Dehydration of Dimeric 6-Hydroxycyclohexa-2,4-dienones—an Alternative Course for These Reactions and A Model for the Maytenone to Anhydromaytenone Transformation

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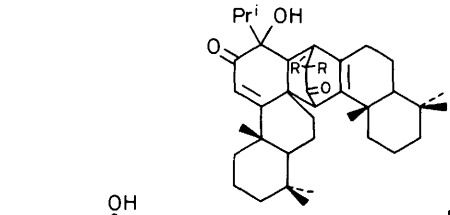
Periodate oxidation of thymol gave the dimeric 6-hydroxycyclohexa-2,4-dienone (12), 3,10-dihydroxy-3,10-di-isopropyl-6,11-dimethyltricyclo[6.2.2.$0^{2,7}$]dodeca-5,11-diene-4,9-dione, and dehydration of this yields 4,11-di-isopropyl-7,12-dimethyl-13-oxapentacyclo[7.2.1.$1^{4,12}$.$0^{2,11}$]tridec-6-ene-5,10-dione (13). The structure of (13) rests upon its ozonolysis to yield *anti*-7-acetyl-4,9-di-isopropyl-1-methyl-5-oxo-10-oxatetracyclo[4.4.0.$0^{2,4}$.$0^{3,8}$]decane-9-carboxylic acid (15) which can be isomerised to give 1-hydroxy-2,7-di-isopropyl-5-methyl-10-oxo-6-oxapentacyclo[7.2.1.$0^{2,4}$.$0^{3,8}$.$0^{5,12}$]dodecane-7-carboxylic acid (21) with dilute aqueous sodium hydroxide. Alternatively acid catalysed isomerisation of (15) gives the *syn* isomer (19) and the *X*-ray crystal structure of the corresponding methyl ester *syn*-7-acetyl-4,9-di-isopropyl-1-methyl-5-oxo-10-oxatetracyclo[4.4.0.$0^{2,4}$.$0^{3,8}$]decane-9-carboxylic acid methyl ester (20) is reported. The dehydration of (12) to give (13) is considered to be a model for the transformation of the bis-diterpene maytenone into anhydromaytenone.

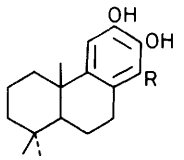
The isolation of the first bis-diterpene maytenone (1), $C_{40}H_{60}O_4$ was reported by Grant and Johnson in 1957.[1] The constitution (1) for maytenone was established [2] after the unprecedented thermal transformation which maytenone underwent on melting (197 °C) was rationalised. The diterpene related pyrocatechols (2) and (3) together with propene were identified [3,4] as the sole products of the thermolysis of maytenone, and a concerted mechanism for this reaction was proposed.[2] Model compounds, for example the dimeric 6-hydroxy-2,4-dienone (4) were found to behave in a similar way to maytenone upon melting,[5] and this gave weight to the structural proposal (1) for maytenone. We have recently carried out an *X*-ray crystallographic analysis [6] on maytenol, $C_{40}H_{62}O_4$ which can be obtained from maytenone by reduction of the saturated carbonyl function. This determination allows the deduction of the absolute stereochemistry of maytenone as (5). In the original publication [2] it was reported that maytenone gave a dehydration product anhydromaytenone ($C_{40}H_{58}O_3$) either on attempted acetylation (Ac_2O–$HClO_4$) or on treatment with boiling formic acid. No detailed structural proposals were advanced for this product although it was pointed out that the compound retained the two carbonyl groups ($\nu_{max.}$ 1 725 and 1 680 cm^{-1}) of maytenone. Further the i.r. spectrum showed no absorption due to hydroxy functions, a band at 1 050 cm^{-1} was assigned to an ether grouping and it was concluded that the dehydration reaction involved both of the hydroxy groups in maytenone.

Dehydration of dimeric 6-hydroxycyclohexa-2,4-dienones has been reported upon previously, thus the dimer (6) with sodium acetate/acetic anhydride gives [7] the aromatic acetate (9) albeit in very low yield. Higher yields of phenolic products related to (9) have been obtained by alkaline hydrolysis of dimeric 6-acetoxycyclohexa-2,4-dienones.[8] The course of the acid catalysed hydrolysis of the acetates (7) and (8) depends [9] upon the stereochemistry at C-3. Thus the stereoisomer (7) gives rise to (10), formally a dehydration product of the parent dimeric 6-hydroxycyclohexa-2,4-dienone. However the acetate (8) gives the cleaved product (11) on treatment with dilute aqueous ethanolic sulphuric acid. It was clear from the limited spectroscopic data quoted above for the maytenone ⟶ anhydromaytenone transformation that this reaction could not be interpreted in terms of any of the dehydration/aromatisation reactions described previously for dimeric 6-hydroxycyclohexa-2,4-dienones.

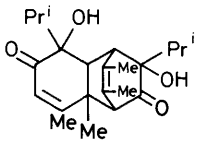
Since supplies of maytenone were no longer available we



(1) R = OH, R′ = Pr^i



(2) R = Pr^i
(3) R = H



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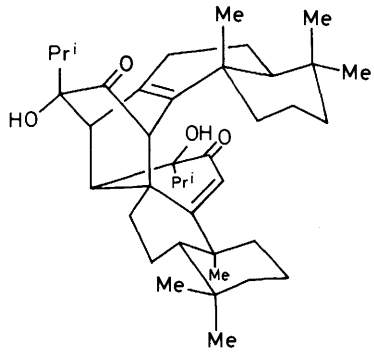
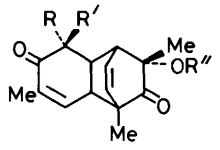
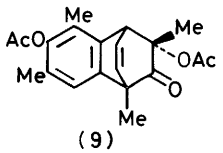


(5)

have turned our attention towards model compounds in order to try and deduce the course of the maytenone ⟶ anhydromaytenone transformation. Oxidation of thymol with sodium metaperiodate in dilute aqueous ethanol gave the dimeric 6-hydroxycyclohexa-2,4-dienone (12), $C_{20}H_{28}O_6$, in acceptable yield. The constitution (12) for the dimer follows from the precedents established by the extensive work of Adler [7,8] and others [10] in this field, and from a detailed consideration of the spectral characteristics of the compound. Examination of the high resolution ^1H n.m.r. (360 MHz, $CDCl_3$ solution) allowed a complete assignment of all resonances together with appropriate coupling constants, and these assignments were all confirmed by decoupling experiments. In addition preparation



(6) R = Me, R′ = OH, R″ = H
(7) R = Me, R′ = OAc, R″ = Ac
(8) R = OAc, R′ = Me, R″ = Ac



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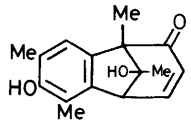

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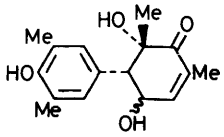


(11)

of the [5,7,8,12-$^2H_4$]-analogue of (12) from [2,4-$^2H_2$]thymol was carried out, and the ^1H n.m.r. spectrum of this confirmed the assignments due to 1-H and 2-H. The dimer is thus represented as the *endo* adduct as shown in (12); the tertiary hydroxy substituents at C-3 and C-10 are orientated as shown by analogy with previous studies.[8] In addition the ^1H n.m.r. spectrum of the dimer shows a highfield methyl doublet (δ 0.56, *J* 7 Hz) assigned to one of the methyl groups of the isopropyl residue attached to C-10 and shielded by the C(11)–C(12) double bond.

