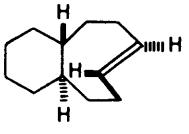
trans-Cycloalkenes. Part 9.[1] Optically Active *trans*-Cyclo-octenes *via* Resolution of β-Hydroxyphosphine Oxides. Proof of Configuration of Bicyclic *trans*-Cyclo-octenes constrained in Chair and Twist Conformations

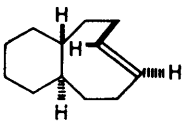
By **Paul F. Newton** and **Gordon H. Whitham,*** The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY

β-Hydroxyphosphine oxide precursors to *trans*-cyclo-octenes have been resolved by crystallisation of their menthoxyacetates. Subsequent fragmentation using sodium hydride gives the respective optically active *trans*-cyclo-octenes. In this way (*S*)-(+)- and (*R*)-(−)-*trans*-cyclo-octene, (*S*)-(+)-*cis,trans*-cyclo-octa-1,5-diene, and 4,5-epoxy-*trans*-octene [(+)-(12)] have been obtained in high optical purity. The epoxy-olefin (+)-(12) can be converted *via* addition of butadiene, and epoxide opening with lithium diphenylphosphide, into the optically active hydroxyphosphine oxides (+)-(14) and (+)-(15) which are respectively precursors of the optically active bicyclic twist and chair *trans*-cyclo-octenes (+)-(3) and (−)-(4). Addition of butadiene to (+)-(3) gave (+)-(17) while addition to (−)-(4) gave the *meso*-compound (18). In this way the twist and chair olefins were identified. Absolute configurations to all the optically active compounds have been assigned by correlation with (*S*)-(+)-*trans*-cyclo-octene.

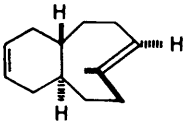
We have described in the previous paper syntheses of the twist and chair bicyclic *trans*-cyclo-octenes (1) and (2) and their unsaturated analogues (3) and (4), though their actual identification was left unsolved. The aim of the work in this paper was to identify unambiguously each member of these pairs of diastereoisomeric olefins. The method chosen required that (3) and (4) be obtained in optically active form followed by a reaction of these to give products, containing a further element of symmetry, whose optical properties would distinguish between the isomers.



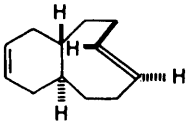
(1)



(2)



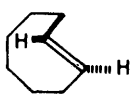
(3)



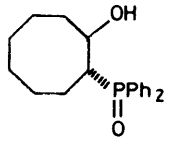
(4)

trans-Cyclo-octene itself had previously been obtained in optically active form (*a*) by direct resolution using diastereoisomeric platinum complexes;[2] (*b*) by kinetically controlled asymmetric transformation using (−)-*sym*-tetraisopinocampheyldiborane;[3] and (*c*) by synthesis from a resolved precursor. In the latter category are the following: fragmentation of the thionocarbonate from optically active *trans*-cyclo-octane-1,2-diol[4] and of the analogous trithiocarbonate,[4] and application of the dioxolan olefin synthesis to the benzylidene derivative of optically active *trans*-cyclo-octane-1,2-diol.[5,6] The absolute configuration of *trans*-cyclo-octene has been determined[7] and confirmed,[8] the (−)-(*R*)-enantiomer being as shown in (5).

For the case in hand it was decided that resolution *via* a precursor would be preferable to direct resolution of



(−)-(5)



(6)

(3) and (4) owing to the lability of the latter. Since the precursors to (3) and (4) were β-hydroxyphosphine oxides,[1] resolution of such compounds using the *trans*-cyclo-octene precursor (6)[9] as a model was investigated first.

