

Cope Rearrangement of Some Germacrane-type Furan Sesquiterpenes. Part IV.¹ Preparation of Some Cyclodeca-*cis,trans*-diene Derivatives and their Cope Rearrangements²

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In order to clarify whether the abnormal Cope rearrangement of the *cis,trans*-cyclodecadienes 6,12-epoxygermacra-3,6,9,11-tetraene (II) and neolinderalactone (6,12-epoxy-8-hydroxygermacra-3,6,9,11-tetraen-14-oic acid γ -lactone) (III) is due to the substituents on the 3,4- and 9,10-double bonds or to the furan ring, the *cis,trans*-compounds (3*Z*,9*E*)-germacra-3,7(11),9-trien-6-one (VII), (3*Z*,9*E*)-germacra-3,7(11),9-triene (XI), (3*Z*,6*Z*,9*E*)-11-formylmethylgermacra-3,6,9-triene (XXII), and (6*E*,10*Z*)-5,8,9,12-tetrahydrobenzocyclodecene (XXIV) were synthesised. They all underwent a normal Cope rearrangement, thus establishing that the abnormal rearrangement is due neither to the groups on the double bonds nor to the benzene ring.

THE mechanism of the Cope rearrangement of cyclodeca-1,5-diene derivatives has been frequently discussed,³⁻⁶ and it is clear that the *trans,trans*-cyclodeca-1,5-diene system rearranges to give the *trans*-1,2-divinylcyclohexane derivative whereas the *cis,trans*-cyclodeca-1,5-diene system gives the *cis*-1,2-divinyl derivative.⁷ In

¹ Part III, K. Takeda, I. Horibe, and H. Minato, *J. Chem. Soc. (C)*, 1970, 2704.

² Preliminary communications, K. Takeda, I. Horibe, and H. Minato, *Chem. Comm.*, 1971, 87, 88.

³ W. v. E. Doering and W. R. Roth, *Tetrahedron*, 1962, **18**, 67.

particular, (1*Z*,4*Z*,8*E*)-1,2-dimethylcyclodeca-1,4,8-triene^{7,8} (I) gives a *cis*-1,2-divinylcyclohexane derivative.

However, in spite of the fact that the *cis,trans*-cyclodeca-1,5-diene type furan sesquiterpenes, *cis,trans*-furanodiene (II) and neolinderalactone (III), have the

⁴ E. Vogel, *Angew. Chem. Internat. Edn.*, 1963, **2**, 1.

⁵ G. B. Gill, *Quart. Rev.*, 1968, **22**, 386.

⁶ R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 395.

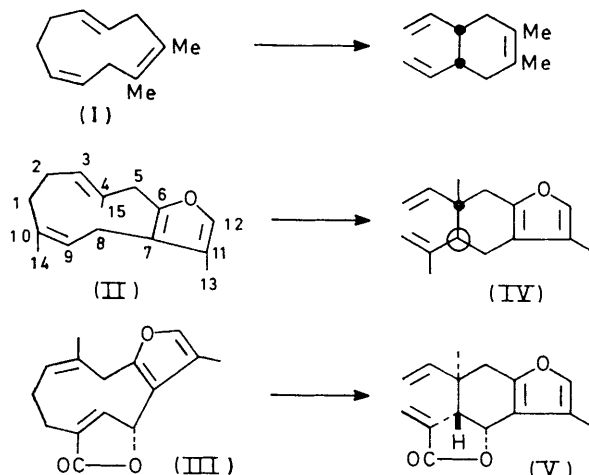
⁷ P. Heimbach, *Angew. Chem. Internat. Edn.*, 1964, **3**, 702.

⁸ W. Brenner, P. Heimbach, and G. Wilke, *Annalen*, 1969, **727**, 194.

same double bond system as (I), they undergo abnormal Cope rearrangement⁹ to give the *trans*-1,2-divinylcyclohexane derivatives, isofuranogermacrene (IV) and isolinderalactone (V), respectively. It is suggested that the discrepancy for compounds (II) and (III) is due to the effect of either the groups on the 3,4- and 9,10-double bonds,* or the furan ring, and the present work examines whether the presence or absence of the methyl groups on the double bonds has an important effect on the stereoselectivity of this rearrangement.

To obtain compounds having the *cis,trans*-1,5-diene system, we prepared some *cis,trans*-germacatriene derivatives. Photoisomerisation of cyclodecadienes affords the geometrical isomers¹⁰ of one or both double bonds, although positional isomers¹¹ or intramolecular cycloaddition products¹² are also obtained in some cases. Germacrene (VI) was therefore photoisomerised.

Upon irradiation in ether in the presence of acetophenone under nitrogen atmosphere at room temperature, using a Pyrex apparatus with a 300 W high-pressure mercury-vapour lamp, germacrene (VI) was



transformed into two photoisomers, the *cis,trans*-germacrone (VII) and the *cis,cis*-germacrone (VIII).

Application of the intramolecular nuclear Overhauser effect¹³ (n.O.e.) to (VII) showed that a vinyl methyl (δ 1.88) and a vinyl proton (δ 5.28) are in a *cis*-relationship; there was an increase of 17% in the intensity of the vinyl proton signal on double irradiation at the vinyl methyl signal. However, it was not possible to decide whether the vinyl methyl was situated at C-4 or C-10 and whether the vinyl proton was at C-3 or C-9. Compound (VII) was heated under reflux in 1*N*-ethanolic

* All germacrene derivatives in this paper are numbered using the system exemplified by compounds (II) and (VI).

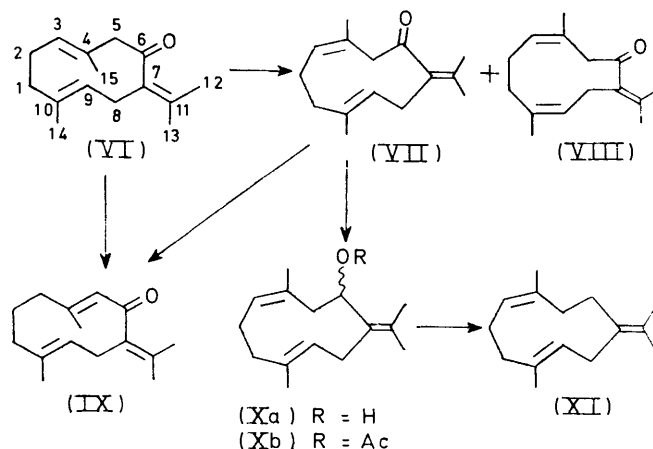
⁹ K. Takeda, I. Horibe, and H. Minato, *J. Chem. Soc. (C)*, 1970, 2704.

¹⁰ J. G. Traynham and H. H. Hsieh, *Tetrahedron Letters*, 1969, 3905; J. Dale and C. Moussebois, *J. Chem. Soc. (C)*, 1966, 264; P. Radlick and W. Fenical, *Tetrahedron Letters*, 1967, 4901.

¹¹ P. Heimbach, *Angew. Chem. Internat. Edn.*, 1966, 5, 595.

¹² A. Soni, *Tetrahedron Letters*, 1968, 5175; J. R. Scheffer and M. L. Lungle, *ibid.*, 1969, 845; J. R. Scheffer and B. A. Boire, *ibid.*, p. 4005; H. Yoshioka, T. J. Mabry, and A. Higo, *J. Amer. Chem. Soc.*, 1970, 92, 923.

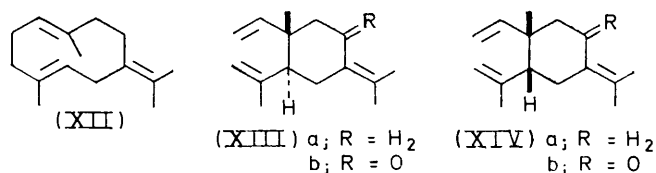
KOH for 6.5 h giving isogermacrene¹⁴ (IX), m.p. 50–52°, indicating therefore that (VII) should possess a *cis*-3,4-double bond and a *trans*-9,10-double bond.



