17. *Homolytic Aromatic Substitution. Part XXXII.* Some Reactions with* meta-*Substituted Phenyl Radicals.*

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Measurements of relative rates have been made for the arylation of benzene and nitrobenzene, and of nitrobenzene and chlorobenzene, with *m*-nitro-, *m*-chloro-, and *m*-methyl-phenyl radicals. In order to complete the information required to substantiate the theoretical treatment, the corresponding relative rates for *o*-chlorophenylation have been measured. Isomer ratios for the *m*-nitro-, *o*- and *m*-chloro-, and *m*-methyl-phenylation of nitrobenzene have been determined and the relevant partial rate factors derived. The results are discussed in terms of the hypothesis of polarised radicals. A number of new disubstituted biphenyls are described.

The results of measurements of relative rates and ratios of isomers for the arylation of several monosubstituted benzene derivatives with *ortho*- and *para*-substituted aryl radicals, obtained from the appropriate diaroyl peroxides, have been reported in earlier Papers in this series.[1-4] These results have been shown to be in general agreement with the hypothesis that the pattern of homolytic substitution is modified in a predictable manner by polar and steric influences which are dependent upon the nature of the attacking radicals. In an attempt to provide further evidence on this question and to obtain further light on the mechanism of the transmission of polar influences in aryl free radicals, similar measurements have now been made of the relative rates of the reactions of three *meta*-substituted aryl radicals, namely *m*-nitro-, *m*-chloro-, and *m*-methyl-phenyl, with mixtures of benzene and nitrobenzene, and of nitrobenzene and chlorobenzene. In order to complete a series, the relative rates of the reactions of *o*-chlorophenyl radicals with these substrates have also been determined. In addition, isomer ratios have been measured for the reactions of *m*-nitrophenyl, *o*- and *m*-chlorophenyl, and *m*-methylphenyl radicals with nitrobenzene.

Nitrobenzene has been used as a reference compound in all the competitive experiments and the compositions of the mixtures of biaryls obtained have been determined by means of the volumetric estimation of the nitro-group by reduction with titanous sulphate.[3] A further advantage of this procedure is that, since nitro-compounds were present in all the competitive reaction mixtures, high-boiling residues were formed only in small quantities.[5] Nevertheless, as can be seen from the experimental details, small quantities of material remained unidentified in all the competitive experiments, and are shown in the Tables as "Residue." The magnitude of the greatest possible errors in the relative rates can be calculated if it is assumed that the "Residues" consist entirely of products of further reactions of intermediates in the arylation of one or the other of the competing solvents. Such calculations lead to the conclusion that, although the amounts of residue obtained varied somewhat from one experiment to another, it would, in almost all cases, be reasonable to assume that differences in rate ratios of more than 20% are of theoretical significance. This assumption has therefore been adopted in the following discussion. It applies, however, only to directly determined relative rates, since the derivation of rates of arylation relative to benzene by multiplication of directly determined values, as described in previous papers (see, for example, Augood, Hey, and Williams [6]), can give rise to multiplication of errors, and some supporting evidence of the validity of such derived values is usually

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* Part XXXI, *J.*, 1964, 3412.

[1] Cadogan, Hey, and Williams, *J.*, 1955, 1425.

[2] Chang Shih, Hey, and Williams, *J.*, 1958, (*a*) 1885, (*b*) 2600, (*c*) 4403.

[3] Hey, Moulden, and Williams, *J.*, 1960, 3769.

[4] (*a*) Hambling, Hey, and Williams, *J.*, 1960, 3782; (*b*) Hambling, Hey, Orman, and Williams, *J.*, 1961, 3108; (*c*) Hambling, Hey, and Williams, *J.*, 1962, 487.

[5] Hey, Perkins, and Williams, *Chem. and Ind.*, 1963, 83.

[6] Augood, Hey, and Williams, *J.*, 1952, 2094.

desirable.[6] The use of such figures is therefore not considered advisable in the present context, when the errors attendant upon the direct determinations are rather larger than in most of the determinations previously reported, and when the differences expected to arise from changes in the polar characteristics of the radicals are, in any case, small.

The results obtained on the relative rates of arylation are shown in Table 1, which also includes, for reference, some results reported previously. Since the nitro-group is the more strongly electron-attracting of the directing groups present in the substrates used, namely nitrobenzene and chlorobenzene, the relative rates ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ and ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCl}}K$ would be expected to decrease with increasing electrophilic character, and to increase with increasing nucleophilic character, of the attacking radicals, if steric effects are neglected. These steric effects have, however, been shown to be important in some, but not all, reactions with *ortho*-substituted radicals.[3] In particular, the reactions with *o*-chlorophenyl radicals would be expected to be affected, and possibly also those with *o*-methylphenyl radicals and of *o*-nitrophenyl radicals with chlorobenzene. The relative rate ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ for *o*-nitrophenylation has, however, been shown not to be influenced by a steric effect,[3] and the absence of such an effect in this instance was considered to be due to the rotation of the nitro-groups, attached to both the radical and the substrate molecule, out of the plane of their respective nuclei as the transition state leading to *ortho*-substitution is formed. Circumvention of the steric effect in this manner is not possible with methyl and chloro-substituents, neither of which is planar.

TABLE 1.

Relative rates of arylation.

