

1957

# Mechanism of aromatic substitution by phenyl radicals

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MECHANISM OF AROMATIC SUBSTITUTION BY PHENYL RADICALS

by

John Fredric Garst

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
The Requirements for the Degree of  
DOCTOR OF PHILOSOPHY

Major Subject: Physical-Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

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Dean of Graduate College

Iowa State College

1957

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## INTRODUCTION

In the past ten years there has been a revival of interest in the reactions leading to the replacement of aromatic hydrogen by phenyl or substituted phenyl groups. The earlier studies in the field, those of the period 1920-1935, were mainly concerned with the qualitative nature of the products, the applicability of the reactions as synthetic tools, and the mechanisms of the reactions insofar as could be determined using the relatively crude techniques then at hand. It was recognized late in that period that the attacking entities were probable free phenyl radicals.

Since the advent of quantitative infrared spectroscopy and improved methods and equipment for ultraviolet spectroscopy, interest has turned to detailed quantitative product analyses. From these studies have come much data on the relative reactivities of various substituted benzenes and on the orientations of phenyl groups entering the rings of substituted benzenes. In addition, quantum mechanical calculations based on hypothetical models for transition states, or on ground state characteristics which might affect the course of the reaction, have been made.

In spite of this, little has been done giving direct experimental evidence for the mechanism of the substitution reaction itself. This work is an attempt to obtain such evidence. The work has taken two courses: (1) a study

designed to provide kinetic evidence pertaining to the molecularity of the substitution with respect to radicals, and (2) a study providing evidence pertaining to the state of benzoyloxy radicals in solution.

## HISTORICAL

Since several reviews of free radical aromatic substitution have been published in the past year, no attempt will be made here to give a complete review of the field. The review of Augood and Williams<sup>1</sup> is by far the most complete. These authors are former co-workers of D. H. Hey, and the view that they present is largely that which Hey has expressed in his various papers. Dermer and Edmison's review<sup>2</sup> is a summary of the more practical aspects of aromatic substitution by radicals of all types, in contrast to that of Augood and Williams, who discuss arylation almost exclusively. Rondestvedt and Blanchard's article<sup>3</sup> is one of a series of research papers on the subject, but they have briefly reviewed the field and proposed their own mechanism in the same paper. Nelson's review<sup>4</sup> is less complete than that of Augood and Williams and offers essentially the same material.

The article of Augood and Williams<sup>1</sup> contains an extended compilation of the results of most of the more important papers which have been published on the subject. These

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<sup>1</sup>D. R. Augood and G. H. Williams, Chem. Rev., 57, 123 (1957).

<sup>2</sup>O. C. Dermer and M. T. Edmison, ibid., 57, 77 (1957).

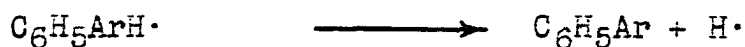
<sup>3</sup>C. S. Rondestvedt, Jr. and H. S. Blanchard, J. Org. Chem., 21, 229 (1956).

<sup>4</sup>F. F. Nelson, J. Chem. Ed., 32, 606 (1955).

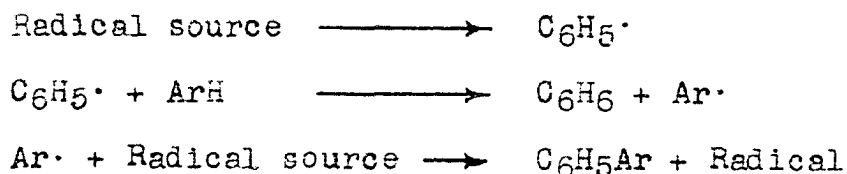
authors discuss in detail the background material which forms the basis of common knowledge in the field. Furthermore, the bibliography presented there is far more complete than one which might have been given here. Since this is true, no attempt at giving comprehensive references will be made here, but the reader is referred to this article for references and summary discussion of background material presented here without annotation. Where tables of data are presented, their source will be indicated, though this may also be the article of Augood and Williams.

The author will defer his discussion of the nature of the reaction to the Discussion section of this dissertation. However, the more important mechanisms which have been proposed for the free radical phenylation of aromatic compounds are presented here:

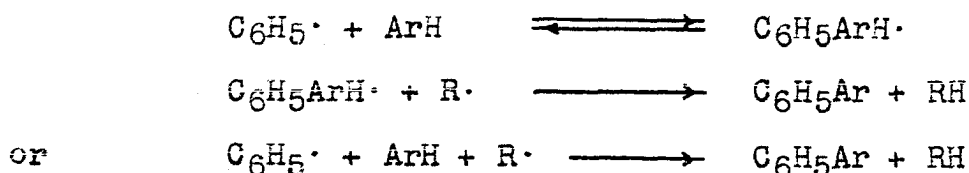
I. The mechanism of Augood and Williams:<sup>1</sup>



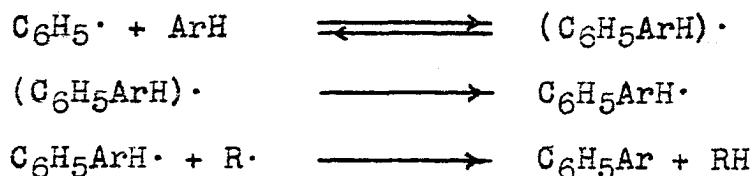
These workers visualize the reaction as a direct displacement of a hydrogen atom, probably through an intermediate quinonoid adduct, though there is no strong evidence on this point. As previously mentioned, their views are generally those of D. H. Hey.

II. The mechanism of DeTar and Sagmanli:<sup>5</sup>

In this mechanism the biaryl is formed in an induced decomposition step.

III. The mechanism of Hammond, Rudesill, and Modic:<sup>6</sup>

This mechanism has been proposed in the literature only for the tritylation of benzene in the presence of benzoyl peroxide. Allusions to it have appeared elsewhere,<sup>7</sup> though.

IV. The mechanism of Rondestvedt and Blanchard:<sup>3</sup>

These authors have patterned the mechanism after a general mechanism for electrophilic aromatic substitution. ( $\text{C}_6\text{H}_5\text{ArH}$ ).

<sup>5</sup>D. F. DeTar and S. V. Sagmanli, J. Am. Chem. Soc., 72, 965 (1950).

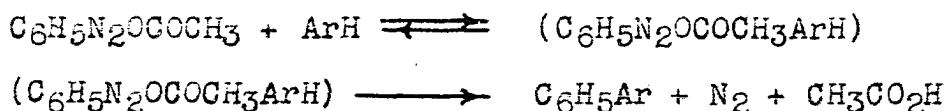
<sup>6</sup>G. S. Hammond, J. T. Rudesill, and F. J. Modic, ibid., 73, 3929 (1951).

<sup>7</sup>G. S. Hammond, in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1956, p. 200.



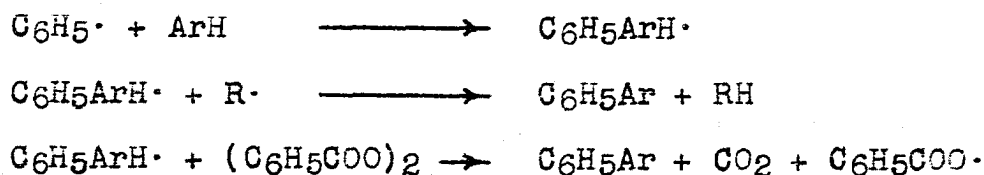
represents a "preliminary complex," perhaps a "pi complex."  $C_6H_5ArH\cdot$  is a "sigma complex." Röndestvedt and Blanchard feel that formation of the sigma complex is usually the rate determining step.

V. The mechanism of Huisgen and Horeld:<sup>8</sup>



This is a concerted mechanism which was presented for phenylations by N-nitrosoacetanilide.

VI. The mechanism of Lynch and Pausacker:<sup>9,10</sup>



These workers propose a mechanism in which biaryl is generated in two ways. One is essentially the mechanism of Augood and Williams. The other is an induced decomposition reaction of benzoyl peroxide.

Other mechanisms could be written which involve hydrogen abstraction from solvent as a first step, followed by coupling with phenyl radicals. Such mechanisms are not seriously being considered at the present time, principally because the

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<sup>8</sup>R. Huisgen and G. Horeld, Ann., 562, 137 (1949).

<sup>9</sup>B. M. Lynch and K. H. Pausacker, Australian J. Chem., 10, 49 (1957).

<sup>10</sup>K. H. Pausacker, ibid., 10, 49 (1957).

resultant solvent derived radicals must be very similar to the phenyl radicals from the radical source, yet biaryl derived entirely from solvent, i.e., dimethylbiphenyl from solvent toluene, is never found and biaryl derived entirely from the radical source, i.e., biphenyl from benzoyl peroxide, is found only in very small quantities in aromatic solvents, about 1%.

## EXPERIMENTAL

## The Reaction of Benzoyl Peroxide with Toluene

Preparation of p-methylbiphenyl

p-Methylbiphenyl was prepared by the method of Gomberg and Pernert.<sup>11</sup> Seven moles of p-toluidine were diazotized and the resulting solution added, with cooling by addition of ice and stirring, to a mixture of a potassium hydroxide solution and benzene. The diazotization was carried out in a 4 liter beaker, and the addition to the basic benzene mixture was done in a battery jar (capacity approximately 12 liters). The temperature was maintained at 5°C during the addition and for 1 hour afterward. The temperature was then allowed to rise to room temperature and stirring continued for 4 more hours. The organic layer was separated by siphoning, dried over calcium chloride, and distilled. When the solvent was practically removed, the remaining portion was distilled at 20 mm pressure. A fraction boiling at 148-153°C was collected as product. This was recrystallized several times from methanol (decolorizing charcoal was used in the first recrystallization). Accidental overheating of the material on a hot plate resulted in the loss of a considerable quan-

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<sup>11</sup>M. Gomberg and J. C. Pernert, J. Am. Chem. Soc., 48, 1372 (1926).

tity. Approximately 35 g of the purified material (0.2 mole) were obtained. The melting point was determined using a Hershberg apparatus and a thermometer calibrated in tenths of a degree. The corrected melting point of this material was 47.3-47.9°C (lit.,<sup>11</sup> 47.7°C). This material was used as the carrier in runs 2-4 and 14. A portion of the p-methylbiphenyl was again recrystallized from methanol and dried. The melting point, taken as before, was 47.3-47.9°C (corrected), identical with the previous one. This material was used as carrier in the other runs.

#### Purification of toluene

Toluene was purified by the method of Fieser.<sup>12</sup> Reagent grade commercial toluene was washed with successive portions of sulfuric acid at cool room temperature (water bath) until the sulfuric acid layer showed no coloration in 5 minutes of contact with the toluene. It was then washed with sodium hydroxide solution, distilled water, and dried over sodium sulfate. The toluene was then distilled through a 1 in. diameter, 30 plate Oldershaw column, a constant boiling middle fraction (109°C uncorrected) being taken for use in these experiments. The distilled toluene was further dried by storing in contact with sodium ribbons until use.

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<sup>12</sup>L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Company, Boston, Mass., 1955, p. 292.

Preparation of benzoyl peroxide 1-C<sup>14</sup>

Benzoic acid 1-C<sup>14</sup> was received from Tracerlab<sup>13</sup> in small vials containing 0.5, 0.2, 0.2, and 0.1 millicuries each. One of the vials containing 0.2 millicuries was opened and the contents dissolved in a small beaker of hot water. This was poured into a 1 liter Erlenmeyer flask, along with several further rinsings of the beaker with more hot water. Twenty g of inactive benzoic acid was added to this flask. The flask was heated and water added until all the benzoic acid was dissolved. This required about 600 ml of water. The flask was wrapped with a towel and set aside to cool. Six hours later crystals had formed. The flask was then refrigerated overnight. The crystals were filtered by suction and placed in a desiccator containing calcium chloride. After drying, a small amount was set aside for radio-assay. The specific activity of the material was found to be 1820 c/min/ $\mu$  mole (counts/minute/micromole) using the apparatus and counting procedure described later.

Benzoyl chloride 1-C<sup>14</sup> was prepared from the benzoic acid 1-C<sup>14</sup> using the procedure described by Vogel.<sup>14</sup> The benzoic acid 1-C<sup>14</sup> diluted as in the above paragraph was

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<sup>13</sup>Tracerlab, Inc., 130 High Street, Boston 10, Massachusetts.

<sup>14</sup>A. I. Vogel, "Practical Organic Chemistry," 2nd ed., Longmans, Green and Company, New York, N. Y., 1951, p. 751.

placed in a 100 ml round bottomed flask containing boiling stones and 15 ml of freshly distilled thionyl chloride, and fitted with a reflux condenser with a calcium chloride drying tube at the top. This mixture was refluxed for 1 hour. The condenser was then replaced by a small Claisen distilling head and condenser, and all material which would distill below 30°C at 15 mm pressure (aspirator) was stripped. This was done in a well operating hood in order to avoid breathing of benzoyl chloride  $1-C^{14}$ .

Benzoyl peroxide  $1-C^{14}$  was prepared from the benzoyl chloride  $1-C^{14}$  by the method of Gambarjan,<sup>15</sup> as quoted by Tobolsky and Mesrobian.<sup>16</sup> Forty ml of acetone were added to the flask containing the benzoyl chloride  $1-C^{14}$  prepared as above. This mixture was slowly added to a stirred solution of 8 g of sodium peroxide in 80 ml of ice water, with occasional further addition of ice. Benzoyl peroxide  $1-C^{14}$  separated. This was filtered the next day and recrystallized from chloroform and Skelly B (petroleum ether, boiling point 60-70°C) by dissolving it in minimum amount of chloroform and pouring this solution into three or four times its volume of Skelly B, with stirring. The yield of benzoyl peroxide  $1-C^{14}$  was 4 g. Titration with sodium thiosulfate by the method of

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<sup>15</sup>S. Gambarjan, Ber., 42, 4004 (1909).

