17. *Aspects of Polyphenyl Chemistry. Part II.*[1] *Synthesis of Sexiphenyls.*

By J. A. CADE and A. PILBEAM.

The syntheses and some physical properties of several sexiphenyls have been investigated. Four new isomers are described while independent routes to two others have served to confirm their structures.

THE products of irradiation of *p*-terphenyl with electrons, or the mixed radiation from a nuclear reactor, include hydrogen, methane, C_2 hydrocarbons, and polymers (*i.e.*, having a molecular weight greater than the starting material).[2] Available evidence indicates that the polymer is a mixture of polyphenyls (predominantly sexiphenyls), alkylpolyphenyls, polyphenylenes,[3] and partially hydrogenated products of all these compounds. Since the rate of formation of polymer decreases with increase in the total radiation dose, it was of interest to discover which, if any, of these classes of compound exert the apparent " protection " effect. Of particular interest was the incidence of partial ring hydrogenation, because good scintillator properties in organic compounds appear to parallel high radiation stability, and partially hydrogenated quaterphenyls are reported to exhibit some of the highest relative pulse heights as scintillators.[4]

For this reason, synthetical routes to the polyphenyls which involved partially

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[1] Part I, Cade and Pilbeam, AERE Report R-3039; *Tetrahedron*, in the press.

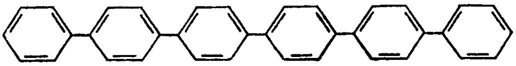
[2] Bates, Burns, *et al.*, AERE Reports C/R 2121; C/R 2185; M/412; R/3564; R/3743; R/3989 and references therein.

[3] Keen, NAA-SR-3850, II-B-3, 1959.

[4] Gilman, Weipert, and Hayes, *J. Org. Chem.*, 1958, **23**, 910.

hydrogenated precursors in the penultimate stage were avoided where possible. This increased the difficulty of obtaining certain sexiphenyls, but ensured that their absorption spectra would be free from extraneous absorption due to even slight contamination by substances whose presence was ultimately to be detected and determined in polymers.

The general synthetical approach was to couple appropriate halogenoterphenyls by the Ullmann reaction or *via* the corresponding lithium aryls prepared by halogen–metal interconversion. Improvements could be made at some stages in the preparation of the intermediate halogenoterphenyls. For example, although small quantities of 3-bromo-*p*-terphenyl had previously been obtained from the mixture of isomeric bromo-*p*-terphenyls formed by interaction of 4-nitrosoacetamidobiphenyl and bromobenzene,[5] a far more effective route to this substance was reaction of 3′-bromobiphenyl-4-diazonium hydroxide with benzene. Other intermediate halogenoterphenyls were made by similar homolytic substitutions. We observed that, in general, the Gomberg–Bachmann reaction[6] was superior to the nitrosoacetamido-method[5] for compounds having electron-withdrawing substituents, whereas the converse obtained for unsubstituted compounds, or those having electron-releasing groups.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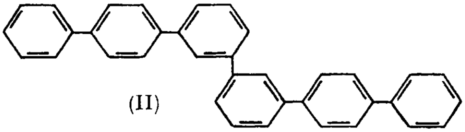
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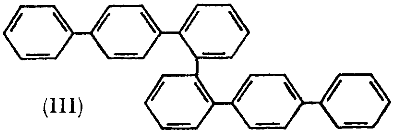
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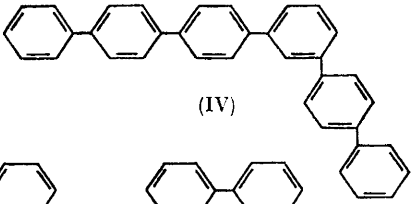
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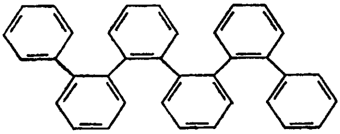
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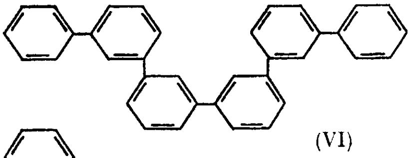
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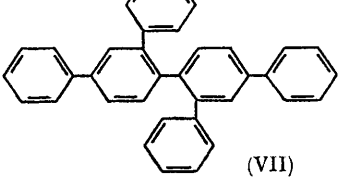
(VII)

Some physical properties of the sexiphenyls are given in Table 1, and Table 2 contains analytical data. The main features of the u.v. spectra are recorded, but will be discussed in a subsequent paper in relation to other polyphenyls, as also will the infrared spectral studies.