Radical	Relative rates ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$	Relative rates ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCl}}K$	Reference	Radical	Relative rates ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$	Relative rates ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCl}}K$	Reference
o-Nitrophenyl......	0·26	0·31	3	Phenyl	2·9	2·9	6, 7, 8
m-Nitrophenyl ...	0·43	0·76	This work	*o*-Methylphenyl...	2·2	1·4	9
p-Nitrophenyl ...	0·94	0·75	4*a*	*m*-Methylphenyl	3·0	2·6	This work
o-Chlorophenyl ...	0·82	0·92	This work	*p*-Methylphenyl...	3·4	2·5	4*b*
m-Chlorophenyl ...	1·3	1·2	This work				
p-Chlorophenyl ...	1·5	1·5	1				

The polar effects in the radicals are therefore most clearly displayed by the values of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ for *o*-, *m*-, and *p*-nitrophenylation, which are uncomplicated by steric influences, and it is clear from the results given in Table 1 that the electrophilic character of the nitrophenyl radicals increases in the order *p*- < *m*- < *o*-. No significant differences are displayed between the values of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCl}}K$ for *m*- and *p*-nitrophenylation, but the value of this relative rate for *o*-nitrophenylation is significantly lower. Since the operation of a steric effect should tend to raise this value (chlorobenzene, but not nitrobenzene, is rendered less reactive by the steric effect) the observed low value must be indicative of the enhanced electrophilic character of the *o*-nitrophenyl radical. The relative rates for nitrophenylation therefore fall into a self-consistent pattern, and indicate that the influence of a polar group (nitro in this case) on the properties of a radical containing it depends primarily on its proximity to the atom which formally carries the unpaired electron, and appears not to be affected by the presence of a conjugated system in such a radical.[3] The dominant influence of the nitro-group appears to be its direct effect, since transmission of polarisation through the conjugated system of the nucleus would be expected to result in selection of the *ortho*- and *para*-positions, and the electrophilic character of the nitrophenyl radicals to vary in the order *o*-, *p*- > *m*-.

The electrophilic character of the *m*- and *p*-chlorophenyl radicals is clearly demonstrated by the relative rates given in Table 1, since the values of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ and ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCl}}K$ for arylation with these radicals are considerably lower than those for phenylation. The small differences

[7] Hey, Orman, and Williams, *J.*, 1961, 565.
[8] Hey, Pengilly, and Williams, *J.*, 1956, 1463.
[9] Moulden, Ph.D. Thesis, University of London, 1959.

displayed between the values for the *meta*- and *para*-substituted radicals are hardly significant. The reactions with *o*-chlorophenyl radicals again illustrate the electrophilic character of these radicals, although these relative rates may well also be influenced by the operation of the steric effect, as has been shown to operate in reactions with *o*-bromophenyl radicals.[3] It seems likely that the steric effect is also responsible for the low values of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ and ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCl}}K$ for *o*-methylphenylation, since the *o*-methylphenyl radical would be expected, if anything, to be slightly nucleophilic, and the operation of the polar effect would tend to give rise to values of these relative rates which are higher than those for phenylation. The polar characteristics of the *p*-methylphenyl radical have been discussed previously.[4b]

The ratios of isomers for the arylation of nitrobenzene are reported in the Experimental section. Partial rate factors (F_o, F_m, and F_p) derived from these results and from the appropriate directly determined relative rates of arylation, are given in Table 2, which also contains partial rate factors for some other reactions of arylation of nitrobenzene, for comparison. The influence of the formation of high-boiling residues on the reliability of ratios of isomers formed in phenylation reactions has been investigated recently,[5,10] and has been shown to be negligible. Moreover, only small quantities of residues were formed in the reactions now reported.

It is clear that any change in the effective size of an attacking radical should exert its greatest influence on the reactivity of the *ortho*-positions of the substrate molecule, whilst the *para*-position should be the least affected. It was noted above that the extent of the polarisation of the nitrophenyl radicals appears to increase in the order *p*- < *m*- < *o*-. The consequent variation in the electrophilic character of these radicals is clearly indicated by the partial rate factors for the nitrophenylation of nitrobenzene. Moreover, the absence of a steric effect with any of them is shown by the closeness of the value F_o/F_p for all three nitrophenyl radicals to the value of this ratio for phenylation. On the other hand, the progressive decrease in F_p/F_m in the series of radicals phenyl, *p*-, *m*-, *o*-nitrophenyl is consistent with a progressive increase in the electrophilic character of the radicals in this series.

TABLE 2.

Partial rate factors for the arylation of nitrobenzene.

Radical	F_o	F_m	F_p	F_o/F_p	F_p/F_m	Ref.
o-Nitrophenyl	0·43	0·14	0·42	1·0	3·0	3
m-Nitrophenyl	0·68	0·73	0·75	0·91	3·3	This work
p-Nitrophenyl	1·6	0·43	1·6	1·0	3·6	4*a*
o-Chlorophenyl	0·88	0·60	2·0	0·45	3·3	This work
m-Chlorophenyl	2·2	0·58	2·2	1·0	3·8	This work
p-Chlorophenyl	2·7	0·63	2·5	1·1	3·9	1, 2*a*
Phenyl	5·5	0·86	4·9	1·1	5·7	2*a*, 7
o-Methylphenyl	2·7	1·2	5·2	0·51	4·3	3
m-Methylphenyl	5·5	1·2	4·7	1·2	4·0	This work
p-Methylphenyl	6·1	1·2	5·8	1·0	5·7	4*b*

