Tetrahedron, 1964, Vol. 20, pp. 519 to 529. Pergamon Press Ltd. Printed in Northern Ireland

ASPECTS OF POLYPHENYL CHEMISTRY—I

SYNTHESIS AND VAPOUR PHASE CHROMATOGRAPHY OF QUATERPHENYLS

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(*Received* 16 *April* 1963)

Abstract—Quaterphenyl isomers have been prepared by a variety of synthetic methods, which have served to corroborate or clarify former structure assignments and physical properties. Incidentally, new formation has been obtained concerning different modes of interaction of various polyphenylyl radicals, relevant to an understanding of the radiolysis of polyphenyls. The behaviour of mixtures of polyphenyls including quaterphenyls on a high temperature gas/solid VPC column is described.

INTEREST in the polyphenyls, notably biphenyl and the terphenyls, has been stimulated by their application as moderator-coolants in nuclear reactors.[2] As an aid to the interpretation of radiation damage in these substances, various polyphenyls and substituted polyphenyls which could be used for systematic spectroscopic studies and comparison with polymer fragments formed under irradiation have been synthesized, suitable processes for separation of the radiolysis products have been developed, and attempts have been made to simulate chemically, processes occurring as a result of irradiation, in order to elucidate their mechanism.

The primary technological interest lay in assessing radiation damage in isomeric terphenyls,[3] and initially our work was concerned with the chemistry of these systems. Subsequently however we reverted to the chemical problems associated with biphenyl radiolysis. These were several compelling reasons for this.

First, it seemed likely that the most useful contribution we could make to an understanding of the mechanism of radiolysis would be to discern from an analysis of the relative abundance of various isomers of a given higher molecular weight polyphenyl, the probable nature, in terms of nucleophilic or electrophilic power, of the immediate precursors of the products. Theoretically, four isomeric terphenylyl radicals or monovalent ions can be derived from each terphenyl isomer, and these can presumably substitute for hydrogen in four different ways, on attacking another terphenyl molecule. Thus from pure *para*-terphenyl one might expect to obtain among numerous other products of irradiation, at least ten isomeric sexiphenyls,

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[2] For reviews see W. N. Bley, NAA-SR-2420 (1958); C. A. Trilling, D. W. Bareis, J. G. Burr and R. H. J. Grecke, A/CONF.15/P/1779; C. A. Trilling, A/CONF.15/P/421, *Proc. 2nd. International Conference on the Peaceful Uses of Atomic Energy*, Geneva 1958.

[3] T. H. Bates, W. G. Burns, B. Morris, R. W. Wilkinson and T. F. Williams, *AERE* C/R-2121 (1957); *AERE* C/R-2185 (1959); T. H. Bates and R. W. Wilkinson, *AERE* M-412 (1959); T. H. Bates, R. F. Cumberland, W. G. Burns and C. R. Reed, *AERE* R-3564 (1960); T. H. Bates, W. G. Burns, M. East, B. Morris, C. R. Reed, P. Stanaway, R. W. Wilkinson and J. A. Winter, *AERE* R-3743 (1962); W. G. Burns, C. R. Reed, R. W. Wilkinson and J. A. Winter, *AERE* R-3989 (1962).

most of which would be unknown compounds which might have to be synthesized for the purpose of unambiguous identification. Some of the difficulties associated with synthesizing and handling unsymmetrical or branched sexiphenyls have already been described.[4,5] Biphenyl can form three isomeric biphenylyl radicals or monovalent ions, which can give rise in substitution-addition reactions to only six linear isomeric quaterphenyls, all of which are now known and comparatively easily handled.

Then too, the problems associated with all the analytical techniques available would be aggravated when applied to compounds of such relatively high molecular weight as sexiphenyls. For example we have found that a VPC column operating above 400°, and suitable for the separation of terphenyl isomers, could also be used to analyse quantitatively, isomeric mixtures of quaterphenyls. But *para*-quaterphenyl represented a practical upper limit to such analyses in terms of molecular weight and involatility. Even comparatively volatile sexiphenyl isomers such as *meta*-sexiphenyl tended to decompose on the column and the peaks obtained on the recorder trace were of such a shape as to preclude the possibility of accurate quantitative measurement.

In order to familiarize ourselves with the behaviour of quaterphenyls with regard to their physical properties, their separation from isomeric mixtures, and their quantitative isomer ratio analyses, it was necessary to prepare samples of these compounds, as only two isomers were commercially available. Furthermore, when this work was begun, there was some doubt about the nature or properties of some of the isomers.

The nine isomers of quaterphenyl and some of their physical properties are shown in Table A.

(I) was prepared by the method of Bowden[6] who first obtained it via an Ullmann reaction with 2-iodobiphenyl, and as a by-product from the synthesis of *ortho*-sexiphenyl by a method similar to that of Wittig and Lehmann's.[7] It was also obtained together with II and III from the neutral products of the thermal decomposition of 2-phenylbenzoyl peroxide in liquid biphenyl. These homolysis experiments will be described in detail in another paper.[8] Compound II had been obtained previously via a partially hydrogenated precursor.[9] We wished to avoid such methods for reasons explained elsewhere,[7] although this precaution eventually proved to be unnecessary.

We also obtained IV and VI by Bowden's method from the appropriate iodobiphenyls.

