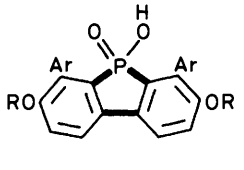
Synthesis of Substituted Dibenzophospholes. Part 2. Syntheses of Intermediate Biphenyls and Quaterphenyls †

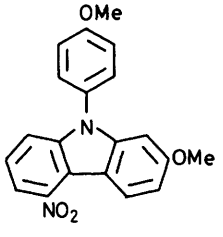
By **Sir John Cornforth,* Andrew F. Sierakowski,** and **Timothy W. Wallace,** School of Molecular Sciences University of Sussex, Brighton BN1 9QJ

A general procedure for synthesis of 4'',6'-dialkoxy-2',2''-diamino-*m*-quaterphenyls has been established. Copper(I) t-butoxide is used to prepare 2,6-dinitrobiphenyls from 1,3-dinitrobenzene and aryl iodides. One of the nitro-groups is then exchanged for a methoxy-group by sodium methoxide in hexamethylphosphoramide; the resulting 2-methoxy-6-nitrobiphenyls are then iodinated in the 5 position. Ullmann coupling then gives the dinitroquaterphenyls which are reduced to the diamines. An alternative route from 2,2',4,4'-tetranitrobiphenyl was explored; arylation was easy but alkoxydenitration was indiscriminate. Some 71 new derivatives of biphenyl, terphenyl, and quaterphenyl are reported.

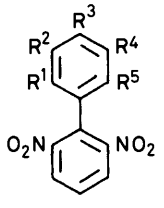
THE approach, described in Part 1,[1] to a convenient synthesis of substances having the general structure (1) proved difficult in practice. We therefore examined the alternative of generating suitably substituted biphenyls that could be joined at a later stage by the bonds indicated in structure (1) by bold lines.



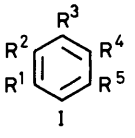
(1)



(2)



(3a)



(4a)

All R^n = H unless stated otherwise

b; R^3 = OMe
c; R^1 = Me, R^2 = OMe
d; R^3 = NO_2
e; R^1 = NO_2
f; R^2 = R^4 = Cl, R^3 = OMe
g; R^2 = R^4 = Bu^t, R^3 = OMe
h; R^1 = R^2 = R^4 = Me, R^3 = OMe
i; R^1 = R^2 = R^4 = R^5 = Me, R^3 = OMe
j; R^1R^2 = R^4R^5 = $[CH_2]_4$

The method eventually found and already briefly reported [2] has its origin in Forrest's [3] observation that Ullmann coupling of iodobenzene to biphenyl by copper was accompanied by formation of 2,6-dinitrobiphenyl when 1,3-dinitrobenzene was present. Björklund and Nilsson [4] showed that cuprous oxide in hot (220—240 °C) quinoline mediated condensation of 1,3-dinitrobenzene with a number of aryl iodides to give 2,6-dinitrobiphenyls. In our experience this procedure gives products contaminated from side-reactions and difficult to purify. A by-product from 4-iodoanisole and 1,3-dinitrobenzene, unnoticed by the original authors, is assigned the carbazole structure (2) from its composition and spectra.

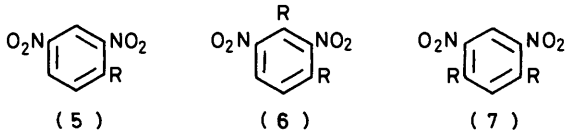
Björklund and Nilsson's suggestion that a complexed 2,6-dinitrophenylcopper(I) compound might be an intermediate in their procedure prompted us to examine derivatives of copper(I) more basic than the oxide. Copper(I) t-butoxide [5] is capable, for example, of metalating phenylacetylene slowly at room temperature. We originally prepared pure copper(I) t-butoxide by Saegusa's method.[5] When a solution of 1,3-dinitrobenzene in pyridine was mixed with this substance and iodobenzene was then added, the mixture after heating, yielded 2,6-dinitrobiphenyl (3a) in satisfactory yield and purity. Following a suggestion of Whitesides *et al.*[6] that mixtures of alkali metal alkoxides with cuprous chloride in 1,2-dimethoxyethane (DME) are, for some purposes, equivalent to copper(I) alkoxides, we substituted for copper(I) t-butoxide a mixture of potassium t-butoxide and cuprous chloride in DME. The presence of pyridine (1—2 mol/mol) was still necessary to promote formation of 2,6-dinitrobiphenyl when 1,3-dinitrobenzene and iodobenzene were subsequently added, but the process was smooth and the yield high (87%). A slight excess of potassium t-butoxide over cuprous chloride seems desirable and we tended to prepare the potassium butoxide *in situ* after erratic results with some commercial samples.

The scope of the synthesis was explored. In general, the aryl iodides (4i) and (4j) substituted in both *ortho*-positions reacted sluggishly and without positional preference. Thus 1,2,3,4,5,6,7,8-octahydro-9-iodoanthracene (4j)‡ afforded not only the 2-aryl- (3j) but, also the 4-aryl- (5a), the 2,4-diaryl- (6a), and the 4,6-diaryl- (7a) derivatives of dinitrobenzene. When at least one *ortho*-position was free, reaction was normal and the derivatives (3a)—(3h) were prepared from the iodides (4a)—

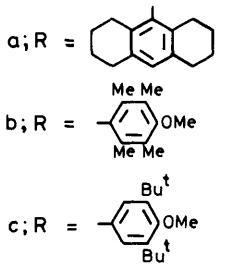
† No reprints available.

‡ This iodide was prepared by direct iodination of the hydrocarbon, but we also investigated the inferior route of nitration–reduction–diazotization. The properties of our 1,2,3,4,5,6,7,8-octahydro-9-nitroanthracene differed in all respects except elementary analysis from those reported (ref. 7) for a specimen prepared otherwise.

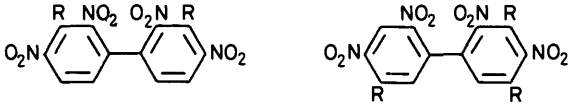
(4h) without trouble. The successful preparation of trinitrobiphenyl (3e) is notable since Björklund and Nilsson's procedure failed to afford it. We tried a few substitutes for 1,3-dinitrobenzene (methyl 3-nitro-



(5) (6) (7)

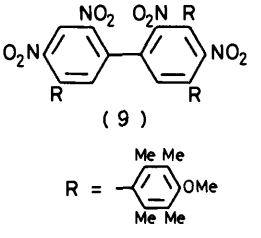


benzoate, 1,3-dicyanobenzene, 3-nitrophenyl methoxymethyl ether) without observing appreciable reaction. With 2,2′,4,4′-tetranitrobiphenyl (8a), however, the procedure readily yielded the quaterphenyls (8b) and (8c). Here again, the fully substituted iodide (4i) gave a product (9) of indiscriminate attack. The only other 'abnormal' by-products noticed were 2-nitrophenyl t-butyl ether (10) and 2,2′-dinitrobiphenyl in the preparation of compound (3e) from 2-iodonitrobenzene.

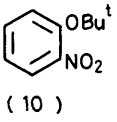


(8)

a; R = H
b; R = Ph
c; R = C_6H_4OMe-4

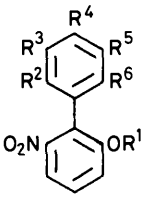


(9)



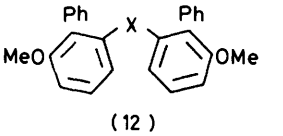
(10)

2,6-Dinitrobiphenyl could be converted into 2-methoxy-6-nitrobiphenyl (11b) by the classical methods of selective reduction, diazotization, and methylation of the nitrophenol (IIa). However, Kornblum's [8] elegant methoxydenitration by sodium methoxide in hexamethylphosphoramide proved applicable in the 2,6-dinitrobiphenyl series and gave the same 2-methoxy-6-nitrobiphenyl (11b) directly from 2,6-dinitrobiphenyl. An excess of sodium methoxide gave the dimethoxyazoxybiphenyl (12a) as the major product and this could be reduced to the diarylhydrazine (12b). This hydrazine was oxidized to the azobiphenyl (12c).



(11a)

All R^n = H unless stated otherwise
b; R^1 = Me
c; R^1 = Me, R^4 = OMe
d; R^1 = R^2 = Me, R^3 = OMe
e; R^1 = Me, R^3 = R^5 = Cl, R^4 = OMe
f; R^1 = Me, R^3 = R^5 = Bu^t, R^4 = OMe
g; R^1 = R^2 = R^3 = R^5 = Me, R^4 = OMe
h; R^1 = R^2 = R^3 = R^5 = R^6 = Me, R^4 = OMe



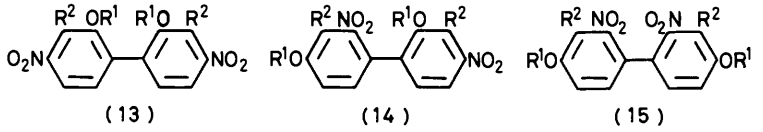
(12)

a; X = –N=N–
b; X = –NH–NH–
c; X = –N=N–

Another product from an excess of sodium methoxide was 2,6-dimethoxybiphenyl.

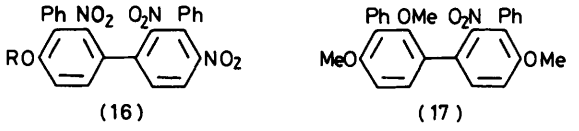
This methoxydenitration was applied further to prepare the methoxynitrobiphenyls (11c)—(11h). No difficulty was experienced with any of these when the optimum conditions for compound (11a) were used. It was hoped that the different environments of the 2′,2″- and 4″,6′-nitro-groups in the tetranitroquaterphenyls (8b) and (8c) would promote selective methoxydenitration. In fact, the three possible dimethoxydinitro-compounds (13a), (14a), and (15a) were obtained from compound (8b) and the monomethoxy- (16a) and trimethoxy- (17) derivatives were obtained in other experiments. Assignment of structures was easy because of a characteristic shielding effect in the n.m.r. spectra of methoxyhydrogens situated between two benzene rings, as well as a chemical correlation to be described later in this paper. The use of more bulky alkoxy-groups (ethoxy and neopentyloxy) led to no better result. The three diethoxydinitro-compounds (13b), (14b), and (15b) were isolated along with the monoethoxy-derivative (16b), and the dineopentyloxydinitro-derivative (15c) was separated from an analogous mixture. The dimethoxytetranitroquaterphenyl (8c) gave a mixture from which the isomer (13d) was isolated. Finally, an attempt to apply Knudsen and Snyder's [9] method by treatment of the tetranitro-compound (8b) with sodium benzaldoxime led to an unwanted dibenzofuran synthesis, the compound (18a) being among the products along with the trinitroquaterphenyl (19a). Both substances were characterized as their methyl ethers (18b) and (19b).

The plan for synthesis of 4,6-diaryldibenzophospholes (1) from biphenyl derivatives called now for preparation of di-biphenylylphosphinic acids [*e.g.* compound (24)] followed by an oxidative cyclization. Some model experiments were done while the necessary intermediates were being prepared. Bis-(3-methoxyphenyl)phosphinic acid (20a) was made by applying Kosolapoff's method [10] and it was converted into its methyl ester (20b) and into the dihydroxy-acid (22c), a known substance.[11] The methyl ester (20b) with vanadium



(13) (14) (15)

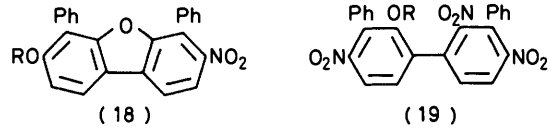
a; R^1 = Me, R^2 = Ph
b; R^1 = Et, R^2 = Ph
c; R^1 = CH_2Bu^t, R^2 = Ph
d; R^1 = Me, R^2 = C_6H_4OMe-4



(16) (17)

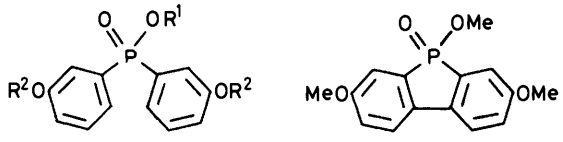
a; R = Me
b; R = Et

oxytrifluoride [12] in trifluoroacetic acid–trifluoroacetic anhydride gave, in 57% yield, the dibenzophosphole (21), a substance already in hand (Part I, preceding paper). 2-Methoxy-6-nitrobiphenyl (11b) was reduced easily to the amine (22a), and the amines (22b) and (22c) were prepared similarly from the appropriate nitro-compounds (11c) and (11f). The catalysed reduction of nitro-compounds with hydrazine [13] proved an excellent method throughout our work. The amines were converted into the iodides (23a)—(23c) by conventional diazonium-salt chemistry. We found that the 2-lithiobiphenyls, formed by exchange with butyl-lithium from these iodides and from 2-iodobiphenyl itself, gave good yields of the requisite phosphinic esters (24a)—(24e) by reaction with ethyl or methyl dichlorophosphate.



(18) (19)

a; R = H
b; R = Me

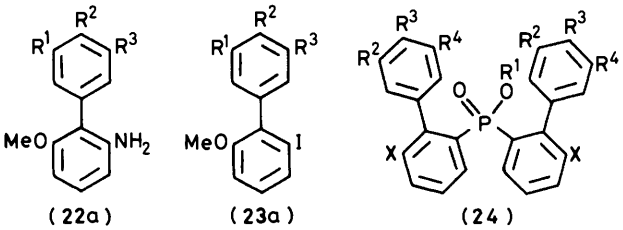


(20) (21)

a; R^1 = H, R^2 = Me
b; R^1 = R^2 = Me
c; R^1 = R^2 = H

Many attempts were made to cyclize these phosphinic esters or acids, or the phenols (24f) and (24g) derived by demethylation, to dibenzophospholes. These failures are tabulated in the Experimental section. When, later, the dibenzophospholes became available it was possible to prove that in no case had cyclization been successful. A product isolated from the action of vanadium oxytrifluoride on the phosphinic ester (24d) proved to be the dienone (25). Analogous cyclizations have been noted by Kupchan *et al.*[12]

If it had been possible to halogenate the phosphinates (24) in the positions *ortho* to phosphorus, an Ullmann synthesis would probably have generated the dibenzophosphole system; but despite several trials only in-



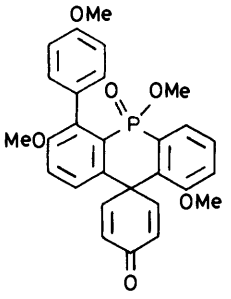
(22a) (23a) (24)

All R^n = H unless stated otherwise

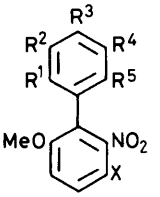
b; R^2 = OMe
c; R^1 = R^3 = Bu^t, R^2 = OMe

a; R^1 = Me, X = H
b; R^1 = Et, X = H
c; R^1 = Me, X = OMe
d; R^1 = Me, R^3 = X = OMe
e; R^1 = Me, R^2 = R^4 = Bu^t, R^3 = X = OMe
f; R^1 = Me, X = OH
g; X = OH

tractable mixtures were produced. It was the more gratifying to discover that halogenation of the nitro-compounds (11) proceeded smoothly in the desired manner, and yielded the halides (26a)—(26h). No tendency to halogenation in other positions of that ring was noted, but halogenation in the other ring could also



(25)



(26)

All R^n = H unless stated otherwise

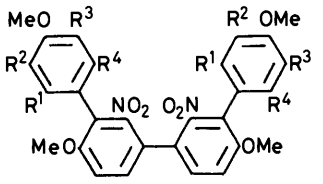
a; X = I
b; X = Br
c; R^3 = X = Br
d; R^2 = X = I, R^3 = OMe
e; R^2 = R^4 = X = I, R^3 = OMe
f; R^1 = X = I, R^2 = R^4 = R^5 = Me, R^3 = OMe
g; R^2 = R^4 = Cl, R^3 = OMe, X = I
h; R^2 = R^4 = Bu^t, R^3 = OMe, X = I

occur if promoted by substitution or [as in the formation of the dibromide (26c)] by forcing conditions. Iodination was generally preferred since the *o*-iodonitrobiaryls produced were good subjects for Ullmann coupling, leading to quaterphenyls of type (15).

In this way the dinitroquaterphenyls (15a) and (27a)—(27e) were prepared, and they were reduced to the diamines (28a)—(28d). Yields from halogenation, coupling, and reduction were generally good, the limitation being the occurrence of unsymmetrical coupling when more than one iodine atom was present in a precursor of type (26). This difficulty was later overcome (see following paper) by a different coupling procedure. Another device was to block unwanted iodination by t-butyl substitution [as in compound (26h)] which, after coupling, was removed by catalytic dealkylation (27e)→(27f).

Several correlations were possible at the dinitro (27) and diamine (28) stage. Compound (15a) can be prepared in this way and from tetranitroquaterphenyl. The hydrazobiphenyl (12b), on rearrangement with acid, gave the three products (28a), (29), and (30) of *ortho*-, *ortho–para*-, and *para*-coupling. These were identified with the reduction products from (13a), (14a), and (15a) and one of them with the diamine prepared by the route (26a)→(15a)→(28a). These correlations, in conjunction with *X*-ray crystallographic results reported in Part 3 (following paper), establish beyond doubt the correctness of the orientations assigned to the compounds produced in the syntheses of these diamines from 1,3-dinitrobenzene and from tetranitroquaterphenyl.