Similar considerations may be applied to the partial rate factors for the chlorophenylation of nitrobenzene. Here, however, the low value of F_o for *o*-chlorophenylation, and the corresponding sharp reduction in F_o/F_p, is clearly indicative of the operation of a steric effect which reduces the reactivity of the *ortho*-positions in nitrobenzene towards attack by *o*-chlorophenyl radicals. A similar conclusion was reached for the reaction of nitrobenzene with *o*-bromophenyl radicals.[3] The values of the ratio F_p/F_m confirm that the *meta*-position in the substrate (nitrobenzene) is less sensitive to changes in the polar characteristics of the attacking radical than the *para*-position, as for the nitrophenylation reactions, and as might be predicted from elementary considerations. Moreover, comparison of these ratios with the corresponding ratio for phenylation reveals

[10] Morrison, Cazes, Samkoff, and Howe, *J. Amer. Chem. Soc.*, 1962, **84**, 4152.

the electrophilic character of all three chlorophenyl radicals, and whilst there appears to be little difference between the *meta*- and *para*-radicals, the *o*-chlorophenylradical is the most electrophilic of them. Once again, the " proximity effect " is displayed, as the *m*-chlorophenyl radical appears to be not less electrophilic than its *para*-analogue.

The operation of a steric effect is again apparent in the *o*-methylphenylation reaction. The partial rate factors for *p*-methylphenylation do not indicate any pronounced polar characteristics and, whilst the values of F_p/F_m are numerically less than the corresponding values for phenylation, it is unlikely that this difference is theoretically significant, since with these radicals the amount of the *meta*-isomer formed is small, and a slight error (2%) in its value would cause a substantial change in F_p/F_m. The method of analysis of the mixtures of biaryls used is incapable of a greater degree of accuracy than this. The results, therefore, indicate that the introduction of the methyl group in the *meta*- or *para*-position causes no appreciable change in the properties of the phenyl radical. These radicals would, of course, be expected to possess some slight nucleophilic character [4b] but the influence of the methyl group on the polarity of the ground-states of the methylphenyl radicals must be very small and the resultant influences on the pattern of aromatic substitution by them are not sufficiently pronounced to be detectable by the present experiments. This is not surprising, especially in view of the conclusion reached above that it is the direct effect of the group present in the radical which is the most important in determining its polar characteristics.

EXPERIMENTAL

All solids were recrystallised to constant m. p. Melting points are uncorrected.

Reagents.—Benzene, chlorobenzene, and nitrobenzene were purified as described in Part II.[6] *m*-Nitrobenzoyl peroxide, m. p. 136°, and *m*-chlorobenzoyl peroxide, m. p. 122—123° (decomp.), were prepared by Hey and Walker's method.[11] *o*-Chlorobenzoyl peroxide, m. p. 102—103° (decomp.) and *m*-methylbenzoyl peroxide, m. p. 52—53°, were prepared by Price and Krebs's method.[12]

A specimen of 2,3′-dinitrobiphenyl, m. p. 118—119° was kindly donated by Dr. H. N. Moulden. 3,4′-Dinitrobiphenyl was crystallised from ethanol, m. p. 189—190°. 3,3′-Dinitrobiphenyl, m. p. 205° (Found: C, 58·6; H, 3·4. Calc. for $C_{12}H_8N_2O_4$: C, 59·0; H, 3·3%), was prepared by means of the Ullmann reaction with *m*-iodonitrobenzene and copper powder, which was prepared by Gore and Hughes's method.[13]

3-Chloro-3′-nitrobiphenyl was prepared by heating a mixture of *m*-iodonitrobenzene (106 g.), *m*-chloroiodobenzene (100 g.), and copper powder [13] (85 g.) at 200° for 4 hr. Extraction with ethanol, and crystallisation gave 3,3′-dinitrobiphenyl (10 g.). Ethanol was removed from the mother-liquor and distillation of the residue under reduced pressure gave (i) *m*-chloroiodobenzene (13 g.), b. p. 53°/0·03 mm., (ii) a yellow solid (3 g.), b. p. 120—130°/0·02 mm., and (iii) 3,3′-dinitrobiphenyl (1 g.), b. p. 135—180°/0·02 mm. Fraction (ii), on repeated crystallisation from light petroleum (b. p. 40—60°), slow sublimation *in vacuo*, and final recrystallisation from light petroleum (b. p. 40—60°) gave 3-chloro-3′-nitrobiphenyl (2 g.), m. p. 91° (lit.,[14] 89°) (Found: C, 62·1; H, 3·4; Cl, 14·9. Calc. for $C_{12}H_8ClNO_2$: C, 61·7; H, 3·5; Cl, 15·2%).

3-*Chloro-2′-nitrobiphenyl* was prepared by the decomposition of *m*-chlorobenzoyl peroxide (25 g.) in nitrobenzene (500 ml.) at 80° for 72 hr. After removal of the bulk of the nitrobenzene by distillation *in vacuo*, the residue was extracted with saturated aqueous sodium hydrogen carbonate (6 × 50 ml.), washed with water (2 × 100 ml.), and dried (Na_2SO_4). After removal of the residual nitrobenzene by distillation (b. p. 35°/0·01 mm.), fractional distillation of the residue gave a pale yellow oil (8 g.), b. p. 110—125°/0·05 mm., and a yellow semi-solid (3·5 g.), b. p. 145—160°/0·05 mm. Chromatography of the former fraction on alumina, and elution with light petroleum (b. p. 60—80°)–benzene (4 : 1; v/v) gave (i) a pale yellow oil (1·4 g.), (ii) a yellow oil (4 g.), and (iii) a yellow solid (2 g.). Fraction (iii) was combined with the less volatile fraction from the distillation, and crystallisation of the combined fraction from light petroleum

[11] Hey and Walker, *J.*, 1948, 2213.
[12] Price and Krebs, *Org. Synth.*, Coll. Vol. 3, 649.
[13] Gore and Hughes, *J.*, 1959, 1615.
[14] Woods, Reed, Arthur, and Ezekiel, *J. Amer. Chem. Soc.*, 1951, **73**, 3854.

