Pergamon

Tetrahedron, Vol. 53, No. 6, pp. 2103-2110, 1997
Copyright © 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4020/97 $17.00 + 0.00

PII: S0040-4020(96)01159-3

Total Synthesis of (±)-Silphinene[1] : non photochemical cyclobutenic route to a crucial intermediate.

Michel Miesch, Laurence Miesch-Gross, Michel Franck-Neumann

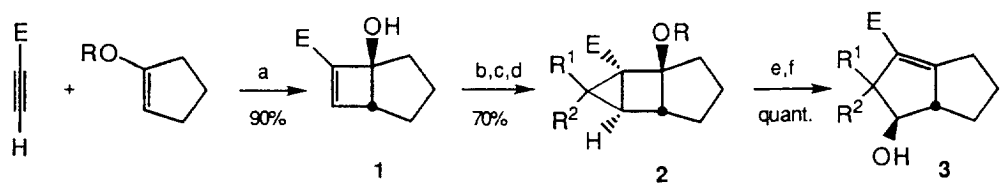
Laboratoire de Chimie Organique Synthétique, associé au CNRS,
Institut de Chimie, Université Louis Pasteur, 1, rue Blaise Pascal 67008 - Strasbourg (France).

Abstract : The cyclobutenic ester **1**, readily available by thermal [2+2] cycloaddition of the silyl enol ether derived from cyclopentanone with ethyl propynoate, is easily transformed into the diquinanic alcohol **3** via the bicyclo [2.1.0] pentane intermediate **2**. After protection as the thexyldimethylsilyl ether, an allylic oxidation stereospecifically introduces a hydroxyl group at position 8. Following formation of the benzyl ether, the diquinane **9** was then transformed in four steps into the triquinane **20** using a silyl-assisted Nazarov type cyclisation. From this intermediate, (±)-silphinene has previously been synthesized. © 1997, Elsevier Science Ltd. All rights reserved.

Silphinene is a natural sesquiterpene, isolated from *Silphium perfolatium*, and characterized by a tricyclo [6.3.0.$0^{4,8}$] undecane skeleton[2]. The synthesis of this molecule with its, at that time, rather unusual triquinane structure became a challenge for the organic chemist and made silphinene as well as the other angular triquinane, pentalenene (see next article), a major goal for natural product synthesis. Of about ten total syntheses of silphinene[3-13], several made use of small ring intermediates such as cyclopropanes[7] or cyclobutanes[8,9] both being obtained by photochemical reactions. Our interest in small ring chemistry in total synthesis[14] led us now to investigate a *non photochemical* cyclobutenic route to a crucial intermediate for the synthesis of (±)-silphinene[14b].

We had shown that the thermal $ZrCl_4$ catalyzed [2+2] cycloaddition of ethyl propynoate with the trimethylsilyl enol ether derived from cyclopentanone led to the cyclobutenic alcohol **1**. After protection of the alcohol as its trimethylsilyl ether, cyclopropanation of the electrophilic double bond could easily be achieved by 1,3-dipolar cycloaddition with various diazoalkanes, followed by sensitized photochemical nitrogen cleavage. The resultant bicyclo [2.1.0] pentanic derivatives **2** were then solvolysed in an acidic medium, giving the difunctionalized diquinanes **3**[15] quantitatively and stereospecifically.

E = CO_2Et; R = $SiMe_3$; R^1,R^2 = H , Me



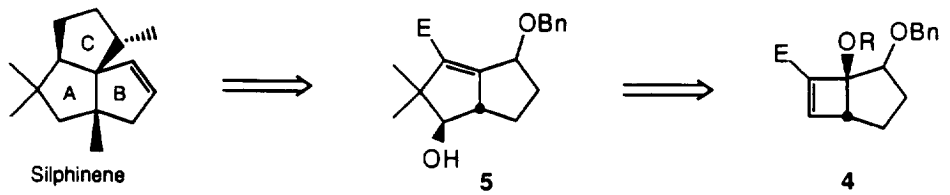
a : $ZrCl_4$, CH_2Cl_2 , 20°C ; b : $CF_3SO_3SiMe_3$, NEt_3 , CH_2Cl_2 , 20°C ; c : $R^1R^2CN_2$ -50°C / 0°C
d : hυ , acetone , $C_6H_5COCH_3$; e : TBAF , CH_2Cl_2 , 20°C ; f : H_2SO_4 10%/H_2O , Et_2O , 20°C .

