

dark brown. Then, the mixture was poured into a mixture of 100 ml. of ether, 150 ml. of benzene and 150 ml. of water in a separatory funnel. After separation of the organic layer, the water layer was extracted with 100 ml. of an ether-benzene mixture. The combined organic extracts were thoroughly washed with dilute sulfuric acid and then water, sodium bicarbonate solution and water. Removal of solvent, followed by recrystallization of the residual crystalline material from *n*-pentane-benzene, gave 1,5-diphenylbicyclo[3.1.0]hexan-3-one in quantitative yield, colorless blocks, m.p. 135.0–135.5°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.72  $\mu$  (1748  $\text{cm}^{-1}$ ).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{16}\text{O}$ : C, 87.06; H, 6.50. Found: C, 87.18; H, 6.52.

**1,3,5-Triphenylbicyclo[3.1.0]hexan-3-ol (XV).**—To a solution of phenyllithium in 20 ml. of absolute ether, prepared from 0.148 g. of lithium metal and 1.28 g. of bromobenzene, 0.5 g. of 1,5-diphenylbicyclo[3.1.0]hexan-3-one in 25 ml. of anhydrous benzene and ether (1:2) was added dropwise at room temperature under nitrogen and with stirring. After heating at reflux for 2 hours, 20 ml. of water was added and organic layer was washed with water. Removal of the solvent and recrystallization of the resulting crystals from *n*-pentane-benzene or cyclohexane gave colorless crystals of 1,3,5-triphenylbicyclo[3.1.0]hexan-3-ol, m.p.

150.5–151.5° (the first crop of crystals, recrystallized twice from *n*-pentane-benzene, showed m.p. 102.5–103.5°, but after one more recrystallization it melted at 150.5–151.5°), yield 0.35 g. (53%),  $\lambda_{\text{max}}^{\text{CHCl}_3}$  2.75 (3636  $\text{cm}^{-1}$ ) and 2.89  $\mu$  (3460  $\text{cm}^{-1}$ ). In a subsequent run on larger scale a 76% yield of XV, m.p. 150–151.5°, was obtained.

*Anal.* Calcd. for  $\text{C}_{24}\text{H}_{22}\text{O}$ : C, 88.31; H, 6.79. Found: C, 88.49; H, 6.81.

The carbinol XV gave no color with 1% sulfuric acid in glacial acetic acid or with trifluoroacetic acid. With boron fluoride etherate a rose-red color developed immediately and a crystalline precipitate rapidly separated, m.p. 177.5–178.5° (43% yield), which was identified as 1,3,5-triphenylbenzene by m.p., infrared absorption, n.m.r. spectrum and elemental analysis. Reaction of the carbinol XV with thionyl chloride in ether at reflux for 1 hour also produced 1,3,5-triphenylbenzene. At higher concentrations of sulfuric acid in acetic acid, triphenylbenzene was formed rapidly. The carbinol could be recovered unchanged after treatment (in solution) with acetyl chloride (excess) in benzene at reflux for 40 minutes, conditions which convert triphenylcarbinol to the corresponding chloride.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.]

## Reactions of Benzyne Intermediates in Non-basic Media<sup>1</sup>

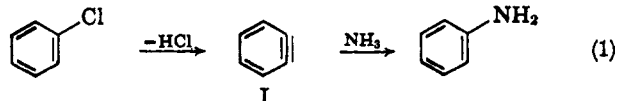
BY MARTIN STILES,<sup>2a</sup> ROY G. MILLER<sup>2b</sup> AND URS BURCKHARDT

RECEIVED JANUARY 14, 1963

Diazotization of anthranilic acid or variously substituted anthranilic acids leads to crystalline inner salts, the diazonium-2-carboxylates. Mild pyrolysis (35–60°) of these substances causes the elimination of nitrogen and carbon dioxide and formation of benzyne intermediates. The nature of the intermediates was revealed by trapping with furan, with anthracene, with carboxylic acids and with *tert*-butyl alcohol. The mixture of products obtained from each of the latter two reactions indicated that carbon atoms 1 and 2 of the inner salt III become equivalent during the reaction. Certain aspects of the mechanism of addition to the benzyne intermediate are discussed.

### Introduction

Evidence presented in 1953<sup>3</sup> established that the reaction of chlorobenzene with potassium amide in liquid ammonia was not a simple displacement reaction. The amino group in the product had become attached with nearly equal probability to the carbon atom which had borne the chlorine and to one of the *ortho* carbons. This discovery placed rigid requirements upon any attempt to write a mechanism for the reaction, and led Roberts<sup>3</sup> to propose, as the simplest explanation, that chlorobenzene first undergoes an elimination reaction to form benzyne (I). This intermediate resembled one which Wittig,<sup>4</sup> on the basis of very different evidence, had envisioned some years earlier, and it was almost simultaneously advanced<sup>5</sup> to account for the rearrangements which accompany the reaction of phenyllithium with fluoronaphthalenes and fluoroanisoles. Research activity on a broad front was stimulated by these startling proposals.



Several recent reviews<sup>6</sup> summarize research during the past decade which has defined the benzyne concept

more fully and greatly extended its scope. The use of reactive dienes to trap a  $\text{C}_6\text{H}_4$  fragment, generated from *o*-fluorobromobenzene and lithium amalgam, provided very satisfying evidence for the existence of benzyne.<sup>7</sup> Various alternatives to the elimination-addition mechanism for the reaction of eq. 1 have now been eliminated,<sup>8</sup> and the mechanism of the elimination step has been clarified by kinetic<sup>9</sup> and deuterium exchange studies.<sup>10</sup> Some progress has also been made in understanding the mechanism of the addition step.<sup>11</sup> Experiments with 9,10-phenanthryne and 1,2-naphthylene have suggested that these two substances are more stable than benzyne, as reflected by their greater discrimination between phenyllithium and lithium piperidide.<sup>12</sup> On the practical side, the benzyne concept has stimulated the development of new, potentially important methods for effecting cyclization to an aromatic ring under alkaline conditions.<sup>13,14</sup>

At the outset of the present research, benzyne was within the province of the metallo-organic chemist. The only reactions in which it had been discovered were those of aryl halides, ethers or sulfonates with

(6) (a) R. Huisgen, in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp. 36–87; (b) J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961); (c) G. Wittig, *Angew. Chem.*, **69**, 245 (1957); **74**, 479 (1962); (d) H. Heaney, *Chem. Rev.*, **62**, 81 (1962).

(7) G. Wittig and L. Pohmer, *Angew. Chem.*, **67**, 348 (1955); *Chem. Ber.*, **89**, 1334 (1956); for other papers on experiments of this type, see ref. 6.

(8) M. Panar and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3629 (1960).

