# 683. *Homolytic Aromatic Substitution. Part IV.* Partial Rate Factors for the Phenylation of Fluorobenzene, Bromobenzene, and Iodobenzene.*

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The rates of attack relative to nitrobenzene by phenyl radicals (generated from benzoyl peroxide) on fluorobenzene, bromobenzene, and iodobenzene have been measured, and from these measurements the rates of attack on these compounds relative to benzene have been calculated. The ratios of the *ortho*-, *meta*-, and *para*-isomerides formed in these reactions have also been measured, thus enabling partial rate factors to be calculated. The values obtained are discussed with reference to free valence numbers calculated by the molecular-orbital method.

The determination of partial rate factors for the homolytic phenylation of nitrobenzene and chlorobenzene was reported in Parts I, II, and III (Hey, Nechvatal, and Robinson, *J.*, 1951, 2982; Augood, Hey, and Williams, *J.*, 1952, 2094; *loc. cit.**), and these and other results were discussed by Hey and Williams (*Discuss. Faraday Soc.*, 1953, **14**, 216). In the present work the survey of homolytic aromatic substitution in the halogenobenzenes is completed by the determination of partial rate factors for the phenylation of fluorobenzene, bromobenzene, and iodobenzene.

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* Part III, *J.*, 1953, 44.

The phenylation of bromobenzene by means of the Gomberg reaction, with aryldiazoic acids, was studied in a qualitative manner by Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1924, **46**, 2339), who isolated 2- and 4-bromodiphenyls from the reaction between bromobenzene and diazotised aniline. The same orientation was observed with $MeO_2C{\cdot}C_6H_4{\cdot}$ radicals derived from methyl *p*-aminobenzoate and from methyl anthranilate by Heilbron, Hey, and Wilkinson (*J.*, 1938, 113), and with *p*-tolyl radicals derived from *p*-toluidine by Gomberg and Pernert (*J. Amer. Chem. Soc.*, 1926, **48**, 1372). Some *meta*-substitution was observed in bromobenzene by France, Heilbron, and Hey (*J.*, 1938, 1364), who used 4-diphenylyl radicals derived from 4-nitrosoacetamidodiphenyl. The arylation of fluorobenzene and iodobenzene has not been investigated. The proportions of isomerides isolated from these preparative experiments differ widely from those found in the present investigation, in which the mixtures of substituted diphenyls were analysed by infra-red spectroscopy. The reason for these discrepancies is that, as pointed out in Part III (*loc. cit.*), the 4-substituted diphenyls are less soluble and are higher-melting substances than the 2- and the 3-isomerides, and hence, in preparative experiments, are isolated preferentially, and losses of the 2- and 3-isomerides are very substantial. The results of Dannley (personal communication), however, who has measured by ultra-violet spectroscopy the proportion of isomerides obtained in the phenylation of bromobenzene, are in agreement with those reported in the present paper.

## EXPERIMENTAL METHODS AND RESULTS

*Direct Determination of* ${}^{\mathrm{PhF}}_{\mathrm{PhNO_2}}K$.—Benzoyl peroxide (6 g.) was allowed to decompose in an equimolar mixture (200 ml.) of nitrobenzene and fluorobenzene in a thermostat at 80° for 72 hr. The mixed product was isolated from the reaction mixture and analysed by estimation of the nitro-compound by titration with titanous chloride. The standard procedure described in Part II (*loc. cit.*) was employed. The results are given in Table 1. Fore-runs, *i.e.*, mixed fractions containing nitrobenzene and fluorodiphenyls, were collected separately from the diaryl fractions, so that the latter should not be contaminated with the last traces of nitrobenzene. The fore-runs were analysed for fluorine, and a correction in terms of fluorodiphenyls applied to the composition of the diaryl fraction. It may safely be assumed that the fore-runs contained no nitrodiphenyls, since these were found not to distil until a temperature 60° above that at which the fore-runs were collected had been reached.

TABLE 1.*

| Expt. No. | Diaryl fraction, g. | Nitro-diphenyl, % | Fore-run, g. | F (%) in fore-run | Correction $C_6H_4PhF$, mg. | Corr. wt. of diaryl fraction, g. | Nitro-diphenyl, % (corr.) | ${}^{\mathrm{PhF}}_{\mathrm{PhNO_2}}K$ | Benzoic, acid, g. | $(Ph{\cdot}CO_2)_2$ accounted for, % |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2·993 | 88·84 | 1·390 | 3·5 | 441 | 3·434 | 77·43 | 0·34 | 2·673 | 81·1 |
| 2 | 2·951 | 92·98 | 2·065 | 2·9 | 543 | 3·494 | 78·52 | 0·33 | 2·594 | 80·2 |

Hence, ${}^{\mathrm{PhF}}_{\mathrm{PhNO_2}}K = 0{\cdot}34$.

