204. Photochemical Reactions

139th Communication[1])

Photochemistry of Acylsilanes: 1. Siloxycarbene Formation *versus* γ-H-Abstraction

by **Markus E. Scheller**[2]) and **Bruno Frei***

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, Universitätstrasse 16, CH-8092 Zürich

(7.VIII.84)

Summary

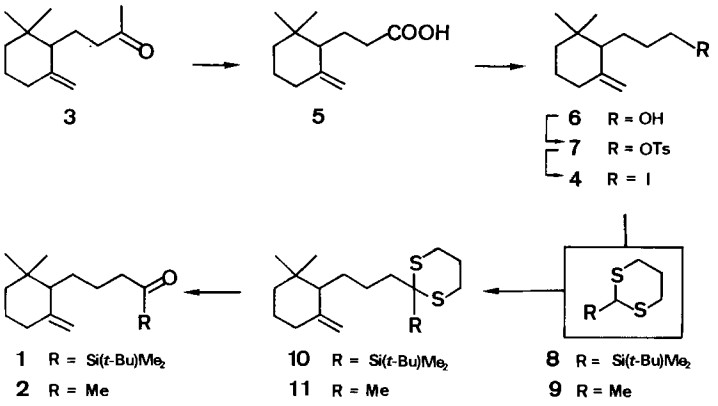
The syntheses and the photolyses of the acylsilane **1** and the corresponding methyl ketone **2** are described. On n,π*-excitation, the silyl ketone **1** as well as the methyl ketone **2** undergo a *Norrish* type II reaction involving γ-H-abstraction and fragmentation to the diene **12**, and acetone (**20**) or the acylsilane **26**, respectively. The methyl ketone **2**, but not the acylsilane **1**, isomerizes to cyclobutanols (**21A–D**). Additionally, compound **1** shows photochemical behavior typical of acylsilanes undergoing rearrangement to the siloxycarbene intermediate **c**. Insertion of **c** into the O–H-bond of the enol **28** leads to compound **13**. Initial trapping of the siloxycarbene **c** by H_2O, however, gives rise to the formation of compounds **16–18.** As minor photolysis products of **1**, the isomers **14** and (*Z*)-**15** were formed; however, on vapor phase thermolysis (520°) of **1**, compounds **14** and (*E*/*Z*)-**15** were obtained in 92% combined yield. To a small extent the acylsilane **1** also undergoes *Norrish* type I cleavage leading to the acid **19**.

1. Introduction. – In recent years, the photochemistry of acylsilanes has attracted considerable interest [2–8]. The pioneering studies of *Brook et al.* [2–4] disclosed that acylsilanes undergo rapid photoisomerization to siloxycarbene intermediates which show intermolecular reaction with alcohols or electron-poor olefins in competition with rearrangement to the starting acylsilanes. A second, slower and less efficient process is the *Norrish* type I photocleavage to silyl and acyl radicals. In the present investigation, the photolysis of the (*t*-butyl)dimethylsilyl ketone **1** was studied in comparison with the corresponding methyl ketone **2** (see *Scheme 1*). The acylsilane **1** was considered to be a suitable model to delineate the intramolecular reactivity of the expected siloxycarbene intermediate which could undergo addition to the C=C bond or an insertion reaction into a C–H bond.

[1]) 138th Communication: [1].

[2]) Part of the planned Ph. D. thesis of *M. E. S.*

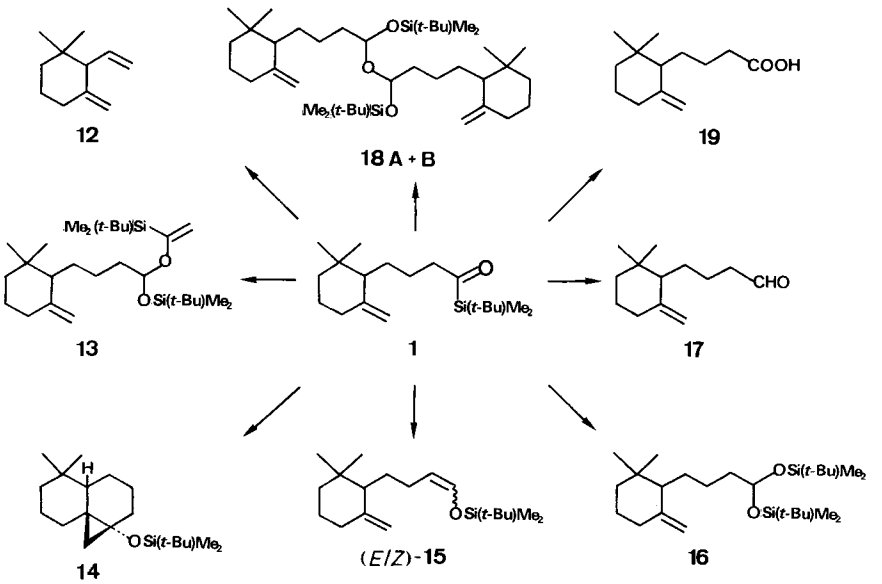
Scheme 1



2. Preparation of the Compounds 1 and 2. – The acylsilane **1** and the methyl ketone **2** were synthesized starting from 7,8-dihydro-γ-ionone **3** in 17 and 30% overall yields, respectively (see *Scheme 1*). Reaction of the iodide **4** (obtained from **3** *via* **5**→**6**→**7** with the 2-lithio derivatives of **8**[3]) and **9** [9] [10] gave the 1,3-dithianes **10** (92%) and **11** (94%) which were dethioacetalized by treatment with $Tl(NO_3)_3 \cdot 3H_2O$ [11] [12] affording **1** (54%) and **2** (88%), respectively.

3. Photolysis Experiments. – 3.1. *Irradiation of the Acylsilane* **1**. The results are given in the *Table* and the photoproducts depicted in *Scheme 2*.

Scheme 2



[3]) Prepared by reaction of 2-lithio-1,3-dithiane with (*t*-butyl)dimethylsilyl chloride.

Table. *Results of the Photolysis of* **1** ($\lambda > 347$ nm)

Solvent	Concentration	Conversion	Product Distribution [%][a]							
	[M]	[%]	**12**	**13**[b]	**14**	(*Z*)-**15**	**16**	**17**	**18A+B**	**19**
MeCN	0.03	90	16	16	3	4	22	3	3	*ca.* 2
THF	0.01	85	60	11	3	–	–	–	–	–
MeCN[c]	0.03	100	–	–	–	–	61	–	–	–

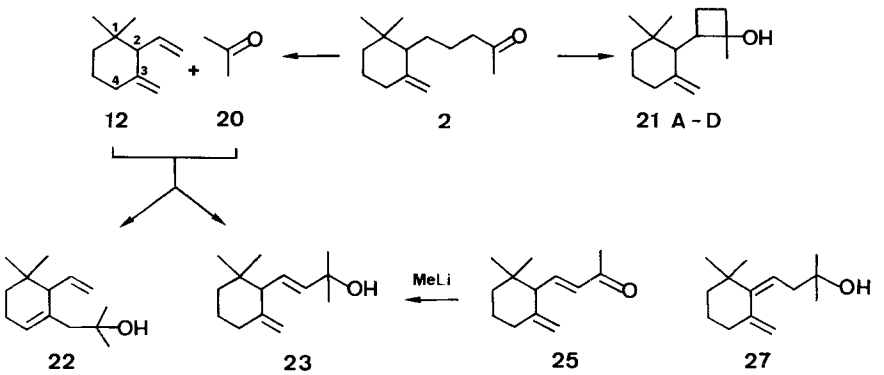
[a]) Based on converted starting material. Yields were determined after chromatography on SiO_2 by ^{1}H-NMR and GC analysis of the fractions.

[b]) Mixture of diastereomers (*ca.* 1:1).

[c]) In the presence of 1 equiv. of (*t*-butyl)dimethylsilanol.

3.2. *Irradiation of* **2** *in pentane* ($\lambda > 280$ nm, 93% conversion) afforded the diene **12** (45%), acetone (**20**, 26%)[4]), the stereoisomeric cyclobutanols **21A** (7%), **21B** (7%), **21C** (6%), and **21D** (6%), and the alcohols **22** (2%), and **23** (3%). On photolysis of **2** in MeCN, the following product distribution was determined: **12** (*ca.* 20%), **21A** (2%), **21B** (5%), **21C+D** (9%), **22** (*ca.* 1%), and **23** (*ca.* 1%). Compounds **22** and **23** were also obtained in 6 and 5% yield, respectively, on photolysis of **12** in the presence of acetone (**20**).

Scheme 3



4. Thermolysis of 1 and 2. – Vapor-phase thermolysis of the acylsilane **1** (520°) afforded **14** (9%), (*E*)-**15** (32%) and (*Z*)-**15** (51%). Under these conditions the methyl ketone **2** proved to be stable and was recovered in 80% yield.

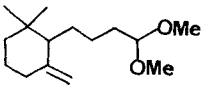
5. Structure of the Products. – The structures of all new compounds were deduced from the spectral data, of which only the most relevant are discussed herein together with the chemical transformations which confirmed the assigned structures. Full data and the assignment of the NMR data are presented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

Acylsilane **1** *and Methyl Ketone* **2**. The acylsilane **1** shows in the IR spectrum the expected long-wavelength carbonyl-stretching absorption at 1635 cm^{-1} as well as in the UV spectrum strong n,π*-bands at $\lambda = 357$ ($\varepsilon = 120$), 372 ($\varepsilon = 160$) and 387 nm ($\varepsilon = 135$) [4] [13]. In comparison, the methyl ketone **2** shows a strong IR band at 1715 cm^{-1} and an UV-maximum at $\lambda = 280$ nm ($\varepsilon = 20$). In the ^{13}C-NMR spectrum, the carbonyl signal of **1** (246 ppm) is shifted *ca.* 40 ppm downfield relative to that of **2**.

[4]) Isolated and identified as its 2,4-dinitrophenylhydrazone.

Acetals **13**, **16**, *and* **18A+B**. The molecular weight determination of **13** (*ca.* 1:1 mixture of diastereomers) and of the two diastereomers **18A** and **18B** indicated the molecular formulas $C_{27}H_{54}O_2Si_2$ and $C_{38}H_{74}O_3Si_2$, respectively. Furthermore, compounds **13** and **18A+B** were treated with aq. HCl in MeOH leading to the dimethylacetal **24** which was also obtained from the aldehyde **17**. The acetal **16** was hydrolyzed to the aldehyde **17**.

24



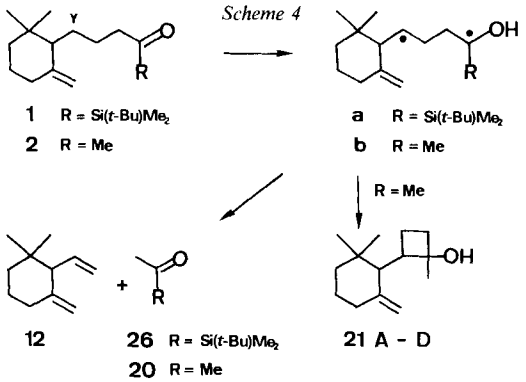
Tricyclic Compound **14**. The configuration was assigned by X-ray analysis of the *p*-nitrobenzoate of a decalol obtained from **14** in two steps: hydrolysis and subsequent reduction of the resulting ketone with $NaBH_4$ (see [14]).

*The enol ethers (*E*)- and (*Z*)-***15*** were synthesized in 43% yield (3:7 mixture) by the reaction of the aldehyde **17** with (*t*-butyl)dimethylsilyl chloride/Et_3N in DME [15]. The configuration of the enol-ether moiety was assigned by the ^{1}H-NMR coupling constants J = 12 and 6 Hz, for (*E*)- and (*Z*)-**15**, respectively.

Cyclobutanols **21A–D**. The spectral data of the 4 isomers are very similar. In particular, the cyclobutanol moiety is evidenced by the MS peaks m/z = 180 ($M^+ - C_2H_4$) and m/z = 150 ($M^+ - C_3H_6O$). *The alcohol* **23** was prepared by reaction of γ-ionone (**25**) with MeLi.