✆ : (33).03.88.41.68.11 ; fax : (33).03.88.60.42.48 ; e-mail : mfneu@chimie.u-strasbg.fr

This prompted us to use the same reaction sequence for the total synthesis of the natural angular triquinanes silphinene (this article) and pentalenene (following article).

The first retrosynthetic scheme we considered started from the electrophilic cyclobutene **4**. By applying our reaction sequence to this compound, we should obtain the diquinane **5**, an intermediate in our previous synthesis of silphinene[14b].

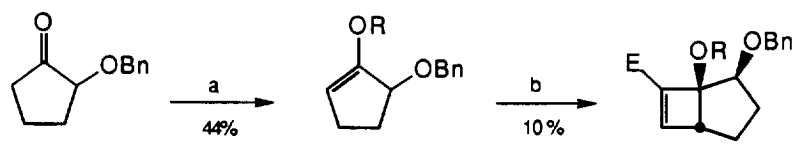
E = CO_2Et Bn = $CH_2C_6H_5$ R = TBDMS



Silphinene **5** **4**

For that purpose, we used as starting material the ketone **6**[16] which was transformed into the silyl enol ether **7** (TBDMSOTf, NEt_3, 44 %). However the [2+2] cycloaddition with ethyl propynoate in the presence of $ZrCl_4$ gave the desired cyclobutenic ester **8** in only 10 % yield. All attemps to increase this yield using different Lewis acids ($TiCl_4$ or $HfCl_4$) and different reaction conditions were unsuccessful, probably due to the fact that the Lewis acid can be coordinated here by several oxygen bearing functions.

E = CO_2Et R = TBDMS



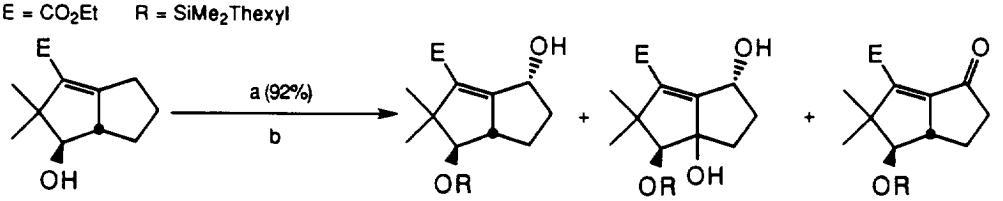
6 **7** **8**

a : TBDMSOTf, NEt_3, CH_2Cl_2, 20°C , b : E—≡—H , $ZrCl_4$, -78°C

We therefore modified our retrosynthetic scheme, using the readily available diquinane **3** as starting material (70 % overall yield from the cyclobutenic ester **1**). An allylic oxydation followed by protection of the resulting hydroxyl group as a benzyl ether should again give the diquinane **5**.

After protection of alcohol **3** as the thexyldimethylsilyl ether, allylic oxydation[17] (SeO_2, dioxane reflux) stereospecifically introduced the hydroxyl group at position 8, giving the diquinane **9** along with diol **10** (5 %) resulting from a double allylic oxydation, and ketone **11** (4 %). These compounds were easily separated by chromatography on silica gel.

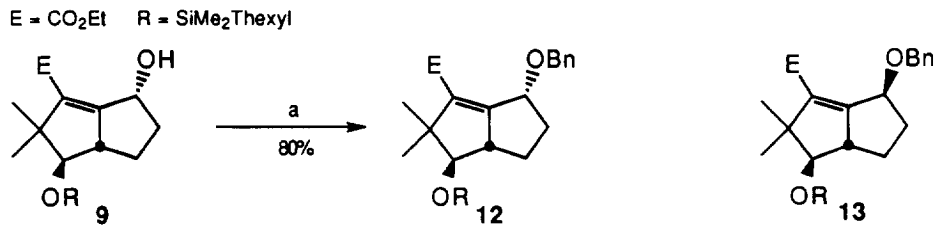
E = CO_2Et R = $SiMe_2Thexyl$



3 **9** (70%) **10** (5%) **11** (4%)