Treatment of the dimer (12) with formic acid at 100 °C during 1 h gave the anhydro dimer $C_{20}H_{26}O_3$ ($\nu_{max.}$ 1 720 and 1 680 cm^{-1}, bands assigned to saturated and α : β unsaturated ketones respectively, no absorption due to hydroxy groups was present). It was clear that the dehydration reaction of the dimer (12) was not following a course that could be accommodated within any of the schemes outlined previously for related dimeric 6-hydroxycyclohexa-2,4-dienones.[7-9] Rather the spectroscopic data indicated that the dehydration of the dimer (12) was following a similar course to that reported for maytenone.[2] We now formulate the anhydro dimer as the oxapentacyclo[7.2.1.1^{4,12}.0^{2,11}]tridec-6-ene derivative (13) and the ^1H n.m.r. spectrum confirmed this assignment; in particular a complete assignment of the protons attached to the critical carbon sequence C(1)–C(2)–C(3)–C(8)–C(9) was possible. Thus the cyclopropyl protons 1-H and 2-H appear as a doublet δ 2.12 (*J* 7.5 Hz) and a double doublet δ 1.97 (*J* 7.5, 6 Hz), 3-H is a lowfield triplet δ 2.8 coupled to 2-H and 8-H; 8-H is identified as a doublet (*J* 5 Hz) at δ 2.31. Finally, 9-H is a singlet δ 1.78; inspection of a Dreiding model of the anhydro dimer (13) shows that the torsion angle H(9)–C(9)–C(8)–H(8) is *ca.* 90°. Another significant feature of the n.m.r. spectrum is the absence of any highfield methyl absorption, the secondary methyl groups of the isopropyl groups now appearing as a series of four doublets (*J* 7 Hz) between δ 0.93 and 1.21. Finally the n.m.r. spectrum indicates the absence of the unconjugated C(11)–C(12) double bond of the dimer; that is, signals due to the olefinic proton and associated methyl group are absent. The dimer (4) $C_{22}H_{32}O_4$ was available from previous studies[5] on the maytenone thermolysis reaction and this compound also furnished an anhydro dimer (14) $C_{22}H_{30}O_3$ with hot formic acid. Interestingly, like (12) the dimer (4) also showed a highfield methyl signal in its ^1H n.m.r. spectrum (δ 0.58), and again this was absent in the spectrum of the anhydro product (14). The remaining spectroscopic data relating to the pair of compounds (4) and (14) agrees with that quoted above for the pair (12) and (13).

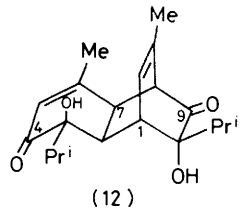
Formation of the anhydro dimer (13) is pictured as involving protonation of the 10-hydroxy group in the dimer (12); loss of water then occurs with participation of the C(11)–C(12) double bond, the resulting tertiary carbocation at C-11 being neutralized by transannular cyclisation with the remaining tertiary hydroxy group at C-3.

Confirmation of the structural proposal (13) for the anhydro dimer was next sought. Ozonolysis of the anhydro dimer gave the *anti*-7-acetyloxatetracyclo[4.4.0.0.^{2,4}.0^{3,8}]-decane derivative (15) * in 70% yield, together with some minor products, *vide infra*. Again a full ^1H n.m.r. assignment (see Experimental section) was possible for this compound based on the appropriate spin-spin decoupling results, and in addition degradation of the tetradeuterio anhydro dimer (13; ^2H at C-5, C-7, C-8, and C-12) gave the [2,6,7-$^2H_3$]-analogue of (15). Treatment of the ozonolysis product (15) with sodium borohydride resulted in the reduction of the more accessible carbonyl of the acetyl group, and this was followed by spontaneous cyclisation to give the lactone (17), $C_{19}H_{26}O_4$, $\nu_{max.}$ 1 742 and 1 733 cm^{-1}. Significant signals occurred in the ^1H n.m.r. spectrum at δ 4.27 (octet, *J* 6 and 3.5 Hz, 7-H) coupled to 8-H, δ 2.08 (dd, *J* 6.5, 3.5 Hz) and also to a methyl group δ 1.32 (d, *J* 6.5 Hz). The value of coupling between 7-H and 8-H indicates that the most probable orientation of the methyl group attached to C-7 is equatorial, and that the lactone ring adopts a chair-like conformation.

The ozonolysis product (15) was further degraded by the Curtis procedure to give the tricyclo[3.2.1.0^{2,7}]octan-6-one derivative (18), but in very disappointing yield. The ^1H n.m.r. spectrum of (18) is similar to those reported [11] for other synthetic tricyclo[3.2.1.0^{2,7}]octan-6-one derivatives. The ozonolysis product (16) underwent two interesting isomerisation reactions. Treatment of (15) with dilute aqueous sodium hydroxide caused epimerisation at C-7 and the resulting *syn*-7-acetyl compound (19) underwent an internal aldol reaction to give the oxapentacyclo[7.2.1.0^{2,4}.0^{3,8}.0^{5,12}]dodecane-7-carboxylic acid (21) isolated after acidification. The course of this reaction was monitored conveniently by ^1H n.m.r. spectroscopy, and this showed a decrease in the acetyl methyl signal δ 1.98 with concomitant appearance of a new AB system δ 2.88 and 2.47 *J* 18 Hz, assigned to the CH_2 protons at C-11. When the experiment was repeated using NaOD–D_2O these signals were absent as was the signal δ 2.02 (d, *J* 8 Hz, 9-H).

