272. *Studies in the Terphenyl Series. Part II. Hydroxy- and Methyl-*p*-terphenyls.*

By H. France, I. M. Heilbron, and D. H. Hey.

2- and 4-*Methoxy*-p-*terphenyl* are formed by the action of 4-nitrosoacetamidodiphenyl on anisole, and the corresponding *hydroxy*-compounds are obtained on demethylation. The constitutions of these compounds are proved by unambiguous methods. Quinol dimethyl ether yields 2 : 5-dimethoxy-*p*-terphenyl with 4-nitrosoacetamidodiphenyl and 2 : 5 : 2″ : 5″-*tetramethoxy*-p-*terphenyl* with dinitrosodiacetyl-1 : 4-phenylenediamine. The reaction of 4-nitrosoacetamidodiphenyl with toluene gives a mixture of 2-, 3-, and 4-*methyl*-p-*terphenyl*, and both 2- and 4-methyl-*p*-terphenyl are synthesised from the appropriate nitroso-4-acetamidomethyldiphenyl and benzene. *p*-Xylene with dinitrosodiacetyl-1 : 4-phenylenediamine yields 2 : 5 : 2″ : 5″-*tetramethyl*-p-*terphenyl.* Whereas oxidation of 4-methyl-*p*-terphenyl gives *p*-terphenyl-4-carboxylic acid, that of 2-methyl-*p*-terphenyl gives an acid regarded as 2-*methyldiphenyl*-4′-*carboxylic acid.*

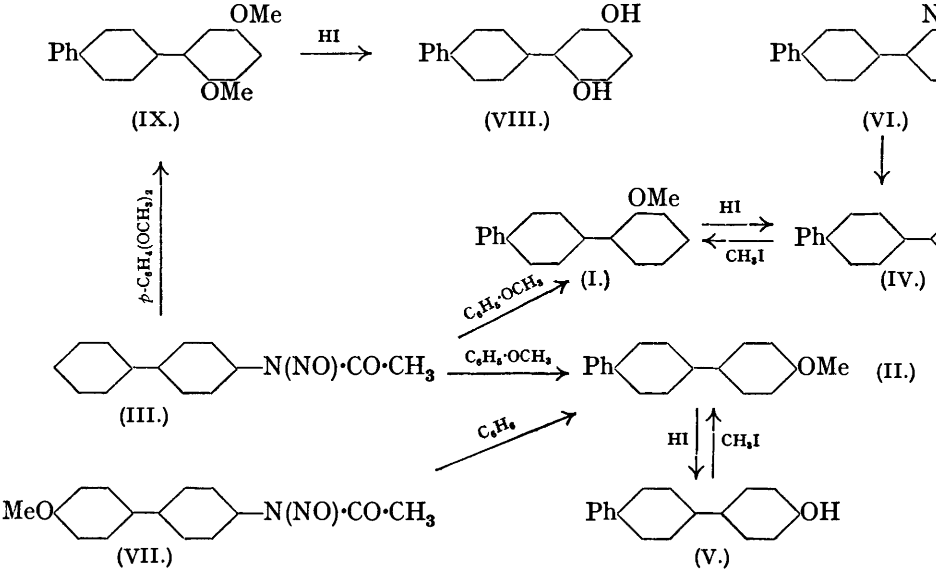
Part I of this series (J., 1938, 1364) consisted of a study of *p*-terphenyl and certain of its nitro-, amino-, and halogeno-derivatives, and this investigation has now been extended on similar lines to certain hydroxy- and methyl derivatives of the hydrocarbon.

