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THE SYNTHESIS OF A PRECURSOR TO PENTALENENE USING A PALLADIUM(0) CATALYSED (3 + 2) CYCLOADDITION

RAYMOND BAKER and RONA B. KEEN

Department of Chemistry, University of Southampton, Southampton SO9 5NH (Great Britain)

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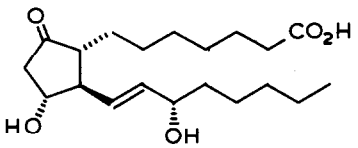
Summary

A precursor to pentalenene has been synthesised by a route involving a cycloaddition reaction of a 2-alkyl-2-cyclopentenone with 2-methylene-3-trimethylsilylpropyl acetate in presence of a palladium(0) catalyst.

Introduction

The importance of the cyclopentanoid natural products was recognised nearly twenty years ago by the discovery of structures such as the prostaglandins [1], e.g. PGE_1 (**1**) and hirsutic acid (**2**) [2], which are based on a cyclopentane unit. Since



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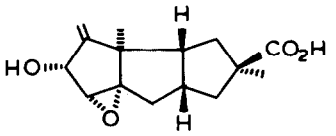

(2)

then, many methodologies have been designed to produce variously functionalised cyclopentane units, which have been used in the synthesis of several natural products [3]. One of the most popular approaches has been the (3 + 2) cycloaddition, usually involving organometallic complexes of a metal such as lithium [4], iron [5], nickel [6] or palladium [6,7]. The use of palladium complexes has possibly produced the most interesting results. Trost and Chan [7] have extensively investigated the mechanism and limitations of the reaction between 2-methylene-3-trimethylsilylpropyl acetate (**3**) and electron-deficient olefins, in the presence of palladium(0) catalysts (Scheme 1).

These reactions have been performed with electron-withdrawing groups (EWG) such as esters, nitriles, sulphones, and ketones, producing a range of cyclopentane units with various substituents on the ring. The recent total synthesis of (±) albene [8] was based on one of these palladium-catalysed reactions.

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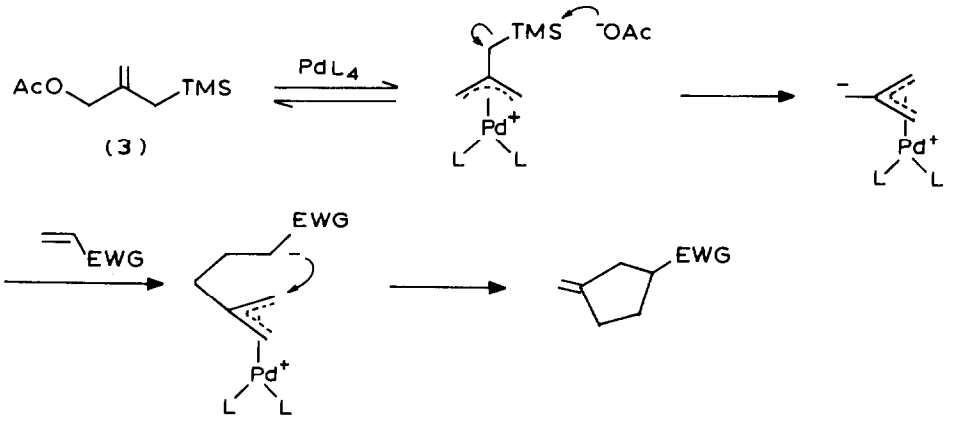
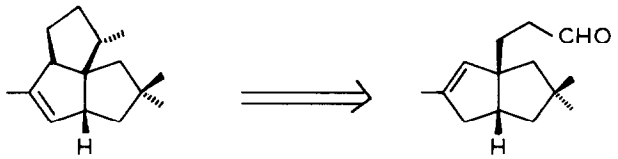
SCHEME 1. EWG = electron-withdrawing group.



