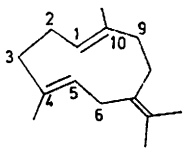
Medium-ring 1,5-Dienes. Part III.[1] Cyclisation of Germacra-1(10),4,7-(11)-triene Oxides

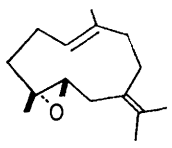
By **Edward D. Brown, James K. Sutherland,*** and (in part) **Teng W. Sam,** Chemistry Department, Imperial College, London SW7, and Chemistry Department, The University, Manchester M13 9PL

The mono-oxides of germacra-1(10),4,7(11)-triene (1) have been prepared and an explanation is offered for the relative proportions obtained. Cyclisation of the 1,10-oxide yields selinane derivatives, whereas guaianes are obtained from the 4,5-oxide. Reductive cyclisation of the latter gives a guaiane, and on pyrolysis it is converted into a bicyclo[4.1.0]heptane derivative having the carbon skeleton found in the carabrone group of sesquiterpenes.

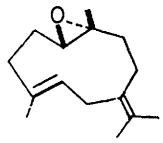
In the preceding paper [1] we have shown that the predominant cyclisation mode of germacratriene (1) with electrophilic and radical reagents affords selinane derivatives. We now extend the cyclisation studies to the epoxides (2) and (3) which were prepared by reaction of the triene (1) with peracetic acid (1 mol. equiv.). The pure epoxide (2) could be crystallised directly from the oxidation mixture, leaving mother liquors containing *ca.* 80% of the isomer (3); this mixture was used in subsequent cyclisation studies. It was not possible to determine the composition of the epoxide mixture accurately by spectroscopic methods; however chromatography on alumina under precisely controlled conditions established that a reproducible fraction (82%) of (2) could be recovered while (3) was completely destroyed. Thus by chromatography of a 1 : 1 mixture of pure (2) and the epoxidation mixture it was estimated that the ratio of (2) : (3) present in the original epoxidation mixture was 7 : 3. Confirmation of this came from studies on the cyclisation of the mixture, which also led to the isolation of 2% of the oxide (4) which survived the acidic conditions. The structure of (4) was assigned by n.m.r. spectroscopy which showed the presence of two shielded vinylic methyl groups (τ 8.49), two vinyl protons (τ 5.22), and two quaternary methyl groups (τ 8.68 and 8.72). The structures of (2) and (3) followed from the nature of their cyclisation products. Reaction



(1)



(2)



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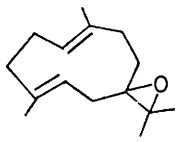

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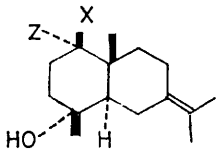
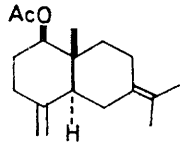




(10)

(5) Z=H, X=OH

(6) Z=H, X=OAc

(7) Z=H, X=$SO_3C_7H_7$

(8) XZ=:O

(9) X=Z=H

of the mixture rich in (3) with 0.5N-sulphuric acid in acetone gave the diol (5) which could be isolated by

[1] Part II, E. D. Brown, T. W. Sam, J. K. Sutherland, and A. Torre, preceding paper.

direct crystallisation. Its structure and stereochemistry were established by oxidation to the ketone (8) followed by Wolff–Kishner reduction to the known alcohol (9); the equatorial disposition of the secondary hydroxy-group was clear from the $W_{\frac{1}{2}}$ value of the C-1 proton signal [*ca.* 16 Hz in (5), (6), and (7) [2]]. From the mother liquors a mixture of olefinic alcohols (τ 4.75, 5.23, and 5.45) was isolated by chromatography and, after acetylation and chromatography on silver nitrate–silica gel the crystalline acetate (10), $\nu_{max.}$ 895 cm^{-1}, τ 5.3 (3 H, m), was obtained. The same compound was the major product isolated after dehydration of the acetate (6) with phosphoryl chloride–pyridine. Since the diol (5) is not converted into the dehydration product mixture under the cyclisation conditions, the original epoxidic oxygen atom is present at C-1 in the diol (5), and this leads to assignment of structure (3) to the precursor epoxide. The epoxide (3) thus cyclises in the same structural [3] and stereochemical [4] mode as does pyrethrosin.

