trans-Cycloalkenes. Part 8.[1] Bicyclic *trans*-Cyclo-octenes constrained in Chair and Twist Conformations

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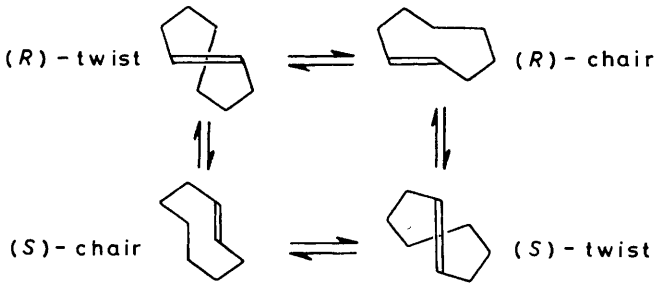
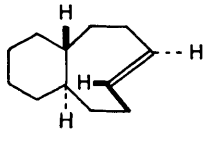
Bicyclic *trans*-cyclo-octenes locked in twist (1) and chair (2) forms and their unsaturated analogues (18) and (19) have been synthesised. Key steps are: the Diels–Alder addition of the epoxide (7) to butadiene to generate (6) directly, ring-opening of the bicyclic epoxides (6) and (12) to give diastereoisomeric pairs of β-hydroxyphosphine oxides, and stereospecific fragmentation of the latter to the bicyclic *trans*-cyclo-octenes.

THE configurational and conformational relationships for *trans*-cyclo-octene can be summarised as in Scheme 1. Recent work [2] indicates that the preferred conformation is the twist, that the barrier to conversion of (*R*)-twist to

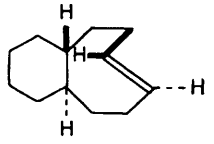


SCHEME 1

(*R*)-chair [or of (*S*)-twist to (*S*)-chair] is relatively low (*ca.* 40 kJ mol^{-1}) and that the main barrier to racemisation [3] of optically active *trans*-cyclo-octene is the conversion of (*R*)-twist to (*S*)-chair or of (*S*)-twist to (*R*)-



(1)

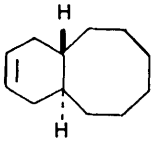


(2)

chair. We considered that further verification of these relationships might be obtained by the synthesis of bicyclic *trans*-cyclo-octenes possessing a *trans*-fused six-membered ring attached to positions 5 and 6 across the ring from the double bond. In such compounds the placement of the six-membered ring should not significantly distort the eight-membered ring by affecting the partial conformation about C-4, C-5, C-6, and C-7, and conversion of (*R*)-twist to (*R*)-chair and of (*S*)-twist to (*S*)-chair should be prohibited. Thus, for example, olefin (1) would be a locked-twist *trans*-cyclo-octene and olefin (2) a locked-chair *trans*-cyclo-octene.

RESULTS AND DISCUSSION

There are two basic problems associated with the synthesis of compounds of type (1) and (2). These are (*a*) formation of the *trans*-fused bicyclo[6.4.0]dodecane skeleton and (*b*) introduction of the *trans* double bond. The first problem was readily solved using the known ability of *trans*-cyclo-octene to participate as a dienophile in Diels–Alder reactions, *e.g.* addition to butadiene to give the bicyclo[6.4.0]dodec-10-ene (3).[4] Although the *trans*-ring junction of (3) had not been rigorously proved, verification was subsequently provided when the compound was obtained optically active (see following paper). The second problem required the placement of a *cis* double bond at position 4,5 so that further application of a suitable olefin inversion procedure might permit generation of the *trans* double bond there. A step forward in this direction was provided by the discovery that *cis,trans*-cyclo-octa-1,5-diene underwent addition to butadiene to give the bicyclic diene (4).[5] However, it did not prove possible either to hydrogenate selectively the double bond in the six-membered ring or to epoxidise selectively the double bond in the eight-membered ring.[5] An obvious way round the selectivity problem was *via*



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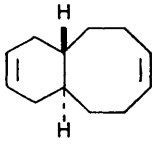

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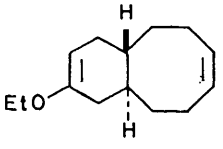

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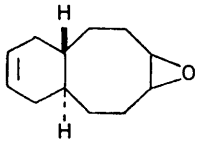

