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Total Synthesis of (±)-Pentalenene[1] via small ring intermediates.

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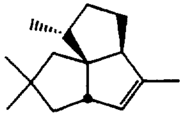
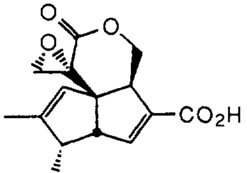
Abstract : The cyclopropanation of the starting cyclopentacyclobutene **4** was achieved by a 1,3-dipolar cycloaddition using diazoethane followed by sensitized photolysis. The resulting bicyclo [2.1.0] pentan-2-ol derivative **8** was cleaved by reflux in acetic acid, giving the diquinanes **9**. The third five membered ring present in (±)-pentalenene was introduced via a silyl assisted Nazarov cyclization leading to the triquinane **3** which was transformed into (±)-pentalenene.

Pentalenene is an angularly fused triquinane isolated from *Streptomyces griseochromogenes*[2]. This sesquiterpene, characterized by a tricyclo[6.3.0.0^{4,8}]undecane skeleton, is the parent hydrocarbon of the pentalenolactone family of sesquiterpenoid antibiotics. Since the first total synthesis of Paquette *et al.* in 1982, more than twenty syntheses have been described[3-24]. Of the various strategies used several took advantage of small ring chemistry, featuring cyclopropanic[6,11,12,14,17,19] or cyclobutanic[3-5,10,13,20,23] intermediates, the latter resulting from photochemical[5,10,13] or ketene [2+2] cycloadditions[3,4]. In continuation of our interest in small ring intermediates in total synthesis (preceding article), we describe here a stereocontrolled approach to (±)-pentalenene, based on the thermal $ZrCl_4$ catalyzed [2+2] cycloaddition of a silyl enol ether of a properly substituted cyclopentanone with ethyl propynoate.

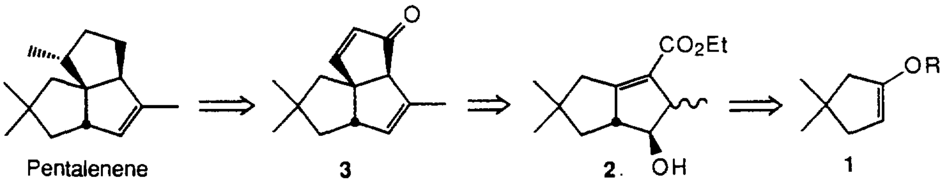


Pentalenene



Pentalenolactone

The retrosynthetic scheme we considered started from the silyl enol ether **1**. By using our reaction sequence (see preceding publication) we should be able to obtain diquinane **2**. The introduction of the third five membered ring could be achieved by means of a Nazarov cyclization leading to triquinane **3** which has previously been transformed into pentalenene[3,4].



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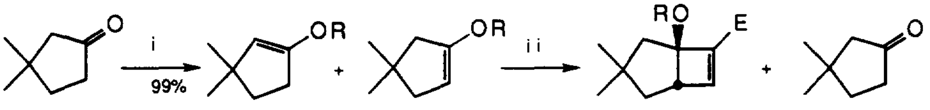
In order to obtain silyl enol ether **1** in a regiospecific manner, we followed the procedure developed by Magnus *et al.*[25] for the catalytic hydrosilylation (Et_3SiH, RhP $(C_6H_5)_3$ Cl) of 4,4-dimethyl cyclopenten-2 one. However this silyl enol ether did not undergo [2+2] cycloaddition with ethyl propynoate in the presence of $ZrCl_4$, 3,3-dimethylcyclopentanone being the sole product recovered, which indicates that under our reaction conditions deprotection of the triethylsilyl enol ether occurred before cycloaddition.

We then used the TBDMS silyl enol ether derived from 3,3-dimethylcyclopentanone as starting material. Under standard conditions (TBDMSOTf, NEt_3, CH_2Cl_2, -78°), 3,3-dimethylcyclopentanone gave a 1/1 mixture of the TBDMS silyl enol ethers **1a** and **1b**. When subjected to our usual [2+2] cycloaddition conditions, the desired cyclobutenic ester **4** was obtained (32 %) along with 3,3-dimethylcyclopentanone (41 %) which could be recycled.