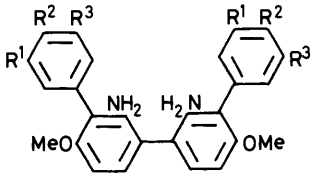
Completion of the synthesis of 4,6-diaryldibenzophospholes from the diamines (28a), (28b), and (28d) is described in the following paper (Part 3).



(27e)

All R^n = H unless stated otherwise

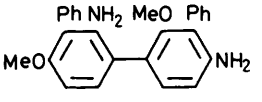
a; R^2 = I
b; R^1 = I, R^2 = R^3 = R^4 = Me
c; R^2 = R^3 = Cl
d; R^2 = R^3 = Bu^t



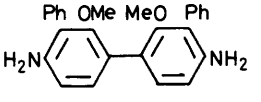
(28a)

All R^n = H unless stated otherwise

b; R^2 = OMe
c; R^1 = R^3 = Cl, R^2 = OMe
d; R^1 = R^3 = Bu^t, R^2 = OMe



(29)



(30)

EXPERIMENTAL

Melting points were determined on a Kofler hot stage. I.r. spectra, except where otherwise stated, were of liquid paraffin pastes on sodium chloride plates, recorded on Perkin-Elmer 257 (grating) or 297 instruments. N.m.r. spectra were measured in deuteriochloroform (unless otherwise stated) with tetramethylsilane as internal standard, at 60 MHz on a Varian T60 instrument or at 90 MHz on a Perkin–Elmer R32. Mass spectra (m.s.) were recorded on an AEI MS30 double beam instrument or occasionally on a Hitachi RMU-6E. Gas–liquid chromatography (g.l.c.) was performed in a Pye-Unicam GCD machine with flame-ionization detector. Solvents were routinely purified by standard techniques. Organic solvent extracts were dried over anhydrous sodium sulphate and evaporated under reduced pressure in a rotary evaporator. Thin layer chromatography (t.l.c.) was executed on silica gel GF_{254} (Merck); preparative t.l.c. was on 1 mm thick layers of the same. 'Alumina' refers to Spence Grade H alumina. Compositions of mixtures of solvents are quoted as ratios of volume. 'Hexane' refers to a light petroleum fraction, b.p. 60—68 °C. Where colour is not mentioned, new compounds were colourless.

Condensations of Aryl Iodides with 1,3-Dinitrobenzenes 2,6-Dinitrobiphenyl (3a).—Potassium t-butoxide was pre-

pared [14] from t-butyl alcohol (1.25 l) and potassium (47.5 g) (*Note*. Attention is drawn again [15] to the convenience of dioxan for preparation of clean potassium. Lump potassium is blotted from covering oil and put into dry, peroxide-free dioxan in a beaker covered with a clock glass. This is heated on a hot-plate; when the metal melts it frees itself from crust, which sinks leaving a floating globule of clean potassium that can be removed when cold. A larger molten globule can be divided by gentle pressure with a spatula into smaller globules as desired; they do not coalesce while molten, but should be kept apart while solidifying. Any residual potassium in the dioxan is destroyed by addition of isopropyl alcohol. The procedure avoids or minimizes the cutting of potassium). Final drying of the butoxide at 100—110 °C/1 mmHg for 1—2 h was sufficient. Under nitrogen, the white solid was suspended by stirring into freshly purified 1,2-dimethoxyethane (DME) (1 l), the suspension was cooled in ice–water, and freshly purified [6] powdered cuprous chloride (120.6 g) was added during 30 min. The suspension, now thinner and greenish in colour, was stirred at 0—5 °C for 30 min more and then at room temperature for several hours. Dry pyridine (120 ml) was added, followed after 10 min by a solution of 1,3-dinitrobenzene (168 g) in DME (400 ml). After a further 10 min iodobenzene (120 ml, 218.8 g) was added to the purple solution and the well stirred mixture was heated slowly to 80 °C. After 4 h the mixture was cooled to room temperature; 12 h later it was poured into water (6 l) and acidified with concentrated hydrochloric acid (200 ml). The solid was washed on a filter with water (10 l), dried under reduced pressure over silica gel, mixed with an equal bulk of alumina, and placed on a pad of Celite in a 20-cm Buchner funnel. The solid was repeatedly extracted with portions (1.5 l) of hot ethyl acetate. Extracts were evaporated to remove solvent (which was recycled) and the residues were collected on a filter with the aid of methanol. When *ca.* 220 g of solid had been collected thus, it was boiled with ethyl acetate (3 l), and the hot mixture was put through a pre-heated funnel covered with Celite (2 cm) and alumina (3 cm). The filtrate deposited 2,6-dinitrobiphenyl (176.3 g); the mother liquors, concentrated after passage through a short alumina column, yielded four more crops and a total yield of 212.2 g (87% from dinitrobenzene), m.p. 191—192 °C (lit.,[4] 189—191 °C; lit.,[3] 188—190 °C); $\nu_{max.}$ 1 530, 823, 777, 755, 730, and 702 cm^{-1}; δ([$^2H_6$]acetone) 7.3—7.6 (5 H, m, Ph), and 7.77—8.37 (3 H, m, 3-,4-,5-H). The procedure for work-up is the result of many experiments, the insolubility of this product making isolation difficult.

4-Methoxy-2′,6′-dinitrobiphenyl (3b).—To potassium t-butoxide (from 1.62 g potassium as above) was added dry DME (50 ml) and then, with stirring and ice-cooling under nitrogen, cuprous chloride (4.12 g). After 1.5 h at room temperature there were added successively pyridine (8 ml), 1,3-dinitrobenzene (5.8 g), and 4-iodoanisole (8.5 g). The mixture was stirred at 67 °C (bath) for 20 h, poured into hydrochloric acid (200 ml of 2M), and extracted with ethyl acetate (400 ml). The washed, dried extract was evaporated, the residue in chloroform (150 ml) was passed through a plug (5 cm × 5cm) of alumina and the solid recovered by evaporation was recrystallized from methanol giving in three crops the product (3b) (8.95 g; 95%), m.p. 117—118 °C (lit.,[4] 117—119 °C). The m.p. was undepressed on admixture with a specimen prepared by the literature method [4] (see next experiment).

2-Methoxy-9-(4-methoxyphenyl)-5-nitrocarbazole (2).—1,3-Dinitrobenzene (20 g), 4-iodoanisole (28 g), cuprous oxide (8.6 g), and quinoline (50 ml) were heated at reflux for 2.5 h. The product, obtained by pouring into dilute acid and extraction with ethyl acetate, yielded, on trituration with methanol and recrystallization of the solid from diethyl ether, the above biphenyl (3b). The mother liquors were chromatographed on alumina and eluted with acetone–hexane (1 : 3). Crystallization of the later fractions gave more biphenyl (total yield 32.5%) and a substance crystallizing from methanol in deep yellow plates. This was recrystallized from ethyl acetate–methanol. The *carbazole* (2) had m.p. 141—143 °C (Found: C, 68.8; H, 4.62; N, 8.0. $C_{20}H_{16}N_2O_4$ requires C, 69.0; H, 4.63; N, 8.0%); $\lambda_{max.}$ (methanol) 383 (log ε 3.95), 296sh (4.06), 273sh (4.26), and 234 nm (4.79). The mass spectrum was almost featureless apart from a peak at *m/e* 348 (M^+, 100%) and another at *m/e* 302 ($M - NO_2^+$, 20%). The i.r. spectrum showed no N–H stretching band, complex absorption at *ca.* 1 600 cm^{-1} ($\nu_{max.}$ 1 620, 1 600, 1 580, 1 570, and 1 560 cm^{-1}), and a band at 1 510 cm^{-1} attributable to NO_2. The n.m.r. spectrum (90 MHz) showed δ 3.81 (3-H, s, OMe) 3.91 (3-H, s, OMe), 6.70 (1 H, d, *J* 2.5 Hz, 1-H), 6.98 (1 H, dd, *J* 9 and 2.5 Hz, 3-H), 7.1—7.5 (6 H, incompletely resolved), 8.08 (1 H, dd, *J* 7 and 2 Hz, 6-H), and 8.70 (1 H, d, *J* 9 Hz, 4-H). The resonances at δ 6.98 and 8.70 were coupled as were those at δ 6.70 and 6.98. The strong deshielding of 4-H is attributed to the 5-nitro-group; a similar effect has been found in the dibenzophospholes (see Part 3).

3-Methoxy-2-methyl-2′,6′-dinitrobiphenyl (3c).—Copper(I) t-butoxide (4.9 g), prepared [5] as a mixture with lithium chloride, was treated under nitrogen with dry pyridine (20 ml) and 1,3-dinitrobenzene (5 g) in pyridine (10 ml) was added. The mixture was stirred at 85 °C (bath) and a solution of 2-iodo-6-methoxytoluene (7.5 g) in pyridine (10 ml) was added. The mixture was heated at 65—85 °C for 20 h, boiled under reflux for 5 h more, and heating continued at 65—80 °C for a further 16 h. The brown solid, obtained by pouring the reaction mixture into dilute sulphuric acid, was dried and extracted (Soxhlet) with light petroleum (b.p. 60—80 °C). Prolonged extraction and trituration of the evaporated extracts with diethyl ether gave a solid (m.p. 175—180 °C; 3.73; 49%) appearing homogeneous by t.l.c. (silica; ethyl acetate–hexane, 1 : 3). On recrystallization from ethanol the *biphenyl* (3c) formed colourless leaflets, m.p. 179 °C (Found: C, 58.4; H, 4.3; N, 9.6. $C_{14}H_{12}N_2O_5$ requires C, 58.3; H, 4.2; N, 9.7%). The m.s. showed strong peaks at *m/e* 288 (M^+), 241 ($M^+ - NOH_2$), 211, and 152. The n.m.r. and i.r. spectra confirmed the presence of Me, OMe, and NO_2 groups.

2,4′,6-Trinitrobiphenyl (3d).—The preparation was carried out essentially as described for 4-methoxy-2′,6′-dinitrobiphenyl (see above). From 1,3-dinitrobenzene (5 g) and 4-iodonitrobenzene (8.45 g), after 17 h at 90 °C (bath), there were obtained, by crystallization from ethyl acetate and ethyl acetate–ethanol, a total of 8.31 g (87%) of the trinitrobiphenyl (3d), m.p. 183—185 °C (lit.,[4] m.p. 185—187 °C).

2,2′,6-Trinitrobiphenyl (3e).—The preparation, from 1,3-dinitrobenzene (3.6 g) and 2-iodonitrobenzene (5.6 g), was carried out as for 4-methoxy-2′,6′-dinitrobiphenyl (18 h at reflux). The product, after chloroform–alumina treatment (above), was a yellow oil. Trituration of this with ethanol–hexane (1 : 3) gave a cream solid which was crystallized from acetic acid and from chloroform–hexane to give 2,2′,6-trinitrobiphenyl (3e), m.p. 135 °C (lit.,[16] m.p. 134—135 °C).

The total yield from this and other fractions was 2.5 g (40%). The ethanol–hexane extract was distilled at 120—130 °C (bath) and 0.01 mmHg pressure to give, in two fractions, a yellow oil. The more volatile fraction (0.08 g) was purified by t.l.c. on silica (ethyl acetate–hexane, 1 : 4; then hexane developed, 4 ×) to give *2-nitrophenyl t-butyl ether* (10) as a mobile, yellow oil (Found: C, 61.6; H, 6.7; N, 7.2. $C_{10}H_{13}NO_3$ requires C, 61.5; H, 6.7; N, 7.2%). The second fraction (1.68 g) appeared by t.l.c. to be a mixture of this substance and 1,3-dinitrobenzene. One-fifth of the involatile residue (1.92 g) was purified by preparative t.l.c. on silica (ethyl acetate–hexane, 1 : 4; twice developed). This separated 1,3-dinitrobenzene, the trinitrobiphenyl already isolated, and a new product which was recrystallized from chloroform–hexane and identified as 2,2′-dinitrobiphenyl by m.p. (124 °C) and mixed m.p. with an authentic sample. The yield was *ca.* 28% (from 2-iodonitrobenzene).

3,5-Dichloro-4-methoxy-2′,6′-dinitrobiphenyl (3f).—The preparation from 1,3-dinitrobenzene (4.5 g), and 1,3-dichloro-5-iodo-2-methoxybenzene (8.5 g) [the latter was prepared in 80% overall yield by iodination of 2,6-dichlorophenol in acetic acid by iodine chloride, followed by methylation in acetone with potassium carbonate and methyl sulphate; m.p. 82—83 °C, lit.,[17] m.p. 75—76 °C)] followed the procedure for compound (3b) (above) (17 h at 75 °C). The solid, which precipitated on pouring the mixture into acid, was collected, dried, and digested with chloroform–ethyl acetate (1 : 1). The solution was filtered through Celite, concentrated to *ca.* 300 ml, filtered through alumina, and evaporated. The residue was triturated with warm ethanol (150 ml) to yield a product (7.37 g; 80%), homogeneous by t.l.c. Recrystallization from ethyl acetate gave the *biphenyl* (3f) as pale yellow needles, m.p. 195.5—196 °C (Found: C, 45.6; H, 2.4; Cl, 20.7; N, 7.8. $C_{13}H_8Cl_2N_2O_5$ requires C, 45.5; H, 2.4; Cl, 20.7; N, 8.2%); *m/e* 342—346 (M^+) and 307 and 309 (M^+ − Cl); δ($CDCl_3$) 4.22 (3 H, s, OMe), 7.50 (2 H, s, 2-, 6-H), and 7.83—8.40 (3 H, m, 3′-,4′-, 5′-H).

5-Iodo-2-methoxy-1,3-di-t-butylbenzene (4g).—2,6-Di-t-butylphenol (Aldrich; purified by passage in hexane through alumina; 80 g) in DME (dry, 200 ml) was added at a fast drop rate to a stirred suspension of commercial potassium t-butoxide (53 g) in DME (dry, 400 ml). After 1 h, methyl iodide (70 ml) was added, and a further 30 ml after 20 min more. Next day the mixture was poured into water (2l) and extracted twice with hexane (1 l; 300 ml). Evaporation of the dried extract left a golden oil (85.3 g). This in carbon tetrachloride (500 ml) was treated at 0—5 °C with a solution of iodine monochloride (24 ml) in carbon tetrachloride (100 ml). Nitrogen was bubbled through the mixture to remove hydrogen chloride and the mixture was allowed to regain ambient temperature. After 2 h the mixture was heated at 50 °C for 2 h. Next day it was poured into aqueous sodium hydrogensulphite and shaken to discharge the iodine colour. The washed (water) organic layer was dried and evaporated. Trituration of the residue with cold methanol gave a cream solid which crystallized from ethanol–methanol to yield the *iodide* (4g) (85.1 g; 63% overall) in two crops as needles, m.p. 47—49 °C. Recrystallization gave the analytical sample, m.p. 51.5 °C (Found: C, 52.2; H, 6.7; I, 36.5. $C_{15}H_{13}IO$ requires C, 52.0; H, 6.7; I, 36.7%); δ(CCl_4) 1.40 (18 H, s, 2 × Bu^t); 3,68 (3 H, s, OMe), and 7.42 (2 H, s, 4-,6-H).

4-Methoxy-2′,6′-dinitro-3,5-di-t-butylbiphenyl (3g).—The preparation, from 1,3-dinitrobenzene (6 g) and the above iodide (4 g) (13.8 g), followed the procedure for compound (3b) (above) except that the heating time was 6 h at 80 °C and the passage through alumina was in ethyl acetate–hexane (1 : 1). The crude product (14.85 g) crystallized from ethanol–hexane, yielding the *biphenyl* (3g) (13.14 g; 95%; 3 crops) as pale yellow needles, m.p. 146—147 °C (Found: C, 65.1; H, 6.8; N, 7.3. $C_{21}H_{26}N_2O_5$ requires C, 65.3; H, 6.8; N, 7.3%); *m/e* 386 (50%, M^+) and 371 (100, M^+ − Me); *m** 357 (386→371), 356 (12%), 341 (7), 299 (12), and 257 (10); δ($CDCl_3$) 1.40 (18 H, s, 2 × Bu^t), 3.70 (3 H, s, OMe), 7.13 (2 H, s, 2-, 6-H), and 7.43—8.00 (3 H, m, 3′-,4′-,5′-H).

In another (larger scale) experiment the mother liquors were worked up by chromatography on alumina. Diethyl ether eluted a fraction which crystallized when cooled to −30 °C with methanol. This product gave pale yellow crystals (from pentane) of *4,4″-dimethoxy-2′,6′-dinitro-3,3″,5,5″-tetra-t-butyl-m-terphenyl* (6c), m.p. 137—140 °C (Found: C, 71.8; H, 8.0; N, 4.5. $C_{36}H_{48}N_2O_6$ requires C, 71.5; H, 8.0; N, 4.6%); *m/e* 604 (M^+, 90%), 589 (100), and 574 (30); δ 1.40 and 1.43 (36 H, 2 ×, 4 × Bu^t), 3.70 and 3.73 (6 H, 2 × s, 2 OMe_3), 7.20 (2 H, s, 2″-,6″-H?), 7.34 (2 H, s, 2′-, 6′-H), 7.60 (1 H d, *J* 9 Hz, 4′-H) and 8.00 (1 H, d, *J* 9 Hz, 5′-H).