(b. p. 60—80°) gave 3-chloro-4′-nitrobiphenyl (3 g.), m. p. 90—91° (lit.,[2b] 91°). This compound (m. p. and mixed m. p. 91°) was also prepared by means of the Gomberg reaction from *m*-chloroaniline and nitrobenzene (Found: C, 61·0; H, 3·5; Cl, 15·4. Calc. for $C_{12}H_8ClNO_2$: C, 61·7; H, 3·5; Cl, 15·2%). Fraction (ii) could not be crystallised and was assumed to be a mixture. Fraction (i) solidified at −80°, and was recrystallised from light petroleum (b. p. 40—60°) to give *prisms* (1·0 g.), m. p. 29—30° (Found: C, 62·1; H, 3·6; Cl, 14·7. $C_{12}H_8ClNO_2$ requires C, 61·7; H, 3·5; Cl, 15·2%). Since this compound was different from both 3-chloro-3′-nitrobiphenyl and 3-chloro-4′-nitrobiphenyl, it must be 3-chloro-2′-nitrobiphenyl. Its infrared spectrum was consistent with this assignment.

2-Chloro-2′-nitrobiphenyl was prepared by heating a mixture of *o*-iodonitrobenzene (50 g.), *o*-chloroiodobenzene (50 g.), and copper powder (45 g.) at 225° for 5 hr. with stirring. The resulting mixture was extracted with boiling ethanol until the extracts were colourless, and the extracts were treated with activated charcoal and evaporated to about 250 ml. 2,2′-Dinitrobiphenyl (11·4 g.), m. p. 124—125°, was deposited on cooling, and fractional distillation of the residue obtained by evaporation of the mother-liquors gave unchanged *o*-chloroiodobenzene (7 g.), b. p. 57—65°/0·04 mm., 2,2′-dichlorobiphenyl (2·7 g.), b. p. 72—85°/0·02 mm., m. p. 56—58°, 2,2′-dinitrobiphenyl (2·3 g.), b. p. 122—140°/0·01 mm., m. p. 125°, and a solid fraction which was collected at 95—115°/0·01 mm. This fraction, on crystallisation from methanol or light petroleum (b. p. 40—60°), gave 2-chloro-2′-nitrobiphenyl (7·6 g.), m. p. 70° (lit.,[15] 71°) (Found: C, 62·2; H, 3·5; Cl, 15·0%. Calc. for $C_{12}H_8ClNO_2$: C, 61·7; H, 3·5; Cl, 15·2%).

2-Chloro-3′-nitrobiphenyl was prepared from *m*-nitroaniline and chlorobenzene by means of the Gomberg reaction. A solution of sodium hydroxide (40 g.) in water (200 ml.) was added during 2 hr. to a stirred mixture of chlorobenzene (1 l.), crushed ice, and a solution prepared by diazotisation of *m*-nitroaniline (100 g.) in concentrated hydrochloric acid (180 ml.) and water (100 ml.), with a solution of sodium nitrite (50 g.) in water (100 ml.). After being stirred for 36 hr. at room temperature, the mixture was separated and the organic layer washed twice with 10% v/v hydrochloric acid, and twice with water, and dried (Na_2SO_4). After removal of the excess of chlorobenzene by distillation the residue was fractionally distilled, fractions being collected at 120—136°/0·05 mm. and 140—160°/0·02 mm. The former, on crystallisation from light petroleum (b. p. 40—60°) gave 2-chloro-3′-nitrobiphenyl (2 g.), m. p. 64—65° (lit.,[16] 64—65°) (Found: C, 62·4; H, 3·6; Cl, 15·1%). A further crop (4·5 g.) was obtained by chromatography on alumina of the second fraction from the distillation, elution with light petroleum (b. p. 60—80°)–benzene (4 : 1), and crystallisation from light petroleum (b. p. 40—60°).

2-Chloro-4′-nitrobiphenyl was prepared from *o*-chloroaniline (80 g.) and nitrobenzene (1 l.) by means of the Gomberg reaction, as described above. Distillation of the product gave a semi-solid fraction of b. p. 90—130°/0·01 mm. Filtration and crystallisation of the residue from light petroleum (b. p. 40—60°) gave 2-chloro-4′-nitrobiphenyl (6·4 g.), m. p. 79—80° (lit.,[2b] 77—78°). A further crop (1 g.) was obtained by chromatography of the filtrate on alumina, elution with light petroleum (b. p. 60—80°)–benzene (3 : 1), and crystallisation from light petroleum (b. p. 40—60°). 2-Chloro-3′-nitrobiphenyl (3 g.), m. p. and mixed m. p. 62—63°, was eluted first in the chromatography, followed by a liquid fraction which was presumed to be a mixture of isomers. 2-Chloro-4′-nitrobiphenyl was also prepared, in low yield, by Chang Shih, Hey, and Williams's method.[2b]