<sup>16</sup>A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 38.

Kokatnur and Jelling,<sup>17</sup> which involves the use of isopropyl alcohol for a solvent, indicated 93% purity. The material was recrystallized from chloroform and Skelly B once more. Titration indicated that the peroxide content of this sample was 98.3%, and the material was used directly in the reactions with toluene. The ultimate yield of benzoyl peroxide  $1-C^{14}$  was 3 g. Acidification of the aqueous solution from the preparation precipitated benzoic acid. Evaporation of the mother liquor from the recrystallization of the peroxide led to a residue, probably containing more peroxide. The benzoic acid and the residue were reserved. The activity of the benzoyl peroxide  $1-C^{14}$  was found to be within 2% of twice that observed for the benzoic acid  $1-C^{14}$ .

The reaction of benzoyl peroxide  $1-C^{14}$  with toluene

The following is a description of the general technique used in each run. Benzoyl peroxide  $1-C^{14}$  was weighed into a reaction vessel with a constricted neck and a small, sealed side arm. The amount of peroxide used in all runs was approximately 150 mg. Toluene was added through the constricted neck from pipettes. As it was added, the stream was directed in such a fashion that all of the inner surface of the neck was washed down thoroughly. The amount of

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<sup>17</sup>V. R. Kokatnur and M. Jelling, J. Am. Chem. Soc., **63**, 1432 (1941).

toluene used was such as to result in a solution of approximately  $10^{-1}M$ ,  $10^{-2}M$ ,  $3 \times 10^{-3}M$ , or  $10^{-3}M$ . The flask was then attached to a vacuum system by means of a rubber stopper and cooled in a dry ice-trichloroethylene bath for at least 15 minutes before evacuation was begun. It was then evacuated to at least 0.5 mm and flushed with nitrogen. "Prepurified" nitrogen (Matheson<sup>18</sup>) was further purified by passing it through a series of gas wash bottles containing Fieser's solution,<sup>19</sup> concentrated sulfuric acid, and lead acetate, and through a drying tower containing sodium hydroxide and calcium chloride. The evacuation and flushing procedure was repeated twice and the reaction vessel was sealed off under reduced pressure. After the vessel and its contents had warmed to room temperature, it was placed in an oil bath maintained at  $80^{\circ}$ . The reaction was allowed to proceed at this temperature for 3 days. The half life of benzoyl peroxide in toluene at this temperature (based on the unimolecular rate constant of Nozaki and Bartlett<sup>20</sup>) is about 6 hours. Three days represents, then, at least 12 half lives, indicating that not more than 0.02% of the original peroxide remained. The actual amount remaining after 3 days is less

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<sup>18</sup>The Matheson Company, Inc., Joliet, Ill.

<sup>19</sup>L. F. Fieser, op. cit., p. 299.

<sup>20</sup>K. Nozaki and P. D. Bartlett, J. Am. Chem. Soc., **68**, 1686 (1946).



than 0.02% because some of the peroxide decomposes in radical induced reactions.<sup>20</sup> The reaction vessel was then allowed to cool to room temperature. The small side arm was broken to release the pressure of carbon dioxide which built up during the reaction, and the top of the flask was cut off by scratching the neck with a file and touching a hot glass rod to the scratch. The contents of the vessel were poured into a clean volumetric flask (1000 ml if the run was  $10^{-3}M$ , 250 ml if  $3 \times 10^{-3}M$ , 100 ml if  $10^{-2}M$ , or 25 ml if  $10^{-1}M$ ) through a funnel. The funnel was washed down and the flask filled to the mark with Skelly B. The contents were then thoroughly mixed. The run was separated into three portions of approximately equal size by pipetting two portions into Erlenmeyer flasks and leaving the third portion in the volumetric flask. p-Methylbiphenyl (approximately 50 mg) was weighed into one of the flasks and washed into the solution with Skelly B. The contents were mixed by swirling. The remaining two portions were reserved for use in case of accidental invalidation of the results of the first or for use later in the estimation of m- or o-methylbiphenyl. The solution was allowed to stand in contact with sodium carbonate for at least 4 hours in order to remove carboxylic acids. It was then placed in a pear shaped distilling flask of the proper size fitted with a side arm for a capillary bubbler, and as much of the liquid as possible was distilled

at about 25 mm pressure through a small (30 cm high) vacuum jacketed column containing a glass spiral. The residue was dissolved in as small as possible volume of Skelly B which had been purified by washing with sulfuric acid, treating with alkaline permanganate, washing with distilled water, drying over magnesium sulfate, and distilling. The resulting solution was chromatographed on 4 g of neutral alumina in order to remove esters. The first 25 ml of Skelly B eluent were collected in a 50 ml round bottomed centrifuge tube. The solvent was removed by impinging a stream of air on it while warming gently over a heating mantle. The residue was dissolved in 1-2 ml of glacial acetic acid. The centrifuge tube was then placed in a water bath maintained (on a hot plate) at approximately 45°C. Two ml of a chromic acid oxidizing solution (a solution of 35 g chromium trioxide in a mixture of 80 ml water, 130 ml acetic acid, and 25 ml concentrated sulfuric acid<sup>21</sup>) were added and reaction was allowed to proceed for 1 1/2 hours. At the end of this time, 30 ml of water were added, precipitating the solids, including the desired product, p-phenylbenzoic acid. The solids were washed several times with water to remove most of the chromium salts. The liquid and solid layer were separated by centrifugation followed by removal of the liquid by means

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<sup>21</sup>D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 30.

of a capillary pipette. Frequently the solid floated on the surface of the liquid after centrifugation, or part floated and part went to the bottom of the tube. The residue was then treated with two 5 or 6 ml portions of 5% potassium hydroxide in order to extract the acids present. A small wad of cotton was dropped into the tube and the residue thoroughly triturated with the basic solution by swabbing the cotton wad around the sides of the tube and into the bottom. The basic solution was separated from the residue by inserting the tip of a capillary pipette into the wad of cotton, thus using it for a filter. The basic solution was transferred to a 15 ml conical centrifuge and acidified with concentrated hydrochloric acid, precipitating the organic acids. These were separated by centrifugation and washed several times with water. The acids were treated with about 2 ml of ether (terephthalic acid, one of the by-products of the reaction, is not soluble in ether) and the ether solution separated with a capillary pipette and placed in another 15 ml centrifuge cone. The ether was evaporated by impinging air on its surface. The residue was dissolved in about 2 ml of ethyl alcohol, water was added until a heavy precipitate formed, and the mixture was heated to boiling over a heating mantle. It was found that bumping could be prevented by letting a stirring rod of just smaller size than the bottom of the cone rest in it during the heating. The alcohol and

water were adjusted so that the material just dissolved at the boiling temperature. In some cases a yellow gum formed which would not dissolve. As much of this as possible was removed with the stirring rod. The solution was cooled slowly and p-phenylbenzoic acid crystallized. The product was separated by centrifugation and dried in the cone in a vacuum desiccator. A piece of pyrex tubing about 2 feet long and just large enough for the centrifuge cone to slip into was sealed at one end and the cone inserted. The tubing was tilted so that the cone fell to the sealed end and a vacuum pump was attached by means of a rubber stopper to the open end. The closed end was inserted into a warm combustion furnace. The pump was started and the p-phenylbenzoic acid sublimed to a region of the glass tube just outside the furnace. The sublimation was repeated once or twice by inserting the tube further into the furnace. The furnace was removed and the tube allowed to cool. The tube was sealed off about 2 inches on each side of the region containing the sublimate. The material was stored in this form until just before its activity was determined. At this time, the tube was cut off on one side of the sublimate and drawn into a funnel on the other. The p-phenylbenzoic acid was washed into a fresh 15 ml centrifuge cone with a fine stream of ether, which was then evaporated as before. Enough of the p-phenylbenzoic acid for a radioanalysis was weighed into a combustion tube.

The sublimation process was repeated, each sample being sublimed three or four times, and that portion of the sublimation tube from which the sample was sublimed being sealed off between sublimations. Samples were removed for radioanalysis by scraping them from the surface of the tube with a nickel spatula. The sublimation process was then again repeated, four or five times, in the same manner.

Microscope hot plate melting points were taken on the samples used for carbon and radioanalyses. It should be noted that the melting points observed were quite variable, even within one sample. The larger aggregates of crystals tended to melt much lower than single crystals or smaller aggregates. In one case a microscope melting point of 210-222°C was obtained, while the same sample was observed to melt at 217.5-218.5°C (uncorrected) in a sealed capillary (Hershberg melting point apparatus).<sup>22</sup> In another case the opposite effect was obtained, the capillary melting point being lower. Since the *p*-phenylbenzoic acid tends to sublime readily above 195°, it was difficult to follow single crystals as the plate was warmed up. In general, smaller aggregates were reduced even further in size by the time the melting point was reached, and these were chosen for melting point

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<sup>22</sup>N. D. Gheronis, "Micro and Semimicro Methods," vol. VI of A. Weissberger, "Technique of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p. 149.

data wherever possible. It should be noted that the melting points of the material used in the first series of radioanalyses were taken, in general, on larger aggregates than those used in the second and third series of radioanalyses. There are indications that the sublimation process did not purify the p-phenylbenzoic acid in all cases. A capillary melting point (sealed tube) taken on the material from run 15-A used for the third series of radioanalyses was 208-214°C. Sufficient material for capillary melting points on the other runs was not at hand. It is apparent, however, that the melting points in most cases did improve with sublimation, indicating purification.

In order to avoid cross contamination of the runs, the following procedures were adopted. Centrifuge tubes and volumetric flasks were used once only and set aside. A fresh stirring rod was used in connection with each run and discarded after use. Capillary pipettes were discarded after one use. Acetone was refluxed through the distilling column for at least 1 hour after each use. Distilling flasks and capillary bubblers were cleaned in chromic acid cleaning solution after each use.

#### The determination of carbon and its radioactivity

The benzoic acid  $1-C^{14}$  from which the benzoyl peroxide  $1-C^{14}$  was made, the benzoyl peroxide  $1-C^{14}$ , and the p-

phenylbenzoic acid isolated from each run were analyzed for carbon and its radioactivity by the method of Van Slyke and co-workers<sup>23,24,25,26</sup>. The manometric apparatus used was a commercial<sup>27</sup> one with a magnetic stirrer. The connecting tube (joining the combustion tube and the apparatus) was received fitted with a hemispherical joint, but this was found to be a source of leakage, and was removed. The connection was made with a piece of rubber vacuum tubing. As recommended, the joint and stopcock on the combustion tube and connecting piece were lubricated with syrupy phosphoric acid. Apiezon N grease<sup>28</sup> was used on other joints and stopcocks on the system. The procedure followed was that given by Van Slyke and co-workers in the papers cited above. The procedure is also given (up to the reading of  $P_1$ , the pressure of carbon

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<sup>23</sup>D. D. Van Slyke and J. Folch, J. Biol. Chem., 136, 509 (1940).

<sup>24</sup>D. D. Van Slyke, J. Plazin, and J. R. Weisiger, ibid., 191, 299 (1951).

<sup>25</sup>D. D. Van Slyke, R. Steele, and J. Plazin, ibid., 192, 769 (1951).

<sup>26</sup>F. M. Sinex, J. Plazin, D. Clareus, W. Bernstein, D. D. Van Slyke, and R. Chase, ibid., 213, 673 (1955).

<sup>27</sup>A. H. Thomas Company, 230-2-4 South 7th Street, Philadelphia 5, Pa.

<sup>28</sup>J. G. Biddle Company, 1615 Arch Street, Philadelphia 7, Pa.

dioxide plus a small amount of foreign gases) by Steyermark.<sup>29</sup> There are several possible minor variations in the procedure developed by Van Slyke and co-workers. The modifications used will be pointed out here. The reagents were prepared according to Van Slyke, Plazin, and Weisiger.<sup>24</sup> The amounts used and general procedure followed were those for "micro-analyses." All utensils used for delivering reagents to the apparatus were kept covered except when in use. The air free lactic acid was stored in the container described by Van Slyke, Steele, and Plazin.<sup>25</sup> It was delivered to the apparatus by running about 2 milliliters into the cup in such a fashion that it did not fall through the air, then admitting the lower 1 milliliter only to the apparatus. The gas phase proportional counting procedure used was that described by Van Slyke, Steele, and Plazin<sup>25</sup> as modified by Sinex, *et al.*<sup>26</sup> The scaler employed was a Nuclear Instrument and Chemical Corporation Model 162.<sup>30</sup> Although this instrument incorporates an amplifier for use in proportional counting, it was not found to be of sufficient sensitivity. Moreover, overloading from large pulses resulted in spurious counts. Accordingly, an amplifier-discriminator of the type described

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<sup>29</sup>A. Steyermark, "Quantitative Organic Microanalysis," The Blakiston Company, New York, N. Y., 1951, p. 251.

<sup>30</sup>Nuclear Instrument and Chemical Corporation (Nuclear-Chicago), 223 West Erie Street, Chicago 10, Ill.



by Sinex, et al.<sup>26</sup> was employed. A cathode follower was added to the system in order that fairly long connecting cables could be used. The units were connected to the 110 V line through an isolation transformer. The high voltage supply used was that of the scaler. A circuit diagram is on file with the Instrumentation Group of the Ames Laboratory of the Atomic Energy Commission, Iowa State College, as drawing MF-60, "Non-Overloading Pulse Amplifier."