1-Iodo-4-methoxy-2,3,5-trimethylbenzene (4h).—The methyl ether (b.p. 94 °C/15 mmHg) was prepared in 92% yield from 2,3,6-trimethylphenol by successive treatment in tetrahydrofuran (THF) with sodium hydride and methyl iodide. This ether (18.75 g) in acetic acid (400 ml) and water (40 ml) was treated with concentrated sulphuric acid (5 ml), iodine (12.7 g), and iodic acid (4.5 g). The mixture was stirred at 50—60 °C for 85 h, decolorized by aqueous sodium hydrogensulphite (50 ml of 10% w/v), diluted with water (500 ml), and extracted with hexane (3 × 100 ml). The extracts were washed successively with water, saturated aqueous sodium hydrogencarbonate (2 × 100 ml), water, and brine; they were then dried (Na_2SO_4) and evaporated. The *iodide* (4h) (29.7 g, 86%) distilled at 100 °C/0.55 mmHg as an oil. For analysis a centre cut was taken on redistillation (Found: C, 43.8; H, 4.8; I, 45.7. $C_{10}H_{13}IO$ requires C, 43.5; H, 4.8; I, 46.0%); δ($CDCl_3$) 2.17, 2.23, and 2.34 (9 H, 3 s, 3 × Me), 3.63 (3 H, s, OMe), and 7.50 (1 H, s, 6-H).

4-Methoxy-2,3,5-trimethyl-2′,6′-dinitrobiphenyl (3h).—Commercial potassium t-butoxide (6.34) in DME (60 ml) was stirred and treated with cuprous chloride (5.6 g) in portions during 10 min, and then left for 20 h. Pyridine (5 ml) was added and 10 min later 1,3-dinitrobenzene (8 g) in DME (15 ml). No purple colour appeared at this point, indicating a possible deficiency of potassium t-butoxide. The above iodide (13.54 g) was added and the mixture was heated to reflux; after 1.5 h, more pyridine (5 ml) was added. After 27 h of reflux, vapour phase chromatography (v.p.c.) of the product (SE-30 column; 225 °C) showed < 10% of the organic reactants and a large product peak. The bath temperature was lowered to 75 °C and maintained for a further 65 h. Addition to aqueous acid, extraction with ethyl acetate, filtration, and drying followed as usual. The ethyl acetate solution was put through alumina (100 g) and evaporated, leaving an oil (which was freed from a little cuprous iodide by filtration of a chloroform solution). The oil, after careful removal of chloroform, was triturated with ethanol–hexane (1 : 2). The yellow solid was collected and a further quantity was obtained from the mother liquors after chromatography on alumina

with 2% ethyl acetate in light petroleum (b.p. 60—80 °C) as eluant. The total of solid product, homogeneous by t.l.c. (silica, ethyl acetate–hexane 1 : 4, 2 × developed), was 9.14 g (61%). The *biphenyl* (3h) crystallized from methanol as small yellow prisms, m.p. 116—118 °C (Found: C, 60.6; H, 5.0; N, 9.0. $C_{16}H_{16}N_2O_5$ requires C, 60.8; H, 5.1; N, 8.9%); *m/e* 316 (M^+) and 269 ($M^+ - NO_2H$); δ($CDCl_3$) 2.01 (3 H, s, Me), 2.25 (6 H, s, 2 × Me), 3.70 (3 H, s, OMe), 6.73 (1 H, s, 6-H), and 7.4—8.15 (3 H, m, 3′-,4′-,5′-H). A fraction from the chromatography gave spectra indicative of a terphenyl formed from two equivalents of iodide and one of dinitrobenzene.

1-*Iodo*-4-*methoxy*-2,3,5,6-*tetramethylbenzene* (4i).—2,3,5,6-Tetramethylphenol (16.3 g) was methylated using sodium hydride and methyl iodide in THF.[18] The crude crystalline product (17.2 g) was iodinated as for the trimethyl analogue (4h) (above). Total heating time was 41 h at 65—75 °C and more iodic acid (2 mmol) was added after 18 h. After precipitation by water (1 l) the solid product was collected and dissolved in ethyl acetate (300 ml) which was washed successively with aqueous sodium hydrogensulphite, water, saturated aqueous sodium hydrogencarbonate, water, and brine; it was then dried and evaporated. The residue crystallized from methanol as colourless plates (25.45 g in 2 crops; 84% from phenol), m.p. 115—119 °C (subl.). The analytical sample of the *iodide* (4i), recrystallized from methanol, had m.p. 118—119 °C (subl.) (Found: C, 45.7; H, 5.3; I, 44.2. $C_{11}H_{15}IO$ requires C, 45.5; H, 5.2; I, 43.7%); *m/e* 290 (100%; M^+) and 275 (36%; M^+ — Me); δ($CDCl_3$) 2.30 (6 H, s, 3-,5-Me), 2.48 (6 H, s, 2-,6-Me), and 3.64 (3 H, s, OMe).

4-*Methoxy*-2,3,5,6-*tetramethyl*-2′,6′-*dinitrobiphenyl* (3i).—Copper(I) t-butoxide was prepared from potassium (1.7 g), t-butyl alcohol (50 ml), and cuprous chloride (4.32 g) as previously described, except that diethylene glycol dimethyl ether (diglyme, 50 ml) was used instead of DME. Pyridine (5.1 ml) was added, followed by a solution of 1,3-dinitrobenzene (6 g) in diglyme (50 ml). The above iodide (4i) (11 g) was then added and the mixture was heated at 140—145 °C for 90 h. It was then poured into water (600 ml), stirred with chloroform, and filtered. The chloroform layer was evaporated and lower pressure was provided to remove diglyme. The residue in ethyl acetate–hexane (1 : 1) was passed through alumina giving a crude mixture (10.35 g). A portion (3%) of this was subjected to preparative t.l.c. on silica (ethyl acetate–hexane, 1 : 9 4 × developed). The 2′,6′-dinitro-isomer (3i) was the slowest running product, but was eluted as a mixture with 1,3-dinitrobenzene (83 mg; 39 : 44); δ($CDCl_3$) 1.88 (6 H, s, 2-,6-Me), 2.22 (6 H, s, 3-,5-Me), 3 H, s, OMe); and 7.67—8.02 (m, 3 H, overlapped by a dinitrobenzene peak). The structure was established by conversion into the methoxy-dinitro-derivative (11h) (see below). [A pure specimen was made by Ullmann condensation of 1-chloro-2,6-dinitrobenzene (0.81 g) with the iodide (4i) (1.45 g) and copper powder (1.25 g) in boiling DMF (15 ml). After 1 h the mixture was worked up to yield 2,2′,6,6′-tetranitrobiphenyl (75 mg) and a mixture, separated by t.l.c. (ethyl acetate–hexane, 3 : 17; 2 elutions) into 1-*chloro*-4-*methoxy*-2,3,5,6-*tetramethylbenzene*, m.p. 55—57 °C (from aqueous ethanol) (Found: C, 66.5; H, 7.5; Cl, 17.6. $C_{11}H_{15}ClO$ requires C, 66.5; H, 7.6; Cl, 17.8%); δ 2.22 (6 H, s), 2.32 (6 H, s), and 3.62 (3 H, s); *m/e* 200, 198, 185, 183, 163, 155, and 119; and the *biphenyl* (3i) as yellow needles (from acetone–hexane), m.p. 108—109 °C (Found: C, 61.6; H, 5.6; N, 8.6. $C_{17}H_{18}N_2O_5$ requires C, 61.8; H, 5.5; N, 8.5%); *m/e* 330 (M^+, 100%), 315 (5), 300 (5), 299 (5), 283 (20), and 266 (15); δ 1.87 (6 H, s), 2.18 (6 H, s), 3.67 (3 H, s), and 7.50—8.17 (3 H, m). This substance coincided in v.p.c. retention time with the major component of the above mixture.] The second slowest band yielded a crude 2′,6′-dinitroterphenyl derivative (6b). The third band yielded 4-*methoxy*-2,3,5,6-*tetramethyl*-2′,4′-*dinitrobiphenyl* (5b) as cream-coloured crystals (from hexane), m.p. 148—150 °C (Found: C, 61.9; H, 5.6; N, 8.5. $C_{17}H_{18}N_2O_5$ requires C, 61.8; H, 5.5; N, 8.5%); *m/e* 330 (M^+, 100%), 315 (6), 313 (9), 300 (26), 299 (20), 298 (16), 275 (17), 273 (34), and 268 (20); δ 1.80 (6 H, s), 2.19 (6 H, s), 3.66 (3 H, s), 7.43 (1 H, d, *J* 8.5 Hz, 6′-H), 8.44 (1 H, dd, *J* 8.5, 2 Hz, 5′-H), and 8.77 (1 H, d, *J* 2 Hz, 3′-H).

9-*Nitro*-1,2,3,4,5,6,7,8-*octahydroanthracene*.—Octahydroanthracene (18.6 g) was suspended in nitromethane (200 ml) and methyl nitrate (7.80 g) was added. Boron trifluoride gas was passed slowly over the surface of the stirred mixture. After 5 min the hydrocarbon had dissolved. The gas flow was stopped and the mixture was stirred for 2 h. Cold aqueous sodium acetate (150 ml of 20%) was stirred in and the mixture was extracted with ethyl acetate (filtration was necessary). The ethyl acetate extract (500 ml) was dried and evaporated. The residue was extracted with hot methanol (500 ml) and the filtered extract was boiled with charcoal for 1 h. The filtrate, now yellow, deposited pale yellow needles (16.21 g; 70%) m.p. 106—107 °C in two crops. A sample, recrystallized from methanol, afforded the product as large flattened needles, m.p. 107—108 °C (lit.,[7] 89 °C) (Found: C, 72.5; H, 7.3; N, 6.1. Calc. for $C_{14}H_{17}NO_2$: C, 72.7; H, 7.4; N, 6.1%); *m/e* 231 (M^+), 185 ($M^+ - NO_2$), and 184 ($M^+ - NO_2H$); δ($CDCl_3$) 1.60—1.90 (8 H, m), 2.45—2.85 (8-H, m), 6.87 (1 H, s, 10-H); ν(CCl_4) 3 005w (Ar-H), 1 615w, 1 592w (Ar), 1 525vs (NO_2), and 1 380s cm^{-1} (lit.,[7] 3 030, 1 605, 1 560, and 1 350 cm^{-1}).

9-*Amino*-1,2,3,4,5,6,7,8-*octahydroanthracene*.—The above nitro-compound (12.85 g) in warm ethanol (100 ml) with Raney nickel (*ca.* 1 g) was treated with hydrazine hydrate (6 ml of 64%). After 1 hour at reflux the additions of nickel and hydrazine were repeated. After a further 1.5 h at reflux more hydrazine (6 ml) was added and reflux was continued for 1 h (this caused the disappearance of an intermediate, detected by t.l.c.). After dilution with more ethanol the mixture was filtered hot and concentrated. The amine (10.59 g; 95%) was obtained in 3 crops, m.p. 84—84.5 °C (lit.,[19] m.p. 84—85 °C). The mass, n.m.r. and i.r. spectra were in accord with the structure assigned.

9-*Iodo*-1,2,3,4,5,6,7,8-*octahydroanthracene* (4j).—(*a*) The above amine (0.47 g) in diethyl ether (15 ml) was treated with a solution of sulphuric acid (0.24 g) in ethanol (2 ml of 95%). The precipitated salt was collected and dried. This salt (0.47 g), in ethanol (10 ml) and aqueous sulphuric acid (3 ml of 2M), was treated with isoamyl nitrite (0.24 ml) in ethanol (1 ml) at 0 °C. After 15 min a solution of potassium iodide (0.5 g) in water (0.5 ml) was added. The mixture, after addition of a little copper powder, was heated to 80 °C for 1 h. An ethyl ether extract of the product gave an oil which, on preparative t.l.c. (hexane), gave the product (4j), which crystallized from ethanol–hexane and then from acetic acid as needles (75 mg), m.p. 67—68 °C (lit.,[20] m.p. 72—73 °C) (Found: C, 53.7; H, 5.4. Calc. for $C_{14}H_{17}I$: C, 53.9; H, 5.5%); *m/e* 312 (M^+) and 185 ($M^+ - I$); δ($CDCl_3$) 1.50—1.90 (8 H, m), 2.55—2.80 (8 H, m), and 6.75 (1 H, s, 10-H).

(*b*) Octahydroanthracene (18.6 g) was heated at 75 °C (bath) for 120 h with iodine (10.2 g), periodic acid (4.56 g, dihydrate), and sulphuric acid (3 ml, *d* 1.84) in acetic acid (100 ml) and water (20 ml). After dilution with water (1 l) the product was taken into diethyl ether and freed from acetic acid and iodine by extractions with sodium hydrogencarbonate and thiosulphate. The oily product, in acetic acid (350 ml), afforded a white crystallizate (22.4 g; m.p. 64—66 °C). This was suitable for preparative use though it contained a little octahydroanthracene (v.p.c.). The n.m.r. spectrum was essentially identical with the preparation (*a*) (above). In an experiment using more iodine, 9,10-*di-iodo*-1,2,3,4,5,6,7,8-*octahydroanthracene* was obtained as laths (from chloroform), m.p. 204—207 °C (decomp. sealed capillary) (Found: C, 38.5; H, 3.7. $C_{14}H_{16}I_2$ requires C, 38.4; H, 3.7%); *m/e* 438 (M^+), 311 ($M^+ - I$), and 184 ($M^+ - 2I$). The substance blackened on keeping. The procedure for iodination follows a published method.[21]

Condensation of Octahydroiodoanthracene with Dinitrobenzene.—Potassium (0.62 g) was dissolved in t-butyl alcohol (15 ml). Diglyme (15 ml; dry) was added and the excess of butyl alcohol was distilled off under nitrogen through a short column. The mixture was cooled and cuprous chloride (1.488 g) was added, with stirring. After 1.5 h pyridine (1.81 ml) was added followed by a mixture of 1,3-dinitrobenzene (2.52 g) and the above monoiodide [4.20 g; method (*b*)] dissolved in a little warm diglyme. The mixture was stirred and heated at 105 °C (bath) under nitrogen for a total of 90 h. Hydrochloric acid (10 ml of 4M) was added and a prolonged steam-distillation removed the diglyme and most of the unchanged reagents. The water-insoluble residue was extracted with ethyl acetate. The filtered extract was evaporated and the residue was mixed with Celite and exhaustively extracted (Soxhlet) with hexane. The extract (4.07 g) was heated at 110 °C/0.01 mmHg under a water-cooled finger condenser. The condensed product was distilled at 130 °C (bath)/0.05 mmHg to remove the remaining dinitrobenzene. The residue (1.20 g) from this distillation was chromatographed by t.l.c. (acetone–hexane, 1 : 19). Five bands were visible; the one nearest the origin yielded an eluate (5.5 mg), essentially of dinitrobenzene. The next band gave an eluate which crystallized from methanol in small yellow prisms (116 mg, 2 crops) of 9-(2,6-*dinitrophenyl*)-1,2,3,4,5,6,7,8-*octahydroanthracene* (3j) m.p. 231—233 °C (Found: C, 68.1; H, 5.8; N, 7.8. $C_{20}H_{20}N_2O_4$ requires C, 68.2; H, 5.7; N, 7.95%); δ($CDCl_3$, 90 MHz) 1.6—1.8 (8 H, m), 2.0—2.35 (4 H, m), 2.55—2.9 (4 H, m), 6.90 (1 H, s, 10-H), 7.76 (1 H, d, *J* 8 Hz, 4′-H), and 8.08 (2 H, d, *J* 8 Hz, 3′,5′-H). The third band yielded large yellow prisms (469 mg), from ethanol, of 9-(2,4-*dinitrophenyl*)-1,2,3,4,5,6,7,8-*octahydroanthracene* (5a), m.p. 147—148 °C (Found: C, 68.2; H, 5.7; N, 7.7. $C_{20}H_{20}N_2O_4$ requires C, 68.2; H, 5.7; N, 7.95%); *m/e* 352 (M^+), 335 ($M^+ - OH$), 318, 317, and 296 ($M^+ - C_4H_8$, base peak); δ($CDCl_3$) 1.40—1.90 (8 H, m), 1.95—2.35 (4 H, m), 2.60—2.90 (4 H, m), 6.92 (1 H, s, 10-H), 7.47 (1 H, d, *J* 8 Hz, 6′-H), 8.50 (1 H, dd, *J* 8 and 2 Hz), and 8.88 (1 H, d, *J* 2 Hz). The fourth band yielded, after the eluate (25 mg) had been heated under reduced pressure to remove the more volatile components, 1,3-bis-(1,2,3,4,5,6,7,8-*octahydro*-9-*anthryl*)-4,6-*dinitrobenzene* (7a) as yellow-orange rods (5 mg) (from hexane), m.p. 269—271 °C (decomp.) (Found: C, 76.0; H, 6.9; N, 5.0. $C_{34}H_{36}N_2O_4$ requires C, 76.1; H, 6.8; N, 5.2%); *m/e* 536 (M^+), 519, 502, 474, 446, and 418; δ($CDCl_3$) 1.56—1.87 (16 H, m), 2.05—2.30 (8 H, m), 2.56—2.84 (8 H, m), 6.87 (2 H, s, 2 × 10′-H), 7.16 (1 H, s, 5-H), and 8.70 (1 H, s, 2-H). This compound had been obtained in larger quantity from a previous condensation (in boiling pyridine). The original involatile residue, from sublimation in high vacuum, also contained this substance (t.l.c.), but on crystallization from chloroform, ethyl acetate, acetic acid, and ethyl acetate (five times) the residue yielded small pale yellow needles of the isomeric 1,3-*bis*-(1,2,3,4,5,6,7,8-*octahydro*-9-*anthryl*)-2,6-*dinitrobenzene* (6a), m.p. 216—218 °C (Found: C, 75.9; H, 6.8; N, 5.2. $C_{34}H_{36}N_2O_4$ requires C, 76.1; H, 6.8; N, 5.2%); *m/e* 536 (M^+), 519, 501, 488, 473 (100%), and 446; δ($CDCl_3$, 90 MHz) 1.7—1.9 (16 H, m), 2.2—2.45 (8 H, m), 2.6—2.9 (8 H, m), 6.88 and 6.90 (2 H, unresolved d, 2 × 10′-H), 7.42 (1 H, d, *J* 8 Hz, 4-H), and 8.12 (1 H, d, *J* 8 Hz, 5-H).

