A Synthesis of an Alkylated Taxane Model System

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A new synthesis of the model compound 8,12,15,15-tetramethyltricyclo[9,3.1.$0^{3,8}$]pentadecane using $LiCMe_2SePh$ in a method to produce highly substituted dienes is reported.

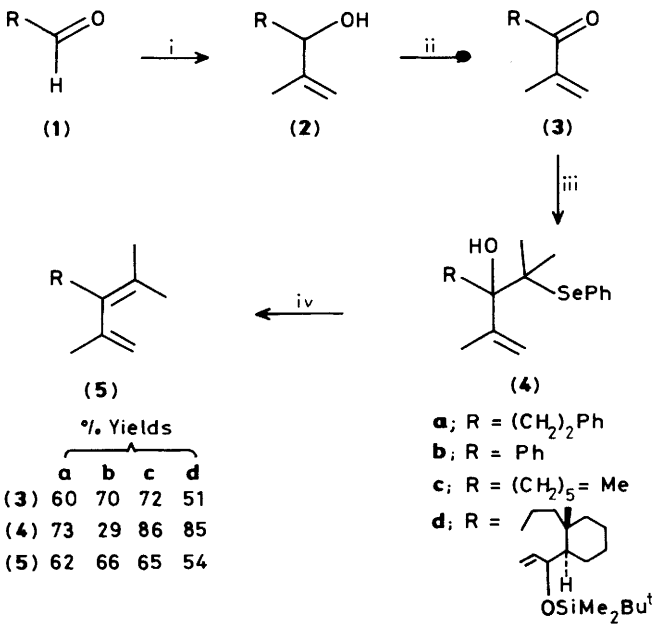
The taxane group of natural products continues to attract considerable attention from synthetic chemists.[1] Our approach has resulted in a stereocontrolled route to the ring system which contains three chiral centres in the same relative configuration as taxinine.[2] However, this model lacked three methyl groups present in the natural product. Adaptation of our synthetic route to incorporate these methyl substituents has involved us in extensive studies on the synthesis and reactions of highly substituted dienes.[3] We have used the reagent $LiCMe_2SiMe_3$ in a route to dienes,[4] however, when applied to the required precursor of a taxane ring system it reacted as a base and not as a nucleophile, consequently the synthesis was not successful. We now report in full[5] that the reagent $LiCMe_2SePh$ is a useful reagent for the synthesis of dienes and that it has enabled us to synthesize an alkylated taxane model system.

Results and Discussion

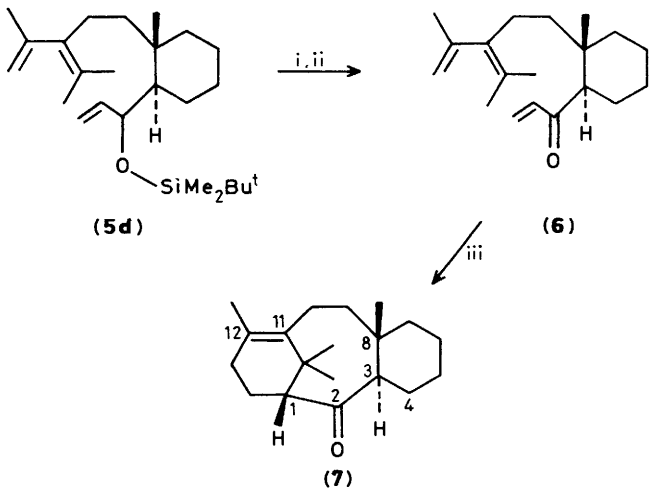
Scheme 1 shows the route for converting three simple aldehydes (**1a**—**c**) and the taxane model aldehyde (**1d**), prepared as previously described,[2] into dienes (**5a**—**d**). Addition of the propenyl Grignard reagent to the aldehydes (**1a**—**d**) produced allylic alcohols (**2a**—**d**) which afforded the enones (**3a**—**d**) on Collins oxidation. Reaction of $Me_2C(SePh)_2$ with BuLi following a literature procedure[6] gave $LiCMe_2SePh$ which added smoothly to the enones (**3a**—**d**) leading to the hydroxy selenides (**4a**—**d**). Elimination was achieved using thionyl chloride and the dienes (**5a**—**d**) were obtained in good yield. The dienes (**5b**) and (**5c**) were characterised as crystalline Diels–Alder adducts with 4-phenyl-1,2,4-trizoline-3,5-dione. Addition of the anion to the enone (**3a**) led to the selenide (**4a**) in lower yield as a result of a side reaction in which $LiCMe_2SePh$ reacted with the enone in a Michael addition.

Conversion of a 2-methylselenobut-3-enol unit into a diene had been mentioned by Krief as unpublished results,[7] and reported in full by Reich[8] using α-lithio selenoxides followed by reduction to prepare the β-hydroxy selenide.

Having established a reliable route to highly substituted dienes further transformations were carried out on the diene (**5d**) as indicated in Scheme 2. Firstly, deprotection and oxidation of (**5d**) gave the enone (**6**) which underwent an intramolecular Diels–Alder reaction on treatment with $BF_3 \cdot OEt_2$ at 40 °C to give the alkylated taxane model system (**7**) as an oil in 56% yield from (**5d**).



Scheme 1. *Reagents:* i, CH_2=CMeMgBr (1.1 equiv.), THF, 0 °C; ii, CrO_3 (6 equiv.), pyridine (12 equiv.), CH_2Cl_2, room temp.; iii, $Me_2C(SePh)_2$, BuLi, THF, −78 °C; iv, $SOCl_2$ (2 equiv.), Et_3N (7 equiv.), CH_2Cl_2, room temp.



Scheme 2. *Reagents:* i, HF, H_2O, MeCN, room temp., 6 h; ii, CrO_3 (6 equiv.), pyridine (12 equiv.), CH_2Cl_2, room temp.; iii, $BF_3 \cdot OEt_2$ (1 equiv.), toluene, −40 °C, 24 h

The stereochemistry of the intramolecular Diels–Alder reaction (**6**)→(**7**) is shown in Figure 1. The eight-membered ring is formed in a chair-boat conformation as in the case of our previous unalkylated model.[2] Nuclear Overhauser difference spectroscopy was used to assign the stereochemistry of (**7**); the results are shown in Figure 2. The strongest evidence in favour of structure (**7**) is the nuclear Overhauser effect between 3-H and 12-Me. This effect would not be present in the alternative Diels–Alder cyclisation product (**8**) obtained *via* the twist chair-boat conformation shown in Figure 3.

In conclusion, we have developed a useful procedure for the preparation of highly substituted dienes using the reagent $LiCMe_2SePh$, and have used it in a synthesis of an alkylated taxane model system.