6. Discussion. – On n,π^*-excitation, the acylsilane **1** as well as the methyl ketone **2** react by γ-H-abstraction leading to the 1,4-diradicals **a** and **b**, respectively. These intermediates fragment to give the diene **12** and – *via* their enol forms – the ketones **26** and **20** (see *Scheme 4*). This process is quite common of carbonyl compounds[5]), however, to the best of our knowledge it has not been reported for acylsilanes until now. In competition to the *Norrish* type II fragmentation, the diradical **b** undergoes cyclization to the diastereomeric cyclobutanols **21A–D**. With the acylsilane **1**, this process was not observed; the lack of formation of the cyclobutanols analogous to **21A–D** may be due to the steric interaction of the bulky (*t*-butyl)dimethylsilyl group with the cyclohexyl moiety. The novel products **22** and **23** (see *Scheme 3*) isolated on n,π^*-excitation of **2**, arise by reaction of acetone (**20**) with the diene **12**, as could be demonstrated by photolysis of **12** in the presence of acetone (see *above*). Presumably compound **22** is formed by a photo-ene reaction of acetone involving addition to the CH_2=C(3) group and abstraction of an H-atom at C(4) (see *Scheme 3*). The alternative photo-ene reaction involving acetone addition to the ethenyl moiety and abstraction of the H–C(2) would lead to the conjugated diene **27** (see *Scheme 3*). Under the irradiation conditions, compound

Scheme 4

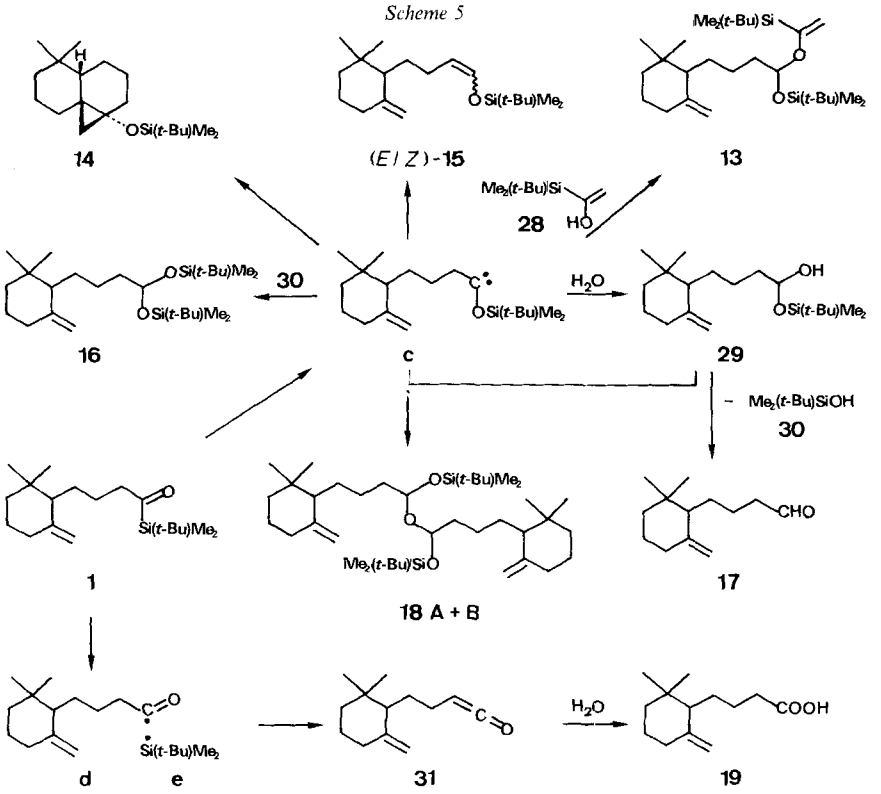


[5]) For a recent review, see [16].

23 could then be formed in a secondary process by a 1,3-H-shift from **27** which was, however, not detected.

As expected, **1** undergoes photoreactions *via* the siloxycarbene **c** (see *Scheme 5*). However, it is surprising that the intermediate **c** reacts efficiently with the enol **28** arising from *Norrish* type II reaction of **1** (see *above*). An insertion reaction of the carbene center into the O–H bond leads to compound **13**. This finding indicates that the trapping rate of the siloxycarbene **c** by the enol **28** is faster than the tautomerization of **28** to the ketone **26**. In contrast to **13**, the products **16**, **17**, and **18A+B** arise from initial trapping of the siloxycarbene **c** with H_2O leading to the intermediate hemiacetal **29**[6]). The latter can react with the siloxycarbene **c** furnishing compound **18A+B**. Alternatively, **29** can decompose to the aldehyde **17** and the silanol **30** which also undergoes addition to the siloxycarbene intermediate **c** affording the acetal **16**. On irradiation of **1** in the presence of 1 equiv. of the silanol **30**, the acetal **16** was isolated as the only product (see the *Table*)[7]).

Scheme 5



[6]) The variable yields of **16**, **17**, and **18A+B** are due to the varying amounts of H_2O present in the photolyses systems, although the irradiations were carried out as far as possible under anhydrous conditions.

[7]) A mechanistic study by *Dalton et al.* disclosed that the formation of acetals upon irradiation of acylsilanes in the presence of alcohols occurred exclusively *via* the siloxycarbene intermediate formed from the acylsilane triplet state [6].

The isomers **14** (2%) and (*Z*)-**15** (4%) were formed as minor products on photolysis of **1**. Thermolysis of **1**, however, led to **14** and (*E*/*Z*)-**15** as the only isolated products in 92% combined yield. The formation of enol ethers is a known type of reaction on thermolysis of acylsilanes [5] [17]. As has been postulated previously for analogous substrates, the siloxycarbene intermediate **c** may undergo a 1,2-H-shift leading to (*E*/*Z*)-**15**[8]). On the other hand the transformation of **1**→**14** represents a novel type of process involving an intramolecular addition of the carbene center of **c** to an electron-rich methylidene group. Due to the low yields of compounds **14** and (*E*/*Z*)-**15** on photolysis of **1** (see the *Table*), a kinetic analysis could not be carried out, which would have made clear whether the siloxycarbene **c** is an actual intermediate, or whether the addition reaction to the electron-rich double bond and the 1,2-H-shift involve other – *e.g.* ionic – intermediates[9]).

Finally, the acid **19** presumably arises by a *Norrish* type I photoreaction (**1**→**d** + **e**; see *Scheme 5*) which was previously reported for acylsilanes [3] [4]. Disproportionation of the acyl and silyl radicals **d** and **e** to the ketene **31** and silane followed by hydration of **31** leads to the acid **19**.

7. Conclusion. – On n,π^*-excitation the acylsilane **1** shows as main process *Norrish* type II fragmentation (**1**→**12** + **26**), thus behaving analogously to the corresponding methylketone **2**. Most interestingly, the initially formed enol **28** reacts rapidly with the siloxycarbene intermediate **c** leading to **13**. *Norrish* type I reaction (**1**→**19**) and the isomerization of **1** to **14** and (*Z*)-**15**) are only minor processes. In the presence of hydroxy compounds, the siloxycarbene **c** is trapped rapidly and the other photoprocesses are suppressed (*cf.* the formation of the acetal **16** as the only isolated product on photolysis of **1** in the presence of the silanol **30**). These findings demonstrate that *the siloxycarbene* **c** *reacts preferentially by an intermolecular insertion into an O–H bond rather than by an intramolecular addition to a C=C bond or by an insertion into a neighboring C–H bond.*

This work was supported by the *Swiss National Science Foundation* and *Ciba-Geigy Ltd.*, Basle. We are indebted to the following persons for their help: Miss *B. Brandenberg*, Mr. *F. Fehr* and *M. Langenauer* (NMR), Mrs. *L. Golgowsky* and Prof. *J. Seibl* (MS) and Mr. *D. Manser* (elemental analysis). We are also grateful to Mr. *K. Job* for the preparation of starting material, and would like to acknowledge the generous gift of 7,8-dihydro-γ-ionone by Dr. *G. Ohloff, Firmenich S.A.*, Geneva.

Experimental Part

General. See [18] except as noted below. Analytical gas chromatography was performed using a 25 m × 0.33 mm *Ucon 50 HB 5100* glass capillary. Column chromatography was carried out on silica gel *60 Merck* 0.040–0.063 mm, 230–400 mesh ASTM (SiO_2) according to [19] ('flash chromatography'). Analytically pure samples were obtained, in general, after repeated column chromatography 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. All UV spectra were taken in pentane solutions. In general, ^{1}H-NMR spectra were taken in $CDCl_3$-

---

[8]) Prior attempts to trap the siloxycarbene intermediates intermolecularly on thermolysis of acylsilanes, however, have not been successful [8] [17].

[9]) *Dalton et al.* have shown that the formation of cyclopropanes on photolysis of acylsilanes in the presence of dimethyl fumarate results from reaction of both the S_1 and T_1 states of the acylsilane rather than *via* addition of a photochemically generated siloxycarbene to the electron poor olefin [7].

solutions on a *Varian HA-100* instrument (100 MHz) or, exceptionally (as indicated below), on a *Bruker WP-80 CW* (80 MHz) or *WM 300* (300 MHz) instrument in $CDCl_3$-solutions. Photolysis experiments were carried out under Ar using a 125-W Hg medium pressure lamp [18]. *Filter solution A* ($Pb(NO_3)_2$/KBr), see [20]. Abs. THF and Et_2O were obtained by distillation from Na/benzophenone (under Ar). Abs. MeCN was obtained by filtration through Al_2O_3 *Woelm bas. Super*, activity I.

1. Preparation of the Acylsilane 1. – 1.1. *Degradation of* **3** *to* **5**. To a solution of I_2 (26.1 g, 103 mmol) in pyridine (35 ml) was added at r.t. **3** (18.15 g, 93 mmol). The mixture was stirred at 100° for 1 h, concentrated under reduced pressure and stirred with 2N NaOH (300 ml) at 100° overnight. At 0°, the mixture was acidified with 2N HCl and extracted with Et_2O. The org. phase was then concentrated to *ca.* half of its volume, extracted with 4N Na_2CO_3, and the aq. phase was again acidified with 2N HCl and extracted with Et_2O. After washing with *ca.* 20% $Na_2S_2O_3$ this org. phase was worked up affording the acid **5** (9.35 g, 51%).

3-(2',2'-Dimethyl-6'-methylidenecyclohexyl)propionic Acid (**5**). IR: 3500–2500*m* br., 2920*s*, 2860*s*, 1700*s*, 1640*m*, 1440*m* (sh), 1410*s*, 1380*m*, 1365*m*, 1290*s*, 1235*m*, 1215*m*, 1160*w*, 930*m* br., 890*s*. ^{1}H-NMR (80 MHz): 0.88, 0.93 (2*s*, 2 CH_3–C(2')); 1.10–2.60 (*m*, 2H–C(2), 2H–C(3), H–C(1'), 2H–C(3'), 2H–C(4'), 2H–C(5')); 4.55, 4.79 (2*m*, $w_{1/2}$ = 4.5, CH_2=C(6')); 9.75–10.60 (*m*, COOH). Full spectral data are given of the corresponding methyl ester which was obtained by reaction of **5** with CH_2CN_2.