3-Methyl-2′- and -4′-nitrobiphenyl were prepared from *m*-methylbenzoyl peroxide (27 g.) and nitrobenzene (540 ml.) heated at 80° for 72 hr. After removal of the bulk of the solvent under reduced pressure, the residue was washed with saturated aqueous sodium hydrogen carbonate (4 × 100 ml.) and water (2 × 100 ml.), and dried (Na_2SO_4). It was then distilled and fractions of b. p. 110—122°/0·05 mm. and 123—145°/0·05 mm. were collected. Crystallisation of the less volatile fraction, which solidified on cooling, from light petroleum (b. p. 40—60°) gave *3-methyl-4′-nitrobiphenyl* (1·2 g.), m. p. 58—59° (Found: C, 73·2; H, 5·0; N, 6·8. $C_{13}H_{11}NO_2$ requires C, 73·2; H, 5·2; N, 6·6%). This compound was identical with one prepared, but not fully characterised, by Dr. J. K. Hambling from *m*-toluidine and nitrobenzene by means of the Gomberg reaction.[17] Its non-identity with 3-methyl-3′-nitrobiphenyl, whose preparation is described below, and a comparison of its m. p., b. p., and infrared spectrum with those of the other, isomeric, product of this reaction, are consistent with the structure now assigned to it.

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[15] Mascarelli, Gatti, and Pirona, *Gazzetta*, 1931, **61**, 782.

[16] Kaslow and Summers, *J. Org. Chem.*, 1955, **20**, 1738.

[17] Hambling, Ph.D. Thesis, University of London, 1957.

Chromatography of the more volatile fraction from the distillation, and elution with light petroleum (b. p. 40—60°) gave a liquid fraction (i). Further elution with light petroleum–benzene (3 : 1) gave fractions (ii), a liquid (3 g.) which was rejected, and (iii) which, on crystallisation from light petroleum (b. p. 40—60°) gave 3-methyl-3′-nitrobiphenyl (0·1 g.), m. p. and mixed m. p. 54—56°, the preparation of which by an unambiguous route is described below. Fraction (i) was distilled, and a middle fraction, b. p. 198°/25 mm., collected and again subjected to chromatography as described above. No apparent separation occurred, and redistillation of

TABLE 3.

Determination of ${}_{\mathrm{PhH}}^{\mathrm{PhNO_2}}K$ for *m*-nitrophenylation.

Expt. No.:	1		2	
Portion:	(A)	(B)	(A)	(B)
Biaryls (b. p. 80—158°/0·01 mm.) (g.)	1·844	1·353	1·961	1·266
Dinitrobiphenyls in biaryl fraction (%)	34·30	34·79	34·55	34·95
Forerun (b. p. 15—35°/0·01 mm.) (g.)	1·137	1·250	1·267	1·354
Nitrobenzene in forerun (%)	99·83	100·0	98·42	99·77
3-Nitrobiphenyl in forerun (g.)	0·002	0·000	0·036	0·003
Corr. wt. of biaryls (g.)	1·846	1·353	1·997	1·269
Dinitrobiphenyls in biaryl fraction (corr.) (%)	34·26	34·79	33·91	34·86
${}_{\mathrm{PhH}}^{\mathrm{PhNO_2}}K$	0·43	0·44	0·42	0·44
Free *m*-nitrobenzoic acid (m. p. 136—137°) (g.)	2·74		2·75	
m-Nitrobenzoic acid from hydrolysis of esters (g.)	0·37		0·37	
Residue (g.)	0·130		0·136	
Peroxide accounted for (%)	95·7		96·8	

Hence ${}_{\mathrm{PhH}}^{\mathrm{PhNO_2}}K$ (mean) for *m*-nitrophenylation = 0·43.

TABLE 4.

Determination of ${}_{\mathrm{PhH}}^{\mathrm{PhNO_2}}K$ for *m*-chlorophenylation.

Expt. No.:	3		4	
Portion:	(A)	(B)	(A)	(B)
Biaryls (b. p. 55—154°/0·01 mm.) (g.)	1·899	1·456	1·924	1·401
Chloronitrobiphenyls in biaryl fraction (%)	62·09	61·12	62·19	60·78
Forerun (b. p. 18—35°/0·01 mm.) (g.)	0·687	1·072	0·306	1·702
Chlorine in forerun (%)	0·000	0·000	0·130	0·180
3-Chlorobiphenyl in forerun (g.)	0·000	0·000	0·002	0·016
Corr. wt. of biaryls (g.)	1·899	1·456	1·926	1·417
Chloronitrobiphenyls in biaryl fraction (corr.) (%)	62·09	62·12	62·13	60·10
${}_{\mathrm{PhH}}^{\mathrm{PhNO_2}}K$	1·32	1·27	1·32	1·25
Free *m*-chlorobenzoic acid (m. p. 150—151°) (g.)	2·66		2·70	
m-Chlorobenzoic acid from hydrolysis of esters (g.)	0·46		0·47	
Residue (g.)	0·180		0·169	
Peroxide accounted for (%)	92·1		93·3	

Hence ${}_{\mathrm{PhH}}^{\mathrm{PhNO_2}}K$ (mean) for *m*-chlorophenylation = 1·3.

TABLE 5.

Determination of ${}_{\mathrm{PhH}}^{\mathrm{PhNO_2}}K$ for *o*-chlorophenylation.

