5. Syntheses of Cyclopropyl Silyl Ketones

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Dedicated to Prof. Dr. *H. R. Christen*

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The synthesis of the cyclopropyl silyl ketones **1**–**4** is described. The trimethylsilyl ketone **1** was prepared from geraniol ((*E*)-**5**) in *ca.* 10% overall yield by cyclopropanation leading to **6**, CrO_3 oxidation to the aldehyde **8**, reaction of the latter with trimethylsilyl anion to **14A** + **B**, and CrO_3 oxidation to **1**. Also for the (*t*-butyl)dimethylsilyl ketones **2**–**4**, an efficient four-step synthesis with overall yields of 48%, 85%, and 13%, respectively, was elaborated, starting from the allylic alcohols (*E*)-**5**, (*Z*)-**5**, and **23**. The method of preparation involves as the key step a *Wittig* rearrangement of the silylallyl ethers ((*E*/*Z*)-**20**, **24**) to the silyl alcohols ((*E*/*Z*)-**21**, **25**), subsequent cyclopropanation (**19A** + **B**, **22A** + **B**, **26**), and oxidation to the cyclopropyl silyl ketones **2**–**4**.

1. Introduction. – One aspect of our continuing interest in the photochemistry of acylsilanes [2] involves the intramolecular trapping of siloxycarbenes by reaction with various neighboring groups. As a part of the investigation of cyclopropyl acylsilanes, we describe the synthesis of four examples (**1**–**4**) of this new class of compounds. The photochemical and thermal behavior of the new compounds will be discussed in a forthcoming paper.

2. Results and Discussion. – Since the dithiane route for the preparation of silyl ketones [3] [4] was previously shown to be convenient, although possessing some limitations, initial attempts were made to obtain compounds **1** and **2** by this method. Hence, cyclopropanation of (*E*)-**5** with CH_2I_2/Zn/AgOAc [5] afforded the cyclopropyl alcohol **6** (80%)[3]). Oxidation of **6** with CrO_3/pyridine [7] or with Ag_2CO_3/*Celite* [8] gave the aldehyde **8** in 72 and 88% yield, respectively. Thioacetalization of the latter with 1,3-propanedithiol ($BF_3 \cdot Et_2O$, CH_2Cl_2) furnished the 1,3-dithiane **9** (98%) which was transformed to **10** (60%) by reaction with BuLi and (*t*-Bu)Me_2SiCl. Dethioacetalization with $Tl(NO_3)_3 \cdot 3H_2O$ [9], $HgO/HgCl_2$ [4], or even under mild conditions using $Me(MeS)_2S^+SbCl_6^-$ at −78° [10] led only to intractable material in which the acylsilane **2** could not be detected.

In a second attempt, the aldehyde **8** was oxidized with Ag_2O [11] to the acid **11** (84%) and the latter transformed *via* the silyl ester **12** to the acid chloride **13** (63%) [12]. The reaction of **13** with trimethylsilyl anion [13] produced a complex mixture in which the acylsilane **1** could not be detected.

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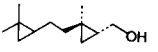
[3]) Preliminary experiments on the cyclopropanation of (*E*)-**5** with CH_2I_2/I_2/Cu [6] produced a *ca.* 3:1 mixture (71%) of **6** and the dicyclopropyl compound **7**, which could not be completely separated.



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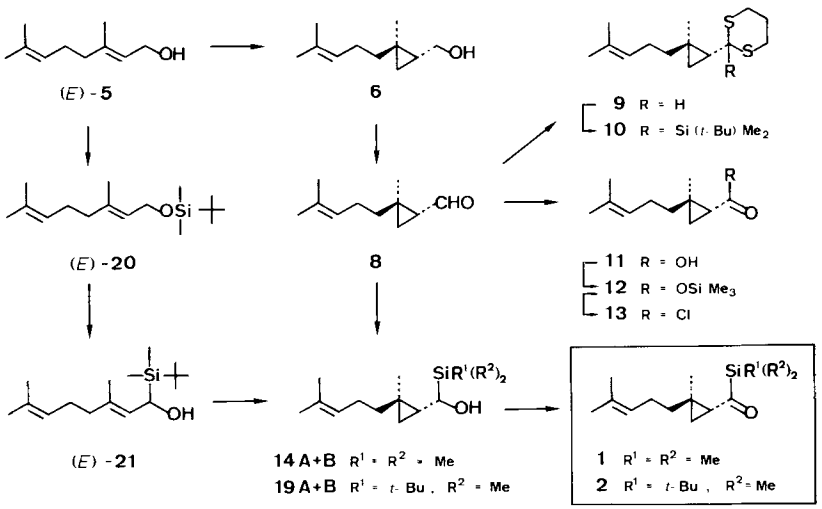
Scheme 1



On the other hand, the successful preparation of the trimethylsilyl ketone **1** was achieved as follows: the reaction of the aldehyde **8** with trimethylsilyl anion [13] led to the diastereoisomeric alcohols **14A + B** (28%). The oxidation of **14A + B** to **1** was carried out successfully with CrO_3/pyridine [7] (55%). So far, other methods reported for the oxidation of silylalcohols to acylsilanes (*e.g.* CrO_3/H_2SO_4 [14] or DCC/DMSO [15]) did not lead to the desired acylsilane **1**.

Due to the low overall yield of the transformation (*E*)-**5**→**6**→**8**→**14A + B**→**1** (*ca.* 10%, *Scheme 1*) and with regard to the generally observed lower stability of trimethylsilyl ethers (the expected photoproducts of **1**), compared with (*t*-butyl)dimethylsilyl ethers, an alternative synthesis leading to the (*t*-butyl)dimethylsilyl cyclopropyl ketone **2** was explored[4]).

The successful oxidation of **14A + B**→**1** encouraged us to search for an efficient new approach to the (*t*-butyl)dimethylsilyl alcohols **19A + B**. Thus, geraniol ((*E*)-**5**) was converted to the (*t*-butyl)dimethylsilyl ether (*E*)-**20** ((*t*-Bu)Me_2SiCl/imidazole/DMF [19]; 81%) which was subjected to a *Wittig* rearrangement [20] (*sec*-BuLi/TMEDA/THF/−30°) furnishing stereospecifically the silyl alcohol (*E*)-**21** (83%). The cyclopropanation of the latter was successfully carried out with CH_2I_2/Zn/AgOAc [5] leading to diastereoisomeric alcohols **19A + B** (73%), which were finally oxidized (CrO_3/pyridine) to the acylsilane **2** (98%; overall yield 48%).

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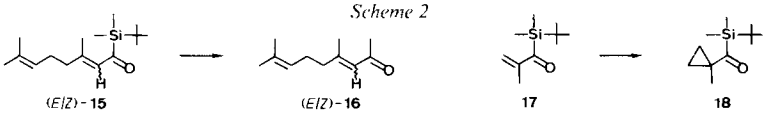
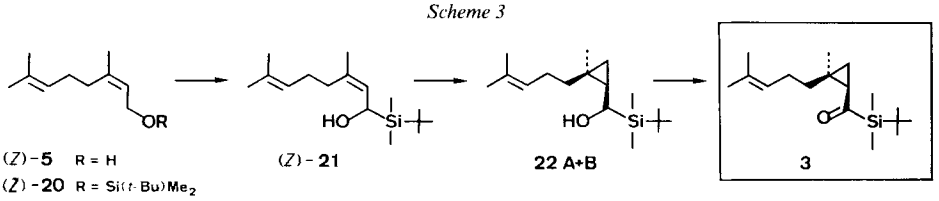
[4]) Attempts of direct cyclopropanation of the α,β-unsaturated acylsilanes (*E*/*Z*)-**15** to **2** failed. The reaction of (*E*/*Z*)-**15** with dimethylsulfoxonium methylide in DMSO [16] led surprisingly to the methyl ketones (*E*/*Z*)-**16** (66%) [17]. During the preparation of this manuscript, however, *Danheiser et al.* [18] reported the successful cyclopropanation of the α,β-unsaturated acylsilane **17** *via* reaction with CH_2N_2 leading to the cyclopropyl silyl ketone **18**.