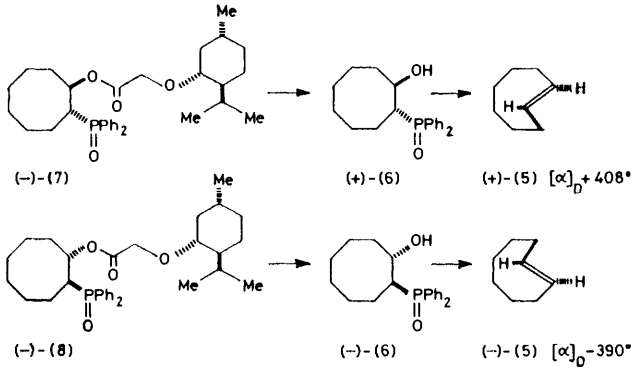
RESULTS AND DISCUSSION

After preliminary attempts to resolve (6) *via* the half-phthalate ester had proved discouraging, attention was turned to the menthoxyacetate. Treatment of (±)-(6) with the acid chloride † of (−)-menthoxyacetic acid in methylene chloride using 1,4-diazabicyclo[2.2.2]octane (DABCO) as base gave the diastereoisomeric menthoxyacetates (−)-(7) ‡ and (−)-(8). Fortunately the two protons of the O-CH_2-CO grouping in (7) and (8) are diastereotopic, and cleanly separated AB quartets for the two isomers were observed in the n.m.r. spectrum of the mixture. These two sets of signals, due to the two diastereoisomers, proved an invaluable monitor of the isomer ratio, and fractional crystallisation gave (−)-(7), $[\alpha]_D$ −32.8°, and (−)-(8), $[\alpha]_D$ −50.7°. The menthoxyacetates were separately hydrolysed to the enantiomeric hydroxyphosphine oxides (+)-(6), $[\alpha]_D$ +21.6°, and (−)-(6), $[\alpha]_D$ −21.5°, and the latter were fragmented in

† An improved preparation of menthoxyacetyl chloride compared to that in the literature[10] was developed (see Experimental section).

‡ Structural formulae for all optically active compounds represent the absolute configuration based on subsequent correlations.

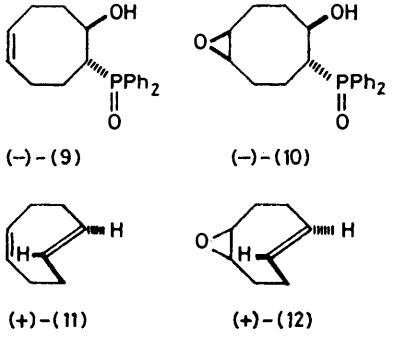
turn using sodium hydride in DMF to give (*S*)-(+)- and (*R*)-(−)-*trans*-cyclo-octene (Scheme 1).



SCHEME 1

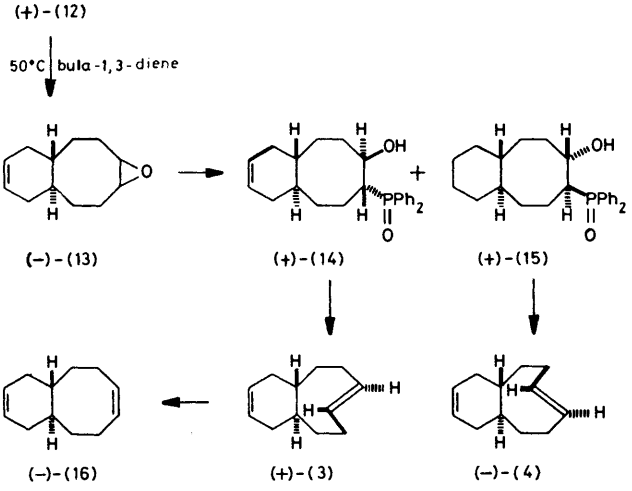
That the specific-rotation values fall short of those in the literature for optically pure *trans*-cyclo-octene, (lit.,[11] [α] −42.6°) is considered to be a consequence of the small scale of the preparations rather than a failure to effect complete resolution of the β-hydroxyphosphine oxides. Thus even after micro-distillation at *ca.* 50 °C, g.l.c. indicated traces of light petroleum remaining, together with a small amount of *cis*-cyclo-octene produced by isomerisation during distillation.

In a similar way (see Experimental section) resolution *via* the menthoxyacetates gave the optically active hydroxyphosphine oxides (−)-(9) and (+)-(9) and the epoxy-analogue (−)-(10). The absolute configuration of (−)-(9) was confirmed *via* correlation with (−)-(7), and fragmentation of (−)-(9) with sodium hydride in DMF gave optically active (*S*)-(+)-*cis,trans*-cyclo-octa-1,5-diene (11), $[\alpha]_D$ +171°; this is higher than the previously reported value (152°) [12] for which the authors stated that resolution might be incomplete. The synthesis identifies the absolute configuration of *cis,trans*-cyclo-octa-1,5-diene. Fragmentation of (−)-(10) gave the optically active epoxy-olefin (+)-(12).



To return to the main purpose of the present paper, it turned out that the hydroxyphosphine oxide precursor of the olefin (4) only gave a poor yield of menthoxyacetates and separation of the latter by crystallisation also led to difficulties. To circumvent these problems, and in any case to avoid two resolutions, it was decided to prepare the optically active precursors of (3) and (4) from the optically active epoxy-olefin (+)-(12) described above, by the procedure developed in the previous paper [1] (Scheme 2). This approach also had the advantage that the products would be of the same stereochemical series.