Epimerisation at C-7 in (15) and suppression of the internal aldol reaction was achieved by using trifluoroacetic acid in deuteriochloroform, again with ^1H n.m.r. monitoring. In this way the *syn*-7-acetyl isomer (19) was isolated, although it failed to crystallise; the corresponding methyl ester (20) $C_{20}H_{28}O_5$ was, however, readily prepared and identified. The significant difference between the ^1H n.m.r. spectra of the isomeric compounds (15) and (19) occurred in the region δ 3.6—2.0. For example 6-H which had appeared as a singlet δ 2.72 in (15) was a doublet δ 2.75 *J* 7 Hz in (19). In the *anti* compound (15) a coupling of 5 Hz was observed between 7-H and 8-H; however, in the *syn* compound no coupling was observed between these protons since the relevant torsion angle is now nearly 90°. Another interesting feature detected in the spectrum of the *syn* methyl ester (20) was the long range (*W*) coupling (*J ca.* 1.5 Hz) observed between 3-H and 7-H, coupling between these protons was not observed in the *anti* compound (15).

* The prefixes *anti* and *syn* are used to denote the orientation of the acetyl group with respect to the carbonyl group at C-5.[11]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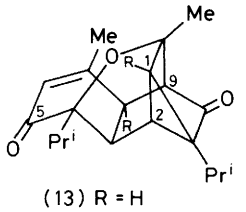
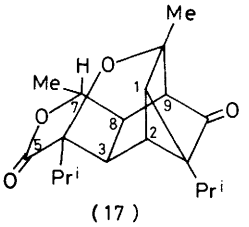

(13) R = H
(14) R = Me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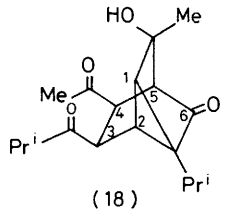
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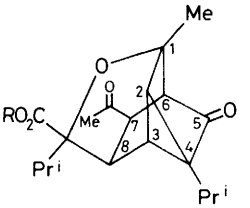
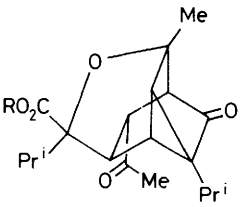
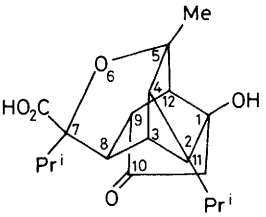

(15) R = H
(16) R = Me


(19) R = H
(20) R = Me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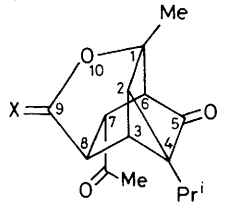
(22) X = CMe_2
(23) X = O

Whilst the structural proposal (13) for the anhydro dimer now seemed to be well founded we were mindful of the skeletal rearrangements that had been reported previously [9] as occurring during dehydration of dimeric 6-hydroxycyclohexa-2,4-dienones, and also those commonly found in the chemistry of the related bicyclo[2.2.2]octyl systems.[12] Accordingly we sought confirmation of our structure by *X*-ray crystallography. A survey of the various compounds available showed that crystals of the methyl ester of the isomerised ozonolysis product (20) would be suitable. The structure was readily solved using direct methods (see Experimental section for crystal data *etc.*), and refined to a final discrepancy index of 7.57% for 2 249 reflections. The molecular structure of (20) is shown in the Figure which contains the crystallographic numbering system, refined atomic co-ordinates are included in Table 2, while bond lengths and angles appear in Table 3. During the refinement it was discovered that the isopropyl substituent at C-6 was disordered and accordingly one of the methyl groups was included in two positions (C-18 and C-21) with arbitrary occupation factors of 0.5, no attempt was made to refine these occupation factors. The structure of the methyl ester (20) as revealed by *X*-ray crystallography confirms in all details the constitution of the anhydro dimer (13) deduced by the degradative sequence outlined above. In addition, the critical spin-spin coupling constants calculated [13] from the observed torsion angles obtained from the *X*-ray structure of (20) agree closely with those observed, and these are included in Table 1. It should be pointed out however that these torsion angles are

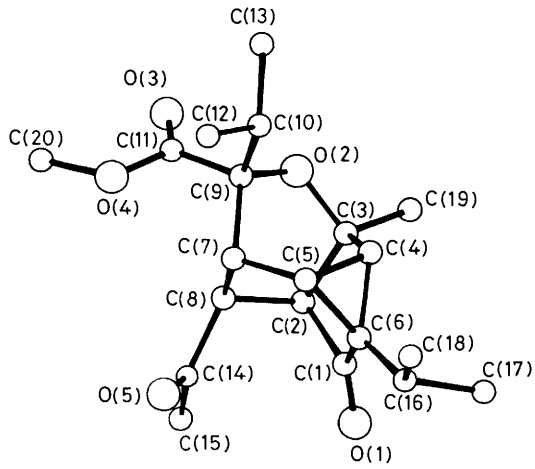

Figure. The molecular structure of *syn*-7-acetyl-4,9-di-isopropyl-1-methyl-5-oxo-10-oxatetracyclo[4.4.0.$0^{2,4}$.$0^{3,8}$]decane-9-carboxylic acid methyl ester (20)

Table 1. Selected torsion angles (°) for the compound (20), with calculated and found spin-spin coupling constants (Hz)

	Angle	*J*(calc) [13]	*J*(found)
H(2)–C(2)–C(3)–H(3)	6	8.1	7.9
H(3)–C(3)–C(8)–H(8)	25.5	6.6	6.1
H(8)–C(8)–C(7)–H(7)	85.6	0	0
H(7)–C(7)–C(6)–H(6)	38.2	5.0	6.0

based on calculated hydrogen positions, these fixed in turn by reference to the refined ' heavy ' atom co-ordinates.

Finally, besides the formation of the expected ozonolysis product (15) a number of minor products were obtained in very low yield; these were separable by column chromatography or h.p.l.c. In this way the isopropylidene compound (22), $C_{18}H_{24}O_3$, $\nu_{max.}$ 1 725 cm^{-1} was obtained. The ^1H n.m.r. spectrum of (22) showed *inter alia* resonances due to two olefinic methyl groups (δ 1.33 and 1.32 as singlets). Since a coupling of 5 Hz is observed between 6-H (δ 2.26) and 7-H (δ 2.68) it seems most probable that the 7-acetyl group assumes the *syn* configuration. In addition, the lactone (23) ($C_{15}H_{18}O_4$, $\nu_{max.}$ 1 780 and 1 725 cm^{-1}) was obtained in a yield of <1% from the ozonolysis degradation; alternatively, this compound could also be obtained by ozonolysis of the isopropylidene compound (22). Again the configuration of the acetyl group at C-7 is represented as *syn* to the ketone carbonyl function; here 6-H appears as a doublet (δ 2.08, *J* 5.4 Hz) coupled to 7-H (δ 2.37, dd, *J* 7 and 5.4 Hz).