Scheme 2

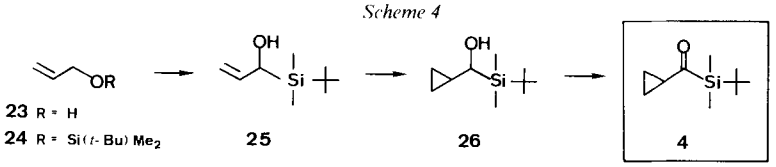


Scheme 3



Analogously, nerol ((*Z*)-**5**) was transformed to the acylsilane **3** (85% overall yield) *via* the silyl ether (*Z*)-**20** (94%), the silyl alcohol (*Z*)-**21** (95%), the cyclopropyl silyl alcohols **22A** + **B** (98%), and final oxidation to **3** (97%).

Scheme 4



Furthermore, by the same method, (*t*-butyl)dimethylsilyl cyclopropyl ketone (**4**)[5]) was obtained from allyl alcohol (**23**) by transformation to the silyl ether (**23**→**24**, 94%), *Wittig* rearrangement (**24**→**25**, 66%), cyclopropanation (**25**→**26**, 30%)[6]), and oxidation (**26**→**4**, 70%; overall yield 18%).

3. Spectral Characteristics of the Cyclopropyl Silyl Ketones 1–4. – In particular, compounds **1–4** show IR bands shifted to extremely long wavelength: 1610–1620 cm^{-1}. In the UV spectra, the expected structured n,π^* bands in the region of 330–395 nm are observed. In the ^{13}C-NMR spectra, the C=O groups are evidenced by low-field shifted signals at *ca.* 245 ppm. In comparison, the analogous methyl ketones show IR bands at *ca.* 1690 cm^{-1}, UV maxima at *ca.* 285 nm, and in the ^{13}C-NMR spectra signals for the C=O group at *ca.* 205 ppm [1]. For spectral data of **1–4** as well as for the other new compounds, see *Exper. Part.*

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Experimental Part

General. See [2]. ^{1}H-NMR spectra were taken in $CDCl_3$ solns. on a *Bruker WP-80 CW* instrument (80 MHz) or, exceptionally (as indicated below), on a *Bruker WM 300* instrument (300 MHz).

1. Preparation of 10. – 1.1.1. *Cyclopropanation of Geraniol* ((*E*)-**5**). To a soln. of AgOAc (50 mg, 0.30 mmol) in AcOH (50 ml), heated under reflux, Zn granulate (mesh 20, 5.58 g, 85.4 mmol) was added at once. After stirring for 30 s, the acid was decanted and the black Ag/Zn-complex washed with abs. Et_2O (5 × 50 ml). Under Ar, abs. Et_2O (40 ml) and I_2 (1 crystal) were added and the mixture was heated at reflux temp. After the dropwise addition of

[5]) Trimethylsilyl cyclopropyl ketone was recently postulated as an intermediate in the flash vacuum pyrolysis of 2-trimethylsilyl-4,5-dihydrofuran [21].

[6]) The low yield of the volatile product **24** is due to the difficult removal of excess CH_2I_2.

CH_2I_2 (3.40 ml, 42.10 mmol), stirring was continued for 15 min under reflux and for 1 h at r.t. A soln. of (*E*)-**5** (663 mg, 4.30 mmol) in abs. Et_2O (10 ml) was added dropwise. After 1 h, the mixture was filtered through *Celite* into a soln. of sat. aq. NH_4Cl and ice, Et_2O (200 ml) was added and the org. phase washed with sat. aq. NH_4Cl, sat. aq. $NaHCO_3$, and sat. aq. NaCl solns. CC (Et_2O/hexane 2:3) gave **6** (580 mg, 80%).

1.1.2. *Cyclopropanation According to the Method of* Kawabata [6]. To benzene (480 ml) and Cu (70 g, 1.1 mol) was added I_2 (14.4 g, 113 mmol), and the mixture was stirred until the Cu color disappeared. After heating to 70°, (*E*)-**5** (36 g, 233 mmol) and CH_2I_2 (96 g, 359 mmol) were added, and the mixture was stirred at 100° for 7 d. Filtration, workup, and CC (Et_2O/hexane 1:3) of the mixture afforded **6**[7]) (35 g, 84%).

[(1RS,2RS)-2-Methyl-2-(4'-methyl-3'-pentenyl)cyclopropyl]methanol (6). B.p. 130°/0.2 Torr. IR: 3620*w*, 3400*w* (br.), 3055*w*, 2960*s*, 2950*s* (sh), 2920*s*, 2880*s*, 2850*s*, 1715*w*, 1635*w*, 1600*w* (br.), 1500*w*, 1485*w*, 1455*m* (sh), 1445*s*, 1405*m*, 1380*m*, 1370*m*, 1250*m*, 1135*w*, 1085*m*, 1025*m*, 1005*m*, 940*w*, 890*w*. ^{1}H-NMR (80 MHz): 0.00–0.20, 0.30–0.60, 0.70–1.10 (3*m*, H–C(1), 2 H–C(3)); 1.09 (*s*, CH_3–C(2)); 1.61, 1.68 (2*s*, CH_3–C(4'), 3 H–C(5')); 1.10–1.50, 1.70–2.30 (2*m*, OH, 2 H–C(1'), 2 H–C(2')); 3.58 (*AB* system, J = 12, δ_A = 3.48 split into *d*, J = 8, δ_B = 3.68 split into *d*, J = 6, CH_2–OH); 5.06 (*tm*, J = 7, $w_{1/2}$ = 4, H–C(3')). MS: 168 (< 1, M^+, $C_{11}H_{20}O$), 150 (3), 109 (27), 107 (12), 95 (15), 83 (11), 82 (27), 81 (38), 75 (11), 73 (14), 70 (13), 69 (100), 68 (12), 67 (21), 55 (36), 53 (11), 43 (20), 41 (67).

1.2. *Oxidation of* **6** *with* CrO_3. To a soln. of pyridine (3.74 ml, 47.3 mmol) in CH_2Cl_2 (*Fluka p.a.*, 30 ml), CrO_3 (2.05 g, 20.5 mmol) was added carefully at 0° and the mixture stirred at r.t. for 15 min. At once, a soln. of **6** (580 mg, 3.45 mmol) in CH_2Cl_2 (2.1 ml) was added. After stirring for 1 h at r.t., the mixture was worked up in Et_2O, and CC (Et_2O/hexane 1:4) afforded **8** (414 mg, 72%).

1.3. *Oxidation of* **6** *with* Ag_2CO_3. To a soln. of **6** (996 mg, 5.92 mmol) in hexane (60 ml), Ag_2CO_3/*Celite* (17.23 g, 30.2 mmol) was added at r.t. The mixture was heated under reflux for 24 h, cooled to r.t., and the solvent evaporated. CC (Et_2O/hexane 1:10) yielded **8**[8]) (93% pure (GC), 952 mg, 88%).

[(1RS,2RS)-2-Methyl-2-(4'-methyl-3'-pentenyl)cyclopropane]carbaldehyde (**8**). B.p. 110°/0.1 Torr. IR: 3050*w*, 2990*s* (sh), 2960*s*, 2920*s*, 2845*s*, 2820*m*, 2720*m*, 1700*s*, 1455*m* (sh), 1445*s*, 1435*s*, 1395*m*, 1380*s*, 1375*s*, 1320*w*, 1170*s*, 1145*w*, 1105*w*, 1075*s*, 1040*m* (br.), 975*m*, 930*w*, 860*m*. ^{1}H-NMR (80 MHz): 1.00–1.90, 1.90–2.30 (2*m*, H–C(1), 2 H–C(3), 2 H–C(1'), 2 H–C(2')); 1.26 (*s*, CH_3–C(2)); 1.61, 1.68 (2*s*, CH_3–C(4), 3 H–C(5')); 5.08 (*tm*, J = 7, $w_{1/2}$ = 4, H–C(3')); 9.37 (*d*, J = 5, CHO). ^{13}C-NMR (75 MHz, contaminated with *ca.* 25% of the corresponding dicyclopropyl compound derived from **7**) characteristic signals: 40.8 (*t*, C(2')); 35.9 (*d*, C(1)); 123.6 (*d*, C(3')); 201.3 (*d*, CHO); 131.8 (*s*, C(4')). MS: 166 (1, M^+, $C_{11}H_{18}O$), 123 (14), 122 (16), 109 (13), 107 (11), 95 (12), 83 (11), 82 (11), 81 (14), *69* (100), 67 (18), 55 (21), 41 (66).