Expt. No.:	5		6	
Portion:	(A)	(B)	(A)	(B)
Biaryls (b. p. 50—154°/0·01 mm.) (g.)	1·568	1·510	1·483	1·516
Chloronitrobiaryls in biaryl fraction (%)	51·47	51·71	51·72	51·40
Forerun (b. p. 18—35°/0·01 mm.) (g.)	0·664	2·182	0·904	1·197
Nitrobenzene in forerun (%)	96·17	98·35	94·41	97·82
2-Chlorobiphenyl in forerun (g.)	0·026	0·036	0·051	0·026
Corr. wt. of biaryls (g.)	1·594	1·546	1·534	1·542
Chloronitrobiphenyls in biaryl fraction (corr.) (%)	50·53	50·54	50·04	50·54
${}_{\mathrm{PhH}}^{\mathrm{PhNO_2}}K$	0·83	0·83	0·80	0·83
Free *o*-chlorobenzoic acid (m. p. 140—141°) (g.)	2·70		2·95	
o-Chlorobenzoic acid from hydrolysis of esters (g.)	0·39		0·39	
Residue (g.)	0·291		0·280	
Peroxide accounted for (%)	90·3		93·3	

Hence ${}_{\mathrm{PhH}}^{\mathrm{PhNO_2}}K$ (mean) for *o*-chlorophenylation = 0·82.

the product, b. p. 94°/0·01 mm., caused no detectable change in the infrared spectrum. The product (1·5 g.), $n_D^{21\cdot5}$ 1·6043 (Found: C, 73·2; H, 5·1; N, 6·7. $C_{13}H_{11}NO_2$ requires C, 73·2; H, 5·2; N, 6·6%) was assumed to be *3-methyl-2′-nitrobiphenyl* on the grounds of its non-identity

TABLE 6.

Determination of $_{\mathrm{PhH}}^{\mathrm{PhNO_2}}K$ for *m*-methylphenylation.

Expt. No.:	7 *		8 *	
Portion:	(A)	(B)	(A)	(B)
Biaryls (b. p. 54—138°/0·01 mm.) (g.)	1·898	1·502	1·909	1·505
Methylnitrobiphenyls in biaryl fraction (%)	79·67	79·56	80·36	80·15
Forerun (b. p. 18—35°/0·01 mm.) (g.)	1·328	0·545	0·934	0·570
Nitrobenzene in forerun (%)	98·11	98·49	97·50	98·19
3-Methylbiphenyl in forerun (g.)	0·025	0·008	0·023	0·010
Corr. wt. of biaryls (g.)	1·923	1·510	1·932	1·515
Methylnitrobiphenyls in biaryl fraction (corr.) (%)	78·65	79·09	79·39	79·62
$_{\mathrm{PhH}}^{\mathrm{PhNO_2}}K$	2·91	2·98	3·05	3·08
Free *m*-toluic acid (m. p. 110—111°) (g.)	2·48		2·50	
m-Toluic acid from hydrolysis of esters (g.)	0·49		0·49	
Residue (g.)	0·159		0·204	
Peroxide accounted for (%)	83·4		84·8	

Hence $_{\mathrm{PhH}}^{\mathrm{PhNO_2}}K$ (mean) for *m*-methylphenylation = 3·0.

* In these experiments the bulk of the nitrobenzene was removed by distillation at a relatively high pressure (105 mm.) in order to prevent loss of the rather volatile 3-methylbiphenyl.

TABLE 7.

Determination of $_{\mathrm{PhCl}}^{\mathrm{PhNO_2}}K$ for *m*-nitrophenylation.

Expt. No.:	9		10	
Portion:	(A)	(B)	(A)	(B)
Biaryls (b. p. 55—144°/0·01 mm.) (g.)	1·947	1·704	2·036	1·476
Dinitrobiphenyls in biaryl fraction (%)	45·81	45·42	46·08	48·78
Forerun (b. p. 17—35°/0·01 mm.) (g.)	2·095	1·308	1·107	1·284
Chlorine in forerun (%)	0·55	0·00	1·39	1·92
Chloronitrobiphenyls in forerun (g.)	0·076	0·000	0·101	0·162
Corr. wt. of biaryls (g.)	2·023	1·704	2·137	1·638
Dinitrobiphenyls in biaryl fraction (corr.) (%)	43·72	45·42	44·51	43·96
$_{\mathrm{PhCl}}^{\mathrm{PhNO_2}}K$	0·74	0·79	0·77	0·75
Free *m*-nitrobenzoic acid (m. p. 136—137°) (g.)	2·68		2·54	
m-Nitrobenzoic acid from hydrolysis of esters (g.)	0·35		0·57	
Residue (g.)	0·094		0·092	
Peroxide accounted for (%)	93·8		95·5	

Hence $_{\mathrm{PhCl}}^{\mathrm{PhNO_2}}K$ (mean) for *m*-nitrophenylation = 0·76.

TABLE 8.

Determination of $_{\mathrm{PhCl}}^{\mathrm{PhNO_2}}K$ for *m*-chlorophenylation.

Expt. No.:	11		12	
Portion:	(A)	(B)	(A)	(B)
Biaryls (b. p. 60—160°/0·01 mm.) (g.)	2·904	1·423	1·946	2·130
Chloronitrobiphenyls in biaryl fraction (%)	55·77	57·01	56·65	56·46
Forerun (b. p. 19—35°/0·01 mm. (g.)	0·842	1·134	1·247	0·722
Nitrobenzene in forerun (%)	100·0	98·87	100·0	98·11
Dichlorobiaryls in forerun (g.)	0·000	0·014	0·000	0·014
Corr. wt. of biaryls (g.)	2·904	1·437	1·946	2·144
Chloronitrobiphenyls in biaryl fraction (corr.) (%)	55·77	56·36	56·65	56·10
$_{\mathrm{PhCl}}^{\mathrm{PhNO_2}}K$	1·20	1·23	1·25	1·22
Free *m*-chlorobenzoic acid (m. p. 151—153°) (g.)	2·63		2·64	
m-Chlorobenzoic acid from hydrolysis of esters (g.)	0·52		0·57	
Residue (g.)	0·189		0·140	
Peroxide accounted for (%)	99·8		98·2 *	

Hence $_{\mathrm{PhCl}}^{\mathrm{PhNO_2}}K$ (mean) for *m*-chlorophenylation = 1·2.