Compounds (I), (V), and (VI) have been described before. We made (I)[7] to extend our experience with this type of compound, it being the most intractable member of the class. Recrystallisation from *o*-dichlorobenzene, the recommended solvent was very unsatisfactory. The best procedure was repeated vacuum sublimation, many arbitrary fractions being taken. When several successive fractions exhibited uniformity as shown by spectrophotometric examination, we assumed that the product was pure.

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[5] France, Heilbron, and Hey, *J.*, 1938, 1364.

[6] Bachmann and Hoffman, *Org. Reactions*, 1944, **2**, 224.

[7] Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1952, p. 378.

TABLE 1.

Some physical properties of sexiphenyls.

Structure	M. p.	$\lambda_{max.}$ (Å)	$10^{-3}\varepsilon$	Purification
(I)	465°	3080	60·0	Sublimed (three times), 390—400°/0·01 mm.
(II)	247·5	2740	72·5	Recryst. (C_6H_6), chromatographed in C_6H_6 (alumina column), and recryst. (C_6H_6).
(III)	189—190	2730	47·3	Recryst. (light petroleum), chromatographed in C_6H_6 (alumina column), and recryst. (light petroleum).
(IV)	312—314	2910	62·5	Sublimed (twice), 280—290°/0·005 mm., and recryst. (4 times) (C_6H_6).
(V)	216—217	2350	39·8	Recryst. (4 times) (EtOH), and from C_6H_{12}.
(VI)	146—147	2490	102·0	Recryst. (3 times) (EtOH).
(VII)	234·5	2910 2530	28·6 57·0	Chromatographed in benzene (alumina column), and sublimed, 200—300°/0·01 mm.).

TABLE 2.

Analytical data.

Compound [Found]	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)
Carbon (%)...	94·3, 94·4	94·35, 94·45	94·35, 94·4	94·4, 94·3	94·2	94·15	93·5, 93·1
Hydrogen (%)	5·7, 5·65	5·7, 5·65	5·7, 5·4	5·7, 5·65	5·8	5·55	5·75, 5·5
Mol. wt.	*	472 ± 15	470 ± 14	462 ± 12	460 ± 8	468 ± 9	468 ± 12

(I)—(VII) require C, 94·3; H, 5·7%; *M*, 459.

TABLE 3.

Compound	M. p.	$\lambda_{max.}$ (Å)	$10^{-3}\varepsilon_{max.}$	Solubility in ether
B	290,[11] 260—280 [2]	2870,[11] 2970 [2]		Insoluble
(IV) Forecast	312 [11]	2870 [11]		
(IV) Found	312—314	2910	62·5	<10 mg./l.
C (A[2])	155—220 [2]	2750 [2]	51·3 [2]	Soluble [2]
(II) Found	247·5	2740	72·5	80 mg./l.

Compound (V) had been prepared in low yield, together with many other substances, by treatment of 2,2′-dilithiobiphenyl and 2,2′-di-iodobiphenyl in ether with transition-metal halides.[8] We considered this method to be somewhat ambiguous, and based our approach on attempts to prepare 2-iodo-*o*-terphenyl, followed by coupling. The latter compound, however, was extremely difficult to obtain, and then attempts to couple it gave triphenylene as the only product isolated. One route involved coupling of 2-amino-2′-iodobiphenyl with benzene, but the chief products of this reaction were biphenylene iodonium halide, di-iodobiphenyl, and carbazole. Another attempt was based on thermal decomposition of the tervalent iodine compound [9] obtained by treatment of biphenylene iodonium iodide with phenyl-lithium or phenylmagnesium halide, but this was also unsuccessful.

Ultimately, compound (V) had to be made by a method similar to that previously used.[8]

Compound (VI) had been prepared [10] *via* a partially hydrogenated precursor. Our approach was based on coupling of 3-halogeno-*m*-terphenyls made either *via* 3-amino-3′-halogenobiphenyl and benzene or from 3-nitro-3′-phenylbiphenyl obtained *via* 3-amino-3′-nitrobiphenyl and benzene.