Dale[10] described 2,4′-diphenylbiphenyl (III), obtained together with I and VI from a mixed Ullmann reaction between 2-iodobiphenyl and 4-iodobiphenyl, as having m.p. 117·5–118°, λ_{max} 205, 248, and 276 mμ. No mixed melting point with I (m.p. 118·5°) was recorded, and the separation from I involved a laborious mechanical procedure. Wiley and Wakefield[11] described III, obtained in low yield from decomposition in benzene of the tetrazonium hydroxide derived from 2,4′-diaminobiphenyl, as

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[4] G. F. Woods, D. D. Centola, H. E. Ruskie and C. D. Miller, *J. Amer. Chem. Soc.* **82**, 5227 (1960).

[5] G. F. Woods, J. C. Oppelt and R. B. Isaacson, *J. Amer. Chem. Soc.* **82**, 5232 (1960).

[6] S. T. Bowden, *J. Chem. Soc.* 1111 (1931).

[7] J. A. Cade and A. Pilbeam, *AERE* R-3038 (1961); *J. Chem. Soc.* in the press.

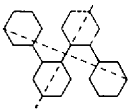
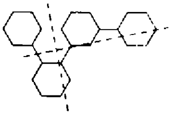
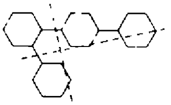
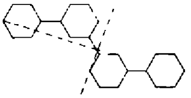
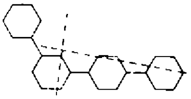
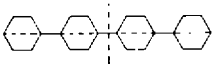
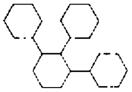
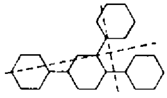
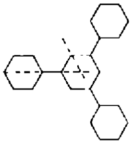
[8] J. A. Cade and A. Pilbeam, *AERE* R-3796 (in preparation).

[9] G. F. Woods, A. L. van Artsdale and F. T. Reed, *J. Amer. Chem. Soc.* **72**, 3221 (1950).

[10] J. Dale, *Acta Chemica Scand.* **11**, 650 (1957).

[11] R. H. Wiley and B. J. Wakefield, *J. Org. Chem.* 25, **25**, 132 (1960).

TABLE A

		M.P., °C	B.P., °C	r^3, Å[a]	λ_{max}, Å	$\varepsilon_{max} \times 10^{-4}$
I		118–119	403 ± 2 420[b]	125	2286	3·39
II		90·5–91[c]			2315	4·5
III		121	438 ± 2	267·1	2760 2480	2·2 2·6
IV.		86–87	469 ± 2	343	2470	5·94
V		169	482 ± 5	402	2675	3·705
VI		322	489 ± 5	481·9	2940	4·59
VII		150–155[d]				
VIII		119–120	439 ± 2	267·1	2500	4·66
IX		173	463 ± 2	184·2	2525	5·78

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[a] Radii were determined both graphically and by calculation, using mean values for the ring C—C bonds (1·39 Å) and interannular C—C bonds (1·52 Å) based on data from *Tables of Interatomic Distances* Special Publn. No. 11, Chemical Society, London (1958). Moments about the relevant inertial axis were taken to determine its position in the isomers with no centre of symmetry.

[b] M. S. Shvartsberg and I. L. Kotlyarevskii, *Uspekhii Khim.* **24**, 1439 (1960).

[c] See reference 9.

[d] E. Knoevenagel, *Liebig's Ann.* 27 (1894).

having m.p. 209–210°, λ_{max} 257 and 274 mμ. No molecular weight was recorded. Copeland *et al.*[12] obtained by catalytic dehydrogenation of 4-(bicyclohex-1-en-2-yl) biphenyl, a substance having properties similar to Dale's compound, but made no reference to Wiley and Wakefield's claims, having submitted their work before the appearance of the latter's paper.

We attempted to prepare III by substitution in benzene of the 4-phenyl-2'-biphenylyl radical derived from 2-amino-4'-phenylbiphenyl[13] via either the diazonium acetate or the nitrosoacetamido derivative.[13] *para*-Terphenyl (m.p. 211–212°, λ_{max} 276 mμ) was the only substance obtained in good yield ($>60\%$). The other neutral products of the reaction were examined using the high temperature VPC equipment described below. This analysis showed that biphenyl was another product of the reaction, but that the yield of III did not exceed 2 per cent, the limit of sensitivity of the determination. Thus the 4-phenyl-2'-biphenylyl radical appears to be sterically hindered, giving instead of homolytic substitution, an hydrogen abstraction reaction. In view of this observation, it seems likely that Wiley and Wakefield's product was also *para*-terphenyl.[11]

We prepared III by coupling, following Karasch and Reynolds,[14] of the mixed lithium aryls obtained from interaction of 2-iodo-4'-phenylbiphenyl[15] and excess of lithium phenyl. In this reaction a five-fold molar excess of lithium phenyl was used to minimize the formation of sexiphenyl and to facilitate separation of the products. The reaction was, however, complicated by the slow rate of metalation of the terphenyl and the disproportionately slow rate of asymmetric coupling, as evidenced by the large amounts of *para*-terphenyl and biphenyl obtained relative to the amount of III isolated.

