

o-Quinonoid Compounds. Part VI.¹ Spiroconjugation in the Ethylene Acetal of 1,3-Diphenylinden-2-one and Derivatives of Benzo[*c*]phosphole 2-Oxide

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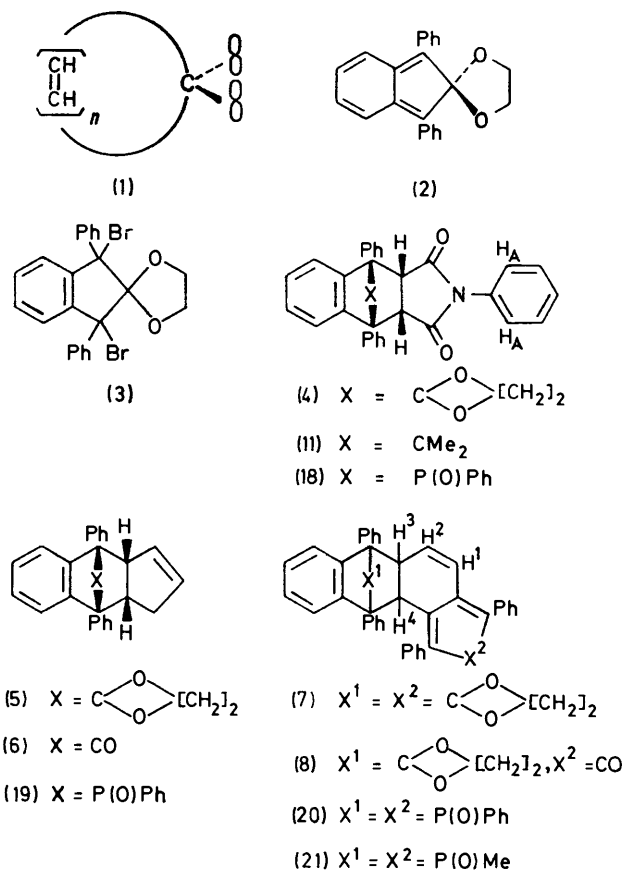
The ethylene acetals of 1,3-diphenylinden-2-one, 1,2,3-triphenylbenzo[*c*]phosphole 2-oxide, and 2-methyl-1,3-diphenylbenzo[*c*]phosphole 2-oxide have been generated by reduction of their dibromides, and characterised by u.v. spectroscopy and trapping experiments. The long-wavelength u.v. absorption and rapid [4 + 2] π dimerisation of these compounds, in comparison with the properties of 2,2-dimethyl-1,3-diphenyl-2*H*-indene, are attributed to spiroconjugation.

THE prediction of spiroconjugation between the termini of a conjugated cyclic polyene and the *p* orbitals of substituents attached to an insulating carbon atom as in (1)^{2,3} encouraged an extension of our study of 1,3-diphenylinden-2-one⁴ to the related ethylene acetal (2).⁵

ambiguities^{2,8} associated with possible non-planarity of the polyene framework.

The ethylene acetal of 1,3-diphenylinden-2-one was prepared from the ketone in the usual way, and gave the dibromide (3) with *N*-bromosuccinimide. Reduction of the product (3) with copper powder in boiling benzene gave a violet-red colour (λ_{max} 537 nm) attributed to the inden-2-one acetal (2) since it was instantly discharged on addition of *N*-phenylmaleimide. Dehalogenation of the dibromide (3) in the presence of *N*-phenylmaleimide produced no colour but gave the adduct (4). The *endo*-configuration of this adduct follows from the resonance of the protons H_A at high field, as a result of shielding by the phenylene ring.⁹ Reaction of the dibromide (3) with sodium iodide in boiling acetone also gave the acetal (2), for in the presence of cyclopentadiene the adduct (5) was produced (45%). The configuration of the latter follows from its preparation from the *endo*-1,3-diphenylinden-2-one-cyclopentadiene adduct (6).⁴ In the absence of a trap the violet-red colour of (2) faded rapidly (30 min in boiling benzene) and isolation then gave the Diels-Alder dimer (7) of the acetal (2). The structure of the dimer (7) rests on its n.m.r. spectrum, τ 4.0 (d, H¹, *J* 10 Hz), 4.22 (dd, H², *J* 10 and 3.5 Hz), 5.66 (dd, H³, *J* 8.5 and 3.5 Hz), and 5.31 (d, H⁴, *J* 8.5 Hz). With toluene-*p*-sulphonic acid hydrate in ethanol the dimer (7) gave the cyclopentadienone (8), which has an appropriate n.m.r. spectrum and i.r. and u.v. properties similar to those of tetraphenylcyclopentadienone. The dimer (7) reacted with *N*-phenylmaleimide in boiling xylene to give the adduct (4) as well as the expected 1 : 1 adduct. Unlike reduction with iodide ion reduction of (3) with copper powder gave an appreciable quantity of the enol ether (9), which may arise from the acetal (2) by a thermal or Lewis-acid-catalysed 1,5-oxygen shift.