This paper reports the application of a palladium-catalysed cycloaddition reaction in a synthesis of a precursor to pentalenene (**4**). Pentalenene [9] was isolated in 1980 and identified as a less oxidised, neutral precursor to pentalenolactone, the latter being well-known for its antibiotic and antitumour activity [10]. The first synthesis of pentalenene (**4**) described by Annis and Paquette [11], began from 4,4-dimethyl-2-cyclopenten-1-one and involved the key intermediate (**5**).

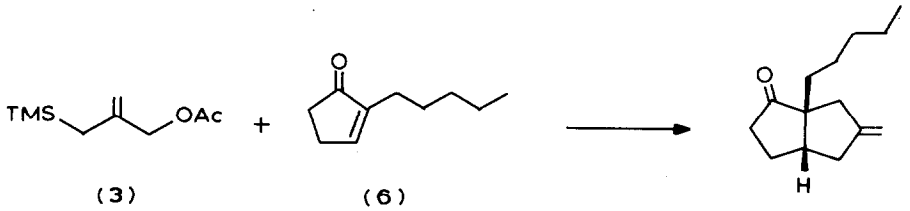


(4) (5)

Results and discussion

The approach used in this synthesis was reaction of the allyl acetate **3** with a 2-alkyl-2-cyclopentenone, in the presence of a palladium complex. Model studies were undertaken to investigate the reactivity of a cyclopentenone derivative, by the reaction of **6** with allylacetate **3** (Scheme 2). 2-Methylene-3-trimethylsilylpropyl

SCHEME 2



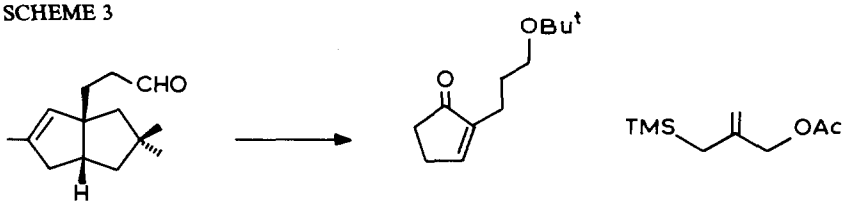
(3) (6) (7)

acetate (**3**) was prepared from methallyl alcohol by the method of Trost and Chan [7]. This was treated with three equivalents of enone **6**, in the presence of a catalytic amount of palladium(II) acetate and triisopropyl phosphite [8]. The product, **7**, was isolated in 45% yield (unoptimised).

Synthesis of the precursor

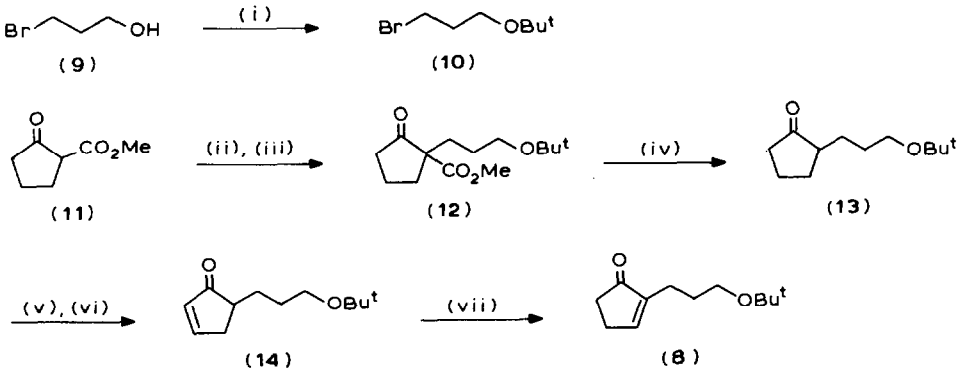
Retrosynthetic analysis of **5** led to choice of **8** as a suitable enone for the annulation reaction (Scheme 3). The aldehyde group of **5** is masked as a protected primary alcohol in **8**. The synthesis of **8** is summarised in Scheme 4.

