trans-Cycloalkenes. Part 12.[1] *trans,trans*- and *cis,trans*-Cyclonona-1,5-diene

A. Christopher Connell and Gordon H. Whitham *
The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY

Possible synthetic routes to *trans,trans*-cyclonona-1,5-diene from the *cis,cis*-isomer have been investigated using the β-hydroxyphosphine oxide olefin inversion procedure. A stepwise approach *via* the epoxy-*trans*-cyclononene (10) failed. However consecutive double elimination involving the bis-β-hydroxyphosphine oxides (11) and (12) gave *cis*- and *trans*-1,2-divinylcyclopentane which are believed to have been obtained by rapid Cope rearrangement of first formed ' parallel ' and ' crossed ' *trans,trans*-cyclonona-1,5-diene (1A) and (1B) respectively.

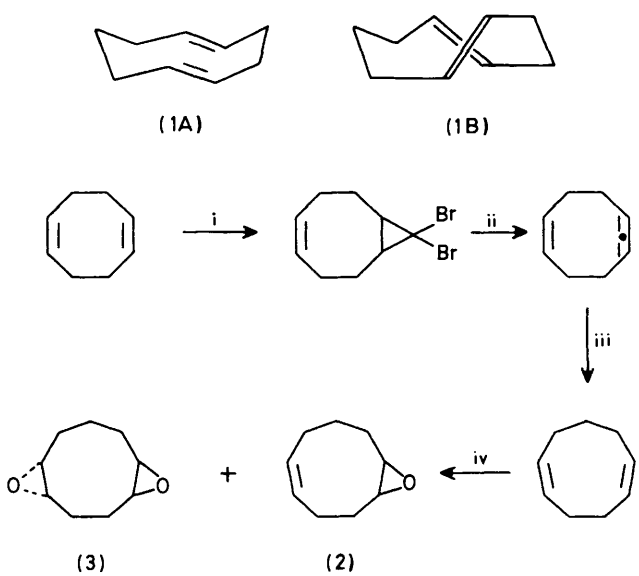
Arising out of our experiences with *trans*-cyclonona-1,2,6-triene described in the previous paper in this series, we decided to attempt the preparation of *trans,trans*-cyclonona-1,5-diene. An additional incentive was provided by a recent statement in the literature[2] that the latter ' should be more stable than the known *cis,trans*-isomer.' This statement was based on examination of molecular models. It is supported by early force-field calculations[3] but not by more recent ones.[4]

trans,trans-Cyclonona-1,5-diene might be expected to exist in two diastereoisomeric forms or at least two conformational isomers with a relatively high energy barrier between them. These two forms are the parallel and crossed structures (1A) and (1B) respectively. In designing routes to these, it was decided to utilise the β-hydroxyphosphine oxide elimination[5] since this olefin inversion procedure was known to proceed with high stereospecificity in suitable cases, and by appropriate choice of precursors it might be possible to direct formation of either (1A) or (1B).

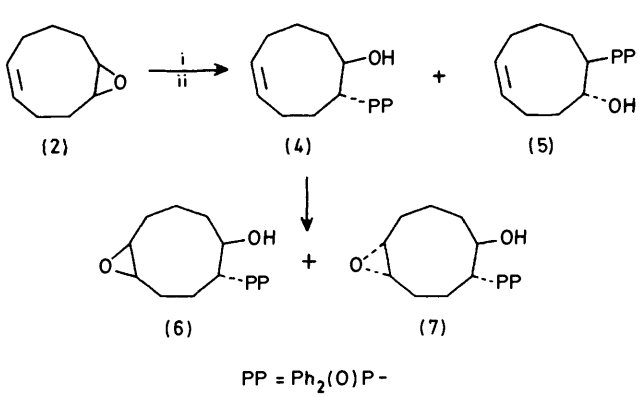
Clearly one can adopt either a stepwise approach in which the *trans*-double bonds are introduced one at a time or a simultaneous one in which they are introduced together in a ' one pot ' reaction. We tried both approaches. Either way a key intermediate is the mono-epoxide (2) of *cis,cis*-cyclonona-1,5-diene which was prepared as shown in Scheme 1. Unexpectedly, and in contrast to *cis,cis*-cyclo-octa-1,5-diene, the selective mono-epoxidation of *cis,cis*-cyclonona-1,5-diene was not efficient, and appreciable amounts of the bis-epoxide (3) were formed. Again in contrast to the eight membered ring where the corresponding bis-epoxide formed with peroxy acid is *syn*,[6] the bis-epoxide (3) is the *anti*-isomer as is shown subsequently.

Further elaboration of mono-epoxide (2) along the stepwise route is summarised in Scheme 2. Two regioisomeric β-hydroxyphosphine oxides were obtained from (2) in the ratio 92 : 8 as shown by the ^{31}P n.m.r. spectrum of the mixture. From the point of view of the stereochemistry of the subsequent reactions it is immaterial which is which of the two regioisomers, but for convenience of discussion it is *assumed* that the major one has structure (4). The high regioselectivity in the epoxide opening is noteworthy. Epoxidation of the unsaturated hydroxyphosphine oxide, essentially (4), gave two epoxides (6) and (7) in the ratio 4 : 6. The major epoxide (7) deteriorated on standing or attempted recrystallisation owing to formation of a transannular ether (which attested to the *trans*-relationship of the OH group to the epoxide ring) and this approach was therefore abandoned. Similarly, opening of one epoxide ring of the bis-epoxide (3) with Ph_2PLi was frustrated by formation of a transannular ether [which demonstrated the *anti*-relationship between the two epoxide rings in (3)].

