# Synthesis of an Isolable 4a*H*-Benzocycloheptene, Ethyl 4-Methoxy-4a-methyl-4a*H*-benzocycloheptene-5-carboxylate, and a Study of its Thermal Rearrangement [1]

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A synthesis of ethyl 4-methoxy-4a-methyl-4a*H*-benzocycloheptene-5-carboxylate (12), the first isolable 4a*H*-benzocycloheptene, is described. The skeleton is constructed by Cope rearrangement of the divinyl-cyclopropane (8). Further unsaturation is then introduced by the use of dichlorodicyanobenzoquinone to give the tetraenone (10), from which an extended enolate anion is generated by means of sodium hydride in 1,2-dimethoxyethane. *O*-Methylation of the anion gives the ether (12). At 138 °C this compound undergoes unimolecular skeletal rearrangement and gives a mixture of three products. It is proposed that these are formed from a common bis-norcaradiene intermediate (17). A new type of rearrangement, which involves the conversion of the bis-nor-caradiene (17) into a second bis-norcaradiene by a $(_\sigma 2_s + _\pi 4_a + _\pi 4_s)$ process, is suggested to explain the formation of the product (19). The methoxy-ester (12) also undergoes 4 + 2 cycloaddition with 4-phenyl-1,2,4-tri-azolinedione and an acid-catalysed methyl group migration.

4-Methoxy-4a-methyl-4a*H*-benzocycloheptene (28) has been generated by an analogous route; at room temperature this undergoes a skeletal rearrangement, of the same type as observed with the ester (12).

BICYCLIC polyenes in which the peripheral conjugation is interrupted by a tetrahedral carbon centre have been investigated very little and few derivatives of such poly-enes have been isolated. Our interest in this class of compound arose from work on imidoyl nitrenes, in which the 3a*H*-benzimidazoles (1) were considered to be generated as intermediates.[2] The all-carbon analogue of this system is 3a*H*-indene (2). We have investigated routes to derivatives of 3a*H*-indene[3] and to other bicyclic polyenes of this general type, in order to under-stand their chemistry, particularly their rearrangement pathways. This paper concerns derivatives of the next higher member of the group, 4a*H*-benzocycloheptene (3).



(1)   (2)   (3)

a; R = H

b; R = Me
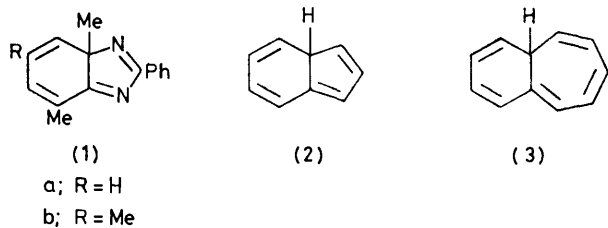
The main objectives of the work were to prepare a simple, isolable derivative of 4a*H*-benzocycloheptene and to study its rearrangement and cycloaddition reactions. In ring systems such as (2) and (3) there is a formal pos-sibility of interaction of the terminal atoms of the con-jugated π-electron systems. In the case of compound (3), this results in its potential classification as a ' homo-aromatic ' system.[4] Homoaromatic stabilisation is, at best, weak in neutral polyenes, and it is very sensitive to the separation of the interacting termini; in the case of 4a*H*-benzocycloheptene it seemed that the separation of the termini of the polyene (as indicated by models) would probably be too great to allow any significant interaction. On the other hand, thermal electrocyclic reactions in-volving the polyene or sigmatropic shifts of substituents

at the tetrahedral centre were feasible and, indeed, had some precedent in earlier work. We also aimed to in-vestigate the possibility of cycloadditions in which the pentaene (3) might act as a 10π-electron unit.

4a*H*-Benzocycloheptenes with a hydrogen atom at the 4a-position have been implicated as transient inter-mediates in several reactions.[5-8] In each case, aromatic 7*H*-benzocycloheptenes were the final products, these presumably being formed by low-energy sigmatropic hydrogen-shifts. In considering possible targets for the synthesis of an isolable 4a*H*-benzocycloheptene it was, therefore, essential to incorporate a substituent at the 4a-position which would be much less susceptible than hydrogen to thermal migration. A methyl group was selected, since there is evidence that methyl groups do not undergo sigmatropic migration readily.[9] None of the reactions in which 4a*H*-benzocycloheptenes have been implicated seemed to be adaptable to the synthesis of a 4a-methyl derivative, and a new route was sought.

*Synthesis of Ethyl 4-Methoxy-4a-methyl-4a*H*-benzo-cycloheptene-5-carboxylate* (12).—Marino and Kaneko have devised a route to dihydroazulenes and other fused seven-membered ring compounds in which the key step is the Cope rearrangement of a suitable divinyl-cyclo-propane derivative.[10] By following a sequence of reac-tions analogous to those used in some of this earlier work we prepared the bicyclic ketone (4), as shown in Scheme 1. The previously unknown oxosulphonium ylide (5) was prepared in moderate yield from 3-chloro-2-methylcyclo-hex-2-en-1-one and dimethyloxosulphonium methylide. With an excess of acrolein the ylide gave the cyclopro-panecarbaldehyde (6) as a 1 : 5 mixture of the *cis*- and *trans*-isomers. The next step, a Wittig reaction, was first performed with a stabilised ylide, triphenylphos-phonium ethoxycarbonylmethylide, since this had been used successfully in earlier work with the dihydro-azulene series.[10] The mixture of *cis*- and *trans*-carb-aldehydes (6) reacted readily with this phosphorane to

give a mixture of the *trans*-divinyl-cyclopropane (7) (86%) and the bicyclic ketone (4) (8%). Evidently the *cis*-divinyl-cyclopropane (8) had cyclised directly to the ketone (4) at room temperature; this was to be expected on the basis of the known propensity of such compounds

(5)   (6)

(7)   +   (8)

(4)
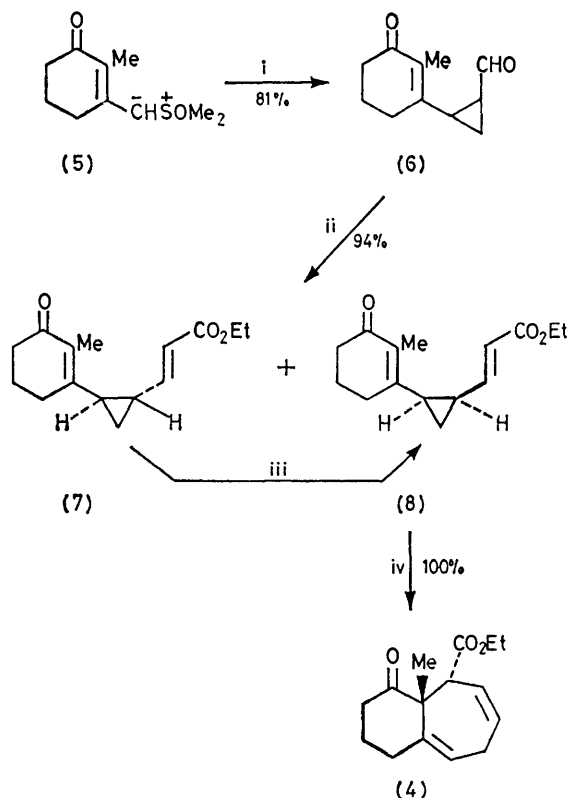
SCHEME 1   *Reagents:* i, CH₂=CHCHO; ii, Ph₃PCHCO₂Et,
   tetrahydrofuran (THF); iii, 140 °C, xylene; iv, 20 °C

for rearrangement. The *trans*-divinyl cyclopropane (7) was cyclised quantitatively to the ketone (4) when heated in xylene and the *cis*-compound (8) was, presumably, an intermediate.