We also prepared III together with V and VI or together with I and II by homolytic substitution in biphenyl of biphenylyl radicals derived from 4-phenylbenzoyl or 2-phenylbenzoyl peroxides respectively.[8] The physical properties of our product support Dale,[10] although the melting point (121°) is somewhat higher than quoted.

Recently Hey *et al.*[16] have also confirmed Dale's result by two independent routes to III.

Woods and Tucker[17] obtained V from dehydrogenation of 1-phenyl-2-(4-biphenylyl)-cyclohexadiene in one of a series of elegant syntheses of *meta*-polyphenyls. We avoided routes involving such hydrogenated intermediates, and obtained V directly from homolysis experiments using 3-phenylbenzoyl of 4-phenylbenzoyl peroxides in biphenyl; from coupling in excess of lithium phenyl of the latter with 3-lithium-4'-biphenyl derived from 3-bromo-4'-phenylbiphenyl; from the aluminium chloride catalysed isomerization[18] of IV in benzene; and unexpectedly from an attempt to prepare 1,2,4-triphenylbenzene (VIII).

When this work commenced, there were several conflicting claims[19] concerning the properties of VIII; e.g. the melting point was reported variously as 99·5–100°,

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[12] P. G. Copeland, R. E. Dean and D. McNeil, *J. Chem. Soc.* 4522 (1960).

[13] H. France, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.* 1364 (1938).

[14] M. S. Karasch and W. B. Reynolds, *J. Amer. Chem. Soc.* **63**, 3239 (1941).

[15] J. A. Cade and A. Pilbeam, *Chem. & Ind.* 1578 (1959).

[16] D. H. Hey, M. J. Perkins and G. H. Williams, *J. Chem. Soc.* 784 (1961).

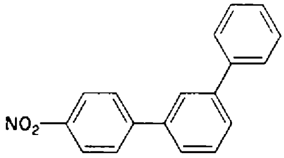
[17] G. F. Woods and I. W. Tucker, *J. Amer. Chem. Soc.* **60**, 3340 (1948).

[18] C. F. H. Allen and F. P. Pingert, *J. Amer. Chem. Soc.* **64**, 1365 (1942).

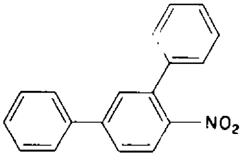
[19] C. G. Overberger and J. M. Whelan, *J. Org. Chem.* **24**, 1155 (1959).

101·5–102°, 109°, 119–120°, and 119·5–120°. Although we were primarily interested in the linear quaterphenyl isomers, it appeared worthwhile to try to resolve this confusion since it seemed that an easy and unambiguous route to VIII would be interaction with benzene of the 3-phenyl-4-biphenylyl radical derived via the amine, from 4′-nitro-*meta*-terphenyl, since the latter had been reported as the sole product of direct mononitration of *meta*-terphenyl.[20] We also required VIII for VPC studies. Thus the crude product from mild nitration[20] of *meta*-terphenyl was reduced to the amine, and coupled with benzene via either the diazonium acetate[21] or the nitrosoacetamido derivative.[13] Each reaction readily gave small yields of a substance m.p. 169–170° which was eventually shown to be 3,4′-diphenylbiphenyl (V). We considered at first that this could have arisen owing to a hitherto unrecognized rearrangement of the aromatic radical; aralkyl radicals can undergo rearrangements which can be satisfactorily explained in terms of migration of a phenyl group.[22,23] However our subsequent studies on the thermal decomposition of phenylbenzoyl peroxides in benzene[8] gave no indications of rearrangements of such a kind.

We therefore reinvestigated the nitration of *meta*-terphenyl and showed that mononitration affords a mixture of 4-nitro-*m*-terphenyl (X) and 4′-nitro-*m*-terphenyl (X). Details of these experiments will appear in another paper, but the results obtained are similar to those of certain other investigations of electrophilic substitution in *meta*-terphenyl.[24,25]



X



XI

On reduction and coupling, X gave 3,4′-diphenylbiphenyl whereas XI gave predominantly *meta*-terphenyl by a deamination process, and only a small amount of VIII. In this respect the radical derived from XI resembles the radical derived from 2-amino-*p*-terphenyl, and provides another example of hindrance to substitution by *ortho* substituted 2-biphenylyl radicals which give preferentially an hydrogen abstraction reaction.

These facts, emerging from the synthetic studies, were eventually of great assistance towards understanding otherwise unexpected isomer ratio distributions in the products of liquid biphenyl radiolysis which will be described in another part.[26]

Boiling points of polyphenyls

Although the effect of structural change on the melting points of polyphenyls has been discussed,[27] correlation of molecular size or shape with the boiling points has not

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[20] H. France, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.* 1289 (1939).

[21] W. E. Bachmann and R. A. Hoffmann, *Organic Reactions* Vol. II; p. 224. Wiley, New York (1944).

[22] H. Pines and C. N. Pillai, *J. Amer. Chem. Soc.* **82,** 2921 (1960).

[23] C. E. Smith and L. C. Anderson, *J. Amer. Chem. Soc.* **82,** 656 (1960).

[24] C. K. Bradsher and I. Swerlick, *J. Amer. Chem. Soc.* **72,** 4189 (1950).

[25] J. J. E. Schmidt, J. A. Krimmel and T. J. Farrell, *J. Org. Chem.* **25,** 252 (1960).

