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SYNTHESIS OF FUNCTIONALISED CYCLOPENTANES BY INTRAMOLECULAR RADICAL-MEDIATED CYCLISATIONS OF TERMINAL ALLENIC KETONES

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Abstract - Electrolysis of a series of terminal allenic ketones e.g. (7), (10), (17) and (21) is shown to result in intramolecular reductive cyclisation, through the exo-mode, producing five-membered rings, viz (8), (9), (20) and (22) respectively, incorporating a bridgehead hydroxyl group. The unsaturated alcohols (8), (20) and (22), are also obtained when the allenic ketones (7), (17) and (21) are treated with sodium naphthalenide. By contrast treatment of (10) in the sodium naphthalenide gives a low yield (ca 7%) of the isomeric indenol (11) by cyclisation through the endo-mode.
Reductive cyclisations of the terminal acetylenic ketones (14) and (30) produce the corresponding unsaturated alcohols (26) and (31) respectively. Treatment of the alcohols (26) and (31) with catalytic selenium dioxide then provides the enediols (27) and (32) respectively, which make up the B/C ring systems of the novel marine natural products capnellenediol (1) and isoamijiol (2).

The construction of ring systems is a fundamental process in synthesis, and an enormous array of procedures involving carbon-to-carbon and carbon-to-heteroatom bond formation by the coupling of nucleophilic and electrophilic centres, and by pericyclic processes have been developed for this purpose. By contrast, the corresponding use of free radical intermediates in the synthesis of ring systems, has until recently been limited to studies of a more mechanistic bias.[1,2]

These mechanistic investigations have however served to illustrate the potential for free radicals in synthesis, and in particular the wide potential for intramolecular radical-mediated reactions in both the regio-and stereoselective synthesis of all types of ring systems.[3] This feature is perhaps nowhere better illustrated than in the area of reductive cyclisations.[4,5,6]

In connection with our investigations of the total synthesis of the marine terpenoids capnellenediol (1)[7], and isoamijiol (2)[8] we required a method for the annulation of a carbocyclic ring with concomitant introduction of unsaturation and a bridgehead hydroxyl group in the fused ring system. We were attracted to the possibility of achieving this aim by intramolecular radical coupling of the corresponding terminal allenic ketones viz (3)→(4).[9] Although an analogy was drawn with the previously reported radical coupling of terminal acetylenic ketones,[5a,10] to our knowledge the intramolecular radical coupling of terminal allenic ketones hitherto has not been described. Indeed, with a few exceptions,[11-14] little is known concerning the role of the allene function as an electron acceptor in radical cyclisation reactions.

We began our investigation of the reductive cyclisation of terminal allene ketones using the δ-allenic ketone (7), which was prepared by alkylation of the anion derived from isobutyl-cyclopentyl imine (5) with 1-bromobuta-2,3-diene (6),[15] followed by mild hydrolisis. Cyclic

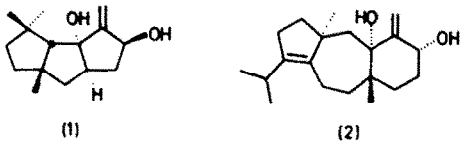
voltammetry studies showed that the reduction of (7) occurs at -2.45 to -2.49V (versus Ag/AgI), and that optimum conditions are achieved with a mercury cathode using solutions in dry dimethylformamide and tetraethylammonium *p*-toluenesulphonate as co-electrolyte. Under these conditions, electrolysis of (7) resulted in smooth reductive cyclisation to the cyclopentenol (8) in 41% isolated yield. Radical addition to the allene system in (7) had therefore occurred in a regioselective manner to give (8) via a 5-exo-dig process. The kinetic preference for radical trapping to occur with 1,5-cyclisation in an exo-manner is well known from studies of δ-alkenyl radicals.[16] The origins of the selectivity have been attributed to either steric,[17] stereoelectronic[18] or entropic[19] effects, although it is likely that all three effects play a contributing role. The same selective mode of cyclisation of (7) was observed when the allene ketone was treated with sodium naphthalene radical anion in tetrahydrofuran, and (8) was the sole product. The product yield, however, was reduced substantially (30%) with the recovery of starting material due to enolate formation with sodium naphthalenide, during the reaction. It is interesting to note that attempts to synthesise cyclic tertiary alcohols, such as (8), via intramolecular radical additions in the reverse mode, that is, addition to ketones by means of organometallic reagents have proved difficult.[20]

With the establishment that allenes can participate as electron acceptors in radical mediated cyclisation reactions, it was of interest to determine the role that the size of ring already present in the starting allene ketone, had on the course of the cyclisation. Accordingly, the six-ring allene ketone (10) was prepared in a similar manner to that described for (7). Electroreduction of the ketone (10) under the same conditions as employed for the cyclopentanone (7) again produced a bicyclic allylic alcohol viz (9) by way of a selective 5-exo-dig cyclisation. To our surprise however, when the allene ketone (10) was treated with sodium naphthalenide, the only product isolated, albeit in only 7% yield, was the isomeric indenol (11) ostensibly produced by a thermodynamically preferred 5-endo-dig process. Separate studies established that the endo-(9) and exo-indenols (11) do not undergo isomerisation under the radical forming conditions.

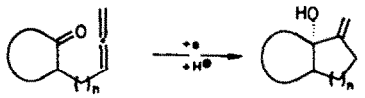
A possible explanation for the formation of (11) may rest in the greater potential of sodium naphthalene radical anion (-3.09V versus Ag/AgI)[21] as compared with the electrode potential of -2.43V employed in the electrochemical generation of the ketyl-radical (12) from (10). This might serve to provide a ketyl radical of higher energy, capable of surmounting thermodynamic activation energy barriers.

