# Synthesis of Substituted Dibenzophospholes. Part 8.[1] Synthesis and Resolution of Atropisomers of a 4,6-Diaryldibenzophosphole

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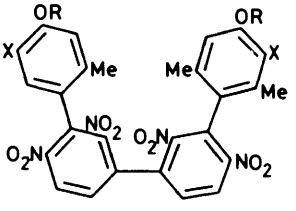
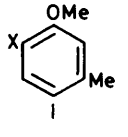
Regiospecific replacement of the 4″- and 6′-nitro groups in a 2′,2″,4″,6′-tetranitro-*m*-quaterphenyl by alkoxy groups has been effected in two ways: (*i*) the dialkali salts of α-oximinoalkanoic acids replaced one nitro group by a hydroxy group; after *O*-alkylation the other alkoxydenitration was effected by sodium benzaldehyde oxime followed by *O*-alkylation; (*ii*) both nitro groups were replaced by treatment with sodium 2,2-dimethoxy-1,2-diphenylethanone oximate followed by acidic hydrolysis, alkaline cleavage, and *O*-alkylation. From the product, synthetic procedures already developed gave 3,7-di-isopropoxy-5-methoxy-4,6-bis-(4-methoxy-2-methyl)dibenzophosphole 5-oxide, separated by chromatography into one racemic and two *meso* forms. The thermal interconversion of the three forms was demonstrated and measured. The racemic form was resolved by high-performance liquid chromatography (h.p.l.c.) on a chiral column.

In the preceding paper[1] a specific solution of the problem of selective alkoxydenitration of the 4″- and 6′-nitro groups in 2′,2″,4″,6′-tetranitro-*m*-quaterphenyls was described: intramolecular cyclization to a bibenzochromenyl. A general solution was still needed, as became evident[2] in experiments with the quaterphenyl (**1**). There, alkoxydenitration with primary alkoxides was quite unselective, and reasonable selectivity was attained only by the use of secondary alkoxides. This procedure had both a general and a specific disadvantage: the yields were low, apparently because secondary alkoxides enter more readily into redox reactions with the nitro groups; and specifically for this series, a distinction in chemical reactivity was desired between the alkoxy groups on the terminal and on the interior rings. We therefore switched to the methoxy analogue (**2**). This was easily made from 2-iodo-5-methoxytoluene (**4**) and tetranitroquaterphenyl by means of copper(I) t-butoxide. A substituted analogue (**3**) was also made from the iodide (**5**), prepared by iodination of a known t-butylmethoxytoluene.



(**1**) R = Pr$^i$, X = H
(**2**) R = Me, X = H
(**3**) R = Me, X = Bu$^t$



(**4**) X = H
(**5**) X = Bu$^t$

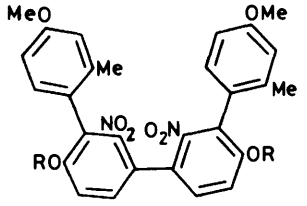
Experiments with the use of secondary alkoxides on the compound (**2**) were even more unpromising than with (**1**), although it was possible to isolate the desired bis(pentan-3-yloxy) derivative (**6**). After many unfruitful attempts to improve the procedure we turned to an apparently unlikely variant already explored in Part 2.[3] There, the use of sodium benzaldehyde oxime to replace nitro by hydroxy (as used by Knudsen and Snyder[4]) had led to a dibenzofuran resulting from primary attack on one of the 'wrong' nitro groups. When this reagent in hexamethylphosphoric triamide (HMPT) was tried with compound (**2**), no dibenzofuran was observed; instead, a mixture of the phenols (**8**) and (**9**) was formed in high yield. Reaction with isopropyl iodide then gave a corresponding mixture of the ethers (**10**) and (**11**), easily analysed by n.m.r. spectroscopy as preponderantly (*ca.* 2:1) the desired isomer (**10**), which could be isolated by direct crystallization in 40% yield. Moreover, when this ether was treated again with sodium benzaldehyde oxime and the product was alkylated without isolation, the dinitro diether (**7**) was obtained in excellent yield without any indication of attack on the 2″-nitro group.