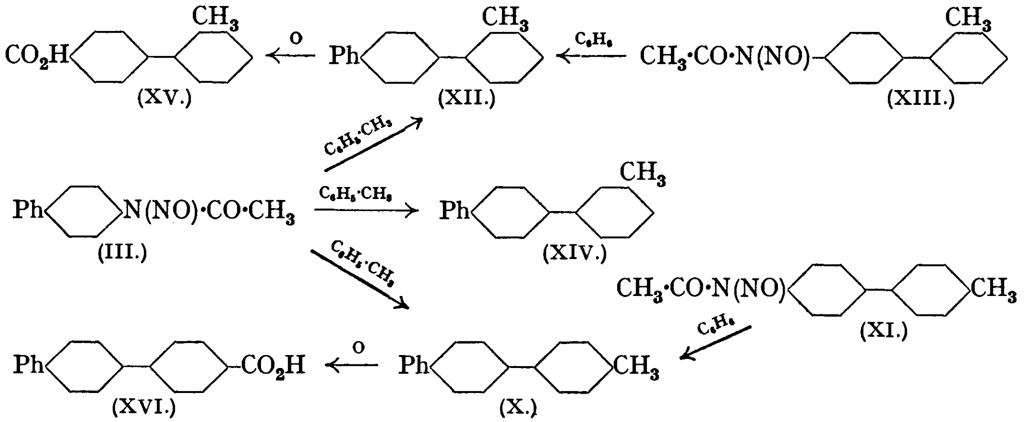
Hydroxy-derivatives.—Monohydroxy-derivatives of *p*-terphenyl have not been prepared hitherto, but 2-*methoxy*-p-*terphenyl* (I) and 4-*methoxy*-p-*terphenyl* (II) are now obtained by interaction of 4-nitrosoacetamidodiphenyl (III) with anisole and on demethylation yield the corresponding *hydroxy*-compounds, (IV) and (V), the constitutions of which are determined by unambiguous methods. 2-Hydroxy-*p*-terphenyl (IV) is prepared by the decomposition of the diazonium sulphate of 2-amino-*p*-terphenyl (VI) (cf. Part I, *loc. cit.*) in hot aqueous solution, and on methylation yields 2-methoxy-*p*-terphenyl (I) identical with the corresponding product isolated in the above reaction with anisole. The structure of 4-methoxy-*p*-terphenyl (II) is demonstrated by its identity with the compound synthesised by the interaction of 4′-*nitrosoacetamido*-4-*methoxydiphenyl* (VII) (from 4′-acetamido-4-methoxydiphenyl) and benzene.

2 : 5-Dihydroxy-*p*-terphenyl (VIII) has been prepared (I.G., D.R.P. 566521, 1931) by condensation of diphenyl-4-diazonium chloride and benzoquinone, followed by reduction of the resulting diphenylbenzoquinone : methylation yielded 2 : 5-dimethoxy-*p*-terphenyl (IX), which is now prepared from the reaction between 4-nitrosoacetamidodiphenyl (III) and liquid quinol dimethyl ether at 50—55° and on demethylation yields the corresponding 2 : 5-dihydroxy-compound (VIII). These compounds are apparently identical with those previously described, although in each case the m. p. now recorded is somewhat higher.

2 : 5 : 2″ : 5″-*Tetramethoxy*-p-*terphenyl* is in a like manner obtained from the interaction of dinitrosodiacetyl-1 : 4-phenylenediamine with quinol dimethyl ether.

The attempted preparation of a nitroso-compound from 2-methoxydiacetyl-1 : 4-phenylenediamine (from 2 : 5-diaminoanisole) with a view to the synthesis of 2′-methoxy-*p*-terphenyl led to the production of a compound regarded as 5-*nitro*-2-*methoxy*-NN′-*diacetyl*-1 : 4-*phenylenediamine*. This recalls a similar attempted nitrosation of aceto-*p*-phenetidide, which yielded 3-nitro-4-acetamidophenetole (Grieve and Hey, J., 1935, 691). It was also found that 2 : 5-diethoxydiacetyl-1 : 4-phenylenediamine failed to react with nitrous fumes.





Methyl Derivatives.—4-Methyl-*p*-terphenyl (X) was prepared by von Braun, Irmisch, and Nelles (*Ber.*, 1933, **66**, 1471) from *p*-tolylmagnesium bromide and 4-*cyclo*hexyl*cyclo*-hexanone, followed successively by dehydration and dehydrogenation. Monomethyl derivatives of *p*-terphenyl have now been prepared by the reaction between 4-nitrosoacetamidodiphenyl (III) and toluene, in which a mixture of three isomerides is formed. After separation by fractional crystallisation, they had m. p.'s 207—208°, 169—170°, and 91—92°. The first compound corresponds with the 4-methyl-*p*-terphenyl (X) described by von Braun, Irmisch, and Nelles (*loc. cit.*), and its identity is further confirmed by its synthesis from the reaction between the nitroso-derivative (XI) of 4-acetamido-4′-methyldiphenyl and benzene. The third compound, m. p. 91—92°, is shown to be 2-*methyl*-p-*terphenyl* (XII) by its identity with the compound synthesised from the reaction between the nitroso-derivative (XIII) of 4-acetamido-2′-methyldiphenyl and benzene. By elimination, the compound of m. p. 169—170°, which is present only in small quantity, must be 3-*methyl*-p-*terphenyl* (XIV). The isolation of all three isomerides in this reaction recalls the analogous reactions with chlorobenzene and bromobenzene (Part I, *loc. cit.*). From the reaction between dinitrosodiacetyl-1 : 4-phenylenediamine and *p*-xylene at 50—55° 2 : 5 : 2″ : 5″-*tetramethyl*-p-*terphenyl* was obtained. It should be noted that in the reactions with quinol dimethyl ether and with *p*-xylene the *para*-derivatives were specifically chosen, since these alone of the isomeric disubstituted benzene derivatives could give rise to one product only in their reaction with the above nitrosoacylarylamines.