In conclusion we propose that the maytenone→anhydromaytenone dehydration reaction [2] is of the same type as that reported here for the dehydration of the dimers (4) and (12) to yield, respectively, the anhydro dimers (14) and (13). However, final proof of this proposal must await the availability of additional supplies of maytenone.

Experimental

M.p.s are uncorrected. Light petroleum refers to the fraction b.p. 60—80 °C. Unless stated ^1H n.m.r. spectra were recorded using solutions in deuteriochloroform, and the following instruments were used: 360 MHz spectra Bruker WH-360 spectrometer, 220 MHz spectra Perkin-Elmer R34, and 100 MHz spectra Varian HA-100 spectrometer. I.r. spectra were measured in chloroform solution using a Perkin-Elmer Infracord 137B instrument, u.v. spectra were obtained in ethanol

solution. Mass spectra were recorded using either an A.E.I. MS-9 or a Kratos MS 80 mass spectrometer.

Periodate Oxidation of Thymol: Formation of 3,10-*Dihydroxy*-3,10-*di-isopropyl*-6,11-*dimethyltricyclo*[6.2.2.$0^{2,7}$]*dodeca*-5,11-*diene*-4,9-*dione* (12).—Thymol (50 g) dissolved in ethanol (95%, 600 ml) was added to a stirred solution of sodium metaperiodate (175 g) in water (3 l). After 20 h glycerol (50%, 100 ml) was added and the solution extracted with dichloromethane (4 × 150 ml, 2 × 100 ml, 2 × 50 ml). The combined dichloromethane extracts were washed with water, dried, and evaporated to give a dark red oily residue. The *dimer* (12) was obtained as an orange crystalline mass on addition of light petroleum; recrystallisation from light petroleum gave colourless prisms (13.5 g, 24.5%), m.p. 168—170 °C (decomp.) (Found: C, 72.05; H, 8.55%; M^+, 332. $C_{20}H_{28}O_4$ requires C, 72.25; H, 8.49%; M^+, 332); $\lambda_{max.}$ 237.5 nm; $\nu_{max.}$ 3 508, 3 435, 1 714, 1 672, 1 460, 1 375, 1 300, 1 152, 1 120, 1 015, 870, and 830 cm^{-1}; δ (360 MHz) 0.56 (3 H, d, *J* 7 Hz) and 0.95 (3 H, d, *J* 7 Hz) [10-CH(CH_3)$_2$], 0.8 (3 H, d, *J* 7 Hz) and 0.83 (3 H, d, *J* 7 Hz) [3-CH(CH_3)$_2$], 1.58 [1 H, sept, *J* 7 Hz, 10-C*H*(CH_3)$_2$], 1.59 (3 H, d, *J* 2 Hz, 11-CH_3), 1.76 [1 H, sept, *J* 7 Hz, 3-C*H*(CH_3)$_2$], 1.96 (3 H, d, *J* 1.5 Hz, 6-CH_3), 2.33 (1 H, s, OH), 3.08 (1 H, dd, *J* 8.5, 2.5 Hz, 7-H), 3.15 (1 H, dd, *J* 2.5, 2 Hz, 8-H), 3.26 (1 H, dd, *J* 8.5, 2 Hz, 2-H), 3.29 (1 H, dd, *J* 7, 2 Hz, 1-H), 3.79 (1 H, s, OH), 5.82 (1 H, d, quin, *J* 7 Hz, 2 Hz, 12-H), and 5.97 (1 H, quint, *J* 2 Hz, 5-H).

Dehydration of the Dimer: Formation of 4,11-*di-isopropyl*-7,12-*dimethyl*-13-*oxapentacyclo*[7.2.1.1^{4,12}.0^{2,11}]*tridec*-6-*ene*-5,10-*dione* (13).—The preceding dimer (10 g) was dissolved in formic acid (200 ml) and boiled under reflux during 2 h. The solution was diluted with ice–water (1 l) and extracted several times with ether. The combined ethereal extracts were washed with water and aqueous sodium hydrogen carbonate and then dried. The volume of ether was reduced and then chromatographed over alumina; elution with ether gave a fraction evaporation of which furnished the *anhydro dimer* (13) (7 g, 74%), m.p. 129—131 °C (Found: C, 76.4; H, 8.25%; M^+, 314. $C_{20}H_{26}O_3$ requires C, 76.40; H, 8.33%; M^+, 314); $\lambda_{max.}$ 238.5 nm; $\nu_{max.}$ 2 925, 1 720, 1 680, 1 460, 1 380, 1 140, 1 115, 1 020, 955, 920, and 860 cm^{-1}; δ (360 MHz) 0.93 (3 H, d, *J* 7 Hz, CH_3), 0.99 (3 H, d, *J* 7 Hz, CH_3), 1.03 (3 H, d, *J* 7 Hz, CH_3), 1.21 (3 H, d, *J* 7 Hz, CH_3), 1.29 (3 H, s, 12-CH_3), 1.78 (1 H, bs, 9-H) 1.81 (3 H, d, *J* 2 Hz, 7-CH_3), 1.90 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$] 1.97 (1 H, dd, *J* 7.5, 6 Hz, 2-H), 2.12 (1 H, d, *J* 7.5 Hz, 1-H), 2.31 (1 H, d, *J* 5 Hz, 8-H), 2.40 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 2.8 (1 H, t, *J* 6 Hz, 5 Hz, 3-H), and 5.65 (1 H, q, *J* 2 Hz, 6-H).

Ozonolysis of the Anhydro Dimer: Formation of anti-7-*Acetyl*-4,9-*di-isopropyl*-1-*methyl*-5-*oxo*-10-*oxatetracyclo*[4.4.-0.$0^{2,4}$.$0^{3,8}$]*decane*-9-*carboxylic Acid* (15), anti-7-*Acetyl*-4-*isopropyl*-1-*methyl*-10-*oxatetracyclo*[4.4.0.$0^{2,4}$.$0^{3,8}$]*decane*-5,9-*dione* (22), *and* anti-7-*Acetyl*-4-*isopropyl*-9-*isopropylidene*-1-*methyl*-10-*oxatetracyclo*[4.4.0.$0^{2,4}$.$0^{3,8}$]*decan*-5-*one* (23).—The anhydro dimer (1 g) in dry ethyl acetate (100 ml) was treated with dried ozonised oxygen (*ca.* 7% O_3) at −25 °C during 45 min. The solvent was evaporated under reduced pressure, water was added, and the mixture boiled under reflux for 15 min. The cooled solution was extracted several times with ether and the combined ether layers were washed with dilute aqueous sodium hydrogencarbonate (for the further treatment of the ethereal layer see below). The hydrogencarbonate extract was acidified and extracted with ether; after washing and drying of the ether extract, evaporation gave a yellow gum. Trituration of the latter with light petroleum yielded the *ozonolysis product* (15) (740 mg, 70%) as colourless prisms, m.p. 126—127 °C after recrystallisation from light petroleum–ether (Found: C, 68.0; H, 7.6%; M^+, 334. $C_{19}H_{26}O_5$ requires C, 68.24; H, 7.84%; M^+, 334); $\lambda_{max.}$ 260 nm; $\nu_{max.}$ 3360, 2 930, 1 764, 1727, 1 460, 1 360, 1 300, 1 180, 1 150, 1 110, 1 025, 995, 972, 910, and 874 cm^{-1}; δ (C_6D_6, 220 MHz) 1.00 (3 H, d, *J* 7 Hz, CH_3), 1.07 (3 H, d, *J* 7 Hz, CH_3), 1.11 (3 H, d, *J* 7 Hz, CH_3), 1.14 (3 H, d, *J* 7 Hz, CH_3), 1.35 (3 H, s, 1-CH_3), 1.78 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 1.92 (1 H, d, *J* 8 Hz, 2-H), 1.98 (3 H, s, $COCH_3$), 2.07 (1 H, dd, *J* 8, 5 Hz, 3-H), 2.37 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 2.72 (1 H, s, 6-H), 2.84 (1 H, d, *J* 5 Hz, 7-H), and 3.37 (1 H, t, *J* 5 Hz, 8-H).