1.4. *Thioacetalization of* **8**. To a soln. of **8**[8]) (227 mg, 1.36 mmol) in AcOH (2.5 ml) and abs. CH_2Cl_2 (2.5 ml), a soln. of 1,3-propanedithiol (0.16 ml, 1.60 mmol), AcOH (0.85 ml), and $BF_3 \cdot Et_2O$ (0.123 ml) was added dropwise at 0°. After stirring for 45 min at 0° and 3 h at r.t., ice (20 ml) and CH_2Cl_2 (100 ml) were added, and the mixture was worked up furnishing **9**[8]) (342 mg, 98%), which was transformed to **10** without purification.

(1'RS,2'RS)-2-[2'-Methyl-2'-(4''-methyl-3''-pentenyl)cyclopropyl]-1,3-dithiane (**9**)[8]). IR: 3060*m*, 2990*s* (sh), 2970*s*, 2950*s*, 2930*s*, 2900*s*, 2850*s*, 2830*m*, 2820*m*, 2730*w*, 1720*w*, 1445*s*, 1430*s*, 1420*s*, 1410*m*, 1380*s*, 1375*s*, 1275*s*, 1240*m*, 1195*w*, 1175*m*, 1170*m*, 1110*w*, 1075*m*, 1020*w*, 950*w*, 910*m*, 885*m*, 840*w*. ^{1}H-NMR (80 MHz): 0.15–2.25 (*m*, 2 H–C(5), H–C(1'), 2 H–C(3'), 2 H–C(1''), 2 H–C(2'')); 1.13 (*s*, CH_3–C(2')); 1.59, 1.65 (2*s*, CH_3–C(4''), 3 H–C(5'')); 2.70–2.96 (*m*, 2 H–C(4), 2 H–C(6)); 3.58 (*d*, J = 10, H–C(2)); 5.06 (*tm*, J = 7, $w_{1/2}$ = 4, H–C(3'')). MS: 256 (6, M^+, $C_{14}H_{24}S_2$), 187 (17), 145 (17), 132 (53), 119 (23), 113 (13), 109 (21), 107 (22), 106 (12), 99 (23), 93 (12), 84 (46), 81 (26), 79 (19), 73 (20), 69 (71), 67 (14), 56 (64), 55 (42), 53 (12), 45 (12), 43 (15), 42 (19), *41* (100).

1.5. *Transformation of* **9** *to* **10**. To a soln. of **9**[8]) (342 mg, 1.33 mmol) in abs. THF (12 ml) and HMPT (0.5 ml) was added at −78° BuLi (1.2M in hexane, 1.25 ml, 1.48 mmol). After stirring for 1.5 h at −30°, the mixture was again cooled to −78°, and a soln. of (*t*-Bu)Me_2SiCl (241 mg, 1.60 mmol) in abs. THF (10 ml) was added. After stirring for 4 h at r.t., the mixture was worked up and chromatographed (Et_2O/hexane 1:15) affording **10**[8]) (105 mg, 36%; conversion 60%).

(1'RS,2'RS)-2-[(tert-Butyl)dimethylsilyl]-2-[2'-methyl-2'-(4''-methyl-3''-pentenyl)cyclopropyl]-1,3-dithiane (**10**). IR: 3050*w*, 2950*s*, 2920*s*, 2830*s*, 1460*m* (sh), 1455*m*, 1420*m*, 1380*m*, 1370*m*, 1360*w*, 1260*w*, 1245*s*, 1215*w*, 1110*w*, 1070*w*, 1045*w*, 1000*w*, 955*w*, 930*w*, 910*m*, 890*w*. ^{1}H-NMR (300 MHz): 0.22, 0.24 (2*s*, 2 CH_3Si); 0.66–0.70, 0.79–1.58 (2*m*, H–C(1'), 2 H–C(3'), 2 H–C(1'')); 1.07 (*s*, 3 CH_3–C–Si); 1.46 (*s*, CH_3–C(2')); 1.60, 1.67 (*s* and *d*, J = 1, CH_3–C(4''), 3 H–C(5'')); 1.88–2.11, 2.56–2.67, 2.80–2.89, 2.93–3.02 (4*m*, 2 H–C(4), 2 H–C(5), 2 H–C(6), 2

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[7]) Contaminated with (*E*)-**5** (15%) and compound **7** (25%; ^{1}H-NMR).

[8]) Contaminated with the dicyclopropyl compound derived from **7**.

H–C(2″)); 5.10 (*tm*, $J = 7$, $w_{1/2} = 4$, H–C(3″)). ^{13}C-NMR: –4.9, –4.7 (2*q*, 2 CH_3Si); 17.6, 18.1, 25.7 (3*q*, CH_3–C(2′), CH_3–C(4″), C(5″)); 28.8 (*q*, 3 CH_3–C–Si); 18.8 (*t*, C(3′)); 24.4, 25.1, 25.8, 26.8 (4*t*, C(4), C(5), C(6), C(1″)); 43.5 (*t*, C(2″)); 36.1 (*d*, C(1′)); 124.7 (*d*, C(3″)); 20.2, 21.9 (2*s*, CSi, C(2′)); 39.5 (*s*, C(2)); 131.0 (*s*, C(4″)). MS: 313 (2, $M^+ - C_4H_9$), 301 (9), 246 (10), 189 (58), 147 (14), 131 (13), 115 (13), 99 (10), 91 (13), 75 (16), *73* (100), 69 (22), 59 (10), 41 (23).

1.6. *Dethioacetalization of* **10**. *a*) To a soln. of **10**[8]) (49 mg, 0.133 mmol) in THF (1 ml) and H_2O (1 drop) was added at once at 0° a soln. of $Tl(NO_3)_3 \cdot 3H_2O$ (80 mg, 0.18 mmol) in abs. MeOH (1.2 ml). After 5 min, the mixture was filtered and worked up. GC and ^{1}H-NMR showed an intractable mixture; compound **2**, however, could not be detected. *b*) To a soln. of **10**[8]) (14 mg, 0.04 mmol) in abs. MeOH (1 ml) was added at r.t. a soln. of $HgCl_2$ (28 mg, 0.105 mmol) and HgO (13 mg, 0.06 mmol). After stirring for 1 min at r.t., TLC of the mixture indicated intractable material; however, compound **2** could not be detected. *c*) To a soln. of **10**[8]) (140 mg, 0.38 mmol) in abs. CH_2Cl_2 (12 ml) was added at –77° a soln. of $CH_3(CH_3S)_2SO^+SbCl_6^-$ (360 mg, 0.76 mmol) in abs. CH_2Cl_2 (7 ml) within 10 min. After 10 min, the mixture was poured into sat. aq. Na_2CO_3 soln., extracted with Et_2O, and washed with H_2O (3 × 20 ml). The intractable mixture did not contain **2** (^{1}H-NMR).

2. Preparation of 13. – 2.1. *Oxidation of* **8** *to* **11**. To a soln. of **8** (270 mg, 1.62 mmol) in EtOH (5 ml) and $AgNO_3$ (268 mg, 1.58 mmol) in H_2O (3 ml) was added at r.t. a soln. of NaOH (270 mg, 6.75 mmol) in H_2O (10 ml). After stirring vigorously for 1 h, the mixture was worked up and chromatographed (Et_2O/hexane 1:1) yielding **11** (228 mg, 84%; based on 92% conversion).

