trans-Cycloalkenes. Part II.[1] Application of the Dioxolan Olefin Synthesis to the Stereospecific Formation of *trans*-Cyclo-octene Derivatives. (1*SR*,2*RS*)-*trans*-Cyclo-oct-2-en-1-ol

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The reaction of benzylidene derivatives of 3-substituted *trans*-cyclo-octane-1,2-diols with n-butyl-lithium leads to 3-substituted *trans*-cyclo-octenes. By appropriate choice of precursors the stereochemistry of the products can be controlled, and diastereoisomeric derivatives of *trans*-cyclo-octene where the 3-substituent is MeO, OH, or Bu^n have been prepared.

In Part I[1] the reasons for our interest in 3-substituted *trans*-cyclo-octenes were outlined and the preparation of (1*RS*,2*RS*)-*trans*-cyclo-oct-2-en-1-ol (I) † was described. Preliminary attempts to invert configuration at C-1 in structure (I), either by S_N2 displacement on a suitable derivative, or by oxidation to the ketone[3] followed by

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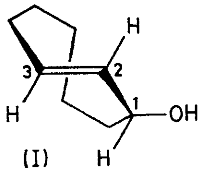
† Although all compounds in this series were obtained as racemic modifications it is convenient to use the Cahn–Ingold–Prelog system[2] to differentiate between diastereoisomers.

[1] Part I, G. H. Whitham and M. Wright, preceding paper.

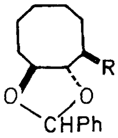
[2] R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem. Internat. Edn.*, 1966, **5**, 385.

[3] P. E. Eaton and K. Lin, *J. Amer. Chem. Soc.*, 1964, **86**, 2087.

reduction, all failed. It was decided therefore to investigate the possibility of a stereospecific synthesis which might at the same time provide a chemical proof of configuration. We had previously explored an olefin synthesis involving the fragmentation of the benzylidene derivative of a 1,2-diol under the influence of an alkyllithium,[4] and had shown that it provided an efficient route to *trans*-cyclo-octene itself. Application of this 'dioxolan olefin synthesis' to a dioxolan of type (II) should give a (1*RS*,2*RS*)-*trans*-cyclo-oct-2-enyl derivative, whereas one of type (III) should give the (1*SR*,2*RS*)-diastereoisomer. We describe here some examples of such reactions culminating in a synthesis of (1*SR*,2*RS*)-*trans*-cyclo-oct-2-en-1-ol (IV).



(I)



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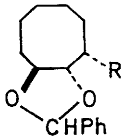

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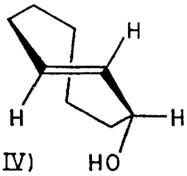


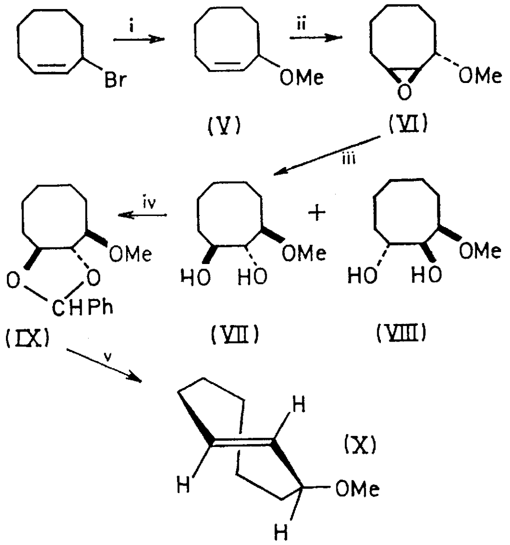
(IV)

RESULTS AND DISCUSSION

We initially investigated the application of the dioxolan olefin synthesis to the methyl ethers (II; R = OMe) and (III; R = OMe) since fewer difficulties were anticipated with compounds bearing the methoxy-substituent.

