

*Anal.* Calcd. for  $C_{22}H_{14}O_2$ : C, 76.26; H, 9.89. Found: C, 76.40; H, 9.64.

b.—To a solution of 100 mg. of XII in 50 ml. of methylene chloride was added 1 ml. of a 2% solution of chromium trioxide in 80% aqueous acetic acid, and the two-phase system was shaken for 70 hours at room temperature. The

methylene chloride layer was washed with water, dried over sodium sulfate and evaporated to dryness. The crystalline residue was recrystallized from ether to give 80 mg. of XIII in long prisms, m.p. 170–172°. The product showed the same infrared spectrum as the product obtained by bismuthate oxidation, and the mixed melting point was not depressed.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, S. C.]

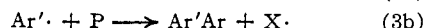
## Intramolecular Free Radical Arylation and Related Reactions<sup>1</sup>

BY DELOS F. DETAR AND CHIN-CHIUN CHU<sup>2,3</sup>

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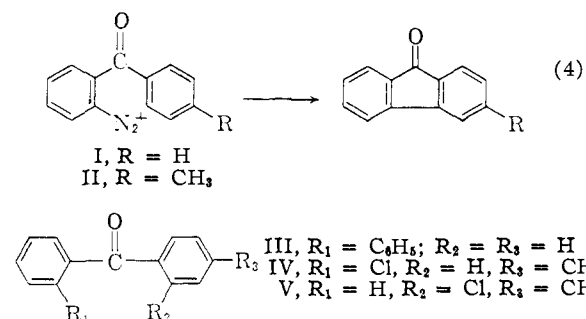
A study has been made of the reactions of the 2-*o*-terphenyl free radical as obtained both from the peroxide of *o*-terphenyl-2-carboxylic acid and from the diazonium salt derived from 2-amino-*o*-terphenyl. Cyclization to triphenylene (IX) occurs to the exclusion of the intermolecular reaction with benzene or with carbon tetrachloride. However, bromine abstraction from bromotrichloromethane does compete with cyclization. This behavior is in contrast to that of the *o*-benzoylphenyl radical, which was found in previous work to give a higher yield of 2-phenylbenzophenone by intermolecular reaction with benzene than of the intramolecular cyclic product, fluorenone. The peroxide of *o*-(1-naphthyl)-benzoic acid (VI) was also investigated, but the acyloxy radical failed to decarboxylate. The main product found was the lactone VIII of *o*-(2-hydroxy-1-naphthyl)-benzoic acid.

A number of mechanisms have been proposed for the free radical arylation reactions which take place on decomposing a diacyl peroxide in an aromatic solvent, in the Gomberg-Bachmann reaction of diazonium salts, and in other related reactions.<sup>4–6</sup> In these reactions a carbon-carbon bond is formed and a carbon-hydrogen bond is broken. If carbon-carbon bond formation is the key step, then mechanisms of type I (eq. 1 or 2) result. If the carbon-hydrogen bond is broken first, then the mechanisms are of type II (eq. 3a and 3b). The



complete over-all mechanisms must also specify the source of the radicals Ar. and the detailed fate of radicals formed in eq. 2 and 3a, etc.

Some years ago we sought to distinguish between type I and type II mechanisms by a study of diazonium ring closure reactions (eq. 4).<sup>7,8</sup> Thus the diazonium salt (I) was allowed to react under alkaline conditions so that a free *o*-benzoylphenyl radical would be formed. A type I mechanism would then give fluorenone if the reaction were intramolecular or, in the presence of benzene, 2-benzoylbiphenyl (III) if the reaction were intermolecular. A type II mechanism (eq. 3a and b) would give mainly the intermolecular product III, for there is no reason to expect that a radical X· (X = ·OH, *e.g.*) will preferentially attack the 2'-position of a diazo-spe-



cies.<sup>9</sup> This approach is based on one of the important empirical generalizations of organic chemistry; namely, that the reaction of two functional groups to form a five- or a six-membered ring wins out over intermolecular reactions of these same groups.

The Gomberg-Bachmann reaction of 2-benzoylbenzenediazonium salts (I) in the presence of benzene and of alkali gave the usual complex mixture (*i.e.*, tars are formed). Some fluorenone was present, but the principal isolable product was 2-phenylbenzophenone (15%) (III).<sup>7</sup> This experiment was repeated during the present investigation and the products (analyzed by gas chromatography) were benzophenone (6%), fluorenone (6%) and 2-phenylbenzophenone (13%); the remaining products were less volatile and were not identified. On decomposition in alkaline media in the absence of an added organic solvent the fluorenone yield ranges from 5–25%.<sup>10,11</sup> On the other hand, under acidic conditions the fluorenone yield is 65–75%, the other product being 2-hydroxybenzophenone.<sup>10–12</sup> The diazonium salt derived from 2-

(1) Intramolecular Reactions VI. Previous paper: D. F. DeTar and T. E. Whiteley, *THIS JOURNAL*, **79**, 2498 (1957).

(2) From the Ph.D. dissertation of Chin-Chiun Chu.

(3) We gratefully acknowledge the support of this work by the Air Force Office of Scientific Research under contract AF 49(638)-88.

(4) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 474, 518.

(5) (a) O. C. Dermer and M. T. Edmison, *Chem. Revs.*, **57**, 77 (1957); (b) D. R. Augood and G. H. Williams, *ibid.*, **57**, 123 (1957).

(6) E. L. Eliel, S. Meyerson Z. Welvart and S. H. Wilen, *THIS JOURNAL*, **82**, 2936 (1960).

(7) D. F. DeTar and S. V. Sagmani, *ibid.*, **72**, 965 (1950).

(8) D. F. DeTar, *Org. Reactions*, **9**, 409 (1957).

(9) In these equations P represents some such species as a diahydroxide and X· would then be a hydroxyl radical. The species actually involved in the Gomberg-Bachmann reactions have not been identified. If a peroxide source were used then P would represent a peroxide molecule and X· would refer to an acyloxy radical.

(10) D. F. DeTar and D. I. Relyea, *THIS JOURNAL*, **76**, 1680 (1954).