(1RS,2RS)-2-Methyl-2-(4′-methyl-3′-pentenyl)cyclopropanecarboxylic Acid (**11**). IR: 3500–2300*m* (br.), 3050*s*, 2970*s*, 2920*s*, 1690*s*, 1465*m* (sh), 1455*s* (sh), 1445*s*, 1425*s*, 1380*m*, 1375*m*, 1330*m*, 1295*m*, 1270*s*, 1215*s*, 1115*m*, 1075*m*, 1045*m*, 940*m* (br.), 865*m*. ^{1}H-NMR (80 MHz): 0.33–0.54, 0.80–1.58 (2*m*, H–C(1), 2 H–C(3), 2 H–C(1′)); 1.04 (*s*, CH_3–C(2)); 1.61, 1.69 (2*s*, CH_3–C(4′), 3 H–C(5′)); 1.88–2.29 (*m*, 2 H–C(2′)); 5.08 (*tm*, $J = 7$, $w_{1/2} = 4$, H–C(3′)); 10.7 (*m*, $w_{1/2} = 14$, COOH). MS: 182 (3, M^+, $C_{11}H_{18}O_2$), 139 (5), 137 (5), 113 (9), 109 (15), 95 (23), 83 (13), 82 (19), 81 (18), 70 (10), *69* (100), 68 (11), 67 (18), 55 (35), 53 (12), 43 (10), 41 (69).

2.2. *Esterification of* **11**. Et_3N (0.66 ml, 4.74 mmol) was added dropwise by means of a syringe to a soln. of **11** (785 mg, 4.31 mmol) and Me_3SiCl (0.60 ml, 4.73 mmol) in abs. THF (5 ml), heated at reflux temperature. After 30 min, the mixture was cooled to r.t., filtered through *Celite* and the residue washed with pentane. The filtrate was concentrated and distilled (140°/0.6 Torr) yielding **12** (825 mg, 75%).

Trimethylsilyl (1RS,2RS)-2-Methyl-2-(4′-methyl-3′-pentenyl)cyclopropanecarboxylate (**12**). B.p. 140°/0.6 Torr. IR: 3050*w*, 2960*s*, 2920*s*, 2850*m*, 1700*s*, 1455*m* (sh), 1450*m*, 1435*m*, 1390*s*, 1370*m*, 1345*m*, 1280*m*, 1260*s*, 1250*s*, 1210*m*, 1180*s*, 1075*m*, 1045*w*, 1020*w*, 960*w* (br.), 860*s*, 850*s*. ^{1}H-NMR (80 MHz): 0.29 (*s*, 3 CH_3Si); 0.25–0.50, 0.60–1.60 (2*m*, H–C(1), 2 H–C(3), 2 H–C(1′)); 1.04 (*s*, CH_3–C(2)); 1.62, 1.69 (2*s*, CH_3–C(4′), 3 H–C(5′)); 1.90–2.30 (*m*, 2 H–C(2′)); 5.09 (*tm*, $J = 7$, $w_{1/2} = 4$, H–C(3′)).

2.3. *Preparation of the Acid Chloride* **13**. To a soln. of **12** (657 mg, 2.58 mmol, freshly dist.) in CCl_4 (*Fluka*, 1 ml) was added $SOCl_2$ (dist., 0.29 ml, 4.03 mmol), and the mixture was heated to 60° for 1 h. The remaining $SOCl_2$ and the solvent were evaporated, and distillation (96°/0.6 Torr) of the residue yielded **13** (425 mg, 84%).

(1RS,2RS)-2-Methyl-2-(4′-methyl-3′-pentenyl)cyclopropanecarbonyl Chloride (**13**). B.p. 96°/0.6 Torr. IR: 3050*w*, 2960*s*, 2920*s*, 2850*m*, 1780*s*, 1455*m* (sh), 1445*s*, 1430*s*, 1380*m* (sh), 1370*s*, 1340*m*, 1245*w*, 1145*w*, 1105*m*, 1065*s*, 1030*m*, 1020*m*, 975*s*, 945*m*, 905*m*, 880*s*. ^{1}H-NMR (80 MHz): 0.40–0.58, 1.00–1.65 (2*m*, 2 H–C(3), 2 H–C(1′)); 1.06 (*s*, CH_3–C(2)); 1.65, 1.72 (2*s*, CH_3–C(4′), 3 H–C(5′)); 2.00–2.40 (*m*, H–C(1), 2 H–C(2′)); 5.10 (*tm*, $J = 7$, $w_{1/2} = 4$, H–C(3′)). MS: 200 (1, M^+, $C_{11}H_{17}ClO$), 165 (4), 137 (6), 123 (8), 109 (16), 95 (28), 83 (13), 82 (22), 81 (26), *69* (100), 68 (12), 67 (20), 55 (40), 53 (14), 41 (64).

2.4. *Reaction of* **13** *with Trimethylsilyl Anion*. To a soln. of hexamethyldisilane (0.3 ml, 1.5 mmol), a soln. of Bu_4NF (0.5M in THF, 0.2 ml) was added dropwise at r.t. Abs. HMPT (2 ml) was added and the mixture stirred at r.t. for 5 min. After the dropwise addition of **13** (223 mg, 1.11 mmol) in THF (3.5 ml), the mixture was stirred for 1 h at r.t. After workup, an intractable mixture was obtained which did not contain any **1**.

3. Preparation of 1. – 3.1. *Reaction of* **8** *with Trimethylsilyl Anion*. To an ice-cold soln. of Bu_4NF (0.5M in abs. THF, 1.0 ml) was added hexamethyldisilane (1.5 ml, 7.5 mmol) followed by the dropwise addition of abs. HPMT (10 ml). After stirring the mixture for 5 min at r.t., a soln. of **8** (830 mg, 5.0 mmol) in abs. THF (3.5 ml) was added dropwise and stirring continued for further 2 h at r.t. Then, a soln. of 10% HCl in MeOH (5 ml) was added and the mixture worked up in Et_2O. CC (Et_2O/hexane 1:5) yielded **14A** (132 mg, 11%) and **14B** (200 mg, 17%).

[(1RS,2RS)-2-Methyl-2-(4′-methyl-3′-pentenyl)]trimethylsilylmethanol (**14**; contaminated with *ca.* 30% of the corresponding dicyclopropyl compound derived from **7**). *Isomer A* (**14A**). IR: 3600*w*, 3050*w*, 2980*s*, 2950*s*, 2920*s*, 2850*m*, 2730*w*, 1455*w* (sh), 1450*m*, 1435*w*, 1380*m*, 1375*m*, 1305*w*, 1255*m* (sh), 1245*s*, 1180*w*, 1120*w*, 1075*w*, 1030*w*, 980*s*, 910*m*, 875*m* (sh), 855*s* (sh), 840*s*. ^{1}H-NMR (80 MHz): 0.05 (*s*, 3 CH_3Si); 0.30–0.40, 0.40–0.60,

0.75–0.85 (3*m*, H–C(1), 2 H–C(3)); 1.13 (*s*, CH_3–C(2)); 1.10–1.50 (*m*, 2 H–C(1'), OH); 1.59, 1.65 (2*s*, CH_3–C(4'), 3 H–C(5')); 1.95–2.25 (*m*, 2 H–C(2')); 2.90 (*d*, J = 11, CH–OH); 5.09 (*tm*, J = 7, $w_{½}$ = 4, H–C(3')).