On the basis of their u.v. absorption spectra, melting points, solubility, and colour, two substances, sexiphenyl [3] B and C [11] (B and A [2]) isolated from the polymer produced on pyrolysis [11] or radiolysis [2] of *p*-terphenyl, had been provisionally assigned structures (IV) and (II), respectively. In Table 3 the properties of substances B and C [11] are

[8] Wittig and Lehmann, *Chem. Ber.*, 1957, **90**, 875.
[9] Sandin and Hay, *J. Amer. Chem. Soc.*, 1952, **74**, 274.
[10] Alexander, *J. Org. Chem.*, 1956, **21**, 1464.
[11] Silverman, Trego, Shideler, and Houk, NAA-SR-1203, 1955.

compared with those of (IV) and (II) and with the properties forecast.[11] We attach little significance to colour as a criterion of structure in the polyphenyls (cf. ref. 11) as, with perseverance, all the polyphenyls we have encountered can be obtained white, except that (I) and (IV) when highly purified exhibit a weak pale green fluorescence. We have also observed that qualitative solubility comparisons can be an unreliable guide to structural similarity, since traces of other isomers can greatly modify the solubility of a given polyphenyl without appreciably affecting the melting point. Despite these reservations it appears that (IV) is undoubtedly a product of *p*-terphenyl pyrolysis or radiolysis, and that (II) very probably is also.

This observation accords with data on the polar nature of polyphenylyl free radicals, which indicate that they attack an aromatic nucleus at positions deactivated with respect to electrophilic substitution. These data will be discussed in a subsequent paper.

EXPERIMENTAL

Melting points are uncorrected. Intermediates were prepared by established procedures or by the improved methods described. The yields given are for the crude sexiphenyls, before final rigorous purification (see Table 1). u.v. spectra refer to solutions in cyclohexane. Molecular weights were determined by a sensitive ebullioscopic method described elsewhere.[12]

p-*Sexiphenyl* (I).—(a) 4-*Bromo*-p-*terphenyl*. A solution of *p*-terphenyl (23·1 g., 0·1 mole) in hot bromobenzene (200 c.c.) was cooled rapidly to deposit fine crystals. Ferric chloride (0·2 g.) and bromide (20 g., 0·25 mole) were added to the stirred suspension, hydrogen bromide was evolved, and the mixture was decolourised within 1 hr. It was set aside overnight, heated to dissolve solids and expel hydrogen bromide, recooled, and treated with more bromine (5 g.), which reacted rapidly. Volatile products were distilled off, and the residue was extracted several times with boiling petroleum (b. p. 100—120°) by decantation. Recrystallisation of the product gave 4-bromo-*p*-terphenyl (15 g., 48·5%) in plates, m. p. 220—222°.

(*b*) p-*Sexiphenyl*. Butyl-lithium[13] [20 c.c. of a light petroleum (b. p. 100—120°) solution containing $8{\cdot}8 \times 10^{-4}$ mole/c.c.] was added with stirring under argon to a suspension in ether (100 c.c.) of 4-bromo-*p*-terphenyl (5 g.) at 25°. The mixture turned pink but the solid remained undissolved. Cobalt chloride (0·05 g.) and butyl bromide (2 c.c.) were added, and the mixture, which cooled perceptibly, was stirred overnight. The brown solid (4·5 g.) which remained after steam-distillation of by-products was washed successively with dilute hydrochloric acid, water, and three portions of hot benzene to yield the sexiphenyl (2·2 g., 59·2%), m. p. >450°, which was purified by sublimation.