SCHEME 3



(5) (8) (3)

SCHEME 4. Reagents: (i) conc. H_2SO_4, iso-butylene; (ii) KOH; (iii) **10**, DMSO; (iv) LiI, DMF; (v) LDA, PhSeCl; (vi) H_2O_2; (vii) KOH, heat.



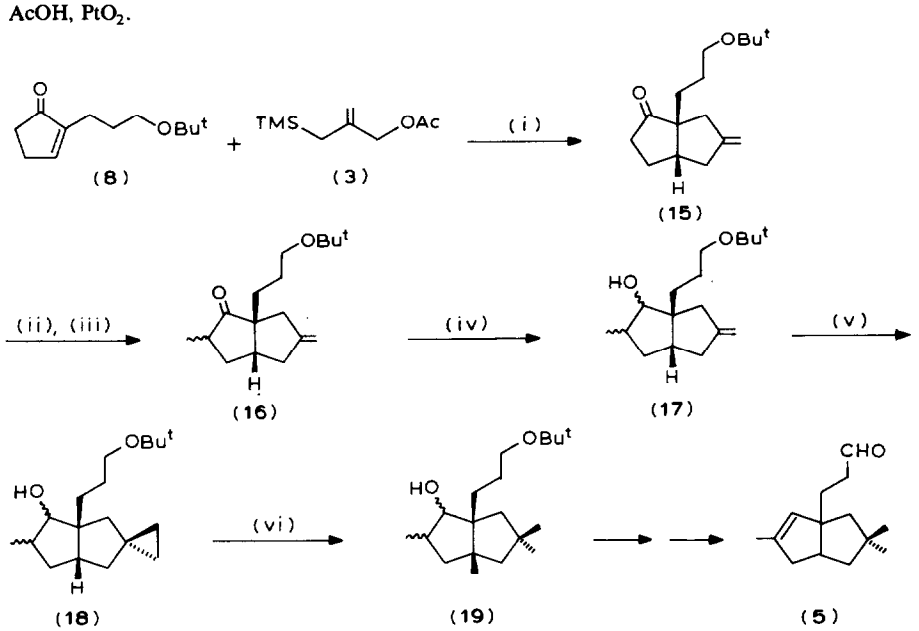
The protection of 3-bromopropan-1-ol (**9**) was accomplished in 76% yield compared to that previously reported in the literature [12] (44%). This improvement in isolated yield was probably due to the more efficient separation of **10** from various side products, by changing the purification procedure from that involving alumina chromatography to the "flash" chromatography procedure of Still et al. [19]. Alkylation of **11** was achieved in 78% yield, but of this only 70% was *C*-alkylated. The high level of *O*-alkylation was probably due to interaction between the potassium ion of the enolate and the oxygen atom in **10**. Decarboxylation of **12** with lithium iodide *N*,*N*′-dimethylformamide (DMF) was carried out in 75% yield to produce cyclopentanone **13**.

Initial attempts to introduce a double bond at the C(2) position of **13** in one step were not successful. Reagents such as copper(II) bromide [13] and iron(III) chloride [14] failed to effect the transformation, yielding polymeric products. The introduction of a phenylselenyl group, followed by oxidation [15] was then considered. The reaction could not be attempted on the thermodynamic enol acetate as the acidic preparation of this compound would result in deprotection of the primary alcohol. An attempt was made to form the thermodynamic enolate of the ketone [16], by using an excess of **13** and raising the reaction temperature to 25°C. Reaction of the enolate with phenylselenyl chloride, followed by oxidation, only yielded a small amount of **14** and none of the desired product. The transformation was finally accomplished by preparing **14** via reaction with an excess of phenylselenyl chloride

and subsequent oxidation, followed by isomerisation of the double bond at C(4) (**14**) to the C(2) position in **8**.

