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# Mechanism of aromatic substitution by free radicals

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MECHANISM OF AROMATIC SUBSTITUTION BY FREE RADICALS

by

James Harvey Waters

A Dissertation Submitted to the  
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DOCTOR OF PHILOSOPHY

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Approved:

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1961

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## INTRODUCTION

The substitution reactions of aromatic systems by electrophilic and by nucleophilic reagents have been subjected to detailed quantitative study extending over a number of years. While some problems remain, the broad mechanistic outlines of these reactions are securely established at present.

By contrast, the substitution reactions of aromatic nuclei by free radicals are still very incompletely understood. Accurate quantitative investigation of these reactions is difficult for two reasons. First, the free radicals of interest as substituting agents in such reactions are extremely reactive, with the result that they cannot be manipulated and their concentrations controlled directly in the fashion that is possible for ionic reagents. Instead they must be produced in low, steady state concentrations which are difficult to measure. In many cases of importance, the radical of interest results from decomposition of the radical first produced from the reagent. Consequently there is a potential ambiguity regarding the nature of the radical that effects the substitution. Second, the reactions do not proceed cleanly to give a small number of well-defined products. A large number of side reactions occur to produce a variety of products, some of which are difficult to separate from the products of the substitution

process. In a number of important cases, a large fraction (up to 50%) of the total product mixture consists of intrac-table tars, the formation of which competes with the substitution process. Partly as a result of these difficulties, and partly because the development of organic free radical chemistry in general has come later than that of ionic organic chemistry, reliable quantitative results in this field have begun to be available only recently.

In the past ten years, a number of careful studies have been made of product distributions, relative reactivities, substituent directive effects, and isotope effects in substitution reactions of aromatic compounds by alkyl and aryl free radicals from various sources. However, only a very little information is available about the variation in product distribution for any given reaction as the concentration of radical source is changed. Such information would be highly relevant to considerations of the mechanism of the reaction. Information of this kind should be of particular interest in the reaction of free radicals with toluene. In this case a second, rather well-understood reaction, hydrogen abstraction from the methyl group, competes with the substitution reaction. Abstraction produces benzyl radicals, which are relatively stable, and react largely by coupling. The present research was designed to measure the variation in yields of methylbiphenyls and bibenzyl

produced by attack on toluene of phenyl radicals derived from decomposition of benzoyl peroxide as the concentration of radical source is changed.

## HISTORICAL

The field of aromatic substitution by free radicals has been reviewed in detail quite recently.<sup>1,2,3</sup> Consequently, no attempt will be made in this dissertation to provide a comprehensive account of investigations in this area. Readers desiring a complete bibliography of work in this field are referred to the reviews cited. The present section will be concerned only with a brief outline of the key developments in the chemistry of such processes, and statement of the mechanistic ideas that have been advanced to correlate and explain them.

It has been known for many years that certain aromatic diazo compounds undergo reaction with aromatic substrates with production of biaryls. The former include diazo esters, diazotates<sup>4,5</sup> and N-nitrosoacylarylamides.<sup>6</sup> Both reactions

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<sup>1</sup>G. H. Williams, "Homolytic Aromatic Substitution", Pergamon Press, London, 1960.

<sup>2</sup>D. R. Augood and G. H. Williams, Chem. Rev., 57, 123 (1957).

<sup>3</sup>O. C. Dermer and M. T. Edmison, ibid., 57, 77 (1957).

<sup>4</sup>(a) E. Bamberger, Ber., 28, 403 (1895); (b) E. Bamberger, ibid., 29, 446 (1896).

<sup>5</sup>(a) O. Kühling, ibid., 28, 41, 523 (1895); (b) O. Kühling, ibid., 29, 165 (1896).

<sup>6</sup>E. Bamberger, ibid., 30, 366 (1897).



have been developed as synthetic methods, the former by Gomberg and his co-workers<sup>7,8</sup>, the latter by Hey and his group<sup>9</sup>. The most distinguishing feature of these arylation reactions is the absence of the usual orienting influences of substituents evident in polar reactions. The earliest work tended to indicate that all substituents were o,p-directing; later, evidence mounted<sup>9b,9c,10,11</sup> that all three isomers were usually formed in these reactions, and that substituent effects were very small, producing only minor deviations from a random substitution pattern.

The first careful study of the products of the decomposition of benzoyl peroxide in aromatic solvents was carried out by Gelissen and Hermans<sup>12</sup>. They found as major

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<sup>7</sup>(a) M. Gomberg and W. E. Bachmann, J. Am. Chem. Soc., 46, 2339 (1924); (b) M. Gomberg and J. C. Fernert, ibid., 48, 1372 (1926).

<sup>8</sup>W. E. Bachmann and R. A. Hoffman, "Organic Reactions", Vol. 2, John Wiley & Sons, Inc., New York, N.Y., 1944, p. 224.

<sup>9</sup>(a) W. S. M. Grieve and D. H. Hey, J. Chem. Soc., 1797 (1934); (b) H. France, I. M. Heilbron, and D. H. Hey, ibid., 1364 (1938); (c) H. France, I. M. Heilbron, and D. H. Hey, ibid., 1283 (1939).

<sup>10</sup>D. H. Hey, ibid., 1966 (1934).

<sup>11</sup>D. H. Hey, A. Nechvatal and T. S. Robinson, ibid., 2892 (1951), and subsequent papers.

<sup>12</sup>H. Gelissen and P. H. Hermans, Ber., 58, 285, 476, 764 (1925).

products the unsymmetrical biaryl and benzoic acid, together with large quantities of intractable resin containing hydrolysable benzoate groups, and small amounts of benzene, phenylbenzoic acids, aryl benzoates, terphenyls, and quaterphenyls. Hey<sup>10</sup> found that the distributions of biaryl isomers formed in the decomposition of benzoyl peroxide in aromatic solvents were similar to those produced in the corresponding reactions of the azo compounds, and were insensitive to the polar nature of the substituent.

The suggestion that aryl free radicals are intermediates in these reactions was advanced by Hey<sup>9a,10,13</sup> and is now generally accepted. Hey<sup>10</sup> also demonstrated that phenylazotriphenylmethane, which had been shown earlier to undergo decomposition with the production of free radicals<sup>14</sup>, also brings about a similar phenylation of aromatic compounds. The ability of aroyl peroxides<sup>15</sup>, phenylazotriphenylmethane<sup>16</sup>

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<sup>13</sup>D. H. Hey and W. A. Waters, Chem. Rev., 21, 169 (1937).

<sup>14</sup>H. Wieland, E. Popper and H. Seefried, Ber., 55B, 1816 (1922).

<sup>15</sup>See, for example, C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p. 70.

<sup>16</sup>G. V. Schulz, Naturwissenschaften, 27, 659 (1939).

and N-nitrosoacylarylamides<sup>17</sup> to initiate normal free-radical polymerization provides at least supporting evidence for the role of free radicals in arylations by these compounds.

In the past decade, accurate quantitative measures of isomer distributions resulting from the arylation reactions have become available for the first time, as a result of intensive researches by a number of workers<sup>11,18,19,20,21</sup>. The same investigators have determined relative reactivities of various aromatic substrates in the arylation reactions by means of competitive experiments. Detailed material balances have been obtained by Dannley<sup>20</sup>, and especially by Lynch and Pausacker<sup>22</sup>. For cases in which the substrate is

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<sup>17</sup>(a) A. T. Blomquist, J. R. Johnson and H. J. Sykes, J. Am. Chem. Soc., 65, 2446 (1943); (b) D. H. Hey and G. S. Misra, Discussions Faraday Soc., 2, 279 (1947); (c) D. F. DeTar and C. S. Savat, J. Am. Chem. Soc., 75, 5116 (1953).

<sup>18</sup>O. Simamura, T. Inukai and M. Kazanishi, Bull. Chem. Soc. Japan, 23, 205 (1950), and subsequent papers.

<sup>19</sup>D. F. DeTar and S. V. Scheifele, J. Am. Chem. Soc., 73, 1442 (1951).

<sup>20</sup>R. L. Dannley, E. C. Gregg, R. E. Phelps and C. B. Coleman, J. Am. Chem. Soc., 76, 445 (1954), and subsequent papers.

<sup>21</sup>(a) C. S. Rondestvedt and H. S. Blanchard, ibid., 77, 1769 (1955); (b) C. S. Rondestvedt and H. S. Blanchard, J. Org. Chem., 21, 229 (1956).

<sup>22</sup>B. M. Lynch and K. H. Pausacker, Austral. J. Chem., 10, 40 (1957), and subsequent papers.

an alkylbenzene, the relative extents of nuclear substitution and attack on the alkyl side chain have been investigated<sup>21a,23,24,25</sup>. A very careful and highly significant study of the deuterium isotope effect in arylation by free radicals has been carried out by Eliel and his co-workers<sup>26</sup>.

In most of the quantitative investigations of arylation by free radicals, the source of radicals has been an aroyl peroxide. The kinetics of decomposition of benzoyl peroxide have been investigated by a number of workers<sup>27,28,29,30,31</sup>.

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<sup>23</sup>J. I. G. Cadogan, D. H. Hey and G. H. Williams, J. Chem. Soc., 3352 (1954).

<sup>24</sup>D. H. Hey, B. W. Pengilly and G. H. Williams, ibid., 6 (1955).

<sup>25</sup>D. H. Hey, B. W. Pengilly and G. H. Williams, ibid., 1463 (1956).

<sup>26</sup>E. L. Eliel, S. Meyerson, Z. Welvart and S. H. Wilen, J. Am. Chem. Soc., 82, 2936 (1960).

<sup>27</sup>(a) K. Nozaki and P. D. Bartlett, ibid., 68, 1686 (1946); (b) P. D. Bartlett and K. Nozaki, ibid., 69, 2299 (1947).

<sup>28</sup>P. F. Hartman, H. G. Sellers and D. Turnbull, ibid., 69, 2416 (1947).

<sup>29</sup>B. Barnett and W. E. Vaughan, J. Phys. Coll. Chem., 51, 926, 942 (1947).

<sup>30</sup>(a) G. S. Hammond, J. Am. Chem. Soc., 72, 3737 (1950); (b) G. S. Hammond and L. M. Soffer, ibid., 72, 4711 (1950).

<sup>31</sup>C. G. Swain, L. J. Schaad and A. J. Kresge, ibid., 80, 3313 (1958).

Substituted aroyl peroxides also have been studied.<sup>32,33</sup> In the presence of scavengers for free radicals, the decomposition of benzoyl peroxide is first order<sup>30,31,32</sup>. In the absence of scavengers, a higher-order induced decomposition occurs<sup>27,28</sup> in most solvents. The first step in the unimolecular decomposition has been shown to be the formation of two benzoyloxy radicals<sup>30b</sup>. These decarboxylate to give phenyl radicals to an extent that varies with experimental conditions<sup>29a</sup>.

A substantial number of other procedures have been shown to result in similar arylations of aromatic solvents. These include the acid-catalysed decomposition of 1-aryl-3,3-dialkyltriazenes at 90-140°<sup>34</sup>; the thermal decomposition of 1,3-diaryltriazene<sup>35</sup>; the oxidation of phenylhydrazine at low temperatures by silver oxide and other oxidizing agents<sup>36</sup>; the thermal decomposition of silver halide dibenzoates<sup>37</sup>;

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<sup>32</sup>C. G. Swain, W. H. Stockmayer and J. T. Clarke, J. Am. Chem. Soc., 72, 5426 (1958).

<sup>33</sup>A. T. Blomquist and A. J. Buselli, ibid., 73, 3883 (1951).

<sup>34</sup>J. Elks and D. H. Hey, J. Chem. Soc., 441 (1943).

<sup>35</sup>R. L. Hardie and R. H. Thomson, ibid., 1286 (1958).

<sup>36</sup>R. L. Hardie and R. H. Thomson, ibid., 2512 (1957).

<sup>37</sup>D. Bryce-Smith and P. Clarke, ibid., 2264 (1956).

the electrolysis of benzoic acid<sup>38</sup>; the thermal decomposition of lead tetrabenzoate<sup>39</sup> and of phenyliodosodibenzoate<sup>40,41</sup>; and the photolysis of triphenylbismuth<sup>42</sup>. In several cases, explicit comparisons of the isomer ratios produced by two or more sources of the same radical in the same solvent under the same conditions have been made; the agreement is remarkably close.

The relative reactivities of a large number of aromatic compounds toward methyl and other alkyl radicals have been investigated by Szwarc and his co-workers<sup>43</sup>; the reaction involved is presumed to be an addition corresponding to the first step in the substitution by aryl radicals. Very recently, the isomer distributions in the methylation of several aromatic substrates by free radicals have been meas-

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<sup>38</sup>P. J. Bunyan and D. H. Hey, J. Chem. Soc., 3787 (1960).

<sup>39</sup>D. H. Hey, C. J. M. Stirling, and G. H. Williams, ibid., 2747 (1954).

<sup>40</sup>D. H. Hey, C. J. M. Stirling and G. H. Williams, ibid., 3963 (1955).

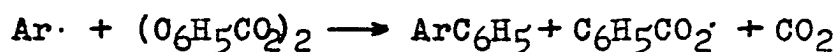
<sup>41</sup>D. H. Hey, C. J. M. Stirling and G. H. Williams, ibid., 1475 (1956).

<sup>42</sup>D. H. Hey and co-workers, unpublished investigations cited in reference 1, p. 42.

<sup>43</sup>M. Levy, M. Steinberg and M. Szwarc, J. Am. Chem. Soc., 76, 3439 (1954), and subsequent papers.

ured<sup>44</sup>.

Among the possible paths for such substitution reactions by free radicals are those involving abstraction of a hydrogen atom from the substrate by radicals derived from the reagent, followed by some reaction of the radicals thus formed to give the product. Such a mechanism has been suggested<sup>45</sup>, with attack of the substrate-derived radical on the radical source as the product-forming step:



Such mechanisms are now considered unlikely as major pathways for the reaction, since coupling of the substrate-derived radicals to give the symmetrical biaryl would be expected to occur to a significant extent. In fact, products of this type are rarely found, and in the few cases in which they are observed<sup>46</sup>, alternative explanations<sup>47</sup> of their formation are available<sup>47</sup>.

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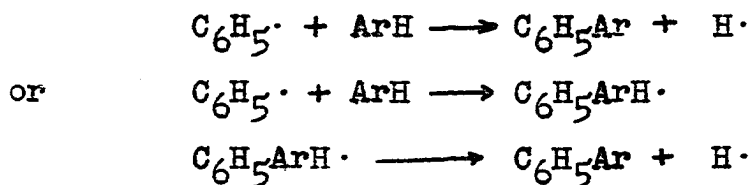
<sup>44</sup>B. R. Cowley, R. O. C. Norman and W. A. Waters, J. Chem. Soc., 1799 (1959).

<sup>45</sup>D. F. DeTar and S. V. Sagmanli, J. Am. Chem. Soc., 72, 965 (1950).

<sup>46</sup>D. I. Davies, D. H. Hey and G. H. Williams, J. Chem. Soc., 1878 (1958).

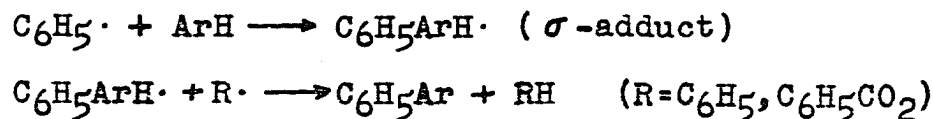
<sup>47</sup>D. F. DeTar and R. A. J. Long, J. Am. Chem. Soc., 80, 4742 (1958).

Hey and co-workers<sup>9a,2</sup> have suggested a mechanism in which a hydrogen atom is displaced by the substituting radical, either directly or via an adduct which unimolecularly expels a hydrogen atom:



It seems to be generally considered by other authors<sup>48</sup> that the high energy required to produce free hydrogen atoms renders this mechanism improbable.

A third class of mechanisms consists of those involving addition of the substituting radical to the substrate, followed by abstraction of a hydrogen atom from the adduct by another radical. Most of the mechanisms that are seriously considered at present belong to this category, with differences as to possible reversibility of the addition step, the detailed nature of the adduct, and the nature of the termination step. Lynch and Pausacker<sup>22</sup> have proposed this mechanism in its simplest form for arylations with benzoyl peroxide:

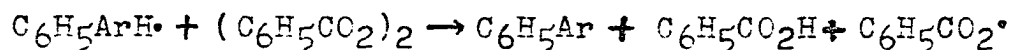



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<sup>48</sup>See for example p. 483 of the reference cited in footnote 15.

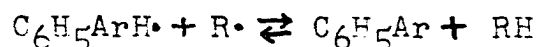


with the additional assumption<sup>49</sup> that part of the biaryl arises from induced decomposition of the peroxide by the adduct radical:



Elie<sup>26</sup> discusses the reaction in terms of essentially the same mechanism, except that at most concentrations the major termination step is considered to be disproportionation of two adduct radicals.

Hammond and co-workers<sup>50,51</sup> have suggested an effectively termolecular reaction, in which very rapid reversible formation of a  $\pi$ -complex of the radical with substrate occurs, followed by hydrogen abstraction from this adduct by another radical:



Rondestvedt<sup>21b</sup> suggests a similar mechanism in which the first-formed loose complex is converted unimolecularly to a  $\sigma$  complex, and the latter loses a hydrogen atom to another radical to produce biaryl.

<sup>49</sup>K. H. Pausecker, Austral. J. Chem., 10, 49 (1957).

<sup>50</sup>G. S. Hammond, J. T. Rudesill and F. J. Modic, J. Am. Chem. Soc., 73, 3929 (1951).

<sup>51</sup>J. F. Garst, "Mechanism of Homolytic Aromatic Substitution", Unpublished Ph. D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1957.

## EXPERIMENTAL

Reagents

Toluene was purified essentially by the method of Fieser<sup>52</sup>. Two liters of Reagent Grade toluene were stirred mechanically with 160 ml. concentrated sulfuric acid in an ice-water bath for half an hour. The acid was separated, and the process was repeated twice more. The acid from the second washing was only faintly colored, and that from the third washing was colorless. The toluene was washed with two 200 ml. portions of water, dried for at least six hours over anhydrous sodium sulfate, and fractionally distilled through a 26 inch Wheeler column packed with metal helices. A center fraction, boiling point 109.8-110.1°, was retained and stored over sodium ribbon.

Inactive benzoyl peroxide was purified by recrystallization. It was dissolved in the minimum volume of chloroform, and the solution was added to three times its own volume of ligroin (boiling range 60-70°). The solution was allowed to stand overnight in the refrigerator, and filtered the following day. The product was assayed for peroxide by the method of Kokatnur and Jelling<sup>53</sup>, and was found to contain

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<sup>52</sup>L. F. Fieser, "Experiments in Organic Chemistry", 2nd ed., D. C. Heath and Company, Boston, Mass., 1941, p. 364.

<sup>53</sup>V. R. Kokatnur and M. Jelling, J. Am. Chem. Soc., 63, 1432 (1941).

99.0% active peroxide.

Biphenyl was recrystallized twice from methanol, melting point 70.0-70.5°.

Diphenylmethane was Eastman Practical Grade. It was faintly yellow, but gas chromatography on an asphalt column at 196° showed only one peak at other than very early retention times. It was used without further purification.

Bibenzyl was purified earlier by Dr. Fabian T. Fang. It melted at 53-54°.

o-Methylbiphenyl and m-methylbiphenyl were prepared previously by Dr. John F. Garst.

p-Methylbiphenyl was prepared by the method of Gomberg and Pernert.<sup>7b</sup> p-Toluidine (300 gm, 2.8 moles), obtained from Matheson, Coleman and Bell, was dissolved in 550 ml. concentrated hydrochloric acid, and the resulting solution was cooled to 0°. A solution of 200 gm. sodium nitrite in 300 ml. water, previously cooled to 10°, was added slowly with rapid manual stirring and occasional addition of crushed ice to keep the temperature of the mixture below 10°. A mixture of 1800 ml. technical grade benzene with 825 ml. of an aqueous solution containing 330 gm. sodium hydroxide was cooled to about 5° in a three gallon battery jar. The mixture was stirred rapidly, and the diazotized p-toluidine solution was added over an interval of two to three minutes. Ice was added frequently during this time and for an hour

thereafter to keep the temperature of the mixture below 5°. Stirring was continued for an additional three and one-half hours while the mixture warmed to room temperature. After the mixture stood overnight, the lower (aqueous) layer was removed by siphoning, and the upper layer was distilled to remove excess benzene. The black tarry residue was steam-distilled, at a pot temperature rising from 100 to 175°. The organic layers from the distillate fractions were combined and cooled in the refrigerator until crystallization occurred. The oily, reddish-yellow crude product was dissolved in ligroin (boiling range 30-60°) and chromatographed on acid-washed alumina. The product was slightly yellow, and the chromatography was repeated to give a colorless product which was recrystallized twice from methanol. The exact yield was not recorded, but was of the order of 10%, melting point 46.8-47.2°. Gas chromatography of a concentrated solution of the product in benzene showed, besides the solvent peak, one very large peak and two very small, barely discernible ones.

