

204. Photochemical Reactions

139th Communication¹⁾

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

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Summary

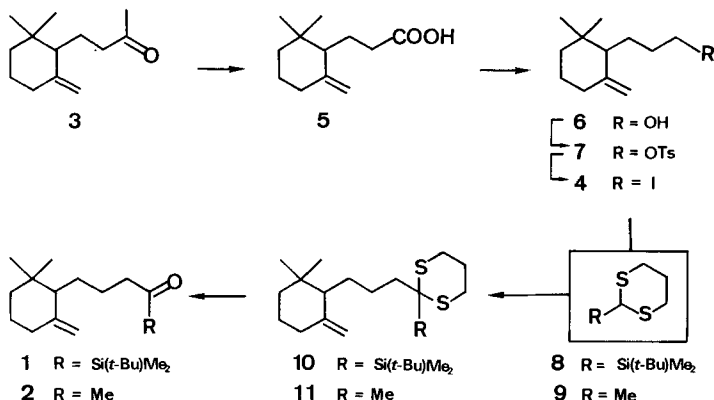
The syntheses and the photolyses of the acylsilane **1** and the corresponding methyl ketone **2** are described. On n,π^* -excitation, the silyl ketone **1** as well as the methyl ketone **2** undergo a *Norrish* type II reaction involving γ -H-abstraction and fragmentation to the diene **12**, and 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 H₂O, 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.*

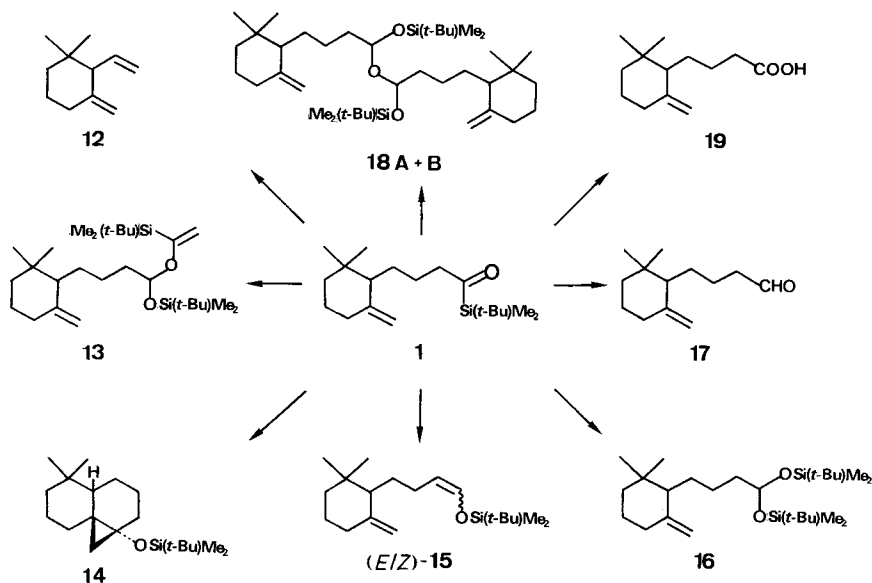
Scheme 1



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** $\rightarrow$ **6** $\rightarrow$ **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 $\text{Ti}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ [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 [M]	Conversion [%]	Product Distribution [%] ^{a)}							
			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	–	–	–

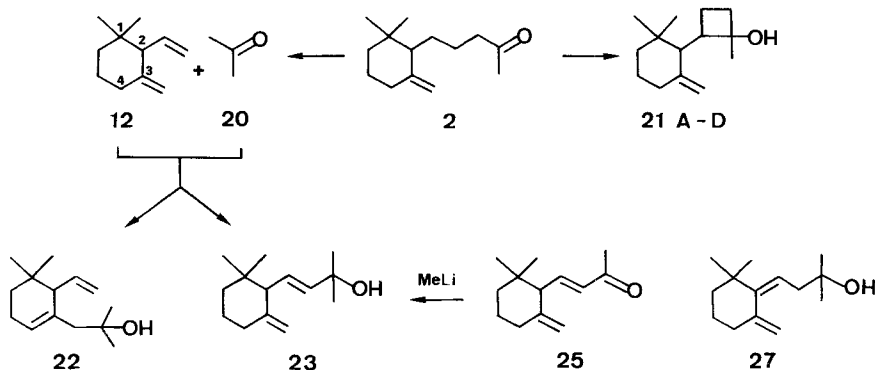
^{a)} Based on converted starting material. Yields were determined after chromatography on SiO₂ by ¹H-NMR and GC analysis of the fractions.