(9) R. Huisgen and J. Sauer, *Ber.*, **92**, 192 (1959); R. Huisgen, W. Mack, K. Herbig, N. Ott and E. Anneser, *ibid.*, **93**, 412 (1960).

(10) J. D. Roberts, D. A. Semenov, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Am. Chem. Soc.*, **78**, 601 (1956).

(11) W. Mack and R. Huisgen, *Chem. Ber.*, **93**, 608 (1960).

(12) R. Huisgen, W. Mack and L. Möbius, *Tetrahedron*, **9**, 29 (1960).

(13) (a) R. Huisgen and H. König, *Angew. Chem.*, **69**, 268 (1957); *Chem. Ber.*, **92**, 203 (1959); (b) R. Huisgen, H. König and N. Blecker, *ibid.*, **92**, 424 (1959); (c) R. Huisgen, H. König and A. R. Lepley, *ibid.*, **93**, 1446 (1960); (d) H. König and R. Huisgen, *ibid.*, **92**, 429 (1959).

(14) B. F. Hrutford and J. F. Bunnett, *J. Am. Chem. Soc.*, **80**, 2021 (1958); J. F. Bunnett and B. F. Hrutford, *ibid.*, **83**, 1691 (1961).

(1) (a) A preliminary communication described some of the results reported here: M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, **82**, 3802 (1960). (b) Presented before the Division of Organic Chemistry, American Chemical Society National Meeting, Washington, D. C., March 29, 1962; Abstracts, p. 31-O. (c) Taken in part from the Ph.D. Thesis of R. G. Miller, University of Michigan, 1962. (d) This research was supported by a grant from the Petroleum Research Fund of the American Chemical Society.

(2) (a) Fellow of the Alfred P. Sloan Foundation. (b) E. C. Britton Fellow in Organic Chemistry (Dow Chemical Co.) 1960–1961; Minnesota Mining and Manufacturing Co. Fellow, 1961–1962.

(3) J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith and C. W. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953).

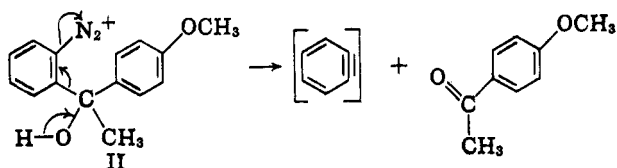
(4) G. Wittig, *Naturwissenschaften*, **30**, 696 (1942).

(5) R. Huisgen and H. Rist, *ibid.*, **41**, 358 (1954); *Ann.*, **594**, 137 (1955).

metallic bases sufficiently strong to cause metallation. Progress in assessing the chemical reactivity of benzyne, which might lead to a clearer picture of its electronic structure and to useful synthetic procedures, has been limited largely by the restrictions imposed by this severely alkaline environment.

In a search for other aromatic compounds which might yield benzyne under milder conditions, diazonium salts appeared worthy of consideration. The diazonium group is probably the most labile substituent known. However, the displacement reactions of diazonium salts have not been reported to occur with rearrangement of substituents on the benzene nucleus, which is diagnostic of the benzyne mechanism, and such reactions are adequately explained<sup>15</sup> in terms of radical or cationic intermediates, the reaction path depending upon *pH*,<sup>15c</sup> *inter alia*. Evidently the point of attack by a strong base upon benzenediazonium ion is at the terminal nitrogen, to form a diazotate, rather than at one of the *ortho* hydrogens.

In this connection, however, an observation by Sisti<sup>16</sup> was of interest. Compound II was found to decompose in acid solution to a mixture of products from which *p*-methoxyacetophenone could be isolated in low yield (as its dinitrophenylhydrazone). The possibility that this fragmentation process involved the elimination of benzyne prompted a search for other *ortho*-substituted diazonium salts which might exhibit this reactivity in greater degree.



Benzenediazonium-2-carboxylate (III), a compound described briefly by Hantzsch and Davidson,<sup>17</sup> was found to lose both nitrogen and carbon dioxide when pyrolyzed in certain media, and to yield products suggestive of benzyne formation. In this paper we describe experiments with III and with several substituted analogs. Emphasis here is on reactions with carboxylic acids and with *tert*-butyl alcohol, compounds not previously reported as reactive toward benzyne. The following paper describes the reaction of benzyne with aromatic hydrocarbons.

Since our preliminary report,<sup>1a</sup> other promising techniques for generating benzyne in non-alkaline media have been described.<sup>18-20</sup>

## Results

Benzenediazonium-2-carboxylate (III) crystallizes from ether-alcohol, containing a little water (*ca.* 5%), as light buff-colored, water-soluble, needles. The ultraviolet and infrared spectra, as well as the solubility properties, are in good agreement with the zwitterion formula III. The compound can be stored for several days in a desiccator at 0° without appreciable decomposition, and more or less indefinitely at -70°, but it darkens at room temperature during 24 hours and forms water-insoluble products. Aqueous solutions of the substance undergo rapid decomposition when warmed to produce a high yield of salicylic acid.

(15) (a) W. E. Bachmann and R. A. Hoffman, "Organic Reactions," Vol. 2, R. Adams, Ed., J. Wiley and Sons, Inc., New York, N. Y., 1944, p. 224; (b) C. S. Rondestvedt, *ibid.*, Vol. 11, p. 189; (c) D. F. DeTar, *ibid.*, Vol. 9, p. 412 ff.

(16) M. Stiles and A. J. Sisti, *J. Org. Chem.*, **26**, 3639 (1961).

(17) A. Hantzsch and W. B. Davidson, *Ber.*, **29**, 1535 (1896).

(18) G. Wittig and H. F. Ebel, *Angew. Chem.*, **72**, 564 (1960); *Ann.*, **650**, 20 (1961).

(19) G. Wittig and R. W. Hoffmann, *Angew. Chem.*, **73**, 435 (1961).

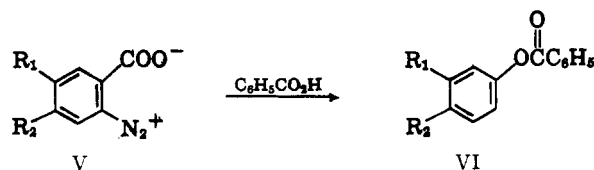
(20) E. LeGoff, *J. Am. Chem. Soc.*, **84**, 3786 (1962).

Refluxing a suspension of the inner salt in furan led to evolution of both nitrogen and carbon dioxide, and formation of 1,4-dihydronaphthalene-1,4-endoxide (IV). Similarly, decomposition of the salt in a benzene solution of anthracene yielded triptycene. Both of these dienes had been used previously by Wittig and his students to trap benzyne,<sup>7</sup> and these present results were tentatively interpreted<sup>1a</sup> as an indication that the diene had successfully intercepted benzyne, formed by the fragmentation of III. However, it was pointed out<sup>1a</sup> that this "trapping" experiment, in the absence of other information, could not be taken as proof of any particular intermediate. The critical question, which must be asked of any reaction for which a benzyne mechanism is proposed, is the symmetry question. Experiments were therefore undertaken to determine whether carbon atoms 1 and 2 become equivalent in the decomposition of the diazonium carboxylate III.



