1074. *Homolytic Aromatic Substitution. Part XXVIII.** *The Nature of the Involatile Products of Reactions of Aroyl Peroxides with Benzene and Chlorobenzene.*

By D. H. HEY, M. J. PERKINS, and GARETH H. WILLIAMS.

The terphenyls produced as by-products of the reaction of benzoyl peroxide with benzene are shown to be formed in the amounts expected for phenylation of the primary reaction product, biphenyl. When the reaction is carried out in dilute solution (~0·02M), followed by oxidation with *o*-chloranil, the main products are biphenyl and a mixture of quaterphenyls. The mechanism of the formation of the quaterphenyls is discussed. This reaction has been extended to provide a convenient synthetical route to a number of substituted quaterphenyls. An earlier report that chloroterphenyls are significant by-products of the reaction of benzoyl peroxide with chlorobenzene has been shown to be incorrect.

LYNCH and PAUSACKER,[1a] in a study of the products formed in the thermal decomposition of benzoyl peroxide in benzene, suggested that the *pp'*-quaterphenyl isolated from the higher-boiling fractions might arise from dimerisation of phenylcyclohexadienyl radicals (I), formed by the attack of phenyl radicals on benzene, followed by dehydrogenation of the resulting tetrahydro-*pp'*-quaterphenyl. In support of this view it was observed that the yield of *p*-terphenyl was *less* than that of *pp'*-quaterphenyl. Milyutinskaya, Bagdasaryan, and Israelevich [2] found that the decomposition of benzoyl peroxide in deuterated benzene gave a high-boiling product, the deuterium content of which agreed closely with that required on the basis of dimerisation of phenylcyclohexadienyl radicals. These views were substantiated by DeTar and Long,[3] who were able to isolate in small yield one of the stereoisomers of tetrahydro-*pp'*-quaterphenyl from the decomposition of benzoyl peroxide in dilute solution in benzene under nitrogen. These workers also isolated 1,4-dihydrobiphenyl, which results, together with biphenyl, from the disproportionation of the phenylcyclohexadienyl radical. Further support for these views has been provided by Eliel, Meyerson, Welvart, and Wilen,[4] who showed that some dideuterobiphenyl is formed in the phenylation of deuterobenzene. This product is supposed to arise by oxidation of dideuterodihydrobiphenyl formed by disproportionation of deuterium-containing phenylcyclohexadienyl radicals. Razuvaev, Petukhov, and Zateev,[5] who also used isotopic labelling, demonstrated that only two of the aromatic rings in the *pp'*-quaterphenyl arose from the peroxide. It is thus clear that the quaterphenyls formed in the reaction of benzoyl peroxide with benzene arise mainly by the dimerisation mechanism rather than by the phenylation of terphenyls. On the other hand terphenyls are most probably derived from the phenylation of biphenyl. This is in agreement with the results of Razuvaev, Petukhov, and Zateev,[5] who showed that two of the nuclei in the *p*-terphenyl arose from the peroxide. This hypothesis has now been confirmed by a quantitative study of the ratio of isomeric terphenyls formed in the reaction of benzoyl peroxide with benzene. The yields of the three isomeric terphenyls formed in this reaction, when a fairly high initial concentration of peroxide is used, are in reasonable agreement with those predicted from the known values of the partial rate factors for the phenylation of

---

* Part XXVII, *J.*, 1962, 487.

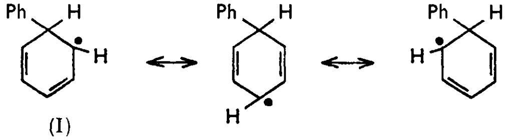
[1] Lynch and Pausacker, *Austral. J. Chem.*, 1957, **10**, (a) 40; (b) 165.
[2] Milyutinskaya, Bagdasaryan, and Israelevich, *J. Phys. Chem. U.S.S.R.*, 1957, **31**, 1019.
[3] DeTar and Long, *J. Amer. Chem. Soc.*, 1958, **80**, 4742.
[4] Eliel, Meyerson, Welvart, and Wilen, *J. Amer. Chem. Soc.*, 1960, **82**, 2936.
[5] Razuvaev, Petukhov, and Zateev, *Proc. Acad. Sci., U.S.S.R.*, 1960, **130**, 336.

biphenyl,[6] by assuming a 40% yield in the conversion of benzene into biphenyl and a 70% yield in the conversion of biphenyl into terphenyls,[6] as reported by previous workers.[1,7]

This agreement between experiment and theory suggests that the formation of terphenyls does not occur appreciably by alternative routes, such as combination of phenyl and phenylcyclohexadienyl radicals with subsequent dehydrogenation, and indicates that terphenyl formation should occur more extensively at high initial concentrations of peroxide.