Methyl 3-(2',2'-Dimethyl-6'-methylidenecyclohexyl)propionate. B.p. 90°/0.02 Torr. IR: 3060*w*, 2930*s*, 2900*s* (sh), 2860*s*, 1735*s*, 1640*m*, 1455*m* (sh), 1445 *m* (sh), 1430*s*, 1415*w* (sh), 1380*m*, 1360*m*, 1320*m*, 1290*m*, 1255*m*, 1230*m*, 1190*m*, 1160*s*, 1050*w*, 890*s*, 860*w*. ^{1}H-NMR: 0.84, 0.90 (2*s*, 2 CH_3–C(2')); 1.00–2.45 (*m*, 2H–C(2), 2H–C(3), 2H–C(3'), 2H–C(4'), 2H–C(5'), 2H–C(1')); 3,60 (*s*, CH_3O); 4.51, 4.75 (2*m*, $w_{1/2}$ = 4, CH_2=C(6')). ^{13}C-NMR: 26.4, 28.3 (2*q*, 2 CH_3–C(2')); 51.2 (*q*, CH_3O); 21.8, 23.6, 32.1, 32.7, 36.0 (5*t*, C(2), C(3), C(3'), C(4'), C(5')); 109.7 (*t*, CH_2=C(6')); 53.5 (*d*, C(1')); 34.8 (*s*, C(2')); 148.5 (*s*, C(6')); 174.3 (*s*, C=O). MS: 210 (9, M^+, $C_{13}H_{22}O_2$), 195 (46), 163 (21), 154 (40), 136 (11), 135 (18), 123 (26), 122 (11), 121 (44), 119 (14), 109 (59), 107 (19), 99 (16), 95 (33), 94 (29), 93 (47), 91 (25), 82 (23), 81 (60), 80 (14), 79 (43), 77 (25), 74 (13), *69* (100), 68 (16), 67 (38), 65 (13), 59 (14), 55 (38), 53 (26), 43 (18), 41 (92). Anal. calc. for $C_{13}H_{22}O_2$ (210.32): C 74.24, H 10.54; found: C 74.39, H 10.52.

1.2. *Reduction of* **5**. A solution of the acid **5** (4.15 g, 21.1 mmol) in abs. Et_2O (30 ml) was added dropwise over 10 min. to a suspension of $LiAlH_4$ (1.20, 31.6 mmol) in abs. Et_2O (100 ml). After stirring for 2 h at r.t., the mixture was worked up by adding *Celite*, sat. aq. NH_4Cl and $MgSO_4$ and chromatographed (hexane/Et_2O) affording **6** (3.39 g, 88%).

3-(2',2'-Dimethyl-6'-methylidenecyclohexyl)-1-propanol (**6**)[10]. B.p. 115°/0.05 Torr. IR: 3620*w* (sh), 3590*w*, 3490*w* br., 3060*w*, 2930*s*, 2860*s*, 1640*w*, 1445*m* br., 1380*m*, 1365*m*, 1270*m* br., 1225*w*, 1180*w*, 1105*w*, 1060*m* br., 1020*m* (sh), 950*w*, 895*s*. ^{1}H-NMR: 0.82, 0.90 (2*s*, 2 CH_3–C(2')); 1.00–1.80 (*m*, 2H–C(2), 2H–C(3), 2H–C(3'), 2H–C(4')); 1,80–2,20 (*m*, 2H–C(5'), H–C(1')); 3.32 (*m*, $w_{1/2}$ = 6, OH); 3.40–3.70 (*m*, 2H–C(1)); 4.52, 4.73 (2*m*, CH_2 = C(6')). ^{13}C-NMR: 26.4, 28.4 (2*q*, 2CH_3–C(2')); 22.6, 23.7, 31.3, 32.3, 36.1 (5*t*, C(2), C(3), C(3'), C(4'), C(5')); 62.8 (*t*, C(1)); 109.0 (*t*, CH_2=C(6')); 53,9 (*d*, C(1')); 34.8 (*s*, C(2')); 149.2 (*s*, C(6')). MS: 182 (10, M^+, $C_{12}H_{22}O$), 167 (28), 149 (28), 126 (14), 123 (28), 121 (20), 109 (51), 108 (16), 107 (16), 95 (49), 93 (44), 91 (16), 82 (24), 81 (43), 79 (27), 77 (16), 71 (14), 70 (12), *69* (100), 68 (18), 67 (43), 55 (40), 53 (19), 43 (19), 41 (88). Anal. calc. for $C_{12}H_{22}O$ (182.31): C 79.06, H 12.16; found: C 78.86, H 11.97.

1.3. *Transformation of* **6** *into* **7**. To a solution of **6** (789 mg, 4.32 mmol) in pyridine (10 ml) was added in portions TsCl (1.12 g, 5.87 mmol) under Ar. After stirring for 5 min. at r.t., the mixture was kept at *ca.* 5° overnight, diluted with Et_2O, and the org. phase was washed with sat. aq. $CuSO_4$ and worked up as usual yielding **7** (1.18 g, 81%).

3-(2',2'-Dimethyl-6'-methylidenecyclohexyl)propyl p-Toluenesulfonate (**7**). UV (0.373 mg in 20 ml): 223 (11900); UV (4.06 mg in 5 ml): 256 (340), 261 (430), 267 (400), 272 (350). IR: 3060*w*, 3030*w*, 2920*s*, 2860*s*, 1635*w*, 1595*w*, 1440*m*, 1360*s*, 1350*s* (sh), 1305*w*, 1285*w*, 1175*s*, 1095*w*, 950*s*, 940*s* (sh), 920*s*, 890*s*, 860*m*. ^{1}H-NMR: 0.75, 0.85 (2*s*, 2 CH_3–C(2')); 1.00–1.75 (*m*, 2H–C(2), 2H–C(3), 2H–C(3'), 2H–C(4')); 1.75–2.10 (*m*, 2H–C(5'), H–C(1')). 2.41 (*s*, CH_3-Ph); 3.9–4.1 (*m*, 2H–C(1)); 4.43, 4,68 (2*m*, $w_{1/2}$ = *ca.* 5, CH_2=C(6')); 7.54 (*AA'*,*BB'*-system, *J* = 8, δ_A = 7.31, δ_B = 7.76, 4 arom. H). ^{13}C-NMR: 21.5 (*q*, CH_3-Ph); 26.4, 28.2 (2*q*, 2 CH_3–C(2'); 22.1, 23.5, 27.4, 31.9, 35.7 (5*t*, C(2), C(3), C(3'), C(4'), C(5')); 70.9 (*t*, C(1)); 109.4 (*t*, CH_2=C(6')); 53.3 (*d*, C(1')); 127.8, 129.8 (2*d*, 4 arom. C); 34.7 (*s*, C(2')); 133.4 (*s*, C(arom.)–CH_3); 144.6 (*s*, C(arom.)–SO_3); 148.6 (*s*, C(6')). MS: 336 (< 1, M^+, $C_{19}H_{28}O_3S$), 164 (24), 163 (22), 149 (81), 123 (23), 122 (24), 121 (35), 109 (28), 108 (87), 107 (52), 105 (21), 96 (12), 95 (55), 94 (24), *93* (100), 92 (14), 91 (64), 82 (13), 81 (59), 80 (21), 79

[10]) The alcohols (+)- and (–)-**6** have been prepared previously [21].

(84), 78 (16), 77 (35), 69 (52), 68 (12), 67 (49), 65 (21), 57 (16), 55 (48), 53 (23), 44 (61), 43 (42), 41 (84). Anal. calc. for $C_{19}H_{28}O_3S$ (336.50): C 67.82, H 8.39, S 9.53; found: C 67.94, H 8.53, S 9.39.

1.4. *Transformation of* **7** *into* **4**. To a solution of **7** (1.18 g, 3.51 mmol) in dimethoxyethane (35 ml) was added in portions NaI (1.0 g, 6.67 mmol) at r.t. with stirring. After stirring for 18 h at 50°, the mixture was diluted with Et_2O, washed with H_2O and 20% aq. $Na_2S_2O_3$ and worked up. Distillation (90°/0.02 Torr) afforded **4** (986 mg, 96%).

2-(3'-Iodopropyl)-1,1-dimethyl-3-methylidenecyclohexane (**4**). UV (5.880 mg in 5 ml): 257 (310). IR: 3060*w*, 2920*s*, 1635*w*, 1520*w* br., 1435*m*, 1380*w*, 1360*m*, 1210*m*, 1160*w*, 965*w*, 890*m*. ^{1}H-NMR: 0.83, 0.89 (2*s*, 2 CH_3–C(1)); 1.0–1.8 (*m*, 2H–C(2'), 2H–C(1'), 2H–C(5), 2H–C(6)); 1.8–2.1 (*m*, H–C(2), 2H–C(4)); 3.0–3.3 (*m*, 2H–C(3')); 4.53, 4.73 (2*m*, $w_{1/2} \approx 4$, CH_2=C(3)). ^{13}C-NMR (75 MHz): 26.4, 28.3 (2*q*, 2 CH_3–C(1)); 7.8 (*t*, C(3')); 23.6, 27.4, 32.0, 32.2, 35.9 (5*t*, C(1'), C(2'), C(4), C(5), C(6)); 109.2 (*t*, CH_2=C(3)); 53.0 (*d*, C(2)); 34,7 (*s*, C(1)); 148.8 (*s*, C(3)). MS: 292 (5, M^+, $C_{12}H_{21}I$), 249 (13), 123 (20), 109 (45), 95 (51), 93 (16), 91 (17), 83 (15), 81 (51), 79 (22), *69* (100), 67 (33), 57 (17), 55 (36), 53 (15), 43 (20), 41 (63).

1.5. *Preparation of* **8**. To a solution of 1,3-dithiane (4.08 g, 33.9 mmol) in abs. THF (80 ml) was added under Ar dropwise at –78° BuLi (1.6M in hexane, 25.2 ml, 40.3 mmol). The mixture was stirred for 1 h at –30°, again at –78° a solution of (*t*-butyl)dimethylchlorosilane (6.08 g, 40.3 mmol) in abs. THF (20 ml) was added dropwise, and the mixture was allowed to come to r.t. slowly. After *ca.* 2 h, the reaction was complete (TLC), the mixture was worked up with Et_2O and distillation (115°/0.03 Torr) afforded **8** (7.49 g, 94%).

*2-[(*tert*-Butyl)dimethylsilyl]-1,3-dithiane* (**8**). UV (3.178 mg in 20 ml): 244 (720). IR: 2920*s*, 2890*s*, 2850*s*, 1460*m*, 1420*m*, 1410*m*, 1390*m*, 1360*m*, 1270*m*, 1250*s*, 1160*m*, 1080*m* br., 995*w*, 935*w*, 910*m*, 875*m*. ^{1}H-NMR: 0.10 (*s*, 2 CH_3–Si); 0.98 (*s*, 3 CH_3–C–Si); 1.95–2.20 (*m*, 2H–C(5)); 2.50–3.05 (*m*, 2H–C(4), 2H–C(6)); 3.79 (*s*, H–C(2)). ^{13}C-NMR: –7.2 (*q*, 2 CH_3–Si); 27.0 (*q*, 3 CH_3–C–Si); 26.2 (*t*, C(5)); 31.4 (*t*, C(4), C(6)); 32.5 (*d*, C(2)); 17.6 (*s*, C–Si). MS: 234 (10, M^+, $C_{10}H_{22}S_2Si$), 177 (49), 149 (42), 119 (17), 87 (72), *73* (100), 59 (24), 41 (17). Anal. calc. for $C_{10}H_{22}S_2Si$ (234.51): C 51.22, H 9.46, S 27.35; found: C 51.20, H 9.53, S 27.24.

1.6. *Reaction of* **4** *with* **8**. To a solution of **8** (2.50 g, 10.7 mmol) in abs. THF (77 ml) and abs. HMPA (7 ml) was added under Ar dropwise at –78° BuLi (1.2M in hexane, 10 ml, 12.0 mmol). After stirring for 1.5 h at –30°, again at –78° a solution of **4** (2.66 g, 9.10 mmol) in abs. THF (55 ml) was added. The mixture was stirred for 2.5 h at r.t., diluted with Et_2O, washed with 2M HCl and H_2O and worked up as usual. Distillation (210°/0.02 Torr) afforded **10** (3.35 g, 92%).