The synthesis of **19** is summarised in Scheme 5 and the palladium(0)-catalysed

SCHEME 5. Reagents: (i) PdL_4; (ii) LDA, HMPA; (iii) MeI; (iv) $LiAlH_4$; (v) Zn/Ag, CH_2I_2; (vi) H_2, AcOH, PtO_2.



annulation reaction was applied to **8** with considerable success. Enone **8** was initially treated with one equivalent of **3**, using the same catalytic system as in the model study, yielding **15** (42%); this yield was raised to 65% when **3** was used in excess. Methylation of **15** was achieved in 78% yield using lithium diisopropylamine/hexamethylphosphoramide (HMPA), followed by methyl iodide *. Reduction of the product **16** with lithium hydride produced **17**, as mixture of two epimers, in 89% yield. An attempt to cyclopropanate the exocyclic double bond in **17** with diazomethane and palladium(II) acetate [17] did not prove successful, yielding unchanged starting material. The transformation was accomplished in 61% yield via a modified Simmons–Smith procedure [18] using a zinc-silver couple with diiodomethane. Opening of the resultant cyclopropane ring in **18** was achieved in 59% yield by hydrogenolysis in acetic acid with platinum(IV) oxide catalyst.

The structure (**19**) is a synthetic precursor of pentalenene. Dehydration of the secondary hydroxyl group, followed by hydrolysis and oxidation of the t-butyl ether, would yield the key intermediate **5**, which can be converted into the natural product.

Experimental

All organometallic operations were performed under pure argon, using solvents which had recently been dried and distilled under N_2. Ether refers to diethyl ether and petrol to petroleum ether boiling between 40 and 60°C. The IR spectra were

* Only one epimer appeared to be formed but the structure was not fully assigned.

taken on a Pye Unicam SP3-100 spectrophotometer, generally as solutions. ^{1}H NMR spectra were obtained at 60 MHz using a Hitachi Perkin–Elmer R-24B high resolution spectrometer and at 100 MHz using a Varian Associates XL-100-12 (deuterium lock) spectrometer. Tetramethylsilane was used as an external standard for organosilicon compounds and as an internal standard in all other cases. Mass spectra were run on a Kratos MS-30 spectrometer at an ionisation potential of 70 eV. Elemental analyses were recorded by Butterworth Laboratories Ltd., University College, London. Flash column chromatography [19] was performed with 230–400 mesh silica gel (Macherey-Nagal Kieselgel 60).

Reaction of 2-methylene-3-trimethylsilylpropyl acetate (3)

General procedure

A mixture of **3** [7], the enone, palladium(II) acetate and triisopropyl phosphite in tetrahydrofuran (THF) was heated at reflux, under argon. After the reaction was completed, the solution was cooled and the solvent removed under reduced pressure. The residue was purified by flash chromatography.

(a) Reaction with 2-n-pentyl-2-cyclopenten-1-one (6)

The general procedure was followed, using **6** (1.3 g, 8.5 mmol), palladium(II) acetate (40 mg), triisopropyl phosphite (210 mg) and THF (4 ml); reaction was complete after 16 h. Flash chromatography (20% ethyl acetate in petrol) yielded the desired product, **7**, (45% yield, b.p. 88–90°C/0.1 mmHg (Kugelrohr); ν_{max} ($CHCl_3$) 1740s (C=O, ketone), δ 4.84 (2H, m, C=CH_2), 2.82–1.95 (9H, m, CH/CH_2 ring), 1.90–1.06 (8H, m, CH_2 chain), 0.90 (3H, t, J 5 Hz, CH_3); m/z 206 (M^+, 8%), 188 (6), 178 (12), 135 (100) (Found: M^+ 206.1759, $C_{14}H_{22}O$ calcd.: M^+, 206.1665).