The 2*H*-indene (10) required for comparison with the acetal (2) can apparently¹⁰ be isolated when prepared by



Spiroconjugative effects have been detected in a variety of molecules,^{6,7} including acetals of cyclopentadienone (1; *n* = 2).^{2,7} Similar effects might be expected in structure (2), a bridged variant of (1; *n* = 4) free of

¹ Part V, D. W. Jones and R. L. Wife, *J.C.S. Perkin I*, 1972, 2722.

² H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, 1967, **89**, 5208.

³ R. Hoffmann, A. Imamura, and G. D. Zeiss, *J. Amer. Chem. Soc.*, 1967, **89**, 5215.

⁴ J. M. Holland and D. W. Jones, *J. Chem. Soc. (C)*, 1971, 608.

⁵ Preliminary communication, J. M. Holland and D. W. Jones, *Chem. Comm.*, 1970, 122.

⁶ H. H. Jaffé and O. Chalvet, *J. Amer. Chem. Soc.*, 1963, **85**, 1561; D. R. Williams, D. L. Coffen, P. E. Garrett, and R. N. Schwartz, *J. Chem. Soc. (B)*, 1968, 1132; H. Durr and L. Schrader, *Z. Naturforsch.*, 1969, **24b**, 536. A. Zweig and J. B. Gullivan, *J. Amer. Chem. Soc.*, 1969, **91**, 260; R. Baschi, A. S. Dreiding, and E. Heilbronner, *ibid.*, 1970, **92**, 123; U. Weidner and A. Schweig, *Angew. Chem. Internat. Edn.*, 1972, **11**, 513.

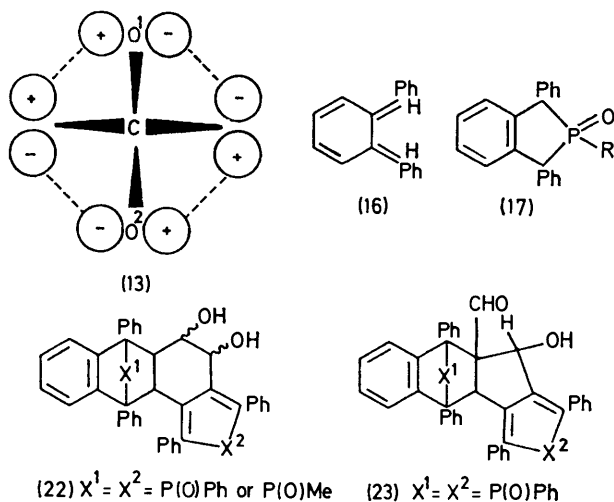
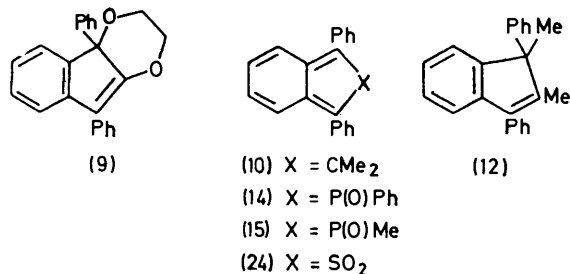
⁷ E. W. Garbisch and R. F. Sprecher, *J. Amer. Chem. Soc.*, 1966, **88**, 3434; 1970, **91**, 6785.

⁸ I. O. Sutherland, *Ann. Reports*, 1967, **64**, 273.

⁹ D. W. Jones and G. Kneen, *Chem. Comm.*, 1971, 1356.

¹⁰ K. Alder and M. Fremery, *Tetrahedron*, 1961, **14**, 190.

reaction of its dibromide with zinc amalgam. We found that the corresponding dehalogenation with copper powder in boiling benzene provided solutions of compound (10) suitable for spectral and reactivity comparisons with (2). The 2*H*-indene (10) prepared in



this way reacted rapidly with *N*-phenylmaleimide to give the adduct (11); it also absorbed at considerably shorter wavelengths (λ_{max} , 444 nm) than the acetal (2) and gave no isolable dimer even on prolonged heating in boiling benzene. When the 2*H*-indene was prepared in boiling xylene the initial strong yellow colour slowly faded and the indene (12) was isolated. In contrast to compound (2) the 2*H*-indene prefers rearrangement to dimerisation.