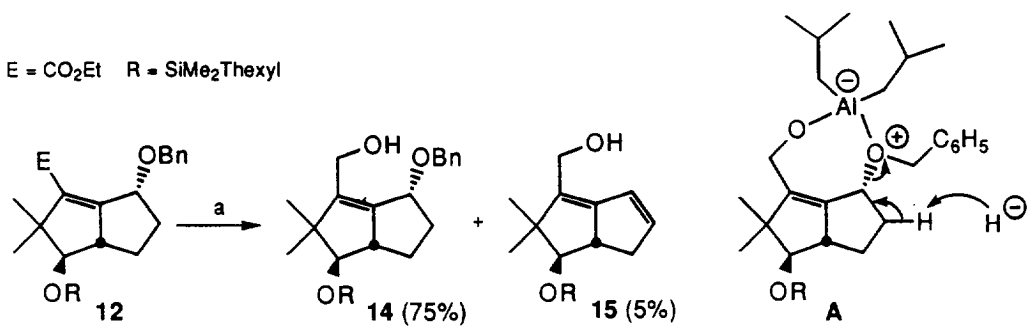
a : $CF_3SO_3SiMe_2Thexyl$, NEt_3, 25°C ; b : SeO_2, dioxane, 110°C

Diquinane alcohol **9** was then protected as its benzyl ether **12** with benzyltrichloroacetimidate in the presence of a catalytic amount of triflic acid[18]. It should be noted that other classical methods of benzylation failed or gave only poor yields (< 20 %). The relative configuration at position 8 of diquinane **12** was secured by NOESY spectroscopy and also by comparison with the ^{1}H-NMR spectrum of the diquinane epimer **13** obtained previously[14b].



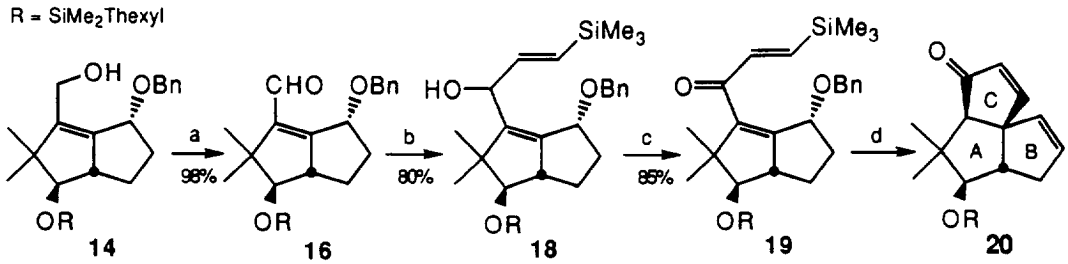
a : $C_6H_5CH_2OCNHCCl_3$, CF_3SO_3H cat., CH_2Cl_2, C_6H_{12}, 40° C

Diquinane **12** was reduced with DIBAH. If this reduction was performed at room temperature, the desired alcohol **14** was obtained (75 % yield) along with minor amounts of olefin **15** (5 % yield). However if the reduction was performed at -10° C, the olefin **15** was the major compound formed (43 % yield) accompanied by alcohol **14** (21 % yield). This may result from the stabilization at low temperature of the intermediate complex **A** from which a hydride ion can now induce elimination of the benzyl group.



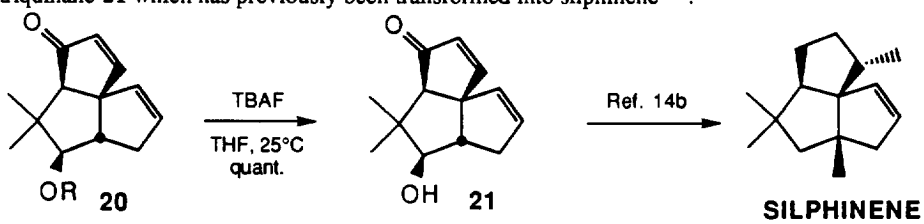
a : DIBAH, benzene, 20°C

Aldehyde **16**, obtained by oxidation of alcohol **14** with MnO_2, was treated with bromovinylsilane **17**[19], leading to alcohol **18**. After reoxidation to ketone **19**, a silyl-assisted Nazarov[20] cyclization ($BF_3.Et_2O$, ethylbenzene, reflux) led to triquinane **20**. Under these reaction conditions, ring C and the double bond in ring B are introduced in one step.



a : MnO_2 , CH_2Cl_2 , 20°C ; b : **17** : $BrMg(CH{=}CH)SiMe_3$, THF , -30°C ;
c : MnO_2 , CH_2Cl_2 , 40°C ; d: $BF_3.Et_2O$, C_6H_5Et , 125°C .