#### Analysis of hydrocarbon mixtures by gas chromatography

The first studies were carried out using an Aerograph instrument, made by Wilkens Instrument and Research, Inc., Walnut Creek, California. The columns used were five feet in length by one-fourth inch in diameter. Usual operating conditions were: temperature 190-215°, filament current 200

milliamperes, inlet pressure 8-15 lb/in.<sup>2</sup>, flow rate 6-10 calibration units, corresponding to 31.1-87.5 ml./min.

A series of known solutions of the low-molecular weight hydrocarbon products expected from the decomposition of benzoyl peroxide in toluene were prepared. Approximately 2-3 ml. of biphenyl, diphenylmethane, bibenzyl, and o-, m-, and p-methylbiphenyl, as the liquid or crystalline solid, were transferred to small test tubes and dissolved in an equal volume of toluene. These were used to identify peaks on the gas chromatograph traces of reaction mixtures and to determine retention times of the products under various operating conditions. For runs on individual compounds, 2-5  $\mu$ l. of solution was injected into the column; for runs with mixtures, 2-3  $\mu$ l. of each of the appropriate solutions were drawn into the syringe and the resulting mixture injected.

A mixture of o- and p-methylbiphenyl solutions showed two widely separated peaks, after that for solvent, on the Asphalt column at 201°. Under the same conditions, a mixture of o-, m-, and p- isomers showed the same first peak, while the second became a doublet cleft a little less than halfway to the base line. At 191° on the same column, separation of the three-isomer mixture was poorer, with the later peak only slightly divided. At 192° a mixture of the three methylbiphenyls with bibenzyl showed the early peak

again unchanged, while the second was large and asymmetric, with a plateau at the beginning.

A mixture of the three isomeric methylbiphenyls on the Silicone column at 203° showed two sharp, symmetrical peaks cleanly separated but quite close together, the second larger than the first. With Apiezon and Paraffin columns under similar conditions separation was again inferior to that on the Asphalt column.

Solutions of each of the six hydrocarbons were passed through the Asphalt column at 208-212° to determine retention times of the corresponding peaks. The results were: o-methylbiphenyl 540 sec., biphenyl 635 sec., diphenylmethane 670 sec., m-methylbiphenyl 865 sec., p-methylbiphenyl 945 sec., and bibenzyl 900 sec. The numbers are not strictly comparable due to imperfect reproducibility of operating conditions, especially temperature, from one run to the next. Passage of a mixture of all six components through the column at 210° gave a peak at 530 sec., a second, compound, peak with a maximum at 620 sec. and a shoulder at about 635 sec., and a third peak, also compound, with an initial shoulder at about 880 sec. and at 940 sec. The first peak presumably corresponds to o-methylbiphenyl, the second to biphenyl and diphenylmethane, and the third to the remaining three components. A mixture of all of these hydrocarbons except o-methylbiphenyl gave an identical trace except that

the first peak was absent. This establishes that o-methylbiphenyl is separated cleanly from the other products, and corresponds to the first peak in the trace.

Benzoyl peroxide (0.1498 gm., 0.618 millimole) was decomposed in toluene (6 ml.) at 80° according to the procedure described in detail below in connection with the numbered runs. The product mixture was concentrated to about 1 ml. by distillation of most of the excess toluene through a small column. A portion of the concentrated crude product was subjected to gas chromatography on the Asphalt column at 201.5°. The trace showed, after peaks ascribable to solvent, a series of six early, very small blips, a large peak at a retention time (665 sec.) reasonable for o-methylbiphenyl in view of the lower temperature, and a still larger, asymmetric peak at 1160 sec. The crude product mixture from a second, identical run was chromatographed on acid-washed alumina and eluted with ligroin (boiling range 30-60°) (fraction 1) and toluene (fraction 2). The volumes of eluent were not recorded, but were around 50 ml. The fractions were evaporated to small volume and passed through the Asphalt.gas chromatograph column at 200°. Fraction 1 gave a symmetrical peak at the appropriate position for o-methylbiphenyl and another peak, asymmetric with a plateau at the beginning, at the position for the m- and p- isomers and bibenzyl. The only other peak besides those for solvent

was a very small one a little before that for o-methylbiphenyl. The trace for fraction 2 was qualitatively similar, but the peaks were smaller and the unidentified early peak was absent.

At this stage in the investigation a second gas chromatograph became available. The instrument was a Leonco Model 15 Chromat-O-Flex, made by Loe Engineering Company, Pasadena, California. It had the advantages of greater sensitivity, much closer temperature control, and availability of somewhat longer columns than the Aerograph. The column used was six feet in length by one-fourth inch diameter, with a Silicone grease as stationary phase. Operating conditions used for most work were 208-211°, inlet pressure 10-15 lb./in.<sup>2</sup>, detector potential 11 volts. Flow rates were not measured in the early work with this machine; the inlet pressure was set and the needle valve opened all the way, which gave a fairly reproducible flow. In later work, the flow rate was measured using a Fisher and Porter Company Precision Bore Flowrator Tube No. 1/16-20-4/36; the flow rates used were in the range 15-19 calibration units, corresponding to 177-252 ml./min.

Retention times for the six expected hydrocarbon products were determined on the Loe instrument with the Silicone column in the same fashion as before. At 208° a mixture of all six components gave, after solvent, a large peak at



a retention time of 1280 sec., a smaller one, incompletely separated from the first, at 1490 sec., a large one at 1850 sec., and an only partially separated smaller one at 2070 sec. Under the same operating conditions, the pure compounds have peaks at the following retention times: biphenyl 1265 sec., diphenylmethane 1420 sec., bibenzyl 1980 sec., o-methylbiphenyl 1310 sec., m-methylbiphenyl 1620 sec., and p-methylbiphenyl 1760 sec. While the retention times found for the individual components do not correspond exactly to those found for the six-component mixture, it appears that in the trace for the mixture, the first peak corresponds to biphenyl and o-methylbiphenyl, the second to diphenylmethane, the third to m- and p-methylbiphenyl, and the fourth to bibenzyl.

A portion of the concentrated crude product mixture from the preliminary run was subjected to gas chromatography on the Loe instrument under the same conditions. A series of five low blips was observed, followed by a major peak at 1230 sec. (biphenyl and o-methylbiphenyl) with a bump on the tail that may correspond to diphenylmethane, another large peak at 1695 sec. (m- and p-isomers) and a smaller, incompletely separated peak at 1920 sec. (bibenzyl). Thus the peaks obtained with an actual product mixture correspond reasonably well to those for known samples of the hydrocarbons.

A mixture of biphenyl and diphenylmethane solutions on the same column at 210° showed two peaks close together, at 1150 and 1365 sec., but almost completely separated. A mixture of biphenyl and o-methylbiphenyl solutions gave one large peak at 1175 sec. These results definitely establish that the first peak in the six-component mixture corresponds to biphenyl and o-methylbiphenyl, which are not separated on this column, and that the second corresponds to diphenylmethane.

A mixture of naphthalene, o-methylbiphenyl, and bibenzyl solutions on the Silicone column at 210° gave three peaks, that for naphthalene coming earlier than the others and well separated from them. Thus naphthalene is usable as an internal "marker" for quantitative determination of product yields from this reaction by measurement of peak areas.

Solutions containing accurately measured quantities of naphthalene and of each of the six expected hydrocarbon products, except diphenylmethane, were prepared. About 0.3 gm. of each compound was weighed accurately into a 10 ml. volumetric flask, dissolved in toluene, and made up to the mark with more toluene. These solutions were used to obtain calibration peaks for the quantitative gas chromatographic determination of product yields. A 20- $\mu$ l portion of the appropriate solution was injected into the Silicone column

on the Loe instrument. Operating conditions were: temperature 210°, detector potential 11 volts, inlet pressure 15 lb./in.<sup>2</sup>, flow rate 16.5 units on the meter (205ml./min. estimated from the calibration chart for air in Bulletin No. 202-6 published by the Matheson Company, Inc., East Rutherford, New Jersey), sensitivity scale 10. All six calibration peaks were obtained in the same day's operation of the instrument, and operating conditions were quite steady over the relevant period. Tracings of the resulting peaks were made on high-quality tracing paper. The peak tracings were cut out carefully and weighed, and the weights obtained were taken as proportional to peak areas, which in turn were assumed proportional to weights of the corresponding compound. The results are shown in Table 1.

Table 1. Calibration of gas chromatographic peak areas

	weight of hydrocarbon in standard solution, gm.	weight of cut-out peak, gm.
biphenyl	0.3077	0.2912
bibenzyl	.3016	.2584
o-methylbiphenyl	.3069	.2501
m-methylbiphenyl	.3050	.2729
p-methylbiphenyl	.3084	.2749
naphthalene	.3071	.2743

Decomposition of benzoyl peroxide in toluene

The reaction vessels were prepared from round-bottom Pyrex flasks, 200 ml. capacity for the 0.1, 0.03, and 0.01 M runs, 500 ml. for the 0.003 M run, and 1000 ml. for the 0.001 M run. The necks of the flasks were extended by sealing on a piece of tubing of the same diameter (22-25 mm.) as the neck, and approximately eight inches in length. The extended necks then were heated near the end to give a thick-walled constriction. The flasks were cleaned carefully with chromic acid-sulfuric acid cleaning solution, rinsed with distilled water, and dried in an oven. The benzoyl peroxide and toluene were added to the flask, which was then cooled in a Dry Ice-trichloroethylene mixture. The constriction in the neck was heated and drawn out to a narrow tube, which was cut to remove the end of the neck. The tube was then attached via rubber tubing to a vacuum system. The flask was evacuated to about 1 mm. and flushed with nitrogen three times, and finally evacuated a fourth time and sealed under reduced pressure. The flask was then placed in an oil bath at  $80.0 \pm 0.1^\circ$  for 72 hours. The half-life for the unimolecular decomposition of benzoyl peroxide at  $80^\circ$  is about six hours<sup>27a</sup>, so 72 hours constitute twelve half-lives for the decomposition at this temperature. At the end of this time the flasks were cooled and opened and the contents transferred to a distilling flask. The solution was con-

centrated to a volume of 1-2 ml. by distillation of the excess toluene through a 9-inch vacuum-jacketed column packed with a wire coil. The residue was taken up in ligroin and chromatographed on a column consisting of a 25 ml. buret half filled with acid washed alumina.

Three runs were carried out at different concentrations of benzoyl peroxide (Run 1 0.1 M, Run 2 0.03 M, Run 3 0.01 M approximately) to determine qualitatively how the relative yields of products vary with initial concentration of radical source. Portions of the crude concentrated product mixtures from the first two runs (but not from the third) were subjected to gas chromatography on the Loe instrument at 210°. The traces in both cases showed the peaks for o-methylbiphenyl and biphenyl, for m- and p-methylbiphenyl, and for bibenzyl. Besides the peaks for the major products there were only a few small blips, all between solvent and the first major product peak. The crude product mixture from each run was chromatographed on alumina and eluted with 75 ml. light ligroin (boiling range 30-60°). In the case of Run 1 only this was followed by elution with 50 ml. of a mixture of equal volumes of light ligroin and benzene, and then in all three runs with 50 ml. benzene. For Run 1 only, the column was then eluted with 50 ml. diethyl ether, and finally in all three runs with 50 ml.

acetone. The fractions from the alumina column were evaporated to small volume on the steam bath and subjected to gas chromatography. In all three runs the products of interest were eluted completely by ligroin and benzene, as evidenced by the absence from the gas chromatographic traces for the ether and acetone fractions of peaks corresponding to these products. The ratios o-methylbiphenyl: m- and p-methylbiphenyl: bibenzyl in the various fractions, as measured by peak heights, are displayed in Table 2. In Run 1, the ligroin-benzene fraction showed only very small rises at the positions for the major products, and no other peaks except solvent. The benzene and ether fractions showed solvent peaks only. In none of the runs was there any indication of any unidentified product in the ligroin and benzene fractions, except as noted below, although the possibility of an unknown product with the same retention time in the gas chromatographic procedure as one of the known major products is not rigorously excluded.

The gas chromatographic results from Runs 2 and 3 indicate a tendency for o-methylbiphenyl and bibenzyl to be eluted from alumina by ligroin preferentially to one or both of m- and p-methylbiphenyl. In these two runs also, the o-methylbiphenyl peak in the trace for the benzene fraction tailed very strongly, suggesting the presence of diphenylmethane and/or possibly some other product.

The ratios of peak heights determined for the crude product mixtures in this series of runs were too similar to permit any definite conclusions about trends in the relative yields of products as initial benzoyl peroxide concentration is changed.

Table 2. Gas phase chromatographic analysis

Run	benzoyl peroxide (gm.)	toluene, (ml.)	ratios of peak heights o: m & p: bz		
			crude mixture	ligroin eluate	benzene eluate
1	0.1453	6	25:12 1/2:15	55:28:36	-----
2	0.1446	20	35:20:26	48:21:36	15:25:23 1/2
3	0.1461	60	not run	38:16:30	10:18:19

Runs 4-11 were carried out with the purpose of determining the yields of hydrocarbon products at various concentrations by accurate measurement of peak areas. A known volume of a standard solution of naphthalene was added to the product mixture after chromatography on alumina and reconcentration, and a portion of the resulting solution passed through the gas chromatographic column. Comparison of the area of the peak obtained for naphthalene with that of the calibration peak for a known quantity of naphthalene gave the amount of naphthalene in the sample injected; comparison of this

quantity with the known quantity of naphthalene added to the product mixture permitted calculation of a sampling factor which is the fraction of the total product mixture that was subjected to gas chromatography. Since the weight of a given product in the sample injected was calculable by comparison of the peak area for that product with its calibration peak, the weight of product in the total reaction mixture could be calculated. This procedure has the advantage that accurate measurement of the sample subjected to gas chromatography is unnecessary.

The crude concentrated product mixture was chromatographed on alumina as described earlier, and eluted with 75-175 ml. (in most cases 150 ml.) light ligroin, with 50 ml. benzene, and with 50 ml. acetone. The acetone fraction was evaporated to small volume and passed through the Silicone gas chromatography column. In no case were peaks corresponding to the product of interest found. The ligroin and benzene fractions, were collected in the same receiver, and the combined solution was concentrated to 7-11 ml. (3 ml. in the case of Run 4) by distillation of the solvent through a 9-inch vacuum jacketed column. To the concentrated solution was added 0.250 ml. (0.375 ml. in the case of Run 4) of a solution prepared by dissolving 1.2028 gm. naphthalene in toluene in a 10 ml. volumetric flask and making up to the mark. A volume of 75-150 l., roughly



measured, of the resulting product solution was subjected to gas chromatography on the Loe instrument using the Silicone column. Duplicate gas chromatographic runs were made on the product mixtures in most cases. Operating conditions were: temperature 210°, inlet pressure 15 lb./in.<sup>2</sup>, detector potential 11 volts, flow rate 16.1-16.7 units on the meter (197-209 ml./min.), sensitivity scale 10.

Difficulties from two sources were encountered in the determination of peak areas. First, the chromatographed product mixtures were concentrated only to about 10 ml., with the result that it was necessary to use a relatively large volume of solution in the gas chromatography in order to obtain peaks of a satisfactory size. Consequently, the column was somewhat overloaded with solvent, so that the solvent peak had a tail that extended into the region of the product peaks. As a result, it was necessary to take the level of the solvent tail as an approximate base line for the measurement of the first product peak. Second, the second and third product peaks were incompletely separated, and the first product peak usually exhibited a tail that suggested the presence of a small amount of diphenylmethane. Consequently it was necessary to carry out an approximate freehand decomposition of the compound peaks into their components, judging the appropriate shapes for the invis-

ible portions of the component peaks by comparison with the visible portions and with the shapes of peaks obtained by gas chromatography under the same conditions of known solutions of the hydrocarbons taken singly.

Measurement of the peak areas was originally essayed using a polar planimeter. However, it was found that measurements made in this way were poorly reproducible, and, with the instrument available, depended heavily on the position of the pole relative to the peak. Ultimately, the area measurements were made by tracing the peaks and cutting them out and weighing them, as described above for the calibration peaks for the individual products.

### Calculations

The sampling factor  $F$  for the gas chromatograph of a given sample is given by:

$$F = \frac{C_M V_M A_C}{C_C V_C A_S}$$

where  $C_M$  is the concentration of the marker solution of naphthalene added to the product mixture,  $V_M$  is the volume of marker solution added,  $C_C$  is the concentration and  $V_C$  is the volume of the naphthalene solution used to obtain the calibration peak,  $A_C$  is the area of the resulting calibration peak for naphthalene, and  $A_S$  is the area of the naphthalene peak in the trace for the individual sample in question.

Since all these values but  $A_S$  are constant from one sample trace to the next, a simple expression for F in terms of  $A_S$  is obtained:

$$F = \frac{(1.2028) (0.250) (10.00) (0.2743)}{(10.00) (0.3071) (0.020) A_S} = \frac{13.43}{A_S}$$

Similarly, the factor  $m_X$  for the number of moles of product X corresponding to the peak for that product in a given trace is

$$m = \frac{A_X C_{CX} V_{CX}}{A_{CX} M_X}$$

where  $A_X$  is the area of the peak for product X in the trace in question,  $C_{CX}$  is the concentration and  $V_{CX}$  is the volume of the standard solution of product X used to obtain the calibration peak for that product,  $A_{CX}$  is the area of the calibration peak obtained, and  $M_X$  is the molecular weight of product X.

$$\text{o-methylbiphenyl: } m_o = \frac{(0.3069) (0.020) A_o}{(0.2501) (10.00) (168.2)} = 1.46 \times 10^{-5} A_o$$

m- and p-methylbiphenyl:

$$m_{mp} = \frac{(0.3067) (0.020) A_{mp}}{(0.2739) (10.00) (168.2)} = 1.33 \times 10^{-5} A_{mp}$$

bibenzyl:

$$m_b = \frac{(0.3016) (0.020) A_b}{(0.2584) (10.00) (182.2)} = 1.28 \times 10^{-5} A_b$$

The values 0.3067 and 0.2739 for  $C_{Cmp}$  and  $A_{Cmp}$  are averages of those for the two isomers. The yield  $Y_X$  in moles of

product X in a given product mixture is than given simply by  $Y_X = Fm_X$ . The results are displayed in Table 3.

The agreement of measurements from duplicate gas chromatographic runs on the same product mixture is very poor. Several sources of serious error exist in the present procedure which may account for the scatter. First and most obvious, the decomposition of the overlapping peaks into components that accurately approximate the peaks that would be obtained if the hydrocarbons were run separately is difficult and uncertain, and the method used to effect the decomposition is inherently crude. The validity of the assumption that the two overlapping components behave independently of each other on the column, and that it is proper to expect the peak for one component to be unchanged by the proximity on the column of the other component is by no means certain. Second, the tailing of the solvent peak and resulting presence of some solvent on the column while the first product is coming out may similarly affect the product peak. Third, the measurement of the volume of standard solution used to obtain calibration peaks is not very accurate; the microsyringes used probably are accurate only within several percent at volumes of 20  $\mu$ l. Fourth, it seems very likely that imperfect reproducibility of the flow rate between gas chromatographic runs is an important factor causing variation in peak areas. It was necessary

to use high flow rates in order to obtain sharp peaks. This entailed operation in a range in which small variations in the calibration reading of the flow meter corresponded to fairly large variations in the absolute flow rate, since the flow meter calibration is not linear. Finally, it is known that some biphenyl is formed in the reaction, and that biphenyl would be counted as o-methylbiphenyl in the present procedure. This would not be manifested as irreproducibility of results from the same product mixture, but would contribute to obscuring any clear trend in the variation in yield of ortho isomer with concentration of radical source.

Table 3. Yields of hydrocarbon products by gas chromatography<sup>a</sup>

Run 5, 0.4712 gm. benzoyl peroxide in 20 ml. toluene (0.0972M)

	o- isomer	m- and p- isomers	hibenzyl
I. $A_S = 0.0838$ gm., $F = 160$			
A, gm.	0.230	0.202	0.225
$10^6$ m, moles	3.36	2.69	2.88
$10^4$ Y, moles	5.39	4.31	4.62
moles/mole <sup>b</sup>	29.0	23.1	24.9
II. $A_S = 0.128$ gm., $F = 105$			
A, gm.	0.392	0.302	0.364
$10^6$ m, moles	5.72	4.02	4.66
$10^4$ Y, moles	5.99	4.22	4.89
moles/mole	32.2	22.7	26.3

<sup>a</sup>See text for explanation of symbols

<sup>b</sup>Moles of product per mole of benzoyl peroxide

Table 3 (Continued).

Run 6, 0.4534 gm. benzoyl peroxide in 60 ml. toluene (0.0312M)			
	o- isomer	m- and p- isomers	bibenzyl
I. $A_S = 0.0992$ gm., $F = 135$			
A, gm.	0.265	0.219	0.323
$10^6$ m, moles	3.87	2.92	4.14
$10^4$ Y, moles	5.23	3.95	5.60
moles/mole	28.0	21.2	30.0
II. $A_S = 0.0980$ gm., $F = 137$			
A, gm.	0.262	0.251	0.381
$10^6$ m, moles	3.82	3.34	4.88
$10^4$ Y, moles	5.23	4.58	6.68
moles/mole	27.8	24.4	35.6
Run 7, 0.4498 gm. benzoyl peroxide in 200 ml. toluene (0.00929M)			
	o- isomers	m- and p- isomers	bibenzyl
I. $A_S = 0.102$ gm., $F = 132$			
A, gm.	0.310	0.258	0.418
$10^6$ m, moles	4.53	3.44	5.35
$10^4$ Y, moles	5.96	4.53	7.03
moles/mole	32.0	14.4	37.8
II. $A_S = 0.0921$ gm., $F = 146$			
A, gm.	0.257	0.202	0.318
$10^6$ m, moles	3.75	2.69	4.08
$10^4$ Y, moles	5.47	3.92	5.95
moles/mole	29.4	21.2	32.0

Table 3 (Continued).