Treatment of (+)-(14) with sodium hydride gave the optically active twist *trans*-cyclo-octene (+)-(3), $[\alpha]_D$ +165.5°. Similar treatment of (+)-(15) gave (−)-(4), $[\alpha]_D$ −79.5°, which contained about 2% of (+)-(3) and 5% of (−)-(16). If the specific rotation is corrected for these contaminants the estimated value of $[\alpha]_D$ for (−)-(4) is −88.5°. As anticipated for *trans*-cyclo-octenes with opposite configurations of the *trans*-double bonds, these isomers have rotations of opposite sign (but not equal rotations since they are diastereoisomeric). They could each be isomerised to the same *cis*-olefin (−)-(16) on treatment with iodine.

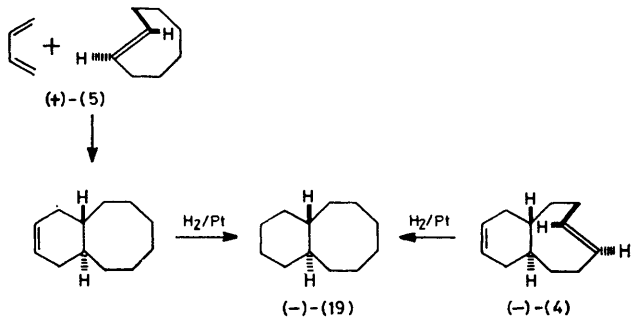


SCHEME 2

It was reasoned that the twist and chair olefins (3) and (4) could be distinguished by way of the products from the Diels–Alder addition of butadiene. The adduct from (+)-(3) should be (17), which, though it possesses three C_2 axes of symmetry, belongs to the chiral point group D_2. In contrast the adduct from (−)-(4) should be (18) belonging to the achiral point group C_{2h} with a plane of symmetry.

Thus addition of (+)-(3), $[\alpha]_D$ +165.5°, to butadiene gave (+)-(17), $[\alpha]_D$ +236°, thereby demonstrating that (3) was indeed the twist *trans*-cyclo-octene. Addition of (−)-(4) to butadiene gave (18) with a small residual rotation, $[\alpha]_D$ −0.7°, attributed to the presence of a small amount of (−)-(16) which was difficult to remove on a small scale. It is considered that the very large specific rotation found for (+)-(17) leaves no ambiguity about the configurational conclusions.

For the assignment of absolute configuration to the optically active bicyclic compounds described above, it was necessary to correlate them with a compound of known absolute configuration. This was achieved *via* (+)-(*S*)-*trans*-cyclo-octene as shown in Scheme 3, the saturated bicyclic hydrocarbon (−)-(19) having the same specific rotation, $[\alpha]_D$ −9.1°, from both routes.



SCHEME 3

Since the olefins (1) and (2) had earlier[1] been correlated with (3) and (4) it follows that they are respectively the twist and chair bicyclic *trans*-cyclo-octenes.

The work described in this paper demonstrates an additional advantage of the β-hydroxyphosphine oxide routes to olefins,[9] namely that resolution by way of menthoxyacetates, which have a convenient built-in monitor for the progress of the resolution, allows optically active olefins to be synthesised.

EXPERIMENTAL

For general points see the previous paper in this series.[1]

(−)-*Menthoxyacetic Acid.*—(−)-Menthol (39.02 g, 0.25 mol) in dry DMF (700 ml) was added to sodium hydride (20 g, 80% oil dispersion, washed twice with light petroleum) and the mixture was stirred under dry nitrogen until hydrogen evolution ceased. Dry chloroacetic acid (25 g, 0.265 mol) in dry DMF (200 ml) was added slowly with vigorous stirring, and stirring was continued for 7 h, then the mixture was heated on a steam-bath for 12 h. Water (200 ml) was added and the solvent was removed at reduced pressure. The residue was dissolved in water (500 ml), washed with benzene (75 ml), acidified with concentrated hydrochloric acid, and extracted with benzene (3 × 200 ml). The extracts were washed with brine (100 ml), combined, and dried ($MgSO_4$). Removal of the solvent and distillation gave (−)-menthoxyacetic acid (34.1 g, 64%), b.p. 133 °C at 0.2 mmHg; $[\alpha]_D$ −94.6° (*c* 2.1, ethanol) {lit.,[13] b.p. 134—137 °C at 2 mmHg, $[\alpha]_D$ −95.1° (*c* 2.0, 95% ethanol)}.

(−)-*Menthoxyacetyl Chloride.*—Menthoxyacetic acid was treated with thionyl chloride according to Leffler,[10] and the acid chloride was distilled (92% yield), b.p. 86 °C at 0.3 mmHg (lit.,[10] 117—120 °C at 3 mmHg). Some solidification in the condenser occurred although the compound is reported as a liquid.

