Synthesis of Substituted Dibenzophospholes. Part 7.[1] Regiospecific Synthesis of 4,6-Diaryl-3,7-dioxydibenzophospholes from 2,2'4,4'-Tetranitrobiphenyl

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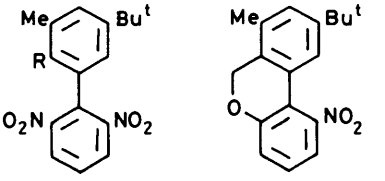
3,3'''-Dimethyl-2',2'',4'',6'-tetranitro-5,5'''-di-t-butyl-*m*-quaterphenyl did not undergo selective alkoxydenitration at the 2' and 4'' positions, but when acetoxymethyl groups were placed at the 2 and 2''' positions, treatment with sodium methoxide caused regiospecific cyclization at these positions and formation of a bibenzochromenyl. Other reagents led to a mixture of two regioisomers. The two remaining nitro groups were replaced *via* a diamine and a di-iodide by a phosphinic ester bridge. The pyran rings could then be opened by boron tribromide to afford a 4,6-diaryldibenzophosphole. The two bromomethyl groups in this intermediate were converted after acetylation into dimethylphosphonomethyl groups and one atropisomer (the *meso* isomer) was isolated. Some analogous experiments in the biphenyl series are reported.

In the preceding paper,[1] some success was reported in effecting selective replacement of the 2' and 4'' nitro groups in 2',2'',4'',6'-tetranitro-*m*-quaterphenyls by alkoxy groups. The procedures there reported did not promise high yields in the case of the quaterphenyl (**10**), though the desired regioisomers were obtained with alkoxides from propan-2-ol and 2,4-dimethylpentan-3-ol. The present paper describes a solution to this problem combined with the introduction of modifiable substituents at the 2 and 2''' positions of the quaterphenyl, leading to a desired chirality (due to atropisomerism) in the eventual products.

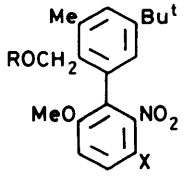
The additional substitution was explored first in the biphenyl series. The biphenyl (**1**)[1] was easily chloromethylated in the 2-position and conversion of the product (**2**) into the acetoxymethyl analogue (**3**) presented no difficulty. Brief treatment of this with potassium carbonate in methanol at room temperature gave the hydroxymethyl derivative (**4**) but at reflux the benzo[*c*]chromene (**5**) was formed, slowly but almost quantitatively. This is a new synthesis of this heterocycle and the mildness of the reagent is remarkable. Similar conditions applied to the chloromethyl derivative (**2**) gave a minor proportion of the chromene, the major product being the methoxymethyl compound (**6**). One of the nitro groups in this compound was replaced smoothly by a methoxy group by a procedure described previously.[2] The product (**7**), when iodinated in the usual manner,[2] suffered acetolysis as well, giving the acetoxymethyl compound (**8**). The analogous hydroxymethyl compound (**9**) was produced from (**8**) by solvolysis on an alumina column. Attempted iodination of the benzo[*c*]chromene (**5**) also led to attack at the benzyl ether function and entry into the quaterphenyl series by way of these intermediates was not attempted further.

Chloromethylation of the quaterphenyl (**10**) gave in 95% yield, the bischloromethyl derivative (**11**) and conversion of this into the bisacetoxymethyl analogue (**12**) by potassium acetate in hexamethylphosphoric triamide was equally smooth. Potassium carbonate in boiling methanol did indeed convert this intermediate, obtained as a mixture of atropisomers, into a bibenzo[*c*]chromenyl, but analysis by high-performance liquid chromatography (h.p.l.c.) showed that this was a mixture of the desired product (**13**) with an almost equal proportion of the regioisomer (**14**). However, sodium methoxide in 1,2-dimethoxyethane gave almost quantitative conversion into the bibenzochromenyl (**13**), homogeneous by h.p.l.c. We welcomed this difference, but cannot explain it. The methylene protons in (**13**) gave a split n.m.r. signal; this suggests that the benzochromene rings are not planar and do not oscillate very rapidly between non-planar forms. No indication of isolable atropisomers was seen, however.