Isomer B (**14B**). IR: 3580*w*, 3050*m*, 2960*s*, 2950*s*, 2920*s*, 2900*s* (sh), 2860*s*, 2730*w*, 1455*m* (sh), 1450*m*, 1435*m* (sh), 1400*w*, 1380*m*, 1370*m*, 1310*m*, 1255*m* (sh), 1245*s*, 1180*w*, 1110*w*, 1075*w*, 1020*m*, 1010*m*, 1000*m*, 965*m*, 940*m*, 910*m*, 880*m*, 855*s* (sh), 835*s* (br.). ^{1}H-NMR (80 MHz): 0.06 (*s*, 3 CH_3Si); 0.30–0.40, 0.40–0.60, 0.75–0.85 (3*m*, H–C(1), 2 H–C(3)); 1.03 (*s*, CH_3–C(2)); 1.10–1.50 (*m*, 2 H–C(1'), OH); 1.58, 1.65 (2*s*, CH_3–C(4'), 3 H–C(5')); 1.75–2.25 (*m*, 2 H–C(2')); 2.85 (*d*, J = 11, CH–OH); 5.06 (*tm*, J = 7, $w_{½}$ = 4, H–C(3')). ^{13}C-NMR (75 MHz, mixture of **14A** + **B**) characteristic signals: –3.50, –3.55 (2*q*, 3 CH_3Si); 18.1 (*t*, C(3)); 41.8 (*t*, C(2')); 67.5 (*d*, CH–OH); 124.8 (*d*, C(3')); 15.4 (*s*, C(2)); 131.1 (*s*, C(4')).

3.2. *Oxidation of* **14A** + **B** *to* **1**. A soln. of **14A** + **B** (330 mg, 1.37 mmol) in abs. CH_2Cl_2 (2.3 ml) was added at once to a soln. of CrO_3 (813 mg, 8.13 mmol) in pyridine (1.5 ml) and abs. CH_2Cl_2 (6 ml). After stirring for 1 h, the mixture was worked up. CC (Et_2O/hexane 25:1) gave **1** (179 mg, 55%).

(1RS,2RS)-2-Methyl-2-(4'-methyl-3'-pentenyl)cyclopropyl Trimethylsilyl Ketone (**1**). UV (2.078 mg in 1 ml): 345 (40), 361 (75), 376 (100), 393 (80). IR: 3060*w* (br.), 2990*m*, 2960*s*, 2920*s*, 2880*m*, 2850*m*, 2730*w*, 1615*s*, 1455*m* (sh), 1450*m*, 1430*m*, 1380*m*, 1375*s*, 1355*m* (sh), 1320*w*, 1260*m*, 1245*s*, 1105*w*, 1080*m*, 1070*m*, 1030*m*, 1000*m*, 945*w* (br.), 905*m*, 845*s* (br.). ^{1}H-NMR (80 MHz): 0.24 (*s*, 3 CH_3Si); 0.77 (*dd*, J_1 = 7.5, J_2 = 3.5) and 0.90–1.10 (*m*, 2 H–C(3)); 0.99 (*s*, CH_3–C(2)); 1.25–1.60 (*m*, 2 H–C(1')); 1.65, 1.71 (2*s*, CH_3–C(4'), 3 H–C(5')); 1.95–2.33 (*m*, 2 H–C(2')); 2.44 (*dd*, J_1 = 7.5, J_2 = 5.5, H–C(1)); 5.11 (*tm*, J = 7, $w_{½}$ = 4, H–C(3')). MS: 238 (1, M^+, $C_{14}H_{26}OSi$), 223 (1), 195 (2), 181 (6), 155 (13), 75 (13), *73* (100), 69 (15), 45 (11), 41 (17).

4. Cyclopropanation of (*tert*-Butyl)dimethylsilyl 2,6-Dimethyl-1,5-heptadienyl Ketone ((*E*/*Z*)-15). A mixture of NaH dispersion (80 mg, 60%, 2.00 mmol; washed with 3 × 10 ml abs. pentane *Fluka*) and abs. DMSO (2.3 ml) was stirred for 20 min at r.t. At 0°, a soln. of (*E*/*Z*)-**15** (*ca.* 1:1 mixture, 493 mg, 1.85 mmol) in abs. DMSO (1 ml) was added in one portion, and after stirring for 40 min at r.t., pentane (150 ml) was added, the mixture washed with H_2O (2 × 50 ml) and worked up. CC (Et_2O/hexane 1:25) gave *(E/Z)-4,8-dimethyl-3,7-nonadien-2-one* ((*E*/*Z*)-**16**; 203 mg, 66%) [17], which was separated by prep. GC (5% *SE-30*, 140°).

5. Preparation of 2 and 3. – 5.1. *Transformation of (E)-***5** *and (Z)-***5** *to the Silyl Ethers (E)-***20** *and (Z)-***20**. *a*) A mixture of (*E*)-**5** (2.00 g, 12.97 mmol), (*t*-Bu)Me_2SiCl (2.35 g, 15.56 mmol), imidazol (1.32 g, 19.46 mmol), and abs. DMF (4.2 ml) was stirred under Ar for 1 h at r.t. The mixture was worked up in Et_2O; CC (Et_2O/hexane 1:25) and distillation (140°/0.5 Torr) gave (*E*)-**20** (2.83 g, 81%).

(E)-[(tert-Butyl)dimethylsilyloxy]-3,7-dimethyl-2,6-octadiene ((*E*)-**20**). B.p. 105°/0.1 Torr. IR: 2950*s*, 2920*s*, 2880*s*, 2850*s*, 2730*w*, 2710*w*, 1665*w*, 1460*m* (sh), 1455*s*, 1440*s* (sh), 1400*m*, 1375*s*, 1355*m*, 1325*w*, 1250*s*, 1190*w*, 1150*w*, 1095*s*, 1055*s* (br.), 1000*m*, 935*w*. ^{1}H-NMR (80 MHz): 0.14 (*s*, 2 CH_3Si); 0.96 (*s*, 3 CH_3–C–Si); 1.66 (6 H), 1.73 (3 H) (2*s*, CH_3–C(3), CH_3–C(7), 3 H–C(8)); 2.08 (*m*, $w_{½}$ = 5, 2 H–C(4), 2 H–C(5)); 4.23 (br. *d*, J = 6.5, 2 H–C(1)); 5.00–5.25 (*m*, H–C(6)); 5.34 (br. *t*, J = 6.5, H–C(2)). ^{13}C-NMR: –5.0 (*q*, 2 CH_3Si); 16.3, 17.7, 25.7 (3*q*, CH_3–C(3), CH_3–C(7), C(8)); 26.0 (*q*, 3 CH_3–C–Si); 26.4, 39.6 (2*t*, C(4), C(5)); 60.3 (*t*, C(1)); 124.2, 124.5 (2*d*, C(2), C(6)); 18.4 (*s*, CSi); 131.4, 136.7 (2*s*, C(3), C(7)). MS: 268 (2, M^+, $C_{16}H_{32}OSi$), 211 (9), 147 (15), 135 (9), 93 (6), 76 (7), *75* (100), 73 (21), 69 (33), 41 (23).

b) The analogous reaction of nerol ((*Z*)-**5**[9]), 3.00 g, 19.45 mmol), (*t*-Bu)Me_2SiCl (4.60 g, 30.52 mmol), and imidazol (2.60 g, 38.19 mmol) and abs. DMF (8.5 ml) afforded after distillation (140°/0.5 Torr) (*Z*)-**20**[10]) (4.93 g, 94%).