The longer-wavelength u.v. absorption and more ready dimerisation of the acetal (2) are fully consistent with a spiro-interaction between the acetal oxygen atoms and the termini of the π -system. The disposition and phases of the relevant orbitals about the spiro-centre are shown in (13). The O¹-O² orbital compounded from two oxygen lone pair *p* orbitals is of the correct symmetry to interact with the highest occupied molecular orbital (HOMO) of a polyene with an *even* number of double bonds. Since the O¹-O² orbital is lower in energy than the HOMO, the perturbed HOMO is of higher energy.² This description accounts for both the long wavelength u.v. absorption and the ready [4 + 2] π dimerisation of (2). The rates of Diels-

Alder reactions involving electron-rich dienes are largely determined by interaction of the diene HOMO with the lowest vacant molecular orbital of the dienophile.¹¹ This interaction will be greater the higher the energy of the HOMO. The bathochromic shift observed for the acetal (2) relative to the 2*H*-indene (10) corresponds to an increase of 11.1 kcal mol⁻¹ in the energy of the HOMO. This value is comparable to that observed for cyclopentadienone acetals.²

In related work directed towards the preparation of derivatives of benzo[*c*]phosphole we generated the *o*-quinonoid phosphole oxides (14) and (15) and found them to have properties similar to those of the acetal (2). McCormack reaction¹² between the *o*-quinonoid tautomer (16) of diphenylbenzocyclobutene and phenylphosphonous dichloride gave a salt which on hydrolysis afforded the phospholene oxide (17; R = Ph). The related phospholene oxide (17; R = Me) was prepared from methylphosphonous dichloride. Reactions of the oxides (17; R = Ph) and (17; R = Me) with *N*-bromosuccinimide gave the corresponding dibromides, which on reduction with copper powder in boiling benzene gave the phosphole oxides (14) and (15). These compounds showed long-wavelength u.v. absorption at 573 and 550 nm, respectively. The phosphole oxide (14) reacted as generated with both *N*-phenylmaleimide and cyclopentadiene to give the adducts (18) and (19), respectively. Like the acetal (2), both phosphole oxides dimerised rapidly under the conditions used to generate them. The dimers are allocated the structures (20) and (21) on the basis of their spectroscopic properties (see Experimental section). The dimers dissociate to the monomers (14) and (15) in boiling xylene. Thus the characteristic colour (λ_{max} , 550 nm) of (15) appears on heating the dimer (21) and is replaced by the yellow colour of the dimer on cooling to room temperature. Similarly with *N*-phenylmaleimide in boiling xylene the dimer (20) gives the adduct (18). On hydroxylation (OsO₄) both dimers afford diols of structure (22); attempted cleavage of the diols with lead tetra-acetate was complicated by probable aldolisation of the expected dialdehydes. Thus n.m.r. examination of the product from the diol [22; X¹ = X² = P(O)Ph] indicated the presence of both compound (23) and the expected dialdehyde. The properties of the oxides (14) and (15), whilst completely consistent with spiro- and homo-conjugation respectively, do not exclude a less important *p* π -*d* π orbital overlap between the π -system and a phosphorus *d* orbital. Indeed the λ_{max} values given show a dependence on the nature of the spiro-atom suggestive of an interaction other than spiroconjugation. The same may be said of the sulphone (24) prepared by Cava and McGrady,¹³ although here the λ_{max} value (550 nm) is close to that observed for the acetal (2). The yellow decomposition products obtained¹³ on attempted iso-

¹¹ R. Sustmann, *Tetrahedron Letters*, 1971, 2721; for related work see M. N. Paddon-Row, *Tetrahedron Letters*, 1972, 1409.

¹² W. B. McCormack, U.S.P. 2,663,736 and 2,663,737/1953; for a review see L. D. Quin, '1,4-Cycloaddition Reactions,' ed. J. Homer, Academic Press, New York, 1967, ch. 3.

¹³ M. P. Cava and J. McGrady, *Chem. Comm.*, 1968, 1648.

lation of the sulphone (24) may arise by dimerisation and loss of a molecule of sulphur dioxide. Spiro-conjugation has been invoked to explain the remarkable properties of thiophen 1,1-dioxide.⁷ The properties of simple phosphole oxides¹⁴ are consistent with spiro-conjugation.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise specified, i.r. spectra refer to Nujol mulls, u.v. spectra to ethanolic solutions, and n.m.r. spectra to solutions in deuteriochloroform measured with a Varian A60A spectrometer. Mass spectra were obtained with an A.E.I. MS902 instrument. Petroleum refers to light petroleum, b.p. 60–80°, and chromatography on silica to short-column chromatography¹⁵ over Kieselgel G (Merck).

2,2-Ethylenedioxy-1,3-diphenylindan.—1,3-Diphenylindan-2-one¹⁶ (3.5 g), ethylene glycol (32 ml), toluene-*p*-sulphonic acid monohydrate (0.14 g), and toluene (175 ml) were heated under reflux in a Dean-Stark apparatus with azeotropic removal of water (20 h). Further ethylene glycol (20 ml) was added and heating continued (10 h). After a final addition of ethylene glycol (15 ml) and heating (18 h) the product was diluted with ether (200 ml), washed with saturated sodium hydrogen carbonate solution, dried (MgSO₄), and evaporated to give a mixture of the *cis*- and *trans*-forms of the ethylene acetal (2.69 g, 67%), m.p. 103–113° (from petroleum) (Found: C, 84.25; H, 6.15. C₂₃H₂₀O₂ requires C, 84.1; H, 6.1%), τ (CCl₄) 2.5–3.2 (14H, m, aromatic), 5.50 and 5.57 (2H, singlets, benzylic), 6.2–6.85 (3H, m, CH₂), and 7.05–7.4 (1H, m, CH₂). Material from one preparation was chromatographed on silica in benzene-petroleum (4 : 1) to give one isomer of the acetal, m.p. 126–131°, τ 2.5–3.2 (14H, m, aromatic), 5.50 (2H, s, benzylic), 6.67 (2H, t, *J* 6 Hz, CH₂), and 7.18 (2H, t, *J* 6 Hz, CH₂).