The *cis,cis*-Germacrene (VIII) was shown to be a geometrical isomer of germacrene (VI) by n.m.r. [two vinyl protons at δ 5.32 (m) and 5.15 (tq)]: measurement of the n.O.e. (in benzene) indicated that a vinyl methyl (δ 1.74) and a vinyl proton (δ 5.32) are in a *cis*-relationship (n.O.e. value, 19%), as are another vinyl methyl (δ 1.57) and vinyl proton (δ 5.15) (n.O.e. value, 17%), thus confirming the structure of (VIII).

When (VII) was reduced with lithium aluminium hydride, it gave the *cis,trans*-alcohol (Xa), m.p. 124–125°, and treatment of the acetate (Xb) with lithium in liquid ammonia gave the *cis,trans*-germacatriene (XI).

The Cope rearrangement of the triene (XI) was investigated, and the *cis,trans*-germacrone (VII), which has *sp*² carbon atoms at positions 6 and 7, was also subjected to the rearrangement because *cis,trans*-furanodiene (II) and compound (I) have a furan ring and a double bond, respectively, at positions 6 and 7. Although the *trans,trans*-diene derivatives germacatriene¹⁵ (XII) and germacrene¹⁶ (VI) underwent Cope rearrangement to give the *trans*-1,2-divinylcyclohexane derivatives γ -elemene (XIIIa) and pyrogermacrone (XIIIb), respectively, the *cis,trans*-diene derivatives



(XI) and (VII) gave oily compounds (XIVa) and (XIVb), respectively. Physical data and g.l.c. and t.l.c. data for (XIVa) and (XIVb) were similar to, but

¹³ K. Takeda, K. Tori, I. Horibe, and H. Minato, *J. Chem. Soc. (C)*, 1970, 985 and references cited therein.

¹⁴ M. Suchý, V. Herout, and F. Šorm, *Coll. Czech. Chem. Comm.*, 1961, 26, 1358.

¹⁵ E. D. Brown, M. D. Solomon, J. K. Sutherland, and A. Torie, *Chem. Comm.*, 1967, 111.

¹⁶ G. Ohloff, *Angew. Chem.*, 1959, 71, 162; V. Herout, M. Horak, B. Schneider, and F. Šorm, *Chem. and Ind.*, 1959, 1089.

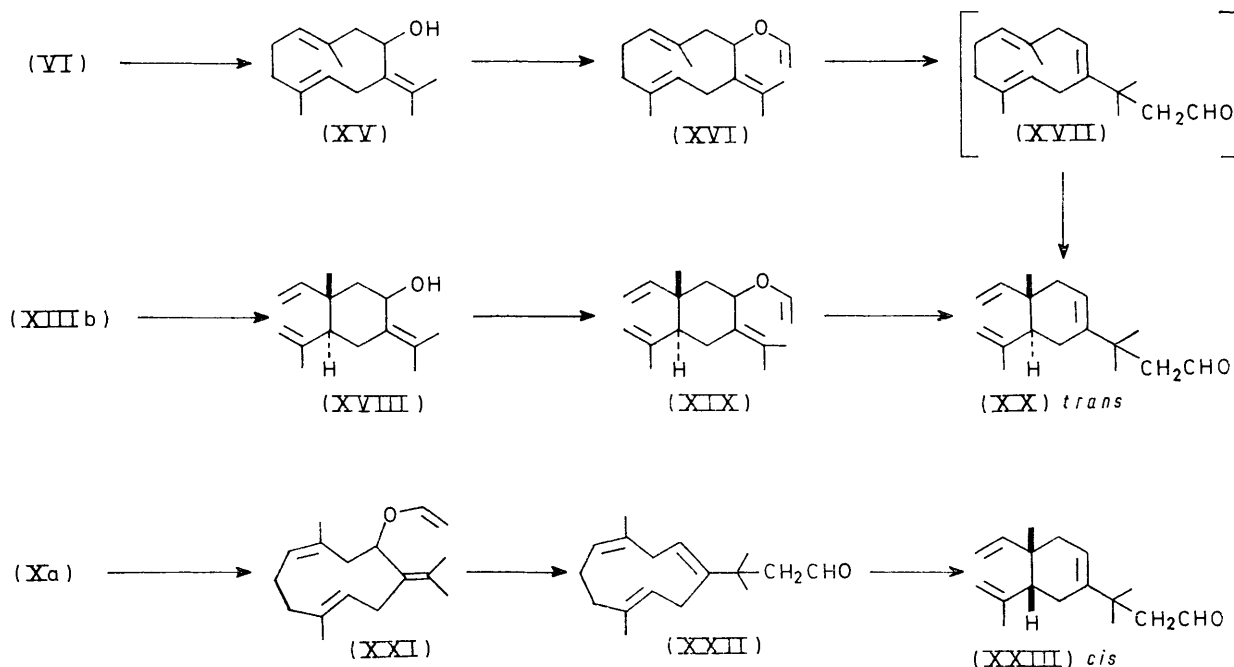
not identical with, those for γ -elemene (XIIIa) and pyrogermacrone (XIIIb), respectively, thus establishing that (XIVa) and (XIVb) are both *cis*-1,2-divinylcyclohexane derivatives. We then decided to synthesize a germacatriene having a *cis*-double bond at positions 6 and 7.

Alcohol^{15,16} (XV) derived from germacrone (VI) was heated under reflux in ethyl vinyl ether with mercury(II) acetate for 20 h under nitrogen to give an oily vinyl ether (XVI). Although (XVI) should have given the *trans*-3,*cis*-6,*trans*-9-triene (XVII) by Claisen rearrangement, it was in fact converted, on heating at 110°, into an oil

arrangement in the same way as (I), giving a *cis*-1,2-divinylcyclohexane derivative.

From these results, it was concluded that the abnormal rearrangement of (II) and (III) is caused not by the methyl groups on the double bonds at C-4 and C-10 but probably by the furan ring. We therefore examined the stereochemistry of the Cope rearrangements of some *cis,trans*-cyclodeca-1,5-diene derivatives in which the furan ring is replaced by a benzene ring.

For this purpose, the tetrahydrobenzocyclodecene (XXIV) was synthesised. Diels-Alder reaction of 1,4-naphthoquinone (XXV) with butadiene gave a quinone¹⁷



(XX), ν_{\max} 2711, 1727, 1638, 912, and 893 cm^{-1} , by a simultaneous Cope rearrangement. Pyrogermacrone (XIIIb), a *trans*-1,2-divinylcyclohexane derivative, was reduced with lithium aluminium hydride in ether to give an alcohol (XVIII), which was converted into a vinyl ether (XIX) under the same conditions as those used for (XV). Claisen rearrangement of (XIX) occurred on treatment at 100° for 15 h to give compound (XX). Thus, (XX) is a *trans*-1,2-divinylcyclohexane derivative.

