

## Medium-ring 1,5-Dienes. Part IV.<sup>1</sup> Reactions of Germacra-1(10),4,7(11)-triene with Singlet Oxygen and with the Triphenyl Phosphite–Ozone Adduct

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In the reaction of  $^1\text{O}_2$  with germacatriene the isopropylidene double bond is attacked *ca.* 9 times more rapidly than the endocyclic double bonds, in contrast to the results in epoxidation. The triphenyl phosphite–ozone adduct reacts primarily at the torsionally most strained double bond, in support of the view that an oxiranium intermediate is formed in the rate-determining step.

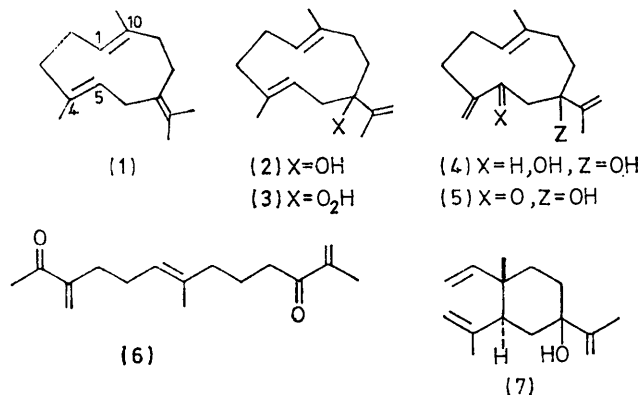
PREVIOUS work<sup>1</sup> has shown that germacatriene (1) undergoes preferential attack at the 1,10-double bond with electrophilic and radical reagents and that this attack is invariably concerted with or followed by cyclisation. However, in the cheletropic epoxidation of (1) there is preferential attack on the 4,5-double bond and no cyclisation, though this can be brought about

under mildly acidic conditions leading to selinanes from the 1,10-epoxide and guaianes from the 4,5-epoxide. These facts led us to believe that a study of the reaction of the triene (1) with  $^1\text{O}_2$  might supply evidence on the question of the intermediacy of an epidioxide in the formation of allylic hydroperoxides.<sup>2</sup> If the formation of an epidioxide were the rate-determining step then the

<sup>1</sup> (a) Part III, E. D. Brown and J. K. Sutherland, preceding paper; (b) Part II, E. D. Brown, T. W. Sam, J. K. Sutherland, and A. Torre, *J.C.S. Perkin I*, 1975, 2326.

<sup>2</sup> K. R. Kopecky and H. J. Reich, *Canad. J. Chem.*, 1965, **43**, 2265.

reactivities of the two endocyclic double bonds should parallel those observed in epoxidation where relief of torsional strain is dominant. The similarities between epoxidation and  $^1\text{O}_2$  reactions have already been discussed.<sup>2</sup> In addition, it was possible that the epidioxides might cyclise rather than rearrange to the allylic hydroperoxides. In the event, reaction of the triene (1) with  $^1\text{O}_2$  (irradiation, with Methylene Blue as sensitiser<sup>3</sup>) followed by reduction with sodium borohydride gave two products, (2) and (4), in a combined yield of 50–60%.



The presence of a 1,5-diene system in (2) [ $\tau$  8.63 (3 H, s), 8.18 (3 H, s), 5.1–5.35 (2 H, m), and 5.00br (2 H, s)] followed from its pyrolysis to give the elemene (7) [ $\tau$  9.04 (3 H, s), 8.26 (3 H, s), 8.18 (3 H, s), 5.40 (1 H, m), 5.25 (3 H, m), 5.00 (2 H, m), and 4.11 (1 H, dd,  $J$  16 and 10 Hz)]. The structure of (2) was confirmed by acid-catalysed cyclisation to a 9 : 1 mixture of diols (8A and B). That the diols were epimeric at C-7 followed from their preparation from (9) in a 2 : 1 ratio by reaction with  $^1\text{O}_2$  followed by reduction. We have no conclusive evidence for stereochemistry, but the major conformer of (2) present in solution should be that with the isopropenyl group equatorial, and since there should be little difference in the rates of cyclisation of the two conformers it is anticipated that the major product of cyclisation (8A) has an equatorial isopropenyl group.