Although this method already gave a better overall result then direct alkoxydenitration, it had the disadvantage of being a two-step process in which separation of the required intermediate, in less than satisfactory yield, was essential. Evidently, in the formation of the phenol:

$$ArNO_2 + PhCH{=}NO^- \longrightarrow NO_2^- + ArON{=}CHPh \longrightarrow ArOH + PhCN,$$

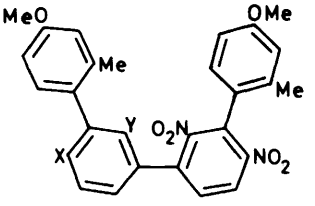
elimination of benzonitrile from the intermediate oxime ether is so fast that the nitro group in the other ring is not attacked at this stage. After formation of the phenoxide anion, the aromatic system is not electrophilic enough to permit further reaction, which can occur only after *O*-alkylation of the phenol. These considerations led us to look for an oxime that would allow formation and cleavage of the oxime ether to be separate processes. This should permit replacement of both nitro groups before a final cleavage leading directly to the diphenol. The first idea was to use α-oximino esters, with which cleavage might be effected by alkaline hydrolysis after oxime ether formation; but the anions of these compounds proved to be suicidal, the ester and oximate groups reacting with each other. α-Oximino acids were then examined, in the hope that decarboxylative

cleavage of the oxime ethers might be slow. That hope was not realized, for the dianions from α-oximino-propanoic, -butanoic, -hexanoic and -4-methylpentanoic acids all gave, with the tetranitroquaterphenyl (**2**), a monohydric phenol only. An unexpected compensation, however, was that these products on



(**6**) R = R$^1$ = $Et_2CH$

(**7**) R = R$^1$ = Pr$^i$



(**8**) X = OH, Y = $NO_2$

(**9**) X = $NO_2$, Y = OH

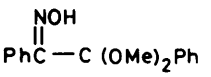
(**10**) X = OPr$^i$, Y = $NO_2$

(**11**) X = $NO_2$, Y = OPr$^i$

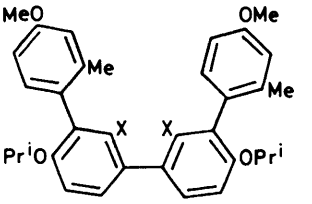
*O*-alkylation all gave the preferred monoether (**10**), with no sign of the isomer (**11**); we thus had a high-yielding regiospecific conversion of (**2**) to (**7**), even though this still required two stages. The dipotassium salt of 2-oximinohexanoic acid was the reagent of choice, since this was most soluble in the HMPT used for the reaction. It was found necessary to use 6—8 equivalents of reagent to obtain complete reaction because the oximinohexanoate dianion, though stable enough alone, decomposed gradually to carbonate and pentanonitrile during the reaction. This requirement made it more convenient to use benzaldehyde oxime, as before, for the second denitration.

The search for a 'one-step' reagent was not abandoned. Anions from benzoin oxime and benzil monoxime both led to the monohydric phenol, with high but not total selectivity for the preferred phenol (**8**). Success was at last attained with the dimethyl acetal (**12**) of benzil monoxime, a compound originally made by Meisenheimer[5] but more conveniently by oximation of benzil monoacetal. A moderate excess of the dianion from this reagent in HMPT gave double denitration of the tetranitroquaterphenyl (**2**); the product was subjected first to acetal hydrolysis (moist acetone–toluene-4-sulphonic acid), then alkaline cleavage (sodium methoxide in methanol, yielding benzonitrile, methyl benzoate, and the dianion of the diphenol), and *O*-alkylation with isopropyl iodide. In this way the dinitro diether (**7**) was obtained without isolation of intermediates and without significant formation of regioisomers, though the overall yield was lower than with the composite process.

The dinitro compound (**7**) was converted into the diamine (**13**), and thence *via* the bis-diazonium iodomercurate into the di-iodide (**14**), by procedures which have become standard in this series. All three compounds are mixtures of three atrop-isomers generated by restricted rotation about the 1:1′ and the 1″:1‴ bonds in the quaterphenyl. One isomer is *meso* and the other two form a racemic pair of enantiomers. When the di-iodide (**14**) was converted by successive reaction with butyl-

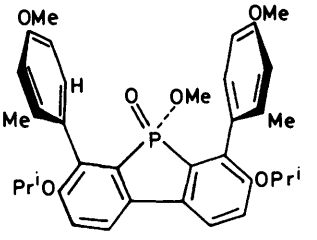


(**12**)