Combined with the closer proximity of the reacting centres in (10) compared to (7), this allows for the opportunity of radical addition via either the kinetically preferred pathway and exo-closure, or via the thermodynamically preferred endo-mode and formation of the indenol (11). In the cyclohexanone system (10), the sp^2 hybridised ketyl carbon, and the central sp-hybridised carbon of the allene system are sufficiently close in the transition state to allow at least some degree of orbital overlap between the SOMO of the ketyl radical and both of the LUMO's of the allene residue (Scheme 1). This orbital overlap together with the higher energy of the ketyl radical when produced chemically, enables radical addition onto the allene system to proceed via the thermodynamically preferred pathway to give the more stable secondary radical (13), and hence ring closure via an endo-mode. The lower energy of the electrochemically produced ketyl radical limits the addition to the kinetic pathway, and hence exo-ring closure. For the corresponding cyclopentanone allene system (7) orbital overlap is only viable with one LUMO system of the allene residue (Scheme 1) and this confines radical addition to the exo-ring closure mode, via both electrochemical and chemical methods.

The size of the cycloalkanone ring used in the reductive cyclisations of terminal allene substituted ring ketones is therefore of significance, since it affects the nature of the orbital overlap between the reacting centres. Of equal importance is the role played by the length of the allene side-chain; that is, the number of intervening carbon atoms between the two reaching



(1) (2)



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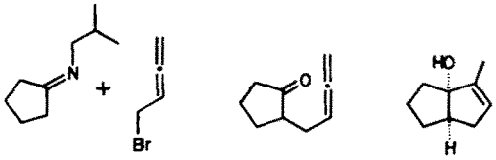
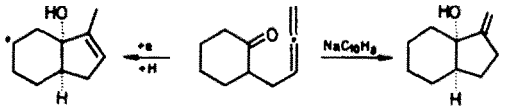
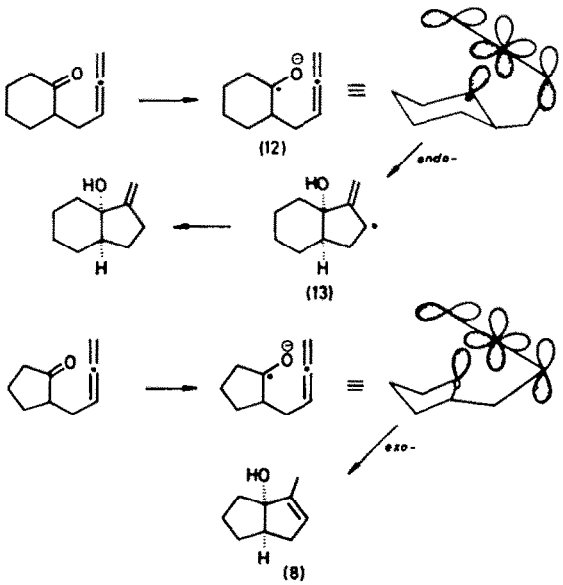


(5) (6) (7) (8)



(9) (10) (11)



(12) (13) (8)

Scheme 1

centres in the cyclisation. We have investigated this effect using the allene ketone (17) which was produced from the known acetylenic ketone (14),[10b] following reduction to the carbinol (15), chain extension to (16),[22] and oxidation of (16) using barium manganate.[23]

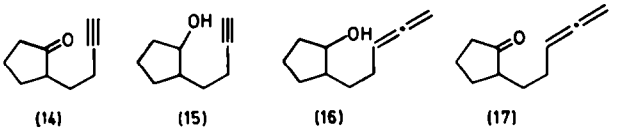
Radical mediated cyclisation of the allene ketone (17) was found to be completely regio- and stereoselective, and using either electrochemical or chemical radical generation conditions, proceeded via and exo-trig cyclisation to give the pentalenol (20). The stereochemistry at the ring juncture in (20) was assigned as cis-, since the corresponding trans-bicyclo[3.3.0] octane is highly strained, and the trans-relationship between the vinyl group and the bridgehead hydroxyl group in the bicycle followed from inspection and comparison of n.m.r. shift data with those of related systems.[24]

The origin of the selectivity observed in the cyclisation of (17) can perhaps be rationalised in terms of the mechanism outlined in Scheme 2. The radical addition of the initially generated oxy-anion radical (18) to the inner terminus of the allene system generates the vinyl radical intermediate (19). In this intermediate at least some negative charge resides in both the oxygen atom, and the recipient radical bearing carbon atom. The respective electron densities therefore repel each other, and the moieties adopt orientations of maximum distance, so leading to the formation of the trans-homoallylic alcohol (20). The result is in agreement with the findings of Shono et al,[25] in their comparative studies of the radical cyclisations of δ-olefinic ketones, where a similar pattern of selectivity was observed.

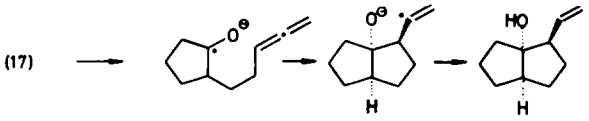
The observations made with the cyclic ketone (17) were reinforced when we examined the reductive cyclisation of the acyclic allene ketone (21). Thus, controlled potentional electrolysis of (21) again promoted a 5-exo-trig cyclisation leading to the selective formation of the cyclopentanol (22) in 55% yield. These last two examples of the cyclisation of allenic ketones viz (17)-(20) and (21)-(22) serve to illustrate some of the salient features of radical reactions, namely (i) that carbon-to-carbon bond formation can, and does occur in a predictable regio- and stero-chemically defined manner, and (ii) that this can be accomplished without the net loss of functionality. These situations are not always achieved with a number of conventional ionic ring-forming reactions.

The present studies thus established that the intramolecular reductive cyclisation of terminal allenic ketones provides an expeditious synthesis of fused-ring cyclopentanes with simultaneous incorporation of a bridgehead hydroxyl group. Our original aim of using this strategy to synthesise the ene-diol units making up the B/C ring portions of the natural products capnellenediol (1) and isoamijiol (2) was somewhat thwarted however, since the aforementioned cyclisations led largely to the endo-ene alcohols e.g. (8) and (9) instead of the corresponding exo-isomers viz (4). Although the ene-diol unit in (1) could be elaborated from the corresponding endo-ene alcohol (25) by way of the epoxide derived from the latter, we found it convenient to instead proceed via the exo-ene alcohol (23) produced from intramolecular reductive cyclisation of the acetylenic ketone (24). This chemistry, which has now been published,[26] was first modelled with the 2-methylenebicyclo [3.3.0]octanediol (28).