The *cis,trans*-germacatrien-6-ol (Xa) afforded a vinyl ether (XXI) under the same conditions as those for the *trans,trans*-isomer (XV). Claisen rearrangement of (XXI) occurred at a low temperature, 80°, to give an aldehyde (XXII) as an oil, ν_{\max} 2706, 1727, and 824 cm^{-1} . When (XXII) was heated at 110° for 17 h in a sealed tube, it smoothly underwent Cope rearrangement to give an oil (XXIII) in good yield, ν_{\max} 2710, 1728, 1638, 912, and 892 cm^{-1} . These physical data correspond to, but are not identical with, those for (XX), thus establishing (XXIII) as a *cis*-1,2-divinylcyclohexane derivative. We had thus shown that the *cis,trans*-derivatives (XI), (VII), and (XXII) all underwent a normal Cope re-

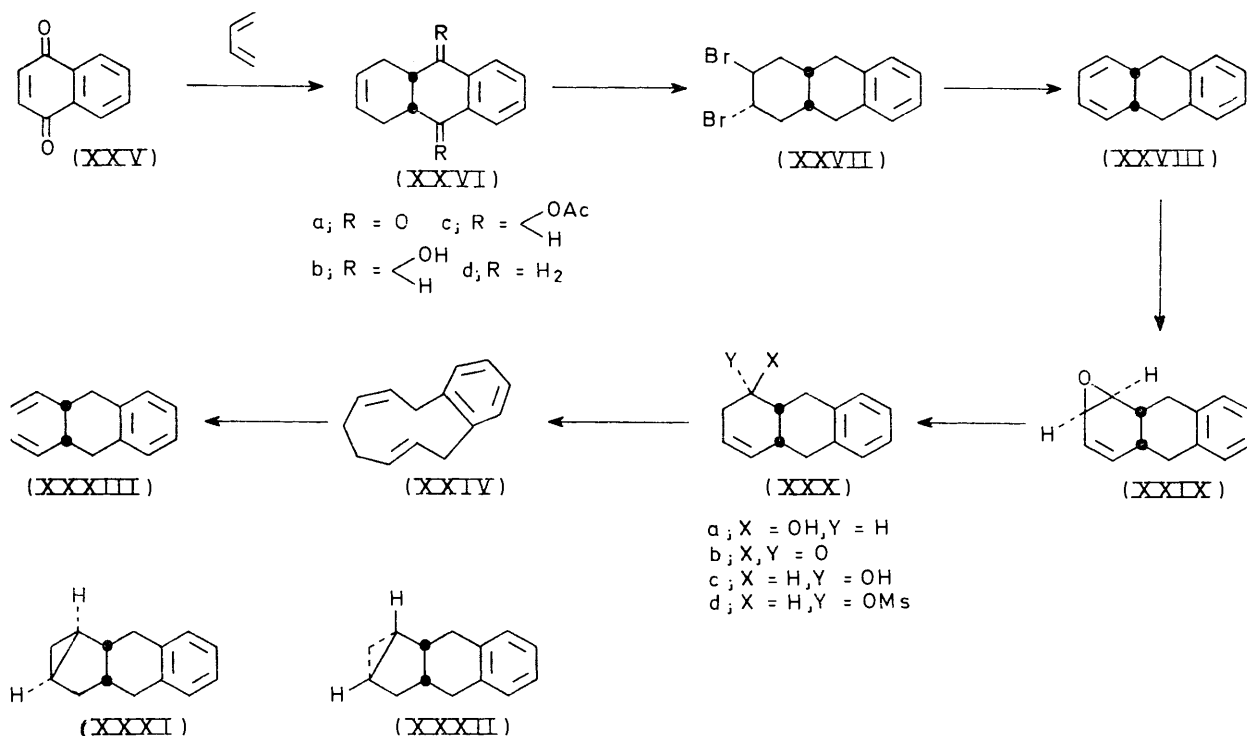
(XXVIa), m.p. 102–103°, which was reduced with lithium aluminium hydride to give a diol (XXVIb), m.p. 245–246°, in a quantitative yield. Its diacetate (XXVIc) afforded an oily compound (XXVIId) in 63% yield on reduction with lithium in liquid ammonia. When an ethereal solution of compound (XXVIId) was treated with a solution of bromine and sodium acetate in acetic acid at 0°, dibromide (XXVII) was obtained as prisms, m.p. 130.5–131°, in 80% yield. Dehydrobromination of the dibromide by heating with lithium chloride and lithium carbonate in hexamethylphosphoric triamide¹⁸ at 95° for 19 h under a nitrogen atmosphere afforded an oily diene (XXVIII), which was oxidized without purification with *m*-chloroperbenzoic acid (1.1 mol. equiv.) in dichloromethane to give an oily monoepoxide (XXIX). An alcohol (XXXa) was obtained in 45% yield as prisms, m.p. 93–94°, by reduction of (XXIX) with aluminium hydride in ether, followed by alumina chromatography. Oxidation of the alcohol (XXXa) with Collins reagent gave a $\beta\gamma$ -unsaturated

¹⁷ O. Diels and K. Alder, *Annalen*, 1928, **460**, 98.

¹⁸ A. de Meijere, *Angew. Chem. Internat. Edn.*, 1970, **9**, 899.

ketone (XXXb), ν_{\max} 1725 cm^{-1} , which was converted into an $\alpha\beta$ -unsaturated ketone, ν_{\max} 1672 cm^{-1} , by treatment with alumina. As the diene (XXVIII) was derived from Diels-Alder adduct (XXVI), its ring junction should be assigned as *cis*. In the oxidation of (XXVIII) with peracid, the reagent should attack the diene from the less hindered β -face of the molecule to give a β -epoxide (XXIX). The stereochemistry of the alcohol should therefore be represented by structure (XXXa). When the ketone (XXXb) was reduced with lithium aluminium hydride, it gave an epimer (XXXc) of (XXXa), an α -alcohol, m.p. 76–77.5°, in 72% yield. This α -alcohol was also obtained by treatment of the mesylate of (XXXa) with lithium carbonate in dimethylformamide¹⁹ to give a formate, followed by lithium aluminium hydride reduction of the formate. This indicates that isomerisation of the ring junction in

(XXXc) by reaction with mesyl chloride in triethyl amine, was treated with diborane in tetrahydrofuran at 0° to give dialkylborane derivatives. Sodium hydroxide (10%) was added to the reaction solution, and the mixture was heated under reflux for 4 h under a nitrogen atmosphere. The oily product was separated by silica gel and then by 10% AgNO_3 -silica gel chromatography to give (XXIV), m.p. 60–60.5° in 12.5% yield, and an oily compound (XXXII) in 24% yield. Compound (XXIV) showed four allylic protons at δ 1.75–2.28, four diallylic protons at 3.05–3.63, four vinyl protons at 4.90–5.63, and four aromatic protons at 7.10 in the n.m.r. spectrum. In the i.r. spectrum, (XXIV) showed strong absorption bands at 972 and 959 cm^{-1} corresponding to a *trans*-disubstituted ethylenic double bond and a strong band at 709 cm^{-1} due to a *cis*-disubstituted one. These physical data and the mechanism of boronate



(XXXc) had not occurred during the processes of oxidation of (XXXa) and reduction of (XXXb).

When the mesylate of (XXXa) was treated with diborane and the product subjected to boronate fragmentation,²⁰ it gave an oily product (XXXI), M^+ 184, which showed signals corresponding to cyclopropane ring protons, δ 0.13 (1H), 0.45 (1H), and 1.24 (2H) in the n.m.r. spectrum. This indicates that the mesylate of (XXXa) does not possess the preferred stereostructure for boronate fragmentation to give a cyclodeca-1,5-diene derivative, so the epimeric mesylate (XXXd) was subjected to the same reaction.

The mesylate (XXXd) obtained from the alcohol

¹⁹ G. A. Selter and R. D. McMichael, *J. Org. Chem.*, 1967, **32**, 2546.

fragmentation indicate that compound (XXIV) is (6*E*,10*Z*)-5,8,9,12-tetrahydrobenzocyclodecene.

Compound (XXXII), M^+ 184, showed signals corresponding to cyclopropane ring protons, δ 0.27 (1H), 0.50 (1H), and 1.24 (2H) in the n.m.r. spectrum, and is therefore, a stereoisomer of compound (XXXI). The mechanisms of these reactions are shown in the Scheme, compound (XXXI) having a cyclopropane ring on the β -face and compound (XXXII) on the α -face of the molecule.

