389. *Homolytic Aromatic Substitution. Part II.* Competitive Experiments on the Phenylation of Benzene, Nitrobenzene, Chlorobenzene, and Pyridine. Partial Rate Factors for Nitrobenzene.*

By D. R. Augood, D. H. Hey, and Gareth H. Williams.

Competitive experiments have been carried out on the action of phenyl radicals derived from benzoyl peroxide on all of the combinations in pairs of the four compounds, benzene, nitrobenzene, chlorobenzene, and pyridine. In this manner a series of rate ratios has been derived, which, coupled with the results reported in Part I on the orienting influence of the nitro-group in homolytic substitution, provides values for the partial rate factors for the phenylation of nitrobenzene at each nuclear position. The reaction with pyridine proceeds at approximately the same rate as does the reaction with benzene, the reaction with chlorobenzene about 1·3 times faster, and that with nitrobenzene about four times as fast. The implications of these results are discussed.

(I) *Introduction.*

(I. 1) *Aims and Scope of the Work.*—The determination of the ratio of isomerides produced when nitrobenzene is attacked by aryl radicals (phenyl, *p*-tolyl, and *p*-bromophenyl) was reported in Part I.* A complete knowledge of the influence of any atom or group on the substitution reactions of an aromatic structure in which this atom or group is present involves a knowledge, not only of the so-called directing influence of that atom or group, *i.e.*, the ratio of isomerides produced, but also of its activating or deactivating influence. Any investigation of directing influences should logically, therefore, involve a parallel

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* Part I, Hey, Nechvatal, and Robinson, *J.*, 1951, 2892.

investigation of activating or deactivating influences. In this manner the influence of a substituent atom or group on the homolytic substitution process may be completely specified in terms of " partial rate factors," a concept introduced in 1927 in a study of heterolytic aromatic substitution by Ingold and Shaw (*J.*, 1927, 2918; see also Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959), who pointed out (see also Ingold and Smith, *J.*, 1938, 905; Bird and Ingold, *J.*, 1938, 918) that two lines of approach to such a problem are possible, namely, the direct measurement of the velocity constants for attack on the substituted and unsubstituted compounds, and the competitive method, whereby the ratio of the velocity constants for attack on two compounds is obtained by analysis of the mixed product obtained when a mixture of the two compounds of known composition is allowed to react, in homogeneous solution, with a limited quantity of the substituting agent. The ratio of the velocity constants is equal to the ratio of the amounts of the two products formed from an equimolar mixture of the two components, provided that two conditions are satisfied. First, the excess of the two components over the attacking reagent must be sufficiently large so that the molar composition of the mixture is not appreciably disturbed by the unequal rates of disappearance of the two components : it is possible (Ingold and Shaw, *loc. cit.*) to make a correction for this factor in the calculation of the rate ratio, but such a correction is unnecessary if a sufficient excess of the two components is employed. Secondly, the reactions leading to the formation of the two products must be of the same kinetic order. This is the basis of Wegscheider's test for simultaneous side reactions of the same order.

The direct kinetic approach is possible only when, of the various reaction stages, the one in which the actual substitution is effected is very much slower than any other, *i.e.*, when this stage is rate-determining. This is not so in any of the reactions leading to the production of aryl radicals, which have so far been studied kinetically. The decomposition of benzoyl peroxide has been the subject of a number of kinetic investigations (Brown, *J. Amer. Chem. Soc.*, 1940, **62**, 2657; 1948, **70**, 1208; Cuthbertson, McClure, and Robertson, *Canad. J. Res.*, 1942, **20**, *B*, 103; Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686; 1947, **69**, 2299; Cass, *ibid.*, 1946, **68**, 1976; Hartman, Sellers, and Turnbull, *ibid.*, 1947, **69**, 2416; Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216), which indicate that the homolytic fission of the central O–O bond, leading to the formation of two benzoyloxy-radicals, is the rate-determining stage, although the kinetics are complicated by various side-reactions. The decomposition of acylarylnitrosamines has also been studied by several groups of workers (Grieve and Hey, *J.*, 1934, 1797; 1935, 689; Butterworth and Hey, *J.*, 1938, 116; Haworth and Hey, *J.*, 1940, 361; Hey, Stuart-Webb, and Williams, *Research*, 1951, **4**, 385; Huisgen and Horeld, *Annalen*, 1949, **562**, 137; Huisgen, *ibid.*, 1951, **573**, 163; Huisgen and Nakaten, *ibid.*, p. 181; DeTar, *J. Amer. Chem. Soc.*, 1951, **73**, 1446), and in this case it appears that the rate-determining stage is the cationotropic rearrangement of the acylarylnitrosamine to its corresponding diazoacetate, itself a heterolytic reaction. Of other reactions which lead to the production of aryl radicals one, the decomposition of arylazotriarylmethanes, has not been studied kinetically, although such a study is feasible; while the decomposition reactions of the diazoic acids and of the 3 : 3-dialkyl-1-aryltriazens are conducted in a two-phase system and, hence, are not suitable for kinetic study.