Cyclisation, under identical conditions, of the epoxide (2) again yielded a mixture of mono-ol and diol. The n.m.r. spectrum of the diol [τ 8.83 (3 H, s), 8.63 (3 H, s), and 8.28 (6 H, s)] was consistent with the structure (11), which was established by its formation in 5% yield by solvolysis of the tosylate (7) with lithium carbonate–water–dioxan. The major product of solvolysis was the alcohol (12) [τ 8.86 (3 H, s), 8.40 (3 H, s), and 8.34 (6 H, s)], which was identical with the mono-ol obtained in the cyclisation. The conversion of (7) into (11) establishes the stereochemistry of (11) at C-1, C-4, and C-5; that at C-10 is assigned on the basis of hydration from the least hindered face of the molecule. During this work a similar cyclisation of parthenolide to a guaianolide was reported [5] but the stereochemistry of the cyclisation was not established. The stereochemistry of both epoxide cyclisations is in accord with the epoxides (2) and (3) reacting in the crown conformation (13). In the formation of (11) there is anti-Markovnikov addition to the oxiran; presumably the energy debt incurred by this direction of ring opening is more than compensated by the steric strain inherent in a Markovnikov bicyclo[6.2.0]decane transition state. It is relevant that cyclisation of germacratriene (1) with *N*-bromosuccinimide in aqueous acetone gave some guaiane product whereas proton-initiated cyclisation did not; it is probable that anti-Markovnikov addition to bridged intermediates is easier than similar additions in proton-initiated reactions.

* *X*-Ray work has shown that (*Z*,*Z*,*Z*)cyclonona-1,4,7-triene [8] has the same structural parameters as its $AgNO_3$ complex, within experimental error.[9] In addition, the double bond stretching frequency of the germacratriene complex shows no change and theoretical calculations support this view.[10]

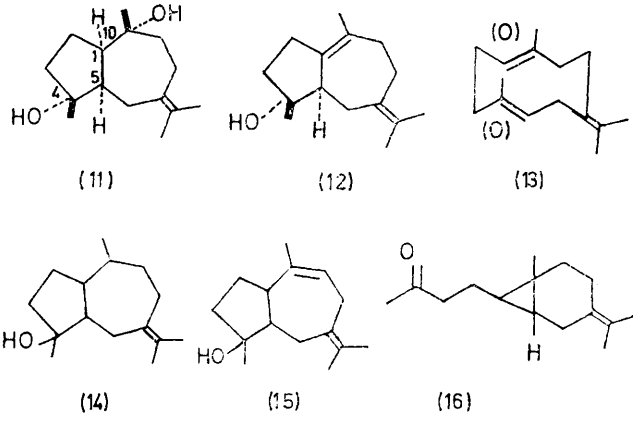
[2] K. L. Williamson and W. S. Johnson, *J. Amer. Chem. Soc.*, 1961, **83**, 4623.

[3] D. H. R. Barton, O. C. Bockmann, and P. de Mayo, *J. Chem. Soc.*, 1960, 2263.

[4] S. Iriuchijima and S. Tamara, *Tetrahedron Letters*, 1967, 1965.

[5] T. R. Govindachari, B. S. Joshi, and V. N. Kamat, *Tetrahedron*, 1965, **21**, 1509.

The relative proportions of the epoxides (2)—(4) obtained on epoxidation of the triene (1) deserve comment. The small yield of (4) implies that the endocyclic double bonds of (1) are abnormally reactive in comparison with aliphatic models; this has been noted previously for medium-ring *E*-olefins.[6] The probable



explanation for this abnormal reactivity and for the relative proportions of (2) and (3) obtained comes from the *X*-ray structure data on the silver nitrate adduct [7] of the triene (1). If we accept that the structural parameters for the adduct are close to those for the triene in solution, the similarity of the C(1),C(2) and C(5),C(6) and of the C(3),C(4) and C(9),C(10) torsion angles shows that there is no difference in steric hindrance for any reagent approaching either bond. The isopropylidene double bond should have a slight electron-withdrawing effect on the 4,5-double bond but this should reverse the reactivity observed. There remains only one significant difference between the 1,10- and 4,5-bonds; both are torsionally strained but the deviation from planarity of the 4,5-bond (20°) is significantly larger than for the 1,10-bond (13°). Co-ordination with silver ion appears to have little perturbing influence on olefinic double bonds * but, even if the silver co-ordination does increase the actual torsion angles in the complex slightly, it is likely that in the free molecule the 4,5-bond is more strained. If we accept this, relief of strain in the transition state for epoxidation will be greater in the formation of (2) than in (3). Rough calculations support these views.[11]