2′,2″,4″,6′-*Tetranitro*-m-*quaterphenyl* (8b).—2,2′,4,4′-Tetranitrobiphenyl was prepared[22] by adding biphenyl (19.8 g), in small portions during 1 h, to an ice-cold, stirred mixture of nitric acid (80 ml; *d* 1.5) and sulphuric acid (100 ml; *d* 1.84). After being allowed to attain room temperature the mixture was heated at 100 °C for 20 h and poured onto crushed ice. The solid product, washed well with water, was recrystallized from acetic acid (350 ml) containing acetic anhydride (5 ml), to give a pale yellow solid (yield 31.1 g; 74%) m.p. 160—162 °C (lit.,[23] 163—164 °C).

Potassium t-butoxide was prepared as usual from potassium (1.63 g) and suspended in DME (60 ml) under nitrogen. Cuprous chloride (4.72 g) was added, with cooling, and after 45 min at room temperature pyridine (8.5 ml), tetranitrobiphenyl (6.7 g), and iodobenzene (9.1 g) were successively added. The mixture was stirred at 80 °C (bath) for 18 h, poured into acid (200 ml, 2M HCl) and chloroform (350 ml), and filtered. The water-washed chloroform layer was concentrated to 100 ml, passed through alumina (7 × 4 cm), and evaporated. The residue crystallized from ethyl acetate–ethanol as fine pale yellow needles, m.p. 183—185 °C, raised to 185—186 °C by a further crystallization. A small, further quantity was obtained from the mother liquors after chromatography on silica (chloroform–hexane, 1 : 1; first fractions contained iodobenzene). The total yield of the *quaterphenyl* (8b) was 7.49 g (77%) (Found: C, 59.3; H, 3.1; N, 11.5. $C_{24}H_{14}N_4O_8$ requires C, 59.3; H, 2.9; N, 11.5%); *m/e* 486 (M^+), 469, 458, and 395; δ($CDCl_3$) 7.19—7.60 (12 H, m) and 7.97 (2 H, d, *J* 8.5 Hz, 5′-, 5″-H).

4,4‴-*Dimethoxy*-2′,2″,4″,6′-*tetranitro*-m-*quaterphenyl* (8c).—Cuprous chloride (1.24 g) was added to a suspension of potassium t-butoxide (1.4 g, commercial) under nitrogen. Next day pyridine (2 ml), tetranitrobiphenyl (2 g), and 4-iodoanisole (3 g) were added and the mixture was stirred and heated for 5 h at 90 °C. It was worked up as for earlier examples; the crude product, after filtration in chloroform through alumina, was a pale yellow solid (2.93 g). Crystallization from acetone–ethanol yielded 1.82 g which was largely the desired product but containing a persistent impurity. T.l.c. (chloroform–hexane, 3 : 1; 2 × developed) gave, with 75% recovery (42% yield), the pure *dimethoxytetranitroquaterphenyl* (8c) as prismatic pale yellow needles (from acetone–hexane), m.p. 201—203 °C (Found: C, 57.1; H, 3.4; N, 10.4. $C_{26}H_{18}N_4O_{10}$ requires C, 57.2; H, 3.3; N, 10.3%); *m/e* 546 (M^+), 529, and 516; δ 3.80 (6 H, s, 2 × OMe), 6.83—7.27 (8 H, dd, *J* 8 Hz, 2-,3‴-,3-,3‴-,5-,5‴-,6-,6‴-H), 7.47 (2 H, d, *J* 9 Hz, 4′-,6″-H), and 7.90 (2 H, d, *J* 9 Hz, 5′-,5‴-H).

4,4‴-Dimethoxy-5′-(4-methoxy-2,3,5,6-tetramethylphenyl)-2,2‴,3,3‴,5,5‴,6,6‴-octamethyl-2′,4″,6′,6″-tetranitro-m-quaterphenyl (9).—Tetranitrobiphenyl (0.5 g) in dry pyridine (10 ml) was treated with copper(I) butoxide (0.54 g) under nitrogen. After a few minutes the iodide (4i) (1.2 g) was added and the mixture was heated at 75 °C for 70 h. After the usual work-up with acid and ethyl acetate the product was chromatographed on silica (25 × 2.5 cm). Elution with acetone–hexane (3 : 17) gave first the iodide (0.94 g) and then a yellow solid (0.27 g) which was purified by t.l.c. (chloroform–hexane, 3 : 2). The major component gave a pale yellow solid (26 mg) on trituration with methanol. Recrystallization from acetone–methanol afforded the *phenyl–quaterphenyl* (9) as yellow prisms, m.p. 296—298 °C (decomp.) (Found: C, 65.6; H, 5.9; N, 6.7. $C_{45}H_{48}N_4O_{11}$ requires C, 65.8; H, 5.9; N, 6.8%); *m/e* 820 (M^+) and 789; δ (90 MHz) 1.82 (6 H, s), 1.93 (3 H, s), 2.02 (9 H, s), 2.13 and 2.18 (18 H, d), 3.59, 3.61, 3.65 (9 H, m, 3 × OMe), 7.25 (1 H, s, 4′-H), 7.42 (1 H, s, 2″-H), and 8.78 (1 H, s, 5″-H). The noteworthy non-equivalences of the methyl groups can be ascribed to restricted rotations.

Methoxydenitration of Biphenyls and Quaterphenyls

2-Methoxy-6-nitrobiphenyl (11b).—(*a*) The preparation of 2-amino-6-nitrobiphenyl [24] was improved. To a suspension of 2,6-dinitrobiphenyl (2.99 g) at gentle reflux in ethanol (75 ml) and pyridine (5 ml) was added, over 1 h, aqueous ammonium sulphide (10% w/w; 25 g). Sublimate in the condenser was washed down with water and refluxing continued for 2 h; more sulphide solution (5 g) was then added as drops. Next day the mixture was poured onto ice (250 g) and water (250 ml), stirred to coagulation, diluted with more water (200 ml), and filtered. The residue was extracted with hot hydrochloric acid (250 ml of 4M) and then with hot 2M acid until no amine hydrochloride was detected (cloudiness with ammonia). The total acid filtrate was then made alkaline (85 ml, 0.880 ammonia), the product was extracted with ethyl acetate (3 × 50 ml), and the extract washed with water (2 × 100 ml) and brine (100 ml). Evaporation of the dried extract gave the yellow crystalline amine (2.19 g, 84%). A sample crystallized from cyclohexane–ethyl acetate as needles, m.p. 74—75 °C (lit.,[24] m.p. 75—76 °C) (Found: C, 67.1; H, 4.7; N, 13.1. Calc. for $C_{12}H_{10}N_2O_2$: C, 67.3; H, 4.7; N, 13.1%). The hydrogensulphate was made by precipitation from diethyl ether with ethanolic sulphuric acid; a portion (624 mg) in sulphuric acid (10 ml of 4M) was diazotized at 0—5 °C with sodium nitrite (147 mg) in water (1 ml). After 1 h the solution was added dropwise to boiling, vigorously stirred sulphuric acid (30 ml of 8M). Boiling was continued for 5 min after the addition and the mixture then poured onto ice (150 g) and extracted with chloroform. The phenol was separated by extraction with sodium hydroxide (2 × 50 ml of 1M), returned to chloroform solution, and chromatographed on silica. The *phenol* (IIa) (193 mg, 45%) was eluted with chloroform–hexane (1 : 1). The analytical sample, obtained by sublimation (60—70 °C/0.8 mmHg) formed yellow, foliated crystals, m.p. 60—62 °C (Found: C, 67.2; H, 4.2; N, 6.6. $C_{12}H_9NO_3$ requires C, 67.0; H, 4.2; N, 6.5%); *m/e* 215 (M^+, 92%), 198 (M^+ − OH, 100), 139 (87), and 115 (96); $\nu_{max.}$ 3 400, 1 610, 1 515, 1 295, 820, 800, 780, 750, 730, 720, and 700 cm^{-1}. On methylation in diethyl ether with an excess of ethereal diazomethane the methyl ether (11b), m.p. 90—91 °C, was formed and was identical (mixed m.p., n.m.r. and i.r. spectra, and t.l.c.) with the sample prepared as in method (*b*).

(*b*) Sodium methoxide (52 g) was added to a stirred solution of 2,6-dinitrobiphenyl (195.2 g) in hexamethylphosphoramide (HMPT) (1.7 l). The deep purple solution was stirred for 28 h, poured into water (6 l), acidified slightly (2M hydrochloric acid), and diluted to 10 l. The product was collected, washed with water, dissolved in chloroform, and filtered through alumina (45 × 8 cm). Chloroform eluted the product in the yellow fore-run. Crystallization from methanol gave *2-methoxy-6-nitrobiphenyl* (IIb) as yellow crystals (in three crops) (159.9 g, 87%), m.p. 90—91 °C (Found: C, 68.0; H, 4.8; N, 6.2. $C_{13}H_{11}NO_3$ requires C, 68.1; H, 4.8; N, 6.1%); *m/e* 229 (M^+, 90%), 212 (40), 201 (50), 168 (60), and 139 (100); $\nu_{max.}$ 1 610, 1 600, 1 520, 1 270, 1 050, 920, 900, 808, 800, 765, 750, 740, and 700 cm^{-1}.

6,6′-Dimethoxy-2,2′-azoxybiphenyl (12a).—2,6-Dinitrobiphenyl (3 g) in HMPT (50 ml) was stirred with sodium methoxide (2.4 g) under nitrogen for 22 h. The product (12a) was precipitated by pouring onto ice. After crystallization from chloroform the *oxide* (12a) had m.p. 244—247 °C (Found: C, 76.0; H, 5.4; N, 7.0. $C_{26}H_{22}N_2O_3$ requires C, 76.1; H, 5.4; N, 5.8%); *m/e* 410 (M^+, 20%), 409 (40), 394 (27), 393 (54), and 197 (100); δ(90 MHz) 3.66, 3.67 (both 3 H, s, OMe), and 6.0—7.4 (16 H, m). In another experiment 2,6-dimethoxybiphenyl was isolated by chromatography; laminated needles (from cyclohexane) m.p. 86—87 °C (lit.,[25] m.p. 87—88 °C) alone or mixed with an authentic specimen.

NN′-Di-(6-methoxybiphenyl-2-yl)hydrazine (12b).—To a stirred suspension of the azoxybiphenyl (12a) in ethanol (25 ml) at 65 ± 5 °C, palladium–carbon (50 mg of 10%) and hydrazine hydrate (1 ml, dropwise) were added; these additions were repeated after 1 and 2 h and the temperature was maintained at 80 °C for 3 h more. The mixture was cooled and filtered, and the residue was washed with hot chloroform (100 ml). Evaporation of the filtrates, dissolution in chloroform (75 ml), and evaporation of the washed (3 × 100 ml water) solution left a solid that was collected and washed with diethyl ether. The *dibiphenylylhydrazine* (12b) crystallized as colourless needles (from ethyl acetate), m.p. 200—210 °C (decomp.) (Found: C, 78.9; H, 6.2; N, 7.1. $C_{26}H_{24}N_2O_2$ requires C, 78.8; H, 6.1; N, 7.1%); *m/e* 396 (M^+, 78%), 394 (53), 199 (100), 183 (68), 168 (53), and 154 (23); δ 3.71 (6 H, s, 2 × OMe), 5.34br, (2 H, s, 2 × NH), 6.4—6.75 (4 H, m), and 7.05—7.5 (12 H, m); $\nu_{max.}$ 3 410, 1 600, 1 260, and 1 085 cm^{-1}. The same compound was also made in 24% yield by reduction of the nitro-compound (11b) with zinc and sodium hydroxide in methanol–water.

6,6′-Dimethoxy-2,2′-azobiphenyl (12c).—A cold solution of sodium hypobromite [from bromine (0.5 ml) added to sodium hydroxide (0.95 g) in ice–water (12 ml)] was added in portions to a stirred solution of the above hydrazine (12b) (204 mg) in chloroform (10 ml). The mixture was stirred for 1 h more, and diluted with chloroform; the solution was washed (2 × water, 10% NH_4Cl, water, brine), dried, and evaporated. The residue, on trituration with ethanol, gave the *azobiphenyl* (12c) (183 mg, 90%). The analytical sample crystallized from methanol as orange prisms, m.p. 221—223 °C (Found: C, 79.3; H, 5.6; N, 7.2. $C_{26}H_{22}N_2O_2$ requires C, 79.2; H, 5.6; N, 7.1%); *m/e* 394 (M^+, 47%), 211 (25), 183 (27), 168 (40), and 40 (100); δ 3.77 (6 H, s, 2 × OMe), 6.7—7.4 (6 H, m), and 7.36 (10 H, s, 2 × Ph); $\nu_{max.}$ 1 585, 1 260, 1 085, 1 070, 805, 765, 735, and 700 cm^{-1}. A number of attempts were made to dehydrogenate this

compound to a benzocinnoline, but vanadium oxyfluoride, aluminium chloride, and thallium(III) trifluoroacetate all gave mixtures in which none of the desired product (see the following paper) was detected by t.l.c.

2,4′-Dimethoxy-6-nitrobiphenyl (11c).—The preparation from methoxydinitrobiphenyl (3b) (8.45 g) and sodium methoxide (2.18 g) in HMPT (75 ml) for 48 h followed the procedure for compound (11b) (above). The work-up was also similar except that the crude product was not collected, but extracted with ethyl acetate. Passage in chloroform through alumina followed by recrystallization from methanol gave the *dimethoxynitrobiphenyl* (11c) as yellow leaflets (7.18 g, 90%), m.p. 103—104 °C (Found: C, 64.8; H, 5.0; N, 5.6. $C_{14}H_{13}NO_4$ requires C, 64.9; H, 5.1; N, 5.4%); *m/e* 259 (100%), 176 (30), 155 (30), 139 (40), and 127 (50); δ 3.77 and 3.80 (2 × 3 H, s, 2 × OMe), and 6.80—7.41 (7 H, m).

2,3′-Dimethoxy-2′-methyl-6-nitrobiphenyl (11d).—Prepared from the methoxymethyldinitrobiphenyl (3c) (1.078 g), sodium methoxide (0.246 g), and HMPT (10 ml) for 45 h, as for compound (11b), the product after precipitation was crystallized directly from methanol (50 ml), giving the *dimethoxymethylnitrobiphenyl* (11d) as pale yellow needles (0.814 g, 80%, 2 crops), m.p. 141—143 °C (on recrystallization) (Found: C, 65.9; H, 5.5; N, 5.2. $C_{15}H_{15}NO_4$ requires C, 65.9; H, 5.5; N, 5.1%); *m/e* 273 (M^+, 100%), 256 (35), 242 (45), and 226 (60); δ 1.97 (3 H, s, Me), 3.75 (3 H, s, OMe), 3.83 (3 H, s, OMe), and 6.5—7.5 (6 H, m).

3,5-Dichloro-2′,4-dimethoxy-6′-nitrobiphenyl (11e).—Prepared from the dinitrobiphenyl (3f) (2 g) and sodium methoxide (420 mg) in HMPT (15 ml) for 66 h and worked up by extraction of the precipitated product with ethyl acetate and purification by passage in chloroform through alumina the *dichlorodimethoxynitrobiphenyl* (11e) was crystallized from methanol as pale yellow plates (1.6 g, 84%), m.p. 139—140 °C (Found: C, 51.6; H, 3.5; Cl, 21.6; N, 4.3. $C_{14}H_{11}Cl_2NO_4$ requires C, 51.2; H, 3.4; Cl, 21.6; N, 4.3%); *m/e* 327, 329, and 341 (M^+, ratio *ca.* 9 : 6 : 1); δ 3.80 (3 H, s, OMe), 3.93 (3 H, s, OMe), and 7.03—7.50 (5 H, m).

2′,4-Dimethoxy-6′-nitro-3,5-di-t-butylbiphenyl (11f).—From the methoxydinitrodi-t-butylbiphenyl (3g) (12 g) and sodium methoxide (2.49 g) in HMPT (90 ml) for 66 h, with work-up as for (11b), the *dimethoxynitrodi-t-butylbiphenyl* (11f) crystallized from methanol as pale yellow rods (10.74 g, 93%, 2 crops), m.p. 100—101 °C (Found: C, 71.1; H, 7.9; N, 3.8. $C_{22}H_{29}NO_4$ requires C, 71.1; H, 7.9; N, 3.8%); *m/e* 371 (M^+, 65%) and 358 (100); *m** 342 (371→356); δ 1.43 (18 H, s), 3.68 and 3.75 (6 H, 2 × s, 2 × OMe), and 6.95—7.32 (5 H, m).

