 CH_3Si); 0.90, 0.93 (3 H); 0.97, 0.98 (4*s*, 2 CH_3–C(4"), 2 CH_3–C(4)); 1.10–1.16 (*m*, H–C(5)); 1.46–1.54 (*m*, 2 H–C(5"), H–C(5)); 1.70, 1.72 (2*m*, $w_{1/2} = 5$, CH_3–C(2)); 1.97 (*m*, $w_{1/2} = 15$, 2 H–C(6)); 2.13 (*d*, $J = 7$, H–C(3)); 4.44–4.46 (*m*, H–C(1")); 5.41 (*m*, $w_{1/2} = 8$, H–C(1)); 5.50–5.70 (*m*, H–C(1'), H–C(2')). ^{13}C-NMR (25.2 MHz, C_6D_6): –4.5, –2.6 (2*q*, 2 CH_3Si); 22.1 (*q*, *C*H_3–C(2)); 22.9, 23.2 (2*q*, 2 *C*H_3–C(4")); 26.1, 26.6 (2*q*, 2 *C*H_3–C(4)); 22.4 (*t*, C(5)); 30.9 (*t*, C(6)); 49.5 (*t*, C(5")); 53.2 (*d*, C(3)); 74.9 (*d*, C(1")); 120.0 (*d*, C(1)); 129.3, 134.7 (2*d*, C(2'), C(1')); 21.5 (*s*, C(4")); 31.1 (*s*, C(4)); 133.4 (*s*, C(2)). MS: 292 (4, $M^{+\cdot}$, $C_{18}H_{32}OSi$), 236 (21), 221 (19), 180 (11), 170 (16), *169* (100), 165 (16), 123 (15), 113 (86), 105 (15), 91 (17), 77 (10), 75 (86), 59 (12), 41 (13).

4. Additional Experiments. – 4.1. *Hydrolysis of* **27A + B**. A soln. of **27A + B** (104 mg, 0.195 mmol) in Et_2O (5 ml) was stirred with 2N aq. HCl (1 ml) overnight. The mixture was worked up in Et_2O, and CC (hexane/Et_2O 30:1) afforded (*E*/*Z*)-**7** (14 mg, 27%), (*E*/*Z*)-**10** (28 mg, 94%), and **28** (36 mg, 69%).

4.2. *Hydrolysis of* **30A** *and* **30B**. a) A soln. of **30A** (77 mg, 0.125 mmol) in Et_2O (10 ml) was stirred with 5% aq. HCl (5 ml) for 72 h at r.t. The mixture was worked up with Et_2O, and CC (Et_2O/hexane 1:50) afforded (*Z*)-**8** (15 mg, 40%), and **11** (16 mg, 33%). b) Hydrolysis of **30B** (93 mg, 0.15 mmol) as described above gave, after CC, (*Z*)-**8** (21 mg, 45%), and **11** (20 mg, 34%).

4.3. *Hydrolysis of* **31A + B**. A soln. of **31A + B** (260 mg, 0.45 mmol) in Et_2O (15 ml) and 5% aq. HCl (5 ml) was stirred for 24 h at r.t. The mixture was worked up in Et_2O, and CC (Et_2O/pentane 1:4) yielded **12** (83 mg, 52%).

4.4. *Hydrolysis of (*E*)-**8** and (*E*)-**9***. a) A soln. of (*E*)-**8** (19 mg, 0.06 mmol) in Et_2O (3 ml) was stirred with 10% aq. HCl (1 ml) for 24 h at r.t. Workup in Et_2O and CC (Et_2O/hexane 1:3) gave **11** (10 mg, 83%). b) Hydrolysis of (*E*)-**9** (18 mg, 0.06 mmol) in Et_2O (3 ml) with 5% aq. HCl (1 ml) for 24 h at r.t. afforded, after CC, **12** (10 mg, 88%).

4.5. *Synthesis of* **32** *and (*E/Z*)-***33**. Citral ((*E*/*Z*)-**10**; 1.00 g, 6.57 mmol; freshly distilled) was added to a soln. of (*t*-Bu)Me_2SiCl (1.18 g, 7.86 mmol) in abs. Et_3N (2.2 ml, 1.59 g, 15.76 mmol) and abs. DMF (1.7 ml), which had been filtered through *Celite*. The mixture was heated at reflux temp. for 3 d, then cooled to 0°, diluted with pentane, and washed with 0.1N aq. HCl. CC (hexane/Et_2O 10:1) gave a mixture of **32** and (*E*/*Z*)-**33** (668 mg, 92%; at 42% conversion; ratio *ca.* 1:1:1). Repeated CC (hexane) afforded an anal. sample of **32** and a 5:1 mixture of (*E*/*Z*)-**33**.