Cyclisation of the epoxide (2) under reductive and under pyrolytic conditions was also observed. Reduction of (2) with lithium in ammonia gave in low

[6] V. Prelog, K. Schenker, and W. Kung, *Helv. Chim. Acta* 1953, **36**, 471; V. Prelog, K. Schenker, and H. H. Gunthart, *ibid.*, 1952, **35**, 1602; A. Aebi, D. H. R. Barton, and A. S. Lindsey, *J. Chem. Soc.*, 1953, 3124.

[7] F. H. Allen and D. Rogers, *Chem. Comm.*, 1967, 588.

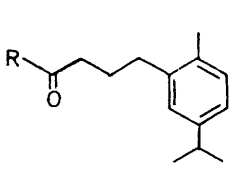
[8] R. B. Jackson and W. E. Streib, *J. Amer. Chem. Soc.*, 1967, **89**, 2539.

[9] W. R. Roth, P. Gobel, R. L. Sass, R. B. Turner, and A. Yu, *J. Amer. Chem. Soc.*, 1964, **86**, 3178.

[10] R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, 1970, **92**, 5589.

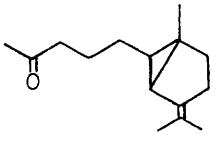
[11] F. H. Allen, E. D. Brown, D. Rogers, and J. K. Sutherland, *Chem. Comm.*, 1967, 1116.

yield a compound with properties consistent with structure (14) [τ 9.13 (3 H, d, J 6.5 Hz), 8.77 (3 H, s), and 8.35 (6 H, s)]; presumably a radical anion derived from the epoxide attacks the endocyclic double bond. Similar cyclisations of ketyls have been observed.[12] Pyrolysis of the epoxide (2) yielded two products; the more polar was an alcohol whose properties were consistent with structure (15), and the second was a methyl ketone (16) [$\nu_{max.}$ 1 710 cm^{-1}, τ 7.95 (3 H, s)] containing an isopropylidene group [τ 8.42 (6 H, s)], an angular methyl group [τ 8.95 (3 H, s)], and a cyclopropane ring bearing two protons [τ 9.60 (2 H, m)]. Dehydrogenation of (16) with palladium–charcoal gave the aromatic ketone (17), which was synthesised by the reaction of the



(17) R=Me

(18) R=OH



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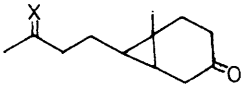
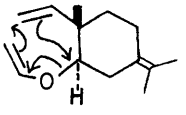


(20) X=O

(21) X= H,OH



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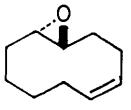

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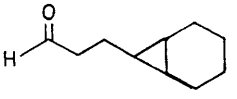

(24)

acid [13] (18) with methyl-lithium. These data leave two alternatives for the structure of the ketone, *viz.* (16) and (19), and a decision was made by ozonolysis of (16) to the dione (20) and of the alcohol derived from (16) to the ketol (21); they showed ε_{215} 220 and 275, respectively, and $\nu_{max.}$ 1 700 cm^{-1}. These values are not those expected [14] for a cyclopropyl conjugated ketone of the type derivable from (19). A similar rearrangement has been reported on pyrolysis of shiromodiol acetate [15] and a radical mechanism has been proposed. We prefer to formulate it as an electrocyclic or cheletropic process, *i.e.* (2) would undergo a [3,3]sigmatropic shift to (22) which would then rearrange to (16) or the combination of the forbidden scission of the epoxide to ketone and carbene concerted with carbene addition to the double bond * which, overall, is an allowed cheletropic reaction.[16] However, the latter process has geometrical requirements which might be difficult to attain within the constraints of a medium ring. Not unexpectedly this rearrangement does not appear to be a general one for mono-epoxides of 1,5-dienes and the only other case in which we have observed this change is the pyrolysis of (23) to give (24). We have not determined the stereochemistry of the side-chain in either of these products and it is only predictable theoretically if the reaction is indeed a cheletropic process. These rearrangements must raise the question of whether carabrone-type sesquiterpenes with the same carbon skeleton as (16) are artefacts, or if such a rearrangement has a biochemical analogue.