Table 1 tabulates counting rate versus voltage for a number of discriminator settings for a moderately active sample. The discriminator dial was not calibrated, so the figures have nothing but relative significance. The same tube was employed for all counts. The counting was done at 2000 V with a discriminator setting of 60. It was demonstrated that a second tube counted essentially the same background as the one used for the active samples. Counter tube #1 showed a background counting rate of  $93 \pm 2$  c/min while counter tube #5 showed a background of  $98 \pm 2$  c/min. Background was counted alternately with the two tubes for a total time of 66 minutes. This tube was filled with counting gas and an inactive carbon dioxide sample and used to count background only for all counts. The counting gas used was 90% argon-10% methane, commonly called P-10, supplied by Matheson.<sup>18</sup>

Since the procedure and the modifications mentioned

Table 1. Plateau characteristics of counter tube #1<sup>a, b</sup>

D <sup>d</sup>	Voltage <sup>c</sup>						
	1600	1700	1800	1900	2000	2100	2200
5					117	798	2810
10	708	1415	2049	2305	2375	2510	4818
25	1825	2232	2341	2412	2498	2515	4740
35	1989	2322	2399	2470	2525	2598	7939
60	2232	2363	2442	2460	2498	2596	5579
80	2270	2415	2469	2460	2578	2623	4290
96	2334	2418	2346	2497	2550	2641	4017

<sup>a</sup>Counter tube #1 was used for counting all active samples in this work. It was operated at a discriminator setting of 60 and a voltage of 2000.

<sup>b</sup>The figures in the table are counts per minute for the same sample.

<sup>c</sup>Voltage applied to the counter tube.

<sup>d</sup>Discriminator setting. This dial is calibrated from 0 to 100, but the figures have no absolute meaning. As the figure increases, the voltage of the lowest pulse the system will count decreases, *i.e.*, the system discriminates at low pulse heights when D is large.

above, except for the addition of the cathode follower, are described fully in the sources cited, it will not be given in detail here. However, the following is the general procedure. The compound is weighed into a combustion tube with a microbalance. The weighing is by difference using a small aluminum scoop or porcelain boat. The amount of carbon is

the sample is generally 2-3 mg for "microanalyses." The combustion tube is attached to the apparatus and most of the air expelled from the system. An alkaline hydrazine solution is introduced into the manometric chamber and the combustion performed. The carbon dioxide evolved from the sample is adsorbed by the alkaline hydrazine. The combustion tube is disconnected and the unabsorbed gases expelled. Air free lactic acid is admitted to the manometric chamber in order to liberate the carbon dioxide.  $P_1$  is read. The carbon dioxide is then distilled into a counter tube which has been evacuated to 0.3 mm or less. Condensation is accomplished by immersing the end of the counter tube in liquid nitrogen. The counter tube is disconnected and  $P_2$  (pressure after removal of carbon dioxide) is read. The difference  $P_1 - P_2$  is taken to be the pressure of the carbon dioxide evolved. This difference less a reagent blank gives the pressure of the carbon dioxide from the sample. This pressure is multiplied by a factor tabulated by Van Slyke and Folch<sup>23</sup> to yield milligrams of carbon.

Van Slyke and Folch<sup>23</sup> recommend that knowns be run on systems which may not be exactly calibrated and the resulting theoretical factor be used for subsequent analyses. This procedure was followed here, since the calibrated chamber was broken in cleaning the apparatus at one time. The results of some analyses of knowns are given in Table 2. The factors calculated from these are given in Table 3.

Table 2. Van Slyke manometric analysis of known pure compounds

Compound		%C (theoretical)	%C (found) <sup>a</sup>	Correction factor
Potassium acid phtalate <sup>b</sup>	1	47.05	45.72	1.029
	2	47.05	46.31	1.016
Benzoic acid <sup>c</sup>	1	68.85	66.70	1.032
	2	68.85	66.50	1.035
				Average 1.028

<sup>a</sup>Calculated using the factors of Van Slyke and Folch<sup>23</sup>.

<sup>b</sup>"Primary Standard" grade.

<sup>c</sup>Recrystallized twice from water.

Table 3. Corrected Van Slyke manometric factors

T(°C)	Factor
20	0.007149
21	7116
22	7083
23	7051
24	7019
25	6988
26	6959
27	6929
28	6899
29	6870
30	6841
31	6814
32	6786
33	6759
34	6732
35	6706

After the counter tube has warmed to near room temperature, it is filled to atmospheric pressure with P-10. It is then ready for counting.

#### Statistical treatment of radiochemical data

Since the disintegrations of radioactive nuclei appear to be random, it is proper to treat data obtained by counting these disintegrations by statistical methods. The following is a summary of the methods conventionally used by radiochemists. A discussion of this topic is given, for example, by Friedlander and Kennedy.<sup>31</sup> The reader is referred to that text for derivation of formulae and elaboration on the ideas presented here.

The standard deviation is a measure of the degree of internal agreement among a set of measurements. If this set is averaged, then the standard deviation gives a measure of the precision of the measurement. It is found that the expected standard deviation of a measurement of the number of radioactive disintegrations occurring in a given time interval is the square root of the number of disintegrations counted if that number is large. Counting rates are generally presented as the observed rate  $\pm$  the expected standard deviation.

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<sup>31</sup>G. Friedlander and J. W. Kennedy, "Nuclear and Radiochemistry," John Wiley & Sons, Inc., New York, N. Y., 1955, p. 252.

This convention is followed in presenting the data given here. If a measurement is divided by a constant, both the observed figure and the standard deviation are divided by the same constant. If two counting rates are added (or subtracted) the standard deviation of the sum (or difference) is the square root of the sum of the squares of the standard deviations of original rates. If the standard deviation for each of two rates to be multiplied (or divided) is on the order of 1% of the counting rate, then the standard deviation of the product (or quotient) is on the order of 1.4% of the product (or quotient). If the distribution law of a series of events is known, then the standard deviations of measurements of these events can be given a concrete significance. Using the Gaussian distribution for radiochemical disintegrations leads to the conclusion that the probability that the actual error in a measurement is greater than the standard deviation is 0.32. Similarly, the probability that the actual error in the measurement is greater than three times the standard deviation is 0.0027. Thus, if the standard deviation is about 1.4% of the rate measured, then the probability that the measurement is less than 4.2% in error is 0.9973. The probability that the measurement is less than 1.4% in error is 0.68. All the counting rates measured in this work were measured in such a fashion that the standard deviation was on the order of 1% of the observed rate. Thus,

the above statistical considerations apply to all derived data given in Table 4. Standard deviations are given in Table 4, therefore, only for directly observed data.

Bleuler and Goldsmith<sup>32</sup> give a formula for the most efficient partitioning of counting time between background counting and sample counting. Generally, this formula was followed approximately. In addition, for samples which it was necessary to count for more than 10 minutes, background was counted for a short time (usually 10 minutes), then sample was counted for a similar time, then background and sample alternately until the count was finished. In this manner errors due to actual variations in the background during the counting period were minimized.

#### The calculation of the yields of p-methylbiphenyl

The active benzoic acid used in these experiments was ring labeled. Since the p-methylbiphenyl formed consists of a phenyl group from the original benzoic acid and a p-tolyl group from the solvent, which was inactive toluene, the specific activity of the p-methylbiphenyl is the same (on a molar basis) as the benzoic acid from which it was made, 1820 c/min/ $\mu$  mole. The p-methylbiphenyl was not isolated directly, however, it was converted to p-phenylbenzoic acid

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<sup>32</sup>E. Bleuler and G. J. Goldsmith, "Experimental Nuclear-  
onics," Reinhardt & Company, Inc., New York, N. Y., 1952,  
p. 66.

Table 4. Summary of data on the reaction of benzoyl peroxide with toluene

Run <sup>a</sup>	Conc. <sup>b</sup> (moles/l)	C <sup>c</sup> ( $\mu$ moles)	p <sup>d</sup> ( $\mu$ moles)	Count rate <sup>e</sup> (c/min)	S <sup>f</sup> ( $\mu$ moles)	B <sup>g</sup> (c/min/ $\mu$ mole)	Carbon <sup>h</sup> (%)	Y <sup>i</sup> (%)	MP <sup>j</sup> (°C)
4A-1	10 <sup>-1</sup>	235.5	221.5	2212 $\pm$ 13	13.60	163 $\pm$ 1.0	76.18	10.5	205-214
-2				578 $\pm$ 8	5.00	116 $\pm$ 1.6	78.83	7.2	216-218
-3				258 $\pm$ 4	1.98	130 $\pm$ 2.0	76.27	8.1	---
15A-1	10 <sup>-1</sup>	307.5	230.0	2460 $\pm$ 23	18.74	131 $\pm$ 1.2	74.76	10.4	210-222
-2				1164 $\pm$ 12	12.29	94.8 $\pm$ 1.0	80.23	7.4	218-222
-3				1558 $\pm$ 14	11.78	132 $\pm$ 1.2	79.18	10.5	(215)

<sup>a</sup>The second number refers to the series of the analysis, i.e., whether the sample has been subjected to one, two, or three sets of sublimations.

<sup>b</sup>Concentration of benzoyl peroxide 1-C<sup>14</sup> at the beginning of the reaction.

<sup>c</sup>Amount of carrier, inert p-methylbiphenyl, added before the reaction mixture was worked up.

<sup>d</sup>Amount of benzoyl peroxide used in the reaction.

<sup>e</sup>Counting rate for the sample taken for radioanalysis.

<sup>f</sup>Amount of sample of p-phenylbenzoic acid taken for carbon and radioanalyses.

<sup>g</sup>Specific activity of the p-phenylbenzoic acid isolated.

(Footnotes continued on next page)



Table 4. (Continued)

Run	Conc. (moles/l)	C ( $\mu$ moles)	P ( $\mu$ moles)	Count rate (c/min)	S ( $\mu$ moles)	B (c/min/ $\mu$ mole)	Carbon <sup>1</sup> (%)	Y <sup>1</sup> (%)	MP (°C)
3B-1	10 <sup>-2</sup>	296.0	203.5	1250±10	12.99	96.3±0.8	80.20	8.1	205-222
-2				592±7	7.90	74.9±0.9	80.08	6.2	220-222
-3				207±3	3.05	67.8±1.0	80.18	5.6	(220)
2A-1	3x10 <sup>-3</sup>	282.0	195.5	961±11	10.78	89.2±1.0	78.06	7.4	205-212
-2				---	---	---	---	---	---
-3				---	---	---	---	---	---

<sup>1</sup>Van Slyke manometric carbon analysis of the p-phenylbenzoic acid isolated. It was discovered that the liquid combustion reagent used for the first series of analyses had deteriorated. A fresh solution was used for the second series. This, too, began to give questionable analyses after 2 days of use, so it was replaced with another fresh solution. Unfortunately, no blanks were run using the second reagent employed. A blank was run on the third, which was made from the same reagents as the second. The blank was run at one temperature only. The approximation was made that the blank might be considered all carbon, and the blank was accordingly corrected to other temperatures using the carbon factors. The theoretical amount of carbon for p-phenylbenzoic acid is 78.77%.

<sup>1</sup>Yield of p-methylbiphenyl from the reaction, based on the expectation of getting 1 mole of p-methylbiphenyl from 1 mole of benzoyl peroxide.

(Footnotes continued on next page)

Table 4. (Continued)

Run	Conc. (moles/l)	G ( $\mu$ moles)	P ( $\mu$ moles)	Count rate (c/min)	S ( $\mu$ moles)	B (c/min/ $\mu$ mole)	Carbon (%)	Y (%)	MP <sup>J</sup> (°C)
12A-1	$3 \times 10^{-3}$	275.0	186.6	3956 $\pm$ 37	18.22	217 $\pm$ 2.0	73.46	20.0	218-221
-2				1172 $\pm$ 14	7.89	148 $\pm$ 1.8	79.65	13.1	216-218
-3				1353 $\pm$ 13	10.48	129 $\pm$ 1.2	77.08	11.5	215-219
11A-1	$10^{-3}$	269.0	188.0	1702 $\pm$ 16	17.16	99.3 $\pm$ 0.9	78.82	8.2	---
-2				371 $\pm$ 4	5.10	72.8 $\pm$ 0.8	82.67	6.0	218-222
-3				767 $\pm$ 7	10.21	75.2 $\pm$ 0.7	66.02	6.2	(220)
14B-1	$10^{-3}$	348.0	192.5	1150 $\pm$ 13	13.62	84.4 $\pm$ 1.0	69.11	8.8	215-223
-2				496 $\pm$ 4	6.78	73.2 $\pm$ 0.6	79.55	7.6	220-222
-3				345 $\pm$ 4	4.54	76.0 $\pm$ 0.9	79.98	7.9	(220)

<sup>J</sup>These melting points were made on a microscope hot plate. In addition, two sealed capillary melting points were made on a copious sample, 15A, and a Fisher-Johns melting point was taken on 2A-1.

Sealed capillary: 15A-1 217.5-218.5°C  
15A-3 208 -214

Fisher-Johns: 2A-1 221

The values enclosed in parentheses represent temperatures at which the sample under observation had completely sublimed without melting.

after a known quantity of inactive p-methylbiphenyl had been added to the final reaction mixture. If no inactive p-methylbiphenyl had been added, the specific activity of the p-phenylbenzoic acid isolated would have been the same as that of the benzoic acid from which the benzoyl peroxide was made. Thus, by measuring the specific activity of the p-phenylbenzoic acid which was isolated, one obtains directly from the specific activity of the starting benzoic acid the factor by which the product p-methylbiphenyl was diluted:

$$\text{Dilution factor} = \frac{A}{B}$$

where A is the specific activity of the starting benzoic acid (1820 c/min/ $\mu$  mole), and B is the specific activity of the p-phenylbenzoic acid finally isolated. The dilution factor can also be expressed in terms of the unknown quantity (X,  $\mu$  moles) of p-methylbiphenyl which is formed in the reaction and the known quantity (C,  $\mu$  moles) of inert p-methylbiphenyl added before the mixture was worked up.

$$\text{Dilution factor} = \frac{C + X}{X}$$

Thus, equating the two expressions for the dilution factor and substituting 1820 for A, we obtain:

$$X = \frac{B C}{1820 - B}$$

The percent yield of p-methylbiphenyl from the reaction is obtained by dividing X by P ( $\mu$  moles of benzoyl peroxide used

in the reaction) and multiplying by 100. The percent yield calculated in this fashion is that based on the expectation of obtaining 1 mole of p-methylbiphenyl from each mole of benzoyl peroxide. This convention for expressing the yield is followed throughout this dissertation.

