

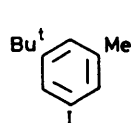
Synthesis of Substituted Dibenzophospholes. Part 6.¹ Preparation of Symmetrical and Non-symmetrical Quaterphenyl Intermediates

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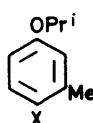
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Further examples are given of the synthetic approach to 4,6-diaryldibenzophospholes by arylation of 1,3-dinitrobenzene and coupling of the resulting biphenyls to symmetrically substituted quaterphenyls. Satisfactory procedures are described for the monoarylation of 2,2',4,4'-tetranitrobiphenyl and for arylation of the products to provide non-symmetrically substituted tetranitroquaterphenyls. Some procedures for the regioselective alkoxydenitration of tetranitroquaterphenyls are described.

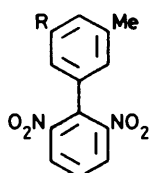
Part 2 of this series² described a synthesis of symmetrically substituted quaterphenyls suitable for transformation into 3,7-dialkoxy-4,6-diaryldibenzophosphole 5-oxides. 2-Arylation of 1,3-dinitrobenzene with copper(I) *t*-butoxide and an aryl iodide is followed by methoxydenitration and iodination to give a 3-aryl-4-methoxy-2-nitroiodobenzene, which undergoes Ullmann coupling to give the quaterphenyl.



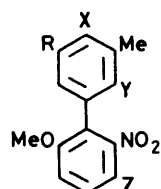
(1)



(2) X = I

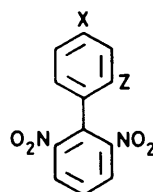
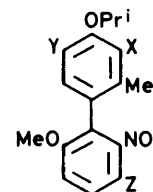
(6) X = CO₂H(3) R = Bu^t

(5) R = H

(8) R = Bu^t, X = Y = Z = H

(10) R = X = Y = Z = H

(11) R = Y = H, X = Z = I

(12) R = Bu^t, X = H, Y = Z = I(4) X = OPrⁱ, Z = Me(7) X = Me, Z = OPrⁱ

(9) X = Y = Z = H

(13) X = Z = H, Y = I

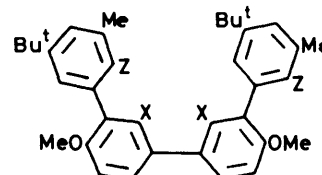
(14) X = H, Y = Z = I

(15) X = Y = I, Z = H

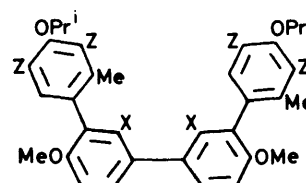
(16) X = Y = Z = I

and the methoxynitrobiphenyls (8), (9), and (10) were then iodinated with iodine and periodic acid. Introduction of iodine *ortho* to the nitro group was in each case accompanied or preceded by iodination of the other ring. The di-iodides (11) and (12) were obtained from (10) and (8) respectively. With (9), iodination led successively to the mono-iodide (13), a mixture of the di-iodides (14) and (15), and the tri-iodide (16), the only one obtainable in high yield and with iodine at the position desired.

It has previously³ been shown that Ullmann coupling of polyiodides such as (12) and (16) could be confined to the

(17) X = NO₂, Z = I(19) X = NH₂, Z = H

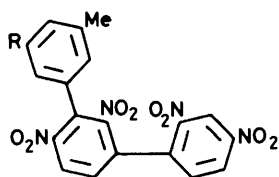
(21) X = I, Z = H

(18) X = NO₂, Z = I(20) X = NH₂, Z = H

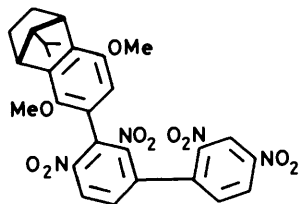
(22) X = I, Z = H

We were interested in developing quaterphenyl syntheses from the aryl iodides (1) and (2), prepared respectively by a Friedel-Crafts reaction between 3-iodotoluene and *t*-butyl chloride and by iodination of the isopropyl ether of *m*-cresol. These iodides condensed smoothly with 1,3-dinitrobenzene, to give the 2,6-dinitrobiphenyls (3) and (4). The biphenyl (3) was also made from 3-iodotoluene by an initial reaction with dinitrobenzene and *t*-butylation of the intermediate biphenyl (5). The orientation of the iodide (2), not obvious from the n.m.r. spectrum, was proved by conversion *via* the aryl-lithium into the carboxylic acid (6). The n.m.r. spectrum of this acid was unambiguous, and it was also dealkylated to a phenolic acid which agreed in its properties with those of the known 4-hydroxy-2-methylbenzoic acid. From the crude iodide (2), a small amount of the isomeric biphenyl (7) was formed: an indication that some iodination *ortho* to oxygen had occurred.

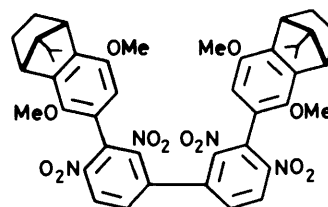
Replacement of one nitro group by a methoxy group in each of the biphenyls (3), (4), and (5) was effected by treatment with sodium methoxide in hexamethylphosphoric triamide (HMPT)



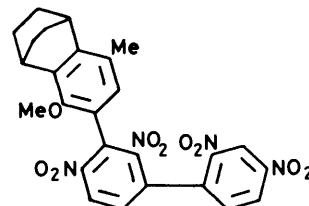
(23) R = H

(24) R = Bu^t

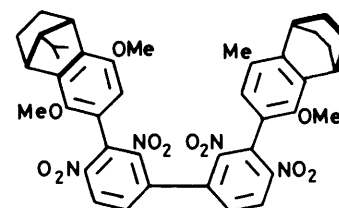
(25)



(26)



(27)



(28)

position *ortho* to a nitro group by the use of Cohen's reagent.^{4,5} We find that higher yields of purer products are obtained—more slowly—when coupling proceeds at 0 °C. Thus the quaterphenyls (17) and (18) were formed in high yields when the iodides (12) and (16) were stirred with copper(I) trifluoromethanesulphonate in cold acetonitrile and aqueous ammonia. Reduction and de-iodination by hydrazine and Raney nickel² was not easy with these quaterphenyls, but the diamines (19) and (20) were produced smoothly when zinc-copper couple in acetic acid was tried. Each of these diamines was converted into the corresponding di-iodide (21) and (22) by the diazonium iodomercurate method.²

The syntheses described above illustrate both the advantages and the limitations of this approach to 4,6-diaryldibenzophospholes. The procedures are generally smooth and overall yields are good, but the coupling means that in practice the terminal aryl groups must be the same. In principle, the alternative (and shorter) route² starting from 2,2',4,4'-tetranitrobiphenyl does not have this limitation, but selective replacement of two nitro groups by alkoxy groups was previously found to be difficult. In this and in the two following papers, procedures for overcoming this difficulty are described and tetranitrobiphenyl is established as a convenient source of unsymmetrically substituted quaterphenyls.

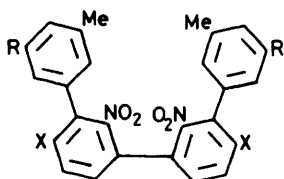
It was found that formation of quaterphenyls in the arylation of tetranitrobiphenyl could be largely suppressed by taking an excess (*ca.* threefold) of the biphenyl. Copper(I) *t*-butoxide in an equivalent excess was sometimes used but the condensation also succeeded with an amount equivalent to the aryl iodide. In this way the terphenyls (23) and (24) were prepared from 3-iodotoluene and from the iodide (1); *t*-butylation of (23) also gave (24). Similarly the bridged aryl iodides described in Part 5¹ gave the bridged naphthylbiphenyls (25) and (27); the bisnaphthylbiphenyl (26) was obtained as a by-product. Treatment of either (25) or (27) with the complementary aryl iodide gave the non-symmetrical bisnaphthylbiphenyl (28). It was always necessary to separate the product of monoarylation by chromatography and the products (25), (26), and (28) were mixtures of atropisomers. Interestingly, the naphthylbiphenyl (27) showed n.m.r. signals indicating atropisomerism: apparently, rotation of the terminal dinitrophenyl group is not fast.

The symmetrically substituted tetranitroquaterphenyls (29), (30), and (31) were readily made from 3-iodotoluene and the iodides (1) and (2) by reaction with tetranitrobiphenyl. Again, *t*-butylation of (29) gave (30); we were examining the possibilities of alkylation at various stages of the synthesis with an eye to the use of other alkyl groups if these were needed. The quaterphenyls (30) and (31) served as models in several experi-

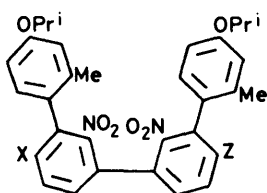
ments designed to replace the 4' and 6' nitro groups (the 'outside' nitro groups) by alkoxy groups.