(b) Reaction with 2-(3-t-butoxypropyl)-2-cyclopenten-1-one (8)

The general procedure was followed, using **8** (1.41 g, 7.1 mmol), **3** (2.31 g, 12.4 mmol), palladium(II) acetate (275 mg), triisopropylphosphite (1.4 g) and THF (7 ml). The reaction was complete after 16 h and flash chromatography (20% ethyl acetate in petrol) yielded the product **15**, *cis*-1-(3-t-butoxypropyl)-7-methylenebicyclo[3.3.0]-octan-2-one, (65% yield, b.p. 80–82°C/0.1 mmHg (Kugelrohr)); ν_{max} ($CHCl_3$) 1735s (C=O, ketone); δ 4.83 (2H, m, C=CH_2), 3.29 (2H, t, J 5 Hz, CH_2O), 2.82–1.94 (9H, m, CH_3/CH ring), 1.84–1.26 (4H, m, CH_2 chain), 1.19 (9H, s, CH_3); m/z 194 ($M^+ - C_4H_8$, 24%), 177 (22), 135 (22), 57 (100) (Found: C, 76.50; H, 10.32. $C_{16}H_{26}O_2$ calcd.: C, 76.75; H, 10.47%).

3-Bromo-1-t-butoxypropane (10)

Liquified isobutylene (~ 200 ml), at ~ −30°C, was added rapidly to a mixture of 3-bromo-1-propanol (**9**) (25 g, 0.18 mmol), dichloromethane (200 ml) and concentrated sulphuric acid (0.8 ml), at 0°C. The flask was sealed with a Subaseal and stirred efficiently for 16 h at room temperature. The mixture was then brought to atmosphere pressure via the introduction of a syringe needle to the system, and was then washed with saturated sodium bicarbonate ($NaHCO_3$) solution (2 × 100 ml) and water (100 ml). After drying over magnesium sulphate ($MgSO_4$), the solvent was removed under reduced pressure. Purification by flash chromatography (8% ethyl acetate in petrol) gave **10** (76% yield, b.p. 75°C/30 mmHg; δ 3.48 (4H, m, CH_2Br, CH_2O), 2.30 (2H, m, CH_2), 1.18 (9H, s, CH_3).

Methyl 1-(3-t-butoxypropyl)-2-oxocyclopentanecarboxylate (12)

Methyl 2-oxocyclopentanecarboxylate (2.5 g, 17.6 mmol) was added dropwise, at 0°C, to a solution of potassium hydroxide (0.99 g, 17.6 mmol) in methanol (4.9 ml) and water (0.3 ml). After stirring for 10 min (manually), cold ether (0.9 ml) was added and the solid filtered, washed with cold methanol and cold ether. The white solid was dried overnight in a desiccator.

To a solution of the above enolate (2.72 g, 15.1 mmol) in dimethyl sulphoxide (DMSO) (29 ml) was added **10** (3.24 g, 16.6 mmol) and the mixture stirred under nitrogen for 2 h. The reaction mixture was then poured into water (19 ml) and petrol (38 ml). The layers were separated and the aqueous layer extracted with petrol. The combined organic phases were washed with water (10 ml), brine (10 ml) and dried ($MgSO_4$). Filtration, solvent removal under reduced pressure and flash chromatography of the residue (30% ethyl acetate in petrol) yielded **12** (0.87 g, 55%, b.p. 90°C/0.1 mmHg); ν_{max} (CH_2Cl_2) 1750s (C=O ketone), 1735s (C=O ester); δ 3.69 (3H, s, CO_2CH_3), 3.29 (2H, t, J 6 Hz, CH_2O), 2.60–1.30 (10H, m, CH_2), 1.16 (9H, s, CH_3); m/z 199 ($M^+ - C_4H_9$, 15%), 183 (62), 142 (33), 123 (100) chemical ionization mass spectrometry, CI-MS: (CH_4) (Found: $M^+ + 1$, 257.1682. $C_{14}H_{25}O_4$ calcd.: $M^+ + 1$, 257.1746).

