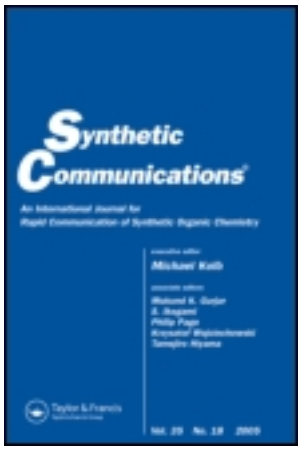

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Version of record first published: 20 Aug 2006

To cite this article: Helen C. Hailes, Ben Isaac & M. Hashim Javaid (2003): The Synthesis of 2-Alkylated Cyclopentene-1,3-diones: Novel Compounds with Olfactory Properties, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 33:1, 29-41

To link to this article: http://dx.doi.org/10.1081/SCC-120015556

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SYNTHETIC COMMUNICATIONS®
Vol. 33, No. 1, pp. 29–41, 2003

The Synthesis of 2-Alkylated Cyclopentene-1,3-diones: Novel Compounds with Olfactory Properties

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ABSTRACT

The syntheses of 2-butyl-4,5-dimethylcyclopent-4-ene-1,3-dione, possessing a buttery jasmine odor, and a series of analogues have been carried out via the synthesis of butenolactones, with subsequent conversion to 4,5-dimethylcyclopent-4-ene-1,3-dione and an alkylation strategy. The compound with the strongest odor characteristics, has also been synthesised using a Pauson–Khand reaction and selective oxidative route.

Key Words: Butenolactones; Cyclopentene-1,3-diones; Pauson-Khand.

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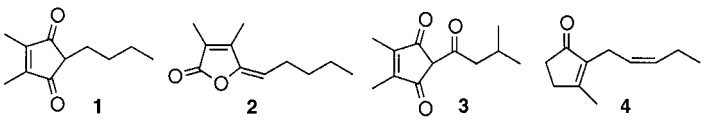
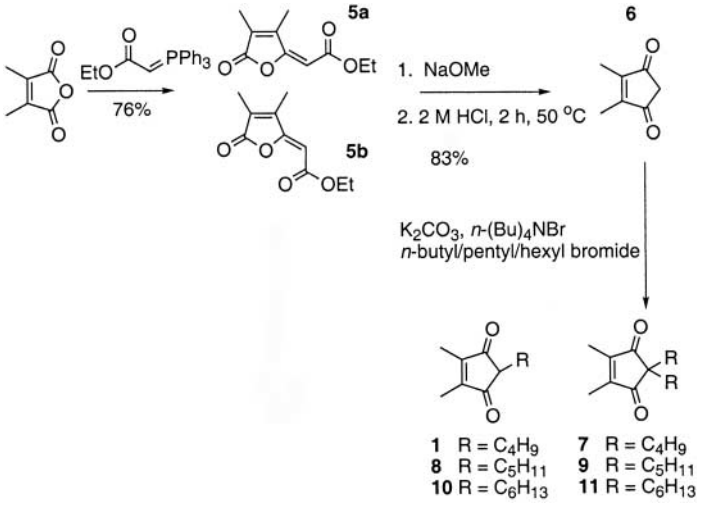
DOI: 10.1081/SCC-120015556 0039-7911 (Print); 1532-2432 (Online)

2-Butyl-4,5-dimethylcyclopent-4-ene-1,3-dione **1** was first identified[1] during the synthesis of bovilide **2**, an ylidenebutenolactone found in, for example, peppermint oil[2] and green tea leaves.[3] It possesses a buttery jasmine odor, and since the jasmonate fragrances are both highly prized and sought after, as well as being extensively used, its synthesis, together with analogues, was of great interest for potential use in perfumery applications. Compound **1** is structurally related to calythrone **3**, a member of a unique group of naturally occurring cyclopentene-1,3-dione β-triketones.[4–7] Calythrone itself possesses a floral odor, reminiscent of *cis*-jasmone **4**. Herein we report the synthesis of **1** and related analogues via a 2-ylidenebutenolactone and also the synthesis of **1** using a Pauson–Khand and selective oxidative strategy.