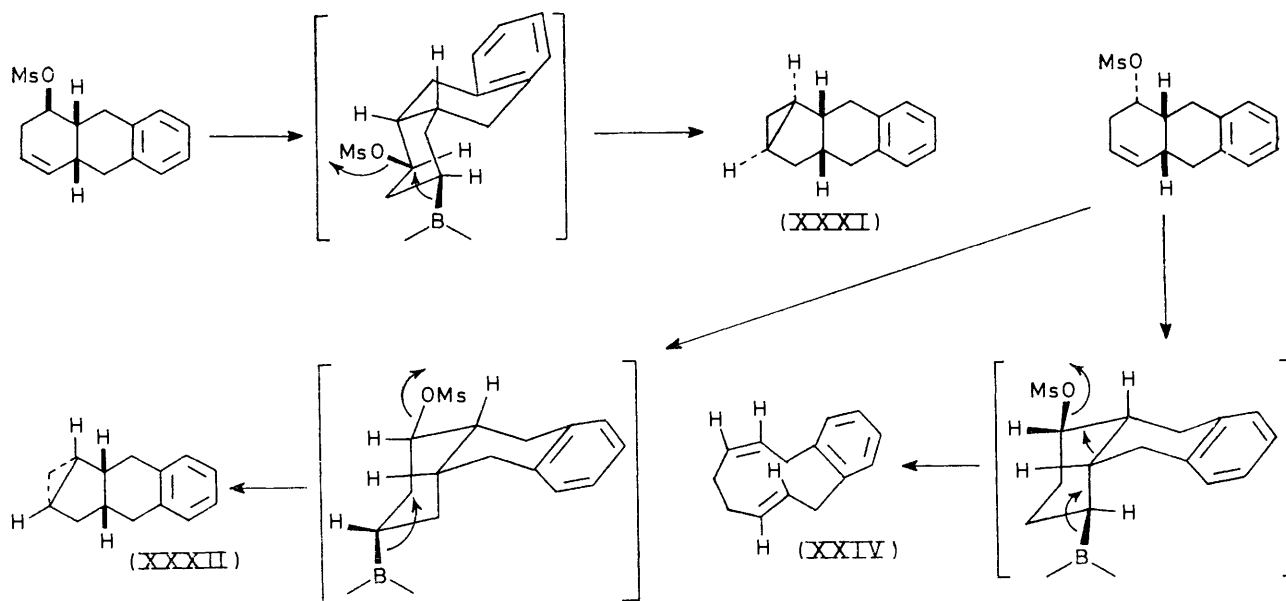
When compound (XXIV) was heated at 140° for 3.5 h in a sealed tube, it quantitatively underwent Cope

²⁰ J. A. Marshall, *Synthesis*, 1971, 229; P. S. Wharton, C. E. Sundin, P. W. Johnson, and H. C. Kleunder, *J. Org. Chem.*, 1972, **37**, 34.

rearrangement to give an oily 1,2-divinyl compound (XXXIII). This product was shown to be identical with an authentic sample of *cis*-2,3-divinyltetralin, synthesised as described below, by comparison of i.r., n.m.r., and mass spectra.

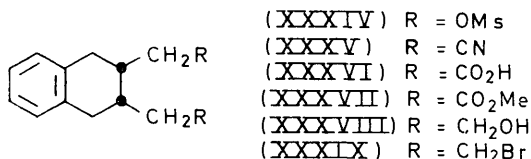
On heating the *cis*-dimesylate²¹ (XXXIV) with sodium cyanide in dimethyl sulphoxide at 90–95° for 2 h, a *cis*-dinitrile (XXXV), m.p. 96–97° was obtained. Compound (XXXV) afforded a *cis*-bismethoxycarbonyl derivative (XXXVII) on hydrolysis with 10% sodium

abnormal Cope rearrangement only occurred with furanoid germacrane-type sesquiterpenes, and it seems reasonable that this abnormality is caused by the five-membered nature of the aromatic furan ring. *cis,trans*-Furanodiene (II) and neolinderalactone (III) did not undergo the rearrangement⁹ unless heated at 200° and 300°, respectively, and the yield was poor in both cases. It is possible that a ten-membered ring having *cis*- and *trans*-double bonds at relative positions 1 and 5, respectively, loses a considerable degree of flexibility on



SCHEME

hydroxide in ethanol, followed by esterification of the carboxylic acid (XXXVI), m.p. 204–205°, with diazomethane. The diester (XXXVII) was reduced with lithium aluminium hydride to give a *cis*-diol (XXXVIII),



the mesylate of which was converted into an oily *cis*-dibromide (XXXIX) on heating under reflux with lithium bromide in acetone for 18 h under a nitrogen atmosphere. When compound (XXXIX) was dehydrobrominated by treatment with potassium *t*-butoxide in *t*-butyl alcohol and dimethyl sulphoxide (1 : 1) at room temperature under a nitrogen atmosphere, it gave *cis*-2,3-divinyltetralin (XXXIII) as a colourless, mobile oil.

Thus, all the synthetic *cis,trans*-cyclodeca-1,5-diene derivatives having no furan ring gave the normal Cope rearrangement products in good yield. The results showed that, in the cases which we examined, the

the introduction of a furan ring at relative positions 8 and 9. Probably it is less difficult for a derivative having a *cis*-double bond or a six-membered aromatic ring between these positions (C-8 and C-9) to meet the stereochemical requirement for transformation into the preferred transition state for this rearrangement. Further work on this problem is now in progress in our laboratory.

EXPERIMENTAL

Unless otherwise stated, n.m.r. spectra were taken for solutions in [²H]chloroform with a Varian A-60 instrument; i.r. spectra were taken for solutions in carbon tetrachloride, and u.v. spectra for solutions in 95% ethanol. Mass spectra were measured using a Hitachi RMU-6 single focus mass spectrometer. G.l.c. was carried out with an Aerograph model 1520 instrument, column dimensions 10 ft × 1/8 in (i.d.). M.p.s were measured with a Kofler hot-stage apparatus. N.O.e. experiments were performed with a Varian HA-100 spectrometer using *ca.* 5% (w/v) degassed solutions in [²H]chloroform for (VII) and [²H₆]benzene for (VIII) in the frequency-swept and internal tetramethylsilane-locked mode. The enhancement is expressed in % with accuracies to ±2%.

Sensitised Photoisomerisation of Germacrone (VI).—A solution of (VI) (2.0 g) and acetophenone (2.0 g) in ether (400 ml) was irradiated with a 300 W high-pressure

²¹ K. Alder and M. Fremery, *Tetrahedron*, 1961, **14**, 190; H. Peters, R. A. Archer, and H. S. Mosher, *J. Org. Chem.*, 1967, **32**, 1382.

mercury-vapour lamp through Pyrex for 5 h under nitrogen. The solvent was carefully evaporated and the residual oil was chromatographed on alumina (80 g) to give a mobile oil (1.55 g), which showed two peaks, t_R 5.95 and 6.8 min, ratio *ca.* 1:2 on g.l.c. (5% Carbowax 20 M; 160°; N_2 50 ml min⁻¹). This oil was separated by 5% silver nitrate-alumina chromatography into (3Z,9E)-germacra-3,7(11),9-trien-6-one (VII), an oil, b.p. 100° (bath) at 1 mmHg, t_R 5.95 min, ν_{max} 1699, 1661, 1299, 1152, 991, and 857 cm⁻¹, λ_{max} 245 (ϵ 2100) and 301 nm (230), δ 1.58 (Me), 1.64 (Me), 1.73 (Me), 1.88 (Me), 5.07 (1H), and 5.28 (1H) (Found: C, 82.2; H, 10.05. C₁₅H₂₂O requires C, 82.5; H, 10.15%), and (3Z,9Z)-germacra-3,7(11),9-trien-6-one (VIII), an oil, b.p. 100° (bath) at 1 mmHg, t_R 6.8 min, ν_{max} 1684, 1668, 1614, 1297, and 832 cm⁻¹, λ_{max} 255 (ϵ 5000) and 311sh nm (182), δ (CCl₄) 1.68 (2Me), 1.78 (2Me), 5.12 (1H), and 5.42 (1H), δ (C₆D₆) 1.48 (Me), 1.57 (Me), 1.74 (Me), 1.80 (Me), 5.15 (1H), and 5.32 (1H) (Found: C, 82.4; H, 10.4. C₁₅H₂₂O requires C, 82.5; H, 10.15%).