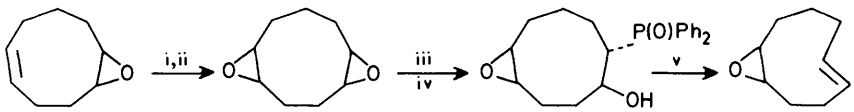
To avoid the complications of transannular ether formation, further work on the stepwise route was carried out on the *syn*-diepoxide (8), obtained by base-catalysed cyclisation of the bromohydrins derived from the mono-epoxide (2) by addition of HOBr (Scheme 3). In practice the regioselectivity of opening the *syn*-diepoxide (8) with Ph_2PLi was even more marked than that of epoxide (2) and in the opposite sense.



Scheme 1. *Reagents:* i, $CHBr_3$–KOBu^t; ii, Mg–THF; iii, Na–liq. NH_3; iv, CH_3CO_3H–CH_2Cl_2

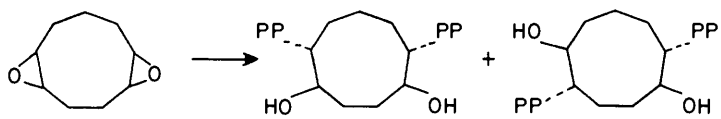


Scheme 2. *Reagents:* i, Ph_2PLi–THF; ii, H_2O_2–AcOH; iii, CH_3CO_3H–CH_2Cl_2



(2) (8) (9) (10)

Scheme 3. *Reagents:* i, NBS–Me_2CO–H_2O–$HClO_4$; ii, K_2CO_3–MeOH–H_2O; iii, Ph_2PLi–THF; iv, H_2O_2–AcOH; v, NaH–DMSO



(8) PP = $Ph_2(O)P$- (11) (12)

Scheme 4. *Reagents:* i, excess Ph_2PLi–THF; ii, H_2O_2–AcOH

Thus only one product was isolated, clearly distinguishable from (6) and hence assigned structure (9) given the earlier assumption about the constitution of (4). Elimination of diphenylphosphonate from the anion of (9) gave the *trans*-alkene epoxide (10). Unfortunately attempts to prepare a hydroxyphosphine oxide from (10) by treatment with Ph_2Li *etc.* failed, a complex mixture of products being obtained. The stepwise approach to *trans,trans*-cyclonona-1,5-diene was therefore abandoned.

The alternative approach, a ' one pot ' preparation of the *trans,trans*-cyclononadiene was therefore explored. The appropriate bis-β-hydroxyphosphine oxide precursors were obtained as summarised in Scheme 4, two diastereoisomers being formed in the ratio 6 : 4. The major one showed only five lines in the aliphatic region of the ^{13}C n.m.r. spectrum and, given the presumption (Scheme 3) that the monoepoxide (9) is the intermediate, the structure (11) with a plane of symmetry is assigned. The minor diastereoisomer is therefore the unsymmetrical one (12). Only the symmetrical isomer was obtained pure, the other, though enriched, was contaminated with isomer (11).

The stereochemistry of the symmetrical bis-hydroxyphosphine oxide (11) is such that successive elimination of two diphenylphosphinates without incursion of conformational change at the half way stage should lead to the parallel isomer (1A) of the diene while the unsymmetrical form (12) should lead to the crossed isomer (1B).

Preliminary attempts to effect the double elimination involved treatment of a 6 : 4 mixture of (11) and (12) with sodium hydride in dimethylformamide (DMF) at 0 ⟶ 18 °C. Two hydrocarbon products were obtained in the ratio 17 : 83. The minor product was identified as *cis*-1,2-divinylcyclopentane (DVCP) (17) by comparison with an authentic sample,[7] the major one was shown spectroscopically to be *trans*-DVCP (18). Neither *cis,cis*- nor *cis,trans*-cyclonona-1,5-diene, known to be stable to the reaction conditions, was detected, thereby demonstrating the high stereospecificity of the eliminations.

We propose that *cis*- and *trans*-DVCP are formed by rapid Cope rearrangement of transient *trans,trans*-cyclonona-1,5-diene (see Scheme 5). The parallel isomer (1A) is constrained to react *via* a boat transition state to give *cis*-DVCP (17) while the crossed isomer (1B) should give *trans*-DVCP (18) *via* a chair transition state.* Since the 6 : 4 mixture of (11)/12 gave (17)/(18) in the ratio 17 : 83 it is clear that stereospecificity in the sense (11) ⟶ (17) and (12) ⟶ (18) is not observed and some interconversion between intermediates must occur.

Table. Products from treatment of the bis-β-hydroxyphosphine oxides (11) and (12) with bases