^{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



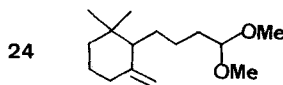
4. Thermolysis of **1** and **2**. – Vapor-phase thermolysis of the acylsilane **1** (520°) afforded **14** (9%), (*E*)-**15** (32%) and (*Z*)-**15** (51%). Under these conditions the methyl ketone **2** proved to be stable and was recovered in 80% yield.

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 $\lambda = 357$ ($\epsilon = 120$), 372 ($\epsilon = 160$) and 387 nm ($\epsilon = 135$) [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 ($\epsilon = 20$). In the ¹³C-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**.

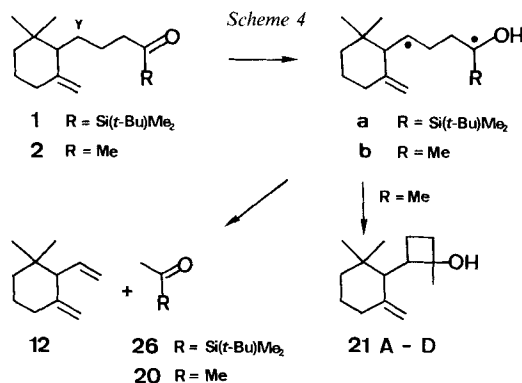


Tricyclic Compound 14. The configuration was assigned by X-ray analysis of the *p*-nitrobenzoate of a decalol obtained from **14** in two steps: hydrolysis and subsequent reduction of the resulting ketone with $NaBH_4$ (see [14]).

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 1H -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.

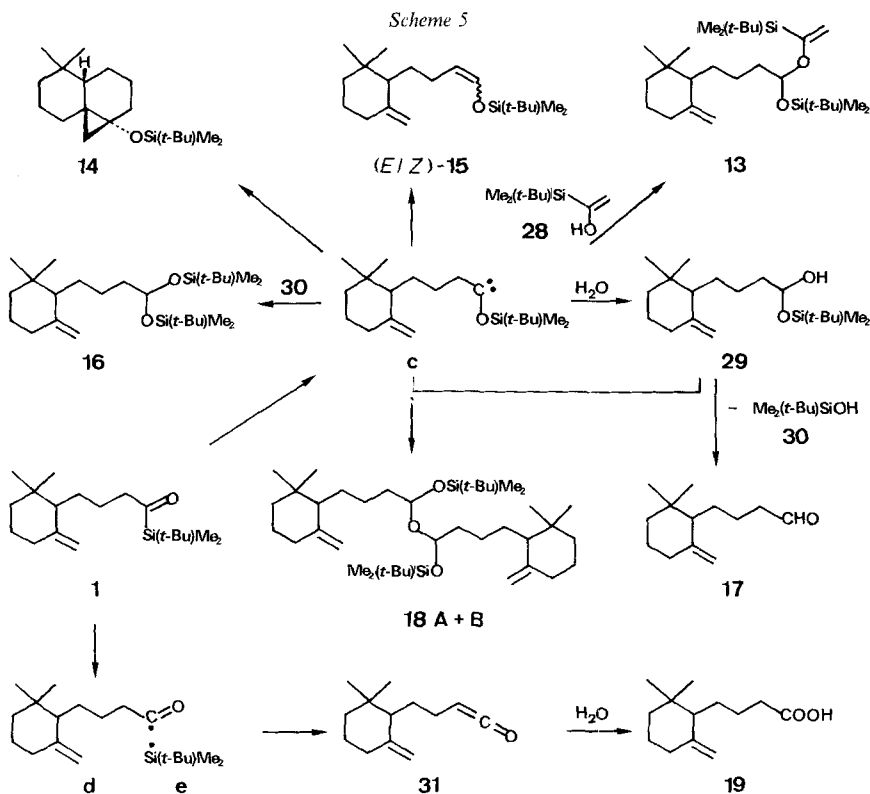
6. Discussion. – On n, π^* -excitation, the acylsilane **1** as well as the methyl ketone **2** react by γ -H-abstraction leading to the 1,4-diradicals **a** and **b**, respectively. These intermediates fragment to give the diene **12** and – via their enol forms – the ketones **26** and **20** (see Scheme 4). This process is quite common of carbonyl compounds⁵⁾, 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



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 H₂O 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 Table⁷⁾).



⁶⁾ The variable yields of **16**, **17**, and **18A+B** are due to the varying amounts of H₂O 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 methylenide 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 – intermediates⁹.