The results described in this and in the previous paper,[1] as well as those from other workers,[17] demonstrate the overwhelming preference for cyclisation *via* a chair-like transition state. Since this conformation is, in most cases, the preferred one, the stereochemistry of cyclisation of cyclodeca-1,5-dienes can be predicted with some degree of certainty.

EXPERIMENTAL

For general details, see preceding paper.[1]

Epoxidation of Germacra-1(10),4,7(11)-triene (1).—Germacratriene (1) (5.8 g) was dissolved in dichloromethane (150 ml), solid sodium carbonate (18 g) was added, and the suspension was stirred vigorously at room temperature. Peracetic acid (5.5 ml, 1.2 mol. equiv.) was added dropwise over 50 min to the stirred suspension and stirring was continued for a further 30 min. Work-up in the usual way gave a semi-crystalline product (6.2 g). Crystallisation from methanol at −70 °C gave 4,5-*epoxygermacra*-1(10),7(11)-*diene* (2) (2.4 g), as a white, crystalline solid, m.p. 55—65 °C (Found: C, 81.6; H, 10.8. $C_{15}H_{24}O$ requires C, 81.8; H, 11.0%). The mother liquors from the first crystallisation of the crude product were evaporated to yield an oil (1.3 g) which could not be crystallised. This oil contained *ca.* 80% of 1,10-epoxygermacra-4,7(11)-diene (3).

Chromatography of the Epoxides (2) *and* (3).—(*a*) The pure 4,5-epoxide (2) (134 mg) was chromatographed over alumina (17 g; grade III). Petroleum (40 ml), followed by petroleum–benzene (80 ml; 3 : 1) eluted the 4,5-epoxide (2) (110 mg, 82%), pure by pyrolytic determination. (*b*) The total epoxidation product (150 mg) and the pure 4,5-epoxide (2) (150 mg) were mixed and chromatographed over alumina (30 g; grade III). Petroleum (80 ml) eluted hydrocarbons (19 mg), and petroleum–benzene (150 ml; 3 : 1) eluted the 4,5-epoxide (2) (194 mg), pure by pyrolytic determination. This was equivalent to 237 mg of the

* We thank Dr. C. E. Moppett for this suggestion.

[12] J. M. Greenwood, I. H. Qureshi, and J. K. Sutherland, *J. Chem. Soc.*, 1965, 3154; M. Eakin, W. Parker, *Chem. Comm.*, 1965, 347.

[13] S. Dev and P. G. Guha, *J. Indian Chem. Soc.*, 1948, **25**, 13.

[14] W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, 1967, **89**, 3449.

[15] K. Wada, Y. Enomoto, and K. Munakata, *Tetrahedron Letters*, 1969, 3357.

[16] R. Hoffmann and R. B. Woodward, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

[17] For a review see J. K. Sutherland, *Tetrahedron*, 1974, **30**, 1651.

4,5-epoxide (2) before chromatography. As the sample of the 4,5-oxide (2) used contained 10 mg of hydrocarbons, 97 mg of the 4,5-epoxide (2) was contained in 141 mg of the epoxidation mixture, *i.e.* the mixture contained 69% of the 4,5-epoxide (2) and 31% of the 1,10-epoxide (3).

7,11-*Epoxygermacra*-1(10),4-*diene* (4).—The epoxidation product of germacratriene (1) (5.3 g) was dissolved in acetone (180 ml), sulphuric acid (0.5N; 30 ml) was added, and the solution was stirred at room temperature for 15 min. Work-up in the usual way gave an oil (5.6 g). This was chromatographed over alumina (300 g; grade V). Petroleum eluted hydrocarbons followed by the 7,11-*epoxide* (4) (116 mg, 2%) as a white, crystalline solid, m.p. 56—58 °C (Found: C, 81.2; H, 11.1%), $\nu_{max.}$ (Nujol) 1 665 cm^{-1}.

