trans-Cycloalkenes. Part 11.[1] *trans*-Cyclonona-1,2,6-triene, a Transient Precursor of 2,3-Divinylcyclopentene

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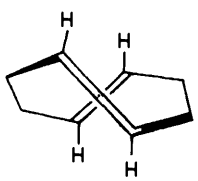
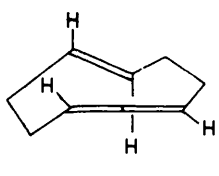
Three potential precursors of *trans*-cyclonona-1,2,6-triene (1), namely the allene-dioxolan (7), the allene-oxathiolan (14), and the dichlorocyclopropane (16) have been prepared starting ultimately from cyclo-octa-1,5-diene. Treatment of these precursors with Bu^{n}Li under conditions appropriate to each case gave 2,3-divinylcyclopentene in moderate to good yields. It is considered that *trans*-cyclonona-1,2,6-triene is formed as a transient intermediate.

We have developed previously some synthetic procedures for introducing a strained *trans*-disubstituted double bond into a medium ring. Three methods have emerged as particularly useful in this respect: the alkyl-lithium induced fragmentation of 2-phenyl-1,3-dioxolans derived from *trans*-1,2-diols (dioxolan olefin synthesis);[2] the related lithium dialkylamide promoted reaction of corresponding oxathiolans (oxathiolan olefin synthesis);[3] and the elimination of diphenylphosphinic acid from *trans*-β-hydroxyphosphine oxides effected by strong bases.[4] Partly with the intention of exploring further the potential of these olefin syntheses, and partly because of intrinsic interest in the compound, it was decided to attempt the synthesis of *trans*-cyclonona-1,2,6-triene. The latter, which could exist as two chiral diastereoisomeric forms (1a) and (1b), related to the twist and chair conformers of *trans*-cyclo-octene,[5] might show interesting chemical and physical properties owing to the close juxtaposition across the ring of the *trans*-double bond and the allene unit.†


(1a)


(1b)

The allene-dioxolan (7) and the allene-oxathiolan (14) potential precursors of the triene (1) were prepared as indicated in Schemes 1 and 2 respectively.

The gem-dibromocyclopropane epoxide (2)[6] required for the sequences shown in the two Schemes, was obtained as a mixture of two diastereoisomers in the ratio 3 : 1 by epoxidation of 9,9-dibromobicyclo[6.1.0]non-4-ene[7] with peracetic acid in dichloromethane. The two diol monoacetates (3a) and (3b) were obtained in a 1 : 1 ratio presumably because of intramolecular acetate exchange under the reaction conditions. Two diastereoisomers of the dioxolan (6) were also obtained in a 1 : 1 ratio as shown by the presence of two singlets at δ 5.74 and 5.84 (benzylic protons) in the n.m.r. spectrum. Furthermore the allene-dioxolan (7) was obtained as a mixture of two diastereoisomers (*ca.* 4 : 1). These must be as represented in structures (8) and (9), though which is which is not known. On one occasion distillation gave a mixture in which the ratio of diastereoisomers had changed from (85 : 15) to (3 : 7). Hydrogenation of either mixture gave the same product (10) thereby corroborating the suggestion that they are indeed diastereoisomers. The observation appears to indicate that a process akin to a thermal racemisation of an optically active allene is occurring on distillation, though lack of analogy[8] makes it difficult to say whether this behaviour of (7) is unusual.

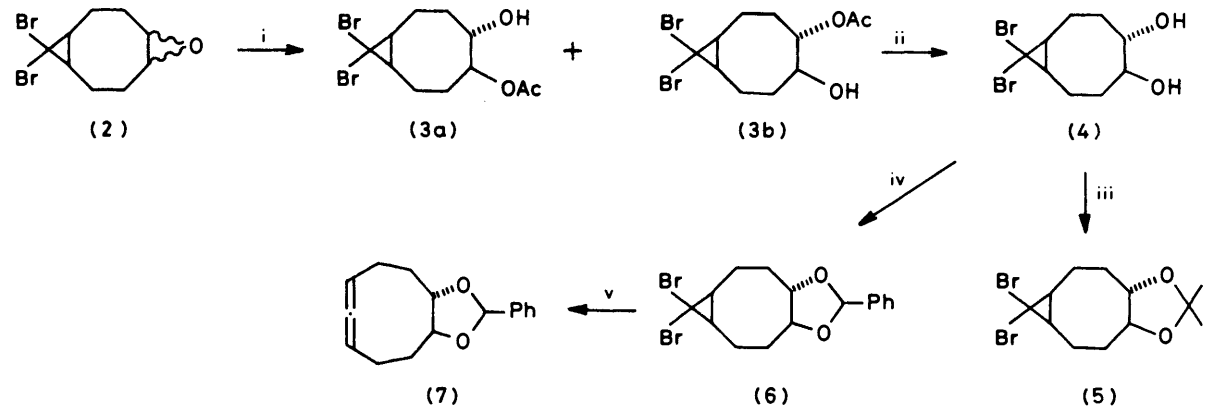
A number of points relevant to Scheme 2 need comment. For reduction of the diastereoisomeric mixture of disulphides (11) with lithium aluminium hydride, conditions had to be carefully established to avoid reduction of the gem-dibromo-group—a well precedented reaction.[9] The mercapto alcohols (12), a 3 : 1 mixture of diastereoisomers, were converted into a mixture of oxathiolans (13) containing all four of the possible diastereoisomers. This mixture could be partially separated by chromatography or crystallisation but, in general, a recrystallised sample containing one major and one minor isomer was used for further reaction. It was originally hoped that the oxathiolan (13) could be converted selectively into (15) owing to the mild conditions ($LiNEt_2$–THF–18 °C) under which some 2-phenyl-1,3-oxathiolans can be converted into olefins.[3] However, (13) was recovered unchanged from these conditions and the oxathiolan ring proved to be sufficiently resistant to base in this instance to allow conversion of (13) into (14) on treatment with methyl-lithium. Spectroscopic evidence for the presence of three of the four possible stereoisomers of (14) was obtained.