Run 8, 0.4549 gm. benzoyl peroxide in 6 ml. toluene (0.313M)			
	o- isomer	m- and p- isomers	bibenzyl
$A_S = 0.166$ gm., $F = 81.0$			
A, gm.	0.446	0.364	0.459
$10^6$ m, moles	6.51	4.85	5.88
$10^4$ Y, moles	5.27	3.93	4.76
moles/mole	28.0	21.0	25.4
Run 9, 0.1492 gm. benzoyl peroxide in 200 ml. toluene (0.00308M)			
	o- isomer	m- and p- isomers	bibenzyl
I. $A_S = 0.0702$ gm., $F = 191$			
A, gm.	0.0726	0.0698	0.0965
$10^6$ m, moles	1.06	0.930	1.24
$10^4$ Y, moles	2.03	1.78	2.36
moles/mole	33.0	28.8	38.4
II. $A_S = 0.0590$ gm., $F = 228$			
A, gm.	0.0623	0.0554	0.0793
$10^6$ m, moles	0.909	0.738	1.02
$10^4$ Y, moles	2.07	1.68	2.31
moles/mole	33.6	27.2	37.6
Run 10, 0.1486 gm. benzoyl peroxide in 600 ml. toluene (0.00102M)			
	o- isomer	m- and p- isomers	bibenzyl
I. $A_S = 0.1864$ gm., $F = 72.1$			
A, gm.	0.181	0.164	0.271
$10^6$ m, moles	2.64	2.18	3.48
$10^4$ Y, moles	1.91	1.57	2.51
moles/mole	31.2	25.6	41.0

Table 3 (Continued).

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Run 10, 0.1486 gm. benzoyl peroxide in 600 ml. toluene  
(0.00102M)

	o- isomer	m- and p- isomers	bibenzyl
II. $A_S = 0.1204$ gm., $F = 112$			
A, gm.	0.133	0.127	0.223
$10^6$ m, moles	1.94	1.69	2.86
$10^4$ Y, moles	2.16	1.89	3.19
moles/mole	35.3	30.9	52.1

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Run 11, 0.4508 gm. benzoyl peroxide in 6 ml. toluene  
(0.310M)

	o- isomer	m- and p- isomers	bibenzyl
$A_S = 0.1153$ gm., $F = 116$			
A, gm.	0.312	0.255	0.288
$10^6$ m, moles	4.18	3.39	3.68
$10^4$ Y, moles	4.87	3.95	4.29
moles/mole	26.2	21.2	23.0

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#### Preparation of 1,4-dihydrobiphenyl

1,4-dihydrobiphenyl was prepared by the method of Hückel and Schwen<sup>54</sup>. A 1-liter 3-neck flask was fitted with a mechanical stirrer, an open-ended gas inlet tube, and

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<sup>54</sup>W. Hückel and R. Schwen, Ber., 89, 150 (1956).



a branching adapter which in turn was fitted with a Dry Ice condenser and a 125-ml. addition funnel. The flask was packed in powdered Dry Ice and filled with approximately 500 ml. liquid ammonia through the gas inlet tube by distillation from a cylinder of the liquid. A stream of nitrogen was then passed through the flask to provide an inert atmosphere, and this was continued through the entire preparation. Small chunks of freshly cleaned sodium, 9.2 gm. in all, were added with stirring, and 15 minutes were allowed for the metal to dissolve. A solution of 30.8 gm. (0.2 mole) biphenyl in 20 ml. diethyl ether was added from the addition funnel over an interval of 20 minutes. A portion of the biphenyl was deposited on the sides of the adapter tube, and 50 ml. more ether was added to wash this into the solution. The mixture was stirred another ten minutes, after which 22.0 gm. solid ammonium chloride was slowly poured in through the adapter tube. The mixture was allowed to warm to room temperature over a period of several hours with the nitrogen stream still passing through the solution. Two hundred ml. water was added to the mixture, which was transferred to a separatory funnel and the phases separated. The flask was washed with a small portion of ether, and this was combined with the main organic fraction. The combined ether solutions were washed quickly with two portions of water, and dried for two hours over anhydrous sodium sulfate

in an atmosphere of nitrogen. The solvent was distilled from the product, and the product was distilled under reduced pressure through a 6-inch vacuum-jacketed column packed with small cylinders of fine metal gauze. A fraction boiling at 106-107° under 9-10 mm. pressure was collected. The product was stored in a screw-cap bottle in an atmosphere of nitrogen. After several days the initially clear product became hazy, presumably as a result of slow oxidation by atmospheric oxygen.

A sample of the product was hydrogenated in glacial acetic acid at atmospheric pressure with platinum dioxide as catalyst. A sample of 0.080 gm. (0.512 millimole) of the product absorbed 57.2 ml. hydrogen (corrected to standard temperature and pressure), corresponding to 4.99 double bonds per molecule in the hydrocarbon.

A solution of 1,4-dihydrobiphenyl in toluene was subjected to gas chromatography on the Loe instrument with the Silicone column at 210°. A large product peak with a low hump on the tail was observed. A mixture of equal volumes of this solution with a solution of biphenyl in toluene gave a similar trace with the small hump augmented to a second major peak. Thus the small hump probably corresponds to biphenyl formed by air oxidation of the dihydro compound. This experiment also demonstrates that 1,4-dihydrobiphenyl is stable at 210° at least for short periods

in the absence of air.

A second preparation of the hydrocarbon was carried out by the same procedure with the following changes. The crude product was fractionally distilled through a small spinning-band column at a pressure of 8-9 mm. of mercury, under a current of nitrogen. Pressure control during the distillation was poor. Fractions of about 5 ml. were collected in long test tubes with ground joints, and sealed off under vacuum. Fraction 1 had a boiling point of 89.5° at 9.0 mm., fraction 2 boiled at 84.0° at 8.5 mm., and fraction 3 boiled at 88.0° at 6.0 mm.

#### Bromination of 1,4-dihydrobiphenyl

Partially reoxidized 1,4-dihydrobiphenyl (1.978 gm.) from the first preparation was dissolved in 35 ml. Reagent grade carbon tetrachloride in a 250 ml. round bottom flask with a standard taper joint. The flask was fitted with a straight standard taper vacuum take-off adapter tube with an inner tube. A standard taper addition funnel was attached to the upper joint of the adapter, and the side arm led to a three-way stopcock connected to nitrogen and vacuum lines. The flask was cooled to -10° in a salt-ice bath and evacuated until boiling of the solvent commenced, flushed with nitrogen, and the procedure repeated twice. A solution of 5.54 gm. bromine in 40 ml. carbon tetrachloride was cooled in an ice bath and added through the addition funnel, and a

slight positive pressure of nitrogen was applied to the system. The mixture was allowed to stand for one hour with occasional swirling while the temperature increased from  $-10$  to  $0^{\circ}$ . Considerable fuming was observed when the system was vented to the atmosphere at the end of that time, due presumably to spontaneous decomposition of the adduct with liberation of hydrogen bromide. The excess bromine and solvent were drawn off at the water aspirator, and the last traces removed by means of a vacuum pump. The yellow oil crystallized completely on standing 24 hours. The solid evolved fumes, presumably of hydrogen bromide, on standing. The product was recrystallized from methanol to give 2.4 gm. slightly off-white crystals with no biphenyl-like odor, 81% yield if the product was a bromobiphenyl. Sodium fusion of a small amount of the product and a test of the resulting solution with aqueous silver nitrate gave a heavy precipitate, indicating the presence of a halogen. Gas chromatography of a portion of the product on the Loe instrument and Silicone column at  $245^{\circ}$  showed a peak soon after solvent which tailed off very slowly, in a manner indicative of decomposition on the column. This could be due either to adduct from which elimination of hydrogen bromide had not proceeded to completion, or possibly to decomposition of a methoxy compound formed during the recrystallization.

The preparation was repeated using a portion of fraction

1 from the second preparation of 1,4-dihydrobiphenyl. Conditions and quantities were almost exactly as before. The solid product, which was nearly colorless this time, was dissolved in 10 ml. benzene, and 5 ml. of the resulting solution was pipetted into a 50 ml. round bottom flask containing 20 ml. benzene and 4 ml. pyridine. The mixture was heated at reflux for 30 minutes, and allowed to cool. A dirty brown precipitate formed on the sides of the flask, and the solution was yellow. The precipitate dissolved on addition of a small amount of water; the organic solution was washed with three 30 ml. portions of 2N sulfuric acid and one 30 ml. portion of water. The resulting colorless benzene solution was evaporated to dryness on the steam bath. The test for halogen on the solution from sodium fusion of a sample of the product again was strongly positive. Gas chromatography with the Aerograph instrument with a Paraffin column of a solution of the product in toluene exhibited a small peak followed by a large one at the appropriate retention time for biphenyl. It appears that the bromine-containing product from bromination of 1,4-dihydrobiphenyl followed by elimination has the same retention time on this column as has biphenyl.

In an experiment carried out under the same conditions as those used for the bromination of the dihydro compound, biphenyl failed to react at all. This was demonstrated by

the negative result obtained when the solid material recovered was subjected to sodium fusion and the resulting solution tested with aqueous silver nitrate.

Oxidation of 1,4-dihydrobiphenyl with potassium permanganate

Approximately 0.5 gm. 1,4-dihydrobiphenyl from the first preparation was dissolved in 10 ml. light ligroin and combined with 100 ml. acetone and 12 ml. of a 5% aqueous solution of potassium permanganate. The mixture was allowed to stand for one hour. At the end of this time, the permanganate color was gone, and the mixture contained a copious precipitate of manganese dioxide. About 5 ml. more potassium permanganate solution was added, and the mixture was allowed to stand for an additional 20 minutes. It was then filtered and the filter was washed with acetone. The purple filtrate solution was boiled to remove the acetone, with the result that the color faded and a little more brown precipitate was formed. The resulting small volume of brown slurry was combined with 50 ml. water and 100 ml. benzene in a separatory funnel, and a small amount of sodium bisulfite was added to destroy the remaining manganese dioxide. The yellow benzene layer was evaporated on the steam bath to about 75 ml., and the solution was extracted with two 50 ml. portions of 2% aqueous sodium hydroxide. The yellow color was extracted into the aqueous phase. The organic phase

was evaporated to dryness on the steam bath to give a quantity of off-white to yellowish solid with an odor of biphenyl.

#### Epoxidation of 1,4-dihydrobiphenyl

Epoxidation by means of trifluoroperacetic acid was investigated as a method for destruction of dihydrobiphenyls from reaction mixtures without converting them to biphenyls. The procedure was an adaptation of that of Emmons<sup>55</sup>. Using peracid made from 95% hydrogen peroxide, practically complete conversion of 1,4-dihydrobiphenyl to non-hydrocarbon could be effected; only a trace of material that could have been biphenyl was found. In a control experiment, however, it was found that p-methylbiphenyl also was appreciably attacked by the reagent under the same conditions. Similar experiments were performed with p-methylbiphenyl using peracid made from hydrogen peroxide of lower strength. With peracid from 75% peroxide, the extent of attack was diminished and when the concentration of the peroxide used was reduced to 50%, a 96% recovery of p-methylbiphenyl was achieved. The reagent from 50% peroxide also was shown to convert 1,4-dihydrobiphenyl essentially completely to non-hydrocarbon products.

A solution of 1.0257 gm. 1,4-dihydrobiphenyl (fraction 2

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<sup>55</sup>W. D. Emmons and A. S. Pagano, J. Am. Chem. Soc., 77, 89 (1955).

from the second preparation) was transferred with the aid of 40 ml. dichloromethane to a 100 ml. 3-neck flask containing 20 gm. anhydrous sodium carbonate and fitted with a reflux condenser, a stirrer, and a 50 ml. pressure-equalized dropping funnel. The peracid solution was prepared by slow addition with swirling of 13.0 ml. trifluoroacetic anhydride to a mixture of 1.020 ml. water, 0.725 ml. 98% hydrogen peroxide, and 20 ml. dichloromethane in an ice bath. The reaction flask was swept out with nitrogen, stirring was commenced, and the peracid solution was added dropwise over about 30 minutes. Stirring was continued at room temperature for 30 minutes more, after which a warm water bath was placed around the flask, and the mixture was refluxed for one hour. The product mixture was filtered through a fritted funnel, the solids were triturated with two 20 ml. portions of dichloromethane, and the washings were combined with the main filtrate. The solvent was evaporated at the water aspirator.

The residue was dissolved in 10 ml. benzene and chromatographed on a column with a diameter of 0.70 inch and a length of 7.0 inches, consisting of 55 gm. acid-washed alumina. The column was washed with 150 ml. benzene (fraction 1), a further 100 ml. benzene (fraction 2), 200 ml. dichloromethane (fraction 3), and 50 ml. acetone (fraction 4). Fraction 4 was evaporated to dryness on the steam bath, leaving a yellow, very viscous residue which was not in-



investigated further. Solvent was removed from fraction 3 at the water aspirator, leaving a white residue, melting point 123.5-126°. Fraction 2 was distilled to remove solvent, and the last traces were drawn off at the water aspirator to give an off-white residue, melting point 117-125°, perhaps the same material as fraction 3 in less pure form. Fraction 1 was treated similarly to fraction 2. It provided a yellow, rather dirty-looking residue, a portion of which was subjected to gas chromatography. It showed a peak a little too early to correspond to biphenyl, followed by a very broad, diffuse rise suggesting decomposition on the column; the latter could have obscured a little biphenyl.

Chromatography of 0.50 gm. biphenyl on an alumina column similar to that used for the epoxidation, elution with benzene, and evaporation of the eluted fractions to dryness on the steam bath provided only a little residue from the first fraction (30 ml.), most of the biphenyl in the second fraction (30 ml.), small amounts in the third and fourth fractions (20 ml. each), and no trace in the fifth fraction (20 ml.). Thus 90 ml. of benzene removes biphenyl essentially completely from such a column.

Since it appeared that a portion of the epoxidation products would be eluted even in the first 90 ml. of benzene, it was necessary to devise a method of converting the epoxidation products to something that would be more strong-

ly retained by alumina. Fractions 1 and 2 from chromatography of the epoxidation product were combined, dissolved in 30 ml. 95% ethanol, and refluxed gently for two hours with 6 ml. concentrated hydrochloric acid. The solvent was distilled away, and the last traces removed by passing a slow stream of air over the concentrated solution at room temperature. The solid residue was extracted with three 10 ml. portions of boiling benzene, chromatographed as described above, and eluted with 90 ml. (fraction 1) and 100 ml. (fraction 2) of benzene. Evaporation of fraction 2 to dryness on the steam bath left only a thin film on the bottom of the flask. Thus hydrochloric acid converts the original epoxidation product to something that is strongly held on alumina. The solvent was distilled from fraction 1 until only a few milliliters remained, and the concentrated solution was evaporated nearly to dryness by means of a slow stream of air. Gas chromatography of a portion of the small volume remaining was performed, using the Loe instrument and Silicone column at 210°. The trace showed only a tiny peak at approximately the retention time for biphenyl under these conditions.

The epoxidation procedure was repeated under identical conditions using 1.68 gm. p-methylbiphenyl as the hydrocarbon substrate. Filtration of the reaction mixture and washing of the filter gave a slightly yellow solution,

which on evaporation of the solvent at the water aspirator left a yellow solid. This was dissolved in benzene, chromatographed on alumina, and eluted with benzene as above. The colorless eluate was evaporated to dryness. The weight of faintly yellow crystalline material was 1.61 gm.

#### Preparation of active benzoyl peroxide

Benzoic acid labelled with carbon-14 at one of the ring positions was obtained from Tracerlab<sup>56</sup>. A vial containing 0.5 millicuries of activity in 0.148 gm. benzoic acid was opened and the contents transferred with the aid of several washings of hot water to a 1-l. Erlenmeyer flask. To this was added 20 gm. inactive benzoic acid, together with enough water to bring all the benzoic acid into solution at a temperature just below 100°. The solution was allowed to cool to room temperature, then stored in a refrigerator overnight. The crystals were collected on a Buchner funnel, and dried in a desiccator over calcium chloride. Determination of the activity of the diluted material is described below.

The first attempt to convert the diluted active acid to benzoyl peroxide was carried out by the procedure described by Tobolsky and Mesrobian<sup>57</sup>, by conversion of the

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<sup>56</sup>Tracerlab, Inc., 130 High Street, Boston 10, Massachusetts.

<sup>57</sup>A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 38.

acid to benzoyl chloride and reaction of the product with ice-cold aqueous sodium peroxide. However, it was found that even at 0° the sodium peroxide solution evolved gas very rapidly, and the product of the reaction was a yellow oil from which a white solid was isolated which analysed for only 25% peroxide. This result may have been due to contamination of the available sodium peroxide.

The second method tried consisted of dropwise addition of pyridine to a rapidly stirred solution of benzoyl chloride and a slight excess of 95% hydrogen peroxide in dichloromethane in an ice bath. The method was found very satisfactory in a preliminary experiment with unlabelled material, giving a fair yield of benzoyl peroxide which assayed 99.0% active peroxide without recrystallization. However, two successive attempts to convert the active benzoic acid, recovered from the previous attempt and carefully repurified, to benzoyl peroxide by this method failed to give material with high peroxide assay, and resulted in the vigorous evolution of gas containing chlorine and the development of a yellow solution apparently containing substituted pyridines. Further studies of this method using inactive benzoic acid indicated that there is a fine balance between the reaction to give benzoyl peroxide and that evolving gas and giving yellow products, and that relatively minor differences in experimental conditions can critically affect the course

of reaction. In the majority of cases the reaction proceeded smoothly to give a good yield of benzoyl peroxide of high oxidizing activity. However, in a substantial fraction of cases, due to influences that never were satisfactorily identified, the system evolved gas, turned yellow, and gave low-activity peroxide.

A third attempt to apply this method to the recovered carbon-14 labelled benzoic acid was successful. 4.7 gm. active benzoic acid was converted to benzoyl chloride by refluxing with 10 ml. thionyl chloride, and the excess reagent was drawn off at 40° over 2.5 hours. To the benzoyl chloride was added 20 ml. dichloromethane and 0.75 ml. 98% hydrogen peroxide. The solution was cooled in an ice bath, and 5.0 ml. pyridine was added slowly with swirling. The resulting mixture was allowed to stand 30 minutes more in the ice bath, then 30 minutes at room temperature. It was washed with two 50 ml. portions of water, dried over anhydrous sodium sulfate over night, and concentrated to 7 ml. by drawing the solvent off at the water aspirator. The concentrated solution was poured into 30 ml. ligroin (boiling range 60-70°). The crystals were collected on a Buchner funnel and sucked dry to give 2.2 gm. of very slightly off-white material which assayed 98.5% peroxide.

A second vial containing 48.7 mg. benzoic acid with an activity of 0.2 millicurie was opened and diluted with

12.0 gm. inactive benzoic acid by the same procedure used for the first vial. A new batch of labelled benzoyl peroxide was prepared from this acid by a different method. Active benzoic acid (7.8 gm.) from the second batch was combined with 10 ml. thionyl chloride, and the mixture was heated at reflux for one hour. The excess thionyl chloride was distilled off at 70° and slightly reduced pressure. The solution was cooled in an ice bath, and 30 ml. dichloromethane and 2.0 ml. 98% hydrogen peroxide were added. The solution was stirred with a magnetic stirrer while a solution of 3.8 gm. sodium hydroxide in 15 ml. water was added dropwise. The mixture was allowed to stand in the ice bath with stirring for one hour, then washed with three 50 ml. portions of water and dried over anhydrous sodium sulfate for three hours. The solvent was evaporated at the pressure of the water aspirator. The residue was dissolved in 18 ml. chloroform, and the solution was poured into 70 ml. ligroin (boiling range 60-70°). The resulting solution was stored in the refrigerator to crystallize. The product weighed 3.4 gm., and assayed 99.4% peroxide.

Decomposition of benzoyl peroxide in toluene: procedure for active runs

Reaction flasks were made and cleaned, and reaction mixtures were made up, degassed, sealed, and allowed to

react at  $80^{\circ}$  as described earlier for the runs for gas chromatographic analysis. The reaction flasks were cooled in an ice bath, opened, and flushed immediately with nitrogen. A previously weighed quantity of o-methylbiphenyl (0.052-.057 gm.), which served as diluent for the active material, was transferred quickly and quantitatively, with the aid of six to eight 2 ml. portions of toluene, to the opened reaction flask, and the solution was thoroughly mixed by swirling. In the case of the runs of 60 ml. volume or less, the solution was transferred immediately to a 100 ml. 3-neck flask fitted with a nitrogen inlet tube, a 6-inch unpacked vacuum-jacketed distilling column, and a stopper. The flask previously had been thoroughly flushed with nitrogen. In the case of the runs of 200 ml. and 600 ml. volume, the stopper was replaced with a 250 or 500 ml. pressure-equalized addition funnel, and the solution was transferred to this and, in part, to the flask.