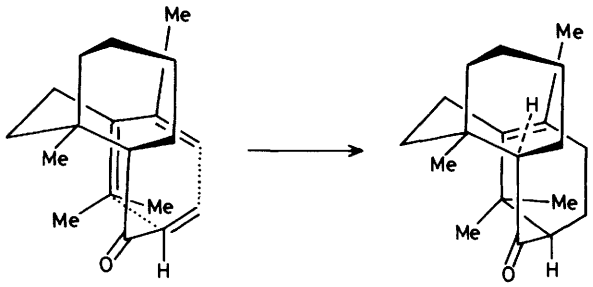


Figure 1. Intramolecular Diels–Alder cyclisation of (**6**) to give (**7**) with the eight-membered ring in the chair-boat conformation

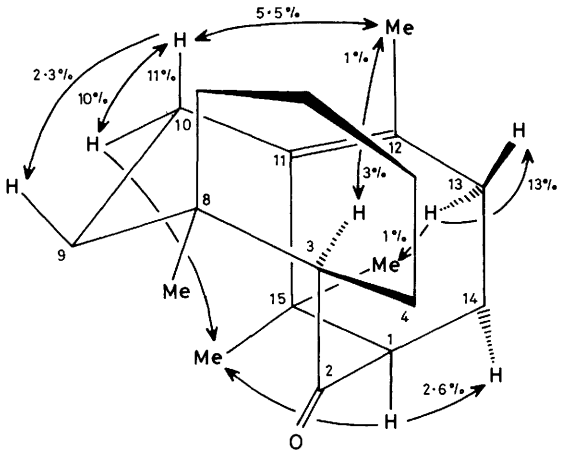


Figure 2. N.O.e. experiments on structure (**7**)

Experimental

All 90 MHz ^{1}H n.m.r. spectra were recorded on a Varian EM-390 spectrometer. Highfield ^{1}H n.m.r. (300 MHz) and ^{13}C n.m.r. (75 MHz) spectra were recorded on a Bruker AM-300 spectrometer at the University of Leicester. ^{1}H N.m.r. (400 MHz) and ^{13}C n.m.r. (100 MHz) spectra were recorded using the highfield n.m.r. service at the University of Warwick. Accurate mass measurements were made at the S.E.R.C. mass spectrometry centre, University College of Swansea and standard mass spectra were recorded on a micromass 16B spectrometer. Elemental analysis was carried out by CHN Analysis, Wigston, Leicester or Butterworth Laboratories, Teddington, Middlesex. I.r. spectra were recorded on a Perkin-Elmer 298 spectrometer and u.v. spectra on a Shimadzu UV-240 spectrometer. M.p.s were determined on a Kofler hot-stage and are uncorrected.

Flash chromatography was carried out according to the method of Still *et al.*[9] using silica gel manufactured by Merck and Co., Kiesel 60, 230—400 mesh (ASTM). Purifications by Chromatotron were performed using mode 7924T and Merck and Co. Kieselgel 60 PF254 silica plates. T.l.c. was conducted on precoated aluminium sheets (60—254) with a 0.2 mm layer thickness, manufactured by Merck and Co.

The concentration of the butyl-lithium was determined by back titration with 0.1M hydrochloric acid from solutions in dibromoethane and water using phenolphthalein as an indicator.

Light petroleum refers to the 40—60 °C fraction; both light petroleum and ethyl acetate were distilled prior to use. Tetrahydrofuran (THF) and toluene were distilled from sodium metal in the presence of benzophenone. Ether refers to diethyl ether and was distilled from $LiAlH_4$. Dichloromethane, triethylamine, and pyridine were distilled from powdered calcium hydride, chromium trioxide was dried over P_2O_5 at 60 °C *in vacuo* overnight, and thionyl chloride was distilled from linseed oil.

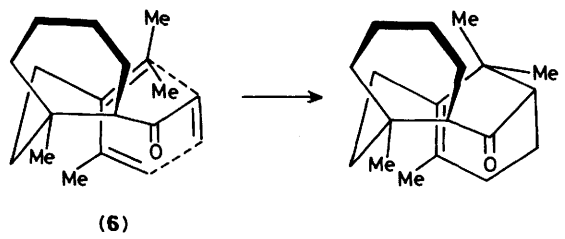


Figure 3. Intramolecular Diels–Alder cyclisation of (**6**) leading to a product with the eight-membered ring in the twist chair-boat conformation

Selenophenol.—Phenylmagnesium bromide (0.3 mol) was prepared in the usual way from bromobenzene (31.6 ml, 0.3 mol) and magnesium (7.2 g, 0.3 mol) in ether (300 ml). Dry powdered black selenium (22.75 g, 0.29 mol) was then added. After work-up and distillation selenophenol[10] was obtained as a colourless oil (32.9 g, 73%), b.p. 62—64 °C at 15 mmHg (lit.,[11] b.p. 72—75 °C at 15 mmHg).

2,2-*Bis*(*phenylseleno*)*propane.*—Hydrogen chloride gas was passed through a mixture of selenophenol (32.8 g, 0.21 mol) and acetone (7.7 ml, 0.104 mol) for 0.5 h at 0 °C. After work-up and flash chromatography (light petroleum) of the crude product in two portions 2,2-bis(phenylseleno)propane was obtained as a pale yellow solid (9.6 g, 26%);[11] R_F 0.25 (light petroleum); δ_H(90 MHz; $CDCl_3$) 1.70 (6 H, s, CH_3) and 7.1—7.8 (10 H, m, C_6H_5).

2-*Methyl*-5-*phenylpent*-1-*en*-3-*ol* (**2a**).[12]—2-Bromopropene (0.89 g, 7.4 mmol) in THF (9 ml) was added to magnesium turnings (0.18 g, 7.5 mmol) in THF (1 ml), under nitrogen, at such a rate so as to maintain a gentle reflux. After the addition, the mixture was heated under reflux for a further 1 h and then cooled in ice; 3-phenylpropanal (1 g, 7.4 mmol) was then slowly added in THF (5 ml). After a further 0.5 h the mixture was poured into saturated aqueous NH_4Cl (75 ml) and extracted with ether (3 × 50 ml). The extracts were combined, dried ($MgSO_4$), and evaporated under reduced pressure, and the residue was flash chromatographed (light petroleum–ether, 7:1) to give the title compound (**2a**) as a colourless oil (0.7 g, 53%); R_F 0.35 (light petroleum–ether, 7:1); $\nu_{max.}$(film) 3 400br s (OH), 3 080m, 3 060m, 3 025m, 2 945s, 2 860m, 1 604m, 1 495m, 1 450s, 1 060br s, 1 030s, 900s, and 700s cm^{-1}; δ_H(90 MHz; $CDCl_3$) 1.5 (1 H, s, OH), 1.72 (3 H, s, 2-Me) overlapping 1.7—1.95 (2 H, m, 4-H), 2.58—2.76 (2 H, m, 5-H), 4.05 (1 H, t, *J* 6 Hz, 3-H), 4.85 (1 H, br s, 1-H), 4.93 (1 H, br s, 1-H), and 7.18 (5 H, s, C_6H_5).

