## Biphenylenes. Part XIV.<sup>1</sup> Synthesis of 1- and 2-Phenyl-, 2,7-Dimethyl-, and 2,3,6,7-Tetramethyl-biphenylene

By P. R. Constantine, G. E. Hall, Charles R. Harrison, J. F. W. McOmie, and R. J. G. Searle

1- and 2-Phenylbiphenylene have been made from 1- and 2-lithiobiphenylene, respectively, by treatment with cyclohexanone followed by dehydration and dehydrogenation. 2-Phenylbiphenylene has also been made by pyrolysis of 4- and 5-phenyl-biphenylene-2,2'-iodonium iodide with cuprous oxide.

One new synthesis of 2.7-dimethyl- and two new syntheses of 2.3.6.7-tetramethyl-biphenylene are described.

HOMOLYTIC aromatic substitution in biphenylene has been little studied,<sup>2</sup> and as a preliminary to a kinetic investigation<sup>3</sup> into free radical phenylation of biphenylene it was necessary to prepare authentic samples of 1- and 2-phenylbiphenylene. This Paper records the details of the synthetic work.

1-Phenylbiphenylene (I; R = Ph) was made by converting biphenylene into its 1-lithio-derivative<sup>4</sup> (I; R = Li) and treating this with an excess of cyclohexanone. The resulting tertiary alcohol was dehydrated by boiling with formic acid, and the 1-cyclohexenylbiphenylene thus produced was dehydrogenated by treatment with chloranil. 1-Phenylbiphenylene has m. p. 46.5°, while the 2-phenyl isomer has m. p.  $125.5^{\circ}$  (see below), cf. 1- and 2-phenylnaphthalene, m. p. 45 and 103°, respectively.

2-Phenylbiphenylene was prepared by three routes. Firstly, by pyrolysis with cuprous oxide of 4-phenylbiphenylene-2,2'-iodonium iodide (II;  $R^1R^2 = I^+_I I^-$ ), which was obtained from a mixture of the iodo-p-terphenyls (II;  $R^1 = I$ ,  $R^2 = H$ ) and (II;  $R^1 = H$ ,  $R^2 = I$ ) by successive treatment with peracetic acid and concentrated sulphuric acid (method of Collette

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et  $al.^{5}$ ), the same product being obtained from each of the iodo-p-terphenyls in the mixture.

In the second route *m*-terphenyl (III; R = H) was converted into 4'-iodo-m-terphenyl<sup>6-8</sup> (III; R = I),



which in turn gave 5-phenylbiphenylene-2,2'-iodonium iodide under standard conditions.<sup>5</sup> Pyrolysis of this iodonium iodide in the same way as for 4-phenylbiphenylene-2,2'-iodonium iodide then gave 2-phenylbiphenylene. For the third route 2-lithiobiphenylene was prepared from 2-bromobiphenylene 9 by transmetallation

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<sup>7</sup> C. A. Wardner and A. Lowry, J. Amer. Chem. Soc., 1932, **54**, 2510.

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with n-butyl-lithium and then converted into 2-phenylbiphenylene by the method described above for 1-phenylbiphenylene. This route gave pure 2-phenylbiphenylene, m. p. 125.5°, whereas the two routes involving pyrolysis gave products which were difficult to purify completely.

For an attempted synthesis of di(biphenylene-2,7-dimethylene) [cf. the synthesis of di(naphthalene-2,7-dimethylene)]<sup>10</sup> it was necessary to prepare 2,7-bisbromomethylbiphenylene. However, erratic results were obtained on bromination of 2,7-dimethylbiphenylene made from 4,4'-dimethyl-2,2'-dinitrobiphenyl by the method of Lothrop.<sup>11</sup> These results were found to be due to the presence of traces of 2,7-dimethylcarbazole,<sup>11</sup> which is difficult to remove; a new synthesis of 2,7-dimethylbiphenylene was therefore devised in order to avoid formation of the carbazole (see Experimental section). Bromination of pure 2,7-dimethylbiphenylene with N-bromosuccinimide proceeded smoothly, but 2,7-bisbromomethylbiphenylene was unstable and difficult to purify. All attempts to convert it into di(biphenylene-2,7-dimethylene) failed. 6-Bromomethylbiphenylene-2-aldehyde was obtained as a by-product of the bromination.

During early studies on substitution reactions of biphenylene<sup>2</sup> it was found that reaction of the latter with chlorodimethyl ether and concentrated hydriodic acid (iodomethylation reaction) followed by reduction with zinc and hydrogen chloride in acetic acid yielded a tetramethyl compound which was considered to be 2,3,6,7-tetramethylbiphenylene. This structure has now been confirmed by two syntheses of this biphenylene (see Experimental section).