The solution was warmed to a temperature of  $70-80^{\circ}$  by means of an oil bath, and the pressure in the system was slowly reduced until distillation commenced at a vapor temperature of  $40-55^{\circ}$ ; the pressure was not directly measured. Distillation was continued in a slow stream of nitrogen until the volume of material in the flask was reduced to about 1 ml. The flask was cooled to room temperature, and more nitrogen was admitted to bring the pressure to

atmospheric. The thermometer at the top of the column was removed, and 40 ml. dichloromethane was added through the opening. With a fairly rapid stream of nitrogen passing through the solution, the stopper or addition funnel was removed, 5 gm. anhydrous sodium carbonate added, and the flask fitted with a 50 ml. pressure-equalized dropping funnel. The distilling column was replaced with a stirrer and the nitrogen inlet tube was replaced with a reflux condenser. A pipet reaching almost into the flask was quickly put down through the condenser to serve as a nitrogen inlet, and the mixture was again blanketed with nitrogen. The oxidizing solution was prepared ahead of time from 20 ml. dichloromethane, 1.68 ml. 50% hydrogen peroxide<sup>58</sup>, and 13.0 ml. trifluoroacetic anhydride by the procedure described previously. (In the first two runs, 0.725 ml. 98% hydrogen peroxide and 1.0 ml. water were used instead of the 50% hydrogen peroxide.) A fresh batch of peracid solution was prepared for each run. An 8.5 ml. portion of this solution was transferred to the dropping funnel. Stirring was commenced, and the peracid solution was added dropwise during a period of 5-15 minutes. Stirring was continued for 30-45 minutes more, and the product mixture was filtered through a Buchner funnel into a 100 ml. round bottom flask.

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<sup>58</sup>Becco Chemical Division, Food Machinery and Chemical Corporation, Buffalo 7, New York.



The solid cake was triturated on the filter with two 25 ml. portions of dichloromethane, and these were drawn into the main filtrate. The light yellow solution was concentrated to 1-2 ml. by distillation of the solvent at atmospheric pressure through the vacuum-jacketed column used before.

To the concentrated solution was added 10 ml. benzene and 25 ml. of the solution prepared by absorbing 40 gm. hydrogen chloride gas in 250 ml. 95% ethanol. (In runs 1 and 2, 30 ml. 95% ethanol and 6 ml. concentrated aqueous hydrochloric acid were used.) The column was replaced by the reflux condenser, and the mixture was refluxed 30-60 minutes. The condenser was again replaced by the column, and the solution was distilled until most of the solvent was removed, and there remained a few milliliters of a dark-colored heterogeneous mixture containing some water. The residue was transferred with the aid of 20 ml. benzene to a column of acid washed alumina approximately seven inches long and 0.7 inches in diameter. The column was eluted with another 80 ml. benzene, the eluate was collected in a 100 ml. round bottom flask, and the resulting solution was again reduced to 1-2 ml. by distillation. The residual solution was transferred with the aid of 1 ml. more benzene to a small test tube. The remaining solvent was largely removed by impinging a slow stream of clean air on the surface of the solution. This gave finally 0.1-0.2 ml. of

dark-colored, rather viscous solution in which fine crystals were sometimes suspended. The dark color indicates that some product other than the desired simple hydrocarbon products is eluted from alumina by benzene.

Separation of the concentrated mixture was effected by gas chromatography and collection of the effluent when the peak corresponding to o-methylbiphenyl appeared. The Aerograph instrument and asphalt column were used, since it was shown earlier that o-methylbiphenyl is separated cleanly from the other expected products on the asphalt column. Operating conditions were: temperature 210° for most runs, 205° beginning with run 19; inlet pressure approximately 15 lb./in.<sup>2</sup>; flow rate 6-7 calibration units (31.1-43.0 ml./min.) for runs 1-18, 3-4 units (7.2-13.2 ml./min.) beginning with run 19; detector current 200 milliamperes. The collector system consisted of a 1 foot length of 3 mm. Pyrex tubing bent to form a U-shaped tube with a horizontal arm. The horizontal arm of the tube was inserted through a tight-fitting gasket as far as possible into the outlet tube of the instrument, and the U-shaped portion was immersed in a Dry Ice-trichloroethylene bath.

Since precise reproducibility of operating conditions for the instrument was difficult, a known mixture was passed through the column immediately before each gas chromatographic separation of an active run in order to

assure that the conditions were such as to permit clean separation of o-methylbiphenyl from the other products, and to provide an estimate of the time at which the product could be expected to appear. A 2:1:1 mixture by volume of solutions of o-methylbiphenyl, biphenyl, and diphenylmethane of approximately equal concentrations was injected into the column. The appearance of two cleanly separated peaks of approximately equal size was taken to indicate that the conditions were satisfactory. The outlet tube of the instrument was then wiped out thoroughly with absorbent tissues to remove any traces of contaminants. The cap nut and gasket were placed over the end of the tube, and a 3 mm. tube with a right angle bend which dipped into a receptacle containing toluene was inserted through the gasket into the outlet. This system served to absorb the unwanted fractions from the column and to prevent escape of radioactive material into the atmosphere. The concentrated product solution was drawn into a 0.25 ml. hypodermic syringe as nearly quantitatively as possible, and injected into the column. When the peak corresponding to o-methylbiphenyl appeared and had reached one-third to one-half its expected total height, the tube leading to the toluene absorbent was replaced by the collector tube. When the peak had fallen to two-thirds to one-half its maximum height, the collector was removed and the absorbent tube replaced. The gas flow through the hot

column was continued at least two hours longer to remove any slightly volatile products from the column. The product in all cases consisted of 2-10  $\mu$ l. of colorless liquid, completely clear in the majority of runs, but in a significant number having a cloudiness that disappeared on standing for a few hours. The recorder traces obtained usually showed a solvent peak, a small to medium-sized peak halfway between solvent and the o-methylbiphenyl peak, a large peak for o-methylbiphenyl with a bump, presumably corresponding to diphenylmethane and/or biphenyl, on the tail, and a large broad peak for the m- and p- isomers and bibenzyl. The early peak was never identified, but the small amount of material that came out when this peak appeared was colorless. No other extraneous peaks were observed. Apparently all the colored material in the crude product mixture injected was non-volatile.

#### Combustion system

The combustion gas used was medical oxygen, containing 5% carbon dioxide. The function of the carbon dioxide in the combustion gas was to exchange with the carbon retained on the packing of the combustion tube and insure that all active carbon was flushed into the ionization chamber. The oxygen was led past a pressure release bottle which consisted of a 50 ml. chamber with an outlet at the bottom which dipped into a dish of mercury. The gas was then passed through a

capillary bubbler partially filled with syrupy phosphoric acid. After the bubbler, a T-tube allowed the gas to be passed through the combustion tube or directly to the final three-way stopcock leading to the ionization chamber. The combustion tube was Vycor, 520 mm. in length and 10.5 mm. in diameter (Corning 18680). A 0.75-inch length of 3 mm. Vycor tubing was sealed to the capillary outlet tube to provide a connection to the smallest available Tygon tubing. The tube was packed according to Steyermark<sup>59</sup>, with two minor variations. The platinized asbestos was omitted, since combustion of compounds with angular methyl groups was not contemplated; and the length of the copper oxide-lead chromate portion of the packing, about six inches, was greater than in Steyermark's description, because of the greater length of the furnace used. The combustion furnace was that described by Niemann and Danford<sup>60</sup>. The lead dioxide mortar was from Arthur H. Thomas Company. The exit gas from the combustion tube was passed through a 10 mm. drying tube containing a 3-inch column of indicating Drierite, and then through a Fischer and Porter "Flowrator" flow

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<sup>59</sup>A. Steyermark, "Quantitative Organic Microanalysis," The Blakiston Company, New York, N. Y., 1951.

<sup>60</sup>C. Niemann and V. Danford, Ind. Eng. Chem., Anal. Ed., 12, 563 (1940).

meter, SA 18808, graduated 2-8. This was connected to a three-way stopcock, which in turn was connected to the bypass line from the capillary bubbler and to an ionization chamber in which the active carbon dioxide was collected and counted.

#### Combustion procedure

The temperature of the combustion furnace was adjusted to 690-710°. The radiation background was determined for the ionization chamber as described below. It was then evacuated and attached to the three-way stopcock in the combustion train. A portion of 2-6  $\mu$ l. of the liquid product was transferred by means of a capillary tube to a small pan made of platinum foil 0.00025 inch in thickness. The material was weighed on a Cahn electrobalance, using the 10 mg. scale. On this scale weights can be read directly to three places and the fourth place can be fairly accurately estimated. The vapor pressure of o-methylbiphenyl is very low at room temperature, and it was found that the weight of a sample of about 3 mg. diminished by only 13  $\mu$ g. in 30 minutes. Since the elapsed time between reading of the weight and commencement of combustion usually was only five to ten minutes, and other much larger sources of error exist in the procedure, the loss of sample by evaporation from the pan was not expected to be significant. A more serious

drawback to this procedure lies in the fact that it is very easy to get a little of the liquid on the outside of the pan during the initial transfer, in which case contact of the pan with the stirrups of the balance and with the forceps used to handle the pan result in loss of weighed sample. A procedure utilizing a sealed capillary tube would have been better.

The pan containing the liquid sample was placed in a platinum combustion boat, which was inserted into the combustion tube and positioned about halfway between the end of the tube and the point at which the tube entered the furnace. The open end of the tube was tightly corked, the pressure at the oxygen tank was set at 2 lb./in.<sup>2</sup>, the needle valve was opened slowly until gentle bubbling from the pressure release chamber occurred, and the stopcock on the ionization chamber was opened until the flow meter reading was 3-4 units (3.7-7.7 ml./min.). The flow was maintained at this rate throughout the combustion. Combustion was commenced immediately, using a Bunsen burner. The burner was applied as close to the inlet to the tube as possible, and slowly moved forward during the course of 10-12 minutes, ending with strong heating at the point of entry of the tube into the furnace. It was necessary to move the burner forward very slowly and with great care to avoid explosion of the sample vapor in the oxygen stream and resulting de-

position of solid particles of products of partial combustion in the inlet where the tube could not be heated to burn them out completely. Despite all efforts, such explosions occurred occasionally; the runs in which this occurred are noted below. The burner was then returned to the beginning of the tube, and the heating cycle was repeated over 8-10 minutes more. At the end of that time the chamber was usually almost full, as evidenced by the decrease in flow rate. The stopcock was opened all the way, then closed before flow ceased completely.

The combustion procedure for samples of benzoic acid from which active benzoyl peroxide was prepared was entirely analogous to that just described.

The ionization chamber and counting system were manufactured by the Applied Physics Corporation of Pasadena, California. The ionization chamber consists essentially of a metal case with an insulated rod in the center; a potential of 90 volts from six 15-volt batteries connected in series is applied between the center rod and the case so that ions produced in the decomposition of carbon-14 are collected on the rod. Counting of the background or of active samples is accomplished by attachment of the chamber to an electrometer head on which is mounted a turret switch and which is connected to a vibrating-reed electrometer and an automatic recorder. The turret switch in the non-operating position



short-circuits the current produced by the ions from decomposition of carbon-14. To count, the switch is moved to place any of several resistors in the circuit; in the present work, position 3, which inserts a resistor of approximately  $10^{-12}$  ohms resistance, was used. The vibrating reed electrometer serves as a stable amplifier for the very small voltage produced by the ionization in the chamber, and measures the voltage drop across the resistor. This voltage drop, registered on the recorder, is proportional to the activity of the sample. Background was measured on the 100 millivolt scale of the recorder, activities of samples from combustion on the 1000 scale. Absolute activities of samples were not determined, since it was only necessary to know the relative activities of starting materials and products, and comparison of millivolt readings on the recorder provided this information.

A portion of the product collected from gas chromatography of the product from run 5 was passed through the asphalt column a second time to determine whether the procedure effected a clean separation of o-methylbiphenyl from other products. The trace obtained showed a small trace of material at about the retention time for solvent, a trace of some other material slightly later, and a large peak for o-methylbiphenyl which appeared identical to peaks obtained with pure material. The peak tailed somewhat (which

also occurs with pure material), so that it was not possible to be certain that absolutely no biphenyl was present; control runs showed that a few percent of biphenyl could be obscured by the tail of the o-methylbiphenyl peak.

Run 26 was a control designed to show that the epoxidation procedure actually was effective in removing dihydro compounds that otherwise would be converted to o-methylbiphenyl and would increase the measured yield. The reaction mixture, after addition of inactive o-methylbiphenyl, was reduced to a volume of 1-2 ml. by slow distillation as usual, except that a stream of air was passed through the system. The liquid residue was chromatographed on alumina, concentrated, and subjected to gas chromatography as usual. The yield of o-methylbiphenyl determined for this run was nearly twice as great as those for runs at the same concentration of benzoyl peroxide which were carried through the epoxidation procedure.

Runs 1-14 were made using the first batch of active benzoyl peroxide, and runs 15-28 using the second batch.

It was observed in some of the early runs that the freshly prepared and sealed reaction mixtures contained what appeared to be small droplets of water, which dissolved in the course of a few hours after the flasks were warmed to room temperature. Beginning with run 15, the freshly sealed flasks were carefully inspected to see if water was present.

It seemed possible that some of the scatter in the early results was due to hydrolysis of a portion of the benzoyl peroxide at 80° by this water. Several variations of the procedure described above for preparing and sealing reaction mixtures were tried, but none was dependable in excluding water entirely. A different procedure finally was adopted, beginning with run 24. A section of Pyrex tubing about ten inches in length and 12 mm. in diameter, with a standard taper joint at the end, was used as the extension neck for the flask. No constriction was made in the neck. The flask, after cleaning and drying in the oven, was flushed thoroughly with dry nitrogen. The active benzoyl peroxide was quickly weighed into the flask, and the toluene was added. The flask was flushed again with dry nitrogen, and attached to a vacuum manifold. Without cooling the flask, the stopcock to the vacuum manifold was opened and the pressure in the flask was reduced until activity of the liquid surface was visible. The stopcock was then closed, and the flask was cooled in a Dry Ice-trichloroethylene bath. After a few minutes, the stopcock was reopened, and the flask was evacuated to a pressure of one micron for ten minutes. After the pumping period, the stopcock was closed, and the flask was warmed to room temperature for ten minutes. Finally the flask was cooled again in the Dry Ice bath. This cycle

was repeated three times, and the flask was sealed under vacuum. No more than a few very small specks of water were ever observed in reaction mixtures prepared in this way. Loss of solvent in the evacuation, measured by the amount retained in the traps in the vacuum line, amounted to only a few milliliters at the most.

Another possible source of serious error in the early runs appeared to be contamination of the o-methylbiphenyl by neighboring fractions, specifically biphenyl, in the gas chromatographic procedure. Reference to the recorder traces for the early runs showed that in many cases the o-methylbiphenyl fraction had been cut rather late, quite close to the small biphenyl peak. Any such contamination would lead to a large error, since all the products other than o-methylbiphenyl were undiluted and considerably more active; small amounts of biphenyl would significantly increase the measured activity of the sample. In order to minimize this difficulty, the operating conditions for the instrument were changed beginning with run 19 so as to spread the peaks further apart, and care was taken to cut the fractions earlier. The temperature was lowered to 205°, and the flow rate was reduced to 3-4 units.

### Calculations

Specific activities were calculated in terms of milli-

volts per milligram of sample. The specific activities of benzoic acid samples used to prepare active benzoyl peroxide are shown in Table 4. The values of the specific activities,  $B$ , of the *o*-methylbiphenyl initially formed in the decomposition in toluene of this benzoyl peroxide are given by

$$B = \frac{A_B M_B}{M_O}$$

where  $A_B$  is the specific activity of the benzoic acid from which the product is derived,  $M_B$  is the molecular weight of benzoic acid, and  $M_O$  is the molecular weight of *o*-methylbiphenyl. The dilution factor  $D$  for a run is given by

$$D = \frac{B}{A} = \frac{W_O + W_D}{W_O}$$

where  $A$  is the measured specific activity of the diluted *o*-methylbiphenyl isolated,  $W_D$  is the weight of inactive *o*-methylbiphenyl diluent added, and  $W_O$  is the weight of *o*-methylbiphenyl produced in the reaction. Then

$$W_O = \frac{A W_D}{B - A}$$

The number of moles of *o*-methylbiphenyl formed per mole of benzoyl peroxide decomposed is given by

$$N = \frac{W_O M_p}{M_O W_p}$$

where  $M_p$  is the molecular weight of benzoyl peroxide and  $W_p$

is the weight of benzoyl peroxide used in making the run.  
The results for the active runs are displayed in Table 5.

Table 4. Specific activities of samples of benzoic acid

Sample	weight of sample for combustion, mg.	activity of sample, mv.	specific activity mv./mg.	average	B <sup>a</sup>
I - I	3.357	310.0	92.34		
- 2	4.397	410.5	93.36	93.53	67.90
- 3	3.446	327.0	94.89		
II - I	3.830	305.2	79.69		
- 2	3.601	289.4	80.37	79.79	57.92
- 3	5.053	400.8	79.32		

<sup>a</sup>Calculated specific activity of o-methylbiphenyl initially formed in decomposition of the benzoyl peroxide from this batch of benzoic acid.

Table 5. Yields of o-methylbiphenyl by isotope dilution analysis

Run no. <sup>a</sup>	1	4 <sup>b</sup>	5	6 <sup>c</sup>	7 <sup>d</sup>	8 <sup>d,e</sup>
W <sub>P</sub> , gm. <sup>f</sup>	0.1471	0.1450	0.1458	0.1470	0.1457	0.1462
Toluene, ml.	6	60	200	6	60	600
W <sub>D</sub> , gm. <sup>g</sup>	0.0535	0.0558	0.0545	0.0555	0.0520	0.0530
Wt. of Sample for Combustion, mg.	1.840	2.699	4.986	5.049	4.468	4.157
Activity of sample, mv. <sup>h</sup>	25.7	28.0	94.0	92.0	60.0	59.5
A <sub>O</sub> , mv./mg. <sup>i</sup>	14.0	10.6	18.9	18.3	13.5	14.4
W <sub>O</sub> , mg. <sup>j</sup>	14.0	10.3	21.0	20.4	12.9	14.3
10 <sup>4</sup> Y, moles <sup>k</sup>	0.832	0.612	1.25	1.21	0.767	0.850
Yield <sup>l</sup>	0.137	0.102	0.208	0.200	0.128	0.141

<sup>a</sup>Runs 2, 3, 13 and 25 were lost; run 20 contained water, and was not carried out.

<sup>b</sup>Some loss occurred in weighing sample for combustion.

<sup>c</sup>Product solution was yellow, probably due to imperfect degassing.

<sup>d</sup>Fraction from gas chromatography was cut late; contamination of sample by the next component is likely.



Table 5 (Continued).

Run no. <sup>a</sup>	9 <sup>d,e</sup>	10	11 <sup>m</sup> ,	12 <sup>d,e</sup>	14	15 <sup>d, e, n</sup>
W <sub>P</sub> , gm <sup>f</sup>	0.1482	0.1526	0.1544	0.1453	0.1460	0.1529
Toluene, ml.	60	20	200	6	6	200
W <sub>D</sub> , gm. <sup>g</sup>	0.1528	0.0544	0.0537	0.0539	0.0549	0.0522
Wt. of Sample for Combustion, mg.	4.602	6.060	5.049	5.489	2.855	4.791
Activity of sample, mv. <sup>h</sup>	52.9	74.5	58.3	79.2	42.2	62.7
A <sub>0</sub> , mv./mg. <sup>i</sup>	11.65	12.4	11.6	14.4	14.8	13.1
W <sub>O</sub> , mg. <sup>j</sup>	11.0	12.0	11.0	14.6	15.3	15.2
10 <sup>4</sup> Y, moles <sup>k</sup>	0.651	0.713	0.654	0.865	0.910	0.907
Yield <sup>l</sup>	0.107	0.112	0.103	0.144	0.151	0.144

<sup>e</sup>Explosion occurred during combustion.

<sup>f</sup>Weight of active benzoyl peroxide used in the reaction. Benzoyl peroxide used in Runs 1-14 was prepared from benzoic acid of specific activity 93.53 mv./mg. That used in Runs 15-28 was from acid of specific activity 79.79 mv./mg.

<sup>g</sup>Weight of inactive o-methylbiphenyl added to product mixture as diluent.

<sup>h</sup>Corrected for background.

<sup>i</sup>Measured activity of diluted active o-methylbiphenyl.

Table 5 (Continued).

Run no. <sup>a</sup>	16	17	18 <sup>m</sup>	19 <sup>m</sup>	21	22
$W_p$ , gm. <sup>f</sup>	0.1480	0.1516	0.1472	0.1476	0.1463	0.1463
Toluene, ml.	60	20	200	20	200	20
$W_D$ , gm. <sup>g</sup>	0.0531	0.0519	0.0534	0.0536	0.0547	0.0537
Wt. of Sample for Combustion, mg.	4.280	3.261	4.086	5.799	5.403	5.266
Activity of sample, mv. <sup>h</sup>	44.1	43.2	49.8	65.6	51.7	65.7
$A_o$ , mv./mg. <sup>i</sup>	10.3	13.2	12.2	11.3	9.57	12.5
$W_o$ , mg. <sup>j</sup>	11.5	15.4	14.2	13.0	10.6	14.8
$10^4 Y$ , moles <sup>k</sup>	0.684	0.916	0.844	0.773	0.630	0.880
Yield <sup>l</sup>	0.112	0.146	0.136	0.127	0.104	0.115

<sup>j</sup>Calculated weight of o-methylbiphenyl produced in the reaction.