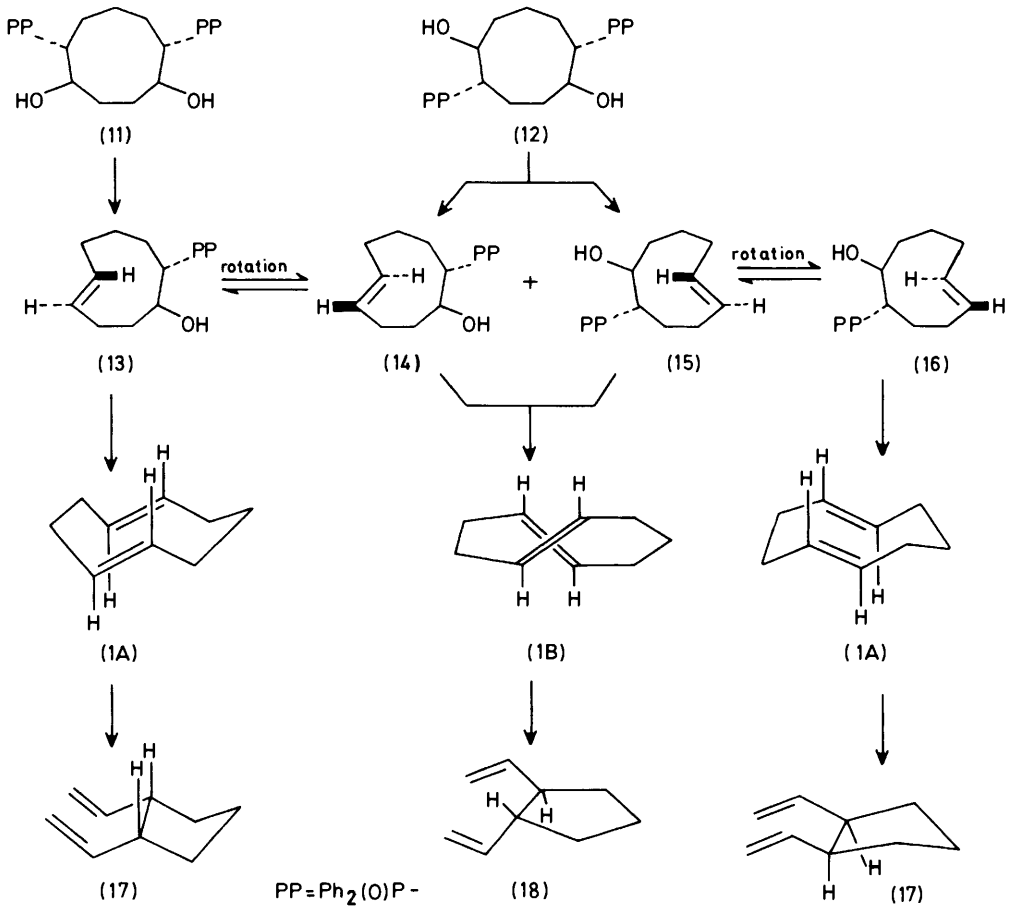
Compound	Base	Solvent	Yield (%)	Ratio of (17) : (18)
(11)	Bu^{t}OK	DMSO	44	85 15
(11)	Bu^{t}OK	DMSO	46 [a]	80 20
(11)	Bu$^n_4$NOH	DMSO	39	54 46
(11)	NaH	DMSO	54	30 70
(11)	NaH	DMF	32	22 78
(11)	NaOMe	DMF	48	36 64
Mixture A [b]	Bu^{t}OK	DMSO	72	70 30
Mixture A	NaH	DMSO	22	33 67
Mixture A	NaH	DMF	50	34 66
Mixture A	NaOMe	DMF	56	36 64
Mixture B [c]	Bu^{t}OK	DMSO	53	36 64
Mixture B	Bu$^n_4$NOH	DMSO	59	24 76

[a] In presence of 18-crown-6 ether. [b] (11)/(12), 2 : 1. [c] (11)/(12), 1 : 2.

The influence of reaction conditions on the stereochemical outcome of the reaction was examined using a sample of pure (11) and two different mixtures of (11) and (12), with the results shown in the Table. Although some inconsistencies are apparent it is clear that the ratio of *cis*- and *trans*-DVCP is dependent on the nature of the starting material (11) or (12) and on the nature of the base/solvent combination. Highest stereospecificity is obtained with potassium t-butoxide in dimethyl sulphoxide (DMSO), while using sodium hydride as base gave (18)/(17) ratios close to 2 : 1 from either starting material. We suggest that this indicates that the conformational interconversion occurs after elimination of the first diphenyl phosphinate unit leading to (13) ⇄ (14) and (15) ⇄ (16). The half-life for racemisation of optically active *trans*-cyclononene is *ca.* 20 s at 20 °C [9] which should be a reasonable model for these interconversions. This interpretation implies that the rate of fragmentation of the anion of a β-hydroxyphosphine oxide is strongly dependent on the associated cation with $K^+ > Na^+$. Such cation dependence has been implicated before,[10] particularly from the point of view of the relative stability of the Li^+ complexes. Interestingly the ratio of (18) to (17) formed under the sodium hydride conditions roughly reflects the energy difference between (1B) and (1A) calculated by White and Bovill.[4]

Attempts were made to trap the postulated intermediate *trans,trans*-cyclonona-1,5-diene by carrying out the base-

* See ref. 8 for chair *vs.* boat transition states in the Cope rearrangement.



Scheme 5.

induced fragmentation of (11) and (12) in the presence of 1,3-diphenylbenzisofuran but without success, only *cis*- and *trans*-DVCP being obtained.

Attempts were also made to isolate one or more of the intermediate mono-β-hydroxyphosphine oxides (13), (14), (15), or (16) by treatment of (11) with one equivalent of sodium methoxide in DMF at 0 °C. A product with an n.m.r. spectrum consistent with the expected structure was isolated which on further treatment with sodium hydride in DMSO gave *cis*- and *trans*-DVCP in the ratio 21 : 79.

The availability of the hydroxyphosphine oxide (4) gave an opportunity of preparing a sample of *cis,trans*-cyclonona-1,5-diene which previously had not been fully characterised.[11] Treatment of (4) with sodium hydride in DMF gave this diene in 62% yield.

In summary, therefore, evidence has been obtained for *trans,trans*-cyclonona-1,5-diene as a transient species in both the parallel and crossed forms. The much greater rate at which it undergoes Cope rearrangement compared with the *cis,cis*- and the *cis,trans*-isomers is in line with expectations from the force-field calculations of White and Bovill [4] which place (1A) and (1B) respectively 55 and 52.5 kJ/mol higher in energy than the preferred conformation for the *cis,cis*-isomer compared to values of 23 and 33 kJ/mol for the two lowest energy conformations of the *cis,trans*-isomer.

Experimental

For general points see previous paper.[1]

cis-*Cyclonona*-1,2,6-*triene*.—(a) *Using methyl-lithium*. Methyl-lithium (0.76M; 0.3 mol in ether) was added during 2 h to a cooled (acetone–CO_2), stirred solution of 9,9-di-bromobicyclo[6.1.0]non-4-ene [1] (70 g, 0.25 mol) in dry ether (200 ml), under nitrogen. After 30 min at −78 °C and 30 min at 18 °C, water (200 ml) was added and the product isolated with ether. Distillation gave *cis*-cyclonona-1,2,6-triene (25 g, 83%), b.p. 67 °C at 18 mmHg (lit.,[12] 61—62 °C at 13 mmHg), δ 1.7—2.4 (8 H, m), 5.0—5.3 (2 H, m), and 5.35—5.65 (2 H, m).