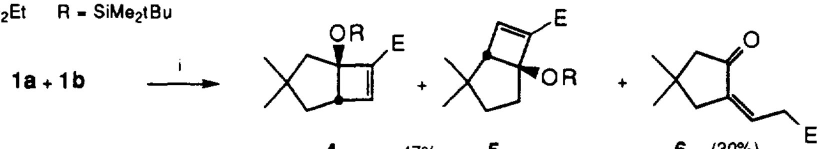


1a 1/1 **1b** **4** 32% 41%

i : TBDMSOTf, NEt_3,CH_2Cl_2, 20°C ; i i : $ZrCl_4$,CH_2Cl_2, -78°C

The same reaction performed in the presence of $TiCl_4$ as Lewis acid, gave cycloadduct **4** <u>and</u> the cycloadduct **5** (1/1, unseparable mixture, 47 %) along with the enone **6** (30 %).

E = CO_2Et R = $SiMe_2tBu$

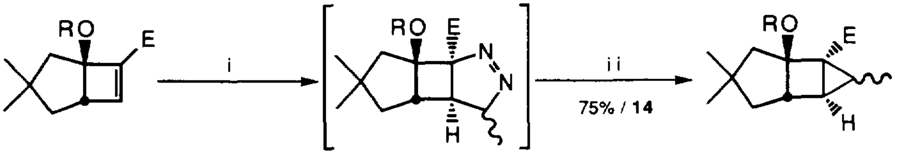


4 47% **5** **6** (30%)

i : $\equiv$—E , $TiCl_4$, -78°C

Cyclopropanation of the electrophilic double bond was carried out as follow : 1,3-dipolar cycloaddition with diazoethane led to two diastereomeric Δ^{-1} pyrazolines **7a** and **7b** which were not isolated but directly subjected to photocleavage in acetone in the presence of acetophenone as a sensitizer, affording the bicyclopentanic derivatives **8a** and **8b*** in 75 % overall yield.

E = CO_2Et ; R = TBDMS



4 **7a,7b** **8a,8b**

i : Diazoethane, Et_2O, 0°C ; i i : hυ , $-N_2$, acetone, acetophenone

The bicyclopentan-2-ols **8a** and **8b** were refluxed in acetic acid yielding quantitatively and stereospecifically the acetates **9a** and **9b** which were transformed into the alcohols **10a** and **10b** by saponification.

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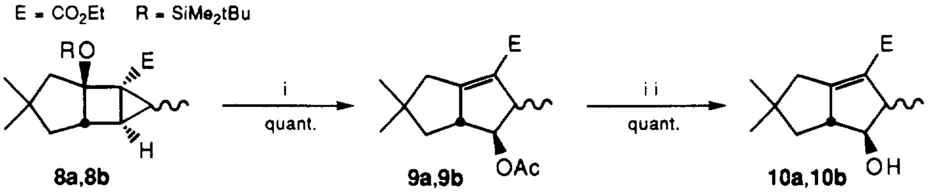
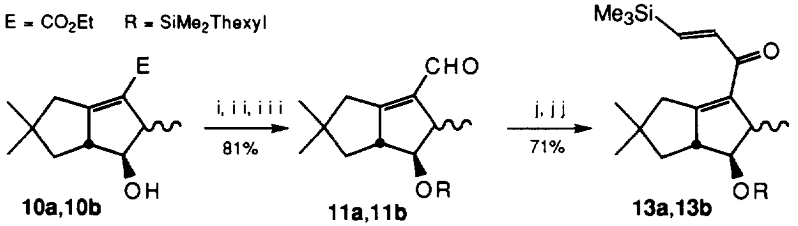
* Two diastereomers were formed in a 1/1.3 ratio which was conserved during the following steps. We did not try to separate them because a double bond was to be introduced at the epimeric position at the end of the synthesis.



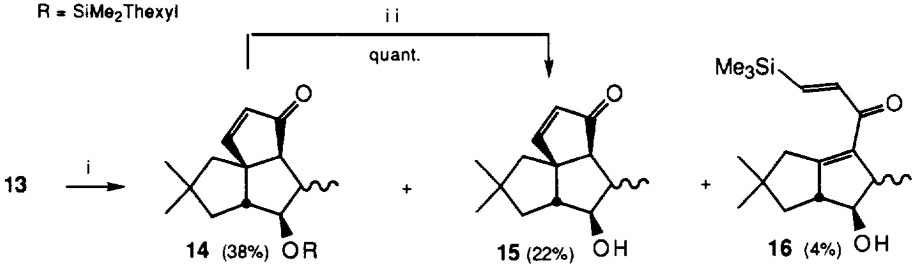
i : AcOH, 120°C ; ii : K_2CO_3, EtOH, 60°C

Elaboration of the third five membered ring present in pentalenene was realized by means of the strategy previously used for the synthesis of silphinene (preceding publication). After protection of the hydroxyl group as a silyl ether, the α,β-unsaturated esters **10** were transformed into aldehydes **11** by reduction (DIBAH, toluene) and reoxidation (MnO_2, CH_2Cl_2). Addition of Grignard reagent **12** followed by oxidation (MnO_2, CH_2Cl_2) gave to the cross-conjugated ketones **13**.