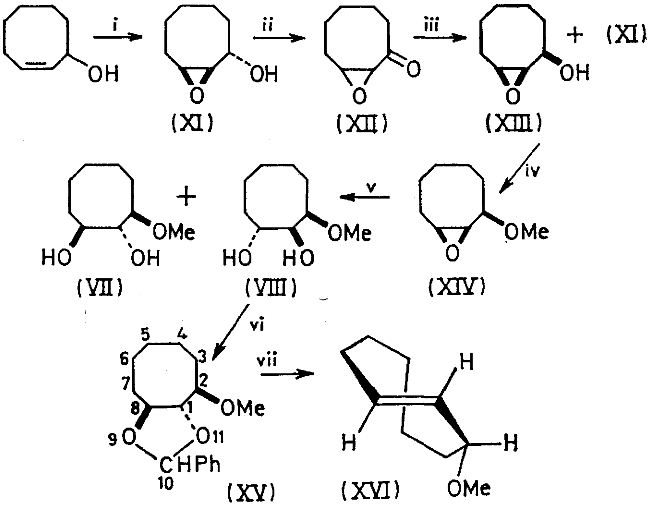
The preparation of the appropriate dioxolan methyl ether (IX) and its fragmentation to (1*RS*,2*RS*)-*trans*-cyclo-oct-2-enyl methyl ether (X) are summarised in Scheme 1. Epoxidation of the allylic ether (V) gave a single epoxy-ether (VI) which was initially assumed to have the epoxide ring *trans* to the methoxy-group for steric reasons;[5] this assumption was subsequently verified by the preparation of the *cis*-isomer (see later). The inductive effect of the methoxy-group would be expected to favour attack at C-3 in opening of the epoxy-ether (VI), an expectation justified by analogy.[6] Ring-opening was carried out with sodium acetate in refluxing acetic acid to minimise transannular processes. Saponification of the product gave two glycols (VII) and (VIII) in the ratio 4 : 1, the major isomer being assigned structure (VII) on the basis of the foregoing reasoning. The dioxolan (IX) derived from (VII) was treated with n-butyl-lithium in tetrahydrofuran (THF) to give the (1*RS*,2*RS*)-ether (X) identified by comparison with an authentic sample prepared by methylation of (1*RS*,2*RS*)-*trans*-cyclo-oct-2-en-1-ol.[1]

The sequence of reactions leading to (1*SR*,2*RS*)-*trans*-cyclo-oct-2-enyl methyl ether (XVI) is summarised in Scheme 2. In order to prepare the methoxy-glycol (VIII) efficiently, the *cis*-epoxy-ether (XIV) was required. Since epoxidation both of *cis*-cyclo-oct-2-enyl methyl ether (see before) and of *cis*-cyclo-oct-2-en-1-ol[7] occurs *trans* to the functional group, it was necessary to devise the route shown to compound (XIV). The epoxy-ketone (XII), prepared by Jones oxidation of the *trans*-epoxy-alcohol (XI) was reduced stereoselectively to the



SCHEME 1

Reagents: i, MeOH–$CaCO_3$; ii, AcO·OH; iii, (a) NaOAc–AcOH, (b) OH^-; iv, PhCHO, H^+; v, Bu^{n}Li.



SCHEME 2

Reagents: i, AcO·OH; ii, H_2CrO_4; iii, $NaBH_4$; iv, NaH–DMF–MeI; v, (a) NaOAc–AcOH, (b) OH^-; vi, PhCHO, H^+; vii, Bu^{n}Li.

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[4] J. N. Hines, M. J. Peagram, G. H. Whitham, and M. Wright, *Chem. Comm.*, 1968, 1593.

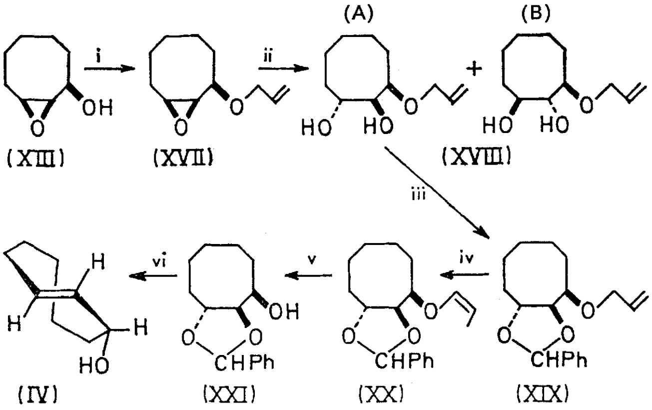
[5] H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1957, 1958.

[6] E. J. Langstaff, E. Hamanaka, G. A. Neville, and R. Y. Moir, *Canad. J. Chem.*, 1967, **45**, 1907.

[7] (*a*) P. Chamberlain, M. L. Roberts, and G. H. Whitham, *J. Chem. Soc.* (*B*), 1970, 1374; (*b*) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, and G. W. Wood, *J. Amer. Chem. Soc.*, 1957, **79**, 3900.

cis-epoxy-alcohol (XIII), only 5% of the *trans*-isomer being formed. The structure and stereochemistry of the *cis*-epoxy-alcohol (XIII) were verified (*a*) by re-oxidation to the parent ketone (XII) with chromic acid, and (*b*) by the i.r. spectrum, which showed the presence of an intramolecular OH · · · O hydrogen bond ($\nu_{max.}$ 3563 cm.$^{-1}$ for a dilute solution in carbon tetrachloride). Methylation of the epoxy-alcohol, followed by opening of the epoxide ring by the procedure used previously gave a mixture of the two glycols (VII) and (VIII) (7 : 93), with the latter now predominant. The dioxolan (XV), obtained as a mixture of isomers epimeric at C-10, gave a mixture of the *trans*-cyclo-octenyl methyl ether (XVI) and 3-n-butyl-*cis*-cyclo-oct-1-ene * on treatment with excess of n-butyl-lithium in THF. The (1*SR*,2*RS*)-*trans*-cyclo-oct-2-enyl methyl ether (XVI) was identified from the characteristic i.r. absorption due to *trans*-–CH=CH ($\nu_{max.}$ 930, 990, and 1650 cm.$^{-1}$) and from the n.m.r. spectrum, which showed in particular the low $J_{1,2}$ value (2·1 Hz) expected for the cisoid C(1)–H,C(2)–H relationship.