The corresponding *methyl ester* (16), m.p. 139.5—140.5 °C was prepared by reaction of the carboxylic acid with ethereal diazomethane; it crystallised from light petroleum (Found: C, 69.1; H, 7.9%; M^+, 348. $C_{20}H_{28}O_5$ requires C, 68.96; H, 8.05%; M^+, 348); $\nu_{max.}$ 2 930 and 1 724, cm^{-1}; δ ($CDCl_3$, 100 MHz) 0.9 (3 H, d, *J* 7 Hz, CH_3), 0.97 (3 H, d, *J* 7 Hz, CH_3), 0.99 (3 H, d, *J* 7 Hz, CH_3), 1.05 (3 H, d, *J* 7 Hz, CH_3), 1.43 (3 H, s, 1-CH_3), 1.94 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 2.07 (1 H, m, 2-H or 3-H), 2.10 (4 H, bs, $COCH_3$ and 2-H or 3-H), 2.40 [1 H, sept, C*H*(CH_3)$_2$], 2.53 (1 H, s, 6-H), 2.74 (1 H, d, *J* 4.5 Hz, 7-H), 3.42 (1 H, m, 8-H), and 3.62 (3 H, s, CO_2CH_3).

The ether layers remaining after the removal of the major ozonolysis product (15) were evaporated and the residue dissolved in chloroform and chromatographed over alumina; alternatively the separation could be achieved by h.p.l.c. The following compounds were separated and identified.

(a) anti-7-*Acetyl*-4-*isopropyl*-9-*isopropylidene*-1-*methyl*-10-*oxatetracyclo*[4.4.0.$0^{2,4}$.$0^{3,8}$]*decan*-5-*one* (22) 1%), m.p. 172—173 °C (decomp.) (Found: C, 74.85; H, 8.3%; M^+, 288. $C_{18}H_{24}O_3$ requires C, 74.96; H, 8.39%; M^+ 288); $\nu_{max.}$ 2 950, 1 725, 1 375, 1 133, 1 070, and 940 cm^{-1}; δ (C_6D_6, 220 MHz) 0.93 (3 H, d, *J* 7 Hz, CH_3), 0.99 (3 H, d, *J* 7 Hz, CH_3), 1.27 (6 H, s, $COCH_3$ and 1-CH_3), 1.32 (3 H, s, vinylic CH_3), 1.33 (3 H, s, vinylic CH_3), 1.84 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 2.04 (1 H, d, *J* 6 Hz, 3-H), 2.22 (1 H, d, *J* 6 Hz, 2-H), 2.26 (1 H, d, *J* 5 Hz, 6-H), 2.68 (1 H, dd, *J* 7, 5 Hz, 7-H), and 3.09 (1 H, d, *J* 7 Hz, 8-H).

(b) anti-7-*Acetyl*-4-*isopropyl*-1-*methyl*-10-*oxatetracyclo*-[4.4.0.$0^{2,4}$.$0^{3,8}$]*decane*-5,9-*dione* (23) (<1%), m.p. 85—86 °C (Found: C, 68.3; H, 6.7%; M^+, 262. $C_{15}H_{18}O_4$ requires C, 68.68; H, 6.92%; M^+, 262]; $\nu_{max.}$ 2 960, 1 780, 1 725, 1 375, 1 115, and 930 cm^{-1}; δ (C_6D_6, 220 MHz) 0.75 (3 H, d, *J* 7 Hz, CH_3), 0.81 (3 H, d, *J* 7 Hz, CH_3), 1.15 (3 H, s, 1-CH_3), 1.21 (3 H, s, $COCH_3$), 1.68 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 1.71 (1 H, d, *J* 6 Hz, 3-H), 1.95 (1 H, dd, *J* 7.2, 1.8 Hz, 2-H), 2.08 (1 H, d, *J* 5.4 Hz, 6-H), 2.37 (1 H, dd, *J* 7.2, 5.4 Hz, 7-H), and 2.72 (1 H, dd, *J* 7.2, 1.8 Hz, 8-H).

Reduction of the Ozonolysis Product (15)*: Formation of* 4,11-*Di-isopropyl*-7,12-*dimethyl*-6,13-*dioxapentacyclo*[7.2.1.1^{4,12}.-0^{2,11}]*tridecane*-5,10-*dione* (17).—The ozonolysis product (15) (200 mg) in methanol (100 ml) was stirred at room temperature during the addition of sodium borohydride (120 mg). After 5 h the solution was diluted with water and acidified with dilute hydrochloric acid. The crude product was obtained as a clear gum by extraction with ether, the *lactone* (17) was obtained by preparative t.l.c. and crystallisation from light petroleum (80 mg, 42%), m.p. 129—130 °C (Found: C, 71.65; H, 7.95%; M^+ 318. $C_{19}H_{26}O_4$ requires C, 71.67; H, 8.23%; M^+, 318); $\nu_{max.}$ 2 950, 1 742, 1 733, 1 476, and 1 142 cm^{-1}; δ ($CDCl_3$, 220 MHz) 0.95 (3 H, d, *J* 7 Hz, CH_3), 1.02 (3 H, d, *J* 7 Hz, CH_3), 1.08 (3 H, d, *J* 7 Hz, CH_3), 1.30 (3 H, d, *J* 7 Hz, CH_3), 1.32 (3 H, d, *J* 6.5 Hz, 7-CH_3), 1.37 (3 H, s, 12-CH_3), 1.89 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 1.94 (1 H, s, 9-H), 1.95 (1 H, d, *J* 6 Hz, 2-H), 2.08 (1 H, dd, *J* 6, 3.5 Hz, 8-H), 2.13