The acceptance of the above hypothesis is, however, in conflict with results previously reported on the nature of the higher-boiling fractions resulting from the reaction of benzoyl peroxide with chlorobenzene. These, on analytical evidence, appeared to be mainly monochloroterphenyls and not dichloroquaterphenyls. Lynch and Pausacker,[1b] however, had isolated a small quantity of *pp*′-quaterphenyl from the products of the reaction of benzoyl peroxide with chlorobenzene and they suggested that this was formed by dimerisation of the phenylchlorocyclohexadienyl radical followed by dehydrochlorination of the dichlorotetrahydro-*pp*′-quaterphenyl. The occurrence of dehydrochlorination, either during the reaction or during the working-up procedure, might account for the anomalous composition of the high-boiling product formed in the reaction between benzoyl peroxide and chlorobenzene referred to above. The complex mixture of dichlorotetrahydroquaterphenyls, which can arise from the dimerisation, can have a proportion of readily eliminated (non-vinyl) chlorine atoms such that, after dehydrochlorination, the product could fortuitously have a chlorine content similar to that required by a mixture of monochloroterphenyls. This possibility has now been substantiated by a quantitative study of the reaction. These findings thus bring the reaction of benzoyl peroxide with chlorobenzene into line with the more detailed experimental work on the corresponding reaction with benzene, which indicates that the higher-boiling fractions resulting from these reactions are derived mainly by dimerisation, sometimes followed by further reactions of the resulting derivatives of tetrahydroquaterphenyls. The experimental results indicate that, in the reaction with chlorobenzene, dehydrochlorination of the high-boiling products occurs mainly during the alkaline hydrolysis of phenolic esters. Biphenyl, which occurs to a relatively small extent in the biaryl fractions obtained from these experiments, is probably formed by dehydrochlorination of dihydrochlorobiphenyls formed by disproportionation of phenylchlorocyclohexadienyl radicals, although phenyl-radical attack at the chlorine-substituted carbon atom cannot be entirely discounted. It is noteworthy that the high-boiling resin from the reaction of benzoyl peroxide with chlorobenzene was found, on elementary analysis, to contain little, if any, oxygen. This contrasts with the resin from the reaction with benzene.[1]

The formation of quaterphenyls by the dimerisation of the mesomeric phenylcyclohexadienyl radical (I), followed by dehydrogenation, implies that three isomeric quaterphenyls should be obtained, namely *pp*′-, *oo*′-, and *op*′-quaterphenyl. These three isomeric hydrocarbons have now been isolated from the high-boiling products of the reaction of benzoyl peroxide with benzene, after dehydrogenation with *o*-chloranil.[8] This technique was employed in order to reduce the number of isomeric compounds present as, in principle, twenty-three stereoisomers of the corresponding tetrahydroquaterphenyls can be formed. *o*-Chloranil was a suitable oxidising agent for this purpose, as the reaction proceeded smoothly at relatively low temperatures, and the probability of thermal cleavage of the tetrahydroquaterphenyls, as observed by DeTar and Long [3] during dehydrogenation under



(I)

---

[6] Hey, Orman, and Williams, *J.*, 1961, 565.

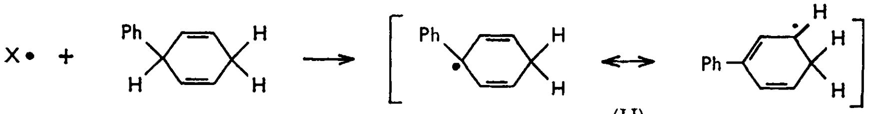
[7] Cadogan Ph.D. Thesis, London, 1954.

[8] Jackman, " Advances in Organic Chemistry, Methods and Results," Vol. II, Interscience, New York, 1960, p. 329.

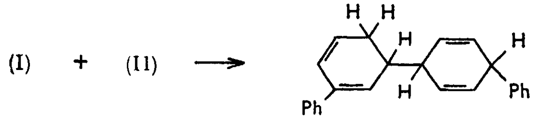
more vigorous conditions, was therefore reduced. The probability of the occurrence of further reactions of the tetrahydroquaterphenyls with the radicals present was reduced as far as possible by conducting the reaction in dilute solution. The decomposition of benzoyl peroxide in 0·021M-solution in benzene gave the following tetranuclear products after dehydrogenation (the yields given in parentheses are in moles per mole of peroxide decomposed): *oo′*-quaterphenyl (0·007), *op′*-quaterphenyl (0·12), *pp′*-quaterphenyl (0·16), and *mp′*-quaterphenyl (0·002).