In seeking to extend these successful syntheses of *trans*-cyclo-octene derivatives to the ' missing ' diastereoisomeric alcohol (IV), it was clear that we would require a protecting group for the putative 1-hydroxy-group which would withstand conditions of epoxide opening and direct dioxolan formation to bridge the requisite oxygen atoms, and yet be removable under conditions which would not lead to equilibration of 1,3-dioxolan and 1,3-dioxans. These conditions appeared to be satisfied by the allyl ether group developed by Gigg and his co-workers.[8] The use of this group in the stereoselective synthesis of the dioxolan (XXI) and the conversion of the latter into the alcohol (IV) are summarised in Scheme 3.



Scheme 3

Reagents: i, NaH–CH$_2$:CH·CH$_2$Br–DMF; ii, (a) NaOAc–AcOH, (b) OH$^-$; iii, PhCHO–H$^+$; iv, KOBu^t–Me$_2$SO; v, HgCl$_2$–HgO; vi, Bu^{n}Li–THF.

The allyl ether (XVII) prepared from the *cis*-epoxy-alcohol (XIII) was converted into a mixture of glycols (XVIII) in which (A) predominated. This was converted into the dioxolan (XIX), which again was obtained as a mixture of epimers. The allyl ether grouping was removed by successive treatment with potassium t-butoxide in dimethyl sulphoxide (DMSO) [to isomerise to the prop-1-enyl ether (XX)] followed by mercury(II) chloride–mercury(II) oxide in aqueous acetone (to ' hydrolyse ' the propenyl ether under neutral conditions). The basic conditions used to isomerise the allyl ether (XIX) did not significantly affect the dioxolan grouping; clearly the conditions needed to fragment a 2-phenyl-1,3-dioxolan (Bu^{n}Li in THF) are much more basic than potassium t-butoxide in DMSO. The hydroxydioxolan (XXI) was treated with three equivalents of n-butyl-lithium in a larger than usual amount of THF to allow for the lower solubility of the lithium alkoxide. After heating under reflux the *trans*-alcohol (IV) was isolated *via* its silver nitrate adduct. The (1*SR*,2*RS*)-alcohol (IV) was identified by its i.r. ($\nu_{max.}$ 945, 965, 990, and 1650 cm.$^{-1}$) and n.m.r. spectra (in particular $J_{1,2}$ 2·0 Hz). It was characteristically different from its epimer (I) and, with a knowledge of its gas chromatographic behaviour, we were able to confirm the high stereospecificity of the solvolytic reaction in which (I) was formed.[1]

In the following paper a number of reactions of derivatives of the alcohols (I) and (IV), which bear particularly upon their diastereoisomeric relationship, are described and discussed. The diastereoisomeric 3-n-butyl-*trans*-cyclo-oct-1-enes were required for comparison purposes in the course of this work. These hydrocarbons were synthesised by methods entirely analogous to those just described, *via* the dioxolans (II; R = Bu^n) and (III; R = Bu^n).[9] They are not described here since no special features were encountered.

EXPERIMENTAL

For general experimental details see previous paper.

cis-*Cyclo-oct-2-enyl Methyl Ether*.—3-Bromocyclo-oct-1-ene (150 g.; prepared by the method of Cope and Estes [10] without purification) was added to a stirred slurry of calcium carbonate (180 g.) in methanol (800 ml.; distilled from magnesium methoxide) during 45 min. and the reflux was maintained for a further 1 hr. The calcium carbonate was filtered off and the filtrate was concentrated to yield an oil, which was distilled through a short column packed with Dixon rings to give cis-*cyclo-oct-2-enyl methyl ether* (36 g., 33%), b.p. 59°/9·5 mm.; one peak on g.l.c. (B) (Found: C, 77·25; H, 11·25. $C_9H_{16}O$ requires C, 77·1; H, 11·5%), $\nu_{max.}$ (film) 715, 760, 950, 1105, and 1650 cm.$^{-1}$, τ 4·1—4·7 (2H, m, olefinic), 5·75—6·05 (1H, m, 1-H), 6·73 (3H, s, OMe), and 7·5—9·0 (10H, ring CH$_2$).

cis-2,3-*Epoxy*-trans-*cyclo-octyl Methyl Ether* (VI).—To a stirred solution of *cis*-cyclo-oct-2-enyl methyl ether (26·5 g.) in chloroform (150 ml.) was added peracetic acid (40% w/v; 57 ml.) containing sodium acetate trihydrate (12 g.; to neutralise the sulphuric acid present) during 3 hr. at 40°.