<sup>k</sup>Number of moles of o-methylbiphenyl produced  $\times 10^4$ .

<sup>l</sup>Moles per mole of benzoyl peroxide decomposed.

<sup>m</sup>Water globules visible in freshly sealed reaction flask.

Table 5 (Continued).

Run no. <sup>a</sup>	23 <sup>e,m</sup>	24 <sup>b,e</sup>	26 <sup>e,o</sup>	27 <sup>p</sup>	28 <sup>e</sup>
W <sub>P</sub> , gm. <sup>f</sup>	0.1479	0.1471	0.1466	0.1473	0.1481
Toluene, ml.	600	60	20	600	60
W <sub>D</sub> , gm. <sup>g</sup>	0.0534	0.0534	0.0535	0.0558	0.0556
Wt. of Sample for Combustion, mg.	3.688	3.630	5.837	3.840	4.579
Activity of sample, mv. <sup>h</sup>	25.7	31.2	108.8	33.0	47.5
A <sub>O</sub> , mv./mg. <sup>i</sup>	6.97	8.60	18.6	8.59	10.4
W <sub>O</sub> , mg. <sup>j</sup>	7.31	9.22	25.4	9.72	12.2
10 <sup>4</sup> Y, moles <sup>k</sup>	0.435	0.548	1.51	0.578	0.719
Yield <sup>l</sup>	0.071	0.0904	0.250	0.0950	0.118

<sup>n</sup>Temperature of bath was 0.5-1.0° low during the first 1.5 hours of the run.

<sup>o</sup>Control run, worked up without epoxidation procedure; see text.

<sup>p</sup>Two rather violent explosions occurred during the first minutes of the combustion, probably due to acetone vapor in the gas inlet line.

## DISCUSSION

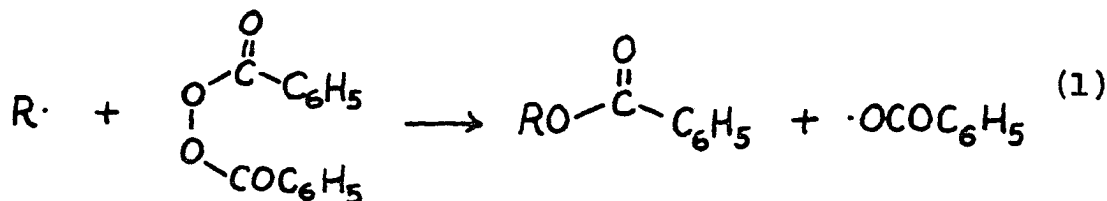
In most of the reactions that result in arylation of aromatic compounds by free radicals, a large number of other products are formed. These by-products seem to be derived from the same free radicals that lead, immediately or ultimately, to arylation. The competition of the reactions forming by-products with one another and with the arylation reaction depends on experimental conditions, and this dependence is of considerable significance to the establishment of the sequence of events in the arylation. Most of the available data concerning the variation in product distribution with experimental conditions derive from studies in which the source of aryl radicals was an aroyl peroxide.

The kinetics of the decomposition of benzoyl peroxide in the absence<sup>27,28,29</sup> and in the presence<sup>30,31</sup> of free-radical scavengers have been studied. The kinetics of decomposition of a number of substituted benzoyl peroxides have also been measured<sup>32,33</sup>. In the presence of scavengers, the decomposition of aroyl peroxides is strictly first order. It has been shown by means of scavenging experiments<sup>30</sup> that the primary process in the decomposition of benzoyl peroxide is cleavage to two benzoyloxy radicals; in moist carbon tetrachloride, essentially 100% of the

benzoyloxy radicals are captured by iodine, and may be recovered as benzoic acid.

In the absence of scavengers, a higher-order induced decomposition is superimposed upon the unimolecular decomposition in almost all solvents<sup>27,28</sup>. The benzoyloxy radicals that are formed in the initial decomposition process undergo decarboxylation to an extent that depends on the temperature, the solvent, and the concentration of benzoyl peroxide<sup>28,29</sup>. Radicals derived from benzoyl peroxide attack solvent molecules at least to some extent in every case that has been studied; no exceptions to this statement are known. Induced decomposition of the peroxide may be effected either by radicals derived from decomposition of the peroxide or by radicals derived from the solvent.

The most obvious position for attack of a radical on benzoyl peroxide to induce decomposition of the latter is at the O-O bond:

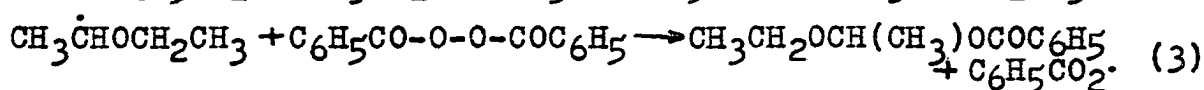
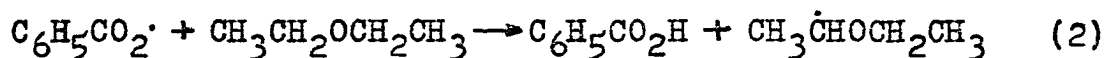


It has been shown conclusively by Cass<sup>61</sup>, from kinetics

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<sup>61</sup>(a) W. E. Cass, J. Am. Chem. Soc., 68, 1976 (1946); W. E. Cass, ibid., 69, 500 (1947).

and from product studies, that the chief process occurring in the decomposition of benzoyl peroxide in ethers such as diethyl ether is an induced decomposition of this type:



It has been shown recently<sup>62</sup> by labelling with oxygen-18 that attack by the radical occurs at the ether rather than the carbonyl oxygen atom of the peroxide.

In other non-aromatic solvents<sup>28,63</sup>, little ester is produced, although in most cases induced decomposition remains significant<sup>27</sup>. In aromatic solvents, somewhat more ester is formed, but still not enough to account for the amount of induced decomposition expected on the basis of the kinetics<sup>28</sup>. Furthermore, the phenols produced by hydrolysis of the esters resulting from the decomposition of benzoyl peroxide in substituted benzenes are largely substituted.<sup>64</sup> Thus it is clear that a considerable part of

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<sup>62</sup>W. von E. Doering, K. Okamoto and H. Krauch, J. Am. Chem. Soc., 82, 3579 (1960).

<sup>63</sup>P. H. Hermans and J. Van Eyk, J. Polymer. Sci., 1, 407 (1946).

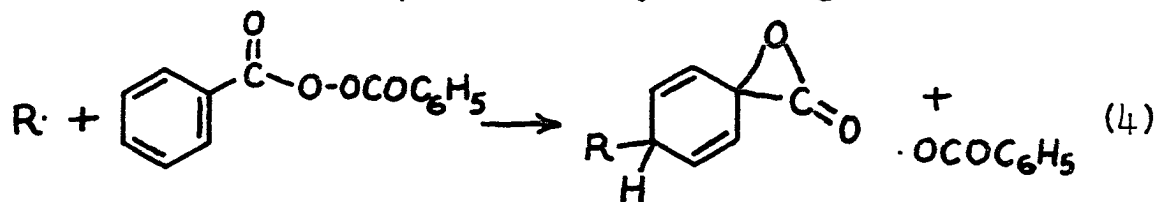
<sup>64</sup>B. M. Lynch and K. H. Pausacker, Austral. J. Chem., 10, 165 (1957).

the ester that is formed in aromatic solvents must arise from processes other than induced decomposition by phenyl radicals.

The substituted aryl benzoates presumably arise in large part from benzoyloxylation of the substrate. Apparently the only data relating to the fraction of the aryl benzoate product in which the phenol fragment is unsubstituted, and hence could result from attack by phenyl radicals on the O-O bond of the peroxide, is that of Lynch and Pausacker<sup>64</sup>. These workers found that hydrolysis of the ester fraction from the decomposition of 0.0825 M benzoyl peroxide in nitrobenzene yielded 0.08 mole of phenols per mole of peroxide. Of this quantity, 83% could be actually recovered and characterized as o- and p-nitrophenols. Only a very little unsubstituted phenol was found, perhaps 5-10% of the total phenolic fraction. Extrapolation of this result to other systems is hazardous, since nitrobenzene is one of the most reactive substrates to free radical substitution, and since there is little information as to the spread in substrate reactivities in benzoyloxylation. However, inasmuch as the yields of simple aryl benzoates in most solvents are less than 0.10 mole per mole of peroxide decomposed, the yield of phenyl benzoate arising from induced decomposition seems likely never to exceed

0.02-0.03 mole per mole<sup>65</sup>.

Walling<sup>65</sup> has suggested that the major induced decomposition reaction in cyclohexane, carbon tetrachloride, and many other solvents is attack by solvent-derived radicals at the o- and p- position of the aromatic nucleus of benzoyl peroxide, with concerted cleavage of the O-O bond to form an  $\alpha$ -lactone, followed by rearrangement of the



lactone by hydrogen migration to give the substituted benzoic acid. Such a reaction would provide an explanation of the formation of considerable quantities of benzoic acids substituted by solvent-derived fragments in the decomposition of benzoyl peroxide in these solvents.<sup>63,66</sup> A similar reaction of phenyl radicals would account for the formation of phenylbenzoic acids in the decomposition in aromatic solvents.

It would be possible for part of the substituted benzoic acids to arise from attack of radicals on benzoic acid formed in the reaction. However, although good quantitative data are scarce, the quantities observed seem too

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<sup>65</sup>All yield data are expressed in terms of moles of product per mole of peroxide decomposed.

<sup>66</sup>C. Walling and E. S. Savas, J. Am. Chem. Soc., 82, 1738 (1960).



large for this to be the sole source of substituted benzoic acids, if a reasonable value for the relative reactivity of benzoic acid toward substitution by phenyl radicals is assumed. For instance, Lynch and Pausacker<sup>22</sup> found by decomposition of 6.0 gm. (0.0248 mole) benzoyl peroxide in 300 ml. (3.39 moles) benzene a yield of free acid of 0.45 mole per mole, or 0.012 mole of acid. The reactivity of benzoic acid toward phenylation relative to that of benzene has not been measured directly, but it seems unlikely<sup>1</sup> to be greater than 3.0. Thus even if the yield of benzoic acid observed had been present at the beginning of the reaction, the yields of biphenyl and phenylbenzoic acids should be in the ratio of 0.36 to 3.39 if the latter product resulted from phenylation of benzoic acid. The yields of these products actually found in this reaction were 0.44 and approximately 0.02 mole per mole, respectively.

The process envisioned by Walling is again effectively a free-radical aromatic substitution reaction, but the reactivity of benzoyl peroxide as a substrate for substitution presumably is enhanced by the concerted cleavage of the O-O bond. It must be noted, however, that Dannley<sup>20,67</sup> has determined the isomer distribution of the phenylbenzoic

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<sup>67</sup>R. L. Dannley and E. C. Gregg, J. Am. Chem. Soc., 76, 2997 (1954).

acids produced in the decomposition of benzoyl peroxide in two different mixtures of aromatic solvents. While the results were not considered to be highly accurate, and those from the two systems were not in quantitative agreement, it was found that all three isomers were present in proportions characteristic of a normal free-radical substitution process. If the reaction suggested by Walling were the main route to formation of phenylbenzoic acids, the *o*- and *p*- isomers should be found almost exclusively.

In aromatic solvents, the yield of phenylbenzoic acids is quite small except in experiments involving very high concentrations of peroxide. For instance, Lynch and Pausacker<sup>22</sup> found that at a concentration of 0.0825 M benzoyl peroxide in benzene, 0.42 mole of free acid per mole of peroxide was produced. The acidic fraction had a neutralization equivalent consistent with the presence of 5% phenylbenzoic acids, assuming that these were the only impurities in the benzoic acid. This corresponds to a yield of phenylbenzoic acids of 0.02 mole per mole. The combination of this yield with the portion of the ester yield that is plausibly ascribable to attack of phenyl radicals on benzoyl peroxide remains too small to account for the observed extent of induced decomposition.

It is also possible that induced decomposition by benzoyloxy radical occurs to some extent. The most reason-

able process of this kind would seem to be a reaction with decarboxylation to give phenyl benzoate. Alternatively, a process analogous to that suggested by Walling<sup>65</sup>, involving attack of the radical on the nucleus to give a benzoyloxybenzoic acid, could be visualized. However, it appears that only a small fraction of the free acid formed during arylations with benzoyl peroxide consists of compounds other than unsubstituted benzoic acid<sup>22</sup>. Thus, induced decomposition by benzoyloxy radical probably is not a reaction of importance in these systems.

The fraction of the benzoyl peroxide that undergoes induced decomposition can be calculated from the kinetic data of Nozaki and Bartlett<sup>27a</sup>. The fraction that would undergo unimolecular decomposition in a given time in the absence of induced decomposition can be calculated from the rate constant of Hammond<sup>30a</sup>. This value is used because it is the smallest yet obtained for the decomposition in benzene, and probably the most reliable. The difference between the calculated and observed decrease in concentration of benzoyl peroxide in a given time gives an approximation to the amount of induced decomposition occurring during the interval. The calculation assumes that the amount of peroxide present and undergoing unimolecular decomposition at any time is that which would result from the operation of unimolecular decomposition only, rather than the lower,

true value. Consequently, this procedure underestimates the extent of induced decomposition. If the comparison is made over an interval that constitutes a major fraction of the reaction, the error is very large. The error can be minimized by making the calculation from point to point, over small fractions of the reaction, and summing the calculated portions of induced decomposition over the entire reaction. The calculation of the extent of induced decomposition occurring in the run of Nozaki and Bartlett<sup>27a</sup> at 0.197 M and 79.8° is summarized in Table 6. The measured value of the peroxide concentration at each kinetic point is taken as the initial value for a calculation of the expected extent of unimolecular decomposition during the interval up to the next kinetic point. By this procedure we find that in the decomposition of 0.197 M benzoyl peroxide, a minimum of 38.0% of the total decomposition is induced, at 0.0206 M the figure is 24.3%, again a minimum. Therefore another path for induced decomposition of benzoyl peroxide must exist.

Pausacker has found<sup>47</sup> that bis-m- and p-nitrobenzoyl peroxides undergo decomposition in benzene to produce the corresponding nitrobiphenyls, nitrobenzoic acids, and carbon dioxide in nearly equimolar quantities, and only small amounts of other products. Swain, Stockmayer and Clarke<sup>32</sup> found that aroyl peroxides with electron-with-

Table 6. The extent of induced decomposition of 0.197 M benzoyl peroxide in benzene at 79.8°<sup>a</sup>

Interval	$P_0$ , m./l. <sup>b</sup>	t, hr. <sup>c</sup>	$P_1$ , m./l. <sup>d</sup>	P, m./l. <sup>e</sup>	$P_0 - P_1$ , m./l. <sup>f</sup>	$P_1 - P$ , m./l. <sup>g</sup>
I	0.197	1.0	0.180	0.166	0.019	0.014
II	.166	1.25	.148	.131	.018	.017
III	.131	1.75	.112	.0975	.019	.014
IV	.0975	2.0	.0813	.0703	.016	.011
V	.0703	2.25	.0573	.0485	.013	.0088
VI	.0485	3.75	.0345	.0277	.014	.0068
VII	.0277	4.25	.0188	.0159	.009	.0029
Totals					.108	.0745

<sup>a</sup>Calculated from the kinetic data of Nozaki and Bartlett<sup>27a</sup> and the unimolecular rate constant of Hammond<sup>37a</sup>.

<sup>b</sup>Actual concentration of peroxide at the beginning of the interval.

<sup>c</sup>Length of the interval.

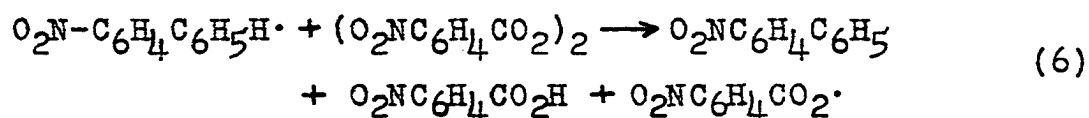
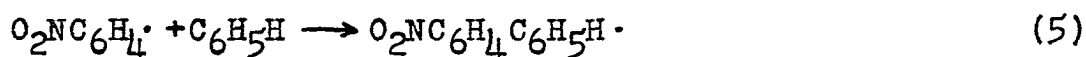
<sup>d</sup>Expected concentration of peroxide at the end of the interval, calculated on the basis of first order reaction only.

<sup>e</sup>Actual concentration of peroxide at the end of the interval.

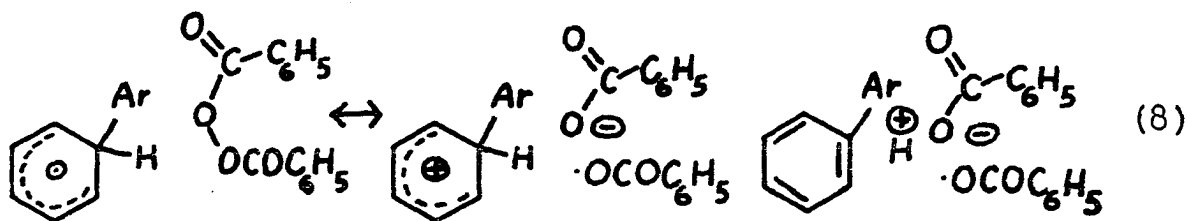
<sup>f</sup>Calculated extent of unimolecular decomposition during the interval.

<sup>g</sup>Calculated extent of induced decomposition during the interval.

drawing substituents are highly susceptible to induced decomposition. In the case of nitro-substituted peroxides, induced decomposition was too rapid to be suppressed entirely with a good inhibitor. It appears that the main reaction is an induced decomposition of the peroxide by the adduct radical resulting from addition of the aryl radical to the substrate:



The reaction is facilitated by good polar resonance structures in the transition state.



Pausacker suggests<sup>47</sup> that a similar reaction of adduct radicals accounts for a major portion of the induced decomposition observed with other aryl peroxides in aromatic solvents. It seems plausible that this might be the most important route for induced decomposition of aryl peroxides in aromatic solvents, except possibly at extremely

high concentrations. Such a conclusion is consistent with the finding of Nozaki and Bartlett that the decomposition of benzoyl peroxide in several aromatic solvents fits rather well a kinetic equation of the form:

$$-\frac{dP}{dt} = k_1P + k_iP^{3/2} \quad (9)$$

This rate law is derived from the proposed reaction sequence if it is assumed that the major termination step is reaction of two solvent-derived radicals. We will argue below that this assumption is reasonable at least at moderately low concentrations. It does not appear to be possible to devise a scheme involving induced decomposition predominantly by phenyl or benzoyloxy radicals that is consistent with this equation.

It is a little difficult to decide whether the assumption that all the remaining induced decomposition is due to this reaction is supported by the available data for the yield of benzoic acid formed in the decomposition. Interpolation from the data both of Lynch and Pausacker<sup>22</sup> and of Barnett and Vaughan<sup>29a</sup> permits an estimate of 0.40-0.44 mole of acid per mole of peroxide at 0.197 M benzoyl peroxide, which is consistent with the estimate made above from kinetic data. On the other hand, De Tar and Long<sup>47</sup> found a yield of only 0.10 mole per mole from the decomposition of 0.0206 M peroxide, which is much less than the

amount of induced decomposition estimated from the kinetics. Further, while it is hard to tell for certain from the description of their experimental procedure, Barnett and Vaughan apparently determined yields of acid in their runs after only about 55% reaction. Now, induced decomposition is most important in the early stages of the decomposition. Again from the data of Nozaki and Bartlett<sup>27a</sup> we may calculate by the method used above that in the decomposition of 0.197 M peroxide in benzene, at least 56% of the decomposition occurring during the first 50.5% reaction is induced. In the run at 0.0206 M, a minimum of 34% of the decomposition in the first 51.5% reaction is induced. On this basis, the acid yields of Barnett and Vaughan seem too low to account for the amount of induced decomposition expected.

One other possible source of induced decomposition may be considered. Evidence has been presented<sup>68</sup> that a molecule-induced decomposition of acetyl peroxide may occur. Since olefinic materials have been shown to be among the products resulting from decomposition of benzoyl peroxide in benzene<sup>47</sup>, it is conceivable that a similar molecule-induced decomposition of benzoyl peroxide could

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<sup>68</sup>J. C. Martin and E. H. Drew, Abstracts of Papers, 137th Meeting of the American Chemical Society, Cleveland Ohio, April 14-19, 1960, p. 8-0.



occur in arylation reaction mixtures. In this connection, it is of interest that the decomposition of benzoyl peroxide at a given concentration has been found<sup>69</sup> to be more rapid in solutions resulting from partial decomposition of benzoyl peroxide initially at a higher concentration than in fresh solutions at the given concentration. However, it has not been shown that such a molecule-induced decomposition can occur with benzoyl peroxide, and there appears to be no way to estimate its possible importance.

