96. Photochemical Reactions

152nd Communication[1])

Photochemistry of Acylsilanes: Photolysis and Thermolysis of Cyclopropyl Silyl Ketones

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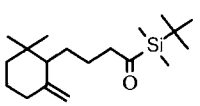
Dedicated to Prof. Dr. *H. R. Christen* on the occasion of his 65th birthday

(17.IV.90)

The photolysis and thermolysis of the cyclopropyl silyl ketones **3**, **4**, and **5** are described. On n,π^* excitation, the silyl ketones **3** and **4** undergo a *Norrish*-type-II reaction involving γ-H abstraction, cyclopropyl ring cleavage followed by retro-enolization to the acylsilanes **6** and (*E*/*Z*)-**12**, respectively. As a common product of **3** and **4**, the dihydrofuran **7** is formed *via* the alternative C(α)-C(β) cleavage of the cyclopropyl moiety. Compounds **6**, **7**, and (*E*/*Z*)-**12** are new types of acylsilane photoproducts. The irradiation of acylsilane **5** gave the analogous dihydrofuran **15** as the only product. On photolysis of **3** and **4**, products **8A** + **B** and **13A** + **B**, derived from a siloxy carbene intermediate, were found as well. On thermolysis of **3** and **4**, the acylsilanes **6** (80%), and (*E*)-**12** (33%) and (*Z*)-**12** (34%), respectively, are formed as the only products. Their formation may occur *via* a [1,5] sigmatropic H-shift. The thermolysis of **5** gave the diene **16** whose formation can be explained by insertion of a siloxycarbene into the neighboring cyclopropane leading to the cyclobutene **28** as thermally unstable intermediate.

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



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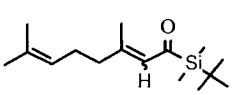


(*E*/*Z*)-**2**

Continuing our studies of the influence of neighboring groups on the reactivity of siloxycarbenes, we prepared some new model compounds. Thus, in our laboratory various syntheses of the cyclopropyl silyl ketones **3**, **4**, and **5** (*Schemes 1* and *3*) were

[1]) 151st communication: [1].

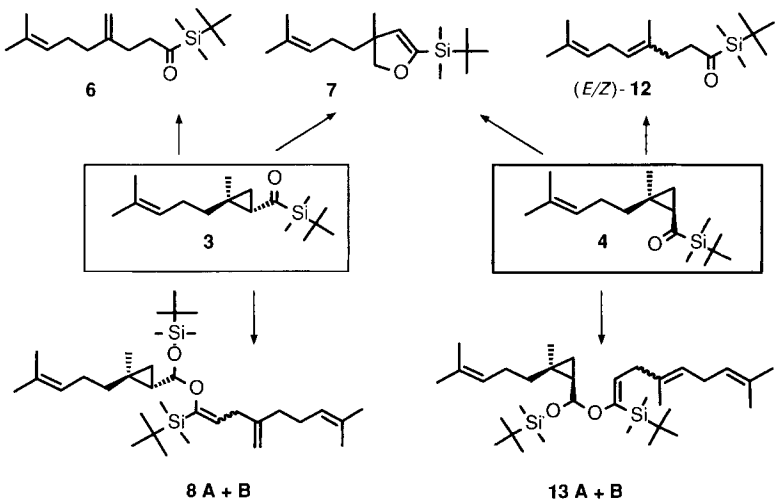
[2]) Taken in part from the Ph.D. thesis of *M.E.S.* Diss. ETHZ No. 7896 (1985) [2].

[3]) New address: *Ciba-Geigy Ltd.*, Additives Division, CH–4133 Schweizerhalle.

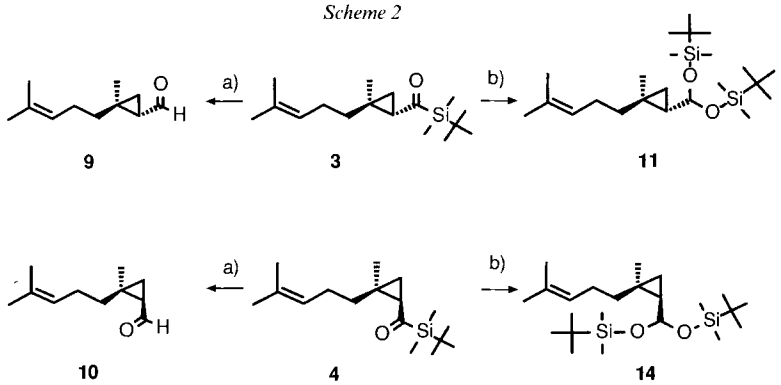
[4]) New address: *Ciba-Geigy Ltd.*, Agricultural Division, CH–4002 Basel.

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

Scheme 1



Scheme 2



a) *hv*, H_2O. b) *hv*, (*t*-Bu)Me_2SiOH.

developed [5]. Until now, there is little known about the reactivity of cyclopropyl-acylsilanes [6]. In the present paper, we describe the photolyses and thermolyses of **3**, **4**, and **5** as three representatives of this interesting class of compounds.

2. Photolysis Experiments. – 2.1. Irradiation of the acylsilane **3** in abs. MeCN ($\lambda > 347$ nm, 100% conversion) afforded the γ,δ-unsaturated acylsilane **6** (15%), the dihydrofuran **7** (7%; *Scheme 1*), the dimers **8A** + **B**[6]) (25%; *Scheme 1*), and the aldehyde **9**[7]) (32%; *Scheme 2*). In the presence of (*t*-Bu)Me_2SiOH, the addition product **11** (78%; *Scheme 2*) was formed as the only product.

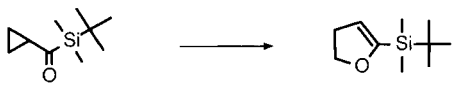
[6]) The terms **A**, **B**, and **C** are used for the description of diastereoisomers whose configurations were not assigned conclusively.

[7]) If H_2O was not strictly excluded from the photolysis mixture, the aldehydes **9** and **10** (*Scheme 2*) were obtained as the major products.

2.2. Irradiation of the acylsilane **4** in abs. MeCN ($\lambda > 347$ nm, 100% conversion) afforded the dihydrofuran **7** (4%; *Scheme 1*), the aldehyde **10**[7]) (2%, *Scheme 2*), the acylsilanes **12** (40%), and the dimers **13A** + **B** (12%; *Scheme 1*). In the presence of the (*t*-Bu)Me_2SiOH, the addition product **14** (76%) was formed as the only product.

2.3. Irradiation of the acylsilane **5** in abs. MeCN ($\lambda > 347$ nm, 72% conversion) afforded the dihydrofuran **15** (74%; *Scheme 3*) as the only product.