(11) D. H. Hey and R. D. Mulley, *J. Chem. Soc.*, 2276 (1952).

(12) D. F. DeTar and T. E. Whiteley, *THIS JOURNAL*, **79**, 2498 (1957).

aminodiphenyl ether also gave more phenyl replacement (2-phenoxybiphenyl) than cyclic product under Gomberg-Bachmann conditions with benzene.<sup>7</sup> These results were originally interpreted as evidence in favor of a type II mechanism for the arylation reaction.<sup>7,13</sup>

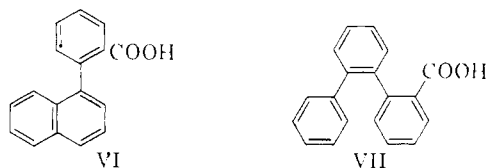
Subsequent work on the mechanism of biaryl formation has shown that this conclusion is wrong. The evidence now is entirely in support of a type I mechanism based on eq. 2.<sup>4,6,15,16</sup> While it would be out of place to give an extensive summary, two lines of evidence may be mentioned. Pausacker obtained evidence of the proposed intermediate radical  $\text{ArAr}'\text{H}\cdot$  by showing that the quaterphenyls formed from decomposition of substituted benzoyl peroxides in benzene had just two substituent groups.<sup>15</sup> Recently the combination product, a tetrahydroquaterphenyl, and the disproportionation products, 1,4-dihydrobiphenyl (and biphenyl) have been isolated from the reaction of benzoyl peroxide with benzene in dilute solutions.<sup>16</sup>

Diazonium salts have certain disadvantages as sources of free radicals. The high reactivity of the diazonium grouping leads to extensive side reactions such as coupling to give complex azo compounds. Furthermore, the cleavage of the carbon-nitrogen bond can give either an aryl carbonium ion or an aryl free radical.<sup>8,10</sup> It is most difficult to determine the relative amounts of these two types of cleavage under a given set of reaction conditions. Now that the mechanism of the arylation reaction has been shown to involve radical addition (eq. 2), the formation of 2-phenylbenzophenone can be taken as evidence that *o*-benzoylphenyl radicals are formed to some extent under the Gomberg-Bachmann conditions. Further evidence is the production of 2-chloro-4'-methylbenzophenone (IV) and of 2-chloro-4-methylbenzophenone (V) on reaction of 2-(4'-methylbenzoyl)-benzenediazonium salts (II) with carbon tetrachloride in the presence of alkali.<sup>17</sup> Since the rate of decomposition of the diazonium salt under alkaline conditions in the presence of benzene is some 500 times faster than under acidic conditions, it is likely that the cyclic product is also formed by a free radical process.<sup>10</sup>

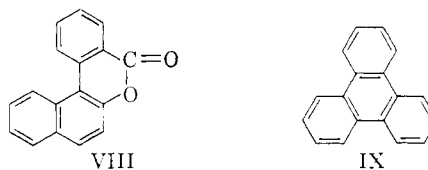
One of the alternatives that should be explored is that of utilizing another source for the production of the requisite free radicals. Diacyl peroxides are by far the best choice since the mechanisms of their reactions are better worked out than have been those of other proposed sources. Unfortunately, the use of peroxides has been frustrated by certain technical difficulties. Thus *o*-phenoxybenzoyl peroxide (the radical source parallel to *o*-phenoxybenzenediazonium salts) reacted in benzene without

detectable decarboxylation to give the interesting rearrangement product, phenyl salicylate, in 25% yield.<sup>18</sup> Attempts to prepare the peroxides of *o*-benzoylbenzoic acid (the source parallel to *o*-benzoylbenzenediazonium salts, I) or of *cis*-stilbene-2-carboxylic acid failed to give simple products. Presumably the neighboring carbonyl and ethylenic bridge groups interfered.

We decided to make a further attempt to obtain a peroxide of suitable structure to permit a direct comparison with the parallel diazonium salt. Two examples were selected, the peroxides of *o*-(1-naphthyl)-benzoic acid (VI) and of *o*-terphenyl-2-



carboxylic acid (VII). The peroxide of the former acid (VI) was obtained in about 70% purity, but when heated in benzene solution gave no carbon dioxide. The principal products were the lactone VIII of *o*-(2-hydroxy-1-naphthyl)-benzoic acid, (40 mole per cent.) and the *o*-(1-naphthyl)-benzoic acid (VI). It is known that benzoyl peroxide re-



acts with naphthalene to give more ester (30% naphthyl benzoates) and less phenyl substitution (20% phenylnaphthalenes)<sup>19</sup> than in its reaction with benzene (2-10% phenyl benzoate, 25-40% biphenyl).<sup>20</sup> Since there is no reason to suppose that the peroxide behaves abnormally, we believe that the lactone VIII results from the intramolecular addition of the *o*-(1-naphthyl)-benzoyloxy radical to the naphthalene ring. Furthermore, this intramolecular reaction competes effectively with decarboxylation. We wish also to comment in passing on the very facile ring closure of *o*-(2-hydroxy-1-naphthyl)-benzoic acid to the lactone VIII.

The peroxide of *o*-terphenyl-2-carboxylic acid (VII) behaved more satisfactorily. The products obtained on decomposition in benzene, carbon tetrachloride and in bromotrichloromethane appear to be typical of those expected for a free radical mechanism. The results are summarized in Table I. The only product traceable to the 2-*o*-terphenyl free radical from the reaction in benzene or in carbon tetrachloride was triphenylene (IX). *o*-Quaterphenyl and 2-chloro-*o*-terphenyl, the possible intermolecular reaction products, were absent. Also absent was 2-hydroxy-*o*-terphenyl, a compound which might have been expected among the hydrolysis products if the 2-*o*-terphenyl radical

(13) The proposed type II mechanism involved an induced decomposition of P (peroxide or diazo compound). Depending on the termination steps this would appear as a kinetic term involving P to the half, the first or the three-halves power.<sup>14</sup> The form of the kinetic expression for peroxide decomposition in an aromatic solvent thus does not constitute evidence against this mechanism, as has been claimed.<sup>13b</sup>

(14) C. G. Swain, W. H. Stockmayer and J. T. Clarke, *THIS JOURNAL*, **72**, 5426 (1950).