*(1*E*,3*Z*)-[(*tert-*Butyl)dimethylsilyloxy]-3,7-dimethyl-1,3,6-octatriene* ((*Z*)-**33**; *ca.* 1:5 mixture with (*E*)-**33**). B.p.: 100°/0.07 Torr. Characteristic signals assigned to (*Z*)-**33**: ^{1}H-NMR (300 MHz, C_6D_6): 0.09 (*s*, 2 CH_3Si); 0.94 (*s*, 3 CH_3CSi); 1.53 (*s*, CH_3–C(7)); 1.62 (*m*, $w_{1/2}$ = 4, 3 H–C(8)); 1.81 (*m*, $w_{1/2}$ = 4, CH_3–C(3)); 2.88 (*t*, *J* = 7, 2 H–C(5)); 5.23 (*m*, $w_{1/2}$ = 9, H–C(4), H–C(6)); 6.58 (*AB*, *J* = 12, δ_A = 6.47, δ_B = 6.69, H–C(2), H–C(1)). ^{13}C-NMR (75 MHz, C_6D_6): –5.0 (*q*, 2 CH_3Si); 20.9, 25.9 (overlapping with additional *q*), 30.3 (3*q*, 3 CH_3CSi, CH_3–C(3), CH_3–C(7), C(8)); 27.1 (*t*, C(5)); 112.0 (*d*, C(2)); 123.8 (*d*, C(6)); 125.6 (*d*, C(4)); 142.4 (*d*, C(1)); 18.5 (*s*, CSi); 129.6, 131.5 (2*s*, C(3), C(7)).

4.6. *Hydrolysis of* **35**. A soln. of **35** (20 mg, 0.065 mmol) in THF (5 ml), and 5% aq. HCl (2 ml) was stirred for 3 h at r.t. The mixture was worked up with Et_2O, and CC (Et_2O/hexane 1:10) gave **38** (12 mg, 95%).

2,2,6,8-Tetramethylbicyclo[4.3.0]non-4-en-7-one (**38**). IR: 3020*m*, 2950*s*, 2920*s*, 2860*s*, 2830*m*, 1645*w*, 1730*s*, 1470*m*, 1445*m*, 1380*m*, 1370*w*, 1360*m*, 1345*w*, 1325*w*, 1280*w*, 1260*w*, 1240*w*, 1195*m*, 1165*w*, 1145*w*, 1105*w*, 1040*w*, 990*m*, 955*w*, 925*w*, 895*w*, 705*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.00, 1.02 (2*s*, 2 CH_3–C(2)); 1.08 (*d*, *J* = 6, CH_3–C(8)); 1.25 (*s*, CH_3–C(6)); 1.68 (*ddm*, *J* = 18, 5.5, $w_{1/2}$ = 3, H–C(3)); 1.74 (br. *dd*, *J* = 11.5, 6, H–C(1)); 1.91 (*dm*, *J* = 18, $w_{1/2}$ = 6, H–C(3)); 2.10–2.30 (*m*, H–C(8), H–C(9)); 5.32 (*ddm*, *J* = 10, 2.5, $w_{1/2}$ = 3, H–C(5)); 5.61 (*ddd*, *J* = 10, 5.5, 2, H–C(4)). MS: 192 (16, $M^{+\cdot}$, $C_{13}H_{20}O$), 135 (14), 134 (64), 122 (22), 121 (19), 108 (12), *107* (100), 93 (11), 91 (24), 79 (10), 77 (10), 41 (15).

4.7. *Hydrolysis of* **36**. A soln. of **36** (36 mg, 0.12 mmol) in THF (6 ml) was stirred with 5% aq. HCl (2.5 ml) for 1 h. Workup in Et_2O and CC (Et_2O/hexane 1:1) yielded **39** (20 mg, 88%).