The formation of *mp′*-quaterphenyl is unexpected, since no canonical form of the phenylcyclohexadienyl radical can be written in which the unshared electron is situated at a position *meta* to that occupied by the phenyl group. The possibility that this compound was formed by thermal rearrangement of the *op′*-isomer during distillation was discounted, since an authentic specimen of *op′*-quaterphenyl was recovered unchanged after being heated at 360° for 24 hours, although rearrangement to the *mp′*-isomer did take place when *op′*-quaterphenyl was heated with aluminium chloride in benzene solution, by a method reported [9] for the conversion of *o*- into *m*-terphenyl.

An alternative mechanism for the formation of *mp′*-quaterphenyl involves homolytic hydrogen-abstraction from 1,4-dihydrobiphenyl, giving the radical (II) which, on combination with a phenylcyclohexadienyl radical, gives the tetrahydroquaterphenyl (III). This compound would then give *mp′*-quaterphenyl on dehydrogenation. The tetrahydroquaterphenyl (III) might also be formed by the addition of a phenylcyclohexadienyl radical at the 3-position of 1,4-dihydrobiphenyl, followed by loss of a hydrogen atom to another radical.



(II)



(III)

The relatively low yield of *oo′*-quaterphenyl compared with the *mp′*- and *pp′*-isomers may be attributable to steric factors, or to the high reactivity of the diene systems in its hydroaromatic precursors in further reactions with free radicals, as suggested by Szwarc,[10] or to a combination of these causes.

The possibility that tetrahydroquaterphenyl derivatives are formed in these reactions by a concerted reaction or " cage " process involving one molecule of peroxide and two of solvent was eliminated by the isolation of the symmetrical compounds *pp′*-quaterphenyl and 2,2‴-dichloro-1,1′ : 4′,1″ : 4″,1‴-quaterphenyl, as well as the unsymmetrical 2-chloro-compound, from the reaction of benzoyl *o*-chlorobenzoyl peroxide with benzene.[11] This result provides strong evidence for the formation of *free* arylcyclohexadienyl radicals in this reaction.

The formation of quaterphenyls by the dimerisation of phenylcyclohexadienyl radicals, followed by dehydrogenation with *o*-chloranil, provides a useful method for the preparation of symmetrically substituted quaterphenyls. In view of their possible application as β-scintillator solutes [for example, 4,4′-di-*m*-tolylbiphenyl (3,3‴-dimethyl-1,1′ : 4′,1″ : 4″,1‴-quaterphenyl) compares favourably with phenyl-*p*-biphenylyloxadiazole

---

[9] Allen and Pingert, *J. Amer. Chem. Soc.*, 1942, **64**, 1365.
[10] Szwarc, quoted in ref. 4.
[11] Foster and Williams, *J.*, 1962, 2862.

as a β-scintillator solute [12]] a number of 4,4′-diarylbiphenyls have been prepared by this method. The compounds *p*-Ar·C_6H_4·C_6H_4·Ar-*p*, where Ar = *m*-BrC_6H_4, *o*-ClC_6H_4, *m*-ClC_6H_4, *p*-ClC_6H_4, *m*-MeC_6H_4, *p*-PhC_6H_4, and β-$C_{10}H_7$, were prepared in yields of about 0·15 moles/mole of peroxide. 2,4′-Di-*m*-tolylbiphenyl was also isolated from a large-scale preparation of 4,4′-di-*m*-tolylbiphenyl.

EXPERIMENTAL

Benzoyl peroxide, benzene, and chlorobenzene were purified as described in Part II.[13] Symmetrical diaroyl peroxides were prepared by the methods given by Vogel.[14] Benzoyl *o*-chlorobenzoyl peroxide (m. p. 54°) was prepared by Wieland, Schapiro, and Metzger's method [15] (lit. m. p. 49°). *o*-Chloranil (m. p. 130—132°) was prepared by a modification of Jackman's method [16] (lit. m. p. 133°). The most important modification of Jackman's procedure was concerned with the technique for oxidising tetrachlorocatechol with nitric acid. It was found essential to wait for the colour of the reaction mixture to change (suddenly) from dark red to light red (1—5 min. after mixing) before quenching it with ice–water. If this precaution was not taken, only an intractable red tar was obtained. Secondly, it was noted that crystallisation from 1 : 5 benzene–light petroleum was not practicable as this yielded the benzene complex of *o*-chloranil.[17] Carbon tetrachloride was the preferred solvent.[18] Commercial samples of *o*-, *m*-, and *p*-terphenyl, anthracene, and phenanthrene were purified by crystallisation; each gave only a single peak when subjected to gas chromatography. *oo*′- and *pp*′-Quaterphenyl were prepared according to the procedures given by Bowden.[19] *op*′-Quaterphenyl was prepared as previously described.[20]