2-*Methyl*-5-*phenylpent*-1-*en*-3-*one* (**3a**).[13]—Chromium trioxide (2.39 g, 23.9 mmol; dried at 60 °C *in vacuo* overnight) was added to a stirred solution of pyridine (3.86 ml, 47.7 mmol) in dichloromethane (60 ml) under nitrogen.[14] Rapid stirring was continued for 0.5 h at room temperature to produce a deep red solution. 2-Methyl-5-phenylpent-1-en-3-ol (**2a**) (0.7 g, 4.0 mmol) in dichloromethane (5 ml) was added in one portion when the solution immediately turned brown. After *ca.* 5 min the mixture was filtered through a short silica column and the chromium residues were washed with ether (2 × 75 ml). The eluant was evaporated under reduced pressure and the residue

flash chromatographed (light petroleum–ether, 20:1) to give the title compound (**3a**) as a colourless oil (0.48 g, 69%); R_F 0.40 (light petroleum–ether, 20:1); $\nu_{max.}$(film) 3 020m, 2 950m, 1 675s (C=O), 1 630m, 1 490m, 1 450s, 1 410m, 1 368m, 1 312w, 1 090m, 1 070m, 1 030m, 935m, 750m, and 700s cm^{-1}; δ_H(90 MHz; $CDCl_3$) 1.83 (3 H, s, CH_3), 2.90 (4 H, s), 5.68 (1 H, s, 1-H), 5.87 (1 H, s, 1-H), and 7.15 (5 H, s, C_6H_5); *m/z* 174 (M^+, 90), 159 (20), 91 (80), 69 (90), and 41 (100).

2,4-*Dimethyl*-3-(2′-*phenylethyl*)-4-*phenylselenopent*-1-*en*-3-*ol* (**4a**).—Butyl-lithium (2.4M; 0.48 ml, 1.15 mmol) was added to a stirred solution of 2,2-bis(phenylseleno)propane (0.407 g, 1.15 mmol) in THF (5 ml), at −78 °C, under nitrogen. After 0.5 h at −78 °C, a solution of 2-methyl-5-phenylpent-1-en-3-one (0.2 g, 1.15 mmol) in THF (1 ml) was added and stirring was continued for 1 h at −78 °C and 1 h at room temperature. The reaction mixture was poured into water and extracted with ether (3 × 20 ml), and each extract was washed with saturated brine (10 ml). The combined ether extracts were dried ($MgSO_4$) and evaporated under reduced pressure and the crude product was purified by flash chromatography (light petroleum–ether) to give the *title compound* (**4a**) as a colourless oil (0.313 g, 73%); R_F 0.33 (light petroleum–ether, 20:1); $\nu_{max.}$(film) 3 480br m, 3 060s, 3 025s, 2 965s, 2 870s, 1 625m, 1 605m, 1 580m, 1 498m, 1 475m, 1 455s, 1 438s, 1 380s, 1 120s, 1 022m, 1 000m, 905m, 740s, and 695s cm^{-1}; δ_H(300 MHz; $CDCl_3$) 1.37 (3 H, s, CH_3), 1.44 (3 H, s, CH_3), 1.91 (3 H, d, *J* 0.6 Hz), 2.07—2.19 (2 H, m, 1′-H), 2.48 (1 H, ddd, *J* 13.7, 9.4 and 6.8 Hz, 2′-H), 2.71 (1 H, s, OH), 2.80 (1 H, ddd, *J* 13.7, 9.5, and 7.8 Hz, 2′-H), 5.08 (1 H, s, 1-H), 5.18 (1 H, m, 1-H), 7.14—7.33 (8 H, m), and 7.58—7.64 (2 H, m); δ_C(75 MHz; $CDCl_3$) 22.69 (q), 26.87 (q), 27.01 (q), 30.27 (t, C-1′), 38.33 (t, C-2′), 60.93 (s, C-4), 81.85 (s, C-3), 114.92 (t, C-1), 125.61 (d), 127.92 (s), 128.28 (d), 138.65 (d), 138.46 (d), 142.75 (s), and 145.20 (s); *m/z* 355 (M^+ − 18%), 111 (15), 105 (67), and 91 (100).

2,4-*Dimethyl*-3-(2′-*phenylethyl*)*penta*-1,3-*diene* (**5a**).—Thionyl chloride (42 µl, 0.58 mmol) in dichloromethane (2 ml) was added to a stirred mixture of the pent-1-en-3-ol (**4a**) (0.108 g, 0.29 mmol) and triethylamine (0.282 ml, 2 mmol) in dichloromethane (2 ml) under nitrogen, at room temperature. The reaction was monitored by t.l.c. and after 2 h no starting material remained. The mixture was then poured into water (10 ml) and extracted with ether (2 × 20 ml). The combined extracts were washed with 1M HCl (10 ml) and saturated brine (10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue, after purification by a Chromatotron (light petroleum) gave the title compound (**5a**) as a colourless oil (36 mg, 62%); R_F 0.5 (light petroleum) (Found: C, 90.05; H, 10.15. $C_{15}H_{20}$ requires C, 89.94; H, 10.06%); $\lambda_{max.}$(CH_3CN) 235 (ε 2 050 dm^3 mol^{-1} cm^{-1}); $\nu_{max.}$(film) 3 080m, 3 060m, 3 030m, 2 920s, 2 880s, 1 632m, 1 605m, 1 496m, 1 435s, 1 372m, 895s, 750m, and 700s cm^{-1}; δ_H(300 MHz; $CDCl_3$) 1.61 (3 H, s, CH_3), 1.68 (3 H, s, CH_3), 1.80 (3 H, dd, *J* 1.5 and 0.9 Hz, CH_3), 2.32—2.41 (2 H, m), 2.58—2.66 (2 H, m), 4.63 (1 H, dq, *J* 2.8 and 0.9 Hz, 1-H), 4.98 (1 H, dq, *J* 2.8 and 1.5 Hz, 1-H), and 7.10—7.28 (5 H, m, C_5H_5); δ_C(75 MHz; $CDCl_3$) 19.51 (q), 21.74 (q), 22.74 (q), 33.36 (t), 34.81 (t), 113.4 (t, C-1), 125.59 (d + s), 128.19 (d), 128.34 (d), 135.94 (s), 142.62 (s), and 146.33 (s); *m/z* 200 (M^+, 70%), 109 (100), 96 (80), 91 (60), 81 (70), and 67 (90).