Finally, the deprotection of silyl ether **20** was carried out with TBAF, leading quantitatively to triquinane **21** which has previously been transformed into silphinene[14b].



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 :

* *Diquinane 9 :*

At room temperature, triethylamine (452 mg ; 4.87 mmol) was added to a solution of alcohol 3[15] (473 mg ; 1.25 mmole) in CH_2Cl_2 (20 ml). Thexyldimethylsilyl triflate (570 mg ; 1.95 mmol) was added and the resulting mixture was stirred for 30 min at room temperature. Water (20 ml) was added and after extraction with Et_2O (2 x 20 ml), the organic layer was washed with brine (20 ml), dried ($MgSO_4$), filtered and concentrated in vacuo to give 731 mg of crude material which was purified by chromatography (15 g SiO_2 ; hexane) yielding the corresponding silyl ether as a colorless oil (654 mg ; 92 %).

$C_{21}H_{37}O_3Si$; colorless oil ; Anal.: calc % C : 68.80, H : 10.45 ; found : C : 69.0, H : 10.5 ; IR (CCl_4) : 1710 (C=O), 1654 (C=C) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 4.16 (2H, qd, J = 7 Hz and J = 1.4 Hz), 3.51 (1H, d, J = 8 Hz), 2.75-2.95 (1H, m), 2.25-2.65 (2H, m), 1.95-2.15 (2H, m), 1.65 (1H, h, J = 7 Hz), 1.28 (3H, t, J = 7 Hz), 1.21 (3H, s), 1.10-1.20 (1H, m), 1.09 (3H, s), 0.91 (3H, d, J = 7 Hz), 0.90 (3H, d, J = 7 Hz), 0.87 (3H, s), 0.86 (3H, s), 0.09 (6H, s).

To a solution of the silyl ether (1.19 g ; 3.24 mmol) in dioxane (50 ml), SeO_2 (1.79 g ; 16.2 mmol) was added. The yellow mixture was heated at reflux for 4 hours. After cooling to room temperature, the resulting green solution was filtered through a pad of Celite. Water (20 ml) was added and after extraction with Et_2O (3 x 25 ml), the organic layer was washed with brine (50 ml), dried over $MgSO_4$, filtered and concentred in vacuo to give 1.30 g of crude material. Separation by chromatography (15 g SiO_2 ; Et_2O/hexane : 5/95) gave **9** (1.03 g ; 83 %) along with **10** (0.06 g ; 5 %) and **11** (0.05 g ; 4 %).

9 : $C_{21}H_{38}O_4Si$; yellow oil ; Anal.: calc % C : 65.92, H : 10.01 ; found : C : 66.0, H : 10.2 ; IR (CCl_4) : 3470 (OH), 1722 (C=O), cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 4.17 (1H, t, J = 4 Hz), 4.22 and 4.28 (2H, ABX_3, J_{AB} = 10 Hz, J_{AX} = 7 Hz and J_{BX} = 7 Hz; $\Delta\nu$ = 12), 3.63 (1H, d, J = 8 Hz), 2.90 (1H, dt, J = 11 Hz and J = 8 Hz), 1.85-2.15 (3H, m), 1.65 (1H, h, J = 7 Hz), 1.40 (1H, m), 1.33 (3H, t, J = 7 Hz), 1.20-1.30 (1H, m), 1.18 (3H, s), 1.10 (3H, s), 0.90 (3H, d, J = 7 Hz), 0.89 (3H, d, J = 7 Hz), 0.86 (3H, s), 0.85 (3H, s), 0.09 (6H, s).

10 : $C_{21}H_{38}O_4Si$; yellow oil ; Anal.: calc % C : 63.28, H : 9.61 ; found : C : 63.4, H : 9.7 ; IR (CCl_4) : 3532 (OH), 1726 (C=O) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 4.91 (1H, dd, J = 7.5 Hz and J = 1.5 Hz), 4.27 (2H, qd, J = 7 Hz and J = 2 Hz), 3.72 (1H, s), 2.45-2.70 (1H, m), 1.95-2.10 (1H, m), 1.50-1.80 (5H, m), 1.34 (3H, t, J = 7 Hz), 1.25 (3H, s), 1.22 (3H, s), 0.94 (3H, d, J = 7 Hz), 0.93 (3H, d, J = 7 Hz), 0.92 (3H, s), 0.91 (3H, s).