(b) *Using magnesium-THF*. 9,9-Dibromobicyclo[6.1.0]non-4-ene (70 g, 0.25 mol) in dry THF (100 ml) was added during 1 h to a mechanically stirred suspension of magnesium (previously flamed under nitrogen) (9 g, 0.38 mol) in dry THF (200 ml), under nitrogen. After the reaction had been initiated by the addition of 1,2-dibromoethane (2 ml), the mixture was heated under reflux for 2 h, cooled, water (100 ml) was added, and the product isolated with light petroleum. Distillation gave *cis*-cyclonona-1,2,6-triene (19.28 g, 64%), b.p. 67 °C at 18 mmHg.

cis,cis-*Cyclonona*-1,5-*diene*.[13]—To a stirred, refluxing deep blue solution of sodium (27.6 g, 1.2 mol) in liquid ammonia (*ca.* 500 ml) was added during 1 h *cis*-cyclonona-1,2,6-triene (24 g, 0.2 mol) in dry ether (40 ml). After 2 h, ether (400 ml) was added and ammonia removed slowly by evaporation over 60 h. Ice–water (150 ml) was cautiously added and the product isolated with ether. Distillation gave *cis,cis*-cyclonona-1,5-diene (21.7 g, 89%), b.p. 64—66 °C at 24 mmHg (lit.,[13] 56 °C at 17 mmHg), δ 1.3—2.2 (10 H, m) and 5.2—5.9 (4 H, m, =CH) (lit.,[13] 5.35).

cis-10-*Oxabicyclo*[7.1.0]*dec*-4-*ene* (2).—*cis*,*cis*-Cyclonona-1,5-diene (21.26 g, 0.175 mol) in dichloromethane (150 ml) was epoxidised with peracetic acid (37%; 43 ml, 0.21 mmol), in the usual way, with the rate of addition being such that the temperature did not rise above 9 °C. After 15 min, water (50 ml) was added and the mixture worked up with dichloromethane. Distillation through a column packed with helices gave, after a fore-run of unchanged diene (2.68 g, 13%), the monoepoxide cis-10-*oxabicyclo*[7.1.0]*dec*-4-*ene* (2) (12.26 g, 51%), b.p. 97 °C at 17 mmHg (Found: C, 77.95; H, 10.4. $C_9H_{14}O$ requires C, 78.2: H, 10.2%), δ 1.0—2.65 (10 H, m), 2.75—3.2 (2 H, m, 1-H and 9-H), 5.2—5.55 (1 H, m, 4-H or 5-H), and 5.65—6.0 (1 H, m, 5-H or 4-H).

The distillation residue separated into liquid and solid fractions and distillation of the former gave further monoepoxide (1.16 g, 5%) plus a solid residue. Recrystallisation of the solid fraction from light petroleum (b.p. 40—60 °C) gave the *trans*-diepoxide (3) (3.95 g, 15%) (see below for data). The distillation residue and crystallisation mother liquors were combined and recrystallised from light petroleum (b.p. 40—60 °C) to give more *trans*-diepoxide (3) (1.24 g, 5%). Distillation of the mother liquors gave the monoepoxide (2) (0.39 g, 2%).

The β-*Hydroxyphosphine Oxides* (4) *and* (5).—Following the general procedure, $LiPPh_2$ (40 mmol) in dry THF (50 ml) was added to the monoepoxide (2) (2.78 g, 20 mmol) in dry THF (50 ml). After 20 h at 18 °C, glacial acetic acid (2.31 ml, 45 mmol) and a solution of hydrogen peroxide (30%; 5.82 ml, 57 mmol) were added. The normal work-up from dichloromethane gave a solid which crystallised on trituration with ether. Recrystallisation from toluene gave a mixture of the β-hydroxyphosphine oxides (1*RS*,2*RS*)-2-diphenylphosphinoylcyclonon-5-enol (4) and (1*RS*,2*RS*)-2-diphenylphosphinoylcyclonon-6-enol (5) (5.37 g, 78%), m.p. 161—165 °C (Found: C, 73.95; H, 7.6; P, 8.9. Calc. for $C_{21}H_{25}O_2P$: C, 74.1; H, 7.4; P, 9.1%), δ 1.1—2.6 (10 H, m), 2.75—3.15 (1 H, m, CHP), 4.0—4.3 (1 H, m, CHO), 5.35—6.0 (3 H, m, HC=CH and OH, D_2O exch.), 7.3—7.95 (10 H, m, Ph); δ_C 20.7 (s, CH_2), 24.3 (s, CH_2), 25.5 (d, J_{PC} 12.2 Hz, CH_2), 26.5 (s, CH_2), 33.3 (d, J_{PC} 11.0 Hz, CH_2), 40.2 (d, J_{PC} 68.4 Hz, CHP), 70.1 (d, J_{PC} 3.7 Hz, CHO), 128—132.9 (aromatic and olefinic carbons), δ_P 39.5, 36.9 in the ratio 92 : 8. Although the ^{31}P n.m.r. spectrum suggested the presence of the two possible regioisomers (4) and (5), the relative amount of the less abundant was sufficiently small that it did not confuse the ^{13}C n.m.r. spectrum. Since the ^{13}C n.m.r. spectrum did not distinguish between the two possibilities, the more abundant isomer was arbitrarily assigned the structure (4).