2-(3-t-Butoxypropyl)cyclopentan-1-one (13)

A mixture of **12** (773 mg, 3 mmol), lithium iodide monohydrate (1.4 g, 9 mmol) and dimethyl formamide (DMF) was heated at reflux under nitrogen and heating continued for 16 h. After cooling, water (15 ml) was added and the mixture acidified to pH = 6 with dilute hydrochloric acid. The mixture was extracted with petrol and the organic solvent back-washed with water (10 ml) and brine (10 ml). The petrol layer was dried ($MgSO_4$) and the solvent removed under reduced pressure, to produce a residue which was distilled to yield **13** (446 mg, 75%, b.p. 70°C/0.5 mmHg); ν_{max} (CH_2Cl_2) 1740s (C=O ketone); δ 3.34 (2H, t, J 6 Hz, CH_2O), 2.38–1.26 (11H, m, CH_2/CH), 1.20 (9H, s, CH_3); m/z 142 ($M^+ - C_4H_8$, 23%), 141 (38), 125 (64), 97 (56), 57 (100) (Found: C, 72.24; H, 10.95. $C_{12}H_{22}O_2$ calcd.: C, 72.68; H, 11.18%).

5-(3-t-Butoxypropyl)-2-cyclopenten-1-one (14)

n-Butyllithium (0.63 ml, 1.6 M in hexane, 1 mmol) was added to a solution of diisopropylamine (101 mg, 1 mmol) in THF (3.5 ml) at −5°C, and the mixture was stirred at this temperature for 30 min. It was then sooled to −78°C and a solution of **13** (172 mg, 0.87 mmol) in THF (2 ml) was added and stirring continued at the temperature for 30 min. Finally, phenylselenyl chloride (192 g, 1 mmol) was added rapidly and after stirring for 1–2 min, the mixture was poured into dilute hydrochloric acid (5%, 9 ml), ether (4 ml) and petrol (4 ml). The layers were shaken, separated and the organic layer washed with water (5 ml), saturated $NaHCO_3$ solution (5 ml) and brine (5 ml). The solvents were removed under reduced pressure and the residue dissolved in dichloromethane (4–5 ml) and pyridine (0.2 ml).

This solution was treated with a mixture of water (1 ml) and hydrogen peroxide (30%, 1 ml) and stirred vigorously for 30 min. The phases were then separated and the organic phase washed with sodium carbonate solution (25%, 2 ml), dilute hydrochloric acid (2 × 3 ml) and brine (2 ml). The extract was dried ($MgSO_4$), and the solvent removed under reduced pressure to yield a yellow residue. Flash

chromatography (30% ethyl acetate in petrol) gave **14** (67% yield, b.p. 82°C/0.6 mmHg); ν_{max} (CH_2Cl_2) 1710s (C=O, ketone); δ 7.65 (1H, m, CH_2CH=CH), 6.14 (1H, m, CH=*CH*–CO), 3.33 (2H, t, *J* 5 Hz, CH_2O), 2.76 (1H, m, CO–C*H*–CH_2), 2.52–2.18 (2H, m, CH–CH_2–CH), 1.96–1.38 (4H, m, CH_2chain), 1.17 (9H, s, CH_3); *m/z* 140 ($M^+ - C_4H_8$, 23%), 139 (46), 123 (100) (Found: C, 73.09; H, 10.22. $C_{12}H_{20}O_2$ calcd.: C, 73.43; H, 10.27%).

