A Quantitative Product Study and a Critical Evaluation of the Thermal Decomposition of Benzoyl Peroxide in Benzene[1–3]

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Abstract: The thermal decomposition of benzoyl peroxide in benzene constitutes a prototype reaction for the production of aryl radicals and for the arylation of aromatic rings. A detailed quantitative study has been made of the products formed. Present results have been combined with values reported by others to give a definitive account of product distribution as a function of initial peroxide concentration.

The thermal decomposition of benzoyl peroxide in benzene has long been an important source of benzoyloxy and phenyl free radicals.[4] The reactions occurring in benzene have served as a primary example of the free-radical arylation reaction.[5,6] Although the reaction products have been studied since the 1920's,[7] several major products were identified only rather recently.[3] The over-all reaction in dilute solution is summarized in eq 1.

$$(C_6H_5COO)_2 + C_6H_6 \longrightarrow CO_2 + C_6H_5COOH + C_6H_5C_6H_5 + C_6H_5C_6H_7 + C_6H_5C_6H_6C_6H_6C_6H_5 + C_6H_5COOC_6H_5 + \text{other products} \quad (1)$$

The present paper summarizes our extensive series of investigations of the products of the reaction, both quantitative and qualitative. The discussion is based primarily on our observations, but these are correlated with the extensive work reported by others. An attempt has been made to give as complete a description of the reaction as possible. The following paper considers in more detail the problems of mechanisms.[10]

Quantitative analysis of these reaction mixtures is quite difficult. The products are labile; the mixture is complex in solutions of moderate initial peroxide concentration and dilution brings other problems: a 0.01 M solution starts with 2.4 g of peroxide/l. Quantitative recovery of even CO_2 and of benzoic acid requires careful technique. It is not surprising that the analyses show considerable scatter. Our best results are summarized in Table IV in the Experimental Section. These have been combined with other values of ours from somewhat fragmentary experiments and with the best values from the literature.[6,11–13] Some data on tetrahydroquaterphenyls[11] have been omitted because results of the dehydrogenation procedure cannot be interpreted quantitatively. These combined data are summarized in Figures 1 and 2 and smoothed values are presented in Table I. The curve for phenyl benzoate has been omitted since it is very flat. The solid lines in the figures represent values calculated from the semitheoretical data in part II.[10]

The reactions under consideration have all been run in the absence of oxygen. In the present work the reaction solvents were swept under reflux with high-purity nitrogen before peroxide was introduced. In the presence of oxygen, the yield of biphenyl is somewhat larger.[12] As discussed later[10] there are theoretical reasons to believe that the observed diphydrobiphenyl yields are somewhat low and the biphenyl yields are high (Table IV). This might be due to incomplete removal of oxygen. The analysis is believed to be correct since it was done by gas phase chromatography (gpc) on unhydrogenated reaction mixtures in direct comparison with standards. Disproportionation occurs on hydrogenation,[14] so that phenylcyclohexane yield underestimates the dihydrobiphenyl although the sum of dihydrobiphenyl plus biphenyl presumably corresponds to the sum of the phenylcyclohexane plus biphenyl present after hydrogenation.

The material balance for CO_2 and phenyl fragments based on the listed products is reported in the last two columns of Table I. The remaining fragments are to be found among the "other products" consisting mostly of nonvolatile residues, but it is probable that some of the phenyl radicals abstract allylic hydrogen atoms from products to produce benzene as discussed later.

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(2) With the technical assistance of Mr. E. Heimer.

(3) A portion of the material was reported at the 17th National Organic Symposium at Bloomington, Ind., June 1961. A preliminary report of this has appeared: D. F. DeTar and R. A. J. Long, *J. Am. Chem. Soc.*, **80**, 4742 (1958).

(4) First established by W. S. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934); D. H. Hey, *ibid.*, 1966 (1934); D. H. Hey and W. A. Waters, *Chem. Rev.*, **3**, 169 (1937).

(5) For reviews see: (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 474; (b) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p 72; (c) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press Ltd., London, 1960.

(6) For a recent study see G. B. Gill and G. H. Williams, *J. Chem. Soc.*, 995, 7127 (1965); W. R. Foster and G. H. Williams, *ibid.*, 2862 (1962).

(7) Benzoyl peroxide was first prepared in 1864[8] but was first extensively studied by Gelissen and Hermans.[9]

(8) C. Brodie, *J. Chem. Soc.*, **17**, 266 (1864).

(9) (a) H. Gelissen and P. H. Hermans, *Ber.*, **58**, 285 (1925); (b) *ibid.*, **58**, 476 (1925).

(10) D. F. DeTar, *J. Am. Chem. Soc.*, **89**, 4058 (1967).

(11) D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.*, 5604 (1963); 3412 (1964).

(12) (a) M. Eberhardt and E. L. Eliel, *J. Org. Chem.*, **27**, 2289 (1962); (b) E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Am. Chem. Soc.*, **82**, 2936 (1960).

(13) (a) B. Barnett and W. E. Vaughan, *J. Phys. Chem.*, **51**, 926 (1947); (b) *ibid.*, **51**, 942 (1947).

(14) E. A. Braude and R. P. Linstead, *J. Chem. Soc.*, 3544 (1954); E. A. Braude, R. P. Linstead, and P. W. D. Mitchell, *ibid.*, 3578 (1954).