Due to previous work on the rearrangement of ylidenebutenolactones,[6,7] and our aim of generating analogues of **1**, the synthetic route shown in Sch. 1 was explored. The treatment of 2,3-dimethylmaleic



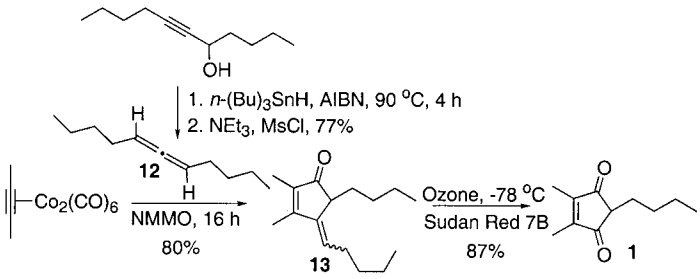
Scheme 1.

anhydride with ethoxycarbonylmethylenetriphenylphosphorane in toluene gave the butenolactones **5a** and **5b** in 76% yield, in an isomeric ratio of *E*:*Z* of 2:3.[8,9] Whilst a geometric mixture of isomers was not problematical due to the rearrangement in the next step, we noted that the use of THF or aqueous CTAB (cetyltrimethylammonium bromide) media led to product formation in higher *E*:*Z* ratios (yields 69% and 52% and ratios of 1:1 and 3:2 respectively) due to solvent effects on the stability and rate of decomposition of the *threo* and *erythro* betaines. The mixture of **5a** and **5b** was treated with sodium in methanol followed by hydrolysis and decarboxylation to generate 4,5-dimethylcyclopent-4-ene-1,3-dione **6**, in an overall yield of 83%.[10] We noted that the use of methoxide, rather than ethoxide, led to superior yields in this system.

The selective *C*-alkylation of 1,3-dicarbonyl compounds is often problematical due to competing self condensation and *O*-alkylation. We initially wished to access quantities of the mono and dialkylated materials (Compounds **1**, **7**–**11**) for analysis purposes. An alkylation method using alumina impregnated with sodium ethoxide[11] unfortunately led to the formation of self condensation products only. However, the use of a biphasic procedure using tetrabutylammonium bromide as a phase transfer catalyst[12] with bromobutane led to the formation of the mono and dialkylated products **1** and **7**, which were readily separable, in 57% and 11% yields respectively. The use of pentyl- and hexylbromide generated the corresponding analogues (**8**–**11**), and further attempts to improve the yields of the monoalkylated materials were not fruitful. 2-Butyl-4,5-dimethylcyclopent-4-ene-1,3-dione **1** possessed the strongest odor characteristics, and therefore a novel alternative route to **1** was sought which would avoid the alkylation procedure which had led to a mixture of products.

The Pauson–Khand reaction has emerged as a useful method for the construction of five membered rings, particularly with the use of allenic compounds as unsaturated partners to the alkyne cobalt complexes.[13,14] We envisaged using this technique to assemble the five membered ring, together with a selective oxidative cleavage, and the route explored is given in Sch. 2.

Dicobalthexacarbonylbut-2-yne complex was prepared from but-2-yne in almost quantitative yield as previously reported.[14,15] Undec-6-yn-5-ol[16] was heated with tributyltin hydride and AIBN to give the completely regioselective hydrostannylation product which was converted into the mesylate, and which underwent spontaneous elimination to form 5,6-undecadiene **12** in 77% yield.[17] The Pauson–Khand reaction was then carried out in the presence of *N*-methylmorpholine



Scheme 2.

N-oxide monohydrate to generate 4-pentylidene-5-butyl-2,3-dimethyl-cyclopent-2-enone **13** in 80% yield.[14]

Since exocyclic alkenes are normally more reactive than endocyclic alkenes, we anticipated high selectivity in the oxidation of the trisubstituted olefin to afford **1**. When using a catalytic osmium tetraoxide/sodium periodate oxidation procedure[18,19] under various conditions, **1** was isolated at best in 65% yield. The use of an ozonolysis procedure was then investigated to improve the yield, together with an azo-dye to serve as a marker to indicate completion of the required oxidation. Ozone was expected to react with the more electron-rich trisubstituted olefin first prior to oxidation of the azo-dye, the consumption of which will result in a color loss. Sudan Red 7B[20] (also known as Solvent Red 19) served as an excellent indicator, and the use of this procedure gave rise to **1** in an isolated yield of 87%.

In summary, we have synthesised the novel compounds **1** and **7**–**11** via a rearrangement and alkylation strategy, and also **1** via a Pauson–Khand reaction and oxidative route. Compound **1** possessed the strongest odor characteristics, and is an important addition to the family of compounds with jasmine-like fragrance properties.