Another potential route to the cyclononatriene (1) already mentioned above is *via* precursors of the type (15) and (16), and we tried to prepare these by the β-hydroxyphosphine oxide approach. Attempts to open the epoxide ring in (2) using lithium diphenylphosphide were foiled owing to preferential halogen-metal exchange giving the allene-epoxide (17) together with products derived by further attack of $LiPPh_2$ on the allene group in (17). The allene-epoxide (17) was obtained in better yield by treatment of (2) with methyl-lithium. Control experiments showed that $LiPPh_2$ reacted with cyclonona-1,2-diene to give, after protonation-oxidation 1-diphenylphosphinoxycyclononene.

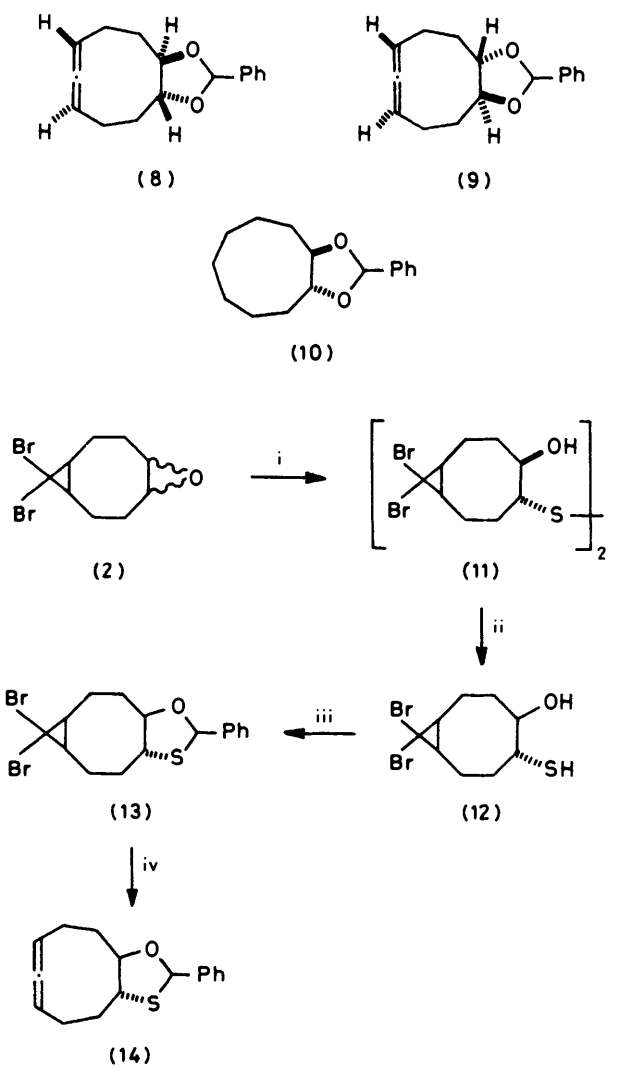
In contrast to the difficulties encountered in attempts to make (15) it proved practicable to prepare (16) by the route summarised in Scheme 3. Compound (20) was obtained as one diastereoisomer apparently because only the major diastereoisomer of (19) reacted under the conditions used. Fragmentation of (20) to give the bicyclic *trans*-cycloalkene (16) proceeded satisfactorily using sodium hydride in dimethylformamide (DMF). Attempts were made to convert (20) into the allene-hydroxyphosphine oxide (18), a possible precursor to (1) analogous to (7) and (14); however treatment with alkyl-lithium reagents under a variety of conditions failed to effect the transformation.

With the dioxolan (7), the oxathiolan (14) and the dichlorocyclopropane (16) at hand, attempts were made to convert them into *trans*-cyclonona-1,2,6-triene (1) by appropriate

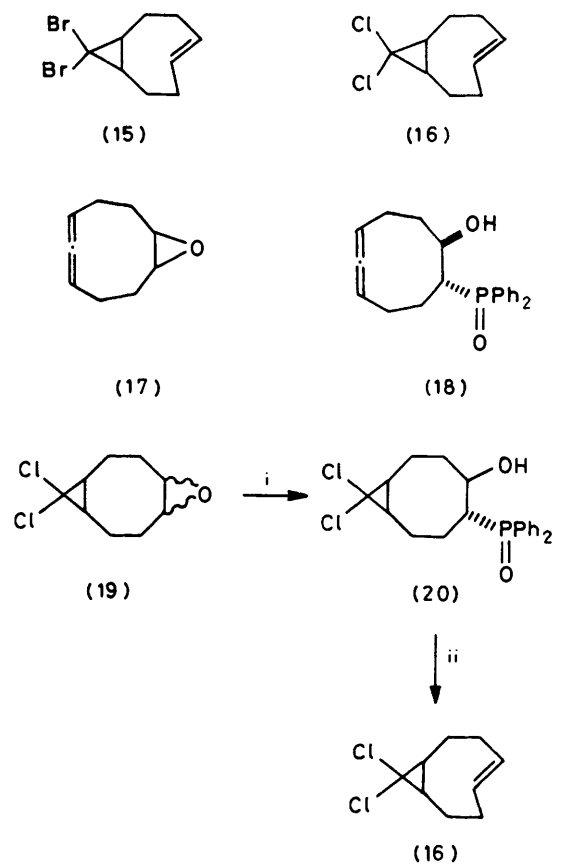
† Throughout, the use of the term 'allene' is taken to mean the presence of a $-CH=C=CH-$ unit.