In cases where direct kinetic data have not been available, the competitive method has in the past been used with conspicuous success (Ingold and Shaw, *loc. cit.*, and *J.*, 1949, 575; Ingold, Lapworth, Rothstein, and Ward, *loc. cit.*; Ingold and Smith, *loc. cit.*; Bird and Ingold, *loc. cit.*; Bordwell and Rohde, *J. Amer. Chem. Soc.*, 1948, **70**, 1191). Moreover, when the direct kinetic data have subsequently become available, the agreement between the results obtained by the two methods has been very satisfactory (Hughes, Ingold, and Reed, *J.*, 1950, 2400, and subsequent papers). In view of the difficulties mentioned above, it is apparent that the only satisfactory method of obtaining information concerning relative rates of attack by aryl radicals is by the use of the competitive method.

Five reactions which may be used as sources of phenyl radicals have been surveyed in Part I (*loc. cit.*). Of these, two (the triazen reactions and the diazoic acid decomposition, generally referred to as the Gomberg reaction) are conducted in two-phase systems, and their behaviour will therefore be governed partly by purely mechanical factors, such as rates of stirring, which are not capable of exact specification. The decomposition of arylazotriarylmethanes is not suitable, because in certain cases (*e.g.*, with nitrobenzene itself) anomalous results are obtained (Hey, *J.*, 1934, 1966), which are thought to be due to the presence in solution of the stable triphenylmethyl radical. The decomposition of acylarylnitrosamines, while giving rise to almost quantitative yields of nitrogen, gives yields of the diaryl which rarely exceed 50% (cf. Bachmann and Hoffman, " Organic Reactions," John Wiley & Sons, New York, 1944, Vol. II, pp. 253 *et seq.*). Thus the fate of more than half of the phenyl radicals is unknown, and a large uncertainty is introduced into any quantities derived from product analyses. Competitive reactions have, however, been performed by Huisgen and Sorge (private communication), using this source of phenyl radicals. Comparison of their results with those reported in the present communication, and in the present authors' preliminary publication (*Research*, 1951, **4**, 386), reveals a high measure of agreement.

Consideration of the difficulties mentioned above led to the choice of benzoyl peroxide as the source of the phenyl radical in the reactions now described. The yields reported in preparative experiments are, in general, much higher for this reaction than for the others mentioned, and in the present work it has frequently been found possible to account for 85—90% of the reagent as identified products.

It is proposed to extend this work to include other aryl radicals, such as tolyl, bromophenyl, and nitrophenyl. It is also intended to carry out competitive experiments with other sources of aryl radicals, although any results obtained in this way are of necessity less reliable and should be regarded only as supplementary to those obtained with the benzoyl peroxides.

(I. 2) *General Methods.*—The four compounds, benzene, nitrobenzene, chlorobenzene, and pyridine, were taken in pairs and allowed to compete for phenyl radicals. The analytical problem involves an estimation of the proportions in which the two binuclear products are formed. The fraction of the product containing the diphenyl and substituted diphenyls was, in most cases, capable of quantitative isolation by careful distillation of the mixture, provided that certain unwanted products (benzoic acid and aryl benzoates) were removed before distillation. This was accomplished by saponification with aqueous alkali, followed by extraction with benzene. The analysis of the mixture of diaryls is facilitated if one of the components of the solvent mixture is nitrobenzene, since it was found possible to determine the nitrodiphenyls in these products accurately by titration with titanous chloride. Thus the rate of attack of phenyl radicals on a compound PhX compared with the rate of attack on nitrobenzene, the quantity designated as ${}^{\mathrm{PhX}}_{\mathrm{Ph\cdot NO_2}}K$, could generally be determined. The activating, or deactivating, influence of the group X, however, is expressed by the quantity ${}^{\mathrm{PhX}}_{\mathrm{PhH}}K$, the rate of attack on PhX compared with the rate of attack on benzene. This quantity can be determined provided that the influence of the nitro-group, *i.e.*, the quantity ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$, is known. Thus

$${}^{\mathrm{PhX}}_{\mathrm{PhH}}K = {}^{\mathrm{PhX}}_{\mathrm{Ph\cdot NO_2}}K \times {}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$$

Competitive experiments designed to determine ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$ directly proved, however, unsatisfactory, because the difference in boiling point between diphenyl and nitrobenzene was too small to allow a complete separation of these two fractions to be made by distillation. Some diphenyl was inevitably lost at this stage, leading to high values for the rate-ratio ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$. The results of these experiments, in which steps were taken with varying degrees of success to prevent the loss of diphenyl, are quoted in Section (II. 3) and provide a *maximum* value for ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$.