2,4′-Dimethoxy-2′,3′,5′-trimethyl-6-nitrobiphenyl (11g).—The methoxytrimethyldinitrobiphenyl (3h, 15.8 g) and sodium methoxide (3.16 g) in HMPT (100 ml) after 46 h was worked up as for compound (11c). Crystallization from methanol gave the *dimethoxytrimethylnitrobiphenyl* (11g) (13.09 g, 87%, 2 crops). A recrystallized sample formed yellow prisms, m.p. 127—128 °C (Found: C, 67.8; H, 6.2; N, 4.7. $C_{17}H_{19}NO_4$ requires C, 67.8; H, 6.4; N, 4.7%); *m/e* 301 (M^+); δ 1.98 (3 H, s), 2.26 (6 H, s), 3.73 (3 H, s), 3.77 (3 H, s), 6.70 (1 H, s, 6′-H), and 7.0—7.5 (3 H, m); $\nu_{max.}$ 1 535, 1 270, 1 095, 1 055, and 915 cm.[1]

2,4′-Dimethoxy-2′,3′,5′,6′-tetramethyl-6-nitrobiphenyl (11h).—A mixture of the dinitro-compound (3i) with dinitrobenzene [1.73 g, *ca.* 1.24 g of compound (3i)] with sodium methoxide (0.44 g) in HMPT (15 ml) was stirred for 68 h, poured into water (100 ml), and extracted with chloroform. The extract was washed (water, brine), dried, and passed through alumina. The evaporated residue still contained HMPT; it was washed in hexane with water (3 ×) and brine. Evaporation and trituration with methanol then gave yellow crystals (0.47 g). The product was purified further by chromatography on silica using ethyl acetate–hexane (1 : 4). Crystallization from methanol then gave the *dimethoxytetramethylnitrobiphenyl* (11h) (0.23 g, 19%) as yellow rods, m.p. 156—158 °C (after recrystallization) (Found: C, 68.7; H, 6.8; N, 4.5. $C_{18}H_{21}NO_4$ requires C, 68.6; H, 6.7; N, 4.4%); *m/e* 315 (M^+, 100%), 285 (30), 284 (33), 268 (80), 253 (34), and 238 (24); δ 1.85 (6 H, s), 2.20 (6 H, s), 3.66 (3 H, s), 3.73 (3 H, s), and 7.05—7.5 (3 H, m); $\nu_{max.}$ 1 605, 1 575, 1 520, 1 270, 1 100, 1 060, 910, 900d, and 740 cm^{-1}.

Action of Sodium Methoxide on 2′,2″,4″,6′-Tetranitro-m-quaterphenyl (8b).—Several experiments were necessary to isolate all the products described below. In general the tetranitro-quaterphenyl (8b) in HMPT (or dimethyl sulphoxide–HMPT) was treated with sodium methoxide 1—2.7 mol equiv.) for 20—96 h. T.l.c. (acetone–hexane, 1 : 4; repeated development) was invariably necessary to separate components.

4″,6′-Dimethoxy-2′,2″-dinitro-m-quaterphenyl (15a).—This *substance*, which moved on t.l.c. more slowly even than the tetranitro-compound (8b), crystallized from acetone–ethanol as colourless needles, m.p. 260—261.5 °C (Found: C, 68.6; H, 4.4; H, 6.2. $C_{26}H_{20}N_2O_6$ requires C, 68.4; H, 4.4; N, 6.1%); *m/e* 456 (M^+, 75%), 410 (100), and 105 (62); δ(90 MHz) 3.77 (6 H, s, 2 × OMe), 7.05 (2 H, d, *J* 9 Hz, 5′-, 5″-H), and 7.39 (12 H, s, overlapping d).

2′,2″-Dimethoxy-4″,6′-dinitro-m-quaterphenyl (13a).—Found in the fastest running bands, this *substance* crystallized from acetone–ethanol as pale yellow needles, m.p. 201—203 °C (Found: C, 68.3; H, 4.4; N, 6.2. $C_{26}H_{20}N_2O_6$ requires C, 68.4; H, 4.4; N, 6.1%); *m/e* 456 (M^+, 100%), 439 (6), 428 (30), and 369 (25); δ 3.17 (6 H, s, 2 × OMe), 7.40 (s), 7.43 (d), and 7.62 (d, *J* 8.5 Hz) (total 14 H).

2′,4″-Dimethoxy-2″,6′-dinitro-m-quaterphenyl (14a).—This *substance* was recovered from bands running slightly faster than the tetranitro-compound (8b). Compound (14a) crystallized from acetone–ethanol as pale yellow needles, m.p. 153—154 °C (Found: 68.8; H, 4.5; N, 6.2. $C_{26}H_{20}N_2O_6$ requires C, 68.4; H, 4.4; N, 6.1%); *m/e* 456 (M^+, 100%), 439 (<5), and 424 (<5); δ 3.17 (3 H, s, 2′-OMe), 3.80 (3 H, s, 4″-OMe), 7.10br (2 H, d, *J* 9 Hz); the phenyl groups showed as a singlet, δ 7.38, with overlapping multiplets (total 12 H).

6′-Methoxy-2′,2″,4″-trinitro-m-quaterphenyl (16a).—Formed by the action of sodium methoxide (1 equiv.), this product was isolated by t.l.c. of a crystallizate (from diethyl ether) of the crude product. It was separated in this way from the unsymmetrical dimethoxy-compound (14a), running somewhat slower than this. Crystallization from acetone–ethanol gave the *methoxytrinitro-quaterphenyl* (16a) as yellow needles, m.p. 190—193 °C (change in crystal form during heating) (Found: C, 63.6; H, 3.7; N, 8.9. $C_{25}H_{17}N_3O_7$ requires C, 63.7; H, 3.6; N, 8.9%); δ(90 MHz) 3.80 (3 H, s, OMe), 7.12 (1 H, d, *J* 8.5 Hz), 7.2—7.5 (11 H, m), 7.58 (1 H, d, *J* 8.5 Hz), and 7.99 (1 H, d, *J* 8.5 Hz).

2′,4″,6′-Trimethoxy-2″-nitro-m-quaterphenyl (17).—This was the major product in an experiment with 2.68 mol equiv. of sodium methoxide. The principal band on t.l.c. was eluted and the *trimethoxynitroquaterphenyl* (17) was

recrystallized from ethanol as colourless needles, m.p. 182—183 °C (Found: C, 73.5; H, 5.3; N, 3.2. $C_{27}H_{23}NO_5$ requires C, 73.5; H, 5.3; N, 3.2%); *m/e* 441 (M^+, 100%), and families of minor peaks at *m/e ca.* 410, 394, 380, 365, and 350; δ 3.12 (3 H, s, 2'-OMe), 3.79 (3 H, s, OMe), 3.85 (3 H, s, OMe), 6.67 (1 H, d, *J* 8.5 Hz, H-5'), 7.09 (2 H, apparent t, apparent *J* 8.5 Hz, 4'-,6''-H), and 7.3—7.5 (11 H, m).

*Action of Sodium Ethoxide on 2',2'',4'',6'-Tetranitro-*m*-quaterphenyl* (8b).—The tetranitroquaterphenyl (8b) (309 mg) in HMPT (6 ml) was stirred with sodium ethoxide (95 mg; 2.2 equiv.) for 48 h. The crude product, isolated by extraction with ethyl acetate after addition to dilute acid, was applied to four 40 × 20 cm silica plates. Continuous elution with acetone–hexane (1 : 4) gave four major bands. In order of decreasing mobility these gave the following compounds.

*2',2''-Diethoxy-4'',6'-dinitro-*m*-quaterphenyl* (13b) (19 mg, 6%, crude) crystallized from ethanol–hexane as pale yellow needles, m.p. 181—182 °C (Found: C, 69.4; H, 5.1; N, 5.8. $C_{28}H_{24}N_2O_6$ requires C, 69.4; H, 5.0; N, 5.8%); *m/e* 484 (M^+, 100%); δ 0.74 (6 H, t, *J* 7 Hz), 3.28 (4 H, q, *J* 7 Hz), and 7.37 (s) overlapping 7.45 (d) and 7.62 (d) (*J* 9 Hz) (total 14 H).

*2',4''-Diethoxy-2'',6'-dinitro-*m*-quaterphenyl* (14b) (79 mg, 26% crude) crystallized from ethanol as pale yellow prismatic needles, m.p. 167—168 °C (Found: C, 69.5; H, 5.0; N, 5.7. $C_{28}H_{24}N_2O_6$ requires C, 69.4; H, 5.0; N, 5.8%); *m/e* 484 (M^+, 100%) and 467 (5); δ 0.70 (3 H, t, *J* 7 Hz), 1.24 (3 H, t, *J* 7 Hz), 3.30 (2 H, q, *J* 7 Hz), 4.01 (2 H, q, *J* 7 Hz), 7.08 (1 H, d, *J* 9 Hz), and 7.25—7.60 (13 H, m).

*4'',6'-Diethoxy-2',2''-dinitro-*m*-quaterphenyl* (15b) (105 mg, 34% crude) formed needles (after several crystallizations from ethanol), m.p. 185 °C (Found: C, 69.5; H, 5.0; N, 5.9. $C_{28}H_{24}N_2O_6$ requires C, 69.4; H, 5.0; N, 5.8%); *m/e* 484 (M^+, 100%), and 438 (75); δ 1.25 (6 H, t, *J* 7 Hz), 3.99 (4 H, q, *J* 7 Hz), 6.98 (2 H, d), and 7.32 (s) overlapping 7.30 (d) (total 12 H).

*6'-Ethoxy-2',2'',4''-trinitro-*m*-quarterphenyl* (16b) (53 mg, 17% crude) crystallized from acetone–ethanol as pale yellow prisms, m.p. 178—179 °C (Found: C, 64.4; H, 3.9; N, 8.7. $C_{26}H_{19}N_3O_7$ requires C, 64.3; H, 3.9; N, 8.7%); *m/e* 485 (M^+, 100%), 457 (40), 439 (50), and 411 (12); δ 1.23 (3 H, t, *J* 7 Hz), 3.98 (2 H, q, *J* 7 Hz), 7.00 (1 H, d, *J* 9 Hz), 7.31 (s) and 7.33 (s) overlapping 7.29 (d) and 7.50 (d) (total 12 H), and 7.90 (1 H, d, *J* 9 Hz).

*4'',6'-Di-(2,2-dimethylpropoxy)-2',2''-dinitro-*m*-quaterphenyl* (15c).—The tetranitroquaterphenyl (8b) (200 mg) in HMPT (5 ml) was treated with sodium neopentyl oxide (100 mg) and stirred for 24 h. The product, isolated as above, was chromatographed on two plates (acetone–hexane, 3 : 17, twice developed). The fastest running band gave, on crystallization from acetone–hexane, the *dineopentyloxydinitroquaterphenyl* (15c) as fine needles, m.p. 127—128 °C (Found: C, 71.8; H, 6.4; N, 4.9. $C_{34}H_{36}N_2O_6$ requires C, 71.8; H, 6.4; N, 4.9%); *m/e* 568 (M^+, 100%), 498 (10), 452 (32), 382 (90), and 352 (55); δ 0.8 (18 H, s), 3.55 (4 H, s), 7.00 (2 H, d, *J* 8.5 Hz), and 7.35 (d) overlapping 7.38 (s) (total 12 H). The reaction mixture showed three major components by t.l.c. The yield of the above product was raised to 22% by use of an excess of alkoxide.

*2',2'',4,4'''-Tetramethoxy-4'',6'-dinitro-*m*-quaterphenyl* (13d).—The dimethoxytetranitroquaterphenyl (8c) (0.29 g) in HMPT (5 ml) was treated with sodium methoxide (68 mg). After 43 h the mixture was worked up as usual. The product was a mixture; on t.l.c. only the *2',2''-dimethoxy-isomer* was separated analytically pure, as small yellow prisms, m.p. 201—202 °C (from ethanol) (Found: C, 65.1; H, 4.7; N, 5.3. $C_{28}H_{24}N_2O_8$ requires C, 65.1; H, 4.7; N, 5.4%); *m/e* 516 (M^+, 100%), 486 (8), and 484 (10); δ 3.12 (6 H, s, 2'-,2''-OMe), 3.80 (6 H, s, 4-,4'''-OMe), 6.91 (4 H, d, *J* 9 Hz, 3-,5-,3'''-,5'''-H), 7.26 (4 H, d, *J* 9 Hz, 2-,6-,2'''-,6'''-H), 7.37 (2 H, d, *J* 8 Hz, 4'-,6''-H), and 7.55 (2 H, d, *J* 8 Hz, 5'-,5''-H). Indications of other isomers were obtained.

*Action of Sodium Benzaldoxime on 2',2'',4'',6'-Tetranitro-*m*-quaterphenyl* (8b).—The tetranitro-compound (8b) (252 mg) in HMPT (10 ml) was treated with the sodium salt of benzaldoxime (300 mg, dried at 114 °C/0.4 mmHg for 3 h). After 1.5 h under nitrogen formation of two products, more polar than the starting material, appeared to be complete (t.l.c.) and the mixture was poured into hydrochloric acid (100 ml of 2M). The product was collected and chromatographed on silica plates (chloroform–hexane, 3 : 2, 2 elutions). The less polar product (60 mg) crystallized from ethanol–hexane in clusters of yellow prisms, m.p. 215—216 °C (M^+, 381). Its identification as 3-hydroxy-7-nitro-4,6-diphenyldibenzofuran (18a) was based on analysis of the methyl ether, *3-methoxy-7-nitro-4,6-diphenyldibenzofuran* (18b), prepared by methylation (methyl sulphate, potassium carbonate, acetone); it formed lemon-yellow needles, m.p. 209—210 °C (from acetone–ethanol) (Found: C, 76.0; H. 4.3; N, 3.7. $C_{25}H_{17}NO_4$ requires C, 75.9; H, 4.3; N, 3.5%); *m/e* 395 (M^+, 100%), 378 (24), 363 (15), 334 (35), and 305 (50); δ 3.85 (3 H, s, OMe), 7.03 (1 H, d, *J* 8.5 Hz), 7.38 (s) overlapping 7.2—7.87 (m) (total 13 H). The more polar product (50 mg) crystallized from ethanol–hexane as pale yellow prisms, m.p. 184—186 °C (M^+, 457). Identification of this as 2'-hydroxy-2'',4'',6'-trinitro-*m*-quaterphenyl (19a) was confirmed by methylation (as above) to *2'-methoxy-2'',4'',6'-trinitro-*m*-quaterphenyl* (19b), cream microprisms (from ethanol), m.p. 213 °C (Found: C, 6.38; H, 4.1; N, 8.9. $C_{25}H_{17}N_3O_7$ requires C, 63.7; H, 4.3; N, 8.9%); *m/e* 471 (M^+, 100%), 453 (20), and 442 (55); *m** 415 (471→442); δ 3.14 (3 H, s, OMe), 7.38 (s) overlapping 7.2—7.73 (m) (total 13 H), and 8.01 (1 H, d, *J* 9 Hz).

Preparation of Diarylphosphinic Acids and Esters

Bis-(3-methoxyphenyl)phosphinic Acid (20a).—A solution of 3-bromoanisole (5 g) in dry diethyl ether (15 ml) was added gradually to magnesium (0.65 g) under dry diethyl ether (15 ml). When the reaction started, the rate of addition (over 45 min) was adjusted to allow gentle reflux. Dry THF (10 ml) was added to dissolve the precipitate and the mixture was boiled under reflux for 2 h before the addition, as drops, of diethylphosphoramidic dichloride (Et_2NPOCl_2, 2.54 g) in diethyl ether (5 ml). After a further 1 h at reflux the cooled mixture was diluted with water (10 ml) and aqueous ammonium chloride (20 ml). The ethereal layer yielded a residue (4.4 g) which was heated for 5 h (bath, 110 °C) with hydrochloric acid (50 ml, *d* 1.18). After cooling, the pale yellow solid (1.9 g; 59%) that had separated was collected and recrystallized from aqueous ethanol; the *phosphinic acid* (20a) formed plates m.p. 185—187 °C (Found: C, 60.5; H, 5.1; P, 11.5. $C_{14}H_{15}O_4P$ requires C, 60.4; H, 5.4; P, 11.1%); *m/e* 278 (M^+, 100%), 277 (95), 259 (20), 250 (12), and 248 (10); δ[$(CD_3)_2SO$] 3.80 (6 H, s, OMe) and 7.0—7.57 (8 H, m); $\nu_{max.}$ 2 680m (POOH) and 1 240s cm^{-1} (PO). *Methyl bis-(3-methoxyphenyl)phosphinate* (20b) was made from this acid (0.5 g), potassium carbonate (1.25 g), and methyl sulphate (0.5 g)

in boiling acetone (25 ml; 5 h; reflux). The acetone, on evaporation, left a residue which was taken up in diethyl ether, washed (water, 10% NH_4OH, water), dried, and distilled; the *ester* (20b) was a colourless oil, b.p. 240 °C (block temperature)/0.15 mmHg (0.48 g, 91%) (Found: C, 61.4; H, 6.0; P, 10.4. $C_{15}H_{17}O_4P$ requires C, 61.6; H, 5.9; P, 10.6%); *m/e* 292 (M^+, 100%) and 291 (95); *m** 290 (292→291), 261 (28), and 258 (20); δ 3.80 (s) overlapping 3.80 (d, *J* 11 Hz) (total 9 H), 6.97—7.23 (2 H, m), and 7.27—7.62 (6 H, m); δ(^{31}P) 96.594 p.p.m. (s) upfield of trimethylphosphine.