Scheme 1. *Reagents.* i, AcOH–NaOAc, 60 °C; ii, KOH–EtOH; iii, Me_2CO–*p*-TsOH, reflux; iv, PhCHO–*p*-TsOH–C_6H_6–reflux; v, MeLi–Et_2O, −78 °C ⟶ 18 °C



Scheme 2. *Reagents:* i, $NaBH_2S_3$–THF; ii, $LiAlH_4$–Et_2O; iii, PhCHO–*p*-TsOH–C_6H_6, reflux; iv, MeLi–Et_2O, −78 ⟶ 18 °C



Scheme 3. *Reagents:* i, Ph_2PLi–THF, then H_2O_2–AcOH; ii, NaH–DMF

treatment with n-butyl-lithium. In no case was direct evidence for formation of the cyclic allene (1) obtained, the major significant product being 2,3-divinylcyclopentene (21). Optimum conditions in each case were (a) from (7), Bu^nLi–THF, −78 °C ⟶ 18 °C, 83% yield (by g.l.c.); (b) from (14), Bu^nLi–Et_2O, −78 °C ⟶ 18 °C, 51% yield (by g.l.c.); (c) from (16), Bu^nLi–Et_2O, −78 °C ⟶ 18 °C, 67% yield (by g.l.c.). In neither of the first two cases was *cis*-cyclonona-1,2,6-triene detected, thus confirming the high stereospecificity of these olefin-forming reactions.

It is attractive to speculate that the immediate product of

the three reactions was *trans*-cyclonona-1,2,6-triene which underwent rapid Cope rearrangement to the divinylcyclopentene (21). This suggestion seems reasonably firmly based in the case of the precursors (7) and (14). From the third precursor (16) there also exists the possibility that the intermediate carbenoid could fragment to give (21) directly, *e.g.* (22). This point is also relevant to the formation of (21) in a related study of diastereoisomers of (16) described in a brief communication.[10]

Attempts to trap the postulated *trans*-cyclonona-1,2,6-triene failed. Thus *trans*-cyclo-octenes are known to react with alkyl-lithium reagents, but none of the possible products which would be derived by addition of n-butyl-lithium to (1) were detected in the above reactions.

We believe therefore that *trans*-cyclonona-1,2,6-triene undergoes rapid Cope rearrangement to 2,3-divinylcyclopentene at or below room temperature. This contrasts sharply with the behaviour of the *cis*-isomer, the rearrangement of which to (21) has a half-life of over 30 min at 150 °C.[11] The large difference in reactivity must be the result of relief of ground-state steric strain in the *trans*-isomer which occurs on rearrangement. We consider this to be true for either of the diastereoisomers of (1) since both would be expected to be formed from the diastereoisomeric mixtures of (7) and (14). Diastereoisomer (1a) is constrained to react by a chair-like and (1b) by a boat-like transition state.

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 WH90 machine operating at 22.63 MHz for solutions in $CDCl_3$. Chemical shifts are quoted in p.p.m. downfield of internal $SiMe_4$.

9,9-*Dibromobicyclo*[6.1.0]*non*-4-*ene*.—Bromoform (202.4 g, 71.3 ml, 0.8 mol) in dry light petroleum (b.p. 40—60 °C) (100 ml) was added during 6 h to a cooled (−10 to −15 °C), mechanically stirred suspension of potassium t-butoxide (107.5 g, 0.96 mol) in *cis,cis*-cyclo-octa-1,5-diene (347 g, 3.2 mol) and dry light petroleum (b.p. 40—60 °C) (200 ml), under nitrogen. After 16 h at 18 °C, water (500 ml) was added and the product isolated with light petroleum (b.p. 40—60 °C). Distillation gave 9,9-dibromobicyclo[6.1.0]non-4-ene (189 g, 85%), b.p. 96 °C at 0.5 mmHg (lit.,[7] 86 °C at 0.3 mmHg), δ 1.5—2.7 (10 H, m) and 5.4—5.7 (2 H, m, 4-H and 5-H).

10,10-*Dibromo*-5-*oxatricyclo*[7.1.0.0^{4,6}]*decane* (2).—9,9-Dibromobicyclo[6.1.0]non-4-ene (56 g, 0.2 mol) in dichloromethane (100 ml) was treated with peracetic acid (37%, 82 ml, 0.4 mol) at 0 °C. After 16 h at 18 °C, water (50 ml) was added and the product isolated with dichloromethane. Recrystallisation of the solid from ether gave 10,10-*dibromo*-5-*oxatricyclo*[7.1.0.0^{4,6}]*decane* (45.6 g, 78%), m.p. 61—64 °C, shown by h.p.l.c. to comprise two diastereoisomers in the ratio 3 : 1 (Found: C, 36.5; H, 4.1; Br, 54.0. $C_9H_{12}Br_2O$ requires C, 36.6; H, 4.0; Br, 54.0%), δ 1.0—2.5 (10 H, m) and 2.8—3.2 (2 H, m, 4-H and 6-H).

Separate samples of the two diastereoisomers (A) and (B) were isolated by p.l.c. and recrystallised from light petroleum. The major diastereoisomer (A) had: m.p. 68—73 °C, $\nu_{max.}$ 2 940, 1 110, and 915 cm^{-1}; δ 1.4—2.6 (10 H, m), 2.9—3.1 (2 H, m, 4-H and 6-H); δ_C 21.1 (C-2, C-8 or C-3, C-7), 25.4 (C-3, C-7 or C-2, C-8), 32.4 (C-1, C-9), 36.8 (C-4, C-6), and 56.0 (C-10). The minor diastereoisomer (B) had: m.p. 68—76 °C, δ 0.8—2.6 (10 H, m), 2.9—3.15 (2 H, m, 4-H, 6-H), δ_C 21.5 (C-2, C-8 or C- C3,-7), 25.1 (C-3, C-7 or C-2, C-8), 32.3 (C-1, C-9), 35.1 (C-4, C-6), 55.9 (C-10). The latter ^{13}C n.m.r. spectrum was obtained by subtraction of that for (A) from that for a mixture of (A) and (B). The following data was obtained from a sample of (B) which had been prepared [6] by the base-induced cyclisation of the bromohydrin obtained by treatment of 9,9-dibromobicyclo[6.1.0]non-4-ene with hypobromous acid: m.p. 81—85 °C, δ 0.8—2.6, and 2.7—3.2. The epoxide (A) had a longer retention time on h.p.l.c. but was the more mobile of the two on t.l.c. Repeated recrystallisation of the original mixture of (A) and (B) from light petroleum and then methanol gave a mixture containing at least 95% of (A) (by h.p.l.c.). The diastereoisomer (A) was assumed to have the *cis,syn,cis*-configuration.