EXPERIMENTAL

Unless otherwise indicated, reagents were obtained from commercial suppliers and were used without further purification. THF was freshly distilled from sodium/benzophenone. Toluene was freshly distilled from sodium. Triethylamine was distilled from and stored over potassium hydroxide. Methanol was distilled from magnesium turnings and

stored over 3 Å molecular sieves. 'Ethanol' refers to absolute ethanol (> 99.7%) and was used as received. Flash column chromatography[21] was carried out using silica gel (particle size 40–63 μm) purchased from BDH.

Proton NMR spectra were recorded at 400 MHz on a Varian VXR-400 instrument or at 200 MHz, on a Varian XL-200 instrument. Carbon-13 NMR spectra were recorded at 100.6 MHz on a Varian VXR-400 instrument. Residual protic solvent was taken as internal standard, with $CDCl_3$ as solvent unless otherwise stated, stored over 4 Å molecular sieves and filtered through basic alumina prior to use. Coupling constant (J) values are given in Hz.

Mass spectra were taken on an Autospec Q, VG 7070, or VG 7070B instrument with sources for EI. Infra red spectra were recorded on a Perkin–Elmer FT-IR 1605 spectrometer. CHN analyses were carried out on a Perkin–Elmer 2400 CHN Elemental Analyzer. Melting points were taken on a Reichert hot stage instrument and are uncorrected.

Ethoxycarbonylmethylenetriphenylphosphorane was prepared as previously reported.[22] Dicobalt hexacarbonylbut-2-yne was prepared as previously reported.[14,15]

Ethyl (*E*)-3,4-dimethyl-5-oxo-2,5-dihydrofuran-2-ylidene ethanoate (5a) Ethyl (*Z*)-3,4-dimethyl-5-oxo-2,5-dihydrofuran-2-ylidene ethanoate (5b): To a solution of 2,3-dimethylmaleic anhydride (3.50 g, 27.8 mmol), in dry toluene (140 mL), ethoxycarbonylmethylenetriphenylphosphorane (8.88 g, 27.8 mmol) was added in one portion, and the mixture was stirred for 18 h at room temperature. The solvent was removed in vacuo to afford a white solid. The crude material was dissolved in petroleum spirit (40–60°C) (50 mL) and the triphenylphosphinoxide removed by filtration. The filtrate was reduced in vacuo to give an oil (containing the *E*:*Z* compounds in a ratio of 2:3 by ^{1}H NMR) which was purified by flash column chromatography (petroleum ether 40–60°C/ethyl acetate, 20:1 to 5:1). The two products (**5a** and **5b**) were isolated in a combined yield of 76%, R_f 0.75 (*E*), 0.45 (*Z*) (7:1 petroleum ether 40–60°C/ethyl acetate). Due to confusion arising from a previous publication[9] which reported the *Z*-isomer as having the higher R_f, more comprehensive NMR spectral data was obtained for **5a** and **5b** to confirm their assignment below.

Ethyl (*E*)-3,4-dimethyl-5-oxo-2,5-dihydrofuran-2-ylidene ethanoate (5a)[9]: ν_{max}(film)/cm^{-1} 2985s, 2938s, 1787s (C=O), 1723s (C=O), and 1649s (C=C); δ_H(400 MHz; $CDCl_3$) 1.29 (3H, t, J 7.1, OCH_2CH_3), 1.93 (3H, s, C4-Me), 2.29 (3H, s, C3-Me), 4.18 (2H, q, J 7.1, OCH_2CH_3), and 5.90 (1H, s, $CHCO_2Et$); δ_C(100 MHz; $CDCl_3$) 9.0, 13.4, 14.1 (CH_2CH_3),

60.9 (O*C*H_2), 102.9 (*C*HCO_2Et), 131.7 and 146.5 (C-3 and C-4), 158.8 (C-2), 164.4 (C=O), and 168.8 (C=O); *m*/*z* (EI) 196 (M^+, 16%), 151 (M − OEt, 60), and 127 (100).