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 photo-processes 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. Brandenburg*, 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 $\times$ 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 $\times$ 23.6 mm SiO_2 column. All UV spectra were taken in pentane solutions. In general, ^1H -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* ($\text{Pb}(\text{NO}_3)_2/\text{KBr}$, 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% $\text{Na}_2\text{S}_2\text{O}_3$ this org. phase was worked up affording the acid **5** (9.35 g, 51%).

3-(2',2'-Dimethyl-6'-methylidenecyclohexyl)propionic Acid (5). IR: 3500–2500m br., 2920s, 2860s, 1700s, 1640m, 1440m (sh), 1410s, 1380m, 1365m, 1290s, 1235m, 1215m, 1160w, 930m br., 890s. $^1\text{H-NMR}$ (80 MHz): 0.88, 0.93 (2s, 2 $\text{CH}_3\text{-C}(2'')$); 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 (2m, $w_{\text{H}} = 4.5$, $\text{CH}_2=\text{C}(6')$); 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_3CN_2 .

Methyl 3-(2',2'-Dimethyl-6'-methylidenecyclohexyl)propionate. B.p. $90^\circ/0.02$ Torr. IR: 3060w, 2930s, 2900s (sh), 2860s, 1735s, 1640m, 1455m (sh), 1445 m (sh), 1430s, 1415w (sh), 1380m, 1360m, 1320m, 1290m, 1255m, 1230m, 1190m, 1160s, 1050w, 890s, 860w. $^1\text{H-NMR}$: 0.84, 0.90 (2s, 2 $\text{CH}_3\text{-C}(2'')$); 1.00–2.45 (m, 2H–C(2), 2H–C(3), 2H–C(3'), 2H–C(4'), 2H–C(5')); 3.60 (s, CH_3O); 4.51, 4.75 (2m, $w_{\text{H}} = 4$, $\text{CH}_2=\text{C}(6')$). $^{13}\text{C-NMR}$: 26.4, 28.3 (2q, 2 $\text{CH}_3\text{-C}(2'')$); 51.2 (q, CH_3O); 21.8, 23.6, 32.1, 32.7, 36.0 (5t, C(2), C(3), C(3'), C(4'), C(5')); 109.7 (t, $\text{CH}_2=\text{C}(6')$); 53.5 (d, C(1')); 34.8 (s, C(2'')); 148.5 (s, C(6')); 174.3 (s, C=O). MS: 210 (9, M^+ , $\text{C}_{13}\text{H}_{22}\text{O}_2$), 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 $\text{C}_{13}\text{H}_{22}\text{O}_2$ (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. $115^\circ/0.05$ Torr. IR: 3620w (sh), 3590w, 3490w br., 3060w, 2930s, 2860s, 1640w, 1445m br., 1380m, 1365m, 1270m br., 1225w, 1180w, 1105w, 1060m br., 1020m (sh), 950w, 895s. $^1\text{H-NMR}$: 0.82, 0.90 (2s, 2 $\text{CH}_3\text{-C}(2'')$); 1.00–1.80 (m, 2H–C(2), 2H–C(3'), 2H–C(4'), 2H–C(5')); 1.80–2.20 (m, 2H–C(5'), H–C(1')); 3.32 (m, $w_{\text{H}} = 6$, OH); 3.40–3.70 (m, 2H–C(1)); 4.52, 4.73 (2m, $\text{CH}_2=\text{C}(6')$). $^{13}\text{C-NMR}$: 26.4, 28.4 (2q, 2 $\text{CH}_3\text{-C}(2'')$); 22.6, 23.7, 31.3, 32.3, 36.1 (5t, C(2), C(3), C(3'), C(4'), C(5')); 62.8 (t, C(1)); 109.0 (t, $\text{CH}_2=\text{C}(6')$); 53.9 (d, C(1')); 34.8 (s, C(2'')); 149.2 (s, C(6')). MS: 182 (10, M^+ , $\text{C}_{12}\text{H}_{22}\text{O}$), 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 $\text{C}_{12}\text{H}_{22}\text{O}$ (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: 