$1^1,1^2{:}4^2,1^3{:}3^3,1^4{:}3^4,1^5{:}4^5,1^6$-*Sexiphenyl* (II).—(a) 4-*Acetamido*-4′-*nitrobiphenyl*. 4-Nitrobiphenyl[14] (86 g.) was converted into 4,4′-dinitrobiphenyl[15] (58·8 g., 56%), m. p. 234—236°, and purified[16] by Soxhlet extraction of the 2,4-dinitro-isomer with ethanol (500 c.c.). To the product (12 g.) heated under reflux in ethanol (200 c.c.), was added, drop-wise with stirring, sodium sulphide (14 g.) and sulphur (3·6 g.) in water (45 c.c.); the mixture was heated for 3 hr., left for *ca.* 12 hr., and poured into water. The precipitate was collected with the aid of cellulose powder on a funnel, washed repeatedly with boiling water, and extracted with N-hydrochloric acid (4×220 c.c.). The hot acid extracts were treated with an excess of ammonia solution, and the separated and washed precipitate (m. p. 198—199°) crystallised from ethanol (1 l.) gave 4-amino-4′-nitrobiphenyl (9 g., 80%) as platelets, m. p. 199—200° (lit.,[15] m. p. 197—198). In other experiments extraction of the base with boiling 5% aqueous perchloric acid was shown to be superior.

The product (9 g.) was heated under reflux (45 min.) in acetic acid (50 c.c.) and acetic anhydride (4·5 g.), treated with water (12·7 c.c.), reheated (1 hr.), and cooled. The crystals of 4-acetamido-4′-nitrobiphenyl which separated were washed with acetic acid (80%) and water, and dried (10·1 g., 93·6%), m. p. 240—241° (lit.,[15] m. p. 240°).

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[12] Ray, *Trans. Faraday Soc.*, 1952, **48**, 809; Bates, AERE Report M919.
[13] *Org. Reactions*, 1945, **3**, 285.
[14] Bell, Kenyon, and Robinson, *J.*, 1926, 1239.
[15] Bell and Kenyon, *J.*, 1926, 2707.
[16] Walls, *J.*, 1947, 72.

(*b*) 4-*Amino-3′-bromobiphenyl.* 3-Bromo-4′-nitrobiphenyl (23·8 g.) obtained by bromination [17] of 4-acetamido-4′-nitrobiphenyl followed by hydrolysis (1 : 1 aqueous sulphuric acid) and deamination [18] of the product, was heated with stannous chloride (60 g.) in ethanol (400 c.c.) under reflux for 15 hr. Most of the alcohol was distilled off and the base, liberated with sodium hydroxide (40 g.) in water (145 c.c.), was extracted into ether. Hydrogen chloride was passed into the dried ether extracts, and the precipitated base hydrochloride was separated off, washed with acetone, and treated with ammonia solution (50 c.c.). The oil which separated (19 g., 90%) solidified slowly; it had m. p. 48—50° and was satisfactory for the next stage.

(*c*) 3-*Bromo*-p-*terphenyl.* 4-Amino-3′-bromobiphenyl hydrochloride (10·53 g., 0·037 mole) in hydrochloric acid (50 c.c.) and water (100 c.c.) was treated with sodium nitrite (3·67 g.) in water (50 c.c.) at 5—10° with stirring. To the suspension of diazonium salt formed, benzene (375 c.c.) at 10°, and sodium acetate (120 g.) in water (140 c.c.) were added, and the mixture was stirred at ambient temperature for 40 hr. Steam distillation and cooling gave a residue (11·3 g.) which was filtered off, washed, and dried (70—80°). Sublimation (110—130°/0·01 mm.) gave crops of crystals contaminated with yellow material. Recrystallisation from ethanol (75 c.c./g.) gave the pure bromoterphenyl (5·7 g., 50%) as platelets, m. p. 148—148·5° (lit.,[5] m. p. 147—148°). Inferior yields of product (<5%) and unchanged 4′-acetamido-3-bromobiphenyl were obtained from the latter when coupling *via* the nitrosoacetamido-derivative was attempted.

(*d*) *The sexiphenyl* (II). By the method [19] described for the preparation of (I), 3-bromo-*p*-terphenyl (1·5 g.), butyl-lithium (10 c.c.), cobalt chloride (0·01 g.), and butyl bromide (1 c.c.) gave the crude *product* (0·5 g., 45%), m. p. 228—238° (from benzene).

$1^1,1^2{:}4^2,1^3{:}2^3,1^4{:}2^4,1^5{:}4^5,1^6$-*Sexiphenyl* (III).—2-Iodo-*p*-terphenyl [18] (1·1 g.) and copper bronze (1 g.) were heated at 230°, and then to 290° (10 min.). Extraction with benzene of the cooled mass, followed by evaporation; and recrystallisation of the residue from ethanol and petroleum, gave the *product* (0·35 g., 49·5%) as white crystals, m. p. 188—189°.