Table I. Smoothed Product Yields from Thermal Decomposition of Benzoyl Peroxide in Benzene

Initial $(C_6H_5COO)_2$, *M*	Products[a]						Peroxide fragments[b]	
	CO_2	C_6H_5-COOH	Biphenyl	$C_{12}H_{12}$[c]	$C_{24}H_{16}$[d]	Phenyl benzoate	% CO_2	% phenyl
0.001	192	5.0			70	4.1	100.5	...
0.002	189	5.5	40	28	65	3.9	99.5	104
0.005	184	6.0	39	23	58	3.7	97.0	94
0.010	178	8.0	38	18	51	3.5	95.0	81
0.020	171	12.0	37	14	43	3.3	93.0	76
0.050	159	20.0	36	6	32	3.1	91.0	65
0.100	150	28.0	36	5	19	2.9	90.5	55
0.200	140	35.0	35	3	9	2.7	89.0	47
0.500	125	44.0	34	1	2	2.5	86.0	43.0
Error[e]	±3[f]	±10%[g]	±10%[g]	±15%[g]	±2[f]	±0.3[f]		

[a] Entries are mole % (100 × moles of product/mole of peroxide). Values were taken from the original graphs of Figures 1 and 2. [b] Per cent of peroxide fragments accounted for by products listed. Careful gravimetric evaluation of total reaction residues invariably showed an increasing discrepancy in phenyl groups accounted for as the peroxide concentration increased. Tentatively this is considered to be due to formation of benzene from hydrogen atom abstraction from initial products by phenyl radicals. The amount of benzene may be from 10 to 20 mole % for 0.2 *M* peroxide. [c] Dihydrobiphenyl. These yields may be too low and the biphenyl yields correspondingly high. See text. [d] Tetrahydroquaterphenyls. [e] Estimate of standard deviation for the smoothed average value. [f] Scalar error. [g] Relative error.

Further product information is presented in Table II. From reactions in very concentrated solutions in toluene and in chlorobenzene *p*-phenylbenzoic acid has been isolated;[9b,15] however, in 0.3 *M* solutions in benzene the amount formed is small. Our estimate is based on determinations of the neutral equivalents of several samples of isolated benzoic acid. The low neutral equivalents also exclude RC_6H_4COOH where R is a complex cyclohexyl group of the types described elsewhere.[10] Such a product would be analogous to the cyclohexylbenzoic acids formed in cyclohexane,[16,17] and its absence is remarkable. *p*-Quaterphenyl is highly insoluble and separates from reactions 0.2 *M* or even less, but the amount is small. Presumably the corresponding *o,p'*-quaterphenyl is also formed but remains in solution. Hexahydroquaterphenyls are present upon reductive work-up and emerge after the corresponding dodecahydroquaterphenyls upon gas chromatography. Dihydroquaterphenyls are expected products intermediate between tetrahydroquarterphenyls and quaterphenyls but the hexahydroquaterphenyls may also arise from disproportionation upon the catalyst.[14]

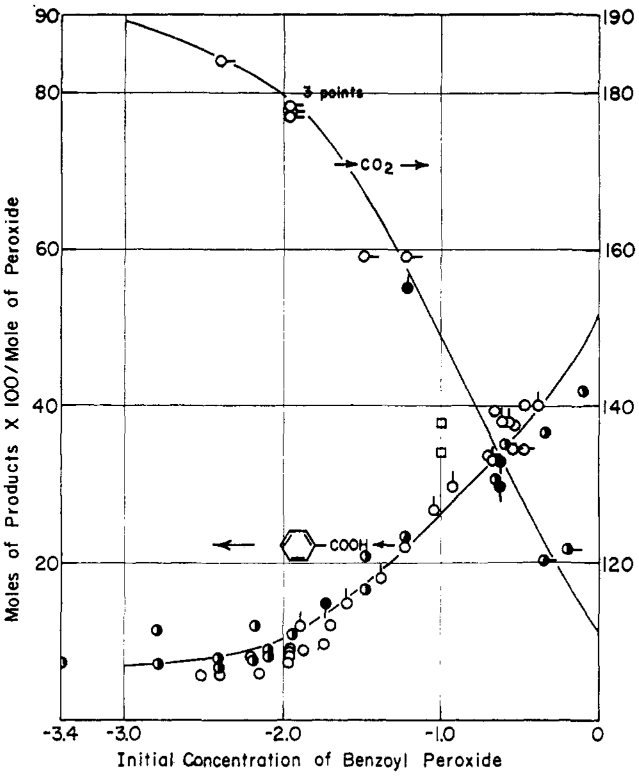

Figure 1. Yield of CO_2 (right-hand scale) and of benzoic acid (left-hand scale) as a function of peroxide concentration (logarithmic scale): ○-, Table IV, CO_2; ○, Table IV, benzoic acid; ◑-, ◑, present work, fragmentary; ȯ, ref 11; ●̍, ref 13; ●̩, ref 15; □, ref 17. Solid lines represent yields predicted by the mechanism in ref 10.

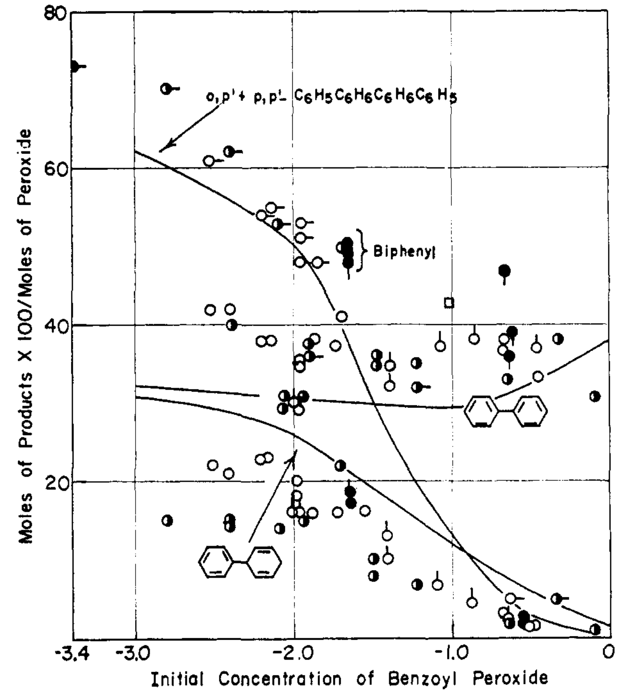

Figure 2. Yield of total tetrahydroquaterphenyls, biphenyl, and dihydrobiphenyls. Points and lines as for Figure 1.

Evidence for the structure of the 1,4-dihydrobiphenyl should be mentioned briefly. An analytical sample was isolated and compared directly with an authentic specimen.[18,19] The ultraviolet absorption in the 260-mμ region (ε 500) is similar to that of 3-phenylcyclo-

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(15) D. I. Davies, D. H. Hey, and G. H. Willams, *J. Chem. Soc.*, 562 (1961).

(16) P. H. Hermans and J. Van Eyk, *J. Polmer Sci.*, 1, 407 (1946).