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* The origin of this hydrocarbon will be discussed in the following paper.

[8] J. Gigg and R. Gigg, *J. Chem. Soc.* (*C*), 1966, 82; R. Gigg and C. D. Warren, *ibid.*, 1968, 1903.

[9] M. Wright, D.Phil. Thesis, Oxford, 1968.

[10] A. C. Cope and L. L. Estes, *J. Amer. Chem. Soc.*, 1950, **72**, 1129.

The mixture was stirred for 3 days at 20° and then poured into a large volume of water. Sodium hydrogen carbonate was added until no more carbon dioxide was evolved, and the chloroform layer was removed, dried ($MgSO_4$), and concentrated. The crude oil (38·4 g.) was distilled on a spinning-band column to afford the *epoxy-ether* (20 g., 68%), b.p. 89°/10 mm.; one peak on g.l.c. (B) (Found: C, 68·5; H, 10·6. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%), $\nu_{max.}$ (film) 755, 890, 950, 1095, and 1110 cm.$^{-1}$, τ 6·55 (3H, s, OMe), 6·6—6·95 (1H, m, 1-H), 7·0—7·3 (2H, m, 3-H and 2-H), and 7·7—9·0 (10H, m, ring CH_2), *m/e* 156 (M^+).

cis- *and* trans-3-*Methoxycyclo-octane*-1,trans-2-*diol* (VII) *and* (VIII).—The epoxy-ether (VI) (19·0 g.) in glacial acetic acid (76 ml.) and sodium acetate trihydrate (43 g.) were heated under reflux during 4 days. Most of the acetic acid was removed under reduced pressure and the residue was treated with saturated aqueous sodium hydrogen carbonate until carbon dioxide evolution had ceased. The aqueous mixture was extracted with ether (3 × 200 ml.); the extracts were combined, dried ($MgSO_4$), and concentrated. The oil (18·0 g.) was heated at reflux for 45 min. with ethanolic potassium hydroxide (125 ml., 10%), and the ethanol was removed under reduced pressure. Isolation with ether gave compounds (VII) and (VIII) (9·9 g., 47%), which were shown by g.l.c. (B) to be in the ratio 4 : 1. Their identities were later confirmed by g.l.c. comparison with authentic samples prepared from *cis*-2,3-epoxycyclo-octyl methyl ether. The mixture of diols (6·0 g.) was adsorbed from light petroleum–ether (1 : 1) on to alumina deactivated with 5% of water (400 g.). After a small quantity of unchanged starting material had been eluted the polarity of the eluant was gradually increased (to 100% ether) and *trans*-3-methoxycyclo-octane-1,*trans*-2-diol (3·1 g.) and a mixed fraction of *cis*- and *trans*-3-methoxycyclo-octane-1,*trans*-2-diol (1·8 g.) were collected (in order of increasing polarity). The mixed fraction was adsorbed from ether on to a 1 m. preparative layer chromatography (p.l.c.) plate, which was then eluted three times with ether. Two bands were obtained; from the first was isolated by continuous extraction with ether a further quantity of *trans*-3-methoxycyclo-octane-1,*trans*-2-diol (0·8 g.), $\nu_{max.}$ (film) 750, 1040, and 3800 cm.$^{-1}$, τ 6·05 (2H, s, exchangeable, OH), 6·3—6·55 (2H, m, 1-H and 2-H), 6·65 (3H, s, OMe), 6·8—7·0 (1H, m, 3-H), and 8·0—8·9 (10H, m, ring CH_2), and from the second was obtained *cis*-3-methoxycyclo-octane-1,*trans*-2-diol (0·37 g.), $\nu_{max.}$ (film) 920, 985, 1010, 1045, and 3800 cm.$^{-1}$, τ 5·9—6·15 (1H, m, 1-H or 2-H), 6·25—7·0 (7H, m; singlets at τ 6·47 and 6·57; OH, OMe, 3-H, and either 1-H or 2-H), and 8·0—8·6 (10H, m, ring CH_2).

10-*Phenyl*-9,11-*dioxa*-trans-*bicyclo*[6,3,0]*undecan*-trans-2-*yl Methyl Ether* (IX).—*trans*-3-Methoxycyclo-octane-1,*trans*-2-diol (3·1 g.) in toluene (80 ml.) was heated at reflux for 6 hr. under nitrogen in a Dean and Stark apparatus with benzaldehyde (6 ml.) and toluene-*p*-sulphonic acid (0·01 g.). Isolation with ether gave an oil which crystallised from light petroleum to give the *dioxolan* (IX) (3·7 g., 80%), m.p. 71—72°; one peak on g.l.c. (B) (Found: C, 72·55; H, 8·4. $C_{16}H_{22}O_3$ requires C, 73·25; H, 8·45%), $\nu_{max.}$ (film) 700, 725, 890, 920, and 3100 cm.$^{-1}$, τ 2·4—2·8 (5H, m, aromatic), 4·23 (1H, s, 10-H), 5·8—6·2 (2H, m, bridgehead), 6·55 (4H, s, OMe and 2-H), and 7·6—8·8 (10H, m, ring CH_2).