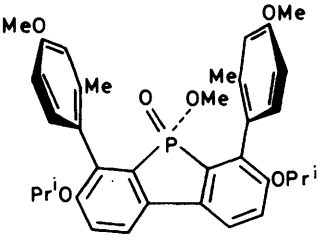
(**13**) X = $NH_2$

(**14**) X = I

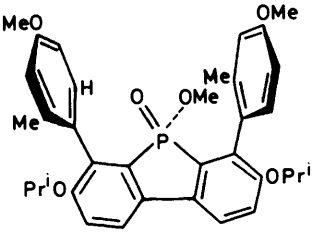


(**15**)

lithium, phosphorus trichloride, water, hydrogen peroxide, and diazomethane into the cyclic phosphinic ester, chromatography of the product separated it into three isomeric products. Two of these were the two possible *meso* esters [(**15**) and (**16**)]; the third was the racemic ester (**17**; only one enantiomer shown). The stereochemistry of the isomers was established by n.m.r. methods; for example, all signals in the two *meso* esters, but not in the racemic ester, are paired. The nuclear Overhauser effect was used to distinguish between (**15**) and (**16**): irradiation of the POMe protons in (**15**) caused enhancement of the signal for the 2- and 2‴-protons which must therefore lie on the same side of the dibenzophosphole ring plane as the phosphinic ester methyl group.



(**16**)



(**17**)

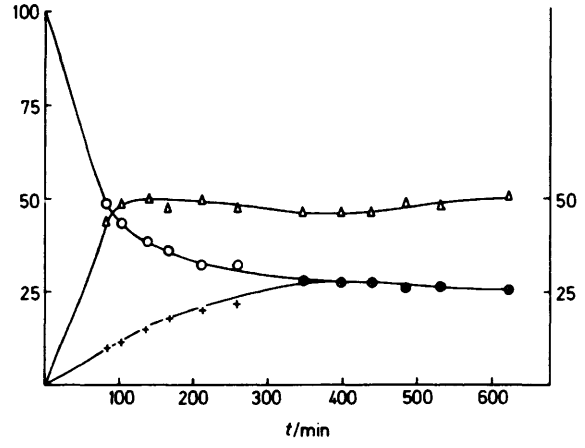



**Figure 1.** Stereomutation of the *meso* ester (**15**) in $C_6D_5NO_2$ at 130 °C. ○ = *meso* ester (**15**); + = *meso* ester (**16**); △ = racemic ester (**17**)

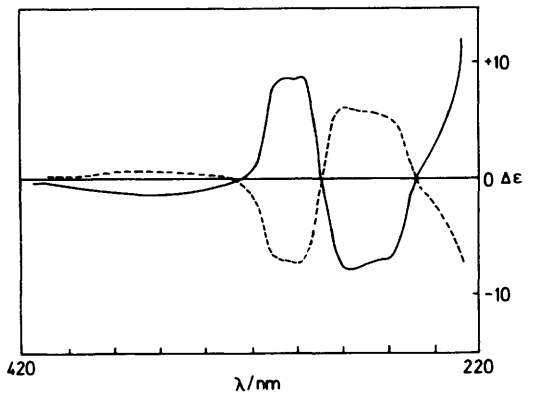



**Figure 2.** Circular dichroism spectra (in methanol) of separated enantiomers comprising the racemic ester (**17**)

The availability of these isomers, and the finding that mixtures of them could be analysed by high-resolution n.m.r. techniques, invited experiments on stereomutation. Starting from one of the *meso* esters, a thermally activated rotation about one of the rotationally hindered bonds would give with equal probability the two enantiomers composing the racemic form. A second rotation would then give, with approximately equal probability, the original *meso* ester and the other *meso* ester. Assuming no significant differences in energy between the four molecular species concerned, the equilibrium composition would be one part each of the two *meso* esters and two parts of the racemic ester. A preliminary experiment controlled by t.l.c. showed that the *meso* ester (**15**) in boiling xylene generated a mixture of itself with (**16**) and (**17**) and that equilibrium was approached after a few hours. A quantitative experiment, conducted in pentadeuterionitrobenzene at 130 °C and monitored at 360 MHz, gave the results incorporated in Figure 1. The calculated activation energy of stereomutation at this temperature is 133 kJ $mol^{-1}$.