1,3-Dibromo-2,3-ethylenedioxy-1,3-diphenylindane (3).—The foregoing product (656 mg, 2.0 mmol), *N*-bromosuccinimide (712 mg, 4.0 mmol), and carbon tetrachloride (30 ml) were stirred with illumination (5 h), with additions of benzoyl peroxide (3 × 4 mg). The product was cooled in ice and filtered, and the filtrate was evaporated under reduced pressure to give the *cis*- and *trans*-forms of the dibromide (3) (810 mg, 83%), m.p. 170–180° (from benzene) (Found: C, 57.2; H, 3.65; Br, 32.5. C₂₃H₁₈Br₂O₂ requires C, 56.8; H, 3.7; Br, 32.9%), τ (CCl₄) 2.15–3.0 (14H, m, aromatic) and 5.8–7.2 (4H, m, CH₂).

Reduction of the Dibromo-acetal (3) with Iodide Ion in the Presence of Cyclopentadiene.—The product (3) (200 mg, 0.41 mmole), sodium iodide (500 mg, 3.3 mmol), cyclopentadiene (1.0 ml), and dry acetone (15 ml) were heated under reflux with stirring in nitrogen (1.5 h). Heating was then similarly continued (5 h) with further additions of cyclopentadiene (2 × 1.0 ml). The product was evaporated, washed with sodium thiosulphate solution, washed with water, dried (MgSO₄), and evaporated. The product (190 mg) was chromatographed on silica. Elution with benzene-petroleum (4 : 1) gave the adduct (5) (73 mg, 45%), m.p. 180–184° (from ethanol) (Found: C, 85.8; H, 5.9. C₂₈H₂₄O₂ requires C, 85.7; H, 6.2%), ν_{\max} 1185 and 1604

cm⁻¹, τ 2.1–3.3 (14H, m, aromatic), 4.5–5.0 (2H, m, olefinic), 5.35–5.80 (1H, m, allylic methine), 5.83–6.30 (1H, td, *J* 9.5 and 4 Hz, homoallylic methine), 6.45–7.00 (4H, octet, O-CH₂-CH₂-O), and 7.2–8.5 (2H, m, allylic methylene). The product was recovered unchanged after heating under reflux in acetone-sulphuric acid (2N) for 1.75 h.

Preparation of the Adduct (5) from the endo-Cyclopentadiene-1,3-Diphenylindan-2-one Adduct.—The endo-cyclopentadiene-1,3-diphenylindan-2-one adduct (27 mg), ethylene glycol (0.3 ml), benzene (2 ml), and toluene-*p*-sulphonic acid (2 mg) were heated under reflux with azeotropic water removal (20 h). After slow distillation to dryness, the product was diluted with ether, washed with water, dried (MgSO₄), and evaporated to give the adduct (5) (25 mg, 82%), m.p. 180–185° (from ethanol), identical with the material prepared before (mixed m.p. and i.r. spectrum).

Reaction of the Dibromo-acetal (3) with Iodide Ion in the Absence of a Trap.—The dibromo-acetal (3) (200 mg), sodium iodide (500 mg), and dry acetone (15 ml) were heated under reflux in nitrogen (20 h). The product was evaporated to dryness, diluted with ether, washed with sodium thiosulphate solution, washed with water, dried (MgSO₄), and evaporated. The product, an oil (161 mg), was chromatographed on silica with benzene as eluant to give the dimer (7) (102 mg, 45%) as a resin [Found: *M*⁺, 652.263. C₄₈H₃₆O₄ requires *M*, 652.261. Found: *M* (osmometer), 587], λ_{\max} 350 nm (ϵ 6520), τ 2.2–3.25 (24H, m, aromatic), 4.0 (1H, d, *J* 10 Hz, olefinic), 4.22 (1H, dd, *J* 10 and 3.5 Hz, olefinic), 5.31 (1H, d, *J* 8.5 Hz, methine), 5.66 (1H, dd, *J* 8.5 and 3.5 Hz, methine), and 6.2–6.6 and 6.7–7.2 (8H, m, O-CH₂-CH₂-O).

Reduction of the Dibromo-acetal (3) with Enneacarbonyliron.—The dibromide (3) (200 mg, 0.41 mmol), enneacarbonyliron (728 mg, 2 mmol), and ether (30 ml) were stirred at 20° in nitrogen for 20 h. The red colour which developed during the first hour had disappeared after this time. The product was filtered, the filtrate evaporated, and the oily residue (156 mg) chromatographed on silica. Elution with benzene-petroleum (4 : 1) gave the dimer (7) (58 mg, 43%), identical with the material previously prepared (i.r. and n.m.r. spectra).