**Reaction of Benzyne with Carboxylic Acids.**—Suspensions of III in benzene decompose slowly in the temperature range 40–60° to furnish both nitrogen and carbon dioxide. Products can be isolated which result from attack upon the solvent.<sup>21</sup> However, benzene is sufficiently unreactive in this respect to allow its use as a medium for bringing other reagents into contact with diazonium carboxylate. Thus, decomposition of III in a benzene solution of benzoic acid produced phenyl benzoate (25%) as the major product, together with a smaller quantity of a hydrocarbon mixture from which biphenyl could be isolated, and polymeric material. *m*-Toluic acid reacted in similar fashion to produce phenyl *m*-toluate as the only ester.

For 4-iodoanthranilic acid and 5-iodoanthranilic acid the two isomeric diazonium carboxylates Va and Vb were prepared. Each compound was readily obtained as a pure crystalline substance, closely resembling III in physical properties. In parallel experiments each of these compounds was treated with benzoic acid in benzene solution to produce a mixture of *p*-(VIa) and *m*-(VIb) iodophenyl benzoates. The ratio of the two isomers (VIa/VIb) was the same (Table I), within the experimental error, from the two reactions. Each reaction also afforded an oily fraction from which *p*-iodobiphenyl could be isolated.



- a,  $R_1 = H, R_2 = I$   
 b,  $R_1 = I, R_2 = H$   
 c,  $R_1 = H, R_2 = F$   
 d,  $R_1 = H, R_2 = NO_2$

5-Fluorobenzenediazonium-2-carboxylate (Vc) and 5-nitrobenzenediazonium-2-carboxylate (Vd) were prepared in a similar manner. Each compound reacted with benzoic acid in benzene to yield a mixture of *m*- and *p*-substituted phenyl benzoates (Table I). In each case a less polar fraction was also obtained, and from the nitrobenzenediazonium carboxylate this fraction yielded both *m*- and *p*-nitrobiphenyl.

The results obtained with Va–Vd demand an interpretation in which the benzoate group becomes attached to C-1 or C-2 without regard for its previous substituent. Thus the deviation from a 50/50 *para*/

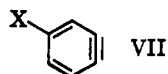
(21) R. G. Miller and M. Stiles, *ibid.*, **85**, 1798 (1963).

TABLE I  
ISOMER RATIOS IN THE ADDITION OF BENZOIC ACID AND *tert*-BUTYL ALCOHOL TO SUBSTITUTED BENZYNES

Subst. benzyne (VII)	Benzoates		<i>t</i> -Butyl ethers	
	Yield, %	<i>para/meta</i>	Yield, %	<i>para/meta</i>
X = I <sup>a</sup>	38	1.6 ± 0.2		
I <sup>b</sup>	34	1.5 ± .2		
F	25	3.5 ± .1		
NO <sub>2</sub>	16	3.8 ± .2	79	3.6 (3.0) <sup>c</sup>
H	25, 22 <sup>d</sup>	.....	20	.....

<sup>a</sup> Generated from Va. <sup>b</sup> Generated from Vb. <sup>c</sup> Value in parentheses obtained by infrared analysis; the higher value was obtained by ultraviolet analysis and is more accurate. <sup>d</sup> Using *p*-xylene instead of benzene as solvent.

*meta* product ratio must be due to the effect of the other ring substituent (I, F, NO<sub>2</sub>) rather than to any "memory" of the structure of the starting material. The intermediacy of a substituted benzyne (VII) is the only explanation for which any precedent exists.



A series of experiments was performed in which the diazonium carboxylate was allowed to decompose in the presence of two different carboxylic acids, each in large excess. The results (Table II) may suggest a slight preference for reaction with the stronger acid. However, the similarity of all of the product ratios and the lack of consistently good yields in these experiments argue against drawing any important conclusions from the data. One may merely note the absence of any great influence of polar substituents in the acid reactant, in contrast to the great influence of substituents in the benzyne reactant.

TABLE II  
COMPETITION BETWEEN BENZOIC ACID (A) AND A SUBSTITUTED BENZOIC ACID (B) FOR A LIMITED QUANTITY OF I

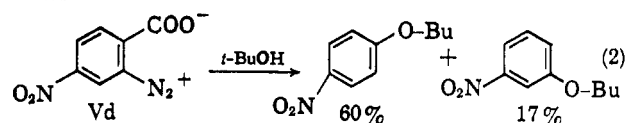
Competing acid (B)	Total esters, %	Ratio	B ester
			phenyl benzoate
<i>p</i> -Anisic	46	0.72	
<i>m</i> -Toluic	35	1.0	
<i>p</i> -Toluic	11	0.82	
<i>m</i> -Nitrobenzoic	11 <sup>a</sup>	1.2 <sup>a</sup>	
<i>p</i> -Nitrobenzoic	45	1.0	

<sup>a</sup> Only approximate; see Experimental.

**Reaction of Benzyne with *tert*-Butyl Alcohol.**—In the strongly basic systems previously used to generate benzyne, alcohols are present as metal alkoxides. In spite of their high basicity and their high nucleophilic reactivity toward many electrophiles, alkoxides are very unreactive toward benzyne. No phenyl *tert*-butyl ether could be found from the reaction of bromobenzene and potassium amide in the presence of potassium *tert*-butoxide.<sup>22</sup> Similarly, in a study of intramolecular additions to the benzyne function, alkoxides gave very poor results.<sup>13c</sup>

The generation of benzyne by the present method provided an opportunity for the examination of its behavior toward free alcohols. *tert*-Butyl alcohol was chosen in order to avoid reduction of the diazonium function, which primary and secondary alcohols could bring about. It also seemed likely that simple nucleophilic displacement of nitrogen by the alcohol oxygen would be minimized in the case of a tertiary alcohol.<sup>23</sup> The diazonium carboxylate proved moderately soluble in dry *tert*-butyl alcohol, and its decomposition

was considerably faster than that of a suspension in benzene. The products isolated were salicylic acid (9–12%) and phenyl *tert*-butyl ether (20%). The origin of the acid is not yet clear, but the ether is derived from benzyne, as the following experiment (eq. 2) shows.



The decomposition of 5-nitrobenzenediazonium-2-carboxylate (Vd) in *tert*-butyl alcohol led to a virtually quantitative yield of carbon dioxide and only a very small acidic fraction. A mixture of *m*- and *p*-nitrophenyl *tert*-butyl ethers was produced in 77% yield. In this case, at least, the alcohol function has proved very effective in intercepting the intermediate. Wittig and Hofmann<sup>19</sup> have recently reported equally good yields in the reaction of methanol with benzyne, generated by the diazotization of 2-aminobenzenesulfonic acid.