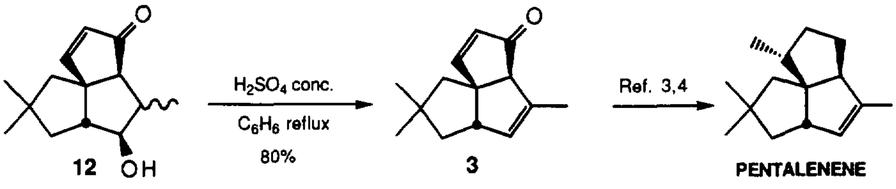
i : $CF_3SO_3SiMe_2$ Thexyl, NEt_3, CH_2Cl_2, 20°C ; ii : DIBAH, benzene, 20°C; iii: MnO_2, CH_2Cl_2, 20°C ;
j : 12 : BrMg (CH=CH)$SiMe_3$, THF, -30°C ; jj : MnO_2, CH_2Cl_2, 40°C

When the cross-conjugated ketones **13** were treated with 2.8 equivalents of $BF_3.Et_2O$ in refluxing ethylbenzene, triquinanes **14** (R = $SiMe_2$thexyl, 38 %) and **15** (R = H, 22 %) were obtained alongside the deprotected starting hydroxy dienones **16** (4 %). The triquinanes **14** were quantitatively deprotected with tetrabutylammonium fluoride.



i : $BF_3.Et_2O$, C_6H_5Et, 125°C ; ii : TBAF, THF, 25°C

Dehydration of alcohols **15** yielded the sole triquinane **3**, which had already been transformed into pentalenene[3,4].



Acknowledgment : We thank the BASF for gifts of ethyl propynoate.

EXPERIMENTAL SECTION

General information :

IR spectra were recorded on a Perkin-Elmer IR-457 instrument (CCl_4 solution). ^{1}H-NMR spectra were recorded on a Bruker WSP 200 spectrometer at 200 MHz. Chemical shifts (δ/TMS) were measured in ppm relative to chloroform as internal standard unless otherwise stated and coupling constants (J values) are in Hertz (Hz). Multiplicities are designated as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Analytical thin-layer chromatography (TLC) was performed on Merck silica gel (60F254) plates (0.25 mm). Visualization was effected with UV light and with ethanol-vanillin-H_2SO_4. Chromatography was carried out on Merck silica gel 60 (230-400 mesh ASTM) under low pressure (CFG pump). Chromatotron chromatography (Harrison Research Model 7924 T) was carried out on Merck silica gel 60 ($SiO_2$60 PF_{254} gipshaltig). Melting points (mp) were determined with a Reichert melting point apparatus and are uncorrected. Elemental analyses were performed by the "Service de Microanalyse du Département de Chimie de l'ULP de Strasbourg". Photolyses were carried out in a Pyrex photoreactor with a Mazda 250 W medium pressure Hg- lamp and stopped when the stoichiometric amount of nitrogen gas + 10 % was obtained.
Before use, ether was distilled over CaH_2, CH_2Cl_2 was distilled over P_2O_5 and THF was distilled over sodium/benzophenone. All reactions were performed under an argon atmosphere in flame dried glassware.

Experimental :

* *Silyl enol ethers **1a** and **1b** :*

Triethylamine (2.83 g ; 28.05 mmol) followed by ter-butyldimethylsilyl triflate (3.26 g ; 12.34 mmol) were added at room temperature to 3,3-dimethylcyclopentanone (1.26 g ; 11.22 mmol) in CH_2Cl_2 (30 ml). After 1 hour stirring at room temperature, water (30 ml) was added and the mixture was extracted with Et_2O (2 x 50 ml). The organic layer was washed with brine (50 ml), dried ($MgSO_4$) and evaporated in vacuo to give 3.05 g of crude material. This was purified by chromatography (15 g SiO_2 ; hexane) yielding silyl enol ethers **1a** and **1b** (2.51 g ; 99 % ; ratio 1/1).