Scheme 3



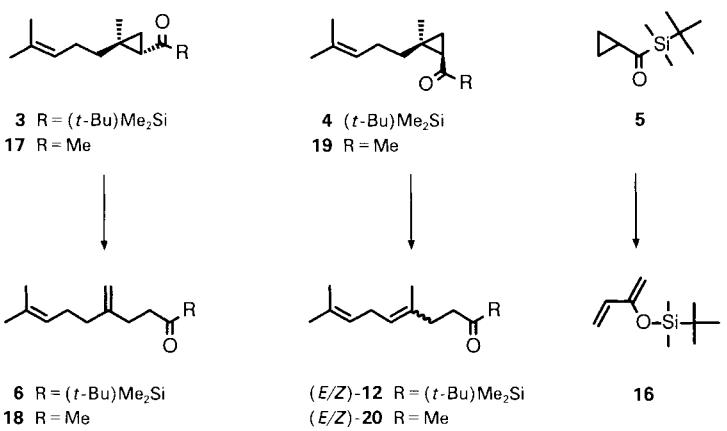
5 **15**

3. Thermolysis Experiments (*Scheme 4*). – 3.1. *Flash Vacuum Thermolysis* (FVT) [7] of the acylsilane **3** (400°, conversion 80%) afforded **6** (80%).

3.2. FVT of the acylsilane **4** (400°, conversion 97%) afforded (*E*/*Z*)-**12** (*ca.* 1:1; 60%).

3.3. FVT of the acylsilane **5** (500°, conversion 100%) afforded the dienyl silyl ether **16** (73%).

Scheme 4



3 R = (*t*-Bu)Me_2Si
17 R = Me

4 (*t*-Bu)Me_2Si
19 R = Me

5

6 R = (*t*-Bu)Me_2Si
18 R = Me

(*E*/*Z*)-**12** R = (*t*-Bu)Me_2Si
(*E*/*Z*)-**20** R = Me

16

3.4. FVT of the methyl ketone **17** (500°, conversion 78%) afforded **18** (74%).

3.5. FVT of the methyl ketone **19** (500°, conversion 86%) afforded a 1.5:1 mixture (*E*/*Z*)-**20** (87%).

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 are presented in the *Exper. Part.*

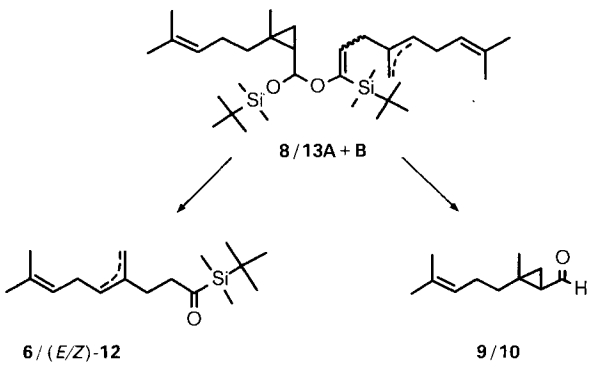
Acylsilane **6** (*Schemes 1* and *4*). The acylsilane **6** shows in the IR spectrum the expected long-wavelength C=O stretching absorption at 1640 cm^{-1} as well as in the UV spectrum characteristic structured n,π^* bands at 374 nm ($\varepsilon = 160$). In the ^{13}C-NMR spectrum, the *s* of the C=O group (246.6 ppm) is shifted *ca.* 40 ppm downfield relative to

the analogous methyl ketones **17** and **19**. Furthermore, the *t* (109.0 ppm) is characteristic of the methylidene moiety.

Dihydrofuran **7** (*Scheme 1*). The ^{1}H-NMR shows an *AB* system (3.94 ppm, $J = 8.6$) for the geminal H-atoms in α-position to the ether-O-atom, as well as a *s* (5.04 ppm) of the olefinic H-atom. ^{13}C-NMR confirmed the structure with a *s* (43.3 ppm), a *t* (81.5 ppm), and a *s* (159.7 ppm).

Dimers **8A + B** *and* **13A + B** (*Schemes 1* and *5*). The hydrolyses of **8A + B** and **13A + B** with oxalic acid gave the acylsilanes **6** and (*E*/*Z*)-**12**, respectively, and the aldehydes **9** and **10**, respectively, in a ratio of *ca.* 1:1 each.

Scheme 5

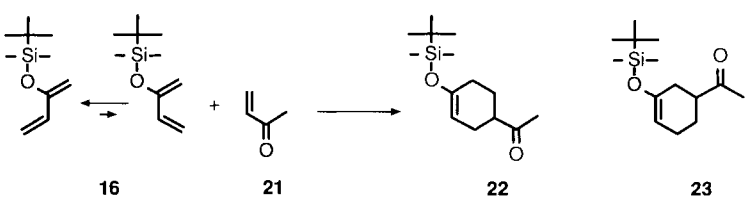


Acylsilanes (E/Z)-**12** (*Schemes 1* and *4*). The spectra of these compounds are similar to those of **6**. The (*E*)- and consequently the (*Z*)-configuration was established by NOE experiments (see *Exper. Part*).

Dihydrofuran **15** (*Scheme 3*). The IR spectrum of **15** shows an enol-ether band at 1585 cm^{-1}. The ^{1}H-NMR spectrum confirms the proposed structure by a *td* (2.55 ppm) for the two allylic H-atoms, a *t* (4.25 ppm) for the H-atom in α-position to the O-atom, and a *t* (5.20 ppm) for the olefinic H-atom.

Diene **16** (*Scheme 4*). The UV maximum at 233 nm ($\varepsilon = 11\,500$) is characteristic for the diene chromophore, and the IR spectrum shows an enol-ether band at 1580 cm^{-1}. In the ^{1}H-NMR, a br. *s* (4.31 ppm) for the upfield shifted methylidene H-atoms, a *dm* and *dd* (5.06 ppm), and a down-field shifted *dd* (6.21 ppm) are assigned to the 3 olefinic H-atoms. The structure of **16** was confirmed by its synthesis from methyl vinyl ketone (**21**) followed by a *Diels-Alder* reaction with methyl vinyl ketone (**21**). As expected [8], the silyl enol-ether **22** (71%; *Scheme 6*) was obtained, whereas the alternative addition product **23** was not detected.