## EXPERIMENTAL

1-Phenylbiphenylene (I; R = Ph).—A mixture of bibiphenylene (4.0 g.) in ether (50 ml.) with a ten-fold excess of n-butyl-lithium in ether (250 ml.) was kept at room temperature for 4 days. The resulting solution of 1-lithiobiphenylene<sup>4</sup> was then added, under nitrogen, to a stirred mixture of cyclohexanone (30 ml.) and ether (100 ml.). After 10 min. an excess of dilute hydochloric acid was added cautiously, and the ethereal layer was washed three times with water. After removal of the solvent on a waterbath, the residual oil was boiled under reflux with 98% formic (100 ml.) for 1 hr. The mixture was cooled, then extracted with ether, and the ethereal extract was washed successively with water, aqueous sodium carbonate, and water. The ether and other volatile material were removed by distillation up to 200° and the residue was chromatographed on alumina in light petroleum (b. p. 60-80°). The pale yellow fraction was collected and was distilled at 150°/10<sup>-3</sup> mm., the colourless, lower-boiling fractions being rejected. The yellow oil was dissolved in xylene (15 ml.) and heated under reflux with a large excess of chloranil for 4 hr. The mixture, after being cooled, was

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diluted with light petroleum (b. p. 60-80°), filtered, and washed in turn with water, aqueous sodium carbonate, and water. The solvents were removed by distillation and the residue was chromatographed and distilled twice under reduced pressure, in the same way as before the dehydrogenation stage. After a few days the yellow oil began to solidify, and was recrystallised twice from methanol (retaining a crystal for seeding each time) giving 1-phenylbiphenylene (0.15 g., 2.5%) as yellow plates, m. p. 46.5° (Found: C, 94.5; H, 5.2. C<sub>18</sub>H<sub>12</sub> requires C, 94.75; H, 5.25%);  $\lambda_{max.}$  (in 95% EtOH) 229, 267, 342 infl., 358, and 376 mµ (log ɛ 4·30, 4·38, 3·36, 3·56, and 3·53, respectively).

2-Phenylbiphenylene.-(a) From p-terphenyl. p-Terphenyl (1.2 g.) was mononitrated 12 and the resulting mixture of 2- and 2'-nitro-p-terphenyl was reduced 13 and then converted by diazotisation into a mixture of 2- and 2'-iodo*p*-terphenyl (1.2 g.), which was oxidised by peracetic acid to give the corresponding iodoso-compounds. Treatment<sup>5</sup> of the latter with concentrated sulphuric acid then gave 4-phenylbiphenylene-2,2'-iodonium iodide (1.3 g.) as a grey powder, m. p. 199—201° (decomp.) (Found: C, 43.7; H, 2.4.  $C_{18}H_{12}I_2$  requires C, 44.8; H, 2.5%). An intimate mixture of the iodonium iodide (1.0 g) and cuprous oxide (20 g.) was heated at 450° for 20 min. in a rotating flask.<sup>14</sup> The sublimate was crystallised from ethanol, sublimed at 120°/0.05 mm., and recrystallised from ethanol to give 2-phenylbiphenylene (0.08 g., 17%) as pale yellow plates, m. p. 111-113° [Found: C, 94.6; H, 5.4% cf. (c) below].

(b) From m-terphenyl. 4-Amino-m-terphenyl was made from *m*-terphenyl via the 4-nitro-derivative by the method of France et al.6 and purified by the method of Wardner and Lowry.7 It was then converted into 5-phenylbiphenylene-2,2'-iodonium iodide, m. p. 155-157° (decomp.) as for the *p*-terphenyl series. Pyrolysis with cuprous oxide then gave 2-phenylbiphenylene (15% yield on last step), m. p. and mixed m. p. with the above material, 112-113°.

(c) From 2-bromobiphenylene. n-Butyl-lithium (3 equivalents) in ether (100 ml.) was added under nitrogen to a stirred solution of 2-bromobiphenylene<sup>9</sup> (2.0 g.) in ether (100 ml.). After 10 min. the solution was added to cyclohexanone (3 ml.) in ether (100 ml.). The product was converted into 2-phenylbiphenylene by the method described above for 1-phenylbiphenylene, omitting the final chromatography and distillation. The crude product was recrystallised from methanol and then from hexane to give 2-phenylbiphenylene as pale yellow plates (0.1 g., 5.0%), m. p. 125.5° (Found: C, 94.5; H, 5.5.  $C_{18}H_{12}$  requires C, 94.75; H, 5.25%);  $\lambda_{max}$  (in 95% EtOH) 238, 265, 335 infl., 351, and 368 mµ (log z 4.39, 4.75, 3.75, 3.96, and 4.03, respectively). The infrared spectra of the products from (a), (b), and (c) were almost identical.