9,9-*Dichlorobicyclo*[6.1.0]*non*-4-*ene*.—Freshly prepared, ice-cold aqueous sodium hydroxide (50%; 32 ml, 0.4 mol) was added dropwise to a vigorously stirred solution of *cis,cis*-cyclo-octa-1,5-diene (10.8 g, 0.1 mol) in chloroform (48.1 g, 32.5 ml, 0.4 mol), containing triethylbenzylammonium chloride (0.229 g, 1 mmol) and ethanol (1 ml). After 1 h at 18 °C and 16 h at 50 °C, the solution was acidified and the product isolated with chloroform. Distillation gave 9,9-dichlorobicyclo[6.1.0]non-4-ene (9.08 g, 48%), b.p. 52 °C at 0.1 mmHg (lit.,[12] 115—116 °C at 12 mmHg), δ 1.5—2.6 (10 H, m) and 5.4—5.7 (2 H, 4-H and 5-H).

10,10-*Dichloro*-5-*oxatricyclo*[7.1.0.0^{4,6}]*decane* (19).—9,9-Dichlorobicyclo[6.1.0]non-4-ene (4.78 g, 25 mmol) in dichloromethane (30 ml) was epoxidised with peracetic acid (37%, 10.3 ml, 50 mml) at 0 °C. After 16 h at 18 °C, water (20 ml) was added and the product isolated with dichloromethane. Distillation gave 10,10-dichloro-5-oxatricyclo-[7.1.0.0^{4,6}]decane (4.60 g, 95%), b.p. 92 °C at 0.2 mmHg (lit.,[12] 136—137 °C at 7 mmHg) (Found: C, 52.4; H, 5.9; Cl, 34.55. Calc. for $C_9H_{12}Cl_2O$: C, 52.2; H, 5.85; Cl, 34.25%), $\nu_{max.}$ (liquid film) 1 470, 1 120, 920, 910, 895, and 810 cm^{-1}; δ 1.05—2.5 (10 H, m) and 2.85—3.1 (2 H, m). The ^{13}C n.m.r. spectrum had two sets of 5 signals, in the average ratio 72 : 28, which were assumed to be associated with the two possible diastereoisomers (A) and (B). The major diastereoisomer (A) was considered to have the *cis,syn,cis*-stereochemistry. The diastereoisomer (A) had: δ_C 18.8 (CH_2), 25.6 (CH_2), 31.5 (C-1, C-9), 55.8 (C-4, C-6), and 65.1 (C-10). The diastereoisomer (B) had: δ_C 19.2 (CH_2), 25.6 (CH_2), 34.4 (C-1, C-9), 56.0 (C-4, C-6), and 65.4 (C-10). Two close spots were observed on t.l.c.

10-*Oxabicyclo*[7.1.0]*deca*-4,5-*diene* (17).—(*a*) Lithium diphenylphosphide (13.4 mmol) from triphenylphosphine and lithium in dry THF was added to a solution of diastereoisomeric 10,10-dibromo-5-oxatricyclo[7.1.0.0^{4,6}]decanes (2.96, 10 mmol) in dry THF (20 ml). After 4 h at 18 °C, acetic acid (0.77 ml, 14.8 mmol) followed by hydrogen peroxide solution (30%; 1.84 ml, 16.1 mmol) was added. Isolation with dichloromethane was followed by chromatography on silica gel. Elution with ether (2%) in benzene gave mixed fractions containing the allene-epoxide [see (*b*)] (0.3 g, 22%) and recovered starting material (1.77 g, 60%) (yields estimated from the n.m.r. spectrum of the mixture.

(*b*) Methyl-lithium (0.94M; 32 ml, 30 mmol) was added during 15 min to a cooled (acetone–CO_2), stirred solution of 10,10-dibromo-5-oxatricyclo[7.1.0.0^{4,6}]decane (7.4 g, 25 mmol) in dry ether (50 ml), under nitrogen. After 30 min the cooling was removed and the mixture allowed to reach 18 °C. Water (30 ml) was added and the product isolated with ether. Distillation gave 10-oxabicyclo[7.1.0]deca-4,5-diene (3.11 g, 89%), b.p. 55 °C at 0.35 mmHg. A satisfactory microanalysis was not obtained; $\nu_{max.}$ (liquid film) 1 965 cm^{-1} (allene),

δ 1.2—2.6 (8 H, m), 2.65—3.05 (2 H, m, 1-H and 9-H), 5.1—5.6 (2 H, m, =CH); δ_C 21.2, 23.0, 24.2 and 30.5 (C-2, C-3, C-7, C-8), 57.9, 59.2 (C-1, C-9) 89.1, 93.4 (C-4, C-6), and 207.3 (C-5).

The β-Hydroxyphosphine Oxide (20).—Following the general procedure, $LiPPh_2$ (10 mmol) in dry THF (15 ml) was added to the 72 : 28 mixture of the epoxides (19) (1.035 g, 5 mmol) in dry THF (20 ml). After 1 h at 0 °C and 5 h at 18 °C, glacial acetic acid (0.77 ml, 15 mmol) and hydrogen peroxide (30%; 1.93 ml, 16.5 mmol) were added. Work-up with dichloromethane produced a solid foam which was triturated with cooled (acetone–CO_2) ether, leaving a gum which was recrystallised from ethyl acetate to give the β-hydroxyphosphine oxide 9,9-*dichloro*-5-*diphenylphosphinoylbicyclo*[6.1.0]*nonan*-4-*ol* (20), (0.81 g, 40%), m.p. 205—209 °C, shown by ^{31}P n.m.r. to be single isomer (Found: C, 61.9; H, 5.75; Cl, 16.95; P, 7.4. $C_{21}H_{23}Cl_2O_2P$ requires C, 61.65; H, 5.65; Cl, 17.3; P, 7.7%), $\nu_{max.}$ ($CHCl_3$) 3 360 cm^{-1}; δ 1.0—2.3 (10 H, m), 2.3—2.65 (1 H, m, CHP), 4.1—4.5 (1 H, m, C*H*OH), 4.7—4.8 (OH, D_2O exch.), 7.2—7.9 (10 H, m, phenyl); δ_C 20.2 (CH_2) 26.7 (d, *J* 18.31 Hz, Cα to CHP), 27.4 (CH_2), 31.8 (2 × CH), 36.6 (d, *J* 3.66 Hz, Cα to CHOH), 45.8 (d, *J* 70.80 Hz, CHP), 64.78 (CCl_2), 73.3 (d, *J* 6.10 Hz, CHOH), and 128.27—137.7 p.p.m. (aromatic C); δ_p 33.3 p.p.m. The single diastereoisomer that was obtained was considered to have the stereochemistry (1*RS*,4*SR*,5*SR*,8*SR*).