Estimation of the Isomeric Terphenyls formed in the Reaction of Benzoyl Peroxide with Benzene.—In two experiments benzoyl peroxide (2 g.) was allowed to decompose in benzene (25 ml.) at 80° for 40 hr. The solutions were cooled and a measured quantity of a marker compound, either anthracene or phenanthrene (~15 mg.), was added, as well as chlorobenzene (3 ml.) as high-boiling solvent. The benzene was distilled off through a 30-cm. helix-packed column until the residual volume was about 6 ml., and each mixture was then analysed by gas–liquid chromatography, a Pye argon chromatograph being used. The column used was of Apiezon " L " grease on Celite, the column temperature was 225°, and the argon flow-rate about 60 ml./min. The quantities of the components of the mixture which had retention times corresponding to the isomeric terphenyls were estimated by their peak-heights relative to the height of the marker peak. It was necessary to compare the results with those given by synthetic mixtures of known composition. The size of sample chromatographed was adjusted so that the peak heights were approximately the same as those given by a synthetic mixture, and a linear relation between peak-height and quantity of compound was assumed. This linearity of response was not ideally realised and, with widely differing sample sizes, a spread of some 20% in the results was noted. However, detailed calibration did not appear to be justified, owing to the poor base-line stability obtained with the large samples of reaction mixture necessary for the detection of the terphenyls. The results of the analyses are given in Table 1. When phenanthrene was used as marker there was some overlap with *o*-terphenyl on the chromatograms, and a correction was made for this. Consequently, a larger margin of error has been allowed in the results of this experiment. The spread of results

TABLE 1.

		Wt. (mg.) of terphenyl from 2 g. of benzoyl peroxide		
Expt. no.	Marker compd.	*o*-	*m*-	*p*-
1	Phenanthrene	7·5 ± 2	4·5 ± 2	7 ± 2
2	Anthracene	8·7 ± 1·5	4·7 ± 1·5	7·2 ± 1·5
	Calcd. yields *	~11	~5	~7

* For these reaction conditions and with the assumptions mentioned above.

---

[12] Nay, Eichoff, Herrmann, and Wirth, *Z. Elektrochem.*, 1960, **64**, 1098.

[13] Augood, Hey, and Williams, *J.*, 1952, 2094.

[14] Vogel, " Practical Organic Chemistry," 3rd edn., Longmans, London, 1956, pp. 807 and 808.

[15] Wieland, Schapiro, and Metzger, *Annalen*, 1934, **513**, 93.

[16] Jackman, see ref. 8, p. 359.

[17] Pfeiffer, *Annalen*, 1916, **412**, 294.

[18] Rocklin, U.S.P. 2,920,082.

[19] Bowden, *J.*, 1931, 1111.

[20] Hey, Perkins, and Williams, *J.*, 1961, 748.

noted above for different analyses on the same reaction mixture suggests a maximum error of ±10% on the measured values for each isomer. More generous allowance than this has been made, in view of the poor base-line stability, the effect of which was not readily estimated.

The Reaction of Benzoyl Peroxide with Chlorobenzene.—In expt. 3, benzoyl peroxide (12 g.) was dissolved in cold chlorobenzene (400 ml.) which had been dried by azeotropic distillation, and oxygen-free nitrogen passed for 40 min. through the cold solution and then through two wash-bottles containing, respectively, distilled water and dilute aqueous sodium hydroxide. The solution was then heated rapidly to 80° and maintained at this temperature (thermostat) for 72 hr., with slow passage of nitrogen. A solution of potassium hydroxide (12 g.) in " AnalaR " ethanol (100 ml.) was added to the yellow mixture, which was then heated at 80° for a further 18 hr. to hydrolyse phenolic esters, and then cooled, and water (300 ml.) added to dissolve the inorganic precipitates. The whole apparatus was washed with some of this water to collect any hydrogen chloride which might have been carried from the solution by the gas stream, but which had not reached the wash-bottles. The mixture was filtered through hardened paper to remove *pp'*-quaterphenyl (0·68 g.; m. p. 315—319°, and mixed m. p. 317—319°). After separation, the organic layer was washed with 1N-sodium hydroxide (2 × 60 ml.) and then with water (2 × 60 ml.). A further aqueous washing, on acidification with nitric acid, gave no reaction with silver nitrate solution. The washings and the original aqueous layer were combined and extracted with chlorobenzene (2 × 30 ml.), which was itself then washed with water (2 × 50 ml.). All the organic solutions were combined and dried ($CaCl_2$). The aqueous solutions were combined and made faintly acid with dilute nitric acid which had been freed from oxides of nitrogen by boiling. The volume was made up to 1 l. with water and the chloride content (0·795 g. as hydrogen chloride) estimated by Volhard's method. The same procedure was employed to estimate the chloride content (0·055 g. as hydrogen chloride) of the solution from the first wash-bottle. It was confirmed that a negligible amount of hydrogen chloride in a stream of nitrogen penetrated to the second wash-bottle. In a second control experiment, chlorobenzene (40 ml.) was heated at 80° for 18 hr. with potassium hydroxide (1·2 g.) in ethanol (10 ml.). The mixture was extracted in a manner similar to that described above, and the aqueous extract was shown not to contain chloride ions. It was, therefore, concluded that hydrolysis of chlorobenzene could be neglected under the conditions of the reaction.