2,7-Dimethylbiphenylene.—Peracetic acid (12%, 10 ml.) was added to 2-iodo-4,4'-dimethylbiphenyl<sup>15</sup> (2.0 g.) in acetic anhydride (10 ml.). Next day, water (0.5 ml.) was added and, after keeping for 3 hr. (to hydrolyse any iodosoacetate), the mixture was cooled to 0° and concentrated sulphuric acid (2 ml.) was added with stirring, keeping the temperature below 15°. Water (20 ml.) was

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then added and after 0.5 hr. the pale yellow 5,5'-dimethylbiphenylene-2,2'-iodonium bisulphate (1.9 g.) was collected. This was dissolved in boiling water and treated with an excess of potassium iodide to give a 100% yield of the corresponding iodonium iodide. Pyrolysis of the latter (10 g.) with cuprous oxide (10 g.) and copper oxalate (10 g.) gave 2,7-dimethylbiphenylene (35%) as pale yellow plates, m. p. 111—112°, raised to 115° (lit.,<sup>11</sup> m. p. 112°) by crystallisation from ethanol (Found: C, 92.7; H, 7.0. Calc. for  $C_{14}H_{12}$ : C, 93.3; H, 6.7%);  $\lambda_{max}$  (in EtOH) 243, 252, 333 infl., 347, and 365.5 mµ (log  $\varepsilon$  4.80, 5.07, 3.51, 3.83, and 3.97).

The n.m.r. spectrum consisted of two broad peaks with centres at  $\tau$  3.50 (aromatic) and  $\tau$  7.88 (methyl protons).

Bromination of 2,7-Dimethylbiphenylene.--A mixture of benzoyl peroxide (50 mg.), 2,7-dimethylbiphenylene (0.5 g.), and N-bromosuccinimide (1.15 g.) in carbon tetrachloride was boiled under reflux for 25 min. The hot solution was filtered and evaporated and the residue chromatographed on thick layers of silica supported on glass, using as eluent carbon tetrachloride (49%), benzene (49%), and acetic acid (2%). This procedure gave 2,7-bisbromomethylbiphenylene (0.5 g., 53%) as needles, m. p. 141-143° raised to 148° by recrystallisation from carbon tetrachloride (Found: C, 49.9; H, 3.05.  $C_{14}H_{10}Br_2$  requires C, 49.7; H, 3.0%). The biphenylene was characterised by conversion into the 2,7-bisthiouronium dipicrate, m. p. 215° (decomp.) (Found: C, 40.2; H, 3.2. C<sub>12</sub>H<sub>6</sub> (C<sub>2</sub>H<sub>5</sub>N<sub>2</sub>S, C<sub>6</sub>H<sub>3</sub>N<sub>3</sub>O<sub>7</sub>)<sub>2</sub>, 3H<sub>2</sub>O requires C, 40.0; H, 3.4%). A mixed m. p. of this picrate with a repurified sample of that derived from x,y-bisiodomethylbiphenylene,<sup>2</sup> m. p. 210-211° (decomp.), was 203-205° (decomp.).

In one experiment, the above chromatographic procedure also gave 7-bromomethylbiphenylene-2-aldehyde which, after recrystallisation from carbon tetrachloride, formed yellow

<sup>16</sup> P. S. Varma and K. S. V. Raman, J. Indian Chem. Soc., 1935, **12**, 245.

needles (0·1 g., 13%), m. p. 140—140·5° (Found: C, 61·0; H, 3·2.  $C_{14}H_9BrO$  requires C, 61·5; H, 3·3%).

2,3,6,7-*Tetramethylbiphenylene*.—(a) (With S. D. THATTE). 4-Bromo-5-iodo-1,2-dimethylbenzene<sup>16</sup> (10 g.) in ether (50 ml.) was added during 0.5 hr. to a stirred suspension of magnesium (1.15 g.) in ether (50 ml.), under nitrogen. Stirring was continued for 2 hr. more, then the mixture was set aside for 2 days. Removal of the ether and crystallisation of the residue from ethanol gave 2,3,6,7-tetramethylbiphenylene (0.17 g., 12%) as straw-coloured needles, m. p. 224—225°, alone or mixed with the product obtained from biphenylene by iodomethylation followed by reduction with zinc<sup>2</sup> (Found: C, 92.3; H, 7.6. Calc. for C<sub>16</sub>H<sub>16</sub>: C, 92.3; H, 7.7%);  $\lambda_{max}$  (in EtOH) 246, 256, 352, and 372 mµ (log  $\epsilon$  4.7, 4.9, 3.8, and 4.0).

(b) Iodic acid (3 g.) in water (5 ml.) was added to a boiling solution of 3,4,3',4'-tetramethylbiphenyl <sup>17</sup> (1.5 g.) and iodine (8 g.) in acetic acid (500 ml.) during 15 min. The mixture was boiled under reflux for 20 hr., then poured into a solution of sodium hydrogen sulphite (5 g.) in water (500 ml.). Extraction with ether (3 × 100 ml.) then yielded 2,2'-di-iodo-4,5,4',5'-tetramethylbiphenyl as pale yellow plates (0.9 g., 26%), m. p. 182—184° after two recrystallisations from ethanol (Found: C, 41.4; H, 3.3.  $C_{16}H_{16}I_2$  requires C, 41.6; H, 3.5%).

The di-iodobiphenyl (1.0 g.) mixed with cuprous oxide (15 g.) was pyrolysed at  $380-400^{\circ}$ ; the resulting biphenylene was purified *via* its complex with 2,4,7-trinitrofluorenone, m. p. 168-170°, to give tetramethylbiphenylene (22 mg., 5%), m. p. and mixed m. p. 224-225°.

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THE UNIVERSITY, BRISTOL.

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