The results of these experiments are given in Table 4.

### The Reaction of Benzoyl Peroxide with Durene and Mesitylene

#### Durene

Eastman white label durene was recrystallized from ethanol and water. The melting point as determined in a Thiele tube was 79-80°C (uncorrected).

#### Benzoyl peroxide

Eastman benzoyl peroxide was recrystallized by dissolving it in the least possible amount of chloroform and pouring the solution slowly and with vigorous stirring into Skelly A. The peroxide was filtered and dried under vacuum.

#### Mesitylene

Matheson, Coleman, and Bell mesitylene was used directly.

The reaction of benzoyl peroxide  
with durene at approximately 100°C

Two g durene (0.0150 moles) and 0.366 g benzoyl peroxide (0.00151 moles) were placed in constricted tubes, evacuated and flushed with nitrogen three times, and finally sealed off under vacuum. These were placed in an oven regulated to 100±5°C. After 12 hours at this temperature the tubes were opened and worked up for products.

Chromatography on an alumina column 2.5 x 50 cm gave the products given in Table 5.

Table 5. Chromatography of benzoyl peroxide-durene reaction mixture

Fraction	Eluent	Melting point	Amount	Description
1-4	Skelly A		0	
5-10	Skelly A	80°C	Large	Durene
11	Skelly A		0	
12	Skelly A	46°C	Trace	A liquid which deposited crystals on standing
13	Skelly A		0	
14	Skelly A- Benzene	125-129°C	0.221 g	White crystals with faint bluish cast
15-44	Benzene Methylene chloride Methanol Acetic acid	Indefinite gum	Traces	

Fraction 14 of the above chromatography was recrystallized from ethanol and water. It was then sublimed and dried in a drying pistol over  $P_2O_5$ . The following properties were observed:

Melting point - 131-132.5°C (uncorrected).

Solubility - The compound was insoluble in water, 5% aqueous hydrochloric acid, 5% aqueous sodium hydroxide, concentrated sulfuric acid, and syrupy phosphoric acid. This places the compound in solubility class I of Shriner, Fuson, and Curtin's scheme of analysis.<sup>33</sup> In view of the reaction this compound is probably a hydrocarbon.

Infrared spectrum - The infrared spectrum in carbon disulfide showed no carbonyl band, indicating that the compound must be derived from phenyl radicals and/or durene. The spectrum showed an overall resemblance to that of durene.

Elementary analysis - A sample of the compound was sent to Geller Laboratories of Hackensack, New Jersey for an elementary analysis. The results are given in Table 6 together with the theoretical analyses for two of the most likely suspects. The analysis

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<sup>33</sup>R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 64.

Table 6. Carbon analyses of unknown compound and suspects

Compound	Carbon (%)	Hydrogen (%)
2,3,5,6-tetramethylbiphenyl	91.43	8.57
2,2',4,4',5,5'-hexamethylbibenzyl	90.17	9.83
Unknown	89.97	9.85

corresponds very closely to the theoretical one for 2,2',4,4',5,5'-hexamethylbibenzyl. The other data are also consistent with this identification.

Fractions 5-10 were combined and sublimed at atmospheric pressure. The sublimation was interrupted before it was completed and infrared spectra of the sublimate and the residue were made. No distinctive differences between the spectra could be seen. Anomalously, both showed a carbonyl band,  $5.80\mu$ . Otherwise, they were durene spectra. Since the solvent used for combination of the fractions was acetone, perhaps the carbonyl band is due to traces of unremoved acetone.

Other reactions were carried out in exactly the same fashion and were analyzed for carbon dioxide and acids as follows:

Carbon dioxide - Nitrogen was passed through tubes containing ascarite and anhydrous into a thick walled

suction flask containing the unbroken reaction ampule, through two more absorption tubes containing ascarite, and finally through a bubbler tube containing sulfuric acid. After 20 minutes of flushing the system in this manner, the connecting tubes to the absorption tubes between the flask and the bubbler were pinched off with clamps. The absorption tubes were removed, weighed, and replaced in the system. The reaction ampules were then broken by vigorously shaking the suction flask. Nitrogen was passed through the system for 30 minutes to an hour. The absorption tubes were then reweighed, the difference being taken as carbon dioxide.

**Acids** - The acids were titrated with 0.1052 N aqueous base in the suction flask used in the carbon dioxide measurement. The contents of the flask were first dissolved in Skelly A and the titrations were done heterogeneously with vigorous shaking. Phenolphthalein was used as the indicator. The acid measured is taken to be benzoic acid. An experiment described below confirms this. The results of the carbon dioxide and benzoic acid determinations are given in Table 7. The confidence placed in the carbon dioxide determinations



is not high, since durene is relatively volatile and could possibly also have deposited in the ascarite tubes. Nevertheless, two determinations gave good agreement in both acid titre and carbon dioxide. A third gave a lower acid titre and a lower carbon dioxide analysis. It is not included in Table 7.

Table 7. Products of the reactions of benzoyl peroxide with durene and mesitylene

Solvent	Temperature (°C)	Moles of solvent	Yields <sup>a, b</sup>	
			Carbon dioxide	Benzoic acid
Durene	100±5	0.0150	61.6	99.8
			61.0	100.4
	89	0.0150	--	129.6
			28.6	129.6
			27.2	--
			27.2	132.8
	0.0300	33.2	127.4	
Mesitylene	89	0.0718	99.4	87.8
		0.0288	102.4	88.6

<sup>a</sup>Percent yields based on the expectation of 1 mole of carbon dioxide or 1 mole of benzoic acid per mole of benzoyl peroxide.

<sup>b</sup>The yield of 2,2',4,4',5,5'-hexamethylbibenzyl, based on the expectation of 1 mole per mole of benzoyl peroxide, was 55% (crude weight) when the reaction was carried out at approximately 100°C.

In one instance the Skelly A solution of the reaction mixture was separated after titration with base and dried over calcium chloride. The Skelly A was then evaporated and infrared spectrum of the residue obtained. This spectrum showed a carbonyl peak at  $5.83\mu$  with a shoulder at  $5.80\mu$ . The residue was then triturated with concentrated sulfuric acid and the mixture poured into water. The water was extracted with ether. Extraction of the ether with 5% aqueous base was followed by saturating the basic solution with carbon dioxide. The ether layer was evaporated and an infrared spectrum of the residue made. The carbonyl peak at  $5.83\mu$  had disappeared, but the shoulder at  $5.80\mu$  remained. The resultant aqueous solution was then extracted with ether and the ether evaporated, yielding no material. The aqueous basic solution was then neutralized and extracted with ether. Evaporation of this ether layer also led to no material. It is probable that this treatment would not lead to recovery of such water soluble compounds as benzoic acid when the quantities present were so small. The infrared spectra indicate the presence of two carbonyl compounds one of which is removed by the treatment described. The most likely carbonyl compounds resulting from reactions of benzoyl peroxide with hydrocarbons are esters. The probable ester products of this reaction are phenyl benzoate, 2,3,5,6-tetramethylphenyl benzoate (duryl benzoate), and 2,4,5-trimethylbenzyl benzoate.

The reaction of benzoyl peroxide  
with durene at 89°C

Special ampules fitted with two inlets containing "Break-offsky" seals were used as reactions vessels. Durene and benzoyl peroxide were introduced into the ampules, they were evacuated and flushed with nitrogen three times and sealed under vacuum. The amount of benzoyl peroxide used was always 0.366 g (0.00151 moles). The amount of durene used was 2.00 g (0.0150 moles) except in one case in which 4.00 g (0.030 moles) were used. The ampules were placed in an oil bath maintained at 89°C. After 2 days they were removed and inserted in a system including the same features as the one already described plus a dry ice-acetone trap between the reaction vessel and the absorption tubes. U-tubes with stopcocks were used for absorption tubes. All connecting tubes of the system were flushed with nitrogen before the analysis was begun. The ascarite u-tubes were fitted with stopcocks which could be opened and closed to regulate the flow of gases through them. After flushing the system well with nitrogen the ascarite absorption tubes were weighed and reinserted into the system. The "Breakoffsky" seals were broken by raising small magnets which had been inserted above the seals before the ampules were put into the system, and dropping these on the seals. Nitrogen was then passed through the system for 20 minutes or more. The ascarite tubes were

reweighed. Further flushing with nitrogen was found in all cases to produce small variable changes in the weight of the tubes. These changes were present even when the gases being flushed through the system by-passed the reaction vessel. Since they were variable, no blank correction could be made. The variations were usually within 5% of the total weight change in actual runs. This would lead to a 2-3% difference in the percent yield of carbon dioxide from the reactions. This is the magnitude of the probable error in these measurements. It is thought that the small variable weight differences might be due to variations in the amount of surface moisture absorbed, since these tubes have quite a large surface. After the carbon dioxide measurement was completed, the ampules were removed from the system and opened. The contents were washed into a flask with Skelly A for titration of acids. The acids were titrated as before. The results of these analyses are presented in Table 7. The basic solutions from two of these titrations were acidified and extracted with ether, leading to a 97% yield (based on the titration) of a material melting at 121-122°C after one recrystallization from water. The infrared spectra of both the crude and recrystallized material were identical with that of benzoic acid.

The reaction of benzoyl peroxide  
with mesitylene at 89°C

The procedure used here was exactly the same as that for the reaction of benzoyl peroxide with durene at 89°C. The results of the carbon dioxide and benzoic acid analyses are given in Table 7.

Miscellaneous Experiments

The reaction of N-nitrosoacetanilide  
with benzene and iodine

N-nitrosoacetanilide was prepared by bubbling nitrogen dioxide through a solution of 5 g of acetanilide in 25 ml of glacial acetic acid until the solution turned dark green.<sup>34</sup> The solution was maintained at 5°C or below throughout the operation. The solution was then poured into 25 ml of ice and water, precipitating the N-nitrosoacetanilide. The yield was 2.74 g.

Next 2.24 g of N-nitrosoacetanilide (0.0136 moles) and 4.34 g of iodine (0.0171 moles) were placed in a 100 ml round bottomed flask with 75 ml of benzene. The benzene had been purified by washing with concentrated sulfuric acid until no yellow color developed on treatment with more sulfuric acid until no yellow color developed on treatment with

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<sup>34</sup>W. S. M. Grieve and D. H. Hey, J. Chem. Soc., 1797 (1934).

more sulfuric acid, then distilling through a column packed with nichrome wire. The flask was kept in a dry ice-acetone bath until the contents had been degassed by evacuating and flushing three times with nitrogen. The flask was then warmed to room temperature and the contents dissolved by shaking. The reaction mixture was kept under a positive pressure of nitrogen at all times. After the mixture had been at room temperature for 12 hours, it was refluxed for 1 hour. The mixture was washed with distilled water, then with basic sodium thiosulfate solution, and finally with distilled water. The benzene was distilled through a nichrome packed column and the column washed down with Skelly A. The residue was chromatographed on a 1 inch x 15 inch alumina column. Some of the early fractions eluted by Skelly A were mixed with chloroform and treated with chlorine.<sup>35</sup> A yellow solid which decomposed at 122-123°C (uncorrected) was obtained. Nichol and Sandin give 120-121°C as the decomposition point for phenyliodosochloride. Thus, the presence of iodobenzene is indicated. A total of 1.25 g of phenyliodosochloride was isolated. This corresponds to a 33.4% yield of iodobenzene. It is not believed, however, that the formation and isolation of the phenyliodosochloride is quantitative.

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<sup>35</sup>J. C. Nichol and R. B. Sandin, J. Am. Chem. Soc., 67, 1307 (1945).

A later fraction eluted by Skelly A deposited a white solid on evaporation of the solvent. The material was sublimed. The melting point of the sublimed material was 66-69°C (uncorrected), and a mixed melting point with biphenyl was 67-70°C (uncorrected; lit.<sup>36</sup>, 69-70°C). Furthermore, the infrared spectrum of the material was identical with that of an authentic sample of biphenyl. The yield of biphenyl was about 1% in another similar experiment.

Later fractions eluted with Skelly A showed a pale yellow color. Evaporation of the solvent from these led to a deep yellow-orange solid. It was sublimed and blotted dry. Its melting point was 64-66°C (uncorrected; lit.<sup>37</sup> for azobenzene, 68°C). The infrared spectrum (Perkin Elmer potassium bromide pellet) was identical with that of an authentic sample of azobenzene. The total yield of azobenzene was 0.035 g (about 1.5%).

The reaction of phenylazotriphenylmethane  
with benzene in the presence of added triphenylmethyl

Triphenylmethyl was prepared under nitrogen from 8 g of triphenylmethyl chloride and 30 g of mercury in 50 ml of benzene by the method of Hammond, Raave, and Modic.<sup>38</sup> The

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<sup>36</sup>N. A. Lange, "Handbook of Chemistry," 6th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1948, p. 472.

<sup>37</sup>N. A. Lange, *ibid.*, p. 364.