Concentration of the ether-soluble fraction, followed by crystallisation from ethyl acetate also gave the β-hydroxyphosphine oxide (20) (254 mg, 12%). T.l.c. analysis of the crude reaction product suggested the presence of some unchanged epoxide (19). The i.r. spectrum did not contain a significant absorption around 1 950 cm^{-1}.

9,9-*Dichloro*-trans-*bicyclo*[6.1.0]*non*-4-*ene* (16).—A solution of the hydroxyphosphine oxide (2.05 g, 5 mmol) in dry DMF (10 ml) was added to sodium hydride (80% dispersion in oil; 0.225 g, 7.5 mmol). After 1 h, light petroleum (50 ml) and water (25 ml) (cautiously) were added and the product isolated with light petroleum. Distillation gave (1RS,8SR)-9,9-*dichloro*-trans-*bicyclo*[6.1.0]*non*-4-*ene* (16) (0.65 g, 69%), b.p. 48 °C at 0.1 mmHg (Found: C, 56.25; H, 6.2; Cl, 37.3. $C_9H_{12}Cl_2$ requires C, 56.6; H, 6.3; Cl, 37.0%), $\nu_{max.}$ (liquid film) 1 640, 988, 845, and 790 cm^{-1}; δ 0.75—2.6 (10 H, m), 5.0—5.4 (1 H, m, =CH), and 5.55—5.95 (1 H, =CH).

Treatment of the Epoxide (2) *with Sulphurated Sodium Borohydride*.—Sulphurated sodium borohydride was produced by the method of Lalancette.[13] Dry THF (80 ml) was rapidly added to an ice-cooled, stirred mixture of sodium borohydride (3.8 g, 0.1 mol), and sulphur (9.6 g, 0.3 mol), under nitrogen. After evolution of hydrogen had ceased (15 min), the 3 : 1 mixture of the epoxides (2) (14.8 g, 0.05 mol) was added and the mixture left at 18 °C for 16 h. Solvent was removed under reduced pressure, dichloromethane (100 ml) and aqueous sodium hydroxide (cautiously) (2M; 150 ml) added and the product isolated with dichloromethane. The disulphide (11) thus obtained was used without further purification.

The Mercapto Alcohol (12).—(*a*) A solution of the disulphide (11) (6.58 g, 100 mmol) in dry ether (40 ml) was added during 30 min to a stirred suspension of lithium aluminium hydride (0.46 g, 12 mmol) in dry ether (100 ml). After 90 min, hydrochloric acid (2M; 100 ml) was cautiously added and the acidic aqueous layer separated and extracted with ether (3 × 30 ml). The combined ethereal layers were washed with aqueous sodium hydroxide (0.3M; 3 × 50 ml), brine (50 ml) and then dried (Na_2SO_4) and concentrated under reduced pressure to give recovered disulphide (1.36 g, 20%). Acidification of the alkaline washings and re-extraction into dichloromethane gave the mercapto alcohol (12) (4.14 g, 63%) which was used without further purification since it deteriorated rapidly, $\nu_{max.}$ (CCl_4) 3 480 (OH) and 2 480w cm^{-1} (SH); δ 0.4—2.5 (10 H, m), 2.8—3.15 (2 H, m and OH, SH, D_2O exch.), 3.15—3.5, 3.55—3.85 (2 H, m). The n.m.r. spectrum suggested that the two possible diastereoisomers were present in the ratio 76 : 24. The major diastereoisomer was considered to have the configuration (1*RS*,4*RS*,5*RS*,8*SR*).

(*b*) The disulphide (6.58 g, 10 mmol) in dry ether (40 ml) was added during 45 min to a stirred solution of anhydrous aluminium chloride (1.59 g, 12 mmol) in dry ether (80 ml) containing lithium aluminium hydride (0.456 g, 12 mmol). After 8 h at 18 °C, the work-up as described in (*a*) gave recovered disulphide (1.92 g, 28%) and the mercapto alcohol (4.42 g, 67%).

The Oxathiolan (13).—A solution of the 76 : 24 mixture of the mercapto alcohols (12) (3.3 g, 10 mmol), freshly distilled benzaldehyde (1.17 g, 11 mmol), and toluene-*p*-sulphonic acid (5 mg) in dry benzene (50 ml) was heated under reflux for 4 h in a Dean and Stark apparatus. After removal of solvent under reduced pressure and dilution with dichloromethane (50 ml) the solution was washed with aqueous sodium hydroxide (0.3M; 3 × 15 ml) and brine (15 ml) and then dried (Na_2SO_4) and concentrated under reduced pressure. Final traces of benzaldehyde were removed by azeotropic distillation with toluene, leaving a residue (3.7 g). The n.m.r. spectrum contained 4 singlets at δ 5.95, 6.05, 6.09, and 6.2, ascribed to the benzylic protons of the four possible oxathiolan diastereoisomers. Trituration of the residue with ether generated a solid (2.25 g), containing two diastereoisomers in the ratio 23 : 77, which was crystallised from methanol to give a mixture (1.54 g, 37%) of the two oxathiolans in the ratio 14 : 86 (ratios from the n.m.r. spectrum). Further recrystallisation from methanol gave the major diastereoisomer of 12,12-*dibromo*-5-*oxa*-6-*phenyl*-7-*thiatricyclo*-[9.1.0.$0^{4,8}$]*dodecane*, m.p. 142—144 °C (Found: C, 46.1; H, 4.4; Br, 38.15; S, 7.45. $C_{16}H_{18}Br_2OS$ requires C, 45.95; H, 4.35; Br, 38.2; S, 7.65%), δ 1.0—2.65 (10 H, m), 3.2—3.5 (1 H, m, 8-H), 3.9—4.2 (1 H, m, 4-H), 6.05 (1 H, s, 6-H), and 7.2—7.6 (5 H, m, phenyl). The stereochemistry is considered to be (1*RS*,4*RS*,8*RS*,11*SR*).