3060w, 3030w, 2920s, 2860s, 1635w, 1595w, 1440m, 1360s, 1350s (sh), 1305w, 1285w, 1175s, 1095w, 950s, 940s (sh), 920s, 890s, 860m. $^1\text{H-NMR}$: 0.75, 0.85 (2s, 2 $\text{CH}_3\text{-C}(2'')$); 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, $\text{CH}_3\text{-Ph}$); 3.9–4.1 (m, 2H–C(1)); 4.43, 4.68 (2m, $w_{\text{H}} = \text{ca. } 5$, $\text{CH}_2=\text{C}(6')$); 7.54 (AA',BB'-system, $J = 8$, $\delta_A = 7.31$, $\delta_B = 7.76$, 4 arom. H). $^{13}\text{C-NMR}$: 21.5 (q, $\text{CH}_3\text{-Ph}$); 26.4, 28.2 (2q, 2 $\text{CH}_3\text{-C}(2'')$); 22.1, 23.5, 27.4, 31.9, 35.7 (5t, C(2), C(3), C(3'), C(4'), C(5')); 70.9 (t, C(1)); 109.4 (t, $\text{CH}_2=\text{C}(6')$); 53.3 (d, C(1')); 127.8, 129.8 (2d, 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^+ , $\text{C}_{19}\text{H}_{28}\text{O}_3\text{S}$), 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: 3060w, 2920s, 1635w, 1520w br., 1435m, 1380w, 1360m, 1210m, 1160w, 965w, 890m. 1H -NMR: 0.83, 0.89 (2s, 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 (2m, $w_{1/2} \approx 4$, CH_2 =C(3)). ^{13}C -NMR (75 MHz): 26.4, 28.3 (2q, 2 CH_3 -C(1)); 7.8 (t, C(3')); 23.6, 27.4, 32.0, 32.2, 35.9 (5t, 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: 2920s, 2890s, 2850s, 1460m, 1420m, 1410m, 1390m, 1360m, 1270m, 1250s, 1160m, 1080m br., 995w, 935w, 910m, 875m. 1H -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: 3060w, 2900s, 2850s, 2660w, 1635w, 1460m (sh), 1445m, 1420m (sh), 1410m (sh), 1380m, 1360m, 1245m, 1160w, 1005w, 930w, 890m. 1H -NMR: 0.20, 0.24 (2s, 2 CH_3 -Si); 0.88, 0.96 (2s, 2 CH_3 -C(2'')); 1.04 (s, 3 CH_3 -C-Si); 1.20-2.60 and 2.9-3.25 (2m, 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 (2m, $w_{1/2} = 4$, CH_2 =C(6'')); ^{13}C -NMR: -5.2, -5.3 (2q, 2 CH_3 -Si); 26.7 (q, CH_3 -C(2'')); 28.4 (q, CH_3 -C(2''), 3 CH_3 -C-Si); 23.6¹¹⁾, 23.7, 25.1, 26.9, 27.1, 32.2, 36.1, 38.4 (9t, C(4), C(5), C(6), C(1'), C(2'), 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: 3060w, 2940s (sh), 2920s, 2900s, 2850s, 1635s, 1460m, 1390w (sh), 1380m, 1360m, 1245m, 1000w, 945w, 890m. 1H -NMR (300 MHz): 0.16 (s, 2 CH_3 -Si); 0.80, 0.89 (2s, 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 (2m, $w_{1/2} = 4$, 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 (5t, 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: 3060w, 2930s, 2905s, 2860s, 1640m, 1460m (sh), 1445s, 1420m, 1415m, 1380m, 1370m, 1365m, 1340w, 1315w, 1295w, 1275m, 1235m, 1210w, 1185w, 1180w, 1170w, 1160w, 1145w, 1115w, 1080w, 1045w, 1035w, 1000w, 975w, 940w, 910m, 890s, 870w. ¹H-NMR: 0.80, 0.89 (2s, 2 CH₃-C(2'')); 1.57 (s, CH₃-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 (2m, w_{1/2} = 4, CH₂=C(6)). ¹³C-NMR: 15.2 (q, CH₃-C(2)); 27.7, 28.4 (2q, 2 CH₃-C(2'')); 22.7, 23.6, 25.4, 26.2, 26.4¹¹⁾, 32.3, 36.1, 41.7 (9t, C(4), C(5), C(6), C(1'), C(2'), C(3'), C(3''), C(4''), C(5'')); 108.9 (t, CH₂=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⁺, C₁₇H₃₀S₂), 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 C₁₇H₃₀S₂ (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 H₂O (75 drops) was added at 0° at once a solution of Ti(NO₃)₃·3H₂O (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/Et₂O 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: 3060w, 2930s, 2910s (sh), 2860s, 1715s, 1640m, 1460m (sh), 1450m, 1440m (sh), 1410m, 1380m, 1360s, 1285w, 1225w, 1180m, 1155m, 890s. ¹H-NMR (80 MHz): 0.75, 0.85 (2s, 2 CH₃-C(2')); 1.10–1.80 and 1.85–2.10 (2m, 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 (2m, w_{1/2} ≈ 4, CH₂=C(6')). ¹³C-NMR: 26.4, 28.3 (2q, 2 CH₃-C(2')); 29.5 (q, C(1)); 22.5, 23.7, 25.9, 32.3, 36.1 (5t, C(4), C(5), C(3'), C(4'), C(5')); 43.6 (t, C(3)); 109.1 (t, CH₂=C(6')); 53.9 (d, C(1')); 34.7 (s, C(2')); 148.9 (s, C(6')). MS: 208 (10, M⁺, C₁₄H₂₄O), 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 C₁₄H₂₄O (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/Et₂O gradient, O→5% Et₂O) yielded fractions from which the following product distribution was determined (¹H-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: 3070m, 3010w, 2960s (sh), 2940s (sh), 2920s, 2900s (sh), 2860s, 2840s, 1640m, 1455m, 1450m (sh), 1435m, 1420m, 1380m, 1360m, 1210w, 1220w, 1190w, 1145w, 1005m, 990m, 915s, 890s, 870w, 860w, 845w. ¹H-NMR (300 MHz): 0.81, 0.90 (2s, 2 CH₃-C(1)); 1.20–1.65 (m, 2H-C(5), 2H-C(6)); 1.95–2.15 and 2.20–2.35 (2m, 2H-C(4)); 2.42 (d, J = 10, H-C(2)); 4.58, 4.73 (2m, w_{1/2} = 5, CH₂=C(3)); 4.98–5.09 (m, CH=CH₂); 5.92 (ddd, J₁ = 17, J₂=J₃ = 10, CH=CH₂). ¹³C-NMR (75 MHz): 23.2, 29.4 (2q, 2 CH₃-C(1)); 23.5, 34.7, 39.2 (3t, C(4), C(5), C(6)); 108.3 (t, CH₂=C(3)); 116.4 (t, CH=CH₂); 59.1 (d, C(2)); 137.5 (d, CH=CH₂); 34.9 (s, C(1)); 149.9 (s, C(3)). MS: 150 (25, M⁺, C₁₁H₁₈), 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: 3060w, 3020w, 2945s (sh), 2920s, 2900s (sh), 2850s, 1645m, 1460m, 1435m (sh), 1390m br., 1360m, 1340w, 1250s, 1200w, 1170w, 1115m, 1100m, 1055m, 980w br., 935w, 890m, 870m, 835s. ¹H-NMR (300 MHz): 0.06, 0.065, 0.07, 0.11 (4s, 2(CH₃)₂Si); 0.83, 0.91 (2s, 2 CH₃-C(2')); 0.88, 0.92 (2s, 2(CH₃)₃CSi); 1.00–1.85 and 1.95–2.10 (2m, 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 (2m, w_{1/2} ≈ 4, 2H-C(1)); 4.52, 4.72 (2m, w_{1/2} ≈ 4, CH₂=C(6'')); 5.28 (dd, J₁=J₂ = 5, H-C(4)). ¹³C-NMR (75 MHz): -6.3, -6.2, -4.0, -3.9, -3.3 (5q, 2(CH₃)₂Si); 25.9, 26.9 (2q, 2(CH₃)₃CSi, CH₃-C(2'')); 28.5 (q, CH₃-C(2'')); 23.4, 23.5, 23.8¹¹⁾, 26.5¹¹⁾, 32.1, 32.3, 36.0, 36.1 (10t, C(6), C(7), C(3'), C(4'), C(5'')); 37.1, 37.3 (2t, C(5)); 98.2, 98.3 (2t, C(1)); 109.2 (t, CH₂=C(6'')); 54.3, 54.4 (2d, C(1'')); 96.0 (d, C(4)); 16.5, 18.2 (2s, 2(CH₃)₃CSi); 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 CH₃N₂.