Two indirect determinations of ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$ were made. In the first, chlorobenzene was used as the intermediate compound, *i.e.*, ${}^{\mathrm{PhCl}}_{\mathrm{PhH}}K$ and ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhCl}}K$ were measured; and in the second, pyridine was used in place of chlorobenzene. The quantity ${}^{\mathrm{PhCl}}_{\mathrm{PhH}}K$ was determined by isolating the mixed diaryl fraction, and analysing it by means of a micro-Carius determination of chlorine. ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhCl}}K$ was determined in a similar manner, but in this case the Carius estimation was confirmed by a titanous chloride titration. The experiments with pyridine involved separation of the mixture before distillation into neutral and basic fractions by acid extraction. These two fractions were distilled and weighed. The agreement between the results obtained by the two methods is good, and provides a value for ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$ which is sufficiently accurate to allow the use of nitrobenzene as a sub-standard in other competitive experiments.

(II) *Experimental Methods and Results.*

(II. 1) *Saponification.*—Synthetic mixtures containing known quantities of benzoic acid, *p*-nitrophenyl benzoate, and phenyl benzoate, in addition to diphenyl, nitrodiphenyls, *p*-diphenylbenzene, and nitrobenzene, were refluxed with 100 ml. of aqueous sodium hydroxide of various strengths for 24 hours. The unsaponified material was extracted with benzene, and the aqueous portion titrated against standard hydrochloric acid, with phenolphthalein as indicator. A blank control solution was similarly treated. The proportion of the sodium phenoxide (and nitrophenoxide) which is titrated under these conditions can be calculated from the acid dissociation constants of phenol and *p*-nitrophenol, and a correction applied to the results. The percentage of the esters which has been saponified can then be calculated. It was found that the esters were saponified quantitatively by 1·5—2N-aqueous sodium hydroxide on refluxing for 24 hours. This procedure was therefore adopted in the competitive experiments.

(II. 2) *Analytical Methods.*—For the estimation of the nitrodiphenyls, Kolthoff and Robinson's method (*Rec. Trav. chim.*, 1926, **45**, 169) was used with some modifications. This method involves the reduction by titanous chloride of the solution of the nitro-compounds buffered to pH 5·9 by the addition of trisodium citrate. The buffer is then destroyed by the addition of concentrated hydrochloric acid, and the excess of titanous chloride is estimated by titration with ferric alum, ammonium thiocyanate being used as indicator. The whole operation is conducted in an atmosphere of carbon dioxide. Titanous chloride ($\sim$ N/20) was stored in an automatic burette under hydrogen. Ferric alum ($\sim$ N/30) was similarly stored under carbon dioxide. The solutions were standardised against *p*-nitroaniline in acetone solution.

By the titration of solutions prepared to simulate the solutions that would be obtained from competitive experiments, the following procedure was evolved, which was used in all estimations and standardisation : 30 ml. of aqueous trisodium citrate (20% w/v solution, containing 1% of sodium hydrogen carbonate) were placed in the titration flask, and to it were added acetone (10 ml.) and the acetone solution (20 ml.) containing the nitro-compounds. The mixture was saturated with carbon dioxide by passage of the gas for 25 minutes. The titanous chloride solution (20 ml.) was then added from the burette, the mixture being shaken during the addition. The mixture was kept at room temperature for 10 minutes while reduction took place, at the end of which time the brownish-green colour of the titanous chloride–sodium citrate complex which is formed at this pH had faded. Concentrated hydrochloric acid (20 ml.) was added to destroy the buffer, and the solution was then pale violet in colour. Ferric alum was added from the burette until the colour was discharged, whereupon ammonium thiocyanate (5 ml.; 10%) was added. The titration was continued until a permanent pink colour denoted the end-point. Approximately 0·05N-titanous chloride was employed, and the concentration of the nitro-compounds was adjusted so that 20 ml. of this solution provided a convenient excess for back-titration. The solution was made up from 100 ml. of 13% titanous chloride solution (May & Baker) by dilution with 75 ml. of hydrochloric acid and 1500 ml. of water. The ($\sim$ N/30) ferric alum solution was prepared by dissolving " AnalaR " reagent (42 g.) in water (2500 ml.) to which had been added sulphuric acid (245 g.; 136 ml.).