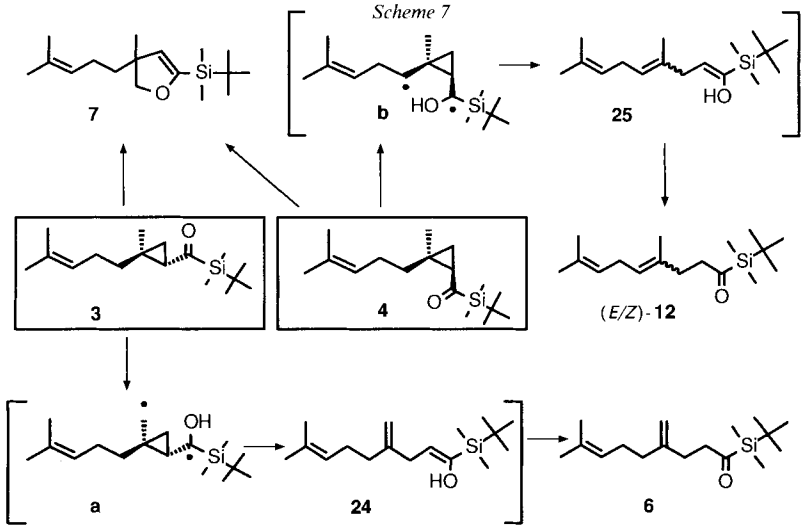
Scheme 6



Methyl Ketones **18** *and (*E/Z*)-***20*** (Scheme 4*). Their structures can be established by comparison of their spectral data with those of the related acylsilane **6** and (*E/Z*)-**12**.

5. Discussion. – 5.1. *Photolyses. n,π** Excitation ($\lambda > 347$ nm) of the acylsilanes **3** and **4** gives rise to the formation of three types of products: the acylsilanes **6** and (*E/Z*)-**12**, the dimers **8A** + **B** and **13A** + **B**, and the aldehydes **9** and **10**. The formation of **6** and (*E/Z*)-**12** may be explained *via* a γ-H abstraction, leading to the 1,4-diradicals **a** and **b**, followed by a cyclopropyl-ring cleavage, furnishing the dienols **24** and **25**, which tautomerize to **6** and (*E/Z*)-**12**, respectively.

Scheme 7



The alternative bond cleavage of the cyclopropyl ring of **3** and **4** is evidenced by the formation of **7**. The dihydrofuran **7** represents the product of a new type of reaction in the photochemistry of acylsilanes, involving an intramolecular addition of the C=O group. This finding demonstrates that in competition to the γ-H abstraction, a C–C bond cleavage of the cyclopropane, without migration of the silyl group to the O-atom, is possible.

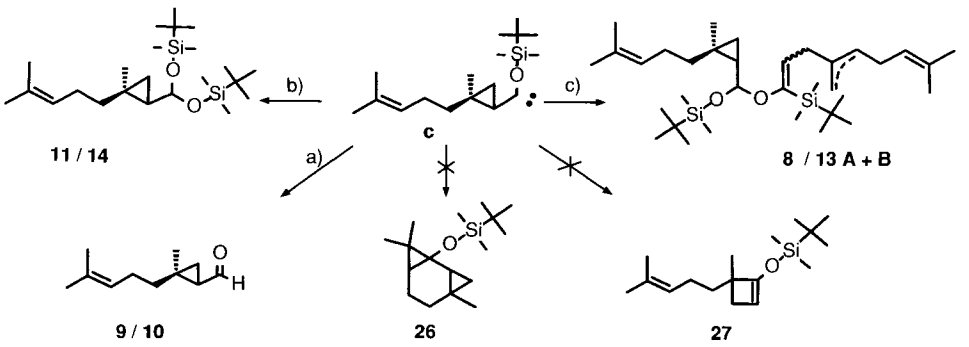
On photolyses of cyclopropyl ketones, (*E/Z*)-isomerization of the cylopropane ring as well as dihydrofurane formation are known [9–13]. In contrast to the acylsilanes **3** and **4**, however, in the methyl ketones, the more substituted cyclopropyl bond is usually cleaved. A photochemical epimerization of **3** and **4** could not be detected.

On n,π* excitation of the acylsilane **5** the lack of γ-H-atoms results in the formation of **15** as the only product.

The formation of the dimers **8A** + **B** and **13A** + **B** as well as the aldehydes **9** and **10** may be due to the addition of the siloxycarbene **c** to the enols **24** and **25** and to H_2O, respectively (*Scheme 8*).

To compare the siloxycarbene reactivity of earlier investigated acylsilanes [2] [3], **3** and **4** were photolyzed in the presence of 1.5 equiv. of the (*t*-Bu)Me_2SiOH. Thus, only addition products to the siloxycarbene **c**, the acetals **11** (78%) and **14** (76%), respectively, were isolated. On GC analysis, however, the acylsilanes **6** and (*E/Z*)-**12**, respectively,

Scheme 8



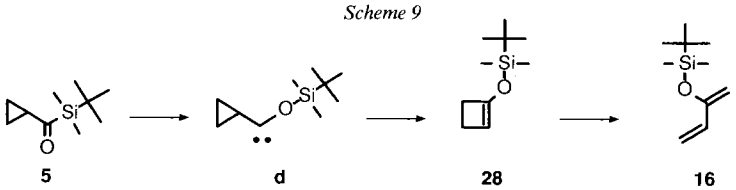
a) H_2O. b) (*t*-Bu)Me_2SiOH. c) Compounds **24** and **25**, resp.

were isolated. On GC analysis, however, the acylsilanes **6** and (*E*/*Z*)-**12**, respectively, were also detected in trace amounts. This finding indicates clearly, that the presence of the cyclopropyl moiety did not influence the fast trapping reaction of the siloxycarbene **c** with (*t*-Bu)Me_2SiOH. Although the siloxycarbenes formed from **3** and **4** are seemingly not significantly different from those of other silyl ketones [3] [4], no other siloxycarbene addition product was detected. Thus, for example an intramolecular addition of the siloxycarbene center in **c** to the double bond (→ **26**) or an insertion reaction into the neighboring cyclopropane (→ **27**) did not occur (*Scheme 8*).

5.2. On *thermolysis*, cyclopropyl methyl ketones have been reported to undergo a thermal ring opening, leading to γ,δ-unsaturated ketones [14]. This process may be explained *via* a [1,5]-homosigmatropic H-shift. The same mechanism may be assumed for the conversion of the methyl ketones **17** and **19** to the ketones **18** and (*E*/*Z*)-**20**, respectively (*Scheme 4*).

The transformations of **3** and **4** to the acylsilanes **6** and (*E*/*Z*)-**12**, respectively, may be explained analogously. However, this reactivity is not typical for the thermal behavior of acylsilanes, which lead in general to siloxycarbene intermediates [15] [16]. However, thermolysis of **5**, which has no H-atoms in γ-position, leads exclusively to the diene **16**. Its formation may be explained *via* the siloxycarbene intermediate **d** (*Scheme 9*), which reacts *via* an insertion into the C(α)–C(β) bond, leading to the labile cyclobutene **28**, which is further transformed to **16** by an electrocyclic reaction[8]).

Scheme 9



[8]) An analogous mechanism was proposed by *Barton* and *Groh* [17] to explain the thermolysis of the trimethylsilyl analog of the dihydrofuran **15**. They postulated an acylsilane corresponding to **5** as an intermediate, but were not able to isolate or synthesize this compound for verification of this hypothesis. The here presented transformation of **5** → **16** proves it.