1a and **1b** : $C_{13}H_{26}OSi$; colorless oil ; ^{1}H-NMR ($CDCl_3$) : 4.51 (1H, s), 2.30 (2H, ddd, J = 8 Hz, J = 7 Hz and J = 1.5 Hz), 1.62 (2H, dd, J = 8 Hz and J = 7 Hz), 1.04 (6H, s), 0.93 (9H, s), 0.15 (6H, s).

* *Cyclopentacyclobutene **4** :*

$ZrCl_4$ (884 mg ; 3.79 mmol) was suspended at room temperature in CH_2Cl_2 (20 ml). Ether (3 ml) was added until the mixture became clear. At -78° C, ethyl propynoate (525 mg ; 5.86 mmol) was added followed by addition of the mixture of silyl enol ethers **1a**, **1b** (ratio 1/1) (780 mg ; 3.45 mmol). The resulting mixture turned red. After 30 minutes stirring a saturated $NaHCO_3$ solution was added and the mixture was extracted with CH_2Cl_2 (2 x 20 ml), and ether (2 x 20 ml). The organic layers were washed with brine (30 ml), dried ($MgSO_4$) and evaporated in vacuo to give 1.16 g of crude material. This was purified by chromatography (15 g SiO_2 ; hexane) yielding cycloadduct **5** (358 mg ; 32 %) along with 3,3-dimethylcyclopentanone (158 mg ; 41 %).

4 : $C_{18}H_{37}OSi_2$; colorless oil ; Anal.: calc % C : 66.61, H : 9.94 ; found : C : 66.6, H : 10.0 ; IR (CCl_4) : 1718 (C=O), 1603 (C=C) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 6.88 (1H, d, J = 1 Hz), 4.22 (2H, dq, J = 7 Hz and J = 2 Hz), 3.03 (1H, ddd, J = 8.5 Hz, J = 2.5 Hz and J = 1 Hz), 2.06 and 1.62 (2H, AB, J_{AB} = 13 Hz, $\Delta\nu$ = 89.5), 1.66 and 1.35 (2H, ABX, J = 13.5 Hz, J = 8.5 Hz and J = 2.5, $\Delta\nu$ = 134.3), 1.31 (3H, t, J = 7 Hz), 1.08 (3H, s), 0.97 (3H, s), 0.87 (9H, s), 0.05 (6H, s).

* *Cyclobutene 5* :

Ethyl propynoate (0.99 g ; 10.09 mmol) followed by $TiCl_4$ (1.23 g ; 6.53 mmol) in CH_2Cl_2 (15 ml) were added at -78° C to a solution of **1a** and **1b** (1.34 g ; 5.94 mmol ; ratio 1/1) in CH_2Cl_2 (20 ml). The mixture was stirred for 10 min at -78° C and turned yellow. A saturated solution of $NaHCO_3$ (20 ml) was added, the aqueous phase was separated and extracted with CH_2Cl_2 (2 x 20 ml) and Et_2O (2 x 20 ml), dried ($MgSO_4$), filtered and evaporated in vacuo. The crude material (2.03 g) was purified by chromatography (15 g SiO_2 ; hexane) yielding cyclobutenes **4** and **5** (910 mg ; 47 % ; ratio 1/1) and ketone **6** (384 mg ; 30 %).

5 : $C_{18}H_{32}OSi_2$; colorless oil ; IR (CCl_4) : 1726 (C=O) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 6.85 (1H, s), 4.22 (2H, qd, J = 7 Hz and J = 2 Hz), 2.45 (1H, s), 2.03 and 1.64 (2H, AB, J_{AB} = 13.5 Hz, $\Delta\nu$ = 77.13), 1.60-1.85 (1H, m), 1.31-1.45 (1H, m), 1.31 (3H, t, J = 7 Hz), 1.01 (3H, s), 0.93 (3H, s), 0.87 (9H, s), 0.05 (6H, s).

6 : $C_{12}H_{18}O_3$; yellow oil ; Anal.: calc % C : 68.54, H : 8.62 ; found : C : 68.3, H : 8.7 ;IR (CCl_4) : 1742, 1729 (C=O) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 6.69 (1H, tt, J = 7.5 Hz and J = 3 Hz), 4.17 (2H, q, J = 7 Hz), 3.15 (2H, dt, J = 7.5 Hz and J = 1.5 Hz), 2.41 (2H, dt, J = 3 Hz and J = 1.5 Hz), 2.21 (2H, s), 1.27 (2H, t, J = 7 Hz), 1.11 (6H, s).