The second product from the  $^1\text{O}_2$  reaction was a diol (4) [ $\tau$  8.35 (3 H, s), 8.22 (3 H, s), 5.72 (1 H, m), and 5.20–4.67 (5 H, m)], characterised as a 3,5-dinitrobenzoate. Oxidation of (4) with manganese dioxide gave the ketol (5) [ $\lambda_{\text{max}}$  ( $\text{C}_6\text{H}_{12}$ ) 225 nm ( $\epsilon$  4 600),  $\nu_{\text{max}}$  1 670  $\text{cm}^{-1}$ ,  $\tau$  ( $\text{CCl}_4$ ) 8.42 (3 H, s), 8.22 (3 H, s), 7.53 (1 H, d,  $J$  16 Hz), 7.10 (1 H, d,  $J$  16 Hz), 5.25 (1 H, s), 5.22 (1 H, s), 4.80 (1 H, m), 4.73 (1 H, s), and 4.67 (1 H, s)]. The AB quartet in the n.m.r. spectrum of (5) excludes the alternative structure arising from reaction of the 1,10-bond. Confirmation of structure (5) came from retro-aldolisation to give the dione (6) [ $\lambda_{\text{max}}$  ( $\text{C}_6\text{H}_{12}$ ) 216 nm ( $\epsilon$  9 750),  $\nu_{\text{max}}$  1 680  $\text{cm}^{-1}$ ,  $\tau$  8.43 (3 H, s), 8.20 (3 H, s), 7.88 (3 H, s), 4.98 (1 H, m), 4.38 (2 H, s), and 4.12 (2 H,

s)], characterised as its bis-semicarbazone. The de-aldolisation could be effected either by chromatography on alumina or by treatment with sodium carbonate solution. We have no definitive evidence for the relative stereochemistry of (4), but we believe that attack on the more stable conformer of (3) occurs leading to a *trans*-disposition of the hydroxy-groups. The  $W_1$  value of the H-5 n.m.r. signal is 15 Hz, suggesting that H-5 is pseudoaxial.

The total yield of compounds (2) and (4) was reasonably constant if the reaction time was increased, but the ratio of (2) to (4) varied from 3.2 : 1 to 0.6 : 1, suggesting that a major portion of (4) was produced by further reaction of (3). Crude measurements of  $-d(1)/dt$  and  $-d(2)/dt$  (9 : 2) support this if it is accepted that the reactivities of the endocyclic double bonds of the two compounds are similar. The reaction of (2) with  $^1\text{O}_2$  yielded the diol (4) (40%) after reduction. The conclusions which can be drawn from these results are necessarily limited by our inability to account for all the starting material consumed. However, it is clear that the isopropylidene double bond is only *ca.* 9 times more reactive than the endocyclic double bonds rather than the 30–50 times expected from studies on unstrained models.<sup>4</sup>

Work on isotope effects has not given clear and unequivocal evidence on whether C–H bond breaking occurs in the rate-determining step.<sup>5</sup> If there is an epidioxide intermediate formed in a rate-determining step then it is difficult to explain the relative rate changes between  $^1\text{O}_2$  and  $\text{RCO}_3\text{H}$  reactions with germacatriene as compared with simple models. If rearrangement of the epidioxide is rate-determining then, as pointed out by Foote,<sup>4</sup> it is difficult to account for the rate enhancement caused by alkyl groups and to rationalise the enhanced, albeit small, reactivity of the endocyclic double bonds of germacatriene. In an 'ene' type of reaction<sup>6</sup> on torsionally strained bonds there are probably two opposing effects, the rate-enhancing relief of torsional strain and a rate-retarding steric effect due to the allyl system being 'bent' towards the  $^1\text{O}_2$  molecule.

In order to check that the relative reactivities of the 1,10- and 4,5-bonds had not changed dramatically in going from (1) to (2), the latter was epoxidised with 1 mol. equiv. of peracetic acid. Since it was not possible to determine the composition of the epoxide mixture by chromatographic or spectroscopic methods, the mixture was cyclised with dilute sulphuric acid in the expectation that the 1,10-oxide (11) would yield decalins whereas the 4,5-oxide (10) would afford guaianes.<sup>1</sup> Separation of the mixture gave a secondary alcohol fraction (48%) consisting of a mixture of double-bond isomers (12).