This work was supported by the *Swiss National Science Foundation* and *Ciba-Geigy Ltd.*, Basel. We are indebted to the following persons for their help: Miss *B. Brandenberg*, Mr. *F. Bangerter*, Mr. *F. Fehr*, and Mr. *M. Langenauer* (NMR), Mrs. *L. Golgowski*, Dr. *J. Meili*, and Prof. *J. Seibl* (MS), and Mr. *D. Manser* (elemental analysis). We are also grateful to Mr. *A. Wiget* for his help with the experiments.

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 cm × 23.6 mm SiO_2 column. In general, ^{1}H-NMR spectra were taken in $CDCl_3$ solns. on a *Bruker WP-80 CW* (80 MHz) or *WM 300* (300 MHz) instrument. For the description of the thermolysis procedures and the silylation of the thermolysis tubes, see [7].

1. Photolyses. – 1.1. *Photolyses of* **3**. 1.1.1. *In MeCN.* A soln. of **3** (910 mg, 3.24 mmol) in abs. MeCN (200 ml) was irradiated (lamp *B*, filter *A*, conversion 100%). CC of the photolysis mixture (SiO_2, Et_2O/hexane 1:25 and 1% Et_3N) yielded **6** (133 mg, 15%), **7** (64 mg, 7%), **8A** + **B** (230 mg, 25%), and **9** [5] (172 mg, 32%).

*1-[(*tert*-Butyl)dimethylsilyl]-8-methyl-4-methylidenenon-7-en-1-one* (**6**). B.p. 150°/0.1 Torr. UV (2.579 mg in 2 ml): 345 (sh, 70), 360 (120), 374 (160), 389 (140). IR: 3260*w*, 3080*w*, 2950*s*, 2930*s*, 2900*s*, 2880*s*, 2860*s*, 2740*w*, 2720*w*, 1640*s*, 1470*s*, 1465*s*, 1440*s*, 1405*m*, 1390*m*, 1375*m*, 1365*m*, 1340*w*, 1330*w*, 1290*w*, 1255*s* (sh), 1250*s*, 1105*w*, 1095*w*, 1060*w*, 1040*w*, 1010*w*, 985*w*, 940*w*, 910*w*, 890*s*. ^{1}H-NMR (80 MHz): 0.23 (*s*, 2 CH_3Si); 0.98 (*s*, $(CH_3)_3$C); 1.64, 1.71 (2*m*, $w_{1/2}$ = 4, CH_3–C(8), 3H–C(9)); 2.00–2.40 (*m*, 2H–C(3), 2H–C(5), 2H–C(6)); 2.60–2.90 (*m*, 2H–C(2)); 4.70 (*m*, $w_{1/2}$ = 7, CH_2=C(4)); 5.10 (*m*, $w_{1/2}$ = 12, H–C(7)). ^{13}C-NMR (75 MHz): −6.8 (*q*, 2 CH_3Si); 15.4, 25.8 (2*q*, CH_3–C(8), C(9)); 26.6 (*q*, $(CH_3)_3$C); 26.6, 28.1, 36.5, 48.7 (4*t*, C(2), C(3), C(5), C(6)); 109.0 (*t*, CH_2=C(4)); 124.1 (*d*, C(7)); 16.7 (*s*, C–Si); 131.7, 148.9 (2*s*, C(4), C(8)); 246.6 (*s*, C(1)). MS: 280 (< 1, M^+, $C_{17}H_{32}OSi$), 265 (< 1), 252 (< 1), 237 (1), 223 (4), 211 (2), 115 (15), 107 (1), 75 (24), *73* (100), 69 (15), 59 (9), 41 (18).

*5-[(*tert*-Butyl)dimethylsilyl]-3-methyl-3-(4′-methylpent-4′-enyl)-2,3-dihydrofuran* (**7**). IR: 3050*w* (br.), 2950*s*, 2920*s*, 2880*s*, 2850*s*, 2740*w*, 2710*w*, 1635*w*, 1590*w*, 1465*m*, 1460*s*, 1410*w*, 1385*m*, 1370*m*, 1360*m*, 1245*s*, 1170*w*, 1095*w*, 1060*m*, 1005*m*, 950*s*, 865*m*. ^{1}H-NMR (300 MHz): 0.09 (*s*, 2 CH_3–Si); 0.92 ($(CH_3)_3$C); 1.11 (*s*, CH_3–C(3)); 1.36–1.42 (*m*, 2H–C(1′)); 1.59, 1.67 (2*m*, $w_{1/2}$ = 4, CH_3–C(4′), 3H–C(5′)); 1.90–2.05 (*m*, 2H–C(2′)); 3.94 (*AB* system, *J* = 8.6, δ_A = 3.86, δ_B = 4.03, 2H–C(2)); 5.04 (*s*, H–C(4)); 5.10 (*tm*, *J* = 7, $w_{1/2}$ = 4, H–C(3′)). ^{13}C-NMR: −6.5 (*q*, 2 CH_3–Si); 17.6, 25.7, 26.0 (3*q*, CH_3–C(3), CH_3–C(4′), C(2)); 26.5 (*q*, $(CH_3)_3$C); 23.9, 40.6 (2*t*, C(1′), C(2′)); 81.5 (*t*, C(2)); 123.0, 124.7 (2*d*, C(4), C(3′)); 16.3 (*s*, C–Si); 43.3 (*s*, C(3)); 131.3 (*s*, C(4′)); 159.7 (*s*, C(5)). MS: 280 (1, M^+, $C_{17}H_{32}OSi$), 223 (4), 197 (38), 115 (7), 83 (8), 75 (22), *73* (100), 69 (12), 59 (9), 41 (16).