*2-[3'-(2'',2''-Dimethyl-6''-methylidenecyclohexyl)propyl]-2-[(*tert*-butyl)dimethylsilyl]-1,3-dithiane* (**10**). UV (2.247 mg in 5 ml): 232 (900), 245 (970). IR: 3060*w*, 2900*s*, 2850*s*, 2660*w*, 1635*w*, 1460*m* (sh), 1445*m*, 1420*m* (sh), 1410*m* (sh), 1380*m*, 1360*m*, 1245*m*, 1160*w*, 1005*w*, 930*w*, 890*m*. ^{1}H-NMR: 0.20, 0.24 (2*s*, 2 CH_3–Si); 0.88, 0.96 (2*s*, 2 CH_3–C(2'')); 1.04 (*s*, 3 CH_3–C–Si); 1.20–2.60 and 2.9–3.25 (2*m*, 2H–C(4), 2H–C(6), 2H–C(1'), 2H–C(2'), 2H–C(3'), H–C(1''), 2H–C(3''), 2H–C(4''), 2H–C(5'')); 4.59, 4.78 (2*m*, $w_{1/2} = 4$, CH_2=C(6'')). ^{13}C-NMR: –5.2, –5.3 (2*q*, 2 CH_3–Si); 26.7 (*q*, CH_3–C(2'')); 28.4 (*q*, CH_3–C(2''), 3 CH_3–C–Si); 23.6[11]), 23.7, 25.1, 26.9, 27.1, 32.2, 36.1, 38.4 (9*t*, C(4), C(5), C(6), C(1'), C(2'), C(3'), C(3''), C(4''), C(5'')); 109.0 (*t*, CH_2=C(6'')); 54.1 (*d*, C(1'')); 19.8 (*s*, C–Si); 34.8 (*s*, C(2'')); 41.1 (*s*, C(2)); 149.5 (*s*, C(6'')). MS: 398 (< 1, M^+, $C_{22}H_{42}S_2Si$), 175 (16), 165 (14), 145 (15), 115 (11), 101 (12), 95 (17), 91 (26), 81 (17), 79 (11), 77 (12), *75* (100), 73 (85), 69 (28), 67 (15), 59 (20), 57 (14), 56 (14), 55 (22), 44 (12), 43 (22), 42 (11), 41 (49). Anal. calc. for $C_{22}H_{42}S_2Si$ (398.79): C 66.26, H 10.62, S 16.08; found: C 66.29, H 10.60, S 16.27.

1.7. *Transformation of* **10** *into* **1**. To a solution of **10** (712 mg, 1.78 mmol) in THF (14 ml) and H_2O (15 drops) was added at 0° at once a solution of $Tl(NO_3)_3 \cdot 3H_2O$ (1.11 g, 2.50 mmol) in abs. MeOH (19 ml, *Fluka*). After stirring at r.t. for 5 min, the mixture was diluted with hexane, filtered through *Celite*, washed with sat. NaCl and dried ($MgSO_4$). Chromatography (hexane/Et_2O 20:1) yielded **1** (297 mg, 54%).

*4-(2',2'-Dimethyl-6'-methylidenecyclohexyl)-1-[(*tert*-butyl)dimethylsilyl]-1-butanone* (**1**). B.p. 150°/0.07 Torr; m.p. 62–64°. UV (1.7414 mg in 2 ml): 357 (120), 372 (160), 387 (135). IR: 3060*w*, 2940*s* (sh), 2920*s*, 2900*s*, 2850*s*, 1635*s*, 1460*m*, 1390*w* (sh), 1380*m*, 1360*m*, 1245*m*, 1000*w*, 945*w*, 890*m*. ^{1}H-NMR (300 MHz): 0.16 (*s*, 2CH_3–Si); 0.80, 0.89 (2*s*, 2 CH_3–C(2')); 0.92 (*s*, 3 CH_3–C–Si); 1.00–1.65 (*m*, 2H–C(3), 2H–C(4), 2H–C(3'), 2H–C(4')); 1.68 (*dd*, $J_1 = 8$, $J_2 = 7$, H–C(1')); 1.93–2.10 (*m*, 2H–C(5')); 2.47–2.66 (*m*, 2H–C(2)); 4.53, 4.73 (2*m*, $w_{1/2} = 4$, CH_2=C(6')). ^{13}C-NMR (75 MHz): –6.9 (*q*, 2 CH_3–Si); 26.5 (*q*, 3 CH_3–C–Si, CH_3–C(2')); 28.3 (*q*, CH_3–C(2')); 20.8, 23.8, 26.2, 32.3, 36.1 (5*t*, C(3), C(4), C(3'), C(4'), C(5')); 50.5 (*t*, C(2)); 109.1 (*t*, CH_2=C(6')); 54,1 (*d*, C(1')); 16.6 (*s*, C–Si); 34.8 (*s*, C(2')); 149.1 (*s*, C(6')); 246.7 (*s*, C(1)). MS: 308 (1, M^+, $C_{19}H_{36}OSi$), 293 (1), 280 (1), 265 (2), 251 (8), 115 (31), 75 (35), *73* (100), 69 (7), 59 (9), 41 (9). Anal. calc. for $C_{19}H_{36}OSi$ (308.58): C 73.95, H 11.76; found: C 73.79, H 11.76.

---

[11]) *Presumably* 2 signals overlapping.

2. Preparation of the Butanone 2. – 2.1. *Transformation of* **4** *into* **11**. Reaction of lithio 2-methyl-1,3-dithiane [prepared from 2-methyl-1,3-dithiane (**9**, 1.35 g, 10.1 ml, *Fluka purum*) in abs. THF (100 ml) and HMPA (2 ml) with BuLi (1.6M in hexane, 7.8 ml, 12.5 mmol)] and **4** (2.94 g 10.1 mmol) in abs. THF (20 ml) as described in *Sect. 1.5* afforded after distillation (200°/0.06 Torr) **11** (2.82 g, 94%).

2-Methyl-2-[3'-(2",2"-dimethyl-6"-methylidenecyclohexyl)propyl]-1,3-dithiane (**11**). UV (2.3075 mg in 5 ml): 226 sh (620), 250 (760). IR: 3060*w*, 2930*s*, 2905*s*, 2860*s*, 1640*m*, 1460*m* (sh), 1445*s*, 1420*m*, 1415*m*, 1380*m*, 1370*m*, 1365*m*, 1340*w*, 1315*w*, 1295*w*, 1275*m*, 1235*m*, 1210*w*, 1185*w*, 1180*w*, 1170*w*, 1160*w*, 1145*w*, 1115*w*, 1080*w*, 1045*w*, 1035*w*, 1000*w*, 975*w*, 940*w*, 910*m*, 890*s*, 870*w*. ^{1}H-NMR: 0.80, 0.89 (2*s*, 2 CH_3–C(2")); 1.57 (*s*, CH_3–C(2)); 0.80–2.20 (*m*, 2H–C(5), 2H–C(1'), 2H–C(2'), 2H–C(3'), H–C(1"), 2H–C(3"), 2H–C(4"), 2H–C(5")); 2.65–2.90 (*m*, 2H–C(4), 2H–C(6)); 4.55, 4.75 (2*m*, $w_{1/2}$ = 4, CH_2=C(6)). ^{13}C-NMR: 15.2 (*q*, CH_3–C(2)); 27.7, 28.4 (2*q*, 2 CH_3–C(2")); 22.7, 23.6, 25.4, 26.2, 26.4[11]), 32.3, 36.1, 41.7 (9*t*, C(4), C(5), C(6), C(1'), C(2'), C(3'), C(3"), C(4"), C(5")); 108.9 (*t*, CH_2=C(6")); 53.5 (*d*, C(1")); 34.7 (*s*, C(2")); 49.1 (*s*, C(2)); 148.9 (*s*, C(6")). MS: 298 (32, M^+, $C_{17}H_{30}S_2$), 223 (38), 191 (14), 190 (16), 175 (19), 161 (18), 150 (19), 136 (14), 135 (19), *133* (100), 121 (14), 109 (16), 107 (14), 106 (26), 101 (10), 99 (26), 95 (19), 93 (14), 91 (10), 81 (28), 79 (20), 73 (11), 69 (30), 67 (16), 59 (19), 55 (21), 53 (10), 41 (40). Anal. calc. for $C_{17}H_{30}S_2$ (298.56): C 68.39, H 10.13; found: C 68.57, H 10.10.

2.2. *Transformation of* **11** *into* **2**. To a solution of **11** (2.59 g, 8.67 mmol) in THF (70 ml) and H_2O (75 drops) was added at 0° at once a solution of $Tl(NO_3)_3 \cdot 3H_2O$ (5.31 g, 12.0 mmol) in MeOH (*Fluka*, 90 ml). After 5 min, the mixture was worked up as described for **1** and chromatographed (hexane/Et_2O 20:1) yielding **2** (1.59 g, 88%).

5-(2',2'-Dimethyl-6'-methylidenecyclohexyl)-2-pentanone (**2**). B.p. 120°/0.08 Torr. UV (11.17 mg in 2 ml): 280 (20). IR: 3060*w*, 2930*s*, 2910*s* (sh), 2860*s*, 1715*s*, 1640*m*, 1460*m* (sh), 1450*m*, 1440*m* (sh), 1410*m*, 1380*m*, 1360*s*, 1285*w*, 1225*w*, 1180*m*, 1155*m*, 890*s*. ^{1}H-NMR (80 MHz): 0.75, 0.85 (2*s*, 2 CH_3–C(2')); 1.10–1.80 and 1.85–2.10 (2*m*, 2H–C(4), 2H–C(5), H–C(1'), 2H–C(3'), 2H–C(4'), 2H–C(5')); 2.05 (*s*, 3H–C(1)), 2.20–2.50 (*m*, 2H–C(3)); 4.51, 4.72 (2*m*, $w_{1/2} \approx 4$, CH_2=C(6')). ^{13}C-NMR: 26.4, 28.3 (2*q*, 2 CH_3–C(2')); 29.5 (*q*, C(1)); 22.5, 23.7, 25.9, 32.3, 36.1 (5*t*, C(4), C(5), C(3'), C(4'), C(5')); 43.6 (*t*, C(3)); 109.1 (*t*, CH_2=C(6')); 53.9 (*d*, C(1')); 34.7 (*s*, C(2')); 148.9 (*s*, C(6')); 207.7 (*s*, C(2)). MS: 208 (10, M^+, $C_{14}H_{24}O$), 193 (19), 190 (18), 175 (14), 152 (27), 150 (62), 147 (12), 135 (41), 123 (30), 121 (14), 109 (52), 108 (12), 107 (40), 95 (31), 94 (65), 93 (23), 91 (15), 84 (13), 82 (32), 81 (46), 80 (12), 79 (42), 77 (13), 71 (11), *69* (100), 68 (14), 67 (25), 55 (25), 53 (14), 43 (85), 41 (51). Anal. calc. for $C_{14}H_{24}O$ (208.35): C 80.71, H 11.61; found: C 80.60, H 11.62.

3. Photolyses of the Acylsilane 1. – 3.1. *In MeCN*. A solution of **1** (1.19 g, 3.86 mmol) in abs. MeCN (120 ml) was irradiated (lamp *B*, filter *A*, 90% conversion) under Ar. Chromatography (hexane/Et_2O gradient, O→5% Et_2O) yielded fractions from which the following product distribution was determined (^{1}H-NMR, GC): **12** (16%), **13** (16%), **14** (3%), (*Z*)–**15** (4%), **16** (22%), **17** (3%), **18A**+**B** (3%), and **19**[12]) (*ca.* 2%).