Several attempts were made to remove the ethoxy-carbonyl group from compound (4). The ester was hydrolysed in good yield (87%), but the product showed an absorption in the i.r. spectrum for the carbonyl group at ν 1 745 cm⁻¹, indicating that it exists predominantly as the tricyclic tautomer (9) rather than as the free acid.

(9)
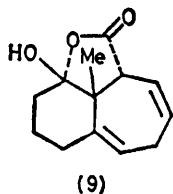
Attempts at oxidative decarboxylation, using lead tetra-acetate, were not encouraging and it was therefore decided to continue the synthesis with the ethoxycar-bonyl group in the system.

The most effective way we found for the introduction of further unsaturation was direct dehydrogenation using dichlorodicyanobenzoquinone (DDQ). When heated with 2.2 mol equiv. of DDQ, the ketone (4) was converted into a mixture of two compounds which were assigned the structures (10) and (11). The n.m.r. spectrum of the major component (10) shows only one methine hydrogen signal as a doublet (J 8.6 Hz) at δ 4.38; this signal was assigned to 9-H. The extended conjugation is indicated by the u.v. spectrum which shows a maximum at λ 400 nm. The trienone-ester (11) is an intermediate in the formation of compound (10); when 1 mol equiv. of DDQ was used for the oxidation, compound (11) was the major product and it was converted into the tetraenone-ester (10) when treated with an excess of DDQ. These transformations are summarised in Scheme 2.

(11)   iv   (10)

(12)
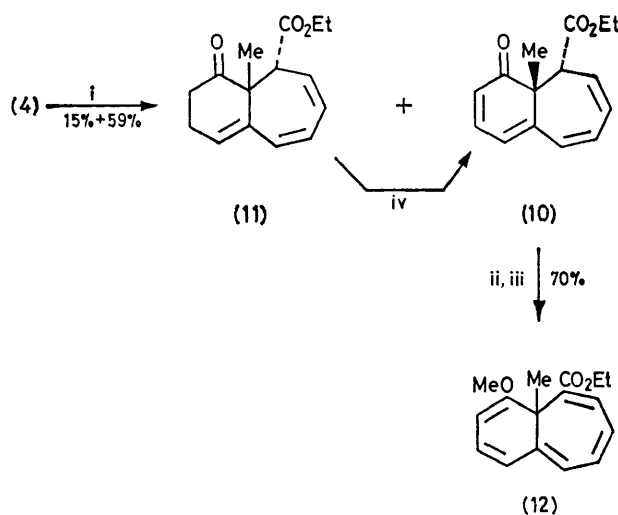
SCHEME 2   *Reagents:* i, DDQ (2.2 mol equiv.), dioxan, acetic
    acid, heat; ii, NaH–MeO[CH₂]₂OMe, −10 °C; iii, MeOSO₂F,
    −10 °C; iv, excess DDQ

Compound (10) is a conjugated keto-ester and, as a consequence, the hydrogen atom at C-5 is quite acidic. A turquoise-coloured anion was generated by reaction of the keto-ester (10) with sodium hydride in 1,2-dimethoxy-ethane (DME) at −10 °C (other bases and other solvents were found to be much less effective in this step; it was also essential to use carefully purified starting materials). The addition of freshly distilled methyl fluorosulphonate resulted in rapid *O*-alkylation of the anion and the clean formation of the 4a*H*-benzocycloheptene derivative (12), which was isolated as a red oil.

The spectra of compound (12) are fully consistent with the structure shown. The u.v. spectrum has maxima at λ 283 and 435 nm and the i.r. spectrum shows a carbonyl absorption at ν 1 695 cm⁻¹. The ¹H n.m.r. spectrum was analysed and gave the chemical-shift values and coupling constants shown in Figure 1. The values of the coupling constants show an alternation round the periphery which is consistent with a pattern of ' fixed ' double bonds.

Extended enolisation and *O*-alkylation of this type

had not previously been described when this work was carried out. The methodology was subsequently adapted to the preparation of methoxylated 3aH-indenes.[3] A recent preparation of 3-methoxy-1,5-methano[10]annulene also makes use of an extended enolisation–alkylation sequence.[11]
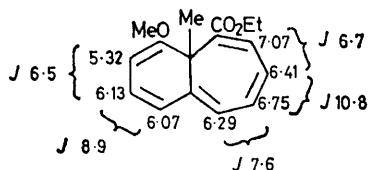

FIGURE 1   Chemical-shift values and coupling constants for peripheral hydrogen atoms of compound (12)

*Thermal Rearrangement of the 4a*H-*Benzocycloheptene* (12).—The ester (12), although very sensitive to moisture and impurities, was found to be thermally stable below *ca.* 100 °C, and was purified by vacuum distillation at 70—75 °C. When the compound was heated in solution to >130 °C it was transformed into a mixture of other substances, its disappearance being indicated by a gradual discharge of the red colour of the solution. Approximate kinetic measurements using u.v. spectroscopy showed that its rearrangement was first order, with a half life of *ca.* 33 min at 138 °C in decalin.

The ester was heated in xylene under reflux until the rearrangment was complete. A mixture of products was obtained, from which only the major component could be isolated, by layer chromatography, in a fairly pure state. This component was identified as the aromatic 7*H*-benzocycloheptene (13) by physical and chemical means. The assignments of the signals in the n.m.r. spectrum to the hydrogen atoms on the seven-membered ring at C-7, C-8, and C-9, and their inter-relationship, were established by decoupling experiments. The structure of the ester (13) was confirmed by its degradation into the known[12] ketone (14). This was achieved by its hydrolysis to the β-keto-ester (15) (which exists predominantly in the enol form) followed by decarbo-alkoxylation to the ketone (16) by heating the keto-ester with sodium chloride in wet dimethyl sulphoxide[13] and catalytic hydrogenation of the double bond (Scheme 3).

The 7*H*-benzocycloheptene (13) is clearly derived from the 4a*H*-benzocycloheptene (12) by a skeletal rearrangement rather than by a sigmatropic shift of the methyl group. A reasonable pathway for its rearrangement, illustrated in Scheme 4, involves, as the first step, the valence tautomerism of the seven-membered ring to produce a ' bis-norcaradiene ' intermediate (17) which can then open in an alternative way to give a different 4a*H*-benzocycloheptene (18). A [1,5] sigmatropic shift of the bridgehead ethoxycarbonyl group can then produce the 7*H*-benzocycloheptene (13). Bis-norcaradienes have previously been generated and detected at low temperatures by spectroscopic means;[7,8] their rearrangement to 7*H*-benzocycloheptenes is postulated to follow a route
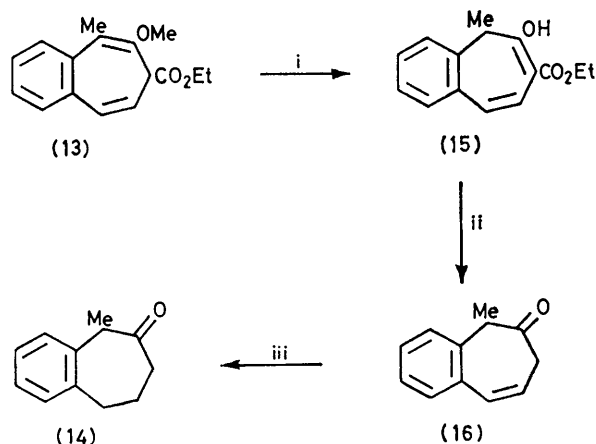
SCHEME 3   *Reagents:* i, NaHSO₄, aqueous dioxan, heat; ii, NaCl, aqueous Me₂SO, 140 °C; iii, H₂/Pd–C

analogous to that shown in Scheme 4. There is therefore good precedent for this pathway.