(17) C. Walling and E. S. Savas, *J. Am. Chem. Soc.*, **82**, 1738 (1960).

(18) A. Rader, M. S. Thesis, University of South Carolina, 1961.

(19) W. Hückel and R. Schwen, *Chem. Ber.*, **89**, 150 (1956).

Table II. Further Products of the Thermal Decomposition of Benzoyl Peroxide in Benzene

$C_6H_5C_6H_4COOH$	$<$1 mole % at 0.2 *M* Bz_2O_2
p-Quaterphenyl[b]	~1 mole % at 0.2*M*
Terphenyl fraction	~1 mole % at 0.2 *M*
$C_6H_5C_6H_5C_6H_6C_6H_5$	About 56% *p,p′*, 42% *o,p′*, 2.5% *o,o′* at 0.01 *M*
$C_6H_5C_6H_7$	$<$10% 1,2-dihydrobiphenyl
Ester	~1 mole % C_{19} ester in 0.01 *M* reaction
Residue	Average formula: $(C_6H_6)_6(C_6H_5\text{-}COOH)_2$[a] (80%) + $(C_6H_6)_7C_6H_5\text{-}COOH$ (20%)

[a] As an approximation this is made up of three phenylcyclohexadienyl residues plus two benozic acid residues plus or minus a hydrogen atom. [b] 11% of the total quaterphenyl fraction was isolated as a crystalline isomer of *p,p′*-tetrahydroquaterphenyl.

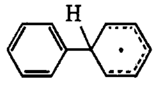
hexene in ethanol: 248 mμ (ε 230), 254 (280), 255 (287), 260 (308), 262 (333), 265 (241), and 268 (265) and of 4-phenylcyclohexene in ethanol: 247 mμ (ε 130), 253 (185), 255 (185), 259 (220), 261 (230), 214 (170), and 268 (190). Conjugated 1-phenylcyclohexene has a maximum at 247 mμ (ε 12,000).[18,20] It is possible that a small amount of 1,2-dihydrobiphenyl is also one of the products.

The evidence for the 1,4,1′,4′-tetrahydro-*p*-quaterphenyl[21] (**2**) is based on isolation of a crystalline isomer with the correct analysis, which can be dehydrogenated to quaterphenyl (plus biphenyl from disproportionation) and which absorbs 4 moles of hydrogen to give a dodecahydroquaterphenyl. The ultraviolet spectra show that the double bonds are not conjugated with each other nor with the aromatic rings; **2** is the only possible structure, but there are six possible stereoisomers. The *cis-syn-cis* isomer is the flatest, and perhaps the least soluble. This structure may be tentatively assigned.

The major portion of the tetrahydroquaterphenyl fraction was an oily residue. No other isomers were obtainable in pure form. Dehydrogenation gave small amounts of *o,p′*-quaterphenyl along with *p,p′*-quaterphenyl showing the presence of the *o,p′* isomer. The hydrogenated material (dodecahydroquaterphenyls, various fractions having the correct analysis) gave two major rather broad peaks on gpc and two minor ones (see Figure 4). Samples of *o,o′*-quaterphenyl and of *o,p′*-quaterphenyl had retention times similar to those of one of the minor peaks (7 min) and to the first of the large peaks (14 min). The dodecahydroquaterphenyls from hydrogenation of crystalline *p,p′*-tetrahydroquaterphenyl had an emergence time of 22 min, corresponding to the second large peak. There is also a miscellany of other data, including infrared and nmr spectra which are consistent with assigning the tetrahydroquaterphenyl structure to the mixture. The second small peak at about 7 min is an ester, and the retention time indicates the presence of one benzoate and two phenyl residues (**10**).

Tetrahydroquaterphenyls disproportionate at about 170° (gpc) into biphenyl and dihydrobiphenyl, the former predominating. Treatment with Pd, with tetrachloro-*o*-benzoquinone, or with other dehydrogenating agents also causes disproportionation.[3,11] We therefore hydrogenated the reaction mixtures at an appropriate stage and analyzed for the resulting dodecahydroquaterphenyls. Hexahydroquaterphenyls that may be formed during hydrogenation[14] emerge with about the same retention time and do not disturb the results.

Relative yields of the tetrahydroquaterphenyl isomers are given in Tables II and V. The tetrahydroquaterphenyls (*e.g.*, **2**) result from coupling of phenylcyclohexadienyl radicals (**1**) at the *ortho* and *para* positions, and the ratio found apparently reflects a sensitivity of the coupling process to steric factors. In these complex systems one must always consider the possible effect of differing susceptibilities of initially formed products to further attack. However, in the dilute solutions used there was relatively little loss to materials of higher molecular weight and the product ratios are expected to represent the formation ratios reasonably well.



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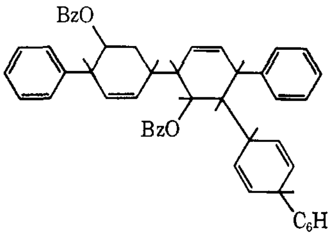
The "terphenyl" fraction is nearly undetectable with 0.01 *M* peroxide, but we have observed a peak (gpc) with 0.2 *M* peroxide and find the absolute and relative yields agree closely with those reported by Hey, *et al.*:[11] 0.55 *ortho*, 0.12 *meta*, and 0.32 *para* in moles of product × 100/moles of peroxide. These materials have not been isolated, however, and other C_{18} hydrocarbons are theoretically possible (*e.g.*, by addition of phenyl radicals to 1,4-dihydrobiphenyl) and could perhaps be confused with the terphenyls. However, the mechanism presented later suggests that most of the C_{18} fraction should arise from phenylation of biphenyl.[10]

We have made a careful examination of the nonvolatile residue to provide partial characterization. It is expected to be a complex mixture. Two important results emerged; the residue consists largely of ester molecules, and there is very little material with an average molecular weight in excess of about 800. From runs in 0.2 *M* peroxide the over-all average molecular weight was 705, and there were about 1.8 benzoate groups per molecule. We believe that these products arise primarily from addition of benzoyloxy



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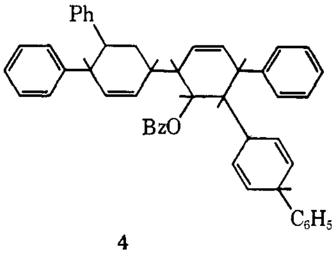

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(20) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy in Organic Chemistry," 2nd ed, Edward Arnold, Ltd., London, 1958, p 97.