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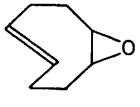

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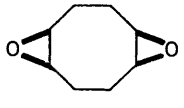

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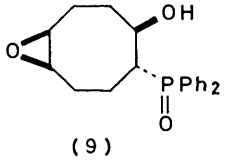

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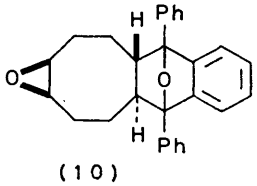

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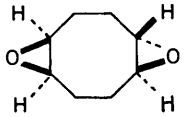
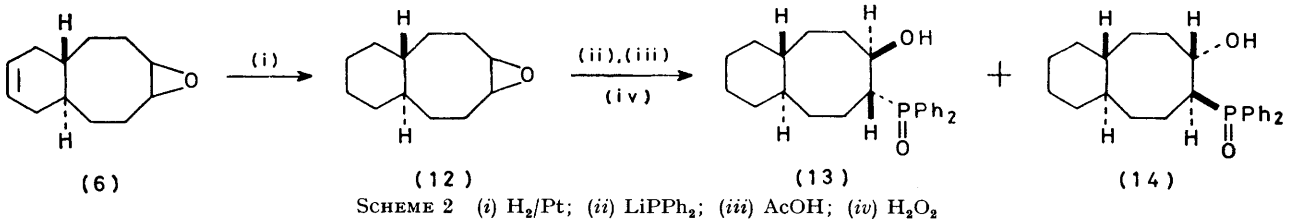


(11)

the compound (5) formed by addition of 2-ethoxybutadiene to *cis,trans*-cyclo-octadiene. In practice the hydrolysis of the enol–ether function in (5) and Wolff–Kishner reduction of the derived ketone gave difficulties which made such a route tedious and unattractive.[5] A significant improvement resulted from the realisation and demonstration that the bicyclic epoxide (6) could be obtained in one step by addition of the ' unnatural ' epoxide (7) of *cis,trans*-cyclo-octa-1,5-diene to butadiene.

The mono-epoxide (7) was obtained most satisfactorily by application of the β-hydroxyphosphine oxide procedure [6] to the diepoxide of *cis,cis*-cyclo-octadiene [(8), known to be the *cis*-isomer [7]]. Thus treatment of (8) with lithium diphenylphosphide followed by oxidation gave the hydroxyphosphine oxide (9) in 68% yield. Fragmentation of (9) using sodium hydride in dimethyl sulphoxide gave (7). The latter was characterised as the 1,3-diphenylisobenzofuran adduct (10); epoxidation of (7) gave the diepoxide (11) which showed eight carbon signals in the ^{13}C n.m.r. spectrum, in agreement with the absence of a plane or axis of symmetry. Addition of butadiene to (7) gave (6) in 87% overall yield from the phosphine oxide (9).



(6) (12) (13) (14)

SCHEME 2 (*i*) H_2/Pt; (*ii*) $LiPPh_2$; (*iii*) AcOH; (*iv*) H_2O_2

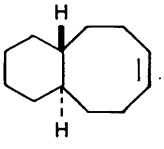
For synthesis of bicyclic *trans*-cylo-octenes of type (1) and (2) it was considered that the β-hydroxyphosphine oxide route [6] would probably be the most suitable since it should provide separable crystalline precursors of the two olefins. The bicyclic epoxide (6) was therefore hydrogenated and treated with lithium diphenylphosphide in the usual way (Scheme 2). Two diastereoisomeric β-hydroxyphosphine oxides (13) and (14) were obtained which could be separated by repeated fractional crystallisation. Given a *syn*-elimination in the subsequent olefin-forming step, (13) should be a precursor of the twist olefin (1) and (14) of the chair olefin (2). The hydroxyphosphine oxides (13) and (14) were very similar compounds, as expected, and no means of identification was apparent at this stage of the investigation. Subsequent work (see following paper) allowed this identification to be made, and the following discussion will presuppose these configurational assignments.

Treatment of (13) with sodium hydride in dimethylformamide gave the twist olefin (1) as an oil which polymerised on standing, but which could be kept for several weeks in solution in light petroleum at 0 °C. It showed signals due to six carbons in the ^{13}C n.m.r. spectrum as expected for the C_2 axis of symmetry and was rapidly isomerised to the corresponding *cis*-olefin (15) on treatment with iodine in ether.