$1^1,1^2{:}4^2,1^3{:}4^3,1^4{:}3^4,1^5{:}4^5,1^6$-*Sexiphenyl* (IV).—This was made (12%) in a similar manner to (I) by coupling 3-lithio-*p*-terphenyl (1 equiv.) with 4-lithio-*p*-terphenyl (5 equiv.). An excess of the latter was used to minimise formation of (II) and hence to facilitate the isolation of the sexiphenyl (IV), which was sublimed, extracted from comparatively insoluble (I) with benzene, and then resublimed.

$1^1,1^2{:}2^2,1^3{:}2^3,1^4{:}2^4,1^5{:}2^5,1^6$-*Sexiphenyl* (V).—(*a*) 2,2′-*Dinitrobiphenyl.* Precipitated copper [20] (80 g.) was added in portions to *o*-chloronitrobenzene (102 g.) stirred mechanically at 215—225°, and then at 225° for 1 hr. The mixture was cooled to 120° and extracted several times with hot benzene. The pale brown product (52 g., 66%) obtained by removal of benzene, charcoal filtration in ethanol (1·2 l.), and recrystallisation, had m. p. 121—122°.

(*b*) 2-*Amino-2′-nitrobiphenyl.* 2,2′-Dinitrobiphenyl (179 g.) in ethanol (3 l.), heated under reflux, was treated with sodium sulphide hydrate (209 g.) and sulphur (53·8 g.) in water (680 c.c.), stirred, and heated for 2—5 hr. Alcohol was distilled from the mixture, which was treated with ether and water and filtered. Removal of solvent from the ether extract dried over sodium hydroxide pellets,[21] yielded an orange oil (149 g.) which was treated with hot hydrochloric acid (146 c.c.) in water (4·5 l.). The aqueous phase, filtered at 40° from residual tar, was treated with charcoal, filtered, and neutralised, giving the amine (98·5 g., 62·5%), m. p. 68—70°.

(*c*) 2-*Iodo-2′-nitrobiphenyl.* 2-Amino-2′-nitrobiphenyl hydrochloride (33 g.) was dissolved in hydrochloric acid (330 c.c.) and water (1·82 l.), diazotised at 5° with sodium nitrite (14·87 g.) in water (330 c.c.), stirred for 10 min., and treated with potassium iodide (69·4 g.) solution, added rapidly. Nitrogen was evolved,* and the mixture was boiled and cooled. The aqueous portion was decanted from the deposited black oil which was washed twice with hot 5% aqueous sodium hydroxide with vigorous stirring, once with water, and then extracted several times with ether. The ether extracts, dried over sodium hydroxide pellets and separated from a

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* *Caution.* In larger scale preparations, nitrogen evolution did not occur spontaneously; a purple complex formed which decomposed explosively as the mixture was warmed.

[17] Case, *J. Amer. Chem. Soc.*, 1938, **60**, 425.
[18] Cade and Pilbeam, *Chem. and Ind.*, 1959, 1578.
[19] Gilman, *J. Org. Chem.*, 1957, **22**, 446.
[20] Gore and Hughes, *J.*, 1959, 1615.
[21] Purdie, *J. Amer. Chem. Soc.*, 1941, **63**, 2276.

black deposit, yielded on removal of solvent a dark solid. Petroleum (350 c.c.) extracts of this substance after treatment with charcoal, filtration, and chilling gave the product (54·2%) in crops (19·7 + 2·8 g.), m. p. 83—84°, which were distilled, b. p. 238—256°/0·01 mm.

(*d*) *2-Amino-2′-iodobiphenyl.*[22] The 2-iodo-2′-nitrobiphenyl (85·2 g.) was reduced with stannous chloride (192 g.) in hydrochloric acid (192 c.c.) and ethanol (420 c.c.) by heating under reflux for 6 hr. The alcohol was distilled, and the base, liberated with sodium hydroxide (240 g.) in water (2 l.), was taken up in benzene (400 c.c.), dried, and obtained on removal of solvent as a viscous brown oil (76·3 g., 99%). This, dissolved in hot hydrochloric acid (90 c.c.) in water (1 l.), treated with charcoal, filtered, treated with hydrochloric acid (1 l.), and chilled overnight, yielded the hydrochloride (78 g.), m. p. 175—194°, which was washed with dilute (1 : 1) acid (250 c.c.) and dried. Alternatively the amine was distilled (b. p. 115—125°/0·1 mm.).

