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TRANSANNULAR CYCLISATION AS A STRATAGEM IN SYNTHESIS. A TOTAL SYNTHESIS OF (±)-PENTALENENE.

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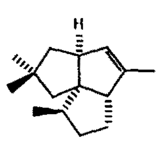
Abstract: - A total synthesis of the triquinane sesquiterpene (±)-pentalenene(1) found in Streptomyces, based on transannular cyclisation of the bicyclo[6.3.0]undecadiene (7) in the presence of boron trifluoride etherate is described. The bicyclo[6.3.0]undecadiene(7) was elaborated from the silyl enol ether(36) using a unique intramolecular [2+2] photocycloaddition - Grob fragmentation sequence leading to (8) [viz (36)→(37) and (38)→(8)], followed by olefination to (40) and isomerisation in the presence of rhodium trichloride trihydrate.

The triquinane sesquiterpene pentalenene(1)[1] is the parent hydrocarbon of the pentalenolactone family of antibiotic antifungal metabolites, e.g.(2), found in Streptomyces[2]. Pentalenene is related structurally to the naturally occurring tricyclo[6.3.0.0^{4,8}]undecanes isocomene(3)[3], silphinene(4)[4] and silphiperfolene(5)[5,6]. It seems likely that the four hydrocarbons(1), (3→5), which differ only in the relative positions and stereochemistries of methyl substituents together with the positional arrangement of double bonds in their carbon frameworks, are all derived in Nature from humulene(6)[7], via a series of cyclisations accompanied by carbocation rearrangements. In continuation of our studies of transannular cyclisations and intramolecular [2+2] photocycloadditions as strategies in the synthesis of natural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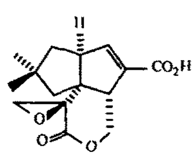

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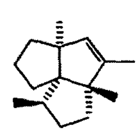
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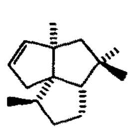
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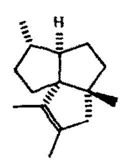

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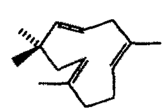
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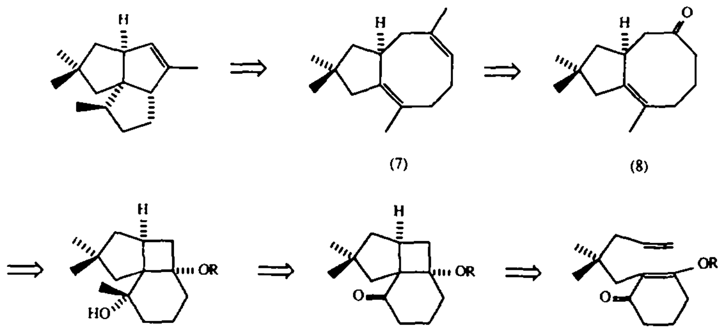
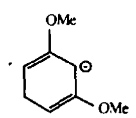
products[8], we now report a total synthesis of (±)-pentalenene(1) which is based on a transannulation of the bicyclo[6.3.0]undecane(7), itself elaborated via a unique intramolecular [2+2] photocycloaddition - Grob fragmentation sequence[9] starting with the enol ether (11) [viz (11)→(10) and (9)→(8)] (Scheme 1)[10].



(7) (8) (9) (10) (11)

Scheme 1

We began our studies of the above approach to (±)-pentalenene(1)[11], by first investigating a synthetic route to the 2-pentenyl substituted cyclohexane-1,3-dione precursor, viz (16), to (11). In the past, we have found that direct alkylation of the anion (12) derived from 2,4-dimethoxycyclohexa-1,4-diene[12] with an appropriate 1-iodopent-4-ene, followed by hydrolysis of the intermediate bis enol ether(13), provides a particularly useful and practical route to 2-substituted cyclohexane-1,3-diones viz (12)→(13)→(14)[8a]. In the event, however, although this method proceeds well and in high yields with primary and secondary iodides, we were not able to effect a similar alkylation of (12) using the sterically encumbered (neopentyl) iodopentene(15). We therefore decided to elaborate the cyclohexanedione(16) by an intramolecular acylation reaction involving the δ-keto ester (17) as a central intermediate, which was conveniently synthesised from the enone(24).



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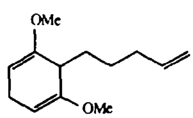

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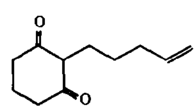

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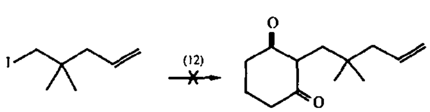

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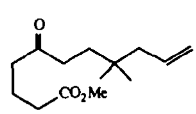

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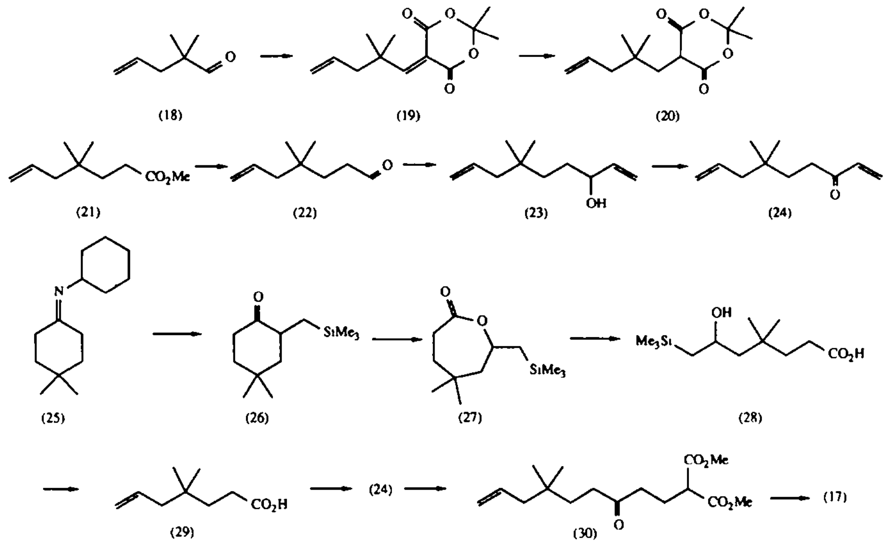
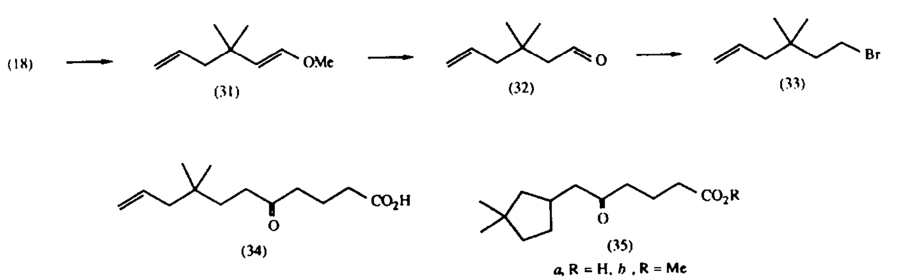
Two principal routes were developed for the preparation of the enone(24) and these are summarised in Scheme 2. Thus, condensation between 2,2-dimethyl-4-pentenal(18) and Meldrum's acid first led to the ylidene-malonate(19), which by reduction to (20)[13] followed by methanolysis[14] was converted into the unsaturated ester(21). After conversion of the ester(21) to the corresponding aldehyde(22), addition of vinylmagnesium bromide followed by oxidation of the resulting carbinol(23) using manganese dioxide, then led to the enone(24). In a second route[15], the cyclohexylimine(25) of