<sup>38</sup>G. S. Hammond, A. Raave, and F. Modic, Anal. Chem., 24, 1373 (1952).

apparatus used was the double flask described by these authors. In the lobe of the flask into which the triphenylmethyl solution was to be filtered was placed 100 ml of benzene and 3.60 g of phenylazotriphenylmethane, which was prepared by the method of Cohen and Wang.<sup>39</sup> The entire system was kept under nitrogen throughout the experiment. The lobe of the flask containing the phenylazotriphenylmethane was kept immersed in a dry ice-acetone bath during the entire period in which the triphenylmethyl was being prepared. When the preparation of the triphenylmethyl was complete the apparatus was tipped so that the solution of triphenylmethyl in benzene filtered through a sintered glass disc into the lobe of the flask containing the phenylazotriphenylmethane. When the filtration was complete, the dry ice-acetone bath was removed and the system allowed to come to room temperature. The solution was stirred with a magnetic stirrer. It was allowed to remain overnight at room temperature, then heated for 2 hours at 70°C. The final reaction mixture was bright red and clear. When oxygen was bubbled through the mixture, the red color disappeared, but no precipitate formed. The benzene was distilled through a nichrome packed column, which was then washed down with ether. When the ether was distilled, a few crystals formed in the distilling flask.

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<sup>39</sup>S. G. Cohen and C. H. Wang, J. Am. Chem. Soc., 76, 1425 (1954).



The column was washed down with Skelly A and the resulting residue filtered (any biphenyl on the column should come down with Skelly A). The precipitate was a white solid, 0.0443 g, melting point 85-90°C (uncorrected), mixed melting point with triphenylmethane 90-92°C (uncorrected; lit.,<sup>40</sup> 95.4°C). The solution was shaken with distilled water (to hydrolyze any remaining triphenylmethyl chloride) and allowed to stand in contact with the water overnight. The Skelly A solution was then separated, dried over magnesium sulfate, and filtered. Chromatography on alumina gave 1.71 g of material which was eluted by Skelly A, but the melting point of this material was not well defined (60 - greater than 100°C). It was probably a mixture of hydrocarbons (biphenyl, triphenylmethane, and tetraphenylmethane). Since tetraphenylmethane is of very limited solubility in both Skelly A and ether, it is not likely that it was a major constituent of the mixture. Some tetraphenylmethane was isolated, however, by treating the mixture with potassium dichromate and sulfuric acid, in the expectation of oxidizing the triphenylmethane present to triphenylcarbinol,<sup>41</sup> and isolating the hydrocarbon fraction from the resultant mixture by chromatography on alumina. The yield was 0.01 g (melting point 283-284°C, uncorrected;

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<sup>40</sup>N. A. Lange, op. cit., p. 658.

<sup>41</sup>C. R. Noller, "Chemistry of Organic Compounds," W. B. Saunders Company, Philadelphia, Pa., 1951, p. 541.

lit.<sup>42</sup> for tetraphenylmethane, 285°C). Since triphenylmethane is much more soluble in ether than tetraphenylmethane, it is surprising that it separated from the ether solution. This fact may be taken as an indication that triphenylmethane was formed in substantial quantity. An investigation of the rate of decomposition of phenylazotriphenylmethane in the presence of added triphenylmethyl showed that the rate is unaffected by the triphenylmethyl.<sup>43</sup>

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<sup>42</sup>N. A. Lange, op. cit., p. 636.

<sup>43</sup>J. F. Garst and G. S. Hammond, J. Org. Chem., in press.

## DISCUSSION

Aromatic phenylations which appear to be free radical in character have been accomplished with benzoyl peroxide, phenylazotriphenylmethane, diazonium salts in basic solutions (Gomberg reaction), diazonium chlorides (thermal decomposition), diazonium chlorides (cuprous catalyzed decomposition),<sup>44</sup> N-nitrosoacetanilide, lead tetrabenzoate, phenyl iodosobenzoate, 1-phenyl-3,3-dialkyltriazenes, and other similar compounds.<sup>2</sup> Mono- and polysubstituted benzenes and hydrocarbons containing condensed ring systems can be used as the substrate with some success in obtaining products of phenylation, though the higher molecular weight condensed systems,<sup>45</sup> as well as some of the substituted naphthalenes,<sup>46,47</sup> tend to yield products of benzoyloxylation if the reaction is carried out with benzoyl peroxide.

The proof that the reactions are free radical in nature rests largely on the facts that the orientation of the phenyl group entering the aromatic ring does not correspond to that

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<sup>44</sup>S. C. Dickerman, K. Weiss, A. K. Ingberman, J. Org. Chem., 21, 380 (1956).

<sup>45</sup>I. M. Roitt and W. A. Waters, J. Chem. Soc., 2695 (1952).

<sup>46</sup>R. L. Dannley and M. Gippin, J. Am. Chem. Soc., 74, 332 (1952).

<sup>47</sup>B. M. Lynch and K. H. Pausacker, Australian J. Chem., 10, 165 (1957).

predicted on the basis of the theory of electrophilic aromatic substitution<sup>48</sup> and that other reactions, such as vinyl polymerization, thought to be typically free radical in character can be initiated by many of the above mentioned reagents.<sup>49</sup> Moreover, evidence for the free radical nature of the phenylations by any particular one of the above reagents speaks for the free radical nature of phenylations by all of them, for it has been demonstrated that essentially the same isomer distribution is obtained when any of the reagents thus far tested (in some cases as many as five) are allowed to react with a particular substrate. One would expect that differences in the nature of the attacking species would be reflected in the isomer distribution, hence the attacking species is probably the same for all the reagents tested. Additional evidence for the free radical nature of the reactions of benzoyl peroxide<sup>50</sup> and phenylazotriphenylmethane<sup>51,52</sup> is that the products of these reactions can be diverted by the inclusion of iodine, a typical free radical scavenger, in the

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<sup>48</sup>G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1955, p. 476.

<sup>49</sup>P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 108.

<sup>50</sup>G. S. Hammond, J. Am. Chem. Soc., 72, 3737 (1950).

<sup>51</sup>R. Huisgen and H. Nakaten, Ann., 586, 70 (1954).

<sup>52</sup>G. L. Davies, D. H. Hey, and G. H. Williams, J. Chem. Soc., 4397 (1956).

reacting system, without changing the unimolecular rate at which the radical source decomposes. The products of the decomposition of N-nitrosoacetanilide in benzene are also diverted by the inclusion of iodine (see Experimental).

The yields of biaryls from these reactions are never large, at least in those cases where the unsubstituted phenyl radical is employed. Most frequently, the biaryl amounts to not more than 0.5 mole per mole of phenylating agent used. Probably the most complete product analysis of the reaction between benzoyl peroxide and benzene thus far reported is that of Lynch and Pausacker.<sup>9</sup> A typical product analysis from one of their runs is given in Table 8. In this table the "first benzoic acid" is that obtained by extracting the reaction mixture with 5% aqueous sodium bicarbonate, while the "second benzoic acid" is the additional amount obtained by alkaline hydrolysis of the mixture. It is seen that benzoic acid, carbon dioxide, esters or other material hydrolyzable to benzoic acid, and high-boiling residue are the major products. The residue formation is common to the reactions of all the common sources of phenyl radicals with aromatic solvents, though the amount of residue varies somewhat. Phenylazotriphenylmethane, decomposed in benzene, leads to biphenyl, triphenylmethane, and residue, while N-nitrosoacetanilide, which reacts as benzenediazoacetate, leads to biphenyl, acetic acid, and residue in the same

Table 8. Yields of products of decomposition of benzoyl peroxide in benzene (initial concentration,  $4 \times 10^{-1} M$ ) at  $78^{\circ}C$

Product	Yield (%) <sup>a,b</sup>
Carbon dioxide	119
First benzoic acid	45
Second benzoic acid	31
Phenol	6
Biphenyl	40
Quaterphenyl	2.5
Terphenyl	1
High boiling residue	72.6 g/mole peroxide

<sup>a</sup>The data are those of Lynch and Pausacker.<sup>9</sup>

<sup>b</sup>The yield is based on the expectation of 1 mole of product from 1 mole of benzoyl peroxide.

solvent. These results are typical for other aromatic solvents except that the biaryl produced is the substituted biphenyl containing one solvent residue and one phenyl group. The quantities of biaryl produced are generally roughly equivalent to or less than the benzoic acid, triphenylmethane, or acetic acid produced, as the case may be. This suggests that the fate of the hydrogen atom which must be lost from the ring in these reactions is to combine with benzoyloxy, triphenylmethyl, and acetyloxy radicals, respectively. It

appears, then, that in phenylation the radicals which accept the ring hydrogen atoms are always, insofar as is known, those which should, on theoretical or experimental grounds, be expected to be among the less reactive radicals in the solution, and thus have a higher steady state concentration<sup>53</sup> than the more reactive phenyl radicals. While this appears to be a unifying principle relating all phenylations about which sufficient information is known concerning the products, it may not be true for aromatic substitutions by other radicals, such as methyl.<sup>54</sup> Pausacker<sup>10</sup> has recently noted that the action of m- or p-nitrobenzoyl peroxide on benzene results in an approximately 0.90-0.94 mole per mole of peroxide yield of nitrobiphenyl and an equivalent yield of nitrobenzoic acid. Hence there is no doubt in this case at least that the fate of the nuclear hydrogen is combination with the nitrobenzoyloxy radical. The residues from the reactions of benzoyl peroxide with aromatic solvents appear to consist largely of conjugated unsaturated compounds. It should be noted (see Table 8) that small amounts of phenyl benzoate, terphenyl, and quaterphenyl are formed when benzoyl peroxide is decomposed in benzene. Of particular interest is the fact that the quaterphenyl yield is indicated to be somewhat greater than

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<sup>53</sup>M. Swarc, Discussions Faraday Soc., 14, 250 (1953).

<sup>54</sup>E. L. Eliel, K. Rabindran, and S. H. Wilan, J. Org. Chem., 22, 860 (1957).

the terphenyl yield.

Any mechanism for free radical aromatic phenylation should be able to accommodate the products summarized above and other outstanding features of the reaction discussed in the following paragraphs. Rondestvedt and Blanchard<sup>3</sup> have mentioned several of these and the reader is referred to their paper for further discussion as well as to Augood and Williams.<sup>1</sup>

Orientation in free radical phenylation of substituted benzenes does not lend itself to explanation by any theory based on the type of considerations that explain orientation in electrophilic aromatic substitution. Table 9 gives some data on orientation in phenylation. In general, the entering phenyl group shows a tendency to substitute ortho to the group already present, irrespective of its nature. Thus, ortho substitution occurs though the extent of 48-67% for each of the following substituents on benzene: nitro, fluoro, chloro, bromo, iodo, cyano, methyl, ethyl, phenyl, and methyl sulfonate. In addition, it is apparent that selectivity among the various positions is not as great as in electrophilic substitution, where frequently the amount of substitution at some position is vanishingly small.

Ortho substitution is subject to steric hindrance. Qualitatively this steric hindrance is similar to that observed in nitration. It is believed to be somewhat less pronounced, though, in the case of phenylation, since even



Table 9. Orientation and reactivity in the phenylation of aromatic compounds at 80°C<sup>a</sup>

Aromatic compound	Ortho or $\alpha$	Meta or $\beta$	Para or $\gamma$	$X_{H^k}^b$	$X_{H^k_o(\alpha)}^c$	$X_{H^k_m(\beta)}^c$	$X_{H^k_p(\gamma)}^c$	o/p <sup>d</sup>	m/p <sup>d</sup>
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	58	10	32	4.00	6.86	1.20	7.68	1.81	0.31
C <sub>5</sub> H <sub>5</sub> N	58	28	14	1.04	1.81	0.87	0.87	4.14 <sup>e</sup>	2.00 <sup>f</sup>
C <sub>6</sub> H <sub>5</sub> F	54.1	30.7	15.2	1.35	2.19	1.50	1.23	3.56	2.02
C <sub>6</sub> H <sub>5</sub> Cl	60.3	25.9	13.8	1.44	2.60	1.12	1.19	4.37	1.88
C <sub>6</sub> H <sub>5</sub> Br	49.3	33.3	17.4	1.75	2.09	1.80	1.83	2.83	1.91

<sup>a</sup>Compiled from data given by Augood and Williams.<sup>1</sup> Detailed references are given by these authors.

<sup>b</sup>The total rate factor; the rate at which phenyl radicals substitute the compound in question relative to the rate at which they substitute benzene.

<sup>c</sup>The partial rate factor for the position indicated by the right subscript; the rate at which phenylation occurs at the indicated position of the compound in question relative to the rate at which it occurs at one position of benzene.

<sup>d</sup>The ratio of ortho to para (o/p) or meta to para (m/p) isomers formed in the phenylation of the compound in question. The statistical value for each of the quantities is 2.00.

<sup>e</sup>The ratio of alpha to gamma isomers.

<sup>f</sup>The ratio of beta to gamma isomers.