(21) The unsubstituted tetrahydroquaterphenyl is indexed in *Chemica Abstracts* as bi-2,5-cyclohexadien-1-yl, 4,4′-diphenyl-. The quaterphenyl-derived names are used in this paper for the sake of clarity.

and to a lesser extent of phenyl radicals to the olefinic double bonds and that the resulting alkyl radicals either abstract hydrogen atoms from allylic hydrogen sites or combine or disproportionate with the dominant phenylcyclohexadienyl radical (**1**). Representative possible structures are shown as **3** and **4**, and purely for purposes of calculation it has been assumed that the residue may be approximated as a mixture of 80% **3** and 20% **4** (average molecular weight 701, 1.8 benzoate groups). The situation is dealt with later.[10]

Nmr spectra of these ester fractions were broad as might be expected for mixtures. It was possible to estimate roughly the ratios of aryl (390–485 cps at 60 Mc), vinyl (300–390), and alkyl (50–240) hydrogen atoms. The ratios calculated for the mixture of **3** and **4** are 57:18:25 and the average ratios observed were 63:13:24.

Two further tests of the consistency of the assigned product yields are summarized in Table III. They are based on the amount of hydrogen required to saturate the double bonds and on the total weight of products, or more particularly the weight of everything except the CO_2 and the benzoic acid, which were stripped from the solution. For computing material balances the averaged product yields of Table I were used and the residue was assumed to have the composition mentioned above. It was further assumed that the number of moles of residue could be estimated from the CO_2 deficit. In 0.01 *M* peroxide 95% of the CO_2 is accounted for; the deficit is therefore 0.1 mole/mole of peroxide. Since each "mole" of residue has 1.8 CO_2 groups, there must be 0.055 mole of residue/mole of peroxide. These contain on the average 4–5 double bonds and hence contribute 0.22–0.27 mole of unsaturation/mole of peroxide.

Table III. Material Balance and Unsaturation Balance for Products of Decomposition of Benzoyl Peroxide in Benzene

	Initial peroxide concn, *M*			
	0.01		0.2	
Product	Wt[a]	Unsat[b]	Wt[a]	Unsat[b]
CO_2	78.0	...	62	...
C_6H_5COOH	10.0	...	43	...
Biphenyl	58.0	...	54	...
Dihydrobiphenyl	28.0	0.36	5	0.06
Tetrahydro-quaterphenyl	158.0	2.04	28	0.36
Phenyl benzoate	7.0	...	5	...
Residue	38.0	0.22	84	0.49
Total	377[c]	2.62[d]	281[e]	0.91[f]

[a] Entries are in grams of product/mole (242 g) of peroxide. Entries for all but the residue are taken directly from Table I. Probable accuracies are given in Table I. [b] Moles of C = C/mole of peroxide. [c] The weight excluding CO_2 and benzoic acid is 289, hence 1.19 g of these remaining products is formed per gram of peroxide. The average value found is about 1.13 (Table IV). However, the observed residue weights averaged 22 g/mole of peroxide and the figure 38 is certainly too high (see text). [d] Value from Table IV is 2.60. [e] Observed residue weight was 82 g/mole of peroxide. The predicted weight of products excluding CO_2 and benzoic acid is 176, hence 0.73 g of these products is formed per gram of peroxide. The observed value is 0.72 (Table IV). [f] The observed value is 0.69. The discrepancy may be due to incorrect assumptions about structure of residue or to presence of bonds difficult to reduce although the completeness of hydrogenation was tested against fresh catalyst.

Comparison between observation and theory as given in the footnotes of Table III showed that the material balance is quite good except for two points. The estimated amount of residue is high for the 0.01 *M* solution, and this probably reflects cumulative errors in the CO_2 estimate; perhaps 97% recovery would be a better value. The other point is that the phenyl residues have not been accounted for quantitatively in the 0.2 *M* solution. The listed residue contributes five phenyl groups for every 1.8 CO_2 groups; hence a deficit of 0.22 mole of CO_2 corresponds to 0.122 mole of residue or 0.61 mole of phenyl groups per mole of peroxide. This gives a recovery of 0.94 + 0.61 or 1.55 moles of phenyl groups. The deficit (0.45) is probably accounted for by three factors: (1) the amount of residue may be somewhat underestimated by the CO_2, (2) the product present as hydrocarbon may contribute a few mole per cent of phenyl groups, and (3) a possibly quite important factor may be allylic hydrogen abstraction by phenyl radicals to give peroxide-derived benzene which is not detectable in the present work.

Such points as the latter one require labeling to identify the origin of products. A few studies were therefore made of the reaction of *p*-chlorobenzoyl peroxide with benzene and of the reaction of benzoyl peroxide with chlorobenzene. These were not pursued in detail since neither hydrogenation nor dehydrogenation proved suitable for quantitative work with these reaction mixtures. All variations of hydrogenation tried led to an intolerable amount of hydrogenolysis of aryl chlorine. Quantitative product studies of the reaction of benzoyl peroxide with chlorobenzene have been reported.[6]

Decomposition of 0.17 *M* *p*-chlorobenzoyl peroxide in benzene at 80° gave the following products (mole %): CO_2, 150; *p*-chlorobenzoic acid, 20; chlorobenzene, 16; biphenyl, 1.5; *p*-chlorodihydrobiphenyl, 18; *p*-chlorobiphenyl, 64; and phenyl *p*-chlorobenzoate, 6.

The identification of the esters as chlorophenyl benzoates (benzoyl peroxide in chlorobenzene) and as phenyl *p*-chlorobenzoate (*p*-chlorobenzoyl peroxide in benzene), along with the virtual absence of chlorophenyl *p*-chlorobenzoates, shows that the acyloxy portion comes from the peroxide and the aryl portion from solvent. This was the conclusion drawn earlier.[15] Some discussions of the reaction have assumed that phenyl benzoate is formed either by attack of a phenyl radical on the peroxide or by combination of phenyl and benzoyloxy radicals. There is a second strong argument against such mechanisms. They clearly require the yield of phenyl benzoate to increase with increasing peroxide concentration.[22] As seen from Table I, the yield is practically invariant.