The phosphine oxide (14) was more resistant to fragmentation, but potassium t-butoxide in dimethyl sulphoxide gave the chair olefin (2), which was less stable than its isomer (1) and polymerised rapidly when neat. The spectroscopic properties of (2) were different from those of (1) and the ^{13}C n.m.r. spectrum showed six carbon signals, again corroborating the C_2 axis of symmetry. Iodine treatment also gave the *cis* isomer (15) thereby corroborating the skeletal identity of (1) and (2). Unfortunately conditions could not be found for separating the two olefins (1) and (2) on g.l.c.

In a similar manner the unsaturated bicyclic epoxide (6) was converted *via* the hydroxyphosphine oxides (16) and (17) into the corresponding twist (18) and chair olefins (19) (Scheme 3). These olefins were required in connection with the configurational assignments to be described in the next paper, but it transpired that there were several advantages in this series of compounds with the extra double bond in the six-membered ring. Thus the hydroxyphosphine oxides (16) and (17) were more readily separable by crystallisation than (13) and (14) and they showed greater difference in mobility on t.l.c. Also the olefins (18) and (19) could be separated by g.l.c. ($AgBF_4$ containing column) and were more stable than (1) and (2) although again one of the pair, (19), was less stable and polymerised at room temperature.

The two series of compounds were interrelated by hydrogenation of the more polar isomer (17) of the unsaturated hydroxyphosphine oxides to give the more polar isomer, (14), of the saturated pair.

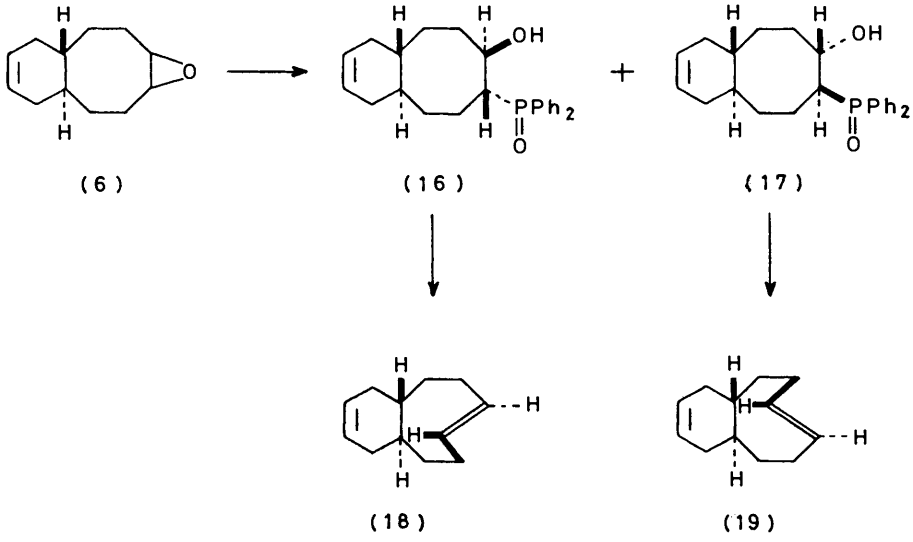


(15)

Thus the initial aim of the investigation, the preparation of isolable chair and twist *trans*-cyclo-octenes, has been achieved. Clearly interconversion between the isomers by rotation of the double bond through the eight-membered ring is a fairly high-energy process. The following paper is concerned with the assignment of configuration to the compounds described in this paper. A third paper deals with some reactions of the chair and twist *trans*-cyclo-octenes in which a more accurate assessment of the energy barrier between them is obtained by direct interconversion.

It should be pointed out that the related pair of olefins (20) and (21) have been prepared by non-stereospecific

routes by Deyrup and Betkouski.[8] In these compounds, however, the presence of the *trans*-fused cyclopropane ring provides an additional element of strain and distortion, and the authors were unable to study interconversion between them.



