751. *Homolytic Aromatic Substitution. Part XIX.* The Arylation of Nitrobenzene and Chlorobenzene with* para-*Substituted Aryl Radicals.*

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The determination, by means of competitive experiments, of the relative rates of *p*-nitrophenylation and *p*-methoxyphenylation of nitrobenzene and chlorobenzene is reported. The ratio of the isomers formed in the *p*-nitrophenylation of nitrobenzene is also determined. The results, which indicate that the *p*-nitrophenyl and *p*-methoxyphenyl radicals are slightly electrophilic in character, are consistent with the hypothesis that the permanent polarisation of the substituent has a small but significant influence on the reactivity of the free aryl radical.

IN Parts IX,[1] XIV, XV, and XVI,[2] determinations were reported of the relative rates of arylation of nitrobenzene, chlorobenzene, and bromobenzene with some *para*-substituted aryl radicals, and of the proportions in which the *ortho*-, *meta*-, and *para*-isomers were formed in some of these reactions. These results supported the hypotheses that the *para*-substituents in the radicals conferred upon them a measure of electrophilic or nucleophilic character, dependent upon the polar properties of the substituents, and that the relative rates at which the radicals attacked the different nuclear positions in the substrates (partial rate factors) consequently became modified. Further results are now reported, which permit examination of the polar properties of the *p*-nitro- and *p*-methoxy-phenyl radicals in their competitive reactions with mixtures of nitrobenzene and benzene or chlorobenzene. In addition, since the modifications in the numerical values of the partial rate factors are generally rather small, it was considered desirable to subject to the most detailed examination a reaction between a radical and a substrate, both of which contain substituent groups of pronounced polar character, namely, the *p*-nitrophenyl radical and nitrobenzene. The ratio of isomers formed in this reaction has, therefore, also been determined.

EXPERIMENTAL

Reagents.—Solids were recrystallised to constant m. p. Benzene, chlorobenzene, and nitrobenzene were purified as described in Part II.[3] *NN*-Dimethylformamide was dried ($CaCl_2$) and fractionally distilled three times; the distillate (b. p. 151°) was stored in the dark under nitrogen. *p*-Nitrobenzoyl peroxide was prepared by Hey and Walker's method [4] (m. p. 155°), and *p*-methoxybenzoyl peroxide by Price, Kell, and Krebs's method [5] (m. p. 127—128°).

2,4'-Dinitrobiphenyl (m. p. 93°) was prepared by nitration of 2-nitrobiphenyl by Gull and Turner's method.[6] The 2-nitrobiphenyl was prepared in two ways, namely, by nitration of biphenyl (cf. Bell, Kenyon, and Robinson [7]) and by reaction of diazotised *o*-nitroaniline with benzene in the presence of sodium acetate using the procedure described by Elks, Haworth, and Hey.[8] The latter method was the more satisfactory.

3,4'-Dinitrobiphenyl was prepared by nitration of 3-nitrobiphenyl, which was obtained from the reaction of *m*-nitrobenzoyl peroxide with benzene. *m*-Nitrobenzoyl peroxide (25 g., prepared by Hey and Walker's method [4]) was heated with benzene under reflux for 24 hr. Excess of solvent was then removed by distillation, and the residue was heated under reflux with 2N-sodium hydroxide for 12 hr. The resulting mixture was extracted thoroughly with benzene, and the combined benzene extracts were dried ($CaCl_2$). Excess of solvent was

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* Part XVIII, preceding paper.

[1] Cadogan, Hey, and Williams, *J.*, 1955, 1425.
[2] Chang Shih, Hey, and Williams, *J.*, 1958, (*a*) 1885, (*b*) 2600, (*c*) 4403.
[3] Augood, Hey, and Williams, *J.*, 1952, 2094.
[4] Hey and Walker, *J.*, 1948, 2216.
[5] Price, Kell, and Krebs, *J. Amer. Chem. Soc.*, 1942, **64**, 1103.
[6] Gull and Turner, *J.*, 1929, 495.
[7] Bell, Kenyon, and Robinson, *J.*, 1926, 1239.
[8] Elks, Haworth, and Hey, *J.*, 1940, 1284.