Two methods were investigated for the estimation of the chlorodiphenyls (Schwenk, Papa, and Ginsberg, *Ind. Eng. Chem. Anal.*, 1943, **15**, 576; Bird and Ingold, *loc. cit.*), but neither yielded satisfactory results. Finally, micro-Carius estimations (by Messrs. Weiler and Strauss) were used.

(II. 3) *Direct Determination of* ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$.—In all the competitive experiments reported in this paper (unless otherwise stated) benzoyl peroxide (6 g.) was allowed to decompose in an equimolar mixture (200 ml.) of the two components kept at 80° in a thermostat for 72 hours. The reaction vessels were 250-ml. flasks with ground-glass joints, to which were fitted Liebig condensers and calcium chloride guard-tubes. The nitrobenzene–benzene runs were worked up according to the following procedure : (i) When the reaction was complete, the benzene and nitrobenzene fractions were removed by distillation through a 25-cm. helix-packed column, the jacket of which was electrically heated. (ii) The benzene was returned to the flask, and the dark red mixture poured through a short alumina column. By this means much of the tar was removed. The benzene was then removed from the eluate by distillation. (iii) The residual 10—15 ml. of mixture were then subjected to the saponification procedure described in Section (II. 1). (iv) The mixture was thoroughly extracted with benzene and the extracts were dried over calcium chloride for 12 hours. (v) The remaining tarry material was removed by pouring the mixture through a 15-cm. alumina column. Benzene washings of the calcium chloride used in (iv) were used as eluent, and elution was completed with benzene containing a little ether. (vi) Solvents were removed by distillation through the small column mentioned above, and the residue was quantitatively transferred (benzene being used as wash-liquid) to the small fractionation apparatus shown in Fig. 1, where the bulk of the residual nitrobenzene was removed at about 15 mm. The 5—8 ml. of mixture remaining were transferred to the small distillation apparatus (Fig. 2), and the benzene used in the transference carefully removed. The pressure was lowered to 0·1 mm. and two fractions were taken off. The first consisted of nitrobenzene, and the second of diphenyl and nitrodiphenyls. It was at this stage that errors were incurred due to loss of diphenyl in the nitrobenzene fraction [cf. Section (I. 2)].

FIG. 2.

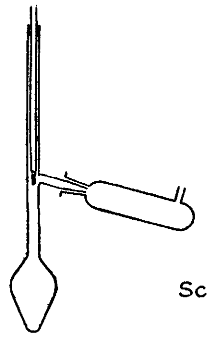
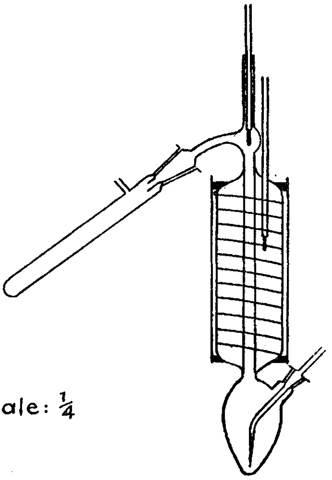


FIG. 1.



(vii) A weighed portion of the diphenyl–nitrodiphenyl fraction was made up to the required strength with acetone, and estimated by the procedure recorded in Section (II. 2).

The results of four such determinations are summarised below. In Expt. 1, stage (ii) in the working-up was omitted. In Expt. 11, the benzoic acid was recovered and weighed and, from this datum, it is possible to calculate that 73·6% of the benzoyl peroxide is accounted for in weighed products. This is a lower percentage than that obtained in most of the later experiments and may be due, at least in part, caused by the loss of diphenyl mentioned above.

Expt. no.	Wt. of diaryl fraction(g.)	Nitrodiphenyl, %	${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$	Expt. no.	Wt. of diaryl fraction (g.)	Nitrodiphenyl, %	${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$
1	2·40	93·73	11·57	3	2·80	87·06	5·21
2	2·64	96·78	23·27	11	2·85	84·35	4·17

Hence, ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K \not< 4{\cdot}17$.