The Epoxy-β-*hydroxyphosphine Oxides* (6) *and* (7).—A solution of the β-hydroxyphosphine oxide [essentially (4)] (1.7 g, 5 mmol) in dichloromethane (20 ml) containing anhydrous sodium carbonate (1 g) was epoxidised with peracetic acid (37%, 1.67 ml, 7.5 mmol) in the usual way. After 72 h at 18 °C, water (15 ml) was added and the mixture worked up with dichloromethane. The product (1.43 g) was generally used without further purification. Recrystallisation of a portion (200 mg) from ethyl acetate gave the *epoxy*-β-*hydroxyphosphine oxides* (6) and (7) (100 mg, 40%), m.p. change of phase above 180 °C with melting until 210 °C (Found: C, 70.5; H, 6.95; P, 8.75. $C_{20}H_{25}O_3P$ requires C, 70.75; H, 7.05; P, 8.7%); δ 1.0—2.6 (10 H, m), 2.6—3.1 (3 H, m, 2 × CHO, CHP), 3.9—4.3 (1 H, m, C*H*OH), and 7.3—8.0 (10 H, m, phenyl); δ_P 35.8 and 39.1 p.p.m. in the ratio 81 : 19 and attributed to the two possible diastereoisomers (7) and (6) respectively.

More generally, recrystallisation of the reaction product from a variety of solvents (ethyl acetate, toluene, chloroform, carbon tetrachloride) was not so straightforward. In a typical example, attempted recrystallisation of the freshly prepared product (reaction scale 5 mmol) from toluene was hindered by the presence of an especially insoluble fraction. This was collected by filtration and recrystallised from chloroform to give a transannular ether, δ 1.1—2.5 (10 H, m), 2.8—3.05 (1 H, m), 3.6—4.2 (3 H, m), and 7.3—8.0 (10 H, m); δ_P 23.9 p.p.m. [by subtraction of the spectrum for (6) and (7)].

A solution of the reaction product was found to change its composition slowly. Initially t.l.c. analysis showed only two close spots, attributed to (6) and (7) plus a third, due to the transannular ether faintly visible only on heavy loading of the t.l.c. plate. As the intensity of the less mobile of the two close t.l.c. spots decreased, that of the third increased. Parallel spectroscopic changes were observed.

The trans-*Diepoxide* (3).—*cis*,*cis*-Cyclonona-1,5-diene (1.22 g, 10 mmol) in dichloromethane (20 ml) was epoxidised with peracetic acid (37%, 6.17 ml, 30 mmol) in the usual way. After 1 h at 0 °C and 4 h at 18 °C, the mixture was worked up with dichloromethane. Recrystallisation of the solid product from light petroleum (b.p. 40—60 °C) gave (1RS,4RS,-6SR,10SR)-5,11-*dioxatricyclo*[8.1.0.0^{4,6}]*undecane* (3) (0.94 g, 70%), m.p. 71—93 °C (Found: C, 70.2; H, 9.25. $C_9H_{14}O_2$ requires C, 70.1; H, 9.15%), δ 0.8—1.58, 1.58—2.5 (10 H, m), and 2.65—3.2 (4 H, m, CHO); δ_C 21.4 (C-2 and C-3 or C-7 and C-9), 21.8 (C-8), 28.8 (C-7 and C-9 or C-2 and C-3), 56.2 (C-1 and C-4 or C-6 and C-10), and 56.8 (C-6 and C-10 or C-1 and C-4). G.l.c. analysis of the crude reaction product showed only a negligible amount of the monoepoxide (2) (OV17 at 200 °C) remaining whilst the *cis*-diepoxide (8) (PEGA at 180 °C) could not be detected.

Treatment of the trans-*Diepoxide* (3) *with* $LiPPh_2$.—Following the general procedure, $LiPPh_2$ (13.4 mmol) in dry THF (20 ml) was added to the *trans*-diepoxide (3) (0.77 g, 5 mmol) in dry THF (20 ml). After 4 h at 18 °C, glacial acetic acid (0.77 ml, 14.8 mmol) and a solution of hydrogen peroxide (30%; 1.84 ml, 16.1 mmol) were added in succession. The normal work-up with chloroform produced a solid which was recrystallised from chloroform–ethyl acetate to give a transannular ether-hydroxyphosphine oxide (1.23 g, 68%), m.p 345—348 °C (Found: C, 70.85, H, 7.25; P, 8.55. $C_{21}H_{25}O_3P$ requires C, 70.75; H, 7.1; P, 8.7%), δ 1.2—2.5 (10 H, m), 2.8—3.1 (1 H, m, CHP), 3.75—4.35 (4 H, m, CHO, C*H*OH and OH, D_2O exch.), and 7.3—8.0 (10 H, m, phenyl); δ_P 23.9 p.p.m.

The crystallisation mother liquors gave seven t.l.c. spots and the least mobile fraction isolated by p.l.c. had δ 1.6—2.1 (10 H, m) 2.6—3.0 (2 H, m), 4.0—4.4 (2 H, m), 4.6—4.8 (OH, D_2O exch.), and 7.3—7.9 (20 H, m)—consistent with being a bis-β-hydroxyphosphine oxide.

The Bromohydrins (1RS,4RS,5RS,9SR)-4-*Bromo*-10-*oxabicyclo*[7.1.0]*decan*-5-*ol and* (1RS,4SR,5SR,9SR)-5-*Bromo*-10-*oxabicyclo*[7.1.0]*decan*-4-*ol*.—Perchloric acid (0.1M; 120 ml, 12 mmol) in acetone (100 ml) and *N*-bromosuccinimide (16.02 g, 90 mmol) in acetone (100 ml) were added to the monoepoxide (2) (8.88 g, 60 mmol), at 0 °C. After 3 h at 0 °C and 1 h at 18 °C, solvent was removed under reduced pressure, at 10 °C. Heating at this stage during one preparation caused complete deterioration of the product. The bromohydrins were isolated with dichloromethane and used without further purification. P.l.c. was used to obtain, in approximately equal amounts, samples of the two isomers and these were then recrystallised from light petroleum (b.p. 40—60 °C). The *bromohydrin* responsible for the more mobile t.l.c. spot had

m.p. 89—102 °C (Found: C, 46.05; H, 6.4; Br, 34.05. $C_9H_{15}BrO_2$ requires C, 45.95; H, 6.45; Br, 34.0%), δ 1.1—2.8 (10 H, m), 2.8—3.2 (2 H, m, CHO), 3.8—4.1 (1 H, m), and 4.1—4.4 (1 H, m) (CHBr, C*H*OH). The *bromohydrin* responsible for the less mobile t.l.c. spot had m.p. 79—94 °C (Found: C, 46.25; H, 6.4; Br, 34.3%), δ 1.1—2.6 (10 H, m), 2.8—3.1 (2 H, m, CHO), and 3.8—4.3 (2 H, m, CHBr and C*H*OH).