Reduction of the Dibromide (3) with Copper Powder.—The dibromide (3) (0.5 g) and copper powder (1.5 g) in benzene (25 ml) were heated under reflux in nitrogen with vigorous stirring. A red-violet colour developed after 5 min heating and had faded after 30 min. After 4 h heating, the product was filtered, and the filtrate evaporated. The residue was chromatographed on silica. Elution with benzene-petroleum (3 : 1) gave 2,3-dihydro-4a,9-diphenyl-4aH-indeno-[1,2-b]-*p*-dioxin (9) (35 mg), m.p. 157–158° (from ethanol) (Found: *M*⁺, 326.1309. C₂₈H₁₈O₂ requires *M*, 326.130), τ 5.95 (4H, m, O-CH₂-CH₂-O) and 2–3.8 (14H, m, aromatic). Continued elution with the same solvent gave the dimer (7) (195 mg), identical (i.r. spectrum) with samples previously prepared.

Hydrolysis of the Dimer (7).—The dimer (200 mg), toluene-*p*-sulphonic acid monohydrate (100 mg), and ethanol (15 ml) were heated on a water-bath (30 min). The deep red crystalline precipitate was filtered off, washed with a little ethanol, and dried to give the ketone (8) (140

¹⁴ G. Märkl and R. Potthast, *Tetrahedron Letters*, 1968, 1755; D. A. Usher and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1964, **86**, 4732; R. Kluger and F. H. Westheimer, *ibid.*, 1969, **91**, 4143; Yuan-Yuan Chiu and W. S. Lipscomb, *ibid.*, 1969, **91**, 4150.

¹⁵ B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1868.

¹⁶ G. Quinkert, K. Opitz, W.-W. Weisdorff, and M. Finke, *Annalen*, 1966, **603**, 44.

mg, 75%), m.p. 286—289° (from chloroform-ethanol) [Found: C, 87.0; H, 5.45%; *M* (osmometer), 597. $C_{44}H_{32}O_3$ requires C, 86.8; H, 5.3%; *M*, 608], ν_{\max} , 1693 cm^{-1} , λ_{\max} , 269, 336, and 493 nm (ϵ 25,400, 4520, and 1970), τ 2.15—3.3 (24H, m, aromatic), 3.58 (1H, d, *J* 10 Hz, olefinic), 3.87 (1H, dd, *J* 10 and 4 Hz, olefinic), 4.97 (1H, d, *J* 8 Hz, methine), 5.51 (1H, dd, *J* 8 and 4 Hz, methine), and 6.7—7.7 (4H, m, $O\cdot CH_2\cdot CH_2\cdot O$).

Reaction of the Dimer (7) with N-Phenylmaleimide.—The dimer (7) (100 mg), *N*-phenylmaleimide (25 mg), and xylene (5 ml) were heated under reflux for 24 h. Further *N*-phenylmaleimide (25 mg) was added and heating was continued for 4 h. The product was evaporated and the residue chromatographed on silica; elution with benzene-ether (1:1) gave a 1:1-adduct (28 mg), m.p. 242—243° (from chloroform-ethanol) (Found: C, 81.3; H, 5.45; N, 1.7. $C_{36}H_{43}NO_6$ requires C, 81.45; H, 5.2; N, 1.7%). Continued elution with the same solvent gave the adduct (4) (55 mg), m.p. 245—247° (from chloroform-ethanol) (Found: M^+ , 499.1788. $C_{35}H_{25}NO_4$ requires *M*, 499.1783), τ 6.7 (4H, m, $O\cdot CH_2\cdot CH_2\cdot O$), 5.4 (2H, s), 3.5 (2H, m, aromatic), 3.1—2.4 (13H, m, aromatic), and 2.15 (4H, m, aromatic).

Reduction of the Dibromide (3) with Copper Powder in the Presence of N-Phenylmaleimide.—The dibromide (243 mg), copper powder (0.75 g), *N*-phenylmaleimide (86.5 mg), and benzene (10 ml) were heated under reflux in nitrogen with stirring. The product was filtered and evaporated to give the adduct (4), identical (mixed m.p. and i.r. spectrum) with the sample previously prepared.

Reduction of 1,3-Dibromo-2,2-dimethyl-1,3-diphenylindan with Copper Powder in the Presence of N-Phenylmaleimide.—The dibromide [m.p. 168—174° (from benzene-petroleum)] (200 mg) and copper powder (800 mg) in benzene (5 ml) were boiled under nitrogen with stirring. A deep yellow colour developed within 1 min and was instantly discharged on adding *N*-phenylmaleimide (76 mg). After boiling under reflux (12 h) the product was filtered and the filtrate diluted with ether and washed with water. The ether layer was dried ($MgSO_4$) and evaporated. Crystallisation of the product from ethanol gave the adduct (11), m.p. 265—266° (Found: M^+ , 469.204. $C_{33}H_{27}NO_2$ requires *M*, 469.204), ν_{\max} , 1718 and 1778 cm^{-1} , τ 9.34 (3H, s, Me), 9.26 (3H, s, Me), 5.43 (2H, s, CH_2), 3.5 (2H, m, aromatic), and 2.2—3 (17H, m, aromatic).