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: 3050w, 2950s, 2925s, 2900s (sh), 2880s (sh), 2855s, 1470m, 1460m, 1450m (sh), 1405w, 1385m, 1360m, 1335m, 1295w, 1280m, 1250s, 1220m, 1210m, 1180w, 1165w, 1155m, 1130m, 1110w, 1085w, 1065m, 1045w, 1035m, 1000m, 985m, 970m, 960m, 940m (sh), 935m, 890w, 880m, 860m, 835s. ¹H-NMR: 0.09, 0.15 (2s, 2 CH₃-Si); 0.47 (AB-system, $J = 5$, $\delta_A = 0.40$, $\delta_B = 0.53$, 2H-C(2)); 0.88 (s, CH₃-C(8)), 3 CH₃-C-Si); 0.97 (s, CH₃-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)). ¹³C-NMR: -3.2, -3.7 (2q, 2 CH₃-Si); 25.5, 29.8 (2q, 2 CH₃-C(8)); 25.8 (q, 3 CH₃-C-Si); 18.4, 18.9, 20.8, 23.5, 28.8, 29.8, 38.6 (7t, 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^+ , C₁₉H₃₆OSi), 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 C₁₉H₃₆OSi (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: 3060w, 3020w, 2940s, 2920s, 2895s, 2845s, 1650s, 1645s, 1465m (sh), 1455m, 1445m, 1395m, 1380m, 1360m, 1250s, 1170w, 1110s, 1095s, 1050m, 1000w, 935w, 885s, 865m, 830s. ¹H-NMR: 0.16 (s, 2 CH₃-Si); 0.86, 0.95 (2s, 2 CH₃-C(2')); 0.96 (s, 3 CH₃-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 (2m, $w_{1/2} \approx 4$, CH₂=C(6')); 6.20 (dt, $J_1 = 6$, $J_2 = 1$, H-C(1)). ¹³C-NMR: -5.3 (q, 2 CH₃-Si); 25.7 (q, (CH₃)₃C-Si); 26.3, 28.5 (2q, 2 CH₃-C(2')); 22.5, 23.8, 26.6, 32.6, 36.5 (5t, C(3), C(4), C(3'), C(4'), C(5')); 108.9 (t, CH₂=C(6')); 53.8 (d, C(1')); 111.0 (d, C(2)); 138.4 (d, C(1)); 18.3 (s, (CH₃)₃C-Si); 34.8 (s, C(2')); 149.2 (s, C(6')). MS: 308 (< 1, M^+ , C₁₉H₃₆OSi), 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 C₁₉H₃₆OSi (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: 3060w, 2950s, 2925s, 2900m, 2850s, 1640w, 1465m, 1460m, 1380m, 1370m (sh), 1360m, 1250s, 1210w, 1140m, 1065m br., 1020m, 995m, 940m, 890m, 860m (sh), 830s. ¹H-NMR (300 MHz): 0.08, 0.10 (2s, 2(CH₃)₂Si); 0.83, 0.91 (2s, 2 CH₃-C(2')); 0.89 (s, 2 (CH₃)₃C-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 (2m, H-C(1'), 2H-C(5')); 4.52, 4.72 (2m, $w_{1/2} \approx 4$, CH₂=C(6')); 5.10 (dd, $J_1 = J_2 = 5$, H-C(1)). ¹³C-NMR (75 MHz): -4.1, -4.0, -3.5¹¹) (4q, 2(CH₃)₂Si); 26.0 (q, 2(CH₃)₃C-Si); 26.9, 28.5 (2q, 2 CH₃-C(2')); 23.5, 23.8, 26.4, 32.2, 36.0 (5t, C(3), C(4), C(3'), C(4'), C(5')); 41.1 (t, C(2)); 109.0 (t, CH₂=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^+ , C₃₅H₅₂O₂Si₂), 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 C₃₅H₅₂O₂Si₂ (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: 3060w, 2930s, 2910s (sh), 2860s, 2810m, 2710m, 1725s, 1640m, 1460m (sh), 1450m, 1440m (sh), 1410w, 1385m, 1365m, 890s. ¹H-NMR: 0.81, 0.90 (2s, 2 CH₃-C(2')); 1.10-1.85 and 1.90-2.10 (2m, 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 (2m, $w_{1/2} \approx 4$, CH₂=C(6')); 9.70 (t, $J = 2$, H-C(1)). ¹³C-NMR: 26.4, 28.3 (2q, 2 CH₃-C(2')); 20.8, 23.6, 25.9, 32.2, 36.1 (5t, C(3), C(4), C(3'), C(4'), C(5')); 43.9 (t, C(2)); 109.2 (t, CH₂=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^+ , C₁₃H₂₂O), 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 C₁₃H₂₂O (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: 3070w, 2950s (sh), 2940s, 2910s (sh), 2870s, 1740s, 1640w, 1460m (sh), 1450m, 1435m, 1415w, 1385m, 1360m, 1250m, 1200m, 1160m, 890s. ¹H-NMR: 0.80, 0.89 (2s, 2 CH₃-C(2')); 1.00-1.85 and 1.90-2.15 (2m, 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, CH₃O); 4.53, 4.74 (2m, $w_{1/2} \approx 4$, CH₂=C(6')). ¹³C-NMR: 26.4, 28.4 (2q, 2 CH₃-C(2')); 51.4 (q, CH₃O); 23.7¹¹), 26.0, 32.3, 34.2, 36.2 (6t, C(2), C(3), C(4), C(3'), C(4'), C(5')); 109.1 (t, CH₂=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^+ , C₁₄H₂₄O₂), 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: 3060w, 2940s (sh), 2920s, 2850s, 1640w, 1465m (sh), 1460m, 1435m (sh), 1380m,