Table 2. Compound (20) Refined atomic co-ordinates ($\times 10^4$); standard deviations in parentheses

	x/a	*y/b*	*z/c*
O(1)	4 612(5)	9 690(3)	8 303(3)
C(1)	4 126(6)	8 376(4)	8 025(4)
C(2)	3 461(5)	7 467(4)	8 781(3)
C(3)	4 244(5)	6 309(4)	8 493(3)
O(2)	3 106(3)	4 932(3)	8 543(2)
C(9)	1 482(5)	4 225(4)	7 668(3)
C(7)	1 248(5)	5 388(4)	7 183(3)
C(8)	1 477(5)	6 654(4)	8 253(3)
C(14)	607(7)	7 615(5)	7 995(5)
O(5)	−227(7)	7 321(5)	7 030(4)
C(15)	782(8)	8 885(6)	8 997(5)
C(5)	2 679(5)	5 837(4)	6 533(3)
C(4)	4 402(5)	6 160(4)	7 230(4)
C(6)	4 111(6)	7 391(4)	6 904(4)
C(16)	4 904(7)	8 031(5)	6 012(5)
C(17)	6 731(9)	8 866(7)	6 423(6)
C(18)	4 480(10)	6 919(9)	4 780(6)
C(21)	5 860(20)	1 280(20)	4 370(20)
C(10)	1 522(6)	2 908(4)	6 471(3)
C(12)	000(8)	2 191(5)	5 682(4)
C(13)	1 701(7)	1 769(5)	7 264(4)
C(11)	97(5)	3 706(4)	8 399(3)
O(3)	333(4)	3 512(3)	9 261(2)
O(4)	−1 449(4)	3 495(3)	7 759(2)
C(20)	−2 872(6)	3 031(6)	8 324(4)
C(19)	5 929(6)	6 758(5)	9 347(5)

(1 H, d, *J* 6 Hz, 1-H), 2.45 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 2.70 (1 H, t, *J* 6 Hz, 3-H), and 4.27 (1 H, oct, *J* 6, 3.5 Hz, 7-H).

Curtius Degradation yf the Ozonolysis Product (15)*: Formation of* 4-*Acetyl*-8-*hydroxy*-3-*isobutyryl*-7-*isopropyl*-8-*methyltricyclo*[3.2.1.$0^{2,7}$]*octan*-6-*one* (18).—The ozonolysis product (700 mg) was treated with an excess of thionyl chloride at 100 °C during.3 h. Excess of reagent was removed under diminished pressure leaving a yellow gum ($\nu_{C=O}$ 1 780 cm^{-1} acid chloride) which was dissolved in ether (20 ml) and added with vigorous stirring to a mixture of hydrazine hydrate (60%, 10 ml) and aqueous sodium hydroxide (1M; 10 ml). After 4 h the ether layer was separated and the ether evaporated, the residue was treated with concentrated hydrochloric acid (10 ml) and saturated aqueous sodium nitrite (5 ml). The mixture was extracted with chloroform after *ca.* 3 h, and the residue from this extract ($\nu_{max.}$ 2 130, azide and 2 250 cm^{-1} isocyanate) was boiled in benzene during 1 h. Ethanol (95%, 50 ml) was then added and the solution heated under reflux for 8 h; subsequently, the solvents were evaporated and the residue separated by t.l.c. The *triketone* (18) (20 mg, 3%), m.p. 82—83 °C crystallised as colourless needles from light petroleum (Found: C, 69.95; H, 8.45%; M^+, 306. $C_{18}H_{26}O_4$ requires C, 70.56; H, 8.55%; M^+, 306); $\nu_{max.}$ 3 400, 2 930, 1 725, 1 695, and 1 145 cm^{-1}; δ ($CDCl_3$, 220 MHz), 0.92 (3 H, d, *J* 7 Hz, CH_3), 0.96 (3 H, d, *J* 7 Hz, CH_3), 1.15 (3 H, d, *J* 7 Hz, COCHC*H*$_3$), 1.22 (3 H, d, *J* 7 Hz, COCHC*H*$_3$), 1.43 (3 H, s, CH_3), 1.88 (1 H, dd, *J* 7, 2 Hz, 2-H), 2.03 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 2.23 (1 H, d, *J* 7 Hz, 1-H), 2.27 (3 H, s, CH_3), 2.46 (1 H, d, *J* 2 Hz, 5-H), 2.91 [1 H, sept, *J* 7 Hz, COC*H*(CH_3)$_2$], 3.31 (1 H, dd, *J* 6, 2 Hz, 3-H), 4.33 (1 H, dd, *J* 6, 2 Hz, 4-H), and 5.34 (1 H, s, OH).

Base-catalysed Isomerisation of the Ozonolysis Product (15)*: Isolation of* 1-*Hydroxy*-2,7-*di-isopropyl*-5-*methyl*-10-*oxo*-6-*oxapentacyclo*[7.2.1.$0^{2,4}$.$0^{3,8}$.$0^{5,12}$]*dodecane*-7-*carboxylic Acid* (21).—The ozonolysis product (15) (100 mg) in aqueous sodium hydroxide (1M; 10 ml) was heated at 60 °C during 15 min.

Table 3. Compound (20) bond length (Å) and bond angles (°); standard deviations in parentheses

Bond lengths

C(1)–O(1)	1.215(5)	C(16)–C(18)	1.541(9)
C(1)–C(2)	1.504(5)	C(16)–C(21)	1.268(13)
C(2)–C(3)	1.564(6)	C(7)–C(8)	1.527(5)
C(2)–C(8)	1.555(6)	C(7)–C(9)	1.549(5)
C(3)–C(4)	1.531(5)	C(8)–C(14)	1.523(6)
C(3)–C(19)	1.511(6)	C(14)–O(5)	1.201(6)
C(3)–O(2)	1.435(4)	C(14)–C(15)	1.490(7)
C(4)–C(5)	1.484(6)	C(9)–C(10)	1.543(5)
C(4)–C(6)	1.534(5)	C(9)–C(11)	1.533(5)
C(5)–C(6)	1.540(5)	C(10)–C(12)	1.521(6)
C(5)–C(7)	1.529(5)	C(10)–C(13)	1.536(6)
C(6)–C(1)	1.469(6)	C(11)–O(3)	1.201(4)
C(6)–C(16)	1.521(5)	C(11)–O(4)	1.336(5)
C(16)–C(17)	1.430(8)	O(4)–C(20)	1.457(5)
		C(9)–O(2)	1.451(4)