The nature of the minor products of thermal rearrangement of the ester (12) could not be determined directly, since no satisfactory means of separating them was found. The problem was overcome by treatment of the total mixture of products from the thermal rearrangement with sodium hydrogensulphate in aqueous dioxan; this gave a mixture which contained three components which were cleanly separable by layer chromatography. The most abundant component was the keto-ester (15) which had been obtained earlier; the others, which were isolated in yields of 15% and 8%, respectively, were a methoxy-ester and a keto-ester.
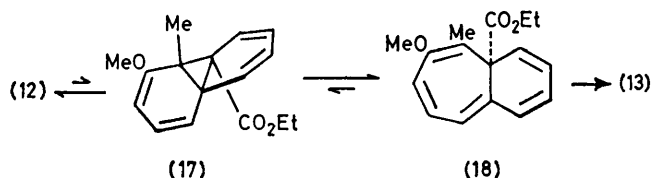
SCHEME 4   Rearrangement pathway for formation of the 7*H*-benzocycloheptene (13)

The retention of the methoxy-group in the methoxy-ester indicates that the methoxy-group is probably attached to a benzene ring. The structure (19) was assigned to the substance on the basis of its n.m.r. spectrum: the chemical-shift values and coupling constants (detailed in the Experimental section) were obtained by analysis and the assignments were supported by decoupling experiments. For the third product of the reaction the available evidence was consistent with either of two structures, (20) and (21), and no definite assignment could be made. Analysis and decoupling of the ¹H n.m.r. spectrum of the third product established the ABX pattern of the signals for 7-Hₐ, 7-Hᵦ, and 8-H, with further coupling to 9-H. This part of the spectrum closely resembles that of the ketone (16). The spectrum also shows that there are three contiguous hydrogen atoms attached to an aromatic ring, but the

position of the ethoxycarbonyl group cannot be established with certainty. The structure of the third component of the mixture obtained by thermal rearrangement of the compound (12) must therefore be either that of compound (22) or (23).

(19)

(20)

(21)

(22)

(23)
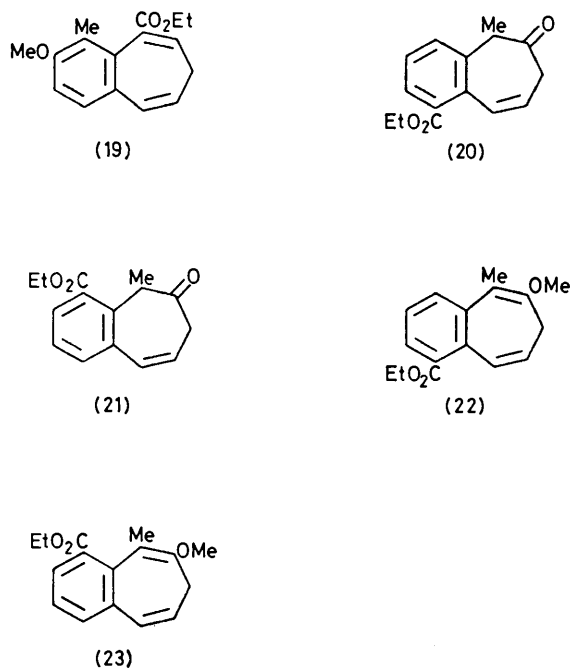
A possible rearrangement pathway which could account for the formation of the anisole (19) and of the enol ether (23) is shown in Scheme 5. It involves the rearrangement of the bis-norcaradiene (17) to another bis-norcaradiene (24) [a thermally allowed $(_\sigma 2_s + _\pi 4_a + _\pi 4_a)$ process (Figure 2) and a sterically feasible one] followed by ring-opening and sigmatropic hydrogen-shifts. Interconversions of bis-norcaradienes by such a pathway have been discussed previously,[6,8] but there is a lack of conclusive evidence. We consider that Scheme 5

shows the most likely route for the formation of compound (19).

A possible source of a product with the alternative structure (22) is a [1,5] shift of the ethoxycarbonyl group of the intermediate (18) onto the six-membered ring. There are thus reasonable pathways to account for the formation of either compound (22) or (23). All three products do, however, arise by skeletal rearrangement of the 4aH-benzocycloheptene (12), and the bis-norcaradiene (17) appears likely to be the first intermediate formed in the rearrangement sequence.
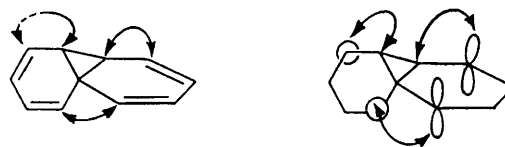

FIGURE 2 A $(_\sigma 2_s + _\pi 4_a + _\pi 4_a)$ rearrangement pathway for bis-norcaradienes

Other Reactions of the 4aH-Benzocycloheptene (12).— Cycloaddition and acid-induced reactions of compound (12) were observed and are summarised in Scheme 6. 4-Phenyl-1,2,4-triazolinedione gave an adduct (25) which is the result of 4 + 2 cycloaddition across the six-membered ring diene system. Attempts to observe cycloadditions with dimethyl acetylenedicarboxylate, maleic anhydride, and 4-toluonitrile oxide were unsuccessful. In particular, there was no evidence for an ' extended ' cycloaddition across the termini of the pentaene system. An acid-catalysed rearrangement was observed to give compound (26), which is presumably the product of two successive 1,2-methyl shifts. In aqueous acid the lactol ether (27) was formed; this is probably the result of protonation of the enol ether double bond followed by cyclisation. The structures of the products (25)—(27) were deduced from their n.m.r. spectra.*

