893. *Homolytic Aromatic Substitution. Part XVI.*[1] *Relative Rates of* p-*Bromophenylation of Nitrobenzene and* p-*Nitrophenylation of Bromobenzene. Derivation and Discussion of Partial Rate Factors.*

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The determination, by means of competitive experiments, of the relative rates of *p*-bromophenylation of nitrobenzene and *p*-nitrophenylation of bromobenzene is reported. Partial rate factors for the arylation with various radicals of nitrobenzene, chlorobenzene, and bromobenzene are derived and discussed from the point of view of the polarity of the attacking free radicals. The validity of the competitive method is also discussed.

In Parts XIV[2] and XV[1] the influence of the polarised radicals on the ratios of isomers obtained in the *p*-bromophenylation and *p*-chlorophenylation of nitrobenzene, and the *p*-nitrophenylation of chlorobenzene and bromobenzene was investigated. The corresponding effect of radical polarisation on the relative rates of arylation of nitrobenzene and chlorobenzene, with use of *p*-chlorophenyl radicals, was reported in Part IX.[3] Further work on this aspect, namely, the measurement of the relative rates of *p*-bromophenylation of nitrobenzene and *p*-nitrophenylation of bromobenzene, is now reported. This, together with the results reported in Parts IX,[3] XIV,[2] and XV,[1] makes possible the calculation of partial rate factors for a number of new arylation reactions, in terms of which the influence of the polarising groups in the radicals may be preliminarily discussed. Further extensions of this work, with a greater variety of both radicals and substrates, will be reported in future publications.

The relative rate ratios $^{\text{PhNO}_2}_{\text{PhH}}K$ and $^{\text{PhNO}_2}_{\text{PhBr}}K$ have been determined for *p*-bromophenylation and *p*-nitrophenylation respectively, Augood, Hey, and Williams's competitive technique[4] being used. The former measurement gives the relative rate of *p*-bromophenylation of nitrobenzene directly, and the relative rate of *p*-nitrophenylation of bromobenzene can be obtained from the latter measurement, in conjuncton with the value of $^{\text{PhNO}_2}_{\text{PhH}}K$ for *p*-nitrophenylation obtained by Hambling, Hey, and Williams.[5]

EXPERIMENTAL

Preparation of Reagents.—Benzene, bromobenzene, and nitrobenzene were purified as described in Parts II[4] and IV.[6] *p*-Bromobenzoyl peroxide (m. p. 142°, decomp.) and *p*-nitrobenzoyl peroxide (m. p. 155°, decomp.) were prepared from *p*-bromobenzoyl chloride and *p*-nitrobenzoyl chloride respectively by Hey and Walker's method.[7]

Determination of $^{\text{PhNO}_2}_{\text{PhH}}K$ *for* p-*Bromophenylation.*—Experiments 1 and 2 were carried out with *p*-bromobenzoyl peroxide (6 g.) in an equimolar mixture (200 ml.) of benzene and nitrobenzene. The reactions were allowed to proceed in a thermostat at 80° for 72 hr. The mixed diaryls from the reaction mixtures were isolated by standard methods (cf. Part II[4]), and the composition of these mixtures determined volumetrically by reduction of the nitrodiaryls with titanous chloride, as described in Part II.[4] In the final distillation, fore-runs were collected, consisting of mixed fractions containing the last traces of nitrobenzene (the higher-boiling solvent) and the first traces of 4-bromodiphenyl (the lowest-boiling diaryl product). The fore-runs were analysed by the micro-Carius method, and a correction in terms of bromodiphenyl was applied to the yield and composition of the diaryl fraction. Fractions taken immediately

[1] Part XV, Chang Shih, Hey, and Williams, *J.*, 1958, 2600.
[2] *Idem, ibid.*, p. 1885.
[3] Cadogan, Hey, and Williams, *J.*, 1955, 1425.
[4] Augood, Hey, and Williams, *J.*, 1952, 2094.
[5] Hambling, Hey, and Williams, to be published.
[6] Augood, Cadogan, Hey, and Williams, *J.*, 1953, 3412.
[7] Hey and Walker, *J.*, 1948, 2213.

before the fore-run consisted entirely of nitrobenzene, showing that neither the fore-run nor the diaryl fraction was contaminated with benzene, and that the whole of the 4-bromodiphenyl formed was contained in the diaryl fraction and the fore-run. The absence of bromonitrodiphenyls from the fore-runs is inferred because they did not distil until a temperature 50° above that at which the fore-runs were collected had been reached. No significant amount of high-boiling residue was left after the distillation. The results are given in Table 1.

TABLE 1.