Bond angles

C(6)–C(1)–O(1)	126.5(4)	C(6)–C(16)–C(18)	113.7(8)
C(6)–C(1)–C(2)	107.6(3)	C(17)–C(16)–C(21)	110.4(5)
O(1)–C(1)–C(2)	125.9(4)	C(17)–C(16)–C(18)	112.6(9)
C(1)–C(2)–C(3)	103.3(3)	C(5)–C(7)–C(8)	111.2(3)
C(1)–C(2)–C(8)	105.0(3)	C(5)–C(7)–C(9)	106.7(3)
C(3)–C(2)–C(8)	107.3(3)	C(8)–C(7)–C(9)	105.4(3)
C(2)–C(3)–C(4)	102.7(3)	C(7)–C(8)–C(2)	105.4(3)
C(2)–C(3)–C(19)	112.5(3)	C(7)–C(8)–C(14)	113.5(3)
C(4)–C(3)–C(19)	114.4(4)	C(2)–C(8)–C(14)	114.5(3)
C(2)–C(3)–O(2)	118.8(3)	C(8)–C(14)–O(5)	120.9(4)
O(2)–C(3)–C(16)	105.9(3)	C(8)–C(14)–C(15)	116.9(4)
O(2)–C(3)–C(4)	109.7(3)	O(5)–C(14)–C(15)	122.3(5)
C(3)–C(4)–C(5)	107.4(3)	C(7)–C(9)–C(10)	114.7(3)
C(3)–C(4)–C(6)	109.3(3)	C(7)–C(9)–C(11)	110.5(3)
C(5)–C(4)–C(6)	61.4(3)	C(7)–C(9)–O(2)	107.7(3)
C(4)–C(5)–C(6)	60.9(3)	O(2)–C(9)–C(10)	108.3(3)
C(4)–C(5)–C(7)	112.3(3)	O(2)–C(9)–C(11)	104.9(3)
C(6)–C(5)–C(7)	123.5(3)	C(10)–C(9)–C(11)	110.3(3)
C(5)–C(6)–C(4)	57.7(3)	C(9)–C(10)–C(12)	113.7(4)
C(5)–C(6)–C(1)	114.3(3)	C(9)–C(10)–C(13)	112.4(3)
C(1)–C(6)–C(4)	103.9(3)	C(12)–C(10)–C(13)	110.5(4)
C(5)–C(6)–C(16)	121.7(4)	C(9)–C(11)–O(3)	125.9(4)
C(1)–C(6)–C(16)	119.3(4)	C(9)–C(11)–O(4)	110.6(3)
C(4)–C(6)–C(16)	124.3(4)	O(3)–C(11)–O(4)	123.5(4)
C(6)–C(16)–C(17)	112.0(5)	C(11)–O(4)–C(20)	115.8(3)
C(6)–C(16)–C(21)	114.8(4)	C(9)–O(2)–C(3)	114.2(3)

After acidification the product was isolated by extraction with chloroform and purified by t.l.c. using benzene–methanol–acetic acid (45 : 8 : 4) as eluant and crystallised from ether–light petroleum. The *isomer* (21) (53 mg, 53%), m.p. 188—190 °C formed colourless prisms (Found: C, 68.3; H, 7.55%; M^+, 334. $C_{19}H_{26}O_5$ requires C, 68.26; H, 7.84%; M^+, 334]; $\nu_{max.}$ 3 350, 2 940, 1 768, 1 754, 1 355, 1 305, 1 142, and 1 013 cm^{-1}; δ ($CDCl_3$, 220 MHz) 0.84 (3 H, d, *J* 7 Hz, CH_3), 0.94 (3 H, d, *J* 7 Hz, CH_3), 0.95 (3 H, d, *J* 7 Hz, CH_3), 1.00 (3 H, d, *J* 7 Hz, CH_3), 1.17 (1 H, t, *J* 8, 6 Hz, 3-H), 1.55 (3 H, s, 5-CH_3), 1.63 (1 H, d, *J* 8 Hz, 4-H), 2.02 (1 H, d, *J* 8 Hz, 9-H), 2.14 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 2.18 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 2.23 (1 H, d, *J* 8 Hz, 12-H), 2.47 (1 H, d, *J* 18 Hz, 11-H), 2.75 (1 H, d, *J* 6 Hz, 8-H), 2.88 (1 H, d, *J* 18 Hz, 11-H), and 3.71 (3 H, s, CO_2CH_3).

Acid-catalysed Isomerisation of the Ozonolysis Product (15)*; Isolation of* syn-7-*Acetyl*-4,9-*di-isopropyl*-1-*methyl*-5-*oxo*-10-*oxatetracyclo*[4.4.0.$0^{2,4}$.$0^{3,8}$]*decane*-9-*carboxylic Acid Methyl Ester* (20).—The ozonolysis product (15) (200 mg) was dissolved in chloroform (10 ml) and treated with trifluoroacetic acid (1.5 ml). The progress of the reaction was monitored by

n.m.r. spectroscopy. After 5 days the reaction mixture was quenched by addition of water (10 ml). The chloroform layer was separated and washed several times with water and then dried and evaporated. The *carboxylic acid* (164 mg) (19) was obtained as a gum which failed to crystallise (Found: M^+, 334. $C_{19}H_{26}O_5$ requires M^+, 334); δ ($CDCl_3$ + TFA, 220 MHz) 0.92 (3 H, d, *J* 7 Hz, CH_3), 1.02 (3 H, d, *J* 7 Hz, CH_3), 1.05 (3 H, d, *J* 7 Hz, CH_3), 1.19 (3 H, d, *J* 7 Hz, CH_3), 1.52 (3 H, s, 1-CH_3), 1.93 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 2.24 (3 H, s, $COCH_3$), 2.32 (1 H, dd, *J* 7, 5 Hz, 3-H), 2.38 (1 H, d, *J* 7 Hz, 2-H), 2.45 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 2.75 (1 H, d, *J* 7 Hz, 6-H), 2.95 (1 H, d, *J* 7 Hz, 7-H), and 3.26 (1 H, d, *J* 5 Hz, 8-H). The gum was dissolved in methanol (20 ml) and treated with an excess of diazomethane in ether solution; evaporation of the solvents afforded the *methyl ester* (20) (127 mg), m.p. 159—160 °C as colourless plates from light petroleum–ether (Found: C, 68.95; H, 7.95%; M^+, 348.1953. $C_{20}H_{28}O_5$ requires C, 68.94, H, 8.09%; M^+, 348.1936); $\nu_{max.}$ 2 930 and 1 725 cm^{-1}; δ (C_6D_6, 220 MHz) 0.92 (3 H, d, *J* 7 Hz, CH_3), 0.95 (3 H, d, *J* 7 Hz, CH_3), 1.01 (3 H, d, *J* 7 Hz, CH_3), 1.05 (3 H, d, *J* 7 Hz, CH_3), 1.14 (3 H, s, 1-CH_3), 1.44 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 1.50 (1 H, d, *J* 7.9 Hz, 2-H), 1.68 (1 H, m, 3-H), 1.73 (3 H, s, $COCH_3$), 2.14 (1 H, bd, *J* 6 Hz, 6-H), 2.57 (1 H, dd, *J* 6, 1.5, 7-H), 3.33 (3 H, s, CO_2CH_3), and 3.39 (1 H, d, *J* 6.1 Hz, 8-H).