The major route to ester is therefore through radical **5** or its analogs.[6] The formation of relatively large amounts of phenyl benzoate from reaction of benzoyl peroxide in chlorobenzene is interesting. Addition of benzoyloxy radicals to give **6** and isomers can lead to **7** and isomers which should lose hydrochloric acid readily upon work-up, and to the radical **8** which could readily lose a chlorine atom to another radical by disproportionation. Attack at the chlorine-bearing carbon has been suggested previously.[12,15]

The formation of benzene and of chlorobenzene in the above reactions indicates that hydrogen abstraction to form solvent-derived aryl radicals is of considerable

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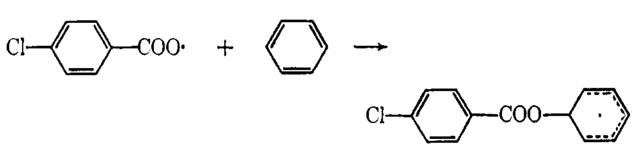
(22) This conclusion has been verified by detailed calculations.



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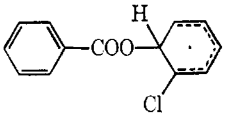

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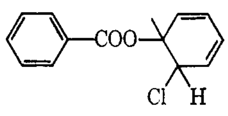

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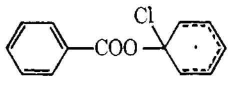

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importance. This reaction has also been postulated to account for part of the dideuteriobiphenyls obtained in the reaction of benzoyl peroxide with monodeuteriobenzene.[12]

Experimental Section

Benzoyl Peroxide. Commercial benzoyl peroxide was dissolved in chloroform and precipitated with methanol, assay 99.5%.

Benzene. The reaction is sensitive to certain types of trace impurities; small amounts of aliphatic compounds decrease the yield of carbon dioxide and increase the yield of benzoic acid. Benzene, Pure Grade (99+ mole %), from Phillips Petroleum Co. shows trace amounts of aliphatic C-H by differential infrared absorption against the Phillips Research Grade benzene (stated purity 99.93%). Gas chromatography (Apiezon) shows three components before benzene and one after. Fractional distillation over a period of several days through a 4-ft Sarnia Mark II fractionator (H. S. Martin and Co.) with collection of the center 60% gave benzene which had only about three times as much impurity (probably cyclohexane) as the very pure Research Grade benzene (estimated by gpc using a polypropylene glycol column). Benzene recovered from reaction mixtures appeared indistinguishable from the original benzene.

Reaction Procedure. Most of the reactions were carried out under reflux in an apparatus with sealed-on reflux condenser and sealed-in nitrogen inlet tube. Benzene was introduced into the tared vessel and distilled under a stream of high-purity nitrogen to remove water. After cooling under a nitrogen stream, the vessel was weighed and benzoyl peroxide added as crystals with a benzene rinse. The mixture was refluxed gently for 48 hr or more (ten half-lives) under very slow nitrogen sweep. Reliable determination of carbon dioxide required careful technique and a fairly elaborate train consisting in series of two cold traps (Dry Ice), a drying tube [Anhydrone, $Mg(ClO_4)_2$], carbon dioxide absorber, and guard tube. Ascarite (NaOH on asbestos) tends to plug if subjected to large volumes of carbon dioxide over a short time. Soda lime with Anhydrone and an Ascarite guard serve very well.

Most of the benzene was removed from the reaction mixture by distillation through a column. When the volume had been reduced to 2.5 l. or less, heating was done with an oil bath at about 100° (good insulation needed) to minimize cracking of labile products. The temperature of the solution did not exceed about 80°, the temperature at which the reactions were carried out.

Distillation was interrupted when the volume had been reduced to 200–500 ml. Benzoic acid was then extracted by prolonged stirring at room temperature with an excess of 0.1 *N* sodium hydroxide and the excess back-titrated. The solution was acidified and the benzoic acid was extracted from the aqueous layer with chloroform; the extractions were checked for completeness. Solid benzoic acid was isolated and retitrated. Agreement between the first two values was nearly always better than 1.5%, and the titer of the isolated benzoic acid averaged 3% low. These results were independent of initial peroxide concentration up to 0.4 *M* initial peroxide. It is therefore estimated that the ratio $C_6H_5C_6H_4$-COOH:C_6H_5COOH was less than about 0.03 even at 0.4 *M*. The amount of such products as $C_6H_5C_6H_6C_6H_4$COOH is even lower.

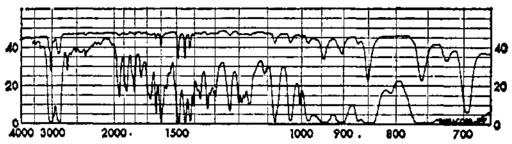

Figure 3. Infrared curve of 1,4-dihydrobiphenyl.

Most of the remaining benzene was removed on a small column. Again the temperature was kept below 85°. An aliquot was taken by weight, and the remaining mixture was hydrogenated over 10% palladium on carbon (60–100 mg/g of peroxide). Since reduction proceeded sluggishly in benzene alone, the solution was diluted with ethyl acetate and ethanol (roughly equal parts, total volume about 25–30 ml/g of peroxide taken). Hydrogenation required 5–7 hr at atmospheric pressure and room temperature.

The hydrogenated mixture was distilled in a special apparatus consisting of a 50-ml flask sealed to an alembic (gutter) and an inner 24/40 joint. The head was constructed of an outer 24/40 water-cooled joint. Solvent was distilled at ice temperature and about 10^{-2} torr. Then the biphenyl and phenylcyclohexane were distilled at 130° and 1–5 × 10^{-3} torr. Finally the dodecahydroquaterphenyl fraction was distilled at 240° and 1–2 × 10^{-3} torr. The distillation was greatly facilitated by use of magnetic stirring.