When the dibromide (300 mg), copper powder (1.2 g), and xylene (10 ml) were boiled under reflux (18 h) under nitrogen and the product was chromatographed on silica in benzene-petroleum (1:1), 1,2-dimethyl-1,3-diphenylindene (12) (130 mg) was obtained (Found: M^+ , 296. $C_{23}H_{20}$ requires *M*, 296), τ 8.35 (3H, s, Me), 8.27 (3H, s, Me), and 2.5—3.3 (14H, m, aromatic).

1,3-Dihydro-1,2,3-triphenylbenzo[c]phosphole 2-Oxide.—1,2-Diphenylbenzocyclobutene¹⁶ (1.5 g) and phenylphosphonous dichloride (15 ml) were kept at 20° for 14 days. The mixture was diluted with cyclohexane (15 ml), and the crystalline precipitate filtered off, washed with cyclohexane, and suspended in water (50 ml). The suspension was warmed briefly on a water-bath, and made alkaline with saturated sodium hydrogen carbonate solution. The product was extracted with chloroform; the organic layer was washed with saturated sodium hydrogen carbonate solution, washed with water, dried ($MgSO_4$), and evaporated to give 1,3-dihydro-1,2,3-triphenylbenzo[c]phosphole 2-oxide (1.65 g, 74%) as needles, m.p. 212—213° (from benzene-

petroleum) (Found: C, 81.85; H, 5.5%; M^+ , 380.1330. $C_{26}H_{21}PO$ requires C, 82.1; H, 5.6%), ν_{\max} , 1195 cm^{-1} , τ 2.4—3.4 (19H, m, aromatic), and 4.83, 4.97, 5.14, and 5.20 (2H, two doublets, benzylic).

Generation of 1,2,3-Triphenylbenzo[c]phosphole 2-Oxide in the Presence of N-Phenylmaleimide.—The foregoing product (100 mg, 0.264 mmol), *N*-bromosuccinimide (95 mg, 0.53 mmol), benzoyl peroxide (2 mg), and carbon tetrachloride (10 ml) were stirred at 30° with illumination (4 h). The product was cooled in ice and filtered, and the filtrate evaporated under reduced pressure to give 1,3-dibromo-1,3-dihydro-1,2,3-triphenylbenzo[c]phosphole 2-oxide (135 mg, 95%) as pale yellow prisms, m.p. 223—226.5°, on trituration with ether; τ 2.1—2.6 (m, aromatic). This product, *N*-phenylmaleimide (46 mg, 0.27 mmol), copper powder (240 mg), and dry benzene (10 ml) were heated under reflux in nitrogen (1.5 h). After evaporation of solvent the product was continuously extracted with dichloromethane (16 h) to yield the adduct (18) (136 mg, 94%) as a powder, m.p. 390° (decomp.) (from trifluoroacetic acid-ethanol) (Found: M^+ , 551.1649. $C_{36}H_{26}NPO_3$ requires *M*, 551.1650), ν_{\max} , 1194 and 1710 cm^{-1} , τ ($CF_3\cdot CO_2H$) 2.05—3.1 (22H, m, aromatic), 3.35—3.6 (2H, m, aromatic), and 4.4 (2H, s, methine), *m/e* 551 (3.5%), 427 (64), 280 (100), 203 (12), and 202 (14), m^* 331 (for 551 — PhPO), 183.7 [for 427 — $PhN(CO)_2$], and 147 (for 280 — Ph).

Reaction of 1,2,3-Triphenylbenzo[c]phosphole 2-Oxide with Cyclopentadiene.—The phosphine oxide (17; R = Ph) (100 mg) was brominated as already described. The product, copper powder (240 mg), cyclopentadiene (1.0 ml), and dry benzene (10 ml) were heated under reflux in nitrogen (1.5 h). The product was filtered, and the filtrate evaporated to give partially crystalline material (179 mg) which was chromatographed on silica. Elution with benzene-ether (3:2) gave the adduct (19) (90 mg, 77%), m.p. 221—223° (from benzene-petroleum) (Found: C, 83.4; H, 5.8%; M^+ , 444.1646. $C_{31}H_{25}PO$ requires C, 83.8; H, 5.7%; *M*, 444.1643), ν_{\max} , 1198 and 1601 cm^{-1} , τ 2.45—3.2 (19H, m, aromatic), 4.28—4.72 (2H, m, olefinic), 4.89—5.38 (1H, m, allylic methine), 5.44—5.86 [1H, triple doublet further split by ^{31}P to doublets, *J* 9 and 4 Hz with *J* ($^{31}P, H$) 1.5 Hz, homoallylic methine], and 7.0—8.3 (2H, m, CH_2), *m/e* 444 (52%), 378.1173 ($C_{26}H_{19}PO$) (100), 331 (27), 320 (23), 319 (29), and 254 (14), m^* 290 (for 378 — PO).