1360m, 1340w, 1250m, 1180w, 1145w, 1110m, 1005m, 985s, 950w, 935w, 890m, 835s. ¹H-NMR (300 MHz): 0.08, 0.10 (2s, 2 CH₃-Si); 0.88, 0.91 (2s, 2 CH₃-C(2')); 0.89 (s, 3 CH₃-C-Si); 1.00-1.65 and 1.95-2.10 (2m, 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 (2m, w_{1/2} ≈ 4, CH₂=C(6')); 4.92 (m, w_{1/2} = 5, H-C(1)). ¹³C-NMR (75 MHz): -4.3, -3.9 (2q, 2 CH₃-Si); 25.9 (q, 3 CH₃-C-Si); 26.6, 28.4 (2q, 2 CH₃-C(2')); 22.5, 22.7, 23.7¹³), 26.4¹¹), 32.2¹¹), 36.0¹¹), (10t, C(3), C(4), C(3'), C(4'), C(5')); 37.4, 37.5 (2t, C(2)); 108.9 (t, CH₂=C(6')); 54.1 (d, C(1')); 94.1, 94.2 (2d, 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 C₃₈H₇₄O₃Si₂: 635.18; found: 618.

Isomer B (18B). B.p. 225°/0.09 Torr. IR: 3060w, 2920s, 2850s, 1640w, 1465m (sh), 1460m, 1435m (sh), 1380m, 1360m, 1340w, 1250s, 1130s, 1005m, 980s br., 950m, 940m, 890s, 875m, 840s. ¹H-NMR (300 MHz): 0.08, 0.10 (2s, 2 CH₃-Si); 0.82, 0.90 (2s, 2 CH₃-C(2')); 0.89 (s, 3 CH₃-C-Si); 1.05-1.75 and 1.90-2.15 (2m, 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 (2m, w_{1/2} ≈ 4, CH₂=C(6')); 4.95 (m, w_{1/2} = 5, H-C(1)). ¹³C-NMR (75 MHz): -3.7, -3.6 (2q, 2 CH₃-Si); 26.0 (q, 3 CH₃-C-Si); 26.6, 28.5, (2q, 2 CH₃-C(2')); 22.8, 23.2, 23.8¹¹), 26.5¹¹), 32.4¹¹), 36.2¹¹) (10t, C(3), C(4), C(3'), C(4'), C(5')); 38.5, 38.6 (2t, C(2)); 109.0 (t, CH₂=C(6')); 54.2, 54.3 (2d, C(1')); 94.9, 95.0 (2d, 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 C₃₈H₇₄O₃Si₂: 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/Et₂O 20:1) gave the starting material **1** (83 mg, 11%), **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/Et₂O 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/H₂SO₄ [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/Et₂O 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: 3560m, 3060w, 2970s, 2930s, 2910s (sh), 2860s, 1635w, 1455m, 1440m, 1430w (sh), 1380m, 1370m, 1360m, 1340m, 1320w, 1290w, 1275w, 1260w, 1230m, 1220m, 1155m, 1100w, 1070w, 970w, 955w, 930m, 915m, 895s, 860w. ¹H-NMR: 0.81, 0.85 (2s, 2 CH₃-C(2')); 1.20 (s, CH₃-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, CH₂=C(6')). ¹³C-NMR (75 MHz): 27.4, 29.2, 29.7 (3q, 2 CH₃-C(2'), CH₃-C(1)); 23.9, 28.0, 32.2, 33.8, 34.7 (5t, C(3), C(4), C(3'), C(4'), C(5')); 109.9 (t, CH₂=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⁺, C₁₄H₂₄O), 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 C₁₄H₂₄O (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: 3610m, 3580-3300w br., 3060w, 2970s, 2920s, 2900s (sh), 2860s, 1640m, 1635w (sh), 1455m (sh), 1450s, 1435m, 1380s, 1370m, 1365m, 1340w, 1320w, 1290w, 1240m, 1220m, 1210m, 1190m, 1165m, 1130m br., 1080m, 1050w, 985w, 960m, 930m, 915m, 890s, 875m, 860w. ¹H-NMR: 0.86, 0.91 (2q, 2 CH₃-C(2')); 1.35 (q, CH₃-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 (2m, w_{1/2} ≈ 5, CH₂=C(6')). ¹³C-NMR (75 MHz): 27.7, 29.2, 29.4 (3q, 2 CH₃-C(2'), CH₃-C(1)); 19.1, 23.3, 32.5, 34.2, 34.6 (5t, C(3), C(4), C(3'), C(4'), C(5')); 109.9 (t, CH₂=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/Et₂O 10:1), and cleavage of the acetates with LiAlH₄.