Product Identification. The 1,4-dihydrobiphenyl was isolated by gas chromatography. Typical conditions utilized a 3 ft × 0.25 in. column with 10% poly-*m*-phenyl ether on diatomaceous earth, column at 130°, inlet at 110°, and a helium flow rate of 60–80 cc/min; emergence times were 7 min for dihydrobiphenyls, 12 min for biphenyl, and 5–6 min for phenylcyclohexane. 1,4-Dihydrobiphenyl could also be isolated by liquid chromatography, on F20 alumina (slightly alkaline, activity grade Brockmann I) 1 × 180 cm, using hexane as eluent (0.8-g load of neat mixture of biphenyl and dihydrobiphenyl). Both techniques showed traces of an early peak that may be 1,2-dihydrobiphenyl in the original mixture. The analytical sample contained less than 0.5% of biphenyl. The infrared curve (Perkin-Elmer Model 137 Infracord) is shown in Figure 3. Principal peaks are at 692, 759, 850, 903, 945, 1420, 1450, 1488, 1600, 1635, 2822, 2860, 2880, and 3028 cm^{-1} (from Perkin-Elmer Model 221 grating spectrophotometer). The absence of the strong 735-cm^{-1} biphenyl peak may be noted. Ultraviolet absorption maxima are 256 mμ (ε 435 l. $mole^{-1}$ cm^{-1}), 262 mμ (ε 510), and 269 mμ (ε 405). The reduction of biphenyl with sodium in liquid ammonia followed by addition of ammonium chloride gives a mixture from which 1,4-dihydrobiphenyl may be isolated. The infrared curves of the two preparations were identical.[18,19] On hydrogenation of the reaction mixture the gpc peak corresponding to 1,4-dihydrobiphenyl was replaced by a phenylcyclohexane peak.

Anal. Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 92.27, 92.02; H, 7.95, 7.79.

Samples of biphenyl and of phenylcyclohexane were collected and had infrared curves indistinguishable from curves of known specimens. Phenyl benzoate was isolated by gas chromatography at somewhat higher temperatures and collected and identified by its infrared curve as well as its emergence time.

Tetrahydroquaterphenyls were isolated by two principal techniques. The benzene was almost completely removed from a reaction mixture and alcohol was added. Crystals of a mixture of tetrahydroquaterphenyls separated and were purified by recrystallization from ethanol. Alternatively the benzene concentrate prior to hydrogenation was chromatographed on neutral alumina using 30–40% benzene and 70–60% hexane as eluent.

Anal. Calcd for $C_{24}H_{22}$: C, 92.90; H, 7.10; mol wt, 310. Found: C, 92.90; H. 7.18; mol wt, 303 (Signer[23] in $CHCl_3$).

Hydrogenation of the crystalline tetrahydroquaterphenyl in ethyl acetate using 10% palladium on carbon gave a mixture of 1′,2′,3′,4′,5′,6′,1′′,2′′,3′′,4′′,5′′,6′′-dodecahydroquaterphenyls (**9**), the principal component of which consisted of colorless plates, from ethyl acetate, mp 214–216° cor.

Anal. Calcd for $C_{24}H_{30}$: C, 90.56; H, 9.43. Found: C, 90.0; H, 9.44.

A 115-mg sample was dehydrogenated using tetrachloro-*o*-benzoquinone in refluxing benzene to give 41 mg (36%) of *p,p′*-

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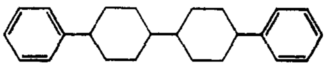
(23) R. Signer, *Ann.*, **478**, 246 (1930); E. P. Clark, *Anal. Chem.*, **13**, 820 (1941).



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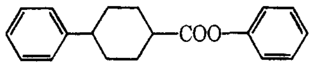

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quaterphenyl; 80 mg of biphenyl was also produced. A 50-mg sample when heated with 10% palladium on carbon gave 9 mg of biphenyl and 20 mg of *p,p'*-quaterphenyl.

The infrared spectra of the crystalline tetrahydroquaterphenyl on a thin layer deposited by melting had the following major peaks: 682, 699, 742, 768, 798, 852, 862, 910, 1032, 1076, 1450, 1600, 2830, 3030, and 3100 cm^{-1}. The peaks observed in carbon disulfide were similar, but a few were somewhat shifted: 682, 697, 732, 760, 793, 852, 908, 1030, 1075, 2820, and 3060 cm^{-1} (Model 137).

The ultraviolet curve in ethanol of the crystalline tetrahydroquaterphenyl had the following maxima (in mμ): 2560, 2620, and 2688, with extinction coefficients, respectively, 920, 1180, and 1015.

Attempts to isolate other tetrahydroquaterphenyl from the mixtures gave little fruitful result. Distillation is difficult, since the compounds dissociate at an appreciable rate at 170°. Gas chromatography of a solution gives peaks corresponding to dihydrobiphenyl and biphenyl and little else. Evidence for the presence of the *o,p'* isomers and the *o,o'* isomers is based on dehydrogenation and on hydrogenation.

Samples of the tetrahydroquaterphenyl fraction from liquid chromatography were dehydrogenated with an equimolar amount tetrachloro-*o*-benzoquinone by refluxing in benzene for 1 hr. *p,p'*-Quaterphenyl precipitated and was removed by filtration. The orange-red solution was chromatographed on neutral alumina. Recoveries of hydrocarbon were 80–95%; these showed gpc peaks corresponding to quaterphenyls and a biphenyl peak. A combination of gas chromatography and recrystallization from ethanol gave a pure sample of *o,p'*-quaterphenyl: colorless needles, mp 117–117.5° cor. (lit.[24] 117.5–118°), and with infrared spectra that matched the published curve.[24] The amount of *o,o'*-quaterphenyl was small, mp 100–112°, but the infrared curve had all the peaks observed with an authentic sample. In gpc, the quaterphenyls come out at nearly the same position as the respective dodecahydroquaterphenyls, except that the quaterphenyls have somewhat longer emergence times.

The Dodecahydroquaterphenyl Fraction. A typical high-temperature gas chromatographic curve of the hydrogenated reaction mixture (see Reaction Procedure) is shown in Figure 4. While a variety of operating conditions was used successfully, the best columns had 10–15% of silicone rubber on Chromosorb W (acid-treated diatomaceous earth) and utilized column temperatures of 225–275°.