2-*Methyl*-1-*phenylprop*-2-*en*-1-*ol* (**2b**).[8]—Propenylmagnesium was prepared as in the preparation of (**2a**) from magnesium turnings (1.25 g, 50 mmol) and 2-bromopropene (3.3 ml, 37 mmol) in THF (40 ml). Benzaldehyde (3 ml, 30 mmol) in THF (10 ml) was added to the Grignard solution which after work-up gave crude title compound (**2b**) (4.22 g, 95%); R_F 0.29 (light petroleum–ether, 10:1); the ^1H n.m.r. spectrum was in agreement with the published data.[8]

2-*Methyl*-1-*phenylprop*-2-*en*-1-*one* (**3b**).[8]—Using the same procedure as for the preparation of (**3a**) a solution of the prop-2-en-1-ol (**2b**) (4.22 g, 28.5 mmol) in dichloromethane (40 ml) was oxidised with a preformed solution of chromium trioxide (17.1 g, 0.171 mol) and pyridine (27 g, 0.34 mol) in dichloromethane (400 ml). Standard work-up and flash chromatography (light petroleum–ether, 10:1) gave the title compound (**3b**) as a colourless oil (2.93 g, 70%); R_F 0.39 (light petroleum–ether, 20:1); the spectroscopic data were in agreement with published data.[8]

2,4-*Dimethyl*-3-*phenyl*-4-*phenylselenopent*-1-*en*-3-*ol* (**4b**) *and* 2,4-*Dimethyl*-1-*phenyl*-4-*phenylselenopentan*-1-*one*.—Using the same procedure as for the preparation of (**4a**), 2-lithio-2-phenylselenopropane (2.06 mmol) and the pent-2-en-1-one (**3b**) (0.3 g, 2.05 mmol) were allowed to react in THF (6 ml) at −78 °C for 1 h then at room temperature for 1 h. After work-up and flash chromatography (light petroleum–ether) the *title compound* (**4b**) was obtained as a pale yellow solid (0.21 g, 29%), m.p. 66—70 °C; R_F 0.59 (light petroleum–ether, 20:1); $\nu_{max.}$(Nujol) 3 480w (OH), 1 338m, 1 118m, 1 038s, 912m, 900m, 762s, 745s, 710m, and 696s cm^{-1}; δ_H(300 MHz; $CDCl_3$) 1.03 (3 H, s, CH_3), 1.61 (3 H, m, CH_3), 1.67 (3 H, s, CH_3), 3.34 (1 H, s, OH), 5.22 (1 H, m, 1-H), 5.73 (1 H, s, 1-H), and 7.20—7.66 (10 H, m, C_6H_5); δ_C(75 MHz; $CDCl_3$) 21.71 (q), 58.71 (s, C-4), 83.64 (s, C-3), 113.64 (t, C-1), 126.96 (d), 127.05 (d), 127.95 (d), 128.49 (s), 128.68 (d), 138.31 (d), 139.30 (s), and 146.85 (s); *m/z* 346 (M^+, 1%), 344 (M^+), 199 (30), 197 (13), 119 (34), and 105 (100); and 2,4-*dimethyl*-1-*phenyl*-4-*phenylselenopentan*-1-*one* was obtained as a pale yellow oil (0.27 g, 38%); R_F 0.47 (light petroleum–ether, 20:1); $\nu_{max.}$(film) 3 060m, 2 970s, 2 930s, 2 875m, 1 680s (C=O), 1 600m, 1 580m, 1 450s, 1 365m, 1 255m, 1 215m, 1 115m, 1 001m, 975s, 795m, and 740 cm^{-1}; δ_H(300 MHz; $CDCl_3$) 1.17 (6 H, s and d overlapping, *J* 7.2 Hz, CH_3), 1.38 (3 H, s, CH_3), 1.56 (1 H, dd, J_{33} 14.8, *J* 2.2 Hz, 3-H), 2.50 (1 H, dd, J_{33} 14.8, *J* 8.8 Hz, 3-H), 3.94—4.04 (1 H, m, 2-H), 7.21—7.63 (8 H, m), and 8.02—8.06 (2 H, m); δ_C(75 MHz; $CDCl_3$) 20.48 (q), 29.29 (q), 31.67 (q), 38.12 (d, C-2), 45.51 (t, C-3), 48.17 (s, C-4), 127.66 (s), 128.31 (d), 128.45 (d), 128.56 (d), 128.59 (d), 132.83 (d), 136.31 (s), 138.04 (d), and 203.81 (s, C=O); *m/z* 346 (M^+, 2%), 344 (M^+, 1), 189 (39), 171 (23), and 105 (100).

2,4-*Dimethyl*-3-*phenylpenta*-1,3-*diene* (**5b**).—Using the same procedure as for the preparation of (**5a**) a solution of the pent-1-en-3-ol (**4b**) (0.195 g, 0.57 mmol) was treated with thionyl chloride (82 µl, 1.13 mmol) and triethylamine (550 µl, 3.96 mmol) in dichloromethane (6 ml). Work-up and purification by Chromatotron (light petroleum) gave the title compound (**5b**) as a colourless oil (64 mg, 66%); R_F 0.65 (light petroleum); $\nu_{max.}$(film) 3 075s, 2 980s, 2 970s, 2 910s, 2 855s, 2 720w, 1 630m, 1 600m, 1 490s, 1 440s, 1 370s, 1 090m, 1 070m, 895s, 763s, and 700s cm^{-1}; δ_H(300 MHz; $CDCl_3$) 1.63—1.64 (6 H, m, CH_3), 1.87 (3 H, s, CH_3), 4.84—4.85 (1 H, m, 1-H), 5.02—5.03 (1 H, m, 1-H), and 7.14—7.3 (5 H, m, C_6H_5); δ_C(75 MHz; $CDCl_3$) 21.66 (q), 22.02 (q), 22.63 (q), 114.05 (t, C-1), 126.12 (d), 127.78 (d), 128.42 (s), 129.21 (d), 139.10 (s), and 141.41 (s).

2,2,4-*Trimethyl*-3,8-*diphenyl*-1,6,8-*triazabicyclo*[4.3.0]*non*-3-*ene*-7,4-*dione*.—4-Phenyl-1,2,4-triazoline-3,5-dione[15] (16 mg, 87 µmol) in acetone (250 µl) was added to a solution of the penta-1,3-diene (**5b**) (15 mg, 87 µmol) in dichloromethane (250 µl) at room temperature. After 1 h the solvent was removed under reduced pressure and the resulting white solid was recrystallised twice from methanol to yield the *title compound* as a white crystalline solid (21 mg, 69%), m.p. 153—155 °C (Found: C, 72.4; H, 6.1; N, 12.0. $C_{21}H_{21}N_3O_2$ requires C, 72.60; H, 6.09; N, 12.09%); $\nu_{max.}$(Nujol) 1 770m, 1 710s (C=O), 1 503m, 1 283m, 1 248w, 1 138m, 760m, 742s, 720m, 700m, and 693m cm^{-1}; δ_H(90 MHz; $CDCl_3$) 1.43 (3 H, s, CH_3), 1.54 (6 H, s, CH_3),

4.08 (2 H, s, 5-H), and 6.95—7.52 (10 H, m, C_6H_5); *m/z* 347 (M^+, 75%), 332 (100), 213 (54), and 129 (38).