11 : $C_{21}H_{36}O_4Si$; yellow solid ; F = 39-40° C ; Anal.: calc % C : 66.27, H : 9.53 ; found : C : 66.3, H : 9.7 ; IR (CCl_4) : 1727 (C=O), 1687 (C=C) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 4.20-4.40 (2H, m), 3.77 (1H, d, J = 8 Hz), 3.20 (1H, d, J = 10 Hz and J = 7 Hz), 2.25-2.70 (3H, m), 1.55-1.75 (1H, m), 1.65 (1H, h, J = 7 Hz), 1.33 (3H, t, J = 7 Hz), 1.23 (3H, s), 1.16 (3H, s), 0.94 (3H, d, J = 7 Hz), 0.90 (3H, d, J = 7 Hz), 0.89 (3H, s), 0.88 (3H, s), 0.12 (3H, s), 0.11 (3H, s).

* *Diquinane 12 :*

Allylic alcohol **9** (1.73 g ; 4.53 mmol) was dissolved in a 2:1 mixture of cyclohexane and methylene chloride (30 ml). Benzyl trichloroacetimidate (1.37 g ; 5.44 mmol) was added, followed by trifluoromethanesulfonic acid (2 µl). The reaction mixture was heated at 40° C for 1.5 hours. Addition of saturated $NaHCO_3$ solution (50 ml), extraction with CH_2Cl_2 (2 x 25 ml) and ether (2 x 25 ml), washing with brine (50 ml), drying ($MgSO_4$), filtration and concentration under vacuum (25° C, 15 mmHg) gave 2.13 g of crude material. Purification on the Chromatotron (ethyl acetate - cyclohexane 1:99) yielded **12** (1.71 g ; 80 %).

12 : $C_{28}H_{44}O_4Si$; yellow oil ; Anal.: calc % C : 71.14, H : 9.38 ; found : C : 71.3, H : 9.3 ; IR (CCl_4) : 1703 (C=O), 1655 (C=C) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 7.36-7.40 (2H, m), 7.13-7.19 (2H,), 7.04-7.09 (1H, m), 4.52 and 4.44 (2H, AB, J_{AB} = 11.5 Hz ; $\Delta\nu$ = 32.5), 4.37 (1H, d, J = 5 Hz), 4.10 and 4.02 (2H, ABX_3, J_{AB} = 10.5 Hz, J_{AX} = 7 Hz, J_{BX} = 7 Hz ; $\Delta\nu$ = 29.9), 3.68 (1H, d, J = 8 Hz), 2.74-2.82 (1H, m), 1.98-2.03 (1H, m), 1.73-1.79 (1H, m), 1.65 (1H, h, J = 7 Hz), 1.44-1.56 (2H, m), 1.49 (3H, s), 1.36 (3H, s), 0.99 (3H, t, J = 7 Hz), 0.98 (3H, d, J = 7 Hz), 0.97 (3H, d, J = 7 Hz), 0.93 (3H, s), 0.91 (3H, s), 0.05 (6H, s).

* *Diquinane* ***14*** :

At room temperature DIBAH 1 M in hexane (2.15 ml ; 2 mmol) was added dropwise to a solution of **12** (504 mg ; 1.07 mmol) in distilled benzene (100 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 (444 mg) was purified on the Chromatotron (ethyl acetate - hexane 5/95) to give **14** (346 mg ; 75 %) and **15** (17 mg ; 5 %).

14 : $C_{26}H_{42}O_3Si$; colorless oil ; Anal.: calc % C : 72.50, H : 9.82 ; found : C : 72.0, H : 10.3 ; IR (CCl_4) : 3452 (OH) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 7.30-7.40 (5H, m), 4.53 (1H, d, J = 9 Hz), 4.47 and 4.61 (2H, AB, J_{AB} = 11 Hz ; $\Delta\nu$ = 22.4), 4.06 and 4.20 (2H, AB, J_{AB} = 16 Hz ; $\Delta\nu$ = 23.3), 3.59 (1H, d, J = 7.4 Hz), 2.70-2.90 (1H, m), 1.85-2.35 (3H, m), 1.65 (1H, h, J = 7 Hz), 1.25-1.50 (1H, m), 0.98 (6H, s), 0.91 (3H, d, J = 7 Hz), 0.90 (3H, d, J = 7 Hz), 0.86 (3H, s), 0.85 (3H, s), 0.08 (3H, s), 0.07 (3H, s).