Ethyl (*Z*)-3,4-dimethyl-5-oxo-2,5-dihydrofuran-2-ylidene ethanoate (5b)[9]: M.p. 45–46°C (from ethyl acetate/hexane) (lit.,[9] 39–40°C); ν_{max}(KBr)/cm^{-1} 3085s, 2981s, 1786s (C=O), 1720s (C=O), and 1654m (C=C); δ_H(400 MHz; $CDCl_3$) 1.30 (3H, t, *J* 7.1, OCH_2CH_3), 1.96 (3H, s, C4-Me), 2.05 (3H, s, C3-Me), 4.24 (2H, q, *J* 7.1, OCH_2CH_3), and 5.40 (1H, s, C*H*CO_2Et); δ_C(100 MHz; $CDCl_3$) 9.1 (C-4), 9.9 (C-3), 14.2 (CH_2CH_3), 60.8 (O*C*H_2), 96.7 (*C*HCO_2Et), 129.0 and 147.4 (C-3 and C-4), 157.6 (C-2), 163.5 (C=O), and 169.1 (C=O); NOE (2%) observed between C3-*Me* and C*H*CO_2Et; *m*/*z* (EI) 196 (M^+, 15%), 151 (M − OEt, 59), and 127 (100).

Use of THF as a solvent: The same procedure was used as outlined above but using 2,3-dimethylmaleic anhydride (0.350 g, 2.78 mmol), dry THF (14 mL), and ethoxycarbonylmethylenetriphenylphosphorane (0.888 g, 2.78 mmol), and the mixture was stirred for 18 h at room temperature. The work-up and purification were as described above to yield the two products (**5a** and **5b**) in a combined yield of 69% and an *E*:*Z* ratio of 1:1.

Use of CTAB in water as a solvent: The same procedure was used as outlined above but using 2,3-dimethylmaleic anhydride (0.350 g, 2.78 mmol), cetyltrimethylammonium bromide (CTAB) (14 mL; 1 mmol dm^{-3} solution in distilled water), and ethoxycarbonylmethylenetriphenylphosphorane (0.888 g, 2.78 mmol), and the mixture was stirred for 18 h at room temperature. The work-up and purification were as described above to yield the two products (**5a** and **5b**) in a combined yield of 52% and an *E*:*Z* ratio of 3:2.

4,5-Dimethylcyclopent-4-ene-1,3-dione (6): To a stirred solution of the butenolactone mixture (**5a** and **5b**) (500 mg, 2.55 mmol), in methanol (100%, 15 mL), was added sodium (90 mg, 3.91 mmol). The reaction was heated to reflux and stirred for 15 h. The orange precipitate formed was filtered and washed with methanol (15 mL), dried, added to hydrochloric acid (2 M, 10 mL) and stirred for 2 h at 50°C. The product was extracted into ethyl acetate (3 × 40 mL) and the combined organics washed with saturated sodium hydrogencarbonate (30 mL), dried (magnesium sulfate), and reduced in vacuo to afford a yellow solid. This was purified by flash column chromatography (petroleum ether 40–60°C/ethyl acetate, 15:1) to give the title compound (261 mg, 83%) as a pale yellow waxy solid which readily decomposed (Found: C, 67.7; H, 6.5. $C_7H_8O_2$ requires C, 67.7; H, 6.5%);

ν_{max}(KBr)/cm^{-1} 2912s, 2887s, 1698s (C=O), and 1640 m (C=C); δ_H(400 MHz; $CDCl_3$) 1.99 (6H, s, $2 \times CH_3$), and 2.83 (2H, s, 2-H); δ_C(100 MHz; $CDCl_3$) 9.3 ($2 \times CH_3$), 40.8 (C-2), 156.4 (C-4, C-5), and 200.5 (C-1, C-3); *m*/*z* (EI) 124 (M^+, 100%), 108 (25), 96 (M − CO, 90), 54 (85).

2-Butyl-4,5-dimethylcyclopent-4-ene-1,3-dione (1) and 2,2-dibutyl-4,5-dimethylcyclopent-4-ene-1,3-dione (7): To a stirred solution of the diketone (**6**) (1.24 g, 10.0 mmol) in toluene (30 mL), was added anhydrous potassium carbonate (6.17 g, 44.6 mmol) and tetra *n*-butylammonium bromide (35 mg, 0.11 mmol). The reaction mixture was heated at reflux for 2 h then cooled to room temperature. Butylbromide (1.37 g, 10.0 mmol) was added in one portion and the reaction stirred for 24 h. The reaction mixture was filtered through Celite and washed with hexane. The filtrate was concentrated in vacuo to afford a brown oil (containing the mono and dialkylated material in a ratio of 5:1 by ^{1}H NMR) which was purified by flash column chromatography (petroleum ether 40–60°C/ethyl acetate, 25:1), to yield *2-butyl-4,5-dimethylcyclopent-4-ene-1,3-dione* (**1**) as an oil (1.03 g, 57%) and *2,2-dibutyl-4,5-dimethylcyclopent-4-ene-1,3-dione* (**7**) as an oil (264 mg, 11%), (unreacted starting diketone (**6**) was also recovered (180 mg)).