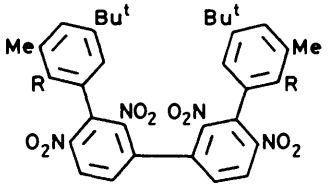


(**1**) R = H
(**2**) R = CH_2Cl
(**3**) R = CH_2OAc
(**4**) R = CH_2OH
(**6**) R = CH_2OMe

(**5**)



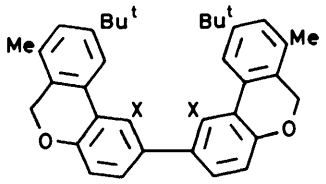
(**7**) R = Me, X = H
(**8**) R = Ac, X = I
(**9**) R = H, X = I



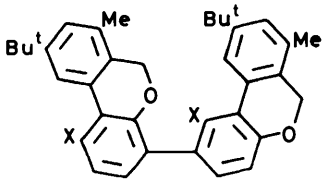
(**10**) R = H
(**11**) R = CH_2Cl
(**12**) R = CH_2OAc

Reduction of the two nitro groups by hydrazine and Raney nickel gave a 90% yield of the diamine (**15**); when the mixture of bibenzochromenyls was reduced, the isomeric diamine (**16**) was also isolated. The next step, formation of the di-iodide (**17**), was the only one for which a high yield could not be obtained. The best procedure, found after many trials, was a variant of our bis-diazonium iodomercurate method,[3] which gave a 50% yield of recrystallized material. The principal by-product was the benzo[*c*]cinnoline derivative (**18**), which was also isolated from some reductions of the dinitro compound (**13**).

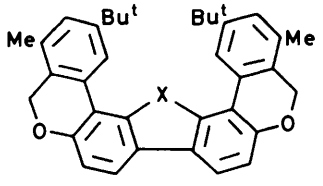
The di-iodide (**17**) readily afforded the cyclic phosphinic ester (**19**) by the procedure already[3] established: butyl-lithium; phosphorus trichloride; water; hydrogen peroxide; diazomethane. Analogous substances had been made by a different synthesis,[4] but not in useful quantity since the final step was an



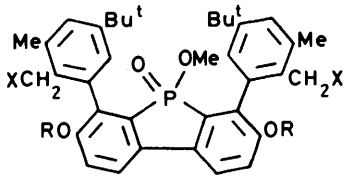
(13) X = NO_2
(15) X = NH_2
(17) X = I



(14) X = NO_2
(16) X = NH_2



(18) X = —N=N—
(19) X = >P(O)OMe



(20) R = H, X = Br
(21) R = Ac, X = Br
(22) R = Ac, X = $P(O)(OMe)_2$

inefficient photolysis. With more material available, alteration of the pyran rings could be explored. Boron tribromide, followed by aqueous work-up, led smoothly to the dibromo diol (**20**). This was unstable, the pyran rings being easily reformed; but acetylation (for which it was necessary to use collidine rather than pyridine) gave a more stable product (**21**). When this was heated with trimethyl phosphite in benzene the diphosphonic ester (**22**) was produced by a double Arbuzov reaction. A single atropisomer was isolated by crystallization, and high resolution n.m.r. spectroscopy showed this to be a single ester of the *meso* form (in compounds of this type, there are two *meso* esters and one racemic ester).

This satisfactory synthesis is now being used to prepare larger amounts of (**22**) and of its racemic analogue, and thence to make water-soluble derivatives for testing as catalysts of alkene hydration.

Experimental

General directions are as described in Part 5.[5]

2-Chloromethyl-3-methyl-2′,6′-dinitro-5-t-butylbiphenyl.—The methyldinitro-t-butylbiphenyl (**1**) (2.5 g; described in the preceding paper) in chloromethyl methyl ether (28 ml) was cooled in ice and aluminium chloride (4 g) was added carefully during 10 min. The mixture was stirred overnight without cooling, then poured on ice. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed ($NaHCO_3$ and brine), dried ($MgSO_4$), and evaporated. Crystallization from ether then gave the *chloromethylbiphenyl* (**2**) (2.75 g), m.p. 181.5—183 °C (Found: C, 59.4; H, 5.2; N, 7.7. $C_{18}H_{19}ClN_2O_4$ requires C, 59.6; H, 5.3; N, 7.7%); δ_H (60 MHz) 1.28 (9 H, s,), 2.45 (3 H, s), 4.25 (2 H, br s), 6.96 (1 H, br s), 7.23 (1 H, br s), and 7.6—8.2 (3 H, m).