SCHEME 3

The syntheses described in the present paper provide additional examples of the power of the stereospecific olefin synthesis based on β-hydroxyphosphine oxides.[6]

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded with Perkin-Elmer R32 or R14 instruments operating at 90 and 100 MHz respectively ($SiMe_4$ as internal standard). Pulsed Fourier-transform ^{13}C n.m.r. spectra were recorded with a Bruker WH 90 operating at 22.63 MHz for solutions in $CDCl_3$. Chemical shifts are quoted in p.p.m. downfield of internal $SiMe_4$. Analytical g.l.c. used 20% 1,2,3-tris-(2-cyanoethoxy)propane containing 0.5% $AgBF_4$ on Embacel (Column A), or 15% Carbowax 20M on Diatomite C-AW (column B).

cis,cis-5,10-*Dioxatricyclo*[7.1.0.0^{4,6}]*decane* (8).—*cis,cis*-Cyclo-octa-1,5-diene (108 g, 1 mol) in methylene chloride (400 ml) with sodium carbonate (120 g) was epoxidised with buffered peracetic acid (45%; 356 ml, 2.1 mol) in the usual way. The mixture was stirred at 15 °C for 3 d, then worked up and distilled to give the diepoxide (8) (93 g, 66%), b.p. 69—70 °C at 0.3 mmHg, which crystallised on standing, m.p. *ca.* 25 °C (lit.,[6] b.p. 65—72 °C at 0.35 mmHg, m.p. 25—27 °C); ^{13}C n.m.r., δ 56.0 (d, C-1) and 22.0 (t, C-2).

(1RS,4RS,5RS,8RS)-5-*Diphenylphosphinyl*-9-*oxabicyclo*-[6.1.0]*nonan*-4-*ol* (9).—Lithium diphenylphosphide[9] (0.354 mol) in THF (200 ml) was added during 1 h to the diepoxide (8) (38.1 g, 0.27 mol) in THF (300 ml). After stirring for 30 min, acetic acid (22 ml) and hydrogen peroxide (40 ml; 30%) were added and the mixture extracted with methylene chloride (3 × 300 ml). Removal of the solvent and crystallisation from ethyl acetate–chloroform (4 : 1) gave (1SR,4RS,5RS,8RS)-5-*diphenylphosphinyl*-9-*oxabicyclo*[6.1.0]*nonan*-4-*ol* (9) (63.2 g, 68%), m.p. 206—207 °C (Found: C, 70.1; H, 6.9. $C_{20}H_{23}O_3P$ requires C, 70.2; H, 6.8%); $\nu_{max.}$(Nujol) 3 450, 1 159, 921, 759, 747, and 700 cm^{-1}; τ 2.0—2.8 (10 H, m, 2 × Ph), 5.37 (1 H, d, *J* 5 Hz, OH, exchanged by D_2O), 5.7 (1 H, m, C*H*O), 7.1 (2 H, m, 1-H and 8-H), and 7.2—9.0 (8 H, m).

(1RS,4RS,5RS,8SR)-9-*Oxabicyclo*[6.1.0]*non*-trans-4-*ene* (7).—A solution of the hydroxyphosphine oxide (9) (1 g) in dry DMSO (25 ml) was added to sodium hydride (0.3 g) in the usual way. The mixture was stirred for 1 h then worked up and the solvent removed to give (1*RS*,4*RS*,5*RS*,8*SR*)-9-oxabicyclo[6.1.0]non-*trans*-4-ene (7) (0.29 g, 80%) as a colourless unstable oil which was normally used immediately for further reaction; $\nu_{max.}$(film) 3 000, 2 850, 1 630, 993, 965, and 747 cm^{-1}; τ(CCl_4) 4.1—5.0 (2 H, m, CH=CH) and 7.1—9.4 (10 H, m); δ_C 137.1 and 132.2 (d, C-4 and C-5), 54.9 and 54.5 (d, C-1 and C-8), 38.8, 32.0, 30.2, 25.2 (t, C-2, C-3, C-6, C-7).

The 1,3-diphenylisobenzofuran adduct (10) was prepared by adding 1,3-diphenylisobenzofuran (0.62 g, 1 equiv.) to a solution of the olefin (7) (0.29 g) in dry benzene (30 ml). The solution was set aside at 18 °C for 2 d. Evaporation of the solvent and crystallisation from benzene–light petroleum (b.p. 40—60 °C) gave the *adduct* (10) (0.6 g, 57%) as pale yellow needles, m.p. 251—255 °C (Found: C, 85.3; H, 6.6. $C_{28}H_{26}O_2$ requires C, 85.1; H, 6.7%); $\nu_{max.}$(Nujol) 3 060, 3 020, 1 603, 1 018, 987, 769, and 710 cm^{-1}, τ 2.1—3.1 (14 H, m, aromatic), 7.25 (2 H, m, CHO), and 7.5—9.7 (10 H, m).