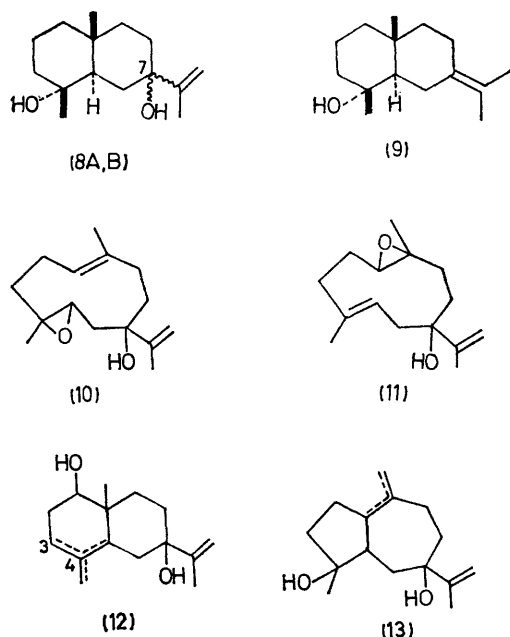
<sup>5</sup> L. M. Stephenson, D. E. McClure, and P. K. Sysak, *J. Amer. Chem. Soc.*, 1973, **95**, 7888; A. Nickon, V. T. Chuang, P. J. A. Daniels, R. W. Denny, J. B. DiGiorgio, J. Tsunetsugu, H. G. Vilhuber, and E. Verstink, *J. Amer. Chem. Soc.*, 1972, **94**, 5517; K. R. Kopecky, J. H. van de Sande, and C. Mumford, *Canad. J. Chem.*, 1968, **46**, 25.

<sup>6</sup> A. Nickon and U. L. Mendelson, *J. Amer. Chem. Soc.*, 1965, **87**, 3921, and earlier papers.

<sup>3</sup> K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, 1964, **9**, 507.

<sup>4</sup> C. S. Foote, *Accounts Chem. Res.*, 1968, **1**, 104.

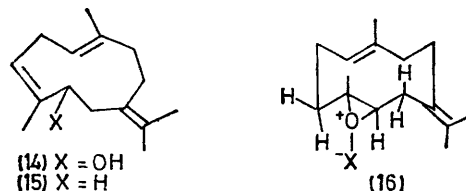
Acetylation of this fraction gave material from which a crystalline 3 : 2 mixture of the  $\Delta^3$ - and  $\Delta^4$ -isomers could be obtained. The second fraction, which did not undergo acetylation with acetic anhydride-pyridine, gave spectra consistent with its being a mixture of the guaiane isomers (13). These results indicate that at least 48% of the epoxide (11) was formed in the mono-epoxidation of the trienol (2), and show a slight change in the relative reactivities of the endocyclic double bonds, perhaps caused by the inductive effect of the hydroxy-group. No hydration product of the intermediate carbocations could be detected; this illustrates the trend that, with increasing oxygen content, the fate of the carbocations changes from total nucleophilic



attack (with germacatriene<sup>1</sup>) to at least 90% elimination with (10) and (11), with the germacatriene epoxides giving intermediate results.

The triphenyl phosphite-ozone adduct<sup>7</sup> has been shown to be a source of  $^1\text{O}_2$  above  $-35^\circ\text{C}$ , but the complex can react with some olefins below this temperature to give products identical with those obtained from  $^1\text{O}_2$ .<sup>8</sup> The adduct reacts with germacatriene (1) at  $-45^\circ\text{C}$ . After reduction of the reaction mixture with lithium aluminium hydride the alcohol (14) (50%) was isolated [ $\tau$  8.32 (12 H, s) and 5.0 (2 H, m)] and characterised as its crystalline 3,5-dinitrobenzoate. The alcohol was converted into its acetate and reduced with lithium in ammonia to yield starting material (14) (35%) and a mixture of three hydrocarbons in the ratio 28 : 38 : 34. The least abundant component was identified by g.l.c. as germacatriene. This was confirmed by

treatment of the reaction mixture with the palladium chloride-benzonitrile complex to yield the complex of  $\gamma$ -elemene.<sup>1b</sup> The two other hydrocarbons were not rearranged and, this, coupled with the 1 : 1 ratio of



vinyl ( $\tau$  5.0) to bis-allylic ( $\tau$  7.3) protons suggested that they had the constitution (15). The constitution of (14) was proved by ozonolysis followed by reduction with sodium borohydride to give trimethylene glycol (21%).