Acid-catalysed Cyclisation of the 1,10-*Epoxide* (3).—The 'liquid' epoxide fraction (940 mg) was treated with acetone (35 ml) and sulphuric acid (0.5N; 6 ml) as in the preparation of the 7,11-epoxide (4). This gave an oil (1.05 g), which on treatment with petroleum (b.p. 60—80 °C) afforded a crystalline solid. Recrystallisation from ethyl acetate yielded *selin*-7(11)-*ene*-1β,4-*diol* (5) (192 mg), as a white, crystalline solid, m.p. 174—175 °C (Found: C, 75.6; H, 11.1. $C_{15}H_{26}O_2$ requires C, 75.6; H, 11.0%). The mother liquors were purified by preparative t.l.c. to give a mono-alcoholic fraction (228 mg) and a fraction containing a mixture of the diols (5) and (11) (345 mg). The diol (5) (114 mg) was treated with reagent grade acetic anhydride (0.5 ml) and pyridine (5 ml). Crystallisation of the product from ethyl acetate gave the 1-*acetate* (6) (123 mg, 92%), as a white, crystalline solid, m.p. 101—105 °C (Found: C, 72.7; H, 9.9. $C_{17}H_{28}O_3$ requires C, 72.8; H, 10.1%).

The Tosylate (7).—The diol (5) (192 mg) was dissolved in pyridine (3 ml), tosyl chloride (143 mg, 1 mol. equiv.) was added, and the solution was kept at room temperature for 7 days. Work-up in the usual way gave a crude product (215 mg) which was purified by preparative t.l.c. to give the 1-*tosylate* (7) (200 mg, 63%) as a white, crystalline solid, m.p. 134—136 °C (Found: C, 67.3; H, 8.1. $C_{22}H_{32}O_4S$ requires C, 67.3; H, 8.2%).

The Ketol (8).—The diol (5) (47 mg) was dissolved in pyridine (0.5 ml), chromium trioxide (23 mg, 1 mol. equiv.) in pyridine (0.5 ml) was added, and the brown solution was stirred for 30 h at room temperature. Work-up in the usual way gave a solid (34 mg) which was subjected to preparative t.l.c. Recrystallisation of the product from ethyl acetate gave 4-*hydroxyselin*-7(11)-*en*-1-*one* (8) (20 mg, 43%), as a white crystalline solid, m.p. 130—131 °C (Found: C, 76.2; H, 10.2. $C_{15}H_{24}O_2$ requires C, 76.2; H, 10.2%), $\nu_{max.}$ (Nujol) 3 450 and 1 705 cm^{-1}.

Huang-Minlon Reduction of the Ketol (8).—The ketol (8) (47 mg) was dissolved in triethylene glycol (3 ml), solid potassium hydroxide (145 mg) and hydrazine hydrate (0.2 ml) were added, and the mixture was heated under reflux (140—150 °C) for 1 h. The condenser was removed and the temperature was allowed to rise to 215 °C. The condenser was replaced and the solution was refluxed at this temperature for 3 h. Work-up in the usual way gave a white solid (31 mg) which was subjected to preparative t.l.c. Recrystallisation from ethanol gave the alcohol (9) (13 mg, 31%), m.p. and mixed m.p. 164—165 °C, identical with a sample prepared previously.[1]

The Acetate (10).—The mono-alcoholic fraction (228 mg) (obtained by the acid-catalysed hydrolysis of the 'liquid' epoxide fraction) was treated with acetic anhydride (1 ml) in pyridine (4 ml). Work-up in the usual way gave an oil (210 mg) which was subjected to preparative t.l.c. to give an acetate fraction (108 mg). The acetate fraction (80 mg) was submitted to preparative t.l.c. on silver nitrate–silica to give *selina*-4(14),7(11)-*dien*-1β-*yl acetate* (10) (37 mg) as a white, crystalline solid, m.p. 65—71.5 °C (Found: C, 77.7; H, 10.1. $C_{17}H_{26}O_2$ requires C, 77.8; H, 10.0%), $\nu_{max.}$ (Nujol) 1 725, 1 645, 1 250, and 895 cm^{-1}. Also isolated was the isomeric acetate.

Dehydration of the Acetate (6).—The acetate (6) (36 mg) was treated overnight with phosphoryl chloride (0.2 ml) in pyridine (2 ml). Work-up gave an oil (28 mg) which contained *ca.* 80% of the acetate (10) and <20% of its isomer. The mixture was separated by preparative t.l.c. on silver nitrate–silica to give the acetate (10) (15 mg, 38%), m.p. and mixed m.p. 66—71.5 °C, identical with a sample prepared from the 1,10-epoxide (3).