* The peroxide accountance is remarkably high, and therefore the biaryl fractions were redistilled to ensure that no extraneous material was present. No loss in weight occurred, and thus no nitrobenzene could be detected in these fractions.

with 3-methyl-3′-nitrobiphenyl and a comparison of its physical properties with those of 3-methyl-4′-nitrobiphenyl.

3-Methyl-3′-nitrobiphenyl was prepared by stirring a mixture of *m*-iodonitrobenzene (50 g.), *m*-iodotoluene (50 g.), and copper powder (45 g.) at 230° for 5 hr. The resulting mixture was extracted with boiling ethanol until the extracts were colourless, and the combined extract was treated with activated charcoal and evaporated to 300 ml. Crystallisation from ethanol of the solid which was deposited on cooling, gave 3,3′-dinitrobiphenyl, m. p. and mixed m. p. 202—203°. Fractional distillation of the residue obtained by eavporation of the original mother-liquor gave unchanged *m*-iodotoluene, 3,3′-dimethylbiphenyl (6·5 g.), b. p. 80—100°/0·05 mm., 3,3′-dinitrobiphenyl (0·5 g.), b. p. 160—180°/0·05 mm., m. p. 205°, and a solid (6 g.), b. p. 110—120°/0·05 mm. Crystallisation of this solid from light petroleum (b. p. 40—60°) gave 3-*methyl*-3′-*nitrobiphenyl* (4·7 g.), m. p. 57—58° (Found: C, 73·1; H, 5·1; N, 6·7%).

Competitive Experiments.—The experiments were conducted, and the mixtures of biaryls and foreruns were collected and analysed for the nitro-group by titration with titanous sulphate as described in Part XXIII.[7] The appropriate peroxide (6 g.) was allowed to decompose in an equimolar mixture (200 ml.) of the two solvents in a thermostat at 80° for 72 hr. Before the final distillation, the mixtures were divided into two portions, (A) and (B), which were distilled and analysed separately. In each experiment, fractions collected immediately before the forerun were shown by analysis to consist of pure nitrobenzene. The absence of the products of arylation of nitrobenzene from the foreruns can be assumed, as in every case there was a sufficient difference between the temperature at which the forerun was collected, and that at which these compounds began to distil. The results are given in Tables 3—10. The percentages of peroxide accounted for given in these Tables do not include the involatile and uncharacterised residues.

Measurement of Ratios of Isomers formed in the Arylation of Nitrobenzene.—The peroxide (6 g.)

TABLE 9.

Determination of ${}^{PhNO_2}_{PhCl}K$ for *o*-chlorophenylation.

Expt. No.:	13		14	
Portion:	(A)	(B)	(A)	(B)
Biaryls (b. p. 55—157°/0·01 mm.) (g.)	2·451	1·538	2·724	1·174
Chloronitrobiphenyls in biaryl fraction (%)	49·83	49·03	49·26	49·67
Forerun (b. p. 18—35°/0·01 mm.) (g.)	0·511	0·352	1·275	0·808
Nitrobenzene in forerun (%)	97·92	98·11	98·05	100·0
Dichlorobiaryls in forerun (g.)	0·011	0·007	0·025	0·000
Corr. wt. of biaryls (g.)	2·462	1·545	2·749	1·174
Chloronitrobiphenyls in biaryl fraction (corr.) (%)	49·51	48·34	48·87	49·67
${}^{PhNO_2}_{PhCl}K$	0·94	0·88	0·91	0·94
Free *o*-chlorobenzoic acid (m. p. 139—140°) (g.)	2·57		2·48	
o-Chlorobenzoic acid from hydrolysis of esters (g.)	0·34		0·33	
Residue (g.)	0·305		0·337	
Peroxide accounted for (%)	93·5		92·8	

Hence ${}^{PhNO_2}_{PhCl}K$ (mean) for *o*-chlorophenylation = 0·92.

TABLE 10.

Determination of ${}^{PhNO_2}_{PhCl}K$ for *m*-methylphenylation.

Expt. No.:	15		16	
Portion:	(A)	(B)	(A)	(B)
Biaryls (b. p. 50—140°/0·01 mm.) (g.)	2·273	1·848	2·331	1·982
Methylnitrobiphenyls in biaryl fraction (%)	74·99	74·91	74·76	74·57
Forerun (b. p. 19—35°/0·01 mm.) (g.)	1·315	1·374	2·479	1·550
Nitrobenzene in forerun (%)	96·28	97·10	95·66	98·23
Chloromethylbiphenyls in forerun (g.)	0·049	0·040	0·108	0·028
Corr. wt. of biaryls (g.)	2·322	1·888	2·439	2·010
Methylnitrobiphenyls in biaryl fraction (corr.) (%)	73·40	73·35	71·45	73·53
${}^{PhNO_2}_{PhCl}K$	2·63	2·63	2·38	2·63
Free *m*-toluic acid (m. p. 105—106°) (g.)	2·36		2·35	
m-Toluic acid from hydrolysis of esters (g.)	0·36		0·32	
Residue (g.)	0·179		0·204	
Peroxide accounted for (%)	89·0		90·6	

Hence ${}^{PhNO_2}_{PhCl}K$ (mean) for *m*-methylphenylation = 2·6.

was allowed to decompose in nitrobenzene (200 ml.) in a thermostat at 80° for 72 hr. The mixtures of biaryls were isolated from the resulting solutions as described above for the competitive experiments, except that the solutions were not divided into two portions. Also, no foreruns were collected as it was found from preliminary experiments that the difference in boiling-point between nitrobenzene and the biaryls was, in all cases, sufficiently large to permit satisfactory separation. The last traces of nitrobenzene were removed slowly over 8 hr. at a pressure of 0·05 mm., the bath temperature being raised gradually to ~80°. Yields of the various products are given in Table 11.