Reduction of both (30) and (31) by sodium sulphide yielded the dinitro diamines (32) and (33) with apparently complete selectivity; in milder conditions the trinitro amine (34) was formed. Unfortunately, conversion to the phenols by diazotization was not found to be possible. The bis-diazonium salts seemed to be formed normally, as judged by the isolation of the di-iodide (36) and the mono-iodide (37) by diazotization of (31) and treatment with potassium iodide. The diamine (30) was converted into the di-iodide (35) by the action of pentyl nitrite and di-iodomethane⁶ and thence to the desired diether (38) by Whitesides' method⁷ using copper(I) isopropoxide. This did solve the problem of regiospecific alkoxydenitration, but three steps were needed and all intermediates had to be isolated.

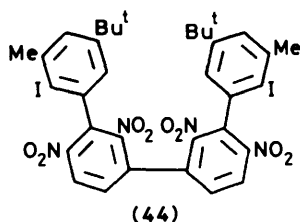
Direct replacement of two nitro groups in a tetranitroquaterphenyl by alkoxy groups had previously² been found to be unselective for a number of primary alkoxides, separation of three products by chromatography being needed. Further examination showed that alkoxides from secondary alcohols showed greater preference for attack on the outside nitro groups. Thus from the tetranitroquaterphenyl (30) and potassium 2,4-dimethylpentan-3-yl oxide, the diether (39) could be obtained in moderate yield by crystallization. Similarly, the tetranitro compound (31) with sodium pentan-3-yl oxide gave the diether (40) in 55% yield by direct crystallization, although the alkoxides from neopentyl, isopropyl, and *s*-butyl alcohol gave mixtures requiring chromatography before the diethers (41), (42), and (43) could be isolated. This partial success was limited by the formation in all cases of highly coloured by-products; evidently, the higher basicity of secondary alkoxides promoted side reactions with the nitro groups leading to azoxy compounds² and other products. A renewed attack on the problem is reported in later papers of this series. An attempt to



- (29) R = H, X = NO₂
 (30) R = Bu^t, X = NO₂
 (32) R = Bu^t, X = NH₂
 (35) R = Bu^t, X = I
 (38) R = Bu^t, X = OPrⁱ
 (39) R = Bu^t, X = OCH(Prⁱ)₂



- (31) X = Z = NO₂
 (33) X = Z = NH₂
 (34) X = NH₂, Z = NO₂
 (36) X = Z = I
 (37) X = I, Z = H
 (40) X = Z = OCH₂Et
 (41) X = Z = OCH₂Bu^t
 (42) X = Z = OPrⁱ
 (43) X = Z = OBu^s



- (45) Ar = C₆H₃Me-*m*, Bu^t-*m*
 (46) Ar = C₆H₃Me-*o*, OPrⁱ-*p*

enhance the selectivity by increasing the steric hindrance had the opposite effect: the di-iodotetranitroquaterphenyl (44) was attacked less selectively than its parent (30).

As by-products in the conversion of the diamines (19) and (20) into the di-iodides (21) and (22), the benzo[*c*]cinnolines (45) and (46) were isolated and characterized.

Experimental

The general experimental procedures were as explained in Part 5.¹

The following general conditions apply to all reactions using copper(I) t-butoxide that are reported here. All procedures prior to work-up were conducted under nitrogen. t-Butyl alcohol was freshly distilled from sodium and most of the excess was distilled back into the same flask after the reaction with potassium to form potassium t-butoxide. The latter was heated (bath) at 100–120 °C for 1–3 h under reduced pressure to decompose the 1:1 complex with t-butyl alcohol. The butoxide was suspended in 1,2-dimethoxyethane (DME) which had been freshly distilled from sodium. Stirring was commenced and was continued until work-up. Copper(I) chloride, freshly purified,⁷ was added with cooling and was followed after a specified time by dry pyridine, then dry powdered dinitrobenzene or tetranitrophenyl, and finally the aryl iodide. After the specified heating period the mixture was cooled and poured into dilute acid.

3-Iodo-5-*t*-butyltoluene.—Aluminium chloride (2 g) was added cautiously over 1–2 min to a stirred, ice-cooled mixture of 3-iodotoluene (106 g) and t-butyl chloride (80 ml). Stirring was continued for 15 min in all. The mixture was poured into water and extracted with chloroform which was then washed (aqueous NaHSO₃) and evaporated. Distillation at 2 mmHg then recovered some 3-iodotoluene (36.5 g) and yielded the iodide (1) (76.3 g) as a colourless oil, b.p. 90 °C. Crystallization from acetone at –15 °C gave prisms, m.p. 33–34 °C (Found: C, 48.0; H, 5.6. C₁₁H₁₅I requires C, 48.2; H, 5.5%); δ_H (60 MHz) 1.45 (9 H, s), 2.27 (3 H, s), 7.15 (1 H, br s), 7.38 (1 H, br s), and 7.53 (1 H, br s); *m/z* 274 (*M*⁺, 50%), and 259 (100).

2,6-Dinitro-3'-methylbiphenyl.—Copper(I) t-butoxide in DME [from potassium (2.4 g) in t-butyl alcohol (100 ml); potassium butoxide dried at 100–110 °C for 2 h; DME (95 ml); CuCl (5.85 g) added with ice cooling; 2 h at room temperature; see general directions above] was treated with pyridine (7 ml) and 1,3-dinitrobenzene (7.97 g), followed after 10 min by 3-iodotoluene (11.37 g). After 21 h at 80 °C, the mixture was cooled and poured into 5% hydrochloric acid. The product was recovered by extraction with ethyl acetate which was then washed (5% HCl then water), dried (MgSO₄), and evaporated. The residue was put on alumina from which ether eluted some iodotoluene. Chloroform then eluted a crystalline solid which was triturated with methanol to give the biphenyl (5) (11.4 g) as yellow prisms, m.p. 177–178 °C (Found: C, 60.4; H, 3.9; N, 10.8. C₁₃H₁₀N₂O₄ requires C, 60.5; H, 3.9; N, 10.9%); *m/z* 258 (*M*⁺, 100%).

3'-Methyl-2,6-dinitro-5'-*t*-butylbiphenyl.—(a) A solution of the above biphenyl (5) (7.74 g) in trichloroethylene (500 ml) was added to ferric chloride (anhydrous; 100 g). The mixture was stirred vigorously during the dropwise addition of t-butyl chloride (35 ml) and stirring was continued overnight. The liquid was decanted and the residue was washed (2 × 200 ml) with trichloroethylene. The solutions were concentrated, then filtered through alumina using chloroform as the eluant. Removal of the solvent and trituration with methanol left the biphenyl (3) (6 g) as pale yellow prisms, m.p. 187–188 °C after recrystallization from dichloromethane-methanol (Found: C, 65.0; H, 5.7; N, 9.1. C₁₇H₁₈N₂O₄ requires C, 65.0; H, 5.7; N, 8.9%); δ_H (90 MHz) 1.28 (9 H, s), 2.33 (3 H, s), 6.89 (1 H, br s), 7.10 (1 H, br s), 7.28 (1 H, s), and 7.5–8.1 (3 H, m); *m/z* 314 (*M*⁺, 14%) and 299 (100).

(b) Copper(I) t-butoxide in DME [from potassium (4 g) in t-butanol (200 ml); potassium butoxide dried 2 h at 100–110 °C; DME (170 ml); CuCl (9.4 g) added with ice cooling; 3 h at room temperature; see general directions above] was treated

with pyridine (10 ml). After 20 min, 1,3-dinitrobenzene (13.1 g) was added and then the iodide (1) [washed in with pyridine (2 ml); 25 g]. After 17 h at 75 °C the mixture was cooled and poured into 5% hydrochloric acid. The work-up was as described for (5) (above) and gave the biphenyl (3) (22.7 g), identical with the specimen prepared by method (a).