Isomerisation of the Germacatrienone (VII) into Iso-germacrone (IX).—A solution of (VII) (30 mg) in *n*-ethanolic potassium hydroxide (5 ml) was heated under reflux for 6.5 h under nitrogen. The solvent was evaporated off and the residue was extracted with ether. The extract was separated by preparative t.l.c. into isogermacrone [(4E,9E)-germacra-4,7(11),9-trien-6-one] (IX) (7 mg) as prisms, m.p. 50—52° (from ethanol), ν_{max} (CHCl₃) 1663, 1624, 1155, 1009, 882, 833, and 821 cm⁻¹, identical with isogermacrone (mixed m.p., and i.r. spectrum), and the starting material (VII) (14 mg).

Reduction of the Germacatrienone (VII) with Lithium Aluminium Hydride.—A solution of (VII) (62 mg) in dry ether (3 ml) was reduced with lithium aluminium hydride (15 mg) at room temperature for 40 min. The product was recrystallised from light petroleum to give (3Z,9E)-germacra-3,7(11),9-trien-6-ol (Xa) (60 mg), m.p. 124—125°, ν_{max} 3585, 3466, 1653, 995, 978, and 839 cm⁻¹ (Found: C, 82.05; H, 10.95. C₁₅H₂₄O requires C, 81.75; H, 11.0%). The acetate (Xb) was a mobile oil, ν_{max} 1735, 1652, 1242, 1012, and 946 cm⁻¹.

Reduction of Acetate (Xb) with Lithium in Liquid Ammonia.—To a stirred solution of lithium (100 mg) in liquid ammonia (10 ml) at -60 to -70° was added dropwise during 5 min a solution of (Xb) (68 mg) in dry ether (6 ml), and the mixture was stirred for 1 h. Ammonium chloride (1.0 g) was then added with stirring at the same temperature. The solvent was evaporated off and the residue was diluted with water and extracted with ether, to yield an oil (55 mg). The product was dissolved in light petroleum and chromatographed on alumina (2 g) to give the alcohol (Xa) (17 mg) and (3Z,9E)-germacra-3,7(11),9-triene (XI) (32 mg) as an oil, b.p. 90° (bath) at 4 mmHg, ν_{max} 1659 and 852 cm⁻¹, δ 1.63 (Me), 1.65 (Me), 1.72 (Me), 1.98 (Me), and 5.12 (2H) (Found: C, 88.3; H, 11.75. C₁₅H₂₄ requires C, 88.15; H, 11.85%).

Cope Rearrangement of the Germacatrienone (VII).—(i) When a solution of (VII) in *p*-cymene was heated at 177° for 2 h under nitrogen, it gave a Cope rearrangement product (XIVb) and the starting material in the ratio, *ca.* 1:1.

(ii) Compound (VII) (50 mg) was heated at 220° in a sealed tube for 2 h. The product was chromatographed on 5% silver nitrate-alumina (1.5 g) to give *r*-4-isopropenyl-2-isopropylidene-5-methyl-*c*-5-vinylcyclohexanone (XIVb) as a mobile oil (39 mg), b.p. 90° (bath) at 0.2 mmHg, ν_{max} 1687,

1640, 1607, 1303, 1282, 1209, 919, and 897 cm⁻¹, λ_{max} 256.5 nm (ϵ 6600), δ 1.07 (Me), 1.78 (Me), 2.05 (Me), 4.78—5.13 (4H), and 5.98 (1H) (Found: C, 82.2; H, 9.9. C₁₅H₂₂O requires C, 82.5; H, 10.15%).

Cope Rearrangement of the Germacatriene (XI).—When compound (XI) (100 mg) was heated at 200° in a sealed tube for 2 h, it gave a mixture containing the starting material (XI) (33%) and a rearrangement product (XIVa) (67%).

This mixture was separated by preparative g.l.c. using a column (10 ft × 3/8 in) of Carbowax 20M (180°; He 100 ml min⁻¹) into (XI) (15 mg) and *r*-2-isopropenyl-4-isopropylidene-1-methyl-*c*-1-vinylcyclohexane (XIVa) (23 mg), an oil, b.p. 90° (bath) at 6 mmHg, ν_{max} 1637, 1001, 911, and 891 cm⁻¹, δ 1.02 (Me), 1.68 (3Me), 4.68—5.15 (4H), and 6.40 (1H) (Found: C, 87.9; H, 11.65. C₁₅H₂₄ requires C, 88.15; H, 11.85%).

Conversion of Alcohol (XV) into Vinyl Ether (XVI).—To a solution of (XV) (500 mg) in ethyl vinyl ether (30 ml) was added mercury(II) acetate (500 mg). The mixture was heated under reflux for 20 h under nitrogen, then glacial acetic acid (0.5 ml) was added with stirring at room temperature, and stirring was continued for 1.5 h. The mixture was diluted with water and extracted with light petroleum. The extract was washed with 2*N*-potassium hydroxide solution and water, dried (Na₂SO₄), and evaporated, leaving an oily residue (830 mg). This was chromatographed on alumina (25 g) to give (3E,9E)-6-vinyloxygermacra-3,7(11),9-triene (XVI) (570 mg), a mobile oil, b.p. 105° (bath) at 0.2 mmHg, ν_{max} 1635, 1614, 1193, 1180, 1063, and 1041 cm⁻¹, δ 1.52 (Me), 1.56 (Me), 1.77 (2Me), 3.95 (1H), 4.22 (1H), 4.75 (2H), and 6.28 (1H) (Found: C, 82.95; H, 10.65. C₁₇H₂₆O requires C, 82.85; H, 10.65%).

Claisen and Cope Rearrangements of Vinyl Ether (XVI).—Compound (XVI) (56 mg) was heated at 110° in a sealed tube for 15 h. The mixture was separated by preparative t.l.c. into 3-(*t*-5-isopropenyl-4-methyl-*r*-4-vinylcyclohex-1-enyl)-3-methylbutanal (XX) (25 mg), an oil, b.p. 100° (bath) at 0.2 mmHg, ν_{max} 2711, 1727, 1638, 912, and 893 cm⁻¹, δ 0.94 (Me), 1.18 (2Me), 1.75 (Me), 2.38 (2H), 4.73—5.08 (4H), 5.51 (1H), 5.82 (1H), and 9.66 (1H) (Found: C, 82.7; H, 10.65. C₁₇H₂₆O requires C, 82.85; H, 10.65%), and the starting material (XVI) (28 mg).

Reduction of Pyrogermacrone (XIIIb) with Lithium Aluminium Hydride.—A solution of (XIIIb) (100 mg) in dry ether (4 ml) was reduced with lithium aluminium hydride (20 mg) in dry ether (4 ml) at room temperature for 1.5 h. The product (103 mg) was purified by p.l.c. to give *r*-4-isopropenyl-2-isopropylidene-5-methyl-*t*-5-vinylcyclohexanol (XVIII) (95 mg), an oil, ν_{max} 3570, 3451, 1636, 1043, 908, and 892 cm⁻¹.