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*. ¹H-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*, $w_{1/2}$ ≈ 4, CH_2 =C(6')). ¹³C-NMR (75 MHz): 22.5, 27.8, 29.4 (3*q*, 2 CH_3 –C(2'), CH_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*, CH_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*. ¹H-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*, $w_{1/2}$ = 5, CH_2 =C(6')). ¹³C-NMR (75 MHz): 21.0, 27.1, 28.7, (3*q*, 2 CH_3 –C(2'), CH_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*, CH_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*. ¹H-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*, $w_{1/2}$ = 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')). ¹³C-NMR (75 MHz): 27.0, 27.9, 29.6, 30.0 (4*q*, C(1), CH_3 –C(2), 2 CH_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*. ¹H-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*, $w_{1/2}$ ≈ 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)). ¹³C-NMR (75 MHz): 23.2, 29.6, 29.9, 30.0 (4*q*, C(1), CH_3 –C(2), 2 CH_3 –C(2')); 23.4, 34.7, 39.3 (3*t*, C(3'), C(4'), C(5')); 108.3 (*t*, CH_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/Et₂O 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/Et₂O 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 $\times$ 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, N₂)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: 3060w, 3020w, 2940s, 2920s, 2900s (sh), 2850s, 1655s, 1650s (sh), 1465m, 1460m, 1440m, 1380m, 1360m, 1255s (sh), 1250s, 1190s, 1175s, 1155s, 1120m, 1000w, 935m (sh), 920m, 890s, 850s (sh), 835s. ¹H-NMR: 0.18 (s, 2 CH₃-Si); 0.86, 0.94 (2s, 2 CH₃-C(2')); 0.97 (s, 3 CH₃-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 (2m, w_{1/2} = 4, CH₂=C(6')); 5.01 (dt, J₁ = 12, J₂ = 7, H-C(2)); 6.24 (dt, J₁ = 12, J₂ = 1, H-C(1)). ¹³C-NMR (75 MHz): –5.0 (q, 2 CH₃-Si); 25.9 (q, 3 CH₃-C-Si); 26.5, 28.5 (2q, 2 CH₃-C(2')); 23.9, 25.9, 27.4, 32.5, 36.3 (5t, C(3), C(4), C(3'), C(4'), C(5')); 109.0 (t, CH₂=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⁺, C₁₉H₃₆OSi), 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 C₁₉H₃₆OSi (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 Et₂O and chromatographed (Et₂O/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: 3060w, 2930s, 2910s (sh), 2860s, 2825s, 1640m, 1465m, 1450m, 1440m (sh), 1385m, 1365m, 1280w br., 1270m, 1245w, 1210w, 1190m, 1165m, 1125s, 1080s (sh), 1070s, 1050s, 1025m, 1010w, 960m, 950m, 940m, 930m, 910m, 890s, 870w, 860w. ¹H-NMR: 0.80, 0.89 (2s, 2 CH₃-C(2')); 1.00–1.80 and 1.85–2.15 (2m, 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 CH₃O); 4.33 (t, J = 5.5, H-C(1)); 4.53, 4.74 (2m, w_{1/2} = 5, CH₂=C(6')). ¹³C-NMR: 26.4, 28.5 (2q, 2 CH₃-C(2')); 52.3, 52.5 (2q, 2 CH₃O); 23.3, 23.8, 26.3, 32.5, 32.6, 36.3 (6t, C(2), C(3), C(4), C(3'), C(4'), C(5')); 108.9 (t, CH₂=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⁺, C₁₅H₂₈O₂), 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 C₁₅H₂₈O₂ (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. Et₃N (dist. from LiAlH₄, 1.7 ml, 12.4 mmol) which was filtered through Celite was added abs. DMF (dist. from CaH₂, 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 Et₂O. Distillation (115°/0.02 Torr) afforded (*E/Z*)-**15** (3:7 mixture (GC, ¹H-NMR), 680 mg, 43%).

5.5. *Hydrolysis of 16.* A solution of **16** (26 mg, 0.059 mmol) in Et₂O (2 ml) and 10% aq. HCl (1 ml) was stirred for 3 d at r.t. The mixture was worked up in Et₂O 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 (Et₂O/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 Et₂O and chromatography (hexane/Et₂O 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 Et₂O 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 Et₂O, 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 Et₂O with sat. aq. (NH₄)₂SO₄. Chromatography (hexane/Et₂O 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. Tschärner, 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).