(15) K. H. Pausacker, *Austral. J. Chem.*, **10**, 49 (1957).

(16) D. F. DeTar and R. A. J. Long, *THIS JOURNAL*, **80**, 4742 (1958).

(17) D. F. DeTar and D. I. Relyea, *ibid.*, **78**, 4302 (1956).

(18) D. F. DeTar and A. Hlynsky, *ibid.*, **77**, 4411 (1955).

(19) D. I. Davies, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 1878 (1958).

(20) B. M. Lynch and K. H. Pausacker, *Austral. J. Chem.*, **10**, 40 (1957).

had attacked the peroxide to give an ester, or if the radical had combined with an acyloxy radical to give this same ester. In bromotrichloromethane some 2-bromo-*o*-terphenyl was produced; this result shows that a sufficiently reactive solvent can compete successfully with the cyclization process. A preliminary measurement of the kinetics at 79° gave a first-order rate constant of  $3.4 \times 10^{-4}$  sec.<sup>-1</sup> in 0.01 *M* solution in benzene. This rate is comparable to those of *o*-chlorobenzoyl peroxide and of *o*-methylbenzoyl peroxide.<sup>21</sup> These rates are all greater than the rate for benzoyl peroxide by a factor of about ten. The behavior of the *o*-terphenyl-2-carbonyl peroxide thus appears to be quite normal.

TABLE I

PRODUCTS OF THE DECOMPOSITION OF *o*-TERPHENYL-2-CARBONYL PEROXIDE IN SOLUTION (80° FOR 60 HOURS)<sup>a</sup>

Solvent	—Free acids—			Triphenylene	Intermolecular product	Lactone	Acid VII after hydrolysis
	CO <sub>2</sub>	VII <sup>b</sup>	Polymeric <sup>c</sup>				
Benzene	0.93	0.1	0.3	0.5	<i>d,e</i>		0.39
Benzene	1.00		(.4) <sup>f</sup>	.56			.48
Benzene	0.85		(.95) <sup>f</sup>	.48			..
CCl <sub>4</sub>	.89	0.4	.4	.58	<i>d,g</i>	0.17 <sup>h</sup>	.40
CBrCl <sub>3</sub>	.44	0.4	.4	.1	0.04 <sup>i,d</sup>	0.58 <sup>h</sup>	.4

<sup>a</sup> All entries in the table are moles of product per mole of peroxide. <sup>b</sup> *o*-Terphenyl-2-carboxylic acid. <sup>c</sup> Acids not volatile at 120–130° and 0.1 mm. ("moles" estimated on basis of mol. wt. of 274, the mol. wt. of VII). <sup>d</sup> No *o*-terphenyl detectable. <sup>e</sup> No *o*-quaterphenyl detectable. <sup>f</sup> Not distilled. <sup>g</sup> No 2-chloro-*o*-terphenyl was detected; the maximum amount present is 0.01 mole. <sup>h</sup> Based on analysis, ease of ring closure, and analogy with the *o*-(1-naphthyl)-benzoyl peroxide reaction this is the lactone of 2'-hydroxy-*o*-terphenyl-2-carboxylic acid. <sup>i</sup> 2-Bromo-*o*-terphenyl.

For purposes of direct comparison the reactions of the diazonium salt derived from 2-amino-*o*-terphenyl were also studied. These results are summarized in Table II. The first six runs utilized conditions previously tested with a series of diazonium salts.<sup>12</sup> The two runs in sulfuric acid indicate the products to be expected of the ionic reaction. The mechanistic interpretations of the reactions in the presence of copper or of cuprous chloride are not entirely clear. Under alkaline conditions the principal intermediate should be the 2-*o*-terphenyl free radical. With benzene as solvent triphenylene is formed, but no quaterphenyl is produced. Carbon tetrachloride also does not compete effectively for the radical, but with the more reactive bromotrichloromethane some 2-bromo-*o*-terphenyl is formed. These results compare as closely as can be expected with those of the peroxide reactions. Incidentally, the Sandmeyer reaction gives triphenylene rather than 2-bromo-*o*-terphenyl.

From the various studies of the cyclization reaction the following points appear to be established: (1) Under ionic conditions cyclization competes with phenol formation by intermolecular reaction with water. The yield of cyclic product ranges from about 35% for *o*-(3-nitrobenzoyl)-benzenediazonium salts to 90% or more for triphenylene formation. The balance of the product is the phenol, 2-hydroxy-3'-nitrobenzophenone or 2-hy-

(21) A. T. Blomquist and A. J. Buselli, *THIS JOURNAL*, **73**, 3883 (1951).

TABLE II

REACTION PRODUCTS FROM DIAZOTIZED 2-AMINO-*o*-TERPHENYL

Conditions <sup>a</sup>	Triphenylene	2-Hydroxy- <i>o</i> -terphenyl	Other
1 <i>N</i> H <sub>2</sub> SO <sub>4</sub>	79	12	
1 <i>N</i> H <sub>2</sub> SO <sub>4</sub> + Cu	78	..	
1 <i>N</i> H <sub>2</sub> SO <sub>4</sub> + CuCl	92	2	
21 <i>N</i> H <sub>2</sub> SO <sub>4</sub>	93	2	
21 <i>N</i> H <sub>2</sub> SO <sub>4</sub> + Cu	75	..	
21 <i>N</i> H <sub>2</sub> SO <sub>4</sub> + CuCl	94	5	
Benzene, 20 ml., aq., pH 12–13			
20 ml. <sup>b</sup>	53	..	None found <sup>c,d</sup>
CCl <sub>4</sub> , 20 ml., aq., pH 12–13, 20 ml. <sup>b</sup>	58		None found <sup>d,e</sup>
CBrCl <sub>3</sub> , 20 ml., aq., pH 12–13, 20 ml. <sup>b</sup>	31		29 <sup>f,d</sup>
CCl <sub>4</sub> , 50 ml., 0.1 <i>F</i> phosphate buffer, pH 11.1, 50 ml. <sup>g</sup>	73		None found <sup>d,e</sup>
CBrCl <sub>3</sub> , 30 ml., 0.1 <i>F</i> phosphate buffer, pH 11.1, 50 ml. <sup>h</sup>	41		27 <sup>f,d</sup>
25 ml. 2 <i>N</i> NaOH + Cu <sup>i</sup>	44		3 <sup>j</sup>