* Analyses for fluorine were carried out through the courtesy of Professor M. Stacey, F.R.S., of the University of Birmingham, to whom the authors express their thanks.

*Direct Determination of* ${}^{\mathrm{PhBr}}_{\mathrm{PhNO_2}}K$ *and* ${}^{\mathrm{PhI}}_{\mathrm{PhNO_2}}K$.—Experiments 3, 4, and 5 were carried out with benzoyl peroxide (6 g.) in an equimolar mixture (200 ml.) of bromobenzene and nitrobenzene, and experiments 6 and 7 with benzoyl peroxide (6 g.) in an equimolar mixture (200 ml.) of iodobenzene and nitrobenzene. The reactions were allowed to proceed in a thermostat at 80° for 72 hr. The isolation and analysis of the mixed products were carried out by the standard procedure described in Part II (*loc. cit.*), except that the fore-runs taken from experiments 6 and 7 were analysed for nitrobenzene by the titanous chloride method, corrections in terms of iododiphenyl being obtained by difference. The results are given in Tables 2 and 3.

*Determination of Ratios of Isomerides.*—The standard procedure outlined in Part II (*loc. cit.*) was used for the isolation of the diaryl fraction from the products of reactions 8—13. In the pairs of experiments 8 and 9, 10 and 11, 12 and 13, 200 ml. of fluoro-, bromo-, and iodo-benzene respectively were used, together with 6, 8, and 6 g. of benzoyl peroxide. All the reactions were allowed to proceed for 72 hr. in the thermostat at 80°.

For the infra-red spectrographic analysis of the mixtures of the 2-, 3-, and 4-halogenodiphenyls, a Grubb–Parsons instrument was used with an automatic pen recorder. In order to determine for each compound the range in which suitable absorption bands occur and so to enable a solvent to be chosen, the spectra of the three pure isomerides were measured. 2-, 3-, and 4-Fluorodiphenyl, 4-bromodiphenyl, and 4-iododiphenyl were used as crystalline powders in Nujol mulls, and 2- and 3-bromodiphenyl and 2- and 3-iododiphenyl, which were liquids, were used as capillary films between rock-salt plates. The frequencies of the absorption bands of the nine compounds investigated are given in Table 4.

TABLE 2.

| Expt. No. | Diaryl fraction, g. | Nitro-diphenyl, % | Fore-run, g. | Br (%) in fore-run | Correction $C_6H_4PhBr$, mg. | Corr. wt. of diaryl fraction, g. | Nitro-diphenyl, % (corr.) | ${}^{\text{PhBr}}_{\text{PhNO}_2}K$ | Benzoic acid, g. | $(Ph{\cdot}CO_2)_2$ accounted for, % |
|---|---|---|---|---|---|---|---|---|---|---|
| 3 | 3·915 | 67·24 | 0·325 | 1·96 | 19 | 3·934 | 66·92 | 0·422 | 2 73 | 83·0 |
| 4 | 3·800 | 69·42 | 1·738 | 5·4 | 274 | 4·074 | 64·75 | 0·465 | 2·80 | 85·4 |
| 5 | 3·963 | 68·18 | 0·875 | 3·61 | 92 | 4·055 | 66·63 | 0·428 | — | 84·8 |

Hence ${}^{\text{PhBr}}_{\text{PhNO}_2}K = 0{\cdot}44$.

TABLE 3.

| Expt. No. | Diaryl fraction, g. | Nitro-diphenyl, % | Fore-run, g. | $PhNO_2$ (%) in fore-run | Correction $C_6H_4PhI$, mg. | Corr. wt. of diaryl fraction, g. | Nitro-diphenyl, % (corr.) | ${}^{\text{PhI}}_{\text{PhNO}_2}K$ | Benzoic acid, g. | $(Ph{\cdot}CO_2)_2$ accounted for, % |
|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 3·447 | 62·64 | 0·698 | 96·72 | 23 | 3·470 | 62·22 | 0·432 | 3·52 | 89·5 |
| 7 | 3·436 | 61·08 | 0·453 | 91·39 | 39 | 3·475 | 60·39 | 0·466 | 3·49 | 88·8 |

Hence ${}^{\text{PhI}}_{\text{PhNO}_2}K = 0{\cdot}45$.