distilled off at atmospheric pressure, and the residue distilled *in vacuo* (b. p. 106°/0·05 mm.). Crystallisation from ethanol gave 3-nitrobiphenyl (12 g., m. p. 61°). The preparation of 3,4'-dinitrobiphenyl by nitration of 3-nitrobiphenyl was first attempted with fuming nitric acid as described by Blakey and Scarborough.[9] This method, however, gave mainly 2,3',4-trinitrobiphenyl, m. p. 137—138° (Found: N, 14·7. Calc. for $C_{12}H_7O_6N_3$: N, 14·5%). Case [10] reported m. p. 137—138°. The following method was therefore used for the nitration. Fuming nitric acid (*d* 1·51) was added dropwise to a vigorously stirred suspension of 3-nitrobiphenyl in an excess of nitric acid (*d* 1·42) until the mixture became homogeneous. Stirring was continued until precipitation of the crude product of nitration, which began soon after the termination of the addition of fuming nitric acid, was complete. This solid product was filtered off, washed with water, and digested with methanol to remove 2,3'-dinitrobiphenyl. The suspension in boiling methanol was cooled to 0°, and the solid removed and repeatedly crystallised from aqueous acetic acid to give 3,4'-dinitrobiphenyl, m. p. 189°.

4,4'-Dinitrobiphenyl (m. p. 233°) was prepared by nitration of biphenyl, by Schultz's method.[11]

Determination of ${}^{PhNO_2}_{PhH}K$ *for* p-*Nitrophenylation.*—Experiments 1 and 2 were carried out with *p*-nitrobenzoyl 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 biaryls were isolated as described in Part II,[3] except that chromatography was unnessary, 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-nitrobiphenyl (the lowest-boiling binuclear product). The fore-runs were analysed by estimation of their content of nitro-group, and corrections in terms of nitrobiphenyl were applied to the yield and composition of the biaryl fractions. Fractions taken immediately before the fore-runs consisted entirely of nitrobenzene, showing that neither the fore-runs nor the biaryl fractions were contaminated with benzene, and that the whole of the 4-nitrobiphenyl formed was contained in the fore-runs and the biaryl fractions. The absence of dinitrobiphenyls from the fore-runs is inferred because they did not distil until a temperature considerably above that at which the fore-runs were collected had been reached. The biaryl fractions and the fore-runs were analysed for nitro-groups volumetrically by reduction with titanous chloride as described in Part II,[3] and the results were confirmed by catalytic hydrogenation at atmospheric pressure over Raney nickel. This confirmation was considered desirable in this instance, since errors in the volumetric analysis might have been caused by the low solubility of 4,4'-dinitrobiphenyl. In the event, however, the agreement between the two methods of analysis was excellent. A standard hydrogenator, in which the hydrogen reservoir was an ordinary gas-burette, was used, and reduction of nitro-groups was complete in about 1 hr. The method was exhaustively tested by analysis of mixtures of known composition, and it was shown that both nitrobenzene and nitrobiphenyls could be estimated in the presence of most other biaryls to an accuracy of ±1%. The method could not, however, be used in the presence of halogenated biaryls, since some halogen was always removed by reduction. The results of some of these tests are given in Table 1.

TABLE 1. *Analysis of mixtures containing nitrobiaryls.*

	Nitrobiphenyls (%)	
Mixture	By hydrogenation	By Ti^{3+} reduction
2-, 3-, and 4-Nitrobiphenyl	100·3	100·0
Nitrobiphenyls + t-butylbiphenyls	86·6	86·8
Nitrobiphenyls + isopropylbiphenyls	66·7	66·6
Nitrobiphenyls + dinitrobiphenyls	53·0	54·0

The results of Experiments 1 and 2 are given in Table 2.

Determination of ${}^{PhNO_2}_{PhH}K$ *for* p-*Methoxyphenylation.*—Experiments 3 and 4 were carried out with *p*-methoxybenzoyl peroxide (6 g.) in an equimolar mixture (200 ml.) of benzene and

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[9] Blakey and Scarborough, *J.*, 1927, 3005.

[10] Case, *J. Amer. Chem. Soc.*, 1942, **64**, 2225.

[11] Schultz, *Annalen*, 1874, **174**, 221.

TABLE 2.

