527. *Homolytic Aromatic Substitution. Part XV.* Ratio of Isomerides formed in the Arylation of Chlorobenzene and Bromobenzene with* p-*Nitrophenyl Radicals.*

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Measurements are reported of the proportions in which homolytic substitution by *p*-nitrophenyl radicals takes place at the *ortho*-, *meta*-, and *para*-positions of chlorobenzene and bromobenzene. In order to resolve inconsistencies revealed on examination of previous work, the proportions in which the 2-, 3-, and 4-isomer are formed in the phenylation of chlorobenzene have been measured. The results thus obtained illustrate the electrophilic character of the *p*-nitrophenyl radical, since significantly less *meta*-substitution takes place in *p*-nitrophenylation than in phenylation of these halogenobenzenes.

It is apparent from previous work (De Tar and Kazimi,[1] Dannley and Sternfeld,[2] Cadogan, Hey, and Williams [3]) that the nitro-group, being powerfully electron-attracting, confers considerable electrophilic character on an aryl radical in which it is situated in the *para*-position. The *p*-nitrophenyl radical is therefore used in the work described in this communication as a typical example of an electrophilic radical. Substitution in the halogenobenzenes by all types of reagents is of special interest, because of the peculiar combination of inductive and tautomeric effects ($-I + T$) exhibited by the halogens, which give rise in electrophilic substitution, as is well known, to deactivation of the nucleus accompanied by *ortho-para*-direction. Similarly the influence of a halogen atom on the nucleophilic replacement of groups present in the same nucleus is also anomalous, such replacement of groups oriented *meta* to the halogen being facilitated to a greater extent than that of groups in the *ortho*- and the *para*-position (see, for example, Bunnett and Zahler [4]). Arylation of the halogenobenzenes by electrophilic radicals is therefore of interest since, if the interpretation of the behaviour of polarised radicals put forward in Parts IX [3] and XIV [5] is correct, the modification of the pattern of substitution in the halogenobenzenes occasioned by the use of an electrophilic radical should be subject to similar influences. Thus, it may be predicted that while the relative rate of substitution by *p*-nitrophenyl radicals should be less than that of phenylation, the amount of the *meta*-isomer produced in *p*-nitrophenylation should be *less* than that produced in phenylation.

The relative rate of *p*-nitrophenylation of chlorobenzene has been shown by Cadogan, Hey, and Williams [3] to be less than that of phenylation, and similar measurements on bromobenzene are to be described in Part XVI,[6] in which partial rate factors are derived.

In the present communication measurements are reported of the ratios of isomerides obtained in the *p*-nitrophenylation of chlorobenzene and bromobenzene. Infrared spectroscopy was used for the analysis. The interest of these results lies in a comparison of them with the corresponding ratios for phenylation. The ratio of isomerides in the phenylation of chlorobenzene measured by Augood, Hey, and Williams [7] appears to be somewhat out of harmony with the results for the other halogenobenzenes which were obtained by Augood, Cadogan, Hey, and Williams,[8] and also with the results of Dannley, Gregg, Phelps, and Coleman.[9] In particular, the proportion of 3-chlorodiphenyl appears

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* Part XIV, *J.*, 1958, 1885.

[1] De Tar and Kazimi, *J. Amer. Chem. Soc.*, 1955, **77**, 3842.

[2] Dannley and Sternfeld, *ibid.*, 1954, **76**, 4543.

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

[4] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 315.

[5] Chang, Hey, and Williams, *J.*, 1958, 1885.

[6] Chang, Hey, and Williams, *J.*, to be submitted.

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

[8] Augood, Cadogan, Hey, and Williams, *J.*, 1953, 3412.

[9] Dannley, Gregg, Phelps, and Coleman, *J. Amer. Chem. Soc.*, 1954, **76**, 445.

to be anomalously low. Accordingly, this measurement was repeated and it was indeed found that the proportion of 3-chlorodiphenyl is higher than that previously reported. These results are summarised in Table 1, in which the ratio of isomerides for the phenylation of bromobenzene obtained by Augood, Cadogan, Hey, and Williams[8] is included for completeness.

Table 1. *Ratios of isomerides formed in the phenylation and* p-*nitrophenylation of chlorobenzene and bromobenzene.*

		Composition (%)		
Compound	Reaction	2-	3-	4-
PhCl	Phenylation	50·1	31·6	18·3
PhCl	*p*-Nitrophenylation	59·6	24·2	16·2
PhBr	Phenylation	49·3	33·3	17·4
PhBr	*p*-Nitrophenylation	60·5	25·1	14·4

The most striking feature of these results is the substantially smaller amount of *meta*-substitution which takes place in both compounds with *p*-nitrophenyl than with phenyl radicals, in accord with the predictions made above. The compensating increase appears to be in substitution at the *ortho*- rather than the *para*-position; indeed, the amount of the 4-isomer appears to decrease slightly. The meaning of this effect at the *para*-position, if real, is at present obscure.