The availability of commercial chiral columns for h.p.l.c. prompted an experiment on optical resolution of the racemic ester. In the event, the two enantiomers were readily separated (though not with total resolution in a single passage); the circular dichroism spectra (Figure 2) demonstrate the resolution. The two *meso* esters were separated from each other and from the two enantiomers on the same column, so that in principle it is possible, using the easy stereomutation described above, to convert the original mixture of esters totally into any one of the four molecular species composing it.

Further manipulations of these and related compounds will be reported in later parts of this series. It may be mentioned that selective removal of *O*-methyl and *O*-isopropyl groups has already been demonstrated: sodium ethanethiolate in HMPT[6] demethylated the ester mixture without effect on the isopropyl groups, and (in a related series) titanium tetrachloride in dichloromethane at 0—20 °C removed isopropyl groups without demethylation.

## Experimental

The general procedures and conventions outlined in Parts 5 and 6 (this volume, pp. 851 and 859) apply here. In addition, $^{31}P$ n.m.r. spectroscopic measurements were made at 32.43 MHz on a Bruker WP80 spectrometer and chemical shifts are quoted in p.p.m. downfield from 85% orthophosphoric acid.

*2-Iodo-5-methoxytoluene.*—3-Methoxytoluene (33 g), iodine (29.4 g), and aqueous periodic acid dihydrate (50%; 11.3 ml) were successively dissolved in a stirred mixture of acetic acid (500 ml), water (50 ml), and sulphuric acid (*d* 1.84; 15 ml). After 6 h, aqueous sodium hydrogen sulphite (10%; 500 ml) and then water (500 ml) were added. The product was extracted into ether which was washed (water then $NaHCO_3$), dried ($MgSO_4$), and evaporated. Distillation then recovered 3-methoxytoluene (5.9 g) and gave the product (**4**) (35 g), b.p. 129—130 °C/12 mmHg, which had m.p. 41—43 °C (lit.,[7] m.p. 43—45 °C) after crystallization from ethanol; $\delta_H$ (60 MHz) 2.37 (3 H, s), 3.72 (3 H, s), 6.41 (1 H, dd, *J* 9, 3 Hz), 6.78 (1 H, d, *J* 3 Hz), and 7.61 (1 H, d, *J* 9 Hz).

*2-Iodo-5-methoxy-4-t-butyl-toluene.*—3-Methoxytoluene (15 g) with t-butyl alcohol (12.6 ml) were stirred at 15—20 °C during the addition (1 h) of sulphuric acid (*d* 1.84; 9 ml). After 4 h the product, an oil (20.7 g) was isolated by means of ether, and iodinated as above (for 16 h), using the same molar proportions of reagents. The product crystallized directly and was recrystallized from ether, yielding the *iodo ether* (**5**) (28.2 g), m.p. 104 °C (Found: C, 47.1; H, 5.7. $C_{12}H_{17}IO$ requires C, 47.4; H, 5.6%); $\delta_H$ (60 MHz) 1.33 (9 H, s), 2.37 (3 H, s), 3.77 (3 H, s), 7.02 (1 H, s), and 7.53 (1 H, s). The compound was best kept in a refrigerator.

*4,4‴-Dimethoxy-2,2‴-dimethyl-2′,2″,4″,6′-tetranitro-m-quaterphenyl.*—See the general directions in Part 6 for arylations of this type. Copper(I) chloride (9.24 g) was added under nitrogen to a cooled stirred mixture of potassium t-butoxide [from potassium (3.8 g)] in 1,2-dimethoxyethane (DME) (300 ml). After 1 h pyridine (10 ml) was added, followed by 2,2′,4,4′-tetranitrobiphenyl (12.8 g) and then the iodide (**4**) (20 g). After 16 h at 80 °C the mixture was poured into dilute hydrochloric (2M; 300 ml) and extracted with ether, which was then washed (brine), dried ($MgSO_4$), and evaporated. The residue in ether was put through a column of alumina and the eluate crystallized slowly from methanol (300 ml). The *quaterphenyl* (**2**) (14.07 g) had m.p. 179—182 °C (Found: C, 58.3; H, 4.0; N, 9.6. $C_{28}H_{22}N_4O_{10}$ requires C, 58.5; H, 3.9; N, 9.8%); $\delta_H$ (60 MHz) 2.13 (6 H, br s), 3.73 (6 H, s), 6.60—7.17 (6 H, m), 7.52 (2 H, d, *J* 9 Hz), and 7.94 (2 H, d, *J* 9 Hz); *m/z* 574 ($M^+$, 62%).