Thus, intramolecular reductive cyclisation of the acetylenic ketone (14), by cathodic electrolysis or using sodium naphthalenide, led to the corresponding known bicyclooctanol (26) in 52% yield. Allylic oxidation of (26), using catalytic selenium dioxide produced a single crystalline ene-diol which was assigned the 1α,3α-configuration (27) on the basis of the expected delivery of the new functionality to the less hindered convex face of the bicycle (26), and also by comparison of p.m.r. spectral data with those of natural capnellene-8α,10β-diol (1). The secondary alcohol group in (27) could be inverted, most conveniently by conversion to the corresponding mesylate followed by reaction with potassium superoxide. This procedure led to the 1α,3β-diol (28) contaminated by the product (29) resulting from simultaneous S_N2' displacement within (27).

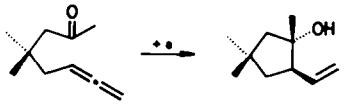


(14) (15) (16) (17)

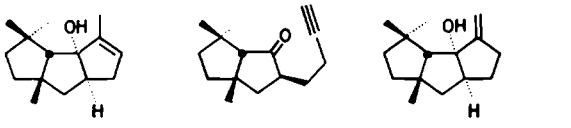


(18) (19) (20)

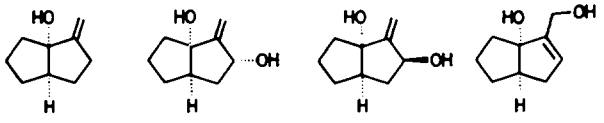
Scheme 2



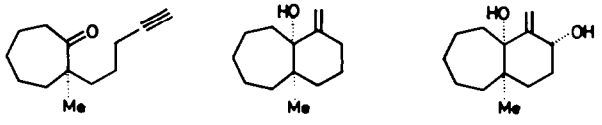
(21) (22)



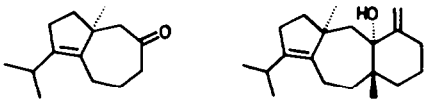
(23) (24) (25)



(26) (27) (28) (29)



(30) (31) (32)



(33) (34)

In a similar manner, reductive cyclisation of the acetylenic ketone (30), derived via alkylation of 2-methylcycloheptanone with 5-iodo-1-pentynyltrimethylsilane, using sodium naphthalenide led to the cis-bicyclic alcohol (31). Treatment of (31) with catalytic selenium dioxide then produced the crystalline 3α,4α,9α-enediol (32), and this model study provided the basis for the completion of our total synthesis of isoamijiol via the bicyclo[5.3.0] decenone intermediate (33), and the tricycle (34).†

EXPERIMENTAL

Proton n.m.r. spectra were recorded on a Perkin-Elmer R32 at 90MHz, or on a Bruker WM 250 PFT for solutions in deuterio-chloroform. Molecular weights were determined from mass spectra measured with a VG MM 7070E or A.E.I. MS-902 instrument.

Analytical t.l.c. plates (Merck Kieselgel $60F_{254}$ on aluminium sheets) were visualised with iodine vapour, 2,4-dinitrophenylhydrazine, basic potassium permanganate or dodecamolybdenum phosphonic acid sprays. All g.l.c. analyses were done on glass columns packed with 10% SE-30 on diatomite.

Organic solvents were distilled before use, and organic solutions were dried over magnesium sulphate.

Electrochemical Reductive Cyclisations : General Procedure

The electrolysis apparatus was a standard H-cell in which the diaphragm was a Nafion cation-exchange membrane, and the cathodic and anodic chambers were 12ml and 5ml respectively. The cell was equipped with a mercury pool cathode (2.2cm diameter), a carbon rod anode (5mm diameter), and a reference electrode comprising a silver wire immersed in a solution of tetra- butylammonium iodide (10g) in dry dimethylformamide (1ml).

The electrolyte, that is, a solution of tetra-ethylammonium tosylate (5g) in dry dimethyl-formamide (DMF) (25ml) was placed in the cathodic and anodic chambers, and the allene ketone was then added to the catholyte. Under the external cooling of a water bath (10°C) the electrolysis was carried out at a cathode potential of -2.43V versus Ag/AgI until g.l.c. analysis (SE30,150-204°C) indicated the consumption of starting material. The catholyte was stirred with a magnetic bar during the electrolysis, and the control reduction potential was maintained with a Hi-tek Instruments DT2101 potentiostat. The catholyte was poured into water (25ml), and the aqueous solution was then saturated with sodium chloride and extracted with ether (3x30ml). Evaporation of the dried extracts gave the crude product which was purified by column chromato-graphy on Silica gel G using ether-hexane (1:2) as eluant.

Reductive Cyclisation Initiated with Sodium Naphthalene Radical Anion : General Procedure

To a solution of dry recrystallised naphthalene (1.92g) in dry tetrahydrofuran (THF) (20ml), stirred under nitrogen at room temperature, was added freshly cut sodium (580mg) in small pieces. The resulting green solution was then stirred at room temperature for 3h. This routinely gave a 0.6M solution of the reagent.

The solution of sodium naphthalenide was added dropwise under nitrogen to a well stirred solution of the allene ketone in dry tetrahydrofuran at room temperature until a faint green end point was reached. The colouration discharged by itself in about 3 min. after turning off the nitrogen. The mixture was poured into water (30ml) and then extracted with ether (3x25ml).