(II. 4) *Direct Determination of* ${}^{\mathrm{PhCl}}_{\mathrm{PhH}}K$.—Expts. 14 and 15 were carried out with an equimolar mixture of benzene and chlorobenzene and were worked up according to the procedure described in Section (II. 3), with the following modifications, which were subsequently employed in all cases : (*a*) Stage (ii) was omitted, and the extraction (Stage iv) was carried out from hot solution. (*b*) The final traces of solvent obtained from the distillation (Stage vi) (the " forerun ") were retained, and analysed for the more volatile diphenyl. A correction was then made to the rate-ratio, if this proved necessary. A very small amount (50 mg.) of crystalline material separated from the residue after the first distillation. Although the quantity was too small to affect the rate-ratio appreciably, and no correction was made for it, the substance was investigated and identified as 4 : 4′-diphenyldiphenyl (quaterphenyl). In addition, a high-boiling resin was left in the distillation flask after removal of the diphenyl fraction. This was thought to consist of a mixture of terphenyls and chlorinated terphenyls, and therefore, after purification by chromatography and distillation, it was analysed (Found: C, 85·5; H, 5·6; Cl, 9·0%; *M*, 244. Calc. for 67% $C_{18}H_{13}Cl$ + 33% $C_{18}H_{14}$: C, 85·7; H, 5·3; Cl, 9·0%; *M*, 253). This analysis shows that the resin was very probably a mixture of terphenyl and chloroterphenyls in the molecular ratio of 1 : 2. The resin was taken into account in the calculation of ${}^{\mathrm{PhCl}}_{\mathrm{PhH}}K$, the results for which are given below.

Expt. no.	Wt. of diaryl fraction (g.)	Wt. of Ph·CO₂H (g.)	Wt. of resin (g.)	Cl, %, in diaryl fraction	${}^{\mathrm{PhCl}}_{\mathrm{PhH}}K$	$(Ph\cdot CO_2)_2$ accounted for, %
14	2·764	1·47	1·75	11·2	1·21	85·2
15	2·661	1·55	1·54	11·9	1·41	81·7

Hence ${}^{\mathrm{PhCl}}_{\mathrm{PhH}}K = 1{\cdot}31$

(II. 5) *Direct Determination of* ${}^{\mathrm{PhCl}}_{\mathrm{Ph\cdot NO_2}}K$.—Expts. 12 and 13 were carried out as already described, an equimolar mixture of chlorobenzene and nitrobenzene being used. In this case it was found that the fore-run contained a very small quantity of chlorodiphenyl, and a correction was made for this in the calculation of ${}^{\mathrm{PhCl}}_{\mathrm{Ph\cdot NO_2}}K$. The results are given herewith.

Expt. no.	Wt. of diaryl fraction (g.)	Nitro-diphenyl, %	Wt. of fore-run (g.)	Cl, %, in fore-run	Correction (mg. $Cl\cdot C_6H_4Ph$)	Corr. wt. of diaryl fraction (g.)	Nitro-diphenyl (corr.), %	${}^{\mathrm{PhCl}}_{\mathrm{Ph\cdot NO_2}}K$	$(Ph\cdot CO_2)_2$ accounted for, %
12	3·578	74·99	0·414	0·71	16	3·594	74·65	0·358	83·0
13	3·519	74·80	0·374	1·07	21	3·540	74·35	0·364	82·5

Hence ${}^{\mathrm{PhCl}}_{\mathrm{Ph\cdot NO_2}}K = 0{\cdot}361$.

(II. 6) *Direct Determination of* ${}^{\mathrm{PyH}}_{\mathrm{PhH}}K$.—Expts. 16—23 were performed with an equimolar mixture of benzene and pyridine. After saponification, the mixture was separated by extraction with aqueous hydrochloric acid into neutral and basic portions. These were worked up separately, and the weights of diphenyl and of phenylpyridines were obtained. A high-boiling residue was obtained from the neutral portion. This was treated in the manner employed for the resins described in Section (II. 4). Its composition corresponded fairly closely to that required for a mixture containing 60% of terphenyl and 40% of diphenylpyridines (Found: C, 90·8; H, 7·2; N, 1·4. Calc. for 60% $C_{18}H_{14}$ + 40% $C_{17}H_{13}N$: C, 91·7; H, 5·9; N, 2·4%). A correction was made for this in the calculation of ${}^{\mathrm{PyH}}_{\mathrm{PhH}}K$. The occurrence of diphenylpyridines in a residue obtained from the neutral portion of the product demonstrates the extremely feeble basicity of such compounds. The results are summarised in the following table.