2-*Methylnon*-1-*en*-3-*ol* (**2c**).[16]—Propenylmagnesium was prepared as in the preparation of (**2a**) from magnesium turnings (0.81 g, 34 mmol) and 2-bromopropene (2.4 ml, 27 mmol) in THF (20 ml). Heptanal (3 ml, 22 mmol) in THF (20 ml) was added to the Grignard solution and after 0.5 h at room temperature the mixture was worked up to yield 2-methylnonen-3-ol (**2c**) as a pale yellow oil (3.47 g, 99%); R_F 0.40 (light petroleum–ether, 10:1); the ^{1}H n.m.r. spectrum was in agreement with published data.[16]

2-*Methylnon*-1-*en*-3-*ol* (**3c**).[17]—Using the same procedure as for the preparation of (**3a**) a solution of 2-methylnon-1-en-3-ol (**2c**) (3.47 g, 22 mmol) in dichloromethane (30 ml) was oxidised with a preformed solution of chromium trioxide (13.3 g, 133 mmol) and pyridine (21.5 ml, 266 mmol) in dichloromethane (300 ml). Standard work-up and flash chromatography (light petroleum–ether, 20:1) gave 2-methylnon-1-en-3-one (**3c**) as a colourless oil (2.4 g, 70%); R_F 0.61 (light petroleum–ether, 20:1); $\nu_{max.}$(film) 2 940br s, 2 860s, 1 675s (C=O), 1 630s, 1 450s, 1 410m, 1 370m, 1 125m, 1 070s, and 930s cm^{-1}; δ_H(90 MHz; $CDCl_3$) 0.80—1.0 (3 H, m, CH_3), 1.23—1.70 (8 H, m), 1.88 (3 H, s, CH_3), 2.68 (2 H, t, *J* 7.5 Hz, 4-H), 5.75 (1 H, s, 1-H), and 5.95 (1 H, s, 1-H); *m/z* 154 (M^+, 10%), 111 (15), 105 (18), 84 (80), and 69 (100).

3-*Hexyl*-2,4-*dimethyl*-4-*phenylselenopent*-1-*en*-3-*ol* (**4c**).—Using the same procedure as for the preparation of (**4a**), 2-lithio-2-phenylselenopropane (3.24 mmol) and 2-methylnon-1-en-3-one (0.5 g, 3.24 mmol) were allowed to react together in THF (14 ml) at −78 °C for 1 h then at room temperature for 1 h. Work-up and flash chromatography (light petroleum–ether, 20:1) gave the *title compound* (**4c**) as a pale yellow oil (0.998 g, 86%); R_F 0.58 (light petroleum–ether, 20:1); $\nu_{max.}$(film) 3 480br m (OH), 2 955s, 2 920s, 2 855m, 1 578w, 1 460m, 1 435m, 1 378m, 1 110m, 1 020m, 900m, 740s, and 693s cm^{-1}; δ_H(300 MHz; $CDCl_3$) 0.86—0.92 (3 H, m, CH_3), 1.24—1.33 (8 H, br s), 1.36 (3 H, s, CH_3), 1.43 (3 H, s, CH_3), 1.78—1.87 (5 H, m), 2.49 (1 H, s, OH), 5.0 (1 H, s, 1-H), 5.08 (1 H, m, 1-H), 7.22—7.38 (3 H, m), and 7.63—7.67 (2 H, m); δ_C(75 MHz; $CDCl_3$) 14.01 (q), 22.59 (t and q overlapping), 23.59 (t), 26.92 (q), 27.07 (q), 29.77 (t), 31.80 (t), 35.91 (t), 60.66 (s, C-4), 81.97 (s, C-3), 114.47 (t, C-1), 128.19 (s), 128.52 (d), 138.49 (d), and 145.56 (s); *m/z* 354 (M^+, 1%), 352 (M^+), 214 (31), 158 (100), and 113 (28).

3-*Hexyl*-2,4-*dimethylpenta*-1,3-*diene* (**5c**).—Using the same procedure as for the preparation of (**5a**) a solution of the pent-1-en-3-ol (**4c**) (0.4 g, 1.13 mmol) was treated with thionyl chloride (165 μl, 2.27 mmol) and triethylamine (1.1 ml, 7.93 mmol) in dichloromethane (15 ml). After work-up and purification by Chromatotron (light petroleum) and Kugelrohr distillation (50 °C at 15 mmHg) the *title compound* (**5c**) was isolated as a colourless oil (0.132 g, 65%); R_F 0.7 (light petroleum) (Found: C, 86.45; H, 13.2. $C_{13}H_{24}$ requires C, 86.59; H, 13.41%); $\lambda_{max.}$(CH_3CN) 236 (ε 1 910 dm^3 mol^{-1} cm^{-1}); $\nu_{max.}$(film) 2 980s, 2 925s, 2 860s, 1 450br m, 1 370m, and 895s cm^{-1}; δ_H(300 MHz; $CDCl_3$) 0.88 (3 H, br t, *J* 6.7 Hz), 1.27 (8 H, br s), 1.66 (6 H, s, CH_3), 2.75 (3 H, dd, *J* 1.5 and 0.9 Hz, CH_3), 2.06 (2 H, br t, *J* 7.4 Hz), 4.53 (1 H, dq, *J* 2.8 and 0.9 Hz, 1-H), 4.90 (1 H, dq, *J* 2.8 and 1.5 Hz, 1-H); δ_C(75 MHz; $CDCl_3$) 14.10 (q), 19.62 (q), 21.72 (q), 22.74 (t and q overlapping), 28.67 (t), 29.35 (t), 31.19 (t), 31.91 (t), 112.72 (t, C-1), 124.52 (s), 137.03 (s), 146.81 (s); *m/z* 180 (M^+, 21), 137 (28), 109 (42), 95 (60), 81 (100), and 66 (65).