We were unable to detect either of the products obtained in the  $^1\text{O}_2$  reaction, nor were we able to detect compound (14) in the  $^1\text{O}_2$  reaction which thus differs from the case of caryophyllene<sup>9</sup> where minor amounts of endocyclic double-bond isomers were formed. Thus the  $^1\text{O}_2$  and  $(\text{PhO})_3\text{P}-\text{O}_3$  reactions differ in both the double bond attacked and the allylic isomer formed. The results for the latter reaction are in accord with a rate-determining attack to form a three-membered ring intermediate (16), with the reagent approaching the least hindered sector of the double bond *syn* to  $\text{CH}_2$  and H. Sigmatropic rearrangement to the allylic hydroperoxide then occurs, involving the geometrically accessible  $3\beta$ -H. This would require inversion of the trivalent oxygen to be slow in comparison with the rearrangement, but this is not unreasonable since decreased rates of nitrogen inversion are observed to result from bonding to electronegative groups and from constraining the nitrogen in a three-membered ring.<sup>10</sup>

#### EXPERIMENTAL

For general information see ref. 1b.

*Photosensitised Oxidation of Germacra-1(10),4,7(11)-triene* (1).—Germacatriene (2.1 g) was dissolved in absolute ethanol (100 ml) containing Methylene Blue (5 mg) in a Pyrex apparatus provided with a cold-finger condenser and a sintered glass bottom through which oxygen was passed rapidly. The solution was then irradiated with a water-cooled medium-pressure mercury lamp (A.E.I. Mazda) through a glass plate filter. After 2 h, the solution was transferred to a 100 ml flask, sodium borohydride (1 g) was added, and the mixture was stirred at room temperature for 3 h. The bulk of the ethanol was then removed from the solution at  $50$ – $60^\circ\text{C}$  by a nitrogen stream. Work-up in the usual way gave a liquid which was chromatographed on grade III neutral alumina. Petroleum eluted hydrocarbons, mainly germacatriene (120 mg). Petroleum-benzene (1 : 1) eluted the mono-ol (2) (430 mg,

<sup>7</sup> R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, 1968, **90**, 537.

<sup>8</sup> P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, 1970, **92**, 6055.

<sup>9</sup> K. H. Schulte-Elte and G. Ohloff, *Helv. Chim. Acta*, 1968, **51**, 494.

<sup>10</sup> D. Felix and A. Eschenmoser, *Angew. Chem. Internat. Edn.*, 1968, **1**, 224; S. J. Brois, *J. Amer. Chem. Soc.*, 1968, **90**, 506, 508, 1680; J. M. Lehn and J. Wagner, *Chem. Comm.*, 1968, 148.

26% based on total recovered material) followed by an intractable mixture (120 mg).

Ether eluted the column residue, which was rechromatographed on silica gel preparative plates (25% ethyl acetate-benzene) to give the diol (4) (710 mg, 43% based on total recovered material) and a residue (170 mg).

Germacra-1(10),4,11-trien-7-ol (2),  $\nu_{\max}$  (film) 3400, 1075, and 900  $\text{cm}^{-1}$ , on distillation (90–95 °C and 1 mmHg) yielded 4-isopropenyl-1-vinyl-o-menth-8-en-4-ol (7),  $\nu_{\max}$  (film) 3400, 1010, 990, and 900  $\text{cm}^{-1}$  (Found: C, 75.3; H, 11.1.  $\text{C}_{15}\text{H}_{26}\text{O}_2$  requires C, 75.6; H, 11.0%).

Germacra-1(10),4(14),11-triene-5,7-diol (4) was characterised as its *mono-3,5-dinitrobenzoate*, m.p. 116–117°,  $\tau$  8.24 (3 H, s), 8.18 (3 H, s), 5.46 (1 H, s), 5.20 (1 H, s), 5.06 (1 H, s), 5.0–5.2 (1 H, m), and 4.52 (1 H, t,  $J$  7 Hz) (Found: C, 61.5; H, 6.3; N, 6.3.  $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_7$  requires C, 61.4; H, 6.1; N, 6.5%). A control experiment showed no reaction in the dark.