EXPERIMENTAL

Reagents.—Unless otherwise stated, the light petroleum used had b. p. 60—80°. Solids were recrystallised to constant m. p.

Benzoyl peroxide, nitromethane, and chlorobenzene were purified as described in Part II,[10] and bromobenzene as described in Part IV.[8] *p*-Nitrobenzoyl peroxide was prepared by Hey and Walker's method.[11] 2-, 3-, and 4-Chlorodiphenyl were kindly presented by Dr. P. Clarke (King's College, London), whom we thank. 2-Chlorodiphenyl was recrystallised from light petroleum (to m. p. 33·5°), and the 4-isomer from ethanol–water (to m. p. 77°). 3-Chlorodiphenyl, which was a colourless oil (n_D^{20} 1·6198), was used without further purification. The preparation of 4-chloro-4′-nitrodiphenyl and 4-bromo-4′-nitrodiphenyl was reported in Part XIV.[5] 3-Bromo-4′-nitrodiphenyl (m. p. 94—95°) was prepared by Case's method.[12]

2-Bromo-4′-nitrodiphenyl.—This was prepared by a modification of Scarborough and Waters's method.[13] A solution of 2-acetamidodiphenyl in glacial acetic acid was treated with a mixture of concentrated sulphuric acid and fuming nitric acid at 0°, the temperature being carefully controlled, to give 2-acetamido-4′-nitrodiphenyl, m. p. 201°. Hydrolysis for 1½ hr. with boiling 10% ethanolic hydrochloric acid gave 2-amino-4′-nitrodiphenyl, m. p. 158°, which was diazotised by Hodgson and Walker's method[14] as follows. A hot solution of 2-amino-4′-nitrodiphenyl (5 g.) in glacial acetic acid (47 ml.) was rapidly cooled to room temperature and added with stirring to a solution of sodium nitrite (1·78 g.) in concentrated sulphuric acid (12·5 ml.), the temperature being maintained below 20° throughout the addition. The resulting solution was added to the mixture obtained by treating a solution of copper sulphate (6·68 g.) and sodium bromide (3·23 g.) in water (21·5 ml.) with one of sodium metabisulphite (1·48 g.) and sodium hydroxide (0·98 g.) in water (11 ml.). The resulting mixture was immediately treated with 48% hydrobromic acid (7 ml.) and kept overnight. The solid residue obtained on filtration crystallised from methanol to give 2-bromo-4′-nitrodiphenyl as yellow needles, m. p. 82—83° (2 g.). Scarborough and Waters[12] reported m. p. 82·5°.

2-Chloro-4′-nitrodiphenyl.—This was prepared by a method analogous to that described above for the preparation of 2-bromo-4′-nitrodiphenyl, except that the diazotisation of 2-amino-4′-nitrodiphenyl and the subsequent Sandmeyer reaction were carried out in the presence of concentrated hydrochloric acid. 2-Chloro-4′-nitrodiphenyl was obtained as pale yellow needles, m. p. 77—78°. Case[15] reported m. p. 74—75°.

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[10] Augood, Hey, and Williams, *J.*, 1952, 2094.
[11] Hey and Walker, *J.*, 1948, 2216.
[12] Case, *J. Amer. Chem. Soc.*, 1945, **67**, 118.
[13] Scarborough and Waters, *J.*, 1927, 89.
[14] Hodgson and Walker, *J.*, 1933, 1620.
[15] Case, *J. Amer. Chem. Soc.*, 1943, **65**, 2137.

3-Chloro-4′-nitrodiphenyl.—(*a*) Dry chlorine was passed at room temperature into a solution of 2-acetamido-4′-nitrodiphenyl (4 g.) and anhydrous sodium acetate (4 g.) in glacial acetic acid (200 ml.) until a gain in weight of about 0·6 g. had occurred. After being kept overnight, the mixture was poured into ice-water, and the chlorinated product collected by filtration. Repeated crystallisation from acetone–ethanol gave 2-acetamido-5-chloro-4′-nitrodiphenyl (1·5 g.; m. p. 204—206°), which was then hydrolysed by boiling dilute sulphuric acid. The 2-amino-5-chloro-4′-nitrodiphenyl thus obtained (4 g.) was diazotised in 50% sulphuric acid (7 ml.) with a saturated aqueous solution of sodium nitrite (1·2 g.). The filtered solution of the diazonium salt was treated with 30% aqueous hypophosphorous acid (18 ml.) at 0°, and the ensuing reaction allowed to proceed at this temperature for 24 hr. Repeated crystallisation of the product from methanol gave *3-chloro-4′-nitrodiphenyl* (1 g.) as yellow needles, m. p. 89° (Found: Cl, 15·8. $C_{12}H_8O_2NCl$ requires Cl, 15·2%).