<sup>a</sup> In the sulfuric acid experiments the conditions were those of DeTar and Whiteley<sup>12</sup>; 160 mg. to 220 mg. (0.46 mmole to 0.64 mmole) of the diazonium fluoborate was dissolved in 25 ml. of aq. solution. <sup>b</sup> The amine hydrochloride (5 mmoles) was diazotized, but the diazonium salt was not isolated. <sup>c</sup> No *o*-quaterphenyl present. <sup>d</sup> No *o*-terphenyl present. <sup>e</sup> No 2-chloro-*o*-terphenyl present. <sup>f</sup> 2-Bromo-*o*-terphenyl. <sup>g</sup> 350 mg. of fluoborate salt. <sup>h</sup> 500 mg. <sup>i</sup> 200 mg. <sup>j</sup> *o*-Terphenyl.

droxy-*o*-terphenyl. (2) Under free radical conditions cyclization competes with a number of other reactions and yields of cyclic product range from 5% for fluorenone formation to some 50–70% for triphenylene formation. In general only a rather small fraction of the other products has been identified.

One significant factor in the interpretation of the results is the distance of approach of the reacting centers as determined by the geometry of the bridging group.<sup>11</sup> In general there is a parallel in that the highest yields of cyclic product result from those compounds that permit the closest approach. It must, however, be noted that the differences involved are not very large energy-wise; they are all of the order of 1–1.5 kcal.

At first view the ionic cyclization appears to be rather better than the free radical cyclization. From the preparative standpoint this is indeed a valid conclusion. However, to consider the free radical process in proper perspective it must be noted that the yield of cyclic product is not necessarily a good measure of the amount of intramolecular radical arylation, for it appears that only part of the radical ArAr'H· (eq. 2) is converted to cyclic product. Part is converted to as yet unidentified materials. Furthermore, the sources of the radical are not very efficient: the acyloxy radicals do not decarboxylate quantitatively, and diazo compounds undergo coupling reactions in which nitrogen is retained. Both of these types of side reactions lower the yield of cyclic product.

There is evidence in triphenylene formation that intermolecular reactions may compete better with cyclization in the ionic mechanisms than in the

radical ones. Under acidic conditions some 2-hydroxy-*o*-terphenyl was formed even when the triphenylene yield was highest. But in the free radical cyclization in benzene and in carbon tetrachloride intermolecular formation of *o*-quaterphenyl or of 2-chloro-*o*-terphenyl were negligible.

The opposite situation is found for fluorenone cyclization. Here the *o*-benzoylbenzenediazonium salt (I) gives 2:1 preference to cyclization over phenol formation under ionic conditions but something like 3:1 preference to intermolecular products over fluorenone under Gomberg-Bachmann conditions in benzene.

In considering more broadly the question of the importance of ring formation over intermolecular reactions, it appears that not many quantitative data are available. Thus, Streitwieser cites rather incomplete figures for ring closure reactions involving attack of neighboring nitrogen, sulfur and oxygen in displacement reactions of an alkyl chloride.<sup>22</sup> The factors favoring closure of five- or six-membered rings appear to range from 20–50,000, but there are considerable uncertainties in the interpretation of the data. What we actually have in the diazonium ring closure reactions are examples that disprove our initial assumption that such ring closures are always favored. A better understanding of the factors involved must await the assembly of more reliable quantitative data for representative systems.

### Experimental

***o*-(1-Naphthyl)-benzoyl Peroxide.**—The acid chloride was obtained by refluxing *o*-(1-naphthyl)-benzoic acid<sup>23</sup> with excess thionyl chloride. The methyl ester,<sup>24</sup> m.p. 83–84°, and the acid both have absorption maxima at 222 m $\mu$ , log  $\epsilon$  4.82, and at 283 m $\mu$ , log  $\epsilon$  3.92. Evaporation left a brown solid that on recrystallization from a benzene-hexane mixture gave colorless crystals, m.p. 74.5–75°. The chloride from 3.2 g. (13 mmoles) of the acid was dissolved in 50 ml. of anhydrous ether and added at 2° over a period of 20 min. to a solution of 4 g. (52 mmoles) of sodium peroxide in 20 ml. of ice-water. After an additional hour at 0° the mixture was filtered, and the crystals were washed in turn with water, methanol, chloroform and ether. This gave 2.3 g. of peroxide, m.p. 108–115°, and of 75% peroxide titer. Attempted recrystallization by solution in chloroform and precipitation with methanol or hexane failed to give purer product.

**Decomposition of *o*-(1-Naphthyl)-benzoyl Peroxide in Benzene.**—Three separate runs were made, but only two were examined in detail. Only the most complete run will be described. In this run 2.22 g. of peroxide of 75% purity (3.36 net mmoles) was heated in 340 ml. of benzene for a week under a slow stream of nitrogen. No carbon dioxide was evolved. The solvent was removed leaving a residue of 2.43 g. An aliquot was dissolved in benzene and extracted with aqueous potassium hydroxide to remove acids (560 mg. crude, m.p. 142–150° referred to the total residue). Based on the yield of sublimate at 150° at 0.22 mm., this corresponds to 510 mg. on 0.61 mole per mole of peroxide of pure *o*-(1-naphthyl)-benzoic acid; m.p. 157–159° (from methanol). A second run gave a yield of 0.47 mole per mole of peroxide.

An examination for hydrocarbons after alkaline hydrolysis or by chromatography showed that none was present. This checks the finding that no carbon dioxide was evolved.