Treatment of the Oxathiolan (13) *with Methyl-Lithium*.—Methyl-lithium (0.94M; 2.35 ml, 2.2 mmol) was added to a cooled (acetone–CO_2), stirred suspension of the oxathiolan (14) major diastereoisomer (418 mg, 1 mmol) in dry ether (15 ml), under nitrogen. After 30 min at −78 °C and 60 min at 18 °C, water (10 ml) was added and the product (285 mg) isolated with ether. P.l.c. was used to obtain the allene-oxathiolan (1RS,9SR)-11-*phenyl*-10-*oxa*-12-*thiabicyclo*[6.3.0]-*dodeca*-4,5-*diene* (14) (113 mg), as an oil (Found: C, 74.1; H, 6.95; S, 12.2. $C_{16}H_{18}OS$ requires C, 74.35; H, 7.05; S, 12.4%), δ 1.5—2.5 (8 H, m), 3.25—3.45, 3.6—3.75, 3.75—4.0, 4.05—4.25 (2 H, m, 1-H, 9-H), 5.3—5.6 (2 H, m, =CH), 6.08 (1 H, s, 11-H), and 7.2—7.6 (5 H, m, phenyl). The n.m.r. spectrum suggested the presence of two diastereoisomers (A) and (B) in the ratio 6 : 1. The n.m.r. spectrum of the crude reaction product indicated that the allene-oxathiolan (14) and the oxathiolan (13) were present in approximately equal amounts. Recovered oxathiolan isolated by p.l.c. was shown to be only the starting diastereoisomer. Quenching the reaction mixture after only 30 min at 18 °C, caused the ratio of (A) to (B) to change to 1 : 2. When the reaction was

quenched after 30 min at −78 °C and 30 min at 0 °C, the n.m.r. spectrum of the product revealed what was probably another allene-oxathiolan diastereoisomer (C), in addition to (A), with the ratio of (A) to (C) being 1 : 2, δ 1.0—2.6 (10 H, m), 3.6—4.0, 4.05—4.25, 4.3—4.6 (2 H, m), 6.10 (1 H, s), and 7.2—7.6 (5 H, m).

Treatment of the Epoxide (2) *with Sodium Acetate–Acetic Acid.*—A solution of the 3 : 1 mixture of the epoxides (2) (8.88 g, 30 mmol) and sodium acetate trihydrate (10.2 g, 75 mmol) in glacial acetic acid (125 ml) was heated at 60 °C for 8 h. Following removal of acetic acid under reduced pressure, water (50 ml) and dichloromethane (75 ml) were added and the aqueous layer separated and extracted with dichloromethane (3 × 15 ml). The combined organic extracts were washed with aqueous saturated sodium carbonate (2 × 30 ml) and brine (30 ml) and dried (Na_2SO_4) and concentrated under reduced pressure. Trituration of the residue with light petroleum gave the hydroxy acetates (3) as a white solid (7.73 g) which was collected by filtration, dried *in vacuo* and then used in the subsequent hydrolysis reaction without further purification.

The Diol (4).—A solution of the crude *trans*-1,2-hydroxyacetates (3) and potassium hydroxide (4.2 g, 37.5 mmol) in ethanol (75 ml) was stirred at 18 °C for 3 h. The solution was concentrated under reduced pressure, water (50 ml) was added, and the product isolated with dichloromethane. Trituration with light petroleum generated a solid which was recrystallised from carbon tetrachloride to give (1RS,4RS,5RS,8SR)-9,9-*dibromo*-trans-4,5-*dihydroxybicyclo*[6.1.0]*nonane* (4) [4.7 g, 52% from epoxide (2)], m.p. 111—113 °C (Found: C, 34.4; H, 4.5; Br, 50.9. $C_9H_{14}Br_2O_2$ requires C, 34.45; H, 4.5; Br, 51.2%), δ 0.9—2.5 (10 H, m), 3.15—3.6 (1 H, m, 4-H or 5-H and 2 × OH, D_2O exch.), and 3.6—3.85 (2 H, m, 5-H or 4-H).

The Acetonide (5).—The diol (4) (314 mg, 1 mmol) in acetone (5 ml), containing toluene-*p*-sulphonic acid (50 mg; 1% w/v) was heated under reflux for 4 h. Solvent was removed by evaporation and the residue subjected to short-column chromatography on silica gel. Elution with light petroleum–ether (95 : 5), concentration under reduced pressure, and crystallisation from methanol gave (1*RS*,4*RS*,8*RS*,11*SR*)-12,12-dibromo-6,6-dimethyl-5,7-dioxatricyclo[9.1.0.0^{4,8}]dodecane (5) (99 mg, 28%), m.p. 90—92 °C (lit.,[14] 84—86 °C) (Found: C, 41.0; H, 5.2; Br, 44.9. Calc. for $C_{12}H_{18}Br_2O_2$: C, 40.7; H, 5.1; Br, 45.15%), δ 0.7—2.5 (10 H, m), 1.38 (6 H, s, Me), 3.5—3.75 (1 H, m, 4-H or 5-H), and 3.85—4.15 (1 H, m, 5-H or 4-H) (lit.,[14] δ 1.38, 3.4—4.2).