3-Methyl-2′,6′-dinitro-5-t-butylbiphenyl-2-ylmethyl Acetate.—The above chloromethylbiphenyl (2.64 g) was heated under reflux with acetic acid (310 ml) and potassium acetate (14.4 g) for 17 h. The cooled mixture was added to ice–water and the white precipitate was collected, dried, and recrystallized from methanol to give the *acetoxymethyl compound* (**3**) (2.66 g) as plates, m.p. 128—129 °C (Found: C, 62.0; H, 5.5; N, 7.2. $C_{20}H_{22}N_2O_6$ requires C, 62.2; H, 5.7; N, 7.3%); δ_H (60 MHz; CCl_4) 1.23 (9 H, s), 1.86 (3 H, s), 2.43 (3 H, s), 4.73 (2 H, br s), 6.87 (1 H, br s), 7.13 (1 H, br s), 7.6 (1 H, dd, $J_{1,2}$ 7 Hz), and 7.85—8.0 (2 H, m).

3-Methyl-2′,6′-dinitro-5-t-butylbiphenyl-2-ylmethanol.—The acetoxymethyl compound (**3**) (386 mg) was dissolved in dry methanol (40 ml) and dry potassium carbonate (1.38 g) was added at 0 °C. After being stirred without cooling for 2 h the mixture was diluted with water. The solid precipitate was collected and dissolved in warm dichloromethane which was dried ($MgSO_4$) and evaporated. Crystallization from methanol then gave the *alcohol* (**4**) (291 mg) as very pale yellow plates, m.p. 182—183 °C (Found: C, 63.1; H, 5.7; N, 8.1. $C_{18}H_{20}N_2O_5$ requires C, 62.8; H, 5.9; N, 8.1%).

7-Methyl-1-nitro-9-t-butyl-6H-benzo[c]*chromene.*—The acetoxymethyl compound (**3**) (1.16 g) was boiled for 26 h under reflux with methanol (120 ml) and potassium carbonate (4.14 g). The cooled mixture was diluted with water and the bright yellow precipitate was collected, dried, and recrystallized from methanol to give the *chromene* (**5**) (857 mg) as large yellow needles, m.p. 143 °C (Found: C, 73.0; H, 6.7; N, 5.1. $C_{18}H_{19}NO_3$ requires C, 72.7; H, 6.4; N, 4.7%); δ_H (60 MHz) 1.28 (9 H, s), 2.31 (3 H, s), 5.06 (2 H, s), and 7.1—7.3 (5 H, m); *m/z* 297 (M^+).

2-Methoxymethyl-3-methyl-2′,6′-dinitro-5-t-butylbiphenyl.—The chloromethyl compound (**2**) (656 mg) was boiled under reflux with methanol (50 ml) and potassium carbonate (1.25 g) for 72 h. The methanol was evaporated and replaced by warm dichloromethane. Filtration through Celite and evaporation, followed by trituration with ether, gave the *methoxymethyl compound* (**6**) (448 mg) as white plates, m.p. 192—193 °C (Found: C, 63.8; H, 6.4; N, 8.0. $C_{19}H_{22}N_2O_5$ requires C, 63.7; H, 6.2; N, 7.8%); δ_H (60 MHz) 1.30 (9 H, s), 2.4 (3 H, s), 3.06 (3 H, s), 4.06 (2 H, s), 7.03 (1 H, br s), 7.23 (1 H, br s), 7.60 (1 H, dd, $J_{1,2}$ 7 Hz), 7.84 (1 H, br s), and 7.95 (1 H, br s). The ether-soluble portion on crystallization from methanol afforded the above chromene (**5**) (113 mg) as the other product.