The above acid-free residue was subjected to alkaline hydrolysis by refluxing it with 10% methanolic potassium hydroxide solution for 6 hours. The resulting acidic material was isolated and found to be entirely soluble in sodium bicarbonate solution, suggesting that phenols are probably absent. The acids were recovered from the sodium bicar-

bonate solution in the form of a brown solid (1.6 g.).<sup>25</sup> This material proved to be only partly soluble in ether. The insoluble material (340 mg., 0.42 mole per mole of peroxide) had a m.p. of 158–160° (159.5–160.0° after recrystallization from a benzene-methanol mixture) and was identified as the lactone VIII of *o*-(2-hydroxy-1-naphthyl)-benzoic acid, synthesis of which is described below. The ultraviolet curve in ethanol had maxima at 222 m $\mu$  (log  $\epsilon$  4.51), 243 (4.54), 313 (4.00) and 342 (3.92).

*Anal.* Calcd. for C<sub>17</sub>H<sub>10</sub>O<sub>2</sub>: C, 82.9; H, 4.1; mol. wt., 246.2. Found: C, 82.6; H, 3.8; mol. wt. (Signer in CHCl<sub>3</sub>), 244.

In another run the lactone yield was 0.36 mole per mole of peroxide.

The ether-soluble acid fraction was esterified with diazomethane. Part of this ester fraction (45 mg.) was soluble in sodium hydroxide solution and had infrared absorption at 3.00 and at 5.78  $\mu$ . This may be the ester of *o*-(8-hydroxy-1-naphthyl)-benzoic acid which would result from hydrolysis of the corresponding lactone. The rest of the ester fraction proved to be mostly the methyl ester of the starting acid VI (1.0 g.), m.p. 82–84° after sublimation (or 83–84° after recrystallization from methanol) (1.2 mole per mole of peroxide). Presumably about 0.6 g. of this acid was derived from the 0.56 g. of impurity present in the peroxide, for this impurity appeared to be the anhydride of VI.

**Lactone of *o*-(2-Hydroxy-1-naphthyl)-benzoic Acid.**— $\beta$ -Naphthol was iodinated in acetic acid solution in the presence of sodium acetate and lead acetate in 68% yield, m.p. 93–95°. Treatment with dimethyl sulfate and alkali gave 1-iodo-2-methoxynaphthalene, m.p. 86–88°, in 24% yield.<sup>26</sup>

A mixture of 0.033 mole of the 1-iodo-2-methoxynaphthalene with 0.034 mole of methyl 2-iodobenzoate was heated to 240° and 0.12 g. atom of copper bronze added. After 3 more hours at 250–280°, the mixture was cooled, extracted with hot acetone, and the acetone removed. Neutral material was removed after alkaline hydrolysis, and the insoluble diphenic acid separated from the acidic residues by benzene extraction. Distillation and recrystallization from ethanol gave 1 g. of colorless crystals of *o*-(2-methoxy-1-naphthyl)-benzoic acid, m.p. 221–222° (reported<sup>27</sup> 218–222°). Because of some doubt about the identity, the material was analyzed.

*Anal.* Calcd. for C<sub>18</sub>H<sub>14</sub>O<sub>3</sub>: C, 77.68; H, 5.07; CH<sub>3</sub>O, 11.15; neut. equiv., 278.3. Found: C, 77.7; H, 5.04; CH<sub>3</sub>O, 12.7; neut. equiv., 276.

Refluxing 200 mg. of the methoxy acid with a mixture of 2 ml. of glacial acetic acid and 2 ml. of 48% hydriodic acid for 12 hours followed by dilution with water and chloroform extraction gave 163 mg. of neutral material, m.p. 158–160°; after recrystallization from a benzene-methanol mixture the m.p. was 160.5–162°. This proved to be identical with the material isolated from the peroxide decomposition. The ease of lactonization noted here is quite common for phenolic acids that can give six-membered ring lactones.

***o*-Terphenyl-2-carboxylic Acid.**—In the Ullmann reaction 0.5 mole of methyl 2-iodobenzoate and 0.75 mole of 2-iodobiphenyl were heated at 230° for 1 hour during the addition of 3 g. atoms of copper bronze, then for 5 hours longer at 230–250°. After cooling, the mixture was extracted with hot acetone, the solvent removed, and the residue distilled. After hydrolysis with 20% ethanolic alkali followed by removal of the alcohol, the residue was taken up in water and extracted with benzene to give 56 g. of *o*-quaterphenyl. The aqueous layer was acidified, extracted with ether, and the ether removed to give a residue of acids. Extraction with benzene gave 44 g. of insoluble diphenic acid. The benzene was removed, the 38 g. of oil taken up in ether, and 30 g. of *o*-terphenyl-2-carboxylic acid obtained, m.p. 124–126°; after several recrystallizations from ether, m.p. 125.5–126.5°.

*Anal.* Calcd. for C<sub>19</sub>H<sub>14</sub>O<sub>2</sub>: C, 83.20; H, 5.15; neut. equiv., 274.3. Found: C, 82.8; H, 5.1; neut. equiv., 275.

The S-benzylthiouranium salt had a m.p. of 155–156°, reported<sup>28</sup> 154.5–155°.

(25) All figures obtained from examination of aliquots are reported in terms of the original total reaction residue.

(26) F. E. Ray and W. A. Moomaw, *THIS JOURNAL*, **55**, 3833 (1933).  
(27) I. M. Heilbron, D. H. Hey and R. Wilkinson, *J. Chem. Soc.*, 699 (1938).

(28) M. Stiles and J. Libbey, Jr., *J. Org. Chem.*, **22**, 1243 (1957).

(22) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 677 (1956).

(23) F. G. Badder and F. L. Warren, *J. Chem. Soc.*, 401 (1938).

(24) W. S. M. Grieve and D. S. Hey, *ibid.*, 108 (1938).

When heated overnight on a water-bath with 10 ml. of thionyl chloride, 400 mg. of the acid gave 260 mg. of 4-phenylfluorenone, isolated by chromatography using activity grade I neutral alumina<sup>29</sup> and benzene-hexane mixtures as eluents; yellow crystals, m.p. 110–112° from benzene-methanol<sup>28,30</sup>. At 30–60° thionyl chloride gave an anhydride that could be hydrolyzed back to the acid.