3-*Hexyl*-2,2,4-*trimethyl*-8-*phenyl*-1,6,8-*triaza*[4.3.0]*bicyclo*-*non*-3-*ene*-7,9-*dione*.—4-Phenyl-1,2,4-triazoline-3,5-dione[15] (79 mg, 0.44 mmol) in acetone (1 ml) was added to a solution of penta-1,3-diene (**5c**) (80 mg, 0.44 mmol) in dichloromethane (1 ml) at room temperature. After 1 h the solvent was removed under reduced pressure and the resulting white solid recrystallised twice from methanol to give the *title compound* as a white crystalline solid (96 mg, 70%), m.p. 88 °C (Found: C, 71.15; H, 8.3; N, 11.95. $C_{21}H_{29}N_3O_2$ requires C, 70.96; H, 8.22; N, 11.82%); $\nu_{max.}$(Nujol) 1 770m, 1 710s, 1 505m, 1 490m, 1 420s, 1 280m, 1 145m, 760s, 750s, 690s, and 650m cm^{-1}; δ_H(300 MHz; $CDCl_3$) 0.91 (3 H, br t, *J* 7 Hz, CH_3), 1.28—1.50 (8 H, m), 1.62 (6 H, s, CH_3), 1.76 (3 H, s, CH_3), 2.01—2.07 (2 H, m), 3.94 (2 H, s, 5-H), and 7.26—7.53 (5 H, m, C_6H_5); δ_C(75 MHz: $CDCl_3$) 13.96 (q), 16.75 (q), 22.57 (t), 23.10 (q), 28.29 (t), 29.90 (t), 31.42 (t), 46.98 (t, C-5), 62.49 (s, C-2), 120.36 (s), 125.42 (d), 127.78 (d), 128.86 (d), 131.32 (s), 135.31 (s), 152.24 (s), and 152.30 (s); *m/z* 355 (M^+, 40), 340 (100), 221 (41), 119 (37), and 109 (38).

trans-5-{2′-[1″-(*Dimethyl*-*t*-*butylsiloxy*)*prop*-2″-*enyl*]-1′-*methylcyclohexyl*}-2-*methylpent*-1-*en*-3-*en*-3-*ol* (**2d**).—Propenylmagnesium was prepared as in the preparation of (**2a**) from magnesium turnings (62 mg, 2.6 mmol) and 2-bromopropene (0.21 ml, 2.4 mmol) in THF (3 ml). The propionaldehyde (**1d**) (0.7 g, 2.2 mmol) in THF (10 ml), was added to the Grignard solution and the mixture was stirred for 0.5 h at room temperature. Work-up and purification by flash chromatography (light petroleum–ether, 4:1) gave the title compound (**2d**) as a colourless oil (0.54 g, 68%); R_F 0.30 and 0.34 (light petroleum–ether, 4:1); $\nu_{max.}$(film) 3 350br m (OH), 2 930s, 2 860s, 1 470m, 1 462m, 1 360m, 1 252s, 1 095s, 1 078s, 1 020s, 920s, 900m, 840s, and 775s cm^{-1}; δ_H(90 MHz; $CDCl_3$, $CHCl_3$ signal set to δ 7.3) −0.05 (3 H, s, $SiCH_3$), 0.05 (3 H, s, $SiCH_3$), 0.87 [9 H, s, $SiC(CH_3)_3$], 0.93 (3 H, s, CH_3), 1.05—1.65 (14 H, m, 6 × CH_2, 2′-H, and OH), 1.73 (3 H, s, CH_3), 4.0 (1 H, br s, 3-H), 4.32 (1 H, br d, *J* 7.5 Hz, 1″-H), 4.81—5.15 (4 H, m), and 5.91 (1 H, ddd, *J* 17.5, 9.6, and 7.0 Hz, 2″H); *m/z* 348 (M^+ − 18), 333 (1), 309 (2), 281 (2), 239 (12), 217 (5), 171 (100), 135 (17), 131 (16), 115 (27), and 109 (21); the ^{13}C n.m.r. spectrum showed the diastereoisomer ratio to be *ca.* 1:1.

trans-5-{2′-[1″-*Dimethyl*-*t*-*butylsiloxy*)*prop*-2″-*enyl*]-1′-*methylcyclohexyl*}-2-*methylpent*-1-*en*-3-*one* (**3d**).—Using the same procedure as for the preparation of (**3a**) a solution of the pent-1-en-3-ol (**2d**) (0.52 g, 1.42 mmol) in dichloromethane (10 ml) was oxidised with a preformed solution of chromium trioxide (0.85 g, 8.5 mmol) and pyridine (1.38 ml, 17 mmol) in dichloromethane (15 ml). Standard work-up and flash chromatography (light petroleum–ether) gave the title compound (**3d**) as a colourless oil (0.383 g, 74%); R_F 0.42 (light petroleum–ether, 20:1); $\nu_{max.}$(film) 2 925s, 2 855s, 1 678s (C=O), 1 460m, 1 370m, 1 252s, 1 094s, 1 020m, 1 005m, 995m, 922s, 888s, and 775s cm^{-1}; δ_H(300 MHz; $CDCl_3$, $CHCl_3$ signal set at δ 7.3) −0.03 (3 H, s, $SiCH_3$), 0.03 (3 H, s, $SiCH_3$), 0.86 [9 H, s, $SiC(CH_3)_3$], 0.94 (3 H, s, CH_3), 1.05—1.78 (15 H should be 11 H, m, 5 × CH_2 and 2′-H), 1.87 (3 H, dd, *J* 1.5 and 0.9 Hz, CH_3), 2.59—2.65 (2 H, m, 4-H), 4.34 (1 H, d, *J* 7.2 Hz, 1″-H), 4.96 (1 H, ddd, $J_{3'',2''cis}$ 10.3, $J_{3'',3''}$ 1.7, *J* 0.9 Hz, 3″-H), 5.03 (1 H, ddd, $J_{3'',2''trans}$ 17.3, $J_{3'',3''}$ 1.7, *J* 1.1 Hz, 3″-H), 5.74 (1 H, m, 1-H), 5.88 (1 H, ddd, $J_{2'',3''trans}$ 17.3, $J_{2'',3''cis}$ 10.3, $J_{2'',1''}$ 7.2 Hz, 2″-H), and 5.94 (1 H, m, 1-H),; δ_C(75 MHz; $CDCl_3$) −4.52 (q), −3.07 (q), 17.78 (q), 18.13 [s, $SiC(CH_3)_3$], 20.50 (q), 21.11 (t), 22.14 (t), 26.02 [q, $SiC(CH_3)_3$]. 26.67 (t), 31.68 (t), 35.75 (s, C-1′), 37.17 (t), 38.62 (t), 50.93 (d, C-2′), 72.82 (d, C-1″), 113.32 (t), 124.10 (t), 142.85 (d), 144.58 (s, C-2), and 202.82 (s, C-3); *m/z* 364 (M^+), 307 (23), and 171 (100) (Found: M^+, 365.2878. $C_{22}H_{40}O_2Si$ requires *M*, 365.2876).