2-Butyl-4,5-dimethylcyclopent-4-ene-1,3-dione (1): ν_{max}(film)/cm^{-1} 2929s, 2859s, 1701s (C=O), and 1647m (C=C); δ_H(400 MHz; $CDCl_3$) 0.86 (3H, t, *J* 7.9, $(CH_2)_3CH_3$), 1.34 (4H, m, $(CH_2)_2CH_3$), 1.75 (2H, m, $CH_2(CH_2)_2CH_3$), 2.02 (6H, s, C4-Me, C5-Me), and 2.60 (1H, t, *J* 6.1, 2-H); δ_C(100 MHz; $CDCl_3$) 9.3, 13.8, 22.7, 26.7, 28.3, 48.8 (C-2), 155.3 (C-4, C-5), and 204.2 (C-1, C-3); *m*/*z* (EI) 180.1145 (M^+, 45%. $C_{11}H_{16}O_2$ requires 180.1150), 166 (10), and 124 (100).

2,2-Dibutyl-4,5-dimethylcyclopent-4-ene-1,3-dione (7): ν_{max}(film)/cm^{-1} 2931s, 2862s, 1706s (C=O), and 1649m (C=C); δ_H(400 MHz; $CDCl_3$) 0.75 (6H, t, *J* 7.4, $2 \times (CH_2)_3CH_3$), 0.86 (4H, m, $2 \times CH_2CH_2CH_3$), 1.13 (4H, quin, *J* 7.4, $2 \times CH_2CH_2CH_3$), 1.58 (4H, m, $2 \times CH_2CH_2CH_2CH_3$), and 1.91 (6H, s, C4-Me, C5-Me); δ_C(100 MHz; $CDCl_3$) 9.1, 13.7, 23.0, 26.8, 34.4, 53.8 (C-2), 155.4 (C-4, C-5), and 207.9 (C-1, C-3); *m*/*z* (EI) 236.1770 (M^+, 35%. $C_{15}H_{24}O_2$ requires 236.1776), 208 (9), 194 (6), 152 (5), and 124 (100).

2-Pentyl-4,5-dimethylcyclopent-4-ene-1,3-dione (8) and 2,2-dipentyl-4,5-dimethylcyclopent-4-ene-1,3-dione (9): The same procedure as that described above was used, but with the diketone (**6**) (124 mg, 1.00 mmol) in toluene (3 mL), anhydrous potassium carbonate (617 mg, 4.46 mmol) and tetra *n*-butylammonium bromide (4 mg, 0.01 mmol). The reaction mixture was heated at reflux for 2 h before being cooled

to room temperature and *n*-pentylbromide (175 mg, 1.2 mmol) added. The work-up and purification procedure was carried out as previously described to yield 2-*pentyl-4,5-dimethylcyclopent-4-ene-1,3-dione* (**8**) as an oil (37 mg, 19%) and *2,2-dipentyl-4,5-dimethylcyclopent-4-ene-1,3-dione* (**9**) as an oil (7 mg, 4%), (unreacted starting diketone was also recovered (48 mg, 38%)).

2-Pentyl-4,5-dimethylcyclopent-4-ene-1,3-dione (8): ν_{max}(film)/cm^{-1} 2930s, 2856s, 1701s (C=O), and 1643m (C=C); δ_H(400 MHz; $CDCl_3$) 0.85 (3H, t, *J* 7.1, $(CH_2)_4CH_3$), 1.27 (6H, m, $(CH_2)_3CH_3$), 1.73 (2H, m, $CH_2(CH_2)_2CH_3$), 2.00 (6H, s, C4-Me, C5-Me), and 2.60 (1H, t, *J* 6.1, 2-H); δ_C(100 MHz; $CDCl_3$) 9.3, 14.0, 22.3, 25.8, 26.9, 31.8, 48.9 (C-2), 155.3 (C-4, C-5), and 204.1 (C-1, C-3); *m*/*z* (EI) 194.1302 (M^+, 30%. $C_{12}H_{18}O_2$ requires 194.1307), 152 (7), and 124 (100).