**Bis-*o*-terphenyl-2-carbonyl Peroxide.**—A solution of 3.4 g. of the *o*-terphenyl-2-carboxylic acid was refluxed for 10 hours with 25 ml. of acetyl chloride. The excess was removed by distillation under reduced pressure, then dry benzene was added and removed twice to help remove the acetic acid. The residual acid chloride was taken up in 25 ml. of anhydrous ether and added in dropwise fashion to 3 g. of sodium peroxide in 30 ml. of ice-water. The temperature was maintained below –4°. After an hour the ether layer was separated, washed, dried, and solvent removed yielding 0.99 g. (30%) of peroxide 99.5% pure by iodometric titer. While variations gave higher yields, the purity was lower.

**Reference Compounds.**—*o*-Terphenyl was obtained from the Ullmann reaction of iodobenzene and 2-iodobiphenyl in 40% yield, m.p. 56–57° from hexane, reported<sup>31</sup> 57°. The ultraviolet curve had a maximum at 233 m $\mu$  (log  $\epsilon$  4.44) in ethanol.

*o*-Quaterphenyl was a by-product from the acid preparation, m.p. 117–119°; reported<sup>30</sup> 119°. The ultraviolet curve had a maximum at 228 m $\mu$  (log  $\epsilon$  4.52) in ethanol.

Triphenylene was prepared from cyclohexanone by sulfuric acid cyclization to the dodecahydro compound which was dehydrogenated over selenium; m.p. 198–199° after sublimation followed by recrystallization from a benzene-ethanol mixture, reported<sup>32</sup> 198°. The ultraviolet curve had maxima at 249 m $\mu$  (log  $\epsilon$  4.82), 258 (5.14), 273 (4.29) and 284 (4.24), in ethanol.

**Decomposition of *o*-Terphenyl-2-carbonyl Peroxide in Benzene.**—A solution of 310 mg. of the peroxide in 70 ml. of freshly distilled and chromatographed benzene was heated under vacuum in a sealed reaction apparatus at 70° for 64 hours. The flask was then connected to a train containing a tube filled with Ascarite (sodium hydroxide on asbestos) for collecting the carbon dioxide. Inlet and outlet seals were broken, and the system was swept with nitrogen. The carbon dioxide yield was 0.93 mole per mole of peroxide. In other runs the yield was 1.00 and 0.85 mole per mole. The solvent was removed, leaving a residue of 295 mg. This was dissolved in 15 ml of benzene, and the solution was extracted with cold 10% aqueous sodium hydroxide solution to remove acids. The crude acidic material (61 mg.) was sublimed at 130° at 0.1 mm.; about 25% was volatile, m.p. 122–124°, and gave no depression on admixture with *o*-terphenyl-2-carboxylic acid. Perhaps the remainder is dimeric or polymeric. In two other runs the total amount of acidic material was about the same, 0.39 and 0.45 "mole" per mole of peroxide based on an assumed molecular weight of 274. The composition of these fractions was not determined.

Triphenylene was estimated in various ways. In one run the neutral residue was hydrolyzed with refluxing 20% ethanolic potassium hydroxide solution. The neutral (hydrocarbon) residue weighed 136 mg. After sublimation and recrystallization (benzene-ethanol) of a portion of this material, pure triphenylene, m.p. 198–199°, was obtained. Gas chromatographic analysis indicated that about 70 mg. (0.5 mole per mole of peroxide) of above residue was triphenylene. In another run the residue remaining after extraction of the acidic materials was hydrogenated before hydrolysis. After alkaline hydrolysis, the hydrocarbon residue was analyzed for triphenylene by measuring the ultraviolet absorption at 249 and at 258 m $\mu$  and was found to contain 52%. Another portion was chromatographed on activity grade I neutral alumina and yielded some 50–60% of pure triphenylene, m.p. 196–197° after recrystallization. The yield of triphenylene in this run was 0.56 mole per mole of peroxide. In the third run the residue after removal of acids was chromatographed directly on activity grade II

neutral alumina<sup>29</sup> and 0.48 mole of triphenylene per mole of peroxide was isolated in pure form.

The triphenylene fraction from the first run was examined for *o*-terphenyl and *o*-quaterphenyl by gas chromatography using a 1.2-meter column packed with high-vacuum silicone grease on Celite (a diatomaceous earth) with a column temperature of 240°, a pressure of 0.8 atm., and a helium flow rate of 40–45 ml. per min. With 20- $\mu$ l. samples of 1% solution the retention times were: benzene (0.5 min.), *o*-terphenyl (9), *o*-quaterphenyl (36) and triphenylene (42). There were no peaks corresponding to *o*-terphenyl or *o*-quaterphenyl, but the peak corresponding to triphenylene was large. There were small unidentified peaks at 6.5 and at 23 min.

The alkaline hydrolysates were examined for the presence of 2-hydroxy-*o*-terphenyl by isolation and by gas chromatography (retention time 7 min. under the above conditions). None could be found.

Attempts to isolate a pure substance from the ester fraction failed.

**Decomposition of *o*-Terphenyl-2-carbonyl Peroxide in Carbon Tetrachloride.**—A solution of 1.51 g. of peroxide of 98% purity was decomposed in carbon tetrachloride (purified by passage through alumina and distillation from phosphorus pentoxide) as described for the run in benzene. The apparent yield of carbon dioxide was 0.89 mole per mole of peroxide; the presence or absence of other acidic materials such as phosgene was not established. Approximately half of the acidic fraction (300 mg. out of 620 mg.) sublimed at 150° at 0.1 mm. and had an infrared curve essentially identical with that of *o*-terphenyl-2-carboxylic acid. The yield was 0.40 mole per mole of peroxide. Hexachloroethane was isolated from the solvent and identified by m.p. (183–185° in sealed tube).

Triphenylene was estimated to constitute 65% of the neutral fraction (560 mg.) after alkaline hydrolysis of the residue both by ultraviolet absorption at 257 m $\mu$  and by gas chromatography. The yield of triphenylene was 0.58 mole per mole of peroxide. *o*-Terphenyl was absent. The residue from sublimation of the triphenylene at 80–90° and 0.1 mm. decolorized 2% aqueous permanganate and bromine in carbon tetrachloride thus indicating the presence of unsaturated materials.