## Discussion

The results of experiments with substituted benzenediazonium-2-carboxylates (Table I) leave no doubt that the pyrolysis of this class of compounds yields an intermediate with the symmetry implied by structure I. Whether the intermediate is chemically identical with benzyne produced from organometallic precursors cannot be said with certainty,<sup>24</sup> but the few data at hand do not suggest that we are dealing here with a different species. Trapping experiments with furan and anthracene led to the same results reported by the earlier investigators.<sup>7</sup> Furthermore, the effect of polar substituents upon the direction of addition of acids and *tert*-butyl alcohol (Table I) is qualitatively in accord with expectations based upon earlier work.<sup>6a</sup> For the remainder of the discussion, therefore, no distinction will be made between arynes produced thermally from different precursors. Whether it will prove possible to extend these conclusions to benzyne produced photochemically<sup>18,25</sup> remains to be seen.

Mack and Huisgen<sup>11</sup> found that free piperidine was as reactive as lithium piperidide toward 9,10-phenanthryne. These authors attributed the effectiveness of the free amine to its ability to attack simultaneously both reactive centers of the aryne, forming a stable compound in one step. Although the present work has not furnished any rigorous evidence on this point, all of the results fit easily into this picture of the addition process. The reactivity of weakly basic carboxylic acids and alcohols toward benzyne may depend upon the presence of both nucleophilic and electrophilic centers in the reagent.

The factors affecting the position of attack on a substituted benzyne have been discussed.<sup>6a,26</sup> The inductive effect of a 3-substituent is of primary importance, but it has been suggested<sup>26</sup> that, in the case of a 4-substituent, conjugative effects may complicate the situation in an unpredictable way. The *para/meta* ratios in Table I are substantially greater than unity, as expected for benzyne with electron-withdrawing substituents. The ratio from the fluoro compound (3.5) is intermediate between that (4.0) reported for the addition of

(24) The hazards in assuming that the two classes of reactions produce identical, energy-rich, intermediates are perhaps best illustrated by the difficulties encountered in trying to predict the behavior of carbenes, carbonium ions or carbanions without regard for their source or their environment.

(25) R. S. Berry, G. N. Spokes and M. Stiles, *J. Am. Chem. Soc.*, **82**, 5240 (1960); **84**, 3570 (1962).

(26) J. D. Roberts, C. W. Vaughan, L. A. Carlsmith and D. A. Semenov, *ibid.*, **78**, 611 (1956).

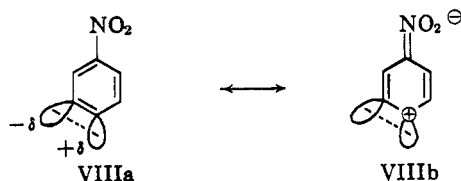
(22) F. Scardiglia and J. D. Roberts, *Tetrahedron*, **3**, 197 (1958).

(23) Subsequent experiments by R. G. Miller and A. Haag have confirmed that reduction and alcoholysis of the diazonium group are observed when methanolic solutions of the diazonium carboxylate III are heated.

potassium amide<sup>26</sup> and that (2.0) reported for the addition of lithium piperidide.<sup>6a</sup> The value for the iodo compound (1.5) is near that (1.4) reported for the addition of lithium piperidide to 4-bromobenzene.<sup>6a</sup>

The *para/meta* ratios in Table I do not correlate well with accepted measures of the inductive effect of substituents. On the basis of the Hammett *meta* substituent constants ( $\sigma_m$  values<sup>27</sup>: F = 0.34, I = 0.35, NO<sub>2</sub> = 0.71) or Taft's polar substituent constants ( $\sigma^*$ -values<sup>28</sup>: F = 1.10, I = 0.85, NO<sub>2</sub> = 1.40) the nitro group should be far more effective than the halogens. Instead, a 4-fluoro and a 4-nitro substituent have virtually the same influence, while a 4-iodo substituent is much less effective.

The usual orbital picture for benzyne<sup>6</sup> leads one to expect that the electrons in the "extra" bond, which are in orbitals orthogonal to the  $\pi$ -system of the ring, would be highly polarizable. The concerted addition of a reagent to benzyne, such as can be accomplished by a molecule having both nucleophilic and electrophilic centers, will be a very exothermic process, and it is appropriate to consider that the geometry and electron distribution in the transition state approximate those in the ground state molecules.<sup>29</sup> The direction of addition of an unsymmetrical reagent would then be governed by the relative electron density in the two  $sp^2$ -orbitals that constitute the highly polarizable "extra" bond. If this picture is accepted, then one must expect substituents in the ring to exert an electrical influence which is different from that observed in most reactions. The nitro group in 4-nitrobenzyne, for example, would decrease the *total* electron density in the vicinity of the *para* carbon atom as a result of both its inductive effect and its conjugative effect. However, the two effects will *oppose* one another as they relate to the "extra" bond, since it is polarized by the former effect in the direction indicated by VIIa, but this polarity tends to be reversed by the conjugative withdrawal of electrons from the orthogonal  $\pi$ -system at the *para* position (VIIb). The same considerations, when applied to



4-fluorobenzene, lead one to the conclusion that the inductive and conjugative effects in this molecule *reinforce* one another in respect to the polarity of the "extra" bond. Thus it may be that the effect of substituents upon the reactions of benzyne cannot be adequately described by measures of polarity which depend upon total charge at various ring positions.

### Experimental<sup>30</sup>

**Benzenediazonium-2-carboxylate (III).**<sup>17</sup>—A solution of 2.74 g. (0.0200 mole) of anthranilic acid in 30 ml. of absolute alcohol was cooled to 0° and treated with 2 ml. of concentrated hydrochloric acid. Cold isoamyl nitrite (5.0 ml., 0.038 mole) was added dropwise to the stirred solution at 0° during approximately 10 minutes. The color of the solution became deep orange as the nitrite was added and changed to a lighter orange near the end of the reaction. Addition of approximately 30 ml. of ether caused precipitation of the diazonium salt,<sup>30a</sup> which was collected and washed with more ether. The funnel containing the precipitate was then transferred to a clean filter flask, and the smallest con-

venient volume (ca. 5–10 ml.) of cold water was then added to the funnel to dissolve the diazonium salt. The aqueous solution was then stirred at 0° with 3 g. of powdered silver oxide for 2 hours. After removal of the solid by filtration, the solution was poured into a mixture of 100 ml. of absolute ethanol and 50 ml. of ether, previously cooled to 0°. Additional ether was added until the diazonium carboxylate began to crystallize. After 10–20 minutes standing at 0°, the product was collected, washed with cold ether, and dried over P<sub>2</sub>O<sub>5</sub> in an evacuated desiccator stored in the refrigerator. The yield of nearly colorless needles<sup>30a</sup> was 1.5–2.0 g. (50–68%). The compound dissolves completely in 2–3 volumes of cold water, and can be stored at 0° for several days without appreciable decomposition. After a few hours at room temperature it darkens and is no longer completely water-soluble; ultraviolet absorption:  $\lambda_{max}$  257 m $\mu$  (log  $\epsilon$  3.87) and 302 m $\mu$  (3.43); infrared peaks at 2283, 1652 and 1624 cm.<sup>-1</sup> (Nujol mull).