2,2-Dipentyl-4,5-dimethylcyclopent-4-ene-1,3-dione (9): ν_{max}(film)/cm^{-1} 2931s, 2851s, 1697s (C=O), and 1639 m (C=C); δ_H(400 MHz; $CDCl_3$) 0.79 (6H, t, *J* 7.5, 2 x $(CH_2)_4CH_3$), 0.92 (4H, m, $2 \times CH_2CH_2CH_3$), 1.19 (8H, m, $2 \times (CH_2)_2CH_2CH_3$), 1.60 (4H, m, $2 \times CH_2(CH_2)_3CH_3$), and 2.03 (6H, s, C4-Me, C5-Me); δ_C(100 MHz; $CDCl_3$) 9.3, 14.0, 19.1, 22.8, 26.8, 34.5, 53.8 (C-2), 155.4 (C-4, C-5), and 204.6 (C-1, C-3); *m*/*z* (EI) 264.0156 (M^+, 25%. $C_{17}H_{28}O_2$ requires 264.0161), 249 (10), 235 (15), 194 (40), and 124 (100).

2-Hexyl-4,5-dimethylcyclopent-4-ene-1,3-dione (10) and 2,2-dihexyl-4,5-dimethylcyclopent-4-ene-1,3-dione (11): The same procedure as that described above was used, but with the diketone (**6**) (124 mg, 1.00 mmol) in toluene (3 mL), anhydrous potassium carbonate (617 mg, 4.46 mmol) and tetra *n*-butylammonium bromide (4 mg, 0.01 mmol). The reaction mixture was heated at reflux for 2 h before being cooled to room temperature and *n*-hexylbromide (175 mg, 1.2 mmol) added. The work-up and purification procedure was carried out as previously described to yield *2-hexyl-4,5-dimethylcyclopent-4-ene-1,3-dione* (**10**) as an oil (32 mg, 11%) and *2,2-dihexyl-4,5-dimethylcyclopent-4-ene-1,3-dione* (**11**) as an oil (9 mg, 3%), (unreacted starting diketone also recovered (51 mg, 42%)).

2-Hexyl-4,5-dimethylcyclopent-4-ene-1,3-dione (10): ν_{max}(film)/cm^{-1} 2929s, 2860s, 1699s (C=O), and 1641w (C=C); δ_H(400 MHz; $CDCl_3$) 0.85 (3H, t, *J* 6.6, $(CH_2)_5CH_3$), 1.27 (8H, m, $(CH_2)_4CH_3$), 1.74 (2H, m, $CH_2(CH_2)_4CH_3$), 2.01 (6H, s, C4-Me, C5-Me), and 2.59 (1H, t, *J* 6.0, 2-H); δ_C(100 MHz; $CDCl_3$) 9.3, 14.1, 22.6, 27.0, 29.3, 29.7, 31.5, 48.9 (C-2), 155.3 (C-4, C-5), and 204.2 (C-1, C-3); *m*/*z* (EI) 208.1458 (M^+, 32%. $C_{13}H_{20}O_2$ requires 208.1453), 178 (10), and 124 (100).

2,2-Dihexyl-4,5-dimethylcyclopent-4-ene-1,3-dione (11): ν_{max}(film)/cm^{-1} 2927s, 2856s, 1696s (C=O), and 1648w (C=C); δ_H(400 MHz; $CDCl_3$) 0.83 (6H, t, *J* 7.2, $2 \times (CH_2)_5CH_3$), 0.90 (4H, m, $2 \times CH_2CH_3$), 1.19 (12H, m, $2 \times (CH_2)_3CH_2CH_3$), 1.65 (4H, m, $2 \times CH_2(CH_2)_4CH_3$), and 2.02 (6H, s, C4-Me, C5-Me); δ_C(100 MHz; $CDCl_3$) 9.0, 13.5, 19.3, 20.4, 23.0, 26.6, 34.4, 53.8 (C-2), 155.4 (C-4, C-5), and 204.1 (C-1, C-3); *m*/*z* (EI) 292.1658 (M^+. $C_{19}H_{32}O_2$ requires 292.1653).