4,4- dimethylcyclohexanone was first deprotonated, and the resulting carbanion was then alkylated with chloromethyltrimethylsilane. Hydrolysis led to the cyclohexanone(26) which by a silicon directed Baeyer-Villiger reaction was next converted into the lactone(27). Saponification of the lactone(27) in the presence of methanolic potassium hydroxide then led to the β-hydroxy-silane(28) which underwent smooth elimination in the presence of boron trifluoride giving the heptenoic acid (29). Finally, addition of vinyllithium to (29) followed by hydrolysis led to the enone(24) which was identical to the same compound produced by the earlier route.



Scheme 2

In a two-step procedure, Michael addition of malonate anion to the enone (24), followed by de-methoxycarbonylation of the resulting di-ester(30) using Krapcho's procedure[16] led to the δ-keto-ester(17). A less practical route to the δ-keto ester(17), but also starting from 2,2-dimethyl-4-pentenal is shown in Scheme 3. Homologation of (18) to (32) via the corresponding vinyl ether (31), followed by reduction and bromination, first led to the bromide(33). After conversion of (33) to the corresponding Grignard reagent, reaction with glutaric anhydride then led to the δ-keto acid (34) which was esterified producing(17). This route to (17) however proved impractical due to co-formation of the compound(35a) produced after initial rearrangement of the Grignard reagent derived from (33)[17].



Scheme 3

Treatment of the δ-keto ester(17) with potassium t-butoxide in ether resulted in clean cyclisation to the cyclohexane-1,3-dione(16) which was isolated as an unstable solid in 98% yield[18]. The dione(16) was immediately converted into the corresponding t-butyldimethylsilyl enol ether(36), in readiness for the next and crucial intramolecular photocycloaddition - Grob fragmentation steps (11)→(10) and (9)→(8)(Scheme 1). We chose the silyl enol ether derivative of (16) instead of the enol ester derivative (i.e. acetate, benzoate) used in our earlier work[9], because of the comparative neutrality of silyl ethers towards organometallic reagents, and because of the known affinity of silicon for fluoride ion to trigger the Grob fragmentation step (see later discussion)[19].

Irradiation of a solution of the silyl enol ether(36) in hexane through Pyrex using a 450W medium pressure mercury lamp, resulted in regioselective intramolecular [2+2] photocycloaddition producing only the tricyclic ketone(37), which was obtained as an oil in 81% yield. The specificity of this [2+2] photocycloaddition, although remarkable, was anticipated by analogy with our earlier described model studies directed towards the synthesis of the marine metabolite precapnelladiene(39)[9].

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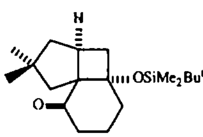

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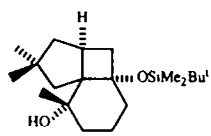

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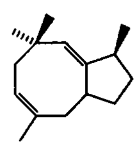
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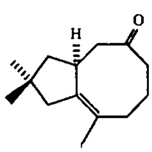

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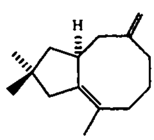

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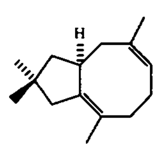
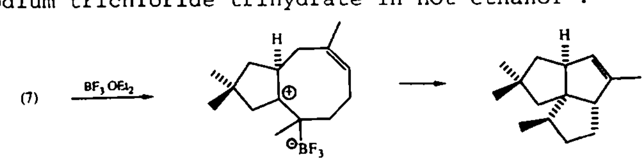


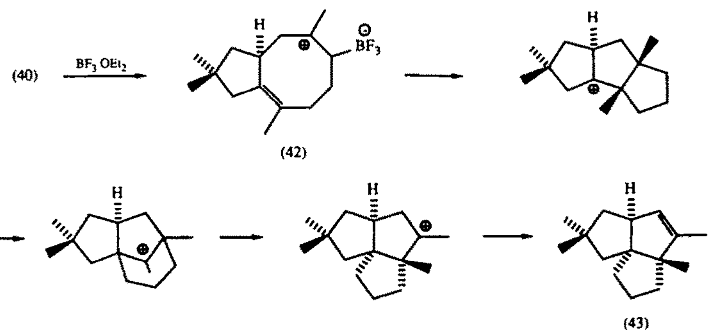
(7)

Addition of the tricyclic ketone(37) to a cold solution of the high order cuprate, Me_3CuLi_2, derived from methyllithium and copper iodide[20], next resulted in stereoselective formation of the crystalline t-alcohol(38) which we presume has the t-alcohol group quasi-axial to the quasi-equatorial silyl ether residue. When the silyl ether(38) was treated with aqueous hydrofluoric acid in tetrahydrofuran, a smooth Grob fragmentation ensued leading to the fused 5,8-ring enone(8), which was obtained as colourless needles in 73% yield. The enone(8) was then converted into the penultimate cycloocta-1,5-diene precursor(7) to pentalenene(1) following Wittig reaction with methylenetriphenylphosphorane[21], leading to (40), and isomerisation of the latter with rhodium trichloride trihydrate in hot ethanol[9].



(41) (1)

Finally, treatment of the cycloocta-1,5-diene(7) with boron trifluoride in methylene dichloride resulted in stereoselective transannular cyclisation, via the carbocation intermediate(41), producing(±)-pentalenene(1), whose n.m.r. spectral data were superimposable on those of an authentic sample. Interestingly, although we found no evidence for the co-formation of the C-9 methyl epimer of pentalenene from transannulation of (7)[22], a minor isomeric hydrocarbon was also produced concurrently. This hydrocarbon, whose proportion in the mixture varied with the reaction conditions, was assigned the structure(43), and we believe that it arises via initial transannular cyclisation from the alternative carbocation(42) derived from (40) in the



Scheme 4

presence of boron trifluoride (Scheme 4). The hydrocarbon (43) is probably identical with a compound reported by Shirahama et al, as a minor product derived via transannulation of humulene(6)[23]. In accordance with the structural assignment(43), we found that as expected, the hydrocarbon was the sole tricyclic compound obtained when the positional isomer (40) of (7) was treated in a similar manner with boron trifluoride etherate.

Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 710B spectrometer, and ultraviolet spectra on either a Pye Unicam SP1700 or SP800 spectrometer. Proton n.m.r. spectra were recorded at 90 MHz on a Perkin Elmer R32 or at 80 MHz on a Bruker WP 80SY PFT, or at 250 MHz on a Bruker WM 250 PFT spectrometer. Carbon n.m.r. spectra were recorded on the Bruker WM 250 PFT instrument, and all samples for n.m.r. analysis were dilute solutions in deuteriochloroform unless otherwise stated. The multiplicities in the n.m.r. spectra were singlets unless otherwise stated when the following abbreviations are used: d, doublet; t, triplet; dd, double doublet; q, quartet; m, multiplet; br, broad.

Mass spectra were recorded on an AEl MS 902, or on a VG 7070E spectrometer, and microanalytical data were obtained on a Perkin-Elmer 2204B elemental analyser.

All organic solvents were dried over magnesium sulphate, and solvents were removed under reduced pressure on a Büchi rotary evaporator.

1-Iodo-2,2-dimethyl-4-pentene(15). - A solution of 2,2-dimethyl-4-pentenal (40g)[24] in dry ether (200ml) was added to a stirred suspension of lithium aluminium hydride (4g) in dry ether (300ml) at a rate sufficient to maintain gentle reflux. The mixture was heated under reflux for 3h, and then cooled to 25°C. Water (10ml) was added dropwise to give a white, granular precipitate. The ether solution was decanted, and the precipitate was then washed with ether (2x50ml). Evaporation of the combined, dried ether extracts and distillation of the residue gave 2,2-dimethyl-4-pentenol (40.2g, 99%) as a colourless liquid b.p. 140-142°C; ν_{max} (film) 3350, 1640 cm^{-1}; δ_H 5.9-5.5(m, :CH), 5.0-4.7(m, :CH_2), 3.35(OH), 3.18(CH_2), 1.95(d, _J_15, CH_2), 0.85(Me_2); (m/z 114.1049; $C_7H_{14}O$ requires _M_ 114.1045).

Tosyl chloride (1.8g) was added portion-wise to a stirred mixture of 2,2-dimethyl-4-pentenol (1g) and dry pyridine (0.73g) whilst the temperature was maintained between 0-5°C. The mixture was stirred at 25°C for 4h then diluted with water (25ml) and extracted with ether (3x30ml). The ether extracts were washed successively with hydrochloric acid (2x25ml, 2M), sodium hydroxide (2x25ml, 2M) and brine (25ml), then dried and evaporated to give 2,2-dimethyl-1-tosyloxy-4-pentene (2.15g, 92%) as a clear oil, b.p. 98-100°C at 0.55mm Hg, ν_{max} (film) 1640, 1600cm^{-1}; δ_H 7.75(d, _J_8, aryl :CH), 7.30(d, _J_8, aryl :CH), 5.9-5.4(m, :CH), 5.1-4.9(m, :CH_2), 3.64(CH_2O), 2.50(Me), 2.00(d, _J_15, CH_2), 0.90(Me_2).

A mixture of 2,2-dimethyl-1-tosyloxy-4-pentene (40g), sodium iodide (44g), hexamethylphosphoramide (200ml) and water (10ml) was heated at 100°C for 18h. The mixture was cooled, then poured into water (1 l) and extracted with ether (3x400ml). The combined extracts were washed successively with hydrochloric acid (2M, 400ml), saturated sodium bicarbonate (100ml) and brine (200ml), then dried and evaporated to give the iodide (30g, 90%) as a light yellow oil, b.p. 56-57°C at 12mm Hg, ν_{max} (film) 1640 cm^{-1}; δ_H 5.8-5.3(m, :CH), 5.0-4.8(m, :CH_2), 2.05(d, _J_15, CH_2), 1.02(Me_2); (m/z 224.0070; $C_7H_{13}I$ requires _M_ 224.0064).

Attempted Alkylation of 1,5-Dimethoxy-1,4-cyclohexadiene with 1-Iodo-2,2-dimethyl-4-pentene(15). - A solution of 1,5-dimethoxy-1,4-cyclohexadiene[12] (1g) in dry tetrahydrofuran (3ml) was added dropwise to _t_-butyllithium (5.17ml, 1.5M) in tetrahydrofuran (40ml) at -78°C. After 1h the yellow solution was treated with hexamethylphosphoramide (1.75ml), and the mixture was stirred at -78°C for 10min, before a solution of 2,2-dimethyl-1-iodo-4-pentene (1.75g) in tetrahydrofuran (3ml) was added. The resulting brown solution was allowed to warm to room temperature, and then brine (10ml) was added. The aqueous layer was separated, and then extracted with pentane (3x20ml). The combined extracts were dried and then evaporated at atmospheric pressure to afford a yellow oil. Column chromatography (Silica gel G, using _n_-hexane as eluant) yielded (a) 4,4,7,7-tetramethyl-1,9-decadiene (0.9g) as an oil, ν_{max} (film) 1640 cm^{-1};δ_H 5.9-5.6(m, CH), 5.0-4.8(m, :CH_2), 1.95(d, _J_15, CH_2), 1.15(CH_2), 0.83(Me_2); δ_C 135.8, 116.4, 46.4, 35.5, 32.8, 27.0 p.p.m.; (m/z 194; $C_{14}H_{26}$ requires _M_ 194), and (b) recovered 1,3-dimethoxybenzene (0.7g).

2,2-Dimethyl-5-(2,2-dimethylpent-4-enylidene)-4,6-diketo-1,3-dioxane(19). - Piperidine (6ml) and glacial acetic acid (20ml) were added to a solution of Meldrum's acid[25] (190g) and 2,2-dimethyl-4-pentenal[24] (120g) in chloroform 1ℓ), and the mixture was then heated under reflux for 14h; the water produced during the condensation was separated by a Dean and Stark trap. The solution was cooled to 25°C, then washed with brine (300ml), dried and evaporated to give the alkylidene malonate (228g, 92%) as a viscous oil; ν_{max} (film) 1740(br), 1620(br) cm^{-1}; δ_H 7.84(:CH), 6.1-5.6(m, :CH), 5.3-4.9(m, :CH_2), 2.49(t, J10, CH_2), 1.74(2 x Me), 1.35(2 x Me); (Found: C,65.8, H,7.9%, m/z 238.1215; $C_{13}H_{18}O_4$ requires: C,65.5, H,7.6%; M 238.1095).