[26] J. A. Cade and A. Pilbeam, *AERE* R-3816 (in preparation).

[27] L. Silverman, K. Trego, M. Shideler and W. Houk. NAA-SR-1203 (1955).

hitherto been noted. The absence of polar substituents suggests little molecular association in the vapour phase. We determined the boiling points of several polyphenyls, and plotted these against the cubed radius of the sphere of revolution of the molecule about the inertial centre of the most extended conformation (Fig. 1.). The approximate positions of the relevant inertial axes are shown in Table A by the intersection of the dotted lines. The rectilinear relationships observed for non-branched isomers, lead us to infer that for a given molecular weight the boiling points are governed primarily by entropy differences consequent upon the relative ease of packing of the molecules in the gaseous state.

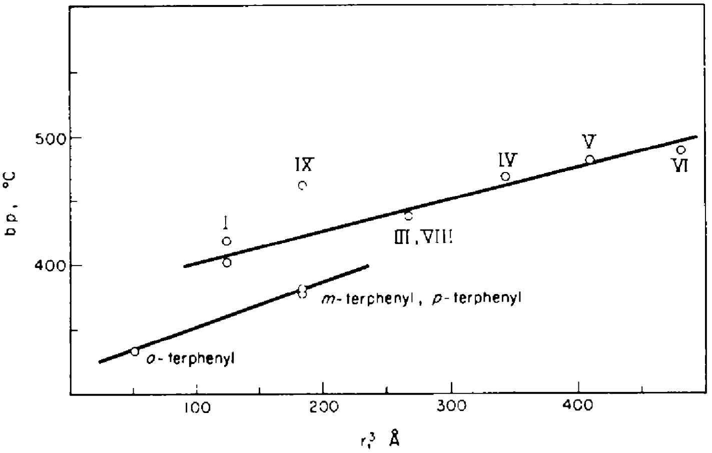

FIG. 1*†

* B.ps of terphenyls measured were somewhat different from figures quoted in *Handbook of Chemistry and Physics* (39th Edition) Chemical Rubber Publishing Co., 1957.

† See footnote b, Table A.

Another fact concerning the boiling points which is of considerable importance in relation to the separation of the radiolysis products of biphenyl, is that the quaterphenyls form a group boiling apart from the terphenyls without overlap of the ranges.

EXPERIMENTAL

Purification of quaterphenyls. The yields of quaterphenyls obtained in the experiments described below are given for products in a reasonable state of purity. To obtain materials for the determination of physical constants the products were further purified by a combination of recrystallization from a suitable solvent, sublimation at low pressure, and passage of a solution in benzene through a column of alumina, until a sample with constant physical properties was obtained.

Melting points. Melting points of pure quaterphenyls were determined on a Fisher–Johns micro-block, and are corrected.

Boiling points. Boiling points were determined at 1 atmosphere by Siwoloboff's method. The samples (ca. 0·5 g) were heated under nitrogen in ignition tubes in a bath of fused nitrates, and the thermometer was standardized by determining the b.p. of pure sulphur and benzophenone in the same apparatus and at the same time as the other determinations.

Molecular weights. These were determined in methylene chloride by a sensitive ebullioscopic method.[18,19] The consistently high experimental values obtained can probably be attributed to variation of the ebullioscopic constant with molecular weight.

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[18] N. H. Ray, *Trans. Farad. Soc.* **48**, 809 (1952).

[19] T. H. Bates, *AERE* M-919 (1961).

Intermediates. 2-Iodobiphenyl was obtained commercially; 4-iodobiphenyl was prepared by direct iodination of biphenyl following Novikov,[30] and 3-iodobiphenyl was made via 3-nitrobiphenyl obtained in high yield from the acetate-buffered Gomberg–Bachmann coupling of 3-nitrophenyldiazonium acetate with benzene. Other starting materials were obtained by the methods referred to.

Acetylation of amines

Aminopolyphenyls are more reactive than aniline, and attempted monoacetylation in the usual way with acetic anhydride often yields a mixture of the monoacetylated and diacetylated products. A simple general procedure for overcoming this was devised. The amine was heated under reflux for a short time in acetic acid containing slightly more than enough anhydride to convert it all into the monoacetylated derivative. Then sufficient water was added, based on the anhydride used, to bring the acid solution to a concentration of about 80% w/v, and the mixture was reheated for 1 hr. This procedure ensured that any N-diacetyl derivative was hydrolysed back to the monoacetyl derivative, which was the exclusive product in all the examples of amines treated in this manner.

3-*Iodobiphenyl*

(a) 3-*Nitrobiphenyl. m*-Nitroaniline (138 g) was diazotized in hydrochloric acid (320 cc) and water (280 cc) at 5–10° by the addition of sodium nitrite (73 g) in water (200 cc). Precooled benzene (1·6 l.) was added, followed immediately by sodium acetate trihydrate (320 g) in water (800 cc) and the mixture was stirred vigorously at ambient temp for 2 days. Excess of benzene was removed with steam, and the residual oil was washed by decantation, separated, dried azeotropically with ethanol and distilled. The distillate (109 g, 56·8%). b.p. 204–210°/12 mm, was crystallized from ethanol, giving the product (100 g), m.p. 56–58°.