(1*RS*,2*RS*)-trans-*Cyclo-oct-2-enyl Methyl Ether* (X).—(*a*) The dioxolan (IX) (0·5 g.) in tetrahydrofuran (10 ml.; distilled from lithium aluminium hydride) was treated with n-butyl-lithium (15% w/v in hexane; 1·6 ml.) under nitrogen at 10° and stirred for 2 hr. The mixture was poured into water (50 ml.); isolation with ether gave an oil (0·48 g.) which was adsorbed on silica (20 g.) and eluted with light petroleum. Unchanged starting material (0·22 g.) was recovered along with a mixture (0·18 g.) which was shown to contain valerophenone by g.l.c. (B) comparison with authentic material. The mixture (0·18 g.) was heated at reflux during 30 min. with an excess of lithium aluminium hydride in ether; isolation with ether in the usual manner gave an oil (0·08 g.) which was adsorbed on silica (5 g.) and eluted with light petroleum. (1*RS*,2*RS*)-*trans*-Cyclo-oct-2-enyl methyl ether (0·018 g.) was collected, $\nu_{max.}$ (film) 835, 940, 965, 990, 1100, and 1650 cm.$^{-1}$, τ 4·1—4·7 (2H, m, olefinic), 6·1—6·35 (1H, m, 3-H), 6·68 (3H, s, OMe), 7·5—8·9 (8H, m, ring CH_2), and 8·9—9·4 (2H, m, ring CH_2), *m/e* 140 (M^+).

(*b*) To (1*RS*,2*RS*)-*trans*-cyclo-oct-2-en-1-ol (1·8 g.) in dimethyl sulphoxide (35 ml.; distilled from calcium hydride) was added n-butyl-lithium (10% w/v in hexane; 9·1 ml.) at 10° under nitrogen, and the mixture was stirred for 10 min. Methyl iodide (1·48 ml.) was added and a white precipitate was observed. The mixture was heated to 35° and maintained at this temperature for 3 hr., after which time it was homogeneous and was poured into water (25 ml.). The aqueous mixture was extracted with light petroleum (2 × 25 ml.); the extracts were combined, dried ($MgSO_4$), and concentrated to give *trans*-cyclo-oct-2-enyl methyl ether (1·88 g., 95%). G.l.c. (C) (R_t 10 min., 100°) showed that the only contaminant present was *cis*-cyclo-oct-2-enyl methyl ether (2%), confirmed by co-injection with an authentic sample. Otherwise the product was identical to material prepared in (*a*).

trans-(2,3-*Epoxy*)*cyclo-octan*-1-*ol* (XI).—To a stirred solution of *cis*-cyclo-oct-2-en-1-ol[11] (113·4 g.) in dichloromethane (500 ml.) was added peracetic acid [220 ml.; 35% w/v, previously treated with sodium acetate trihydrate (33 g.)], during 50 min. at such a rate as to maintain a reaction temperature of 13—15° while the flask was cooled with ice–water. The mixture was stirred overnight at 20° and sodium hydroxide solution (10%; 400 ml.) was added. The aqueous mixture was extracted with ether (3 × 1 l.); the extracts were combined and washed successively with acidified iron(II) sulphate solution, saturated sodium carbonate solution, and brine. The ether layer was dried ($MgSO_4$) and concentrated. Distillation gave the *trans*-epoxy-alcohol (XI) (87 g., 68%), b.p. 99—100°/1 mm. (lit.,[7b] 99—100°/1·8 mm.), g.l.c. (B): one major peak and a trace of 2,3-epoxycyclo-octan-1-one, $\nu_{max.}$ (film) 750, 830, 990, and 3450 cm.$^{-1}$, τ 5·95—6·15 (1H, s, exchangeable, OH), 6·2—6·5 (1H, m, 3-H), 6·85—7·2 (2H, m, 2-H and 3-H), and 7·8—8·9 (10H, m, ring CH_2).

cis-(2,3-*Epoxy*)*cyclo-octan*-1-*ol* (XIII).—To a stirred solution of the *trans*-epoxy-alcohol (XI) (87 g.) in acetone (1400 ml.) was added chromic acid (6N; 135 ml.) during 1 hr. at 0°. The acetone phase was decanted from the green solid, acetone was removed under reduced pressure, and the residue was extracted with ether. Water was added to the green solid and the aqueous solution was extracted with ether. The combined extracts were worked up to afford an oil (80 g.), which was shown by g.l.c. (B) to be a mixture of 2,3-epoxycyclo-octan-1-one (XII) and unchanged starting

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[11] N. Heap and G. H. Whitham, *J. Chem. Soc.* (*B*), 1966, 164.