Oxidation of 2-*methyl*-p-*terphenyl* (XII) with chromic anhydride in acetic acid solution in the usual way gave, not the anticipitated *p*-terphenyl-2-carboxylic acid, but an *acid* which analysis showed to be a methyldiphenylcarboxylic acid. Since the constitution of the 2-methyl-*p*-terphenyl has been established by synthesis, this acid would appear to be 2-*methyldiphenyl*-4′-*carboxylic acid* (XV). On the other hand, oxidation of 4-methyl-*p*-terphenyl (X) in a similar manner gave *p*-terphenyl-4-carboxylic acid (XVI), apparently identical with that described by von Braun, Irmisch, and Nelles (*loc. cit.*).

EXPERIMENTAL.

A. *Hydroxy-derivatives.*

Reaction of 4-*Nitrosoacetamidodiphenyl with Anisole.*—A solution of 4-nitrosoacetamidodiphenyl (10 g.) (prepared by the action of nitrous fumes on 4-acetamidodiphenyl as described in Part I, *loc. cit.*) in anisole (800 c.c.) was kept for 48 hours at 18°, nitrogen being slowly evolved. Removal of excess anisole in steam left a dark solid residue which distilled at 100—150°/10^{-3} mm. as a white solid. Fractional crystallisation from alcohol gave 4-methoxy-*p*-terphenyl, which crystallised from glacial acetic acid in colourless plates, m. p. 223—224°, undepressed on admixture with a synthetic specimen prepared as described below; systematic treatment of the mother-liquors yielded 2-methoxy-*p*-terphenyl, which separated from alcohol in colourless prisms, m. p. and mixed m. p. with an authentic specimen (see below) 118—119°. No other pure substance could be isolated. Both methoxy-*p*-terphenyls were demethylated with hydriodic acid to yield the corresponding hydroxy-*p*-terphenyls, identical with the compounds described below.

2-*Hydroxy*-p-*terphenyl.*—2-Amino-*p*-terphenyl (2 g.) was warmed with a mixture of concentrated sulphuric acid (5 c.c.) and water (40 c.c.), and the stirred suspension of the sulphate, cooled to 5°, was diazotised with an aqueous solution of sodium nitrite (0·6 g.). The diazonium salt separated as an orange-yellow powder, sparingly soluble in water. After addition of sufficient urea to decompose excess nitrous acid, the mixture was diluted with water (153 c.c.) and heated on the steam-bath for 1 hour. The brown product, extracted with ether, distilled at 135°/10^{-2} mm. as a white solid, which crystallised from methyl alcohol in colourless prisms, m. p. 176—177° (Found: C, 88·0; H, 5·3. $C_{18}H_{14}O$ requires C, 87·8; H, 5·7%).

2-*Methoxy*-p-*terphenyl.*—A solution of 2-hydroxy-*p*-terphenyl (0·2 g.) in a mixture of 90% alcohol (5 c.c.), potassium hydroxide (0·1 g.), and methyl iodide (0·5 c.c.) was refluxed for 1 hour. Dilution of the cold solution gave 2-*methoxy*-p-*terphenyl*, which separated from hot alcohol in colourless prisms, m. p. 118—119°, identical with the compound of similar m. p. obtained in the above reaction with anisole (Found: C, 87·5; H, 6·2. $C_{19}H_{16}O$ requires C, 87·7;. H, 6·15%).