15 : $C_{19}H_{34}O_2Si$; yellow oil ; Anal.: calc % C : 70.74, H : 10.62 ; found : C : 70.71, H : 10.87 ; IR (CCl_4) : 3631 (OH) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 6.35 (1H, dt, J = 5.5 Hz and J = 2.5 Hz), 6.20 (1H, dt, J = 5.5 Hz and J = 2.5 Hz), 4.22 (2H, s), 3.58 (1H, d, J = 8.5 Hz), 3.06 (1H, q, J = 8.5 Hz), 2.55 (1H, ddt, J = 22 Hz, 17 Hz and 8 Hz), 2.00-2.20 (1H, m), 1.66 (1H, h, J = 7 Hz), 1.26 (3H, s), 1.07 (3H, s), 0.92 (3H, d, J = 7 Hz), 0.91 (3H, d, J = 7 Hz), 0.88 (3H, s), 0.86 (3H, s), 0.10 (6H, s).

* *Diquinane* ***16*** :

To a solution of **14** (75 mg ; 0.17 mmol) in CH_2Cl_2 (10 ml), MnO_2 (1.25 g ; 14.38 mmol) was added. The reaction mixture was stirred for 7 hours at room temperature, filtered through a pad of Celite and the solvent was evaporated. The crude material obtained (90 mg) was purified by chromatography (3 g SiO_2 ; ether/hexane : 5/95) yielding the aldehyde **16** (73 mg ; 98 %).

16 : $C_{26}H_{40}O_3Si$; colorless oil ; IR (CCl_4) : 1676 (C=O) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 10.08 (1H, s), 7.30-7.40 (5H, m), 4.60-4.70 (1H, m), 4.49 and 4.65 (2H, AB, J_{AB} = 11.5 Hz ; $\Delta\nu$ = 32.2), 3.66 (1H, d, J = 7.7 Hz), 2.92 (1H, q, J = 7.7 Hz), 1.95-2.25 (3H, m), 1.50-1.75 (1H, m), 1.65 (1H, h, J = 7 Hz), 1.27 (3H, s), 1.08 (3H, s), 0.876 (3H, d, J = 7 Hz), 0.875 (3H, d, J = 7 Hz), 0.87 (3H, s), 0.85 (3H, s), 0.09 (6H, s).

* *Bisallylic alcohol* ***18*** :

Mg (154 mg ; 6.34 mmol) was suspended in distilled THF (5 ml). The reaction mixture was brought to reflux (66° C) and a solution of bromide **17** (1.14 g ; 6.34 mmol) in THF (4 ml) was added. As soon as the Mg had been consumed, the mixture was cooled to -30° C and a solution of aldehyde **16** (905 mg ; 2.12 mmol) in THF (6 ml) was added dropwise. The resulting solution was stirred for 2 hours at -30° C, then 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 (1.37 g) was purified by chromatography (15 g SiO_2 ; ether/hexane : 5/95) to give the bisallylic alcohol **18** (894 mg ; 80 %).

18 : $C_{31}H_{52}O_3Si_2$; yellow oil ; Anal.: calc % C : 70.39, H : 9.90 ; found : C : 70.6, H : 10.0 ; IR (CCl_4) : 3458 (OH) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 7.30-7.40 (5H, m), 6.07 (1H, dd, J = 19 Hz and J = 6 Hz), 5.83 (1H, dd, J = 19 Hz and J = 1 Hz), 4.48-4.65 (2H, m), 4.47 and 4.62 (2H, AB, J_{AB} = 11.2 Hz ; $\Delta\nu$ = 23.5), 3.81 (1H, d, J = 8.8 Hz), 3.53 (1H, d, J = 7.4 Hz), 2.74 (1H, q, J = 7.4 Hz), 1.85-1.15 (3H, m), 1.65 (1H, h, J = 7 Hz), 1.34-1.50 (1H, m), 1.01 (3H, s), 0.91 (3H, s), 0.91 (3H, d, J = 7 Hz), 0.90 (3H, d, J = 7 Hz), 0.86 (3H, s), 0.85 (3H, s), 0.09 (3H, s), 0.08 (3H, s), 0.03 (9H, s).