* *Bicyclopentanes 8a and 8b* :

Diazoethane (0.6 M in ether ; 22 ml ; 13.2 mmol) prepared from N-nitrosoethylurea[26] was added at 0° C to a solution of **4** (657 mg ; 2.03 mmol) in ether (25 ml). The reaction mixture was allowed to reach 20° C and the solvent was evaporated. The crude oil was dissolved in acetone (400 ml) and acetophenone (7.2 g ; 5.98 mmol) was added. After photolysis for 30 min, the stoichiometric amount of nitrogen (45 ml) was evolved. After evaporation in vacuo (15 mmHg and then 10^{-1} mmHg) the crude reaction mixture (709 mg) was purified by chromatography (15 g SiO_2, hexane) to give the tricyclic adducts **8a** and **8b** (536 mg ; 75 % ; ratio 1/1.3).

8a and **8b** : $C_{20}H_{36}O_3Si$; colorless oil ; Anal.: calc % C : 68.33, H : 10.45 ; found : C : 68.1, H : 10.3 ; IR (CCl_4) : 1711 (C=O) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 4.10-4.30 (2H, m), 1.65-2.55 (7H, m), 1.39 (3H, d, J = 6.5 Hz), 1.30 (3H, t, J = 7 Hz), 1.27 (3H, t, J = 7 Hz), 1.20 (3H, d, J = 6.4 Hz), 1.07 (3H, s), 1.06 (3H, s), 1.04 (3H, s), 1.02 (3H, s), 0.86 (9H, s), 0.84 (9H, s), 0.19 (3H, s), 0.15 (3H, s), 0.10 (3H, s), 0.09 (3H, s).

* *Diquinanes 9a and 9b* :

The mixture of tricyclic adducts **8a** and **8b** (1.65 g ; 4.69 mmol ; ratio 1/1.3) was treated with concentrated acetic acid (5 ml) at 120° C for 1.5 hours. Water was added (20 ml) and the aqueous phase was separated and extracted with CH_2Cl_2 (3 x 20 ml). The organic layer was neutralized with a saturated of $NaHCO_3$ solution (2 x 20 ml) and dried ($MgSO_4$). After filtration and evaporation in vacuo, the crude material (1,90 g) was purified by chromatography (15 g SiO_2 ; hexane) yielding acetates **9a** and **9b** (1.32 g ; 100 % ; ratio 1/1.3).

9a and **9b** : $C_{16}H_{24}O_4$; colorless oil ; IR (CCl_4) : 1708, 1738 (C=O), 1658 (C=C) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 5.03 (1H, t, J = 8 Hz), 4.78 (1H, t, J = 8 Hz), 4.00-4.20 (2H, m), 3.75 (1H, t, J = 7 Hz), 3.30-3.60 (2H, m), 2.98 (1H, m), 2.58 (1H, dt, J = 19 Hz and J = 2.5 Hz), 2.48 (1H, dd, J = 19 Hz and J = 2 Hz), 2.32 (1H, dd, J = 19 Hz and J = 1.5 Hz), 2.21 (1H, dt, J = 19 Hz and J = 2 Hz), 1.86 (1H, dd, J = 13 Hz and J = 7.5 Hz), 1.76 (3H, s), 1.75 (3H, s), 1.70 (1H, dd, J = 13 Hz and J = 7.5 Hz), 1.56 (3H, d, J = 7 Hz), 1.30 (3H, d, J =

7 Hz), 0.85-1.25 (2H, m), 1.06 (3H, d, J = 7 Hz), 1.05 (3H, t, J = 7 Hz), 0.96 (3H, s), 0.95 (3H, s), 0.88 (3H, s), 0.87 (3H, s).

* *Diquinanes **10a** and **10b** :*

To a solution of **9a** and **9b** (92 mg ; 0.32 mmol ; ratio 1/1.3) in EtOH (10 ml), K_2CO_3 (55 mg ; 0.32 mmol) was added. The reaction mixture was warmed to 40° C for 4 hours and water (10 ml) was added. After extraction with CH_2Cl_2 (10 ml) and ether (2 x 10 ml), the combined organic layers were washed with brine (10 ml) and dried ($MgSO_4$). Evaporation in vacuo gave the crude material (113 mg) which was purified by chromatography (3 g SiO_2 ; Et_2O/hexane : 20/80) yielding alcohols **10a** and **10b** (76 mg ; 0.32 mmol; ratio 1/1.3).