*4,4‴-Dimethoxy-2,2‴-dimethyl-2′,2″,4″,6′-tetranitro-5,5‴-di-t-butyl-biphenyl.*—This was prepared as above from copper(I) chloride (7.73 g), potassium t-butoxide [from potassium (3.15 g)], DME (200 ml), pyridine (8.3 ml), tetranitrobiphenyl (10.5 g), and the iodide (**5**) (20.4 g). After 40 h at 80 °C the mixture was worked up as before. Crystallization from methanol gave

the *tetranitroquaterphenyl* (**3**) (16.2 g), m.p. 219 °C (Found: C, 63.3; H, 5.8; N, 7.9. $C_{36}H_{38}N_4O_{10}$ requires C, 63.0; H, 5.6; N, 8.2%); $\delta_H$ 1.38 (18 H, s), 2.12 (6 H, br s), 3.80 (6 H, s), 6.65 (2 H, s), 6.93 (2 H, s), 7.53 (2 H, d, *J* 9 Hz), and 7.97 (2 H, d, *J* 9 Hz).

*4″,6′-Bis(diethylmethoxy)-4,4‴-dimethoxy-2,2‴-dimethyl-2′,2″-dinitro*-m-*quaterphenyl*.—A mixture of dry sodium pentan-3-yl oxide [from sodium (0.8 g) in pentan-3-ol] and degassed hexamethylphosphoric triamide (HMPT) (20 ml) was stirred under nitrogen and cooled in ice–salt during the dropwise addition of a degassed solution of the quaterphenyl (**2**) (5.74 g) in HMPT (30 ml). After 30 min the ice–salt was replaced by water; 1 h later the deep blue solution was poured into ice (100 g) and dilute hydrochloric acid (2M; 100 ml). The product, a brown oil, was recovered by means of ether, dissolved in ether–hexanes (1:3 v/v) and passed through an alumina column. The solid yellow eluate was recrystallized from ethyl acetate–hexanes to afford pale cream crystals of the *dinitroquaterphenyl* (**6**) (1.34 g), m.p. 207—208 °C (Found: C, 69.2; H, 6.6; N, 4.2. $C_{38}H_{44}N_2O_8$ requires C, 69.5; H, 6.8; N, 4.3%); $\delta_H$ (60 MHz) 0.58—0.97 (12 H, apparent q), 1.27—1.68 (8 H, m), 2.15 (6 H, br s), 3.82 (6 H, s), 4.0—4.12 (m, 2 H), and 6.65—7.32 (10 H, m); *m/z* 656 ($M^+$, 62%) and 516 (78).

*6′-Isopropoxy-4,4‴-dimethoxy-2,2‴-dimethyl-2′,2″,4″-trinitro*-m-*quaterphenyl*.—(*a*) Sodium benzaldehyde oxime was prepared in HMPT (50 ml) from benzaldehyde oxime (4.8 g) and sodium hydride (60% in oil; freed from oil by washing with hexanes; 1.6 g). To this was added under nitrogen with stirring a degassed solution of the quaterphenyl (**2**) (4.8 g) in HMPT (50 ml). After 1 h isopropyl iodide (5 ml) was added and stirring was continued at room temperature for 30 min and then at 60 °C for 1 h. The orange mixture was poured into ice–water (400 ml) containing sodium chloride (5 g), and extracted with ether. The extracts were washed twice with aqueous sodium hydroxide (10%), once with water, dried ($MgSO_4$), and evaporated. After benzonitrile had been removed by heating under reduced pressure, t.l.c. indicated that two compounds were present. The n.m.r. spectrum indicated that these were the product named above, with about half its weight of the 2′-isopropoxy-6′-nitro isomer (**11**) in which the methyl signals of the isopropoxy group were shifted *ca.* 0.5 p.p.m. upfield of those from the 6′-isopropoxy isomer (*cf.* ref. 3). The mixture was boiled under reflux for 2 h with methanol (60 ml) and cooled slowly. The yellow solid (2.36 g in two crops) was pure enough for the next stage. A sample recrystallized from methanol gave the *trinitroquaterphenyl* (**10**), m.p. 192—193 °C (Found: C, 63.4; H, 4.9; N, 7.4. $C_{31}H_{29}N_3O_9$ requires C, 63.4; H, 5.0; N, 7.2%); $\delta_H$ (60 MHz) 1.18 (6 H, br t, $Me_2CHO$), 2.10 (6 H, br s), 3.75 (6 H, s), 4.47 (1 H, br m), 6.55—6.95 (8 H, m), 7.25 (1 H, d, *J* 8 Hz), and 8.08 (1 H, d, *J* 8 Hz); *m/z* 587 ($M^+$, 100%).