Bis-(3-hydroxyphenyl)phosphinic Acid (20c).—Neither pyridinium chloride nor boron tribromide gave complete demethylation of the acid (20a), but this was effected by boiling for 15—20 min with hydriodic acid (d 1.7). The product, after dilution, was recrystallized from water, a drop of concentrated hydrochloric acid being added after filtration. The dihydroxy-acid (20c) formed small white needles, m.p. 239—240 °C (lit.,[11] m.p. 226—229 °C) (Found: C, 57.3; H, 4.4. Calc. for $C_{12}H_{11}O_4P$: C, 57.6; H, 4.4%).

3,5,7-Trimethoxydibenzophosphole 5-Oxide (21).—A stirred suspension of vanadium oxytrifluoride (1.65 g) in trifluoroacetic acid (10 ml) and trifluoroacetic anhydride (2 ml) was treated at −20 °C with a solution of the ester (20b) (201 mg) in trifluoroacetic acid (7.5 ml), dropwise over 0.5 h. After 5 h at −20 °C the mixture was decomposed by careful addition of saturated sodium carbonate (25 ml), poured slowly into a further 100 ml of carbonate, and extracted with ethyl acetate (2 × 50 ml). The residue (176 mg) on evaporation of the washed (brine) and dried solution, was chromatographed (preparative t.l.c., ethyl acetate, continuous development) and the product (which unlike the starting material showed strong blue fluorescence in u.v. radiation) was eluted to give crystalline solid (114 mg, 57%), m.p. 138 °C, homogeneous on t.l.c. Recrystallization from acetone–hexane gave clusters of colourless needles of the trimethoxydibenzophosphole oxide (21), m.p. 139—140 °C alone or mixed with a specimen prepared from the trihydroxy-analogue (see the preceding paper). The i.r. spectra were identical; δ 3.88 (s) overlapping with 3.73 (d, *J* 11.5 Hz) (total 9 H) and 6.95—7.73 (6 H, m).

Methyl (24a) *and Ethyl* (24b) *Bisbiphenyl-2-yl)phosphinate*. To a stirred solution of 2-iodobiphenyl (560 mg) in pentane (10 ml) under nitrogen at room temperature was added butyl-lithium (4 ml of 0.5M). After 18 h, diethyl ether (10 ml) was added and then dropwise a solution of methyl dichlorophosphate (149 mg) in diethyl ether (5 ml). After 1 h, water (35 ml) and diethyl ether (25 ml) were added. The aqueous layer was washed with more diethyl ether and the combined ether solutions were washed (1M HCl, 2 × water, brine), dried, and evaporated. The solid (205 mg, 53%) was collected as a white crystalline powder by washing with hexane. Crystallization from acetone gave the *methyl ester* (24a), m.p. 130—132 °C (Found: C, 78.0; H, 5.5; P, 8.0. $C_{25}H_{21}O_2P$ requires C, 78.1; H, 5.5; P, 8.1%); *m/e* 384 (M^+, 100%), 383 (90), 353 (20), 307 (20), 231 (60), 199 (50), and 152 (40); δ 3.54 (3 H, d, *J* 11 Hz, OMe) and 6.8—7.7 (18 H, m); $\nu_{max.}$ 1 220, 1 050, and 1 040 cm^{-1}. The *ethyl ester*, prepared similarly from ethyl dichlorophosphate (67% yield), crystallized from acetone and had m.p. 89—91 °C (Found: C, 78.4; H, 5.8; P, 7.8. $C_{26}H_{23}O_2P$ requires C, 78.4; H, 5.8; P, 7.8%); *m/e* 398 (M^+, 100%), 369 (20), 245 (33), 217 (30), 199 (50), 152 (50), 95 (35), and 93 (60); δ 1.14 (3 H, t, *J* 7 Hz), 3.90 (2 H, dq, $^3J_{PH}$ 7, J_{HH} 7 Hz), and 6.8—7.7 (18 H, m); $\nu_{max.}$ 1 220 and 1 040 cm^{-1}.

2-Amino-6-methoxybiphenyl (22a).—To a stirred solution of 2-methoxy-6-nitrobiphenyl (25.14 g) in ethanol (250 ml), pre-heated to 60 °C, was added Raney nickel (1—1.5 g) and then, dropwise, hydrazine hydrate (20 ml) at a rate allowing gentle reflux without external heating. After the addition (40 min) the mixture was stirred for 20 min and refluxed for 1 h. Reduction being incomplete (t.l.c.), more catalyst (0.5 g) and hydrazine hydrate (5 ml, dropwise) were added and reflux was continued (2 h). Filtration and evaporation left a dark oil which was dissolved in diethyl ether (300 ml), washed (10% aqueous $NaHSO_3$, water, brine), dried, and treated with a solution of sulphuric acid (11 g; *d* 1.84) in ethanol–water (19 : 1, 100 ml). The amine hydrogensulphate (27.55 g, 84%) was collected, washed with diethyl ether, and dried. The amine, an oil, has been prepared previously by a different route.[26] It had δ 3.4br (2 H, s, NH_2), 3.63 (3 H, s, OMe), 6.28—6.55 (2 H, m), and 6.9—7.4 (6 H, m), and was characterized as the benzamide, which crystallized from diethyl ether–hexane as prismatic needles, m.p. 104—105.5 °C (lit.,[26] m.p. 106—107 °C).

2-Iodo-6-methoxybiphenyl (23a).—A cold suspension of the above hydrogensulphate (24.9 g) in sulphuric acid (20 ml of 1M) and water (65 ml) was vigorously stirred at 0—5 °C during the addition, as drops, of sodium nitrite (6.24 g) in water (15 ml). After 20 min, sulphuric acid (1.7 ml, *d* 1.84) was added, followed by potassium iodide (16.7 g) in ice-cold water (17 ml). Copper powder (*ca.* 0.1 g) was added and the mixture was allowed to warm. Nitrogen evolution was complete after a final heating to 75—80 °C. The cooled mixture was extracted with chloroform (3 × 50 ml) which was then washed (10% aqueous $NaHSO_3$, 2M NaOH, 0.5M HCl, water, brine), dried, and distilled. The *iodide* (23a), b.p. 140—144 °C/0.5 mmHg, was a viscous oil (17.3 g, 67%) which crystallized from methanol as large crystals (15.7 g, 60%) (in three crops), m.p. 42—43 °C (on recrystallization) (Found: C, 50.4; H, 3.5; I, 41.2. $C_{13}H_{11}IO$ requires C, 50.4; H, 3.6; I, 40.9%); *m/e* 310 (M^+, 100%), 168 (50), and 139 (40); δ 3.7 (3 H, s, OMe), and 6.9—7.7 (8 H, m).

Methyl Bis-(6-methoxybiphenyl-2-yl)phosphinate (24c).—To a stirred solution of the above iodide (4.65 g) in diethyl ether (25 ml) under nitrogen at 0—5 °C was added dropwise butyl-lithium (10 ml; 1.54M in hexane). After 15 min stirring was continued for 18 h at room temperature. Pentane (50 ml) was added, the mixture was cooled to −10 °C, and the supernatant removed through a filter-stick. After one washing (by settling and removal of supernatant) with pentane (50 ml) the precipitate was suspended in diethyl ether (25 ml), cooled to 0 °C, and stirred during the addition (30 min) of methyl dichlorophosphate (1.14 g) in diethyl ether (15 ml). After 2.5 h at room temperature water was added and the mixture was extracted with ethyl acetate (120 ml, 40 ml). The combined organic phase was washed [water (2 × 40 ml), brine], dried, and evaporated. The residue, on trituration with diethyl ether, gave the *phosphinic ester* (24c) (2.01 g, 60%) which crystallized from acetone as small, soft prisms, m.p. 165—167 °C (Found: C, 73.0; H, 5.8; P, 6.9. $C_{27}H_{25}O_4P$ requires C, 73.0; H, 5.7; P, 7.0%); *m/e* 444 (M^+, 100%), 443 (54), 367 (38), 261 (85), 299 (25), 184 (65), and 57 (65); δ 3.46 (3 H, d, *J* 11.5 Hz, P–OMe), 3.63 (3 H, s, OMe), and 6.7—7.3 (16 H, m); $\nu_{max.}$ 1 260, 1 230, and 1 030 cm^{-1}.

Methyl Bis-(6-hydroxybiphenyl-2-yl)phosphinate (24f).—The above ester (333 mg) in dichloromethane (10 ml) was stirred and cooled at −78 °C, under nitrogen during addition of boron tribromide (0.5 ml). After 15 min at −78 °C followed by 45 h at room temperature the mixture was

poured onto ice and diluted with chloroform (25 ml). The aqueous layer was washed with chloroform and the united organic layers were washed (2 × water, brine), dried, and evaporated. The residual oil solidified on trituration with acetone–toluene; it was collected and washed with diethyl ether (225 mg, 72%). The white solid was difficult to crystallize; the analytical sample of the *ester* (24f), a colourless amorphous solid, was obtained by preparative t.l.c. (methanol–dichloromethane, 1 : 19, 2 × developed); it was dried at 150 °C/0.2 mmHg for 2 h (Found: C, 72.1; H, 5.1. $C_{25}H_{21}O_4P$ requires C, 72.1; H, 5.1%); *m/e* 416 (M^+, 100%), 415 (56), 247 (80), 215 (45), and 83 (24); δ 3.42 (3 H, d, *J* 11.5 Hz, P–OMe), 4.0br (2 H, s, OH), and 6.6—7.3 (16 H, m); $\nu_{max.}$ 3 410, 1 572, 1 280, 1 173, 1 153, 1 045, 1 010, 800, 768, 700, and 670 cm^{-1}.

Bis-(6-hydroxybiphenyl-2-yl)phosphinic Acid (24g).—The dimethoxy ester (24c) was heated with pyridine hydrochloride (12 equiv.) at 170—190 °C for a few hours. The product was freed of pyridine by boiling it with 2M sodium hydroxide. Acidification then gave the *acid* (24g), which crystallized from acetone–hexane as microscopic prisms, m.p. 306—307 °C (decomp.) (Found: C, 71.5; H, 5.0; P, 7.5. $C_{24}H_{19}O_4P$ requires C, 71.6; H, 4.8; P, 7.7%); *m/e* 402 (M^+), 401, 383, 325, 260, 234, 233, 232, 231, 216, and 215; $\nu_{max.}$ 3 540, 3 380b, 1 165, 1 160, 1 135, 970, 895, 765, 745, 700, and 675 cm^{-1}.

2-*Amino*-4′,6-*dimethoxybiphenyl* (22b).—Compound (22b) was prepared from the corresponding nitro-compound (11c) (11.2 g) by reduction with hydrazine and nickel as described for compound (22a). Evaporation of the filtered solution left an oil which crystallized slowly. Recrystallization from acetone–hexane yielded the *amine* (22b) as large prisms (9.2 g; 93%; 3 crops), m.p. 76 °C (Found: C, 73.3; H, 6.6; N, 6.0. $C_{14}H_{15}NO_2$ requires C, 73.3; H, 6.6; N, 6.1%); *m/e* 229 (M^+, 100%), 214 (10), 199 (5), and 198 (5); δ 3.5br (2 H, s, NH_2), 3.70 (3 H, s, OMe), 3.85 (3 H, s, OMe), 6.45 (2 H, d, *J* 9 Hz), 6.97—7.18 (3 H, m), and 7.22—7.40 (2 H, m); $\nu_{max.}$ 3 480m, 3 380m, and 1 600s cm^{-1}. The *N-benzoyl-derivative* crystallized from chloroform–hexane as prisms, m.p. 99—100 °C (Found: C, 75.7; H, 5.8; N, 4.2. $C_{21}H_{19}NO_3$ requires C, 75.7; H, 5.7; N, 4.2%); *m/e* 333 (M^+, 18%), 228 (<5), and 105 (100); δ 3.72 (3 H, s, OMe), 3.85 (3 H, s, OMe), 6.75 (1 H, d, *J* 8.5 Hz), 6.92—7.70 (10 H, m), 7.83br (1 H, s, NH), and 8.20 (1 H, d, *J* 8.5 Hz). The deshielding of one proton is noteworthy.

2-*Iodo*-4′,6-*dimethoxybiphenyl* (23b).—The amine (22b) (9.2 g) with water (40 g) containing sulphuric acid (4.82 g), was warmed (steam-bath) to dissolve it; the mixture was cooled to 0 °C, stirred, and diazotized by the addition of sodium nitrite (2.89 g) in water (6 ml) during 50 min. After 20 min more, sulphuric acid (1.59 g) was added dropwise followed by a solution of potassium iodide (8.03 g) in water (8 ml). Copper powder (40 mg) was added and the mixture was heated (steam-bath) for 1 h. The dark oil was taken up in chloroform which was then washed (10% aqueous $Na_2S_2O_3$, 2M NaOH, water, 2M HCl, water, brine) and dried. Distillation gave the crude product (9.6 g), b.p. 153—160 °C/0.35 mmHg; a further 1.2 g was obtained in the first eluate from passage of a solution of the residue in dichloromethane–hexane (1 : 1) through alumina (170 g in a 50 mm diameter column). The whole (10.8 g) was recrystallized from methanol to give the *iodide* (23b) as bladed prisms (9.93 g, 73%, 3 crops), m.p. 82—83 °C (Found: C, 49.4; H, 3.9; I, 37.5. $C_{14}H_{13}IO_2$ requires C, 49.4; H, 3.9; I, 37.3%); *m/e* 340 (M^+, 100%), 198 (20), and 183 (15); δ 3.63 (3 H, s, OMe), 3.80 (3 H, s, OMe), 6.82—7.20 (6 H, m), and 7.50 (1 H, dd, *J* 8.5 and 2 Hz, 3-H).

Methyl Bis-(4′,6-dimethoxybiphenyl-2-yl)phosphinate (24d).—A solution of the iodide (23b), (6.4 g) in diethyl ether (50 ml) under nitrogen was treated at 0 °C with butyl-lithium (14 ml of 1.4M in hexane). After 20 min at 0 °C the mixture, from which the aryl lithium had precipitated, was left at room temperature for 20 h; then a solution of methyl dichlorophosphate (1.45 g) in diethyl ether (10 ml) was added during 1.75 h at 0 °C. After 1 h more the mixture was brought to room temperature during 3 h. The mixture worked by addition of water and ethyl acetate gave a product from the organic layer that afforded the *ester* (24d) as a cream solid (2.78 g, 59%) on trituration with acetone–hexane (2 : 3, *ca.* 250 ml). Recrystallization from acetone (charcoal) gave prisms, m.p. 219.5—220.5 °C (Found: C, 69.2; H, 5.8; P, 6.0. $C_{29}H_{29}O_6P$ requires C, 69.0; H, 5.8; P, 6.1%); *m/e* 504 (M^+, 100%), 503 (35), 398 (25), and 291 (50); δ 3.50 (d, *J* 11 Hz) overlapping 3.67 (s) (total 9 H), 3.83 (6 H, s, 2 × OMe), and 6.52—7.27 (14 H, m).

2-*Amino*-4′,6-*dimethoxy*-3′,5′-*di-t-butylbiphenyl* (22c).—The nitro-compound (11f) (8.24 g) was reduced as for compounds (22a) and (22b), but in ethoxyethanol (100 ml). The mixture was poured into water (300 ml) and the product recovered by means of diethyl ether. It was dissolved in dichloromethane (25 ml) and passed through a short alumina column with dichloromethane–hexane (1 : 1) as eluant. The crude amine (7.57 g) crystallized slowly. Recrystallization from hexane gave the *amine* (22c) as prismatic needles, m.p. 152—153.5 °C (Found: C, 77.6; H, 9.1; N, 4.1 $C_{22}H_{31}NO_2$ requires C, 77.4; H, 9.2; N, 4.1%); *m/e* (M^+, 100%) and 326 (9); *m** 312 (341→326); δ 1.42 (18 H, s), 3.73 (s) and 3.76 (s) overlapping 3.70br (s) (total 8 H, 2 × OMe and NH_2), 6.43 (2 H, d, *J* 8 Hz, 3-,5-H), 7.03 (1 H, d, *J* 8 Hz, 4-H), and 7.27 (2 H, s, 2′-,6′-H).

2′-*Iodo*-4,6′-*dimethoxy*-3,5-*di-t-butylbiphenyl* (23c).—A solution of the amine (22c) (200 mg) in DMF (2.5 ml) was treated with aqueous hydrochloric acid (5 ml of 2M) and cooled to 0 °C. To the stirred suspension sodium nitrite (125 mg) in water (1 ml) was added over 1 h. Cold DMF (3 ml) was added and stirring continued at 0 °C for 2.5 h more, urea (125 mg) in water (1 ml) being added after 1 h. A solution of potassium iodide (0.75 g) in cold water (2 ml) was then added and the brown suspension heated at 90 °C for 1 h. Iodine was removed from the cooled mixture by addition of sodium hydrogensulphite (10%) solution. Extraction with diethyl ether then gave a product, separable into two pure components by t.l.c. on silica (ethyl acetate–hexane, 1 : 9). The more mobile product (31 mg) was 4,6′-*dimethoxy*-3,5-*di-t-butylbiphenyl*, obtained as large prisms (from ethanol), m.p. 101—102 °C (Found: C, 81.1; H, 9.2. $C_{22}H_{30}O_2$ requires C, 80.9; 9.3%); *m/e* 326 (M^+, 100%) and 311 (48); *m** 297 (326→311); δ 1.46 (18 H, s), 3.73 (3 H, s, OMe), 3.83 (3 H, s, OMe), 6.80—7.35 (4 H, m), and 7.40 (2 H, s, 2-,6-H). The less mobile product (174 mg, 66%) was the required *iodide* (23c), obtained as needles (from hexane), m.p. 134—135 °C (Found: C, 58.6; H, 6.4; I, 28.3. $C_{22}H_{29}IO_2$ requires C, 58.4; H, 6.5; I, 28.1%); *m/e* 452 (M^+, 100%) and 437 (97); *m** 422 (452→437); δ 1.47 (18 H, s), 3.73 (s) and 3.76 (s) (6 H), 6.85—7.00 (2 H, m), 7.15 (2 H, s, 2-,6-H), and 7.52—7.60 (1 H, m).