Conversion of Alcohol (XVIII) into Vinyl Ether (XIX).—To a solution of (XVIII) (93 mg) in ethyl vinyl ether (10 ml) was added mercury(II) acetate (100 mg). The mixture was heated under reflux for 15 h under nitrogen, and worked up in the same manner as that used for compound (XV). The product (106 mg) was chromatographed on alumina (8 g) to give *r*-2-isopropenyl-4-isopropylidene-1-methyl-*t*-1-vinyl-5-vinylcyclohexane (XIX) (40 mg), an oil, ν_{max} 1635, 1610, 1191, 1180, 911, and 893 cm⁻¹ and the starting material (XVIII) (46 mg).

Claisen Rearrangement of Vinyl Ether (XIX).—Compound (XIX) (30 mg) was heated at 100° in a sealed tube for 15 h. The product was purified by p.l.c. to yield an aldehyde (22 mg), as an oil, which was identical with (XX) derived

from vinyl ether (XVI) (i.r. and n.m.r. spectra, and t.l.c. R_F values).

Conversion of Alcohol (Xa) into Vinyl Ether (XXI).—To a solution of (Xa) (340 mg) in ethyl vinyl ether (25 ml) was added mercury(II) acetate (340 mg). The mixture was heated under reflux for 17 h under nitrogen, and worked up in the same manner as that used for compound (XV). The product (410 mg) was chromatographed on alumina (15 g) to give (3Z,9E)-6-vinylxygermacra-3,7(11),9-triene (XXI) (333 mg), a mobile oil, b.p. 110° (bath) at 0.3 mmHg, ν_{\max} 1635, 1609, 1188, 1177, 1027, and 827 cm^{-1} , δ 1.63 (Me), 1.72 (Me), 1.78 (Me), 1.84 (Me), 3.93 (1H), 4.27 (1H), 4.82 (1H), 5.09 (1H), and 6.22 (1H) (Found: C, 82.75; H, 10.6. $\text{C}_{17}\text{H}_{26}\text{O}$ requires C, 82.85; H, 10.65%).

Claisen Rearrangement of Vinyl Ether (XXI).—Compound (XXI) (238 mg) was heated at 80° for 15 h in a sealed tube. The product was chromatographed on alumina (20 g) to give the starting material (XXI) (174 mg) and an aldehyde mixture [(XXII) + (XXIII)] (62 mg) as an oil. This oil was separated by p.l.c. into (3Z,6Z,9E)-11-formylmethylgermacra-3,6,9-triene (XXII) (45 mg), a mobile oil, ν_{\max} 2706, 1727, and 824 cm^{-1} , δ 1.19 (2Me), 1.67 (Me), 1.72 (Me), 2.39 (2H), 4.97 (1H), 5.08 (1H), 5.63 (1H), and 9.67 (1H), and a Cope rearrangement product (XXIII) (5 mg) (see below).

Cope Rearrangement of Aldehyde (XXII).—Compound (XXII) (63 mg) was heated at 110° for 17 h in a sealed tube. The product was purified by p.l.c. to give 3-(c-5-isopropenyl-4-methyl-r-4-vinylcyclohex-1-enyl)-3-methylbutanal (XXIII) (54 mg), an oil, b.p. 90° (bath) at 0.3 mmHg, ν_{\max} 2710, 1728, 1638, 912, and 892 cm^{-1} , δ 1.02 (Me), 1.18 (2Me), 1.72 (Me), 4.72—5.08 (4H), 5.55 (1H), 6.02 (1H), and 9.67 (1H) (Found: C, 82.9; H, 10.65. $\text{C}_{17}\text{H}_{26}\text{O}$ requires C, 82.95; H, 10.65%).

Reduction of cis-1,4,4a,9a-Tetrahydroanthraquinone (XXVIa).—A solution of (XXVIa) (16 g) in dry tetrahydrofuran (200 ml) was added dropwise to suspension of lithium aluminium hydride (3.1 g) in dry ether (150 ml) and dry tetrahydrofuran (100 ml) with stirring in an ice-bath and the mixture was stirred for 1.5 h at room temperature. To this mixture was slowly added water (10 ml) in an ice-bath and stirring was continued for 1 h. A small amount of anhydrous sodium sulphate was added and the mixture was filtered and evaporated, leaving a crystalline residue, which was recrystallised from methanol to give cis-1,4,4a,9,9a,10-hexahydroanthracene-9,10-diol (XXVIb) (15.5 g, 95%) as colourless prisms, m.p. 245—246°, ν_{\max} (Nujol) 3412, 3320, 1324, 1122, 1049, 1031, 1014, 958, 765, 758, 659, and 645 cm^{-1} (Found: C, 77.95; H, 7.55. $\text{C}_{14}\text{H}_{16}\text{O}_2$ requires C, 77.75; H, 7.45%).

Compound (XXVIb) (15 g) was acetylated with acetic anhydride (15 ml) and pyridine (60 ml) to give cis-1,4,4a,9,9a,10-hexahydroanthracene-9,10-diyl diacetate (XXVIc) (14.4 g, 70%), an oil, ν_{\max} (CCl_4) 1738, 1600, 1372, 1225, 1041, 1016, and 950 cm^{-1} .

Reduction of Diacetate (XXVIc).—A solution of (XXVIc) (14.4 g) in dry ether (100 ml) was added dropwise to a stirred solution of lithium (5.5 g) in liquid ammonia (500 ml) at -60° to -70°. After 1 h ammonium chloride (30 g) was added in portions over 1 h, and ammonia was allowed to evaporate. The residue was diluted with water and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated, leaving an oily residue (9.5 g). This oil was dissolved in light petroleum and chromatographed on alumina (50 g) to give cis-1,4,4a,9,9a,10-

hexahydroanthracene (XXVIId) (4.92 g, 63%), a mobile oil, b.p. 88—89° at 0.3 mmHg, ν_{\max} (CCl_4) 3022, 1653, 1582, 1494, 671, and 644 cm^{-1} (Found: C, 91.0; H, 8.85. $\text{C}_{14}\text{H}_{16}$ requires C, 91.25; H, 8.75%).

Bromination of cis-1,4,4a,9,9a,10-Hexahydroanthracene (XXVIId).—A solution of sodium acetate (335 mg) and bromine (4.8 g) in glacial acetic acid (30 ml) was added dropwise to a solution of (XXVIId) (5.0 g) in dry ether (100 ml) with stirring in an ice-bath. After 10 min the solution was poured into ice-water (100 ml) and the product was extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and evaporated. The residue (9.02 g) was recrystallised from ether to give trans-2,3-dibromo-cis-1,2,3,4,4a,9,9a,10-octahydroanthracene (XXVII) (7.34 g, 80%), prisms, m.p. 130.5—131°, ν_{\max} (Nujol) 1580, 1492, 1259, 1163, 803, 759, 750, 717, 680, and 673 cm^{-1} (Found: C, 49.15; H, 4.75; Br, 46.2. $\text{C}_{14}\text{H}_{16}\text{Br}_2$ requires C, 48.85; H, 4.7; Br, 46.45%).

Dehydrobromination of trans-Dibromide (XXVII).—Anhydrous lithium chloride (2.7 g) and lithium carbonate (2.36 g) were added to a stirred solution of dibromide (7.34 g) in hexamethylphosphoric triamide (30 ml), and the solution was heated at 95° for 19 h under nitrogen. The mixture was diluted with water and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated, to leave an oil (4.1 g). This oil was chromatographed on silica gel (40 g) to give cis-4a,9,9a,10-tetrahydroanthracene (XXVIII) (3.84 g) as a mobile oil, ν_{\max} (CCl_4) 3038, 1680, 1583, 1491, 709, and 699 cm^{-1} , δ 1.90—2.90 (6H), 5.83 (4H), 6.93 (2H), and 6.97 (2H).