Preparation of 1,2,3-Triphenylbenzo[c]phosphole 2-Oxide in the Absence of a Trap.—Phosphine oxide (17; R = Ph) (200 mg) was brominated with *N*-bromosuccinimide (190 mg) as already described. The product, copper powder (400 mg), and benzene (35 ml) were heated under reflux in nitrogen for 2 h, after which time the initially formed violet colour (λ_{\max} , 573 nm) had disappeared. The product was filtered, the filtrate evaporated, and the residue chromatographed on silica. Elution with benzene-acetone (1:1) gave the dimer (20) (166 mg, 84%) as yellow prisms, m.p. 237—239° (from benzene-petroleum) [Found: C, 82.25; H, 5.2; *M* (osmometer), 725. $C_{52}H_{38}P_2O_2$ requires C, 82.5; H, 5.1%; *M*, 756), ν_{\max} , 1190 and 1200 cm^{-1} , ν_{\max} ($CHCl_3$) 1187 and 1220 cm^{-1} , λ_{\max} , 395 nm (ϵ 6780), τ 2.2—3.4 (34H, m, aromatic), 3.61 (1H, d, *J* 12 Hz), 3.93 (1H, doublet triplet, *J* 12 and 3 Hz), 4.1—4.35 (1H, obscured quintet), and 4.88—5.19 (1H, m), τ (90 MHz) 3.74 (1H, d, *J* 13 Hz), 4.07 (1H, double triplet, *J* 12.5 and 3.3 Hz), 4.3—4.6 (1H, quintet), and 5.3—5.7 (1H, m), *m/e* 378.1173 ($C_{26}H_{19}PO$) (100%).

Dissociation of the Dimer of 1,2,3-Triphenylbenzo[c]-phosphole 2-Oxide.—The dimer (38 mg, 0.05 mmol), *N*-phenylmaleimide (18 mg, 0.104 mmol), and xylene (2 ml) were heated under reflux in nitrogen (2.75 h). The product was filtered and the crystalline precipitate washed with ether to give the adduct (18) (48 mg, 86%) identical with the product previously prepared (i.r. spectrum).

Dissociation of the Dimer of 1,2,3-Triphenylbenzo[c]-phosphole 2-Oxide in Acetic Acid.—The dimer (100 mg), glacial acetic acid (4 ml), and anhydrous sodium acetate (300 mg) were heated under reflux in nitrogen (5 days). The product was diluted with ether, washed with saturated sodium hydrogen carbonate solution, washed with water, dried (MgSO_4), and subjected to layer chromatography on silica. Development with benzene-acetone (3:2) gave starting material (80 mg) and a compound (12 mg) with m.p. 246–247.5° (from benzene-petroleum), ν_{max} 1202 cm^{-1} .

1,3-Dihydro-2-methyl-1,3-diphenylbenzo[c]phosphole 2-Oxide.—Diphenylbenzocyclobutene¹⁶ (200 mg), and methylphosphonous dichloride (2.0 ml) were kept at 20° for 14 days. The product was evaporated under reduced pressure, saturated sodium hydrogen carbonate solution (10 ml) was added, and the oily suspension was heated on a water-bath (5 min). The product was extracted with chloroform; the organic layer was washed with saturated sodium hydrogen carbonate solution, dried (MgSO_4), and evaporated to give one isomer of 1,3-dihydro-2-methyl-1,3-diphenylbenzo[c]-phosphole 2-oxide (109 mg, 44%), m.p. 244–247° (from benzene-petroleum) (Found: M^+ , 318.1172. $\text{C}_{21}\text{H}_{19}\text{PO}$ requires M , 318.1173), ν_{max} 1203 cm^{-1} , τ 2.55–2.9 (14H, m, aromatic), 5.18 [2H, d, $J(^{31}\text{P},\text{H})$ 21.5 Hz, benzylic], and 9.17 [3H, d, $J(^{31}\text{P},\text{H})$ 12.5 Hz, CH_3]. Evaporation of the mother liquor after removal of this isomer gave a second isomer (88 mg, 35%), m.p. 162–165°, ν_{max} 1203 cm^{-1} , τ 2.5–3.0 (14H, m, aromatic), 5.01, 5.36, 5.40, and 5.57 (2H, two doublets, benzylic), and 8.72 [3H, d, $J(^{31}\text{P},\text{H})$ 12 Hz, CH_3].