Acid-catalysed Cyclisation of the 4,5-*Epoxide* (2).—The 4,5-epoxide (2) (64 mg) was treated with sulphuric acid (0.5N; 1 ml) in acetone (4 ml) as in the preparation of the 7,11-epoxide (4). Separation of the product (62 mg) by preparative t.l.c. gave a faster and a slower moving component. Crystallisation of the former from petroleum (b.p. 60—80°) gave *guaia*-1(10), 7(11)-*dien*-4-*ol* (12) (11 mg, 22%), as a white, crystalline solid, m.p. 83—86.5 °C (Found: C, 81.9; H, 11.1. $C_{15}H_{24}O$ requires C, 81.8; H, 11.0%). The slower moving component gave *guai*-7(11)-*ene*-4,6α-*diol* (11) (25 mg, 42%), as a white, crystalline solid, m.p. 102—106 °C (from benzene) (Found: C, 75.6; H, 10.9. $C_{15}H_{26}O_2$ requires C, 75.6; H, 11.0%).

Solvolysis of the Tosylate (7) *in Aqueous Dioxan.*—The tosylate (7) (147 mg) was dissolved in water (4 ml) and dioxan (8 ml), lithium carbonate (286 mg) was added, and the stirred suspension was refluxed for 84 h. The solvent was removed *in vacuo* and the residue was washed with boiling chloroform (4 × 5 ml). The combined extracts were cooled, filtered, and evaporated to give a crystalline product (84 mg). This was separated by preparative t.l.c. into a crystalline mono-alcoholic fraction (70 mg), mainly (12), and a crystalline diol fraction (11 mg). The latter was subjected to further preparative t.l.c. and the product crystallised from petroleum (b.p. 60—80°) to give the diol (11) (4 mg, 5%), m.p. and mixed m.p. 98—106 °C, identical (i.r. spectrum) with a sample obtained from the 4,5-epoxide (2).

The Ketone (16).—The 4,5-epoxide (2) (171 mg) was heated at 155 °C in a sealed, evacuated Carius tube for 24 h. The tube was then cooled and opened and the oily product was subjected to preparative t.l.c. to give a faster and a slower moving component. The former was 2-(4-isopropylidene-1-methylbicyclo[4.1.0]heptan-7-yl)ethyl methyl ketone (16) (76 mg, 41%), an oil, $\nu_{max.}$ (film) 1 710 and 1 160 cm^{-1}, characterised as its crystalline *semicarbazone*, m.p. 147—149 °C (from ethanol) (Found: C, 69.1; H, 10.0; N, 15.2. $C_{16}H_{27}N_3O$ requires C, 69.3; H, 9.8; N, 15.2%). Crystallisation of the slower moving component from petroleum (b.p. 60—80°) gave guaia-7(11),9-dien-4-ol (15) (61 mg, 36%), as a white, crystalline solid, m.p. 72—80 °C, $\nu_{max.}$ (Nujol) 1 635 and 895 cm^{-1}. On heating in refluxing tetralin the same two products were obtained and this procedure could be used for determination of the purity of the epoxide as follows. The epoxide mixture (50 mg) was added to a refluxing solution of diphenyl ether (25 mg) in purified tetralin (3 ml) and the

refluxing was continued for 1 h under nitrogen. The solution was then cooled and a sample (1.5 μl) was submitted to g.l.c. analysis under standard conditions. The peaks which corresponded to the diphenyl ether standard and to the ketone were cut out of the trace and weighed. The ratio R = (wt. of ketone peak)/(wt. of standard peak) was then calculated. A value of R = 0.71—0.74 indicated that the sample under test was the pure 4,5-epoxide (2). A sample which contained *ca.* 85% of the 4,5-epoxide (2) had R 0.54.

Dehydrogenation of the Ketone (16).—The ketone (101 mg) was added to 10% palladised carbon (200 mg) in a sublimation tube which was inserted into a small Carius tube and sealed under vacuum. The sealed tube was heated to 325 °C and maintained at this temperature for 4 h. A Soxhlet extraction with petroleum (b.p. 40—60 °C) gave a light yellow oil, from which a semicarbazone, m.p. 119—122 °C, was prepared, identical with that described below.