(b) 3-*Aminobiphenyl.* 3-Nitrobiphenyl (86 g) was *cautiously* mixed with stannous chloride dihydrate (301 g) in ethanol (1·05 l.) and the mixture was heated under reflux (8 hr). Alcohol was removed by distillation, and from the residue, poured into water, the base was liberated with sodium hydroxide, extracted into ether, dried, and precipitated as the hydrochloride by passing anhydrous hydrogen chloride into the ethereal solution. The yield was quantitative.

The base on diazotization and treatment with potassium iodide solution, gave by the usual procedure, a brown oil which was steam distilled, washed successively with sodium thiosulphate solution and water, dissolved in carbon tetrachloride and dried. Distillation following removal of solvent yielded 3-iodobiphenyl (55 g, 45%), b.p. 114–115°/0·1 mm, n_D^{20} 1·677.

Symmetrical linear quaterphenyls (I, IV and VI)

3-Iodobiphenyl (8·6 g) was heated with copper bronze (8·6 g) at 225°. The temp of the mixture rose spontaneously to 312°, and further heat was supplied (20 min) at 260°. The mixture was cooled and extracted with hot benzene. The residue obtained after removal of solvent gave on repeated crystallization from ethanol, IV as a white solid (0·75 g), m.p. 78–79°.

Similarly, 2-iodobiphenyl (2·83 g) and copper bronze (3 g) gave I, (0·8 g), m.p. 118·5°, and 4-iodobiphenyl (5·66 g) and copper bronze (6 g) gave after recrystallization of the products from benzene VI as leaflets (3 g), m.p. 320–321°.

Attempted preparation of 2,4′-*diphenylbiphenyl* (III)

(a) *From aminoterphenyl.* (i) 2-Amino-4′-phenylbiphenyl[16] (4·9 g, 0·02 g mole) was diazotized in hydrochloric acid (25 cc) and water (500 cc) with sodium nitrite (3 g) at 10°, and the mixture was treated with benzene (500 cc) and sodium acetate (60 g) and stirred (48 hr). Benzene was removed with steam and the mixture was cooled and filtered. The solid collected on a funnel was washed with water, dried, dissolved in benzene–ethanol, filtered and re-isolated by evaporation of the solvent. Sublimation at 100–110°/0·01 mm gave an orange product, from which by a combination of recrystallization and passing in solvent through a column of alumina, *para*-terphenyl (3 g), m.p. 209–211°, M.Wt. 230 ± 6, was obtained. Careful examination of all residues and mother liquids failed to reveal the presence of the quaterphenyl sought.

In other experiments, coloured basic products were removed by extraction with conc. sulphuric acid from a solution in benzene of the primary reaction products. *para*-Terphenyl was again the only product isolated.

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[30] A. N. Novikov, *Zh. Obsch. Khim.* **29**, 58 (1959).

(ii) 2-Amino-4′-phenylbiphenyl (2·5 g, 0·01 g mole) was acetylated by the procedure described above. The product, m.p. 124–125°,[15] was dissolved in acetic acid (25 cc) and acetic anhydride (5 cc) containing potassium acetate (3 g) and phosphorus pentoxide (0·2 g) and treated at −10° with freshly prepared nitrosyl chloride solution (7 cc containing 1 g NOCl). The mixture was left to stand (2 hr) and poured into ice-cold water. The yellow solid thrown down, was centrifuged, washed with ice-water and dissolved in precooled benzene (150 cc), and the solution was dried rapidly over anhydrous magnesium sulphate, filtered, and left to stand (48 hr). Solvent was removed and the residue following sublimation, crystallization and chromatography on alumina yielded *para*-terphenyl (0·7 g), m.p. 210–211°, M.Wt. 232 ± 5, and various coloured products. There was no indication of the presence of (III).

(iii)[31] The amine (4·9 g, 0·02 g mole) was suspended in acetic acid (50 cc) and added at 0–5° to a solution of sodium nitrite (5 g) in conc sulphuric acid (25 cc) prepared at −5°. The dark green-brown product was treated with ether (250 cc) and the solid thrown down was collected on a sintered funnel, washed with ether, added quickly to a mixture of benzene (250 cc) and ammonium acetate (10 g) in water (50 cc), and stirred for 3 days. The resulting mixture was processed in the manner described in (i) above, to yield *para*-terphenyl (2·2 g) m.p. and mixed m.p. 209–210°, and various intensely coloured small fractions.

(b) *From iodoterphenyl.* (i) Lithium butyl[32] (40 cc of n-hexane solution containing $9{\cdot}76 \times 10^{-4}$ moles/cc) was added to 2-iodo-4′-phenylbiphenyl[15] (1·7 g, 0·0048 g mole) and bromobenzene (3·75 g, 0·024 g mole) in ether (30 cc). The solution became warm and turned yellow. Anhydrous cobalt chloride (0·05 g) in tetrahydrofuran (2 cc) was added, followed by butyl bromide.[14] The reaction mixture which became hot and turned black was left overnight, treated with water, steam distilled and cooled. The suspended solid (1·05 g) was collected on a funnel, washed and dried. Sublimation of the yellow solid at 0·001 mm gave various fractions from which by crystallization, resublimation and recrystallization, *para*-terphenyl (0·35 g) m.p. 207–210°, M.Wt. 228 ± 10, and unidentified needles [not (III)] (0·13 g), m.p. 130–140°, M.Wt. 300 ± 10, were obtained. Examination on a high temp VPC column of the combined residues and mother liquors from the recrystallization revealed the presence of *para*-terphenyl and III which were identified by spiking with authentic samples.