**Hydrolysis of Benzenediazonium-2-carboxylate.**—The inner salt III (0.598 g., 0.00404 mole) was dissolved in 25 ml. of water and kept at 35–45° for 36 hours. The needles which crystallized from the solution were fairly pure salicylic acid, 0.443 g. (80%), m.p. 156–159°. Extraction of the aqueous filtrate with ether afforded an additional 0.050 g. (8%), m.p. 150–155°. Recrystallization of the combined product from water raised the melting point to 157.5–159.0°, undepressed by authentic material. No phenol was found in this experiment.

**1,4-Dihydronaphthalene-1,4-endoxide.**—The diazonium carboxylate (III) (0.407 g., 0.00275 mole) was suspended in 35 ml. of dry furan and the mixture was stirred at reflux for 64 hours. A small amount of insoluble material was removed and the excess furan was distilled at reduced pressure. Sublimation of the residue provided 0.217 g. (55%) of the colorless adduct, m.p. 55.2–56.2° (reported<sup>7</sup> 56°).

Treatment of the adduct with methanolic hydrogen chloride as described previously<sup>7</sup> converted it to 1-naphthol in 81% yield.

**Triptycene.**—In 70 ml. of dry benzene, 1.2 g. (0.0067 mole) of anthracene and 0.614 g. (0.00414 mole) of benzenediazonium-2-carboxylate were mixed and stirred for 63 hours at 35–40°. After removal of solvent the dark residue was dissolved in 15 ml. of hot xylene and Wittig's method<sup>31</sup> for the separation of anthracene from triptycene was followed. Chromatography of the crude triptycene on alumina yielded colorless crystals in four consecutive fractions: (1) 0.129 g., m.p. 248–256°; (2) 0.131 g., m.p. 251–256°; (3) 0.059 g., m.p. 246–253°; and (4) 0.042 g. which melted below 245°. The fractions 1–3 (30%) were combined and recrystallized from cyclohexane to produce material, m.p. 254–256°, which was identical with a sample of triptycene prepared as described previously.<sup>31</sup> (We are indebted to Mr. Roger Kierstead for preparing the authentic material.)

**Substituted Benzenediazonium-2-carboxylates.**—The following compounds were prepared by the same procedure described above for the parent substance III. In all cases the yields were lower, but no attempt was made to change the procedure significantly. In some cases it was necessary to modify the quantities of various solvents to accommodate the different (generally lower) solubilities of these products and the diazonium chloride intermediates. All of the purified products decomposed violently in the flame.

**5-Iodobenzenediazonium-2-carboxylate (Va)** was prepared from 2-amino-4-iodobenzoic acid<sup>32</sup> in 10–15% yield. Infrared peaks occurred at 2290 and 1645 cm.<sup>-1</sup> (Nujol).

*Anal.* Calcd. for C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>I: C, 30.68; H, 1.10; N, 10.22. Found: C, 30.58; H, 1.28; N, 9.99.

**4-Iodobenzenediazonium-2-carboxylate (Vb)** was prepared from 2-amino-5-iodobenzoic acid<sup>33</sup> in 13–15% yield; infrared peaks at 2280, 1665 and 1641 cm.<sup>-1</sup> (Nujol).

*Anal.* Calcd. for C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>I: C, 30.68; H, 1.10; N, 10.22. Found: C, 30.67; H, 1.23; N, 10.10.

**5-Nitrobenzenediazonium-2-carboxylate (Vc)** was prepared in 16% yield from 2-amino-4-nitrobenzoic acid, which was obtained by the hydrolysis of 2-acetamido-4-nitrobenzoic acid (Aldrich). The infrared spectrum (Nujol) exhibited a sharp peak at 2310 cm.<sup>-1</sup> and broader peaks at 1645 and 1605 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>7</sub>H<sub>4</sub>N<sub>4</sub>O<sub>4</sub>: C, 43.53; H, 1.57; N, 21.76. Found: C, 43.83; H, 1.83; N, 21.51.

**5-Fluorobenzenediazonium-2-carboxylate (Vd)** was prepared in 47% yield from 2-amino-4-fluorobenzoic acid, prepared as described below. Sharp peaks in the infrared spectrum occurred at 2290, 1650 and 1625 cm.<sup>-1</sup> (Nujol).

*Anal.* Calcd. for C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>F: C, 50.61; H, 1.82; N, 16.87; F, 11.44. Found: C, 50.48; H, 2.07; N, 17.09; F, 11.17.

(31) G. Wittig, *Org. Syntheses*, **39**, 75 (1959).

(32) H. L. Wheeler and C. O. Johns, *Am. Chem. J.*, **44**, 441 (1910).

(33) V. H. Wallingford and P. A. Krueger, "Organic Syntheses," Coll. Vol. II, J. Wiley and Sons, Inc., New York, N. Y., 1943, p. 349.

(27) J. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(28) R. Taft, in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., J. Wiley and Sons, Inc., New York, N. Y., 1956, pp. 586–629.

(29) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(30) (a) CAUTION: Both the diazonium halides and the diazonium carboxylates are explosive substances which will detonate when solid samples are heated rapidly or scraped against a hard surface. (b) Microanalyses performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

**Reactions of Diazonium Carboxylates with Benzoic Acid.**—The indicated (below) amount of benzoic acid was dissolved in dry benzene and the dry crystalline diazonium carboxylate (III, Va-d) was added. The suspension was stirred at 50–55° until it was homogeneous and no further evolution of carbon dioxide could be detected. Unreacted benzoic acid was removed by extraction with 5% aqueous bicarbonate. The neutral fraction was then dried, freed from solvent, and chromatographed on silica gel (Davidson, untreated) or Florisil (in one case), using mixtures of benzene and petroleum ether (30–60°) as eluent. From the early eluates (benzene-petroleum ether ratios of less than unity) there was obtained hydrocarbon-like material, whose infrared spectrum indicated the absence of esters. In some cases (*vide infra*) biphenyls were crystallized from this early fraction.<sup>34</sup> In each case a later fraction from the chromatogram (benzene-petroleum ether ratios greater than unity) contained the aryl benzoates. The following paragraphs describe the resolution of individual reaction mixtures.