6′-Methoxy-2-methoxymethyl-3-methyl-2′-nitro-5-t-butylbiphenyl.—The methoxymethyldinitrobiphenyl (**6**) (2 g) was dissolved in hexamethylphosphoric triamide (HMPT; 24 ml) at room temperature and sodium methoxide (0.71 g) was added. After 17 h the deep purple solution was poured into dilute acid (5% HCl) and the product was extracted with ethyl acetate. The extracts were washed (5% HCl then brine), dried ($MgSO_4$), and

evaporated. The residue in chloroform–hexanes (1:1 v/v) was passed through a small column of alumina, to yield a colourless oil which crystallized from methanol to furnish the *methoxynitrobiphenyl* (**7**) (1.67 g), m.p. 96—97 °C (Found: C, 70.3; H, 7.7; N, 4.0. $C_{20}H_{25}NO_4$ requires C, 70.0; H, 7.3; N, 4.1%); δ_H (60 MHz) 1.28 (9 H, s), 2.42 (3 H, s), 3.08 (3 H, s), 3.73 (3 H, s), 4.12 (2 H, dd, not resolved), 6.88 (1 H, br s), 7.18 (3 H, m), and 7.36 (1 H, d, *J* 4.5 Hz); *m/z* 343 (M^+).

3′-Iodo-6′-methoxy-3-methyl-2′-nitro-5-t-butyl-biphenyl-2-ylmethanol and its Acetate.—The above methoxynitrobiphenyl (**7**) (411 mg) in acetic acid–water–sulphuric acid (100:10:3; 11 ml) with iodine (144 mg) and periodic acid (50%; 0.11 ml) was stirred and heated at 70 °C under nitrogen for 28 h. The excess of iodine was destroyed ($NaHSO_3$) and the mixture was added to water and dichloromethane. The organic extract was washed well with water, dried ($MgSO_4$), and evaporated. The residue was put on a column of silica from which elution with chloroform–hexane (7:3 v/v) gave the *iodoacetate* (**8**) (480 mg), m.p. 149—150 °C after crystallization from ethanol (Found: C, 50.4; H, 4.8; N, 2.9. $C_{21}H_{24}INO_5$ requires C, 50.7; H, 4.9; N, 2.8%); δ_H (60 MHz; CCl_4) 1.30 (9 H, s), 1.86 (3 H, s), 2.40 (3 H, s), 3.70 (3 H, s), 4.76 (2 H, br s), 6.73 (1 H, d, *J* 8.5 Hz), 6.83 (1 H, br s), 7.16 (1 H, br s), and 7.72 (1 H, d, *J* 8.5 Hz); *m/z* 482 (M^+ − Me; $M^+ < 1\%$). Column chromatography of the crude product on alumina led to extensive hydrolysis and the *alcohol* (**9**) was isolated, m.p. 209 °C (ethanol) (Found: C, 50.2; H, 5.1; N, 3.1. $C_{19}H_{22}INO_4$ requires C, 50.1; H, 4.9; N, 3.1%); δ_H (60 MHz; CCl_4) 1.30 (9 H, s), 2.46 (3 H, s), 3.72 (3 H, s), 4.18 (1 H, br s, OH), 4.22 (2 H, br s), 6.73 (1 H, d, *J* 8 Hz), 6.75 (1 H, br s), 7.16 (1 H, br s), and 7.83 (1 H, d, *J* 8 Hz); *m/z* 455 (M^+).

2,2‴-Bis(chloromethyl)-3,3‴-dimethyl-2′,2″,4″,6′-tetranitro-5,5‴-di-t-butyl-m-quaterphenyl.—The tetranitrobiphenyl (**10**) (see the preceding paper; 11 g) in chloromethyl ether (50 ml) was stirred under nitrogen and cooled in ice during the addition (15 min) of aluminium chloride (14.4 g). Cooling was discontinued and after 6 h the mixture was poured onto ice (250 g) and the product was taken into ethyl acetate which was washed ($NaHCO_3$, then brine), dried ($MgSO_4$), and evaporated. The *bis-chloromethyl compound* (**11**) (11.93 g) crystallized from ethanol as pale yellow needles, m.p. 247—249 °C (Found: C, 59.3; H, 5.2; N, 7.8. $C_{36}H_{36}Cl_2N_4O_8$ requires C, 59.8; H, 5.0; N, 7.7%); δ_H (60 MHz) 1.32 (18 H, s), 2.44 (6 H, s), 4.35 (4 H, m), 7.12 (2 H, br s), 7.34 (2 H, br s), 7.65 (2 H, d, *J* 9 Hz), and 8.18 (2 H, d, *J* 9 Hz).