For all the 2-isomerides, the strong absorption band, which would otherwise be suitable for their estimation, lies very close to a band common to all three isomerides, and hence could not be used. The mixtures were therefore analysed for the 3- and the 4-isomerides only, and the amounts of the 2-isomerides obtained by difference. This procedure had already been adopted for the analysis of mixtures of 2-, 3-, and 4-chlorodiphenyls (Part III, *loc. cit.*). The bands which were used for these estimations were : for 3- and 4-fluorodiphenyl, 876·5 and 843·7 cm.$^{-1}$, for 3- and 4-bromodiphenyl 793·5 and 834·5 cm.$^{-1}$, and for 3- and 4-iododiphenyl 795·0 and 833·0 cm.$^{-1}$. Nitromethane was a suitable solvent for all the compounds, having no absorption bands in the region concerned. The determination is most accurate when absorption is between 50% and 65%. The concentrations of the solutions employed (in g./10 ml.), which absorbed radiation to this extent at the wave-lengths concerned, were as follows : 3-Fluorodiphenyl, 0·4012; 4-fluorodiphenyl, 0·3934; 3-bromodiphenyl, 1·4152; 4-bromodiphenyl, 0·6105; 3-iododiphenyl, 1·6023; 4-iododiphenyl, 0·2534. With the iododiphenyls the accuracy of the determination is diminished because of the relative insolubility of the 3- and 4-isomerides, *e.g.*, 0·2534 g. of 4-iododiphenyl in 10 ml. of nitromethane represents an almost saturated solution and it absorbs radiation to the extent of less than 50%. The amount of the 2-isomeride obtained by difference thus shows a cumulative error.

TABLE 4.

| Diphenyl | Absorption frequency, cm.$^{-1}$ | Diphenyl | Absorption frequency, cm.$^{-1}$ | Diphenyl | Absorption, frequency, cm.$^{-1}$ |
|---|---|---|---|---|---|
| 2-Fluoro- | 821·5, 774,* 760·3 * | 2-Bromo- | 768 *, 759 * | 2-Iodo- ... | 773,* 754 * |
| 3-Fluoro- | 876·5,* 766·3 * | 3-Bromo- | 884, 793·5,* 776·5,* 759 * | 3-Iodo- ... | 886·5, 795,* 759 * |
| 4-Fluoro- | 843·7,* 760 * | | | 4-Iodo- ... | 833,* 767,* 748 |
| | | 4-Bromo- | 834·5,* 764,* 750 | | |

* Strong absorption.

In order to check the accuracy of the determination, the spectra of test solutions containing known amounts of 2-, 3-, and 4-isomerides of the substituted diphenyls were recorded, and their compositions calculated by the method described in Part III (*loc. cit.*). Two such determinations were carried out for each set of isomerides, making six in all. The results were satisfactory in each case; *e.g.*, mixture (*b*) of fluorodiphenyls contained 41% of the 2-, 30% of the 3-, and 29% of the 4-isomeride, while spectrographic analysis gave 41, 31, and 28%, respectively.

The spectra of standard solutions in nitromethane of the diaryl fractions isolated from experiments 8—13 were then recorded, and the compositions of the mixtures calculated. The results are given in Table 5.

TABLE 5. *Analysis of products obtained in phenylation of fluorobenzene, bromobenzene, and iodobenzene.*

| Expt. No. | Compound | Composition, % 2- | 3- | 4- | Expt. No. | Compound | Composition, % 2- | 3- | 4- | Expt. No. | Compound | Composition, % 2- | 3- | 4- |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | PhF | 53·3 | 31·5 | 15·2 | 10 | PhBr | 49·7 | 33·0 | 17·3 | 12 | PhI | 51·5 | 31·7 | 16·8 |
| 9 | ,, | 54·9 | 30·0 | 15·1 | 11 | ,, | 48·9 | 33·7 | 17·4 | 13 | ,, | 51·9 | 31·5 | 16·6 |
|  | Mean | 54·1 | 30·7 | 15·2 |  | Mean | 49·3 | 33·3 | 17·4 |  | Mean | 51·7 | 31·6 | 16·7 |

*Reagents.*—Nitromethane (Light & Co.) was dried ($CaCl_2$), refluxed in a stream of nitrogen, refluxed over animal charcoal, and twice fractionally distilled through a 4-foot helix-packed column (b. p. 101°/760 mm.). Fluoro-, bromo-, and iodo-benzene (B.D.H.) were washed with concentrated sulphuric acid until the washings were colourless, then with aqueous sodium hydrogen carbonate, and finally with water. After drying ($CaCl_2$), they were twice fractionally distilled as above and had b. p. 85°/760 mm., 156°/760 mm., and 83°/20 mm., respectively. Specimens of 2-, 3-, and 4-fluorodiphenyl, kindly given by Mr. A. C. Littlejohn, to whom the authors express their thanks, were crystallised to constant m. p. from aqueous ethanol; m. p.s were 73·5°, 27°, and 74·5°, respectively.