	Expts.	1	2
Diaryl fraction (g.) (b. p. 55—135°/0·1 mm.)		3·096	3·075
Nitrodiaryls (%) in diaryl fraction		67·99	68·31
Fore-run (g.) (b. p. 35—55°/0·1 mm.)		0·998	1·049
Bromodiphenyl in fore-run (g.)		0	0·037
Corr. wt. of diaryl fraction (g.)		3·096	3·112
Nitrodiaryls, corr. (%)		67·99	67·50
$^{PhNO_2}_{PhH}K$		1·78	1·74
p-Br·C$_6$H$_4$·CO$_2$H (g.) (free and from hydrolysis of esters)		3·22	3·19
(p-Br·C$_6$H$_4$·CO·O)$_2$ accounted for (%)		82·0	82·5

Hence, $^{PhNO_2}_{PhH}K = 1·76$

Determination of $^{PhNO_2}_{PhBr}K$ *for* p-*Nitrophenylation.*—Experiments 3 and 4 were carried out with p-nitrobenzoyl peroxide (6 g.) in exactly the same way as above, except that bromobenzene was substituted for benzene, and isolation and analysis of the diaryl fraction were carried out by the standard procedure. Fore-runs were taken and analysed for nitrobenzene by titanous chloride titration. They were found to consist entirely of nitrobenzene, and hence no correction to the yield and composition of the diaryl fraction was necessary. The clean separation of the diaryl fraction from nitrobenzene, which was possible with these mixtures, was due to the considerable difference in b. p. between nitrobenzene and the bromonitrodiphenyls, which were the most volatile of the diaryl products. The absence of dinitrodiphenyls from the fore-runs is inferred because they did not distil until a temperature 80° above that at which the fore-runs were collected had been reached. Fractions taken immediately before the fore-runs consisted entirely of nitrobenzene. The amounts of high-boiling residue left after the distillation were negligible. The results are given in Table 2.

TABLE 2.

	Expts.:	3	4
Diaryl fraction (g.) (b. p. 90—165°/0·2 mm.)		3·734	3·710
Dinitrodiphenyls (%) in diaryl fraction		35·09	35·86
Fore-run (g.) (b. p. 35—90°/0·2 mm.)		3·515	1·473
Bromonitrodiphenyls in fore-run (g.)		0·000	0·000
$^{PhNO_2}_{PhBr}K$		0·62	0·64
p-NO$_2$·C$_6$H$_4$·CO$_2$H (g.) (free and from hydrolysis of esters)		3·15	3·21
(p-NO$_2$·C$_6$H$_4$·CO·O)$_2$ accounted for (%)		83·0	84·0

Hence $^{PhNO_2}_{PhBr}K = 0·63$

DISCUSSION

The results of the above experiments on homolytic p-bromophenylation and p-nitrophenylation, in comparison with the corresponding figures for phenylation (Parts II [4] and IV [6]), are summarised in Table 3.

TABLE 3.

	Phenylation	p-Bromophenylation	p-Nitrophenylation	Decrease (%)
$^{PhNO_2}_{PhBr}K$	2·27	—	0·63	72
$^{PhNO_2}_{PhH}K$	4·00	1·76	—	56

The relative rates for p-bromophenylation and p-nitrophenylation are significantly lower than the corresponding relative rates for phenylation. Considering the properties

towards electrophilic substitution of the substrates used, these changes are in accord with the predictions of Cadogan, Hey, and Williams [3] for substitution by electrophilic radicals. Thus we conclude that bromo- and nitro-substituents, when present in the *para*-position of the aryl radicals, confer some measure of electrophilic character on these radicals. Moreover, the effect appears to be more marked in the case of the *p*-nitrophenyl radical than in that of *p*-bromophenyl. This is consistent with the known polar properties of the groups concerned, if it be assumed that the properties of the radicals are influenced by the permanent polarisation occasioned by the presence of the substituents. Thus both groups are known to cause such permanent polarisation of molecules containing them in the direction of electron-attraction by the substituent, the effect being greater in the case of the nitro-group.