3,3‴-Dimethyl-2′,6′,2″,4″-tetranitro-5,5‴-di-t-butyl-(m-quaterphenyl-2,2‴-diyldimethyl) Diacetate.—The above chloromethyl compound (**11**) (6.5 g) in dry HMPT (total 160 ml) was added under nitrogen to a mixture of potassium acetate (dried *in situ* at 120 °C/0.5 mmHg for 2.5 h; 3 g) and HMPT (50 ml). The mixture was stirred at 50 °C (bath) for 17 h, then poured into a mixture (600 ml) of ice and hydrochloric acid (5%) and stirred for 30 min. The white precipitate was collected and dried at low pressure over silica gel—a slow process. Crystallization from ethanol at 0 °C then gave the *diacetate* (**12**) (6.6 g) as a mixture of atropisomers (Found: C, 62.1; H, 5.6; N, 7.4. $C_{40}H_{42}N_4O_{12}$ requires C, 62.3; H, 5.5; N, 7.3%). The mixture could be separated by fractional crystallization into two isomers, m.p. 210—212 and 171—174 °C. The higher-melting isomer (more polar on t.l.c.) showed δ_H (60 MHz; CCl_4) 1.35 (18 H s), 1.95 (6 H, s), 2.46 (6 H, s), 4.5—4.95 (4 H, m), 6.99 (2 H, br s), 7.20 (2 H, br s), 7.59 (2 H, d, *J* 9 Hz), and 8.10 (2 H, d, *J* 9 Hz); the other showed δ_H 1.38 (18 H, s), 1.95 (6 H, s), 2.50 (6 H, s), 4.5—5.1 (4 H, m), 7.05 (2 H, br s), 7.25 (2 H, br s), 7.60 (2 H, d, *J* 9 Hz), and 8.15 (2 H, d, *J* 9 Hz).

1,1′-Dimethyl-5,5′-dinitro-3,3′-di-t-butyl-10H,10′H-9,9′-dioxa-6,6′-biphenanthrenyl.—(*a*) The diacetate (**12**) (3.85 g) in 1,2-dimethoxyethane (75 ml) under nitrogen was cooled in ice during the addition of sodium methoxide (0.77 g), then left without cooling overnight. Water and ethyl acetate were then added and the aqueous layer was saturated with sodium chloride and extracted thoroughly with ethyl acetate. The organic layers were washed (brine), dried ($MgSO_4$), and evaporated. Crystallization from ether then gave yellow needles, m.p. 236—238 °C, of the *bichromenyl* (**13**) (2.81 g) which was homogeneous by h.p.l.c. [Spherisorb 5μ; ethyl acetate–hexanes (1:9)] (Found: C, 73.1; H, 6.5; N, 4.8. $C_{36}H_{36}N_2O_6$ requires C, 73.0; H, 6.1; N, 4.7%); δ_H (60 MHz) 1.28 (18 H, s), 2.30 (6 H, s), 5.10 (4 H s), 7.1—7.23 (6 H, m), and 7.30 (2 H, br s); *m/z* (c.i. + ve; NH_3) 592 (M^+).

(*b*) The diacetate (8.01 g) in dimethylformamide (150 ml) and methanol (160 ml) was treated with potassium carbonate (8 g) in water (20 ml). The dark red solution was heated under reflux for 65 h. Methanol was removed under reduced pressure and the residue was poured into ice–water (500 ml). Extraction with dichloromethane yielded a yellow solid which was crystallized from ethanol. The bright yellow needles (total 5.94 g), m.p. 236—240 °C, were shown by h.p.l.c. to be a 1:1 mixture of the above product with the non-symmetrical bichromenyl (**14**).