* The stereochemistry at the bridgehead positions of compound (27) could not be deduced from the n.m.r. spectrum, but that shown would result from cyclisation on the face of compound (12) opposite to the 4a-methyl group.
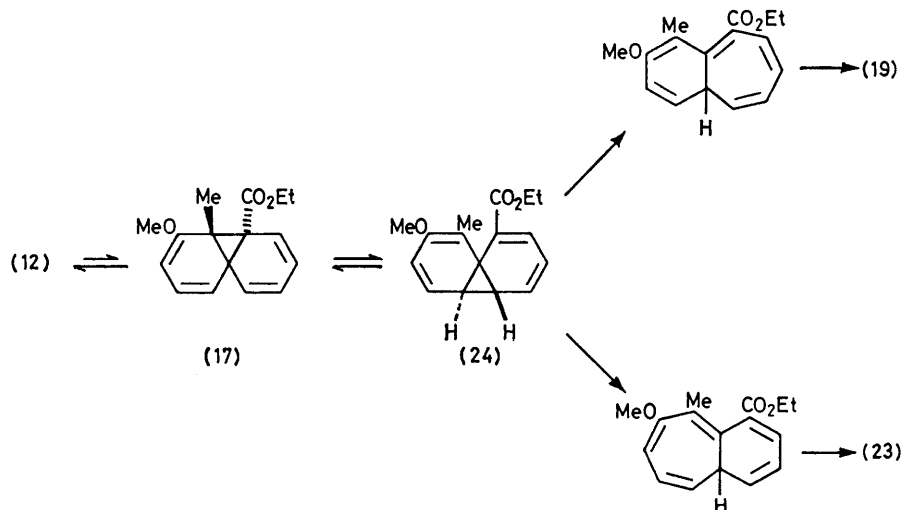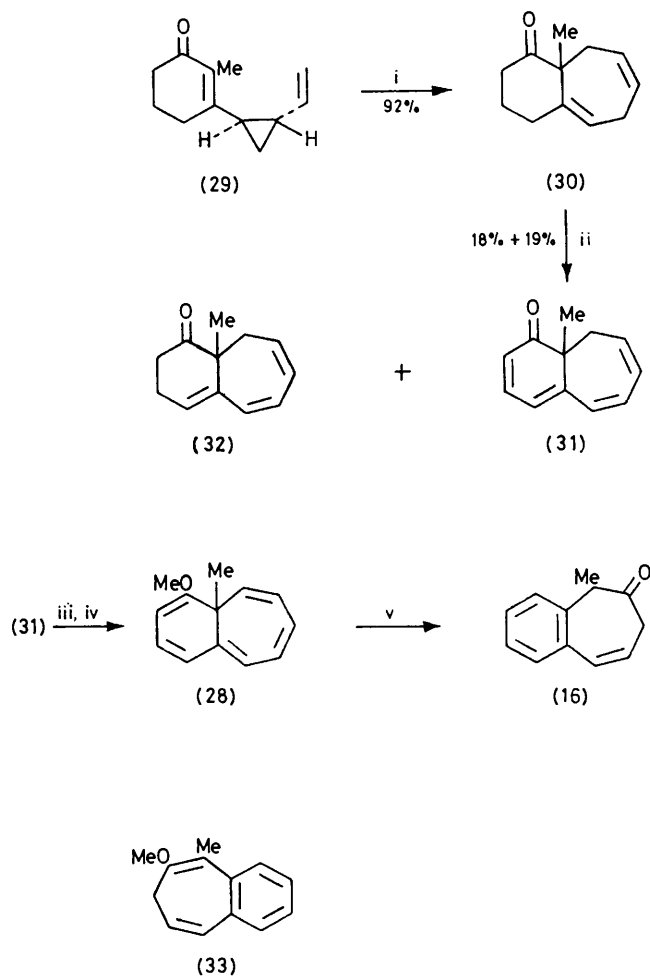

SCHEME 5 Postulated rearrangement pathways for the formation of compounds (19) and (23)

(12)

i ii iii

(25) (26) (27)
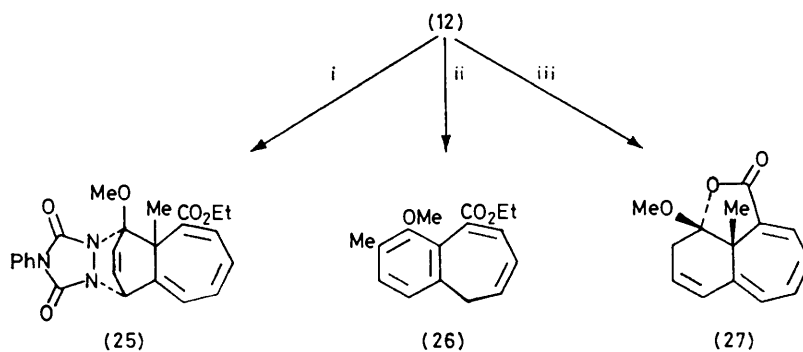
SCHEME 6   *Reagents:* i, 4-phenyl-1,2,4-triazolinedione, CH_2Cl_2; ii, H^+, benzene, 80 °C; iii, HCl, aqueous dioxan, 20 °C

Generation and Rearrangement of 4-*Methoxy*-4a-*methyl*-4aH-*benzocycloheptene* (28).—The route used to prepare the ester (12) was modified in order to prepare the simpler derivative (28) and, possibly, the parent 4a-methyl-4aH-benzocycloheptene. The cyclopropane-carbaldehyde (6) was converted, by means of triphenyl-phosphonium methylide, into the *trans*-divinyl cyclopropane (29), a known compound which had been prepared

(29) (30)

18% + 19% | ii

(32) + (31)

(31) —iii, iv→ (28) —v→ (16)

(33)

SCHEME 7   *Reagents:* i, xylene 140 °C, 10 h; ii, DDQ (2.2 mol equiv.) dioxan, acetic acid, 5 h; iii, KH–18-crown-6, −10 °C; iv, $MeOSO_2F$, −10 °C; v, H_2O, room temperature

earlier by a different route.[14] This gave the bicyclic dienone (30) in high yield when heated. The dehydro-genation of the dienone (30) by DDQ proved to be in-efficient and mixtures of the tetraenone (31) and the trienone (32) were obtained (Scheme 7). Nevertheless, the tetraenone was obtained in sufficient quantity for an enolisation–alkylation sequence to be attempted. The strong base system of potassium hydride complexed with 18-crown-6 [15] was required to generate the deep purple anion of the tetraenone. Methyl fluorosulphonate was then added to produce an unstable substance, presumably the enol ether (28), which could be detected by t.l.c., but which could not be isolated. Instead, a ketone was obtained after concentration of the reaction mixture at room temperature and extraction of the residue with carbon tetrachloride. This ketone was identified as the enone (16) which had been isolated earlier from the degradation of the ester (13). We assume that the enol ether (28) underwent thermal rearrangement *at room temperature*, by a route analogous to that shown in Scheme 4, to give the enol ether (33) which was then hydrolysed to the ketone (16). These reactions are summarised in Scheme 7.

The rates of thermal rearrangement of the 4aH-benzocycloheptenes (12) and (28) are thus dependent upon the nature of the substituents. This could be a consequence of variations in the rate of the initial valence-tautomerism step in Scheme 4 or in the rate of sigmatropic shift of the bridgehead substituent of the rearranged 4aH-benzocycloheptenes [ethoxycarbonyl in compound (18), but hydrogen in the corresponding product from compound (28)]. The greater stability of the methoxy-ester (12) with respect to the methoxy-compound (28) is associated with its greater electron (' push–pull ') delocalisation.

EXPERIMENTAL

I.r. spectra were recorded (for solids) as KBr discs on a Perkin-Elmer 125 instrument and (for liquids) as thin films on a Pye Unicam SP200 spectrometer (calibrated against polystyrene), unless otherwise indicated. U.v. spectra were recorded using a Pye Unicam SP8-100 spectrophoto-meter and were calibrated against holmium glass. [1]H N.m.r. spectra were obtained as $CDCl_3$ solutions using a Perkin-Elmer R34 instrument at 220 MHz. Mass spectra

were obtained on an A.E.I. MS12 or MS902 instrument at 70 eV using a direct insertion probe. Experiments which required anhydrous conditions were carried out in glass apparatus, previously dried at 120 °C and cooled under dry nitrogen. Preparative layer chromatography (p.l.c.) was carried out on plates coated with silica-gel PF254 (Merck) or aluminium oxide GF 254 (Merck). Melting points are uncorrected. Petroleum refers to light petroleum, b.p. 60—80 °C.