The amine (8·9 g.) when heated (1·5 hr.) under reflux in benzene (100 c.c.) and acetic anhydride (2·92 c.c., 1·03 moles) gave, after removal of solvent and successive recrystallisations from light petroleum and aqueous ethanol, crystals (8·6 g., 84·5%) of 2-acetamido-2′-iodobiphenyl, m. p. 88—90°.

(*e*) *Interaction of benzene and 2′-iodobiphenyl-2-diazonium hydroxide.* A suspension of 2-amino-2′-iodobiphenyl hydrochloride (20 g.) in hydrochloric acid (21 c.c.) and water (260 c.c.) was diazotised at 0—5° in the usual manner with sodium nitrite (4·4 g.) in water (40 c.c.) and then treated with benzene (1·3 l.) and sodium acetate (50 g.) in water (60 c.c.) with vigorous stirring for 3 days. Filtration afforded biphenylene iodonium chloride (4·25 g.), m. p. 293—298° (from acetic acid). The benzene solution, separated from the filtrates, was washed and evaporated, yielding a dark oil which was washed with boiling water and hot 3% sodium hydroxide solution and dried. Several extractions of the product with light petroleum (b. p. 100—120°) gave residual tar (7·1 g.) which was rejected, and after removal of solvent, a brown oil which on distillation gave a yellow oil (3·2 g.), b. p. 110—130°/0·002 mm. Fractional crystallisation of the oil from methanol gave 2,2′-di-iodobiphenyl (0·15 g.), m. p. and mixed m. p. 108—109° (Found: *M*, 399 ± 12. Calc. for $C_{12}H_8I_2$: *M*, 406). In another typical experiment, the iodonium chloride (2·4 g.), 2,2′-di-iodobiphenyl (3·1 g.), and carbazole (*ca.* 0·1 g.), m. p. and mixed m. p. 243—245° (Found: N, 8·1%; *M*, 167 ± 6. Calc. for $C_{12}H_9N$: N, 8·4%; *M*, 167) were obtained.

Alternatively, the oily product (13·6 g.) from a number of similar experiments was steam-distilled, and the organic phase separated from the distillates (total 12 l.) yielded (in three fractions) di-iodobiphenyl (1·72 g.) and an oil (3·33 g.) which was shown by high-temperature (425°) vapour-phase chromatography [1] on alumina to contain 2-iodobiphenyl and iodobenzene. Distillation of the residue (5·23 g.) involatile in steam gave uncrystallisable orange oil (*ca.* 4 g.), b. p. 80—140°/0·02 mm. (Found: C, 55·7; H, 3·7; I, 40·15%; *M*, 350·6 ± 8. $C_{18}H_{13}I$ requires C, 60·7; H, 3·7; I, 35·65%; *M*, 356), shown (v.p.c.) to contain three substances (75·2, 16·65, and 8·65% * in order of increasing volatility); the minor constituents were shown to be 2-iodobiphenyl and 2,2′-di-iodobiphenyl respectively, by suitable spiking. Compared with the retention times of 4-iodo-*m*-terphenyl [18] and *o*-terphenyl, that of the main constituent indicated it to be 2-iodo-*o*-terphenyl. Coupling [23] of the crude material (1·06 g.) gave, as the only identifiable product, triphenylene (50 mg.), m. p. and mixed m. p. 196—198°, which was unresolvable from an authentic sample by v.p.c. and infrared analyses. Ullmann coupling (0·95 g.) also gave triphenylene (0·13 g., 28%).

Nitrosation [5] of 2-acetamido-2′-iodobiphenyl (6·74 g.), and treatment of the product with benzene gave unchanged reactant (5·6 g.).