(1R,2R)- *and* (1S,2S)-2-*Diphenylphosphinylcyclo-octyl Menthoxyacetates* (7) *and* (8).—To a solution of the (±)-β-hydroxyphosphine oxide (6) (15 g, 0.046 mol) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (13.5 g, 0.12 mol) in dry methylene chloride (150 ml) was added menthoxyacetyl chloride (13 g 0.056 mol), dropwise with stirring. The mixture was stirred at 18 °C for 100 h, then filtered. The precipitate was washed with methylene chloride (2 × 50 ml), the washings were filtered, and the filtrates combined. This organic layer was washed successively with water (50 ml), dilute hydrochloric acid (50 ml), brine (2 × 50 ml), and dried ($MgSO_4$). Removal of the solvent gave a mixture of diastereoisomers (18 g, 75%) which was separated by fractional crystallisation from ethyl acetate to give (1R,2R)-2-*diphenylphosphinylcyclo-octyl menthoxyacetate* (7), m.p. 180—181 °C; $[\alpha]_D$ −32.8° (*c* 1.0) (Found: C, 73.4; H, 8.4; P, 5.9. $C_{32}H_{45}O_4P$ requires C, 73.25; H, 8.6; P, 5.9%); τ 2.0—2.7 (10 H, m, 2 × Ph), 4.50 (1 H, m, 1-H), 6.54 and 7.12 (2 H, AB q, *J* 16 Hz, OCH_2CO), 7.2 (2 H, m, 2-H and menthoxy −CHO−), and 7.5—9.4 (30 H, m); and (1S,2S)-2-*diphenylphosphinylcyclo-octyl menthoxyacetate* (8) m.p. 177—178 °C; $[\alpha]_D$ −50.7° (*c* 1.0) (Found: C, 73.6; H, 8.3; P, 6.2%); τ 2.0—2.7 (10 H, m, 2 × Ph), 4.50 (1 H, m, 1-H), 6.63 and 7.05 (2 H, AB q, *J* 16 Hz, OCH_2CO), 7.2 (2 H, m, 2-H and menthoxy −CHO−), and 7.6—9.5 (30 H, m).

(1R,2R)-2-*Diphenylphosphinylcyclo-octanol,* (+)-(6).—The menthoxyacetate (7) (2.64 g, 5 mmol) was dissolved in aqueous ethanol (10%) (40 ml) containing potassium hydroxide (800 mg) and set aside at 20 °C for 1 h. The solvent was removed at reduced pressure, water (50 ml) was added, and the solution was extracted with methylene chloride (3 × 50 ml). The extracts were washed with brine (2 × 50 ml), combined, and dried ($MgSO_4$). Removal of the solvent and crystallisation from ethyl acetate–light petroleum (b.p. 40—60 °C) gave (1*R*,2*R*)-2-diphenylphosphinylcyclo-octanol (+)-(6) (1.54 g, 93%) as needles, m.p. 130—131 °C; $[\alpha]_D$ +21.6° (*c* 1.0) (Found: C, 73.2; H, 7.7; P, 9.5. Calc. for $C_{20}H_{25}O_2P$: C, 73.15; H, 7.6; P, 9.4%), with i.r. and n.m.r. spectra identical to those of a racemic sample.

(1S,2S)-2-*Diphenylphosphinylcyclo-octanol,* (−)-(6).—The above procedure was repeated for the menthoxyacetate (8) (780 mg) in aqueous ethanol (10%) (25 ml) containing potossium hydroxide (300 mg). Crystallisation from ethyl acetate–light petroleum gave (1*S*,2*S*)-2-diphenylphosphinylcyclo-octanol (−)-(6) (400 mg, 82%), m.p. 130—131 °C; $[\alpha]_D$ −21.5° (*c* 1.0) (Found: C, 73.5; H, 7.7; P, 9.3. Calc. for $C_{20}H_{25}O_2P$: C, 73.15; H, 7.6; P, 9.4%), spectroscopically identical to the racemic sample.