*(1′*RS*,2′*RS*)-3-[(*tert*-Butyl)dimethylsilyl]-1-{(*tert*-Butyl)dimethylsilyl]oxy}-10-methyl-6-methylidene-1-[2′-methyl-2′-(4″-methylpent-3″-enyl)cyclopropyl]-2-oxaundeca-3,9-diene* (**8A** + **B**; 1:1 mixture of two diastereoisomers). IR: 3050*w*, 2950*s*, 2920*s*, 2890*s*, 2850*s*, 2730*w*, 2705*w*, 1640*w*, 1470*s*, 1465*s*, 1455*s*, 1450*m* (sh), 1405*m*, 1385*m*, 1380*m*, 1375*m*, 1360*m*, 1245*s*, 1175*m*, 1125*s*, 1095*m*, 1030*s*, 1000*s*, 935*m*, 890*m*, 860*m* (sh). ^{1}H-NMR (80 MHz): 0.09, 0.12 (2*s*, 2 (2 CH_3–Si)); 0.25–0.60 (*m*, 2H–C(3′)); 0.75–1.50 (*m*, H–C(1′), CH_3–C(2′), 2H–C(1″), 2 $(CH_3)_3$C); 1.59, 1.68 (2*m*, $w_{1/2}$ = 4, 3H–C(11), CH_3–C(10), 3H–C(5″), CH_3–C(4″)); 1.90–2.25 (*m*, 2H–C(8), 2H–C(2″)); 3.00 (*dm*, *J* = 7, $w_{1/2}$ = 4, 2H–C(5)); 4.60–5.25 (*m*, H–C(1), H–C(4), H–C(9), H–C(3″), CH_2=C(6)). ^{13}C-NMR (75 MHz, C_6D_6, without off-resonance, characteristic signals only): 95.0 (C(1)); 98.9, 99.8 (C(4)); 108.7, 109.0 (CH_2=C(6)); 122.2, 122.8, 123.6, 124.1 (C(9), C(3″)); 129.8, 130.2 (C(10), C(4″)); 148.3, 148.4 (C(6)); 157.5, 159.3 (C(3)). MS: 560 (< 1, M^+, $C_{34}H_{64}O_2Si_2$), 545 (< 1), 517 (< 1), 503 (< 1), 491 (< 1), 425 (< 1), 411 (< 1), 369 (1), 275 (4), 207 (4), 189 (5), 163 (6), 133 (4), 123 (5), 121 (6), 115 (14), 113 (10), 107 (16), 93 (13), 81 (13), 75 (50), *73* (100), 69 (24), 59 (17), 55 (10), 41 (17).

1.1.2. *In the Presence of (*t*-Bu)Me_2SiOH.* A soln. of **3** (50 mg, 0.178 mmol) and (*t*-Bu)Me_2SiOH (37 mg, 0.281 mmol) in abs. MeCN (10 ml) was irradiated (lamp *B*, filter *A*, conversion 100%). CC (SiO_2, Et_2O/hexane 1:30) gave **11** (61 mg, 78%).

*(1′*RS*,2′*RS*)-2′-Methyl-2′-(4″-methylpent-3″-enyl)cyclopropanecarbaldehyde Di[(*tert*-Butyl)dimethylsilyl] Acetal* (**11**). IR: 3050*w*, 2950*s*, 2920*s*, 2890*s*, 2850*s*, 1635*w*, 1610*w*, 1465*m*, 1460*m*, 1455*m* (sh), 1450*m* (sh), 1405*m*, 1385*m*, 1380*m*, 1370*m*, 1355*m*, 1245*s*, 1170*m*, 1120*s*, 1070*m*, 1030*s*, 1000*m*, 935*w*, 890*w*, 860*m* (sh). ^{1}H-NMR (80 MHz): 0.11, 0.16 (2*s*, 2 $(CH_3)_2$Si); 0.10–0.60, 0.75–1.50 (2*m*, H–C(1′), 2H–(C(3′), 2H–C(1″)); 0.94 (*s*, 2 $(CH_3)_3$C); 1.11 (*s*, CH_3–C(2′)); 1.61, 1.69 (2*m*, $w_{1/2}$ = 4, CH_3–C(4″), 3H–C(5″)); 1.85–2.25 (*m*, 2H–C(2″)); 4.78 (*d*, *J* = 7,

H–C(1)); 5.10 (*tm*, $J = 7$, $w_{1/2} = 4$, H–C(3″)). ^{13}C-NMR (75 MHz, *ca.* 80% pure, characteristic signals): –4.2, –3.9, –3.5, –2.9 (4*q*, 2(CH_3)$_2$Si); 25.9, 26.0 (2*q*, 2 (CH_3)$_3$C); 41.4 (*t*, C(2″)); 32.8 (*d*, C(1′)); 95.6 (*d*, C(1)); 124.7 (*d*, C(3″)); 131.0 (*s*, C(4″)). MS: 412 (< 1, M^+, $C_{23}H_{48}O_2Si_2$), 397 (1), 355 (7), 275 (7), 211 (7), 189 (5), 122 (7), 115 (13), 107 (14), 93 (11), 81 (10), 75 (68), *73* (100), 69 (32), 59 (11), 41 (19).

1.2. *Photolyses of* **4**. 1.2.1. *In MeCN*. A soln. of **4** (containing 15% of **3**; 131 mg, 0.538 mmol) in abs. MeCN (50 ml) was irradiated (lamp *B*, filter *A*, conversion 100%). CC of the photolysis mixture (SiO_2, Et_2O/hexane 1:25 and 1% Et_3N) yielded **7** (6 mg, 4%), **10** (*ca.* 3 mg, 2%), (*E*/*Z*)-**12** (*ca.* 1:1; 61 mg, 40%), and **13A** + **B** (18 mg, 12%).

(1RS,2SR)-2-Methyl-2-(4′-methylpent-3′-enyl)cyclopropanecarbaldehyde (**10**). B.p. 100°/0.15 Torr. IR: 3380*w*, 3050*w*, 2950*s*, 2920*s* (sh), 2910*s*, 2850*s*, 2820*m*, 2710*m*, 1690*s*, 1535*w* (br.), 1455*m* (sh), 1435*s*, 1415*m*, 1395*m*, 1380*m*, 1370*m*, 1240*w*, 1210*w*, 1170*m*, 1105*w*, 1070*m*, 1040*w*, 1010*w*, 970*m*, 855*m*. ^{1}H-NMR (80 MHz): 0.90–2.25 (*m*, H–C(1), 2H–C(3), 2H–C(1′), 2H–C(2′)); 1.16 (*s*, CH_3–C(2)); 1.56, 1.63 (2*m*, $w_{1/2} = 4$, CH_3–C(4′), 3H–C(5′)); 5.00 (*tm*, $J = 7$, $w_{1/2} = 4$, H–C(3′)); 9.29 (*d*, $J = 5$, CHO). MS: 166 (1, M^+, $C_{11}H_{18}O$), 151 (2), 123 (8), 122 (18), 110 (10), 109 (69), 107 (20), 97 (12), 95 (14), 83 (14), 81 (19), *69* (100), 67 (27), 55 (24), 53 (13), 43 (13), 41 (86).