**Phenyl Benzoate.**—Several decompositions of benzenediazonium-2-carboxylate (III) in a 2% solution of benzoic acid in benzene (1.5–2.0 equivalents of acid) led to 50–65% yields of carbon dioxide. Chromatography of the neutral product on Florisil afforded phenyl benzoate, m.p. 68–70°, in 22–25% yields. Gas chromatography detected the presence of biphenyl in the hydrocarbon fraction. Phenyl benzoate was obtained in 22% yield when *p*-xylene was used as solvent in place of benzene.

***m*- and *p*-Iodophenyl Benzoates.**—From 0.24 g. (0.88 mmole) of 4-iodobenzenediazonium-2-carboxylate (Vb) and 2.0 g. of benzoic acid (16 mmoles) in 80 ml. of benzene there was obtained 0.030 g. (77%) of carbon dioxide, collected in Ascarite, during 16 hours. The ester fraction from silica gel chromatography (0.098 g., 34%) was identified by a gas chromatogram and infrared spectrum as a mixture of *m*- and *p*-iodophenyl benzoates. Pure *p*-iodophenyl benzoate, m.p. 119.2–120.0°, could be crystallized from the mixture. From the mother liquor the *meta* isomer could be obtained in a less pure condition, m.p. 65–69°, mixed m.p. 66–70°. Separation of the mixture by gas chromatography, using a wide variety of stationary phases, was incomplete. Quantitative analysis was accomplished by ultraviolet spectroscopy of alcohol solutions, using standard mixtures of the pure esters. Measurements of optical density at 230.0, 232.5, 235.0 and 240.0  $\mu$  indicated the composition  $40.7 \pm 3.0\%$  *meta* and  $59.3 \pm 3.0\%$  *para*.

From 5-iodobenzenediazonium-2-carboxylate (Va) (0.30 g., 1.1 mmoles) and 2.0 g. of benzoic acid (16 mmoles) in 95 ml. of benzene there was obtained 0.036 g. (75%) of carbon dioxide during 17 hours. The total ester material from chromatography was analyzed as described in the preceding paragraph and found to consist of  $38.2 \pm 3\%$  *meta* isomer and  $61.8 \pm 3\%$  *para* isomer. As before, the pure *para* isomer and less pure *meta* isomer could be obtained by fractional crystallization.

From both of the reaction mixtures described above it was possible to isolate, from the hydrocarbon-like fraction, *p*-iodobiphenyl, m.p. 113.0–114.5°.

***m*- and *p*-Fluorophenyl Benzoates.**—From 0.20 g. (1.2 mmoles) of 5-fluorobenzenediazonium-2-carboxylate (Vc) and 1.0 g. (8 mmoles) of benzoic acid in 75 ml. of benzene there was obtained, by silica-gel chromatography, 0.063 g. (24%) of an ester mixture. The mixture was only partially resolved by gas chromatography into two peaks, whose retention times were the same as those of *m*- and *p*-fluorophenyl benzoate. The quantitative analysis of the mixture was accomplished *via* infrared spectra of carbon disulfide solutions. Characteristic bands for the *meta* isomer were at 945 and 1123  $\text{cm}^{-1}$ , and for the *para* isomer, 810 and 1190  $\text{cm}^{-1}$ . Using the intensity ratio at 810 and 945  $\text{cm}^{-1}$  the ratio of *para* to *meta* was 3.49, with a total ester yield of 26.4%. A more dilute solution, utilizing the stronger peaks at 1123 and 1190  $\text{cm}^{-1}$ , yielded a ratio of 3.55, with a total ester yield of 24.6%. The infrared spectrum of the mixture was identical with a synthetic mixture prepared from pure samples.

A second reaction carried out under the same conditions was found to contain 29.5% of the mixture of fluorophenyl benzoates, determined by gas chromatography using naphthalene as internal standard. The yield of carbon dioxide in the reaction was 70%.

***m*- and *p*-Nitrophenyl Benzoates.**—From 0.20 g. (1.0 mmole) of 5-nitrobenzenediazonium-2-carboxylate (Vd) and 2.0 g. (16 mmoles) of benzoic acid in 79 ml. of benzene there was obtained an ester fraction, 0.048 g. (20%), the infrared spectrum of which indicated it to be a mixture of *m*- and *p*-nitrophenyl benzoates. Gas chromatography through a 15-ft. column of Silicone gum rubber on Chromosorb was programmed at 2.9°/min. from 150°. The two peaks corresponded in position to the authentic *meta* and *para* isomers, and the composition was 21% *meta*:79% *para*. There was some overlap between the two peaks; the most precise analysis was therefore obtained by preparing mixtures of the two isomers, of known composition in the region indicated, and care-

fully comparing the spectrograms with that of the unknown. The percentages obtained in this way are believed to be accurate to  $\pm 1\%$ . The total yield of esters determined from the chromatogram, using naphthalene as internal standard, was 16% (compared to 20% based on the weight of crude esters).

***m*- and *p*-Nitrobiphenyls.**—From the experiment described in the preceding paragraph a hydrocarbon-like fraction of 0.035 g. (18%) was obtained. Chromatography of this material on 30 g. of ordinary alumina, eluting with 1:3 benzene-petroleum ether (30–60°), led to two series of crystalline fractions separated by an oily fraction. Recrystallization of the crystalline fractions from ethanol yielded *m*-nitrobiphenyl, m.p. 57–59°, from the earlier series, and *p*-nitrobiphenyl, m.p. 112–114°, from the second series. Each sample gave an infrared spectrum which was identical with that of authentic material. Gas chromatography of the nitrobiphenyl mixture obtained from this experiment, using the 15-ft. column described above, indicated the composition to be 54% *meta* and 46% *para*. However, these percentages must be accepted with reservation, owing to the possibility that other isomeric substances, of a type known to be formed in analogous reactions,<sup>31</sup> may have failed to separate from the nitrobiphenyls.

**Reaction of Benzenediazonium-2-carboxylate (III) with *tert*-Butyl Alcohol.**—The diazonium carboxylate (0.815 g., 5.51 mmoles) was stirred at 60° in 20 ml. of dry *tert*-butyl alcohol for 1 hour, during which the theoretical quantity of nitrogen and 30% (1.67 mmoles) of carbon dioxide were evolved. The solution was diluted with ether, extracted successively with 2 *N* sodium bicarbonate, 2 *N* sodium carbonate and 2 *N* sodium hydroxide. From the bicarbonate extract 0.070 g. (9%) of salicylic acid was recovered, m.p. and mixed m.p. 155–157° after sublimation. No organic material was recovered from the sodium carbonate or hydroxide extractions. From the neutral ether layer phenyl *tert*-butyl ether could be recognized as the major product by gas chromatography.