Dimer of 2-Methyl-1,3-diphenylbenzo[c]phosphole 2-Oxide.—The foregoing product (95 mg, 0.3 mmol), *N*-bromosuccinimide (107 mg, 0.6 mmol), benzoyl peroxide (ca. 1 mg), and carbon tetrachloride (5 ml) were stirred at 30° with illumination (2 h). The product was cooled in ice and filtered, and the filtrate was evaporated under reduced pressure. This product, copper powder (160 mg), and benzene (7 ml) were heated under reflux in nitrogen (1.5 h). The product was filtered; the filtrate was evaporated under reduced pressure on a water-bath and subjected to layer chromatography on silica. Development with benzene-acetone (1:1) gave the dimer (21) (54 mg, 57%) as yellow prisms, m.p. 266–267° (from benzene-petroleum) [Found: C, 79.3; H, 5.7; M (osmometer), 587. $\text{C}_{42}\text{H}_{34}\text{P}_2\text{O}_2$ re-

quires C, 79.7; H, 5.4%; M , 633], ν_{max} 1195 cm^{-1} , λ_{max} 384 nm (ϵ 5330), τ 2.3–3.1 (24H, m, aromatic), 3.76 (1H, d, J 10.5 Hz), 4.02 (1H, double triplet, J 10.5 and 3 Hz), 4.40 (1H, double triplet, J 8.5 and 3 Hz), 5.05–5.35 (1H, m), and 8.56, 8.77, 8.95, and 9.16 (6H, two doublets, CH_3), m/e 316.0995 ($\text{C}_{21}\text{H}_{17}\text{PO}$) (100%).

Osmium Tetroxide Hydroxylation of the Dimer (20).—The dimer (334 mg, 0.45 mmol) and dry pyridine (4.4 ml) were stirred at 20° (41 h). After dilution with dichloromethane the product was washed with hydrochloric acid (2*N*), washed with water, dried (MgSO_4), and evaporated to give the osmate ester. This was dissolved in chloroform-ethanol and the solution saturated with hydrogen sulphide. After 15 min the product was heated to boiling, cooled, and filtered (filter-aid), and the filtrate was evaporated under reduced pressure. Filtration through silica in chloroform-ethanol (23:2) gave the diol [22; $\text{X}^1 = \text{X}^2 = \text{P}(\text{O})\text{Ph}$] (278 mg, 80%) as yellow needles, m.p. 292–293° (from ethyl acetate) (Found: C, 78.8; H, 5.25. $\text{C}_{52}\text{H}_{40}\text{P}_2\text{O}_4$ requires C, 79.0; H, 5.1%), ν_{max} 1164 and 1202 ($\text{P}=\text{O}$) and 3470 and 3360sh cm^{-1} (OH), λ_{max} 375 nm (ϵ 6040).

Osmium Tetroxide Hydroxylation of the Dimer (21).—The dimer (273 mg, 0.43 mmol), osmium tetroxide (110 mg, 0.43 mmol), and pyridine (4.5 ml) were stirred at 20° (20 h). Work-up as just described and layer chromatography on silica in chloroform-ethanol (9:1) gave the diol [22; $\text{X}^1 = \text{X}^2 = \text{P}(\text{O})\text{Me}$] (148 mg), m.p. 297–298.5° (from ethanol) (Found: M^+ , 666.2088. $\text{C}_{42}\text{H}_{36}\text{P}_2\text{O}_4$ requires M , 666.2089), ν_{max} 3440 and 3350sh cm^{-1} , λ_{max} 368 nm (ϵ 7170).

Reaction of the Diol [22; $\text{X}^1 = \text{X}^2 = \text{P}(\text{O})\text{Ph}$] with Lead Tetra-acetate.—The diol (122 mg, 0.155 mmol), lead tetra-acetate (75 mg; moist with acetic acid), and benzene (18 ml) were stirred at 30° (1 h). After addition of sulphuric acid (0.2*N*; 5.5 ml) the product was filtered and the filtrate washed with water, dried (MgSO_4), and evaporated. The residue was subjected to layer chromatography on silica. Development with chloroform-ethanol (9:1) gave a yellow oil (119 mg) from which was obtained the supposed aldol (23) (61 mg, 50%), m.p. 265–268° (from ether), ν_{max} 1204, 1706, and 3500w cm^{-1} , λ_{max} 390 nm (ϵ 7700), τ –0.3 (1H, s, CHO), 2.0–3.4 (34H, m, aromatic), 4.2 (1H, apparent t), 4.58–4.92 (1H, two multiplets, J 10 Hz, $\text{CH}\cdot\text{OH}$, simplified to one multiplet at τ 4.66–4.83 with D_2O), and 6.4 (1H, d, J 10 Hz, OH, removed with D_2O). The mother liquors obtained after removal of the aldol probably contained the expected dialdehyde cleavage product, for the n.m.r. spectrum showed τ 0.07 (1H, s, CHO), 1.6 (1H, d, J 1.5 Hz, $\text{CH}\cdot\text{CHO}$), 2.3–3.3 (34H, m, aromatic), 4.6 (1H, dd, J 4.5 and 12 Hz), and 5.3 (1H, dd, J 3 and 12 Hz).