1,1-Dimethyl-3-methylidene-2-vinylcyclohexane (**12**). IR: 3070*m*, 3010*w*, 2960*s* (sh), 2940*s* (sh), 2920*s*, 2900*s* (sh), 2860*s*, 2840*s*, 1640*m*, 1455*m*, 1450*m* (sh), 1435*m*, 1420*m*, 1380*m*, 1360*m*, 1210*w*, 1220*w*, 1190*w*, 1145*w*, 1005*m*, 990*m*, 915*s*, 890*s*, 870*w*, 860*w*, 845*w*. ^{1}H-NMR (300 MHz): 0.81, 0.90 (2*s*, 2 CH_3–C(1)); 1.20–1.65 (*m*, 2H–C(5), 2H–C(6)); 1.95–2.15 and 2.20–2.35 (2*m*, 2H–C(4)); 2.42 (*d*, *J* = 10, H–C(2)); 4.58, 4.73 (2*m*, $w_{1/2}$ = 5, CH_2=C(3)); 4.98–5.09 (*m*, CH=CH_2); 5.92 (*ddd*, J_1 = 17, J_2=J_3 = 10, CH=CH_2). ^{13}C-NMR (75 MHz): 23.2, 29.4 (2*q*, 2 CH_3–C(1)); 23.5, 34.7, 39.2 (3*t*, C(4), C(5), C(6)); 108.3 (*t*, CH_2=C(3)); 116.4 (*t*, CH=CH_2); 59.1 (*d*, C(2)); 137.5 (*d*, CH=CH_2); 34.9 (*s*, C(1)); 149.9 (*s*, C(3)). MS: 150 (25, M^+, $C_{11}H_{18}$), 135 (21), 107 (26), 94 (19), 93 (15), 91 (11), 82 (14), 81 (20), 80 (12), 79 (43), 77 (13), *69* (100), 67 (14), 55 (12), 53 (10), 41 (40).

*2-[(*tert*-Butyl)dimethylsilyl]-4-[(*tert*-butyl)dimethylsilyloxy]-7-(2',2'-dimethyl-6'-methylidenecyclohexyl)-3-oxa-1-heptene* (**13**; *mixture of 2 diastereomers* (*ca.* 1:1)). B.p. 150°/0.03 Torr. IR: 3060*w*, 3020*w*, 2945*s* (sh), 2920*s*, 2900*s* (sh), 2850*s*, 1645*m*, 1460*m*, 1435*m* (sh), 1390*m* br., 1360*m*, 1340*w*, 1250*s*, 1200*w*, 1170*w*, 1115*m*, 1100*m*, 1055*m*, 980*w* br., 935*w*, 890*m*, 870*m*, 835*s*. ^{1}H-NMR (300 MHz): 0.06, 0.065, 0.07, 0.11 (4*s*, 2$(CH_3)_2$Si); 0.83, 0.91 (2*s*, 2 CH_3–C(2')); 0.88, 0.92 (2*s*, 2$(CH_3)_3$CSi); 1.00–1.85 and 1.95–2.10 (2*m*, 2H–C(5), 2H–C(6), 2H–C(7), H–C(1'), 2H–C(3'), 2H–C(4'), 2H–C(5')); 4.38, 4.77 (2*m*, $w_{1/2} \approx 4$, 2H–C(1)); 4.52, 4.72 (2*m*, $w_{1/2} \approx 4$, CH_2=C(6')); 5.28 (*dd*, J_1=J_2 = 5, H–C(4)). ^{13}C-NMR (75 MHz): −6.3, −6.2, −4.0, −3.9, −3.3 (5*q*, 2$(CH_3)_2$Si); 25.9, 26.9 (2*q*, 2($C(CH_3)_3$CSi, CH_3–C(2')); 28.5 (*q*, CH_3–C(2')); 23.4, 23.5, 23.8[11]), 26.5[11]), 32.1, 32.3, 36.0, 36.1 (10*t*, C(6), C(7), C(3'), C(4'), C(5')); 37.1, 37.3 (2*t*, C(5)); 98.2, 98.3 (2*t*, C(1)); 109.2 (*t*, CH_2=C(6')); 54.3, 54.4 (2*d*, C(1')); 96.0 (*d*, C(4)); 16.5, 18.2 (2*s*, 2$(CH_3)_3C$Si); 34.8 (*s*, C(2')); 149.1 (*s*, C(6')); 165.8 (*s*, C(2)).

---

[12]) Full spectral data are given of the corresponding methyl ester which was obtained by reaction of **19** with CH_2N_2.

MS: 409 (1, $M^+ - C_4H_9$), 309 (2), 275 (5), 251 (2), 178 (14), *177* (100), 147 (13), 121 (54), 109 (11), 107 (13), 95 (60), 81 (31), 75 (23), 73 (69), 69 (14). Anal. calc. for $C_{27}H_{54}O_2Si_2$ (466.90): C 69.53, H 11.59; found: C 69.92, H 11.66. Mol. weight calc. for $C_{27}H_{54}O_2Si_2$: 466; found: 460.

*3-[(*tert*-Butyl)dimethylsilyloxy]-8,8-dimethyltricyclo[5.4.0.0^{1,3}]undecane* (**14**). B.p. 130°/0.05 Torr. IR: 3050*w*, 2950*s*, 2925*s*, 2900*s* (sh), 2880*s* (sh), 2855*s*, 1470*m*, 1460*m*, 1450*m* (sh), 1405*w*, 1385*m*, 1360*m*, 1335*m*, 1295*w*, 1280*m*, 1250*s*, 1220*m*, 1210*m*, 1180*w*, 1165*w*, 1155*m*, 1130*m*, 1110*w*, 1085*w*, 1065*m*, 1045*w*, 1035*m*, 1000*m*, 985*m*, 970*m*, 960*m*, 940*m* (sh), 935*m*, 890*w*, 880*m*, 860*m*, 835*s*. ^{1}H-NMR: 0.09, 0.15 (2*s*, 2 CH_3–Si); 0.47 (*AB*-system, $J = 5$, $\delta_A = 0.40$, $\delta_B = 0.53$, 2H–C(2)); 0.88 (*s*, CH_3–C(8), 3 CH_3–C–Si); 0.97 (*s*, CH_3–C(8)); 1.00–1.95 (*m*, 2H–C(4), 2H–C(5), 2H–C(6), H–C(7), 2H–C(9), 2H–C(10), 2H–C(11)). ^{13}C-NMR: –3.2, –3.7 (2*q*, 2 CH_3–Si); 25.5, 29.8 (2*q*, 2 CH_3–C(8)); 25.8 (*q*, 3 CH_3–C–Si); 18.4, 18.9, 20.8, 23.5, 28.8, 29.8, 38.6 (7*t*, C(2), C(4), C(5), C(6), C(9), C(10), C(11)); 45.5 (*d*, C(7)); 18.0 (*s*, C–Si); 24.4 (*s*, C(1)); 33.6 (*s*, C(8)); 60.0 (*s*, C(3)). MS: 308 (6, M^+, $C_{19}H_{36}OSi$), 251 (25), 238 (15), 181 (10), 175 (12), 117 (11), 115 (13), 95 (12), 91 (13), 81 (10), *75* (100), 73 (61), 69 (17), 59 (11), 55 (19), 43 (16), 41 (31). Anal. calc. for $C_{19}H_{36}OSi$ (308.58): C 73.95, H 11.76; found: C 74.05, H 11.78.

*(Z)-1-[(*tert*-Butyl)dimethylsilyloxy]-4-(2',2'-dimethyl-6'-methylidenecyclohexyl)-1-butene* ((*Z*)-**15**). B.p. 115°/0.2 Torr. IR: 3060*w*, 3020*w*, 2940*s*, 2920*s*, 2895*s*, 2845*s*, 1650*s*, 1645*s*, 1465*m* (sh), 1455*m*, 1445*m*, 1395*m*, 1380*m*, 1360*m*, 1250*s*, 1170*w*, 1110*s*, 1095*s*, 1050*m*, 1000*w*, 935*w*, 885*s*, 865*m*, 830*s*. ^{1}H-NMR: 0.16 (*s*, 2 CH_3–Si); 0.86, 0.95 (2*s*, 2 CH_3–C(2')); 0.96 (*s*, 3 CH_3–C–Si); 1.00–2.25 (*m*, 2H–C(3), 2H–C(4), H–C(1'), 2H–C(3'), 2H–C(4'), 2H–C(5')); 4.50 (*dd*, $J_1 = 7$, $J_2 = 6$, H–C(2)); 4.61, 4.79 (2*m*, $w_{1/2} \approx 4$, CH_2=C(6')); 6.20 (*dt*, $J_1 = 6$, $J_2 = 1$, H–C(1)). ^{13}C-NMR: –5.3 (*q*, 2 CH_3–Si); 25.7 (*q*, $(CH_3)_3$C–Si); 26.3, 28.5 (2*q*, 2 CH_3–C(2')); 22.5, 23.8, 26.6, 32.6, 36.5 (5*t*, C(3), C(4), C(3'), C(4'), C(5')); 108.9 (*t*, CH_2=C(6')); 53.8 (*d*, C(1')); 111.0 (*d*, C(2)); 138.4 (*d*, C(1)); 18.3 (*s*, $(CH_3)_3C$–Si); 34.8 (*s*, C(2')); 149.2 (*s*, C(6')). MS: 308 (< 1, M^+, $C_{19}H_{36}OSi$), 251 (14), 184 (10), 176 (34), 175 (27), 171 (21), 170 (40), 161 (42), 155 (33), 133 (19), 128 (16), 127 (49), 119 (22), 115 (23), 105 (15), 99 (18), 91 (24), 81 (16), 75 (68), *73* (100), 69 (22), 59 (22), 41 (29). Anal. calc. for $C_{19}H_{36}OSi$ (308.58): C 73.95, H 11.76; found: C 74.04, H 11.67.

*4-(2',2'-Dimethyl-6'-methylidenecyclohexyl)butanal-bis[(*tert*-butyl)dimethylsilyl]-acetal* (**16**). B.p. 150°/0.03 Torr. IR: 3060*w*, 2950*s*, 2925*s*, 2900*m*, 2850*s*, 1640*w*, 1465*m*, 1460*m*, 1380*m*, 1370*m* (sh), 1360*m*, 1250*s*, 1210*w*, 1140*m*, 1065*m* br., 1020*m*, 995*m*, 940*m*, 890*m*, 860*m* (sh), 830*s*. ^{1}H-NMR (300 MHz): 0.08, 0.10 (2*s*, 2$(CH_3)_2$Si); 0.83, 0.91 (2*s*, 2 CH_3–C(2')); 0.89 (*s*, 2 $(CH_3)_3$C–Si); 1.00–1.65 (*m*, 2H–C(2), 2H–C(3), 2H–C(4), 2H–C(3'), 2H–C(4')); 1.65–1.75 and 1.95–2.10 (2*m*, H–C(1'), 2H–C(5')); 4.52, 4.72 (2*m*, $w_{1/2} \approx 4$, CH_2=C(6')); 5.10 (*dd*, $J_1 = J_2 = 5$, H–C(1)). ^{13}C-NMR (75 MHz): –4.1, –4.0, –3.5[11]) (4*q*, 2$(CH_3)_2$ Si); 26.0 (*q*, 2$(CH_3)_3$C–Si); 26.9, 28.5 (2*q*, 2 CH_3–C(2')); 23.5, 23.8, 26.4, 32.2, 36.0 (5*t*, C(3), C(4), C(3'), C(4'), C(5')); 41.1 (*t*, C(2)); 109.0 (*t*, CH_2=C(6')); 54.3 (*d*, C(1')); 93.8 (*d*, C(1)); 18.1 (*s*, 2 C–Si); 34.8 (*s*, C(2')); 149.3 (*s*, C(6')). MS: 440 (< 1, M^+, $C_{25}H_{52}O_2Si_2$), 425 (< 1), 383 (1), 276 (13), 275 (54), 177 (66), 147 (53), 135 (13), 133 (13), 121 (56), 109 (19), 107 (21), 95 (73), 93 (12), 81 (39), 79 (10), 75 (49), *73* (100), 69 (35), 67 (14), 59 (11), 57 (15), 55 (11), 41 (22). Anal. calc. for $C_{25}H_{52}O_2Si_2$ (440.67): C 68.08, H 11.91; found: C 68.18, H 11.77.