(S)-trans-*Cyclo-octene,* (+)-(5).—A solution of the hydroxyphosphine oxide (+)-(6) (600 mg, 1.8 mmol) in dry DMF (25 ml) was added to sodium hydride (100 mg) in the usual way, and stirred for 2 h. Work-up, and removal of the solvent at reduced pressure and 0 °C gave an oil which was distilled to give (*S*)-*trans*-cyclo-octene (+)-(5) (150 mg, 75%), b.p. 50 °C (bath) at 50 mmHg; $[\alpha]_D$ +408° (*c* 0.5, CH_2Cl_2) (lit.,[11] $[\alpha]_D^{25}$ +414°, *c* 0.55, CH_2Cl_2), with identical g.l.c. (A) retention time and i.r. spectrum to authentic racemic *trans*-cyclo-octene,

(R)-trans-*Cyclo-octene,* (−)-(5).—The above procedure was repeated using the hydroxyphosphine oxide (−)-(6) (250 mg) in dry DMSO (20 ml). Distillation gave (*R*)-*trans*-cyclo-octene (−)-(5), b.p. 80 °C (bath) at 60 mmHg; $[\alpha]_D$ −390° (*c* 1.0, CH_2Cl_2) (lit.,[11] $[\alpha]_D^{25}$ −426°, *c* 0.41, CH_2Cl_2), identical by g.l.c. (A) [1] and i.r. to an authentic racemic sample.

(1S,8S)-*Bicyclo*[6.4.0]*dodec*-10-*ene.*—(*S*)-*trans*-Cyclo-octene (105 mg) was mixed with an excess of butadiene and heated in a sealed flask at 70 °C for 70 h. The excess was allowed to evaporate, and the residue was distilled to give (1*S*,8*S*)-bicyclo[6.4.0]dodec-10-ene (128 mg, 82%), b.p.

90 °C (bath) at 10 mmHg; $[\alpha]_D$ +79.1° (*c* 1.3) (Found: C, 88.0; H, 12.1. Calc. for $C_{12}H_{20}$: C, 87.7; H, 12.3%), spectroscopically identical to a racemic sample.[13]

(1S,8S)-*Bicyclo*[6.4.0]*dodecane*, (−)-(19).—(1*S*,8*S*)-Bicyclo[6.4.0]dodec-10-ene (90 mg) in methanol (10 ml) was hydrogenated at atmospheric pressure over platinum oxide (10 mg; Adams catalyst). The solution was filtered, the solvent was removed and the oil was distilled to give (1S,8S)-*bicyclo*[6.4.0]*dodecane*, (−)-(19) (75 mg, 82%), b.p. 100 °C (bath) at 12 mmHg; $[\alpha]_D$ −8.6° (*c* 2.0) (Found: C, 86.9; H, 13.2. $C_{12}H_{22}$ requires C, 86.7; H, 13.3%); $\nu_{max.}$(film) 2920, 2 850, 1 446, and 850 cm^{-1}, τ(CCl_4) 8.0—9.0 (m).

(1R,2R)- *and* (1S,2S)-2-*Diphenylphosphinylcyclo-oct-5-enyl Menthoxyacetates*.—To a solution of the (±)-β-hydroxyphosphine oxide (9) (9 g, 0.002 76 mol) and DABCO (8 g, 0.0071 mol) in dry methylene chloride (50 ml) was added menthoxyacetyl chloride (8.5 g, 0.003 66 mol) and the mixture was stirred at 20 °C for 107 h, then worked-up as before. Removal of the solvent gave an oil which slowly crystallised, and the crude product was fractionally crystallised from acetone–light petroleum (b.p. 40—60 °C) to give (1R,2R)-2-*diphenylphosphinylcyclo-oct-5-enyl menthoxyacetate* (1.4 g) as needles, m.p. 163.5—164.5 °C, $[\alpha]_D$ −24.2° (*c* 1.0) (Found: C, 73.9; H, 8.0; P, 5.8. $C_{32}H_{43}O_4P$ requires C, 73.5; H, 8.3; P, 5.9%); τ 2.0—2.7 (10 H, m, 2 × Ph), 3.9—4.9 (3 H, m, CH=CH and 1-H), 6.41 and 6.62 (2 H, AB q, *J* 16 Hz, OCH_2CO), 6.75—7.2 (2 H, m, 2-H and menthoxy ⁻CHO⁻), and 7.3—9.5 (26 H, m); and (1S,2S)-2-*diphenylphosphinylcyclo-oct-5-enyl menthoxyacetate* as fine needles, m.p. 151.4—153 °C, $[\alpha]_D$ −59.6° (*c* 1.0) (Found: C, 73.9; H, 7.9; P, 6.1%); τ 2.0—2.7 (10 H, m, 2 × Ph), 3.95—4.9 (3 H, m, CH=CH and 1-H), 6.36 and 6.62 (2 H, AB q, *J* 16 Hz, OCH_2CO), 6.8—7.2 (2 H, m, 2-H and menthoxy ⁻CHO), and 7.3—9.5 (26 H, m).