material, in the ratio 72 : 28. The oil, in ethanol (1200 ml.) and water (240 ml.) was stirred during 2 hr. at 20° with sodium borohydride (8·6 g.). Isolation with ether afforded an oil (69 g.), which was shown by g.l.c. (B) to be a mixture of the *cis*- and *trans*-epoxy-alcohols in the ratio 66 : 34, and was adsorbed on alumina from light petroleum–ether (9 : 1). Elution with light petroleum–ether (6 : 4) gave the *cis*-epoxy-alcohol (XIII) (39·1 g., 52%) as crystals which formed liquid crystals at 50° and became a mobile liquid at 96—97°; one peak on g.l.c. (B), $\nu_{\text{max.}}$ (film) 700, 740, 850, 920, and 3500 cm.$^{-1}$, τ 5·5—5·65 (1H, m, 1-H), 6·95—7·2 (2H, m, 2-H and 3-H), 7·6 (1H, s, exchangeable, OH), and 7·8—9·0 (10H, m, ring CH_2).

The *cis*-epoxy-alcohol (XIII) (1·4 g.) in acetone (25 ml.) was oxidised with chromic acid (8N; 2·2 ml.) to 2,3-epoxycyclo-octan-1-one (1·0 g., 70%). Identity was confirmed by g.l.c. enhancement with material obtained from the *trans*-epoxy-alcohol, and by i.r. spectroscopic comparison.

cis-(2,3-*Epoxy*)*cyclo-octanyl Methyl Ether* (XIV).—Sodium hydride powder (1·37 g.) was added under nitrogen with stirring during 10 min. at 20° to this *cis*-epoxy-alcohol (XIII) (9·0 g.) in dimethylformamide (250 ml.) and methyl iodide (20 ml.). After 1 hr. no more hydrogen was evolved; the mixture was stirred for a further 2 hr. and poured into water (500 ml.). After work-up distillation gave the *epoxy-ether* (XIV) (7·1 g., 72%), b.p. 87—91°/9 mm.; one peak on g.l.c. (B) (Found: C, 68·7; H, 10·45. $C_9H_{16}O_2$ requires C, 69·2; H, 10·35%), $\nu_{\text{max.}}$ (film) 690, 745, 860, 910, and 1120 cm.$^{-1}$, τ 6·0—6·15 (1H, m, 1-H), 6·6 (3H, s, OMe), 7·0—7·25 (2H, m, 2-H and 3-H), and 7·8—8·7 (10H, m, ring CH_2), *m*/*e* 156 (M^+).

trans-3-*Methoxycyclo-octane*-1,trans-2-*diol* (VIII).—The *cis*-epoxy-ether (XIV) (6·65 g.) was heated at reflux during 25 hr. with glacial acetic acid (22 ml.) buffered with sodium acetate trihydrate (15 g.), then poured into water (50 ml.). Sodium hydrogen carbonate was added until evolution of carbon dioxide ceased. Work-up gave an oil (6·5 g.) which was heated at reflux during 1 hr. with ethanolic potassium hydroxide (10%; 50 ml.); the ethanol was removed under reduced pressure. Isolation with ether gave an oil (3·8 g.) which was shown by g.l.c. (B) to contain methoxy-diols (VIII) and (VII) in the ratio 93 : 7. Absorption on three 1 m. p.l.c. plates followed by two elutions with ether–methanol (95 : 5) allowed the removal of one band from each of the plates. These bands were combined and the product was isolated by continuous extraction with ether, giving the methoxy-diol (VIII) (3·15 g., 42%); one peak on g.l.c. (B), $\nu_{\text{max.}}$ (film) 750, 800, 985, 1045, 1090, and 3800 cm.$^{-1}$, τ 6·15—6·3 (2H, m, 1-H and 2-H), 6·4—6·9 [6H, m (sharp s τ 6·62, OMe, broad s τ 6·75, OH and 3-H)], and 8·1—8·6 (10H, ring CH_2).

10-*Phenyl*-9,11-*dioxa*-trans-*bicyclo*[6,3,0]*undecan*-cis-2-*yl Methyl Ether* (XV).—By the procedure already described the methoxy-diol (VIII) (3 g.) was converted into the *dioxolan* (2·1 g., 47%), m.p. 45—46° (from light petroleum) (Found: C, 73·0; H, 8·1. $C_{16}H_{22}O_3$ requires C, 73·25; H, 8·45%). G.l.c. (B; 190°) showed two peaks in the ratio 34 : 66 in order of increasing retention time, which were presumed to be due to the C-10 epimers; $\tau_{\text{max.}}$ 2·4—2·7 (5H, m, aromatic), 4·12 (0·65H, s, 10-H), 4·23 (0·35H, s, 10-H), 5·3—5·6 (1H, m, 8-H), 5·95—6·1 (1H, m, predominantly dd, 1-H), 6·1—6·3 (1H, m, 2-H), 6·55 (3H, s, OMe), and 7·6—9·0 (10H, m, ring CH_2).