2-(3-t-Butoxypropyl)-2-cyclopenten-1-one (8)

To a solution of potassium hydroxide (0.5 g) in water (10 ml) was added **14** (115 mg, 0.6 mmol) and the mixture heated at reflux for 1 h. After cooling, the mixture was neutralised with dilute hydrochloric acid and extracted with ether. The extract was dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was purified by flash chromatography (30% ethyl acetate in petrol) to give **8** (82% yield; b.p. 82–83°C/0.6 mmHg); ν_{max} (CH_2Cl_2) 1705s (C=O, ketone); δ 7.29 (1H, m, C=CH), 3.33 (2H, t, *J* 6 Hz, CH_2O), 2.63–2.09 (4H, m, CH_2 ring), 1.84–1.52 (4H, m, CH_2 chain), 1.16 (9H, s, CH_3); *m/z* 139 ($M^+ - C_4H_9$, 69%), 123 (100), 57 (68) CI-MS (CH_4) (Found: $M^+ + 1$, 197.1038 $C_{12}H_{21}O_2$ calcd.: $M^+ + 1$, 197.1536).

cis-1-(3-t-Butoxypropyl)-3-methyl-7-methylenebicyclo[3.3.0]octan-2-one (16)

n-Butyllithium (3 ml, 1.4 *M* in hexane, 4.2 mmol) was added dropwise, under nitrogen, to a stirred solution of diisopropylamine (425 mg, 4.2 mmol) in THF (18 ml) at −20°C. After stirring at −10°C for 1 h, a solution of **15** (955 mg, 3.8 mmol) in THF (4 ml) was added to the mixture at −78°C. After one hour's stirring at this temperature, hexamethylphosphoramide (1.5 g, 8.4 mmol) was added and stirring continued for 15 min. Finally, iodomethane (752 mg, 5.3 mmol) was added and the mixture stirred for a further hour. The reaction was then treated with saturated ammonium chloride solution (20 ml) and extracted with a 1/1 mixture of ether and petrol. After drying ($MgSO_4$) and solvent removal under reduced pressure, the residue was purified by flash chromatography (15% ethyl acetate in petrol) to give **16** (78% yield, b.p. 85–88°C/0.1 mmHg (Kugelrohr)); ν_{max} (CH_2Cl_2) 1735s (C=O, ketone); δ 4.33 (2H, m, C=CH_2), 3.28 (2H, t, *J* 5 Hz, CH_2O), 2.69–2.01 (8H, m, CH_2/CH ring), 1.75–1.32 (4H, m, CH_2 chain), 1.19 (9H, s, CH_3, t-Bu), 1.14–1.00 (3H, m, CH_3 ring); *m/z* 208 ($M^+ - C_4H_8$, 32%), 207 (16), 149 (30), 148 (32), 91 (40), 57 (100) (Found: C, 77.36; H, 10.51. $C_{17}H_{28}O_2$ calcd.: C, 77.22; H, 10.67%).

cis-1-(3-t-Butoxypropyl-3-methyl-7-methylenebicyclo[3.3.0]octan-2-ol (17)

Lithium aluminium hydride (30 mg, 0.8 mmol) was added to a stirred solution of **16** (372 mg, 1.4 mmol) in dry ether (6 ml) at 0°C. The mixture was allowed to warm to room temperature and stirred for 1 h. A few drops of ice cold water were added to quench the reaction and to react with excess lithium aluminium hydride, the solid was removed by filtration and washed with ether. The solvent was removed under reduced pressure and the residue purified to give two isomeric alcohols (**17 a** and **b**) in 89% yield, the ratio of **a** and **b** being 11/2; b.p. (**a**) 99–102°C/0.1 mmHg; (**b**) 100–102°C/0.1 mmHg; (both Kugelrohr);

(**a**): ν_{max} (CH_2Cl_2) 3460b (OH); δ 4.77 (2H, m, C=CH_2), 3.35 (3H, m, CHO and CH_2O), 2.67–1.75 (8H, m, CH_2/CH ring), 1.64–1.35 (4H, m, CH_2 chain), 1.20 (9H, s, CH_3-t-Bu), 1.06–0.92 (3H, m, CH_3 ring); *m/z* 266 (M^+, 1%), 210 (18), 192 (44), 151 (36), 57 (100) (Found: M^+ 266.1355, $C_{17}H_{30}O_2$ calcd.: M^+ 266.2238.