4-(2',2'-Dimethyl-6'-methylidenecyclohexyl)butanal (**17**). B.p. 90°/0.03 Torr. UV (6.588 mg in 5 ml): 290 (45). IR: 3060*w*, 2930*s*, 2910*s* (sh), 2860*s*, 2810*m*, 2710*m*, 1725*s*, 1640*m*, 1460*m* (sh), 1450*m*, 1440*m* (sh), 1410*w*, 1385*m*, 1365*m*, 890*s*. ^{1}H-NMR: 0.81, 0.90 (2*s*, 2 CH_3–C(2')); 1.10–1.85 and 1.90–2.10 (2*m*, 2H–C(3), 2H–C(4), H–C(1'), 2H–C(3'), 2H–C(4'), 2H–C(5')); 2.25–2.50 (*m*, 2H–C(2)); 4.54, 4.74 (2*m*, $w_{1/2} \approx 4$, CH_2=C(6')); 9.70 (*t*, $J = 2$, H–C(1)). ^{13}C-NMR: 26.4, 28.3 (2*q*, 2 CH_3–C(2')); 20.8, 23.6, 25.9, 32.2, 36.1 (5*t*, C(3), C(4), C(3'), C(4'), C(5')); 43.9 (*t*, C(2)); 109.2 (*t*, CH_2=C(6')); 53.9 (*d*, C(1')); 202.2 (*d*, C(1)); 34.7 (*s*, C(2')); 148.9 (*s*, C(6')). MS: 194 (2, M^+, $C_{13}H_{22}O$), 161 (10), 150 (19), 135 (14), 109 (28), 107 (20), 95 (22), 94 (17), 93 (15), 91 (20), 82 (16), 81 (38), 79 (28), *69* (100), 68 (15), 67 (28), 57 (15), 55 (34), 44 (17), 43 (21), 41 (60). Anal. calc. for $C_{13}H_{22}O$ (194.32): C 80.35, H 11.41; found: C 80.29, H 11.18.

Methyl 4-(2',2'-dimethyl-6'-methylidene-1'-cyclohexyl)-butyrate (*methyl ester of* **19**). IR: 3070*w*, 2950*s* (sh), 2940*s*, 2910*s* (sh), 2870*s*, 1740*s*, 1640*w*, 1460*m* (sh), 1450*m*, 1435*m*, 1415*w*, 1385*m*, 1360*m*, 1250*m*, 1200*m*, 1160*m*, 890*s*. ^{1}H-NMR: 0.80, 0.89 (2*s*, 2 CH_3–C(2')); 1.00–1.85 and 1.90–2.15 (2*m*, 2H–C(3), 2H–C(4), H–C(1'), 2H–C(3'), 2H–C(4'), 2H–C(5')); 2.20–2.40 (*m*, 2H–C(2)); 3.62 (*s*, CH_3O); 4.53, 4.74 (2*m*, $w_{1/2} = 4$, CH_2=C(6')). ^{13}C-NMR: 26.4, 28.4 (2*q*, 2 CH_3–C(2')); 51.4 (*q*, CH_3O); 23.7[11]), 26.0, 32.3, 34.2, 36.2 (6*t*, C(2), C(3), C(4), C(3'), C(4'), C(5')); 109.1 (*t*, CH_2=C(6')); 53.8 (*d*, C(1')); 34.8 (*s*, C(2')); 149.1 (*s*, C(6')); 174.3 (*s*, C(1)). MS: 224 (9, M^+, $C_{14}H_{24}O_2$), 209 (58), 177 (20), 168 (41), 149 (19), 135 (20), 124 (10), 123 (40), 109 (79), 108 (18), 107 (22), 95 (58), 94 (31), 93 (27), 91 (13), 82 (28), 81 (56), 79 (33), 77 (13), *69* (100), 68 (18), 67 (32), 59 (10), 55 (32), 53 (15), 43 (14), 41 (61).

*Bis[1-[(*tert*-Butyl)dimethylsilyloxy]-4-(2',2'-dimethyl-6'-methylidenecyclohexyl)butyl]-ether, Isomer A* (**18A**). B.p. 225°/0.09 Torr. IR: 3060*w*, 2940*s* (sh), 2920*s*, 2850*s*, 1640*w*, 1465*m* (sh), 1460*m*, 1435*m* (sh), 1380*m*,

1360*m*, 1340*w*, 1250*m*, 1180*w*, 1145*w*, 1110*m*, 1005*m*, 985*s*, 950*w*, 935*w*, 890*m*, 835*s*. ^{1}H-NMR (300 MHz): 0.08, 0.10 (2*s*, 2 CH_3–Si); 0.88, 0.91 (2*s*, 2 CH_3–C(2')); 0.89 (*s*, 3 CH_3–C–Si); 1.00–1.65 and 1.95–2.10 (2*m*, 2H–C(2), 2H–C(3), 2H–C(4), H–C(1'), 2H–C(3'), 2H–C(4'), 2H–C(5')); 4.52, 4.72 (2*m*, $w_{1/2} \approx 4$, CH_2=C(6')); 4.92 (*m*, $w_{1/2} = 5$, H–C(1)). ^{13}C-NMR (75 MHz): –4.3, –3.9 (2*q*, 2 CH_3–Si); 25.9 (*q*, 3 CH_3–C–Si); 26.6, 28.4 (2*q*, 2 CH_3–C(2')); 22.5, 22.7, 23.7[11]), 26.4[11]), 32.2[11]), 36.0[11]), (10*t*, C(3), C(4), C(3'), C(4'), C(5')); 37.4, 37.5 (2*t*, C(2)); 108.9 (*t*, CH_2=C(6')); 54.1 (*d*, C(1')); 94.1, 94.2 (2*d*, C(1)); 18.0 (*s*, C–Si); 34.7 (*s*, C(2')); 149.1 (*s*, C(6')). MS: 445 (1), 383 (1), 309 (5), 275 (6), 251 (8), 178 (27), *177* (100), 176 (18), 175 (11), 161 (16), 147 (13), 135 (11), 127 (13), 121 (51), 109 (18), 107 (16), 95 (54), 93 (10), 81 (34), 79 (10), 75 (74), 73 (51), 69 (35), 67 (12), 55 (12), 41 (19). Mol. weight calc. for $C_{38}H_{74}O_3Si_2$: 635.18; found: 618.

Isomer B (**18B**). B.p. 225°/0.09 Torr. IR: 3060*w*, 2920*s*, 2850*s*, 1640*w*, 1465*m* (sh), 1460*m*, 1435*m* (sh), 1380*m*, 1360*m*, 1340*w*, 1250*s*, 1130*s*, 1005*m*, 980*s* br., 950*m*, 940*m*, 890*s*, 875*m*, 840*s*. ^{1}H-NMR (300 MHz): 0.08, 0.10 (2*s*, 2 CH_3–Si); 0.82, 0.90 (2*s*, 2 CH_3–C(2')); 0.89 (*s*, 3 CH_3–C–Si); 1.05–1.75 and 1.90–2.15 (2*m*, 2H–C(2), 2H–C(3), 2H–C(4), H–C(1'), 2H–C(3'), 2H–C(4'), 2H–C(5')); 4.52, 4.71 (2*m*, $w_{1/2} \approx 4$, CH_2=C(6')); 4.95 (*m*, $w_{1/2} = 5$, H–C(1)). ^{13}C-NMR (75 MHz): –3.7, –3.6 (2*q*, 2 CH_3–Si); 26.0 (*q*, 3 CH_3–C–Si); 26.6, 28.5, (2*q*, 2 CH_3–C(2')); 22.8, 23.2, 23.8[11]), 26.5[11]), 32.4[11]), 36.2[11]) (10*t*, C(3), C(4), C(3'), C(4'), C(5')); 38.5, 38.6 (2*t*, C(2)); 109.0 (*t*, CH_2=C(6')); 54.2, 54.3 (2*d*, C(1')); 94.9, 95.0 (2*d*, C(1)); 18.2 (*s*, C–Si); 34.9 (*s*, C(2')); 149.3 (*s*, C(6')). MS: 445 (1), 383 (2), 309 (3), 275 (3), 251 (5), 178 (25), *177* (100), 176 (11), 175 (8), 161 (11), 147 (13), 135 (11), 127 (9), 121 (67), 109 (18), 107 (19), 95 (74), 93 (8), 81 (39), 79 (8), 75 (70), 73 (56), 69 (33), 67 (10), 55 (9), 41 (12). Mol. weight calc. for $C_{38}H_{74}O_3Si_2$: 635.18; found: 677.

3.2. *In THF.* A solution of **1** (509 mg, 1.65 mmol) in abs. THF (200 ml) was irradiated (lamp *B*, filter *A*, 85% conversion). Evaporation of the solvent over a *Vigreux* column and distillation (110°, *ca.* 20 Torr) afforded **12** (129 mg, 60%). Chromatography (hexane/Et_2O 20:1) gave the starting material **1** (83 mg), **13** (68 mg, 11%), and **14** (12 mg, 3%).

3.3. *In MeCN in the Presence of (*tert*-Butyl)dimethylsilanol.* A solution of **1** (1.30 g, 4.22 mmol) and (*tert*-Butyl)dimethylsilanol [22] (560 mg, 4.23 mmol) in abs. MeCN (130 ml) was irradiated (lamp *B*, filter *A*, 100% conversion). Chromatography (hexane/Et_2O 50:1) gave **16** (1.14 g, 61%).

4. Photolyses of the Butanone 2. – 4.1. *In Pentane.* A solution of **2** (1.0 g, 4.80 mmol) in pentane (200 ml) was irradiated (lamp *B*, *Pyrex*, 93% conversion). The solvent was evaporated over a *Vigreux* column and the distillate was treated with a solution of 2,4-dinitrophenylhydrazine in EtOH/H_2SO_4 [23] affording acetone 2,4-dinitrophenylhydrazone (278 mg, 26%; m.p. 127°, subl. ([23]: 128°)). Distillation of the photolysis mixture (110°/12 Torr) gave **12** (302 mg, 45%) and chromatography (hexane/Et_2O 5:1) of the residue afforded the starting material **2** (70 mg), **21A** (69 mg, 7%), **21B** (69 mg, 7%), **21C**+**D**[13]) (1:1 mixture, 127 mg, 12%) **22** (9 mg, 2%), and **23** (13 mg, 3%).

2-(2',2'-Dimethyl-6'-methylidenecyclohexyl)-1-methyl-1-cyclobutanol, Isomer A (**21A**). B.p. 90°/0.06 Torr. IR: 3560*m*, 3060*w*, 2970*s*, 2930*s*, 2910*s* (sh), 2860*s*, 1635*w*, 1455*m*, 1440*m*, 1430*w* (sh), 1380*m*, 1370*m*, 1360*m*, 1340*m*, 1320*w*, 1290*w*, 1275*w*, 1260*w*, 1230*m*, 1220*m*, 1155*m*, 1100*w*, 1070*w*, 970*w*, 955*w*, 930*m*, 915*m*, 895*s*, 860*w*. ^{1}H-NMR: 0.81, 0.85 (2*s*, 2 CH_3–C(2')); 1.20 (*s*, CH_3–C(1)); 0.80–2.80 (*m*, H–C(2), 2H–C(3), 2H–C(4), H–C(1'), 2H–C(3'), 2H–C(4'), 2H–C(5'), OH); 4.75–4.88 (*m*, CH_2=C(6')). ^{13}C-NMR (75 MHz): 27.4, 29.2, 29.7 (3*q*, 2 CH_3–C(2'), CH_3–C(1)); 23.9, 28.0, 32.2, 33.8, 34.7 (5*t*, C(3), C(4), C(3'), C(4'), C(5')); 109.9 (*t*, CH_2=C(6')); 43.3 (*d*, C(2)); 56.6 (*d*, C(1')); 35.6 (*s*, C(2')); 78.4 (*s*, C(1)); 153.6 (*s*, C(6')). MS: 208 (3, M^+, $C_{14}H_{24}O$), 193 (5), 190 (5), 180 (7), 150 (28), 144 (16), 135 (29), 122 (15), 111 (14), 109 (24), 107 (37), 95 (34), 94 (25), 93 (19), 81 (34), 79 (28), *69* (100), 67 (16), 58 (56), 55 (18), 44 (39), 43 (41), 41 (37). Anal. calc. for $C_{14}H_{24}O$ (208.35): C 80.71, H 11.61; found: C 80.60, H 11.72.