2,2-Dimethyl-5-(2,2-dimethylpent-4-enyl)-4,6-diketo-1,3-dioxane(20). - Sodium borohydride (40g) was added portionwise to a stirred solution of 2,2-dimethyl-5-(2,2-dimethylpent-4-enylidene)-4,5-diketo-1,3-dioxane (228g) in ethanol (1.1l). The temperature of the reaction mixture was maintained between 15 and 20°C throughout the addition. The mixture was stirred for 40min. then quenched with ice-cold dilute hydrochloric acid(1l), diluted with brine (1.5l) and extracted with ether (6x800ml). The combined, washed (H_2O), extracts were dried and evaporated to give the alkylmalonate (207g, 90%) as a semi-solid glue, ν_{max} ($CHCl_3$) 1790, 1750, 1640 cm^{-1}; δ_H 6.1-5.6(m, :CH), 5.2-4.9(m, :CH_2), 3.58(t, J10, CH), 2.16(d, J6, CH_2), 2.06(d, J10, CH_2), 1.85(Me), 1.78(Me), 0.94(2xMe); (Found: C,64.9, H,8.6%; m/z 240.1352; $C_{13}H_{20}O_4$ requires: C,65.0, H,8.4%; M 240.1361).

Methyl 4,4-dimethylhept-6-enoate(21). - Copper powder (4g) was added to a solution of 2,2-dimethyl-5-(2,2-dimethylpent-4-enyl)-4,6-diketo-1,3-dioxane (207g) in pyridine (1.51 l) and methanol (250ml). The mixture was heated under reflux for 36h, then cooled to 25°C and evaporated to a volume of approximately 600ml at 12mm Hg. The solution was poured into ice-cold, dilute hydrochloric acid (1.5l,2M) and then extracted with ether (4x600ml). The combined extracts were dried and evaporated to give a yellow oil which was distilled to give the ester (81g, 55%) as a colourless oil, b.p. 78-82°C at 12mm Hg; ν_{max} (film) 1740, 1630 cm^{-1}; δ_H 6.1-5.6(m, :CH), 5.1-4.9(m, CH_2), 3.68(CO_2Me), 2.4-2.2(m, CH_2), 1.98(d, J10, CH_2), 1.7-1.5(m, CH_2), 0.88(Me_2); (Found: C,70.3, H,11.65%, m/z 170.1311; $C_{10}H_{18}O_2$ requires: C,70.5, H,11.8%, M 170.1301).

4,4-Dimethylhept-6-en-1-al(22). - A solution of methyl 4,4-dimethylhept-6-enoate (55g) in dry ether (100ml) was added dropwise to a stirred suspension of lithium aluminium hydride (13g) in dry ether (1.4 l). The mixture was heated under reflux overnight, and then cooled to room temperature. Water was cautiously added dropwise to give a granular precipitate. The supernatant ether was decanted, and the precipitate was then washed with ether (2x600ml). The combined extracts were dried and evaporated to leave a yellow oil, which was distilled to give the 4,4-dimethylhept-6-en-1-ol (42g, 88%) as a colourless oil, b.p. 82-84°C at 12mm Hg; ν_{max} (film) 3350, 1640 cm^{-1}; δ_H 6.1-5.6(m, :CH), 5.1-4.8(m, :CH), 3.62(t, J10, OCH_2), 2.0(br, OH), 1.92(d, J6, CH_2), 1.8-1.1(m, 2xCH_2), 0.88(Me_2); (Found: C,75.6, H,13.2%, m/z 142.1360; $C_9H_{18}O$ requires: C,76.0, H,12.8%; M 142.1358).

4,4-Dimethylhept-6-en-1-ol (2g) was added in one portion, to a stirred mixture of pyridinium chlorochromate (6g), celite (4g)[26] and sodium acetate (1.5g) in dry dichloromethane (60ml). The mixture was stirred for 5h, then ether (160ml) was added and the granular precipitate was filtered off and washed with ether (2x50ml). The combined extracts were carefully evaporated at 12mm Hg, and then the dark brown residue was gently flash distilled at 12mm Hg to give the aldehyde (1.85g, 92%) as a colourless oil, b.p. 56-58°C at 12mm Hg; ν_{max} 2750, 1730 and 1640 cm^{-1}; δ_H 9.84(t, *J*2, CHO), 6.1-5.6(m, :CH), 5.1-4.8(m, :CH_2), 2.41(t, *J*10, CH_2), 1.92(d, *J*6,CH_2), 1.52(t, *J*10, CH_2). The 2,4-dinitrophenylhydrazone derivative crystallised from ethanol and had m.p. 110-111°C; (Found: C,56.2, H,6.4, N,17.65%; $C_{15}H_{20}O_4N_4$ requires: C,56.2, H,6.3, N,17.5%).

6,6-Dimethylnona-1,8-diene-3-ol(23). - Vinylmagnesium bromide (140ml, 1.6M in tetrahydrofuran) was added rapidly to a stirred solution of 4,4-dimethylhept-6-en-1-al (16g) in dry ether (400ml) at-60°C under nitrogen. The buff-coloured suspension was warmed to room temperature, and then treated cautiously with dilute hydrochloric acid (100ml, 2M). The ether layer was decanted, and the aqueous layer was then extracted with ether (2x100ml). The combined extracts were dried and evaporated to give the dienol (18.4g, 96%) as an orange oil, b.p. 70-3°C at 0.1mmHg; ν_{max} (film) 3350, 1640 cm^{-1}; δ_H 6.1-5.6(m, 2 x :CH), 5.4-4.8(m, 2 x :CH_2), 4.1-3.9(m, *H*COH), 2.1(br, HCO*H*), 1.92(d, *J*9, CH_2), 1.6-1.0(m, 2 x CH_2), 0.88(Me_2); (m/z 168.1522; $C_{11}H_{20}O$ requires *M* 168.1514).

6,6-Dimethyl-1,8-nonadien-2-one(24). - (a) Vinyllithium in ether (35ml, 1.2M)[27] was added dropwise to a stirred solution of 4,4-dimethyl-8-heptenoic acid (3g) (see below for details of preparation) in dry glyme (90ml) at room temperature under a nitrogen atmosphere, and the brown suspension was then heated at 40-50°C overnight. The suspension was added dropwise to vigorously stirred iced-water (400ml), and the solution produced was then extracted with ether (4x200ml). The combined extracts were washed with water (100ml), dried and evaporated to leave an orange oil. Column chromatography (Silica gel G, ether-hexane 1:10 as eluant) gave the vinyl ketone (2.1g, 66%) as a yellow oil, b.p. 61-2°C at 2mmHg; ν_{max} (film) 1690, 1635, 1620 cm^{-1}; δ_H 6.5-6.3(m, :CH_2), 6.1-5.6(m, 2 x :CH), 5.2-4.9(m, :CH_2), 2.58(t, *J*10, CH_2), 2.00(d, *J*9, CH_2), 1.55(t, *J*10, CH_2), 0.91(Me_2); δ_C 200.5, 136.6(d), 135(d), 127.4(t), 117.1(t), 46.4(t), 35.6(t), 34.9(t), 32.8(s), 26.7(q) p.p.m.; (Found: C,79.6, H,11.1%, m/z 166.1344; $C_{11}H_{18}O$ requires: C,79.5, H,10.9%; *M* 166.1353).
(b) 6,6-Dimethylnona-1,8-diene-3-ol (10g) was added to a stirred suspension of manganese dioxide (110g) in chloroform (1l), and the mixture was then stirred for 72h at room temperature. The manganese dioxide was removed by filtration through a bed of diatomite which was then washed with further chloroform (4x300ml). The combined filtrates were evaporated to give the enone (9.4g, 95%) which showed identical spectroscopic data to those reported under (a).