In a second experiment, 0.609 g. (4.11 mmoles) of the diazonium carboxylate was decomposed during 40 min. at 50° in a mixture of 20 ml. of *tert*-butyl alcohol and 20 ml. of benzene. The yield of carbon dioxide was 2.68 mmoles (65%). Work-up as described above afforded 0.071 g. (12%) of salicylic acid and a neutral fraction composed of 0.825 mmole (20%) of phenyl *tert*-butyl ether and 0.101 mmole (2.5%) of biphenyl, determined by gas chromatography, using naphthalene as internal standard. Distillation at 70–78° (11 mm.) served to recover 0.062 g. (11%) of the ether, identical in infrared spectrum with a sample prepared as described previously.<sup>35</sup>

**Reaction of 5-Nitrobenzenediazonium-2-carboxylate (Vd) with *tert*-Butyl Alcohol.**—The diazonium carboxylate Vd (0.345 g., 1.79 mmoles) was stirred in 50 ml. of dry *tert*-butyl alcohol at 55–58° for 20 hours, during which 1.74 mmoles (97%) of nitrogen and 1.60 mmoles (89%) of carbon dioxide were collected. The solution was diluted with ether, extracted with 2 *N* sodium hydroxide, dried, and freed of solvent at room temperature. The alkaline extracts yielded 0.030 g. of acidic material which was not further characterized. The neutral fraction possessed an infrared spectrum indicative of *tert*-butyl nitrophenyl ethers. However, attempts to distill the mixture or to resolve it by gas chromatography led to considerable decomposition to nitrophenols and isobutylene. The analysis of the mixture was therefore accomplished by acid-catalyzed cleavage of the ethers to isobutylene and a mixture of *m*- and *p*-nitrophenol, which could be analyzed by means of ultraviolet spectrometry. Illustration of the application of this cleavage reaction to a pure sample of *p*-nitrophenyl *tert*-butyl ether is described in a later paragraph.

The neutral fraction remaining after sodium hydroxide extraction was refluxed in 60 ml. of benzene containing 12 mg. of *p*-toluenesulfonic acid for 2 hours. The solution was diluted with ether and extracted with 2 *N* sodium hydroxide until the extract was colorless. From the alkaline extract there was obtained, after acidification, 0.196 g. (79% based upon Vd) of a mixture of *m*- and *p*-nitrophenols. Quantitative ultraviolet analysis, using the intensities at 269 and 312  $\mu$ , indicated the mixture to contain 1.08 mmoles of *p*-nitrophenol and 0.298 mmole of *m*-nitrophenol the total yield being 77% based upon Vd. The mixture was also analyzed by infrared spectrometry, using the bands at 848 and 1114  $\text{cm}^{-1}$  for the *para* isomer and at 812 and 931  $\text{cm}^{-1}$  for the *meta* isomer. The total yield by this technique was 74%, with a *para/meta* ratio of 3.0. This analysis confirmed the absence of extraneous substances, but the *para/meta* ratio (3.62) obtained by ultraviolet analysis is believed to be more accurate.

***p*-Nitrophenyl *tert*-Butyl Ether.**—*p*-Nitrophenol (69.5 g.) was dissolved in 150 ml. of ether and, after the addition of 0.01 ml. of 75% sulfuric acid, isobutylene was bubbled into the stirred solution for 2 hours at 22°. After dilution with more ether the unreacted phenol was removed by extraction with 2 *N* sodium hydroxide. Distillation of the neutral layer yielded 3.2

(34) Characterization of the hydrocarbons produced in the reaction of benzenediazonium-2-carboxylate with benzene is reported elsewhere.<sup>31</sup>

(35) D. R. Stevens, *J. Org. Chem.*, **20**, 1232 (1955).

g. of *p*-nitrophenyl *tert*-butyl ether, b.p. 76–78° (0.2 mm.) reported<sup>36</sup> 97° (0.2 mm.).

**Cleavage of *p*-Nitrophenyl *tert*-Butyl Ether.**—The ether (0.282 g., 1.46 mmoles) and 8.3 mg. of *p*-toluenesulfonic acid were refluxed in 30 ml. of benzene for 80 min. Isolation of the phenolic product as described above furnished 0.197 g. (97%) of pure *p*-nitrophenol.

***p*-Fluorophenyl benzoate and *m*-fluorophenyl benzoate** were prepared for use as standards in infrared analysis. *p*-Fluorophenol (5.0 g.) and benzoyl chloride (5.8 g.) were dissolved with cooling in 10 ml. of pyridine. The mixture was refluxed for 15 min., cooled, and diluted with ether. After four extractions with 2 *N* sodium carbonate and four extractions with 2 *N* hydrochloric acid, the ether layer was dried and the solvent was removed. Three recrystallizations from petroleum ether, two from methanol, and still another from petroleum ether furnished the analytical sample, m.p. 58.2–58.7°;  $\lambda_{\max}$  232 m $\mu$  ( $\epsilon$  16,600), 263 (3,200), 270 (2,590) and 282 (shoulder) (1,080).

*Anal.* Calcd. for  $C_{13}H_9FO_2$ : C, 72.21; H, 4.20; F, 8.79. Found: C, 72.27; H, 4.26; F, 8.84.

The *meta* isomer was prepared in the same way and recrystallized four times from petroleum ether; m.p. 41.6–42.0°;  $\lambda_{\max}$  232 m $\mu$  ( $\epsilon$  17,200), 259 (shoulder) (3,480), 266 (3,030) and 282 (shoulder) (1,400).

*Anal.* Found: C, 72.23; H, 4.26; F, 8.96.

**4-Fluoro-2-nitrotoluene.**—4-Methyl-3-nitroaniline (68.4 g., 0.45 mole) was suspended in a solution of 94.2 ml. of concentrated hydrochloric acid and 135 ml. of water, cooled to 0°, and diazotized by the addition of 39 g. of sodium nitrite in 110 ml. of water. The resulting solution was filtered, and the filtrate was treated portionwise with 135 g. of 40% aqueous fluoboric acid while stirring at 0°. After stirring for a further 30 min. the crystalline diazonium fluoborate was collected, washed successively with cold water, cold methanol, and ether, and dried under vacuum. The dried material (103 g.) was placed in a flask fitted with a condenser and receiver and pyrolyzed until the evolution of boron trifluoride ceased. The material in the pyrolysis flask and receiver was then combined and steam distilled. The steam distillate was extracted into ether, washed with 5% sodium hydroxide, dried, and distilled to yield 29 g. (42%) of product, b.p. 88–89° (20 mm.).