2-Iodo-5-isopropoxytoluene.—The isopropyl ether of *m*-cresol was prepared in 70% yield by successive treatment of the cresol in dimethylformamide with sodium hydride and a slight excess of isopropyl iodide, followed by heating at 75 °C for 5 h. This formed a colourless oil, b.p. 78–80 °C/14 mmHg, δ_{H} (60 MHz) 1.30 (6 H, d, *J* 6 Hz), 2.30 (3 H, s), 4.48 (1 H, septet, *J* 6 Hz), 6.6–6.9 (3 H, m), 7.0–7.3 (1 H, m). Iodine (26.7 g) was added to a solution of this ether (36.8 g) in a mixture of acetic acid, water, and sulphuric acid (100:10:3; 500 ml). Periodic acid (50% of the dihydrate in water; 10.3 ml) was added and the mixture was stirred for 6 h. The colour was discharged (aqueous NaHSO_3) and water (1.5 l) was added. The product was taken into ether which was then washed (water then NaHCO_3), dried (MgSO_4), and evaporated. The residue was crystallized twice at low temperature from methanol, to yield a solid, m.p. 23 °C. Distillation gave the iodide (2) (52 g), b.p. 102–104 °C/1.5 mmHg (Found: C, 43.5; H, 4.7. $\text{C}_{10}\text{H}_{13}\text{IO}$ requires C, 43.5; H, 4.7%); δ_{H} (60 MHz) 1.32 (6 H, d, *J* 6 Hz), 2.38 (3 H, s), 4.48 (1 H, septet, *J* 6 Hz), 6.43 (1 H, dd, *J* 9 Hz, 3 Hz), 6.79 (1 H, d, *J* 3 Hz), and 7.61 (1 H, d, *J* 9 Hz); *m/z* 276 (M^+ , 18%) and 234 (100). The same product was made in similar yield (71%) by iodination in chloroform with iodine and silver trifluoroacetate.

4-Isopropoxy-2-methylbenzoic acid.—A solution of the iodide (2) (3.04 g) in dry ether (10 ml) was cooled under nitrogen to below –70 °C and a hexane solution of butyl-lithium (1.2M; 10 ml) was added. After 45 min the mixture was poured onto solid carbon dioxide. Next day, ether and dilute hydrochloric acid (5%) were added. The acidic product was recovered by extraction into sodium hydroxide (2.5M), acidification, and re-extraction with ether. Crystallization from methanol–water gave the acid (6) (1.5 g) as prisms, m.p. 113–115 °C before and after recrystallization (EtOAc) (Found: C, 68.4; H, 7.5. $\text{C}_{11}\text{H}_{14}\text{O}_3$ requires C, 68.0; H, 7.2%); δ_{H} (60 MHz) 1.37 (6 H, d, *J* 6 Hz), 2.63 (3 H, s), 4.63 (1 H, septet, *J* 6 Hz), 6.6–6.9 (2 H, m), 8.05 (1 H, d, *J* 10 Hz), and 10.1–10.3 (1 H, br); *m/z* 194 (M^+ , 29%) and 152 (100). Treatment of this acid with boiling hydrobromic acid in aqueous acetic acid gave 4-hydroxy-2-methylbenzoic acid, m.p. 175–176 °C (lit.,⁸ m.p. 177–178 °C; negative ferric chloride test) and thence by esterification ethyl 4-hydroxy-2-methylbenzoate, m.p. 97.5–98.5 °C (lit.,⁹ m.p. 98 °C).

4-Isopropoxy-2'-methyl-2,6-dinitrobiphenyl.—Copper(I) t-butoxide in DME [from potassium (27 g) in *t*-butyl alcohol (900 ml); potassium t-butoxide dried at 100–110 °C/1 mmHg 2 h; DME (500 ml); CuCl (62 g) added with ice cooling, 15 min; 2.5 h at room temperature; see general directions] was treated with a solution of 1,3-dinitrobenzene (87.6 g) in DME (200 ml) and pyridine (100 ml). After 10 min the iodide (2) (144.5 g) was added and washed in with pyridine. After 15 h at 75–80 °C the mixture was cooled and poured into an excess of hydrochloric acid (5%). The product was taken into ether which was washed (5% HCl then water), dried (MgSO_4), passed through alumina, and evaporated. Crystallization of the residue from methanol (100 ml) gave the biphenyl (4) (128.6 g, 2 crops), m.p. 62–63 °C (Found: C, 60.7; H, 5.1; N, 8.9. $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_5$ requires C, 60.8; H, 5.1; N, 8.9%); δ_{H} (60 MHz) 1.35 (6 H, d, *J* 6 Hz), 2.10 (3 H, s), 4.58 (1 H, septet, *J* 6 Hz), 6.6–7.1 (3 H, m), and 7.5–8.1 (3 H, m); *m/z* 316 (M^+ , 58%), 274 (100), and 227 (61).

A similar reaction using a sample of iodide which had not

been crystallized afforded, in small amounts, an isomeric biphenyl from the mother liquors. Recrystallization from methanol gave 2'-isopropoxy-4'-methyl-2,6-dinitrobiphenyl (7) as yellow needles, m.p. 164–165 °C (Found: C, 60.7; H, 5.2; N, 8.9%); δ_{H} (60 MHz) 1.17 (6 H, d, *J* 6 Hz), 2.38 (3 H, s), 4.52 (1 H, septet, *J* 6 Hz), 6.6–7.1 (3 H, m) and 7.4–8.1 (3 H, m); *m/z* 316 (M^+ , 50%), 274 (100), and 207 (44).

The dinitrobiphenyl (4) was also prepared in 59% yield by heating the iodide (2) (5.5 g) and 1-chloro-2,6-dinitrobenzene (3.7 g) in dimethylformamide (40 ml) under nitrogen at 140 °C, adding copper powder (5 g) in portions, and continuing to heat with stirring for 30 min.

2-Methoxy-3'-methyl-6-nitrobiphenyl.—Sodium methoxide (2.25 g) was added to a stirred solution of the dinitrobiphenyl (5) (6.54 g) in hexamethylphosphoric triamide (HMPT; 70 ml). After 24 h, the solution was poured into an excess of dilute acid (5% HCl) and extracted with chloroform which was then washed (5% HCl then water), dried (MgSO_4), passed through alumina, and evaporated. Crystallization from methanol then gave the methoxynitrobiphenyl (10) (5.3 g) as very pale yellow needles, m.p. 89–91 °C (Found: C, 69.4; H, 5.7; N, 5.7. $\text{C}_{14}\text{H}_{13}\text{NO}_3$ requires C, 69.1; H, 5.4; N, 5.8%); δ_{H} (60 MHz) 2.37 (3 H, s), 3.78 (3 H, s), and 6.8–7.4 (7 H, m); *m/z* 243 (69%; M^+) and 215 (100).

2-Methoxy-3'-methyl-6-nitro-5'-*t*-butylbiphenyl.—This was prepared as described in the foregoing example from sodium methoxide (2.74 g), HMPT (85 ml), and the dinitrobiphenyl (3) (12.56 g). After 20 h the mixture was worked up as before except that extraction was carried out with ether and this was replaced by chloroform before passage through alumina. The product was triturated with methanol to afford the methoxynitrobiphenyl (8) (10.6 g), m.p. 110 °C (Found: C, 72.1; H, 7.0; N, 4.6. $\text{C}_{18}\text{H}_{21}\text{NO}_3$ requires C, 72.2; H, 7.0; N, 4.7%); δ_{H} (60 MHz) 1.32 (9 H, s), 2.37 (3 H, s), 3.75 (3 H, s), and 6.8–7.5 (6 H, m); *m/z* 299 (M^+ , 12%), 284 (100), and 271 (80).

4-Isopropoxy-2-methoxy-2'-methyl-6-nitrobiphenyl.—This was made as described for (10) from the dinitrobiphenyl (4) (128.6 g) sodium methoxide (27.4 g) and HMPT (850 ml). The work-up, after 24 h, used ether instead of chloroform. Recrystallization of the product from methanol gave yellow needles of the methoxynitrobiphenyl (9) (110 g), m.p. 90.5–91.5 °C (Found: C, 68.0; H, 6.3; N, 4.8. $\text{C}_{17}\text{H}_{19}\text{NO}_4$ requires C, 67.8; H, 6.3; N, 4.7%); δ_{H} (60 MHz) 1.33 (6 H, d, *J* 6 Hz), 2.05 (3 H, s), 3.75 (3 H, s), 4.52 (1 H, septet, *J* 6 Hz), 6.5–7.0 (3 H, m), and 7.0–7.6 (3 H, m); *m/z* 301 (M^+ , 100%).