From the above value of $^{\mathrm{PhNO_2}}_{\mathrm{PhBr}}K$ for *p*-nitrophenylation, taken in conjunction with the value [5] for the same reaction of $^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K = 0.94$, the rate of *p*-nitrophenylation of bromobenzene relative to benzene ($^{\mathrm{PhBr}}_{\mathrm{PhH}}K$) can be obtained, and is 1·49. This value, together with that of $^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ for *p*-bromophenylation, and the results of Cadogan, Hey, and Williams [3] for *p*-chlorophenylation, can be used in conjunction with the relevant ratios of isomers, the determination of which was reported in Parts XIV and XV, to evaluate partial rate factors for a number of arylations. These results are given in Table 4, which also includes, for comparison, the values for partial rate factors for the phenylation of nitrobenzene, chlorobenzene, and bromobenzene previously reported.[1,2,4,6]

TABLE 4. *Partial rate factors for homolytic arylation.*

Radical	Substrate PhX	$^{\mathrm{PhX}}_{\mathrm{PhH}}K$	F_o	F_m	F_p
p-Br·C₆H₄·	PhNO₂	1·8	3·1	0·7	2·9
p-Cl·C₆H₄·	PhNO₂	1·5	2·7	0·6	2·5
Ph·	PhNO₂ *	4·0	7·5	1·2	6·6
Ph·	PhBr	1·7	2·6	1·7	1·8
p-NO₂·C₆H₄·	PhBr	1·5	2·7	1·1	1·3
p-NO₂·C₆H₄·	PhCl	1·2	2·1	0·8	1·1
Ph·	PhCl *	1·4	2·2	1·4	1·6

* The values quoted here are somewhat different from those previously reported [4,8] since the present values were calculated by using the modified ratios of isomers obtained in the phenylation of nitrobenzene and chlorobenzene, the redetermination of which was reported in Parts XIV [2] and XV.[1]

In the arylation of nitrobenzene it is apparent from Table 4 that all three nuclear positions are considerably less reactive towards attack by *p*-chloro- and *p*-bromo-phenyl than by phenyl radicals, and that there is little difference in properties between *p*-bromo- and *p*-chloro-phenyl radicals. Moreover, the decrease in reactivity occasioned by the change from phenyl to *p*-halogenophenyl radicals is more marked in the *ortho*- and *para*-than in the *meta*-position of nitrobenzene. This is consistent with the known facts concerning electrophilic substitution in nitrobenzene, wherein the nitro-group, by virtue of its polar nature, deactivates the nucleus as a whole, but the *meta*-position less than the *ortho*-and *para*-positions. Thus, when homolytic substitution by electrophilic radicals takes place, it is to be expected that the reactivities of the nuclear positions should be decreased relative to the corresponding reactivities for substitution by neutral radicals in the order *o*, *p* > *m*. The foregoing interpretation of the results obtained with *p*-chloro- and *p*-bromo-phenyl radicals depends on the assumption that free-radical reactions are subject to polar influences, and that the *p*-halogenophenyl radicals are electrophilic when compared with phenyl radicals. This is undoubtedly due to the electron-attracting properties of the halogens, which permanently polarise the radicals containing them in the direction of withdrawal of electrons from the reactive position, which formally carries the unpaired

[8] Augood, Hey, and Williams, *J.*, 1953, 44.

electron. This position therefore suffers an electronic deficiency and the radical would be expected to react most readily, other things being equal, at positions of high electron density. It may be concluded, therefore, that the properties of free radicals are to some degree determined by any permanent polarisation which they may owe to their molecular constitution. It is not clear to what extent, if at all, the properties of radicals are influenced by the time-variable effects of any substituents they may contain on the polarisability of the radicals. The small magnitude of the observed effects indicates that the part played by polar factors in determining the properties of radicals is relatively minor, for even when substitution takes place in such an extensively polarised compound as nitrobenzene, the substitution process is very much more akin to homolytic substitution by neutral free radicals than to electrophilic substitution. It could hardly be expected to be otherwise, since it must always involve entities containing odd numbers of electrons (free radicals by definition), and the pairing of electrons to form covalent bonds must always be the fundamental influence on the behaviour of these reagents.

In the arylation of the halogenobenzenes, it is clear from Table 4 that the aromatic nuclei of these compounds are less reactive towards substitution by the electrophilic p-nitrophenyl radicals than by non-polarised phenyl radicals. This is consistent with the deactivating influence of the halogens in electrophilic substitution. However, as a result of the combination of polar influences displayed by the halogens ($-I + T$ effects) in electrophilic substitution, it is the *meta*-position which suffers the greatest deactivation. Table 4 shows that this property is also displayed in the behaviour of the halogenobenzenes towards homolytic substitution by electrophilic radicals, since the decrease in reactivity occasioned by the change from phenyl to p-nitrophenyl radicals is most marked in the *meta*-positions. This indicates that the polar factors which influence homolytic substitution by polarised free radicals are substantially the same as those which are known to operate in heterolytic substitution.