cis,trans-5,10-*Dioxatricyclo*[7.1.0.0^{4,6}]*decane* (11).—The *trans* olefin (7) (0.7 g) in light petroleum (50 ml) over sodium carbonate (3 g) was epoxidised with buffered peracetic acid (2 ml; 40%) in the usual way. Work-up gave much polymeric material which was filtered off, and the organic extract was dried ($MgSO_4$), evaporated, and distilled to give cis,trans-5,10-*dioxatricyclo*[7.1.0.0^{4,6}]*decane* (11) (140 mg, 18%), b.p. 110 °C (bath) at 0.1 mmHg, which solidified on

cooling to a waxy solid, m.p. 106—112 °C (Found: C, 68.7; H, 8.7. $C_8H_{12}O_2$ requires C, 68.5; H, 8.6%); $\nu_{max.}$(Nujol) 1 279, 1 002, 961, 932, 856, and 754 cm^{-1}; τ 6.8—9.0 (m); δ_C 59.6, 56.6, 55.7, and 55.3 (d, C-1, C-4, C-6, and C-9), 27.5, 27.2, 26.7, and 25.2 (t, C-2, C-3, C-7, and C-8).

(1RS,4SR,6RS,9RS)-5-*Oxatricyclo*[7.4.0.0^{4,6}]*tridec*-11-*ene* (6).—The epoxy-olefin (7) [from the hydroxyphosphine oxide (9), 0.1 mol] was mixed with an excess of buta-1,3-diene and sealed in a flask placed in a water-bath at 50 °C for 20 h. The excess of butadiene was allowed to evaporate and the residue was distilled to give (1RS,4SR,6RS,9RS)-5-*oxatricyclo*[7.4.0.0^{4,6}]*tridec*-11-*ene* (6) (15.5 g, 87% based on 0.1 mol), b.p. 67.5—68.5 °C at 0.05 mmHg (Found: C, 81.0; H, 10.2. $C_{12}H_{18}O$ requires C, 80.85; H, 10.2%); $\nu_{max.}$(film) 3 030, 1 635, 915, and 780 cm^{-1}; τ(CCl_4) 4.20 (2 H, m, CH=CH), 7.25 (2 H, m, CHO), and 7.6—9.1 (14 H, m); δ_C 128.8 and 128.4 (d, C-11 and C-12), 56.4 and 55.4 (d, C-4 and C-6), 39.2 and 37.3 (d, C-1 and C-9), and 32.7, 32.4, 27.8, and 24.7 (t, C-2, C-3, C-7, C-8, C-10, and C-13).

(1RS,4SR,6RS,9RS)-5-*Oxatricyclo*[7.4.0.0^{4,6}]*tridecane* (12).—The unsaturated epoxide (6) (1 g) in ethyl acetate (20 ml) was hydrogenated at atmospheric pressure over platinum oxide (20 mg, Adams catalyst). Filtration, removal of the solvent, and distillation gave (1RS,4SR,6RS,9RS)-5-*oxatricyclo*[7.4.0.0^{4,6}]*tridecane* (12) (0.81 g, 80%), b.p. 74—75 °C at 0.2 mmHg (Found: C, 79.8; H, 10.9. $C_{12}H_{20}O$ requires C, 79.9; H, 11.2%); $\nu_{max.}$(film) 1 015, 915, 850, and 754 cm^{-1}, τ(CCl_4) 7.0—7.4 (2 H, m, CHO) and 7.6—9.3 (18 H, m); δ_C 57.0 and 56.4 (d, C-4 and C-6), 41.3 and 37.0 (d, C-1 and C-9), and 34.2, 33.2, 33.0, 29.9, 26.6, and 25.0 (t, 8 × CH_2).