Isomer B (**21B**). B.p. 90°/0.07 Torr. IR: 3610*m*, 3580–3300*w* br., 3060*w*, 2970*s*, 2920*s*, 2900*s* (sh), 2860*s*, 1640*m*, 1635*w* (sh), 1455*m* (sh), 1450*s*, 1435*m*, 1380*s*, 1370*m*, 1365*m*, 1340*w*, 1320*w*, 1290*w*, 1240*m*, 1220*m*, 1210*m*, 1190*m*, 1165*m*, 1130*m* br., 1080*m*, 1050*w*, 985*w*, 960*m*, 930*m*, 915*m*, 890*s*, 875*m*, 860*w*. ^{1}H-NMR: 0.86, 0.91 (2*q*, 2 CH_3–C(2')); 1.35 (*q*, CH_3–C(1)); 0.7–2.5 (*m*, H–C(2), 2H–C(3), 2H–C(4), H–C(1'), 2H–C(3'), 2H–C(4'), 2H–C(5'), OH); 4.61, 4.74 (2*m*, $w_{1/2} \approx 5$, CH_2=C(6')). ^{13}C-NMR (75 MHz): 27.7, 29.2, 29.4 (3*q*, 2 CH_3–C(2'), CH_3–C(1)); 19.1, 23.3, 32.5, 34.2, 34.6 (5*t*, C(3), C(4), C(3'), C(4'), C(5')); 109.9 (*t*, CH_2=C(6'));

---

[13]) Analytical samples of **21C** and **21D** were obtained by transformation of **21C**+**D** into the corresponding acetates, which could be separated by HPLC (50 bar, hexane/Et_2O 10:1), and cleavage of the acetates with $LiAlH_4$.

44.1 (*d*, C(2)); 51.7 (*d*, C(1')); 33.7 (*s*, C(2')); 75.3 (*s*, C(1)); 149.8 (*s*, C(6')). MS: 208 (1, M^+, $C_{14}H_{24}O$), 193 (4), 190 (3), 180 (11), 150 (25), 135 (25), 122 (15), 111 (20), 109 (28), 107 (37), 95 (29), 94 (30), 93 (19), 82 (23), 81 (33), 79 (33), *69* (100), 67 (17), 55 (21), 43 (46), 41 (39). Anal. calc. for $C_{14}H_{24}O$ (208.35): C 80.71, H 11.61; found: C 80.68, H 11.78.

Isomer C (**21C**). M.p. 75–77°. IR: 3610*m*, 3600–3300*w* br., 3060*w*, 2970*s*, 2930*s*, 2900*s* (sh), 2860*s*, 1640*m*, 1635*w* (sh), 1470*w* (sh), 1465*m* (sh), 1455*m*, 1440*m* (sh), 1435*m* (sh), 1385*m*, 1375*m*, 1365*m*, 1330*m*, 1280*w*, 1255*m*, 1250*m*, 1175*w*, 1160*w*, 1140*w*, 1100*w*, 1080*w*, 1050*w*, 960*m*, 935*m*, 890*s*, 870*w*, 860*w*. ^{1}H-NMR (300 MHz): 0.89, 0.97 (2*s*, 2 CH_3–C(2')); 1.24 (*s*, CH_3–C(1)); 1.00–1.85 (*m*, 2H–C(3), 2H–C(4), 2H–C(3'), 2H–C(4'), H–C(5')); 1.88 (*d*, *J* = 9, H–C(1')); 2.00–2.10 (*m*, H–C(5')); 2.39 (*ddd*, J_1 = 10, J_2=J_3 = 9, H–C(2)); 4.49, 4.67 (2*m*, $w_{½} \approx 4$, CH_2=C(6')). ^{13}C-NMR (75 MHz): 22.5, 27.8, 29.4 (3*q*, 2 *C*H_3–C(2'), *C*H_3–C(1)); 17.4, 23.3, 32.1, 34.3, 34.7 (5*t*, C(3), C(4), C(3'), C(4'), C(5')); 109.2 (*t*, *C*H_2=C(6')); 47.2 (*d*, C(2)); 54.4 (*d*, C(1')); 33.6 (*s*, C(2')); 75.1 (*s*, C(1)); 149.1 (*s*, C(6')). MS: 208 (2, M^+, $C_{14}H_{24}O$), 193 (4), 190 (5), 180 (18), 150 (36), 135 (35), 122 (14), 111 (24), 109 (28), 107 (45), 95 (32), 94 (32), 93 (19), 82 (26), 81 (35), 79 (29), *69* (100), 67 (15), 55 (13), 43 (35), 41 (26).

Isomer D (**21D**; contaminated with *ca.* 20% of **21C**). B.p. 90°/0.06 Torr. IR: 3600*w*, 3065*w*, 2955*s*, 2920*s*, 2860*s*, 2850*s*, 1640*w*, 1460*m* (sh), 1455*m*, 1445*m* (sh), 1435*m* (sh), 1385*m*, 1370*m*, 1365*m*, 1260*m*, 1140*w*, 1090*w*, 975*w*, 950*w*, 940*w*, 910*s*, 895*m*. ^{1}H-NMR (300 MHz): 0.83, 0.88 (2*s*, 2 CH_3–C(2')); 1.32 (*s*, CH_3–C(1)); 1.00–1.85, 1.85–1.95 (2*m*, 2H–C(3), 2H–C(4), H–C(1')), 2H–C(3'), 2H–C(4')); 1.95–2.10, 2.20–2.35 (2*m*, 2H–C(5')); 2.55–2.70 (*m*, H–C(2)); 4.74, 4.84 (2*m*, $w_{½}$ = 5, CH_2=C(6')). ^{13}C-NMR (75 MHz): 21.0, 27.1, 28.7, (3*q*, 2 *C*H_3–C(2'), *C*H_3–C(1)); 23.1, 24.3, 27.0, 33.4, 36.4 (5*t*, C(3), C(4), C(3'), C(4'), C(5')); 110.2 (*t*, *C*H_2=C(6')); 47.2 (*d*, C(2)); 55.8 (*d*, C(1')); 36.2 (*s*, C(2')); 75.2 (*s*, C(1)); 150.6 (*s*, C(6')). MS: 208 (2, M^+, $C_{14}H_{24}O$), 193 (3), 190 (5), 180 (8), 150 (29), 135 (30), 111 (16), 109 (24), 107 (37), 95 (34), 94 (27), 93 (17), 82 (24), 81 (34), 79 (26), 69 (100), 67 (15), 55 (15), 43 (37), 41 (29).

1-(5',5'-Dimethyl-6-vinyl-1'-cyclohexenyl)-2-methyl-2-propanol (**22**). IR: 3610*w*, 3560*w*, 3520–3300*w* br., 3070*w*, 3020*w*, 2960*s*, 2920*s*, 2860*s*, 2840*m* (sh), 1630*w*, 1465*m* (sh), 1455*m*, 1435*m* (sh), 1410*w*, 1380*s*, 1370*s*, 1360*s*, 1345*m*, 1310*w*, 1280*w*, 1255*w*, 1225*w*, 1195*w*, 1145*m*, 1130*m*, 1115*m*, 995*w*, 980*w*, 970*w*, 960*w*, 910*s*, 890*w*, 850*w*. ^{1}H-NMR (300 MHz): 0.84, 0.96 (2*s*, 2 CH_3–C(5')); 1.20 (*s*, 3H–C(3), CH_3–C(2)); 1.10–1.80 (*m*, 2H–C(4')); 1.63 (*m*, $w_{½}$ = 6, OH); 2.10 (*AB*-system, *J* = 13.6, δ_A = 2.02, δ_B = 2.18, overlapping with *m*, 2H–C(3)); 2.00–2.13 (*m*, 2H–C(3')); 2.42 (br. *d*, *J* = 9, *H*–C(6')); 5.00 (*dd*, J_1 = 17, J_2 = 2, H–C(2")); 5.07 (*dd*, J_1 = 10, J_2 = 2, H–C(2")); 5.56 (*m*, H–C(2')); 5.59 (*ddd*, J_1 = 17, J_2 = 10, J_3 = 9, H–C(1")). ^{13}C-NMR (75 MHz): 27.0, 27.9, 29.6, 30.0 (4*q*, C(1), *C*H_3–C(2), 2 *C*H_3–C(5')); 23.2, 30.8, 48.3 (3*t*, C(3), C(3'), C(4')); 116.3 (*t*, C(2")); 55.1 (*d*, C(6')); 125.7 (*d*, C(2')); 139.5 (*d*, C(1")); 32.0 (*s*, C(5')); 71.1 (*s*, C(2)); 135.2 (*s*, C(1')). MS: 208 (1, M^+, $C_{14}H_{24}O$), 193 (1), 190 (2), 150 (15), 135 (10), 95 (14), *94* (100), 93 (11), 79 (45), 69 (13), 59 (72), 43 (16), 41 (16).

4-(2',2'-Dimethyl-6'-methylidenecyclohexyl)-2-methyl-3-buten-2-ol (**23**). IR: 3610*m*, 3600–3200*w* br., 3080*w*, 3070*w*, 3030*w*, 2960*s*, 2920*s*, 2900*s* (sh), 2860*s*, 2840*s*, 1640*m*, 1635*m* (sh), 1465*m* (sh), 1455*m*, 1435*m*, 1380*m*, 1360*m*, 1315*m* br., 1265*w*, 1230*m* br., 1185*w*, 1160*m*, 1155*m*, 1135*w*, 1125*w*, 1105*w*, 980*m*, 970*m*, 955*m*, 910*m*, 890*s*, 875*w*, 870*w*. ^{1}H-NMR (300 MHz): 0.80, 0.88 (2*s*, 2 CH_3–C(2')); 1.32, 1.33 (2*s*, 3H–C(1), CH_3–C(2)); 1.10–1.18 (*m*, 2H–C(3'), 2H–C(4')); 1.95–2.08 and 2.23–2.31 (2*m*, 2H–C(5')); 2.39 (*d*, *J* = 9.2, H–C(1')); 4.54, 4.72 (2*m*, $w_{½} \approx 4$, CH_2=C(6')); 5.68 (*AB*-system, *J* = 15.2, δ_A = 5.60, δ_B = 5.75 split into *d*, *J* = 9.2, H–C(3), H–C(4)). ^{13}C-NMR (75 MHz): 23.2, 29.6, 29.9, 30.0 (4*q*, C(1), *C*H_3–C(2), 2 *C*H_3–C(2')); 23.4, 34.7, 39.3 (3*t*, C(3'), C(4'), C(5')); 108.3 (*t*, *C*H_2=C(6')); 57.1 (*d*, C(1')); 125.7 (*d*, C(4)); 140.2 (*d*, C(3)); 35.3 (*s*, C(2')); 70.8 (*s*, C(2)); 150.3 (*s*, C(6')). MS: 208 (3, M^+, $C_{14}H_{24}O$), 193 (19), 190 (4), 177 (12), 150 (10), 136 (63), 135 (28), 124 (12), 123 (26), 122 (10), 121 (36), 109 (61), 107 (28), 105 (12), 95 (31), 94 (15), 93 (37), 91 (18), 84 (60), 83 (14), 82 (15), 81 (40), 79 (23), 77 (14), 72 (18), 71 (14), 69 (99), 67 (21), 59 (81), 57 (12), 56 (79), 55 (55), *43* (100), 41 (88).

4.2. *In MeCN.* A solution of **2** (680 mg, 3.26 mmol) in abs. MeCN was irradiated (lamp *B*, *Pyrex*, 95% conversion). Evaporation of the solvent and chromatography (hexane/Et_2O 5:1) of the residue (540 mg) gave **21A** (15 mg, 2%), **21B** (36 mg, 5%), and **21C+D** ((1:1)-mixture, 63 mg, 9%). The yields of the diene **12** and the alcohols **22** and **23** were estimated to be as follows (GC): **12** (*ca.* 20%) **22** (*ca.* 1%), and **23** (*ca.* 1%).