Expt. no.	Wt. of phenyl-pyridines (g.)	Wt. of diphenyl (g.)	Wt. of benzoic acid (g.)	Wt. of residue (g.)	${}^{\mathrm{PyH}}_{\mathrm{PhH}}K$	$(Ph\cdot CO_2)_2$ accounted for, %
16	1·263	1·096	3·39	0·10	—	—
17	1·305	—	3·30	—	—	—
18	1·194	—	3·29	—	—	—
19	1·328	1·031	—	0·30	—	—
20	1·259	—	—	0·42	—	—
21	1·259	1·023	—	0·30	—	—
22	1·032	1·000	—	0·55	—	—
23	1·071	1·090	—	0·53	—	—
Mean	1·200	1·090	3·33	0·33	1·04	92·4

(II. 7) *Direct Determination of* ${}^{\mathrm{PhCl}}_{\mathrm{PyH}}K$.—Expts. 24—26 were carried out with chlorobenzene and pyridine as described in Section (II. 6). Again a high-boiling residue was obtained, which was found by analysis to contain about 90% of chloroterphenyls. A correction was made for this in the calculation of ${}^{\mathrm{PhCl}}_{\mathrm{PyH}}K$. The results are summarised in the next table.

Expt. no.	Wt. of phenyl-pyridines (g.)	Wt. of chloro-diphenyls (g.)	Wt. of benzoic acid (g.)	Wt. of residue (g.)	${}^{\mathrm{PhCl}}_{\mathrm{PyH}}K$	$(Ph\cdot CO_2)_2$ accounted for, %
24	1·017	1·030	3·30	0·42	—	—
25	1·020	1·140	3·16	0·59	—	—
26	1·014	1·060	—	0·57	—	—
Mean	1·017	1·078	3·23	0·53	1·15	78·9

(II. 8) *Direct Determination of* ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PyH}}K$.—Expts. 29 and 30 were carried out with nitrobenzene and pyridine as described in Section (II. 6). No residue was found. Experiments 33 and 34 were performed with the concentration of pyridine and nitrobenzene in the molar ratio of 2 to 1. Practically the same value was obtained for ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PyH}}K$, as shown in the next table.

Expt. no.	Wt. of phenylpyridines (g.)	Wt. of nitrodiphenyls (g.)	Wt. of benzoic acid (g.)	${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PyH}}K$	$(\mathrm{Ph\cdot CO_2})_2$ accounted for, %
29	0·540	2·772	2·80	—	—
30	0·535	2·654	2·73	—	—
Mean	0·537	2·713	2·77	3·95	80·2
33	0·760	2·022	3·20	—	—
34	0·874	2·283	3·12	—	—
Mean	0·817	2·153	3·16	4·11	84·6

(II. 9) *Reagents.*—Nitrobenzene (B.D.H.) was shaken three times with concentrated aqueous sodium hydroxide and once with water, steam-distilled, dried ($\mathrm{CaCl_2}$), and twice distilled under reduced pressure through a 4-ft. helix-packed column (b. p. 51°/0·6 mm.). Benzene (" AnalaR") was washed with concentrated sulphuric acid until the washings were colourless, then with aqueous sodium hydrogen carbonate, and finally with water. It was then fractionally distilled after being dried ($\mathrm{CaCl_2}$). Chlorobenzene (B.D.H.) was treated similarly. Pyridine (" AnalaR ") was dried (KOH) and fractionally distilled. *p*-Nitroaniline was treated with carbon in alcohol and crystallised to constant m. p. (147°). 2- and 4-Nitrodiphenyl were prepared by nitration of diphenyl (Bell, Kenyon, and Robinson, *J.*, 1926, 1239). 4-Nitrodiphenyl was purified by distillation *in vacuo* and crystallisation from acetic acid to constant m. p. (almost colourless needles, m. p. 114°). 2-Nitrodiphenyl was distilled *in vacuo*, treated with carbon in alcohol, and crystallised from light petroleum (b. p. 60—80°) to constant m. p. (36·5°). 3-Nitrodiphenyl, prepared by means of the Gomberg reaction from *m*-nitroaniline (Blakey and Scarborough, *J.*, 1927, 3000), was purified by distillation *in vacuo*, and crystallisation from ethanol to constant m. p. (60°). Diphenyl (B.D.H.), phenyl benzoate, *p*-nitrophenyl benzoate, and *p*-terphenyl were treated with carbon in ethanol and crystallised to constant m. p., these being 70° (from ethanol–water), 69·5° (from ethanol), 142° (from ethanol), and 209—210° (from benzene), respectively. Benzoyl peroxide (May and Baker) was dissolved in chloroform and the upper aqueous layer was removed. To the filtered chloroform solution methanol was added slowly with constant stirring and the crystalline solid which separated was filtered off after the solution had been cooled. After repetition of this procedure the product was dried in a vacuum-desiccator over calcium chloride and kept in the dark (m. p. 105°).