N-Cyclohexylimine-4,4-dimethylcyclohexanone(25). - A solution of 4,4-dimethylcyclohexanone[28] (90g) and cyclohexylamine (71g) in benzene (250ml) was heated under reflux through a Dean and Stark trap for 16h. The benzene was evaporated at 14mm Hg and the residue was then distilled to give the imine (115g, 78%) as a colourless oil, b.p. 97-99°C at 0.5mm Hg; ν_{max} (film 1665 cm^{-1}; δ_H 3.5-3.1(m, HCN), 2.5-2.2(t, *J*8, 2 x CH_2), 2.0-1.0(m, 7 x CH_2), 1.02(Me_2); (m/z 207.191; $C_{14}H_{25}N$ requires *M* 207.1987).

4,4-Dimethyl-2-trimethylsilylmethylcyclohexanone(26). - A stirred solution of N-cyclohexylimine-4,4-dimethylcyclohexanone (30g) in tetrahydrofuran (30ml) was treated with ethylmagnesium bromide in tetrahydrofuran (130ml, 1.5M), and the mixture was then heated under reflux for 2h. A solution of chloromethyltrimethylsilane (25g) in tetrahydrofuran (25ml) was added dropwise to the refluxing solution, and the mixture was then heated for a further 48h. The red solution was cooled, treated with brine (100ml), and the tetrahydrofuran layer was then separated. The aqueous layer was extracted with ether (3 x 100ml) and the combined and dried organic extracts were then evaporated to leave a pale yellow oil. A solution of the oil in petroleum ether (400ml, b.p. 40-60°C) and aqueous acetic acid (100ml, 2M) was stirred vigorously for 2.5h at 25°C, and then the aqueous layer was separated and extracted with ether (3 x 100ml). The combined extracts were washed with saturated sodium bicarbonate (150ml), dried and evaporated to leave a yellow oil. Distillation gave the ketone (17g, 49%) as a colourless oil, b.p. 80-84°C at 1mm Hg; ν_{max} (film) 1710 cm^{-1}; δ_H 2.6-2.1(m, 3H), 1.8-1.2(m, 2 x CH_2), 1.24(Me), 1.02(Me), 0.4-0.1(m, CH_2Si), 0.00(Me_3Si); δ_C 212.7, 50.3(t), 42.6(d), 40.1(t), 38.0(t), 31.5(q), 31.0, 24.5(q), 15.9(dd), -0.7 p.p.m.; (m/z 212.1599; $C_{12}H_{24}O_2Si$ requires M 212.1597).

4,4-Dimethyl-6-trimethylsilylmethylheptanolide(27). - m-Chloroperoxybenzoic acid (17g) and disodium hydrogen phosphate (17g) were added in one portion to a stirred solution of 4,4-dimethyl-2-trimethylsilylmethylcyclohexanone (17g) in dichloromethane (250ml) in the dark at 25°C. The mixture was stirred for 3h, then saturated sodium bicarbonate solution (300ml) was carefully added, and the mixture was shaken until two layers separated. The aqueous layer was extracted with dichloromethane (100ml), and the combined extracts were then washed successively with saturated sodium bicarbonate (50ml), water (100ml) and brine (100ml). The extracts were dried and evaporated to leave a pale yellow oil. Distillation gave the lactone (16.8g, 92%) as a colourless oil, b.p. 90-93°C at 1mm Hg; ν_{max} (film) 1730^{-1}; δ_H 4.6-4.2(m, HCO), 2.7-2.1(m, CH_2), 1.7-1.2(m, 2 x CH_2), 0.98(Me), 0.89(Me), 0.00(CH_2Si and Me_3Si); δ_C 175.1, 74.2(d), 50.6(t), 35.8(t), 32.7(q), 32.0, 30.4(t), 25.8(t), 24.0(q), -0.9 p.p.m.; (m/z 213.1317; $C_{15}H_{21}O_2Si$ requires M 213.1311).

4,4-Dimethyl-6-heptenoic acid(29). - Potassium hydroxide solution (25ml, 50%) was added in one portion to a stirred solution of 4,4-dimethyl-6-trimethylsilylmethylheptanolide (17g) and washed with ether (50ml). The aqueous layer was transferred to a 5l separating funnel where it was acidified to pH1 with conc.hydrochloric acid. The white solid of (28) produced was dissolved in dichloromethane (2l), and the organic layer was then separated and dried. The drying agent was filtered off, and the stirred solution was then cooled to 0°C and purged with nitrogen. Boron trifluoride etherate (60ml) was added, and the solution was stirred at 0°C for 2h, and then warmed to 25°C. Saturated sodium carbonate (1l) was added, followed by solid sodium carbonate until the mixture reached pH9. Water (700ml) was added and the lower, organic layer was separated and then extracted with sodium bicarbonate solution (400ml). The combined aqueous extracts were carefully acidified to pH1 with conc.hydrochloric acid, and then extracted with chloroform (4 x 800ml). The combined extracts were dried and evaporated to leave a yellow oil. Distillation gave the acid (10g, 86%) as a colourless oil, b.p. 80-90°C at 1mm Hg; ν_{max} (film) 3500-2500, 1710, 1640 cm^{-1}; δ_H 6.1-5.6 (m, :CH), 5.1-4.9(m, :CH_2), 2.34(t, J10, CH_2), 2.96(d, J9, CH_2), 1.68(t, J10, CH_2), 0.90(Me_2); δ_C 180.8, 134.9(d), 117.2(t), 46.3(t), 36.3(t), 32.8(s), 29.7(t), 26.5(q), p.p.m.; (m/z 156.1160; $C_9H_{16}O_2$ requires M 156.1150). The S-benzylisothiouronium salt derivative recrystallised from water and showed m.p. 140-141°C (Found: C,62.9, H,8.3, N,8.7%; $C_{17}H_{26}N_2O_2S$ requires: C,63.3, H,8.1, N,8.7%).