TABLE 11.

Products of arylation of nitrobenzene.

Expt. No.:	17	18	19	20	21	22	23	24
Peroxide:	*m*-Nitrobenzoyl		*m*-Chlorobenzoyl		*o*-Chlorobenzoyl		*m*-Methylbenzoyl	
Biaryls (g.)	3·537 [a]	3·554 [a]	3·224 [b]	3·127 [b]	3·338 [c]	3·323 [c]	3·854 [d]	3·808 [d]
Free acid (g.)	2·88	2·83	2·67	2·62	2·63	2·62	2·54	2·53
Acid from esters (g.)	0·33	0·32	0·48	0·49	0·28	0·29	0·36	0·38
Residue (g.)	0·238	0·263	0·434	0·372	0·834	0·781	0·433	0·542
Peroxide accounted for (%)	93·0	92·1	90·4	88·5	85·2	85·1	88·8	88·4

[a] B. p. 140—185°/0·01 mm. [b] B. p. 110—136°/0·03 mm. [c] B. p. 108—136°/0·01 mm. [d] B. p. 100—136°/0·03 mm.

TABLE 12.

Determination of ratios of isomers formed in the arylation of nitrobenzene.

		Isomer (%)		
Mixture	Components	2′-	3′-	4′-
S1 (known)	3,*x*′-Dinitrobiphenyls	61·8	14·5	23·7
S1 (found)	,,	61·3	15·5	23·2
Expt. 17	,,	53·0	18·2	28·8
Expt. 18	,,	52·8	17·8	29·4
Mean	,,	52·9	18·0	29·1
S2 (known)	3-Chloro-*x*′-nitrobiphenyls	55·9	19·0	25·1
S2 (found)	,,	54·9	19·1	26·0
S3 (known)	,,	39·8	26·1	34·1
S3 (found)	,,	41·3	26·7	32·0
Expt. 19	,,	55·5	14·5	30·0
Expt. 20	,,	58·0	15·5	26·5
Mean	,,	56·7	15·1	28·2
S4 (known)	2-Chloro-*x*′-nitrobiphenyls	41·9	27·8	30·3
S4 (found)	,,	42·6	28·4	29·0
S5 (known)	,,	47·5	19·2	33·3
S5 (found)	,,	48·0	20·0	32·0
Expt. 21	,,	34·8	24·2	41·0
Expt. 22	,,	36·8	24·2	39·0
Mean	,,	35·8	24·2	40·0
S6 (known)	3-Methyl-*x*′-nitrobiphenyls	60·0	12·2	27·8
S6 (found)	,,	58·1	14·8	27·1
S7 (known)	,,	50·9	19·3	29·8
S7 (found)	,,	49·9	21·6	28·5
Expt. 23	,,	61·6	12·5	25·9
Expt. 24	,,	59·7	13·9	26·4
Mean	,,	60·7	13·2	26·1

The mixtures of isomeric dinitrobiphenyls formed in the *m*-nitrophenylation of nitrobenzene were analysed by the ultraviolet spectrophotometric method described by Cadogan, Hey, and Williams,[18] as the spectra of 2,3′-, 3,3′-, and 3,4′-dinitrobiphenyl exhibit substantial differences in the 220—300 mμ region. The infrared spectrophotometric method [19] was used for the analysis of mixtures of chloronitro- and methylnitro-biphenyls, measurements of optical density being made at the following characteristic maxima: 3-chloro-2′-nitrobiphenyl, 787 cm.$^{-1}$; 3-chloro-3′-nitrobiphenyl, 741 and 889 cm.$^{-1}$; 2-chloro-2′-nitrobiphenyl, 790 cm.$^{-1}$; 2-chloro-3′-nitrobiphenyl, 813 cm.$^{-1}$; 3-methyl-2′-nitrobiphenyl, 786 cm.$^{-1}$; 3-methyl-4′-nitrobiphenyl, 858 cm.$^{-1}$

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[18] Cadogan, Hey, and Williams, *J.*, 1954, 794.

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

The concentrations of 3-chloro-4′-nitrobiphenyl, 2-chloro-4′-nitrobiphenyl, and 3-methyl-3′-nitrobiphenyl were obtained by difference, although the last-named compound had a characteristic maximum at 812 cm.$^{-1}$. Ethanol was used as the solvent for ultraviolet and nitromethane for infrared spectrophotometry. The results of the analysis of all the experimental mixtures, and of synthetic mixtures (S1—S7) of known composition, which were analysed in order to check the accuracy of the determinations, are given in Table 12. The absence of extraneous material from the mixtures of isomeric biaryls obtained from these reactions was inferred from the identity of the positions of absorption maxima in their infrared spectra with those observed in the spectra of the corresponding synthetic mixtures prepared from the three pure components. No unidentified peaks were present in the spectra of the mixtures from the arylations.

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