Dimethyloxosulphonium (2-*Methyl*-3-*oxocyclohex*-1-*en*-1-*yl*)*methylide* (5).—3-Chloro-2-methylcyclohex-2-en-1-one [16] (25.0 g, 173 mmol) in dry THF (50 cm³) was added as drops for 45 min to an ice-cold, stirred solution of dimethyloxosulphonium methylide in THF [17] (650 cm³ of a 0.56M solution, 364 mmol) under nitrogen. The reaction mixture was allowed to warm to room temperature and was then heated under reflux for 18 h. The precipitated trimethyloxosulphonium chloride (13.6 g, 61%) was filtered off and washed with THF (50 cm³). The filtrate and washings were concentrated to 150 cm³ and the ylide (5) (13.0 g, 38%) was precipitated. Crystallisation gave an analytical specimen of the *ylide* (5) as pale yellow crystals, m.p. 152—153 °C (decomp.) from THF (Found: C, 60.2; H, 8.1; S, 16.0. $C_{10}H_{16}O_2S$ requires C, 60.0; H, 8.0; S, 16.0%); $v_{max.}$ 1 560 and 1 495 cm⁻¹; δ 1.67 (3 H), 1.94 (2 H, m), 2.34 (2 H, m), 2.72 (2 H, m), 3.40 (6 H), and 4.10 (1 H, br).

cis- *and* trans-(2-*Methyl*-3-*oxocyclohex*-1-*enyl*)*cyclopropane-carbaldehyde* (6).—A solution of acrolein (redistilled; 6.94 g, 124 mmol) in acetonitrile (dried over type 3A molecular sieves, 30 cm³) was added to the ylide (5) (12.4 g, 62 mmol) in acetonitrile (250 cm³). The solution was kept at 20 °C for 4 h and the solvent was then removed. The residue was dissolved in ethyl acetate (250 cm³) and the solution was washed with water (2 × 100 cm³). The organic layer was dried and evaporated to leave a pale yellow oil (9.0 g, 81%) which slowly crystallised, m.p. 43—48 °C. This was identified as a mixture of the cis- and trans-isomers of the carbaldehyde (6); $v_{max.}$ (CHCl₃) 1 705 and 1 660 cm⁻¹; δ 1.4—2.6 (10 H, m), 1.90 (3 H) and 9.29 and 9.42 (together 1 H, both d, ratio 1 : 5); m/e 178 (M^+). An analytical specimen had m.p. 55—56 °C (from diethyl ether–petroleum) (Found: C, 74.0; H, 8.0. $C_{11}H_{14}O_2$ requires C, 74.2; H, 7.9%). The mixture of isomers was used without further purification in subsequent steps.

Ethyl trans,trans-3-[2-(2-*Methyl*-3-*oxocyclohex*-1-*enyl*)-*cyclopropyl*]*prop*-2-*enoate* (7).—A solution of the aldehyde (6) (4.50 g, 25.2 mmol) and triphenylphosphonium ethoxy-carbonylmethylide [18] (8.80 g, 25.2 mmol) in THF (120 cm³) was left at room temperature for 24 h. The solvent was removed; column chromatography of the residue (silica; diethyl ether as eluant) gave the *ester* (7) (5.40 g, 86%), m.p. 122—123 °C (from dichloromethane–petroleum) (Found: C, 72.7; H, 8.3. $C_{15}H_{20}O_3$ requires C, 72.6; H, 8.1%); $v_{max.}$ 1 700 cm⁻¹ (C=O); δ 1.19—1.40 (2 H, m), 1.27 (3 H, t), 1.8—2.2 (6 H, m), 1.86 (3 H), 2.39 (2 H, m), 4.19 (2 H, q), 5.93 (1 H, d, J 16 Hz), and 6.53 (1 H, dd, J 16 and 10 Hz); m/e 248 (M^+). A faster-moving component of the mixture obtained from the chromatography column was identified as the bicyclic ester (4) (0.51 g, 8%) (see below).

Ethyl trans-2,3,4,4a,5,8-*Hexahydro*-4a-*methyl*-4-*oxo*-1H-*benzocycloheptene*-5-*carboxylate* (4).—The ester (7) (5.2 g) was heated to 140 °C in solution in dry xylene (150 cm³) under reflux for 6 h in a nitrogen atmosphere. This gave the bicyclic *oxo-ester* (4) (100%); bulb-to-bulb distillation gave an analytical specimen as a clear oil, b.p. 70—75 °C at 0.02

mmHg (Found: C, 72.2; H, 8.2. $C_{15}H_{20}O_3$ requires C, 72.6; H, 8.1%); $v_{max.}$ 1 725 and 1 700 cm⁻¹ (C=O); δ 1.19 (3 H, t), 1.24 (3 H), 1.8—2.1 (2 H, m), 2.45—2.60 (4 H, m), 2.89 (2 H, m), 4.09 (2 H, q), 4.16 (1 H, d, J 8 Hz, 5-H), 5.35 (1 H, m), and 5.75—5.95 (2 H, m); m/e 248 (M^+).

Ethyl trans-9,9a-*Dihydro*-9a-*methyl*-1-*oxo*-1H-*benzocyclo-heptene*-9-*carboxylate* (10) *and Ethyl* trans-2,3,9,9a-*Tetra-hydro*-9a-*methyl*-1-*oxo*-1H-*benzocycloheptene*-9-*carboxylate* (11).—A solution of the oxo-ester (4) (4.47 g, 18.0 mmol) and DDQ (8.85 g, 39.0 mmol) in dioxan (140 cm³), which contained acetic acid (1.4 cm³), was heated under reflux under nitrogen for 5 h. The hydroquinone by-product (8.4 g) was filtered off and washed with ether. The filtrate and washings were evaporated under reduced pressure and the residue was redissolved in ether (300 cm³). The solution was washed with aqueous sodium carbonate (1M, 2 × 150 cm³), water (2 × 100 cm³), and saturated brine (100 cm³). It was dried and the solvent was removed to leave a brown oil. Column chromatography (silica, diethyl ether–hexane, 1 : 1, as eluant) gave the *trienone-ester* (11) (0.68 g, 15%) as a pale yellow oil which slowly crystallised, m.p. 28—32 °C; $v_{max.}$ 1 725 and 1 700 cm⁻¹ (C=O); $\lambda_{max.}$ (EtOH) 207 (ε 7 790) and 286 nm (8 610); δ 1.02 (3 H), 1.12 (3 H, t), 2.5—2.8 (4 H, m), 4.01 (2 H, q), 4.29 (1 H, d, J 8.7 Hz, 5-H), 5.70 (1 H, dd, J 12.2 and 6.9 Hz, 4-H), and 5.9—6.2 (4 H, m); m/e 246 (M^+). Further elution gave the *tetraenone-ester* (10) (2.60 g, 59%) as a deep yellow oil. Bulb-to-bulb distillation gave an analytical specimen, b.p. 75—80 °C at 0.03 mmHg (Found: C, 73.6; H, 6.85. $C_{15}H_{16}O_3$ requires C, 73.8; H, 6.6%); $v_{max.}$ 1 725 and 1 665 cm⁻¹ (C=O); $\lambda_{max.}$ (EtOH) 248 (ε 7 690), 257 (7 800), 266 (7 560), and 400 nm (4 820); δ 1.10 (3 H, t), 1.20 (3 H, s), 4.00 (2 H, q), 4.38 (1 H, d, J 8.6 Hz, 9-H), 5.8—6.3 (6 H), and 7.08 (1 H, dd, J 10.0 and 8.6 Hz, 3-H); m/e 244 (M^+).