* *Dienone **19** :*

To a solution of **18** (614 mg ; 1.16 mmol) in CH_2Cl_2 (100 ml), MnO_2 (8 g ; 92 mmol) was added. The reaction mixture was refluxed for 5 hours, diluted with CH_2Cl_2 (100 ml) and filtered through a pad of Celite. After evaporation of the solvent the crude material (530 mg) was purified by chromatography (15 g SiO_2 ; ether/hexane: 2/98) yielding **19** (519 mg ; 85 %).

19 : $C_{31}H_{50}O_3Si_2$; yellow oil ; Anal.: calc % C : 70.66, H : 9.56 ; found : C : 70.9, H : 9.6 ; IR (CCl_4) : 1648 (C=O) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 7.20-7.35 (5H, m), 7.03 (1H, d, J = 18.7 Hz), 6.86 (1H, d, J = 18.7 Hz), 4.35-4.45 (1H, m), 4.40 and 4.50 (2H, AB, J_{AB} = 11.5 Hz ; $\Delta\nu$ = 17.1), 3.71 (1H, d, J = 7.7 Hz), 2.95 (1H, dq, J = 7.7 Hz and 3 Hz), 2.15-2.30 (1H, m), 1.90-2.10 (2H, m), 1.65 (1H, h, J = 7 Hz), 1.50-1.75 (1H, m), 1.24 (3H, s), 1.09 (3H, s), 0.91 (3H, d, J = 7 Hz), 0.90 (3H, d, J = 7 Hz), 0.87 (3H, s), 0.86 (3H, s), 0.09 (6H, s), 0.07 (9H, s).

* *Triquinane **20** :*

To a refluxing solution of dienone **19** (71 mg ; 0.13 mmol) in distilled ethylbenzene (20 ml), freshly distilled $BF_3.Et_2O$ (74 mg ; 0.52 mmol) was added. After 3 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 (37 mg) was purified by chromatography (3 g SiO_2 ; hexane) to give triquinane **20** (23 mg ; 50 %).

20 : $C_{21}H_{34}O_2Si$; yellow oil ; Anal.: calc % C : 72.77, H : 9.88 ; found : C : 72.8, H : 9.8 ; IR (CCl_4) : 1706 (C=O) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 7.32 (1H, d, J = 5.5 Hz), 6.00 (1H, d, J = 5.5 Hz), 5.77 (1H, dt, J = 5.5 Hz and 2.1 Hz), 5.39 (1H, dt, J = 5.5 Hz and 2.1 Hz), 3.45 (1H, d, J = 9.5 Hz), 2.75 (1H, ddt, H = 17 Hz, 8 Hz and 2.1 Hz), 2.30-2.50 (2H, m), 2.25 (1H, s), 1.16 (3H, s), 0.91 (3H, d, J = 7 Hz), 0.90 (3H, d, J = 7 Hz), 0.85 (3H, s), 0.84 (3H, s), 0.78 (3H, s), 0.12 (3H, s), 0.10 (3H, s).

* *Triquinane **21** :*

To a solution of **20** (21 mg ; 0.06 mmol) in THF (10 ml), TBAF (1 M in THF ; 0.18 ml ; 0.18 mmol) was added at room temperature. After stirring for 5 hours, water (10 ml) was added. The organic layer was extracted with ether (3 x 10 ml), washed with brine (2 x 10 ml) and dried ($MgSO_4$). After filtration and evaporation in vacuo, the crude material (93 mg) was purified by chromatography (3 g SiO_2 ; ether/hexane ; 10/90) to yield triquinane **21** (13 mg ; quant.).

21 : $C_{13}H_{16}O_2$; yellow oil ; Anal.: calc % C : 76.44, H : 7.89 ; found : C : 76.6, H : 7.8 ; IR (CCl_4) : 3620, 3540 (OH) 1700 (C=O) 1575 (C=C) cm^{-1} ; ^{1}H-NMR ($CDCl_3$) : 7.32 (1H, d, J = 5.5 Hz), 6.00 (1H, d, J = 5.5 Hz), 5.77 (1H, dt, J = 5.5 Hz and 2.1 Hz), 5.39 (1H, dt, J = 5.5 Hz and 2.1 Hz), 3.45 (1H, d, J = 9.5 Hz), 2.75 (1H, ddt, J = 17 Hz, J = 8 Hz and J = 2.1 Hz), 2.30-2.50 (2H, m), 2.25 (1H, s), 1.22 (3H, s), 0.80 (3H, s).