5-(5-Isopropyl-2-methylphenyl)pentan-2-one (17).—4-(5-Isopropyl-2-methylphenyl)butanoic acid [13] (1.06 g) was dissolved in dry ether (50 ml). Dry, oxygen-free nitrogen was passed through to remove any oxygen present. The rate of nitrogen influx was then adjusted to provide a degree of stirring as well. Methyl-lithium (6 ml, 12 mmol) was then introduced and the mixture was left for 30 min. Work-up gave the ketone (347 mg, 28%), $\nu_{max.}$ (film) 1 715 cm^{-1}; τ (CCl_4) 8.77 (6 H, d, J 7 Hz), 8.02 (3 H, s), 7.80 (3 H, s), and 3.10 (3 H, m). The *semicarbazone*, prepared from a micro-distilled sample of the ketone (50 mg) was purified by high-vacuum sublimation (100 °C and 10^{-2} mmHg), had m.p. 119—122 °C (Found: C, 69.7; H, 9.2; N, 15.7. $C_{16}H_{25}N_3O$ requires C, 69.8; H, 9.2; N, 15.3%).

Ozonolysis of the Ketone (16).—The ketone (97 mg) in dichloromethane (20 ml) containing pyridine (35 mg) was ozonised at −70 °C for 90 min. The solution was flushed with nitrogen and decanted into a conical flask containing zinc (250 mg). Glacial acetic acid (0.5 ml) was then added and the mixture stirred for 30 min. Zinc was filtered off and the solution worked up as usual to give 6-methyl-7-(3-oxobutyl)bicyclo[4.1.0]heptan-3-one (20) (49 mg, 50%), $\nu_{max.}$ (film) 1 700s cm^{-1}; τ 9.44 (2 H, m), 8.79 (3 H, s), and 7.92 (3 H, s). The *bis-semicarbazone* had m.p. 209—211 °C (decomp.) (from ethanol) (Found: C, 54.5; H, 8.1; N, 27.1. $C_{14}H_{24}N_6O_2$ requires C, 54.5; H, 7.8; N, 27.3%).

The Ketol (21).—The ketone (16) (147 mg) dissolved in dry ether (3 ml) was added to a solution of lithium aluminium hydride (62 mg) in ether (20 ml) with stirring, and after 30 min at 0 °C the mixture was refluxed for a further 30 min. Work-up gave the alcohol (21) in 45% yield (68 mg); $\nu_{max.}$ (film) 3 395 cm^{-1}; τ 9.6 (2 H, m), 8.95 (3 H, s), 8.83 (3 H, d, J 6 Hz), 8.5 (1 H, exchangeable), 8.42 (6 H, s), and 6.37 (1 H, m). The alcohol (92 mg) in absolute ethanol (6 ml) was cooled to −23 °C and ozonised for 70 min. After flushing with nitrogen, water (0.5 ml) was added and the solution was left overnight. It was then worked up to give an oil which was purified on silica gel plates (chloroform as solvent) to give 7-(3-hydroxybutyl)-6-methylbicyclo[4.1.0]heptan-3-one (21) in 50% yield (41 mg), which was further purified by micro-distillation at 120 °C and 0.5 mmHg; $\nu_{max.}$ (film) 3 445 and 1 701 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 220 nm (ε 275); τ 9.3 (2 H, m), 8.85 (3 H, s), 8.80 (3 H, d, J 6 Hz), 7.5 (4 H, m), and 6.23 (1 H, m). Jones oxidation of the ketol gave the dione (20).

Pyrolysis of (E,Z)-Cyclodeca-1,5-diene 1,2-Oxide (23).—The oxide (663 mg) was refluxed under nitrogen for 4 h. Chromatography on alumina (grade III; 100 g) with chloroform as solvent gave bicyclo[4.1.0]heptan-7-ylbutyraldehyde (24) in 27% yield (180 mg), $\nu_{max.}$ (film) 1 720 and 2 710 cm^{-1}; τ 9.2 (3 H, m) and 0.18 (1 H, t, J 2 Hz); the *2,4-dinitrophenylhydrazone* had m.p. 76—95 °C (Found: C, 57.7; H, 6.3; N, 16.8. $C_{16}H_{20}N_4O_4$ requires C, 57.8; H, 6.1; N, 16.9%).

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