Undec-6-yn-5-ol[16]: To a solution of 1-hexyne (5.60 mL, 48.8 mmol) at −78°C in dry tetrahydrofuran was added *n*-butyllithium (48.8 mmol) dropwise. The reaction was warmed to −55°C over 20 min and then cooled to −78°C. *n*-Valeraldehyde (5.20 mL, 48.8 mmol) was added and the reaction mixture stirred for a further 2 h (a low reaction temperature was required to avoid the formation of 8-propyl-tridec-6-yne-5,9-diol). The reaction was quenched by the addition of saturated ammonium chloride solution (30 mL) and extracted with ethyl acetate (3×30 mL). The combined organic extracts were dried (magnesium sulfate) and concentrated in vacuo to give a yellow oil. This was purified by flash column chromatography (petroleum ether 40–60°C/ethyl acetate, 10:1) to afford the title compound as a colorless oil (7.12 g, 87%). ν_{max}(film)/cm^{-1} 3346br s (OH), 2220s (alkyne), and 2953s; δ_H(400 MHz; $CDCl_3$) 0.89 (6H, m, 1-H, 11-H), 1.40 (8H, m, 2-H, 3-H, 10-H, 9-H), 1.66 (2H, m, 4-H), 1.97 (1H, s, OH), 2.19 (2H, td, *J* 5.1 and 2.0, 8-H), and 4.33 (1H, tt, *J* 2.8 and 2.0, 5-H); δ_C(100 MHz; $CDCl_3$) 13.6 and 14.0 (C-1 and C-11), 18.4, 21.9, 22.4, 27.4, 30.8, 37.9, 62.7 (C-5), 81.4 (C-6), and 85.4 (C-7); *m*/z (EI) 168.1510 (M^+. $C_{11}H_{20}O$ requires 168.1514).

Undec-6-yn-5-ol was stored under nitrogen to avoid aerial oxidation to the corresponding ketone undec-6-yn-5-one. ν_{max}(film)/cm^{-1} 2960s, 2872s, 2214s (alkyne), and 1672s; δ_H(400 MHz; $CDCl_3$)[23] 0.91 (6H, m, 1-H and 11-H), 1.38 (4H, m, 2-H, 10-H), 1.58 (4H, m, 9-H, 3-H), 2.35 (2H, t, *J* 7.3, 8-H), and 2.50 (2H, t, *J* 7.3, 4-H); δ_C(100 MHz; $CDCl_3$) 13.4 and 13.8 (C-1 and C-11), 18.6, 21.9, 22.1, 26.2, 29.7, 45.2 (C-4), 80.8 (C-6), 94.2 (C-7), and 188.5 (C-5); *m*/*z* (EI) 166 (M^+, 30%), 137 (35), and 123 (100).

Undeca-5,6-diene (12): To a mixture of undec-6-yn-5-ol (1.71 g, 10.2 mmol) and *n*-tributyltin hydride (2.9 mL, 11 mmol), was added AIBN (5 mg). The mixture was heated (in the absence of solvent) at 90°C for 4 h then cooled to room temperature and diluted with dichloromethane (20 mL). Triethylamine (2.8 mL, 20.0 mmol) was added dropwise. The reaction was further cooled to 0°C, methanesulfonyl chloride (1.71 g, 15.1 mmol) was added and the mixture was then warmed to room temperature over 30 min. The reaction was quenched

by adding to hydrochloric acid (2 M, 20 mL). The product was extracted with ethyl acetate (3×30 mL) and the combined organic extracts washed with dilute sodium hydrogencarbonate solution (5%, 20 mL), dried (magnesium sulfate) and concentrated in vacuo to yield an oil. The oil was purified by flash column chromatography (hexane) and then distilled under reduced pressure using a Vigreux column to afford the title compound as a colorless liquid (1.19 g, 77%). ν_{max}(film)/cm^{-1} 2874s, 2953s, 1963w (allene), and 1926w (allene); δ_H(400 MHz; $CDCl_3$) 0.89 (6H, t, *J* 7.0, 1-H, 11-H), 3.71 (8H, m, 2-H, 3-H, 9-H, 10-H), 1.91 (4H, m, 4-H, 8-H), and 5.06 (2H, m, 5-H, 7-H); δ_C(100 MHz; $CDCl_3$), 13.9 (C-1, C-11), 22.2 (C-2, C-10), 28.7 (C-3, C-9), 31.4 (C-4, C-9), 90.9 (C-5, C-7), and 203.8 (C-6); *m*/*z* (EI) 152.1560 (M^+, 17%. $C_{11}H_{20}$ requires 152.1565) and 95 (100).