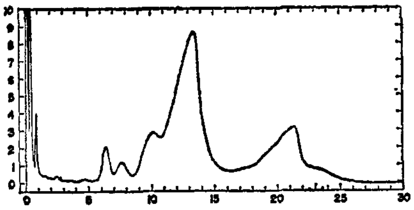

Figure 4. Gas chromatographic analysis of hydrogenated reaction mixture. Abscissa units are minutes, and ordinate is the detector response.

The residues from the distillation of the dodecahydroquaterphenyls averaged about 0.07 g/g of benzoyl peroxide, but gas chromatography at 300° failed to show any peaks beyond those shown in Figure 4. The residues contain esters (infrared absorption at 1720 cm^{-1}).

The peaks in Figure 4 have been identified as follows: 0.5 min, biphenyl and phenylcyclohexane; 1 min, phenyl benzoate; 6.5 min, *o,o'*-dodecahydroquaterphenyl; 7.5 min, an ester, possibly **10**, 10 and 13.5 min, *o,p'*-dodecahydroquaterphenyls; 21.5 min, *p,p'*-dodecahydroquaterphenyls (**9**); 23–24 min, *p,p'*-hexahydroquarterphenyl. This may arise from hydrogenation of dihydroquaterphenyl or from disproportionation during hydrogenation.

Terphenyl derivatives have emergence times of 3–5 min; the amount in this run is estimated as less than one-tenth the amount of phenyl benzoate, which is 0.03 mole/mole of peroxide.

Material from the *p,p'*-dodecahydroquaterphenyl peak (21.5 min) was identified by comparison with the 216° isomer from hydrogenation of crystalline tetrahydroquaterphenyl. Both showed the same emergence time and had nearly identical infrared curves.

A sample of the isolated 13.5-min peak was a viscous oil with the correct analysis and molecular weight. The ultraviolet absorption is consistent with the dodecahydroquaterphenyl structure with maxima (in mμ) 2535, 2585, and 2675(ϵ 1180, 1170, and 850). The extinction coefficients are a bit high (about 2 × 250 expected, based on phenylcyclohexane), and it is possible that 5–10% of hexahydro derivatives are present.

The isolated 6.5–7.5-min material amounted to 15 mg. The ester and hydrocarbon were separated by liquid chromatography on a 10 × 75 mm column of neutral alumina using hexane as eluent. The oily hydrocarbon (9 mg) showed infrared peaks similar to those of the *p,p'*-dodecahydroquaterphenyls and ultraviolet absorption at 255.0, 262.0, and 268.5 mμ with extinction coefficients of the order of 500. The ester (4 mg) was eluted with benzene and showed carbonyl absorption at 1720 cm^{-1} thus indicating an aliphatic (cyclohexyl) benzoate (*e.g.*, **10** or an isomer). Phenyl benzoate and the benzoate of 4-hydroxybiphenyl have the ester peak at 1735 cm^{-1}. Other ester peaks are at 711, 1034, 1074, 1108, 1265, 1280, 1322, 1455, 1720, 2850, and 2920 cm^{-1}. The gpc emergence time is that expected for an ester with three benzene rings.

Except for the 7.5-min peak (Figure 1), no ester was detectable among fractions collected by gas chromatography.

A pure sample of the hydrocarbon with the long elution time, 23–25 min (Figure 4), had an infrared curve very similar to that for the *p,p'*-dodecahydroquaterphenyl, though the aliphatic C–H peaks were somewhat weaker. The ultraviolet curve showed a broad maximum at 255 mμ (ϵ 23,700), and the compound is therefore a hexahydro derivative with an intact biphenyl ring chromophore. This probably arose from disproportionation under hydrogenation conditions.[14]

Anal. Calcd for $C_{24}H_{24}$: C, 92.3; H, 7.75. Found: C, 92.3; H, 7.85.

Frequently the colorless reaction mixtures became yellow, and small amounts of a relatively insoluble yellow solid separated along with the tetrahydroquaterphenyl fraction. The material had a melting point of about 305°, but the infrared curve was very different from that of *p,p'*-quaterphenyl. The material was not investigated further. It may have arisen from the action of light or from the action of bases.

Quantitative Determinations. Relatively large amounts of peroxide (4–5 g) were taken to minimize the effect of minor mechanical losses. An aliquot before hydrogenation was analyzed for biphenyl and for dihydrobiphenyl by gpc using low inlet and column temperatures (130°) to avoid cracking of the tetrahydroquaterphenyls. The method was calibrated against known mixtures. The dihydrobiphenyl:biphenyl ratio before hydrogenation was invariably higher than the phenylcyclohexane:benzene ratio afterwards.[14] The various fractions were carefully weighed, and their compositions were estimated by gas chromatography. The benzene solvent removed on the vacuum train was also checked. The results of the assays are presented in Table IV. The composition of the dodecahydroquaterphenyl fraction is summarized in Table V.

The Nonvolatile Residue. Benzoic acid and *p,p'*-quaterphenyl were removed after decomposition of 7 g of benzoyl peroxide in 90 ml of benzene, and the solvent was stripped (bath temperature during distillation 100°). The residue was chromatographed on neutral alumina using first hexane and then chloroform–hexane (10:90) as eluents. This gave a series of 15 ester fractions totalling 2.32 g. Molecular weights as determined by the vapor-phase osmometer in benzene ranged from 430 to 834 with an average of 709. There were on the average 1.8 moles of benzoyloxy groups/mole of ester as determined by saponification and by ultraviolet absorption.

Bis-*p*-chlorobenzoyl Peroxide. This was prepared in 70% yield in a purity of nearly 100%.[25] *Anal.* Calcd oxidation equiv wt, 155.6. Found: 156.3, 155.6.

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[24] J. Dale, *Acta Chem. Scand.*, **11**, 640 (1957).