Methyl Bis-(4′,6-dimethoxy-3′,5′-di-t-butylbiphenyl-2-yl)-phosphinate (24e).—The iodide (23c) (570 mg) in dry diethyl ether was stirred at −70 °C and treated with butyl-lithium (0.9 ml of 1.47M in hexane). After 1 h, an ethereal solution

of methyl dichlorophosphate (1 ml of 0.79M) was added at a fast drop rate. The cooling bath was removed. Next day water (20 ml) and diethyl ether (150 ml) were added and the washed (water) dried ethereal layer was evaporated. The residue was adsorbed on alumina; elution with dichloromethane–hexane (1 : 1) removed, less polar impurities and the *phosphinic ester* (24e) (369 mg, 80%) was then eluted with dichloromethane. Recrystallization from dichloromethane-hexane gave large prisms, m.p. 237—239 °C (Found: C, 74.2; H, 8.4. $C_{45}H_{61}O_6P$ requires C, 74.2; H, 8.4%); *m/e* 728 (M^+, 100%) and 713 (15); *m** 698 (728→713); δ 1.40 (36 H, s, 4 × Bu^t), 3.60 (s) and 3.72 (s) overlapping 3.72 (d, *J* 11 Hz, P–OMe) (total 15 H), and 6.77—7.17 (10 H, m).

Unsuccessful Attempts to Cyclize Bis-arylphosphinic Acid Derivatives.—Experiments are itemized in the Table. Reaction mixtures were checked by t.l.c. against authentic dibenzophospholes as these became available. No indication of these phospholes was obtained.

Substance	Reagent	Solvent	Result [a]
(20b)	$Pd(OAc)_2$	AcOH	Mainly SM
(20c)	MnO_2	TFA	SM–mixture
(20c)	$Mn(acac)_3$	MeCN	NR
(20c)	VOF_3	TFA–TFAA	Mainly SM
(24c)	VOF_3	CH_2Cl_2–TFA	SM–mixture
(24c)	VOF_3	TFA–TFAA	SM–mixture
(24c)	$Tl(OCOCF_3)_3$	MeCN	NR
(24c)	$Tl(OCOCF_3)_3$	TFA–TFAA	Mixture
(24c)	$Tl(OCOCF_3)_3$	MeCN–TFAA	SM–mixture
(24c)	$Tl(OCOCF_3)_3$	TFA	Mixture
(24f)	Ag_2CO_3–Celite	C_6H_6	SM–mixture
(24f)	$Mn(acac)_3$	MeCN	Mainly SM
(24f)	$K_3Fe(CN)_6$	MeOH–H_2O	Mixture
(24g)	Ag_2CO_3–Celite	C_6H_6	NR
(24d)	VOF_3	MeCN–TFAA	(25)

[a] SM = starting material; NR = no reaction; TFA = trifluoroacetic acid; TFAA = trifluoracetic anhydride.

5,10-Dihydro-1,5,7-trimethoxy-6-(4-methoxyphenyl)spiro-[benzo[b]phospholine-10,1′-cyclohexane-2,5-dien-4-one] 5-Oxide (25).—A solution of the ester (24d) (140 mg) in acetonitrile–trifluoroacetic anhydride (9 : 1, 12.5 ml) was added dropwise at −25 °C, to a stirred suspension of vanadium oxytrifluoride (0.22 g) in the same solvent mixture (7.5 ml). After 6.5 h at −20 °C, the mixture was quenched carefully (2M aqueous Na_2CO_3, 100 ml) and extracted with chloroform (100, 50 ml). The washed (water) and dried extract left a residue which was analysed by preparative t.l.c. (acetone–hexane, 1 : 1, 6 × developed). At least four products were indicated as well as starting material; from a band of intermediate mobility one product (38 mg) was recovered and crystallized from acetone as white rosettes of the *spiro-compound* (25), m.p. 254—255 °C (Found: C, 68.6; H, 5.1. $C_{28}H_{25}O_6P$ requires C, 68.8; H, 5.2%); *m/e* 488.1381 (M^+, Calc. 488.1389, 100%); δ 3.25 (3 H, d, *J* 11 Hz, P–OMe), 3.63 (s) and 3.66 (s) (6 H, 2 × OMe), 3.81 (3 H, s, OMe), 6.30 and 6.42 (2 H, 2 superimposed dd, *J* 8 and 2 Hz, 2′-,6′-H), 6.70—7.66 (11 H, m); $\nu_{max.}$ 1 660s (C=O), 1 620, 1 610, and 1 040 cm^{-1}.

Halogenation of 2-Methoxy-6-nitrobiphenyls

3-Iodo-6-methoxy-2-nitrobiphenyl (26a).—2-Methoxy-6-nitrobiphenyl (120.23 g) was dissolved in a warm solvent mixture (1.5 l; from acetic acid–water–concentrated H_2SO_4 100 : 10 : 3 v/v/v). Iodine (57.15 g) was added, followed by periodic acid dihydrate (21.7 ml of 50% solution). The flask was closed by a balloon to retain vapours and the mixture was stirred at 60—65 °C for 20 h. The warm bath was removed and anhydrous sodium acetate (50 g) was added. Dilution with water (5 l) then gave a solid product that was collected after cooling, washed (water), and dissolved in chloroform (700 ml) which was washed (10% $NaHSO_3$, water, saturated $NaHCO_3$), dried, and evaporated. The yellow oil was warmed and stirred with hot methanol (750 ml), when the *iodo-compound* (26a) crystallized as stout pale yellow prisms (152.4 g, 82%, 2 crops), m.p. 116—118 °C (Found: C, 44.0; H, 2.8; I, 35.9; N, 4.0. $C_{13}H_{10}INO_3$ requires C, 44.0; H, 2.8; I, 35.7; N, 3.9%); *m/e* 355 (M^+, 10%), 338, 327, and 139; δ 3.70 (3 H, s, OMe), 6.81 (1 H, d, *J* 9 Hz, 5-H), 7.1—7.5 (5 H, m), and 7.74 (1 H, d, *J* 9 Hz, 4-H); $\nu_{max.}$ 1 585, 1 532, 1 285, 1 270, 1 245, 1 050, 813, 750, and 695 cm^{-1}.

3-Bromo-6-methoxy-2-nitrobiphenyl (26b).—2-Methoxy-6-nitrobiphenyl (0.23 g) in carbon tetrachloride (10 ml) was stirred with thallium triacetate (1.14 g) during dropwise addition (35 min) of bromine (0.16 g) in carbon tetrachloride (5 ml). After 1 h, the mixture was boiled for 4 h under reflux, then washed with chloroform through a short column of alumina. The eluted oil (300 mg) was chromatographed by t.l.c. (chloroform–hexane, 2 : 3, 4 × developed). From the least mobile band, methoxynitrobiphenyl (77 mg) was recovered. From the next band, the *monobromide* (26b) (166 mg, 81% on converted material) was obtained as prismatic needles (from aqueous ethanol), m.p. 133.5—134.5 °C (Found: C, 50.5; H, 3.3; Br, 25.9; N, 4.3. $C_{13}H_{10}BrNO_3$ requires C, 50.7; H, 3.3; Br, 25.9; N, 4.5%); *m/e* 309/307 (M^+, 50%), 290/292 (10), 183 (25), 182 (20), 155 (20), and 139 (100); δ (CCl_4) 3.73 (3 H, s, OMe), 6.90 (1 H, d, *J* 9 Hz, 5-H), 7.10—7.57 (5 H, m, Ph), and 7.53 (1 H, d, *J* 9 Hz, 4-H).

3,4′-Dibromo-6-methoxy-2-nitrobiphenyl (26c).—2-Methoxy-6-nitrobiphenyl (85 mg) in carbon tetrachloride (10 ml) was stirred with thallium tris(trifluoroacetate) (200 mg during the addition of bromine (100 mg) in carbon tetrachloride (6 ml). After 20 h the mixture was filtered and evaporated. On chromatography as in the monobromination, starting material and the above monobromide were separated and, from the most mobile of the three bands found, the *dibromide* (26c) (54 mg) crystallized as small prisms (from aqueous ethanol), m.p. 167—168 °C (Found: C, 40.4; H, 2.4; Br, 41.4; N, 3.6. $C_{13}H_9Br_2NO_3$ requires C, 40.3; H, 2.3; Br, 41.3 N, 3.6%); *m/e* 389, 387 (100%), and 385 (M^+, ratio 1 : 2 : 1); δ 3.71 (3 H, s, O Me), 6.92 (1 H, d, *J* 9 Hz, 5-H), 7.07 (2 H, d, *J* 8.5 Hz, 2′-,6-H 7.48 (2 H, d, *J* 8.5 Hz, 3′-,5′-H), and 7.55 (1 H, d, *J* 9 Hz, 4-H).

3,3′-Di-iodo-4′,6-dimethoxy-2-nitrobiphenyl (26d).—(a) *By stepwise iodination.* 2,4′-Dimethoxy-6-nitrobiphenyl (243 mg) was stirred at 70—80 °C for 16 h with a mixture of acetic acid (5 ml), aqueous sulphuric acid (0.4 ml of 2M), iodine (102 mg), and iodic acid (34 mg). The mixture was poured into aqueous sodium hydrogen sulphite (10%) and extracted with ethyl acetate which was washed (aqueous $NaHCO_3$), dried, and evaporated. The yellow solid was passed in chloroform through a short column of alumina and then recrystallized from methanol to yield *3-iodo-2′,4-dimethoxy-6′-nitrobiphenyl* as yellow blades (300 mg, 83%) and on recrystallization, as stout prisms, m.p. 155—156 °C (Found: C, 43.9; H, 3.2; N, 3.6. $C_{14}H_{12}INO_4$ requires C, 43.7; H, 3.1; N, 3.6%); *m/e* 385 (M^+, 100%) and 258 (M^+ — I, 15); δ 3.81 (3 H, s, OMe), 3.93 (3 H, s, OMe), 6.85 (1 H, d, *J* 9 Hz, 5-H), 7.10—7.50 (4 H, m), 7.72 (1 H, d, *J* 2 Hz, 2-H). This substance (241 mg) was iodinated (80 °C, 26 h) as above. The *di-iodide* (26d) (227 mg,

77%) crystallized from chloroform–methanol as pale yellow prisms, m.p. 224—226 °C (Found: C, 32.7; H, 2.2; N, 2.8%. $C_{14}H_{11}I_2NO_4$ requires C, 32.9; H, 2.2; N, 2.7%); *m/e* 511 (M^+, 100%); δ[$CDCl_3$ + $(CD_3)_2SO$] 3.80 (s) and 3.90 (s) (total 6 H, 2 × OMe), 6.80—7.32 (3 H, m), 7.61 (1 H, d, *J* 2 Hz, 2'-H), and 7.87 (1 H, d, *J* 9 Hz, 4-H).

(b) *By direct iodination.* 2,4'-Dimethoxy-6-nitrobiphenyl (6.6 g) in acetic acid–water–concentrated sulphuric acid (100 : 10 : 3, v/v/v; 85 ml) at 80 °C was treated with iodine (6.1 g) and periodic acid dihydrate (50% solution, 2.3 ml). After 3 h most of the iodine was gone and the product had crystallized. Work-up was as described in method (*a*). The di-iodide (26d) (7.52 g, 58%) crystallized from chloroform and was identical with the product obtained as in method (a). The mother liquor contained more di-iodide and some tri-iodide (see next section).

3,3',5'-Tri-iodo-4',6-dimethoxy-2-nitrobiphenyl (26e).—The above di-iodide (26d) (120 mg) was iodinated as described in method (b) above. The *tri-iodide* (26e) (102 mg, 68%) crystallized from chloroform–methanol as yellow prisms, m.p. 214—216 °C (Found: C, 26.5; H, 1.6; N, 2.2%. $C_{14}H_{10}I_3NO_4$ requires C, 26.4; H, 1.6; N, 2.2%) *m/e* 637 (M^+, 100%); δ 3.75 (s) and 3.76 (s) (total 6 H, 2 × OMe), 7.15 (1 H, d, *J* 9 Hz, 5-H), 7.64 (2 H, s, 2'-,6'-H), and 7.95 (1 H, d, *J* 9 Hz).

2,3'-Di-iodo-4,6'-dimethoxy-3,5,6-trimethyl-2'-nitrobiphenyl (26f).—The biphenyl (11g) (2.15 g) was iodinated as described for compound (26a) (0.78 g of iodine, 0.48 g of 50% periodic acid, 60—70 °C, overnight). Crystallization from methanol gave the intermediate *2-iodo-2',4-dimethoxy-3,5,6-trimethyl-6'-nitrobiphenyl* (1.94 g, 64%), m.p. 153—155 °C after recrystallization (Found: C, 47.7; H, 4.4; I, 29.6; N, 3.3. $C_{17}H_{18}INO_4$ requires C, 47.8; H, 4.2; I, 29.7; N, 3.3%); *m/e* 427 (M^+, 90%), 300 (100), and 240 (20); δ 1.96 (3 H, s, Me), 2.22 (3 H, s, Me), 2.45 (3 H, s, Me), 3.72 (3 H, s, OMe), 3.80 (3 H, s, OMe), and 7.12—7.62 (3 H, m). This iodide (266 mg), iodine (63.5 mg) acid (22 mg), acetic acid (5 ml), aqueous sulphuric acid (0.5 ml of 2M), and 1,4-dinitrobenzene (2 mg) were stirred at 80—90 °C in the dark for 16 h. The crude product, obtained as for compound (26a), was passed in chloroform through a short alumina column. It crystallized from acetone as very pale yellow prisms (120 mg + 136 mg from mother liquors; total 74%). This material contained traces of starting material (t.l.c.) which were removed by three crystallizations from acetone to yield *compound* (26f), m.p. 236—238 °C (Found: C, 36.8; H, 3.1; I, 45.8; N, 2.5. $C_{17}H_{17}I_2NO_4$ requires C, 36.9; H, 3.1; I, 45.9; N, 2.5%); *m/e* 553 (M^+, 100%) and 426 (35); δ 1.98 (3 H, s, Me), 2.18 (3 H, s, Me), 2.42 (3 H, s, Me), 3.70 (3 H, s, OMe), 3.80 (3 H, s, OMe), 6.87 (1 H, d, *J* 9 Hz, 5-H'), and 8.05 (1 H, d, *J* 9 Hz, 4'-H). The same di-iodide was obtained by a one-step iodination using the conditions of the second step above.

3,5-Dichloro-3'-iodo-4,4'-dimethoxy-2'-nitrobiphenyl (26g).—A mixture of the dichlorodimethoxynitrobiphenyl (11e), (244 mg), iodine (76 mg), iodic acid (26 mg), acetic acid (3 ml), and aqueous sulphuric acid (0.3 ml of 2M) was stirred at 80 °C for 25 h. Worked up as for (26d) [procedure (a)] the product was recrystallized from chloroform–hexane and from methanol to yield the *iodide* (26 g) (230 mg, 68%) as pale yellow prisms, m.p. 161—162 °C; chromatography of the mother liquors gave a further 47 mg (total 82%) (Found: C, 37.0; H, 2.6; Cl, 15.5; I, 28.1; N, 3.1. $C_{14}H_{10}Cl_2INO_4$ requires C, 37.0; H, 2.2; Cl, 15.6; I, 28.0; N, 3.1%); *m/e* 455 and 453 (M^+); δ 3.78 (3 H, s, OMe), 3.93 (3 H, s, OMe), 6.77 (1 H, d, *J* 9 Hz, 5'-H), 7.15 (2 H, s, 2-,6-H), and 7.78 (1 H, d, *J* 9 Hz, 4'-H).

3'-Iodo-4,6'-dimethoxy-2'-nitro-3,5-di-t-butylbiphenyl (26h).—The dibutyldimethoxynitrobiphenyl (11f) (21.66 g) was iodinated with iodine (8 g) and periodic acid (3 ml of 50%) as described for compound (26a) (72 h, 67 °C). The crude product crystallized from methanol to give the *iodide* (26h) (21.04 g, 72.5%, 2 crops), m.p. 110—111 °C (Found: C, 53.3; H, 5.7; I, 25.4; N, 2.8. $C_{22}H_{28}INO_4$ requires C, 53.1; H, 5.7; I, 25.5; N, 2.8%); *m/e* 497 (M^+, 100%) and 482 (M^+ — Me, 75); δ 1.38 (18 H, s, 2 × Bu^t), 3.68 (s) and 3.74 (s) (6 H, 2 × OMe), 6.75 (1 H, d, *J* 9 Hz, 5'-H), 7.03 (2 H, s, 2-,6-H), and 7.67 (1 H, d, *J* 9 Hz, 4'-H).