The cis-*Diepoxide* (8).—A solution of the bromohydrins from (2) (60 mmol) and anhydrous potassium carbonate (15.18 g, 110 mmol) in methanol (50 ml) and water (50 ml) was left at 18 °C for 16 h. The solution was concentrated under reduced pressure and product isolated with dichloromethane. Distillation over a short path gave (1S,4R,6S,10R)-5,11-*dioxatricyclo*[8.1.0.0^{4,6}]*undecane* (8) [8.80 g, 95% from monoepoxide (2)] as a low melting, waxy solid (Found: C, 70.05; H, 9.5. $C_9H_{14}O_2$ requires C, 70.1; H, 9.15%), δ 0.9—2.6 (10 H, m), 2.7—3.0 (2 H, m, CHO), and 3.0—3.3 (2 H, m, CHO); δ_C 20.8 (C-8), 21.2 (C-2 and C-3 or C-7 and C-9), 28.4 (C-7 and C-9 or C-2 and C-3), 54.8 (C-1 and C-4 or C-6 and C-10), and 57.3 (C-6 and C-10 or C-1 and C-4). The *trans*-diepoxide (3) was not detected by g.l.c., t.l.c., or n.m.r. analysis of the crude reaction product.

The Epoxy-β-hydroxyphosphine Oxide (9).—Following the general procedure, $LiPPh_2$ (10 mmol) in dry THF (15 ml) was added to the *cis*-diepoxide (8) (0.77 g, 5 mmol) in dry THF (20 ml). After 2 h at 0 °C, glacial acetic acid (0.77 ml, 15 mmol) and then hydrogen peroxide solution (30%, 1.93 ml, 16.5 mmol) were added. The usual work-up from dichloromethane gave a foam which produced a solid on trituration with cooled (acetone–CO_2) ether. Recrystallisation from chloroform gave an epoxy-β-hydroxyphosphine oxide which was assigned the structure (1SR,4RS,5RS,9RS)-5-*diphenylphosphinoyl*-10-*oxabicyclo*[7.1.0]*decan*-4-*ol* (9) (1.07 g, 60%), m.p. 219—221 °C (Found: C, 70.7; H, 7.0; P, 8.75. $C_{20}H_{25}O_3P$ requires C, 70.75; H, 7.05; P, 8.7%), δ 1.1—2.2 (10 H, m), 2.2—2.6 (1 H, m, CHP), 2.6—3.05 (2 H, m, CHO), 4.2—4.5 (1 H, m, C*H*OH), 4.5—4.8 (OH, D_2O exch.), and 7.4—8.0 (10 H, m, phenyl); δ_P 36.4 p.p.m.

Acetylation of the β-*Hydroxyphosphine Oxide* (9).—Following the general method, the epoxy-β-hydroxyphosphine oxide (9) in dry pyridine (3 ml) containing 4-dimethylaminopyridine (3.6 mg) was acetylated with acetic anhydride (57 μl, 0.6 mmol). After 4 h at 50 °C, water (0.5 ml) was added and the solution worked up with chloroform. Recrystallisation of the solid product from ethyl acetate gave the *acetate*, m.p. 240—243 °C (Found: C, 69.35; H, 7.3; P, 7.55. $C_{23}H_{27}O_4P$ requires C, 69.35; H, 6.85; P, 7.75%), δ 1.0—2.4 (10 H, m) including 1.37 (3 H, s, Me), 2.4—3.05 (1 H, m, CHP), 5.2—5.6 (1 H, m, CHOAc), and 7.3—8.0 (10 H, m, phenyl); δ_P 27.4 p.p.m.

The trans-*Alkene Epoxide* (10).—Following the general procedure, the epoxy-β-hydroxyphosphine oxide (9) (534 mg, 1.5 mmol) in dry DMSO (15 ml) was added to sodium hydride (50% dispersion in oil, 216 mg, 4.5 mmol) in dry DMSO (5 ml). After 2 h, ice-water (40 ml) was cautiously added and product isolated with light petroleum. Distillation gave (1RS,9SR)-10-*oxabicyclo*[7.1.0]*dec*-trans-4-*ene* (10) (170 mg, 82%), b.p. 93 °C at 20 mmHg (Found: C, 78.0; 10.1. $C_9H_{14}O$ requires C, 78.2; H, 10.2%), δ 0.75—2.6 (10 H, m), 2.6—3.05 (2 H, m, CHO), 4.95—5.6 (2 H, m, HC=CH), δ_C 23.5, 25.4, 28.1, 29.4, and 32.2 (C-2, C-3, C-6, C-7, C-8), 58.0 and 60.7 (C-1, C-9), and 130.3 and 130.9 (C-4, C-5).