The combined ether extracts were washed with dilute hydrochloric acid (30ml), followed by water until they were neutral. Evaporation of the dried extracts gave the crude product which was purified by column chromatography on Silica gel G using ether hexane (1:1)as eluant.

4-Bromo-1,2-butadiene (6)

Bromo-allene was prepared from the corresponding carbinol (45%), by treatment with phosphorus tribromide, and showed b.p. 58-64°C at 93mmHg (Lit[15] b.p. 64-6°C at 181mmHg); ν_{max} 1945,1205cm^{-1} δ5.51(m,1H,:CH),4.98 (m,2H,:CH_2),3.68(m,2H,CH_2Br)p.p.m.

N-Cyclopentylidene-2-methyl-1-propanamine (5)

A solution of cyclopentanone (10.00g,0.12mol) and sec-butylamine (8.69g,0.12mol) in dry benzene (100ml) was heated under reflux for 10h. The water produced was separated continuously with a Dean and Stark trap. After cooling, the benzene was evaporated at reduced pressure. The residue was distilled to give the imine (13.55g, 81.9%) as a colourless liquid, b.p. 52°C at 3mmHg; ν_{max} 1680cm^{-1} δ_H 3.04(d,J7,CH_2N:),1.95-2.48(2xapp.t,4H,CH_2C:),1.63-1.95(m,5H),0.94(d,J7, 6H,CH_3) p.p.m.

2-(3,4-Butadienyl) cyclopentanone (7)

A solution of n-butyllithium (1.67M) in hexane (39.0ml,65mmol) was added dropwise to a solution of diisopropylamine (9.1ml,65mmol) in dry HMPA (11.3ml) stirred under nitrogen at -20°C. After stirring at -20°C for 30min, a solution of the freshly distilled imine (5) (8.20g,59mmol) in dry THF (25ml) was added dropwise. The mixture was stirred at 20°C for 20 min. before cooling to -65°C. A solution of the bromide (6) (11.50g,86mmol) was then added dropwise over 40min. After stirring at -65°C for 40 min. the mixture was warmed to -50°C, and then acidified with aqueous

† Unpublished work

tartaric acid solution. The mixture was allowed to warm to room temperature over 3h. The aqueous layer was separated and extracted with ether (3x80ml). The combined organic phases were washed successively with aqueous hydrocholoric acid (2M,40ml), saturated sodium bicarbonate solution (40ml) and brine (40ml). Evaporation of the dried extracts left a red liquid (8.15g), which was purified by column chromatography on silica gel G using ether-hexane (1:2) as eluant to give the allene ketone (3.50g,43.6%) as a pale yellow liquid; ν_{max} 1957,1742cm^{-1}, δ_H 5.10(m,1H,:CH), 4.68,(m,2H,:CH_2),3.00-1.00(m,9H)p.p.m.; δ_C 219.7,209.0,87.7(d), 75.2(t),48.7(d), 38.1(t),29.2(t), 28.6 (t), 20.7(t)p.p.m; (Found:m/z 136.0863; $C_9H_{12}O$ requires M 136.0898). The 2,4-dinitrophenylhydrazone derivative crystallised from methanol as irridescent yellow crystals, m.p. 103-3.5°C (Found :C, 56.84%; H,5.19%,N,17.90%. $C_{15}H_{16}N_4O_4$ requires C,56.95%,H,5.10%,N,17.71%).

cis-2,3,6,6a-Tetrahydro-4-methyl-3a(1H)-pentalenol (8)

(a) Electroreduction of the allene ketone (209.6mg,1.5mmol) by the general procedure, followed by chromatography gave the alcohol (86.8mg,40.8%) as a colourless oil; ν_{max} 3340,3030, 1657cm^{-1}; δ_H 5.37(m,1H,:CH),2.87-1.05(m, 9H), 1.94(s,1H,OH),1.72(m,3H,CH_3C:)p.p.m.;δ_C 142.2, 126.7(d),96.1,50.1(d),38.0(t),37.8(t)35.0(t),25.6(t),11.8(q)p.p.m.; (Found:m/z 138.1044,C,77.85%; H 10.57%. $C_9H_{14}O$ requires M 138.1036; C,78.21%; H,10.51%)

(b) Treatment of a solution of the allene ketone(7) (617mg,4.5mmol) in dry THF (23 ml) with a solution of sodium naphthalene radical anion (0.6M in THF,6.4ml) by the general procedure, followed by chromatography, gave the alcohol (113.2mg,27.8%, eluted second) and recovered starting material (215.8mg,35%, eluted first). The carbinol showed identical spectral data with those of an authentic sample prepared using electrochemical reductive cyclisation.

2-(2,3-Butadienyl)cyclohexanone (10)

A solution of n-butyllithium (1.38M) in hexane (31.8ml,44mmol) was added dropwise to a solution of diisopropylamine (6.2ml,44mmol) in dry THF (50ml), containing HMPA(8ml), stirred under nitogen at -30°C. After stirring at -30°C for 30 min., N-cyclohexylidene-2-methyl-1-propanamine (6.75g,44mmol)[27] in dry THF (18ml) was added dropwise, and the mixture was then stirred at -30°C for 1h. before cooling to -65°C. A solution of the bromide (6) (6.70g,50mmol) in dry THF (18ml) was then added dropwise over 45 min. After stirring at -65°C for 1h. the mixture was warmed to -50°C, and then acidified with aqueous tartaric acid solution. The mixture was shaken vigorously and extracted with ether at 10°C. The combined extracts were washed successively with aqueous hydrochloric acid (2M,40ml), saturated sodium bicarbonate solution (40ml), and brine (40ml). Evaporation of the dried extracts left an orange liquid (5.02g), which was distilled to give the allene ketone (2.12g,32.0%) as an almost colourless liquid, b.p. 92-5° at 5mmHg; ν_{max} 1955,1710cm^{-1} δ_H 5.16(m,1H,:CH), 4.64(m,2H,:CH_2), 2.96-1.80 (m,11H)p.p.m.;δ_C 211.9,209.0,88.0(d).74.7(t), 50.4(d), 42.1(t), 33.7(t), 28.4(t),28.0(t), 25.1(t) p.p.m.; (Found:m/z 150.1029; $C_{10}H_{14}O$ requires M 150.1045).