(1SR,2RS)-trans-*Cyclo-oct-2-enyl Methyl Ether* (XVI).—To the dioxolan (XV) (0·5 g.) in tetrahydrofuran (10 ml.) was added n-butyl lithium (10% w/v in hexane; 3·7 ml.) over 5 min. with stirring under nitrogen at 10°. The mixture was heated under reflux for 90 min. and poured into water (10 ml.). Isolation with ether gave an oil which g.l.c. (B) showed to contain a trace of unchanged starting material (shown to be the benzylic epimer with the shorter retention time), and 3-n-butyl-*cis*-cyclo-oct-1-ene (confirmed by peak enhancement with an authentic sample) and (1*SR*,2*RS*)-*trans*-cyclo-oct-2-enyl methyl ether in the ratio 4 : 6. The oil was adsorbed on alkaline alumina (10 g.) and eluted with light petroleum–ether. The residue from the eluate was adsorbed on a 20 cm. plate made up from Kieselgel and silver nitrate in the ratio 4 : 1. After elution with ether–light petroleum (1 : 1) the band near the origin was removed and continuously extracted with ether to give the ether (XVI) (0·16 g., 60%); one peak on g.l.c. (B and C), $\nu_{\text{max.}}$ (film) 690, 800, 850, 930, 990, 1100, and 1650 cm.$^{-1}$, τ 3·95—4·3 (1H, m, 3-H), 4·53 and 4·7 (1H, 2 × d, 2-H), 5·94br (1H, 1-H), 6·67 (3H, s, OMe), and 7·4—9·3 (10H, m, ring CH_2), *m*/*e* 140 (M^+).

Material from a second band removed from the p.l.c. plate was identified as 3-n-butyl-*cis*-cyclo-oct-1-ene by comparison with authentic material on g.l.c. (B) and by i.r. spectroscopy.

cis-(2,3-*Epoxy*)*cyclo-octyl Allyl Ether* (XVII).—The *cis*-epoxy-alcohol (XIII) (28·4 g.) in dimethylformamide[8] (800 ml.) was stirred under nitrogen at 10° during 6 hr. with sodium hydride powder (5·28 g.) and allyl bromide (18·8 ml.), after which time evolution of hydrogen had ceased and the mixture was poured into water (800 ml.). Work-up gave an oil which was adsorbed on silica (150 g.) from light petroleum–ether (95 : 5); elution with light petroleum–ether (9 : 1) gave the *allyl ether* (XVII) (32·2 g., 88%), b.p. 120°/12 mm.; one peak on g.l.c. (D) (Found: C, 72·4; H, 9·95. $C_{11}H_{18}O_2$ requires C, 72·5; H, 9·95%), $\nu_{\text{max.}}$ (film) 700, 750, 800, 850, 920, 1650, and 3100 cm.$^{-1}$, τ 3·9—4·25 (1H, m, $\mathrm{CH_2{:}}\mathit{CH}$), 4·65—4·95 (2H, m, $\mathit{CH_2}\mathrm{{:}CH}$), 5·65—6·15 (3H, m, $\mathit{CH}\mathrm{{\cdot}O{\cdot}C}$ and 1-H), 7·0—7·3 (2H, m, 2-H and 3-H), and 7·7—8·9 (10H, m, ring CH_2).

trans-3-*Allyloxycyclo-octane*-1,trans-2-*diol* (XVIII A).—The epoxy-ether (XVII) (5 g.) in glacial acetic acid (20 ml.) buffered with sodium acetate trihydrate (13·5 g.) was heated at reflux during 24 hr. Acetic acid was removed under reduced pressure and to the residue was added sodium hydrogen carbonate until evolution of carbon dioxide had ceased. Work-up gave an oil which was heated at reflux during 1 hr. with ethanolic potassium hydroxide (10%; 50 ml.). The ethanol was removed under reduced pressure and work-up gave a residue (4·9 g.) which g.l.c. (B) showed to contain two compounds in the ratio 94 : 6. The mixture was adsorbed on three 1 m. p.l.c. plates and eluted twice with ether. The major, more polar, band was removed and isolated by continuous extraction with ether to give the *allyloxy-diol* (XVIII A) (3·14 g., 57%); one peak on g.l.c. (B) (Found: C, 65·0; H, 10·5. $C_{11}H_{20}O_3$ requires C, 65·95; H, 10·1%), $\nu_{\text{max.}}$ (film) 750, 800, 925, 1140, 1170, 1645, and 3200 cm.$^{-1}$, τ 3·85—4·2 (1H, m, $\mathit{CH}\mathrm{{:}CH_2}$), 4·6—4·9 (2H, m, $\mathrm{CH{:}}\mathit{CH_2}$), 5·75—6·2 (5H, 1-H, 2-H, $\mathit{CH}\mathrm{{\cdot}O{\cdot}C}$, and 3-H), 6·9—7·2 (2H, s, exchangeable, OH), and 8·0—8·8 (10H, m, ring CH_2).