1,1′-Dimethyl-3,3′-di-t-butyl-10H,10′H-9,9′-dioxa-6,6′-biphenanthrenyl-5,5′-diamine.—The dinitrobichromenyl (**13**) (2.4 g) dissolved in dry 2-ethoxyethanol (140 ml) was heated to 75 °C. Dry nitrogen was bubbled through the solution for 1 h, then Raney nickel (freshly made; *ca.* 2 g) was added with stirring which was continued for a further 1 h before the addition, during 1 h, of hydrazine hydrate (10 ml). Further nickel (*ca.* 1 g) was added followed by more hydrazine hydrate (4 ml), added over 15 min. Finally the mixture was stirred at 90 °C for 2 h, then filtered hot (Celite) and the filter washed well with hot ethanol, then with water. The filtrate was diluted with water and the solid precipitate was collected, dried, and crystallized from ether to yield the *diamine* (**15**) (1.92 g) as prisms, m.p. 235—237 °C (Found: C, 81.1; H, 7.8; N, 5.3. $C_{36}H_{40}N_2O_2$ requires C, 81.2; H, 7.6; N, 5.3%); δ_H (60 MHz) 1.32 (18 H, s), 2.35 (6 H, s), 4.27 (4 H, br s), 5.03 (4 H, s), 6.59 (2 H, d, *J* 8 Hz), 7.0—7.3 (4 H, m), and 8.19 (2 H, br s); *m/z* (c.i. + ve; NH_3) 533 (MH^+).

When the mixture of the bichromenyls (**13**) and (**14**) was put through a similar procedure, column chromatography [silica; ethyl acetate–hexanes (1:9)] gave, as the more polar product, the isomeric *1,1′-dimethyl-3,3′-di-t-butyl-10H,10′H-9,9′-dioxa-6,8′-biphenanthrenyl-5,5′-diamine* (**16**), m.p. 260 °C (decomp.) (from dichloromethane–ether) (Found: C, 80.9; H, 7.8; N, 5.3. $C_{36}H_{40}N_2O_2$ requires C, 81.2; H, 7.6; N, 5.3%); δ_H (60 MHz) 1.33 and 1.38 (18 H, 2 overlapping s), 2.32 and 2.38 (6 H, 2 overlapping s), 4.18 (4 H, br s), 4.98 (4 H, m), 6.57 (2 H, d, *J* 8.5 Hz), 6.85—7.1 (4 H, m), and 8.20 (2 H, br s); *m/z* 532 (M^+).

5,5′-Di-iodo-1,1′-dimethyl-3,3′-di-t-butyl-10H,10′H-9,9′-dioxa-6,6′-biphenanthrenyl.—The diamine (**15**) (1.8 g) dissolved in dimethylformamide (40 ml) was cooled (0 °C) and stirred while sulphuric acid (7M; 11.8 ml) was added dropwise. The temperature was lowered to 10 °C and an ice-cold solution of sodium nitrite (1.46 g) in water (25 ml) was added slowly enough to keep the temperature below −5 °C. After a further 30 min below −5 °C, the mixture was treated with a few drops of ether to control foaming and sulphamic acid (1.7 g) in water (12 ml) was added during 30 min. The orange suspension of the bis-diazonium salt was transferred by pipette to a stirred, ice-cooled solution of mercury(II) iodide (3.58 g) and potassium iodide (5.5 g) in water (34 ml) containing some Celite (*ca.* 0.5 g). Dilute sulphuric acid (2.5%; 34 ml) was used to complete the transfer.

The mixture was allowed to warm slowly to room temperature, with control of foaming as necessary, left overnight, and finally warmed briefly to 50 °C. The brown solid was collected, dried at 0.1 mmHg over silica, then suspended in a solution of dried sodium iodide (20 g) in dry degassed dimethyl sulphoxide (50 ml) and stirred at 125 °C for 17 h. After the addition of water the precipitate was filtered off and washed with water followed by dilute sodium thiosulphate. The filter was then washed with toluene which was then filtered through cotton and evaporated to 15 ml. Toluene (5 ml) and hexanes (7 ml) were added and the solution was applied to a column of silica (150 mm × 25 mm). Toluene–hexanes (3:1 v/v) eluted the required product after a small fast-running fraction and crystallization from ethyl acetate gave the *di-iodide* (**17**) (1.25 g) as colourless prisms, m.p. 258 °C (decomp.) (Found: C, 57.3; H, 4.7. $C_{36}H_{36}I_2O_2$ requires C, 57.3; H, 4.8%); δ_H (60 MHz) 1.32 (18 H, s), 2.35 (6 H, s), 4.98 (4 H, s), 7.0—7.2 (6 H, m), and 8.10 (2 H, br s); *m/z* 754 (M^+). Further elution of the column gave fractions containing the cinnoline (455 mg); crystallization from ethanol gave 5,12-*dihydro*-4,13-*dimethyl*-2,15-*di*-*t*-*butyl*-17,18-*diaza*-6,11-*dioxa*-*dibenzo*[a,o]*picene* (**18**) as deep yellow needles, m.p. 310 °C (Found: C, 81.5; H, 7.0; N, 5.0. $C_{36}H_{36}N_2O_2$ requires C, 81.8; H, 6.9; N, 5.3%); δ_H (60 MHz) 1.42 (18 H, s), 2.40 (6 H, s), 5.37 (4 H, s), 7.28 (2 H, br s), 7.60 (2 H, d, *J* 9 Hz), 8.44 (2 H, d, *J* 9 Hz), and 9.15 (2 H, d, *J* 1 Hz); *m/z* 528 (M^+).