3,4'-Di-iodo-6-methoxy-3'-methyl-2-nitrobiphenyl.—Iodine (3.5 g) and periodic acid dihydrate (50% in water; 1.4 ml) were added to a suspension of the methoxynitrobiphenyl (10) (3.1 g) in a mixture (80 ml) of acetic acid–water–sulphuric acid (100:10:3). The flask was closed by a balloon and heated at 77 °C for 23 h. When cooled the product crystallized and was collected after the iodine colour had been discharged (aqueous NaHSO_3) to yield the pure di-iodide (11) (5.4 g). An analytical sample, prisms m.p. 195–197 °C, was recrystallized from dichloromethane–methanol (Found: C, 33.8; H, 2.2; N, 2.5. $\text{C}_{14}\text{H}_{11}\text{I}_2\text{NO}_3$ requires C, 33.9; H, 2.2; N, 2.8%); δ_{H} (60 MHz) 2.42 (3 H, s), 3.75 (3 H, s), 6.74 (1 H, dd, *J* 9 Hz, 3 Hz), 6.82 (1 H, *J* 8 Hz), 7.09 (1 H, d, *J* 3 Hz), 7.79 (1 H, d, *J* 9 Hz), and 7.82 (1 H, d, *J* 8 Hz); *m/z* 495 (M^+ , 100%).

2',3-Di-iodo-6-methoxy-3'-methyl-2-nitro-5'-*t*-butylbiphenyl.—This was prepared essentially as described in the foregoing example from the methoxynitrobiphenyl (8) (3.6 g), iodine (2.87 g), and periodic acid (1.1 ml) in the mixed solvent (110 ml)

at 75 °C for 24 h. The *di-iodide* (**12**) (5.9 g) was recrystallized from dichloromethane–methanol, m.p. 147–148 °C (Found: C, 39.3; H, 3.5; N, 2.5. $C_{18}H_{19}I_2NO_3$ requires C, 39.2; H, 3.5; N, 2.5%); δ_H (60 MHz) 1.28 (9 H, s), 2.50 (3 H, s), 3.78 (3 H, s), 6.85 (1 H, d, *J* 9 Hz), 6.98 (1 H, d, *J* 2 Hz), 7.22 (1 H, d, *J* 2 Hz), and 7.85 (1 H, d, *J* 9 Hz).

5'-Iodo-4'-isopropoxy-6-methoxy-2'-methyl-2-nitrobiphenyl.—The methoxynitrobiphenyl (**9**) (407 mg) was iodinated as in the previous examples [iodine (146.7 mg), periodic acid (0.06 ml), mixed solvent (3.5 ml); 70 °C; 3.5 h]. After the addition of water (15 ml) to the cooled solution, the product was collected and recrystallized from methanol to give yellow plates of the *monoiodide* (**13**) (440 mg), m.p. 133–134 °C (Found: C, 47.9; H, 4.4; N, 3.2. $C_{17}H_{18}INO_4$ requires C, 47.8; H, 4.2; N, 3.3%); δ_H (60 MHz) 1.42 (6 H, d, *J* 6 Hz), 2.05 (3 H, s), 3.78 (3 H, s), 4.55 (1 H, septet, *J* 6 Hz), 6.72 (1 H, s), 7.0–7.6 (m); *m/z* 427 (M^+ , 65%) and 385 (100).

3,5'- and 3',5'-Di-iodo-4'-isopropoxy-6-methoxy-2'-methyl-2-nitrobiphenyl.—Iodination of the methoxynitrobiphenyl (**9**) (1 g) with double proportions of reagents [iodine (0.73 g), periodic acid (0.3 ml), mixed solvent (20 ml); 70 °C; 20 h], followed by discharge of the iodine colour (aqueous $NaHSO_3$) and dilution (50 ml water) gave a precipitate which was separated by crystallizations from dichloromethane–methanol into the *3,5'-di-iodo* compound (**14**), very pale yellow needles, m.p. 208–210 °C (Found: C, 36.9; H, 3.3; N, 2.6. $C_{17}H_{17}I_2NO_4$ requires C, 36.9; H, 3.1; N, 2.5%); δ_H 1.38 (6 H, d, *J* 6 Hz), 2.02 (3 H, s), 3.73 (3 H, s), 4.53 (1 H, septet, *J* 6 Hz), 6.62 (1 H, br s), 6.77 (1 H, d, *J* 9 Hz), 7.37 (1 H, br s), and 7.73 (1 H, d, *J* 9 Hz); *m/z* 553 (M^+ , 8%) and 511 (100); and the more soluble isomer, the *3',5'-di-iodo* compound (**15**), pale yellow needles, m.p. 97–98 °C (Found: C, 36.8; H, 3.1; N, 2.5%); δ_H 1.45 (6 H, d, *J* 6 Hz), 2.22 (3 H, s), 3.80 (3 H, s), 4.9 (1 H, m), 7.0–7.6 (m); *m/z* 553 (M^+ , 8%) and 511 (100).

3,3',5'-Tri-iodo-4'-isopropoxy-6-methoxy-2'-methyl-2-nitrobiphenyl.—The methoxynitrobiphenyl (**9**) (8.75 g) was iodinated as above [iodine, (10.4 g), periodic acid (3.9 ml), mixed solvent (400 ml); 80 °C; 36 h]. From the cooled decolourized mixture most of the product was collected directly; the remainder was recovered by dilution of the filtrate and extraction with chloroform which was washed (water and $NaHCO_3$), dried ($MgSO_4$), and filtered through alumina before evaporation and crystallization from chloroform–methanol. The *tri-iodide* (**16**) (14.45 g) formed colourless prisms, m.p. 142–143 °C (Found: C, 30.4; H, 2.7; N, 2.1. $C_{17}H_{16}I_3NO_4$ requires C, 30.1; H, 2.4; N, 2.1%); δ_H (60 MHz) 1.43 (6 H, d, *J* 6 Hz), 2.20 (3 H, s), 3.75 (3 H, s), 4.85 (1 H, septet, *J* 6 Hz), 6.80 (1 H, d, *J* 9 Hz), 7.43 (1 H, s), and 7.79 (1 H, d, *J* 9 Hz); *m/z* 679 (M^+ , 7%) and 637 (100).

*2,2'''-Di-iodo-6',4''-dimethoxy-3,3'''-dimethyl-2',2''-dinitro-5,5'''-di-*t*-butyl-*m*-quaterphenyl*.—Hydrated copper(II) trifluoromethanesulphonate (7.72 g) was added under nitrogen to a stirred suspension of copper powder (0.99 g) in acetone (155 ml) and acetonitrile (9 ml). Next day the mixture was cooled in ice and a solution of the *di-iodide* (**12**) (5.9 g) in dimethyl sulphoxide (40 ml) was added dropwise, followed by aqueous ammonia (*d* 0.88; 38 ml). The deep blue solution was stirred at 0 °C for 4 h, then at 5 °C for 18 h. Water (250 ml) and chloroform were added and the chloroform layer was washed (5% HCl and water), dried ($MgSO_4$), passed through alumina, and evaporated. The residue after crystallization from methanol gave the *quaterphenyl* (**17**) (3.8 g) as prisms, m.p. 189–190 °C; recrystallized for analysis from dichloromethane–methanol (Found: C, 50.7; H, 4.5; N, 3.1. $C_{36}H_{38}I_2N_2O_6$ requires C, 50.9; H, 4.5; N, 3.3%); δ_H (60 MHz) 1.28 (18 H, s), 2.52 (6 H, s), 3.80 (6

H, s), 7.0 (2 H, d, *J* 9 Hz), 7.03 (2 H, d, *J* 2 Hz), 7.22 (2 H, d, *J* 2 Hz), and 7.47 (2 H, d, *J* 9 Hz).

*3,3'''',5,5'''-Tetraiodo-4,4'''-di-isopropoxy-4'',6'-dimethoxy-2,2'''-dimethyl-2',2''-dinitro-*m*-quaterphenyl*.—Hydrated copper(II) trifluoromethanesulphonate (9.2 g), copper powder (1.2 g), acetone (185 ml), and acetonitrile (11 ml) were mixed under nitrogen and heated with stirring under reflux for 2.5 h, then cooled in ice during dropwise addition of the *tri-iodide* (**16**) (8.6 g) in dimethyl sulphoxide (35 ml), followed by ammonia (*d* 0.88; 42 ml). The mixture was stirred at 0 °C for 8 h, then at 5 °C for 12 h, and was worked up as in the preceding example. The *quaterphenyl* (**18**) (6.3 g) was a pale yellow solid, m.p. 282–283 °C (from MeOH) and was recrystallized (CH_2Cl_2 –MeOH) for analysis (Found: C, 36.7; H, 3.0; N, 2.5. $C_{34}H_{32}I_4N_2O_8$ requires C, 37.0; H, 2.9; N, 2.5%); δ_H (60 MHz) 1.43 (12 H, d, *J* 6 Hz), 2.28 (6 H, br s), 3.82 (6 H, s), 4.86 (2 H, m), 7.06 (2 H, d, *J* 9 Hz), 7.39 (2 H, d, *J* 9 Hz), and 7.53 (2 H, br s); *m/z* (field desorption, Kratos MS50) 1104 (M^+).