REFERENCES

1. Preliminary communication :
   Franck-Neumann, M.; Miesch, M.; Gross, L. *Tetrahedron Lett.* **1991**, *32*, 2135-2136.
2. Bohlmann, F.; Jakupovic, J. *Phytochemistry* **1980**, *19*, 259-260.
3. Leone-Bay, A.; Paquette, L.A. *J. Org. Chem.* **1982**, *47*, 4713-4714.
4. Paquette, L.A.; Leone-Bay, A. *J. Am. Chem. Soc.* **1983**,*105*, 7352-7358.
5. Tsunoda, T.; Kodama, M.; Ito, S. *Tetrahedron Lett.* **1983**, *24*, 83-86.
6. Sternbach, D.D.; Hughes, J.W.; Burdi, D.F.; Banks, A. *J. Am. Chem. Soc.* **1985**, 107, 2149-2153.
7. Wender, P.A.; Ternansky, R.J. *Tetrahedron Lett.* **1985**, *26*, 2625-2628.
8. Crimmins, M.T.; Mascarella, S.W. *J. Am. Chem. Soc.* **1986**, *108*, 3435-3438.
9. Crimmins, M.T.; Mascarella, S.W. *Tetrahedron Lett.* **1987**, *28*, 5063-5066.
10. Rao, Y.K.; Nagarajan, M. *Tetrahedron Lett.* **1988**, *29* , 107-108.
11. Rao, Y.K.; Nagarajan, M. *J. Org. Chem.* **1989**, *54*, 5678-5683.
12. Shizuri, Y.; Ohkubo, M.; Yamamura, S. *Tetrahedron Lett.* **1989**, *30*, 3797-3798.
13. Dickson, J.L.; Fraser-Reid, B. *J. Chem. Soc., Chem. Comm.* **1990**, 1440-1443.
14. a) Hirsutene : Franck-Neumann, M.; Miesch, M.; Lacroix, E. *Tetrahedron Lett.* **1989**, *30*, 3529-3532 ; Franck-Neumann, M.; Miesch, M.; Lacroix, E.; Metz, B.; Kern, J.M. *Tetrahedron* **1992**, *48*, 1911-1926.
    b) Silphinene : Franck-Neumann, M.; Miesch, M.; Lacroix, E. *Tetrahedron Lett.* **1989**, *30*, 3533-3536.
    c) Dihydro-2,3 illudine M : Franck-Neumann, M.; Miesch, M.; Barth, F. *Tetrahedron Lett.* **1989**, *30*, 3537-3540 ; Franck-Neumann, M.; Miesch, M.; Barth, F. *Tetrahedron Lett.* **1993**, *49*, 1409-1420.
    d) Stoechospermol : Miesch, M.; Cotte, A.; Franck-Neumann, M *Tetrahedron Lett.* **1994**, *35*, 7031-7032.
15. Franck-Neumann, M.; Miesch, M.; Gross, L. *Tetrahedron Lett.* **1990**, *31*, 5027-5030 ;
    Franck-Neumann, M.; Miesch, M.; Gross, L. *Tetrahedron* **1995**, *51*, 4969-4984.
16. Smith III, A.B.; Liverton, N.J.; Hirb, N.J.; Sivaramadrisnan, H.; Witzenberg, K. *J. Am. Chem. Soc.* **1986**, *108*, 3040-3048.
17. Furlenmaier, A.; Furst, A.; Langemann, A.; Waldvogel, G.; Kerb, U.; Mocks, P.; Wiechert, R. *Helv. Chim. Acta* **1966**, *49*, 1590-1601.
18. Iversen, T.; Bundle, D.R. *J.C.S. Chem. Comm.* **1981**, 1240-1241.
    Widmer, U. *Synthesis* **1987**, 568-570.
19. Denmark, S.E.; Jones, T.K. *Helv. Chim. Acta* **1983**, *66*, 2377-2396.
20. Nazarov, N.I.; Zaretskaya, *Zh. Obshch . Khim.* **1957**, *27*, 693-705.
    Denmark, S.E.; Jones, T.K. *Helv. Chim. Acta* **1983**, *66*, 2397-2411.
    Santelli-Rouvier, C.; Santelli, M. *Synthesis* **1983**, 429-442.

(*Received in Belgium* 19 *July* 1996; *accepted* 28 *November* 1996)