Ullmann Couplings

4'',6'-Dimethoxy-2',2''-dinitro-m-*quaterphenyl* (15a).—The iodide (26a) (35.5 g) and pure dry copper powder (25.4 g; the copper powder in these couplings was prepared by precipitation,[27] as recommended [28] for *o*-iodonitrobenzene, and activated by washing with disodium ethylenediaminetetra-acetate [29]) were ground together and then transferred to a flask which was immersed in an oil-bath pre-heated to 150—160 °C; when the internal temperature reached 130—140 °C the bath temperature was raised during 15 min to 190—200 °C and maintained there for 3 h; t.l.c. (dichloromethane–hexane, 2 : 3) then showed no iodide. The solid cake obtained on cooling was digested with chloroform to give a smooth suspension; this was filtered through Celite which was then washed with hot chloroform. The filtrate was passed in chloroform through a column of alumina (30 × 4 cm) and the orange eluate evaporated. Trituration with diethyl ether gave the quaterphenyl (16.6 g, 73%) pure enough for the next step. A further 4—5% could be obtained by chromatography of the residues; this also yielded some 2-methoxy-6-nitrobiphenyl (11a) (6%). The recrystallized quaterphenyl had m.p. 261 °C alone or mixed with the previously described product (15a). The same product was also obtained by heating the bromide (26b) with commercial copper powder at 250 °C for 4 h and then, after addition of a little cuprous iodide, at 275 °C for 2 h. The spectra of the specimens (n.m.r., i.r.) were identical.

3,3'''-Di-iodo-4,4'',4''',6'-tetramethoxy-2',2''-dinitro-m-*quaterphenyl* (27a).—The di-iodide (26d) (282 mg) and copper powder (120 mg) were heated at 170 °C for 5.5 h, at 210 °C for 0.5 h, and finally at 180 °C for 4 h. T.l.c. indicated three products. A chloroform extract of the mixture was chromatographed (t.l.c., chloroform–hexane, 1 : 1; 4 × developed). The major and most mobile band afforded a white solid (10 mg, 5%) which crystallized from chloroform–ethanol to give the *quarterphenyl* (27a) as cream-coloured needles, m.p. 300—302 °C (Found: C, 43.5; H, 3.0; N, 3.4. $C_{28}H_{22}I_2N_2O_8$ requires C, 43.8; H, 2.9; N, 3.7%); *m/e* 768 (M^+, 100%) and 722 (M^+ — NO_2, 37); δ 3.76 (6 H, s, 2 × OMe), 3.85 (6 H, s, 2 × OMe), 6.80 (2 H, d, *J* 9 Hz, 5'-, 5''-H), 7.00 (2 H, d, *J* 9 Hz, 5-,5'''-H), 7.15—7.40 (4 H, m), and 7.72 (2 H, d, *J* 9 Hz, 4'-,6''-H).

2,2'''-Di-iodo-4,4'',4''',6-tetramethoxy-3,3''',5,5''',6,6'''-hexamethyl-2',2''-dinitro-m-*quaterphenyl* (27b).—The di-iodide (26f) (588 mg) and copper powder (280 mg) were mixed and heated under nitrogen at 200 ± 10 °C for 3 h. Worked up as for compound (27a), the product on chromatography on alumina (chloroform–hexane 1 : 2 then 2 : 3) gave a fraction purified further by preparative t.l.c. (chloroform–hexane, 1 : 1; 3 × developed) to give the *quaterphenyl*

(27b) as fine needles (from acetic acid), m.p. 295—297 °C (Found: C, 47.9; H, 4.0; I, 26.9; N, 3.2. $C_{34}H_{34}I_2N_2O_8$ requires C, 47.9; H, 4.0; I, 29.8; N, 3.3%); *m/e* 852 (M^+, 100%), 822 (20), and 725 (70); δ 1.99—2.10 (6 H, 3 lines, 2 × Me), 2.19 (6 H, s, 2 × Me), 2.44 (6 H, s, 2 × Me), 3.70 (6 H, s, 2 × OMe), 3.83 (6 H, s, 2 × OMe), 7.07 (2 H, d, *J* 9 Hz, 5′-,5″-H), and 7.48 (2 H, d, *J* 9 Hz, 4′-,6″-H). The high-field methyl signals suggest the presence of atropisomers.

3,3‴,5,5‴-Tetrachloro-4,4″,4‴,6′-tetramethoxy-2′,2″-dinitro-m-*quaterphenyl* (27c).—The iodide (26g) (1.75 g), intimately mixed with copper powder (1 g), was heated at 200—210 °C for 4 h under nitrogen. Extraction with chloroform and trituration of the product with acetone–ethanol gave the *quaterphenyl* (27c) (0.98 g) as clusters of fine needles (from acetone–ethanol), m.p. 251—253 °C (Found: C, 51.6; H, 3.3; Cl, 21.6; N, 4.3; $C_{28}H_{20}Cl_4N_2O_8$ requires C, 51.4; H, 3.1; Cl, 21.7; N, 4.3%); *m/e* 656, 654, 652 (M^+, 100%), 610, 608, and 606 ($M^+ - NO_2$, 65); δ 3.83 (s) and 3.97 (s) (12 H, 4 × OMe), 7.03 (2 H, d, *J* 9 Hz, 5′-,5″-H), and 7.26 (s) overlapping 7.35 (d, *J* 9 Hz) (total 6 H). The mother liquor, on chromatography, yielded the de-iodinated biphenyl (11e) (71 mg).

4,4″,4‴,6′-Tetramethoxy-2′,2″-dinitro-3,3‴,5,5‴-tetra-t-butyl-m-*quaterphenyl* (27 d).—The iodide (26h) (69 g) was divided into three equal portions; each was intimately mixed with copper powder (12 g; Hopkin and Williams, activated by EDTA [29] and dried for 4—5 h at 100 °C/0.1 mmHg) and heated at 180—200 °C for 6 h. After work-up as for compound (27a) the product was triturated with diethyl ether–methanol (1 : 2). The solid product was recrystallized from chloroform–methanol (1 : 3) to yield the *quarterphenyl* (27d) as pale yellow prisms (44.8 g, 87%, 2 crops), m.p. 291—292 °C (Found: C, 71.3; H, 7.6; N, 3.7. $C_{44}H_{56}N_2O_8$ requires C, 71.3; H, 7.6; N, 3.8%); *m/e* 740 (M^+, 100%), 725 (M^+ — Me, 45), and 557 (60); δ 1.45 (36 H, s), 3.73 (s) and 3.85 (s) (12 H, 4 × OMe), 7.03 (2 H, d, *J* 9 Hz, 5′-,5″-H), and 7.23 (s) overlapping 7.33 (d, *J* 9 Hz) (total 6 H).

4,4″,4‴,6′-Tetramethoxy-2′,2″-dinitro-m-*quaterphenyl* (27e).—The above tetramethoxydinitrotetra-t-butylquaterphenyl (27d) (740 mg) in toluene (15 ml) was added to a mixture of toluene-4-sulphonic acid (1.09 g) and toluene (35 ml) which had been concentrated to *ca.* 25 ml to remove water. The solution was distilled slowly until most of the toluene was gone (2—2.5 h), diluted with water, and extracted with ethyl acetate. The washed (2M Na_2CO_3, water, brine) and dried extract was filtered through alumina and evaporated. The residue, on trituration with ethanol, gave the *quarterphenyl* (27e) (324 mg, 63%) as a beige solid. Crystallization from acetone–ethanol gave cream-coloured needles, m.p. 225—226 °C and 237—238 °C (double m.p.) (Found: C, 65.3; H, 4.7; N, 5.2. $C_{28}H_{24}N_2O_8$ requires C, 65.1; H, 4.7; N, 5.4%); *m/e* 516 (M^+, 100%) and 470 ($M^+ - NO_2$, 25); δ 3.72 (s) and 3.73 (s) (total 12 H, 4 × OMe), and 6.83—7.45 (12 H, m).

2′,2″-*Diamino*-m-*quaterphenyls*

2′,2″-Diamino-4″,6′-dimethoxy-m-*quaterphenyl* (28a).—To a solution of the dinitro-compound (15a) (20 g) in 2-ethoxyethanol (500 ml) at 90—95 °C was added Raney nickel (W-2, 2—3 g). Hydrazine hydrate (40 ml) was added dropwise to the stirred mixture so that the temperature remained at 90—95 °C. A second portion of nickel (2—3 g) was then added and, following the reaction by t.l.c. (ethyl acetate–hexane, 1 : 3), portions of hydrazine hydrate (10 ml) were added dropwise until reduction appeared complete (total: 80 ml hydrazine hydrate). The cooled mixture was diluted with water (1.5 l) and the solid was collected and dissolved in chloroform which was washed (brine) and dried. Evaporation left the *diamino-quaterphenyl* (28a) as a pale yellow solid that could be washed free of colour by ethanol or diethyl ether; from the washings a further small crop could be obtained (total yield 90—93%). Recrystallization from ethyl acetate gave fine needles, m.p. 237—238 °C (Found: C, 78.6; H, 6.1; N, 7.0. $C_{26}H_{24}N_2O_2$ requires C, 78.8; H, 6.1; N, 7.1%); *m/e* 396 (M^+, 100%); δ 3.72 (s) overlapping 3.43—3.83br (s) (total 10 H, 2 × OMe + 2 × NH_2), 6.50 (2 H, d, *J* 8.5 Hz, 5′-,5″-H), 7.13 (2 H, d, *J* 8.5 Hz, 4′-,6″-H), and 7.43br (10 H, s).

Isomeric Diamines (28a) (29) *and* (30) *from the Hydrazobiphenyl* (12b).—The hydrazobiphenyl (12b) (0.27 g), 6M-hydrochloric acid (35 ml), and ethanol (5 ml) were boiled, with vigorous stirring, for 2 h. The mixture was filtered (Celite) and the residue washed with water. The filtrate was made alkaline by cautious addition of 4M sodium hydroxide (50 ml). The red oil extracted by chloroform gave on t.l.c. (chloroform, 3 × developed) two main bands. The more mobile band yielded the 2′,2″-diamine (28a) (49 mg), m.p. 235—236 °C, n.m.r. and i.r. spectra identical with those of the product described in the preceding experiment. The less mobile band contained (188 mg) the 4″,6′-diamine (30) in 5 : 1 admixture with the 2′,4″-diamine (29), as analysed by n.m.r. spectroscopy. The pure 4″,6′-*diamino-2′,2″-dimethoxy*-m-*quaterphenyl* (30) was isolated by acetylation, further chromatography, and hydrolysis; it formed flattened needles (from ethanol), m.p. 198—200 °C (Found: C, 78.5; 6.3; N, 7.0. $C_{26}H_{24}N_2O_2$ requires C, 78.8; H, 6.1; N, 7.1%); δ 3.20 (6 H, s, 2 × OMe), 3.47br (4 H, s, 2 × NH_2), 6.55 (2 H, d, *J* 8.5 Hz, 5′-, 5″-H), 7.21 (2 H, d, *J* 8.5 Hz, 4′-,6″-H), and 7.45br (10 H, s). The 2′,4″-diamine (29) was identified only by t.l.c. in comparison with isolated material (see below) and by n.m.r. in admixture with compound (30).

Isomeric Diamines from the Dimethoxydinitroquaterphenyls (13a), (14a), *and* (15a).—2′,2″,4″,6′-Tetranitro-*m*-quaterphenyl (8b) (3.02 g) in HMPT (25 ml) was stirred with sodium methoxide (0.744 g) for 24 h. The mixture was poured into 0.5M hydrochloric acid and the solid product collected. It was reduced in boiling ethanol by hydrazine and Raney nickel, as in the preparation of compound (28a) (above). A chloroform solution of the reduction product was extracted twice with 4M hydrochloric acid and the amines precipitated by addition of ammonia. The crude mixture (1.55 g) in chloroform was applied to a column of silica (80 g) and eluted with chloroform. The first fraction (334 mg) yielded the *m*-quaterphenyl (28a), m.p. 237—238.5° (from ethyl acetate), identical with material prepared as above; the NN′-*diacetyl* derivative crystallized from chloroform–hexane as small prisms, m.p. 279—280 °C (Found: C, 74.9; H, 5.8; N, 5.9. $C_{30}H_{28}N_2O_4$ requires C, 75.0; H, 5.9; N, 5.8%); δ 1.55 (6 H, s, 2 × Ac), 3.75 (6 H, s, 2 × OMe), 6.93 (2 H, d, *J* 9 Hz,) and 7.35 (s) overlapping 7.12—7.40 (m) (total 14 H, including 2 NH). The shielding of the acetate methyl groups is noteworthy. Further elution afforded 2′,4″-*diamino-2″,6′-dimethoxy*-m-*quaterphenyl* (29) (136 mg) as a white solid. Recrystallization from ethyl acetate–ethanol gave fine needles, m.p. 207.5—208 °C (Found: C, 78.6; H, 6.1; N, 7.1. $C_{26}H_{24}N_2O_2$ requires C, 78.8; H, 6.1; N, 7.1%); *m/e* 396 (M^+, 100%), 365 (15), and 350 (65); δ 3.18 (3 H, s, 2″-OMe), 3.66 (s)

overlapping 3.50—3.80 (total 7 H, 6'-OMe and 2 × NH_2), 6.44 (1 H, d, *J* 9 Hz), 6.57 (1 H, d, *J* 9 Hz), 7.08 (d, *J* 9 Hz) and 7.10 (d, *J* 9 Hz) (total 2 H), and 7.34 (s) and 7.37 (s) (total 10 H). The 4'',6'-diamine (30) was eluted last in admixture (427 mg) with a much larger proportion of the unsymmetrical diamine (29); it was identified only by t.l.c. in comparison with the specimen from the hydrazobiphenyl (above).

*2',2''-Diamino-4,4'',4''',6'-tetramethoxy-*m*-quaterphenyl* (28b).—(*a*) The dinitro-compound (27e) (94 mg) was reduced as usual (in 2-ethoxyethanol). The product, isolated by extraction with chloroform, gave the *diamine* (28b) as a white powder (76 mg, 92%) on trituration with diethyl ether. Recrystallization from chloroform–ethanol gave micro-needles, m.p. 291—293 °C (Found: C, 73.7; H, 6.2; N, 6.0. $C_{28}H_{28}N_2O_4$ requires C, 73.7; H, 6.2; N, 6.1%); *m/e* 456 (M^+, 100%).

(*b*) The di-iododinitro-compound (27a) (200 mg) was reduced at 80—100 °C in 2-ethoxyethanol with Raney nickel and an excess of hydrazine, as usual. The product, isolated as in method (*a*), gave, on trituration with acetone–diethyl ether, the diamine (28b) (100 mg, 84%), m.p. 290—292 °C undepressed by the sample prepared as in method (*a*). The i.r. spectra were identical.

*2',2''-Diamino-3,3''',5,5'''-tetrachloro-4,4'',4''',6'-tetramethoxy-*m*-quaterphenyl* (28c).—The dinitroquaterphenyl (27c) (200 mg) was reduced as usual in 2-ethoxyethanol (15 ml) with Raney nickel and hydrazine. Water was added and the solid was collected and digested with hot chloroform (50 ml) which was dried, filtered (Celite), and evaporated. Chromatography (t.l.c., ethyl acetate–chloroform, 1 : 1; 2 × developed) gave, as the main product, the *diamine* (28c) (117 mg, 64%), which crystallized from chloroform–ethyl acetate (1 : 3) as small needles, m.p. 321—323 °C (Found: C, 56.7; H, 4.5; N, 4.6. $C_{28}H_{24}Cl_2N_2O_4$ requires C, 56.6; H, 4.1; N, 4.6%); *m/e* 596, 594, and 592 (M^+, 100%) (tetrachloro-pattern); δ 3.67br (4 H, s, 2 × NH_2), 3.77 (6 H, s, 2 × OMe), 4.00 (6 H, s, 2 × OMe), 6.50 (2 H, d, *J* 8.5 Hz, 5'-,5''-H), and 7.13 (d, *J* 8.5 Hz, 4'-,6''-H) overlapping 7.33 (s, 2-,2''', 6-,6'''-H) (total 6 H).

*2',2''-Diamino-4,4'',4''',6'-tetramethoxy-3,3''',5,5'''-tetra-t-butyl-*m*-quaterphenyl* (28d).—The dinitro-compound (27d) (5.30 g) in 2-ethoxyethanol (150 ml) was reduced at 90 °C with an excess of hydrazine and Raney nickel, as usual. The product was isolated by extraction with chloroform, dissolved in chloroform–hexane (3 : 7), and passed through alumina. Evaporation and crystallization from ethyl acetate–ethanol then gave the *diamine* (28d) (4.05 g, 83%, several crops) as laths, m.p. 241—243 °C (sublimes from 232 °C) (Found: C, 77.5; H, 8.6; N, 4.1. $C_{44}H_{60}N_2O_4$ requires C, 77.6; H, 8.9; N, 4.1%); *m/e* 680 (M^+, 100%); δ 1.45 (36 H, s, 4 × Bu^t), 3.73 (s) overlapping 3.6—3.9br (s) (total 16 H), 6.47 (2 H, d, *J* 8.5 Hz, 5'-, 5''-H), 7.10 (2 H, d, 8.5 Hz, 4'-,6''-H), and 7.25 (4 H, s, 2-,2'''-, 6-, 6'''-H).

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