It is to be expected that coupling of phenyl radicals to form unsubstituted biphenyl, and coupling of phenyl with benzoyloxy radicals to give phenyl benzoate, should occur to some extent. However, in most solvents, including aromatic ones, other reactions of phenyl and/or benzoyloxy radicals compete well with coupling, and very little of the coupling products are actually found. From the products of decomposition of benzoyl peroxide at very high concentration (20-40% by weight), biphenyl has been isolated in yields of 3-4%<sup>70</sup>. It may also be present in smaller quantities among the products of the decomposition at lower concentrations; no careful search for it has been made.

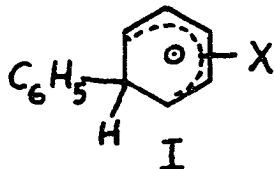
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<sup>69</sup>G. S. Hammond, Pasadena, California, experiments by S. Johnson on the decomposition of benzoyl peroxide, private communication, 1960.

<sup>70</sup>D. F. DeTar, J. Am. Chem. Soc., 72, 1028 (1950).

The yield of phenyl benzoate has been discussed already; the small quantity found must include the product of induced decomposition of peroxide by attack of phenyl radicals at the O-O bond, as well as the phenyl-benzoyloxy coupling product. Swain and co-workers find<sup>31</sup> that 0.003 M benzoyl peroxide in cyclohexane at 91° provides 0.00096 and 0.0138 mole per mole yields of biphenyl and phenyl benzoate respectively. These yields are affected only slightly by the addition of styrene to the reaction mixture, and it is suggested that both products are formed by cage reactions of fragments from benzoyl peroxide.

In most aromatic solvents, the most important reactions of phenyl radicals seem to be addition to the aromatic nucleus, and perhaps reactions with the adduct and with products derived from it. The exact nature of the adduct is not clear, but some variety of adduct seems to be demanded by the nature of the products. For convenience, we will represent it as I, without, however, intending any precise description of the bonding or geometry involved.



In addition to inducing decomposition of benzoyl peroxide, adduct radicals could be expected to be destroyed by reaction with any of the three types of radical present

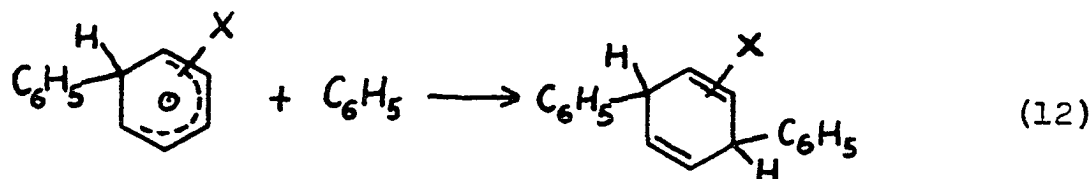


As we have seen, considerable quantities of benzoic acid result from decomposition of benzoyl peroxide in aromatic solvents. It appears necessary to assume that most or all of the benzoic acid produced arises from induced decomposition; however, as we shall see, there are indications that this is not the case. The stable products resulting from hydrogen abstraction from adduct by benzoyloxy radical are the same as those expected from induced decomposition of peroxide by adduct radical according to the formulation above. Consequently, the only way to determine whether the former reaction occurs to an appreciable extent is by comparison of kinetic and product data. The available results are conflicting and of insufficient accuracy to permit a definite conclusion.

The phenyldihydroaryl esters that would result from the coupling reaction have not been isolated. There is some question of the stability of such esters toward elimination to give biaryl and benzoic acid. If they survive the reaction conditions, it is to be expected that they would be oxidized by atmospheric oxygen to phenylaryl esters in the course of work-up of the reaction mixtures as occurs with the dihydrobiphenyls<sup>47,26</sup>. Consistent with this hypothesis is the fact that the quantity of benzoic acid resulting from hydrolysis of the ester portion of the product is always

greater than the quantity of mononuclear phenols<sup>12,22,49,64,71</sup>. For instance,<sup>22</sup> the product formed by decomposition of 0.0825 M benzoyl peroxide in benzene is hydrolysed to yield 0.24 mole of benzoic acid and 0.09 mole phenol per mole of peroxide. The difference may be due in part to the presence of phenylaryl esters, although there are other possibilities. Excess benzoic acid may also arise from benzoyloxy end groups in polymer formed from dihydrobiaryls and related compounds and from high molecular weight esters resulting from attack of benzoyloxy radicals on the substrate.

Coupling of adduct with phenyl radical would lead to an o- or p- dihydroterphenyl:



Workup in air would result in terphenyls. Small amounts (of the order of 0.01 mole per mole) of p-terphenyl have been isolated from the decomposition of benzoyl peroxide in benzene<sup>12,22</sup>, and a material has been obtained<sup>72</sup> from the decomposition in chlorobenzene that appears to be a

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<sup>71</sup>B. M. Lynch and K. H. Pausacker, Austral. J. Chem. **10**, 329 (1957).

<sup>72</sup>D. R. Augood, D. H. Hey and G. H. Williams, J. Chem. Soc., **44** (1953).

chloroterphenyl. Reliable data on yields is essentially non-existent, due to the difficulty of separating the complex mixtures of high-molecular weight compounds. A substantial fraction of the terphenyls formed may also result from further phenylation of initially-formed biaryl. The quantities that have been isolated are not large enough to preclude this possibility, although it is by no means certain that the terphenyls present in the reaction mixture have been quantitatively isolated in any instance.

Abstraction of hydrogen from adduct by phenyl radical would lead to biaryl and benzene. Apparently the only cases in which benzene has been isolated from the phenylation of an aromatic substrate<sup>24, 25, 73</sup> are those in which the substrate was an alkylbenzene having a benzylic hydrogen atom. In these cases at least part of the benzene is almost certainly the product of attack by phenyl radical on the side chain. While no benzene has been found to result from the phenylation of other substrates, no search for it has been made. The first step in most work-up procedures consists of removing the solvent by distillation and discarding it, so benzene would be easy to miss. In a few cases, corresponding products from the decomposition of substituted benzoyl peroxides have been found. Hey and Walker<sup>74</sup> found

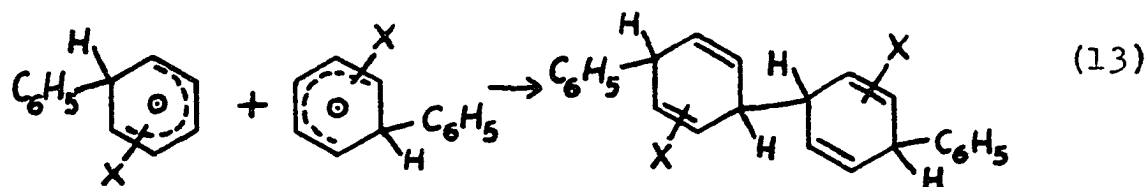
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<sup>73</sup>R. L. Dannley and B. Zaremsky, J. Am. Chem. Soc., 77, 1588 (1955).

<sup>74</sup>D. H. Hey and E. W. Walker, J. Chem. Soc., 2213 (1948).

methyl benzoate among the products of decomposition of bis-o-carbomethoxybenzoyl peroxide in pyridine, and Eliel and co-workers<sup>26</sup> have isolated toluene, anisole, and chlorobenzene from the decompositions in benzene of bis-p-methyl-, p-methoxy, and p-chlorobenzoyl peroxides respectively. Quantitative yields were not reported, but they apparently were moderate, and certainly more than trace amounts.

Coupling of adduct radicals would result in tetrahydroquateraryls:



Atmospheric oxidation during work-up would be expected to convert these to the fully aromatic quateraryls. It was first suggested by Lynch and Pausacker<sup>22</sup> that the quaterphenyl that is formed<sup>12,22</sup> in the decomposition of benzoyl peroxide in benzene results from this reaction. Yields of p-quaterphenyl are of the order of 0.01 to 0.03 mole per mole, together with a similar yield of a compound tentatively identified as a "quinhydrone" of a quaterphenyl with a dihydroquaterphenyl. It is likely that these yields do not represent the total amount of tetrahydroquaterphenyl formed, both because of difficulties in isolation and because the products of ortho coupling are conjugated

dienes, as such they may undergo polymerization to produce materials of still higher molecular weight, at least in runs at relatively high concentration. It seems likely that a large part of the "intractable resin" formed in these reactions consists of such polymers of tetrahydroquaterphenyls, dihydroterphenyls, and dihydrobiphenyls. Even the small yields of quaterphenyls found are large enough to virtually guarantee that the compound is not a product of further phenylation of terphenyls, if any reasonable value is assumed for the relative reactivity of terphenyls toward phenylation.

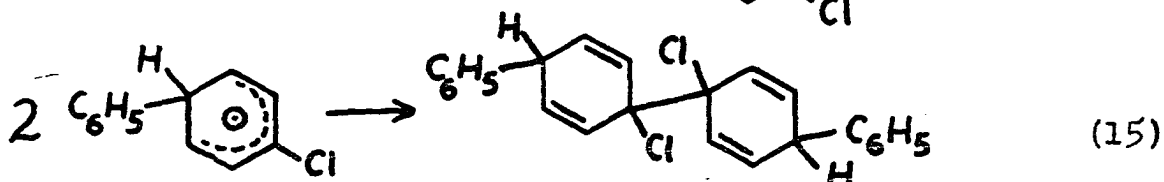
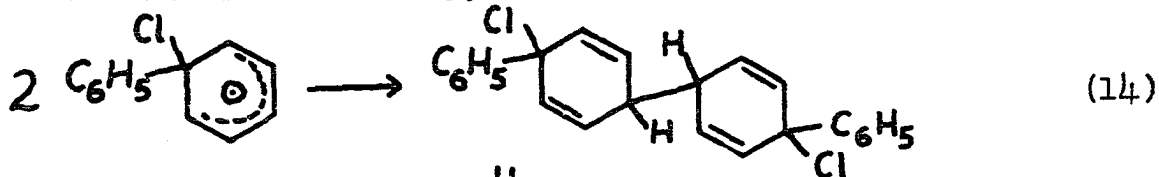
Recently, De Tar and Long<sup>47</sup> actually have isolated 1',4',1'',4''-tetrahydro-p-quaterphenyl in a yield of 0.03 mole per mole from the phenylation of benzene and work-up under non-oxidizing conditions.

It is of interest that Dannley<sup>20</sup> has found that the basic portion of the high molecular weight material from the competitive phenylation of pyridine and bromobenzene contains both nitrogen and bromine. This may well be due to product derived from coupling of two adduct radicals, one derived from each substrate.

Phenylation of chlorobenzene has been reported<sup>64</sup> to yield as one product a small quantity of unsubstituted p-quaterphenyl. This must almost necessarily arise from a similar reaction in which either the adduct is formed



by addition of phenyl radical to the carbon atom attached to chlorine, or by coupling of adduct radicals at the atom substituted with chlorine:

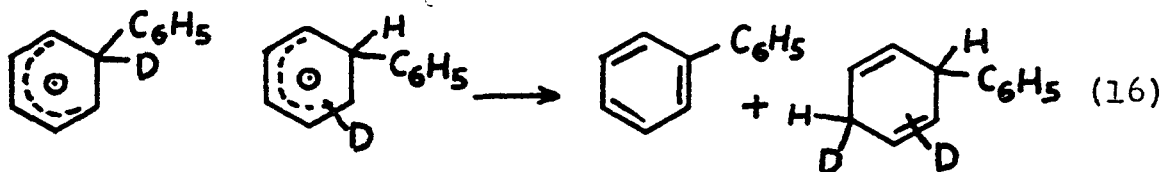


Facile elimination of hydrogen chloride would regenerate the fully aromatic system.

Transfer of a hydrogen atom from one adduct to another (disproportionation) has been demonstrated by De Tar and Long<sup>47</sup>. They found that decomposition of 0.0206 M benzoyl peroxide in benzene, followed by careful work-up with exclusion of air, led to isolation of biphenyl and 1,4-dihydrobiphenyl in yields of 0.6 and 0.4 mole per mole of peroxide, respectively. They also found indications of the presence of a small amount of 1,2-dihydrobiphenyl.

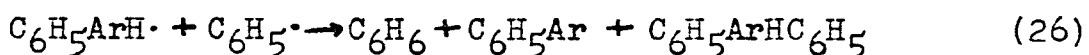
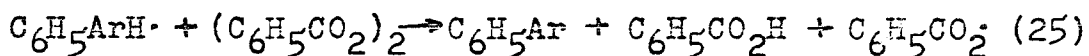
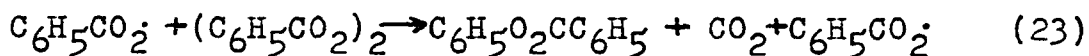
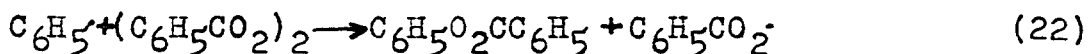
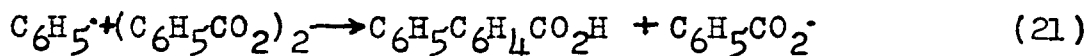
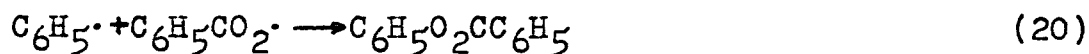
Elie<sup>l</sup> and co-workers<sup>26</sup> also have noted the importance of this reaction. Decomposition of benzoyl peroxide in benzene-d produces biphenyl containing less than the statistically expected amount of deuterium. Presumably this is due to slower breaking of C-D than C-H bonds in the conversion of adduct radicals to biphenyl. Biphenyl isolated by careful work-up in the absence of air shows a much

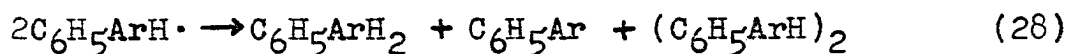
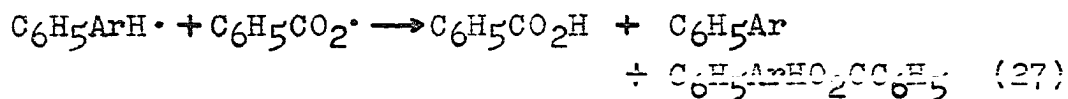
greater isotope effect of this type than does that obtained by work-up under oxidizing conditions. This is explained as being due to dilution in the latter case of the initially formed biphenyl by biphenyl formed by air oxidation of dihydrobiphenyl. The initially formed biphenyl is expected to have a relatively low deuterium content, while the dehydrobiphenyl should contain considerably more. Further, it was found that some biphenyl- $\underline{d}_2$  was formed, presumably by the reaction



followed by oxidation of the dihydro compound.

The reactions considered thus far are the following:





Those of major importance in most cases appear to be 17, 18, 24, 25, 28 and perhaps 26 and 27.

Several other possible reactions must be considered briefly. Attack of benzoyloxy radical on substrate appears to occur to some extent in most cases. With naphthalene<sup>64,75</sup> and other polynuclear aromatic compounds<sup>76</sup>, it apparently represents a major part of the reaction. Presumably<sup>22</sup> an adduct analogous to that with phenyl radical is formed. This adduct could in principle undergo reactions analogous to those of phenyl adduct radicals to give a variety of ester products, both mononuclear and polynuclear. This may be one source both of simple aryl benzoates and of high molecular weight benzoate esters present among the products.

The products of coupling reactions of adduct radicals and of their disproportionation would be expected to be rather active hydrogen donors. Also, since some of these products are conjugated dienes, these should be quite

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<sup>75</sup>D. I. Davies, D. H. Hey and G. H. Williams, J. Chem. Soc., 2213 (1948).

<sup>76</sup>I. M. Roitt and W. A. Waters, ibid., 2695 (1952).

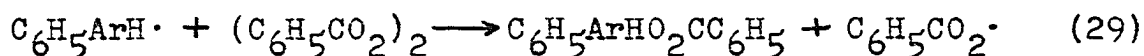
reactive monomers for vinyl polymerization. The reactivity of these compounds toward benzoyloxy and phenyl radicals by either hydrogen transfer or addition to initiate polymerization probably is considerably higher than that of most aromatic substrates. Consequently, despite their low concentration, these products may compete significantly with solvent for phenyl and benzoyloxy radicals, at least in the last stages of reactions and in runs at high concentration. Such polymerization reactions would account for the presence in the product mixtures of tarry materials apparently of still higher molecular weight than quaterphenyls<sup>22, 64</sup>.

The most complete and careful study of the products of the decomposition of benzoyl peroxide in benzene was made by Lynch and Pausacker<sup>22</sup>. They found that over a fivefold range of concentration, from 0.0825 to 0.412 M, the yields of free acid and of biphenyl were nearly equivalent and approximately constant. The yield of acid increased slowly from 0.42 to 0.45 mole per mole of peroxide, while that of biphenyl varied irregularly from 0.38 to 0.44 mole per mole. The products were worked up in the presence of air. The increase in yield of total acids appears to be due in part to an increasing yield of phenylbenzoic acids, since the neutralization equivalent of the acid produced increases slowly with concentration. Such results seem to be straight-

forwardly accommodated by a scheme in which the chief product-forming step is reaction 25 or 27, or some combination of the two. The kinetic considerations mentioned earlier suggest that reaction 25 should be predominant.

By contrast, De Tar and Long<sup>47</sup> found at 0.0206 M, a concentration smaller by only a factor of four than the lowest studied by Lynch and Pausacker, yields of 1.7 moles carbon dioxide, 0.10 mole benzoic acid, 0.60 mole biphenyl, and 0.40 mole 1,4-dihydrobiphenyl, together with a small amount of 1,2-dihydrobiphenyl. Products were worked up in the absence of air. These results indicate that the major process for conversion of adduct radical to biaryl at this concentration is disproportionation of the adduct radical, together with a small amount of induced decomposition or reaction with benzoyloxy radical to give benzoic acid, and perhaps a little reaction with phenyl radical. A puzzling feature is the small yield of benzoic acid. According to the calculations made earlier concerning the extent of induced decomposition, the yield of benzoic acid at this concentration should be around 0.25 mole per mole peroxide. Since biphenyl is produced in both the induced decomposition step and the disproportionation of adduct, its yield should be at least  $0.40 + 0.25 = 0.65$ . It is possible that part of the induced decomposition by adduct radical produces, in part or entirely, a phenyldihydroaryl ester

rather than benzoic acid and biaryl, by the reaction



The yield of carbon dioxide is not too large to preclude the presence among the products of 0.25 mole per mole of the ester produced by such a reaction. However, in runs at higher concentration the observed<sup>22</sup> yields of ester are too small to account for the amount of induced decomposition that is calculated to occur. The alternative appears to be some entirely different induced decomposition reaction which does not produce biaryl. It may be pointed out that Barnett and Vaughan<sup>29</sup> found a higher yield of free acid, 0.21 mole per mole, at nearly the same concentration.

Closer consideration of the results of Lynch and Pausacker casts doubt on the conclusion that the biphenyl and benzoic acid arise almost entirely from induced decomposition. A small yield of quaterphenyl and its "quinhydrone" was found at all concentrations<sup>22</sup>. At 0.0825 M, for instance, the yield was equivalent to 0.09 mole per mole of initially formed tetrahydroquaterphenyl. The total amount formed is probably significantly greater than this, due to the possibility of different isomers, and the possible loss of some of the product by polymerization. Thus reaction of two adduct radicals occurs to some extent at this concentration. The absolute yields of products derived

from adduct radical would be expected to vary with initial concentration of peroxide, but the split between dihydrobiphenyl and tetrahydroquaterphenyl should be concentration-independent, since the reactions forming these products involve the same pair of radicals. Thus if there is very little dihydrobiphenyl produced at 0.0825 M, while a significant amount of tetrahydroquaterphenyl is formed, these products should be formed in the same proportions at 0.0206 M. Since a yield of 1,4-dihydrobiphenyl of 0.40 mole per mole is found at this concentration, the expected yield of tetrahydroquaterphenyls would be enormous, probably corresponding to more than the entire remaining quantity of adduct radical formed. While the 0.03 mole per mole yield of tetrahydroquaterphenyl isolated<sup>47</sup> at this concentration probably does not represent all that was present, it certainly appears that this compound was not a major product of the reaction. Even if it were formed in a yield equivalent to that of 1,4-dihydrobiphenyl, this would mean that 0.0825 M at least 0.09 mole per mole yields each of dihydrobiphenyl and biphenyl must result from disproportionation. The only qualification to this argument is that it must be assumed that dihydrobiphenyl is not preferentially removed by further reaction at the higher concentration. While it is very possible that attack by radicals on dihydrobiphenyl occurs, especially at high concentrations, there is no obvious

reason why attack on tetrahydroquaterphenyl should occur less readily.

Further confirmation of the importance of disproportionation of adduct radicals even at high concentrations is provided by the work of Eliel and co-workers<sup>26</sup>, who found that in monodeuterobenzene, biphenyl-d<sub>2</sub> was found in the products even at 0.4 M. This product is presumed to result from air oxidation of dihydrobiphenyl-d<sub>2</sub> during work-up.

It is of considerable interest in this connection that the yields of free acid and of carbon dioxide at moderate concentration determined by Lynch and Pausacker<sup>22</sup> are considerably different from those found by Barnett and Vaughan<sup>29</sup>. Selected values, determined by several groups of workers, of the yields of carbon dioxide, free acid, and acid bound as ester, are shown in Table 7.

Thus in the vicinity of 0.08 M, the former workers find a considerably greater quantity of acid, and less carbon dioxide, than did the latter. The smaller quantity of acid would be in much better accord with the conclusions reached above about the amount of disproportionation that must occur at 0.0825 M, if it is assumed that the reported yield of biphenyl is correct.