(*f*) *Interaction of biphenylene iodonium iodide and butyl-lithium, and thermal decomposition of the product.* Phenyl-lithium [13] (38·4 c.c. of an ether solution containing 9·6 × 10^{-4} mole/c.c.) was added drop-wise at 0—5° with stirring under argon to biphenylene iodonium iodide [24] (10 g.) suspended in ether (25 c.c.). After being stirred (3 hr.) at ambient temperature, solvent was decanted from the residue which was washed successively with ether, and water and dried

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* The analysis for elemental iodine (40·15%) in the crude 2-iodo-*o*-terphenyl can be compared with the value (39·75%) calculated for a mixture having the composition indicated by the v.p.c. trace, assuming the main peak to be given by 2-iodo-*o*-terphenyl.

[22] Mascarelli and Gatti, *Atti. Accad. naz. Lincei, Rend. Classe Sci., fis. mat. nat.*, 1931, **13**, 891.
[23] Kharasch and Reynolds, *J. Amer. Chem. Soc.*, 1941, **63**, 3239.
[24] Albright, Thesis, Univ. of Illinois, 1958.

(7·27 g.). Treatment with tetrahydrofuran (65 c.c.) gave a residue (0·7 g.), m. p. 191—201°, which was converted on heating [24] into 2-bromo-2′-iodobiphenyl (0·5 g.), m. p. 88—89°, and a solution which after removal of solvent (20—50°/15 mm.) yielded a product of m. p. 149—152°. This substance, when heated (64 hr.) in benzene (100 c.c.) under reflux, gave a solid (0·45 g.), m. p. 170—172° (decomp.), which was converted into 2-bromo-2′-iodobiphenyl [24] (0·2 g.), and a solution which after removal of benzene was distilled, yielding (i) a few drops of oil and crystals, b. p. 80°/0·05 mm., (ii) an oil (1·5 c.c.), b. p. 72—78°/0·02 mm., (iii) an oil, b. p. 90—135°/0·02 mm., and a residue (*ca.* 1 g.) (bath temp. >300°). High-temperature v.p.c. analysis of fractions (i), (ii), and (iii) showed them to contain mostly 2-iodobiphenyl, with (*ca.* 10%) iodobenzene, biphenyl, di-iodobiphenyl, and an unknown substance, probably 2-iodo-*o*-terphenyl. The residue was sublimed, and gave, after an oily forerun (<140°/0·001 mm.), an inhomogeneous glass (0·63 g.), flow point 55—65°, subliming at 140—280°/0·001 mm. (Found: *M*, 531, 688), and a residue (0·14 g.), both of which contained iodine.

Thermal decomposition of the solid phenyl biphenylene iodide gave precisely similar results, even when this substance was prepared *via* butyl-lithium obtained from interaction of lithium with biphenylylmercury.[25]

(*g*) o-*Sexiphenyl* (V). 2,2′-Di-iodobiphenyl (3·6 g.) and 2-iodobiphenyl (12·4 g., 5 equiv.) were coupled [23] *via* the aryl-lithium as described in the preparation of (I), by using butyl-lithium (50 c.c. of n-heptane solution containing $1·12 \times 10^{-3}$ mole c.c.), cobalt chloride (0·5 g.), and butyl bromide (8 c.c.). Fractional sublimation of the residue obtained following hydrolysis, steam distillation, and filtration of the reaction mixture, gave *o*-quaterphenyl (2·15 g., 26·6%), m. p. and mixed m. p. 116—18°, tetraphenylene (0·15 g.), m. p., 225—229°, and *o*-sexiphenyl (0·23 g., 5·7%), m. p. 212—215°.

m-*Sexiphenyl* (VI).—(*a*) 3-*Nitro*-m-*terphenyl.* 3-Amino-3′-nitrobiphenyl [26] (3·76 g.) in acetic acid (44 c.c.) was diazotised [27] with sodium nitrite (4·4 g.) in concentrated sulphuric acid (22 c.c.), and the diazonium salt, precipitated by addition of ether (220 c.c.), was washed and treated immediately with benzene (350 c.c.) and sodium acetate (15·5 g.) in water, and stirred for 36 hr. Steam-distillation afforded a residual tar which neither sublimed nor distilled without decomposition. The crude product was used for reduction.