(III) DISCUSSION

(III. 1) *The Mechanism of the Reaction.*—The kinetics of the decomposition of benzoyl peroxide indicate that in general two types of reaction occur, a unimolecular decomposition and an " induced decomposition," wherein molecules of benzoyl peroxide decompose as a result of collisions with solvent radicals. This induced decomposition is shown (Nozaki and Bartlett, *loc. cit.*; Cass, *loc. cit.*; Hartman, Sellers, and Turnbull, *loc. cit.*) to be of least importance with aromatic solvents. Indeed, consideration of the reaction products leads to the conclusion that solvent radicals are not formed under these conditions. A radical derived by the abstraction of a hydrogen atom from a molecule of the type PhX would be expected to behave in a manner essentially similar to a phenyl radical. In Part I (*loc. cit.*), when the *p*-bromophenyl radical was used in place of the phenyl radical, essentially similar results were obtained. Thus, products derived from the attack of such a radical on the solvent would be expected, *i.e.*, products of the type $\mathrm{X\cdot C_6H_4\cdot C_6H_4X}$. It is a well-known fact, which is substantiated in the present work, that disubstituted derivatives of diphenyl are not found when a phenylation reaction is carried out with a monosubstituted benzene. Hence, it must be concluded that solvent radicals are not formed in any substantial quantity from the aromatic solvents which have been investigated.

The alternative reaction of phenylation by direct substitution requires the ejection of a hydrogen atom from the seat of substitution. Several workers (Wieland *et al.*, *Annalen*, 1934, **514**, 145; Cohen, *J. Polymer Sci.*, 1947, **2**, 511; Huisgen and Horeld, *loc. cit.*) have detected quantities of quinhydrone from reactions of the types under discussion when benzoquinone was present, thus indicating the presence of hydrogen atoms. In addition, in the course of work to be described in a later paper, the present authors have isolated products derived from the reduction of the solvent; *e.g.*, some aniline is formed when the reaction is carried out in nitrobenzene solution.

The entity which brings about the actual phenylation must be either the benzoyloxy-radical derived from the fission of the O–O bond in benzoyl peroxide, which loses carbon dioxide in the process of its attack on the solvent, or alternatively the phenyl radical derived from a benzoyloxy-radical by the loss of carbon dioxide before attack on the solvent. The theory of attack by benzoyloxy-radicals requires the simultaneous occurrence of several processes. The carbon dioxide must be detached from the phenyl residue; the solvent residue must become attached to the phenyl group to form what must become a diphenyl molecule; and the electron residing in the carboxyl group of the benzoyloxy-radical must become transferred to the hydrogen atom which is eliminated from the solvent. The formulation of a transition state for such a reaction presents difficulties which cast doubt on its feasibility as a possible route for the phenylation process. On the other hand, in Part I it is reported that the ratio of isomerides produced in the phenylation of nitrobenzene is essentially the same in both the peroxide and the Gomberg reactions. The work of DeTar and Scheifele (*J. Amer. Chem. Soc.*, 1951, **73**, 1442) shows that this is true also for the acylarylnitrosamine reaction. The same close correspondence is shown for the *p*-tolyl and *p*-bromophenyl radicals (Part I). This indicates that the same entity is responsible for phenylation in each case. The only such entity which is common to all three reactions is the phenyl radical, and hence it is reasonable, in the absence of further experimental evidence, to conclude that this is the phenylating agent.

(III. 2) *Partial Rate Factors.*—The experimental results reported above on the direct measurements of the relative rates of homolytic substitution in benzene, nitrobenzene, chlorobenzene, and pyridine are summarised in the table below, where are also given derived values for the rate-ratios obtained from either two or three combinations of the above results. The general agreement between the derived values and those obtained by direct measurement confirms that none of the latter is grossly in error.