The curve from the gas chromatograph was examined for evidence of 2-chloro-*o*-terphenyl. Since a sample of this material was not available, its retention time can be estimated as being less than 5.5 min. (that of 2-bromo-*o*-terphenyl). The only peak in this region was one at 4.5 min., with an area indicating that this compound would constitute about 2–3% of the neutral (hydrocarbon) fraction or about 0.01 mole per mole of peroxide.

From the alkaline hydrolysis mixture was obtained 490 mg. of black residue after acidification. From this there was obtained 125 g. of a neutral product (lactone), m.p. 171–173° after recrystallization from a benzene-methanol mixture. This had ultraviolet maxima at 227 m $\mu$  (log  $\epsilon$  4.73), 266 (4.08), 275 (4.09) and 315 (3.94) and infrared absorption at 3.3, 5.75 and 5.81 $\mu$ . On the assumption that this was the lactone of 2'-hydroxy-*o*-terphenyl-2-carboxylic acid, the yield was 0.17 mole per mole of peroxide.

**Anal.** Calcd. for C<sub>19</sub>H<sub>12</sub>O<sub>2</sub>: C, 83.8; H, 4.4; mol. wt., 272. Found: C, 82.6, 83.1; H, 4.4, 4.4; mol. wt., 280 (on separate analytical samples).

The rest of the acidic material after separation of the lactone was converted by use of diazomethane to the methyl ester of *o*-terphenyl-2-carboxylic acid (0.40 mole per mole of peroxide).

**Decomposition of *o*-Terphenyl-2-carboxyl Peroxide in Bromotrichloromethane.**—A solution of 2.89 g. of peroxide of 98% purity was decomposed in 500 ml. of bromo-trichloromethane (purified by passage through alumina and distillation from phosphorus pentoxide). The apparent yield of carbon dioxide was 0.44 mole per mole of peroxide; the presence or absence of contaminating acidic materials was not investigated. From an aliquot the amount of free acids was estimated as 1.07 g. and of this 0.54 g. was *o*-terphenyl-2-carboxylic acid (0.39 mole per mole of peroxide). Hexachloroethane was isolated from the total solvent after its removal under reduced pressure.

After hydrolysis of an aliquot of the residue, the neutral material was assayed for triphenylene, for 2-bromo-*o*-terphenyl and for *o*-terphenyl by gas chromatography. The

(29) H. Brockmann and H. Schodder, *Ber.*, **74**, 73 (1941). The activity was checked by the use of the specified dyes.

(30) K. Alder, J. Haydn, K. Heimbach, K. Neufang, G. Hansen and W. Gerhard, *Ann.*, **586**, 130 (1954).

(31) W. E. Bachmann and H. T. Clarke, *This Journal*, **49**, 2089 (1927).

(32) E. Bergmann and O. Blum-Bergmann, *ibid.*, **59**, 1441 (1937).

respective retention times were 14, 5.5 and 3.5 min. The total yields were estimated to be 0.1 mole of triphenylene and 0.04 mole of 2-bromo-*o*-terphenyl per mole of peroxide. There was no peak between 3 and 4 min.

One aliquot of the original reaction product was hydrogenated before application of the isolation procedure. The yield of free acids, of triphenylene and of 2-bromo-*o*-terphenyl were the same as on the other aliquot.

From the acidic fraction obtained after hydrolysis there was obtained 410 mg. of the same lactone found in the carbon tetrachloride runs (0.58 mole per mole of peroxide). After treatment of the remaining material with diazomethane there were isolated 100 mg. of unidentified material, m.p. 128–130° dec., and 550 mg. of the methyl ester of *o*-terphenyl-2-carboxylic acid.

**2-Amino-*o*-terphenyl.**—A mixture of 0.2 mole of *o*-chloronitrobenzene and 0.15 mole of 2-iodobiphenyl was heated at 230° for 30 minutes during the addition of 1.1 g. atom of copper bronze and for an additional 4 hours at 260–270°. Extraction of the cooled mixture with hot acetone and removal of the acetone gave 41 g. of black oil. This was distilled at 3 mm. to give 12.6 g. of mixture, b.p. 190–120°. In order to remove the 2,2'-dinitrobiphenyl the fraction was dissolved in benzene and percolated through a 35-mm. diameter column of 700 g. of activity grade I neutral alumina. The first 520 ml. of benzene eluate gave 2.6 g. of *o*-quaterphenyl, the next 270 ml. gave 8.8 g. of a mixture. Later fractions contained mostly dinitrobiphenyl. The 8.8-g. fraction was adsorbed on a fresh column; the first 500 ml. gave 1.35 g. of *o*-quaterphenyl, the second 40 ml. gave a mixture, and the third 250 ml. gave 6.4 g. of relatively pure 2-nitro-*o*-terphenyl (12% yield). Repeated crystallization from methanol gave pale yellow needles, m.p. 93–94°.

*Anal.* Calcd. for  $C_{18}H_{13}NO_2$ : C, 78.53; H, 4.76; N, 5.09. Found: C, 78.5; H, 4.8; N, 5.03.

Catalytic reduction of the nitro compound over 10% palladium-on-carbon in benzene solution at room temperature and atmospheric pressure gave 2-amino-*o*-terphenyl, colorless crystals from ethanol, m.p. 75–76°.

*Anal.* Calcd. for  $C_{18}H_{15}N$ : C, 88.13; H, 6.16; N, 5.71. Found: C, 87.8; H, 5.9; N, 5.98.

In preparative work it was not necessary to separate the *o*-quaterphenyl from the amine. From 0.5 mole of 2-iodobiphenyl and 0.6 mole of chloronitrobenzene the 2-nitro-*o*-terphenyl fraction was separated from the dinitrobiphenyl by chromatography. After hydrogenation the amine was isolated through the hydrochloride in 21% yield.

Treatment of the amine with acetyl chloride in pyridine gave the diacetyl derivative, m.p. 179–180° from ethanol.