Reaction of the Epoxide (12) *with* $LiPPh_2$.—Following the general procedure, $LiPPh_2$ (0.07 mol) in dry THF (100 ml) was added to the epoxide (12) (9 g, 0.05 mol) in THF (100 ml) and the solution stirred for 4 h, then worked up in the usual way with acetic acid (6 ml) and hydrogen peroxide (10 ml; 30%). Removal of the solvent and crystallisation from ethyl acetate gave the mixture of diastereoisomers (13) and (14) (13.9 g, 72%). The mixture was separated by repeated fractional crystallisation from ethyl acetate to give (1RS,4RS,5RS,8RS)-5-*diphenylphosphinylbicyclo*[6.4.0]-*dodecan*-4-*ol* (13) (*ca.* 5 g), m.p. 163.5—164 °C (Found: C, 75.2; H, 8.15; P, 7.95. $C_{24}H_{31}O_2P$ requires C, 75.4; H, 8.1; P, 8.1%); $\nu_{max.}$(Nujol) 3 400, 3 060, 1 175, 753, 722, and 702 cm^{-1}; τ 2.0—2.7 (10 H, m, 2 × Ph), 4.7 (1 H, s, OH, exchanged by D_2O), 5.95 (1 H, m, C*H*OH), 7.0—7.5 (1 H, m, CHP), and 7.8—9.3 (18 H, m,): and (1RS,4SR,5SR,8RS)-5-*diphenylphosphinylbicyclo*[6.4.0]*dodecan*-4-*ol* (66) (*ca.* 5 g), m.p. 214—215 °C (Found: C, 75.3; H, 8.3; P, 8.0%); $\nu_{max.}$(Nujol) 3 340, 3 050, 1 160, 1 100, and 729 cm^{-1}; τ 2.0—2.7 (10 H, m, 2 × Ph), 4.32 (1 H, s, OH, exchanged by D_2O), 6.05 (1 H, m, C*H*OH), 6.9—7.4 (1 H, m, CHP), and 7.9—9.3 (18 H, m).

High dilution i.r. spectra (CCl_4; 1.7 × 10^{-4}—10 × 10^{-4}M): (13) 3 360 cm^{-1}; (14) 3 330 cm^{-1}.

A sample of the mixture of diastereoisomers (13) and (14) (500 mg) was acetylated under the usual conditions (acetic anhydride–pyridine), and worked up after 43 h, extracting with methylene chloride to give the *acetates* (500 mg, 90%), which were recrystallised from ethyl acetate–light petroleum (b.p. 40—60 °C), m.p. 198—200 °C (Found: C, 73.9; H, 7.9; P, 7.5. $C_{26}H_{33}O_3P$ requires C, 73.6; H, 7.8; P, 7.3%), which could not be separated by t.l.c. [multiple elution in ethyl acetate–light petroleum (1 : 10)]; $\nu_{max.}$(Nujol) 3 055, 1 725, 1 241, 1 175, 1 120, and 726 cm^{-1}, τ 2.0—2.7 (10 H, m, 2 × Ph), 4.60 (1 H, m, C*H*OAc), 7.1 (1 H, m, CHP), 7.7—9.3 (18 H, m), and 8.62 (3 H, s, Me).

(1RS,4SR,5SR,8RS)-*Bicyclo*[6.4.0]*dodec*-trans-4-*ene* (1).—A solution of the hydroxyphosphine oxide (13) (300 mg) in dry DMF (15 ml) was added to sodium hydride (200 mg) in the usual way, and the mixture stirred at 0 °C for 2 h. Work-up, extraction with light petroleum (3 × 50 ml), and removal of the solvent gave (1*RS*,4*SR*,5*SR*,8*RS*)-bicyclo-[6.4.0]dodec-*trans*-4-ene (1) (120 mg, 90%) as a colourless oil. G.l.c. (A) showed <0.2% of the *cis* isomer (15) $\nu_{max.}$(film) 3 000, 1 643, 1 462, 1 333, 1 210, 990, and 839 cm^{-1}; τ(CCl_4) 4.5—4.7 (2 H, m, CH=CH) and 7.4—9.0 (18 H, m); *m/e* 164 (33, M^+), 136 (65), 135 (36), and 121 (95); δ_C 133.4 (d, C-4), 41.8 (d, C-1), and 41.8, 35.6, 27.0, and 18.8 (t, C-2, C-3, C-9, and C-10).

A solution of the *trans* olefin (1) (50 mg) in light petroleum (10 ml) was extracted with aqueous silver nitrate solution (10%; 5 × 3 ml), then concentrated aqueous ammonia was added to the extract which was re-extracted with light petroleum (2 × 10 ml). The organic extracts were washed with water (10 ml) and dried ($MgSO_4$). G.l.c. (A) showed that most of the *trans* olefin (1) remained in the original petroleum phase and that both the *trans* olefin (1) and the *cis* contaminant (15) had been extracted with about the same low efficiency.