	Experiment 1	Experiment 2
Biaryl fraction (g.) (b. p. 40—195°/0·1 mm.)	2·967	3·017
Dinitrobiphenyls in biaryl fraction (%)	54·0	54·0
Fore-run (g.) (b. p. 25—40°/0·1 mm.)	0·743	1·344
Nitrobenzene in fore-run (%)	100·0	98·9
Nitrobiphenyls in fore-run (g.)	0·0	0·012
Corr. wt. of biaryl fraction (g.)	2·967	3·029
Dinitrobiphenyls, corr. (%)	54·0	53·5
${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ for *p*-nitrophenylation	0·95	0·94
Free *p*-nitrobenzoic acid (g.)	2·85	2·66
p-Nitrobenzoic acid from hydrolysis of esters (g.)	0·25	0·26
Residue (g.)	0·147	0·127
(p-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}O)_2$ accounted for (%)	89·1	87·0

Hence, ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ for *p*-nitrophenylation = 0·94

nitrobenzene. The reactions were conducted, and the products isolated and analysed, as described above. The large difference in b. p. between the higher-boiling solvent and the lowest-boiling binuclear product rendered their separation by distillation relatively easy, and hence the fore-runs obtained in these experiments were found on analysis to consist of pure nitrobenzene. No corrections to the weight and composition of the biaryl fraction were therefore necessary. The results are given in Table 3.

TABLE 3.

	Experiment 3	Experiment 4
Biaryl fraction (g.) (b. p. 40—130°/0·1 mm.)	1·720	1·752
Nitrobiaryls in biaryl fraction (%)	78·3	78·5
Fore-run (g.) (b. p. 25—40°/0·1 mm.)	0·554	0·679
Nitrobenzene in fore-run (%)	100·0	100·0
Methoxybiphenyls in fore-run (g.)	0	0
${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ for *p*-methoxyphenylation	2·91	2·93
Free *p*-methoxybenzoic acid (g.)	3·21	3·37
Free *p*-methoxybenzoic acid from hydrolysis of esters (g.)...	0·77	0·63
Residue (g.)	0·084	0·091
(p-$MeO{\cdot}C_6H_4{\cdot}CO{\cdot}O)_2$ accounted for (%)	81·9	82·1

Hence ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ for *p*-methoxyphenylation = 2·9

Determination of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCl}}K$ *for* p-*Nitrophenylation.*—Experiments 5 and 6 were carried out with *p*-nitrobenzoyl peroxide (6 g.) in an equimolar mixture (200 ml.) of nitrobenzene and chlorobenzene. The reactions were conducted, and the biaryl fractions isolated, as described above. The biaryl fractions were analysed for nitro-group content by titanous chloride reduction, and the fore-runs for chlorine by the micro-Carius method. The results are given in Table 4.

TABLE 4.

	Experiment 5	Experiment 6
Biaryl fraction (g.) (b. p. 45—195°/0·1 mm.)	3·112	3·491
Dinitrobiphenyls in biaryl fraction (%)	45·4	45·1
Fore-run (g.)	2·463	1·762
Chloronitrobiphenyls in fore-run (%)	3·51	9·05
Chloronitrobiphenyls in fore-run (g.)	0·087	0·159
Corr. wt. of biaryl fraction (g.)	3·199	3·650
Dinitrobiphenyls, corr. (%)	44·1	43·2
${}^{\mathrm{PhNO_2}}_{\mathrm{PhCl}}K$ for *p*-nitrophenylation	0·76	0·74
Free *p*-nitrobenzoic acid (g.)	2·70	2·60
p-Nitrobenzoic acid from hydrolysis of esters (g.)	0·36	0·34
Residue (g.)	0·150	0·137
(p-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}O)_2$ accounted for (%)	88·2	91·4

Hence ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCl}}K$ for *p*-nitrophenylation = 0·75

Determination of ${}^{PhNO_2}_{PhCl}K$ *for* p-*Methoxyphenylation.*—Experiments 7 and 8 were carried out with *p*-methoxybenzoyl peroxide (6 g.) in an equimolar mixture (200 ml.) of nitrobenzene and chlorobenzene. The reactions were conducted, and the products isolated and analysed, as described above for the determination of the rate-ratio for *p*-nitrophenylation, except that the chromatography stage was included in the working-up procedure. The results are given in Table 5.