*4'',6'-Dimethoxy-3,3'''-dimethyl-5,5'''-di-*t*-butyl-*m*-quaterphenyl-2',2''-diamine*.—Zinc–copper couple [from zinc powder (20 g)] was added to a suspension of the *dinitroquaterphenyl* (**17**) (13.5 g) in water (50 ml) and acetic acid (430 ml). The mixture was heated and stirred for 4 h in a bath preheated to 115 °C, then filtered warm. The filtrate and washings (acetic acid) were diluted with water. The product was collected when cold and purified by dissolution in isopropyl alcohol and precipitation with water. The *diamine* (**19**) (7.3 g) was recrystallized from ethanol for analysis and formed needles, m.p. 118–120 °C (Found: C, 80.2; H, 8.3; N, 5.1. $C_{36}H_{44}N_2O_2$ requires C, 80.6; H, 8.2; N, 5.2%); δ_H (60 MHz) 1.33 (18 H, s), 2.37 (6 H, s), 3.7 (br s, OMe and NH_2), 6.47 (2 H, d, *J* 9 Hz), and 7.0–7.4 (m); *m/z* 537 (35%) and 536 (100, M^+).

*4,4'''-Di-isopropoxy-4'',6'-dimethoxy-2,2'''-dimethyl-*m*-quaterphenyl-2',2''-diamine*.—Zinc–copper couple [from zinc powder (8 g), the *dinitroquaterphenyl* (**18**) (8.1 g), water (25 ml), and acetic acid (200 ml) were brought into reaction as described for the previous example (125 °C, 42 h); two further portions of the couple (6 g) were added at intervals. The combined filtrates were diluted with water until turbid, allowed to cool, and decanted from a small gummy deposit. More water then precipitated the product as a white solid (3.6 g). An identical substance was obtained in 75% yield by shaking the *dinitro* compound (**18**) (1.5 g) and Raney nickel (0.5 g) in methanolic potassium hydroxide (0.5M; 70 ml) under hydrogen (70 psig) for 30 h. Recrystallization from ethyl acetate–ethanol gave the *diamine* (**20**) as a colourless powder, m.p. 143–144 °C (Found: C, 75.8; H, 7.4; N, 5.2. $C_{34}H_{46}N_2O_4$ requires C, 75.6; H, 7.4; N, 5.2%); δ_H 1.38 (12 H, d, *J* 6 Hz), 2.07 and 2.12 (6 H), 3.3–3.7 (4 H, br), 3.73 (6 H, s), 4.62 (2 H, septet, *J* 6 Hz), 6.5 (2 H, d, *J* 8 Hz), and 6.65–7.4 (m); *m/z* 541 (40%) and 540 (100, M^+).

*3-Methyl-2',2'',4'',6'-tetranitro-*m*-terphenyl*.—Copper(I) t-butoxide in DME [from potassium (0.62 g), DME (250 ml), and CuCl (1.54 g); see general directions] was treated in sequence with pyridine (3.5 ml), 2,2',4,4'-tetranitrobiphenyl (16.36 g), and 3-iodotoluene (3.4 g). The mixture was stirred at room temperature for 48 h, poured into dilute acid, and extracted with ethyl acetate which was washed (5% HCl and water), dried ($MgSO_4$), and concentrated. As much as possible of the excess tetranitrobiphenyl was removed by crystallization and the residue was purified by flash chromatography on silica, using chloroform–light petroleum as the eluant. The *terphenyl* (**23**) [4.2 g, 67% (based on iodotoluene)] crystallized from methanol–ether, m.p. 143.5–144.5 °C (Found: C, 54.0; H, 2.9; N, 13.4. $C_{19}H_{12}N_4O_8$ requires C, 53.8; H, 2.8; N, 13.2%); δ_H (60 MHz)

2.37 (3 H, s), 7.15—7.4 (4 H, m), 7.53 (1 H, d, *J* 9 Hz), 7.7 (1 H, d, *J* 9 Hz), 8.1 (1 H, d, *J* 9 Hz), 8.6 (1 H, dd, *J* 9 Hz, 3 Hz), and 9.1 (1 H, d, *J* 3 Hz).

3-Methyl-2',2'',4'',6'-tetranitro-5-*t*-butyl-*m*-terphenyl.—This was prepared essentially as described in the foregoing example [potassium (1.88 g), DME (400 ml), CuCl (4.67 g); 2 h; room temperature; pyridine (7.5 ml), tetranitrobiphenyl (37 g); 10 min; the iodide (1) (7.5 ml); 80 °C; 48 h; worked up as above]. The *terphenyl* (24) (14.1 g) formed colourless crystals from ether, m.p. 159—161 °C (Found: C, 56.6; H, 4.3; N, 11.7. C₂₃H₂₀N₄O₈ requires C, 56.4; H, 4.3; N, 12.0%). An identical substance was formed in 77% yield by alkylation of the *terphenyl* (23) (150 mg) in *t*-butyl chloride (10 ml) by addition of aluminium chloride (0.7 g) at -10 °C and stirring at room temperature for 2 h; δ_{H} (60 MHz) 1.3 (9 H, s), 2.35 (3 H, s), 6.86—7.31 (3 H, m), 7.53 (1 H, d, *J* 9 Hz), 7.7 (1 H, d, *J* 9 Hz), 8.1 (1 H, d, *J* 9 Hz), 8.6 (1 H, dd, *J* 9 Hz, 3 Hz), and 9.1 (1 H, d, *J* 3 Hz).

3-[1,2,3,4-Tetrahydro-9-*syn*-isopropyl-5,8-dimethoxy-1,4-methano-6-naphthyl]-2,2',4,4'-tetranitrobiphenyl.—Copper(I) *t*-butoxide in DME was prepared [from potassium (4.88 g), DME (800 ml), and CuCl (12.38 g)] as in earlier examples. Pyridine (15 ml) and tetranitrobiphenyl (41 g) were added, followed by 1,2,3,4-tetrahydro-6-iodo-9-*syn*-isopropyl-5,8-dimethoxy-1,4-methanonaphthalene (18.65 g; see the preceding paper). After 15 h at 80 °C the mixture was cooled, treated with acetic acid (25 ml) and poured into dilute hydrochloric acid. The product, after work-up as described for (23) and removal of excess tetranitrobiphenyl by crystallization, was a mixture of mono- and diarylation products which were separated by flash chromatography on silica. The *naphthylbiphenyl* (25) (19.7 g) crystallized from benzene as a solvate which was dried at 80 °C/1 mmHg for 3 days, m.p. then 108—110.5 °C (Found: C, 58.1; H, 4.7; N, 9.6. C₂₈H₂₆N₄O₁₀ requires C, 58.1; H, 4.5; N, 9.7%); δ_{H} (60 MHz) 0.84 (6 H, d, *J* 6 Hz), 1.16—2.15 (6 H, m), 3.47—3.78 (8 H, m), 6.48 (1 H, s), 7.47 (1 H, br d, *J* 8.3 Hz), 7.57—7.76 (1 H, m), 8.16 (1 H, br d, *J* 8.3 Hz), 8.55 (1 H, m), and 9.05 (1 H, d).

3,3'-Bis-(1,2,3,4-tetrahydro-9-*syn*-isopropyl-5,8-dimethoxy-1,4-methano-6-naphthyl)-2,2',4,4'-tetranitrobiphenyl.—The other product of the foregoing experiment was the *bisnaphthylbiphenyl* (26) (4.3 g) which crystallized from isopropyl alcohol, m.p. 139—141 °C (Found: C, 63.9; H, 5.8; N, 6.3. C₄₄H₄₆N₄O₁₂ requires C, 64.2; H, 5.6; N, 6.8%); δ_{H} (60 MHz) 0.85 (12 H, br s), 1.10—2.12 (12 H, m), 3.37—3.74 (16 H, m), 6.49 (2 H, m), 7.56 (2 H, m), and 8.02—8.13 (2 H, m).