2,2,6-Trimethylbicyclo[4.3.0]non-4-en-7-one (**39**). IR: 3010*m*, 2950*s*, 2920*s*, 2860*s*, 2830*m*, 1730*s*, 1640*w*, 1470*m*, 1445*s*, 1430*m*, 1405*s*, 1380*s*, 1360*s*, 1345*m*, 1320*w*, 1295*m*, 1270*m*, 1250*m*, 1225*m*, 1205*m* (sh), 1190*s*, 1140*w* (sh), 1130*m*, 1075*s*, 1050*m*, 1030*m*, 1015*m*, 990*m*, 965*m*, 945*m*, 900*m*, 860*w*, 830*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.97, 1.03 (2*s*, 2 CH_3–C(2)); 1.23 (*s*, CH_3–C(6)); 1.45–1.53 (*m*, H–C(9)); 1.74 (*ddm*, *J* = 18, 5.5, $w_{1/2}$ = 3, H–C(3)); 1.82 (br. *dd*, *J* = 10.5, 7, H–C(1)); 1.94 (*dm*, *J* = 18, $w_{1/2}$ = 6, H–C(3)); 1.92–2.06 (*m*, H–C(9)); 2.18 (*ddd*, *J* = 18.5, 11.5, 9, H–C(8)); 2.34 (*ddd*, *J* = 18.5, 8.5, 2, H–C(8)); 5.33 (*ddm*, *J* = 10, 2.5, $w_{1/2}$ = 3, H–C(5)); 5.65 (*ddd*, *J* = 10, 5.5, 2.5, H–C(4)). MS: 178 (24, $M^{+\cdot}$, $C_{12}H_{18}O$), 135 (13), 134 (77), 122 (19), 121 (35), 120 (16), 119 (60), *107* (100), 105 (14), 94 (13), 93 (14), 91 (32), 79 (23), 77 (16), 65 (11), 55 (10), 41 (28).

4.8. *Hydrolysis of* **37A + B**. A soln. of **37A + B** (36 mg, 0.12 mmol) in THF (6 ml) and 5% aq. HCl (3 ml) was heated under reflux for 3 h. Workup in Et_2O and CC (Et_2O/hexane 1:10) gave **40** (11 mg, 32%).

*(4*E*,6*E*)-7-(2′,6′,6′-Trimethyl-2′-cyclohexenyl)-2,3,3-trimethyl-2-sila-4,6-heptadien-2-ol* (**40**). UV (0.156 mg in 10 ml): 250 (28 090). IR: 3680*m*, 3010*m*, 2950*s*, 2920*s*, 2860*s*, 1460*m*, 1380*m*, 1360*m*, 1300*m*, 1250*s*, 1145*w* (br.), 1075*w*, 990*s*, 965*m*, 940*w*, 890*m* (sh). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.10 (*s*, 2 CH_3Si); 0.82, 0.89 (2*s*, 2 CH_3–C(**6′**)); 1.06 (*s*, 2 CH_3–C(3)); 1.18–1.45 (*m*, 2 H–C(5′)); 1.56 (br. *s*, OH); 1.59 (*m*, $w_{1/2}$ = 5, CH_3–C(2′)); 1.99 (*m*, $w_{1/2}$ = 15, 2 H–C(4′)); 2.08 (*d*, *J* = 9.5, H–C(1′)); 5.36 (*dd*, *J* = 15, 9.5, H–C(7)); 5.38 (*m*, $w_{1/2}$ = 6, H–C(3′)); 5.65 (*d*, *J* = 15, H–C(4)); 5.88 (*dd*, *J* = 14.5, 10, H–C(5)); 5.96 (*dd*, *J* = 15, 10, H–C(6)). ^{13}C-NMR (75 MHz, C_6D_6): –3.4 (2*q*, 2 CH_3Si); 22.2 (2*q*, 2 CH_3–C(3)); 23.2 (*q*, CH_3–C(2′)); 27.0, 27.8 (2*q*, 2 CH_3–C(6′)); 23.4 (*t*, C(5′)); 31.8 (*t*, C(4′)); 54.8 (*d*, C(1′)); 120.9 (*d*, C(3′)); 126.6, 132.0, 132.9, 140.3 (4*d*, C(4), C(5), C(6), C(7)); 28.0 (*s*, C(3)); 32.5 (*s*, C(6′)); 134.5 (*s*, C(2′)). MS: 292 (8, $M^{+\cdot}$, $C_{18}H_{32}OSi$), 169 (53), 123 (25), 95 (20), 84 (28), 78 (16), 77 (17), 75 (100), 69 (20), 56 (41), 55 (23), 44 (22), 42 (22), 41 (42).

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