(*Z*)-**20**. B.p. 105°/0.1 Torr. IR: 3010*w*, 2950*s*, 2920*s*, 2880*m*, 2850*s*, 2720*w*, 1660*w*, 1465*m*, 1460*m*, 1445*m*, 1440*m* (sh), 1385*w* (sh), 1375*m*, 1360*w*, 1250*m*, 1090*s*, 1055*s*, 1005*w*, 935*w*. ^{1}H-NMR (80 MHz): 0.10 (*s*, 2 CH_3Si); 0.94 (*s*, 3 CH_3–C–Si); 1.64 (*s*) and 1.73, 1.75 (2*d*, J = 1, CH_3–C(3), CH_3–C(7), 3 H–C(8)); 2.08 (*m*, $w_{½}$ = 5, 2 H–C(4), 2 H–C(5)); 4.19 (br. *d*, J = 6.5, 2 H–C(1)); 4.95–5.24 (*m*, H–C(6)); 5.32 (br. *t*, J = 6.5, H–C(2)). ^{13}C-NMR: –5.0 (*q*, 2 CH_3Si); 17.6, 23.4, 25.7 (3*q*, CH_3–C(3), CH_3–C(7), C(8)); 26.0 (*q*, 3 CH_3–C–Si); 26.7, 32.3 (2*t*, C(4), C(5)); 59.9 (*t*, C(1)); 124.0, 125.4 (2*d*, C(2), C(6)); 18.4 (*s*, CSi); 131.7, 137.2 (2*s*, C(3), C(7)). MS: 268 (5, M^+, $C_{16}H_{32}OSi$), 211 (12), 135 (13), 93 (13), 76 (10), *75* (100), 73 (23), 69 (16), 41 (16).

5.2. Wittig-*Rearrangement of (E)-***20** *and (Z)-***20** *to (E)-***21** *and (Z)-***21**. *a*) To a soln. of (*E*)-**20** (440 mg, 1.54 mmol) in abs. THF (10 ml) was added under Ar at –78° tetramethylethylenediamine (TMEDA; 0.42 ml, 0.38 g, 2.79 mmol) and then *sec*-BuLi (1.30M in cyclohexane; 2.03 ml, 2.65 mmol). After stirring for 50 min at –40°, the mixture was cooled to –78° and quenched with a soln. of AcOH (0.57 ml, 9.96 mmol) in THF (1.7 ml). At r.t., Et_2O

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[9]) Contaminated with (*E*)-**5** (*ca.* 10%).

[10]) Contaminated with (*E*)-**20** (12%).

(50 ml) was added and the mixture worked up, CC (Et_2O/hexane 1:5) gave (*E*)-**20** (209 mg, 53% conversion) and (*E*)-**21** (190 mg, 82%).

(E)-1-[(tert-Butyl)dimethylsilyl]-3,7-dimethyl-2,6-octadien-1-ol ((*E*)-**21**). B.p. 135°/0.1 Torr. IR: 3585*m*, 2950*s*, 2920*s*, 2890*s*, 2880*s*, 2850*s*, 1715*w*, 1465*m*, 1460*m*, 1440*m*, 1410*w*, 1385*m* (sh), 1375*m*, 1360*m*, 1305*w*, 1245*s*, 1160*w*, 1080*w*, 1005*w*, 965*m*, 950*m*, 935*w*, 910*w*. ^{1}H-NMR (80 MHz): −0.11, 0.00 (2*s*, 2 CH_3Si); 0.93 (*s*, 3 CH_3–C–Si); 1.05 (*s*, OH), 1.59, 1.60, 1.65 (3*s*, CH_3–C(3), CH_3–C(7), 3 H–C(8)); 2.05 (*m*, $w_{1/2}$ = 5, 2 H–C(4), 2 H–C(5)); 4.31 (*d*, *J* = 10, H–C(1)); 4.90–5.25 (*m*, H–C(6)); 5.34 (*d*, *J* = 10, H–C(2)). MS: 250 (4, $M^+ - H_2O$), 194 (11), 193 (59), 133 (11), 113 (15), 109 (12), *73* (100), 69 (43), 59 (59), 41 (29).

b) The analogous reaction of (*Z*)-**20**[10] (6.75 g, 25.14 mmol) in abs. THF (120 ml) and TMEDA (5.66 ml, 4.38 g, 37.65 mmol) with *sec*-BuLi (1.16M, in cyclohexane; 32.5 ml, 37.7 mmol) gave after quenching with AcOH (7.5 ml, 7.87 g, 131.0 mmol) in THF (20 ml) and workup (*Z*)-**20** (3.49 g, 48% conversion), and (*Z*)-**21** (3.09 g, 95%).

(*Z*)-**21**. B.p. 135°/0.1 Torr. IR: 3585*m*, 3530*w* (br.), 3020*w*, 2950*s*, 2920*s*, 2880*s*, 2850*s*, 1645*w*, 1465*s*, 1460*s*, 1440*s*, 1410*m*, 1390*m*, 1375*m*, 1360*m*, 1310*w*, 1245*s*, 1195*w*, 1155*w*, 1125*w*, 1105*w*, 1080*w*, 1005*w*, 960*s*, 935*m* (sh). ^{1}H-NMR (80 MHz): −0.11, 0.00 (2*s*, 2 CH_3Si); 0.91 (*s*, 3 CH_3–C–Si); 1.59, 1.66 (2*s*) and 1.71 (*d*, *J* = 1, CH_3–C(3), CH_3–C(7), 3 H–C(8), OH); 2.05 (*m*, $w_{1/2}$ = 8, 2 H–C(4), 2 H–C(5)); 4.26 (*d*, *J* = 11, H–C(I)); 4.90–5.30 (*m*, H–C(6)); 5.35 (*d*, *J* = 11, H–C(2)). MS: 250 (4, $M^+ - H_2O$), 194 (17), 193 (94), 165 (11), 133 (14), 113 (18), 109 (13), 99 (11), 85 (10), 75 (17), *73* (100), 69 (52), 59 (58), 41 (24).

5.3. *Cyclopropanation of (E)-***21** *and (Z)-***21**. *a*) The reaction of (*E*)-**21** (190 mg, 0.71 mmol) as described in *Sect. 1.1.1* afforded after CC (Et_2O/hexane 1:5) and distillation (140°/0.2 Torr) **19A** + **B** (*ca.* 8:1 mixture, 145 mg, 73%).

{(1RS,2RS)-[2-Methyl-2-(4'-methyl-3-pentenyl)]cyclopropyl}[(tert-butyl)dimethylsilyl]methanol (**19A**). B.p. 140°/0.2 Torr. IR: 3580*w*, 3050*w*, 2940*s*, 2920*s*, 2880*s*, 2850*s*, 2740*w*, 1465*m*, 1455*s*, 1445*m*, 1405*w*, 1380*m*, 1370*m*, 1360*m*, 1310*w*, 1245*s*, 1180*w*, 1100*w*, 1075*w*, 1015*m*, 1005*m*, 965*m*, 935*m*, 880*w*, 855*m*. ^{1}H-NMR (80 MHz): 0.04, 0.10 (2*s*, 2 CH_3Si); 0.10–1.00 (*m*, H–C(2), 2 H–C(3)); 1.00 (*s*, 3 CH_3–C–Si); 1.09 (*s*, CH_3–C(2)); 1.10–1.80 (*m*, 2 H–C(1'), OH); 1.64, 1.71 (2*s*, CH_3–C(4'), 3 H–C(5')); 1.85–2.30 (*m*, 2 H–C(2')); 3.08 (*d*, *J* = 11, C*H*–OH); 5.09 (*tm*, *J* = 7, $w_{1/2}$ = 4, H–C(3')). ^{13}C-NMR (75 MHz, 90% pure)[11]: −8.8, −6.9 (2*q*, 2 CH_3Si); 17.6, 18.4, 25.7 (3*q*, CH_3–C(2), CH_3–C(4'), C(5')); 27.1 (*q*, 3 CH_3–C–Si); 17.9 (*t*, C(3)); 25.1, 41.7 (2*t*, C(1'), C(2')); 30.1 (*d*, C(1)); 64.1 (*d*, CH–OH); 124.6 (*d*, C(3')); 16.8 (*s*, CSi); 22.7 (*s*, C(2)); 130.9 (*s*, C(4')). MS: 264 (2, $M^+ - H_2O$), 225 (1), 208 (13), 207 (64), 165 (13), 151 (16), 139 (12), 137 (14), 125 (12), 123 (14), 113 (38), 109 (12), 101 (12), 99 (19), 95 (10), 85 (12), 83 (13), 75 (36), *73* (100), 69 (60), 59 (58), 55 (11), 43 (10), 41 (29).

b) The reaction of (*Z*)-**21** (3.09 g, 11.51 mmol) as described in *Sect. 1.1.1* gave after distillation (140°/0.2 Torr) **22A** + **B** (*ca.* 8:1 mixture, 3.20 g, 98%).