10-*Phenyl*-9,11-*dioxa*-trans-*bicyclo*[6,3,0]*undec*-cis-2-*yl Allyl Ether* (XIX).—The glycol (XVIII A) (13·5 g.) in toluene (150 ml.) was heated at reflux during 6 hr. under nitrogen in a Dean and Stark apparatus with benzaldehyde (27 ml.) and toluene-*p*-sulphonic acid (0·03 g.). The toluene was removed under pressure and the residue was adsorbed from light petroleum on alkaline alumina (350 g.). Elution with light petroleum–ether (95 : 5) gave the *dioxolan* (17·2 g., 89%), two peaks on g.l.c. (B) R_t 36 and 45 min. (180°) in the ratio 32 : 68, believed to be benzylic epimers (Found: C, 75·0; H, 8·4. $C_{18}H_{24}O_3$ requires C, 74·95; H, 8·4%), $\nu_{max.}$ 700, 760, 920, 1215, 1645, 3100, and 3150 cm.$^{-1}$, τ 2·35—2·8 (5H, m, aromatic), 3·8—4·3 [2H, 10-H (2 singlets at τ 4·1 and 4·2 in the ratio 7 : 3) and C*H*:CH$_2$], 4·5—5·0 (2H, m, CH:C*H*$_2$), 5·2—5·6 (1H, m, 8-H), 5·75—6·2 (4H, m, 1-H, 2-H, and C*H*·O·C), and 7·6—9·0 (10H, m, ring CH$_2$).

10-*Phenyl*-9,11-*dioxa*-trans-*bicyclo*[6,3,0]*undecan*-cis-2-ol (XXI).—The allyl ether (XIX) (17·0 g.) in dimethyl sulphoxide (600 ml.) was heated under nitrogen with stirring at 110—115° during 2 hr. with potassium t-butoxide[8] (15 g.) and poured into water (1 l.). Work-up gave an oil (15·3 g.) which was dissolved in acetone–water (10 : 1; 500 ml.) and yellow mercury(II) oxide (15 g.) was added. To this stirred suspension at 20° was added mercury(II) chloride (14·4 g.) in acetone–water (10 : 1; 100 ml.) during 20 min. and the mixture was stirred for a further 30 min. The excess of mercury(II) oxide was filtered off through Celite, and the acetone was removed from the filtrate under reduced pressure. Ether (100 ml.) was added to the residue and the ethereal solution was washed with saturated potassium iodide (2 × 50 ml.). Work-up gave a solid which crystallised from light petroleum to give the *alcohol* (11·2 g., 77%); two peaks on g.l.c. (B) in the ratio 26 : 74 (Found: C, 72·05; H, 7·85. $C_{15}H_{20}O_3$ requires C, 71·75; H, 7·75%), $\nu_{max.}$ 700, 760, 920, 1065, 1090, 1220, 3050, and 3500 cm.$^{-1}$, τ 2·4—2·75 (5H, m, aromatic), 4·13 (1H, s, 10-H), 5·35—5·7 (1H, m, 2-H), 5·7—6·1 (2H, m, 1-H and 8-H), 7·25 (1H, s, OH), and 7·6—8·9 (10H, m, ring CH$_2$).

(1SR,2RS)-trans-*Cyclo-oct-2-en-1-ol* (IV).—n-Butyllithium (7·1 ml.; 11% w/v in hexane) was added under nitrogen to a stirred solution of the dioxolan (XXI) (1 g.) in tetrahydrofuran (45 ml.) at 20°. The homogeneous mixture was heated to reflux, maintained there for 30 min., and then poured into water (100 ml.). Work-up gave an oil (1·13 g.) which was dissolved in light petroleum (20 ml.) and shaken with silver nitrate solution [0·69 g. in water (20 ml.)]. The light petroleum layer was concentrated and gave an oil (0·95 g.) which was shown to contain the dioxolan isomer of shorter g.l.c. retention time and valerophenone. The aqueous layer was washed with light petroleum; an excess of ammonia solution (*d* 0·880) was then added to the aqueous layer, which was extracted with ether (2 × 20 ml.). The ether extracts were combined, dried (MgSO$_4$), and concentrated to give an oil (0·17 g.), which was distilled to give (1*SR*,2*RS*)-*trans*-cyclo-oct-2-en-1-ol (0·15 g., 30%), b.p. 97°/15 mm.; one peak on g.l.c. (C and D), $\nu_{max.}$ (film) 700, 710, 800, 815, 835, 860, 910, 925, 945, 965, 990, 1025, 1070, 1130, 1650, and 3360 cm.$^{-1}$, τ 3·8—4·2 (1H, m, 3-H), 4·35 and 4·5 (1H, 2 × d, 2-H), 5·4 (1H, s, OH), 7·4—7·6 (1H, m, 1-H), and 7·7—9·4 (10H, m, ring CH$_2$), *m/e* 126 (M^+).

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