Hydrogenation of (1R,2R)-2-*Diphenylphosphinylcyclo-oct-5-ethyl Menthoxyacetate*.—The ester (30 mg) in methanol (15 ml) was hydrogenated at atmospheric pressure over platinum oxide (10 mg). Filtration and removal of the solvent gave an ester with an n.m.r. spectrum identical to that of the menthoxyacetate (−)-(7).

(1R,2R)-2-*Diphenylphosphinylcyclo-oct-5-enol*, (−)-(9).—The (1*R*,2*R*)-menthoxyacetate (1.23 g) was hydrolysed in aqueous ethanol (25 ml) containing potassium hydroxide (330 mg). Crystallisation from ethyl acetate–light petroleum gave (1*R*,2*R*)-2-diphenylphosphinylcyclo-oct-5-enol (−)-(9) (600 mg, 78%), m.p. 131—132 °C; $[\alpha]_D$ −32.0° (*c* 1.0) (Found: C, 73.4; H, 7.1; P, 9.2. Calc. for $C_{20}H_{23}O_2P$: C, 73.6; H, 7.1; P, 9.5%), with i.r. and n.m.r. spectra identical to those of a racemic sample.

(+)-(S)-cis,trans-*Cyclo-octa*-1,5-*diene*, (+)-(11).—This was prepared from the (1*R*,2*R*)-hydroxyphosphine oxide by treatment in DMF with sodium hydride in the usual way. It had $[\alpha]_D$ +171° (*c* 1.5, CH_2Cl_2). G.l.c. (A) showed the sample to contain <0.1% of the *cis*,*cis*-isomer, but traces (1—4%) of light petroleum.

(1S,4R,5R,8R)- *and* (1R,4S,5S,8S)-5-*Diphenylphosphinyl*-9-*oxabicyclo*[6.1.0]*non*-4-*yl Menthoxyacetates*.—To a solution of the (±)-hydroxyphosphine oxide (10) (20 g, 0.058 mol) and DABCO (18 g, 0.16 mol) in dry methylene chloride (180 ml) was added menthoxyacetyl chloride (18 g, 0.0775 mol) and the mixture stirred at 18 °C for 40 h, then worked-up as before. The solvent was removed and the crude product was crystallised from ethyl acetate to give (1S,4R,5R,8R)-5-*diphenylphosphinyl*-9-*oxabicyclo*[6.1.0]*non*-4-*yl menthoxyacetate* (9.02 g, 57%) as needles, m.p. 207—208 °C, $[\alpha]_D$ −33.4° (*c* 1.0) (Found: C, 71.1; H, 7.7; P, 6.0. $C_{32}H_{43}O_5P$ requires C, 71.35; H, 8.05; P, 5.75%), τ 2.0—2.7 (10 H, m, 2 × Ph), 4.53 (1 H, m, 4-H), 6.23 and 6.48 (2 H, AB q, *J* 16.5 Hz, OCH_2CO), 6.7—7.15 (4 H, m, 1-H, 5-H, 8-H, and menthoxy ⁻CHO⁻), and 7.15—9.5 (26 H, m). The mother-liquors were concentrated, and gave a non-crystalline gel which could not be induced to crystallise, but which contained predominantly the (1*R*,4*S*,5*S*,8*S*)-isomer contaminated with <10% of the (1*S*,4*R*,5*R*,8*R*)-isomer by n.m.r.; τ 2.0—2.7 (10 H, m, 2 × Ph), 6.55 (1 H, m, 4-H), 6.18 and 6.51 (2 H, AB q, *J* 16.5 Hz, OCH_2CO), 6.8—7.2 (4 H, m, 1-H, 5-H, 8-H, and menthoxy ⁻CHO⁻), and 7.2—9.5 (26 H, m). The material was not further purified.

(1S,4R,5R,8R)-5-*Diphenylphosphinyl*-9-*oxabicyclo*[6.1.0]-*nonan*-4-*ol*, (−)-(10).—The (1*S*,4*R*,5*R*,8*R*)-menthoxyacetate (5g) was hydrolysed in aqueous ethanol (125 ml) containing potassium hydroxide (1 g) as described for the ester (7). Crystallisation from ethyl acetate gave (1*S*,4*R*,-5*R*,8*R*)-5-diphenylphosphinyl-9-oxabicyclo[6.1.0]nonan-4-ol (−)-(10) (3 g, 95%), m.p. 227.5—229.5 °C; $[\alpha]_D$ −69.5° (*c* 1.0), with i.r. and n,m.r. spectra identical to those of a racemic sample.