{(1RS,2SR)-[2-Methyl-2-(4'-methyl-3-pentenyl)]cyclopropyl}[(tert-butyl)dimethylsilyl]methanol (**22A**). B.p. 140°/0.2 Torr. IR: 3580*w*, 3050*w*, 2960*s*, 2920*s*, 2880*s*, 2850*s*, 2740*w*, 2710*w*, 1725*w*, 1465*s*, 1460*s*, 1445*m* (sh), 1410*w*, 1390*m*, 1380*m*, 1375*m*, 1360*m*, 1315*w*, 1275*m*, 1250*s* (sh), 1245*s*, 1175*w*, 1110*w*, 1090*w*, 1065*m*, 1020*m*, 1010*m*, 970*m*, 940*m*, 910*w*, 880*w*, 850*m* (sh). ^{1}H-NMR (300 MHz)[11]: −0.01, 0.05 (2*s*, 2 CH_3Si); 0.25–0.28, 0.46–0.51 (2*m*, 2 H–C(3)); 0.86–0.95 (*m*, H–C(1)); 0.96 (*s*, 3 CH_3–C–Si); 1.05 (*s*, CH_3–C(2)); 1.06–1.57 (*m*, 2 H–C(1'), OH); 1.61 (*s*) and 1.68 (*d*, *J* = 0.9, CH_3–C(4'), 3 H–C(5')); 1.94–2.07, 2.10–2.20 (2*m*, 2 H–C(2')); 3.08 (*d*, *J* = 10.4, C*H*–OH); 5.11 (*tm*, *J* = 7, $w_{1/2}$ = 4, H–C(3')). ^{13}C-NMR: −8.6, −7.1 (2*q*, CH_3Si); 17.8, 20.0, 24.7 (3*q*, CH_3–C(2), CH_3–C(4'), C(5')); 27.1 (*q*, 3 CH_3–C–Si); 17.5, 25.8, 34.9 (3*t*, C(3), C(1'), C(2')); 31.7 (*d*, C(1)); 63.7 (*d*, C–OH); 124.7 (*d*, C(3')); 16.9 (*s*, C–Si); 23.0 (*s*, C(2)); 131.4 (*s*, C(4')). MS: 264 (2, $M^+ - H_2O$), 221 (10), 208 (9), 207 (46), 151 (12), 137 (10), 123 (12), 113 (30), 109 (12), 99 (18), 85 (11), 83 (10), 75 (33), *73* (100), 69 (57), 59 (63), 55 (14), 45 (10), 43 (11), 41 (37).

5.4. *Oxidation of* **19A** + **B** *and* **22A** + **B** *to* **2** *and* **3**, *resp. a*) Oxidation of **19A** + **B** (921 mg, 3.26 mmol) as described in *Sect. 3.2* gave **2** (906 mg, 98%).

(tert-Butyl)dimethylsilyl (1RS,2RS)-2-Methyl-2-(4'-methyl-3'-pentenyl)cyclopropyl Ketone (**2**). B.p. 130°/0.06 Torr. UV (4.553 mg in 2 ml): 336 (30), 347 (55), 362 (110), 378 (160), 395 (130). IR: 3210*w*, 3070*w*, 3020*w* (sh), 2990*m* (sh), 2950*s*, 2920*s*, 2880*s*, 2850*s*, 2740*w*, 2710*w*, 1612*s*, 1465*s*, 1460*s*, 1425*m*, 1405*m*, 1380*s*, 1370*s*, 1360*s*, 1320*w*, 1245*s*, 1145*w*, 1105*w*, 1075*s* (br.), 1030*m*, 995*m* (br.), 935*w*, 900*w*. ^{1}H-NMR (300 MHz): 0.19 (*s*, 2 CH_3Si); 0.78 (*dd*, J_1 = 7.5, J_2 = 4, H–C(3)); 0.95 (*s*, 3 CH_3–C–Si); 1.01 (*s*, CH_3–C(2)); 1.20–1.60 (*m*, 2 H–C(1')); 1.40 (*dd*, J_1 = 5.5, J_2 = 4, H–C(3)); 1.61, 1.69 (*s* and *d*, *J* = 1, CH_3–C(4'), 3 H–C(5')); 2.00–2.15 (*m*, 2 H–C(2')); 2.43 (*dd*, J_1 = 7.5, J_2 = 5.5, H–C(1)); 5.10 (*tm*, *J* = 7, $w_{1/2}$ = 4, H–C(3')). ^{13}C-NMR (75 MHz): −6.9 (*q*, 2 CH_3Si); 15.5, 17.6, 25.7 (3*q*, CH_3–C(2), CH_3–C(4'), C(5')); 26.6 (*q*, 3 CH_3–C–Si); 22.4, 25.6, 41.7 (3*t*, C(3), C(1'), C(2')); 41.0 (*d*, C(1)); 124.0 (*d*, C(3')); 16.9 (*s*, CSi); 33.0 (*s*, C(2)); 131.6 (*s*, C(4')); 245.0 (*s*, C=O). MS: 280 (1, M^+, $C_{17}H_{32}OSi$),

[11]) Contaminated with the other diastereoisomer (*ca.* 10%).

265 (1), 252 (< 1), 237 (1), 223 (7), 197 (6), 115 (21), 75 (28), 73 (100), 69 (12), 41 (9). Anal. calc. for $C_{17}H_{32}OSi$ (280.53): C 72.79, H 11.50; found: C 72.79, H 11.69.

b) Oxidation of **22A + B** (3.20 g, 11.33 mmol) as described in *Sect. 3.2* gave **3** (3.09 g, 97%). An anal. pure sample was obtained by HPLC (Et_2O/hexane 1:160, λ = 371 nm, p = 40 bar).

*(*tert*-Butyl)dimethylsilyl (1RS,2SR)-2-Methyl-2-(4'-methyl-3'-pentenyl)cyclopropyl Ketone* (**3**). B.p. 130°/0.06 Torr. UV (5.435 mg in 2 ml): 335 (30), 347 (50), 363 (90), 379 (120), 397 (100). IR: 3210*w*, 3070*w*, 3010*m*, 2950*s*, 2920*s*, 2890*s* (sh), 2880*s* (sh), 2850*s*, 2730*w*, 2710*w*, 1612*s*, 1465*s* (sh), 1460*s*, 1455*s* (sh), 1430*s*, 1405*m*, 1380*s*, 1370*s*, 1360*s*, 1340*m*, 1310*w*, 1290*w*, 1245*s*, 1140*w* (br.), 1105*m* (sh), 1080*s*, 1020*m* (sh), 995*m* (br.), 935*w*, 900*w*. ^{1}H-NMR (300 MHz): 0.16, 0.21 (2*s*, 2 CH_3Si); 0.75 (*dd*, J_1 = 7.5, J_2 = 3.5, H–C(3)); 0.94 (*s*, 3 CH_3–C–Si); 1.21 (*s*, CH_3–C(2)); 1.23–1.41 (*m*, 2 H–C(1')); 1.44 (*dd*, J_1 = 5.7, J_2 = 3.5, H–C(3)); 1.56, 1.63 (*s* and *d*, J = 1, CH_3–C(4'), 3 H–C(5')); 1.65–1.83, 1.90–2.05 (2*m*, 2 H–C(2')); 2.37 (*dd*, J_1 = 7.5, J_2 = 5.7, H–C(1)); 5.03 (*tm*, J = 7, $w_{1/2}$ = 4, H–C(3')). ^{13}C-NMR (75 MHz): –7.2, –7.1 (2*q*, 2 CH_3Si); 17.4, 24.4, 25.6 (3*q*, CH_3–C(2), CH_3–C(4'), C(5')); 26.4 (*q*, 3 CH_3–C–Si); 22.9, 26.3, 31.1 (3*t*, C(3), C(1'), C(2')); 41.5 (*d*, C(1)); 124.2 (*d*, C(3')); 16.7 (*s*, C–Si); 33.2 (*s*, C(2)); 130.7 (*s*, C(4')); 243.7 (*s*, C=O). MS: 280 (< 1, M^+, $C_{17}H_{32}OSi$), 265 (1), 252 (< 1), 237 (< 1), 223 (2), 211 (18), 197 (1), 115 (15), 75 (16), *73* (100), 69 (10), 59 (10), 41 (11). Anal. calc. for $C_{17}H_{32}OSi$ (280.53): C 72.79, H 11.50; found: C 72.57, H 11.51.