4-*Methoxy*-p-*terphenyl.*—4-Hydroxy-4′-acetamidodiphenyl was prepared from benzidine by the method of Täuber (*Ber.*, 1894, **27**, 2629) and, on treatment with methyl iodide in alcoholic potassium hydroxide in the usual way, yielded 4′-acetamido-4-methoxydiphenyl, m. p. 191—193° from alcohol (cf. Täuber, D.R.P. 85988). On passing nitrous fumes into a solution of 4′-acetamido-4-methoxydiphenyl (2·5 g.) in a mixture of glacial acetic acid (40 c.c.) and acetic anhydride (20 c.c.) cooled to 8° for 2 hours, 4′-*nitrosoacetamido*-4-*methoxydiphenyl* (2·3 g.) separated in yellow plates which detonated at 103° (Found: N, 10·3. $C_{15}H_{14}O_3N_2$ requires N, 10·4%). On reaction with benzene (150 c.c.) in the usual way, the dry nitroso-compound gave a product which, on distillation at 150°/10^{-3} mm., yielded 4-*methoxy*-p-*terphenyl* (1·4 g.). Crystallisation from glacial acetic acid gave plates, m. p. 223—224°, both alone and on admixture with the compound of similar m. p. obtained from the reaction of 4-nitrosoacetamidodiphenyl with anisole (Found: C, 87·6; H, 5·9. $C_{19}H_{16}O$ requires C, 87·7; H, 6·15%).

4-Hydroxy-p-*terphenyl.*—4-Methoxy-*p*-terphenyl (0·5 g.) was heated with hydriodic acid (*d* 1·7, 20 c.c.) at 135—140° for 3 hours, and after treatment with sulphurous acid, 4-*hydroxy*-p-*terphenyl* (0·4 g.) separated; it crystallised from ethyl acetate in colourless prisms, m. p. 264—265° (with partial sublimation at 260°) (Found: C, 87·7; H, 5·8. $C_{18}H_{14}O$ requires C, 87·8; H, 5·7%).

2 : 5-*Dimethoxy*-p-*terphenyl.*—4-Nitrosoacetamidodiphenyl (5 g.) was added gradually with stirring to molten quinol dimethyl ether (100 g.) at 50—55° and, after 1 hour, the temperature was raised slowly to 90°. After removal of excess of quinol dimethyl ether in superheated steam, the residue distilled at 130°/10^{-3} mm. as a solid (0·9 g.) which, after successive crystallisation from alcohol and glacial acetic acid, formed colourless prisms, m. p. 159—160° (Found: C, 82·9; H, 6·1. Calc. for $C_{20}H_{18}O_2$: C, 82·8; H, 6·2%). The m. p. recorded in D.R.P. 566521 is 157—158°. During the earlier stages of the vacuum distillation a small quantity of diphenyl was collected

2 : 5-*Dihydroxy*-p-*terphenyl.*—A solution of 2 : 5-dimethoxy-*p*-terphenyl (0·5 g.) in a mixture of hydriodic acid (*d* 1·7, 20 c.c.) and glacial acetic acid (20 c.c.) was boiled for 3 hours, and the product was isolated as a yellow precipitate on saturation of the diluted reaction mixture with sulphur dioxide. The product, which rapidly turned pink on filtration, crystallised from benzene in pink clusters, m. p. 173—174° (Found: C, 82·4; H, 5·6. Calc. for $C_{18}H_{14}O_2$: C, 82·4; H, 5·3%). The m. p. recorded in D.R.P. 566521 is 171—172°.

2 : 5 : 2'' : 5''-*Tetramethoxy*-p-*terphenyl.*—Dinitrosodiacetyl-1 : 4-phenylenediamine (5 g.) (prepared by the action of nitrous fumes on diacetyl-1 : 4-phenylenediamine as described in Part I, *loc. cit.*) was added in small portions with stirring to molten quinol dimethyl ether (100 g.) maintained at 50—55°. Nitrogen was freely evolved and, after 1 hour, the temperature was gradually raised to 90° during the next 2 hours. The dark residue, left on removal of excess quinol dimethyl ether in superheated steam, distilled at 150°/10^{-3} mm. as a solid (0·4 g.), which crystallised from glacial acetic acid in colourless prisms, m. p. 159—160° (Found: C, 75·7; H, 6·2. $C_{22}H_{22}O_4$ requires C, 75·4; H, 6·2%).