3-(1,2,3,4-Tetrahydro-5-methoxy-8-methyl-1,4-ethano-6-naphthyl)-2,2',4,4'-tetranitrobiphenyl.—To a cold stirred suspension of potassium *t*-butoxide (sublimed; 15 g) in DME (600 ml) was added copper(I) chloride (12.35 g). After 2 h without cooling, pyridine (15 ml) and tetranitrobiphenyl (55.76 g) were added, followed after 30 min by 1,2,3,4-tetrahydro-6-iodo-5-methoxy-8-methyl-1,4-ethanonaphthalene (14.43 g; see the preceding paper). The mixture was heated at 75—80 °C for 12 h. After the usual work-up (using chloroform) tetranitrobiphenyl (46.6 g) was recovered. The remainder was subject to h.p.l.c. on a 250 × 4.5 mm column of 5 μm Spherisorb eluted by hexanes-ethyl acetate (3:2 v/v) at 0.7 ml min⁻¹. The aryl iodide (7.2 g) was recovered along with the *naphthylbiphenyl* (27) (6.44 g) which crystallized from chloroform-ether, m.p. 211—212 °C (Found: C, 58.3; H, 4.3; N, 10.5. C₂₆H₂₂N₄O₉ requires C, 58.4; H, 4.2; N, 10.5%); δ_{H} (360 MHz) 1.15—1.85 (8 H, m), 2.27 (3 H, s), 3.53 and 3.54 (3 H, 2 s), 6.84 (1 H, s), 7.46 and 7.49 (1 H, 2 d, *J* 8.5, 8.3 Hz), 7.63 and 7.72 (1 H, 2 d, *J* 8.2, 8.3 Hz), 8.13 and 8.17 (1 H, 2 d, *J* 8.2, 8.3 Hz), 8.56 (1 H, 2 dd, *J* 8.5, 2 Hz), and 9.06 (1 H, d, *J* 2 Hz).

3-(1,2,3,4-Tetrahydro-5-methoxy-8-methyl-1,4-ethano-6-naphthyl)-3'-(1,2,3,4-tetrahydro-9-*syn*-isopropyl-5,8-dimethoxy-1,4-methano-6-naphthyl)-2,2',4,4'-tetranitrobiphenyl.—Copper(I) *t*-butoxide in DME [from potassium (0.71 g), DME (60 ml), CuCl (1.73 g) added with cooling, 1.5 h at room temperature] was treated successively with pyridine (4 ml), the *naphthylbiphenyl* (25) (8.6 g), and, after 30 min, 1,2,3,4-tetrahydro-6-iodo-5-methoxy-8-methyl-1,4-ethanonaphthalene (5.4 g). After being heated overnight at 75—80 °C the mixture was worked up as usual. Elution from silica by ethyl acetate-light petroleum (15:85 v/v) and crystallization from ether gave the required product (10.1 g) as a microcrystalline mixture, m.p. 108—110 °C, of atropisomers of the *bisnaphthylbiphenyl* (28) (Found: C, 64.8; H, 5.6; N, 6.8. C₄₂H₄₂N₄O₁₁ requires C, 64.8; H, 5.4; N, 7.2%); δ_{H} (60 MHz) 0.86 (6 H, br s), 1.07—2.15 (14 H, m), 2.28 (3 H, br s), 3.15—3.77 (13 H, m), 6.45 (1 H, m), 6.90 (1 H, m), 7.3—7.75 (2 H, m), 8.0—8.22 (2 H, m). The same product was obtained in 86% yield by a similar procedure from the *naphthylbiphenyl* (27) and the complementary iodide.

3,3'''-Dimethyl-2',2'',4'',6'-tetranitro-*m*-quaterphenyl.—Copper(I) *t*-butoxide in DME [from potassium (0.82 g), DME (40 ml), and CuCl (1.95 g)]. After 2 h, pyridine (2.5 ml) was added, then tetranitrobiphenyl (3.04 g), and finally 3-iodotoluene (6.75 g). After 15 h at 80 °C the product, worked up as usual, appeared from t.l.c. to be a mixture of quaterphenyl with minor amounts of *terphenyl* and *quinquephenyl*. Chromatography on alumina (ether-light petroleum) gave the pure *quaterphenyl* (29) (3.1 g), m.p. 194 °C (from methanol) (Found: C, 60.7; H, 3.6; N, 11.0. C₂₆H₁₈N₄O₈ requires C, 60.8; H, 3.5; N, 10.8%); δ_{H} (60 MHz) 2.4 (6 H, s), 7.1—7.5 (8 H, m), 7.64 (2 H, d, *J* 9 Hz), and 8.08 (2 H, d, *J* 9 Hz).

3,3'''-Dimethyl-2',2'',4'',6'-tetranitro-5,5'''-*t*-butylquaterphenyl.—Copper(I) *t*-butoxide in DME was prepared as in the general directions [from potassium (7.05 g), *t*-butyl alcohol (180 ml); potassium *t*-butoxide dried at 120 °C/0.5 mmHg for 3 h; DME (266 ml), CuCl (17.5 g) added with cooling; 75 min at room temperature]. Pyridine (19 ml), tetranitrobiphenyl (27 g), and the iodide (1) (47.3 g) were added in that order and the mixture was heated at 70 °C for 20 h, then cooled in ice and poured into cold hydrochloric acid (1M; 600 ml). Ethyl acetate was added, the mixture was filtered (Celite), and the ethyl acetate layer was washed (1M-HCl and brine), dried (MgSO₄), and evaporated. The residual oil was applied to a column of alumina (500 g) and eluted with chloroform-hexanes (1:3 v/v). The *quaterphenyl* (30) (47 g, 93%) was pure by h.p.l.c. but did not crystallize (Found: C, 65.2; H, 5.7; N, 8.7. C₃₄H₃₄N₄O₈ requires C, 65.0; H, 5.4; N, 8.9%); δ_{H} (60 MHz) 1.3 (18 H, s), 2.35 (6 H, s), 6.9—7.3 (6 H, m), 7.59 (2 H, d, *J* 9 Hz), 8.0 (2 H, d, *J* 9 Hz). The same product was made in 82% yield by alkylation of the *quaterphenyl* (29) with *t*-butyl chloride and aluminium chloride.

4,4'''-Di-isopropoxy-2,2'''-dimethyl-2',2'',4'',6'-tetranitro-*m*-quaterphenyl.—This was prepared by diarylation of tetranitrobiphenyl with the iodide (2) as described for the *quaterphenyl* (30) above [potassium (2.65 g), DME (100 ml), CuCl (6.57 g) added with cooling during 10 min; 1.5 h at room temperature, pyridine (7 ml), tetranitrobiphenyl (10.04 g), iodide (17.9 g); 75—80 °C; 18 h]. The crude product was passed in chloroform through alumina and crystallized from methanol to give the *quaterphenyl* (31) (16.9 g) as yellow needles, m.p. 220—221 °C (Found: C, 60.8; H, 4.8; N, 8.9. C₃₂H₃₀N₄O₁₀ requires C, 61.0; H, 4.8; N, 8.9%); δ_{H} (60 MHz) 1.35 (12 H, d, *J* 6 Hz), 2.13 (6 H, br s), 4.6 (2 H, septet, *J* 6 Hz), 6.6—7.15 (6 H, m), 7.60 (2 H, d, *J* 9 Hz), and 8.02 (2 H, d, *J* 9 Hz). In [²H₆]Me₂SO the broad signal

for the aromatic methyls was resolved into two singlets, still not sharp; δ 1.97 and 2.12.

3,3'''-Dimethyl-2',2''-dinitro-5,5'''-di-*t*-butyl-*m*-quaterphenyl-4'',6'-diamine.—To a solution of the quaterphenyl (30) (1.2 g) in dioxane (50 ml) and water (5 ml), was added at 80 °C during 1 h a solution of sodium sulphide nonahydrate (1.8 g) and sodium hydrogen carbonate (0.85 g) in water (15 ml). The mixture was stirred at 100 °C overnight and the solvent was removed at low pressure. Water (50 ml) and chloroform were added; the chloroform was washed (water), dried (MgSO₄), and evaporated. The residue after passage through alumina in ether–light petroleum was crystallized from methanol to yield the *diamine* (32) (0.43 g), m.p. 287–289 °C (Found: C, 72.3; H, 6.3; N, 10.0. C₃₄H₃₈N₄O₄ requires C, 72.1; H, 6.7; N, 9.9%); δ (60 MHz) 1.33 (18 H, s), 2.35 (6 H, s), 3.81 (4 H, br s), and 6.57–7.18 (10 H, m).