The dried chlorobenzene solution was freed from the excess of solvent by distillation through a 30-cm. column, and the residual liquid (approx. 30 ml.) was transferred to a pear-shaped distillation flask, which had been packed with glass wool, and weighed. The remaining solvent was distilled off at reduced pressure (15 mm.) through a short vacuum-jacketed column, and the distillate redistilled under similar conditions until the residual volume was about 2 ml. This was shown by gas–liquid chromatography to contain a little (0·01 ± 0·005 g.) biphenyl, and a trace of 2-chlorobiphenyl. A fraction was then distilled from the main reaction mixture at 70—90°/0·05 mm. (4·081 g.) (the " biaryl fraction "). Gas–liquid chromatography of this fraction revealed the presence of about 10% of biphenyl. The undistilled residue (6·464 g.) was removed from the distillation flask by repeated extraction with hot benzene, and the benzene distilled off, the last traces being removed at 70° for 24 hr. A portion was removed for analysis (Found: C, 81·5; H, 5·5; Cl, 12·0%) and the remainder (5·01 g.) returned to the distillation flask and distilled. A viscous yellow oil (1·38 g.) distilled predominantly at 205—215°/0·05 mm., and its infrared spectrum was recorded. In addition to other absorptions, the spectrum showed broad maxima which included all the characteristic absorptions of *op'*-quaterphenyl. Before this chromatography, the fraction had been dissolved in benzene and in benzene–light petroleum (b. p. 40—60°). From the first of these solvents *pp'*-quaterphenyl (30 mg.) separated, and a little oil remained undissolved in the second. On cooling, this oil set to a paste (150 mg.), which was crystallised from acetone–light petroleum (b. p. 40—60°), giving a monochloroquaterphenyl as plates, m. p. 163—165° (30 mg.) (Found: C, 84·3; H, 5·1; Cl, 10·9. Calc. for $C_{24}H_{17}Cl$: C, 84·6; H, 5·0; Cl, 10·4%). Chromatography of the mother-liquors on alumina gave only gums. The results are summarised in Table 2.

In another experiment (4) the procedure was similar to that of expt. 3, except that the chlorobenzene was distilled from the mixture at reduced pressure (b. p. approx. 50°/30 mm.) in such a way that the temperature of the heating bath never rose above 75°. The last traces of chlorobenzene were finally removed during ½ hr. at 1 mm., with the oil-bath temperature at approximately 60°. During the distillation of the chlorobenzene, a trap containing moist

TABLE 2.

Composition of products of reaction of benzoyl peroxide with chlorobenzene (Expt. 3.).

	C (g.)	H (g.)	Cl (g.)
Residue (6·464 g.)	5·27	0·356	0·775
pp′-Quaterphenyl (0·68 g.)	0·64	0·040	—
Biphenyl (calc. as 10% of biaryl fraction) (0·4 g.)	0·37	0·026	—
Hydrogen chloride (0·85 g.)	—	0·023	0·825
Totals (g.)	6·24	0·445	1·60
As % of total weight	75·3	5·4	19·3
Calc. for dichlorotetrahydroquaterphenyl ($C_{24}H_{20}Cl_2$) (%)	76·0	5·3	18·7

sodium hydroxide was included between the condenser and the vacuum pump. After distillation, the contents of this trap did not contain chloride ions. The residue, which contained the biaryl fraction in addition to the substance regarded as residue in expt. 3, was weighed and analysed. For the purpose of calculation this combined residue was assumed, on the basis of the yields obtained in expt. 3, to contain 35% by weight of biaryl. The exact value of the biaryl content of this material has, however, little influence on the result, owing to the almost identical elementary compositions of chlorobiphenyls and tetrahydrodichloroquaterphenyls. In this experiment the solution of hydrogen chloride from the first wash-bottle was used to extract inorganic chloride formed in the hydrolysis stage. The total chloride liberated during both the reaction and the hydrolysis was therefore estimated in a single analysis. The results of this experiment are summarised in Table 3.

TABLE 3.

	C (g.)	H (g.)	Cl (g.)
Residue + biaryls (10·394 g.)	8·33	0·591	1·47
pp′-Quaterphenyl (0·798 g.)	0·75	0·047	—
Hydrogen chloride (0·865 g.)	—	0·024	0·84
Total (g.)	9·08	0·662	2·31
As % of total weight	75·3	5·5	19·2
Calc. for mixture containing 65% of $C_{24}H_{20}Cl_2$ and 35% of $C_{12}H_9Cl$ (%)	76·2	5·1	18·7

After a portion of the residue from this experiment had been removed for analysis, the remainder was slowly heated, and a stream of nitrogen bubbled through it and then into aqueous silver nitrate. The temperature of the residue reached 170° before the silver nitrate solution showed any turbidity, and evolution of hydrogen chloride from the residue was only slight below 200°. As the products of expt. 3 had not been heated above 150—160°, the analytical figures obtained in that experiment appear to be acceptable.