*Acid-catalysed Cyclisation of the Mono-ol (2)*.—The mono-ol (2) (130 mg) in acetone (3 ml) containing dilute sulphuric acid (2*N*; 1 ml) was set aside overnight. The mixture was then poured into dichloromethane (25 ml) in a separating funnel and saturated aqueous sodium hydrogen carbonate (3 ml) was added. Work-up in the usual way gave a crystalline mixture of the selin-11-ene-4,7-diols (8A and B) (57 mg, 41%). Multiple t.l.c. (25% ethyl acetate-benzene) on silica gel gave the pure *major epimer* (8A), m.p. 147–149 °C,  $\tau$  ( $\text{CCl}_4$ ) 9.18 (3 H, s), 9.02 (3 H, s), 8.24 (3 H, s), 5.35 (1 H, s), and 5.08 (1 H, s) (Found: C, 75.3; H, 11.1.  $\text{C}_{15}\text{H}_{26}\text{O}_2$  requires C, 75.6; H, 11.0%).

*Photosensitised Oxidation of Juniper Camphor (9)*.—Juniper camphor (1 g) was dissolved in absolute ethanol (100 ml) containing Methylene Blue (2.5 mg). The mixture was irradiated with a 250 W spotlight with constant passage of oxygen at 22–60 °C for 1 h. Reduction of the reaction mixture with sodium borohydride (1 g) and work-up in the usual way gave an oil (850 mg, 85%) whose n.m.r. spectrum showed that it was a 2:1 mixture of the diols (8A and B). Multiple development on a preparative plate (15% EtOH-petroleum) gave, as the most polar fraction, the *epimer* (8B), which was recrystallised from petroleum (b.p. 40–60°) to give pure (8B), m.p. 120–122 °C,  $\tau$  ( $\text{CDCl}_3$ ) 9.09 (3 H, s), 8.94 (3 H, s), 8.22 (3 H, s), 5.03 (1 H, m), 4.94 (1 H, s) (Found: C, 76.0; H, 11.3.  $\text{C}_{15}\text{H}_{26}\text{O}_2$  requires C, 75.6; H, 11.0%). The liquid residue was then chromatographed on preparative plates. Multiple development as above gave as the least polar fraction the *major epimer* (8B), m.p. 147–149 °C, identical with the sample from the hydration of the mono-ol (2).

*Cyclisation of the Epoxides (11) and (10)*.—The mono-ol (207 mg) in dichloromethane (20 ml) containing a suspension of anhydrous sodium carbonate (750 mg) was vigorously stirred at 0 °C while peracetic acid (0.2 ml, 86 mg) was added in one portion. Stirring was continued for 1 h. Work-up in the usual way gave a mixture of epoxides (11) and (13) as a glass (196 mg, 89%). The epoxide mixture (196 mg) in acetone (8 ml) and sulphuric acid (3*N*; 0.5 ml) was stirred at 12–15 °C for 1 h. Saturated aqueous sodium hydrogen carbonate was added (3 ml) and the acetone solvent was removed under reduced pressure. Work-up in the usual way, followed by preparative t.l.c. on silica gel (25% ethyl acetate-benzene; 2 developments) gave as the less polar fraction a secondary alcohol mixture (94 mg) and as the more polar fraction a tertiary alcohol fraction (57 mg). The less polar fraction

(94 mg) was acetylated with acetic anhydride (0.5 ml)-pyridine (3 ml) and, after normal work-up, an acetate mixture (114 mg) was obtained from which was crystallised a mixture of the diols (12) ( $\Delta^3$ - and  $\Delta^4$ -isomers) in the ratio 3:2 (59 mg) (Found: C, 73.5; H, 9.4.  $\text{C}_{17}\text{H}_{26}\text{O}_3$  requires C, 73.3; H, 9.4%).