Epoxidation of cis-4a,9,9a,10-Tetrahydroanthracene (XXVIII).—A solution of diene (XXVIII) (3.84 g) in dichloromethane (100 ml) was stirred at 0° and a solution of *m*-chloroperbenzoic acid (5.0 g; purity 80%) in dichloromethane (100 ml) was added dropwise. After 30 min, the solution was washed with 2*N*-sodium hydroxide and water, dried (Na_2SO_4), and evaporated, leaving a residue (4.6 g). This was chromatographed on silica gel (10 g) to give the starting material (XXVIII) (770 mg, 20%), and 1 β ,2 β -epoxy-cis-1,2,4a,9,9a,10-hexahydroanthracene* (XXIX) (1.04 g, 31%), a mobile oil, b.p. 90° (bath) at 0.2 mmHg, ν_{\max} (CCl_4) 1645, 1584, 1494, 1013, 960, 927, 880, 704, 695, 669, 657, and 638 cm^{-1} , δ 1.92—3.07 (6H), 3.22 (1H), 3.57 (1H), 5.65 (1H), 5.90 (1H), 7.10 (2H), and 7.13 (2H) (Found: C, 84.55; H, 7.15. $\text{C}_{14}\text{H}_{14}\text{O}$ requires C, 84.8; H, 7.1%).

Reduction of Epoxide (XXIX).—Anhydrous aluminium chloride (650 mg, 1 mol. equiv.) was added to a suspension of lithium aluminium hydride (565 mg, 3.3 mol. equiv.) in dry ether (50 ml) with stirring in an ice-bath and the mixture was stirred for 1 h at room temperature. To this solution of aluminium hydride was then added dropwise a solution of epoxide (XXIX) (914 mg) in dry ether (30 ml) at 0°, and the mixture was stirred for 1 h at room temperature. Water (10 ml) was slowly added and the mixture was extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated, leaving a residue (920 mg). This was chromatographed on alumina (30 g) to give cis-1,2,4a,9,9a,10-hexahydroanthracen-1 β -ol (XXXa) (414 mg, 45%), as prisms, m.p. 93—94° (from ether-light

* The configurational notations α and β refer to groups which lie on the opposite and the same side as the angular group, respectively.

petroleum), ν_{\max} . (Nujol) 3364, 3290, 1070, 1046, 1019, 803, 760, 747, 734, and 710 cm^{-1} , δ 1.97—3.00 (8H), 3.81 (1H, ddd, J 8.4, 6.8, and 5.6 Hz), 5.63 (2H), and 7.09 (4H) (Found: C, 84.05; H, 7.75. $\text{C}_{14}\text{H}_{16}\text{O}$ requires C, 83.95; H, 8.05%).

Oxidation of Alcohol (XXXa).—A solution of (XXXa) (414 mg) in dichloromethane (10 ml) was added dropwise to a stirred solution of Collin's reagent prepared from chromium trioxide (1.24 g) and dry pyridine (2.0 ml) in dichloromethane (20 ml). After 30 min the mixture was filtered and the filtrate was washed with water, dried (Na_2SO_4), and evaporated, leaving an oily residue (400 mg). The crude product was purified by silica gel chromatography to give *cis*-4a,9,9a,10-tetrahydroanthracen-1(2H)-one (XXXb) (360 mg, 90%), ν_{\max} . (CCl_4) 1725, 1585, 1121, and 1097 cm^{-1} .

Alumina (1.0 g) was added to a solution of (XXXb) (10 mg) in ether (2.5 ml) and stirred for 1.0 h at room temperature. The crude product was purified by p.l.c. on silica gel to give an $\alpha\beta$ -unsaturated ketone (8 mg), ν_{\max} . (CHCl_3) 1672, 1584, 1493, 1155, and 1108 cm^{-1} .

Reduction of Ketone (XXXb).—A solution of (XXXb) (360 mg) in dry ether (7 ml) was added dropwise to a suspension of lithium aluminium hydride (135 mg) in dry ether (15 ml) with stirring in an ice-bath. The mixture was stirred for 1 h at room temperature and decomposed by addition of water. The product was chromatographed on alumina (10 g) to give *cis*-1,2,4a,9,9a,10-hexahydroanthracen-1 α -ol (XXXc) (295 mg, 80%), as needles, m.p. 76—77.5° (from light petroleum-ether), ν_{\max} . (Nujol) 3388, 3320, 3055, 3018, 1645, 1586, 1497, 1070, 1019, 831, 784, 745, 740, and 642 cm^{-1} , δ 2.03—3.00 (8H), 4.18 (1H, ddd, J 8.5, 6.7, and 3.5 Hz), 5.30—5.73 (2H), and 7.13 (4H) (Found: C, 83.8; H, 8.05. $\text{C}_{14}\text{H}_{16}\text{O}$ requires C, 83.95; H, 8.05%).

Conversion of Alcohol (XXXa) into its Epimer (XXXc).—A solution of methanesulphonyl chloride (350 mg) in dichloromethane (4 ml) was added to a solution of (XXXa) (400 mg) and triethylamine (400 mg) in dichloromethane (15 ml) with stirring in an ice-bath. After 30 min the mixture was poured into 2*N*-sulphuric acid and extracted with dichloromethane. The extract was washed with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and evaporated, leaving an oily methanesulphonate (542 mg, quantitative yield), ν_{\max} . (CCl_4) 1372, 1347, 1177, 968, 946, 934, 917, and 867 cm^{-1} .

To a solution of the above methanesulphonate (240 mg) in *NN*-dimethylformamide (8 ml) was added lithium carbonate (240 mg), and the mixture was heated at 135° for 7.5 h with stirring under nitrogen. The reaction mixture was diluted with water and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated, leaving an oily residue (173 mg) containing a formate. The residue was dissolved in dry ether (8 ml) and reduced with lithium aluminium hydride (50 mg) for 1 h at room temperature to give an oily mixture (160 mg). The mixture was chromatographed on alumina (5 g) to yield an alcohol (30 mg) as needles, which was identical with (XXXc) derived from ketone (XXXb) (m.p. and i.r. and n.m.r. spectra).

Treatment of the Methanesulphonate of (XXXa) with Diborane.—A solution of the methanesulphonate (60 mg) of (XXXa) in dry tetrahydrofuran (3 ml) was added dropwise to a stirred solution of 1.0*M*-diborane in tetrahydrofuran (4.5 ml) in an ice-bath. The mixture was stirred for 30 min at 0° and 1 h at room temperature. To the mixture

in an ice-bath were carefully added water (0.5 ml) and 10% sodium hydroxide (3 ml). The mixture was heated under reflux for 17 h under nitrogen, cooled, and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated, leaving an oily residue (39 mg), which was purified by p.l.c. on silica gel to give 1 β ,3 β -cyclo-*cis*-1,2,3,4,4a,9,9a,10-octahydroanthracene (XXXI) (19 mg, 47%) as an oil, M^+ 184, ν_{\max} . (CS_2) 3060, 3040, 3015, 1018, 814, and 742 cm^{-1} , δ * 0.13 (1H, dd, J 8.4 and 4.0 Hz), 0.45 (1H, dt, J 8.0 and 5.0 Hz), 1.24 (2H, m), and 7.12 (4H, s).

Mesylation of Alcohol (XXXc).—A solution of methanesulphonyl chloride (240 mg) in dichloromethane (4 ml) was added to a solution of (XXXc) (280 mg) and triethylamine (280 mg) in dichloromethane (12 ml) with stirring in an ice-bath. The mixture was stirred for 30 min at the same temperature, and worked up under the same manner as that used for alcohol (XXXa) to give *cis*-1,2,4a,9,9a,10-hexahydroanthracen-1 α -yl methanesulphonate (XXXd) (380 mg) as a light yellow oil, ν_{\max} . (CCl_4) 1373, 1347, 1176, 944, 934, 910, and 867 cm^{-1} .