The Dioxolan (6).—A solution of the diol (4) (3.14 g, 10 mmol) and freshly distilled benzaldehyde (1.17 g, 11 mmol) in dry benzene (50 ml), containing toluene-*p*-sulphonic acid (50 mg, 0.1% w/v) was heated under reflux (3 h). Water (20 ml) was added and the product isolated with dichloromethane. Residual traces of benzaldehyde were removed by azeotropic distillation with toluene and crystallisation from carbon tetrachloride gave (1RS,4RS,8RS,11SR)-12,12-*dibromo*-6-*phenyl*-5,7-*dioxatricyclo*[9.1.0.0^{4,8}]*dodecane* (6) (3.26 g, 81%), m.p. 134—139 °C (Found: C, 47.8; H, 4.55; Br, 39.45. $C_{16}H_{18}Br_2O_2$ requires C, 47.8; H, 4.5; Br, 39.75%), δ 0.8—2.55 (10 H, m), 3.55—3.8, 3.9—4.2 (2 H, m, 4-H, 8-H) 5.74, 5.82 (1 H, 2 × s, 6-H), and 7.3—7.6 (5 H, m, phenyl). The two singlets of equal intensity at δ 5.74 and 5.82 were assigned to the benzylic (6-H) protons of the two possible diastereoisomers.

The Allene-dioxolan (7).—Methyl-lithium (1.1M; 1.49 ml, 1.5 mmol) was added to a cooled (acetone–CO_2), stirred suspension of the 1 : 1 mixture of the dioxolans (6) (402 mg, 1 mmol) in dry ether (10 ml), under nitrogen. After 30 min at −78 °C, the mixture was allowed to reach 18 °C during 60 min. Water (10 ml) was added and the product (249 mg) isolated with ether. T.l.c. analysis revealed complete loss of the dioxolan (6). P.l.c. gave the allene-dioxolan (1RS,9SR)-11-*phenyl*-10,12-*dioxabicyclo*[7.3.0]*dodeca*-4,5-*diene* (7) as an oil which deteriorated with time (Found: C, 78.95; H, 7.5. $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.5%), δ 1.6—2.6 (8 H, m), 3.4—3.7, 3.9—4.2 (2 H, m, 1-H, 9-H), 5.2—5.5 (2 H, m, 4-H, 6-H), 5.80, 5.82 (1 H, 2 × s, 11-H), 7.2—7.6 (5 H, m, phenyl). The two singlets at δ 5.82 and δ 5.80 (and the corresponding multiplets at δ 3.9—4.2 and δ 3.4—3.7), were assigned to two diastereoisomers (A) and (B) which were present in the ratio 85 : 15; δ_C 23.0, 23.5, 29.2, 29.3 (all t, C-2, C-3, C-7, and C-8), 81.1 (d, C-9 or C-1), 82.8 (d, C-1 or C-9), 92.6 (d, C-4 and C-6), 101.9 (d, C-11), 126.4, 128.4, 129.0, 140.8 (q) (aromatic C), 206.4 (q, C-5)—essentially the spectrum of (A).

Distillation of an 85 : 15 mixture of the diastereoisomers (A) and (B) (140 mg) in a short-path distillation apparatus [b.p. (oil bath) 172 °C at 0.1 mmHg] gave a distillate (123 mg), shown to be a mixture of (A) and (B) in ratio 29 : 71, δ 1.6—2.6 (8 H, m), 3.4—3.7, 3.95—4.11 (2 H, m), 5.2—5.5 (2 H, m), 5.80, 5.82 (1 H, 2 × s), and 7.2—7.6 (5 H, m); δ_C [excluding the peaks for (A) given above] 26.3 (×2), 28.9, 29.9 (C-2, C-3, C-7, C-8), 85.5, 87.9 (C-1, C-9), 93.1 (C-4, C-6), 101.9 (C-11), 128.4, 129.1, 129.7, 139.0 (aromatic), and 205.1 (C-5).

The procedure described above was not consistently reproducible. Conversion of (A) into (B) did occur, but not to the same extent. Heating a mixture of (A) and (B) in nitrobenzene at 160 °C for 4 h resulted in the loss of (A) but it was not accompanied by any increase in the amount of (B).

Hydrogenation of the Allene-dioxolan (7).—(*a*) A solution of the 85 : 15 mixture of the allene-dioxolans (A) and (B) (242 mg, 1 mmol) in ethyl acetate (10 ml), containing platinum oxide (10 mg) was hydrogenated at atmospheric pressure until 2 mmol of hydrogen had been absorbed. After removing the catalyst by filtration (Celite), solvent was removed at reduced pressure and the residue subjected to short-column chromatography on silica gel, with ether (5%) in light petroleum (b.p. 40—60 °C) as eluant. Concentration under reduced pressure followed by crystallisation from light petroleum gave (1RS,9SR)-10,12-*dioxa*-11-*phenylbicyclo*[7.3.0]*dodecane* (10) (140 mg, 57%), m.p. 55—57 °C (Found: C, 77.8; H, 9.1. $C_{16}H_{22}O_2$ requires C, 78.0; H, 9.0%), δ 1.4—2.4 (10 H, m), 3.95—4.2 (2 H, m, 1-H, 9-H), 5.84 (1 H, s, 11-H), and 7.2—7.6 (5 H, m, phenyl), δ_C 23.5, 24.1, 26.2, 27.9 (×2), 32.4, 32.8 (C-2 to C-8), 82.5, 84.5 (C-1, C-7), 101.3 (C-11), and 126.6, 128.3, 129.1, and 138.5 (aromatic).

(*b*) The experiment described in part (*a*) was repeated with a 20 : 80 mixture of (A) and (B) giving a product which was identical by m.p., t.l.c., i.r. and n.m.r. with that obtained in part (*a*).

Treatment of trans-9,9-*Dichlorobicyclo*[6.1.0]*non*-4-*ene* (16) *with* n-*Butyl-lithium.*—n-Butyl-lithium (1.6M; 2.8 ml, 4.5 mmol) was slowly added to a cooled (acetone–CO_2), stirred solution of *trans*-9,9-dichloro-*trans*-bicyclo[6.1.0]non-4-ene (16) (0.573 g, 3 mmol) in dry ether (25 ml), under nitrogen. After 30 min, at −78 °C, the solution was allowed to reach 18 °C during 60 min and then added to water (10 ml). The product was isolated with ether and g.l.c. analysis (OV1 at 70 °C) of the solution revealed one major peak which was identified as 2,3-divinylcyclopentene (21) by co-injection with an authentic sample. The estimated yield was 67%. Ether was

removed by distillation under atmospheric pressure and comparison of the n.m.r. spectrum of the residue with that of an authentic sample confirmed the presence of 2,3-divinylcyclopentene, plus n-butyl chloride.