Ethyl 4-*Methoxy*-4a-*methyl*-4aH-*benzocycloheptene*-5-*carboxylate* (12).—A solution of the redistilled tetraenone-ester (10) (1.55 g, 6.35 mmol) in dry DME (15 cm³) was added during 5 min to a suspension of sodium hydride (oil free; 230 mg, 9.58 mmol) in dry DME (45 cm³), stirred at —10 °C under nitrogen. The suspension was stirred at —10 °C for 3 h and a deep turquoise colour, which was attributed to the enolate anion, developed. Methyl fluorosulphonate (redistilled; 0.80 cm³, 10 mmol) was added. The deep red solution was concentrated under reduced pressure at 20 °C to a volume of 5 cm³ and was immediately subjected to p.l.c. (alumina; petroleum–diethyl ether, 2 : 1, as eluant). This gave an intense orange component which was removed from the plate by extraction of the alumina with dry diethyl ether to give the *methoxy-ester* (12) (1.15 g, 70%) as a deep red oil. An analytical specimen was obtained by bulb-to-bulb distillation, b.p. 70—75 °C at 0.02 mmHg (Found: C, 73.9; H, 7.0. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%); $v_{max.}$ 1 695 and 1 640 cm⁻¹; $\lambda_{max.}$ (EtOH) 283 (ε 12 160) and 435 nm (3 590); δ 0.86 (3 H, 4a-Me), 1.28 (3 H, t), 3.62 (3 H), 4.16 (2 H, q), 5.32 (1 H, d, J 6.5 Hz, 3-H), 6.07 (1 H, d, J 8.9 Hz, 1-H), 6.13 (1 H, dd, J 8.9 and 6.5 Hz, 2-H), 6.29 (1 H, d, J 7.6 Hz, 9-H), 6.41 (1 H, dd, J 10.8 and 6.7 Hz, 7-H), 6.75 (1 H, dd, J 10.8 and 7.6 Hz, 8-H), and 7.07 (1 H, d, J 6.7 Hz, 6-H); m/e 258 (M^+).

Thermal Rearrangement of the Methoxy-ester (12).—(a) *Isolation and identification of the major product.* (i) A solution of the ester (12) (190 mg) in dry xylene (5 cm³) was purged with nitrogen and was heated under reflux for 6 h during which period the red colour of the solution was

discharged. P.l.c. (alumina; hexane–diethyl ether, 2 : 1, as eluant) gave a mixture of closely-running components which were only partially separated. The major component (80 mg, 42%; *ca.* 80% purity) was assigned the structure ethyl 6-methoxy-5-methyl-7*H*-benzocycloheptene-7-carboxylate (13); $\nu_{max.}$ 1 725 and 1 640 cm^{-1}; δ 1.09 (3 H, t), 2.10 (3 H, 5-Me), 3.41 (1 H, d, *J* 7.1 Hz, 7-H), 3.63 (3 H, MeO), 4.08 (2 H, q), 6.38 (1 H, dd, *J* 9.5 and 7.1 Hz, 8-H), 6.73 (1 H, d, *J* 9.5 Hz, 9-H), 7.2—7.4 (3 H, m), and 7.56 (1 H, d, *J* 7.8 Hz) (irradiation at δ 6.38 caused the doublets at δ 3.41 and 6.73 to collapse to singlets); *m/e* 258 (*M*$^+$).

(ii) The ester (13) (52 mg, 0.2 mmol) and sodium hydrogensulphate (400 mg) were heated in 50% aqueous dioxan (6 cm^3) under reflux for 5 h. The solution was diluted with water (10 cm^3) and extracted with ethyl acetate (2 × 5 cm^3). The organic solution was washed successively with water and saturated brine, dried, and evaporated to give an oil (42 mg). P.l.c. (silica; hexane–diethyl ether, 1 : 1, as eluant) gave ethyl 6,7-*dihydro-5-methyl-6-oxo-5H-benzo-cycloheptene-7-carboxylate* (15) mg, 30%), m.p. 43–43.5 °C (from hexane at −78 °C) (Found: C, 73.5; H, 6.4. C$_{15}$H$_{16}$O$_3$ requires C, 73.8; H, 6.6%); $\nu_{max.}$ 1 640 and 1 575 cm^{-1}; $\lambda_{max.}$ (EtOH) 235 (ε 19 400), 266 (10 490), and 290 nm (8 050); δ 1.33 (3 H, t), 1.2—1.8 (3 H, br, 5-Me), 2.9—3.2 (1 H, br, 5-H), 4.28 (2 H, q), 6.85 (2 H, m, 8- and 9-H), 7.2—7.45 (4 H, m), and 13.14 (1 H, OH); *m/e* 244 (*M*$^+$). This ester formed a sodium salt in CD$_3$OD, the ^{1}H n.m.r. spectrum of which showed more prominent signals at δ 1.69 (3 H, d, 5-Me) and 3.09 (1 H, 5-H).

(iii) A mixture of the ester (15) (110 mg, 0.45 mmol) and sodium chloride (130 mg) in DMSO (5 cm^3) which contained water (4 drops) was heated and stirred at 140 °C for 0.5 h under nitrogen. Saturated brine (15 cm^3) was added and the emulsion was extracted with ether (3 × 10 cm^3). The organic solution was washed with brine and dried. Evaporation of the solvent left an oil (76 mg) which was eluted through a short column of silica (5 g) with diethyl ether and petroleum (1 : 1) to give 6,7-*dihydro-5-methyl-5H-benzo-cyclohepten-6-one* (16) (64 mg, 82%) as a pale yellow oil; $\nu_{max.}$ 1 695 cm^{-1} (C=O); $\lambda_{max.}$ (EtOH) 246 (ε 12 900) and 275 nm (4 470); δ 1.50 (3 H, d, *J* 7.1 Hz), 2.99 (1 H, m, *A*BXM, 7-H$_a$), 3.24 (1 H, dd, A*B*X, 7-H$_b$), 3.86 (1 H, q, *J* 7.1 Hz, 5-H), 6.01 (1 H, ddd, AB*X*M, 8-H), 6.92 (1 H, dd, AX*M*, 9-H), and 7.29 (4 H, m). Analysis gave $J_{7a,7b}$ 19.1, $J_{7a,8}$ 4.4, $J_{7b,8}$ 7.1, $J_{7a,9}$ 2.2, $J_{8,9}$ 10.8, and $J_{5,7}$ 1.1 Hz; *m/e* 172 (*M*$^+$).

(iv) The enone (16) (52 mg) in ethanol (10 cm^3) was hydrogenated at 1 atm over 5% palladium-on-charcoal and gave 6,7,8,9-tetrahydro-5-methyl-5*H*-benzocyclohepten-6-one (14) (46 mg, 87%), 2,4-dinitrophenylhydrazone m.p. 149—151 °C (from methanol) (lit.,^{12} m.p. 150—151 °C); $\nu_{max.}$ 1 700 cm^{-1} (C=O); δ 1.42 (3 H, d), 1.8—2.2 (2 H, m), 2.5—3.0 (4 H, m), 3.89 (1 H, q), and 7.1—7.3 (4 H, m); *m/e* 174 (*M*$^+$).