Table 9. (Continued)

Aromatic compound	Ortho or $\alpha$	Meta or $\beta$	Para or $\gamma$	$\frac{X_K}{H^K}$	$\frac{X_K}{H^K}_o(\alpha)$	$\frac{X_K}{H^K}_m(\beta)$	$\frac{X_K}{H^K}_p(\gamma)$	o/p	m/p
$C_6H_5I$	51.7	31.6	16.7	1.80	2.08	1.71	1.80	3.10	1.89
$C_6H_5CN$	60	10	30	3.60	6.48	1.08	6.48	2.00	0.33
$C_6H_5CH_3$	66.5	19.3	14.2	1.68	3.5	1.0	1.4	4.68	1.36
$C_6H_5C_2H_5$	53	28	19	1.24	1.97	1.04	1.41	2.79	1.47
$C_6H_5C_3H_7$ - <u>l</u>	31	42	27	0.87	0.81	1.1	1.41	1.15	1.56
$C_6H_5C_4H_9$ - <u>t</u>	24	49	27	0.87	0.63	1.28	1.41	0.89	1.82
$C_6H_5C_6H_5$	48.5	23.0	28.5	4.00	2.91	1.38	3.42	1.70	0.81
$C_{10}H_8$	83.4	16.6	--	23.90	29.90	5.48	--	5.02 <sup>B</sup>	--
$C_6H_5SO_3CH_3$	53	33	14	1.50	2.39	1.49	1.26	3.78	2.36
$C_6H_5CF_3$	20	40	40	0.99	0.59	1.2	2.4	0.50	1.00
$C_6H_5Si(CH_3)_3$	31	45	24	1.06	0.99	1.4	1.5	1.29	1.88

<sup>B</sup>The ratio of alpha to beta isomers.

tert-butylbenzene gives 24% ortho substitution. Moreover, in studying the alkyl benzenes one cannot be sure just how much of the decrease in ortho phenylation to ascribe to the steric effect, since the amount of para substitution increases only slowly from methyl- to tert-butylbenzene, while the fraction of meta substitution goes up rapidly, reaching 49% at tert-butylbenzene, indicating that a secondary effect is influencing the meta position. Furthermore, if one looks at the partial rate factors (see page 58) for phenylation of tert-butylbenzene one immediately notes that the ortho rate factor is somewhat less than that for any position in benzene. However, if one looks at p-ditert-butylbenzene, in which all positions are ortho to a tert-butyl group, one notes that the partial rate factor for any position is nearly that for benzene. Hence the steric hindrance is not necessarily the predominant factor in determining the rate of phenylation ortho to a bulky group. Sym-tri-tert-butylbenzene has not yet been explored in this reaction, but should prove to be of some significance, since each position is flanked by two tert-butyl groups. It is possible that the activating effect of three tert-butyl groups could offset the steric hindrance to phenylation.

Hey and co-workers, Rondestvedt and co-workers, and Dannley and co-workers have studied the relative reactivities of many compounds toward phenylation by the competitive

method. Two substrates are allowed to compete for a single species, in this case, the phenyl radical. Their relative reactivities are measured by the relative yields of products derived from them. In applying this method, a number of assumptions must be made, some of which are justifiable, others of which may be doubtful. It must be assumed that the reaction with each of the substrates is of the same kinetic order in each of the species entering into the transition state, which is reasonable since the same reaction is being examined with similar substrates. It must be further assumed that the side reactions are of the same order for both compounds and that they proceed to similar extents. This assumption has been attacked by Lynch and Pausacker<sup>9,10,47</sup>, who have shown that the amount of residue formed in reactions of benzoyl peroxide (the most commonly used reagent for the competitive experiments) with aromatic substrates varies from one compound to another and does not remain in the same proportions when they are mixed. Furthermore, the reactions must be carried to only a small percent completion, otherwise the selective destruction of one component would change the concentration ratio of the components, making calculations difficult. In spite of these considerations, it is not felt that the relative reactivities measured in this way are grossly in error, although the quantitative aspects of the experiments may not be entirely correct. In any event, these data are

presently the only data available pertaining to the relative reactivities of the various substrates toward free phenyl radicals, and it must be admitted that they show a fairly high degree of internal consistency. In several instances, the reactivity of a substrate A has been measured relative to substrate B, then B measured relative to C, and then A measured relative to C, with the result that the product of the first two relative reactivities agreed quite nicely with the third. The results of experiments such as these are usually expressed in terms of a "total rate factor",  $\frac{X}{H}k$ , where the symbol represents the rate at which  $C_6H_5X$  is attacked to yield biaryls relative to the rate at which  $C_6H_6$  is similarly attacked. The results of these measurements and the isomer distributions may be combined to give "partial rate factors",  $\frac{X}{H}k_o$ , where the symbol represents the rate at which an ortho position of  $C_6H_5X$  is attacked relative to the rate at which one of the six positions of benzene is attacked. Table 9 gives a list of total and partial rate factors. It is apparent that substituents have only a small effect on the reactivities of compounds  $C_6H_5X$ . Nitrobenzene, one of the more reactive substrates toward phenylation, is only four times as reactive as benzene, which factor corresponds to a difference in free energy of activation for phenylation of 0.98 kcal/mole, which is very small. Another feature of the data which strikes one's attention almost

immediately is the fact that practically all substituents are activating. Only in cases in which steric hindrance is prominent does one find that some compounds react more slowly than benzene. Even in these cases, it is generally found that this overall relatively slow rate is due to slow reactions at the hindered positions, and that the partial rate factors for the other positions show that they are at least equal in reactivity to one position of benzene. Some more pronounced electronic effects of substituents may be present in arylations by substituted phenyl radicals. For example, Dannley and Sternfeld<sup>55</sup> have obtained 100% meta compound in the p-nitrophenylation of benzotrichloride. They obtained no ortho isomer when the same compound was phenylated, but this may be at least in part due to steric effects, since the meta/para ratio was less than two, indicating that the most active single position in this case was the para. Simamura and Migita<sup>56</sup> report the following partial rate factors for the p-methoxyphenylation of nitrobenzene:  $\frac{\text{NO}_2}{\text{H}^{\text{ko}}} = 7.24$ ,  $\frac{\text{NO}_2}{\text{H}^{\text{km}}} = 0$ , and  $\frac{\text{NO}_2}{\text{H}^{\text{kp}}} = 8.95$ . Similarly, Morrison and Sweeney<sup>57</sup> have shown that p-nitrophenyl radical is strongly oriented to the

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<sup>55</sup>R. L. Dannley and M. Sternfeld, J. Am. Chem. Soc., 76, 4543 (1954).

<sup>56</sup>O. Simamura and T. Migita, Bull. Chem. Soc. Japan, 27, 228 (1954); C. A., 49, 15720 (1955).

<sup>57</sup>R. T. Morrison and R. F. Sweeney, Abstracts of Papers, 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 16-21, 1956, p. 74-C.

ortho positions of anisole, 89% of the substitution of this radical occurring at those positions. The partial rate factor for this ortho substitution is 8.5, but the total rate factor for anisole relative to benzene is not more than 3.3, since these authors report that the partial rate factors for reaction at the meta and para positions are less than one.

The mechanism presented by Augood and Williams<sup>1</sup> is one in which the controlling step of the reaction is the addition of the phenyl radical to one position of the aromatic system, forming a "sigma complex". In sigma complex the entering group is bound to the particular carbon at which substitution occurs, which carbon has, then, a tetrahedral configuration, and is removed from the conjugated system. Augood and Williams believe that the hydrogen atom from the ring is lost in a rapid step following the addition of the phenyl radical. Though they admit that this step may involve the removal of this hydrogen by another radical (probably benzoyloxy when benzoyl peroxide is the radical source), they prefer the loss of the hydrogen atom per se. They cite as evidence for this the fact that reduced compounds are sometimes found among the products of reactions carried out in the presence of nitrobenzene or quinone (see reference 52 in addition to those given by Augood and Williams). It does not seem to be energetically feasible that this should actually be the

course of the substitution step.<sup>58</sup> The dissociation energy of biphenyl is at most 88 kcal/mole. This is obtained in the following manner. Pitzer<sup>59</sup> gives the bond energy of a carbon-carbon alkane bond as not more than 81 kcal/mole (at 0°K). The carbon-carbon bond of biphenyl should be of this strength except for a slight effect due to hybridization and resonance. The effect due to hybridization is neglected. That due to resonance is theoretically estimated at not more than 3 kcal/mole<sup>60</sup> (i.e., 3 kcal/mole is the difference between the resonance energy of biphenyl and twice that of benzene). Hydrogenation data indicate that the resonance energy of biphenyl is only 1 kcal/mole greater than twice the resonance energy of benzene. Combining the figures for the carbon-carbon alkane bond strength and the maximum estimated resonance energy of biphenyl, and adding 4 kcal/mole in order to lend certainty to the proposal that the figure is a maximum, 88 kcal/mole is obtained for the central carbon-carbon bond energy of biphenyl. The bond dissociation energy for the carbon hydrogen bond of benzene is given by Szwarc and Williams<sup>61</sup> as 102 kcal/mole, obtained from pyrolysis data.

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<sup>58</sup>J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1956, p. 439.

<sup>59</sup>K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953, p. 170.

<sup>60</sup>G. W. Wheland, *op. cit.*, p. 132.

<sup>61</sup>M. Szwarc and D. Williams, *J. Chem. Phys.*, **20**, 1171 (1952).



This means that the activation energy for the reaction proposed by Augood and Williams must be at least 14 kcal/mole. It is difficult to see how a reaction with this activation energy could compete with radical-radical reactions, which are usually very fast, with activation energies of 0-5 kcal/mole and frequency factors on the order of  $10^9$  in many cases.<sup>62</sup> That the phenylation reaction is very fast is emphasized even more by the failure of the decomposition of phenylazotriphenylmethane in benzene to lead to appreciable yields of tetraphenylmethane in the presence of gross quantities of added triphenylmethyl (see Experimental). It is possible that solvation of the radicals involved might be preferentially great with the hydrogen atom, but even in this case it would be difficult to account for complexation of such a high enthalpy change. It is conceivable, however, that the hydrogen atom is lost from the ring to another solvent molecule to form a sigma complex in which one carbon atom binds two hydrogen atoms. This complex could then proceed to react with other radicals (benzoyloxy, for example) to yield its hydrogen. At any rate, the important consideration relative to the mechanism under discussion is the fact that it predicts a substitution step which is kinetically first order in radicals. If one modifies the mechanism so that the hydrogen atom is removed by a second radical, the result is still of

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<sup>62</sup>p. J. Flory, op. cit., p. 158.

the same form kinetically if the first stage, the addition of the phenyl radical to the aromatic ring, is the slow step. The mechanism in which the hydrogen atom is removed from the sigma complex by a second radical is probably the most widely accepted mechanism for free radical aromatic substitution.

A great deal of theoretical work has been done in an attempt to correlate relative reactivities of the various substrates with molecular orbital theories of pi electron systems. Such quantities as the "free valence" and "atom localization energy" have been employed with the most success (see discussion of Augood and Williams<sup>1</sup>). The free valence is a characteristic of the ground state of the molecule. It is an index to the extent to which a particular atom is participating in bonding, relative to the maximum extent it could participate. In a sense, then, it is a measure of the degree of "unsaturation" of a particular atom in a system. It is assumed that in the course of reaction the atom becomes "saturated" in its bonding, and the energy difference between the state of unsaturation and the state of saturation is taken as a measure of the activation energy for the substitution. The method of "atom localization energies" is similar in form, but probably is based on firmer theoretical grounds.<sup>63</sup> In this method, the transition state for the reaction is con-

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<sup>63</sup>H. J. S. Dewar, J. Am. Chem. Soc., 74, 3355 (1952).

sidered to resemble the sigma complex. In the sigma complex, the electrons on the atom being substituted have been removed from the pi electron system. They have been "localized" on that atom. The difference between the pi electron energy in the ground state and that of the transition state (with one atom removed from the system) is taken to be a measure of the energy of activation. The results of calculations of these types are given in Table 10. It should be noted that the calculations involve adjustable parameters in cases where there are substituent groups. Naphthalene, however, and biphenyl, can be treated without the use of any arbitrary parameters. The results of these calculations do not agree extremely well with the experiments. Indeed, it would have been surprising if they had, for the treatments involve many assumptions and approximations. In view of this, no great significance can be attached to the agreement, or lack of it, obtained. It should be noted, though, that using these methods ortho-para activation is generally predicted and that the order of magnitude of the relative reactivities is, usually, proper. However, naphthalene presents somewhat of a problem, for in this case the free valence and atom localization energy treatments are in sharp disagreement. Since this is the prime instance of a calculation which does not involve any arbitrary parameters, it is difficult to rationalize this disagreement without pointing out sharply the

Table 10. Theoretical calculations of reactivities of aromatic compounds toward phenylation<sup>a</sup>

Aromatic compound	Calculated by free valence method				Calculated by atom localization method			
	$\frac{X}{H^k_o}(\alpha)^b$	$\frac{H}{X^k_m}(\beta)^b$	$\frac{H}{X^k_p}(\gamma)^b$	$\frac{H}{X^k_c}$	$\frac{X}{H^k_o}(\alpha)^b$	$\frac{H}{X^k_m}(\beta)^b$	$\frac{X}{H^k_p}(\gamma)^b$	$\frac{H}{X^k_c}$
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	---	---	---	---	2.25	0.85	8.47	2.49
C <sub>6</sub> H <sub>5</sub> F	1.97	1.00	1.34	1.21	---	---	---	---
C <sub>6</sub> H <sub>5</sub> Cl	1.79	1.10	1.34	1.19	5.81	1.42	1.92	2.73
C <sub>6</sub> H <sub>5</sub> Br	2.07	1.10	1.34	1.28	---	---	---	---
C <sub>6</sub> H <sub>5</sub> I	5.12	0.95	1.97	2.35	---	---	---	---
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	---	---	---	---	2.51	0.86	2.14	1.48
C <sub>6</sub> H <sub>5</sub> OH	3.20	0.91	1.97	1.70	32.10	0.76	5.98	11.95

<sup>a</sup>Compiled from data given by Augood and Williams.<sup>1</sup> Detailed references are given by these authors.

<sup>b</sup>The partial rate factor for the position indicated by the right subscript; the rate at which phenylation occurs at the indicated position of the compound in question relative to the rate at which it occurs at one position of benzene.

<sup>c</sup>The total rate factor; the rate at which phenyl radicals substitute the compound in question relative to the rate at which they substitute benzene.

Table 10. (Continued)

Aromatic compound	Calculated by free valence method				Calculated by atom localization method			
	$\frac{X}{H^{k_o}}(\alpha)$	$\frac{H}{X^{k_m}}(\beta)$	$\frac{H}{X^{k_p}}(\gamma)$	$\frac{H}{X^k}$	$\frac{X}{H^{k_o}}(\alpha)$	$\frac{X}{H^{k_m}}(\beta)$	$\frac{X}{H^{k_p}}(\gamma)$	$\frac{H}{X^k}$
<chem>C6H5NH2</chem>	4.95	0.91	1.97	2.28	--	--	--	--
<chem>C6H5N</chem>	2.91	0.82	1.97	1.57	2.33	1.95	1.49	1.68
<chem>C10H8</chem>	13.71	1.34	--	10.03	$8.8 \times 10^4$	19.7	--	$4.4 \times 10^4$
<chem>C6H5C6H5</chem>	804.95	0.86	1.97	538.53	--	--	--	--

invalidity of some of the assumptions, and therefore of the calculations in general. It could not be said that these calculations, in their present state, lend support to any mechanism.