4,4'''-Di-isopropoxy-2,2'''-dimethyl-2',2''-dinitro-*m*-quaterphenyl-4'',6'-diamine.—The quaterphenyl (31) (5 g) was reduced as above in 260 ml dioxane–water (4:1), [70 °C rising to 100 °C over 4 h during the addition of Na₂S (0.2M; 125 ml) containing NaHCO₃ (2.1 g); 14 h at 100 °C]. Water (500 ml) was added and 300 ml of solvent was removed at low pressure. The product was extracted with ethyl acetate which was washed (water), concentrated, and passed through alumina, eluting with chloroform. Removal of the solvent and trituration with methanol gave the *diamine* (33) (3.8 g); the analytical sample, yellow needles, crystallized from dichloromethane–isopropyl alcohol; m.p. 238–240 °C (Found: C, 66.9; H, 6.0; N, 9.7. C₃₂H₃₄N₄O₆ requires C, 67.4; H, 6.0; N, 9.8%); δ_{H} (60 MHz; CDCl₃ with some [2H₆]Me₂SO) 1.32 (12 H, d, *J* 6 Hz), 2.10 (6 H, s), 3.8 (4 H, br s), 4.6 (2 H, septet, *J* 6 Hz), and 6.5–7.2 (8 H, m); *m/z* 570 (*M*⁺, 100%).

4,4'''-Di-isopropoxy-2,2'''-dimethyl-2',2'',4'-trinitro-*m*-quaterphenyl-6'-amine.—To the quaterphenyl (31) (254 mg), suspended in boiling methanol (10 ml) was added dropwise during 1 h, a solution of sodium sulphide nonahydrate (280 mg) and sodium hydrogen carbonate (100 mg) in water (3 ml). After further heating (1.5 h) the mixture was left overnight and diluted with water (3 ml). The product (210 mg) was collected and recrystallized from methanol to give the *monoamine* (34) as yellow prisms, m.p. 203–205 °C (Found: C, 63.8; H, 5.4; N, 9.3. C₃₂H₃₂N₄O₈ requires C, 64.0; H, 5.3; N, 9.3%); δ_{H} (60 MHz) 1.35 (12 H, d, *J* 6 Hz), 2.12 (6 H, br s), 3.9 (2 H, br s), 4.57 (2 H, septet, *J* 6 Hz), 6.6–7.35 (m), 7.58 (1 H, d, *J* 9 Hz), and 7.98 (1 H, d, *J* 9 Hz); *m/z* 600 (*M*⁺, 18%).

4'',6'-Di-iodo-3,3'''-dimethyl-2',2''-dinitro-5,5'''-di-*t*-butyl-*m*-quaterphenyl.—A mixture of the *diamine* (32) (0.5 g), 3-methylbutyl nitrite (3 ml) and di-iodomethane (4 ml) was stirred for 20 h and then heated for 1 h at 75 °C. After evaporation of the reaction mixture under high vacuum, the residue in ether–light petroleum was passed through alumina to yield the *di-iodide* (35) (0.48 g), m.p. 200–203 °C after crystallization from ether (Found: C, 51.8; H, 4.3; N, 3.5. C₃₄H₃₄I₂N₂O₄ requires C, 51.5; H, 4.4; N, 3.1%); δ_{H} (60 MHz) 1.36 (18 H, s), 2.4 (6 H, s), 6.73–7.1 (8 H, m), and 8.05 (2 H, d, *J* 8 Hz).

4'',6'-Di-iodo-4,4'''-di-isopropoxy-2,2'''-dimethyl-2',2''-dinitro-*m*-quaterphenyl.—The *diamine* (33) (1.25 g) in sulpholane (25 ml) and sulphuric acid (75%; 25 ml) was cooled below 0 °C during the dropwise addition of sodium nitrite (0.65 g) in water (5 ml). Urea (0.62 g) in water (5 ml) was added after 1 h and the mixture, still below 0 °C, was stirred for a further 1 h. A saturated solution of potassium iodide (4 g) was then added; 90 min later, the mixture was diluted with water and extracted with dichloromethane which was washed (10% NaHSO₃ and water)

and evaporated. To remove sulpholane the residue in ether was washed well with water. Preparative i.l.c. on silica then gave, as the least polar fraction, the *di-iodide* (36) (0.5 g), which crystallized from chloroform–isopropyl alcohol as pale yellow prisms, m.p. 181–182 °C (Found: C, 48.3; H, 3.8; N, 3.4. C₃₂H₃₀I₂N₂O₆ requires C, 48.5; H, 3.8; N, 3.5%); δ_{H} (60 MHz) 1.35 (12 H, d, *J* 6 Hz), 2.1 (6 H, br s), 4.5 (2 H, septet, *J* 6 Hz), 6.6–7.3 (m), and 8.1 (2 H, d, *J* 8 Hz). From a more polar fraction the corresponding *6'-monoiodide* (37) (0.2 g) was isolated; m.p. 189–190 °C (from Pr'OH) (Found: C, 57.7; H, 4.6; N, 4.3. C₃₂H₃₁IN₂O₆ requires C, 57.7; H, 4.7; N, 4.2%); δ_{H} (60 MHz) 1.35 (12 H, d, *J* 6 Hz), 2.1 (6 H, br s), 4.4 (2 H, septet, *J* 6 Hz), 6.6–7.1 (6 H, m), 7.1–7.6 (4 H, m), and 8.1 (1 H, d, *J* 8 Hz). At 90 MHz the signal at δ 4.4 was resolved into two overlapping septets.

4'',6'-Di-isopropoxy-3,3'''-dimethyl-2',2''-dinitro-5,5'''-di-*t*-butyl-*m*-quaterphenyl.—Potassium isopropoxide [prepared by dissolving potassium (0.2 g) in isopropyl alcohol and removing the excess alcohol] was suspended in dry DME (30 ml) and copper(I) chloride (495 mg) was added under nitrogen with cooling. The *di-iodide* (35) (390 mg) was added and the mixture was heated at 70 °C for 24 h. After dilution with ice cold dilute hydrochloric acid, the product was recovered by means of ether. T.l.c. having shown the presence of some starting material, the product was chromatographed on silica eluting with 1% ether in light petroleum. The *di-ether* (38) (220 mg) crystallized from methanol; m.p. 149–151 °C (Found: C, 73.6; H, 7.4; N, 4.3. C₄₀H₄₈N₂O₆ requires C, 73.2; H, 7.5; N, 4.0%); δ_{H} (60 MHz) 1.18 (12 H, d), 1.33 (18 H, s), 2.32 (6 H, s), 4.2–4.67 (2 H, m), and 6.8–7.2 (10 H, m).

3,3'''-Dimethyl-4'',6'-bis(2,4-dimethylpentan-3-yloxy)-2',2''-dinitro-5,5'''-di-*t*-butyl-*m*-quaterphenyl.—To a stirred solution of potassium 2,4-dimethylpentan-3-yl oxide [made by dissolving potassium (66 mg) in 2,4-dimethylpentan-3-ol and removing the excess of alcohol] in HMPT (20 ml) was added the tetranitroquaterphenyl (30) (250 mg). After 24 h, water (150 ml) was added and the product was recovered by means of ether. Chromatography on alumina and elution with ether–light petroleum (1:4 v/v) gave the *diether* (39) (110 mg); m.p. 249–250 °C (from ethanol) (Found: C, 75.2; H, 8.7; N, 3.3. C₄₈H₆₄N₂O₆ requires C, 75.4; H, 8.4; N, 3.7%); δ_{H} (60 MHz) 0.8 (24 H, dd), 1.34 (18 H, s), 2.34 (6 H, s), 3.88 (2 H, dd), and 6.85–7.35 (10 H, m).

2,2'''-Di-iodo-3,3'''-dimethyl-2',2'',6',6''-tetranitro-5,5'''-di-*t*-butyl-*m*-quaterphenyl.—The tetranitro compound (30) (2.2 g) was heated at 75–80 °C for 3 h in a mixture of acetic acid (20 ml), water (4 ml), sulphuric acid (1.8 g), iodine (2 g), and periodic acid (0.3 g dihydrate). Sodium acetate (5 g) and then water (100 ml) were added to the cooled solution. The product was extracted with ether which was washed (NaHSO₃ then water), dried (MgSO₄), and evaporated, to leave the *di-iodide* (44) (2.48 g) as a colourless solid, m.p. 272–275 °C (ethanol) (Found: C, 46.8; H, 3.7; N, 6.4. C₃₄H₃₂I₂N₄O₈ requires C, 46.5; H, 3.5; N, 6.4%); δ_{H} (60 MHz) 1.19 (18 H, s), 2.55 (6 H, s), 7.0–7.4 (4 H, m), 7.65 (2 H, d, *J* 9 Hz), and 8.13 (2 H, d, *J* 9 Hz).