Methyl 8,8-Dimethyl-5-oxo-2-methoxycarboxylundec-10-enoate(30). - A solution of 6,6-dimethyl-1,8-nonadien-2-one (2g) and dimethyl malonate (1.8g) in dry ether (50ml) was added to a stirred suspension of potassium t-butoxide (0.2g) in dry ether (100ml). The mixture was stirred for 16h, and then hydrochloric acid (20ml, 2M) was added. The ether layer was separated, dried and evaporated to leave the diester (3.5g, 97%) as a pale yellow oil, ν_{max} (film) 1730, 1640 cm^{-1}; δ_H 6.1-5.6(m, :CH), 5.1-4.8(m, :CH_2), 3.67(2 x CO_2Me), 3.0(t, J5, CH), 2.6-2.1(3 x CH_2), 1.92(d, J8, CH_2), 1.6-1.4(m, CH_2), 1.85(Me_2); (m/z 298.1790; $C_{16}H_{26}O_5$ requires M 298.1780).

Methyl 8,8-Dimethyl-5-oxoundec-10-enoate(17). - (a) A mixture of methyl 8,8-dimethyl-5-oxo-2-methoxycarbonylundec-10-enoate (4g), sodium chloride (0.8g) and water (1ml) in dimethyl sulphoxide (50ml) was heated at 150°C for 10h. The dark brown solution was cooled, then diluted with water (200ml) and extracted with ether (5x150ml). The combined extracts were dried and evaporated to give a dark brown oil which was purified by chromatography (Silica gel G, ether-hexane, 1:1 as eluant) to give the keto-ester (2.8g, 87%) as a colourless oil, ν_{max} (film) 1740, 1640 cm^{-1}; δ_H 6.1-5.6 (m, :CH), 5.1-4.8(m, :CH_2), 3.68(MeO_2C), 2.6-2.2(m, 3 x CH_2), 1.98(d, J8, CH_2), 1.6-1.3(m, 2 x CH_2), 0.86(Me_2); δ_C 209.8, 173.3, 135.2(d), 117.1(t), 51.3(q), 46.4(t), 41.5(t), 37.9(t), 33.0(t), 32.7, 26.7(q), 19.1(t) p.p.m.; (m/z 240.1737; $C_{14}H_{24}O_3$ requires M 240.1744).

(b) 1-Bromo-3,3-dimethyl-5-hexene (12.3g) in dry tetrahydrofuran (60ml) was added dropwise to magnesium turnings (2g) which were just covered with tetrahydrofuran and activated by a crystal of iodine. The Grignard solution was heated under reflux for 0.5h, then filtered and added dropwise to a stirred solution of glutaric anhydride (7.4g) in dry tetrahydrofuran (300ml) at -30°C over 2.5h. The mixture was allowed to warm to room temperature, where it was stirred for 1h. before being treated with dilute hydrochloric acid (2M, 70ml). The tetrahydrofuran was evaporated at reduced pressure, and the aqueous solution was then extracted with ether (4 x 100ml). The combined, dried extracts were evaporated to give a yellow coloured oil (10g). A solution of the crude carboxylic acid (10g) in methanol (250ml) and conc. hydrochloric acid (1 drop) was heated under reflux for 12h. The methanol was evaporated at reduced pressure, and the residue was then taken up in ether (70ml). After the ether solution had been washed with brine and dried, it was evaporated to yield the crude keto ester (9.1g, 86%). Careful chromatography (30% silver nitrate on Silica gel G, ether-hexane, 1:5 as eluant) gave the impurity (35b)(R_f 0.6); ν_{max} (film) 1740, 1715 cm^{-1}; δ_H3.68(MeO_2C), 2.6-2.2(m, 3 x CH_2), 2.2-1.1(m, 9H), 1.1-0.9(m, Me_2), and then the keto ester which showed identical spectroscopic properties to those of the same compound prepared as under (a).

3,3-Dimethyl-1-methoxyhexa-1-5-diene(31). - A solution of methoxymethyldiphenylphosphine oxide[29] (26.2g) in tetrahydrofuran (260ml) was added dropwise over 0.5h to a solution of lithium diisopropylamine (12.2g) in tetrahydrofuran (100ml) at 0°C under a nitrogen atmosphere. The cherry-red solution was stirred at 0°C for 0.5h and then a solution of 2,2-dimethyl-4-pentenal (11.8g) in tetrahydrofuran (75ml) was added dropwise over 0.5h. The reaction was stirred for 1h and then heated under reflux for 5h. The light-orange suspension was cooled, then water (10ml) was added and the resulting precipitate was filtered off. The precipitate was washed with petrol (b.p. 40-60°C), and the combined washings were then dried and evaporated at atmospheric pressure to a volume of 75ml. The remaining yellow oil was fractionated at 160mm Hg to give the diene (9.6g, 65%) as a colourless liquid b.p. 86-90°C at 160mm Hg; ν_{max} (film) 1640 cm^{-1}; δ_H 6.27(d, J14, :HCO, cis-isomer), 6.1-5.6(m, 2 x :CH), 5.73(d, J7, :HCO, trans-isomer), 5.1-4.8(m, 2 x CH_2), 4.81(d, J14, :HC, cis-isomer), 4.18(d, J7, :HC, trans-isomer), 3.55 and 3.51(OMe, cis- and trans-isomers), 2.13 and 2.06(d, J9, CH_2, cis- and trans-isomers), 1.01 and 1.10(Me_2, cis- and trans-isomers); 1.01 and 1.10 (Me_2, cis- and trans-isomers); (m/z 140.1205; $C_9H_{16}O$ requires M 140.1201).

3,3-Dimethylhex-5-en-1-al(32). - Sulphuric acid (65ml, 30%) was added to a stirred solution of 3,3-dimethyl-1-methoxyhexa-1,5-diene (21.6g) in tetrahydrofuran (200ml). After the mixture had been stirred for 1h, it was brought to pH9 using saturated sodium bicarbonate solution, and then extracted with ether (6 x 350ml). The combined extracts were washed with brine, then dried and filtered. A small portion was evaporated to yield the aldehyde as a foul smelling, colourless oil; δ_H 9.5(t, J4, HCO), 5.9-5.5(m,:CH), 5.0-4.8(m, :CH_2), 2.18(d, J4, CH_2), 2.06(d, J9, CH_2), 0.98(Me_2). The dinitrophenylhydrazone derivative crystallised from ethanol and showed m.p. 96-97°C, (Found: C,54.95; H,6.05; N,18.7%; $C_{14}H_{18}N_4O_4$ requires: C,54.9; H,5.9; N,18.3%).

1-Bromo-3,3-dimethyl-5-hexene(33). - Lithium aluminium hydride (15g) was added portionwise to a stirred solution of crude 3,3-dimethylhex-5-en-1-al in ether (from above). The grey coloured suspension was stirred for 4h. at room temperature and then water was cautiously added to give a white, granular precipitate. The ether solution was decanted, and the precipitate was then washed with ether (2 x 500ml). Evaporation of the combined, dried ether extracts and distillation of the residue gave 3,3-dimethylhex-5-en-1-ol (21g, 91%) as a colourless liquid b.p. 60-61°C at 4mm Hg; ν_{max} (film) 3350, 1640 cm^{-1}; δ_H 6.1-5.6(m, :CH), 5.1-4.9(m, :CH_2), 3.70(t, J12, CH_2O), 2.1-2.3(OH), 1.98(d, J9, CH_2), 1.51(t, J12, CH_2), 0.92(Me_2); (m/z 128.1205; $C_8H_{16}O$ requires M 128.1201).