**4-Fluoro-2-nitrobenzoic Acid.**—4-Fluoro-2-nitrotoluene (4.9 g., 0.032 mole) was oxidized by stirring at 75–80° for 12 hours in a solution of 14.5 g. of potassium permanganate and 10.3 g. of magnesium sulfate heptahydrate in 650 ml. of water. After removal of manganese dioxide and acidification there was obtained 3.0 g. (50%) of light yellow crystalline acid, m.p. 143–145° (reported<sup>37</sup> 145°).

**2-Amino-4-fluorobenzoic Acid.**—A solution of 3.0 g. (0.016 mole) of 4-fluoro-2-nitrobenzoic acid in 31 ml. of concentrated aqueous ammonia was treated with a solution of 19 g. of ferrous sulfate in 75 ml. of water. After stirring for 1.5 hours at room temperature and 30 min. on the steam-bath, the solution was filtered from ferric hydroxide and neutralized with sulfuric acid. Extraction of the product into ether and removal of the solvent left 0.94 g. (38%) of white crystalline material, m.p. 188–189° (reported<sup>38</sup> 192.5–193.0°).

**Competition Experiments.**—The diazonium carboxylate III was stirred with a large excess of an equimolar mixture of the two acids, dissolved in dry benzene. After the evolution of gases was complete, the homogeneous solution was extracted with sodium bicarbonate until the unreacted acids were removed. The dried organic layer was analyzed by gas chromatography, using a 4-ft. column of 20% Silicone gum rubber on Chromosorb, operated isothermally at 210°, and an ionization detector, operated at 1300 v. and 230°, and using argon (6.0 ml./min., 14

lb./sq. in.) as carrier gas. In each case the ratio of the two esters was established from integrated intensities, and a synthetic mixture of the pure esters was used to check the analytical procedure. The ester ratios and total yields are given in Table II. The standard deviation in the ester ratios determined by gas chromatography was 0.03–0.05. The following paragraphs contain additional details.

***p*-Anisic Acid and Benzoic Acid.**—From 0.50 g. (3.8 mmoles) of III, 4.88 g. (40.0 mmoles) of benzoic acid and 6.09 g. (40.0 mmoles) of *p*-anisic acid, in 600 ml. of benzene, there was obtained, after 9 hr. at 46°, a neutral product weighing 0.737 g. Chromatography on 50 g. of Florisil, using mixtures of benzene and petroleum ether (30–60°) as eluent, provided 0.215 g. of crude phenyl benzoate and 0.236 g. of crude phenyl *p*-anisate. Each ester was purified by further similar chromatography on 30 g. of Florisil, yielding 0.171 g. (0.86 mmole) of phenyl benzoate, m.p. 67–69°, and 0.204 g. (0.89 mmole) of phenyl *p*-anisate, m.p. 73–75°. A second experiment, carried out under closely similar conditions, was analyzed by gas chromatography, which indicated the ester mixture to be 58.2% phenyl benzoate and 41.8% phenyl *p*-anisate.

***m*-Toluic Acid and Benzoic Acid.**—From 0.545 g. (3.7 mmoles) of III, 0.488 g. (4.0 mmoles) of benzoic acid and 0.544 g. (4.0 mmoles) of *m*-toluic acid, in 50 ml. of benzene, after 18 hr. at 42°, there was obtained 0.101 g. (62%) of carbon dioxide. The neutral product was separated on Florisil into a hydrocarbon fraction (0.131 g.), from which biphenyl could be crystallized, and 0.263 g. of a mixture of esters. The ester mixture was revealed by gas chromatography to contain phenyl benzoate and phenyl *m*-toluate in a ratio of 1.00  $\pm$  0.04.

***p*-Toluic Acid and Benzoic Acid.**—From 0.567 g. (3.8 mmoles) of III, 4.88 g. (40.0 mmoles) of benzoic acid and 5.44 g. (40.0 mmoles) of *p*-toluic acid, in 100 ml. of benzene, after 3.5 hr. at 45°, there was obtained 0.057 g. (32%) of carbon dioxide. The neutral product was separated on Florisil to afford 0.052 g. of hydrocarbon material, from which biphenyl could be crystallized, and 0.087 g. of an ester mixture. Gas chromatography indicated the mixture to be 55.0% phenyl benzoate and 45.0% phenyl *p*-toluate.

***p*-Nitrobenzoic Acid and Benzoic Acid.**—From 0.11 g. (0.74 mmole) of I, 0.99 g. (8.1 mmoles) of benzoic acid and 1.35 g. (8.1 mmoles) of *p*-nitrobenzoic acid, in 800 ml. of benzene, after 3.5 hr at 63°, there was obtained 0.187 g. of neutral product which was chromatographed on 30 g. of silica gel. Elution with 1:2 benzene–petroleum ether (30–60°) furnished a small amount of hydrocarbon material; elution with a 9:1 mixture furnished 0.032 g. of phenyl benzoate and 0.042 g. of phenyl *p*-nitrobenzoate. Ultraviolet analysis of the ester fractions indicated 0.031 g. and 0.041 g. of the two esters, respectively. Pure samples of the two compounds, m.p. 70–71° and 125–127°, were obtained by recrystallization from ethanol. A second reaction carried out under the same conditions provided a neutral fraction which was analyzed by gas chromatography, which indicated 51% phenyl benzoate and 49% phenyl *p*-nitrobenzoate. This analysis was accomplished with a 15-ft. column of Silicone gum rubber on Chromosorb, with temperature programmed from 150° at 5.6° per minute.

***m*-Nitrobenzoic Acid and Benzoic Acid.**—From 0.45 g. (3.0 mmoles) of I, 4.44 g. (36.4 mmoles) of benzoic acid and 6.07 g. (36.4 mmoles) of *m*-nitrobenzoic acid, in 650 ml. of benzene, after 22 hr. at 46–49°, there was obtained a crude product weighing 0.541 g. Attempts to separate phenyl benzoate and phenyl *m*-nitrobenzoate by gas chromatography were unsuccessful. Column chromatography on Florisil separated 0.102 g. of hydrocarbon material from 0.035 g. (0.14 mmole) of phenyl benzoate and 0.033 g. (0.11 mmole) of phenyl *m*-nitrobenzoate. Experiments with pure phenyl *m*-nitrobenzoate indicated that only about 60% of it could be recovered from Florisil chromatography carried out in this way. The ester ratio must therefore be considered unreliable; correction for *m*-nitrobenzoate probably lost indicates that the ratio of *m*-nitrobenzoate to benzoate may be approximately 1.2.

(36) K. Bowden and P. N. Green, *J. Chem. Soc.*, 1795 (1954).

(37) B. E. Volkani, S. Sicher, E. D. Bergmann and H. Bendas, *J. Biol. Chem.*, **207**, 411 (1954).

(38) E. A. Steck and L. T. Fletcher, *J. Am. Chem. Soc.*, **70**, 439 (1948).