Table 7. Yields of some products from the decomposition of benzoyl peroxide in benzene near 80°

M	carbon dioxide	free acid	acid from esters	reference
0.412	1.19	0.45	0.31	22
0.344	1.30			29
0.316		0.45		29
0.0825	1.34	0.42	0.24	22
0.0798		0.27		29
0.0770	1.56			29
0.0450	1.66	0.218	0.122	28
0.0383		0.25		29
0.0374	1.68			29
0.0214		0.21		29
0.0206	1.70	0.10		47

Experimental procedures used by the two groups of workers were different, and there are several possible sources for the discrepancy. Barnett and Vaughan carried out their reactions under a stream of nitrogen. Lynch and Pausacker saturated their solutions with carbon dioxide in advance and carried out their decompositions in a closed system; otherwise, no effort was made to protect the system

from air. If some air were still present, a greater yield of acid might result, since Barnett and Vaughan<sup>29</sup> have shown that in the presence of air, the decomposition results in more acid than do runs at the same concentration in the absence of air.

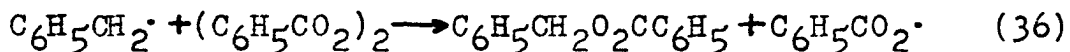
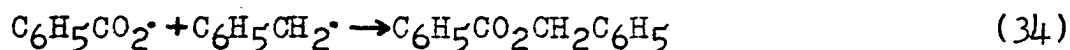
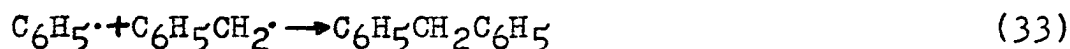
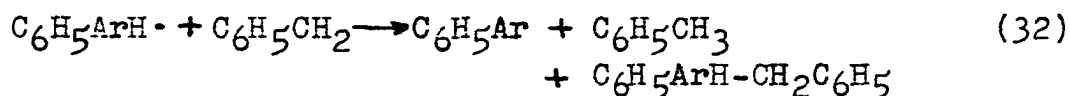
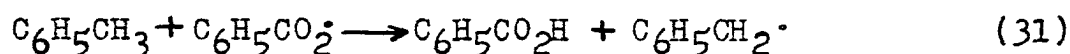
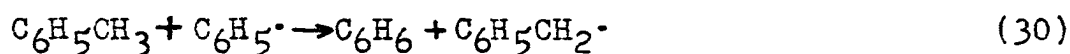
The procedures for determining the yields of acid were different, but the differences are not of such a nature as to render enhancement of the acid yield by hydrolysis of even easily hydrolysed esters likely in either case. Barnett and Vaughan titrated free acid directly in aliquots of the solution, using dilute sodium hydroxide. Lynch and Pausacker extracted the solution with aqueous sodium bicarbonate, and isolated and weighed the acid.

It appears that Barnett and Vaughan carried out their determinations on solutions in which the decomposition reaction was only about 55% complete, while Lynch and Pausacker presumably carried the reactions to completion. It appears possible that the discrepancy could be explained on the basis of accumulation in the solution in the latter stages of the reaction of products that are good hydrogen donors. Such a conclusion is consistent with the fact that at lower concentration, the yields found by Barnett and Vaughan agree reasonably well with those found by Hartman et al.<sup>28</sup>, who also presumably carried the reaction to completion.

There is, however, an objection to such a conclusion. If the benzoic acid which does not arise from attack on the hydrogen-rich products is considered to result from induced decomposition of peroxide, the yield of benzoic acid is too small. According to the discussion of induced decomposition above, the effect of determining the yield of benzoic acid in solutions that have reacted only about halfway to completion should be a strongly enhanced yield of benzoic acid per mole of peroxide decomposed. The expected enhancement in the early stages appears too large to be overbalanced by an enhancement in the later stages due to attack of benzoyloxy radicals on products. Again, the only solution to the dilemma seems to be that at least a large part of the induced decomposition reaction does not produce benzoic acid.

Thus two problems remain. First, it is necessary to devise another source of benzoic acid, one which does not require the concomitant formation of an equimolar amount of biaryl. Second, the benzoic acid and biphenyl are, at least in part, products of reactions other than induced decomposition of peroxide, and the amounts remaining are insufficient to correspond to the amount of induced decomposition previously calculated to occur. Consequently it is necessary to devise another induced decomposition reaction. The nature of these missing reactions is not immediately obvious.

Alkylbenzenes having a benzylic C-H bond undergo attack at the benzylic position, as well as nuclear substitution, by radicals derived from the decomposition of benzoyl peroxide. The radicals produced are relatively stable, and react largely by coupling; they might also be expected to induce decomposition of benzoyl peroxide. In the case of toluene, the reactions that seem plausible are



where  $\text{ArH} = \text{C}_6\text{H}_5\text{CH}_3$ . When the substrate is ethylbenzene or cumene, another group of reactions may be expected to occur. It seems likely that in these cases, benzylic radicals can react with any of the four types of radical present, not only by coupling but by hydrogen transfer to give styrene or  $\alpha$ -methylstyrene. Since these products are very active monomers, they would not be expected to survive in the product mixture, but probably would polymerize and contribute to the yield of high molecular weight residue.

The available quantitative product data from the decomposition of benzoyl peroxide in toluene are summarized in Table 8. The yields determined by various workers of benzene, free benzoic acid, biaryl, and coupling product of the benzylic radical obtained from the reaction in alkylbenzenes are compared in Table 9.

Table 8. Products of the decomposition of benzoyl peroxide in toluene<sup>a</sup>

Investigator	Hey et al. <sup>24</sup>	Rondestvedt <sup>21a</sup>	Dannley <sup>73</sup>
Temperature	80°	80-110°	75°
Benzoyl Peroxide, M	0.124	0.470	0.525
Carbon Dioxide			1.20
Benzoic Acid	0.435		0.79
Phenylbenzoic Acids			0.004
Benzoate Esters	0.073		
Benzene			0.10
Biaryl	0.443	0.37	0.46
Residue, gm. per mole peroxide	83.8		67.0
Bibenzyl	0.0545 <sup>b</sup>	0.078-0.16	c

<sup>a</sup>Yields in moles per mole of peroxide unless otherwise stated.

<sup>b</sup>At 0.412 M.

<sup>c</sup>A yield of 0.08 mole per mole diphenylmethane was reported.

Table 9. Products of the decomposition of benzoyl peroxide in alkylbenzenes

	toluene	ethylbenzene	cumene	<u>tert</u> -butylbenzene
<b>Free Acid<sup>a</sup></b>				
Hey et al. <sup>24,25,83</sup>	0.435	0.477	0.513	0.82
Dannley <sup>73</sup>	0.79	0.81	0.78	
Barnett and Vaughan <sup>29</sup>		0.45	0.54	
Hartman et al. <sup>28</sup>				0.42
<b>Benzene</b>				
Hey		0.207	0.62	
Dannley	0.10	0.57	0.34	
<b>Biaryl</b>				
Hey	0.443	0.237	0.262	0.535
Dannley	0.46	0.14	0.18	
<b>Coupling Product<sup>b</sup></b>				
Hey	0.0585	0.251	0.343	0.00
Dannley		0.24	0.08	
<b>Sum of Biaryl and Coupling Product</b>				
Hey	0.501	0.438	0.605	
Dannley	0.54	0.38	0.26	

<sup>a</sup>Largely benzoic acid.

<sup>b</sup>Bibenzyl, 2,3-diphenylbutane, bicumyl, and 2,5-dimethyl-2,5-diphenylhexane, respectively.

Benzene has been found among the products of decomposition of benzoyl peroxide in toluene<sup>12,73</sup> and other alkylbenzenes<sup>24,25,73</sup>. This probably results, at least in part, from attack of phenyl radical on the side chain. Hey and co-workers<sup>25</sup> originally considered that attack on the alkyl side chain was due entirely to phenyl radical, since "with both ethylbenzene and isopropylbenzene, the amount of benzoic acid formed is grossly insufficient to account for the number of benzoyloxy-radicals which must react in this way to give the observed amounts of the products derived from side-chain attack." This conclusion, as it stands, is not borne out by their own reported quantitative data, as may be seen by reference to Table 9. However, if we compare these yields of benzoic acid with the value of 0.42 reported by Lynch and Pausacker<sup>22</sup> for the yield of benzene at essentially the same concentration, it is apparent that the increase in yield on going to a solvent with an alkyl side chain is unexpectedly small. Unless in these solvents there is a pronounced decrease in the importance of the reactions that produce benzoic acid in benzene, the difference is not great enough to accommodate the observed amount of coupling product. Hence it is likely that a considerable part of the attack on aliphatic side chains is due to phenyl

radical. Hey and co-workers<sup>77</sup> recently have concluded that some attack by aryloxy radical does occur.

Rondestvedt<sup>21a</sup> has observed that the decomposition of N-nitrosoacetanilide in toluene produces a yield of about 0.04 mole per mole of bibenzyl if the temperature of the reaction mixture is allowed to rise to 60-80°. However, if the temperature is kept below 25°, no bibenzyl is found. Simamura<sup>78</sup> also reported no bibenzyl from the decomposition of the same compound in a mixture of toluene and benzene at 21°. However, it is not clear whether any attempt was made to find it in this case. Since phenylation still proceeds readily at the lower temperatures, it would appear that the activation energy for the nuclear substitution process is lower than that for the hydrogen abstraction from the methyl group.

Hydrogen abstraction from adduct by benzyl radical would produce biaryl and toluene. The reaction may occur to some extent, but there seems to be no positive evidence for it. Coupling of adduct with benzyl radical would produce

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<sup>77</sup>D. H. Hey, H. N. Moulden and G. H. Williams, J. Chem. Soc., 3769 (1960).

<sup>78</sup>O. Simamura and T. Inukai, Bull. Chem. Soc. Japan, 28, 444 (1955).



benzylidihydromethylbiphenyls. These products have not been observed, but no search for them has been made. Several isomers are possible, and the compounds are of higher molecular weight than simple biaryls. Consequently they are likely to be hard to separate and identify. We shall argue below that these probably are fairly important products, at least in reactions at low concentrations.

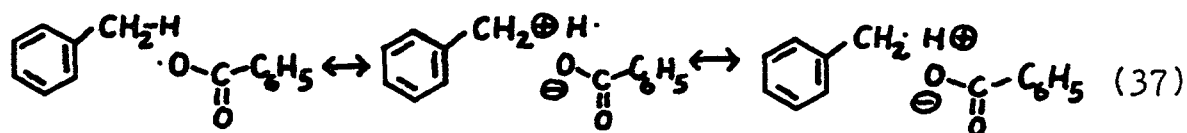
Coupling of benzyl with phenyl radical would produce diphenylmethane. This compound has been reported<sup>73</sup> to be among the products of the decomposition of benzoyl peroxide in toluene, but other workers<sup>21a,24</sup> have been unable to confirm this result. In the present research, gas chromatographs in several cases showed small bumps at the appropriate retention time for diphenylmethane, but no attempt was made to identify the compound. It appears that this product is a minor one if it occurs at all.

The product of coupling of benzyl with benzoyloxy radical would be benzyl benzoate. The same compound would be expected to result from induced decomposition of benzoyl peroxide by benzyl radicals. It has not been reported as a product of the reaction in toluene, but no search for it has been made. In reactions at high concentration, it may well be a significant product.

All investigations to date<sup>21a,24,25,73</sup> indicate that the major product of attack on the side chain of an alkyl-

benzene by radicals from an aroyl peroxide is the product of coupling of two benzylic radicals. The yields of bi-benzyl, 2,3-diphenylbutane, and bicumyl obtained by the decomposition of benzoyl peroxide in toluene, ethylbenzene, and cumene are shown in Table 9.

It is rather remarkable that the reactivity of benzoyloxy radicals in the hydrogen abstraction reaction should be so low. The availability of good polar resonance structures in the transition state would be expected to render this a very facile reaction:



It is conceivable that the predominance of phenyl over benzoyloxy radicals in attack on the side chain is due to rapid decarboxylation of benzoyloxy radicals, and that this process competes strongly with hydrogen abstraction by this radical. The formation in the reaction of considerable quantities of products containing intact benzoyloxy groups argues against this explanation. Otherwise it must be assumed that all such products result either from reactions that are extremely rapid, such as radical-radical reactions, or from processes which give the product without the intermediacy of free benzoyloxy radical.

Hey and co-workers<sup>25,79,80</sup> have stated, on grounds not apparent to the present writer, that attack on the side chain of an alkylbenzene should be favored by nucleophilic character of the attacking radical. Further, data has been quoted<sup>80</sup>, without experimental details, that tends to support this prediction. The extent of attack on the methyl group of toluene relative to phenylation of the nucleus was measured by determining the quantity of bibenzyl produced by the action of radicals, presumably from decomposition of aroyl peroxides, on the solvent. It seems to have been assumed that the aryl radical was solely responsible for the reaction. The quantities found are shown in Table 10. It also has been found that the decomposition of bis-p-nitrobenzoyl peroxide in ethylbenzene and in cumene results in no detectible quantity of the products of coupling of benzylic radicals.<sup>81</sup> However, bis-o-nitrobenzoyl peroxide "anomalously" gives a yield of 0.152 mole per mole bibenzyl (32.8% of the total binuclear hydrocarbon fraction).<sup>76</sup>

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<sup>79</sup>D. R. Augood and G. H. Williams, op. cit., p. 171.

<sup>80</sup>G. H. Williams, op. cit., p. 67.

<sup>81</sup>D. H. Hey, B. W. Pengilly and G. H. Williams, unpublished investigations cited in reference 77.

Table 10. Side-chain attack in the arylation of toluene

Radical <sup>a</sup>	Bibenzyl (%) <sup>b</sup>
p-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	0
p-ClC <sub>6</sub> H <sub>4</sub>	10
C <sub>6</sub> H <sub>5</sub>	13
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	42

<sup>a</sup>Source not stated.

<sup>b</sup>Apparently percent of total binuclear products (biaryl plus bibenzyl).

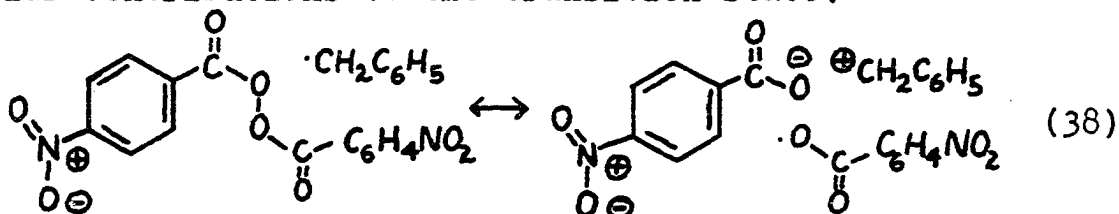
Recently the attack of tert-butoxy radical on a series of substituted toluenes at 110° has been studied by means of competitive experiments<sup>82</sup>. The relative reactivities of substrates, as measured by the yields of the substituted bibenzyls, were found to give a reasonable fit to a Hammett plot with a  $\rho$  value of -0.5. Thus, as would be expected on the basis of polar contributions to the transition state, the reaction is facilitated by substituents that stabilize cationic character in the benzyl moiety. Electrophilic character in the attacking radical then would be expected also to facilitate the reaction.

<sup>82</sup>K. M. Johnston and G. H. Williams, J. Chem. Soc., 1446 (1960).

Objections may be raised to the interpretation of the results shown in Table 10. First, the yield of bibenzyl very probably does not accurately represent the extent of attack on the methyl group of toluene. Coupling reactions of benzyl radical with two other types of radical seem likely to be important at least under some conditions. It is possible, for instance, that polar effects on the coupling of benzyl with aryloxy radical could result in changes in the extent of the competition of this process with the one that produces bibenzyl. Thus, a larger proportion of benzyl radicals well might disappear by reaction with p-nitrobenzoyloxy than with p-methylbenzoyloxy radicals.

Second, it is known that aryl peroxides having electron-withdrawing substituents are highly susceptible to induced decomposition. Swain, Stockmayer and Clarke<sup>32</sup> found that the induced decomposition of nitrobenzoyl peroxides could not be entirely suppressed even by means of a good scavenger such as 3,4-dichlorostyrene. The product data of Pausacker<sup>47</sup> is consistent with the importance of induced decomposition of these compounds. The finding of no benzylic coupling product in the decomposition of bis-p-nitrobenzoyl peroxide in toluene, ethylbenzene, or cumene is explained if benzylic radicals react entirely by attack on peroxide to induce decomposition. This conclusion predicts that benzyl p-nitrobenzoate should be a major product

of the decomposition of this peroxide in toluene. The induced decomposition reaction should be strongly aided by polar contributions to the transition state:



Such a conclusion is also consistent with the formation of substantial amounts of bibenzyl in the decomposition of bis-*o*-nitrobenzoyl peroxide in toluene. In this case, the steric effect of the two ortho substituent groups should interfere with attack on the O-O bond, permitting other reactions to compete.

In spite of all theorizing, however, we are left with the fact that the yields of benzoic acid produced in the decomposition of benzoyl peroxide at concentrations around 0.1 M in toluene, ethylbenzene, and cumene are much lower than those expected if attack of benzoyloxy radical on the side chain were a process of major importance. However, the yields of benzoic acid reported by Dannley<sup>73</sup> for the decomposition of benzoyl peroxide at concentrations of 0.45-0.53 M in alkylbenzenes are nearly twice those found by Hey *et al.* at the lower concentration (Table 9). They are also much higher than those obtained for the reaction in benzene in the same range of concentrations<sup>22,29</sup>. The procedures used by the two groups for separating the acid

were slightly different. The former extracted the acid with 10% sodium hydroxide, whereas the latter used 5% sodium bicarbonate. However, the quantities of benzoic acid bound as ester found by Hey et al. in ethylbenzene and in cumene<sup>25</sup> were too small to account for the differences between the yields of benzoic acid found by the two groups, while the results from runs in toluene were not consistent among themselves<sup>24</sup>. Consequently, the difference cannot be explained on the basis that the excess acid found by Dannley arose by hydrolysis of an unstable ester, but must be, at least in part, a real effect of the difference in concentration. A similar effect appears to occur in tert-butylbenzene. The yield of benzoic acid resulting from decomposition of benzoyl peroxide in this solvent at 0.220 M is 0.842 mole per mole<sup>83</sup>. By contrast, Hartman et al.<sup>28</sup> found a yield of 0.42 mole per mole at 0.024 M. It thus appears that the yield of benzoic acid resulting from the reaction in alkylbenzenes is strongly concentration-dependent, irrespective of whether there is or is not a benzylic hydrogen atom on the side chain.

The kinetic data of Nozaki and Bartlett<sup>27a</sup> for the decomposition of benzoyl peroxide in alkylbenzenes at 80° are

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<sup>83</sup>J. I. G. Cadogan, D. H. Hey and G. H. Williams, J. Chem. Soc., 3352 (1954).

of interest in this connection. Kinetic analysis on the basis of the equation mentioned above showed that the rate constants for both the unimolecular and the induced decompositions were exactly the same in toluene as in benzene. Kinetics in ethylbenzene and in cumene were not studied. However, measurement of the fraction of the benzoyl peroxide initially present that has decomposed after one and four hours in these solvents indicates that the rate constants must be nearly the same as in benzene and toluene. In tert-butylbenzene, kinetic analysis shows that the constant for the spontaneous decomposition is again the same as in benzene. The constant for induced decomposition, however, is nearly four times as large as that found in benzene and toluene.

It should be pointed out that the presence of oxygen in the reaction mixture is likely to affect the yields of the products of the decomposition in aromatic solvents, especially alkylbenzenes. Barnett and Vaughan have shown<sup>29</sup> that even in benzene the yield of acid is greater in the presence of oxygen than in its absence. Further, benzylic radicals are known to be oxygenated very readily<sup>84</sup>. Thus in alkylbenzenes the yields of benzylic coupling products would be expected to be diminished markedly by the presence of oxygen. This expectation is confirmed by the isolation

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<sup>84</sup> See, for example, C. Walling, op. cit., p. 421.



by Hey and co-workers<sup>25</sup> of significant quantities of acetophenone from the decomposition of benzoyl peroxide in ethylbenzene and in cumene. Consequently, it seems important that yields of products of arylation reactions should be determined in reaction mixtures from which air has been carefully excluded. Actually, in only two instances have data been reported concerning the yield of any product of the decomposition of benzoyl peroxide in an alkylbenzene with reasonably careful exclusion of air. These are the yields of acid in ethylbenzene and in cumene determined by Barnett and Vaughan<sup>29</sup>, and in tert-butylbenzene by Hartman et al.<sup>28</sup>. The supply of oxygen to the interior of a reaction mixture is likely to be slow. Consequently yields determined in runs from which air was not excluded are likely to give a fair semiquantitative measure of the amounts of many of the products formed. However, such data cannot be expected to be completely accurate.