Rearrangement of op′-*Quaterphenyl*.—Benzene was dried by azeotropic distillation, shaken for 3 hr. with anhydrous aluminium chloride, and distilled. A mixture of dry benzene (100 ml.), *op*′-quaterphenyl (360 mg.), and anhydrous aluminium chloride (~30 mg.) was boiled for 5 hr. The violet solution was cooled and filtered, and the residue washed with dilute aqueous ethanolic hydrochloric acid to remove the aluminium chloride, leaving *pp*′-quaterphenyl (45 mg.; m. p. 300—310°), which was characterised by its infrared spectrum (Nujol mull). The filtrate was concentrated and then diluted with methanol; the resulting solution, on cooling, deposited crystals, m. p. 165—169° (255 mg.). Recrystallization from benzene-methanol gave *mp*′-quaterphenyl, m. p. 169—170° (Found: C, 94·0; H, 6·0. Calc. for $C_{24}H_{18}$: C, 94·1; H, 5·9%). The infrared spectrum of a Nujol mull showed absorptions attributable to both *meta*- and *para*-disubstituted benzene rings. Woods and Tucker [21] give m. p. 166° for *mp*′-quaterphenyl and, by a method similar to the above, Copeland, Dean, and McNeil [22] rearranged *oo*′-quaterphenyl to a mixture of *mm*′-quaterphenyl, *pp*′-quaterphenyl, and a compound (m. p. 168°) which they also consider to be *mp*′-quaterphenyl. Further evidence that the compound obtained was *mp*′-quaterphenyl was obtained from its rearrangement to *pp*′-quaterphenyl. *mp*′-Quaterphenyl (100 mg.) in dry benzene (50 ml.) was heated under reflux with anhydrous aluminium chloride (100 mg.) for 50 hr.; *pp*′-quaterphenyl was obtained in low yield (10 mg.; m. p. 300—310°; characterised by its infrared spectrum in a Nujol mull).

---

[21] Woods and Tucker, *J. Amer. Chem. Soc.*, 1948, **70**, 3340.

[22] Copeland, Dean, and McNeil, *J.*, 1960, 4522.