(*b*) Potassium t-butoxide (19.6 g) was suspended in HMPT (125 ml) and a solution of 2-oximinohexanoic acid[8] (12.63 g) in HMPT (90 ml) was added. The mixture was warmed to 50 °C for 2 h, cooled, treated with a solution of the tetranitroquaterphenyl (**2**) (10 g) in HMPT (120 ml), and stirred overnight. Isopropyl iodide (20 ml) was then added and after 5 h the mixture was added to water (1 200 ml). The product was recovered by means of ether which was washed (brine; 2 × 200 ml), dried ($MgSO_4$) and evaporated. The residue was left overnight in ethanol (200 ml) and aqueous sodium hydroxide (10%; 160 ml); the product, recovered in the usual manner by extraction with ethyl acetate after removal of ethanol under reduced pressure, formed a yellow solid (10 g) having an n.m.r. spectrum identical with that of the compound (**10**) above.

*4″,6′-Di-isopropoxy-4,4‴-dimethoxy-2,2‴-dimethyl-2′,2″-dinitro*-m-*quaterphenyl*.—(*a*) A solution of the above trinitroquaterphenyl (**10**) (1.18 g) in HMPT (10 ml) was added to a stirred solution of sodium benzaldehyde oxime [from (0.96 g) benzaldehyde oxime as above] in HMPT (10 ml) under nitrogen. After 1 h isopropyl iodide (1 ml) was added and stirring was continued for 1 h. The mixture was worked up as in the foregoing experiment and the product was crystallized from hexanes containing a little chloroform. The *dinitroquaterphenyl* (**7**) (0.97 g) formed cream crystals, double m.p. 160—165 and 205—206 °C (Found: C, 68.1; H, 6.2; N, 4.6. $C_{34}H_{36}N_2O_8$ requires C, 68.0; H, 6.0; N, 4.7%); $\delta_H$ (60 MHz) 1.20 (12 H, br t), 2.12 (6 H, br s), 3.80 (6 H, s), 4.47 (2 H, septet, *J* 6 Hz), and 6.62—7.37 (10 H, m); *m/z* 600 ($M^+$, 100%).

(*b*) A stirred suspension of sodium hydride (1 g) in HMPT (20 ml) was treated under nitrogen with a solution of benzil mono-oxime dimethyl acetal[5] (10.84 g) in HMPT (120 ml). After 2 h the tetranitroquaterphenyl (**3**) (5.74 g) in HMPT (80 ml) was added. The mixture after 4 h was poured into dilute hydrochloric acid (0.33M; 600 ml) and extracted with ethyl acetate (3 × 300 ml). The washed (2 × 100 ml brine), dried ($MgSO_4$) solvent was evaporated and the residue was left for 18 h in moist acetone (300 ml) containing toluene-4-sulphonic acid (0.5 g). The product, recovered by means of ethyl acetate after the addition of water and removal of acetone, was dissolved in methanolic sodium methoxide [from methanol (200 ml) and sodium (2 g)]. After 2 h, water (100 ml) was added and the methanol was removed under reduced pressure. The product, recovered from the acidified (2M-HCl; 100 ml) aqueous residue by means of ethyl acetate, was dissolved in dimethylformamide (150 ml) containing isopropyl iodide (8 ml). Potassium carbonate (12 g) was added and the mixture was stirred overnight under nitrogen. Recovery of the product as before was followed by chromatography on silica, using hexanes–ethyl acetate (19:1; v/v). This gave a yellow solid (3.6 g) with an n.m.r. spectrum identical with that of the product (**7**) above.