Rondestvedt and Blanchard<sup>3</sup> present a several step mechanism incorporating the essential features of the mechanism of Augood and Williams, but invoking a preliminary complex to account for special features. Both Augood and Williams and Rondestvedt and Blanchard believe that the ratio of isomers formed in the phenylation of substituted benzenes is a reflection of the stabilities of the various sigma complexes. Rondestvedt and Blanchard state that they do not know which step of their proposed mechanism is rate determining, however they base their discussion on the assumption that the formation of the sigma complex from the preliminary is the slow step. They feel that the sigma complex might either donate its hydrogen atom to the solvent, the new radicals producing reduced compounds and tars, or, more likely, that a second radical reacts with the sigma complex to abstract its extra hydrogen. They believe that radicals may be somewhat electrophilic, thus tending to complex with sites of high electron density. Using this hypothesis, they postulate that ortho orientation is preferred for most substituents because the incoming phenyl radical can complex with the electron rich (in some manner or another) substituent in the preliminary

complex. The following quotation is taken from their article:

Although resonance stabilization of the isomeric ortho and para sigma complexes is identical (steric effects disregarded here), a difference in the energy contents of the isomeric "preliminary complexes" or in the energy barriers to their formation will result in a higher concentration of the more favored preliminary complex. Therefore one of the sigma complexes will be formed more rapidly, and one isomer will predominate among the products.<sup>3</sup>

This reasoning cannot be valid. That this is true can easily be seen from the fact that at all points up to the transition state the system must be in equilibrium with reactants. In particular, if formation of the sigma complex is the slow step, with the transition state resembling the sigma complex, then the preliminary complexes must be in equilibrium with reactants and with the transition state. This being true, it is seen that the stability of the preliminary complex has no effect on the rate of formation of any isomer, the only factor of importance being the free energy difference between the reactants and the sigma complexes (as models for the transition state). Only if the association with the substituent is important in the sigma complex, then, will its effect be noticed, according to Röndestvedt and Blanchard's mechanism. The authors themselves admit that this is unlikely for such substituents as the halogens, though it may be possible for substituents such as the nitro group, which, incidentally, does not favor ortho substitution over para

except by the statistical factor of two, and hence does not require the explanation. It is seen, thus, that Rondestvedt and Blanchard's postulates concerning the effects of the stabilities of the sigma complexes and the preliminary complexes on the isomer distribution are mutually inconsistent. These authors also believe that in some cases hydrogen abstraction may become the rate determining step, in which case they expect to find a deuterium isotope effect.

The mechanisms of DeTar and Sagmanli<sup>5</sup> and of Lynch and Pausacker<sup>9,10</sup> involve generating biaryl, at least in part, in induced decomposition steps. While there is no doubt that induced decomposition occurs in the case of benzoyl peroxide, no evidence for induced decomposition has been obtained for some of the other sources of free phenyl radicals, notably phenylazotriphenylmethane. As a matter of fact, phenylazotriphenylmethane shows good first order kinetics even to high fractions of decomposition, and these kinetics are not affected by the presence of trityl radical.<sup>43</sup> Thus, while it is possible that some biaryl may be generated in induced decomposition steps when some radical sources are used, there must also be some formed in other reactions, and it is the mechanism of the formation of the latter in which we are primarily interested.

The "kryptoradical" mechanism of Huisgen and Horeld<sup>8</sup> is a concerted mechanism (see Historical section). They applied



it in particular to decompositions of N-nitrosoacetanilide. Similar schemes could be written, probably, for any source of phenyl radicals. However, the mechanism could not be a general one because it has been shown that iodine will scavenge radicals from benzoyl peroxide<sup>50</sup> and phenylazotriphenylmethane<sup>51,52</sup> with about 90% efficiency. This could be accounted for if the iodine reacted with the radical source in a concerted action similar to the proposed reaction with benzene. However, if this were true, one should expect a dependence on the rate of decomposition of benzoyl peroxide and phenylazotriphenylmethane on the iodine present, and this is not found.<sup>50,51</sup> It is unlikely, then, that this mechanism can be the proper one.

The mechanism of Hammond and co-workers<sup>6,7</sup> permits a rationalization of the features of the reaction which have been discussed. In particular, the mechanism readily accommodates the observed small variations in the reactivities of aromatic substrates, the relatively small effect of steric hindrance, and the lack of great selectivity among the various positions of substituted benzenes. The key to the rationalization is the idea that the rate-determining step of the reaction is a radical-radical reaction, and is therefore expected to have a small activation energy. The phenyl radicals are considered to be in rapid equilibrium with a complex of the radical with the aromatic solvent.

This complex must be of a small free energy of formation, otherwise the formation of the complex would probably be the rate determining step of the reaction. The complex would be, most likely, a "pi complex", in which the radical is imbedded in the pi electrons of the substrate, and will be henceforth referred to in that manner (though it is also possible that it could be a sigma complex). The mechanism of Hammond and co-workers differs from that of Rondestvedt and Blanchard<sup>3</sup> in that the pi complex enters into the rate determining step which is bimolecular in radicals, not unimolecular. Hammond<sup>64</sup> has discussed situations in which transition state energy can be correlated with the energy of reactants or products. In the case of highly exothermic reactions, it is thought that the transition state must resemble the reactants. This is particularly true for radical-radical reactions, which are usually very highly exothermic. Since in the mechanism of Hammond and co-workers, the rate determining step is the last one, products must have been determined in the transition state of that reaction. Since that reaction is a radical-radical reaction, the transition state must resemble the reactant radicals. Therefore orientation of the entering phenyl group must be determined in the pi complex. Since the pi complex must have a small energy of formation, it is not

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<sup>64</sup>G. S. Hammond, ibid., 77, 334 (1955).

likely that there would be large differences between the energies of formation of complexes having different orientations of the phenyl radical, thus accounting for the observed lack of great specificity. Similar considerations apply to the variations in reactivity among aromatic substrates. Since the pi complex must have only a small energy of formation, it is probably a "loose" complex, that is, the phenyl radical is probably not in very close proximity (compared to usual bonding distances) to the substrate or its substituent groups. Therefore strong steric interactions will not appear in the transition state for the reaction unless the groups concerned are particularly bulky.

According to the mechanism of Hammond and co-workers only those phenyl radicals which are complexed will lead to products of phenylation. It is likely that phenyl radicals would react upon meeting another radical whether they were complexed with solvent or not. It must be shown, therefore, that enough of the phenyl radicals would be complexed with solvent (at equilibrium) to account for the yields of products observed. If the usual practical ("infinite dilution") standard state<sup>65</sup> is adopted for phenyl radicals and pi complexes, the activity of the solvent being one, and the standard free energy of formation of the complex at 80°C

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<sup>65</sup>I. M. Klotz, "Chemical Thermodynamics," Prentice-Hall, Inc., New York, N. Y., 1950, p. 274.

assumed to be 0 kcal/mole, then at equilibrium 50% of the phenyl radicals will be complexed with benzene. Since the yields of biphenyl from the reactions of benzoyl peroxide and phenylazotriphenylmethane are about 50% (based on the expectation of 1 mole of biphenyl from 1 mole of benzoyl peroxide), it is seen that a free energy of formation of the complex of 0 kcal/mole is sufficient to account for the observed yield if all of the complexes at equilibrium result in product. If the standard free energy of formation of the complex at 80°C is assumed to be -3 kcal/mole, then 98.6% of the phenyl radicals exist at equilibrium as complexes. These estimates of the free energy of formation of the complex are certainly of the proper magnitude to be considered small, and are therefore consistent with previous considerations.

Price and Convery<sup>66</sup> have recently demonstrated that there is no tritium isotope effect when 2,4-dinitrotritiobenzene is phenylated by benzoyl peroxide. Augood and Williams<sup>1</sup> argue that this demonstrates that if a complex is formed, the rate determining step cannot be the conversion of the complex to products, since this reaction must involve the stretching of the carbon-hydrogen bond at the seat of substitution. This argument is not rigorous. As previously

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<sup>66</sup>C. C. Price and R. J. Convery, J. Am. Chem. Soc., 79, 2941 (1957).

mentioned, the transition state of reaction of the pi complex with a second radical to yield products would closely resemble the reactant radicals themselves. Therefore it would not be likely that the carbon-hydrogen bond at the seat of the substitution had stretched to an appreciable extent in the transition state of the reaction, an occurrence which is necessary in order for an isotope effect to be observed.<sup>67</sup> Although the lack of tritium isotope effect fails to distinguish between the mechanism of Hammond and co-workers and that of Augood and Williams, it probably does eliminate the mechanism of DeTar and Sagmanli,<sup>5</sup> on the basis discussed above.

There appears to be substantial precedent now for radical-solvent complexes. Hammond and co-workers<sup>68</sup> have demonstrated there probably exists a radical-inhibitor complex in the inhibition of air oxidation of hydrocarbons by phenols and amines. The evidence is that there is no isotope effect when the hydrogen atom previously thought to be abstracted in the first step of inhibition is replaced by deuterium, and that the kinetics are properly fitted by a mechanism in which radicals form complexes with the inhibitor

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<sup>67</sup>L. Melander, Arkiv Kemi, 2, 211 (1950).

<sup>68</sup>G. S. Hammond, C. E. Boozer, C. E. Hamilton, and J. N. Sen, J. Am. Chem. Soc., 77, 3238 (1955).

in rapid reversible reactions, but not by a mechanism in which the chain carrying radicals abstract hydrogen atoms from the inhibitor. Russell<sup>69</sup> has obtained evidence that chlorine atoms complex with aromatic solvents. He studied the photochlorination of 2,3-dimethylbutane. This hydrocarbon has only two types of hydrogen atoms, six primary and two tertiary. Since tertiary free radicals are generally more stable than primary ones, they are probably more readily formed. The ratio of tertiary to primary hydrogen abstraction will, however, depend not only on the stability of the product, but also on the reactivity of the attacking radical. The more reactive radicals will show less preference for tertiary hydrogens than the less reactive radicals. It is this kinetic criterion that Russell applied. He observed that the ratio of tertiary to primary chloride formed in this reaction is a function of the nature and concentration of small amounts of additives. In particular, it appears that most aromatic compounds when added in small amounts change the tertiary to primary ratio considerably in favor of the tertiary, indicating that attacking species are being stabilized. Furthermore, he was able to correlate the ratio of the yields of tertiary to primary chloride with the concentration of aromatic additive by the following equation:

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<sup>69</sup>G. A. Russell, ibid., 79, 2977 (1957).

$$5^{\circ}/1^{\circ} = k_1 + k_2 (\text{ArH}) + k_3 (\text{ArH})^2$$

This was taken as evidence that some of the hydrogen abstraction was done by uncomplexed chlorine atoms, some by chlorine atoms complexed with one molecule of aromatic compound, and some by chlorine atoms complexed with two molecules of aromatic compound. Others have postulated radical-solvent or radical-substrate complexes as possible explanations for certain facts, but their evidence is not as good as that just presented.

The present work provides some evidence pertaining to radical-solvent complexes. Table II gives some typical yields of carbon dioxide from decompositions of benzoyl peroxide in various aromatic solvents. It is seen that there is a slight variation in the yield of carbon dioxide in most cases with initial concentration of peroxide and with temperature, higher peroxide concentrations resulting in less carbon dioxide and higher temperatures resulting in more. Superimposed on these slight effects are much more pronounced differences from solvent to solvent, the yield of carbon dioxide decreasing as one reads down the table. The yields of carbon dioxide from the decomposition of benzoyl peroxide in durene, naphthalene, and  $\alpha$ -substituted naphthalenes are strikingly smaller than the yields in the aromatic compounds near the top of the table. Generally, the substrates which appear to be more reactive toward benzoyl peroxide are those

Table 11. Yields of carbon dioxide and benzoic acid from the decomposition of benzoyl peroxide in aromatic solvents

Solvent	T(°C)	P/S <sup>a</sup>	Carbon dioxide(%) <sup>b</sup>	Benzoic acid(%) <sup>b</sup>	Reference
Benzene	76	0.0110	136	42	9
	78	.0098	151	--	70
	78	.0147	149	--	70
	79.6	.0040	166	22	71
<u>tert</u> -Butylbenzene	80	.0037	155	42	71
	89	.0037	156	42	71
Toluene	75+2	.0556	120	79	72
Ethylbenzene	75+2	.0632	112	81	72
Cumene	75+2	.0626	111	78	72
Nitrobenzene	78	.0127	93	69	47
Mesitylene	100	.0127	99	73	47
	89	.0210	102	89	c
	89	.0525	99	88	c
Durene	89	.0508	33	127	c
	89	.1015	29	130	c
Naphthalene	100+5	.1015	62	100	c
	100	.0159	42	93	47
$\alpha$ -Bromonaphthalene	70	.0413	1	98	46
$\alpha$ -Chloronaphthalene	70	--	2	91	46
$\alpha$ -Nitronaphthalene	70	.0400	3	92	46

<sup>a</sup>The ratio of the number of moles of benzoyl peroxide to the number of moles of solvent used in the reaction.

<sup>b</sup>Yield of product based on the expectation of 1 mole of product from 1 mole of benzoyl peroxide.

<sup>c</sup>This work.

<sup>70</sup>J. H. McClure, R. E. Robertson, and A. C. Cuthbertson, Can. J. Research, **20B**, 105 (1942).