N-Bromosuccinimide (26.9g) was added portionwise to a stirred solution of 3,3-dimethylhex-5-en-1-ol (19.3g) and triphenylphosphine (40g) in benzene (300ml). The mixture was stirred for 4h and then the benzene was evaporated at reduced pressure. The resulting succinimide was washed repeatedly with hexane, and the combined, dried washings were then evaporated to give the crude bromide as a brown oil. Distillation gave the bromide (1.5g, 54%) as a colourless oil, b.p. 83-85°C at 24mm Hg; ν_{max} (film) 1640 cm^{-1}; δ_H 6.1-5.6 (m, :CH), 5.2-4.9(m, :CH_2), 3.42(t, J10, CH_2Br), 1.98(d, J8, CH_2), 1.84(t, J10, CH_2), 0.92(Me_2); (m/z 190.0366; $C_8H_{15}Br$ requires M 190.0357).

2-(2,2-Dimethyl-4-pentenyl)-cyclohexane-1,3-dione(16). - Methyl 8,8-dimethyl- 5-oxo-10-undecenoate (0.2g) in dry ether (1ml) was added to a stirred suspension of potassium t-butoxide (0.2g) in dry ether (8ml) at 0°C under a nitrogen atmosphere. The yellow suspension was stirred at 0°C for 0.5h, and then ice cold water (6ml) was added. The ether layer was separated, and the basic aqueous layer was then washed with ether (10ml). The aqueous layer was acidified to pH1 with conc.hydrochloric acid and then extracted with chloroform (4x15ml). The combined extracts were dried and evaporated to give the dione (0.17g, 98%) as a white solid m.p. 102-104°C; ν_{max} ($CHCl_3$) 3500-3100, 1695, 1660-1600 cm^{-1}; δ_H 9.5-9.2(OH), 6.1-5.7(m, :CH), 5.2-4.8(m, :CH_2), 2.8-2.4(m, 2 x CH_2), 2.4-2.3(m, CH_2), 2.1-1.8(m, 2 x CH_2), 0.86(Me_2); δ_C 188.8, 136.5(d), 116.2(t), 114.2(s), 47.3(t), 35.7, 33.2, 33.0(t), 26.9(t), 26.6(q), 20.6(t) p.p.m; (Found: C,74.9%, H,10.0%; m/z 208.1451; $C_{13}H_{26}O_3$ requires: C,75.0%; H,9.7; M 208.1463).

2-(2,2-Dimethylpent-4-enyl)-3-t-butyldimethylsilyloxycyclohex-2-en-1-one(36). - Dry triethylamine (3.4ml) was added dropwise to a stirred solution of 2-(2,2-dimethylpent-4-enyl)cyclohexane-1,3-dione (2.1g) and t-butyldimethylsilyl chloride (3.7g) in dry benzene (100ml) under nitrogen. The mixture was heated at 60°C for 16h, then cooled and quickly filtered. The precipitate was washed with dry hexane (3 x 40ml), and then the combined filtrate and washings were evaporated at 12mmHg. The cream coloured residue was taken up in dry hexane (200ml), filtered and re-evaporated to give the siloxy ether (3.2g, 99%) as a red-coloured, moisture sensitive oil, ν_{max} (film) 1720-1630 br.cm^{-1}; δ_H 6.1-5.7(m, :CH), 5.1-4.9(m, :CH_2), 2.5-2.2(m, 3 x CH_2), 2.1-1.8 (m, :CH_2), 0.90(Me_3), 0.85(Me_2), 0.1(Me_2); (m/z 322.2321: $C_{19}H_{34}O_2Si$ requires: M 322.2328), which was used without further purification.

8,8-Dimethyl-6-t-butyldimethylsilyloxytricyclo[6.3.0.$0^{1,6}$]undecan-2-one(37). - A solution of 2-(2,2-dimethylpent-4-enyl)-3-t-butyldimethylsilyloxycyclohex-2-en-1-one (0.5g) in dry degassed, heptane (20ml) was irradiated in a sealed Pyrex tube using a 450W medium presssure Hg lamp. The progress of the reaction was monitored by g.l.c. (10% SE-30, 225°C) and was stopped when chromatography indicated that all the starting material had been consumed (ca. 7h). The crude mixture was filtered, and then evaporated. Chromatography (Silica gel G, ether-hexane, 1:9 as eluant) gave the tricyclic siloxy ketone (0.4g, 81%) as a light yellow oil, ν_{max} (film) 1695 cm^{-1}; δ_H 2.5-1.2(m, 13H), 1.11(Me), 0.81(Me), 0.80(Me_3C), 0.00(MeSi), -0.05(Me_3Si); δ_C 212.2, 74.8, 69.2, 49.7(t), 43.5(t), 43.3(t), 40.4(t), 37.8(t), 37.4(t), 37.4(d), 30.7(q), 30.4(q), 25.6(q), 18.5(t), 17.9(s), -2.8(q), p.p.m; (m/z 322.2323; $C_{19}H_{34}O_2Si$ requires: M 322.2328).

2,8,8-Trimethyl-6-butyldimethylsiloxytricyclo[6.3.0.$0^{1,6}$]undecan-2-ol(38). - Methyl lithium (6.4ml, 1.4M in ether) was added to a stirred suspension of copper iodide (0.6g) in dry ether (30ml) at 0°C under nitrogen, and the mixture was then stirred until it became homogeneous (ca. 0.5h). The light tan solution was cooled to -69°C and 8,8-dimethyltricyclo[6.3.0.0^{1,6}]undecan -2-one (310mg) in dry ether (10ml) was then added dropwise over 10min. The solution was stirred at -68°C for 1h. then poured into saturated ammonium chloride solution (30ml) and the ether layer decanted. The aqueous layer was extracted with ether (3 x 30ml), and the combined extracts were dried and evaporated. Chromatography of the residue (Silica gel G, ether-hexane, 1:4 as eluant) gave the alcohol (0.27g, 82%) as a white solid, m.p. 70-71°C (ether-hexane), ν_{max} ($CHCl_3$) 3600, 1460 cm^{-1}; δ_H 2.4-1.4(m, 14H), 1.28(Me), 1.20(Me), 1.18(Me), 0.9(Me_3), 0.11(MeSi), δ_C 73.5, 72.5, 66.9, 57.5(t), 43.6(t), 41.1, 41.0(t), 40.0(t), 39.6(t), 37.5(d), 33.8(q), 33.3(q), 26.6(q), 25.7(q), 19.6(t), 17.9, - 3.0 p.p.m; (Found: C,71.1; H,10.9%, m/z 338.2654; $C_{20}H_{38}O_2Si$ requires: C,70.9; H,11.3%, M 338.2641).