The 2,4-dinitrophenylhydrazone derivative crystallised from methanol as irridescent orange crystals, m.p. 110.5 - 111.5°C (Found: C,58.20%; H,5.55%, N,17.18%. $C_{16}H_{18}N_4O_4$ requires C,58.17%; H,5.49%,N,16.96%).

cis-1,4,5,6,7,7a-Hexahydro 3-methyl-3a(1H)inden-3a-ol (9)

Electroreduction of the allene ketone (10) (302.3mg,2mmol) by the general procedure, followed by chromatography gave the alcohol (132.5mg, 43.2%) as a colourless oil; ν_{max} 3390, 1652cm^{-1}, δ_H 5.49(m,1H,:CH), 2.56-0.96(m.12H),1.71(m,3H,CH_3C:)p.p.m.δ_C 145.5,126.0(t),83.1,46.6(d), 34.8, 33.0(t), 28.6(t),23.1(t),21.7(t),11.7(q)p.p.m.; (Found:m/z 152.1163;C,79.00%, H,10.88%. $C_{10}H_{16}O$ requires M 152.1201; C,78.89%; H,10.59%).

cis-Octahydro-3-methylene-3a-(1H)-inden-3a-ol(11)

Treatment of a solution of the allene ketone (10) (545.0mg,3.6mmol) in dry THF (17ml) with a solution of sodium naphthalene radical anion (0.6M in THF,5.0ml,3mmol) by the general procedure, followed by chromatography gave the alcohol[10b] (22.3mg,7.0%, eluted second) as an almost colourless oil; ν_{max} 3425,1660cm^{-1},δ_H 5.08 and 4.97 (dt,J_{gem} 1l,J_{vic} 2.5,2H,:CH),2.66-2.37(m,2H,CH_2 C:), 2.66-1.03(M,12H)p.p.m.;δ_C 156.5,105.6(t),79.4,46.4(d),33.8(t),28.1(t),27.1(t),25.7(t),23.2(t), 23.1(t)p.p.m.; (Found:m/z 152.1183; $C_{10}H_{16}O$ requires M 152.1201), together with recovered starting material (263.5mg,48.3%, eluted first).

2-(3-Butynyl)cyclopentanone (14)

p-Toluenesulphonylhydrazide (26.00g,0.14mol) was added to a solution of hexahydroindeno [3a,4-b]oxiren-2(1aH)one (20.28g,0.13mol)[28] in glacial acetic acid (220ml) and dichloromethane (440ml) stirred at -17°C under nitrogen. The resultant yellow solution was stirred at -17°C for 1h, then at -1 to -2°C overnight, and finally at room temperature for 2h to give a clear orange solution. Solid sodium carbonate was added to neutralise the acetic acid, and water (250ml) was then added to dissolve any solid present. The aqueous phase was separated and extracted with dichloromethane (3x300ml). The combined organic phases were washed successively with saturated sodium bicarbonate solution (2x300ml) and brine (300ml). Evaporation of the dried extracts gave an orange-red liquid, distillation of which gave the acetylenic ketone (10.54g, 58.1%) as a colourless liquid, b.p. 65°C at 0.7mmHg (Lit.[10b] b.p.71°C/5mmHg); ν_{max} 3290,2120,1730cm^{-1}; δ_H 2.46-1.40(m,11H),1.96(t,J2.6,1H,:CH)p.p.m.;δ_C 220.2,88.7,69.1(d), 48.1(d),38.1(t),29.6(t),28.7(t),20.8(t),16.8(t)p.p.m.; (Found: m/z 136.0870; $C_9H_{12}O$ requires M 136.0898). The 2,4-dinitrophenylhydrazone derivative crystallised from methanol as irridescent orange crystals, m.p. 129-131°C (Found: C,56.76%; H,5.20%,N,17.65%. $C_{15}H_{16}N_5O_4$ requires C,56.95%; H,5.10%; N,17.71%).

cis-2-(3-Butynyl) cyclopentanol (15)

To a solution of L-Selectride (1M) (3 equiv) in THF (29ml) stirred under nitrogen at -78°C was added a solution of the acetylenic ketone (14) (1.32g,10mmol) in dry THF (6ml). After stirring at -78°C for 2h, the mixture was allowed to warm to room temperature where it was stirred for 4h. The excess hydride was destroyed by the addition of wet THF (6ml). Aqueous sodium hydroxide solution (2M,24ml) was added at 0°C, followed by the slow addition of aqueous hydrogen peroxide (30%,48ml) and the mixture was saturated with sodium chloride and the aqueous layer was then separated and extracted with ether (3x50ml). The combined organic phases were washed with aqeous sodium thiosulphate solution (25ml) and brine (25ml). Evaporation of the dried extracts gave an almost colourless liquid (1.41g) which was purified by column chromatography on Silica gel G using ether - light petroleum (b.p. 40-60°C)(1:1) as eluant, to give the acetylenic alcohol (1.20g,83.0%) as a colourless liquid; ν_{max} 3400(br),3305,2130cm^{-1},δ_H4.20 (m,1H,CHOH),2.54(br s,1H,OH), 2.26(d,J6.5,2H,CH_2C:),1.98(t,J3,1H:CH),2.80-1.00(m,9H)p.p.m.; δ_C85.0,74.1(d),68.4(d),45.0(d),34.9(t),28.7(t),28.1(t),21.8(t),17.2(t)p.p.m.;(Found:m/z 138.1046; $C_9H_{14}O$ requires M 138.1048).

cis-2-(3,4-Pentadienyl)cyclopentanol (16)