Crystal Data.—$C_{20}H_{28}O_5$, M = 348.4. Triclinic, a = 8.534(2), b = 10.441(3), c = 12.185(3) Å, α = 105.487(7), β = 96.46(9), γ = 111.30(7)°, U = 947.9 Å^3, D_c = 1.32, Z = 2, Space group $P\bar{1}$, Cu-K_α radiation λ = 1.5418 Å.

Three-dimensional diffraction data were collected using an Enraf-Nonius CAD-4 diffractometer, out to a value of θ ≤ 66°. A total of 3 315 reflections were scanned and of these 2 249 had $I > 3\sigma(I)$ and were used in the refinement. The structure was solved using the SHELX direct methods program although only 15 of the 25 ' heavy ' atoms were detected. The resulting trial structure was refined using the CRYSTALS program when the missing atoms were located using Fourier methods. Using isotropic thermal parameters the refinement converged with an R value of 12.1%, then further refinement was continued with anisotropic temperature factors. After several cycles of such refinement a peak of high residual electron density in the region of C-16 (*cf.* Figure) was located in a Fourier map, indicating that this isopropyl group was disordered. Accordingly the 18-methyl group was located in two positions each with arbitrary occupation factors of 0.5. The majority of the hydrogen atoms were then detected from a difference map and then located in their calculated positions, further refinement (hydrogen atoms were not refined) gave a final R value of 7.57%.

Observed and calculated structure factors together with refined anisotropic thermal parameters are listed in Supplementary Publication No. SUP. 23744 (23 pp.).*

3,10-*Dihydroxy*-3,10-*di-isopropyl*-6,7,11,12-*tetramethyl*-[6.2.2.0^{2,7}]*dodeca*-5,11-*diene*-4,9-*dione* (4).—The dimer (4), m.p. 186—187 °C (lit.,[5] 185—186 °C), was prepared as described previously; δ (100 MHz) 0.58 (3 H, d, *J* 7 Hz, CH_3), 0.88 (3 H, d, *J* 7 Hz, CH_3), 0.94 (3 H, d, *J* 7 Hz, CH_3), 0.99 (3 H, d, *J* 7 Hz, CH_3), 1.34 (3 H, s, CH_3), 1.46 (3 H, s, CH_3), 1.61 (3 H, s, CH_3), 1.69 [1 H, m, C*H*(CH_3)$_2$], 1.73 [1 H, m, C*H*(CH_3)$_2$], 1.90 (3 H, d, *J* 1.5 Hz, 6-CH_3), 2.53 (1 H, s, OH), 2.79 (1 H, s, 8-H), 2.99 (1 H, d, *J* 2 Hz, 2-H), 3.18 (1 H, d, *J* 2 Hz, 1-H), 3.75 (1 H, s, OH), and 5.95 (1 H, d, *J* 1.5 Hz, 5-H).

Dehydration of the Dimer (4) : *Formation of* 4,11-*Di-isopropyl*-1,7,8,12-*tetramethyl*-13-*oxapentacyclo*[7.2.1.1^{4,12}.0^{2,11}]-*tridec*-6-*ene*-5,10-*dione* (14).—Reaction of the dimer (4) (1.5 g) with hot formic acid (30 ml) furnished the *anhydro dimer* (14) (480 mg, 33%), m.p. 189—190 °C (Found: C, 77.20; H, 8.77%; M^+, 342. $C_{22}H_{30}O_3$ requires C, 77.15; H, 8.83%; M^+ 342); $\nu_{max.}$ 1 718, 1 676, and 1 100 cm^{-1}; δ (100 MHz) 0.95 (3 H, s, CH_3), 0.98 (3 H, d, *J* 7 Hz, CH_3), 1.14 (3 H, s, CH_3), 1.16 (3 H, d, *J* 7 Hz, CH_3), 1.19 (3 H, d, *J* 7 Hz, CH_3), 1.22 (3 H, s, CH_3), 1.24 (3 H, d, *J* 7 Hz, CH_3), 1.54 (1 H, d, *J* 6 Hz, 2-H), 1.57 (1 H, bs, 9-H), 1.73 (3 H, d, *J* 1.5 Hz, 7-CH_3), 2.10 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 2.15 [1 H, sept, *J* 7 Hz, C*H*(CH_3)$_2$], 2.42 (1 H, dd, *J* 6, 1.5 Hz, 3-H), and 5.56 (1 H, d, *J* 1.5 Hz, 6-H).

Formation of the Deuteriated Compounds.—(*a*) *Deuteriated dimer* (12). Thymol was equilibrated with triethylamine and ^2H_2O to give 3-*methyl*-6-*isopropyl*[2,4-$^2H_2$]*phenol* (66.2% $C_{10}H_{12}{}^2H_2O$ by mass spectrometry) and this material was oxidised with sodium metaperiodate as described above to give the [5,7,8,12-$^2H_4$]-dimer (12) [Found: M^+, 332 ($C_{20}H_{28}O_4$) 2.5, 333 ($C_{20}H_{27}{}^2HO_4$) 2.0; 334 ($C_{20}H_{26}{}^2HO_4$) 7.1; 335 ($C_{10}H_{25}{}^2H_3O_4$) 29.5 and 336 ($C_{20}H_{24}{}^2H_4O_4$) 59%]. (*b*) *Deuteriated anhydro dimer* (13). The preceding dimer gave the [1,6,8,9-$^2H_4$]-anhydro dimer (13) with hot formic acid [Found: M^+, 314 ($C_{20}H_{26}O_3$) 5.1; 315 ($C_{20}H_{25}{}^2HO_3$) 1.4; 316 ($C_{20}H_{24}{}^2H_2O_3$) 7.1; 317 ($C_{20}H_{23}{}^2H_3O_3$) 30.5; 318 ($C_{20}H_{22}{}^2H_4O_3$) 56.3%].

The other deuteriated compounds mentioned in the text were prepared according to the experimental procedures discussed above for the non-deuteriated analogues.

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* For details of the Supplementary publications scheme, see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 1*, 1984, Issue 1.

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