4,4'''-Di-isopropoxy-2,2'''-dimethyl-2',2''-dinitro-4'',6'-dipentan-3-yloxy-*m*-quaterphenyl.—Sodium wire (45 mg) was added under nitrogen to pentan-3-ol (3 ml) and the mixture was heated at 80–90 °C. When the reaction had ceased, excess alcohol was removed, finally at 90 °C under reduced pressure (1 h), and the residue was dissolved in HMPT (7 ml). After addition of the tetranitroquaterphenyl (31) (315 mg) the mixture was stirred for 20 h under nitrogen, then poured into hydrochloric acid (5%) and extracted with chloroform. The extracts were diluted

with light petroleum (1/3 vol.), washed (HCl then water), and evaporated. The residue in ether was put through alumina. Evaporation and trituration with methanol gave the *bis*-3-pentyl ether (**40**; 195 mg) as colourless prisms, m.p. 208–209 °C after crystallization from dichloromethane–isopropyl alcohol (Found: C, 71.0; H, 7.3; N, 4.0. $C_{42}H_{52}N_2O_8$ requires C, 70.8; H, 7.3; N, 3.9%); δ_H (60 MHz) 0.6–1.0 (12 H, m), 1.35 (d, *J* 6 Hz), 1.3–1.8 (m), 2.10 (6 H, s), 4.2 (2 H, m), 4.6 (2 H, m), 6.5–6.9 (6 H, m), 6.90 (2 H, d, *J* 8 Hz), and 7.22 (2 H, d, *J* 8 Hz); *m/z* 7.12 (M^+ , 100%).

Similar conditions were used to prepare the following 4'',6'-diethers, which all had to be separated from regioisomers by preparative t.l.c.

(a) From 2,2-dimethylpropanol: 2,2''-dimethyl-4'',6'-bis(2,2-dimethylpropoxy)-4,4''-di-isopropoxy-2',2''-dinitro-m-*quaterphenyl* (**41**), m.p. 195–196 °C (from methanol) (Found: C, 71.0; H, 7.4; N, 3.6. $C_{42}H_{52}N_2O_8$ requires C, 70.8; H, 7.3; N, 3.9%); δ_H (60 MHz) 0.75 (18 H, s), 1.30 (12 H, d, *J* 6 Hz), 2.0 (6 H, br s), 3.45 (4 H, br s), 4.4 (2 H, m), 6.4–6.9 (8 H, m), and 7.2 (2 H, d, *J* 8 Hz); *m/z* 712 (M^+ , 100%). The 2',4''- and the 2',2''-isomers were obtained (non-crystalline) from the same separation; the n.m.r. spectra showed one and both, respectively, of the neopentyl methyl signals at δ 0.4 instead of 0.75.

(b) From isopropyl alcohol: 4,4'',4''',6'-tetraisopropoxy-2,2''-dimethyl-2',2''-dinitro-m-*quaterphenyl* (**42**); m.p. 181–182 °C (Found: C, 69.3; H, 7.1; N, 4.3. $C_{38}H_{44}N_2O_8$ requires C, 69.5; H, 6.7; N, 4.3%); δ_H (60 MHz) 1.0–1.5 (24 H, m), 2.05 (6 H, br s), 4.2–4.7 (4 H, m), 6.5–6.9 (6 H, m), 6.92 (2 H, d, *J* 8 Hz), and 7.22 (2 H, d, *J* 8 Hz); *m/z* 684 (M^+ , 100%).

(c) From butan-2-ol, 4,4''-di-isopropoxy-2,2''-dimethyl-4'',6'-bis(1-methylpropoxy)2',2''-dinitro-m-*quaterphenyl* (**43**), m.p. 178.5–180 °C (from methanol) (Found: C, 70.0; H, 7.1; N, 4.1. $C_{40}H_{48}N_2O_8$ requires C, 70.2; H, 7.0; N, 4.1%); δ_H (60 MHz) 0.6–1.0 (6 H, m), 1.15 (6 H, apparent t, *J* 7 Hz), 1.35 (12 H, d, *J* 6 Hz), 1.4–1.8 (4 H, m), 2.10 (6 H, s), 4.3 (2 H, m), 4.6 (2 H, m), 6.5–7.1 (8 H, m), and 7.3 (2 H, d, *J* 8 Hz); at 90 MHz the highest-field signal appeared as two doublets, *J* 6 Hz, at δ 1.05 and 1.25; *m/z* 684 (M^+ , 100%).

2',2''-Di-iodo-6',4''-dimethoxy-3,3''-dimethyl-5,5''-di-*t*-butyl-m-*quaterphenyl*.—Hydrochloric acid (*d* 1.16; 6 ml) was added to the diamine (**19**) (1 g) in dimethylformamide (32 ml). Sodium nitrite (0.8 g) in water (5 ml) was added with stirring during 1.5 h; the internal temperature was kept between –1 and +1 °C during the addition and for 2 h thereafter. Urea (1.6 g) in water (4 ml) was stirred in and the temperature was kept at 0–5 °C for a further 3 h. Water (5 ml) was added and then a solution of mercuric iodide (2 g) and potassium iodide (1.5 g) in water (20 ml). The brown precipitate was filtered off after the addition of water (to 250 ml), suspended in water (50 ml), and stirred overnight. The brown solid was collected and dried *in vacuo*, suspended in dimethyl sulphoxide (22 ml) along with anhydrous sodium iodide (15 g), and heated under nitrogen at 125 °C for 24 h. The mixture was diluted with water and extracted with chloroform, which was washed (water) and evaporated. The residue in chloroform–light petroleum (1:3 v/v) was passed through alumina to yield a colourless oil which crystallized from isopropyl alcohol to give the *di-iodide* (**21**) (470 mg) as needles, m.p. 172–173 °C (Found: C, 57.0; H, 5.4.

$C_{36}H_{40}I_2O_2$ requires C, 57.0; H, 5.3%); δ_H (60 MHz) 1.33 (18 H, s), 2.38 (6 H, br s), 3.72 (6 H, s), and 6.8–7.4 (10 H, m).

Continued elution of the column with chloroform–light petroleum (3:1 v/v) afforded 3,8-dimethoxy-4,7-bis-(5-*t*-butyl-3-methylphenyl)benzo[*c*]cinnoline [**45**], yellow needles, m.p. 301–303 °C (from CH_2Cl_2 –PrⁱOH) (Found: C, 81.2; H, 7.5; N, 5.3. $C_{36}H_{40}N_2O_2$ requires C, 81.2; H, 7.5; N, 5.3%); δ_H (60 MHz) 1.35 (18 H, s), 2.40 (6 H, s), 3.95 (6 H, s), 7.0–7.4 (m), 7.67 (2 H, d, *J* 8 Hz), and 8.53 (2 H, d, *J* 8 Hz); *m/z* 532 (M^+ , 3%), 476 (35), and 474 (100).

2',2''-Di-iodo-4,4''-di-isopropoxy-4'',6'-dimethoxy-2,2''-di-methyl-m-*quaterphenyl*.—The diamine (**20**) (1 g) was treated as in the foregoing experiment except that the heating with sodium iodide was at 120–125 °C for 22 h. The work-up was also the same except that the product was eluted from alumina with 1:1 (v/v) chloroform–light petroleum. The *di-iodide* (**22**) (1.0 g) crystallized from isopropyl alcohol, m.p. 107–109 °C (Found: C, 53.3; H, 4.7. $C_{34}H_{36}I_2O_4$ requires C, 53.5; H, 4.7%); δ_H (60 MHz) 1.38 (12 H, d, *J* 6 Hz), 2.03 (6 H, s), 3.75 (6 H, s), 4.6 (2 H, br septet, *J* 6 Hz), 6.6–6.85 (m), 6.9 (2 H, d, *J* 7 Hz), and 7.3 (2 H, d, *J* 7 Hz); *m/z* 762 (M^+ , 100%), 636 (60), and 635 (90). The corresponding benzocinnoline was also a product of this reaction but was isolated more easily (15% yield) from a diazotization conducted as above but in which copper(I) bromide was added instead of potassium iodomercurate, with final heating to 65 °C. After passage through alumina [chloroform–light petroleum (1:1)] 3,8-dimethoxy-4,7-bis(4-isopropyl-2-methylphenyl)benzo[*c*]cinnoline (**46**) was obtained as yellow prisms; m.p. 190–191 °C (from methanol) (Found: C, 76.3; H, 6.7; N, 5.2. $C_{34}H_{36}N_2O_4$ requires C, 76.1; H, 6.7; N, 5.2%); δ_H (60 MHz) 1.35 (12 H, d, *J* 6 Hz), 1.99 (6 H, s), 3.90 (6 H, s), 6.6–7.3 (6 H, m), 7.68 (2 H, d, *J* 9 Hz), and 8.70 (2 H, d, *J* 9 Hz); *m/z* 536 (M^+ , 65%) and 521 (100).

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