*Oxidation of the Diol (4)*.—The diol (241 mg) was dissolved in dry benzene (5 ml). Manganese dioxide (commercial; oven-dried for 1 week at 120 °C; 1 g) was added and the suspension stirred overnight at room temperature. The manganese dioxide was then filtered off through Celite 545 (*ca.* 1 in); evaporation left 7-hydroxygermacra-1(10),4(14),11-trien-5-one (5) (198 mg, 83%). The hydroxy-ketone (85 mg) in benzene (1 ml) was applied to a preparative t.l.c. silica gel plate and chromatographed twice with benzene as eluant. It was recovered as a clear liquid (68 mg) which was distilled (Kugelrohr; 95–100 °C; 0.05 mmHg);  $\nu_{\max}$  (film) 3400s, 3050m, and 1670s  $\text{cm}^{-1}$ ;  $\tau$  ( $\text{CCl}_4$ ) 8.42 (3 H, s), 8.22 (3 H, s), 7.53 (1 H, d,  $J$  16 Hz), 7.10 (1 H, d,  $J$  16 Hz), 5.25 (1 H, s), 5.22 (1 H, s), 4.80 (1 H, m), 4.73 (1 H, s), and 4.67 (1 H, s) (Found: C, 76.8; H, 9.6.  $\text{C}_{15}\text{H}_{22}\text{O}_2$  requires C, 76.9; H, 9.5%).

*Retro-aldolisation of the Hydroxy-ketone (5)*.—(a) The hydroxy-ketone (180 mg) was passed slowly through basic alumina (100 g; grade III) with benzene as eluant. Evaporation of the solution (500 ml) left 7,12-dimethyl-3-methylenedodeca-6,12-diene-2,11-dione (98 mg, 54%),  $\nu_{\max}$  (film) 1675s and 1625m  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  (EtOH) 216 nm ( $\epsilon$  9750),  $\tau$  8.43 (3 H, s), 8.20 (3 H, s), 7.88 (3 H, s), 4.98 (1 H, t,  $J$  7 Hz), 4.38 (1 H, m,  $W_{\frac{1}{2}}$  4 Hz), and 4.14 (1 H, m,  $W_{\frac{1}{2}}$  3 Hz). The *bis-semicarbazide* had m.p. 214–219 °C (from ethanol) (Found: C, 58.3; H, 8.2; N, 24.0.  $\text{C}_{17}\text{H}_{28}\text{N}_6\text{O}_6$  requires C, 58.6; H, 8.1; N, 24.1%).

(b) The hydroxy-ketone (102 mg) in ether (5 ml) was stirred in the presence of potassium carbonate (anhydrous, 500 mg) overnight at room temperature. The solid material was filtered off and the ether was evaporated from the filtrate to give products which consisted mainly of the acyclic bis-enone (6) with a little unchanged diol. Percolation of the products through grade II basic alumina (5 g) and elution with benzene (50 ml) gave the bis-enone (64 mg, 63%).

*Photosensitised Oxidation of the Mono-ol (2)*.—The mono-ol (210 mg) in ethanol (100 ml) containing Methylene Blue (5 mg) was irradiated with continuous passage of oxygen for 1 h. Sodium borohydride (500 mg) was added and the mixture was stirred for 3 h. The ethanolic solution was then passed through neutral alumina (grade III; 10 g) to remove inorganic material. After further elution with ether, the combined eluate was evaporated and the residue chromatographed on preparative t.l.c. plates (20% ethyl acetate-benzene) to give unchanged (2) (60 mg, 31%) as the less polar fraction and the diol (4) (60 mg, 31%) as the more polar fraction. The 3,5-dinitrobenzoate of the diol had m.p. 116–120 °C.

*Reaction between Germacatriene and Triphenyl Phosphite-Ozone*.—Redistilled triphenyl phosphite (2 g) dissolved in dichloromethane (50 ml) was cooled to –73 °C. Ozonised oxygen was passed through the mixture until a blue colouration indicated that the dichloromethane solution was saturated with ozone (*ca.* 2 h). The clear solution obtained was then flushed with nitrogen while still at –73 °C for a further 2 h, until the effluent gas no longer showed a reaction with damp starch-potassium iodide paper. Germacatriene (1 g) was then added neat and the mixture