[25] C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

Table IV. Products of the Thermal Decomposition of Benzoyl Peroxide in Benzene at Reflux[a]

Peroxide concn, *M*	CO_2	BzOH	$C_{12}H_{12}$[b]	$C_{12}H_{10}$[c]	$C_{13}H_{10}O_2$[d]	$C_{24}H_{30}$[e]	Residue, g/g	Total products,[f] g/g	H_2[g]
0.011	177	8.1	...	(51)[h]	...	(62)[i]	...	1.13	...
0.011	173	8.3	17	35	2.8	53	0.092	1.15	240
0.011	173	9.2	18	37	3.5	48	0.095	1.10	245
0.011	173	7.7	20	35	3.6	51	0.079	1.13	(200)
0.020	...	12.0	16	41	2.9	...	...	1.01	...
0.006	...	8.3	23	38	3.0	54	0.53	1.11	230
0.018	...	9.5	16	37	3.4	...	...	...	...
0.014	...	8.7	16	38	...	48	...	1.12	260
0.004	...	5.8	21	42	...	...	...	...	290
0.007	...	6.0	23	38	...	55	...	1.18	260
0.003	...	5.5	22	42	...	61	...	1.16	280
Av[j]	174	8.3	20	37	3.3	55	...	1.13	260
Phenyl groups	...	8.3	20	37	3.3	106	...	175[k]	...
CO_2 groups	174	8.3	...	...	3.3	*m*	...	188[k]	...
H balance +	...	8.3	20	...	...	...	...	+28[l]	...
H balance −	...	...	...	37	3.3	...	...	−40[l]	...
Unsat[n]	...	...	40	...	...	312	...	252	...
0.220	134	39	3	38	2	5.2	*n*	1.16	70
0.284	135	38	...	...			*o*		
0.341	134	40	1.5	33	1.8	...	*p*		

[a] Entries are moles of product/mole of peroxide × 100 unless otherwise noted. The top seven entries are considered to be more reliable than the others. These runs utilized 4.8 g of peroxide. [b] Dihydrobiphenyls; about 90% 1,4-dihydrobiphenyl and 10% 1,2-dihydrobiphenyl. [c] Biphenyl. [d] Phenyl benzoate. [e] Tetrahydroquaterphenyls determined in the fm of dodecahydroquaterphenyls. [f] Excluding benzoic acid and carbon dioxide; theoretical is 1.28 g and discrepancy is thought to be due mainly to cumulative mechanical losses. [g] Total amount of hydrogen added to dihydrobiphenyls and tetrahydroquaterphenyls. [h] Sum of biphenyl and dihydrobiphenyl. [i] Total residue including phenyl benzoate and residue. [j] Estimated best value weighting first entries more heavily than last entries which represent earlier runs. [k] Theoretical is 200. [l] A hydrogen atom is lost from a phenylcyclohexadienyl radical to give biphenyl, and this hydrogen atom forms dihydrobiphenyl, benzoic acid, or is perhaps lost to atmospheric oxygen. [m] The hydrogen uptake on hydrogenation (2.60 moles/mole of peroxide) adequately balances the amount of unsaturation estimated (2.52 moles/mole). [n] Terphenyls, 1; *p,p'*-quaterphenyl, 1; mixed esters, 12; molecular weight, 710). [o] *p,p'*-Quaterphenyl, 1.2. [p] *p,p'*-Quaterphenyl, 1.4.

Table V. Composition of Total Dodecahydroquaterphenyl Fraction[a]

	o,o'- Dodeca IV	*o,p'*- Dodeca V	*p,p'*- Dodeca III	Ester "VI"
	2.3	45	51	1.8
	2.3	42	54	1.8
Av	2.3	44	53	1.8
	Av moles/mole of peroxide × 100[b]			
	1.2	22	27	1.0

[a] Entries are in mole per cent and include the dodecahydroquaterphenyls in the distillate plus those precipitated on the hydrogenation catalyst. [b] Based on average yield of the $C_{24}H_{30}$ of 0.55 mole/mole of peroxide (Table I).

Decomposition. In a typical run a solution of 21.7 g of bis-*p*-chlorobenzoyl peroxide was refluxed in 4200 ml of benzene ("pure" grade, not further distilled) for 72 hr. The carbon dioxide yield was 1.51–1.56 moles/mole of peroxide. Most of the benzene was removed on a 90 × 1 cm column packed with glass helices. The approximately 200 ml of solution was filtered to remove the insoluble *p*-chlorobenzoic acid and extracted with 2 *N* sodium hydroxide solution. The yield of *p*-chlorobenzoic acid was 0.22–0.16 mole/mole of peroxide. Further concentration of the reaction mixture to 50 ml led to deposition of 4,4'''-dichloro-1',4',1'',4''-tetrahydro-*p,p'*-quaterphenyl and 0.03 mole/mole of peroxide, including material deposited on further concentration. The reaction mixture was taken to dryness at bath temperatures up to 200°, and addition to ethanol gave varying yields of *p*-chlorobiphenyl, 0.46–0.76 mole/mole of peroxide.

4,4'''-Dichloro-1',4',1'',4''-tetrahydro-*p,p'*-quaterphenyl (I). The compound crystallized from *n*-heptane in the form of almost colorless needles, mp 170–171°.

Anal. Calcd for $C_{24}H_{20}Cl_2$: C, 75.99; H, 5.28; Cl, 18.75; mol wt, 379. Found (on two samples): C, 76.22, 75.84; H, 5.14, 5.55; Cl, 18.71, 18.53; mol wt, 365 (Signer[23] in $CHCl_3$).

A solution of 50 mg of I in 10 ml of ethyl acetate absorbed 12 ml (4 moles) of hydrogen at room temperature in the presence of platinum oxide (prereduced). Colorless needles (40 mg from *n*-heptane) of 4,4'''-dichloro-1',2',3',4',5',6',1'',2'',3'',4'',5'',6''-dodecahydro-*p,p'*-quaterphenyl were obtained.

Anal. Calcd for $C_{24}H_{28}Cl_2$: C, 74.43; H, 7.23; Cl, 18.35. Found: C, 74.63; H, 6.55; Cl, 18.66.

Dehydrogenation of I over selenium at 250° gave 40% of *p*-chlorobiphenyl as the only isolable product. Dehydrogenation over 10% palladium on carbon or on barium carbonate gave mixtures of biphenyl, *p*-chlorobiphenyl, and material melting in the 300° range which had less than half the amount of chlorine expected for 4,4'''-dichloro-*p,p'*-quaterphenyl.