4.3. *Photolysis of* **12** *in the Presence of Acetone* (**20**). A solution of **12** (140 mg, 0.93 mmol) and acetone (**20**, 0.136 ml, 1.85 mmol) in pentane (110 ml) was irradiated (lamp *B*, *Pyrex*, 85% conversion). Evaporation of the solvent and chromatography (hexane/Et_2O 5:1) of the mixture afforded the starting material **12** (22 mg), **22** (10 mg, 6%), and **23** (8 mg, 5%).

5. Additional Experiments. – 5.1. *Thermolysis of* **1**. In a quartz tube (30 cm × 1.7 cm) filled with quartz rings, which was previously silylated by evaporation of bis(trimethylsilyl)acetamide, **1** (161 mg, 0.52 mmol) was thermolyzed in three portions at 520° (0.5 Torr, N_2)[14]. Chromatography (hexane) of the mixture afforded **14** (14 mg, 9%), (*E*)-**15** (51 mg, 32%), and (*Z*)-**15** (82 mg, 51%).

(*E*)-**15**. B.p. 115°/0.2 Torr. IR: 3060*w*, 3020*w*, 2940*s*, 2920*s*, 2900*s* (sh), 2850*s*, 1655*s*, 1650*s* (sh), 1465*m*, 1460*m*, 1440*m*, 1380*m*, 1360*m*, 1255*s* (sh), 1250*s*, 1190*s*, 1175*s*, 1155*s*, 1120*m*, 1000*w*, 935*m* (sh), 920*m*, 890*s*, 850*s* (sh), 835*s*. ^{1}H-NMR: 0.18 (*s*, 2 CH_3–Si); 0.86, 0.94 (2*s*, 2 CH_3–C(2′)); 0.97 (*s*, 3 CH_3–C–Si); 1.00–2.20 (*m*, 2H–C(3), 2H–C(4), H–C(1′), 2H–C(3′), 2H–C(4′), 2H–C(5′)); 4.58, 4.80 (2*m*, $w_{1/2}$ = 4, CH_2=C(6′)); 5.01 (*dt*, J_1 = 12, J_2 = 7, H–C(2)); 6.24 (*dt*, J_1 = 12, J_2 = 1, H–C(1)). ^{13}C-NMR (75 MHz): –5.0 (*q*, 2 CH_3–Si); 25.9 (*q*, 3 CH_3–C–Si); 26.5, 28.5 (2*q*, 2 CH_3–C(2′)); 23.9, 25.9, 27.4, 32.5, 36.3 (5*t*, C(3), C(4), C(3′), C(4′), C(5′)); 109.0 (*t*, CH_2=C(6′)); 53.4 (*d*, C(1′)); 111.9 (*d*, C(2)); 140.1 (*d*, C(1)); 18.5 (*s*, C–Si); 34.9 (*s*, C(2′)); 149.3 (*s*, C(6′)). MS: 308 (< 1, M^+, $C_{19}H_{36}OSi$), 251 (16), 184 (12), 176 (41), 175 (33), 161 (54), 133 (17), 127 (59), 119 (15), 115 (16), 105 (16), 99 (19), 95 (17), 91 (17), 81 (23), 75 (89), *73* (100), 69 (38), 59 (22), 55 (17), 41 (34). Anal. calc. for $C_{19}H_{36}OSi$ (308.58): C 73.95, H 11.76; found: C 73.99, H 11.87.

5.2. *Thermolysis of* **2** (30 mg, 0.14 mmol) as described for **1** gave the starting material **2** (24 mg, 80%).

5.3. *Hydrolysis of* **13**. A solution of **13** (23 mg, 0.049 mmol) in MeOH (3 ml) and 2M HCl (1 ml) was heated under reflux for 1 h. The mixture was worked up in Et_2O and chromatographed (Et_2O/hexane 1:1) yielding **24** (11 mg, 93%).

4-(2′,2′-Dimethyl-6′-methylidenecyclohexyl)butanal-dimethyl-acetal (**24**). B.p. 107°/0.06 Torr. IR: 3060*w*, 2930*s*, 2910*s* (sh), 2860*s*, 2825*s*, 1640*m*, 1465*m*, 1450*m*, 1440*m* (sh), 1385*m*, 1365*m*, 1280*w* br., 1270*m*, 1245*w*, 1210*w*, 1190*m*, 1165*m*, 1125*s*, 1080*s* (sh), 1070*s*, 1050*s*, 1025*m*, 1010*w*, 960*m*, 950*m*, 940*m*, 930*m*, 910*m*, 890*s*, 870*w*, 860*w*. ^{1}H-NMR: 0.80, 0.89 (2*s*, 2 CH_3–C(2′)); 1.00–1.80 and 1.85–2.15 (2*m*, 2H–C(2), 2H–C(3), 2H–C(4), H–C(1′), 2H–C(3′), 2H–C(4′), 2H–C(5′)); 3.26 (*s*, 2 CH_3O); 4.33 (*t*, *J* = 5.5, H–C(1)); 4.53, 4.74 (2*m*, $w_{1/2}$ = 5, CH_2=C(6′)). ^{13}C-NMR: 26.4, 28.5 (2*q*, 2 CH_3–C(2′)); 52.3, 52.5 (2*q*, 2 CH_3O); 23.3, 23.8, 26.3, 32.5, 32.6, 36.3 (6*t*, C(2), C(3), C(4), C(3′), C(4′), C(5′)); 108.9 (*t*, CH_2=C(6′)); 54.0 (*d*, C(1′)); 104.6 (*d*, C(1)); 34.8 (*s*, C(2′)); 149.2 (*s*, C(6′)). MS: 240 (1, M^+, $C_{15}H_{28}O_2$), 208 (8), 177 (17), 176 (26), 161 (15), 150 (32), 135 (16), 133 (10), 121 (12), 109 (26), 107 (23), 101 (23), 95 (19), 94 (18), 93 (13), 84 (22), 81 (22), 79 (17), *75* (100), 71 (24), 69 (39), 67 (14), 55 (15), 41 (33). Anal. calc. for $C_{15}H_{28}O_2$ (240.38): C 74.95, H 11.74; found: C 74.88, H 11.59.

5.4. *Preparation of (*E/Z*)-***15*** from* **17**. To a solution of (t-butyl)dimethylsilyl chloride in abs. Et_3N (dist. from $LiAlH_4$, 1.7 ml, 12.4 mmol) which was filtered through *Celite* was added abs. DMF (dist. from CaH_2, 80°/15 Torr; 1.9 ml) and **17** (1.0 g, 5.15 mmol). The mixture was heated under reflux for 24 h and worked up in Et_2O. Distillation (115°/0.02 Torr) afforded (*E*/*Z*)-**15** (3:7 mixture (GC, ^{1}H-NMR), 680 mg, 43%).

5.5. *Hydrolysis of* **16**. A solution of **16** (26 mg, 0.059 mmol) in Et_2O (2 ml) and 10% aq. HCl (1 ml) was stirred for 3 d at r.t. The mixture was worked up in Et_2O affording (**17**, 11 mg, *ca.* 50% pure).

5.6. *Hydrolysis of* **18A+B**. A solution of **18A+B** 1:2 mixture, (41 mg, 0.064 mmol) in MeOH (5 ml) and 0.1M HCl (0.5 ml) was heated under reflux for 1 h. The mixture was worked up and chromatographed (Et_2O/hexane 1:1) affording **24** (25 mg, 81%).

5.7. *Transformation of the Aldehyde* **17** *to the Acetal* **24**. *a*) A solution of **17** (254 mg, 1.31 mmol), MeOH (25 ml) and 0.1M HCl (3 ml) was heated to reflux for 1.5 h. Workup in Et_2O and chromatography (hexane/Et_2O 5:1) afforded **24** (249 mg, 79%) and the starting material **17** (43 mg). *b*) A solution of **17** (245 mg, 1.26 mmol), MeOH (1 ml), and a catalytic amount of TsOH in benzene (3 ml) was heated to reflux for 2 h and worked up in Et_2O yielding **24** (290 mg, 96%).

5.8. *Preparation of* **23**. To a solution of γ-ionone (**25**, 530 mg, 2.76 mmol) in abs. THF (35 ml) cooled to –10° was added dropwise MeLi (1.6M in Et_2O, 3 ml, 4.8 mmol) under Ar. The mixture was allowed to warm up to r.t., stirred for 1 h and worked up in Et_2O with sat. aq. $(NH_4)_2SO_4$. Chromatography (hexane/Et_2O 7:3) afforded **23** (270 mg, 47%).

[14]) For a detailed description of the thermolysis apparatus, see [24].

REFERENCES

[1] *B. Frei, T. Iizuka, K. Ishii & O. Jeger*, Yuki Gosei Kagaku Kyokai Shi *42*, (1984) in print.
[2] *J.M. Duff & A.G. Brook*, Can. J. Chem. *51*, 2869 (1973).
[3] *A.G. Brook*, Intra – Sci. Chem. Rept. *7*, 131 (1973) and references cited therein.
[4] *A.G. Brook*, Acc. Chem. Res. *7*, 77 (1974) and references cited herein.
[5] a) *A. Hassner & J.A. Soderquist*, Tetrahedron Lett. *1980*, 429; b) J. Org. Chem. *45*, 541 (1980).
[6] *R.A. Bourque, P.D. Davis & J.C. Dalton*, J. Am. Chem. Soc. *103*, 697 (1981).
[7] *J.C. Dalton & R.A. Bourque*, J. Am. Chem. Soc. *103*, 699 (1981).
[8] *C. Shih & J.S. Swenton*, J. Org. Chem. *47*, 2668 (1982).
[9] *A.G. Brook, J.M. Duff, P.F. Jones & N.R. Davis*, J. Am. Chem. Soc. *89*, 431 (1967).
[10] *E.J. Corey, D. Seebach & R. Freedman*, J. Am. Chem. Soc. *89*, 434 (1967).
[11] *E. Fujita, Y. Nagao & K. Kaneko*, Chem. Pharm. Bull. Jpn. *24*, 1115 (1976).
[12] *R.A.J. Smith & D.J. Hannah*, Synth. Commun. *9*, 301 (1979).
[13] *E.M. Dexheimer, G.R. Buell & C. Le Croix*, Spectrosc. Lett. *11*, 751 (1978).
[14] *M.E. Scheller, P. Mathies, W. Petter & B. Frei*, Helv. Chim. Acta *67*, 1748 (1984).
[15] *H.O. House, L.J. Czuba, M. Gall & H.D. Olmstead*, J. Org. Chem. *34*, 2324 (1969).
[16] *P.J. Wagner*, in 'Rearrangements in Ground and Excited States' Vol. 3, ed. P. de Mayo, Academic Press, New York, 1980, pp. 381.
[17] *A.R. Bassindale, A.G. Brook & J. Harris*, J. Organomet. Chem. *90*, C6 (1975).
[18] *A.P. Alder, H.R. Wolf & O. Jeger*, Helv. Chim. Acta *63*, 1833 (1980).
[19] *W.C. Still, M. Kahn & A. Mitra*, J. Org. Chem. *43*, 2923 (1978).
[20] *M. Yoshioka, K. Ishii & H.R. Wolf*, Helv. Chim. Acta *63*, 571 (1980).
[21] *R. Buchecker, R. Egli, H. Regel-Wild, Ch. Tscharner, C.H. Eugster, G. Uhde & G. Ohloff*, Helv. Chim. Acta *56*, 2548 (1973).
[22] *L.H. Sommer & L.J. Tyler*, J. Am. Chem. Soc. *76*, 1030 (1954).
[23] Organikum, Organisch-Chemisches Grundpraktikum, VEB Verlag der Wissenschaften Berlin, 1973, p. 426 and 689.
[24] *M. Karpf & A.S. Dreiding*, Helv. Chim. Acta *60*, 3045 (1977).