*Attempted Nitrosation of 2-Methoxydiacetyl-*1 : 4-*phenylenediamine.*—A suspension of 2-*methoxy*-NN'-*diacetyl*-1 : 4-*phenylenediamine* (3 g.), obtained from 2 : 5-diaminoanisole by boiling with a mixture of glacial acetic acid and acetic anhydride in the usual way (white prisms from alcohol, m. p. 220—222°. Found: N, 12·8. $C_{11}H_{14}O_3N_2$ requires N, 12·6%), in a mixture of glacial acetic acid (70 c.c.) and acetic anhydride (20 c.c.), containing phosphoric oxide (0·5 g.), was cooled to 8° and treated with nitrous fumes for 3½ hours. A yellow solid, regarded as 5-*nitro*-2-*methoxydiacetyl*-1 : 4-*phenylenediamine*, was obtained on pouring the reaction mixture into water; it crystallised from glacial acetic acid in yellow needles, m. p. 258—259° (Found: C, 49·4; H, 4·4. $C_{11}H_{13}O_5N_3$ requires C, 49·4; H, 4·9%).

B. *Methyl Derivatives.*

Reaction of 4-Nitrosoacetamidodiphenyl with Toluene.—4-Nitrosoacetamidodiphenyl (10 g.) was allowed to react with toluene (800 c.c.) at 18° exactly as described above for the corresponding reaction with anisole. Excess toluene was removed by distillation under reduced pressure, leaving a dark brown residue, which distilled at 100—150°/10^{-3} mm. as a white solid (2·5 g.). Fractional crystallisation from alcohol gave three distinct crops of crystals in the following order: (i) 4-methyl-*p*-terphenyl (0·8 g.), in plates from alcohol, m. p. 207—208°, identical with an authentic specimen (see below) (Found: C, 93·3; H, 6·4. Calc. for $C_{19}H_{16}$: C, 93·4; H, 6·6%); (ii) 3-*methyl*-p-*terphenyl* (0·1 g.), in needles from alcohol, m. p. 169—170° (Found: C, 93·2; H, 6·7%); (iii) 2-*methyl*-p-*terphenyl* (0·9 g.), in plates from alcohol, m. p. 91—92°, undepressed on admixture with the synthetic specimen described below (Found: C, 93·3; H, 6·5%).

Reaction of Diazotised p-*Nitroaniline with Toluene in Presence of Alkali.*—An ice-cold suspension of *p*-nitroaniline hydrochloride, prepared by rapid cooling and stirring of a hot mixture of *p*-nitroaniline (70 g.), concentrated hydrochloric acid (270 c.c.), and water (50 c.c.), was diazotised by the slow addition of a solution of sodium nitrite (36 g.) in water (100 c.c.). Toluene (2000 c.c.) was added, and the vigorously stirred mixture treated dropwise with a 40% aqueous solution of sodium hydroxide until just alkaline, the temperature being maintained at 5° by addition of ice, after which stirring was continued at room temperature overnight (cf. Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2339). The mixture, previously rendered just acid to facilitate filtration, was filtered from a tarry residue; the residue was extracted with hot toluene, and this extract combined with the toluene layer from the original filtrate. After removal of excess toluene, the residual oil was distilled under reduced pressure. The fraction, b. p. 195—230°/15 mm., consisted of practically pure 4-nitro-2′-methyldiphenyl (10 g.), which crystallised from alcohol in yellow needles, m. p. 103—104° (Bamberger, *Ber.*, 1895, **28**, 404; cf. Kühling, *ibid.*, p. 43; 1896, **29**, 166; Kliegl and Huber, *ibid.*, 1920, **53**, 1646), while that boiling at 235—255°/15 mm. was mainly 4-nitro-4′-methyldiphenyl (5 g.), which separated from alcohol in pale yellow needles, m. p. 138—139°, identical with the product prepared by Grieve and Hey (J., 1932, 1891) by nitration of 4-methyldiphenyl. On raising the distillation temperature above 260°, violent decomposition occurred.