*4″,6′-Di-isopropoxy-4,4‴-dimethoxy-2,2‴-dimethyl*-m-*quaterphenyl-2′,2″-diamine*.—The dinitroquaterphenyl (**7**) (1.66 g) and Raney nickel (*ca.* 0.6 g) in ethoxyethanol (20 ml) were stirred under nitrogen at 90 °C during the addition of hydrazine hydrate (10 ml) over 1 h. More nickel (0.3 g) was added, followed by the dropwise addition of more hydrazine hydrate (5 ml). After dilution with water (100 ml) and filtration (Celite), the filter was washed through with ether and the filtrate was extracted further with ether. The dried ($MgSO_4$) extracts yielded an oil which was passed through alumina, eluting with ether–hexanes (2:3). The *diamine* (**13**) (1.20 g) was a colourless glass and could not be crystallized; $\delta_H$ (60 MHz) 1.12 (12 H, br d), 2.07 and 2.10 (6 H, two s), 3.48 (4 H, br s), 3.77 (6 H, s), 4.30 (2 H, br septet, *J* 6 Hz), and 6.30—7.07 (10 H, m). The double aromatic methyl signal indicates the presence of *meso* and racemic forms.

*2′,2″-Di-iodo-4″,6′-di-isopropoxy-4,4‴-dimethoxy-2,2‴-dimethyl*-m-*quaterphenyl*.—Hydrochloric acid (6 ml, d 1.16) was added to a solution of the diamine (**13**) (1 g) in dimethylformamide (32 ml). The mixture was stirred and cooled in ice–salt during the addition of sodium nitrite (0.8 g) in water (5 ml). The temperature was kept below −5 °C during this addition and the addition, 2 h later, of sulphamic acid (1.1 g) in water (5 ml). A solution of mercury(II) iodide (2 g) and potassium iodide (1.5 g) in water (20 ml) was then added and after dilution with water (180 ml) the red-brown precipitate was collected, washed with water, suspended in fresh water (50 ml), and stirred overnight. The solid, now brown, was dissolved in chloroform (150 ml) which was then dried ($MgSO_4$) and evaporated. The residue was mixed with dried sodium iodide (15 g) and dry dimethyl sulphoxide (22 ml), degassed, and heated under nitrogen for 22 h at 120—125 °C. Water and chloroform were added and the

chloroform layer was washed (aqueous $NaHSO_3$ then water), dried ($MgSO_4$), and evaporated. The dark oil in hexanes–dichloromethane (1:1 v/v) was chromatographed on alumina to yield a fraction (0.91 g) consisting essentially of the required di-iodide as a mixture of atropisomers. An inefficient recovery of wholly crystalline material (partial dissolution in isopropyl alcohol containing a little dichloromethane, followed by recrystallization from chloroform–methanol) gave the *di-iodide* (**14**), m.p. 153—161 °C (Found: C, 53.3; H, 4.9. $C_{34}H_{36}I_2O_4$ requires C, 53.6; H, 4.8%); $\delta_H$ (60 MHz) 1.22 (12 H, d, *J* 6 Hz), 2.05 (6 H, br s), 3.82 (6 H, s), 4.38 (2 H, septet, *J* 6 Hz), 6.77 (6 H, br s), 6.93 (2 H, d, *J* 8 Hz), and 7.13 (2 H, d, *J* 8 Hz); *m/z* 762 ($M^+$, 16%), 635 (27), 551 (51), 246 (25), 119 (32), and 69 (100).

3,7-*Di-isopropoxy*-5-*methoxy*-4,6-*bis*-(4-*methoxy*-2-*methylphenyl*)*dibenzophosphole* 5-*Oxide*.—Butyl-lithium (1.6M in hexane; 4.5 ml) was added under nitrogen to a cooled (< −70 °C) stirred solution of the di-iodide (**14**) 2.27 g) in tetrahydrofuran (90 ml). After 2 h, phosphorus trichloride (freshly distilled from zinc powder in a stream of dry nitrogen; 1.2 ml) was added and stirring and cooling were continued for 2 h. Water (10 ml) was added; the mixture was brought to room temperature, made alkaline with aqueous sodium hydroxide, treated with hydrogen peroxide (30%; 30 ml), stirred overnight, acidified (2M-HCl), and extracted with chloroform (3 × 150 ml); the extract was then washed (2 × aqueous $NaHSO_3$; brine), dried ($MgSO_4$), and evaporated. The residue in ether (20 ml) was cooled in ice, treated with ethereal diazomethane (1.1M; 20 ml), and left for 2 h. Flash chromatography of the product on silica, using ethyl acetate–hexanes (1:4, v/v), gave a *phosphinic ester* (total 1.32 g), which separated into three fractions, the two *meso* esters sandwiching the racemic ester.