<sup>71</sup>p. F. Hartman, H. G. Sellers, and D. Turnbull, J. Am. Chem. Soc., **69**, 2416 (1947).

<sup>72</sup>R. L. Dannley and B. Zaremsky, ibid., **77**, 1588 (1955).



which result in the lower yields of carbon dioxide. A possible explanation for this observation is that the benzoyloxy radicals produced in the decomposition of benzoyl peroxide decompose relatively slowly and unimolecularly to yield phenyl radicals and carbon dioxide, and that the lifetimes of the free benzoyloxy radicals in the solutions vary in an inverse fashion with the reactivity of the solvent. If it is assumed that the radical-radical reactions in all the solvents occur at similar rates<sup>73</sup> and that benzoyloxy radicals do not decarboxylate at the time of their reaction with another molecule or radical, then the variations in the lifetime of the benzoyloxy radical (and hence the yield of carbon dioxide) must be due to variations among the various solvents in interactions unimolecular in radicals. Three types of such interactions may be easily envisioned. First, the benzoyloxy radicals might add to the aromatic systems of some of the solvents to produce sigma complexes, eventually leading to esters and other products, but probably not leading to benzoic acid as a direct product of a radical-radical reaction (in view of the extensive reorganization which would be required) unless a free benzoyloxy radical were also involved in the reaction. Second, the benzoyloxy radicals might abstract active hydrogen

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<sup>73</sup>The validity of this assumption is questionable. However, it is worthy of note that termination constants given by Flory<sup>62</sup> are similar for most monomers in vinyl polymerization.

atoms (such as benzylic hydrogen atoms) from the solvent in steps faster than the radical-radical reactions. Third, the benzoyloxy radicals might enter into loose pi complexes with the solvent, stabilizing them toward decarboxylation.

If the assumption stated above that sigma complexes do not lead to benzoic acid is true, then about 50% of the benzoyloxy radicals produced in the decomposition of benzoyl peroxide in  $\alpha$ -substituted naphthalenes must react as some other species, i.e., either as free benzoyloxy radicals or as benzoyloxy radicals pi complexed with the solvent. If they react as free benzoyloxy radicals, and if the assumptions that the rates of radical-radical reactions in these systems are all similar and that benzoyloxy radicals do not decarboxylate at the time of their reaction with some other species are true, then the benzoyloxy radicals which lead to benzoic acid in naphthalene must have lived at least as long as those produced in benzene.<sup>74</sup> But, this is inconsistent with the

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<sup>74</sup>This statement is subject to one assumption not mentioned above, that the rates of production of radicals from the peroxide in all the solvents are similar. Nozaki and Bartlett<sup>20</sup> have shown that the rate of decomposition of benzoyl peroxide in various solvents actually varies considerably. Most of this variation is due, however, to variations in the rate of the induced decomposition of the peroxide by radicals. The unimolecular rates of decomposition of benzoyl peroxide varies only slightly among a series of similar compounds. Since the destruction of peroxide in an induced step does not alter the concentration of radicals in the system (it produces one radical and destroys one), the fact that induced decomposition occurs has no bearing  
(Footnote continued on next page)

observed fact that extensive decarboxylation occurs in the decomposition of benzoyl peroxide in benzene.<sup>75</sup> Therefore it is most likely that the failure of benzoyloxy radicals to decarboxylate in  $\alpha$ -substituted naphthalenes (and to a lesser extent in naphthalene itself) is probably due to stabilization of these radicals through the formation of  $\pi$  complexes. This conclusion is, of course, subject to reservations with respect to the validity of the assumptions mentioned above.

The decomposition of benzoyl peroxide in durene might represent a case in which benzoyloxy radicals fail to extensively decarboxylate because their lifetimes are shortened due to a rapid reaction with the solvent to abstract benzylic hydrogen atoms. That such a reaction can actually occur is evidenced by the fact that bibenzyl or substituted bibenzyls are isolated from the decomposition of benzoyl peroxide in toluene, ethylbenzene, cumene, o-xylene,<sup>3</sup> p-xylene, mesitylene, and durene (present work). Eliel, Fang, and Wilen<sup>76</sup> have shown that there is a substantial isotope effect in the

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(Continued from last page) on the kinetic arguments presented here. However, it is possible that the benzoic acid in question may be in whole or part produced in the induced decomposition step.

<sup>75</sup>It is not likely that any large amount of products arise from "cage" reactions of radicals produced from benzoyl peroxide in benzene.<sup>50</sup>

<sup>76</sup>E. L. Eliel, F. T. Fang, and S. Wilen, Abstracts of Papers, 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 16-21, 1956, p. 17-Q.

production of bibenzyl from  $\alpha$ -deuterotoluene by reaction with benzoyl peroxide. This implies that the benzylic carbon-hydrogen bond has been stretched in the transition state of the reaction in which the hydrogen is removed, indicating that the reaction is probably unimolecular in radicals.

It should be noted that the yield of carbon dioxide from the decomposition of benzoyl peroxide in durene is smaller by a factor of three than that obtained when the reaction is carried out in mesitylene at the same temperature. Since durene has one more methyl group than mesitylene, it might be that the effect is merely a statistical one. This is unlikely, since comparison of the yields of carbon dioxide obtained in mesitylene and durene with those obtained in toluene show that the carbon dioxide produced in mesitylene is less than that produced in toluene by a factor of only 1.2, while the carbon dioxide produced in durene is less by a factor of four. More likely, some special interaction occurs in durene that does not occur in mesitylene. Two possibilities suggest themselves. First, the benzylic hydrogen atoms of durene could be particularly reactive because of stabilization of the benzyl type radical resulting from the abstraction of a hydrogen atom from a methyl group by hyperconjugative interactions with two of the other methyl groups. If this is the explanation, then the effect is a large one for interactions of this type. A second, and here favored, explanation is

that the benzoyloxy radicals are stabilized in durene more than in mesitylene by pi complexing with the solvent in the same fashion as postulated above for the interaction between benzoyloxy radicals and naphthalene. It is possible that pi complexes of this type can decompose to yield benzyl type radicals and benzoic acid. Although the arguments presented for stabilization of benzoyloxy radicals by pi complexing with naphthalenes and durene are by no means rigorous, the explanation is considered more satisfactory than the alternatives, especially in view of the known tendency for naphthalenes and durene<sup>77</sup> to enter into more stable molecular compounds than many simple aromatic compounds.

In an effort to distinguish between mechanisms such as that of Hammond and co-workers,<sup>6,7</sup> in which the rate determining step is bimolecular in radicals, and mechanisms such as those of Augood and Williams,<sup>1</sup> Rondestvedt and Blanchard,<sup>3</sup> and Lynch and Pausacker,<sup>9,10</sup> in which the rate determining step is unimolecular in radicals, the present work on the reaction of benzoyl peroxide with toluene was undertaken. The basis for the work is quite simple. Radicals apparently may react with either the nucleus or the side chain of toluene, leading respectively to methylbiphenyls and bibenzyl. In all probability the reaction of the radicals with the side

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<sup>77</sup>L. J. Andrews, Chem. Rev., 54, 713 (1954).

chain of toluene is unimolecular in radicals (see discussion above). Apparently both phenyl<sup>78</sup> and benzoyloxy (present work with durene) radicals can react with side chains of aromatic compounds to abstract  $\alpha$ -hydrogen atoms, while most of the substitution on the nucleus is by phenyl radicals. If the concentration of free radicals in the system is varied, then variations in the relative yields of bibenzyl and methylbiphenyls should result if the nuclear substitution reaction is second order in radicals and the side chain hydrogen abstraction first order. On the other hand, if both reactions are of the same order in radicals, no variation in the relative yields of these two products should be observed. It is not possible to predict the variation of steady state radical concentrations with concentration of radical source for short chain reactions such as the decomposition of benzoyl peroxide without detailed knowledge of the mechanism, but if the concentration of radical source tends toward infinite dilution, so must the concentrations of the radicals produced. Therefore it is to be expected that the yield of methylbiphenyls from the decomposition of a phenylating agent in toluene should decrease as the initial concentration of the radical source tends to infinite dilution if the substitution step is bimolecular in radicals and the side chain hydrogen

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<sup>78</sup>D. H. Hey, B. W. Pengilly, and G. H. Williams, J. Chem. Soc., 1463 (1956).

abstraction step is unimolecular. Mechanisms in which both the nuclear and side chain reactions are unimolecular in radicals (Augood and Williams) predict that the yield of methylbiphenyls will increase as the initial concentration of the radical source tends to infinite dilution if that source is benzoyl peroxide, for at lower concentrations more decarboxylation occurs, resulting in the availability of more phenyl radicals for substitution.

Since methylbiphenyls are quite difficult to isolate quantitatively from solution in aromatic solvents, it was decided to analyze for them by the method of isotopic dilution, using carbon-14 as the isotope. The procedure used and the method of calculation of the results are given in the Experimental section. Only p-methylbiphenyl was determined, the assumption being made that the isomer distribution for the phenylation of toluene does not change with concentration. Benzoyl peroxide 1-C<sup>14</sup> was chosen as the phenylating agent because it could be conveniently prepared from available materials, because it is easily purified and assayed, and because its mode of decomposition is well understood.

The results of the study are given in Table 4 (page 29). It is obvious that the first series of counts was made on materials that were grossly impure, as indicated by the melting points and the fact that purification led to decreases in the specific activities of the materials. It is

likewise obvious that run 12-A is far out of line with the other results and should be discarded. If the remaining analyses are examined, it is seen that the agreement obtained between duplicates is in most cases poor, the differences being as much as 20% of the larger one in some instances. Nevertheless, the yields are generally in good agreement with the values already in the literature, which were obtained by ordinary chemical and spectrophotometric methods. Table 12 gives these comparisons. The principal value of the present work, then, is the corroboration of the published values for the yields of p-methylbiphenyl and the establishment of a method for isolating the desired product from the reaction mixture in quantities and activities conveniently suitable for radioanalysis. Further refinement of the method of purifying the isolated material should increase the precision of the analysis.

Examination of the data of the present work presented in Table 12 shows that the data probably indicate that the yield of p-methylbiphenyl either remains constant or decreases with decreasing concentration. There is no indication that the yield increases with decreasing concentration, as demanded by mechanisms involving substitution steps unimolecular in radicals. The indication is, then, that such mechanisms are probably not correct. That this is so cannot be stated with certainty until the data are further refined and until the



Table 12. Yield of p-methylbiphenyl from the reaction of benzoyl peroxide with toluene

T(°C)	Conc. <sup>a</sup>	Y(%) <sup>b</sup>	Reference
75±2	5.2x10 <sup>-1</sup>	7.36	72
80	1.2x10 <sup>-1</sup>	6.38	79
80-110	4.7x10 <sup>-1</sup>	5.92	80
80	10 <sup>-1</sup>	8.10-10.5	c
80	10 <sup>-2</sup>	5.83- 6.19	c
80	3x10 <sup>-3</sup>	7.44	c
80	10 <sup>-3</sup>	6.17- 7.89	c

<sup>a</sup>Initial concentration of benzoyl peroxide in moles/liter.

<sup>b</sup>Yield of p-methylbiphenyl based on the expectation of obtaining 1 mole of product from 1 mole of benzoyl peroxide.

<sup>c</sup>This work.

data relative to the yields of bibenzyl in the reaction are available.

<sup>79</sup>D. H. Hey, B. W. Pengilly, and G. H. Williams, *ibid.*, 8 (1955).

<sup>80</sup>C. S. Rondestvedt and H. S. Blanchard, *J. Am. Chem. Soc.*, **77**, 1769 (1955).

## SUMMARY

The decomposition of benzoyl peroxide in durene and mesitylene has been studied, with emphasis on the yields of carbon dioxide and benzoic acid obtained. The yield of carbon dioxide from the reaction in durene is particularly low, while that from the reaction in mesitylene is not. These and other similar data are best explained in terms of weak interactions of the benzoyloxy radicals produced in the decomposition of benzoyl peroxide with the solvent ( $\pi$  complexing).

A mechanism for the free radical phenylation of aromatic compounds is presented which involves a rate determining step that is bimolecular in radicals. It is shown that this mechanism can account for the known facts about the reaction.

In an effort to demonstrate that the mechanism is the correct one, the yield of p-methylbiphenyl from the reaction of benzoyl peroxide with toluene at 80°C was studied as a function of the initial concentration of the peroxide, using the method of isotopic dilution. A procedure for isolating a derivative of p-methylbiphenyl from the reaction mixture in quantities and activities convenient for radioanalysis was developed. The values for the yields obtained agree well with those already in the literature, but are not of sufficient precision to allow interpretation in terms of a mechanism.

## ACKNOWLEDGMENTS

The author is indebted to a number of people and institutions that gave him assistance in his work.

The National Science Foundation awarded him predoctoral fellowships for the period September, 1954 to September, 1957.

The Department of Chemistry of Iowa State College provided him with funds for research.

Dr. George S. Hammond advised and encouraged him.

Dr. Fabian T. Fang set up much of the equipment used in the work and graciously allowed the author to perform some of the work in his laboratory.

Dr. A. Voigt permitted the author to do some of the radiochemical work in laboratories under his supervision.

Mr. Milo Voss gave advice and help pertaining to safety procedures, and lent the author a number of lead bricks.

Mr. W. Jones and his staff helped the author in many emergencies pertaining to the fabrication and repair of glassware.

Messrs. Wayne Rhinehart and Ray Prior willingly gave assistance with the electronic circuitry.

Mr. Ray Seymour and his staff built much of the equipment used.

Mr. Roy Dixon and his staff (especially Mr. George Walker) gave prompt supply service.

Mrs. Edna L. Garst, the author's wife, gave him

technical assistance, encouragement, and love.

The author is grateful.