2-*Methyl*-p-*terphenyl*.—A solution of 4-nitro-2′-methyldiphenyl (10 g.) in boiling 95% alcohol (100 c.c.) was treated with a hot solution of stannous chloride (70 g.) in concentrated hydrochloric acid (70 c.c.) in the usual way, and the corresponding base, isolated as a colourless oil, was boiled with a mixture of acetic anhydride (10 c.c.) and glacial acid (30 c.c.) to give 4-acetamido-2′-methyldiphenyl (7·5 g.), which crystallised from aqueous alcohol in plates, m. p. 146—147° (cf. Bamberger, *loc. cit.*). Nitrous fumes were passed for 70 minutes into a solution of the acetyl compound (5 g.) in a mixture of glacial acetic acid (100 c.c.) and acetic anhydride (50 c.c.), containing phosphoric oxide (1 g.), cooled to 8°. The nitroso-compound, obtained as a yellow oil on dilution of the reaction mixture with excess iced water, was immediately extracted with benzene (600 c.c.). The benzene extract, washed twice with water, was kept at room temperature over anhydrous sodium sulphate, whereupon nitrogen was slowly evolved. After 24 hours the decanted solution was concentrated, and distillation of the residue at 80°/10^{-3} mm. gave 2-methyl-*p*-terphenyl (0·9 g.), which crystallised from alcohol in colourless plates, m. p. 91—92°, both alone and on admixture with the corresponding compound described above.

Oxidation of 2-*Methyl*-p-*terphenyl*.—A solution of the hydrocarbon (0·5 g.) in glacial acetic acid (40 c.c.) was boiled with a solution of chromic anhydride (1·5 g.) in dilute acetic acid (10 c.c.) for 4 hours, and the product, precipitated with water, was dissolved in ether and extracted with alkali. Acidification of the alkaline extract gave an acid, regarded as 2-*methyldiphenyl*-4′-*carboxylic acid*, which crystallised from glacial acetic acid in colourless needles, m. p. 173—175° (Found: C, 78·9; H, 5·5. $C_{14}H_{12}O_2$ requires C, 79·2; H, 5·7%).

4-*Methyl*-p-*terphenyl*.—The reduction of 4-nitro-4′-methyldiphenyl, carried out as described above for 4-nitro-2′-methyldiphenyl, yielded 4-amino-4′-methyldiphenyl, m. p. 95—97° (cf. Grieve and Hey, *loc. cit.*), from which 4-acetamido-4′-methyldiphenyl, m. p. 217—219° (cf. Kliegl and Huber, *loc. cit.*), was obtained by boiling with acetic anhydride in the usual way. Nitrous fumes were passed for 1½ hours into a solution of the acetyl compound (4·6 g.) in a mixture of glacial acetic acid (120 c.c.) and acetic anhydride (60 c.c.), containing phosphoric oxide (1 g.), cooled to 8°. The nitroso-compound, which partly separated in yellow prisms (m. p. 105°, decomp.) from the resulting green solution, was isolated in almost theoretical yield by dilution with excess iced water. A solution of the dry nitroso-compound (5 g.) in benzene (300 c.c.) was stirred for 12 hours at room temperature, and the product, obtained after removal of excess benzene, on distillation at 150°/10^{-3} mm. gave 4-methyl-*p*-terphenyl (2·4 g.), which crystallised from glacial acetic acid in colourless plates, m. p. 207—208°, identical with the corresponding compound described above (cf. von Braun, Irmisch, and Nelles, *loc. cit.*, who give m. p. 206—208°). Oxidation, carried out with chromic anhydride in acetic acid solution as previously described for 2-methyl-*p*-terphenyl, gave *p*-terphenyl-4-carboxylic acid (m. p. 303—305° from glacial acetic acid), apparently identical with the acid (m. p. 305°) previously reported by von Braun, Irmisch, and Nelles (*loc. cit.*) (Found: C, 83·0; H, 5·3. Calc. for $C_{19}H_{14}O_2$: C, 83·2; H, 5·1%).

2 : 5 : 2″ : 5″-*Tetramethyl*-p-*terphenyl*.—Dinitrosodiacetyl-1 : 4-phenylenediamine (7 g.) was added gradually with stirring to *p*-xylene (450 c.c.) maintained at 50—55°. Nitrogen was freely evolved, and after 3 hours the temperature was raised to 90° for 2 hours. The reaction mixture was filtered from a small amount of insoluble matter and, after removal of *p*-xylene by distillation first at atmospheric pressure and finally under reduced pressure, the residue distilled at 140—150°/4 mm. The oily distillate (0·8 g.) rapidly solidified, and on crystallisation from methyl alcohol 2 : 5 : 2″ : 5″-*tetramethyl*-p-*terphenyl* separated in almost colourless needles, m. p. 112—113° (Found: C, 92·4; H, 7·6. $C_{22}H_{22}$ requires C, 92·3; H, 7·7%).

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THE UNIVERSITY, MANCHESTER.

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