A solution of paraformaldehyde (1.44g,16mmol) cuprous bromide (1.62g,5.6mmol), diisopropylamine (4.6ml,33mmol), and the alcohol (15) (3.80g,2.8mmol) in dry dioxan (46ml) was stirred under gentle reflux in an atmosphere of nitrogen for 21h. After cooling, the mixture was quenched by the addition of water (50ml). Solid ammonium chloride was added to saturate the solution, and the mixture was then shaken thoroughly and extracted with ether (4x75ml). The combined organic phases were washed successively with saturated silver nitrate solution (30ml), aqueous hydrochloric acid (2M,40ml), saturated sodium bicarbonate solutation (40ml), and brine (40ml). Evaporation of the dried extracts gave an orange liquid, which was purified by column chromatography on Silica gel G using ether hexane (1:2) as eluant, to give the allenic alcohol (1.64g,39.1%) as a pale yellow liquid; ν_{max} 3430,1950cm^{-1},δ_H5.17(m,1H,:CH),4.68(m,2H,:CH_2). 4.17(m,1H,CHOH),2.83(m,1H,OH),3.08-0.78(m,11H)p.p.m.; δ_C208.6,90.2(t),74.7(d),74.5(d), 45.3(d),34.9(t),28.8(t),28.7(t),27.4(t),21.9(t)p.p.m.; (Found:m/z 151.1100(M-1); $C_{10}H_{16}O$ requires M-1 151.1123).

2-(3,4-Pentadienyl)cyclopentanone (17)

A solution of the allenic alcohol (16)$_{23}$(533.6mg,3.5mmol) in dry dichloromethane was stirred with excess barium manganate (9.52g,37mmol) at room temperature for 37h. The excess barium manganate was filtered off under suction, and then washed with dichloromethane (2x75ml). Evaporation of the dichloromethane solution left a pale yellow liquid (345.3mg) which was purified by column chromatography on Silica gel G using ether-hexane (2:1) as eluant to give the allene-ketone (284.3mg,57.0%) as an almost colourless liquid; ν_{max} 1955,1735cm^{-1}; δ_H5.12(m,1H,:CH), 4.68(m,2H:CH_2),2.90-0.90(m,11H)p.p.m. δ_C219.8,208.8,89.5(d),74.9(t),48.4(d),38.0(t),29.7(t), 29.3(t),26.3(t),20.8(t)p.p.m.; (Found :m/z 150.1018; $C_{10}H_{14}O$ requires M 150.1045). The 2,4-dinitrophenylhydrazone derivative crystallised from methanol as a yellow sold, m.p. 75-7°C.

(3α,3aβ,6aβ)-3-Ethenylhexahydro-3a(1H)-pentalenol (20)

(a) Electroreduction of the allene ketone (17) (170.9mg,1.1mmol) by the general procedure followed by chromatography, gave the alcohol (64.4mg,37.2%) as a colourless oil; ν_{max} 3380, 1640cm^{-1};δ_H5.88 (m,1H,:CH),5.07(m,2H,:CH_2),2.47(m,1H,CHC:),1.72(m,2H,CH_2CC:),2.52-1.02(m,1OH) p.p.m.; δ_C138.2(d),115.5(t),92.8,55.6(d),51.5(d),37.7(t),34.8(t),30.1(t),29.9(t),25.9(t)p.p.m.; (Found:m/z 134.1100 (M-H_2O); $C_{10}H_{16}O$ requires M-H_2O 134.1096).

(b) Treatment of a solution of the allene ketone (17)(218.2mg) in dry THF (8ml) with a solution of sodium naphthalene radical anion (0.6M in THF,1.4ml) by the general procedure, followed by chromatography, gave the alcohol (44.0mg,23.3%, eluted second) as a colourless liquid, and recovered starting material (61.7mg,28.3%, eluted first). The carbinol showed identical spectral data with those of an authentic sample prepared using electrochemical reductive cyclisation.

2-Methyl-2-(2,2-dimethyl-4-pentynyl)-1,3-dioxolane

To a solution of 4,4-dimethyl-6-heptyn-2-one[29] (4.57g,33mmol) in dry benzene (200ml), was added ethylene glycol (4.20ml,75mmol) and pyridinium tosylate (0.96g,3.8mmol). The mixture was stirred under reflux for 3h with continuous removal of water (Dean and Stark trap). After cooling, the solvent was evaporated, and the residue was then taken up in ether (100ml) and washed with saturated sodium bicarbonate solution (75ml), followed by brine (75ml). Evaporation of the dried ether extracts gave the crude dioxolane (4.20g,89.4%) sufficiently pure for further use; ν_{max}3300,2125cm^{-1}; δ_H3.97(s,4H,CH_2O). 2.25(d,J2.5,2H,CH_2C:),1.99(t,J2.5,1H,:CH),1.80(s,2H,CH_2 CO),1.36(s,3H,CH_3CO),1.08(s,6H,CH_3)p.p.m.

2-Methyl-2-(2,2-dimethyl-4,5-hexadienyl)-1,3-dioxolane

A solution of paraformaldehyde (1,23g,14mmol),cuprous bromide (1.21g,4.2mmol), diisopropylamine (4.10ml,29mmol) and 2-methyl-2(2,2-dimethyl-4-pentynyl)-1,3-dioxolane (4.20g,28mmol) in dry dioxan (42ml) was stirred under gentle reflux under nitrogen for 17h. After cooling, the mixture was quenched by the addition of water (50ml). Solid ammonium chloride was added to saturate the solution, and the mixture was then shaken thoroughly and extracted with ether (4x75ml).

The combined ether extracts were washed successively with saturated silver nitrate solution (30ml) aqueous hydrochloric acid (2M,40ml), saturated sodium bicarbonate solution (40ml), and brine (40ml). Evaporation of the dried extracts gave the allene(1.67g,36.9%) as a pale yellow liquid,

which was used without further purification; ν_{max} 1950cm^{-1}; δ_H5.14(m,1H,:CH),4.62(dt,J7 and 2,2H,:CH_2),3.94(s,4H,CH_2O),2.04(dt,J7 and 2,2H,CH_2C:),1.69(s,2H,CH_2 CO),1.34(s,3H,CH_3CO),1.00 (s,6H,CH_3)p.p.m.