2-Bromodiphenyl was prepared by a modification of Zaheer and Faseeh's method (*J. Indian Chem. Soc.*, 1944, **21**, 47), which involves diazotisation of 2-aminodiphenyl in hydrochloric acid and decomposition of the diazonium chloride with cuprous bromide. This was found to yield a mixture of 2-chloro- and 2-bromo-diphenyl. The following procedure, however, was satisfactory. A solution of 2-aminodiphenyl (12 g.) in hot constant-boiling hydrogen bromide (21 g., 3 equivs.) was diazotised at 5° with a solution of sodium nitrite (6 g.) in water (10 ml.). Excess of nitrous acid was removed at the end of the reaction by adding urea and stirring the mixture for 20 min. The diazotised solution was added dropwise to a solution of cuprous bromide (from 15 g. of copper sulphate) in constant-boiling hydrogen bromide (20 ml.) with vigorous stirring. The mixture was set aside for 20 min., after which the brown complex was decomposed by warming it on a steam-bath for 2 hr. The dark oil which separated was extracted with ether, and the extract filtered through glass-wool, washed with water, dilute sodium hydroxide, and water again, and dried ($CaCl_2$). Evaporation of the ether, and distillation, gave a pale yellow oil (7 g.), b. p. 146—152°/12 mm. This was dissolved in benzene, passed through alumina, and subsequently eluted with benzene. The solvent was removed and the product distilled under vacuum to give 2-bromodiphenyl as a colourless oil, b. p. 148—150°/10 mm., $n_D^{20}$ 1·6270.

3-Bromodiphenyl was prepared in 13% yield by means of a Gomberg reaction from diazotised *m*-bromoaniline and benzene (Marvel, Ginsberg, and Mueller, *J. Amer. Chem. Soc.*, 1939, **61**, 77). The crude product was redistilled, dissolved in benzene, passed through alumina, and subsequently eluted with benzene. After removal of the solvent the 3-bromodiphenyl was obtained as a colourless oil, b. p. 103°/0·2 mm., $n_D^{20}$ 1·6405.

4-Bromodiphenyl was prepared by Gomberg and Bachmann's method (*Org. Synth.*, **1**, 113) from diazotised *p*-bromoaniline and benzene. It was crystallised to constant m. p. (89·7°) from ethanol.

2-Iododiphenyl was prepared from 2-aminodiphenyl by diazotisation and treatment with potassium iodide (Zaheer and Faseeh, *loc. cit.*). The orange-coloured oil was twice fractionally distilled under vacuum, yielding a pale yellow liquid, b. p. 94—95°/0·07 mm., $n_D^{20}$ 1·6620.

3-Aminodiphenyl (23 g.), dissolved in 5·5N-hydrochloric acid (30 ml.), was diazotised with sodium nitrite (11·5 g.). After 30 min.' stirring to allow the reaction to become complete, a solution of potassium iodide (35 g.) in water (200 ml.) was added dropwise with stirring. Stirring was continued for 1 hr. in the cold and then for 1½ hr. on a steam-bath. The black oil which separated was extracted with ether, and the extract washed with sodium thiosulphate solution, water, sodium hydroxide (three times), and water (twice), and dried ($CaCl_2$). After removal of the ether, 3-iododiphenyl was distilled three times under vacuum and obtained as a colourless oil, b. p. 114·5°/0·3 mm., in 50% yield.

4-Iododiphenyl was prepared in a similar manner from 4-aminodiphenyl (B.D.H.). The crude product, which was obtained as a yellow solid in 70% yield from the distillation, was purified by dissolving it in benzene and shaking the solution with successive portions of concentrated sulphuric acid until the benzene layer was no longer coloured. This was then washed with aqueous sodium hydrogen carbonate, and with water. After removal of the solvent the product was crystallised to constant m. p. from ethanol, and gave 4-iododiphenyl in white plates, m. p. 113·8°.

Benzoyl peroxide (May & Baker) was purified according to the procedure described in Part II (*loc. cit.*).