It is therefore clear that the present results reported and those in Parts XIV[2] and XV[1] are in accord with the general theory of the behaviour of polarised radicals as enunciated by Dannley and Sternfeld,[9] and by Cadogan, Hey, and Williams,[3] and elaborated here. The present results, however, also demonstrate that polar influences play only a relatively small part in determining the course of homolytic reactions. It is, perhaps, an unfortunate consequence of this that the differences, especially in ratios of isomers, which are indicative of the operation of polar influences, are also small and are often only just outside the experimental errors. For this reason it is the more desirable to examine as wide a variety of both radicals and substrates as possible. Further investigation on these lines has therefore been undertaken, and the results will be reported in due course.

The competitive method, whose use to obtain relative rates of homolytic arylation has been described in this and preceding papers, has recently been discussed by Lynch and Pausacker.[10] From reactions of some aroyl peroxides with benzene, chlorobenzene, and naphthalene, they isolated considerable quantities of high-boiling resins which they consider to contain derivatives of the isomeric quaterphenyls together with some esters formed by benzoyloxylation of the various compounds present. The quaterphenyls are considered to arise by dimerisation of the addition complex formed between the aryl radical and the aromatic substrate in the first stage of the arylation process. The differential removal, by this and other processes giving rise to the resins, of the various diaryl products occurring in the reaction mixtures obtained in competitive experiments is considered by them to invalidate the results obtained from competitive reactions in which benzoyl peroxide is used as the source of phenyl radicals. A similar view has been expressed by Walling.[11] This criticism would be serious if it could correctly be applied to the results under discussion. It is therefore necessary to examine its validity, if it be accepted that Lynch and Pausacker's

[9] Dannley and Sternfeld, *J. Amer. Chem. Soc.*, 1954, **76**, 4543.
[10] Lynch and Pausacker, *Austral. J. Chem.*, 1957, **10**, 40, 49, 165.
[11] Walling, " Free Radicals in Solution," John Wiley & Co. Inc., New York, 1957, p. 485.

conclusions are correct and are founded on a sound experimental basis. In this connection, it is relevant that some of their results on the reaction of benzoyl peroxide with naphthalene have been shown by Davies, Hey, and Williams [12] to be in error.

According to Lynch and Pausacker, the results of any competitive reaction in which high-boiling resins are obtained are subject to some uncertainty, owing to the possible differential removal of diaryl products. However, as has been pointed out by Augood and Williams [13] resins are formed only when the substrate consists entirely of relatively unreactive ("slow") solvents such as benzene, pyridine, the alkylbenzenes, or the halogenobenzenes. If the substrate consists of "fast" solvents (*e.g.*, nitrobenzene or diphenyl), either alone or mixed with slow solvents, very little resin is obtained. This conclusion is amply confirmed by the results reported in this series. If only negligible quantities of resin are formed. no significant differential removal of the diaryl products can have taken place, and Lynch and Pausacker's criticism is inapplicable. All the relative rates reported in this and earlier papers are based on competitive experiments in which the reference solvent, which forms one component of the solvent mixture, was nitrobenzene. Only very small quantities of resins were formed in these reactions, and consequently the results cannot be regarded as invalid. In some cases, pyridine was used as reference solvent in competitive experiments conducted for the purpose of confirming the results obtained by using nitrobenzene as reference solvent. In these reactions, resins were obtained when the substrate consisted exclusively of slow solvents, and because of the uncertainty thus introduced, these experiments have never been relied upon alone, but have always been supported by ones with nitrobenzene. Even so, the agreement between results obtained by the two methods has been good, and this suggests that the complications introduced by differential removal of products are, in most cases, not serious, and occasions greater confidence in the reliability of the results. This confidence is also increased by the considerable measure of agreement between the values of a number of relative rates obtained by various cyclic procedures involving competitive experiments with different pairs of solvents, as shown in Part II.[4] The competitive results, and the partial rate factors derived therefrom, have also been shown (Part III [8]) to give rise to predictions of the relative rates of arylation of polysubstituted benzenes which are substantially in agreement with experimentally determined values. The relative rates also agree with theoretical predictions based on the calculation of both atom localisation energies and free valency numbers (cf. Augood and Williams [13]). Thus there appears to be much evidence supporting the published values of these relative rates derived from competitive experiments. It has never been claimed that these figures are accurate to, say, $\pm 1\%$, and indeed, the theoretical interest of these quantities does not lie in such an accurate knowledge of them, but rather in their order of magnitude and in the way in which they vary from one compound to another. It is therefore concluded that, on the experimental evidence at present available, the values reported and the discussions based upon them are unaffected by Lynch and Pausacker's criticisms.

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[12] Davies, Hey, and Williams, *J.*, 1958, 1878.
[13] Augood and Williams, *Chem. Reviews*, 1957, **57**, 123.