*(4E)-1-[(*tert*-Butyl)dimethylsilyl]-4,8-dimethylnona-4,7-dien-1-one* ((*E*)-**12**). B.p. 150°/0.1 Torr. UV (5.149 mg in 2 ml): 345 (sh) (70), 359 (115), 373 (150), 388 (130). IR: 3250*w*, 2940*s*, 2920*s*, 2880*s*, 2850*s*, 2710*w*, 1635*s*, 1465*m* (sh), 1460*s*, 1455*s* (sh), 1440*m*, 1400*m*, 1390*m*, 1380*m*, 1370*m*, 1360*m*, 1335*w*, 1325*w*, 1250*s* (sh), 1245*s*, 1100*w*, 1050*w*, 1005*w*, 980*w*, 950*w*, 935*w*. ^{1}H-NMR (300 MHz): 0.18 (*s*, 2 CH_3–Si); 0.92 (*s*, (CH_3)$_3$C); 1.60[9]), 1.62[9]) (2*m*, $w_{1/2} = 4$, CH_3–C(4), CH_3–C(8)); 1.69 (*m*, $w_{1/2} = 4$, 3H–C(9)); 1.18 (*t*, $J = 7$, 2H–C(3)); 2.60–2.70 (*m*, 2H–C(2), 2H–C(6)); 5.08[9]) (*tm*, $J = 7$, $w_{1/2} = 4$, H–C(5), H–C(7)). ^{13}C-NMR (75 MHz): –7.2 (*q*, 2 CH_3–Si); 15.9, 17.4, 25.4 (3*q*, CH_3–C(4), CH_3–C(8), C(9)); 26.2 (*q*, (CH_3)$_3$C); 26.9, 31.4, 48.4 (3*t*, C(2), C(3), C(6)); 123.0, 123.3 (2*d*, C(5), C(7)); 16.3 (*s*, C–Si); 130.7, 133.5 (2*s*, C(4), C(8)); 245.4 (*s*, C(1)). MS: 280 (< 1, M^+, $C_{17}H_{32}OSi$), 265 (1), 252 (< 1), 237 (< 1), 223 (1), 211 (20), 115 (16), 107 (3), 75 (13), *73* (100), 69 (5), 59 (6), 41 (5). Anal. calc. for $C_{17}H_{32}OSi$ (280.53): C 72.79, H 11.50; found: C 72.67, H 11.52.

*(4Z)-1-[(*tert*-Butyl)dimethylsilyl]-4,8-dimethylnona-4,7-dien-1-one* ((*Z*)-**12**; contains *ca.* 20% of **6**). B.p. 150°/0.1 Torr. UV (4.297 mg in 2 ml): 345 (sh) (70), 364 (sh) (115), 377 (140), 380 (130). IR: 3250*w*, 3050*w*, 3020*w*, 2940*s*, 2920*s*, 2895*s*, 2880*s*, 2850*s*, 2720*w*, 1635*s*, 1465*m* (sh), 1460*s*, 1455*s*, 1440*s*, 1400*m*, 1390*m*, 1370*m*, 1360*m*, 1325*w*, 1275*w*, 1245*s*, 1100*w*, 1055*w*, 1005*w*, 935*w*, 885*m*. ^{1}H-NMR (80 MHz): 0.20 (*s*, 2 CH_3–Si); 0.95 (*s*, (CH_3)$_3$C); 1.61 (3H), 1.68 (6H) (2*m*, $w_{1/2} = 4$, CH_3–C(4), CH_3–C(8), 3H–C(9)); 2.00–2.40, 2.50–2.85 (2*m*, 2H–C(2), 2H–C(3), 2H–C(6)); 5.09 (*m*, $w_{1/2} = 10$, H–C(5), H–C(7)). ^{13}C-NMR (75 MHz): –7.0 (*q*, 2 CH_3–Si); 17.6, 23.3, 25.7 (3*q*, CH_3–C(4), CH_3–C(8), C(9)); 26.4 (*q*, (CH_3)$_3$C); 24.1, 26.9 (2*t*, C(2), C(3)); 48.5 (*t*, C(6)); 123.2, 124.5 (2*d*, C(5), C(7)); 16.5 (*s*, C–Si); 131.0, 134.1 (2*s*, C(4), C(8)); 246.1 (*s*, C(1)). MS: 280 (< 1, M^+, $C_{17}H_{32}OSi$), 265 (1), 252 (1), 223 (3), 211 (14), 115 (18), 107 (8), 75 (18), *73* (100), 41 (6). Anal. calc. for $C_{17}H_{32}OSi$ (280.53): C 72.79, H 11.50; found: C 72.98, H 11.13.

*(1′RS,2′SR)-3-[(*tert*-Butyl)dimethylsilyl]-1-{[(*tert*-Butyl)dimethylsilyl]oxy}-6,10-dimethyl-1-[2′-methyl-2′-(4″-methylpent-3″-enyl)cyclopropyl]-2-oxaundeca-3,6,9-triene* (**13A** + **B**; 1:1 mixture of two diastereoisomers). IR: 2960*s*, 2950*s*, 2930*s*, 2920*s*, 2870*s*, 2850*s*, 2720*w*, 1655*w* (br.), 1615*w* (br.), 1590*w*, 1465*s*, 1460*s*, 1410*m*, 1375*m*, 1360*m*, 1350*w*, 1290*w*, 1245*m*, 1165*m*, 1115*m* (br.), 1030*m* (br.), 1000*m*, 950*w*, 935*m*, 865*m*. ^{1}H-NMR (80 MHz): 0.00, 0.25 (*m*, 2(CH_3)$_2$Si); 0.25–0.60 (*m*, 2H–C(3′)); 0.75–1.55 (*m*, H–C(1′), CH_3–C(2′), 2H–C(1″), 2 (CH_3)$_3$C); 1.60, 1.68 (2*m*, $w_{1/2} = 4$, 3H–C(11), CH_3–C(10), CH_3–C(6), 3H–C(5″), CH_3–C(4″)); 1.90–3.10 (*m*, 2H–C(5), 2H–C(8), 2H–C(2″)); 4.75–5.25 (*m*, H–C(1), H–C(4), H–C(7), H–C(9), H–C(3″)). MS: 428 (< 1, [*M*-(*t*-Bu)Me_2SiOH]$^+$), 355 (< 1), 294 (1), 280 (8), 264 (5), 237 (8), 224 (8), 223 (38), 211 (10), 207 (33), 165 (8), 149 (12), 147 (19), 123 (11), 122 (21), 115 (18), 113 (20), 107 (28), 99 (11), 93 (11), 75 (75), *73* (100), 69 (38), 59 (30), 55 (12), 41 (27).

1.2.2. *In the Presence of (*t*-Bu)Me_2SiOH*. A soln. of **3** (containing 15% or **3**; 50 mg, 0.178 mmol) and (*t*-Bu)Me_2SiOH (37 mg, 0.281 mmol) in abs. MeCN (10 ml) was irradiated (lamp *B*, filter *A*, conversion 100%). CC (SiO_2, Et_2O/hexane 1:30) gave **14** (containing 15% of **11**; 56 mg, 76%).