The most mobile fraction contained (4S,5S,6R)-3,7-*di-isopropoxy*-5-*methoxy*-4,6-*bis*-(4-*methoxy*-2-*methylphenyl*)*dibenzophosphole* 5-*oxide* (**15**) which crystallized from ether, m.p. 160—162 °C (Found: C, 71.5; H, 6.9. $C_{35}H_{39}O_6P$ requires C, 71.7; H, 6.7%); $\delta_P$ +40.71 p.p.m.; $\delta_H$ (360 MHz) 1.11 (6 H, d, *J* 6 Hz), 1.16 (6 H, d, *J* 9 Hz), 2.16 (6 H, s), 2.78 (3 H, d, *J* 11.7 Hz), 3.75 (6 H, s), 4.34 (2 H, septet, *J* 6 Hz), 6.68 (2 H, dd, *J* 2.6, 8.3 Hz), 6.74 (2 H, d, *J* 2.6 Hz), 6.95 (2 H, d, *J* 8.3 Hz), 7.04 (2 H, d, *J* 8.4 Hz), and 7.55 (2 H, dd, *J* 4.4 , 8.4 Hz). Irradiation of the MeOP doublet at δ 2.78 caused a 7% enhancement of the doublet at δ 6.95.

The middle fraction yielded the racemic (4SR,6SR)-*isomer* (**17**), not obtained crystalline; $\delta_P$ +41.31 p.p.m.; $\delta_H$ (60 MHz) 1.13 (12 H, br m), 2.04 (3 H, s), 2.16 (3 H, s), 2.66 (3 H, d, *J* 11 Hz), 3.75 (6 H, s), 4.31 (2 H, br septet, *J* 6 Hz), 6.7—7.23 (8 H, br m), and 7.53 (2 H, dd, *J* 4, 8 Hz).

From the least mobile fraction the other *meso* ester, the (4R,5R,6S)-*isomer* (**16**), crystallized from acetone, m.p. 199 °C (Found: C, 71.4; H, 6.9%); $\delta_P$ +41.00 p.p.m.; $\delta_H$ (60 MHz) 1.13 (12 H, m), 2.03 (6 H, s), 2.54 (3 H, d, *J* 11 Hz), 3.77 (6 H, s), 4.3 (2 H, br m), 6.7—7.2 (8 H, br m), and 7.53 (2 H, dd, *J* 4, 8 Hz); *m/z* 586 ($M^+$, 66%), 502 (100), 487 (70), and 469 (24).

*Interconversion of the Atropisomers* (**15**), (**16**) *and* (**17**).—The *meso* ester (**15**) (3 mg) in xylene (2 ml) was boiled under reflux and changes were monitored by t.l.c. [silica; hexanes–ethyl acetate (1:1 v/v)]. After 2.5 h, three spots corresponding in mobility to the three isomers were seen. After 4.5 h, the middle spot corresponding to (**17**) was more intense than the other two. Accordingly, the *meso* ester (**15**) in $C_6D_5NO_2$ was heated at 130 °C and the changes were monitored at 360 MHz, with periodic scanning of the region δ 2—4 and analysis of the Ar*Me* and POMe peaks. The results are embodied in Figure 1.

*Optical Resolution of the Racemic Ester* (**17**).—The ester (**17**) was subjected to h.p.l.c. on a column (250 mm) of Bakerbond DNBPG, using isopropyl alcohol–hexanes (1:49 v/v) at 1.5 ml $min^{-1}$. Minor amounts of the two *meso* isomers were seen at 30 and 55 min, but the major component formed two peaks at 38 and 41.5 min (not completely resolved). This fraction was run again, fractions corresponding to the outer slopes of the two peaks being collected separately and each run once more. The resolved esters were recovered and dissolved in methanol for examination of the c.d. spectra shown in Figure 2. We are indebted to Dr. Alex F. Drake of the National CD Service (S.E.R.C.) at Birkbeck College, University of London, for running these spectra.

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