*Anal.* Calcd. for  $C_{22}H_{19}NO_2$ : C, 80.22; H, 5.81; N, 4.25. Found (two different anal. samples): C, 80.4, 80.3; H, 5.7, 5.7; N, 4.41, 4.29.

**2-(*o*-Terphenyl)-diazonium Fluoborate.**—Fluoboric acid was added to a filtered aqueous solution of the diazonium chloride. The precipitated fluoborate was purified by solution in methanol and precipitation with ether.

*Anal.* Calcd. for  $C_{18}H_{13}N_2BF_4$ : C, 62.82; H, 3.81; N, 8.14. Found: C, 63.0; H, 3.9; N, 8.12.

The chloride and the bisulfate salts were less convenient to work with.

**Procedure for Decomposition of the Diazonium Salts of 2-Amino-*o*-terphenyl.**—A 160–220 mg. sample of the diazonium fluoroborate was stirred or heated until a spot on filter paper moistened with  $\beta$ -naphthol solution no longer gave a red color. Runs using copper powder or cuprous chloride utilized about 2 g. of these catalysts.

The reaction mixture was extracted with four or five 10–15 ml. portions of chloroform. After removal of the chloroform the residue was assayed by either liquid phase or gas phase chromatography. For the former the product dissolved in 5 ml. of benzene was introduced onto a 10-mm. diameter column of activity grade I neutral alumina. The first 100 ml. of benzene eluate contained the triphenylene, the next 50 ml. contained very little material. The column then was eluted with 200 ml. of a 1:10 methanol-ether mixture of recover 2-hydroxy-*o*-terphenyl, which was

obtained as a thick oil with infrared absorption at 2.80, 7.50 and 8.50 $\mu$ , and was distilled.

*Anal.* Calcd. for  $C_{18}H_{14}O$ : C, 87.8; H, 5.7. Found: C, 86.1; H, 5.6.

The gas phase chromatography utilized a 120 cm. long column of Celite coated with Dow-Corning high-vacuum silicone grease operated at 280° using helium as the carrier. The retention time of triphenylene was 10.5 min., of *o*-terphenyl 3.0, and of 2-hydroxy-*o*-terphenyl 4.0.

For the alkaline 2-phase decomposition reactions the amine hydrochloride (5 mmoles) was diazotized with sulfuric acid and sodium nitrite to give 5–6 ml. of solution. After 15 minutes, 20 ml. of the organic medium (benzene, carbon tetrachloride, or bromotrichloromethane) was added, then 30% sodium hydroxide to give a pH of 12 to 13 at 5–10°. After stirring overnight at room temperature, 15 ml. of benzene was added, and the organic layer introduced onto a column 2.5 cm. in diameter containing 100 g. of activity grade I alumina. The first 200 ml. of benzene eluate contained all of the triphenylene and related products. Continued elution gave small amounts of a reddish material which was not identified.

With benzene and carbon tetrachloride runs the benzene eluate on evaporation gave pure triphenylene, m.p. 198–199°. In order to test the detectability of small amounts of *o*-quaterphenyl, a mixture of 8 mg. of *o*-quaterphenyl and 102 mg. of triphenylene was subjected to the isolation procedure. The first 50 mg. of recovered hydrocarbon had a m.p. of 188–194° (s. at 165) and the second 58 mg. had a m.p. of 193–197° (s. at 170). Thus the reaction mixtures contained something less than 1% of the *o*-quaterphenyl.

The reaction product with bromotrichloromethane appeared to be half triphenylene and half a bromine-containing compound which did not crystallize.

A sample was distilled at 80–90° at 0.1 mm. to give a distillate consisting primarily of 2-bromo-*o*-terphenyl. This distillate was then subjected to gas chromatography to separate a very small amount of triphenylene.

*Anal.* Calcd. for  $C_{18}H_{13}Br$ : C, 69.9; H, 4.24; Br, 25.9. Found (distilled sample): C, 70.0; H, 4.23; Br, 25.9. Found (gas chromatographed sample): C, 70.2; H, 4.2; Br, 25.9.

Attempts to prepare this compound by the Sandmeyer procedure (using cuprous bromide dissolved in hydrobromic acid) gave only triphenylene.

For the quantitative runs a 350–500 mg. sample of the diazonium fluoroborate was added to a vigorously stirred mixture of the halomethane and a phosphate buffer at pH 11.1 and the mixture stirred until the spot test with  $\beta$ -naphthol gave no color. The products were assayed by solution chromatography. The principal by-product was an unidentified red solid.

**Products from the Gomberg-Bachmann Reaction of *o*-Benzoylbenzenediazonium Salts with Benzene.**—Three grams of 2-aminobenzophenone was diazotized in 6 ml. of 1:1 sulfuric acid with 1.2 g. of sodium nitrite in 25 ml. of water at 0°. To the solution was added 40 ml. of benzene and then 30% sodium hydroxide to a pH of 12–13 at 5–12°. The crude residue after removal of the benzene amounted to 2.83 g. This was passed through a 2.0 cm. column of 120 g. of activity grade II alumina and eluted with 100 ml. of 1:1 benzene-pentane to give 0.93 g. of oil with infrared peaks suggesting the presence of fluorenone, benzophenone and 2-benzoylbiphenyl. The oil was analyzed by gas chromatography on the same column used for the other runs. At a temperature of 215° retention times were benzene (0.5 min.), benzophenone (7), 2-hydroxybenzophenone (10.5), 2-benzoylbiphenyl (36). A benzene solution of the above oil had peaks at 0.5, 7, 10.5, and 36 min., but no others. The yields were benzophenone 6.3%, fluorenone 6%, and 2-benzoylbiphenyl 13.4%.

**Kinetics of the Thermal Decomposition of *o*-Terphenyl-2-carbonyl Peroxide in Benzene.**—The solution was made up in a volumetric flask and portions pipetted into tubes which were outgassed and sealed on a vacuum train. The peroxide was titrated as described previously. The reactions were first order. The results at 79.1° were ( $k \times 10^4 \text{sec}^{-1}$ ) concn. 0.0096 *M*, 3.55; 0.0095 *M*, 3.39; 0.109 *M*, 4.27.