To a solution of the *trans* olefin (1) (50 mg) in ether (5 ml) was added iodine (2 mg). After 5 min g.l.c. (A) showed no *trans* isomer (1) remaining; the solution was filtered through neutral alumina and the solvent was removed to give (1*RS*,8*RS*)-bicyclo[6.4.0]dodec-*cis*-4-ene, identical by g.l.c. (A) and i.r. to an authentic sample of (15).

(1RS,4RS,5RS,8RS)-*Bicyclo*[6.4.0]*dodec*-trans-4-*ene* (2).—A solution of the phosphine oxide (14) (400 mg) in dry DMSO (20 ml) was added to potassium t-butoxide (220 mg) and the mixture stirred under nitrogen for 2 h. Water (30 ml) was added, the solution was extracted with light petroleum (2 × 30 ml), and the organic extracts were washed with water (2 × 30 ml). The combined petroleum extract was dried ($MgSO_4$), and the solvent was removed at reduced pressure to give the *trans* olefin (2) containing 4% of the *cis* isomer by g.l.c. (A). No starting material remained under these conditions. The olefin (2) showed $\nu_{max.}$(film) 3 005, 1 645, 1 450, 1 222, 982, 879, and 825 cm^{-1}; τ(CCl_4) 4.1—4.35 (2 H, m, CH=CH) and 7.4—9.1 (18 H, m); *m/e* 164 (33, M^+), 136 (77), 135 (56), and 121 (100); δ_C 137.2 (d, C-4), 43.0 (d, C-1), and 47.5, 36.7, 28.5, and 25.4 (t, C-2, C-3, C-9, and C-10). Alternated and co-injections of the two isomers (1) and (2) on several g.l.c. columns [(A), Carbowax, and support coated open tubular (50 ft) columns: Carbowax, silicone rubber gum SE 30, squalane, and diethylene glycol succinate] showed the isomer (1) to have a slightly longer retention time, but failed to separate the two.

The silver nitrate extraction described for (1) was repeated using a solution of the *trans* olefin (2) (40 mg) in light petroleum (10 ml). The extraction efficiency was again very low, but the process caused slight enrichment in the *trans* (2) relative to *cis* (15) ratio.

The iodine isomerisation described for (1) was repeated using a solution of (2) (30 mg) in ether (10 ml). G.l.c. (A) showed that rapid isomerisation occurred, and filtration through alumina and removal of the solvent gave an oil identified spectroscopically as the *cis* olefin (15).

Reaction of the Epoxide (6) *with Lithium Diphenylphosphide*.—$LiPPh_2$ (0.12 mol) in THF (60 ml) was added to the epoxide (6) (15 g, 0.084 mol) in THF (200 ml) in the

usual way. After addition of acetic acid (9 ml) and hydrogen peroxide (20 ml; 30%), and stirring for 18 h, a precipitate was produced which was filtered off and dissolved in methylene chloride. This solution was washed with water (2 × 100 ml), dried ($MgSO_4$), and evaporated to give a solid (6.44 g) containing predominantly the isomer (17). The filtrate from above was diluted with water (500 ml) and extracted with methylene chloride (3 × 200 ml), the extracts being washed as above. Drying ($MgSO_4$) and removal of the solvent gave a solid (19.6 g, total yield 81%) containing the isomers (16) and (17) in a *ca.* 1 : 1 ratio by t.l.c. (ethyl acetate). The samples were fractionally crystallised from ethyl acetate to give (1RS,4SR,5SR,8RS)-5-*diphenylphosphinylbicyclo*[6.4.0]*dodec*-10-*en*-4-*ol* (16) (*ca.* 7.5 g), m.p. 193—194 °C (Found: C, 75.5; H, 7.6; P, 8.3. $C_{24}H_{29}O_2P$ requires C, 75.8; H, 7.7; P. 8.1%); $\nu_{max.}$(Nujol) 3 340, 3 040, 3 015, 1 435, 1 180, 1 111, 750, and 720 cm^{-1}; τ 2.0—2.7 (10 H, m, 2 × Ph), 4.42 (2 H, m, CH=CH), 4.80 (1 H, s, OH, exchanged by D_2O), 5.9 (1 H, m, 4-H), 7.20 (1 H, m, 5-H), and 7.7—9.0 (14 H, m): and (1RS,4RS,5RS,8RS)-5-*diphenylphosphinylbicyclo*[6.4.0]*dodec*-10-*en*-4-*ol* (17) (*ca.* 7.5 g), m.p. 212—214 °C (Found: C, 76.0; H, 7.8; P, 8.2%); $\nu_{max.}$(Nujol) 3 350, 3 050, 3 010, 1 650, 1 305, 1 180, 1 156, 1 091, 1 029, and 764 cm^{-1}; τ 2.0—2.7 (10 H, m, 2 × Ph), 4.4 (3 H, m, CH=CH and OH, exchanged by D_2O), 6.0 (1 H, m, 4-H), 7.15 (1 H, m, 5-H), and 7.6—9.0 (14 H, m).