That this is no idle worry is clear from the results of the present research. The decomposition of benzoyl peroxide in toluene at 80° was carried out at several concentrations in carefully degassed solutions. The product solutions, which were completely colorless in all cases, were concentrated and chromatographed on alumina to remove acids and esters. No effort was made to exclude air from the mixtures during work-up. The yields of bibenzyl and

o-methylbiphenyl, and the sum of the yields of m- and p-methylbiphenyl were determined by quantitative gas chromatography using naphthalene as an internal marker. Table 11 contains the averaged results, in moles of product per mole of peroxide decomposed. The yield of bibenzyl at 0.1 M is much higher than that reported by Hey et al.<sup>25</sup> (Table 9). The precision of the gas chromatographic results is not high, but the scatter is far too small to account for the difference noted, particularly in view of the fact that runs at other concentrations give similar values. Furthermore, there seems to be no reason to expect systematic errors of a magnitude even remotely approaching that of the difference observed; it would be necessary to assume the existence of another major product with the same retention time as bibenzyl. A part of the difference doubtless is due to the fact that the value reported by Hey et al. was determined by actual isolation; bibenzyl was precipitated from ligroin at  $-80^{\circ}$ . However, it seems probable that the major cause of the lower yield found in the earlier work is the loss of benzyl radicals by oxygenation.

The results in Table 11 also show that there is a steady and marked increase in the yield of bibenzyl as the initial concentration of peroxide is reduced. The precision of the determinations is poor, but the qualitative conclusion can hardly be doubted. The situation is less

Table 11. Average yields of products determined by gas chromatography<sup>a,b</sup>

Concentration, M	0.310	0.0972	0.0312	0.00929	0.00308	0.00102
o-Methylbiphenyl	0.272	0.306	0.280	0.308	0.332	0.332
m- and p-Methylbiphenyls	.212	.228	.228	.228	.280	.282
Bibenzyl	.242	.256	.328	.350	.380	.464
Total Methylbiphenyls	.484	.534	.508	.536	.612	.614
Methylbiphenyls plus Bibenzyl	.726	.790	.836	.886	.992	1.078

<sup>a</sup>Derived from the data of Table 3.

<sup>b</sup>Moles per mole of peroxide.

clear-cut for the yields of the methylbiphenyls, but it appears that the yields of these products also drift upward as the concentration of peroxide is decreased. It is of interest that the total yields of methylbiphenyls at approximately 0.3 and 0.1 M are only slightly larger than those found by Hey et al.<sup>24</sup> and by Dannley<sup>73</sup> at similar concentrations (Table 9). This probably signifies that the yields of biaryls are much less affected by the presence of oxygen than are the yields of bibenzyl, which is not unreasonable. The yield of bibenzyl appears to increase more rapidly than does the yield of biaryls.

The ratio of the yield of o-methylbiphenyl to that of m- and p- isomers may be calculated from the data of Table 11. The values at different concentrations fluctuate irregularly from 1.18 to 1.35. By contrast, Hey and co-workers<sup>25</sup> report an isomer distribution o:m:p = 66.5:19.2:14.3, which yields a ratio of 1.98. The higher value obtained by Hey et al. may be due to unremoved bibenzyl interfering with the accuracy of the spectrophotometric determination of the isomer ratios. It is clear that the large yields of bibenzyl found in the present work are not due to incorrect identification of peaks in the gas chromatographic traces, and resulting inclusion of one of the methylbiphenyls with the bibenzyl peak. Such an error would make the ratio o:m+p appear larger than the true

value; correction for such an error would increase the discrepancy between our results and those of Hey et al.

The yield of o-methylbiphenyl formed in this reaction was determined as a function of concentration by isotope dilution analysis, using benzoyl peroxide labelled on the ring with carbon-14. This technique has the advantage of not requiring quantitative isolation of the product. Reaction mixtures again were carefully degassed, and remained completely colorless in all but one case. In these runs, the crude product mixture, after concentration in the absence of air, was treated with trifluoroperacetic acid to destroy all olefinic compounds. Thus, the yields measured correspond to the quantities of o-methylbiphenyl that are formed directly in the reaction, and do not include the quantity that normally results from air oxidation of dihydro-o-methylbiphenyls during work-up. The results considered most likely to be accurate, selected from those reported in the Experimental section, are shown in Table 12. One run was made (Run 26) omitting the treatment with peracid, and working up the product in the usual way in the presence of air. The yield of o-methylbiphenyl measured in this run was nearly double the yield found in a run at the same concentration that was carried through the peracid procedure. Thus it is fairly certain that dihydromethylbiphenyls are produced in the decomposition of benzoyl

peroxide in toluene, and that the peracid treatment destroys these products without converting them to methylbiphenyls. The yield measured in Run 26 is known to be slightly low, since an explosion occurred during combustion of the product, with resulting loss of some carbon. In view of this circumstance, the agreement between this value and that determined by gas chromatography in a run at the same concentration is tolerable, and provides semi-quantitative confirmation of the validity of the results obtained by gas chromatography.

Table 12. Yields of initially formed o-methylbiphenyl by isotope dilution analysis<sup>a</sup>

Run	Concentration of peroxide, m./l.	Yield, moles/mole
14	0.100	0.151
10	.0314	.112
17	.0312	.146
22	.0302	.145
16	.0102	.112
21	.00302	.104
27	.00101	.095

<sup>a</sup>Selected runs from Table 5.

The results of the decomposition of benzoyl peroxide in toluene may be discussed in terms of the set of reactions presented above (17-28, 30-36). The scheme is far too complicated to permit a complete and quantitative kinetic analysis. However, qualitative kinetic arguments may be used to predict the nature of the expected variation in yields of biaryls and bibenzyl with concentration.

We will consider first a reduced scheme in which no attack of phenyl radical on the solvent and no induced decomposition of peroxide occurs. The reactions included are decarboxylation of benzoyloxy radical, hydrogen abstraction from the methyl group by benzoyloxy radical, coupling of phenyl and benzyl radicals with themselves and with each other, and back-coupling of these with benzoyloxy radical (reactions 2, 31, 19, 33, 35, 20 and 34). The decarboxylation of benzoyloxy radical and its attack on toluene are both first order in radicals; hence the competition between these processes should be independent of concentration. It is expected from kinetic considerations that a decrease in the concentration of benzoyloxy radical also results in a decrease in the concentration of phenyl and benzyl radicals. Since the coupling reactions are second order in radicals, the result of reducing the concentration of peroxide will be to favor the processes converting benzoyloxy to phenyl and benzyl radicals relative to those destroying benzoyloxy

radical by coupling with its descendants. The consequence should be an increased "yield" of phenyl and benzyl radicals, and an increase in the yields of biphenyl, diphenylmethane, and bibenzyl. As the importance of back-coupling of phenyl and benzyl radicals with benzoyloxy radical becomes vanishingly small, the relative yields of these three products would be expected to become concentration-independent.

The perturbation to this scheme arises from rapid reactions of phenyl radical with solvent by addition to the nucleus to give adduct radical (reaction 24), and by abstraction of hydrogen from the methyl group to give benzyl radical (reaction 30). Since these two reactions are first order in radicals, they should compete better with the coupling reactions of phenyl radical with phenyl and with benzyl radicals as the concentration of radicals is diminished. The competition of these first order reactions with the coupling reactions of phenyl radical presumably accounts for the small yields of biphenyl and diphenylmethane.

A situation similar to that discussed for benzoyloxy radical is encountered in the reactions of phenyl radical with solvent and with benzyl and adduct radicals. The radical-radical reactions at this level are the coupling of benzyl radicals, coupling and disproportionation of adduct radicals, reaction of benzyl with adduct radical to couple or abstract hydrogen, coupling of phenyl and benzyl radicals,



and reaction of phenyl with adduct radical to couple or abstract hydrogen (reactions 35, 28, 32, 33 and 26). A decrease in the concentration of radicals again will favor the reactions of phenyl radical with solvent and decrease the importance of the reactions of phenyl radical with its descendants, benzyl and adduct radicals. Consequently the yields of products of reaction of benzyl and adduct radicals with themselves and with each other will increase relative to the products of reaction of these radicals with phenyl radical. As these latter reactions become of small importance, the distribution of products from the remaining reactions should become nearly independent of concentration.

Two complications must be considered. First, benzyl radical results from abstraction of hydrogen from toluene not only by phenyl radical, but probably also to some extent by benzoyloxy radical. This circumstance, while it would complicate a quantitative kinetic expression, should not affect the qualitative conclusions. The existence of a separate source of benzyl radical should not alter the direction in which the yield of any product changes with decreasing concentration. A second complication is the reactions of adduct radical by coupling with or loss of hydrogen to benzoyloxy radical (reaction 27). This well may be a process of some importance at high concentration. The importance of this reaction too must decrease with di-

minishing concentration, due to the more favorable competition by processes first order in benzoyloxy radical, and the increased yield of other radicals with which the adduct may react.

We now may make a fairly detailed accounting of the expected effects on the yield of bibenzyl of lowering the concentration of the radical source. Bibenzyl arises entirely from coupling of two benzyl radicals. This radical is produced by two reactions, the abstraction of a hydrogen atom from the methyl group by benzoyloxy and by phenyl radicals. As the concentration of benzoyloxy radical is decreased, the proportion of this radical that attacks toluene is increased at the expense of the coupling reactions of benzoyloxy radical. The proportion that decarboxylates also increases, by exactly the same factor. Thus while the concentration of phenyl radical decreases, the proportion of the original benzoyloxy radical which is converted to phenyl radicals increases. Since the attack of phenyl radical on solvent to produce benzyl radical is first order in the radical, decreasing concentration should favor this process relative to any coupling reaction of phenyl radical. Thus all effects of lowering the concentration of radicals result in an increase in the yield of benzyl radical.

The reactions that destroy benzyl radical, leaving induced decomposition out of account, are reactions with

benzoyloxy, phenyl, adduct, and benzyl radicals (reactions 34, 33, 32 and 35). The first two of these reactions are less favored relative to reactions first order in benzoyloxy and phenyl radicals at lower concentrations. The relative proportions of the other two reactions probably will not change greatly with concentration; depending on the magnitudes of the relevant rate constants, either could be slightly favored by a decrease in concentration. However, the overall effect of diminishing concentration of radical source should be a definite increase in the proportion of radicals that lead ultimately to bibenzyl.

The reactions of adduct with benzyl radical also should be favored by a decrease in concentration. Consequently, benzylmethyldihydrobiphenyls should constitute a significant part of the product of the reaction, especially at low concentrations. The alternative is to assume that benzyl radical reacts with adduct radical only by hydrogen abstraction, which seems unlikely.

Methylbiphenyls are expected to be derived entirely from adduct radicals. If induced decomposition is not considered, the reactions that may be involved are abstraction of hydrogen by any of the four types of radical present in the solution (reactions 26, 27, 28 and 32). Thus two factors may change the yield of methylbiphenyls as the initial concentration of peroxide is changed. First, the fraction

of the initially formed benzoyloxy radicals that are converted to phenyl and ultimately to adduct radicals may change. Second, changes in the relative extent to which adduct radical undergoes coupling and hydrogen transfer reactions will affect the yield. For the reaction of adduct with any given radical, the competition between coupling and hydrogen transfer is independent of concentration. However, the competition between the two types of process well may be different for reaction with different radicals. Consequently, the second effect can occur only as a result of the influence of concentration on the nature of the radical with which the adduct reacts predominantly.

We already have concluded that the yield of phenyl radical should increase with decreasing concentration of radicals. The reaction of phenyl radical with toluene to give adduct radical also should be favored relative to competing radical-radical reactions by lowering the concentration of radicals. Consequently the total yield of products derived from adduct radical should increase when the concentration of peroxide is reduced. As concentration is decreased, benzyl and adduct radicals should become the predominant radical species to an increasing extent, at the expense of phenyl and benzoyloxy radicals. The extent to which the increased yield of adduct radical is reflected by an augmented yield of methylbiphenyls will depend on the

comparison of the competition between coupling and hydrogen transfer in the reactions of adduct radical with benzyl and with adduct radical, on the one hand, with that in the reaction with phenyl and with benzoyloxy, on the other. In the extreme case, if the reactions of adduct radical both with benzyl and with adduct radical proceeded entirely by coupling, it would be possible for the yield of methylbiphenyl to tend to zero despite the increased proportion of radicals that are converted to adduct.

The effect of including induced decomposition of peroxide in the theoretical discussion is difficult to assess accurately. Fortunately, there is ample experimental evidence<sup>27a,29,30a</sup> that the importance of the reaction or reactions involved decreases as the concentration of peroxide is reduced. Consequently, the occurrence of induced decomposition does nothing to invalidate the conclusions already reached regarding the increase in yield of adduct and of benzyl radicals at low concentration. If biaryl is produced in an induced decomposition reaction, the diminution of the contribution to the yield of biaryl from this source at low concentration must be taken into account.

The yields of products determined in the present research are accommodated by the scheme considered here. The yield of bibenzyl (Table 11) determined by gas chromatography is seen to increase markedly as the initial concen-

tration of benzoyl peroxide is reduced. This behavior is fully in accord with the prediction made on kinetic grounds. It is interesting and somewhat surprising that the yield appears still to be increasing at the lowest concentration studied. Thus even at this low concentration a significant fraction of the phenyl radicals formed still must be undergoing radical-radical reactions. In view of the low yield of diphenylmethane and (apparently, although the matter has not been carefully investigated) of biphenyl and phenyl benzoate, these must be reactions with adduct radical.

The yields of o-methylbiphenyl and the sums of the yields of the m- and p- isomers also were determined by gas chromatography. The reaction mixtures were worked up in the presence of air, so the yield obtained for a given isomer is the sum of the yield of the methylbiphenyl initially formed and those of the dihydromethylbiphenyls corresponding to it. The yields of methylbiphenyls determined in this way appear also to increase slightly over the 300-fold concentration range, although the effect is obscured by the scatter in the experimental data. As the concentration is decreased, an increase in the total yield of adduct radicals, parallel to the increase in the yield of benzyl radical, must occur. However, decreasing concentration will tend to shift the fate of adduct radical from

reaction with phenyl and benzoyloxy radicals to reaction with benzyl and with other adduct radicals. Therefore, the sum of biaryl plus dihydrobiaryl will increase if at least as great a proportion of hydrogen transfer occurs in the reactions with benzyl and with adduct radicals as in those with phenyl and with benzoyloxy radicals. Alternatively, the increase in yield could result from an increase in the fraction of adduct radicals converted to dihydrobiaryl and biaryl in radical-radical reactions, partially balanced by a decrease in biaryl formed in induced decomposition of benzoyl peroxide.

The yields of o-methylbiphenyl determined, by isotope dilution analysis, in runs worked up by treatment with peracid are much lower than those determined by gas chromatography. The difference is believed to be due to the destruction of dihydromethylbiphenyls by the peracid treatment. That it is not due to a major error in one of the analytical techniques is established by the finding that isotope dilution analysis of a run worked up in the presence of air, without the treatment with peracid, leads to a yield value in approximate agreement with the gas chromatographic result at the same concentration. Comparison of the two sets of results shows that the yield of o-methylbiphenyl including the portion derived from oxidation of the o-methyldihydrobiphenyls is virtually double the yield found

when dihydro compounds are first removed. This seems to indicate that even at high concentration biaryls are formed entirely by disproportionation of adduct radicals. Such a conclusion is contrary to the conclusion reached above that some reaction of phenyl with adduct radical must occur even at low concentration. Furthermore, the yields of o-methylbiphenyl determined by the two procedures diverge; at very low concentration the yield of o- isomer including that derived from dihydro compounds is approximately three times that for initially formed o-methylbiphenyl. Clearly it is nonsense for the total yield of dihydrobiaryl to exceed that of initially produced biaryl, since the only reaction that can make dihydrobiaryl also makes an equivalent quantity of biaryl.

Fortunately, the conclusion that all types of adduct radical lose hydrogen entirely by disproportionation even at high concentration is not required by the data. Such a conclusion depends on the assumption that all three isomeric adduct radicals behave similarly, all having the same aptitude for loss (or gain) of hydrogen. This need not be true; one isomer well might be better adapted than the others to serve as a hydrogen acceptor, with the result that the yield of the corresponding dihydrobiaryls would not truly represent the extent of disproportionation of that adduct radical, or the amount of it formed. The ortho adduct radical could



quite plausibly exhibit an increased preference, relative to other isomers, for reaction by gain rather than loss of hydrogen for steric reasons. In such a case a substantial part of the total hydrogen abstraction occurring could be due to radicals other than adducts, but for the yield of o-methyldihydrobiphenyls to be equal to, or even greater than, that of initially formed o-methylbiphenyl. The ratio of dihydrobiaryls to initially formed biaryl then would be much lower for the other isomers, and considerably less than unity.

Some workers<sup>21b,26,56,51</sup> have considered the possibility that the addition of radicals to the nucleus in phenylation and similar reactions is reversible. If the reverse reaction were rapid, so that the addition was essentially an equilibrium process, the overall substitution would be effectively second order in radicals. Hey *et al.*<sup>25</sup> found that in the decomposition of benzoyl peroxide in cumene the relative extents of nuclear and side-chain attack were the same within experimental error at 0.109 M as at 0.275 M. These results indicate that the two processes are of the same kinetic order, presumably unity, and would argue against reversibility of the addition step. However, the range of concentrations involved is small.

Recently, Eliel and co-workers<sup>26</sup> have carried out the decomposition of bis-p-chlorobenzoyl peroxide in a mixture

of benzene and benzene- $d_6$ . Three portions of peroxide, each time at a concentration in the vicinity of 0.2 M, were decomposed in the same portion of solvent, which was re-isolated and purified after each reaction. The solvent recovered after this sequence was analysed by mass spectrometry. Its composition was found to be unchanged; no isotopic fractionation had occurred during the reaction. However, an isotope effect on the deuterium content of the biphenyl resulting from decomposition of the same peroxide in benzene- $d_6$  is found<sup>26</sup>. The conclusion that the addition step is effectively irreversible seems to be justified, although the extent of isotopic fractionation expected in the first experiment if the addition step were reversible is not far outside the experimental error of the analytical technique.

Hammond<sup>85</sup> has pointed out that these experiments do not rule out the possibility of slow reversal of the addition step. The processes converting adduct radical to product are second order in radicals, while the reversal of addition is a unimolecular decomposition of the adduct. It is possible that at the concentrations at which the reaction in benzene-benzene- $d_6$  was studied radicals are

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<sup>85</sup>G. S. Hammond, Pasadena, California, substitution of aromatic nuclei by free radicals, private communication, 1960.

sufficiently plentiful so that essentially all adduct radicals formed undergo some variety of radical-radical reaction, but that at lower concentrations the unimolecular decomposition of adduct competes significantly. Then at high concentrations the substitution reaction would be effectively first order in radicals, but second order at low concentrations.

Such a scheme can also be made to accommodate the results of the present research. The continuing increase in the yield of bibenzyl even at the lowest concentration studied would be very satisfactorily explained in this manner. However, if the addition step were reversible, the yields of the biaryls would be expected to decrease at very high dilution, which is contrary to the observed results. It would be necessary to assume that the expected tendency of the biaryl yield to decrease is offset with increasing availability of phenyl radicals due to decreasing importance of other reactions at low concentration. Thus basically this scheme encounters the same difficulty as did the scheme previously discussed: the extent to which side reactions involving radicals other than benzyl and adduct must occur even at very low concentration is unexpectedly high. Although the explanation of the results via reversibility of the addition step cannot be rigorously ruled out, the scheme originally given is favored by the present writer.

Whichever of these schemes is correct, the disparity and divergence between the yields of o-methylbiphenyl worked up with and without the peracid treatment apparently must be explained on the basis of selectivity among the isomers of the adduct radical in the disproportionation step, as discussed earlier.

Finally, the conclusions reached in this discussion are subject to one important reservation. Arguments that have been presented show that almost certainly the scheme considered is incomplete. Apparently, at least in benzene and probably in toluene also, an unidentified induced decomposition reaction must occur, and perhaps also another reaction producing benzoic acid. Furthermore, we have not explicitly considered reactions of benzoyloxy radical with the solvent. Such reactions must certainly occur, at least to a limited extent. Also, we have entirely neglected the possibility that some products, attributed to reactions of phenyl radical, are actually formed from benzoyloxy radical by complex processes involving simultaneous substitution and decarboxylation. The possible effects of these processes on the conclusions reached here cannot be estimated at present.

## SUMMARY

The decomposition of benzoyl peroxide in toluene has been studied. The yields of some of the products have been determined as a function of the initial concentration of the peroxide over a three hundred-fold range. The yields of bibenzyl and o-methylbiphenyl, and the sum of the yields of m- and p-methylbiphenyls, have been determined by quantitative gas chromatographic analysis. Reaction mixtures were worked up in the presence of air, which oxidizes dihydrobiaryls to biaryls. The yields of bibenzyl observed are considerably higher than those reported in the literature, and increase markedly as the concentration of benzoyl peroxide is reduced. The yields of the methylbiphenyls also appear to increase slightly as the concentration of peroxide is decreased.

The variation in the yield of o-methylbiphenyl initially formed in the reaction was determined as a function of the concentration of benzoyl peroxide by isotope dilution analysis. The product mixtures were treated with trifluoroacetic acid to destroy the corresponding dihydromethylbiphenyls. The yields were found to be much lower than those determined in runs worked up in the presence of air, and to decrease as the initial concentration of benzoyl peroxide is diminished.

A reaction scheme is considered which involves competing irreversible attack of radicals on the nucleus and on the methyl group of toluene. The variations in yields are ascribed to changes in the nature of the predominant radical species at different concentrations. The scheme is shown to account for the observed yield data. An alternative scheme, in which slow reversal of the addition to the nucleus occurs, cannot be ruled out.

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