Treatment of Methanesulphonate (XXXd) with Diborane.—A solution of (XXXd) (380 mg) in dry tetrahydrofuran (10 ml) was added dropwise to a solution of 1.0*M*-diborane in tetrahydrofuran (20 ml) with stirring in an ice-bath. The mixture was stirred for 1 h at 0° and 1 h at room temperature. To the mixture in an ice-bath were carefully added water (2.0 ml) and 10% sodium hydroxide (15 ml). The mixture was heated under reflux for 4 h under nitrogen, and worked up as in the case of the methanesulphonate of (XXXa). The product (283 mg) was dissolved in light petroleum, and chromatographed on silica gel (8 g) to give hydrocarbon mixture (105 mg). This was separated by 10% silver nitrate-alumina (4 g) chromatography into 1 α ,3 α -cyclo-*cis*-1,2,3,4,4a,9,9a,10-octahydroanthracene (XXXII) (60 mg, 24%), an oil, M^+ 184, ν_{\max} . (CS_2) 3060, 3038, 3018, 1018, 813, 764, 746, and 730 cm^{-1} , δ * 0.27 (1H, dd, J 9.5 and 5.0 Hz), 0.50 (1H, m), 1.24 (2H, m), and 7.15 (4H, s); and (6*E*,10*Z*)-5,8,9,12-tetrahydrobenzocyclodecene (XXIV) (31.5 mg, 13%), needles, m.p. 60—60.5° (from ethanol), M^+ 184, ν_{\max} . (CS_2) 3054, 3004, 972, 959, 910, 741, and 709 cm^{-1} , δ 1.75—2.28 (4H, m), 3.05—3.63 (4H, m), 4.90—5.63 (4H, m), and 7.10 (4H, s).

Cope Rearrangement of (XXIV).—When compound (XXIV) was heated at 120° in a sealed tube, it gave a mixture of a Cope rearrangement product and the starting material on a ratio of *ca.* 1 : 4 after 30 min, and 1 : 2 after 1.0 h.

Compound (XXIV) (21 mg) was heated at 140° in a sealed tube for 3.5 h. The product was purified by p.l.c. to give the Cope rearrangement product (18 mg) as a mobile oil, b.p. 90° (bath) at 1.0 mmHg, which was identical with *cis*-2,3-divinyl-1,2,3,4-tetrahydronaphthalene (XXXIII) derived from *cis*-dibromide (XXXIX) (i.r., n.m.r., and mass spectra).

1,2,3,4-Tetrahydronaphthalene-2,3-*cis*-bisacetoneitrile (XXXV).—To a solution of the bismethanesulphonate (XXXIV)²¹ (685 mg) in dimethyl sulphoxide (8 ml) was added sodium cyanide (240 mg), and the mixture was heated with stirring for 2 h at 90°. The mixture was poured into ice-water and extracted with dichloromethane. The extract was washed with water, dried (Na_2SO_4), and evaporated, leaving a crystalline residue, which was

* The n.m.r. spectra were taken with a Varian HR-220 spectrometer operating at 220 MHz using *ca.* 5% solutions in deuteriochloroform containing dichloromethane as internal standard.

crystallised from ethyl acetate to give the *bisacetonitrile* (XXXV) (400 mg, quant.), as needles, m.p. 96–97°, ν_{\max} (Nujol) 2250, 1581, 1494, 1265, 1224, 1115, 950, 751, and 675 cm^{-1} (Found: C, 79.8; H, 6.6; N, 13.4. $\text{C}_{14}\text{H}_{14}\text{N}_2$ requires C, 79.95; H, 6.7; N, 13.3%).

Hydrolysis of the Bisacetonitrile (XXXV).—A solution of (XXXV) (309 mg) in 10% sodium hydroxide–ethanol (10 ml) was heated under reflux for 16 h under nitrogen and then evaporated *in vacuo*, and the residue was dissolved in water (20 ml). The aqueous solution was washed with dichloromethane, and the aqueous layer was acidified with 6*N*-hydrochloric acid and filtered, leaving a white powder (365 mg, quant.), which was recrystallised from ethanol–ethyl acetate (1:1) to give 1,2,3,4-tetrahydronaphthalene-2,3-*cis*-diacetic acid (XXXVI) as prisms, m.p. 204–205°, ν_{\max} (Nujol) 1716, 1697, 1583, 1497, 1300, 1277, 1235, 1207, 1191, 948, 933, 920, 761, 745, and 672 cm^{-1} (Found: C, 67.7; H, 6.6. $\text{C}_{14}\text{H}_{16}\text{O}_4$ requires C, 67.75; H, 6.5%).

Reduction of the Diacetic Acid (XXXVI).—A solution of (XXXVI) (530 mg) in tetrahydrofuran (4 ml) and ether (3 ml) was treated with diazomethane to give dimethyl 1,2,3,4-tetrahydronaphthalene-2,3-*cis*-diacetate (XXXVII) (590 mg).

This was dissolved in dry ether (20 ml) and treated with lithium aluminium hydride (160 mg) at room temperature for 2 h to give 1,2,3,4-tetrahydronaphthalene-2,3-*cis*-diethanol (XXXVIII) (465 mg), an oil, ν_{\max} (film) 3323, 1583, 1495, 1051, 1020, 1001, 745, and 679 cm^{-1} .

2,3-*cis*-Bis-(2-bromoethyl)-1,2,3,4-tetrahydronaphthalene (XXXIX).—A solution of methanesulphonyl chloride (580 mg) in dichloromethane (6 ml) was added to a solution of (XXXVIII) (465 mg) and triethylamine (560 mg) in dichloromethane (20 ml) with stirring in an ice-bath. The

mixture was stirred for 30 min at same temperature, and worked up under the same manner as that used for alcohol (XXXa), giving a bismethanesulphonate (524 mg, 66%) as a light yellow, viscous oil, ν_{\max} (film) 1583, 1356, 1175, 972, 950, 925, and 749 cm^{-1} .

To a solution of this bismethanesulphonate (520 mg) in acetone (15 ml) was added anhydrous lithium bromide (1.0 g), and the mixture was heated under reflux for 18 h with stirring under nitrogen. The solvent was evaporated *in vacuo*, and the residue was extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated to leave a residue (537 mg). The residue was dissolved in benzene and chromatographed on silica gel (10 g) to give 2,3-*cis*-bis-(2-bromoethyl)-1,2,3,4-tetrahydronaphthalene (XXXIX) (480 mg), a mobile oil, ν_{\max} (film) 3017, 1583, 1495, 1267, 1250, and 745 cm^{-1} .

Dehydrobromination of the Dibromide (XXXIX).—Potassium *t*-butoxide (1.45 g) was added in portions to a stirred solution of (XXXIX) (450 mg) in *t*-butyl alcohol (4 ml) and dried (with molecular sieves) dimethyl sulphoxide (4 ml) in an ice-bath under nitrogen, and stirring was continued for 1 h at room temperature. The mixture was slowly poured into ice-water (20 ml) and the product was extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated. The residue (260 mg) was dissolved in light petroleum and chromatographed on silica gel (6 g) to give the *cis*-divinyl derivative (XXXIII) (82 mg, 34%), a mobile oil, b.p. 90° (bath) at 1.0 mmHg, M^+ 184, ν_{\max} (CCl_4) 3076, 3062, 3017, 3000, 2975, 1642, 1582, 1494, 993, and 917 cm^{-1} , δ (CCl_4) 2.55–2.90 (6H, m), 4.83–5.17 (4H, m), 5.83 (1H, ddd, J 15.3, 9.4, and 6.2 Hz), and 6.97 (4H, s).

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