Methyl 1,1′-*Dimethyl*-3,3′-*di*-*t*-*butyl*-10H,10′H-9,9′-*dioxa*-6,6′-*biphenanthrenyl*-5,5′-*diylphosphinate*.—The above di-iodide (**17**) (0.8 g) was dissolved under nitrogen in tetrahydrofuran (freshly distilled from $LiAlH_4$; 32 ml), cooled below −70 °C, and treated with butyl-lithium (1.6M; 1.3 ml), added by syringe. The yellow solution was stirred and cooled for 2 h, then phosphorus trichloride (freshly distilled from zinc in a stream of nitrogen; 0.3 ml) was added. The transiently red, then bright yellow solution was stirred for 2 h; after addition of water (4 ml), cooling and nitrogen cover were discontinued, and after another 30 min the mixture was made alkaline to litmus (8% sodium hydroxide; *ca.* 15 ml required) and hydrogen peroxide (30%; 8 ml) was added. This mixture was stirred for 17 h, then poured into hydrochloric acid (5%; 100 ml). The aqueous layer was extracted with dichloromethane and the organic solutions were washed (10% aqueous $NaHSO_3$ then brine), dried ($MgSO_4$), and filtered, washing the drying agent well with warm dichloromethane. Removal of the solvents left the crude phosphinic acid which was slurried in ether (10 ml) and centrifuged. This process was repeated and left the apparently homogeneous (t.l.c.) acid as a yellow solid (365 mg), which was covered with ether–dichloromethane (20 ml; 1:1 v/v) and treated with excess of diazomethane. Removal of solvent and crystallization from ether gave the *phosphinic ester* (**19**) (360 mg) as yellow clusters, m.p. 320 °C (decomp.) (Found: C, 76.7; H, 6.8. $C_{37}H_{39}PO_4$ requires C, 76.8; H, 6.8%); δ_H (60 MHz) 1.38 (18 H, s), 2.26 (6 H, s), 3.28 (3 H, d, *J* 11.5 Hz), 5.02 (4 H, br s), 7.0—7.2 (4 H, m), 7.50 (2 H, dd, *J* 8, 3 Hz), and 8.86 (2 H, br s); *m/z* 578 (100%; M^+).

4,6-*Bis*-(2-*bromomethyl*-3-*methyl*-5-*t*-*butylphenyl*)-5-*methoxy*-*dibenzophosphole*-3,7-*diol* 5-*Oxide*.—The above phosphinic ester (**19**) (75 mg) in dry dichloromethane (4 ml) was cooled under nitrogen to −100 °C and a solution of boron tribromide in dichloromethane (1M; 0.52 ml) was added dropwise during 15 min. The mixture was allowed to warm very slowly to 0 °C during 17 h. Ice–water (10 ml) was added and the mixture was stirred well for 1 h. Dichloromethane (10 ml) was added and the layers were separated after vigorous shaking. The aqueous layer was further extracted with dichloromethane and the combined organic layers were washed (brine), dried ($MgSO_4$), and evaporated. The residue, a mixture of phosphinic acids and esters, was dissolved in dry ether (30 ml) and treated with ethereal diazomethane (0.5M; 0.4 ml). at 0 °C. After 1 h at room temperature the mixture was evaporated on a warm water-bath and then under reduced pressure. Recrystallization from ether than gave, as straw-coloured clusters, one rotamer of the *dihydroxydibromo ester* (**20**) (52 mg); $\nu_{max.}$($CHCl_3$) 3 530, 2 965, 1 600, 1 460, 1 440, 1 270, 1 200, and 1 040 cm^{-1}; δ_H (60 MHz) 1.25 (18 H, s), 2.42 (6 H, s), 2.63 (3 H, d, *J* 11.5 Hz), 4.46 (4 H, s), 7.0 (2 H, m), 7.2 (4 H, s), 7.55 (2 H, m); *m/z* 564 (M^+ − HBr − CH_3Br). The substance was not stable to chromatography and could not be stored.