kept at  $-40$  to  $-50$  °C for 30 min with a slow nitrogen flow through it. The solution was then allowed to warm to room temperature by removal of the acetone–solid  $\text{CO}_2$  bath. Dichloromethane was then cautiously removed at room temperature by low pressure evaporation. Traces of solvent were finally removed under high vacuum. Dry ether (50 ml) was added to the residue followed by lithium aluminium hydride (2 g). The mixture was cooled to  $-5$  °C during the reaction. After overnight stirring at room temperature, hydrochloric acid (2N; 100 ml) was added and the mixture was worked up in the usual way (crude yield 1.33 g). Preparative scale t.l.c. on silica gel (dichloromethane as solvent) gave germacra-1(10),3,7(11)-trien-5-ol (14) (490 mg, 49%),  $\nu_{\text{max}}$  (film) 3440s  $\text{cm}^{-1}$ ,  $\tau$  8.32 (12 H, s), 3.25 (1 H, exchangeable), and 5.0 (2 H, m); the 3,5-dinitrobenzoate had m.p. 44–47° (from methanol),  $\tau$  8.30 (12 H, s,  $W_{\frac{1}{2}}$  7 Hz), 7.20 (2 H, m), 4.95 (2 H, m), 4.23 (1 H, m), and 0.88 (3 H, m) (Found: C, 64.2; H, 6.5; N, 6.5.  $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_6$  requires C, 63.8; H, 6.3; N, 6.8%).

*Conversion of the Alcohol (14) into Germacrene.*—The mono-ol (1.68 g) was dissolved in dry pyridine (5 ml) and acetic anhydride (5 ml) was added. The mixture was kept at 40–50 °C for 5 h. The acetate (940 mg) in dry ether (25 ml) was added to a solution of lithium (500 mg) in liquid ammonia (*ca.* 100 ml) and the mixture was stirred for 4 h. Ammonium chloride was added to destroy the excess of lithium. The ammonia was allowed to evaporate overnight. Work-up gave a mixture which was separated by column chromatography on basic alumina (20 g) into a hydrocarbon fraction (260 mg; eluant petroleum) and an alcohol fraction (270 mg; eluant ether). Germacrene was identified in the hydrocarbon mixture (28%) by g.l.c. comparison on a 6 ft Carbowax column (150 °C) and on a 3 ft PEGA column (130 °C). The alcohol fraction was

identified as the mono-ol (14) by comparison with an authentic sample (t.l.c. and i.r. spectrum).

A solution of bis(benzonitrile)palladium chloride (100 mg) in benzene (1 ml) was added to a solution of the hydrocarbon mixture in benzene (1 ml). After 10 min petroleum (5 ml) was added and the palladium chloride complex of germacatriene precipitated out (30 mg) and was filtered off. Dimethyl sulphoxide (0.5 ml) was added to the filtrate and the mixture was percolated through basic alumina (grade III; 15 g) with elution by petroleum. Palladium salts were retained at the top of the column. Evaporation of the eluate gave a hydrocarbon mixture (108 mg) consisting of the isomers (15),  $\tau$  8.32 (12 H, s,  $W_{\frac{1}{2}}$  5 Hz), 7.25 (2 H, t,  $W_{\frac{1}{2}}$  21 Hz), and 5.00 (2 H, m), and some  $\gamma$ -elemene.

*Reductive Ozonolysis of the Alcohol (14).*—The alcohol (151 mg) in absolute ethanol (10 ml) was cooled to and maintained at 0 °C while an ozone–oxygen stream was passed through during 1 h. A large excess of sodium borohydride (500 mg) and water (0.5 ml) was added to the solution still at 0 °C. After the initial vigorous reaction had subsided, the mixture was allowed to warm to room temperature with continued stirring over 3 h. The ethanolic solution was then passed through Amberlite IR 120 resin (acid form; 30 g) and the ion-exchange column was washed out with more ethanol (250 ml). Evaporation under reduced pressure of the combined eluate gave products (198 mg) which were dissolved in ethanol (0.5 ml). G.l.c. (4% PEGA at 150 °C and 8% PEGA at 165 °C) comparison with an authentic sample of trimethylene glycol (79 mg in 0.5 ml of ethanol) indicated the presence of trimethylene glycol (by peak enhancement) to the extent of 21% of theoretical yield (11 mg by peak area calculation).

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