Isolation of Isomeric Quaterphenyls from the Reaction of Benzoyl Peroxide with Benzene.—A solution of benzoyl peroxide (20 g.) in benzene (4 l.) was boiled under reflux in a stream of nitrogen for 30 hr. The volume of the solution was reduced to 1·5 l. by distillation, *o*-chloranil (31 g.) added, and the solution boiled under reflux for 24 hr. and cooled. *pp'*-Quaterphenyl (4·05 g.) separated in plates, m. p. and mixed m. p. 318—320°. Tetralin (4·584 g.) was added and the solution boiled under reflux for 3 hr. to convert any unchanged *o*-chloranil into tetrachlorocatechol. The volume was then reduced to 300 ml. by further distillation. On cooling, more *pp'*-quaterphenyl (0·165 g.) separated and was removed by filtration. The filtrate was shaken with 2N-sodium hydroxide (200 ml.), and the black solid so formed was filtered off and discarded. The organic portion of the filtrate was separated and shaken again with 2N-sodium hydroxide (2 × 50 ml.) and with water (2 × 100 ml.). The combined aqueous extracts were washed with benzene (100 ml.). The washings were extracted with water (2 × 50 ml.), and all the benzene solutions were combined and dried ($CaCl_2$). Benzene was distilled from the dried solution through a 30-cm. helix-packed column until the residual volume was about 35 ml. The remaining benzene was removed by distillation at atmospheric pressure through a short vacuum-jacketed column. The pressure was then reduced and the following distillation fractions taken: (i) b. p. 80—125°/15 mm. (7·90 g.), (ii) b. p. 125—135°/15 mm. (3·56 g.), (iii) b. p. 70—105°/0·05 mm. (1·52 g.), (iv) b. p. 105—170°/0·05 mm. (1·46 g.), (v) b. p. 170—230°/0·05 mm. (5·36 g.), and residue (5·36 g.). The column was replaced by a simple distillation head between fractions (i) and (ii). Fraction (iv) gave crystals of *op'*-quaterphenyl (0·053 g.; m. p. and mixed m. p. 118—120°) on treatment with aqueous methanol. The solvent was removed from the mother-liquors and the residue, after combination with fraction (iii), was redistilled. This gave the following fractions: (*a*) b. p. 130—145°/20 mm. (1·68 g.), (*b*) b. p. 100—150°/0·05 mm. (1·03 g.), and residue (0·12 g.). Fraction (i) was shown, by gas–liquid chromatography, to consist of biphenyl, tetralin, and a little naphthalene. Fractions (ii) and (*a*) were predominantly biphenyl. Fraction (*b*) was dissolved in a little hot benzene, and the solution diluted with light petroleum (b. p. 40—60°), and cooled in the refrigerator, whereupon crystals of tetrachlorocatechol separated (m. p. 194°; lit. m. p. 194—195°). Concentration of the mother-liquors, followed by chromatography on alumina and crystallisation from ethanol, gave phenyl benzoate (0·45 g.; m. p. and mixed m. p. 69—70°). Fraction (v), a yellow glass, was dissolved in the minimum of boiling 5 : 1 benzene–light petroleum (b. p. 60—80°), and the hot solution freed from *pp'*-quaterphenyl (0·057 g.) by filtration. On cooling, a solid (2·313 g.) was deposited, which consisted of colourless prisms mixed with clusters of orange needles. A portion of the latter was separated mechanically and shown to be tetrachlorocatechol. The remaining tetrachlorocatechol was removed by ethanol, and the colourless solid (1·857 g.) was then identified as *op'*-quaterphenyl (m. p. and mixed m. p. 119—120°); the infrared spectrum of this compound was identical with that of an authentic specimen. Concentration of the original mother-liquors in methanol gave a second crop (0·980 g.) of this compound, m. p. 116—119°. Attempted further concentration gave no solid products, and removal of the solvent gave a brown oil (1·945 g.) which was separated into three main fractions, and some unidentified tar, by chromatography on alumina and elution with 1 : 4 benzene–light petroleum (b. p. 60—80°). The first fraction crystallised from methanol, giving *oo'*-quaterphenyl (0·168 g.; m. p. and mixed m. p. 116—118°); the infrared spectrum of this compound was identical with that of an authentic specimen. Examination of the infrared spectrum of the second fraction (0·384 g.) suggested that it was largely *op'*-quaterphenyl, but crystalline material could not be obtained. Repeated crystallisation of the third fraction from methanol gave *mp'*-quaterphenyl (0·028 g.; m. p. and mixed m. p. 169—171°). The infrared spectrum of this compound was identical with that of a specimen obtained by the rearrangement of *op'*-quaterphenyl with aluminium chloride. The infrared spectra of later fractions showed broad absorption maxima characteristic of complex mixtures.

Synthesis of Quaterphenyls.—(a) 4,4'- *and* 2,4'-*Di*-m-*tolylbiphenyl.* Di-*m*-toluyl peroxide (22·3 g.) was allowed to decompose in refluxing " AnalaR " benzene (4 l.) for 30 hr. The mixture was then dehydrogenated with *o*-chloranil and worked up as described above. After dehydrogenation, most of the solvent was removed by distillation, and, on cooling, 4,4'-di-*m*-tolylbiphenyl (3,3'''-dimethyl-1,1' : 4',1'' : 4'',1'''-quaterphenyl) separated in plates (4·2 g.), m. p. 214—215° (from benzene) (lit. m. p.[23] 214—215°) (Found: C, 93·6; H. 6·6. Calc. for $C_{26}H_{22}$: C, 93·4;

---

[23] Gilman and Weipert, *J. Amer. Chem. Soc.*, 1957, **79**, 2281.

H, 6·6%). The fraction (4·72 g.) of the neutral product which distilled in the range 180—250°/0·05 mm. was dissolved in light petroleum (b. p. 60—80°) and chromatographed on alumina. Elution with the same solvent, followed by distillation of the solvent from the eluate, gave a glass (3·08 g.), which softened at about 40° and which could not be crystallised. It had an ultraviolet absorption spectrum similar to that of *op'*-quaterphenyl [absorption in ethanol (based on *M*, 334): $\lambda_{\max}$ 249 mμ (ε $2{\cdot}76 \times 10^4$), and a broad band at $\lambda_{\max}$ approx. 273 mμ (ε $2{\cdot}15 \times 10^4$). *op'*-Quaterphenyl has $\lambda_{\max}$ 249 mμ (ε $2{\cdot}72 \times 10^4$), and approx. 277 mμ (ε $2{\cdot}33 \times 10^4$)], and its infrared spectrum supported the view that it was predominantly 2,4'-*di*-m-*tolylbiphenyl* (3,3'''-*dimethyl*-1,1' : 2',1'' : 4'',1'''-*quaterphenyl*). After some months this glassy product slowly crystallised. It was recrystallised to constant m. p. (89—90°) from ethanol (Found: C, 93·6; H, 6·5. $C_{26}H_{22}$ requires C, 93·4; H, 6·6%).