Hydrogenation of β-*Hydroxyphosphine Oxide* (17).—The hydroxyphosphine oxide (17) (1 g) in methanol (60 ml) was hydrogenated over platinum oxide (100 mg, Adams catalyst) at atmospheric pressure. Filtration and concentration gave crystals (0.84 g, 83.5%) identified as the isomer (14), by its i.r. and n.m.r. spectra.

(1RS,4RS,5RS,8RS)-*Bicyclo*[6.4.0]*dodeca*-trans-4-cis-10-*diene* (18).—A solution of the β-hydroxyphosphine oxide (16) (1 g, 2.63 mmol) in dry DMSO (30 ml) was added to sodium hydride (200 mg) in the usual way. After 2 h the mixture was worked up to give (1*RS*,4*RS*,5*RS*,8*RS*)-bicyclo[6.4.0]-dodeca-*trans*-4-*cis*-10-diene (18) (350 mg, 82%) as an oil [containing <0.1% of the *cis,cis* isomer (4) by g.l.c. (A)]; $\nu_{max.}$(film) 3 034, 3 000, 1 645, 1 632, 1 440, 1 182, 989, 870, and 692 cm^{-1}; $\lambda_{max.}$(cyclohexane) 193 nm (ε 11 000); τ 4.13 (2 H, m, 10-H and 11-H), 4.52 (2 H, m, 4-H and 5-H), and 7.5—9.0 (14 H, m); δ_C 133.8 (d, C-4), 129.4 (d, C-10), 42.5 (d, C-1), and 42.3, 35.3, and 31.5 (t, C-2, C-3, and C-9).

A solution of the *trans* olefin (18) (50 mg) in ether (10 ml) was treated with iodine (2 mg). After 30 min the solution was washed with aqueous sodium thiosulphate, then water, dried ($MgSO_4$), evaporated, and distilled to give the *cis* olefin (4) (35 mg, 70%), identified with an authentic sample by g.l.c. (A) and i.r.

(1RS,4SR,5SR,-RS)-*Bicyclo*[6.4.0]*dodeca*-trans-4-cis-10-*diene* (19).—A solution of the β-hydroxyphosphine oxide (17) (500 mg, 1.3 mmol) in dry DMSO (30 ml) was added to sodium hydride (200 mg) at 25 °C in the usual way, and worked-up after 30 min to give (1*RS*,4*SR*,5*SR*,8*RS*)-bicyclo[6.4.0]dodeca-*trans*-4-*cis*-10-diene (19) as an unstable oil [contaminated with 3% of the *trans* isomer (18) and 6.5% of the *cis* isomer (4) by g.l.c. (A)], $\nu_{max.}$(film) 3 015, 2 900, 2 850, 1 647, 990, 848, and 667 cm^{-1}; $\lambda_{max.}$(cyclohexane) 191 nm (ε 12 500); τ(CCl_4) 4.2—4.6 (4 H, m, olefinic), 7.4—9.0 (14 H, m,); δ_C 136.8 (d, C-4), 128.4 (d, C-10), 39.3 (d, C-1), and 40.2, 36.2, and 28.9 (t. C-2. C-3, and C-9).

A sample of the *trans* olefin (19) in ether was treated with iodine as for (18). Distillation gave (1*RS*,8*RS*)-bicyclo-[6.4.0]dodeca-*cis*-4-*cis*-10-diene (4), identified by comparison of the i.r. spectrum with that of an authentic sample.

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