Determination of the Ratio of Isomers formed in the p-*Nitrophenylation of Nitrobenzene.*—In experiments 9 and 10, *p*-nitrobenzoyl peroxide (6 g.) was allowed to decompose in nitrobenzene (200 ml.) in a thermostat at 80° for 72 hr. The standard procedure (Part II [3]) was used for the isolation of the biaryl fractions, which were shown by analysis to contain no extraneous material. The yields of the various products obtained are given in Table 6.

TABLE 5.

	Experiment 7	Experiment 8
Biaryl fraction (g.) (b. p. 45—130°/0·1 mm.)	1·777	1·742
Nitrobiaryls in biaryl fraction (%)	66·4	65·7
Fore-run (g.) (b. p. 25—45°/0·1 mm.)	0·481	0·711
Chloromethoxybiphenyls in fore-run (g.)	0	0
${}^{PhNO_2}_{PhCl}K$ for *p*-methoxyphenylation	1·96	1·91
Free *p*-methoxybenzoic acid (g.)	3·03	3·16
p-Methoxybenzoic acid from hydrolysis of esters (g.)	0·60	0·58
Residue (g.)	0·172	0·043
$(p\text{-MeO}\cdot C_6H_4\cdot CO\cdot O)_2$ accounted for (%)	80·5	82·5

Hence ${}^{PhNO_2}_{PhCl}K$ for *p*-methoxyphenylation = 1·9

TABLE 6.

	Experiment 9	Experiment 10
Biaryl fraction (g.) (b. p. 60—195°/0·1 mm.)	3·041	2·972
Free *p*-nitrobenzoic acid (g.)	2·78	2·68
p-Nitrobenzoic acid from hydrolysis of esters (g.)	0·25	0·30
Residue (g.)	0·328	0·359
$(p\text{-NO}_2\cdot C_6H_4\cdot CO\cdot O)_2$ accounted for (%)	84·6	83·2

The mixtures of isomeric dinitrobiphenyls obtained from expts. 9 and 10 were analysed by infrared spectrography. The procedure described in Part XIV [2(a)] was used, except that *NN*-dimethylformamide was used as solvent instead of the more usual nitromethane, in which 4,4′-dinitrobiphenyl is virtually insoluble. *NN*-Dimethylformamide is a suitable solvent for this analysis, since it has only one intense absorption band (at 870 cm.$^{-1}$) in the region 750—900 cm.$^{-1}$, in which the characteristic bands of the relevant biaryls occur, and this band does not coincide with any of the characteristic biaryl bands used for the analysis, which were as follows: 2,4′- 790 cm.$^{-1}$, 3,4′-dinitrobiphenyl 772 cm.$^{-1}$. The amount of 4,4′-dinitrobiphenyl present in the mixtures was obtained by difference. In order to check the accuracy of the analyses a synthetic mixture (S1) of known composition was made up and analysed. The composition of the two experimental mixtures, and their mean, together with the composition of S1, as determined spectrographically, are given in Table 7.

TABLE 7. *Analysis of mixtures of dinitrobiphenyls.*

	Composition of dinitrobiphenyls (%)		
Mixture	2,4′-	3,4′-	4,4′-
9	56·7	15·2	28·1
10	58·3	15·2	26·5
Mean	57·5	15·2	27·3
S1 (Found)	59·0	10·7	30·3
S1 (Calc.)	57·5	10·1	32·4

DISCUSSION

Relative Rates of Arylation.—The results are summarised in Table 8, which also includes, for comparison, the relative rates of phenylation and *p*-chlorophenylation of these compounds, and the dipole moments of the compounds C_6H_5R from which the radicals *p*-R·C_6H_4· may be regarded as being derived by removal of a hydrogen atom from the *para*-position. This value may be taken as an indication of the polar character of the radicals, if it can be assumed that this is determined wholly or mainly by the permanent effects of the substituents.