(b) *Identification of minor products.* The methoxy-ester (12) (0.85 g) in dry xylene (25 cm^3) was heated under nitrogen for 6 h. The solvent was removed and the residue was then heated in 50% aqueous dioxan (60 cm^3) with sodium hydrogensulphate (5.0 g) for 5 h. The reaction mixture was cooled and diluted with water (100 cm^3). Extraction of the resulting emulsion with diethyl ether (3 × 40 cm^3) gave an oil (0.72 g) which was subjected to p.l.c. (silica; diethyl ether–petroleum, 1 : 1, as eluant). Three components were separated; no others were detected in significant amounts. The major component (at R_F 0.7) was the oxo-ester (15) (0.213 g, 25%). A second component, R_F 0.5, was assigned

the structure ethyl 3-*methoxy-4-methyl-7H-benzocycloheptene-5-carboxylate* (19) (0.124 g, 15%), a pale yellow amorphous solid, m.p. 56—61 °C (from hexane at −78 °C) (Found: *m/e* 258.1253. C$_{16}$H$_{18}$O$_3$ requires *m/e* 258.1256); $\nu_{max.}$ 1 710 cm^{-1}; $\lambda_{max.}$ (EtOH) 225 (ε 11 300), 270sh (7 000), and 310sh nm (1 840); δ 1.25 (3 H, t), 1.9—2.8 (2 H, br, 7-H), 2.15 (3 H, 4-Me), 3.90 (3 H, OMe), 4.21 (2 H, q), 6.02 (1 H, dt, *J* 9.0 and 6.7 Hz, 8-H), 6.70 (1 H, d, *J* 9.0 Hz, 9-H), 6.96 (1 H, d, *J* 9.0 Hz, 2-H), 7.06 (1 H, t, *J* 7.8 Hz, 6-H), and 7.24 (1 H, d, *J* 9.0 Hz, 1-H). Irradiation at δ 6.02 caused collapse of the doublet at δ 6.70 only; irradiation at δ 2.70 caused some loss of resolution in the signals at δ 6.02 and 7.06.

A third component, R_F 0.4, had an n.m.r. spectrum which was consistent with either of the structures ethyl 6,7-dihydro-5-methyl-6-oxo-5*H*-benzocyclohept-ene-1-carboxylate (20) or the 4-carboxylate (21) (61 mg, 8%), a pale yellow amorphous solid, m.p. 38–42 °C (from hexane at −78 °C); $\nu_{max.}$ (film) 1 700 cm^{-1}; $\lambda_{max.}$ (EtOH) 250 (ε 6 170), 272sh (3 250), and 306sh nm (1 560); δ 1.39 (3 H, t), 1.48 (3 H, d, *J* 6.6 Hz, 5-Me), 2.88 (1 H, m, *A*BXM, 7-H$_a$), 3.19 (1 H, dd, A*B*X, 7-H$_b$), 3.91 (1 H, q, *J* 6.6 Hz), 4.39 (2 H, q), 6.20 (1 H, ddd, AB*X*M, 8-H), 7.35—7.52 (3 H, m, includes 9-H), 7.89 (1 H, d, aromatic *ortho* to ester). Irradiation at δ 6.20 caused simplification of the multiplet at δ 7.35—7.52 and showed the 9-H signal to be at δ 7.49. Analysis gave $J_{7a,7b}$ 17.4, $J_{7a,8}$ 4.4, $J_{7b,8}$ 7.6, and $J_{8,9}$ 11.0 Hz; *m/e* 244 (*M*$^+$), 216, 185, 155, 129, and 115.

Cycloaddition of the Methoxy-ester (12) with 4-Phenyl-1,2,4-triazolinedione.—A solution of 4-phenyl-1,2,4-triazolinedione (freshly sublimed; 54 mg, 0.31 mmol) in dichloromethane (5 cm^3) was added as drops for 15 min to an ice-cold, stirred solution of the methoxy-ester (12) (80 mg, 0.31 mmol) in dichloromethane (10 cm^3) under nitrogen. The colouration due to both components was rapidly discharged. The pale yellow solution was evaporated to leave a glassy solid residue, which was triturated with diethyl ether to give ethyl 2,4,4a,10-*tetrahydro-4-methoxy-4a-methyl-1,3-dioxo-2-phenyl-4,10-ethenocyclohepta[d]pyridazino[1,2-a][1,2,4]tri-azole-5-carboxylate* (25) (94 mg, 70%) as crystals, m.p. 161—163 °C (decomp.) (from ethyl acetate) (Found: C, 66.25; H, 5.3; N, 10.0. C$_{24}$H$_{23}$N$_3$O$_5$ requires C, 66.5; H, 5.3; N, 9.7%); $\nu_{max.}$ 1 755 and 1 700 cm^{-1}; δ 1.20 (3 H), 1.30 (3 H t), 3.78 (3 H), 4.21 (2 H, q), 5.20 (1 H, d, *J* 5.7 Hz, methine H), 6.3—6.45 (4 H, m), 6.73 (1 H, dd, *J* 8.7 and 6.1 Hz), 6.91 (1 H, d, *J* 8.9 Hz), and 7.3—7.5 (5 H); *m/e* 433 (*M*$^+$).

Acid-catalysed Rearrangement of the Methoxy-ester (12).—The methoxy-ester (12) (90 mg, 0.35 mmol) in dry benzene (1 cm^3) was added to a previously dried solution of toluene-4-sulphonic acid (40 mg) in benzene (20 cm^3). The solution was heated under reflux for 1 h and was then washed successively with aqueous sodium carbonate, water, and saturated brine. It was dried and the solvent was removed. P.l.c. alumina; petroleum–diethyl ether, 2 : 1, as eluant) gave, as a major component, a clear oil (32 mg, 36%) which was assigned the structure ethyl 1-*methoxy-2-methyl-5H-benzo-cycloheptene-9-carboxylate* (26); $\nu_{max.}$ (film) 1 695 cm^{-1}; $\lambda_{max.}$ (EtOH) 235 (ε 6 450), 257sh (3 610), and 305 nm (2 840); δ 1.35 (3 H, t), 2.30 (3 H, 2-Me), 3.00 (2 H, br, 5-H), 3.81 (3 H, OMe), 4.35 (2 H, q), 6.05—6.22 (2 H, m, 6- and 7-H), 6.72 (1 H, d, *J* 9.0 Hz, 4-H), 7.36 (1 H, d, *J* 9.0 Hz, 3-H), and 7.51 (1 H, d, *J* 4.5 Hz, 8-H). Irradiation at δ 6.15 caused collapse of the doublet at δ 7.51 only; irradiation at δ 3.0 caused simplification of the multiplet at δ 6.05—6.22; *m/e* 258 (*M*$^+$). A second component which was isolated from the plate was identified as the lactol ether (27) (9 mg, 11%),

by comparison with a specimen obtained from the reaction described below.