## DISCUSSION

*Partial Rate Factors.*—The rates of phenylation of fluorobenzene, bromobenzene, and iodobenzene relative to that of benzene may be computed from the results of the determination of the rates of phenylation relative to that of nitrobenzene (Tables 1, 2, and 3), and the rate of phenylation of nitrobenzene relative to benzene, the determination of which was reported in Part II (*loc. cit.*). The values of ${}^{\mathrm{PhF}}_{\mathrm{PhH}}K$, ${}^{\mathrm{PhBr}}_{\mathrm{PhH}}K$, and ${}^{\mathrm{PhI}}_{\mathrm{PhH}}K$ so obtained, together with the mean values obtained by spectrographic analysis for the ratios of isomerides formed in the phenylation of fluoro-, bromo-, and iodo-benzene (Table 5), enable the calculation to be made of partial rate factors for the phenylation of these compounds. These values, together with the total rates of phenylation relative to benzene, are given in Table 6. The corresponding quantities relating to the phenylation of chlorobenzene, the determination of which was reported in Part III (*loc. cit.*), are included for comparison.

TABLE 6. *Partial rate factors for the phenylation of the halogenobenzenes.*

| Compound PhX | $F_o$ | $F_m$ | $F_p$ | ${}^{\mathrm{PhX}}_{\mathrm{PhH}}K$ | Compound PhX | $F_o$ | $F_m$ | $F_p$ | ${}^{\mathrm{PhX}}_{\mathrm{PhH}}K$ |
|---|---|---|---|---|---|---|---|---|---|
| Fluorobenzene ... | 2·20 | 1·25 | 1·20 | 1·35 | Bromobenzene ... | 2·59 | 1·75 | 1·83 | 1·75 |
| Chlorobenzene...... | 2·7 | 1·03 | 1·2 | 1·44 | Iodobenzene ...... | 2·79 | 1·70 | 1·80 | 1·80 |

It may be noted that in all four halogenobenzenes all the positions are activated towards attack by phenyl radicals, and that the activation is greatest in the *o*-position. The *amounts* of the isomerides formed vary in the order $o > m > p$ in all four compounds. In addition, the overall activation of the nucleus towards homolytic attack increases in the order PhF < PhCl < PhBr < PhI. This is in contrast with the results obtained in electrophilic substitution of halogenated aromatic hydrocarbons. It has been found, both for the nitration of the halogenobenzenes (Bird and Ingold, *J.*, 1938, 918) and for the bromination in the 4-position of the 1-halogenonaphthalenes (de la Mare and Robertson, *J.*, 1948, 100), that the chloro- and bromo-compounds react more slowly than either the corresponding fluoro- or iodo-derivatives. Thus, in ascending the series of the halogens, the rates of substitution pass through a minimum, and sequences of the type PhF > PhCl > PhBr < PhI are obtained. This is understandable, because both inductive electron *attraction* and tautomeric electron *repulsion* vary in the order F > Cl > Br > I. The fact that an undisturbed order is obtained for the rates of homolytic substitution in the halogenobenzenes therefore demonstrates that substitution of this type is not susceptible to electrostatic influences on the charge distributions in these molecules. It may also be noted that whereas the *meta*-positions of the halogenobenzenes are completely deactivated towards heterolytic halogenation and nitration, these positions are activated towards homolytic phenylation.

*Comparison with Theoretical Predictions.*—Atom localisation energies, from which partial rate factors may be calculated directly, have been calculated by Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 900) for chlorobenzene only. These were discussed in Part III (*loc. cit.*), where the surprisingly good agreement between them and the experimentally-determined partial rate factors was noted. No values of atom localisation energies are available for comparison with the partial rate factors for the other halogenobenzenes.

Free valence numbers, which are related to partial rate factors for homolytic substitution by the relation

$$\log F_r = 2x\beta(f_r - f_b)/2\cdot 303RT$$

(cf. Brown, *Quart. Reviews*, 1952, **6**, 63), where $F_r$ is the partial rate factor for homolytic substitution at the $r$th position of the molecule, $f_r$ is the free valence at that position, $f_b$ is the free valence at any position in benzene, and $x\beta$ is the change in the resonance integrals $\beta_{rm}$, $\beta_{rn}$---- brought about by the reagent. Since $x\beta$ is not known, partial rate factors cannot be calculated directly from free valence numbers, though qualitative comparisons can be made, since $\log F_r \propto f_r - f_b$. Sandorfy (*Bull. Soc. chim.*, 1949, **16**, 615) has calculated free valence numbers in molecules of the type $C_6H_5X$, using various values for the parameters $\alpha_X$ (the coulomb integral of the atom X), and $\beta_{C-X}$ (the resonance integral of the C–X bond). The calculations predict the activation of all three positions towards homolytic attack, and show that the *ortho*-position is expected to be the most reactive. The values chosen by Sandorfy for $\alpha_X$ and $\beta_{C-X}$ for fluorine, chlorine, bromine, and iodine lead to a small increase in the reactivity of the nucleus towards homolytic attack in the order $F < Cl < Br < I$, in agreement with the experimental determinations.

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