10a and **10b** : $C_{14}H_{22}O_3$; colorless oil ; Anal.: calc % C : 70.55, H : 9.30 ; found : C : 70.4, H : 9.3 ; IR (CCl_4) : 3632, 3390 (OH), 1707 (C=O), 1660 (C=C) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 3.95-4.15 (2H, m), 3.86 (1H, t, J = 8 Hz), 3.40 (1H, t, J = 8 Hz), 2.85-3.30 (2H, m), 2.40-2.60 (1H, m), 2.10-2.30 (1H, m), 1.15-1.80 (2H, m), 1.50 (3H, d, J = 6.7 Hz), 1.27 (3H, d, J = 1 Hz), 1.02 (3H, t, J = 7 Hz), 1.00 (3H, t, J = 7 Hz), 0.95 (3H, s), 0.93 (3H, s), 0.86 (3H, s), 0.85 (3H, s).

* *Aldehydes **11a** and **11b** :*

Triethylamine (893 mg, 8.84 mmol) followed by thexyldimethylsilyl triflate (1137 mg ; 3.89 mmol) were added at room temperature to a mixture of **10a** and **10b** (842 mg ; 3.54 mmol) in CH_2Cl_2 (10 ml). After being stirred for 1.5 hours at room temperature, the mixture was treated with water (20 ml) and extracted with Et_2O (2 x 10 ml). The organic layer was washed with brine (20 ml), dried ($MgSO_4$) and evaporated in vacuo to give 1240 mg of crude material. This was purified by chromatography (15 g SiO_2 ; hexane) yielding a mixture of the corresponding silyl enol ethers (1209 mg ; 90 % ; ratio 1/1.3) as a colorless oil :

$C_{22}H_{40}O_3Si$; colorless oil ; Anal.: calc % C : 69.42, H : 10.59 ; found : C : 69.4, H : 10.5 ; IR (CCl_4) : 1707 (C=O), 1650 (C=C) ; ^{1}H-NMR ($CDCl_3$) : 4.10-4.25 (2H, m), 4 (1H, t, J = 7,5 Hz), 3.61 (1H, t, J = 7.8 Hz), 3.05 (2H, m), 2.62 (1H, dt, J = 19 Hz and J = 2.5 Hz),2.57 (1H, dd, J = 19 Hz and J = 2.5 Hz), 2.33 (1H, d, J = 19 Hz), 2.28 (1H, dt, J = 19 Hz and J = 2 Hz), 1.70-1.80 (2H, m), 1.61 (3H, d, J = 7 Hz), 1.46 (3H, d, J = 7 Hz), 1.10 (3H, t, J = 7 Hz), 0.85-1.30 (1H, m), 1.07 (3H, t, J = 7 Hz), 1.00, 1.04 and 1.07 (12 H, 3 s), 0.98 (6H, s), 0.92 (3H, s), 0.91 (3H, s), 0.19 (3H, s), 0.17 (3H, s), 0.15 (3H, s), 0.14 (3H, s).

DIBAH (4.1 ml ; 1 M in hexane ; 4.1 mmol) was added dropwise at room temperature to a solution of the above silyl enol ethers (791 g ; 2.08 mmol) in distilled benzene (50 ml). The mixture was stirred for 30 minutes and water (50 ml) was added. The viscous mixture was filtered through a pad of Celite, extracted with CH_2Cl_2 (2 x 25 ml) and Et_2O (2 x 25 ml), washed with brine (50 ml) and dried ($MgSO_4$). After filtration and evaporation, the crude material (794 mg) was purified by chromatography (15 g SiO_2 ; ether/hexane : 5/95) to give the corresponding alcohols (630 mg ; 90 % ; ratio 1/1.3) :

$C_{20}H_{38}O_2Si$; colorless oil ; Anal.: calc % C : 70.94, H : 11.31 ; found : C : 71.0, H : 11.4 ; IR (CCl_4) : 3966, 3372 (OH) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 4.08 (2H, s), 3.98 (1H, t, J = 7.5 Hz), 3.46 (1H, t, J = 7.5 Hz), 2.85-3.10 (2H, m), 2.01 (2H, s), 1.55-1.80 (2H, m), 1.20-1.50 (1H, m), 1.05 (6H, s), 0.85, 0.88 and 0.91 (12H, 3s), 0.08 (3H, s), 0.07 (3H, s).

To a solution of the resulting alcohols (610 mg ; 1.8 mmol) in CH_2Cl_2 (50 ml), MnO_2 (10 g ; 114 mmol, Mangan (IV)-oxid gefällt aktiv, Merck 5958) was added. The reaction mixture was stirred for 30 min at room temperature, filtered through a pad of Celite and the solvent was evaporated. The crude material obtained (680 mg) was purified by chromatography (15 g SiO_2 ; ether/hexane : 5/95) yielding the aldehydes **11a** and **11b** (606 mg ; 100 % ; ratio 1/1.3).