The Bis-β-hydroxyphosphine Oxides (11) *and* (12).—Following the general procedure, $LiPPh_2$ (20 mmol) in dry THF (30 ml) was added to the *cis*-diepoxide (8) (0.77 g, 5 mmol) in dry THF (5 ml). After 2 h at 0 °C and 6 h at 18 °C, glacial acetic acid (1.54 ml, 30 mmol) followed by hydrogen peroxide solution (30%; 3.86 ml, 33 mmol) was slowly added. The usual work-up with dichloromethane gave a foam which was triturated with cooled (acetone–CO_2) ether to give a solid which was recrystallised from chloroform–ethyl acetate to give the symmetric *bis-β-hydroxyphosphine oxide* assigned the structure (1*S*,2*S*,6*R*,7*R*)-2,6-bis(diphenylphosphinoyl)cyclononane-1,7-diol (11) (0.53 g, 19%), m.p. 212—220 °C (Found: P, 11.0. $C_{33}H_{36}O_4P_2$ requires P, 11.1%), δ 1.0—2.3 (10 H, m), 2,65—3.15 (2 H, m, CHP), 3.9—4.25 (2 H, m, CHO), 4.3—4.6 (OH, D_2O exch.), and 7.35—7.9 (20 H, m, phenyl); δ_C 26.1 (1C, s), 27.3 (2C, d, J_{PC} 18.1 Hz), and 30.1 (2C, d, J_{PC} 12.0) (all CH_2), 45.5 (2C, d, J_{PC} 68.4 Hz, CHP), 70.9 (2C, d, J_{PC} 2.2 Hz, CHO), and 128.1—133.6 (m, aromatic); δ_P 36.4 p.p.m.

A solution of the mother liquors from the crystallisation in dry pyridine (20 ml) containing 4-dimethylaminopyridine (40 mg) were acetylated with acetic anhydride (1.34 ml, 10 mmol), in the normal way. After 4 h at 50 °C, water (1 ml) was added and the solution worked up with chloroform. Recrystallisation of the solid product from chloroform–ethyl acetate gave the *acetates* of (11) and (12) in the ratio 30 : 70 (by n.m.r.) [664 mg, 21% from (8)], m.p. 285—290 °C (Found: C, 68.7; H, 6.5; P, 9.8. $C_{37}H_{40}O_6P_2$ requires C, 69.15; H, 6.25; P, 9.65%), The acetate of (12) had δ 1.09 (3 H, s, Me), 1.22 (3 H, s, Me), 1.5—2.3 (10 H, m), 2.6—3.05 (2 H, m, CHP), 5.1—5.5 (2 H, m, CHOAc), 7.3—8.0 (20 H, m, phenyl); δ_P 27.6 and 28.9 p.p.m. [by subtraction, the n.m.r. data for the acetate of (11) are given below].

A solution of the acetates of (11) and (12), in the ratio 38 : 62 (1.93 g, 3 mmol) and potassium hydroxide (1.68 g, 30 mmol) in water (30 ml) and methanol (100 ml) was heated under reflux for 2 h. The solution was concentrated under reduced pressure, water (30 ml) added and the product isolated with dichloromethane. Recrystallisation from ethyl acetate gave the bis-β-hydroxyphosphine oxide (11) and (1*SR*,2*SR*,-6*SR*,7*SR*)-2,7-bis(diphenylphosphinoyl)cyclononane-1,6-diol (12) in the ratio 34 : 66 (by ^{31}P n.m.r.), (1.26 g, 75%), δ for (12) 1.0—2.6 (10 H, m), 2.6—3.3 (2 H, m, CHP), 3.9—4.3 (2 H, m, C*H*OH), 5.0, 5.6, 5.85 (OH, D_2O exch.), and 7.3—8.2 (20 H, m, phenyl); δ_P for (12) (by subtraction) 40.2 and 40.1 p.p.m.

The Acetate of (11).—The symmetric bis-β-hydroxyphosphine oxide (11) (112 mg, 0.2 mmol) in dry pyridine (3 ml), containing 4-dimethylaminopyridine (*ca.* 2.4 mg) was acetylated with acetic anhydride (98 μl, 1 mmol), in the usual manner. After 24 h at 50 °C, water (1 ml) was added and the solution worked up with chloroform. Recrystallisation from chloroform–ethyl acetate gave the *acetate* assigned the structure (1*S*,2*S*,6*R*,7*R*)-1,7-bisacetoxy-2,6-bis(diphenylphosphinoyl)cyclononane (93 mg, 72%), m.p. 283—286 °C (Found: C, 69.0; H, 6.15; P, 9.45. $C_{37}H_{40}O_6P_2$ requires C, 69.15; H, 6.25; P, 9.65%), δ 1.42 (6 H, s, Me), 1.6—2.4 (10 H, m), 2.7—3.15 (2 H, m, CHP), 5.2—5.55 (2 H, m, CHOAc), and 7.65—8.0 (20 H, m, phenyl); δ_P 27.9 p.p.m.

Treatment of the Bis-β-hydroxyphosphine Oxides (11) *and* (12) *with* NaH–DMF.—Following the general method, the bis-β-hydroxyphosphine oxides (11) and (12) [total reaction product, from (8) (4 mmol)] in dry DMF (20 ml) was added to sodium hydride (80% dispersion in oil, 450 mg, 15 mmol). After 40 min at 0 °C and 60 min at 18 °C, water (20 ml) was cautiously added and product isolated with light petroleum. The n.m.r. spectrum of the crude product showed peaks in the region δ 4.85—6.0 indicative of the presence of 1,2-

divinylcyclopentane (see below). G.l.c. analysis (OV17 at 90 °C) revealed two close peaks in the ratio 17 : 83. The minor peak, of longer retention time, was identified as *cis*-1,2-divinylcyclopentane (17) by co-injection with an authentic sample. Distillation gave a fraction (112 mg) b.p. 42 °C at 24 mmHg, $\nu_{max.}$ (liquid film) 3 090, 1 645, 995, and 910 cm^{-1}; δ 1.2—2.7 (8 H, m), 4.85—5.1 (4 H, m) and 5.55—5.95 (2 H, m). The ^{13}C n.m.r. spectrum of the fraction contained two sets, each of 5 peaks, with the less intense set identified as coming from *cis*-1,2-divinylcyclopentane (17). The other set was δ_C 23.9 (1C, C-3), 32.6 (2 C, C-2, C-4), 50.9 (2 C, C-1, C-5), 114.0 (=CH_2), and 142.1 (−HC=). G.l.c. analysis (OV17) at 90 °C) of this distillate showed two close peaks in the ratio 19 : 81, with the minor one, of longer retention time, again, identified as *cis*-1,2-divinylcyclopentane, by co-injection with an authentic sample. The spectroscopic data indicated that the major component of the mixture, responsible for the g.l.c. peak of shorter retention time, was *trans*-1,2-divinylcyclopentane (18).