4,6-*Bis*-(2-*bromoethyl*-3-*methyl*-5-*t*-*butylphenyl*)-5-*methoxy*-*dibenzophosphole*-3,7-*diyl Diacetate* 5-*Oxide*.—To the above dihydroxy dibromo ester (**20**) (100 mg; not recrystallized) in benzene (3 ml) and acetic anhydride (2 ml), 2,4,6-trimethylpyridine (2 ml) was added during 5 min. After 17 h the mixture was added to ice-cold hydrochloric acid (5%). The organic layer together with an ethyl acetate extract of the aqueous layer was washed (brine), dried ($MgSO_4$), and evaporated, finally under high vacuum. The residue on crystallization from ether gave the *dibromo ester diacetate* (**21**) (103 mg) as white clusters; m.p. 234—235 °C (Found: C, 59.6; H, 5.8. $C_{41}H_{45}Br_2O_4P$ requires C, 59.7; H, 5.5%); δ_H (90 MHz) 1.21 (18 H, s), 1.89 (6 H, s), 2.45 (6 H, s), 2.62 (3 H, d, *J* 11.5 Hz), 4.36 and 4.55 (4 H, AB system, *J* 12 Hz), 6.95 (2 H, d, *J* 1 Hz), 7.19 (2 H, d, *J* 1 Hz), 7.45 (2 H, d, *J* 8.5 Hz), and 7.85 (2 H, dd, *J* 8.5, 4 Hz).

meso-4,6-*Bis*-(2-*dimethoxyphosphosphorylmethyl*-3-*methyl*-5-*t*-*butylphenyl*)-5-*methoxydibenzophosphole*-3,7-*diyl Diacetate* 5-*Oxide*.—The above dibromo ester acetate (**21**) (34 mg) in dry benzene (1 ml) and trimethyl phosphite (1 ml) were heated under reflux (bath at 110 °C) for 24 h. The product was partitioned between ethyl acetate and water and the ethyl acetate layer was washed (brine), dried ($MgSO_4$), and evaporated. The crude product after treatment with ethereal diazomethane was chromatographed on a silica column which was eluted first with ethyl acetate, and then with methanol–ethyl acetate (1:9 v/v) which eluted the *bisphosphonomethyl ester diacetate* (**22**) (15 mg) as a white non-crystalline hygroscopic solid (collected after trituration with ether), m.p. 210—215 °C (Found: C, 56.8; H, 6.6. $C_{45}H_{57}O_{12}P_3 \cdot 4H_2O$ requires C, 56.6; H, 6.8%); δ_H (360 MHz) 1.19 (18 H, s), 1.65 (br s, H_2O), 1.93 (6 H, s), 2.46 (6 H, s), 2.54 (3 H, d, *J* 12 Hz), 3.20—3.38 (4 H, 2 overlapping AB systems, *J* 16 Hz), 3.53 (6 H, d, *J* 11 Hz), 3.57 (6 H, d, *J* 11 Hz), 6.86 (2 H, s), 7.14 (2 H, d, *J* 1.6 Hz), 7.36 (2 H, d, *J* 8.5 Hz), and 7.77 (2 H, dd, *J* 8.5, 3.9 Hz); *m/z* (c.i. + ve; NH_3) 883 (MH^+). The less polar fraction from the column contained material (8 mg) in which double signals were seen for the t-butyl, methyl, and acetate hydrogens, and in which only one phosphonomethyl group was apparent.

Acknowledgements

We thank the S.E.R.C. for grants, and Janet Buckingham for expert assistance with the experiments.

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Received 7th April 1986; *Paper* 6/688