(*E*)- and (*Z*)-4-Pentylidene-5-butyl-2,3-dimethylcyclopent-2-enone (13): To a stirred solution of dicobalthexacarbonylbut-2-yne (2.72 g, 8.0 mmol) and the allene (**12**) (1.88 g, 12.2 mmol) in dry dichloromethane (80 mL) at 0°C was added *N*-methylmorpholine *N*-oxide monohydrate (6.48 g, 48.0 mmol) gradually over 2 min. The reaction was then stirred for 16 h at room temperature. The reaction mixture was filtered through silica gel and the filtrate was concentrated in vacuo to afford a dark brown oil which was purified by flash column chromatography, (petroleum ether 40–60°C/ethyl acetate, 20:1). The product was isolated as a colorless oil containing an inseparable mixture of the *E* and *Z* isomers (1.49 g, 80%). Although extensive spectral analysis was not carried out because the alkene generated was cleaved in the subsequent step the NMR spectra were consistent with the formation of the isomers in a ratio of 12:1 (*E*:*Z*) based upon extensive literature precedent for the selectivity with this reaction.[14] ν_{max}(film)/cm^{-1} 2928s, 2856s, 1667s (C=O), 1643m (C=C), and 1616s (C=C); *E* isomer δ_H(400 MHz; $CDCl_3$) 0.87 (6H, m, $2 \times (CH_2)_3CH_3$), 1.20 (6H, m, $3 \times CH_2$), 1.65 (2H, m, CH_2), 1.78 (3H, s, C3-Me), 1.93 (2H, m, CH_2), 2.04 (3H, s, C2-Me), 2.56 (2H, m, C=CHCH_2), 2.90 (1H, t, *J* 4.5, 5-H), and 5.67 (1H, t, *J* 7.7, C=C*H*); *E* isomer δ_C(100 MHz; $CDCl_3$) 13.9, 14.0, 22.5, 23.0, 26.6, 29.1, 29.4, 29.7, 30.1, 31.7, 46.3, 124.7, 137.4 (C-2), 141.2, 163.3, and 208.5 (C-1); *Z* isomer δ_H(400 MHz; $CDCl_3$) 0.87 (6H, m, 2 x $(CH_2)_3CH_3$), 1.20 (6H, m, $3 \times CH_2$), 1.65 (2H, m, CH_2), 1.78 (3H, s, C3-Me), 1.93 (2H, m, CH_2), 2.04 (3H, s, C2-Me), 2.56 (2H, m, C=CHCH_2), 2.90 (1H, t, *J* 4.5, 5-H), and 5.67 (1H, t, *J* 7.7, C=C*H*); *Z* isomer δ_C(100 MHz; $CDCl_3$) 13.9, 14.0, 22.5, 23.0, 26.6, 29.1, 29.4, 29.7, 30.1, 31.7, 46.3, 124.7, 137.4 (C-2), 141.2, 163.3, and 208.5 (C-1); *m*/*z* (EI) 234.1978 (M^+, 14%. $C_{16}H_{26}O$ requires 234.1984), 178 (M−Bu, 40), 136 (M−Bu-Pr, 100).

2-Butyl-4,5-dimethylcyclopent-4-ene-1,3-dione (1): Osmium tetraoxide/periodate procedure: To a solution of tetrahydrofuran (3 mL) and osmium tetraoxide (0.2 mL of 0.04 M solution), at 0°C was added the enone (**13**) (102 mg, 0.44 mmol) which was stirred for 10 min. Sodium periodate (307 mg, 1.44 mmol) was added gradually over 20 min and the reaction was sealed and stirred for 72 h at room temperature. The reaction was filtered though a pad of Celite and the filtrate concentrated in vacuo. The crude oil was purified by flash column chromatography (petroleum ether 40–60°C/ethyl acetate, 30:1) to give the target compound as a yellow oil (51 mg, 65%) with identical spectral properties to those above.

Ozone procedure: To a solution of enone (**13**) (0.50 g, 2.14 mmol) in ethanol (30 mL), was added Sudan Red 7B (1 mL of a saturated solution of Sudan Red 7B in ethanol), the reaction mixture was cooled to −78°C and ozone was bubbled through. After 40 min the red color had almost disappeared, and the reaction was purged with nitrogen. The mixture was warmed to room temperature and concentrated in vacuo. The yellow oil was purified by flash column chromatography (petroleum ether 40–60°C/ethyl acetate, 30:1) to afford the target compound (335 mg, 87%) as an oil with identical spectroscopic properties to those above.

ACKNOWLEDGMENTS

We thank Bush Boake Allen for a studentship (MHJ), John Janes for helpful discussions, and Dirk Uwe Hahn. The ULIRS Mass Spectrometry Facility at the University of London School of Pharmacy are acknowledged for high resolution mass spectra.

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Received in the UK December 18, 2001

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