(*b*) 3-*Amino*-m-*terphenyl.* Crude 3-nitro-*m*-terphenyl (equivalent to 4·82 g.) was reduced with stannous chloride (11·86 g.) and hydrochloric acid (11·9 c.c.) in ethanol (44 c.c.) under reflux (7 hr.). Alcohol was removed and the base was liberated, taken up in benzene, filtered from black by-products, dried, evaporated, and redissolved in ether into which hydrogen chloride was passed. The precipitated *base hydrochloride* (2·4 g., 51%), when crystallised from N-hydrochloric acid, had m. p. 198—214° (decomp.). A portion (0·3 g.) gave, on deamination,[18] *m*-terphenyl, m. p. and mixed m. p. 89—90°.

The amine hydrochloride was converted into 3-*iodo*-m-*terphenyl* in the usual way (22·4% yield). The product was an uncrystallisable oil which was purified as far as possible by fractional precipitation from light petroleum–ethanol and chromatography on alumina (Found: C, 57·1, 57·1; H, 3·5, 3·6; I, 36·55, 36·5. $C_{18}H_{13}I$ requires C, 60·7; H, 3·7; I, 35·7%).

(*c*) 3-*Iodo*-m-*terphenyl.* 3-Amino-3′-nitrobiphenyl hydrochloride (21 g.) was converted into 3-iodo-3′-nitrobiphenyl (19·2 g., 70%) in the usual way, and the product, m. p. 98—99° after recrystallisation from aqueous ethanol, was reduced by alcoholic stannous chloride. The 3-amino-3′-iodobiphenyl was purified by precipitation of the hydrochloride from ether, and the product (15 g.) was diazotised and treated with benzene (1 l.) in the presence of excess of sodium acetate (117 g.) solution. The mixture was stirred for two days, and then steam distilled, and the residual dark oil was taken up in benzene, washed with sodium hydroxide solution and water, and dried. Chromatography on alumina, fractional precipitation, and distillation, yielded an oil (4·65 g.), b. p. 150—200°/0·01 mm. (Found: C, 57·0; H, 3·6; I, 39·8. Calc. for $C_{18}H_{13}I$: C, 60·7; H, 3·7; I, 35·7%). V.p.c. analysis gave three peaks, two of which were identified with 3-iodobiphenyl and 3,3′-di-iodobiphenyl. The main peak corresponding to the least volatile component was irresolvable from the main peak given by 3-iodo-*m*-terphenyl prepared *via* 3-amino-*m*-terphenyl.

(*d*) *Purification of* 3-*iodo*-m-*terphenyl, and preparation of* m-*sexiphenyl* (VI). Crude 3-iodo-*m*-terphenyl, prepared *via* 3-amino-*m*-terphenyl (1·85 g.), and 3-amino-3′-iodobiphenyl

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[25] Coates, " Organo-metallic Compounds," Methuen, London, 1958, p. 3.

[26] Mascarelli and Gatti, *Gazzetta*, 1929, **59**, 858.

[27] Hodgson and Mahadevan, *J.*, 1947, 325.

(4·65 g.), were combined and steam-distilled for several days. The residual oil (6 g.) was separated, dried, and coupled in the presence of cobalt chloride *via* the aryl-lithium prepared as described for (I). After working up in the usual way, the residual oil involatile in steam was sublimed during several weeks, yielding oily foreruns (2·22 g.), b. p. 115—170°/10^{-3} mm., and a glass (0·5 g.), b. p. 170—250°/10^{-3} mm. The latter on crystallisation from light petroleum and ethanol gave *m*-sexiphenyl, m. p. 145—147°, mixed m. p. with an authentic sample,[10] 147—148°.

3′,2″-*Diphenyl*-p-*quaterphenyl* (VII).—4′-Iodo-*m*-terphenyl [18] (6·2 g.) and copper bronze (15 g.) were heated at 320° (1 hr.) cooled, and extracted with benzene. The brown extracts were treated with Celite 545 and charcoal and then filtered, and the residue after evaporation gave crystals of the *diphenylquaterphenyl* (0·8 g., 10%), m. p. 230—232° [from light petroleum (b. p. 100—120°)].

We thank Mr. T. H. Bates for recording some of the u.v. spectra and for some molecular-weight determinations; Dr. R. Alexander of the National Heart Institute of the U.S.A. for a sample of *m*-sexiphenyl; and Dr. W. Wild for his interest in the work.

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[*Received, December 4th*, 1962.]