(b) *Other* 4,4'-*Diarylbiphenyls*. A solution of the appropriate diaroyl peroxide (1 g.) in " AnalaR " benzene (200 ml.) was boiled under reflux for 40 hr. *o*-Chloranil (1·5 g.) was then added, and the solution boiled under reflux for a further 15 hr. Most of the solvent was distilled off and the residual solution cooled, when the diarylbiphenyl separated. All the compounds showed strong infrared absorption in the 12—12·4 μ region, characteristic of *p*-disubstituted benzene rings. The details of the syntheses are given in Table 4.

Compound (V) was crystallised to constant m. p. from ethanol. Compounds (IV), (VI), and (VII) were washed with ethanol, but not further purified. A portion of compound (VIII) was crystallised from a large volume of benzene before analysis. Compound (IX), which was obtained from 1 g. of peroxide in 400 ml. of benzene, started to separate from the boiling solution as soon as *o*-chloranil was added. It was not further purified.

Reaction of Benzoyl o-*Chlorobenzoyl Peroxide with Benzene*.—A solution of the peroxide (4 g.) in benzene (800 ml.) was boiled under reflux for 40 hr. *o*-Chloranil (6 g.) was added and the solution was boiled under reflux for a further 24 hr. Benzene was then distilled from the solution until the residual volume was 150 ml. On cooling, *pp'*-quaterphenyl (0·15 g., m. p. and mixed m. p. 314—318°; infrared spectrum identical with that of an authentic specimen) separated. Concentration of the remaining solution to about 25 ml. and treatment with methanol precipitated a solid (0·32 g.; m. p. 175—179°), which was crystallised to constant m. p. (183—185°) from benzene–methanol. The infrared spectrum of this compound again showed an absorption maximum due to a *p*-disubstituted benzene, and it was formulated as 2-*chloro*-1,1' : 4',1'' : 4'',1'''-*quaterphenyl* (Found: C, 84·6; H, 5·15. $C_{24}H_{17}Cl$ requires C, 84·6; H, 5·05%). Further concentration of the original mother-liquor, and treatment with methanol, gave a gum from which a trace (~30 mg.) of 2,2'''-dichloro-1,1' : 4',1'' : 4'',1'''-quaterphenyl (m. p. 164—165°) identical (m. p., mixed m. p., and infrared spectrum) with the specimen obtained from the reaction of bis-*o*-chlorobenzoyl peroxide with benzene, was isolated.

TABLE 4.

Peroxide	Product	Yield (g.)	M. p.	Found (%) C	Found (%) H	Required (%) C	Required (%) H
$(m\text{-BrC}_6\text{H}_4\cdot\text{CO}_2)_2$	3,3'''-*Dibromo*-1,1' : 4'1'' : 4'',1'''-*quaterphenyl* (plates) (IV)	0·12	236—237°	62·6	3·8	62·1	3·5
$(o\text{-ClC}_6\text{H}_4\cdot\text{CO}_2)_2$	2,2'''-*Dichloro*-1,1' : 4',1'' : 4'',1'''-*quaterphenyl* (needles) (V)	0·256	164—165	76·75	4·4	76·85	4·3
$(m\text{-ClC}_6\text{H}_4\cdot\text{CO}_2)_2$	3,3'''-*Dichloro*-1,1' : 4',1'' : 4'',1'''-*quaterphenyl* (plates) (VI)	0·206	224—225	76·9	4·5	76·85	4·3
$(p\text{-ClC}_6\text{H}_4\cdot\text{CO}_2)_2$	4,4'''-Dichloro-1,1' : 4',1'' : 4'',1'''-quaterphenyl (plates) (VII)	0·175	340—342 *	77·15	4·45	76·85	4·3
$(\beta\text{-C}_{10}\text{H}_7\cdot\text{CO}_2)_2$	4,4'-*Di-2-naphthylbiphenyl* (pale yellow plates) (VIII)	0·120	336—338	94·4	5·8	94·5	5·5
$(p\text{-PhC}_6\text{H}_4\cdot\text{CO}_2)_2$	*p*-Sexiphenyl (pale yellow powder) (IX)	0·227	>400 †	93·55	5·75	94·3	5·7

* Pausacker, *Austral. J. Chem.*, 1957, **10**, 49, records m. p. 334°. † Pummerer and Bittner, *Ber.*, 1924, **57**, 84, record m. p. 475°.

M. J. P. thanks the Department of Scientific and Industrial Research for the award of a Studentship during the tenure of which part of this work was carried out.

DEPARTMENT OF CHEMISTRY, KING'S COLLEGE (UNIVERSITY OF LONDON),
STRAND, LONDON W.C.2.

[*Received, December* 29*th*, 1962.]