2,10,10-Trimethylbicyclo[6.3.0]undec -2-en-6-one(8). - Hydrofluoric acid (20ml, 40% in water) was added in one portion to a stirred solution of 2,8,8-trimethyl-6-t-butyldimethylsilyloxytricyclo [6.3.0.0.^{1,6}]undecan-2-ol (500mg) in tetrahydrofuran (25ml). The mixture was stirred at room temperature for 3h, then neutralised with sodium hydroxide (approx. 300ml, 2M) and extracted with ether (3 x 200ml). The combined extracts were washed sequentially with sodium hydroxide (100ml, 2M) and brine (100ml), then dried and evaporated. Chromatography of the residue (Silica gel G, ether-hexane 1:10 as eluant) gave the ketone (0.23g, 73%) as white needles m.p. 40-41°C (hexane), ν_{max} ($CHCl_3$) 1700 cm^{-1}; δ_H 1.7 (:CMe), 3.0-1.0(m, 13H), 1.12(Me), 0.86(Me); δ_C 214.3, 139.5, 126.1, 55.6(t), 48.8(dd), 45.1(t), 39.4(t), 37.6(s), 57.4(d), 32.6(t), 29.1(q), 27.7(q), 21.3(t), 19.4(q), p.p.m; (m/z 206.1675; $C_{14}H_{22}O$ requires: M 206.1671).

2,10,10-Trimethyl-6-methylenebicyclo[6.3.0]undec-1-ene(40). - A solution of methylenetriphenylphosphoranylide[prepared from methyltriphenylphosphonium iodide (4.8g) and n-butyl lithium (7.8ml, 1.54M) in dry ether (80ml)] was added dropwise to a stirred solution of 2,10,10-trimethylbicyclo[6.3.0]undec-1-en-6-one (400mg) in dry ether (15ml) until the ylide colour persisted (approx. 13 ml). After the solution had been stirred for 15min. water (40μl) was added to give a cream coloured suspension which was stirred for 30min. The mixture was treated with further portions (approx. 13ml) of the ylide solution and the water (approx. 40μl), sequentially through a total of four cycles, then stirred at 25°C for 16h. The mixture was poured onto water (100ml) and then extracted with pentane (4 x 70ml). The combined extracts were washed with brine (80ml) then dried and evaporated. Chromatography of the residue (Silica gel G, pentane as eluant) gave the diene (0.33g, 82%) as a colourless oil; ν_{max} (film) 1670, 1640 cm^{-1}; δ_H 4.9-4.8(m, :C$\underline{H}$H), 4.8-4.7(m, :CH$\underline{H}$), 1.63(:Me), 2.8-1.1(m, 13H), 1.10(Me), 0.84(Me); δ_C 150.7, 139.8, 125.4, 111.6(t), 49.4(t), 49.3(t), 45.1(t), 41.7(d), 37.4, 32.2(t), 31.5(t), 29.2(q), 27.7(q), 27.3(t), 28.7(q), 27.3(t), 19.8(q) p.p.m; (m/z 204.1885; $C_{15}H_{24}$ requires: M 204.1878).

2,6,10,10-Tetramethylbicyclo[6.3.0]undeca-1,5-diene(7). - A solution of 2,10,10-trimethyl-6-methylenebicyclo[6.3.0]undec-1-ene (293mg) in ethanol (40ml) was heated under reflux in the presence of rhodium chloride trihydrate

(320mg) for 1h, then cooled and poured into aqueous potassium cyanide (300ml, 5%). The solution was stirred at 25°C for 30min., and then extracted with pentane (5 x 120ml). The combined extracts were washed with brine (180ml), then dried and evaporated. Chromatography of the residue (Silica gel G, pentane as eluant) gave the isomerized diene (0.15g, 51%) as a colourless oil, ν_{max} (film) 1450, 1370 cm^{-1}; δ_H 5.4-5.2(m, :CH), 1.72(:CMe), 1.59(:CMe), 3.3-1.1(m, 11H), 1.05(Me), 0.92(Me); δ_C 138.4, 134.9, 125.6, 123.2(d), 50.0(t), 47.0(t), 41.6(d), 38.0(dd), 36.4, 34.0(t), 29.3(q), 28.1(q), 27.2(q), 26.7(q), 26.7(t), 20.3(q), p.p.m; (m/z 204.1862; $C_{15}H_{24}$ requires: M 204.1878).

(±)-iso-Pentalenene(43). - Boron trifluoride etherate (0.25ml) was added to a stirred solution of 2,10,10-trimethyl-6-methylenebicyclo[6.3.0]undec-1-ene (0.1g) in dry dichloromethane (15ml) at 25°C, and the resulting red solution was stirred at 25°C for 1h. Saturated sodium bicarbonate solution (30ml) was added to the mixture which was then extracted with dichloromethane (3 x 15ml). The combined organic extracts were washed with brine, and then dried (Na_2SO_4) and evaporated *in vacuo*. Chromatography of the residue on silica impregnated with 20% silver nitrate using ether as eluant gave the hydrocarbon (77mg, 77%) as a colourless oil, δ_H 0.97(Me), 0.99(Me), 1.01(Me), 1.05-1.52(m, 6H), 1.56(:CMe), 1.6-1.9(m, 4H),2.62(t, J 2, 1H), 5.18(br,:CH); δ_C 143.4, 128.3, 62.4, 58.6, 58.5, 50.4, 48.9, 45.4, 40.9, 39.5, 30.0, 29.1, 23.9, 23.5, and 13.3 p.p.m.; (m/z 204.1864; $C_{15}H_{24}$ requires: M 204.1878).

(±) Pentalenene(1). - A solution of 2,6,10,10-tetramethylbicyclo[6.3.0] undec-1,5-diene(0.14g) in dichloromethane (20ml) was treated with boron trifluoride etherate in an identical manner to that described for the isomeric undec-1-ene(40). Chromatography on silica impregnated with 20% silver nitrate, using ether as eluant, gave the hydrocarbon (55mg, 38%) (eluted first) as an oil, δ_H 0.9(d, J7, CHMe), 0.98(CMe_2), 1.2-1.5(m, 5H), 1.61(:CMe), 1.6-1.9(m, 4H), 2.54(d, J9, 1H), 2.66(br, 1H), 5.2(:CH); δ_C 140.6, 129.6, 64.9, 62.2, 59.5, 49.0, 47.0, 44.7, 40.6, 33.7, 30.1, 29.2, 27.7, 17.0 and 15.5 p.p.m.; (m/z 204.1875; $C_{15}H_{24}$ requires: M 204.1878), and the *iso*-pentalenene(43) (25-35%)(eluted second) which showed identical spectroscopic properties to those described above.The synthetic pentalenene showed p.m.r. and c.m.r. data which were superimposable on those of naturally derived pentalenene.

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