(**b**): ν_{max} (CH_2Cl_2) 3440b (OH); δ 4.80 (2H, m, $C{=}CH_2$), 3.32 (3H, m, CHO/CH_2O), 2.76–1.76 (8H, m. CH/CH_2 ring), 1.67–1.35 (4H, m, CH_2 chain), 1.19 (9H, s, CH_3-t-Bu), 1.05–0.89 (3H, m, CH_3 ring); *m/z* 266 (M^+, 4%), 210 (49), 192 (100), 151 (74), 57 (89) (Found: M^+ 266.1148, $C_{17}H_{30}O_2$ calcd.: M^+ 266.2238).

*Spiro[cis-1-(3-t-butoxypropyl)-3-methylbicyclo[3.3.0]octan-2-ol-7,1'-cyclopropane] (**18**)*

Granular zinc (315 mg, 4.8 mmol) was added to a hot, stirred solution of silver acetate (2 mg) in acetic acid (2 ml). After 30 s, the couple formed was isolated by decanting the acetic acid and washing with fresh acetic acid (2 ml) and dry ether (5 × 2 ml). A solution of diiodomethane (644 mg, 2.5 mmol) in dry ether (4 ml), together with a small batch of silver wool, was added to the couple, and the mixture stirred at room temperature, under nitrogen for 1 h. A solution of **17a** (106 mg, 0.4 mmol) in ether (1 ml) was then added and the mixture heated at reflux for 60 h. The reaction was cooled and more dry ether (4 ml), followed by pyridine (380 mg, 4.8 mmol) was added. The resulting white precipitate was removed by filtration, the filtrate concentrated under reduced pressure and the residue purified by flash chromatography (20% ethyl acetate in petrol) to yield **18** (67 mg, 61%, b.p. 102–104°C/0.1 mmHg (Kugelrohr)); ν_{max} (CH_2Cl_2) 3400b (OH); δ 3.33 (3H, m, CH_3 ring), 0.39 (4H, s, CH_2 cyclopropyl); *m/z* 224 ($M^+ - C_4H_8$, 2%), 206 (5), 133 (6), 107 (8), 57 (100) (Found: C, 76.56; H, 11.00. $C_{18}H_{32}O_2$ calcd.: C, 77.09; H, 11.50%).

*cis-1-(3-t-Butoxypropyl)3,7,7-trimethylbicyclo[3.3.0]octan-2-ol (**19**)*

A solution of **18** (200 mg, 0.71 mmol) in distilled acetic acid (5 ml) was stirred over activated charcoal for 1 h. The charcoal was removed by filtration and the filtrate placed in a hydrogenation bottle together with platinum(IV) oxide (240 mg) and a trace of concentrated hydrochloric acid. The mixture was placed in a hydrogen atmosphere (3 atm. pressure) and stirred well for 5 d. The mixture was then filtered, the filtrate concentrated under reduced pressure and the residue purified by flash chromatography (20% ethyl acetate in petrol) to yield **19** (118 mg, 59%, b.p. 105–108°C/0.1 mmHg (Kugelrohr)); ν_{max} (CH_2Cl_2) 3400b (OH); δ 3.32 (3H, m, CHO/CH_2O), 2.31–1.43 (12H, m, CH/CH_2), 1.20 (9H, s, CH_3-t-Bu), 1.10–0.97 (9H, m. CH_3 ring); *m/z* 226 ($M^+ - C_4H_8$, 7%), 225 (5), 207 (11), 109 (18), 95 (26), 57 (100) CIMS (NH_3) (Found: $M^+ + 1$ 283.2435; $C_{18}H_{35}O_2$ calcd.: $M^+ + 1$ 283.2628).

Acknowledgements

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