The results indicate that the *p*-nitro-, *p*-chloro-, and *p*-methoxy-phenyl radicals are slightly electrophilic in character, since the relative rates $\frac{PhNO_2}{PhCl}K$ and $\frac{PhNO_2}{PhH}K$ for electrophilic substitution have long been known to be less than unity. Moreover, the electrophilic character of these radicals varies in the order *p*-nitrophenyl > *p*-chlorophenyl > *p*-methoxyphenyl, that is, in the order predicted by an examination of the dipole moments of the corresponding compounds C_6H_5R. It therefore appears that the polarisability (mainly electromeric) effects of chloro- and methoxy-substituents in the radicals do not influence the polar characteristics of the radicals to a large extent, certainly not sufficiently to upset the pattern established by the permanent polarisation induced by these substituents. It is not possible to draw this conclusion for the *p*-nitrophenyl radical since, in this instance, the permanent and time-variable effects of the nitro-group reinforce one another, both being in the direction of electron-withdrawal from the nucleus. Nevertheless, the conclusion is probably a general one, and, indeed, is not entirely unexpected, since polarisability effects can only operate to the extent to which they are called into play by the electronic requirements of the reaction. In reactions of homolytic substitution the only entity which is involved other than the radical itself is the neutral molecule of the aromatic substrate, and this would not be expected to call polarisability effects into play to any marked degree.

TABLE 8. *Relative rates of arylation.*

Radical *p*-R·C_6H_4·	$\frac{PhNO_2}{PhCl}K$	$\frac{PhNO_2}{PhH}K$	Dipole moment of C_6H_5R (D) [12]
p-NO_2·C_6H_4·	0·75	0·94	−3·98
p-ClC_6H_4·	1·49 *	1·53 *	−1·55
p-MeO·C_6H_4·	1·9	2·9	−1·23
C_6H_5·	2·8 †	4·0 *†	0

* Cadogan, Hey, and Williams.[1] † Augood, Hey, and Williams.[3]

Rates of arylation of chlorobenzene compared with those of benzene may be derived from the reported data, since $\frac{PhCl}{PhH}K = \frac{PhNO_2}{PhH}K / \frac{PhNO_2}{PhCl}K$. These are as follows: for *p*-nitrophenylation, 1·3; for *p*-chlorophenylation, 1·02; and for *p*-methoxyphenylation, 1·5. It would, however, be unwise to base any argument concerning the polar characteristics of radicals on these values, since the differences displayed are very small, and the values themselves, being derived, are subject to rather larger errors than directly determined values.

Ratio of Isomers.—The ratio of isomers formed in the *p*-nitrophenylation of nitrobenzene is compared with the corresponding ratio for the phenylation of this compound in Table 9. The difference between the two ratios, though small, is outside experimental error, at least for the percentage of the 3-isomer produced. The electrophilic *p*-nitrophenyl radical appears to attack the least deactivated (*meta*-)position of nitrobenzene to a

TABLE 9. *Arylation of nitrobenzene at* 80°.

	Isomer (%)		
Radical	2-	3-	4-
p-NO_2·C_6H_4·	57·5	15·2	27·3
C_6H_5· *	62·5	9·8	27·7

* Chang Shih, Hey, and Williams.[2a]

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[12] Waters, " Physical Aspects of Organic Chemistry," 4th edn., Routledge and Kegan Paul Ltd., London, 1950, p. 88

greater extent than the phenyl radical, as would be expected. The observed small magnitude of the effects of radical-polarisation on ratios of isomers has been predicted by Rondestvedt and Blanchard.[13]

Similar conclusions can be drawn from a comparison of the partial rate factors for *p*-nitrophenylation of nitrobenzene ($F_o = 1{\cdot}64$, $F_m = 0{\cdot}43$, $F_p = 1{\cdot}56$) with those for phenylation of this compound at 80° ($F_o = 7{\cdot}5$, $F_m = 1{\cdot}2$, $F_p = 6{\cdot}6$ [2c]). The ratio F_m/F_p could be expected to increase with increasing electrophilic character of the radical, if the directing group in the substrate is an electron-attracting group (*ortho*-positions are not considered in this argument because of possible steric complications). The values of this ratio, which for *p*-nitrophenylation of nitrobenzene is 0·275, and for phenylation of this compound is 0·182, are again in agreement with this prediction.

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[13] Rondestvedt and Blanchard, *J. Org. Chem.*, 1956, **21**, 229.