trans-5-{2′-[1″-(*Dimethyl*-*t*-*butylsiloxy*)*prop*-2″-*enyl*]-1′-*methylcyclohexyl*}-3-(1‴-*methyl*-1‴-*phenylselenoethyl*)-2-*methylpent*-1-*en*-3-*ol* (**4d**).—Using the same procedure as for

the preparation of (**4a**), 2-lithio-2-phenylselenopropane (1.05 mmol) and *trans*-5-{2′-[1″-(dimethyl-t-butylsiloxy)prop-2″-enyl]-1′-methylcyclohexyl}-2-methylpent-1-en-3-one (**3d**) (0.38 g, 1.04 mmol) were allowed to react in THF (10 ml) at −78 °C for 1 h and then at room temperature for 1 h. Work-up and flash chromatography (light petroleum–ether, 20:1) gave the title compound (**4d**) as a colourless oil (0.503 g, 85%); R_F 0.63 (light petroleum–ether, 2:1); $\nu_{max.}$(film) 3 480br,w (OH), 2 930s, 2 855s, 1 461s, 1 438s, 1 380s, 1 251s, 1 120s, 1 095s, 1 078s, 1 022s, 1 005s, 920s, 838s, 774s, 740s, and 695s cm^{-1}; δ_H(90 MHz; $CDCl_3$) −0.04 (3 H, s, $SiCH_3$), 0.03 (3 H, s, $SiCH_3$), 0.85 [9 H, s, $SiC(CH_3)_3$], 0.89 (3 H, s, CH_3), 0.89 (3 H, s, CH_3), 1.03—1.73 (19 H, m, 6 × CH_2, 2 × CH_3, and 2′-H), 1.83 (3 H, s, CH_3), 2.44 (1 H, br s, OH), 4.3 (1 H, br t, *J* 6.5 Hz, 1″-H), 4.83—5.23 (4 H, m), 5.61—6.11 (1 H, m, 2′-H), and 7.13—7.68 (5 H, m, C_6H_5): *m/z* 546 (M^+ −18), 544 (M^+ − 18), 205 (52), 171 (100), and 157 (45).

trans-2-[1″-(*Dimethyl-t-butylsiloxy*)*prop-2″-enyl*]-1-*methyl*-1-[4′-*methyl*-3′-(1‴-*methylvinyl*)*pent-3′-enyl*]*cyclohexane* (**5d**).—Using the same procedure as for the preparation of (**5a**) a solution of pent-1-en-3-ol (**4d**) (0.214 g, 0.38 mmol) was treated with thionyl chloride (0.38 ml, 0.76 mmol) and triethylamine (0.365 ml, 2.66 mol) in dichloromethane (4 ml). Work-up and flash chromatography (light petroleum) gave the title compound (**5d**) as a colourless oil (80 mg, 54%); R_F 0.78 (light petroleum); $\nu_{max.}$(film) 3 075m, 2 920br s, 1 633m, 1 470s, 1 460s, 1 445s, 1 371s, 1 360m, 1 253s, 1 094s, 1 020s, 1 005s, 994s, 920s, 895s, 838s, 775s, and 680m cm^{-1}; δ_H(300 MHz; $CDCl_3$, $CHCl_3$ signal was set at δ 7.3) −0.03 (3 H, s, $SiCH_3$), 0.03 (3 H, s, $SiCH_3$), 0.87 [9 H, s, $SiC(CH_3)_3$], 0.92 (3 H, s, CH_3), 1.03—1.57 (13 H should be 11 H, m, 5 × CH_2 and 2-H), 1.66 (5 H, s, CH_3), 1.76 (3 H, dd, *J* 1.4 and 0.9 Hz, CH_3), 1.86—2.09 (2 H, m, 2′-H), 4.36 (1 H, br d, *J* 7.2 Hz, 1″-H), 4.55—4.56 (1 H, m, 2‴-H), 4.89—4.91 (1 H, m, 2‴-H), 4.96 (1 H, ddd, $J_{3^*,2^*cis}$ 10.3, $J_{3^*,3^*}$ 1.7, *J* 0.9 Hz, 3″-H), 5.03 (1 H, ddd, $J_{3^*,2^*trans}$ 17.3, $J_{3^*,3^*}$ 1.7, *J* 1.1 Hz, 3″-H), and 5.89 (1 H, ddd, $J_{2^*,3^*trans}$ 17.3, $J_{2^*,3^*cis}$ 10.3, $J_{2^*,1^*}$ 7.2 Hz, 2″-H); δ_C(75 MHz; $CDCl_3$) −4.58 (q), −3.01 (q), 18.15 [q, $SiC(CH_3)_3$], 19.47 (q), 20.76, 21.11, 21.72, 22.26, 22.87, 24.80 (t), 26.09 [q, $SiC(CH_3)_3$], 26.84 (t), 35.85 (s, C-1), 38.60 (t), 41.03 (t), 50.22 (d, C-2), 72.70 (d, C-1″), 112.73 (t), 113.08 (t), 124.37 (s), 137.14 (s), 143.11 (d, C-2″), and 146.88 (s) (Found: M^+, 390.3313. $C_{25}H_{46}OSi$ requires *M*, 390.3318).

trans-1-{2′-*Methyl*-2′-[4″-*methyl*-3″-(1‴-*methylvinyl*)*pent*-3″-*enyl*]*cyclohexyl*}*prop*-2-*en*-1-*ol*.—A solution of 40% aqueous hydrofluoric acid (0.88 ml) was added *via* an Eppendorf syringe to a stirred solution of the cyclohexane (**5d**) (0.164 g, 0.42 mmol) in acetonitrile (5 ml) in a glass round-bottomed flask.[18] The reaction was monitored by t.l.c. and after 6 h at room temperature the starting material had disappeared. The mixture was poured into water (2 ml) and then neutralised with solid sodium hydrogencarbonate and extracted with ether (3 × 10 ml). The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to yield the title compound as an oil (0.115 g, 99%) which was used without further purification; R_F 0.47 (light petroleum–ether, 5:1); $\nu_{max.}$(film) 3 400br s (OH), 3 070m, 2 920br s, 1 630m, 1 442s, 1 370m, 1 120m, 985m, 920s, 892s, 760s, and 735s cm^{-1}; δ_H(90 MHz; $CDCl_3$) 1.0 (3 H, s, CH_3), 1.12—1.58 (10 H, m), 1.61 (6 H, s, CH_3), 1.72 (3 H, s, CH_3), 1.6—2.2 (overlapping with CH_3, 4 H, m), 4.33—4.57 (2 H, m), 4.81—5.28 (3 H, m), and 5.83 (1 H, ddd, $J_{2,3trans}$ 16, $J_{2,3cis}$ 10, $J_{2,1}$ 6 Hz, 2-H).