*(1′RS,2′SR)-2′-Methyl-2′-(4″-methylpent-3″-enyl)cyclopropanecarbaldehyde Di[(*tert*-butyl)dimethylsilyl] Acetal* (**14**; contains *ca.* of 15% **11**). IR: 3050*w*, 2950*s*, 2920*s*, 2890*s*, 2850*s*, 2735*w*, 2705*w*, 1465*s*, 1460*s*, 1405*m*, 1385*m*, 1380*m*, 1370*m*, 1360*m*, 1250*s*, 1210*w*, 1185*m*, 1170*m*, 1115*s*, 1080*m*, 1070*m*, 1030*s*, 1000*s*, 955*w*, 935*m*, 885*m*, 860*m*. ^{1}H-NMR (80 MHz): 0.09, 0.15 (2*s*, 2(CH_3)$_2$Si); 0.10–0.60, 0.75–1.60 (2*m*, H–C(2), 2H–C(3′), 2H–C(1″)); 0.91 (*s*, 2 (CH_3)$_3$C); 1.01 (*s*, CH_3–C(2′)); 1.61, 1.68 (2*m*, $w_{1/2} = 4$, CH_3–C(4″), 3H–C(5″)); 1.90–2.25 (*m*, 2H–C(2″)); 4.84 (*d*, $J = 7$, H–C(1)); 5.11 (*tm*, $J = 7$, $w_{1/2} = 4$, H–C(3″)). MS: 412 (< 1, M^+, $C_{23}H_{48}O_2Si_2$),

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[9]) These signals show a positive NOE effect on irradiation at 2.65 ppm.

397 (< 1), 355 (6), 275 (9), 211 (4), 189 (9), 171 (7), 115 (4), 107 (15), 93 (15), 81 (15), 75 (52), *73* (100), 69 (38), 59 (10), 41 (19).

1.3. *Photolysis of* **5**. A soln. of **5** (163 mg, 0.886 mmol) in abs. MeCN (50 ml) was irradiated (lamp *B*, filter *A*, conversion 72%). Pentane (200 ml) was added to the photolysis mixture, and the soln. was washed 3 times with sat. aq. NaCl. The solvent was distilled off over a *Vigreux* column, and CC (SiO_2, Et_2O/hexane 1:25) yielded **5** (45 mg) and **15** (87 mg, 74%).

*5-[(*tert*-Butyl)dimethylsilyl]-2,3-dihydrofuran* (**15**; *ca.* 80% pure). IR: 3080*w*, 2950*s*, 2920*s*, 2880*s*, 2850*s*, 2740*w*, 2710*w*, 1585*m*, 1465*s*, 1460*s*, 1445*m*, 1410*w*, 1385*m*, 1375*w*, 1360*m*, 1275*m*, 1245*s*, 1190*w*, 1175*w*, 1105*m* (sh), 1090*s*, 1005*m*, 990*m*, 925*s*, 905*m*, 880*s*. ^{1}H-NMR (80 MHz): 0.08 (*s*, 2 CH_3–Si); 0.90 (*s*, $(CH_3)_3C$); 2.55 (*td*, $J_1 = 10$, $J_2 = 3$, 2H–C(3)); 4.25 (*t*, $J = 10$, 2H–C(2)); 5.20 (*t*, $J = 3$, H–C(4)). ^{13}C-NMR: –6.6 (*q*, 2 CH_3–Si); 26.4 (*q*, $(CH_3)_3C$); 30.7 (*t*, C(3)); 70.3 (*t*, C(2)); 112.5 (*d*, C(4)); 16.4 (*s*, C–Si); 161.0 (*s*, C(5)). MS: 184 (13 M^+, $C_{10}H_{20}OSi$), 169 (1), 128 (26), 127 (28), 125 (12), 113 (19), 109 (18), 103 (10), 99 (15), 98 (14), *97* (100), 75 (96), 73 (28), 69 (12), 59 (16), 57 (11), 43 (16), 41 (14).

2. Thermolyses. – 2.1. *Thermolyses of* **3**, **4**, *and* **5**. 2.1.1. *Thermolysis of* **3** (94 mg, 0.34 mmol) at 400° in a silylated quartz tube (conversion 80%). CC (SiO_2, Et_2O/hexane 1:40) and HPLC (SiO_2, $p = 45$ bar, flow = 33 ml/min, $\lambda_{DET} = 371$ nm, Et_2O/hexane 1:200) yielded **3** (19 mg), and **6** (75 mg, 80%).

2.1.2. *Thermolysis of* **4** (containing 10% of **3**; 599 mg, 2.14 mmol) at 400° in a silylated quartz tube (conversion 97%). CC (SiO_2, Et_2O/hexane 1:40) and HPLC (SiO_2, $p = 45$ bar, flow = 33 ml/min, $\lambda_{DET} = 371$ nm, Et_2O/hexane 1:200) yielded **4** (18 mg), (*E*)-**12** (176 mg, 33%), and (*Z*)-**12** (182 mg, 34%).

2.1.3. *Thermolysis of* **5** (158 mg, 0.857 mmol) at 500° in a silylated quartz tube (conversion 100%). CC (SiO_2, Et_2O/hexane 1:40) gave **16** (115 mg, 73%).

*2-{[(*tert*-Butyl)dimethylsilyl]oxy}buta-1,3-diene* (**16**). B.p. 120°/50 Torr. UV (0.119 mg in 20 ml): 233 (11500). IR: 3120*w*, 3100*w*, 3020*w*, 2960*s*, 2930*s*, 2895*m*, 2890*m*, 2860*m*, 1630*m*, 1580*s*, 1470*m*, 1460*m*, 1405*m*, 1390*m*, 1370*m*, 1360*m*, 1300*s*, 1280*m*, 1250*s*, 1055*s*, 1000*s*, 980*m*, 940*w*, 915*s*, 910*s*, 870*s*. ^{1}H-NMR (80 MHz): 0.16 (*s*, 2 CH_3–Si); 0.96 (*s*, $(CH_3)_3C$); 4.31 (*m*, $w_{1/2} = 4$, 2H–C(1)); 5.06 (*dm*, $J = 10$, $w_{1/2} = 5$, H–C(4)); 5.49 (*dd*, $J = 17$, 2, H–C(4)); 6.21 (*dd*, $J = 17$, 10, H–C(3)). ^{13}C-NMR (75 MHz): –4.6 (*q*, 2 CH_3–Si); 25.9 (*q*, $(CH_3)_3C$); 96.1 (*t*, C(1)); 114.5 (*t*, C(4)); 134.9 (*d*, C(3)); 18.4 (*s*, C–Si); 155.2 (*s*, C(2)). MS: 184 (3, M^+, $C_{10}H_{20}OSi$), 169 (5), 142 (5), 129 (11), 128 (55), *127* (100), 113 (13), 97 (11), 85 (53), 75 (67), 73 (15), 59 (11), 57 (13), 45 (10), 41 (9).

2.2. *Thermolyses of the Methyl Ketones* **17** *and* **19**. 2.2.1. *Thermolysis of* **17**[10]) [2] (130 mg, 0.721 mmol) at 500° in a silylated quartz tube (conversion 78%). HPLC (SiO_2, $p = 45$ bar, flow = 33 ml/min, $\lambda_{DET} = 220$ nm, Et_2O/hexane 1:15) yielded **17** (28 mg) and **18** (75 mg, 74%).