Acid Catalysed Hydrolysis of the Methoxy-ester (12).—A solution of the methoxy-ester (12) (0.180 g, 0.7 mmol) in 2M hydrochloric acid–dioxan (1 : 1, 10 cm³) was stirred at room temperature for 36 h. Water (15 cm³) was added and the resulting emulsion was extracted with ethyl acetate (2 × 10 cm³). The solution was washed, dried, and then evaporated and the residue (0.167 g) was purified by p.l.c. (silica; diethyl ether–petroleum, 2 : 1, as eluant). This gave 9a,9b-di-hydro-9a-methoxy-9b-methylcyclohepta[cd]benzofuran-2(9H)-one (27) (83 mg, 53%), m.p. 168—170 °C (from dichloromethane–hexane); $\nu_{max.}$ 1 735 cm⁻¹; δ 0.71 (3 H), 2.69 (1 H, m, ABXM, 9-H_a), 3.08 (1 H, dd, ABX, 9-H_b), 3.53 (3 H, OMe), 6.01 (1 H, ddd, ABXM, 8-H), 6.34 (1 H, d, J 7.8 Hz, 6-H), 6.42 (1 H, dd, AXM, 7-H), 6.85 (1 H, dd, J 10.9 and 6.5 Hz, 4-H), 7.02 (1 H, dd, J 10.9 and 7.8 Hz, 5-H), and 7.39 (1 H, d, J 6.5 Hz, 3-H) (the assignments were supported by decoupling experiments). Analysis gave $J_{7,8}$ 9.5, $J_{7,9a}$ 3.0, $J_{8,9a}$ 2.3, $J_{8,9b}$ 6.8, and $J_{9a,9b}$ 17.1 Hz; m/e 230 (M^+).

5,7,8,9,9a,9b-*Hexahydro-9a-hydroxy-9b-methylcyclohepta*-[cd]*benzofuran*-2(2aH)-*one* (9).—The ester (4) (1.72 g, 6.93 mmol) was dissolved in aqueous ethanolic sodium hydroxide (0.5M; 50 cm³) and the solution was kept at 20 °C for 4 h. Acidification gave the *lactol* (9) (1.32 g, 87%), m.p. 129—130 °C (from chloroform–diethyl ether) (Found: C, 71.0; H, 7.3. $C_{13}H_{16}O_3$ requires C, 70.9; H, 7.3%); $\nu_{max.}$ 3 340 (OH) and 1 745 (C=O) cm⁻¹; δ 1.45 (3 H), 1.5—2.5 (6 H, m), 2.7—3.1 (2 H, m), 4.04 (1 H, d, J 9 Hz), 5.55 (1 H, m), 5.80 (1 H, m), and 6.05 (1 H, m) (all the signals for ring hydrogen atoms were poorly resolved); m/e 220 (M^+).

trans-3-(2-*Ethenylcyclopropyl*)-2-*methylcyclohex-2-en-1-one* (29).—Sodium hydride (55% dispersion in oil; 0.510 g, 11.7 mmol) was washed with dry hexane and dried under nitrogen. It was then heated with dry DMSO (25 cm³) until the evolution of hydrogen ceased. The solution was cooled and methyltriphenylphosphonium bromide (4.15 g, 11.6 mmol) was added in portions for 15 min. After a further 10 min, the aldehyde (6) (2.0 g, 11.2 mmol) in DMSO (5 cm³) was added. The reaction mixture was stirred for 15 min at room temperature, then added to saturated brine (250 cm³). Extraction by ethyl acetate and column chromatography (silica; diethyl ether–petroleum, 3 : 2) gave the vinylcyclopropane (29)[14] (1.36 g, 66%), b.p. 70—73 °C at 0.1 mmHg (Found: C, 81.9; H, 9.2. Calc. for $C_{12}H_{16}O$: C, 81.8; H, 9.1%); δ 1.0—1.35 (2 H, m), 1.7—2.05 (6 H, m), 1.86 (3 H), 2.36 (2 H, m), 4.97 (1 H, d, J 9 Hz), 5.13 (1 H, d, J 16 Hz), and 5.55 (1 H, ddd, J 16, 10, and 9 Hz); m/e 176 (M^+).

2,3,4,6,9,9a-*Hexahydro-9a-methyl*-1H-*benzocyclohepten-1-one* (30).—The vinylcyclopropane (29) (1.31 g) was heated in dry xylene (30 cm³) under nitrogen at 140 °C for 10 h. The solvent was removed; column chromatography (silica; diethyl ether–petroleum, 3 : 2) gave the ketone (30)[14] (1.21 g, 92%), b.p. 71—73 °C at 0.02 mmHg (Found: C, 81.75; H, 9.2. Calc. for $C_{12}H_{16}O$: C, 81.8; H, 9.1%); $\nu_{max.}$ 1 700 cm⁻¹; δ (CDCl₃) 1.29 (3 H), 1.65 (1 H, m), 1.9—2.2 (2 H, m), 2.3—2.95 (7 H, m), 5.45 (1 H, m), and 5.8—6.0 (2 H, m); m/e 176 (M^+).

9,9a-*Dihydro-9a-methyl*-1H-*benzocyclohepten*-1-*one* (31) *and* 2,3,9,9a-*Tetrahydro-9a-methyl*-1H-*benzocyclohepten*-1-*one* (32).—A solution of the ketone (30) (0.58 g, 3.3 mmol) and DDQ (1.63 g, 7.2 mmol) in dioxan (15 cm³), containing acetic acid (0.15 cm³) was heated under reflux under nitrogen for 5 h. The hydroquinone by-product (1.8 g) was filtered

off and washed with ether. The filtrate and washings were evaporated and the residue was dissolved in ethyl acetate (40 cm³). This solution was washed successively with aqueous sodium carbonate, water, and brine and then dried and evaporated. P.l.c. of the residue (alumina; petroleum–diethyl ether, 2 : 1, as eluant) gave the *tetraenone* (31), the slower of two closely-running compounds, as a deep yellow oil (0.100 g, 18%); $\nu_{max.}$ 1 655 and 1 630 cm⁻¹; δ 1.17 (3 H), 2.37 (1 H, d, J 18.5 Hz, 9-H_b), 2.97 (1 H, dd, J 18.5 and 9.0 Hz, 9-H_a), 5.85—6.2 (6 H), and 7.06 (1 H, dd, J 9.5 and 6.8 Hz, 3-H); m/e 172 (M^+). The faster running component was identified as the *trienone* (32) (0.107 g, 19%); $\nu_{max.}$ 1 695 cm⁻¹; δ 1.09 (3 H), 2.1—2.85 (6 H), 5.7—6.06 (4 H), and 6.16 (1 H, d, J 14 Hz); m/e 174 (M^+).

Attempted Methylation of the Tetraenone (31).—Potassium hydride (20% dispersion in oil; 150 mg, 0.75 mmol) was washed with dry hexane under nitrogen. Dry DME (4 cm³) and 18-crown-6 (105 mg, 0.4 mmol) were added and the suspension was cooled to −10 °C. A solution of the tetraenone (30) (65 mg, 0.38 mmol) in DME (2 cm³) was added to the stirred suspension. A deep purple coloration soon appeared and this intensified as the reaction proceeded. After the mixture had been stirred at −10 °C for 3 h, freshly distilled methyl fluorosulphonate (0.1 cm³, 1.26 mmol) was added. The purple colour was discharged and a red solution was formed. T.l.c. (alumina; petroleum–diethyl ether, 3 : 1, as eluant) showed complete conversion of the initial tetraenone (R_F 0.5) into an orange component (R_F 0.8). The solution was allowed to reach room temperature over 0.5 h and it was then filtered through Celite and concentrated under reduced pressure below 25 °C. The residue was extracted with dry carbon tetrachloride and the solution was evaporated to leave an oil. T.l.c. showed that the orange component (R_F 0.8) had been completely converted into a new substance (R_F 0.6). P.l.c. gave an oil (16 mg) which was identified as the enone (16) by comparison with the specimen prepared previously.

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