trans-1-{2′-*Methyl*-2′-[4″-*methyl*-3″-(1‴-*methylvinyl*)*pent*-3″-*enyl*]*cyclohexyl*}*prop*-2-*en*-1-*one* (**6**).—Chromium trioxide (0.239 g, 2.39 mmol) was added to a stirred solution of pyridine (386 μl, 4.78 mmol) in dry dichloromethane (6 ml) at room temperature. The stirring was continued for a further 30 min after which *trans*-1-{2′-methyl-2′-[4″-methyl-3″-(1‴-methylvinyl)pent-3″-enyl]cyclohexyl}prop-2-en-1-ol (110 mg, 0.4 mmol) in dichloromethane (1 ml) was added. After 5 min the mixture was filtered through a short silica column and the chromium residues were washed with ether (3 × 30 ml). The solvent was removed under reduced pressure and the residue purified by Chromatotron (light petroleum–ether, 40:1) to give the *title compound* (**6**) as a colourless oil (108 mg, 99%); R_F 0.39 (light petroleum–ether, 20:1); $\nu_{max.}$(film) 2 925s, 2 860s, 1 680s, 1 672s, 1 630m, 1 608s, 1 465m, 1 445s, 1 398s, 1 370m, 1 083m, 983m, 965m, 895s, and 758s cm^{-1}; δ_H(300 MHz; $CDCl_3$) 1.00 (3 H, s, CH_3), 1.21—1.32 (4 H, m), 1.45—1.78 (6 H, m) overlapping with 1.62 (3 H, s, CH_3), 1.63 (3 H, s, CH_3), 1.72 (3 H, dd, *J* 1.4 and 0.9 Hz, CH_3), 1.92—2.12 (2 H, m, 2″-H), 2.66 (1 H, dd, $J_{1',6'ax}$ 11.0, $J_{1',6'eq}$ 3.7 Hz, 1′-H), 4.49 (1 H, dq, $J_{2''',2''''}$ 2.8, *J* 0.9 Hz, 2‴-H), 4.86 (1 H, dq, $J_{2''',2''''}$ 2.8, *J* 1.4 Hz, 2‴-H), 5.65 (1 H, dd, $J_{3,2cis}$ 10.4, $J_{3,3}$ 1.5 Hz, 3-H), 6.17 (1 H, dd, $J_{3,2trans}$ 17.4, $J_{3,3}$ 1.5 Hz, 3-H), and 6.40 (1 H, dd, (1 H, dd, $J_{2,3trans}$ 17.4, $J_{2,3cis}$ 10.4 Hz, 2-H); δ_C(75 MHz; $CDCl_3$) 19.16 (q), 19.36 (q), 21.54 (t), 21.65 (q), 22.70 (q), 24.85 (t), 25.01 (t), 25.01 (t), 25.27 (t), 36.12 (s, C-2′), 37.32 (t), 41.75 (t), 54.86 (d, C-1′), 112.89 (t), 124.53 (s), 126.70 (t), 136.61 (s), 137.53 (d, C-2), 146.40 (s), and 203.60 (s, C-1) (Found: M^+, 274.2294. $C_{19}H_{30}O$ requires *M*, 274.2297).

(1R/S,3R/S,8S/R)-8,12,15,15-*Tetramethyltricyclo*[9.3.1.$0^{3,8}$]-*pentadec*-11-*en*-2-*one* (**7**).—Boron trifluoride–ether (18 μl, 0.15 mmol) was added to a stirred solution of the prop-2-en-1-one (**6**) (40 mg, 0.146 mmol) in toluene (1 ml) at −40 °C. After 24 h, since t.l.c. showed the absence of starting material, the mixture was poured into water (5 ml) and extracted with ether (3 × 10 ml). The organic extracts were combined, dried ($MgSO_4$), and evaporated under reduced pressure and the residue was purified by Chromatotron (light petroleum–ether) to give the *title compound* (**7**) as a colourless oil (23 mg, 58%); R_F 0.33 (light petroleum–ether, 20:1); $\nu_{max.}$(CH_2Cl_2) 2 930s, 2 850m, 1 678s (C=O), 1 460m, 1 380m, 1 368m, 1 244m, 1 218m, and 800br m cm^{-1}; δ_H(400 MHz; $CDCl_3$) 0.94 (3 H, s, 8-CH_3), 0.98—1.21 (4 H, m), 1.08 (3 H, s, CH_3), 1.24 (3 H, s, CH_3), 1.47—1.74 (6 H, m), 1.82 (1 H, ddd, *J* 15.1, 12.7, and 5.5 Hz, 9β-H) overlapping 1.83 (3 H, m, CH_3), 1.97 (1 H, dddd, *J* 15.4, 11.3, 8.6, and 2.4 Hz, 14β-H), overlapping 2.02 (1 H, ddd, *J* 18.3, 10.1, and 2.4 Hz, 13α-H), 2.09—2.17 (1 H, m, 10β-H), 2.40 (1 H, d, *J* 6.8 Hz, 1-H), 2.44—2.59 (1 H, m, 13β-H), 2.81 (1 H, ddd, *J* 14.2, 12.7, and 5.6 Hz, 10α-H), and 2.96 (1 H, dd, *J* 12.2 and 3.0 Hz, 3-H); δ 2.96 (3-H), shows a n.O.e. to 1.83 (12-CH_3, 1%); 2.81 (10α-H) shows a n.O.e. to 2.09—2.17 (10β-H, 10%), 1.83 (12-CH_3), 1.82 (9β-H); 2.44—2.59 (13β-H) shows a n.O.e. to 2.02 (13α-H, 13%), 1.08 (1%); 2.40 (1-H) shows a n.O.e. to 1.97 (14β-H, 2.6%), 1.24 (15-CH_3); 2.09—2.17 (10β-H) shows a n.O.e. to 2.81 (10α-H, 11%), 1.24 (15-CH_3); 1.83 (12-CH_3) shows a n.O.e. to 2.96 (3-H, 3%), 2.81 (10α-H, 5.5%); 1.24 (15-CH_3) shows a n.O.e. to 2.40 (1-H, 3.5%), 2.09—2.17 (10β-H, 5%), 1.08 (15-CH_3), 0.94 (8-CH_3); 1.08 (15-CH_3) shows a n.O.e. to 2.96 (3-H), 2.44—2.59 (13β-H), 2.4 (1-H), 1.24 (15-CH_3); δ_C(100 MHz; $CDCl_3$) 18.95 (t), 21.81 (t), 22.09 (q), 22.17 (q), 25.17 (t), 26.02 (q), 26.18 (t), 26.39 (t), 29.16 (t), 29.69 (q), 38.09 (s), 38.78 (s), 39.47 (t), 41.08 (t), 50.83 (d), 62.79 (d), 130.23 (s), 137.68 (s), and 218.95 (s) (Found: M^+, 274.2288. $C_{19}H_{30}O$ requires *M*, 274.2297).

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