4,4-Dimethyl-6,7-octadien-2-one (21)
To a solution of 2-methyl-2(2,2-dimethyl-4,5-hexadienyl)-1,3-dioxolane (2.43g,13mmol) in acetone (90ml) containing 1% water was added, pyridinium tosylate (960mg,3.8mmol) and the mixture was then stirred under reflux for 3h. After cooling, the solvent was evaporated, and the residue was taken up in ether (100ml) and then washed with saturated sodium bicarbonate solution (75ml) followed by brine (75ml). Evaporation of the dried ether phase left an orange liquid (1.69g), which was purified by column chromatography on Silica gel G using ether-hexane (1.2) as eluant to give the allene ketone (6.18.0mg,47.7%) as an almost colourless liquid;ν_{max} 1955,1715cm^{-1};δ_H5.07 (m,1H,:CH),4.63(dt,J6.7 and 2.4,2H,:CH_2),2.36(s,2H,CH_2CO),2.13(s,3H,CH_3CO),2.04(dt,J8 and 2.4,2H,CH_2C:),1.02(s,6H,CH_3)p.p.m.;δ_C210.0,208.0,86.0(d),73.6(t),53.1(t),41.3(t),34.3,32.2(q), 27.0(2xq)p.p.m.;(Found:m/z 152.1203;$C_{10}H_{16}O$ requires M 152.1196). The 2,4-dinitrophenylhydrazone derivative crystallised from methanol as yellow crystals, m.p. 78.9°C (Found:C,57.45%; H,6.04%;N,16.93%. $C_{16}H_{20}N_4O_4$ requires C,57.82%; H,6.07%; N,16.86%).

trans-2-Ethenyl-1,4,4-trimethylcyclopentanol (22)
(a) Electroreduction of the allene ketone(21) (150.4mg,1mmol) by the general procedure followed by chromatography gave the alcohol (83.2mg,54.6%) as a colourless oil; ν_{max} 3370,1640cm^{-1}; δ_H5.84(m,1H,:CH),5.08(m,2H,:CH_2).2.69(m,1H,CHC:)2.20-0.69 (m,5H),1.16(s,3H,CH_3),1.14(s,3H,CH_3COH), 1.06(s,3H,CH_3)p.p.m.; δ_C138.1(d),115.6(t),81.01,56.04(t),55.0(d),45.4(t),37.8,32.1(q),31.6(q), 25.1(q)p.p.m.;(Found:m/z 154.1351;C,78.05%;H,12.17%. $C_{10}H_{18}O$ requires M 154.1357; C,77.86%;H, 11.76%).
(b) Treatment of a solution of the allene ketone (21) (304.2mg) in dry THF (11ml) with a solution of sodium naphthalene radical anion (0.6M in THF,2.8ml) by the general procedure, followed by chromatography, gave the alcohol (97.1mg,55.8%, eluted second), and recovered starting material (132.6mg,22.1%, eluted first). The carbinol showed identical data with those of an authentic sample prepared using electrochemical reductive cyclisation.

cis-Hexahydro-3-methylidene-3a(1H)-pentalenol (26)
Electroreduction of the acetylenic ketone (14) (181.4mg,1.2mmol) by the general procedure gave; after chromatography, the alcohol[10b] (97.3mg,52.8%) as a colourless oil; ν_{max} 3375,1665cm^{-1}; δ_H5.10 (m,1H,:CH_2),4.96(m,1H,:CH_2), 2.92-1.07(m,11H),2.01(s,1H,OH)p.p.m.;δ_C159.1,105.2(t),89.9, 52.2(d),41.0(t),32.6(t),32.4(t),29.5(t),25.7(t),p.p.m.; (Found:m/z 138.0900; C,78.08%;H,10.76%. $C_9H_{14}O$ requires M 138.1043; C,78.21%;H,10.21%).

(2β,3aβ)-Hexahydro-3-methylene-3aH-pentalene-2,3a-diol (27)
A solution t-butyl hydroperoxide (350mg,3.9mmol) in dichloromethane (4ml) was added to a stirred solution of the alcohol (26)(100mg,0.7mmol), seleniumdioxide (20mg,0.2mmol), and salicylic acid (60mg,0.4mmol) in dichloromethane[30] (8ml), and the solution was then stirred at room temperature for 4h. The solution was diluted with benzene (50ml) and then evaporated to a volume of approximately 40ml, before it was washed with aqueous potassium hydroxide solution (2M,30ml). The aqueous wash was back extracted with ether (2x20ml). The combined extracts were dried and evaporated to give a viscous oil which was purified by column chromatography on Silica gel G using acetone-hexane (1:2) as eluant to give the diol (40mg,35.8%) as an amorphous cream-coloured solid, m.p. 60-2°C; ν_{max}($CHCl_3$)3600,3300,1630 (v.weak)cm^{-1};δ_H5.30 and 5.20 (each m,2H,:CH_2),4.52(app.t,1H,CHOH),2.66-2.56(m,2H,OH),2.65-1.14(m,9H)p.p.m.; δ_C160.6,107.4,88.4,75.3(d),49.4(d),41.1(t),39.6(t),33.1(dd),25.7(t)p.p.m.; (Found:m/z 154.0995; C,69.85%;H,9.30%. $C_9H_{14}O_2$ requires M 154.0994;C,70.10%,H,9.15%).