11a and **11b** : $C_{20}H_{36}O_2Si$; yellow oil ; IR (CCl_4) : 1676 (C=O) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 9.71 (1H, s), 4.03 (1H, t, J = 7.5 Hz), 3.55 (1H, t, J = 7.8 Hz), 2.95-3.45 (2H, m), 2.32 (1H, d, J = 19 Hz), 2.50 (1H, dd, J = 19 Hz and J = 2.5 Hz), 1.75-1.90 (1H, m), 1.65 (1H, h, J = 7 Hz), 1.00-1.32 (10H, m), 0.85, 0.88 and 0.91 (12 H, 3s), 0.10 (6H, s), 0.09 (6H, s).

* *Dienones **13a** and **13b** :*

Mg (1.49 mg ; 6.21 mmol) was suspended in dry THF (5 ml). The reaction mixture was brought to reflux (66° C) and a solution of bromide **12** (1.11 g ; 6.19 mmol) in THF (5 ml) was added. As soon as the Mg had been consumed, the mixture was cooled to -30° C and a solution of aldehydes **11a** and **11b** (695 mg ; 2.07 mmol) in THF (5 ml) was added dropwise. The resulting solution was stirred for 2 hours at -30° C. The reaction mixture was warmed to 0° C and a 2 % solution of NH_4Cl (50 ml) was added. The aqueous phase was separated and extracted with CH_2Cl_2 (2 x 30 ml) and ether (2 x 30 ml). The organic layers were combined, washed with brine (50 ml), dried ($MgSO_4$), filtered and evaporated. The crude material (1.11 g) was purified by chromatography (15 g SiO_2 ; hexane) yielding the corresponding bis allylic alcohols (608 mg ; 80 % ; ratio 1/1.3).

$C_{25}H_{48}O_2Si$; colorless oil ; Anal.: calc % C : 68.74, H : 11.07 ; found : C : 68.9, H : 10.9 ; IR (CCl_4) : 3614, 3450 (OH) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 5.80-6.25 (4H, m), 6.16 (1H, dd, J = 18.5 Hz and J = 5 Hz), 6.11 (1H, dd, J = 18.5 Hz and J = 5 Hz), 5.91 (1H, dd, J = 18.5 Hz and J = 1.5 Hz), 5.86 (1H, dd, J = 18.5 Hz and J = 1.5 Hz), 4.60-4.80 (1H, m), 2.65-3.05 (2H, m), 1.85-2.15 (2H, m), 1.45-1.75 (4H, m), 1.11 (3H, d, J = 6.8 Hz), 1.03 and 1.05 (9H, 2s), 0.85, 0.88 and 0.91 (12H, 3s), 0.088 (15 H, s), 0.082 (15H, s).

To a solution of the bisallylic alcohols so obtained (556 mg ; 1.27 mmol), in CH_2Cl_2 (50 ml), MnO_2 (11g ; 125 mmol) was added. The reaction mixture was refluxed for 2 hours, diluted with CH_2Cl_2 (100 ml) and filtered through a pad of Celite. After evaporation of the solvent, the crude material (587 mg) was purified by chromatography (15 g SiO_2 ; hexane) to give the dienones **13a** and **13b** (496 mg ; 90 % ; ratio 1/1.3).

13a and **13b** : $C_{25}H_{46}O_2Si_2$; yellow oil ; Anal.: calc % C : 69.06, H : 10.66 ; found : C : 69.3, H : 10.5 ; IR (CCl_4) : 1638 (C=O) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 7.12 (1H, d, J = 18.6 Hz), 7.05 (1H, d, J = 18.6 Hz), 6.89 (1H, d, J = 18.6 Hz), 6.78 (1H, d, J = 18.6 Hz), 4.01 (1H, t, J = 7.9 Hz), 3.52 (1H, t, J = 7.9 Hz), 3.05-3.40 (1H, m), 2.15-2.50 (1H, m), 1.60-1.90 (1H, m), 1.13 (3H, s), 1.09 (3H, s), 0.95-1.35 (7H, m), 0.86, 0.89 and 0.92 (12H, 3s), 0.16 (15H, s), 0.15 (15H, s).