When the reaction was repeated but with THF as solvent the estimated yield of (21) fell to 58%.

Treatment of the Allene-oxathiolan (15) *with n-Butyl-lithium.*—n-Butyl-lithium (1.6M; 0.94 ml, 1.52 mmol) was added to a cooled (acetone–CO_2), stirred solution of a freshly prepared 6 : 1 mixture of the allene-oxathiolans (15) (97 mg, 0.37 mmol) in dry ether (10 ml), under nitrogen. After 1 h at −78 °C and 2 h at 18 °C, water (10 ml) was added and the aqueous layer separated and extracted with ether (3 × 5 ml). The combined ether layers were washed with brine (10 ml) and dried (Na_2SO_4). G.l.c. analysis (OV1 at 70 °C) of the solution revealed a single major peak of short retention time and this was identified as 2,3-divinylcyclopentene (21) by comparison with an authentic sample. The estimated yield was 51%.

When the reaction was repeated but with THF as the solvent, the estimated yield of 2,3-divinylcyclopentene fell to 21%. The course of the reaction was followed by g.l.c. and this showed that, as the reaction solution was brought to 18 °C, the amount of 2,3-divinylcyclopentene present decreased.

Base Treatment of the Allene-dioxolan (7).—(a) *With n-butyl-lithium.* n-Butyl-lithium (1.6M; 1.59 ml, 2.54 mmol) was added to a cooled (acetone–CO_2), stirred solution of a 3 : 1 mixture of the allene-dioxolans (7) (freshly prepared; 155 mg, 0.64 mmol) in dry THF (5 ml), under nitrogen. After 1 h, the cooling was removed and the solution was allowed to reach 18 °C during 2 h. Light petroleum (10 ml) and water (10 ml) were added, and the product isolated with light petroleum. T.l.c. analysis indicated the presence of unchanged allene-dioxolan (7) whilst the n.m.r. spectrum showed that (B) was now the predominant diastereoisomer. The hydrocarbon product was isolated by short-column chromatography on silica gel. Elution with light petroleum gave a single major product which was identified as 2,3-divinylcyclopentene (21) by g.l.c. (OV1 at 70 °C) and spectroscopic comparison with an authentic sample. The estimated yield, by g.l.c., of (21) was 83%.

(b) *With t-butyl-lithium.* The experiment described above, in (a), was repeated, using t-butyl-lithium. Examination of the hydrocarbon product by g.l.c. and n.m.r. showed only the presence of (21).

2,3-*Divinylcyclopentene.*[11]—*cis*-Cyclonona-1,2,6-triene (0.84 g, 7 mmol) was heated for 1 h at 150 °C in a sealed Pyrex tube (purged with nitrogen prior to sealing). Distillation, followed by preparative g.l.c. (OV1 at 150 °C) gave 2,3-divinylcyclopentene, δ 1.6—2.7 (4 H, m), 3.25—3.6 (1 H, m, 3-H), 4.85—5.3 (4 H, m, $=CH_2$), 5.5—5.95 (2 H, m, =CH), 6.2—6.6 (1 H, d of d, *J* 9, 17 Hz, 1-H) (lit.,[11] 1.5—2.7, 3.4, 4.7—6.7), $\lambda_{max.}$ 234, 228sh, 241 (ε 2.11, 1.89, and 1.52 × 10^4 respectively) [lit.[11] (cyclohexane) 234, 228sh, 241 with ε 2.42, 2.7, and 1.88 × 10^4, respectively].

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References

1 Part 10, P. F. Newton and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 1979, 3077.
2 J. N. Hines, M. J. Peagram, E. J. Thomas, and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 1973, 2332.
3 M. Jones, P. Temple, E. J. Thomas, and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 1974, 433.
4 A. J. Bridges and G. H. Whitham, *J. Chem. Soc., Chem. Commun.*, 1974, 142; P. F. Newton and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 1979, 3067; A. D. Buss and S. Warren, *J. Chem. Soc., Chem. Commun.*, 1981, 100.
5 M. Traetteberg, *Acta Chem. Scand., Sect. B*, 1975, **29**, 29; O. Ermer, *Angew. Chem. Int. Ed. Engl.*, 1974, **13**, 604; *Tetrahedron*, 1975, **31**, 1849; P. F. Newton and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 1979, 3067.
6 D. Duffin and J. K. Sutherland, *J. Chem. Soc., Chem. Commun.*, 1970, 626; J. K. Sutherland, personal communication.
7 L. Skattebøl, *Acta Chem. Scand.*, 1963, **17**, 1683.
8 R. Rossi and P. Diversi, *Synthesis*, 1973, 25; R. Hoffmann, *Tetrahedron*, 1966, **22**, 521.
9 C. W. Jefford, D. Kirkpatrick, and F. Delay, *J. Am. Chem. Soc.*, 1972, **94**, 8905.
10 J. A. Deyrup and M. Betkouski, *Tetrahedron Lett.*, 1973, 1131.
11 (*a*) E. Vogel, W. Grimme, and E. Dinne, *Angew. Chem. Int. Ed. Engl.*, 1963, **2**, 739; (*b*) L. Skattebøl and S. Solomon, *J. Am. Chem. Soc.*, 1965, **87**, 4506; (*c*) K. G. Untch and D. J. Martin, *J. Am. Chem. Soc.*, 1965, **87**, 4501.
12 B. S. Farah and E. F. Gilbert, *J. Chem. Eng. Data*, 1962, **7**, 568.
13 J. M. Lalancette and A. Freche, *Can. J. Chem.*, 1971, **49**, 4047.
14 H. J. J. Loozen, W. A. Castenmiller, E. J. M. Buter, and H. M. Buck, *J. Org. Chem.*, 1976, **41**, 2965.

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