In other experiments, treatment of the reaction mixture with solid carbon dioxide before addition of water, followed by extraction with sodium carbonate solution of the solid residue from the steam distillation stage, yielded small quantities of *o*-(4-biphenylyl)benzoic acid, signifying that although metalation of the terphenyl nucleus had occurred, coupling was incomplete.

(ii) By the procedure described in (i) lithium butyl solution (35 cc), bromobenzene (4 g), 2-iodo-*para*-terphenyl (1·78 g), cobalt chloride (0·05 g) and butyl bromide (5 cc) in ether (50 cc) at 0°, gave a solution to which anhydrous ferric chloride (6 g) was then added. After standing overnight the mixture was treated with water containing sodium bisulphite, steam distilled, and treated with dil. hydrochloric acid. The suspended solid was separated and treated as described in (i). The more volatile sublimates afforded on crystallization from pet. ether, *para*-terphenyl (0·5 g) m.p. 209–211°, M.Wt. 229 ± 7. The less volatile sublimates yielded on crystallization from ethanol 2,4′-diphenylbiphenyl (III), m.p. 121°, M.Wt. 304 ± 6 (Found: C, 93·75; H, 6·5. Calc. for $C_{24}H_{18}$: C, 93·66; H, 6·34%).

3,4′-*Diphenylbiphenyl* (V)

(a) By the procedure described in (i) above, lithium butyl solution (150 cc) bromobenzene (15·7 g, 0·1 g mole), 3-bromo-4′-phenylbiphenyl (3·1 g, 0·01 g mole), cobalt chloride (0·1 g) and butyl bromide (10 cc) in ether (100 cc) gave after reaction and working up in a similar way, biphenyl, *para*-terphenyl (2·15 g) m.p. 210–211°, M.Wt. 240 ± 7, and 3,4′-diphenylbiphenyl (0·65 g) m.p. 166–167°, M.Wt. 312 ± 7 (Found: C, 94·01; H, 6·0. Calc. for $C_{24}H_{18}$: C, 93·66; H, 6·34%).

(b)[18] *meta*-Quaterphenyl (0·67 g) was treated in benzene (17 cc) with anhydrous aluminium chloride (3·4 mg) and the mixture was heated under reflux (21 hr). A portion (1 cc) was diluted in benzene, washed with dil. hydrochloric acid, then with water, dried and evaporated. The residual white solid m.p. 82–84°, was shown to be substantially unchanged IV by VPC analysis. More aluminium chloride (27 mg) was added to the reaction mixture together with benzene (35 cc) and heating was continued (17 hr). The solution became red. A portion (2 cc) gave after the working up treatment

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[31] H. H. Hodgson and A. P. Mahadevan, *J. Chem. Soc.* 325 (1947).

[32] C. W. Kamienski and D. L. Esmay, *J. Org. Chem.* **25**, 115 (1960).

described, a chromatogram showing the presence of *para*-quaterphenyl (IV) and another substance in addition to unchanged reactant (IV). The primary reaction residue was worked up in the same way, and gave on crystallization from benzene–pet. ether, *para*-quaterphenyl (15 mg), m.p. 312°, and V, m.p. and mixed m.p. with the product from (a) 165·5–166·5°, M.Wt. 310 ± 9.

1,2,4-*Triphenylbenzene* (VIII)

(a) The liquid product (47 g) of nitration of *meta*-terphenyl was obtained and distilled as described in the literature,[30] and reduced without further purification with stannous chloride dihydrate (125 g) in hydrochloric acid (125 cc) and ethanol (250 cc) by the procedure described above. The separated base was acetylated, and the product (10·3 g) in acetic acid (135 cc) and acetic anhydride (25 cc) containing potassium acetate (10 g) and phosphoric oxide (0·5 g) was treated at 5–10° with nitrosyl chloride solution (20 cc containing 3 g) in acetic anhydride. The nitrosoacetamido derivative (a sticky semi-solid) was separated in the usual manner, and allowed to decompose thermally in benzene at 25° (12 hr). Removal of solvent gave a tar which on distillation afforded yellow oil (4·6 g) b.p. 200–300°/0·01 mm. Multiple crystallization over a protracted period gave finally white crystals (0·45 g), m.p. 166·5–166 (Found: C, 93·22; H, 6·14; M.Wt. 315 ± 11. Calc. for $C_{24}H_{18}$: C, 93·66; H, 6·34%; M.Wt. 306).

This substance did not depress the m.p. of 3,4′-diphenylbiphenyl (V), was irresolvable from it on a high temperature VPC gas-solid adsorption column, and exhibited identical U.V. light absorption in the range 2200–3600 Å. Examination of the other products of the reaction on the VPC column indicated the presence of *meta*-terphenyl, (V), and 1,2,4-triphenylbenzene (VIII), which was confirmed by spiking with an authentic sample.[19] Careful sublimation of the various fractions (which were combined) followed by recrystallization finally yielded *meta*-terphenyl (2·2 g) m.p. 54–56°, M.Wt. 228 ± 14, more of V (0·15 g), m.p. 163–165°, and VIII (45 mg), m.p. and mixed m.p. 117–119°.