(1R,4S,5S,8S)-9-*Oxabicyclo*[6.1.0]*non*-trans-4-*ene*.— The (1*S*,4*R*,5*R*,8*R*)-hydroxyphosphine oxide (−)-(10) was treated with sodium hydride in DMSO as described for racemic material [1] to give (+)-(12), $[\alpha]_D$ +289° (*c* 1.0).

(1S,4R,6S,9S)-5-*Oxatricyclo*[7.4.0.0^{4,6}]*tridec*-11-*ene*, (−)-(13).—Epoxy-olefin (+)-(12) was treated with butadiene as described for racemic material [1] and gave (−)-(13), b.p. 72 °C at 0.3 mmHg; $[\alpha]_D$ −86.5° (*c* 1.0).

Hydroxyphosphine Oxides (+)-(14) *and* (+)(15).—Ring opening [1] of epoxide (−)-(13) gave (1*S*,4*R*,5*R*,8*S*)-5-diphenylphosphinylbicyclo[6.4.0]dodec-10-en-4-ol (+)-(14), m.p. 150—151 °C; $[\alpha]_D$ +53.2° (*c* 1.0) (Found: C, 75.5; H, 7.7; P, 8.3. Calc. for $C_{24}H_{29}O_2P$: C, 75.8; H, 7.7; P, 8.1%) and (1*S*,4*S*,5*S*,8*S*)-5-diphenylphosphinylbicyclo-[6.4.0]dodec-10-en-4-ol (+)-(15), m.p. 241.5—242 °C; $[\alpha]_D$ +13.6° (*c* 1.0) (Found: C, 75.9; H, 7.4; P, 8.5%).

(1S,4S,5S,8S)-*Bicyclo*[6.4.0]*dodeca*-trans-4-cis-10-*diene*, (+)-(3).—This was prepared from the (+)-hydroxyphosphine oxide (14) using sodium hydride in DMF,[1] worked-up after 30 min. The olefin contained no (4) or (16) by g.l.c. (A); $[\alpha]_D$ +165.5° (*c* 2.0, cyclohexane); c.d. $\lambda_{max.}$(cyclohexane) 202 nm ($\Delta\varepsilon$ 0.284).

A sample of (+)-(3) in ether was treated with iodine. Distillation gave (1*S*,8*S*)-bicyclo[6.4.0]dodeca-*cis*-4-*cis*-10-diene (−)-(16), $[\alpha]_D$ −19.5° (*c* 1.0), with identical g.l.c. (A) retention time and i.r. spectrum to those of racemic material.[1]

(1S,4R,5R,8S)-*Bicyclo*[6.4.0]*dodeca*-trans-4-cis-10-*diene*, (−)-(4), prepared from the hydroxyphosphine oxide (+)-(15) using sodium hydride in DMSO and worked-up after 45 min, contained <5% of the *cis* isomer (−)-(16) and 3% of the *trans* isomer (+)-(3) by g.l.c. (A); $[\alpha]_D$ (corrected for impurity −88.5° (*c* 2.0, cyclohexane); c.d. $\lambda_{max.}$(cyclohexane) 215 nm ($\Delta\varepsilon$ 0.104).

A solution of the *trans* olefin (−)-(4) in ether was treated with iodine as for (3). Distillation gave (1*S*,8*S*)-bicyclo-[6.4.0]dodeca-*cis*-4-*cis*-10-diene (−)-(16); $[\alpha]_D$ −19.8° (*c* 1.5).

Hydrogenation of (1S,4R,5R,8S)-*Bicyclo*[6.4.0]*dodeca*-trans-4-cis-10-*diene*, (−)-(4).—A sample of the *trans* olefin (−)-(4) in cyclohexane was hydrogenated at atmospheric pressure over platinum oxide until g.l.c. (A) indicated only a single component to be present. The solution was filtered,

the solvent was removed, and the residue was distilled to give (1*S*,8*S*)-bicyclo[6.4.0]dodecane (−)-(19), b.p. 100 °C (bath) at 10 mmHg; $[\alpha]_D$ −9.1° (*c* 1.0), identical by i.r. and n.m.r. to the sample obtained from (+)-(*S*)-*trans*-cyclo-octene.

(1RS,8RS)-*Bicyclo*[**6.4.0**]*dodeca*-cis-4-cis-10-*diene*.— A mixture of *cis,trans*-cyclo-octa-1,5-diene [from β-hydroxy-phosphine oxide (±)-(9), 0.012 mol] and an excess of butadiene was sealed in a flask and heated at 50 °C for 20 h. Evaporation of the excess of butadiene and distillation gave (1RS,8RS)-*bicyclo*[6.4.0]*dodeca*-cis-4-cis-10-*diene* (±)-(16) (1.46 g, 73.5%), b.p. 120—125 °C (bath) at 12 mmHg (Found: C, 88.6; H, 11.2. $C_{12}H_{18}$ requires C, 88.8; H, 11.2%); τ 4.2—4.5 (4 H, m, olefinic) 7.1—8.8 (14 H, m); δ_C 129.1 and 127.3 (d, C-4 and C-10), 37.0 (d, C-1), and 33.5, 32.9, and 25.9 (t, C-2, C-3, and C-9).