9-Methyl-5-methylidenedec-8-en-2-one (**18**). IR: 3420*w*, 3080*w*, 3055*w*, 2960*s*, 2920*s*, 2850*s*, 2730*w*, 1715*s*, 1675*w*, 1640*m*, 1440*s* (br.), 1410*m* (sh), 1375*s*, 1355*s*, 1300*w*, 1245*m* (sh), 1225*m*, 1160*s*, 1105*w*, 1030*w*, 980*w*, 890*s*. ^{1}H-NMR (80 MHz): 1.00–2.75 (*m*, 2H–C(3), 2H–C(4), 2H–C(6), 2H–C(7)); 1.63, 1.70 (2*m*, $w_{1/2} = 4$, CH_3–C(9), 3H–C(10)); 2.16 (*s*, 3H–C(1)); 4.71 (*m*, $w_{1/2} = 8$, CH_2); 4.93–5.25 (*m*, H–C(8)). ^{13}C-NMR: 17.7, 25.7, 29.8 (3*q*, C(1), CH_3–C(9), C(10)); 26.4, 29.8, 36.4, 42.0 (4*t*, C(3), C(4), C(6), C(7)); 109.2 (*t*, CH_2=C(5)); 123.9 (*d*, C(8)); 131.7 (*s*, C(9)); 148.2 (*s*, C(5)); 208.3 (*s*, C(2)). MS: 180 (1, M^+, $C_{12}H_{20}O$), 165 (1), 137 (12), 122 (37), 107 (36), 93 (11), 81 (13), 79 (15), *69* (100), 67 (19), 55 (18), 53 (14), 43 (80), 41 (74).

2.2.2. *Thermolysis of* **19**[10]) [2] (64 mg, 0.355 mmol) at 500° in a silylated quartz tube (conversion 86%). HPLC (SiO_2, $p = 45$ bar, flow = 33 ml/min, $\lambda_{DET} = 220$ nm, Et_2O/hexane 1:15) afforded **19** (9 mg) and (*E*/*Z*)-**20** (*ca.* 1.5:1; 48 mg, 87%).

(E/Z)-5,9-Dimethyldeca-5,8-diene-2-one ((*E*/*Z*)-**20**; contains *ca.* 15% of **18**). IR: 3610*w*, 3050*w* (sh), 3030*w* (sh), 2970*s*, 2920*s*, 2910*s*, 2850*s*, 2730*w*, 1715*s*, 1640*w*, 1445*s*, 1435*s*, 1405*m*, 1380*m* (sh), 1375*s*, 1355*s*, 1280*w* (br.), 1225*m*, 1160*s*, 1105*m*, 980*w*, 950*w*, 930*w*, 890*w*, 860*w*. ^{1}H-NMR (80 MHz): 1.66, 1.71 (2*m*, $w_{1/2} = 4$, CH_3–C(5), CH_3–C(9), 3H–C(10)); 2.00–2.90 (*m*, 2H–C(3), 2H–C(4), 2H–C(7)); 4.95–5.25 (*m*, H–C(6), H–C(8)). MS: 180 (1, M^+, $C_{12}H_{20}O$), 165 (1), 147 (1), 122 (58), 109 (13), 108 (10), *107* (100), 93 (13), 91 (14), 81 (21), 79 (15), 69 (35), 67 (21), 55 (16), 53 (13), 43 (80), 41 (49).

3. Additional Experiments. – 3.1. Diels-Alder *Reaction of* **16** *with Methyl Vinyl Ketone* (**21**). A mixture of **16** (23 mg, 0.122 mmol) and **21** (9 mg, 0.128 mmol) was stirred at 80° for 3 h and then cooled to r.t. affording **22** (71%, TLC and ^{1}H-NMR).

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[10]) The synthesis of the cyclopropyl methyl ketones **17** and **19** is described in [2]: cyclopropanation (CH_2I_2, Zn/AgOAc [2]) of geraniol and nerol, respectively, followed by oxidation (CrO_3/pyridine) lead to the aldehydes **9** (58%) [5] and **10** (71%), which were further transformed by *Grignard* reaction (Mg, CH_3I) and oxidation (CrO_3/pyridine) to **17** (80%) and **19** (74%), respectively.

3.2. *Preparation of* **16** *and* Diels-Alder *Reaction with* **21**. To a soln. of (*t*-Bu)Me_2SiCl (6.03 g, 40 mmol) in abs. DMF (20 ml) was added dropwise at r.t. a soln. of **21** (2.5 g, 36 mmol) in abs. Et_3N (5.6 ml) and abs. DMF (2.5 ml). The mixture was stirred at 100–110° for 24 h, cooled to r.t., and worked up in Et_2O. CC (SiO_2, Et_2O/hexane 1:5) afforded a mixture **16**/**22**. Compound **16** was removed by bulb-to-bulb distillation (125°/0.5 Torr) yielding **22** (0.64 g, 7%).

*4-{[(*tert*-Butyl)dimethylsilyl]oxy}cyclohex-3-enyl Methyl Ketone* (**22**). B.p. 125°/25 Torr. UV (3.857 mg in 2 ml): 250 (150). IR: 3050*w*, 3020*w*, 2960*s*, 2960*s*, 2930*s*, 2895*s*, 2885*s*, 2855*s*, 2710*w*, 1710*s*, 1665*s*, 1560*w*, 1470*m*, 1460*m*, 1440*m*, 1430*m*, 1390*m*, 1360*s*, 1350*m* (sh), 1255*s*, 1215*s*, 1190*s*, 1180*s*, 1160*s*, 1050*w*, 1005*m*, 950*w*, 940*m*, 905*m*, 865*s*, 840*s*. ^{1}H-NMR (80 MHz): 0.14 (*s*, 2 CH_3–Si); 0.91 (*s*, $(CH_3)_3C$); 1.25–2.75 (*m*, H–C(1), 2H–C(2), 2H–C(5), 2H–C(6)); 2.15 (*s*, CH_3–C=O); 4.83 (*m*, $w_{1/2}$ = 8, H–C(4)). ^{13}C-NMR: –4.5 (*q*, 2 CH_3–Si); 25.6 (*q*, $(CH_3)_3C$); 27.9 (*q*, CH_3–C=O); 24.9, 25.7, 29.1 (3*t*, C(2), C(5), C(6)); 47.0 (*d*, C(1)); 102.1 (*d*, C(4)); 17.9 (*s*, C–Si); 150.2 (*s*, C(3)); 211.0 (*s*, C=O). MS: 254 (9, M^+, $C_{14}H_{26}OSi$), 211 (12), 197 (26), 128 (13), *127* (100), 85 (12), 75 (35), 73 (41), 59 (8), 43 (12).

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