It was subsequently shown[33] that the isolation of V from this section could be attributed to the presence in the starting material of 3-phenyl-4′-nitrobiphenyl.

Similar results were obtained when the free base was employed, and coupling by the acetate buffered Gomberg–Bachman reaction was carried out.

(b) By the procedure described for III above 3-phenyl-4-iodobiphenyl[15] (1·8 g), bromobenzene (4 g), cobalt bromide (0·1 g) and excess of lithium butyl solution, gave on addition of butyl bromide (5 cc) and working up, an oily paste, which by repeated crystallization and sublimation gave 2,2′,4,4′-tetraphenyl biphenyl[7] (23 mg), m.p. 228–232°, M.Wt. 464 ± 14, *meta*-terphenyl (50 mg), m.p. 52–55°, M.Wt. 230 ± 7, and 1,2,4-triphenylbenzene (VIII), m.p. 118–119°, M.Wt. 310 ± 12.

High temperature vapour-phase chromatographic separation of polyphenyls

The behaviour of mixtures of polyphenyls including quaterphenyls was examined using a simple gas-solid adsorption column of alumina with helium elution, operating at 425°. Details of the construction of the VPC apparatus and ancillary equipment, and of the operating conditions and calibration experiments for mixtures of terphenyls are described elsewhere.[34] With this equipment biphenyl, the terphenyls, eight quaterphenyls, *o*-triphenylene, *o*-tetraphenylene, various phenyl triphenylenes, and some more volatile sexiphenyls were shown to be mutually resolvable.

The shape of peaks obtained for the higher molecular weight compounds indicated severe non-linearity of the adsorption isotherms but there was no serious overlapping and resolution was good for a range of pressure differences across the column from 5 to 30 p.s.i. However, reproducibility of retention times was poor. The latter appeared sensitive to the nature of the mixture being separated, but were also dependent, though not linearly dependent on the load, and were useless as a means of identification of peaks in mixtures. The instrument proved, however, very effective analytically if peaks were identified by spiking with appropriate known polyphenyls.

Correlation of ratios of peak areas with molar ratios of components was accurate to ±4% over a limited range of sample weights. For quaterphenyls, no attempt was made to calibrate the apparatus in an absolute sense i.e. to relate individual peak areas to absolute mass of component in a given mixture, as had been done for mixtures of terphenyls and biphenyl.[34] This was partly because the reproducibility in such calibrations was poor (±12%), and partly because for the purpose of analysing

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[33] J. A. Cade and A. Pilbeam, unpublished work on the nitration of *meta*-terphenyl.

[34] J. A. Winter and R. W. Wilkinson, *AERE* M-820 (1961).

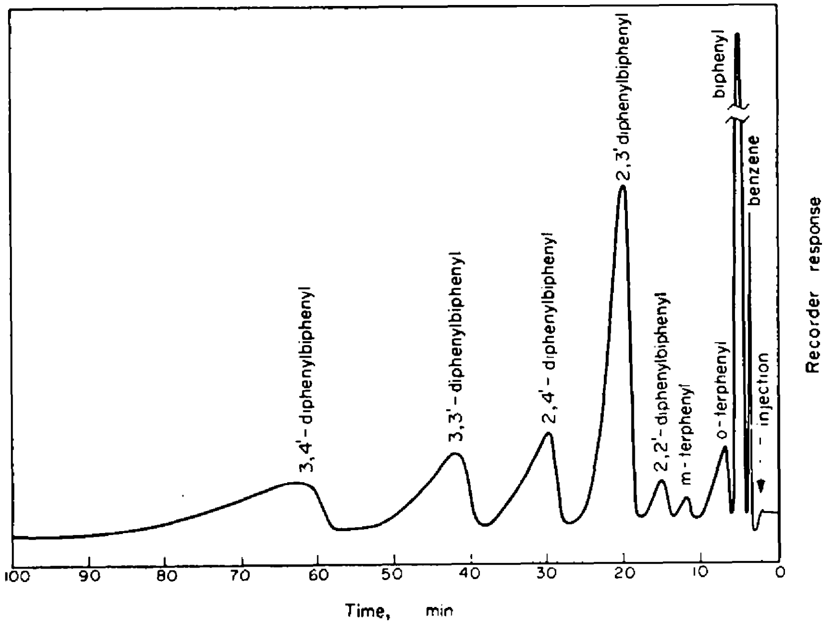
3,4'-diphenylbiphenyl
3,3'-diphenylbiphenyl
2,4'-diphenylbiphenyl
2,3'diphenylbiphenyl
2,2'-diphenylbiphenyl
m-terphenyl
o-terphenyl
biphenyl
benzene
injection
Recorder response
100
90
80
70
60
50
40
30
20
10
0
Time, min