(2α,3aβ)-Hexahydro-3-methylene-3aH-pentalene-2,3a-diol (28) and cis-2,3,6,6a-Tetrahydro-4-(hydroxymethyl)-3a(1H)-pentalenol (29) (S.J. Teague)

A solution of freshly distilled methanesulphonyl chloride (91mg,0.8mmol) in dry dichloromethane (2ml) was added dropwise over 0.5h to a stirred solution of the alcohol (27) (100mg,0.65mmol) and dry triethylamine (150μl,1.1mmol) in dry dichloromethane (20ml) at -25°C under nitrogen. The solution was then stirred for 2h at -20°C, before quenching with iced water (5ml). The mixture was transferred to a cold separating funnel and washed successively with ice-cold aqueous hydrochloric acid (2M,5ml) saturated sodium bicarbonate solution (5ml). The organic phase was separated and dried at 0°C and the solvent carefully evaporated to give the allylic mesylate as a colourless oil which rapidly darkens to a purple slurry above 10°C. The crude mesylate was taken up in an ice-cold mixture of dry dimethylsulphoxide and dimethylformamide (10ml,1:1), and then poured into a stirred solution of potassium superoxide (300mg, 4.2mmol) and 18-crown-6 (200mg,0.8mmol) in ice-cold dimethylsulphoxide (5ml)[31]. The solution was stirred for 2h at 0°C then for 1h at 25°C, before water (20ml) was added and the mixture extracted with chloroform (3x15ml). The combined extracts were stirred with triphenylphosphine (150mg) at room temperature for 1h. Evaporation of the dried extracts left an oil which was chromatographed on Silica gel G using acetone-hexane (1:3) as eluant to give the diols (80mg) consisting of a 1:1 mixture of the alcohols (28) and (29) by n.m.r. analysis;(28)showed; δ_H 5.5 and 5.4(each m,2H, :CH_2),4.8(m,CHOH),2.6-1.2(m,11H); (29) showed: δ_H5.85(m,:CH),4.25(m,CH_2OH), 2.5-1.2(m,11H)p.p.m.

2-Methyl-2-(4-pentynyl)cycloheptanone (30)

A solution of 2-methylcycloheptanone (1.39g,11mmol) in dry DME(8ml) was added to a stirred suspension of oil-free sodium hydride (265mg,11mmol) in dry DME (6ml) and the mixture was then stirred under nitrogen at room temperature for 48h. To the resulting pale yellow slurry of sodium enolate was added dropwise a solution of 5-iodo-1-pentynyltrimethylsilane[32] (2.93g,11mmol) in dry DME (10ml). The pale yellow slurry was allowed to stir and room temperature for 24h and then poured into an ice-cold mixture of aqueous acetic acid (2M,20ml) and ether (30ml). The aqueous phase was separated and extracted with ether (3x10ml). The combined ether extracts were washed successively with aqueous sodium bicarbonate solution (2M,10ml) and water (2x10ml). Evaporation of the dried extracts and bulb-to-bulb distillation of the residue gave acetylenic ketone (1.32g,62.3%) as a colourless liquid, b.p.105°C at 0.5mmHg; ν_{max} 3275,1700cm^{-1}; δ_H 2.96-0.96(m,16H),1.97(t,J3,1H,:CH),1.06(s,3H,CH_3)p.p.m.; δ_C 217.1,83.9,68.7(d),50.6,40.2(t), 38.9(t),37.8(t), 30.7(t),26.6(t),24.5(t),23.3(t),21.6(t).18.9(q)p.p.m.; (Found: m/z 192.1509; C,80.99%;H,10.75%. $C_{13}H_{20}O$ requires M 192.1513;C,81.20%:H,10.48%).

cis-Decahydro-9a-methyl-4-methylene-4aH-benzocyclohepten-4a-ol (31)

Treatment of a solution of the acetylenic ketone (30) (1.05g,5.5mmol) in dry THF (20ml) with a solution of sodium naphthalene radical anion (0.6M in THF,18.0ml,10.8mmol) by the general procedure, followed by column chromatography on Silica gel HF 254 using ether-light petroleum (b.p.40-60°C) (1:4) as eluant gave the alcohol (300.0mg,28.3%, eluted second) as an almost colourless oil; ν_{max} 3455(br),1640cm^{-1}; δ_H 4.84(t,J1.65,1H,:CH_2),4.73(t,J1.3,1H,:CH_2),2.60-2.47 (m,1H, -CH_2C:),2.30-1.42(m,16H),0.85(s,3H,CH_3)p.p.m.;δ_C 153.3,108.4(t),78.1,41.8,37.7(t),37.1(t), 34.3(t),32.3(t)26.6(t),22.9(t),21.7(t),20.5(t),19.0(q)p.p.m.; (Found:m/z 194.1672;$C_{13}H_{22}O$ requires M 194.1669), together with recovered starting material (403.2mg,38.4%, eluted first).

(3β,4aβ,9aβ-)-Decahydro-9a-methyl-4-methylene-4aH benzocycloheptene 3,4a-diol (32)

t-Butyl hydroperoxide (70% solution in water, 25µl) was added to a stirred solution of the alcohol (31) (11.0mg,0.06mmol), selenium dioxide (120µg,1µmol), and salicylic acid (8.3mg,0.06mmol) in dichloromethane (8ml), and the solution was then stirred at room temperature for 8h. The solution was diluted with benzene (20ml) and then evaporated to a volume of approximately 15ml, before it was diluted with ether (10ml) and washed with aqueous potassium hydroxide solution (2M,4x12ml). Evaporation of the dried organic phase left an oily residue which was purified by column chromatography on Silica gel HF 254 using ether-hexane (1:2) to give the diol (4.4mg,37.0%, eluted second) as a white solid. Crystallisation from ether-hexane (1:3) gave white crystals, m.p. 105-6°C; ν_{max} ($CHCl_3$)3350,1630cm^{-1}; δ_H 5.10(d,J0.88,1H,:CH_2),4.97(d,J0,87, 1H.:CH_2),4.33(t,J2.85,1H.CHOH),3.65(m,1H,OH),2.24-1.40(m,14H),0.83(s,3H,CH_3)p.p.m., (Found:m/z 192.1488(M-H_2O);$C_{13}H_{22}O$ requires M-H_2O 192.1514), together with recovered starting material (4.4mg,40%, eluted first).

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