* *Triquinanes :*

To a refluxing solution of dienones **13a** and **13b** (151 mg ; 0.34 mmol) in distilled ethylbenzene (10 ml), freshly distilled $BF_3.Et_2O$ (137 mg ; 0.96 mmol) was added. After 3.5 hours of reflux, a saturated solution of $NaHCO_3$ (10 ml) was added to the warm reaction mixture. The aqueous phase was separated and extracted with CH_2Cl_2 (2 x 10 ml) and ether (2 x 10 ml). The combined organic layers were washed with brine (20 ml), dried ($MgSO_4$), filtered and evaporated. The crude product (123 mg) was purified by chromatography (3 g SiO_2 ; hexane) to yield the triquinanes **14a** and **14b** (47 mg ; 38 %) along with the triquinanes **15a** and **15b** (17 mg ; 22 % ; ratio 1/1,3) and the dienones **16a** and **16b** (4 mg ; 4 % ; ratio 1/1.3).

14a and **14b** : $C_{22}H_{38}O_2Si$; yellow oil ; Anal.: calc % C : 72.86, H : 10.56 ; found : C : 72.9, H : 10.7 ; IR (CCl_4) : 1708 (C=O) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 7.54 (1H, d, J = 5.5 Hz), 7.43 (1H, d, J = 5.5 Hz), 5.82 (1H, d, J = 5.5 Hz), 5.80 (1H, d, J = 5.5 Hz), 3.70-3.80 (1H, m), 2.35-2.70 (1H, m), 1.40-2.20 (6H, m), 1.19 (3H, d, J = 6 Hz), 1.17 (3H, d, J = 7.2 Hz), 1.11 (3H, s), 1.09 (3H, s), 0.75, 0.79, 0.82 and 0.86 (12H, 4s), 0.03 (3H, s), 0.01 (3H, s).

15a and **15b** : $C_{14}H_{20}O_2Si$; yellow oil ; Anal.: calc % C : 76.32, H : 9.15 ; found : C : 76.0, H : 9.2 ; IR (CCl_4) : 3620, 3478 (OH), 1702 (C=O) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 7.58 (1H, d, J = 5.5 Hz), 7.57 (1H, d, J = 5.5 Hz), 5.88 (1H, d, J = 5.5 Hz), 5.86 (1H, d, J = 5.5 Hz), 3.80-3.90 (1H, m), 2.55-2.75 (1H, m), 2.35-2.50 (1H, m), 2.15-2.30 (1H, m), 1.75-2.05 (2H, m), 1.50-1.70 (2H, m), 1.29 (3H, d, J = 7.2 Hz), 1.25 (3H, d, J = 6.9 Hz), 1.13 (6H, s), 1.11 (3H, s), 1.09 (3H, s).

16a and **16b** : $C_{17}H_{28}O_2Si$; yellow oil ; IR (CCl_4) : 3630, 3480 (OH), 1702 (C=O) cm^{-1} ; ^1H-NMR ($CDCl_3$) : 7.12 (1H, d, J = 18.6 Hz), 7.05 (1H, d, J = 18.6 Hz), 6.89 (1H, d, J = 18.6 Hz), 6.78 (1H, d, J = 18.6 Hz), 4.10 (1H, t, J = 7.9 Hz), 3.58 (1H, t, J = 7.9 Hz), 3.05-3.45 (1H, m), 2.20 (1H, m), 1.00-1.95 (5H, m), 1.29 (3H, d, J = 6.8 Hz), 1.28 (3H, d, J = 6.8 Hz), 1.10, 1.13 and 1.16 (6H, 3s), 0.15 (9H, s).

* *Triquinane 3 :*

Four drops of concentrated H_2SO_4 were added to a solution of **15a** and **15b** (34 mg ; 0.15 mmol) in benzene (5 ml). The reaction mixture was heated to reflux for 30 minutes. After cooling, a solution of saturated $NaHCO_3$ (5 ml) was added. The aqueous phase was separated and extracted with Et_2O (2 x 5 ml). The organic layer was washed with brine (2 x 5 ml), dried ($MgSO_4$) and evaporated in vacuo to give triquinane **3** (24 mg ; 80 %).

3 : $C_{14}H_{18}O$; yellow oil ; Anal.: calc % C : 83.12, H : 8.91 ; found : C : 82.8, H : 8.7 ; IR (CCl_4) : 1705 (C=O) cm^{-1} ; ^1H-NMR ($CDCl_3$) : 7.52 (1H, d, J = 5.5 Hz), 5.93 (1H, d, J = 5.5 Hz), 5.30 (1H, s), 2.95-3.10 (1H, m), 2.87 (1H, s), 1.55-1.85 (2H, m), 1.25-1.45 (2H, m), 1.79 (3H, s), 1.08 (3H, s), 1.06 (3H, s).

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