6. Preparation of 4. – 6.1. *Transformation of* **23** *to the Silyl Ether* **24**. Allyl alcohol (**23**; 1.75 g, 30.1 mmol) was reacted with (*t*-Bu)Me_2SiCl as described in *Sect. 5.1* affording after distillation (130°/70 Torr) **24** (4.90 g, 94%).

*3-[(*tert*-Butyl)dimethylsilyloxy]-1-propene* (**24**): B.p. 130°/70 Torr. IR: 3090*w*, 3080*w*, 3060*w*, 3010*w*, 2950*s*, 2930*s*, 2890*s*, 2880*s*, 2850*s*, 2800*w*, 2770*w*, 2740*w*, 2720*w*, 1640*w*, 1470*s*, 1460*s*, 1420*m*, 1400*m*, 1385*m*, 1375*m*, 1360*m*, 1285*w*, 1250*s*, 1185*w*, 1140*s* (br.), 1080*s* (br.), 1030*s*, 1005*m*, 990*m*, 940*m*, 920*s*. ^{1}H-NMR (80 MHz): 0.13 (*s*, 2 CH_3Si); 0.96 (*s*, 3 CH_3–C–Si); 4.20 (*m*, $w_{1/2}$ = 8, 2 H–C(3)); 5.10 (*ddt*, J_1 = 10, J_2 = 2, $J_3 \approx$ 1, H–C(1)); 5.26 (*ddt*, J_1 = 17, J_2 = 2, $J_3 \approx$ 1, H–C(1)); 5.93 (*ddt*, J_1 = 17, J_2 = 10, J_3 = 2, H–C(2)). MS: 172 (13, M^+, $C_9H_{20}OSi$), 147 (6), 116 (12), *115* (100), 85 (24), 75 (18), 73 (15), 59 (28), 41 (6).

6.2. Wittig *Rearrangement of* **24** *to* **25**. As described in *Sect. 5.2*, **24** (2.34 g, 13.58 mmol) was treated with *sec*-BuLi (1.18M in cyclohexane; 17.8 ml, 21.0 mmol) affording after CC (*Florisil*, 200–300 mesh, Et_2O/hexane 1:10) the starting material **24** (0.47 g, conversion 80%) and **25** (1.23 g, 66%).

*1-[(*tert*-Butyl)dimethylsilyl]-2-propen-1-ol* (**25**). B.p. 120°/50 Torr. IR: 3590*w*, 3580*w*, 3080*w*, 3040*w*, 3000*w*, 2950*s*, 2920*s*, 2890*s* (sh), 2880*s*, 2850*s*, 2700*w*, 1625*m*, 1465*m*, 1460*m*, 1405*w*, 1385*w*, 1360*m*, 1320*w* (br.), 1290*w*, 1245*s*, 1135*m*, 1085*m*, 1000*w*, 990*m*, 980*m*, 935*w*, 905*s*, 895*s*. ^{1}H-NMR (80 MHz): 0.01, 0.05 (2*s*, 2 CH_3Si); 1.00 (*s*, 3 CH_3–C–Si); 1.38 (*s*, OH); 4.18 (*dm*, J = 5, $w_{1/2}$ = 4, H–C(1)); 4.90–5.25 (*m*, 2 H–C(3)); 6.09 (*ddd*, J_1 = 17, J_2 = 10, J_3 = 5, H–C(2)). MS: 172 (< 1, M^+, $C_9H_{20}OSi$), 116 (3), 115 (26), 99 (2), 87 (3), 75 (26), 74 (9), *73* (100), 59 (10), 41 (3).

6.3. *Cyclopropanation of* **25**. The reaction of **25** (1.08 g, 6.27 mmol) as described in *Sect. 5.3* followed by CC (*Florisil*, 200–300 mesh, Et_2O/hexane 1:1) and distillation (155°/70 Torr) yielded **26** (356 mg, 30%).

*[(*tert*-Butyl)dimethylsilyl]cyclopropylmethanol* (**26**). B.p. 155°/70 Torr. IR: 3580*m*, 3480*w* (br.), 3080*m*, 3000*m*, 2950*s*, 2920*s*, 2890*s*, 2880*s*, 2850*s*, 2820*m*, 2740*w*, 2720*w*, 1715*w*, 1695*w*, 1625*w*, 1468*s*, 1460*s*, 1440*w*, 1425*w*, 1405*m*, 1390*m*, 1370*m*, 1360*m*, 1320*w* (br.), 1250*s* (sh), 1245*s*, 1195*m*, 1170*w*, 1135*w*, 1105*w*, 1095*m*, 1045*m*, 1020*s*, 1005*m* (sh), 990*s*, 950*w*, 935*m*, 910*m*. ^{1}H-NMR (80 MHz): 0.04, 0.09 (2*s*, 2 CH_3Si); 0.10–0.35, 0.40–0.70 (2*m*, 2 H–C(2'), 2 H–C(3')); 0.98 (*s*, 3 CH_3–C–Si); 1.00–1.40 (*m*, H–C(1')); 2.60 (*d*, J = 10, H–C(1)); 3.25–3.75 (*m*, OH). MS: 186 (< 1, M^+, $C_{10}H_{22}OSi$), 129 (22), 115 (4), 101 (6), 75 (86), 73 (100), 59 (13), 45 (18), 43 (16), 41 (7).

6.4. *Oxidation of* **26** (255 mg, 1.34 mmol) with CrO_3 (792 mg, 7.92 mmol) in CH_2Cl_2 (6 ml) and pyridine (1.5 ml) as described in *Sect. 5.4* gave after CC (Et_2O/hexane 1:20) **4** (176 mg, 70%).

*(*tert*-Butyl)dimethylsilyl Cyclopropyl Ketone* (**4**). UV (2.458 mg in 2 ml): 330 (25), 343 (50), 357 (95), 371 (140), 388 (110). IR: 3210*w*, 3080*w*, 3040*w*, 3000*m*, 2950*s*, 2920*s*, 2890*m*, 2980*m*, 2850*s*, 2710*w*, 1710*w* (br.), 1620*s*, 1465*m*, 1460*m*, 1440*m*, 1410*m*, 1405*w* (sh), 1390*w*, 1360*m*, 1350*s*, 1255*s*, 1245*s*, 1190*w*, 1170*w*, 1120*w*, 1090*m* (br.), 1060*m*, 1040*s*, 1005*m* (sh), 995*m*, 940*w*, 850*s*. ^{1}H-NMR (80 MHz): 0.22 (*s*, 2 CH_3Si); 0.65–1.40 (*m*, 2 H–C(2), 2 H–C(3)); 0.95 (*s*, 3 CH_3–C–Si); 2.30–2.70 (*m*, CH–CO). ^{13}C-NMR (75 MHz): –7.3 (*q*, 2 CH_3Si); 26.4 (*q*, 3 CH_3–C–Si); 11.1 (*t*, C(2), C(3)); 26.1 (*d*, C(1)); 16.3 (*s*, CSi); 245.0 (*s*, CO). MS: 184 (< 1, M^+, $C_{10}H_{20}OSi$), 169 (1), 156 (1), 141 (3), 128 (12), 127 (15), 113 (23), 99 (8), 85 (12), 75 (19), *73* (100), 59 (12), 43 (7), 41 (7).

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