(1RS,4RS,9RS,12RS)-*Tricyclo*[10.4.0.0^{4,9}]*hexadeca*-6,14-*diene* (17).—The *trans* olefin (3) (200 mg) in an excess of butadiene was heated at 50 °C in a sealed tube for 24 h, then the excess was evaporated and the product distilled to give (1*RS*,4*RS*,9*RS*,12*RS*)-tricyclo[10.4.0.0^{4,9}]hexadeca-6,14-diene (17) (210 mg, 80%), b.p. 110 °C (bath) at 0.1 mmHg, which solidified to a waxy solid, m.p. 30—37 °C (Found: C, 88.8; H, 11.3. $C_{16}H_{24}$ requires C, 88.8; H, 11.2%); τ 4.40 (4 H, m, olefinic) and 7.5—8.9 (20 H, m); δ_C 127.5 (d, C-6), 41.6 (d, C-1), and 35.3 and 31.5 (t, C-2 and C-5).

(1S,4S,9S,12S)-*Tricyclo*[10.4.0.0^{4,9}]*hexadeca*-6,14-*diene* (+)-(17), was prepared from the *trans* olefin (+)-(3) and had m.p. 30—37 °C; $[\alpha]_D$ +236° (*c* 1.0) (Found: C, 88.75; H, 10.9%).

(1RS,4SR,9SR,12RS)-*Tricyclo*[10.4.0.0^{4,9}]*hexadeca*-6.14-*diene* (18).—(*a*) The procedure described for (17) was repeated using the *trans* olefin (4) (190 mg), and gave (1RS,-4SR,9SR,12RS)-*tricyclo*[10.4.0.0^{4,9}]*hexadeca*-6,14-*diene* (18) (180 mg, 70%) as an oil, b.p. 120 °C (bath) at 0.4 mmHg (Found: C, 89.1; H, 11.0%); $\nu_{max.}$(film) 3 020, 2 965, 1 664, 1 478, 1 445, 1 059, 963, and 820 cm^{-1}; τ 4.38 (4 H, s, olefinic), 7.7—9.0 (20 H, m); δ_C 126.8 (d, C-6), 37.0 (d, C-1), and 35.0 and 32.8 (t, C-2 and C-5).

(*b*) The tricyclic hydrocarbon was prepared from (−)-(4) and had b.p. 110 °C (bath) at 0.3 mmHg, $[\alpha]_D$ −0.7° (*c* 2.0) (Found: C, 89.1; H, 11.1%).

We thank the S.R.C. for a Research Studentship (to P. F. N.) and Lady Richards and her associates for n.m.r. spectra.

[8/1645 *Received*, 14*th September*, 1978]

REFERENCES

[1] Part 8, P. F. Newton and G. H. Whitham, preceding paper.
[2] A. C. Cope, C. R. Ganellin, and H. W. Johnson, *J. Amer. Chem. Soc.*, 1962, **84**, 3191.
[3] W. L. Waters, *J. Org. Chem.*, 1971, **36**, 1569.
[4] E. J. Corey and J. I. Shulman, *Tetrahedron Letters*, 1968, 3655.
[5] T. Aratani, Y. Nakanishi, and H. Nozaki, *Tetrahedron*, 1970, **26**, 4339.
[6] H. Madden, Part II Thesis, Oxford University, 1971.
[7] A. C. Cope and A. S. Mehta, *J. Amer. Chem. Soc.*, 1964, **86**, 5626.
[8] P. C. Manor, D. P. Shoemaker, and P. S. Parkes, *J. Amer. Chem. Soc.*, 1970, **92**, 5260.
[9] A. J. Bridges and G. H. Whitham, *J.C.S. Chem. Comm.*, 1974, 142.
[10] M. T. Leffler and A. E. Calkins, *Org. Synth., Coll. Vol.* III, 544.
[11] A. C. Cope, C. R. Ganellin, H. W. Johnson, T. V. Van Auken, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, 1963, **85**, 3276.
[12] A. C. Cope, J. K. Hecht, H. W. Johnson, H. Keller, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, 1966, **88**, 761.
[13] K. T. Burgoine, S. G. Davies, M. J. Peagram, and G. H Whitham, *J.C.S. Perkin I*, 1974, 2629.