FIG. 2

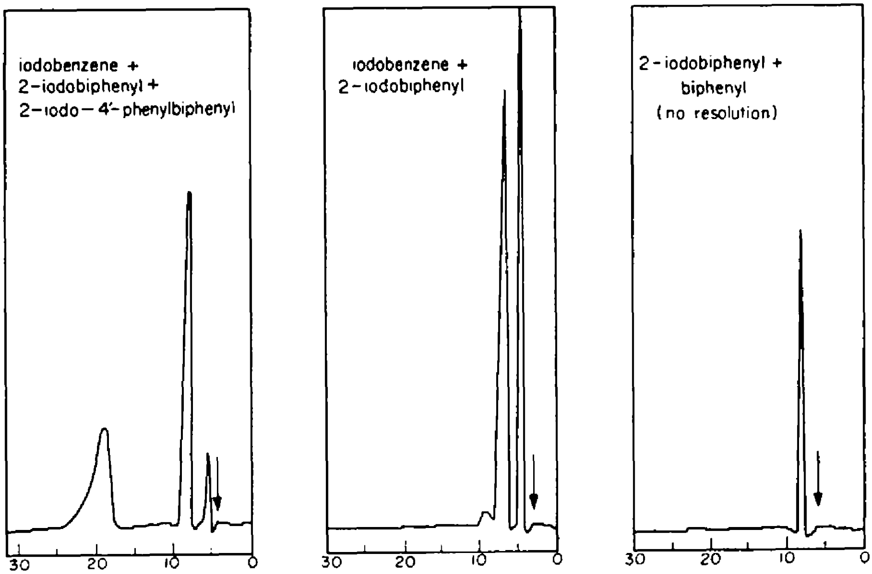
iodobenzene +
2-iodobiphenyl +
2-iodo-4'-phenylbiphenyl
30
20
10
0
iodobenzene +
2-iodobiphenyl
30
20
10
0
2-iodobiphenyl +
biphenyl
(no resolution)
30
20
10
0

FIG. 3

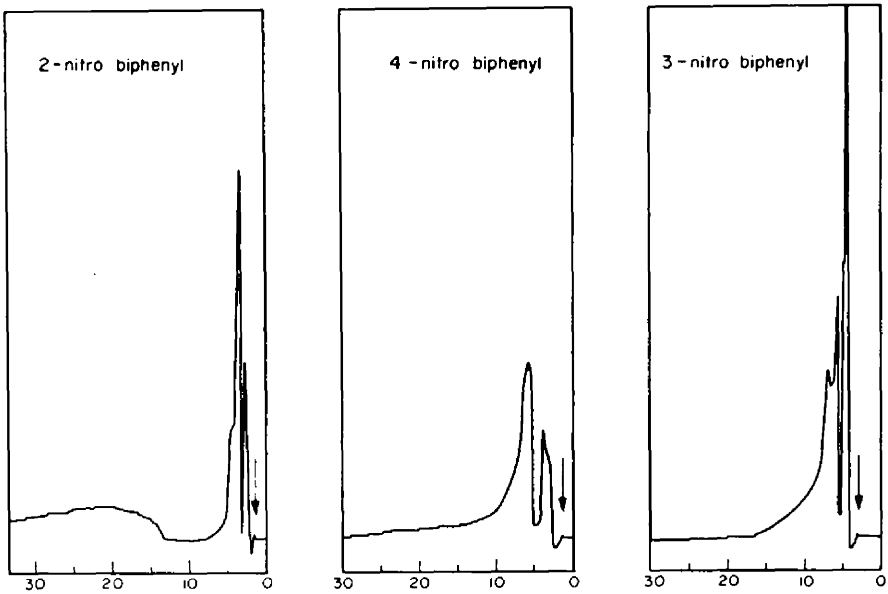

FIG. 4

the polymer obtained from radiolysis[35] or homolysis experiments[8] it was sufficient to know only the isomer ratios. A typical recorder trace for a complex mixture is shown in Fig. 2.

It is interesting to note that the relative retention times of polyphenyls does not correspond with their relative volatilities. Thus for example although *para*-terphenyl must exert a considerably higher vapour pressure (see Fig. 1) than *ortho*-quaterphenyl at the column temp of about 425°, the terphenyl has a higher retention time than the latter which therefore leaves the column first.

As can be seen from the examples in Fig. 3, good results were obtained with mixtures of halogeno polyphenyls, but such compounds caused severe corrosion to the apparatus and drastically shortened the life of the detector plugs. Their study was therefore discontinued at an early stage. Nitro polyphenyls (Fig. 4) extensively pyrolysed on the column, each compound producing multiple peaks.

Hanneman[36] has described a gas-liquid chromatographic apparatus suitable for the study of polyphenyls, in which the stationary phase was a molten inorganic salt mixture supported on firebrick.

Acknowledgements—We thank Mr. T. H. Bates for recording some of the UV spectra which refer to cyclohexane solutions, and for some molecular weight determinations; Dr. C. G. Overberger of the Polytechnic Institute of Brooklyn, U.S.A., for a gift of 1,2,4-triphenylbenzene; Dr. D. D. Lawson of the University of Southern California, U.S.A., for a gift of 2-phenyltriphenylene; Mr. J. Winter for manipulation and maintenance of the VPC column and some analyses; and Dr. W. Wild for his valuable comments and interest in this work.

[35] J. A. Cade and A. Pilbeam, *AERE* R-3779 (in preparation).

[36] W. W. Hanneman, Paper read at *American Chemical Society Meeting*, Cleveland (1960).