cis-1,2-*Divinylcyclopentane*.[7]—*cis,cis*-Cyclonona-1,5-diene (1.22 g, 10 mmol) in a sealed Pyrex tube, purged with nitrogen prior to sealing, was heated at 230 °C for 4 h. Distillation gave a fraction b.p. 63—69 °C at 48 mmHg and from this was isolated, by preparative g.l.c. (OV17 at 140 °C), *cis*-1,2-divinylcyclopentane (17) (Found: C, 88.35; H, 11.65. Calc. for C_9H_{14}: C, 88.45; H, 11.55%), δ 1.3—2.05 (6 H, m), 2.45—2.8 (2 H, m, 1-H, 2-H), 4.85—5.15 (4 H, m, =CH_2), 5.6—6.0 (2 H, m, −HC=); δ_C 23.6 (C-3), 31.1 (C-2, C-4), 48.5 (C-1, C-5), 114.1 (=CH_2), and 140.6 (HC=).

Base Treatment of the Bis-β-hydroxyphosphine Oxides (11) *and* (12): *General Method*.—In the following series of ' g.l.c.-scale ' experiments, the bis-β-hydroxyphosphine oxides (11) or a mixture of (11) and (12) in the ratio 66 : 34 or 35 : 65 (mixtures A and B respectively) (28 mg, 0.05 mmol) were treated with a range of solvent (2 ml)–base (in excess) combinations. Generally, after 2 h at 18 °C water (4 ml) was added and the aqueous solution extracted with light petroleum (3 × 3 ml). The combined organic extracts were washed with brine (3 ml) and examined by g.l.c. (OV17 at 90 °C). The presence of *cis*-1,2-divinylcyclopentane or a mixture of *cis*- and *trans*-1,2-divinylcyclopentane was confirmed by co-injection with authentic samples. The estimated yield and ratio of the two isomers are collected together in the Table.

(a) *Potassium t-butoxide–DMSO*. Dry DMSO was added to (11) and potassium t-butoxide (22.4 mg, 0.2 mmol), under nitrogen and with stirring. Throughout the course of the reaction a homogeneous solution was preserved.

The experiment was repeated with (11) in the presence of 18-crown-6-ether and with mixtures A and B.

(b) *Tetrabutylammonium hydroxide–DMSO*. Tetrabutylammonium hydroxide solution (40% aq.; 78 μl, 1.2 mmol) was added to stirred solution of (11) in dry DMSO, under nitrogen.

The experiment was repeated using mixture B.

(c) *Sodium hydride–DMSO*. A solution of (11) in DMSO was added to sodium hydride (80% dispersion in oil; washed 3 times with light petroleum, 9.6 mg, 0.2 mmol), under nitrogen and with stirring, causing the rapid formation of a thick foam.

The experiment was repeated using mixture A.

(d) *Sodium hydride–DMF*. The reactions described in part (c) were repeated but using dry DMF as the solvent and with an initial period (30 min) at 0 °C.

(e) *Sodium methoxide–DMF*. To an ice-cooled, stirred solution of sodium methoxide (0.2 mmol) in dry DMF (0.5 ml), under nitrogen, was added a solution of (11) in dry DMF (1.5 ml). The mixture was left for 30 min at 0 °C and 90 min at 18 °C and then quenched.

The experiment was repeated using mixture A.

Treatment of the Bis-β-hydroxyphosphine Oxide (11) *with Sodium Methoxide*.—An ice-cooled solution of the bis-β-hydroxyphosphine oxide (11) (112 mg, 0.2 mmol) in dry DMF (4 ml) was added to an ice-cooled, stirred solution of sodium methoxide (0.3 mmol) in dry DMF (0.5 ml), under nitrogen. After 4 h at 0 °C, water (10 ml) was added and the product isolated with dichloromethane. The major component (18 mg) isolated by p.l.c. had δ 1.0—2.85 (11 H, m), 3.9—4.2 (1 H, m), 5.3—5.6 (2 H, m), 7.4—8.05 (10 H, m)—consistent with a structure such as (13). The multiplet δ 5.3—5.6 and the aromatic protons were present in the n.m.r. spectrum of the reaction product in the ratio 8 : 92.

cis,trans-*Cyclonona*-1,5-*diene*.—Following the normal method, a solution of the β-hydroxyphosphine oxide (4) (3.4 g, 10 mmol) in dry DMF (40 ml) was added during 30 min to sodium hydride (80% dispersion in oil; 450 mg, 16.7 mmol). After 30 min, water (30 ml) was cautiously added and the product isolated with light petroleum. Distillation gave cis,trans-*cyclonona*-1,5-*diene* (750 mg, 62%), b.p. 71 °C at 31 mmHg (Found: C, 88.75; H, 11.7. C_9H_{14} requires C, 88.45; H, 11.55%), $\nu_{max.}$ (liquid film) 1 661, 1 645, 971, and 720 cm^{-1} (lit.,[11] 971 and 720 cm^{-1}); δ 1.1—2.7 (10 H, m) and 4.95—5.6 (4 H, m, olefinic H); δ_C 26.1, 28.5, 30.9, 33.0, and 34.3 (C-3, C-4, C-7, C-8, C-9) and 123.3, 129.8, 133.3, and 135.8 (C-1, C-2, C-5, C-6). G.l.c. analysis (TCEP–$AgBF_4$ at 90 °C) revealed only a single peak, identified as *cis,trans*-cyclonona-1,5-diene with no trace of *cis,cis*-cyclonona-1,5-diene. The respective retention times were 14.4 and 3.8 min.

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