Components:				
X	Y	${}^{x}_{y}K$	${}^{x}_{a}K^{a}_{y}K$	${}^{x}_{a}K^{a}_{b}K^{b}_{y}K$
$Ph{\cdot}NO_2$	PhH	$\ngtr$4·17	3·63	3·31
,,	,,		4·11	4·50
PhCl	PhH	1·21	1·50	1·48
,,	,,	1·41	1·20	1·21
PhCl	$Ph{\cdot}NO_2$	0·358	0·29	0·29
,,	,,	0·364	0·31	0·32

Components:				
X	Y	${}^{x}_{y}K$	${}^{x}_{a}K^{a}_{y}K$	${}^{x}_{a}K^{a}_{b}K^{b}_{y}K$
PyH	PhH	1·04	1·14	0·92
,,	,,		1·05	1·30
PhCl	PyH	1·15	1·26	1·44
,,	,,		1·42	1·24
$Ph{\cdot}NO_2$	PyH	3·95	4·00	3·67
,,	,,		3·19	3·50

Note.—The values now accepted for ${}^{x}_{y}K$ differ slightly in some cases from those reported in the preliminary communications (*Nature*, 1951, **167**, 725; *Research*, 1951, **4**, 386), owing to a reassessment of the relevant experimental data in the light of more recent experience.

The value chosen for ${}^{Ph\cdot NO_2}_{Ph\cdot H}K$ is 4·0. Thus, for any compound PhX, ${}^{PhX}_{PhH}K$ will be obtained from ${}^{PhX}_{Ph\cdot NO_2}K$ by multiplying by 4. The value of ${}^{Ph\cdot NO_2}_{PhH}K$ for electrophilic substitution (nitration) is extremely small ($\sim 10^{-4}$), while that of ${}^{PhCl}_{PhH}K$ is 0·033 (Bird and Ingold, *loc. cit.*). Both the nitro-group and the chlorine atom are thus found to have an activating influence in homolytic substitution, but the effects displayed are very much smaller in magnitude than those encountered in electrophilic substitution. This is experimental confirmation of the view that these reactions are free from the powerful electrostatic effects which are important in heterolytic substitution. The neutral radical approaches the reaction-site without experiencing either electrostatic attraction or repulsion, and exerts no polarising influence on the molecule with which it is about to react (cf. Waters, *J.*, 1948, 727). It is also of interest that benzene and pyridine undergo phenylation at approximately the same rates.

If the rates of substitution are expressed in terms of the rate of substitution at any one position in benzene, *i.e.*, the rate for benzene as a whole becomes 6, then that for nitrobenzene becomes 24. If the proportions are known in which the *o*-, *m*-, and *p*-isomerides are formed, the rates of substitution at each position in the compound under consideration may be calculated. These "partial rate factors," ${}^{PhX}_{PhH}F_o$, ${}^{PhX}_{PhH}F_m$, and ${}^{PhX}_{PhX}F_p$, together constitute a complete specification of the influence of the atom or group X on the reactivity of the molecule in which X occurs towards the particular reagent concerned.

The results reported in this paper, together with those reported in Part I, enable the partial rate factors to be calculated for the substitution of nitrobenzene by phenyl radicals. If the percentages in which the three isomerides are formed in the phenylation of nitrobenzene are taken as *ortho* 58%, *meta* 10%, and *para* 32%, the partial rate factors are ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}F_o = 7{\cdot}0$, ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}F_m = 1{\cdot}2$, and ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}F_p = 7{\cdot}9$.

Several attempts have been made to derive theoretically the directing influence of groups in homolytic and heterolytic aromatic substitution (Wheland and Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2086; Wheland, *ibid.*, 1942, **64**, 900; Pullmann, *Ann. Chim.*, 1947, 5; Coulson, *Trans. Faraday Soc.*, 1946, **42**, 265; *Research*, 1951, **4**, 307). Calculation of the partial rate factors for homolytic substitution in nitrobenzene can be made by substitution of Wheland's energy increments into the Arrhenius equation. By this means the following values are obtained:

$${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}F_o = 2{\cdot}25, \quad {}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}F_m = 0{\cdot}85, \quad {}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}F_p = 8{\cdot}7$$

$$\text{since} \quad {}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K = \tfrac{1}{6}\,(2\ {}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}F_o + 2\ {}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}F_m + {}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}F_p),$$

these partial rate factors lead to a value of 2·5 for ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$, which may be compared with the experimentally determined value of 4·0. In agreement with the results now reported, these calculations show that the nitro-group is mildly activating and *ortho-para*-directing in homolytic substitution.

Thanks are accorded to the Department of Scientific and Industrial Research for the award of a Maintenance Grant to D. R. A.

King's College, University of London,
Strand, London, W.C.2.

[*Received, February 5th*, 1952.]