(*b*) A mixture of *m*-chloroaniline (50 g.), concentrated hydrochloric acid (79·5 ml.), and crushed ice was treated with sodium nitrite (29·7 g.) in water (55·5 ml.) until the presence of a slight excess was indicated by starch–iodide paper. After filtration, the solution was vigorously agitated with nitrobenzene (500 ml.) at 0—5°, while 5N-sodium hydroxide solution (99 ml.) was added dropwise. Stirring was continued for 3 hr. at 5°, and for a further 48 hr. at room temperature. The nitrobenzene layer was washed with water, and the solvent removed by distillation under reduced pressure. The resulting tar was extracted repeatedly with boiling light petroleum. The extracts were fractionally distilled and the orange oil (6·0 g.), b. p. 162—172°/0·7 mm., collected and redistilled, the fraction of b. p. 168—172°/0·7 mm. then being collected. Decolorisation with activated charcoal, followed by repeated crystallisation from methanol, gave 3-chloro-4′-nitrodiphenyl (3·8 g.) as pale yellow needles, m. p. 91° (Found: C, 61·7; H, 3·5; N, 5·9; Cl, 14·9. $C_{12}H_8O_2NCl$ requires C, 61·7; H, 3·4; N, 6·0; Cl, 15·2%). A mixed m. p. with the specimen prepared from 2-acetamido-4′-nitrodiphenyl showed no depression. The infrared spectra of the two specimens in nitromethane solution were identical.

Reaction of Benzoyl Peroxide with Chlorobenzene.—In experiments 1 and 2, benzoyl peroxide (6 g.) was allowed to decompose in chlorobenzene (200 ml.) in a thermostat at 80° for 72 hr. The standard procedure (Part II [10]) was used for the isolation of the diaryl fractions. In order to remove the last traces of the high-boiling resin which is formed in this reaction, the mixtures were redistilled twice. The chlorodiphenyl mixtures (b. p. 65—95°/0·15 mm.) were obtained as colourless oils, and the resins as yellow glassy solids, similar to those reported by Augood, Hey, and Williams.[7] The resins were not investigated further. The weights of the various products obtained are given in Table 2.

TABLE 2. *Products obtained in the reactions of benzoyl peroxide with chlorobenzene.*

Expt.	Diaryl fraction (g.)	Resin (g.)	Benzoic acid (g.)	Compositions of chlorodiphenyls (%)		
				2-	3-	4-
1	2·6810	2·4768	1·79	49·2	32·3	18·6
2	2·6202	2·3788	1·80	50·9	31·0	18·1
Mean	—	—	—	50·1	31·6	18·3

Reaction of p-*Nitrobenzoyl Peroxide with Chlorobenzene and Bromobenzene.*—In experiments 3 and 4, *p*-nitrobenzoyl peroxide (6 g.) was allowed to decompose in chlorobenzene (200 ml.) in a thermostat at 80° for 72 hr. In experiments 5 and 6, bromobenzene (200 ml.) was used as solvent. The standard procedure (Part II [10]) was used for the isolation of the diaryl fractions. The mixtures of chloro-4′-nitrodiphenyls obtained from experiments 3 and 4 (4·0120 g. and 3·9602 g. respectively) had b. p. 110—130°/0·1 mm., and the mixtures of bromo-4′-nitrodiphenyls obtained from experiments 5 and 6 (4·0275 g. and 3·9484 g. respectively) had b. p. 110—135°/0·1 mm. All these mixtures were shown by analysis to contain no extraneous material. Only very small quantities (*ca.* 0·1 g.) of high-boiling resinous material were formed in experiments 3—6.

Infrared Analysis of Mixtures of Isomers.—The mixtures of isomers obtained from experiments 1—6 were analysed by the infrared method, the procedure described in Part XIV [5] being used. The " key " absorption bands used for the analyses were as follows: 2-chloro-4′-nitrodiphenyl, 771 cm.$^{-1}$; 3-chloro-4′-nitrodiphenyl, 796·2 cm.$^{-1}$; 2-bromo-4′-nitrodiphenyl, 769 cm.$^{-1}$; 3-bromo-4′-nitrodiphenyl, 793·6 cm.$^{-1}$; 3-chlorodiphenyl, 795 cm.$^{-1}$; 4-chlorodiphenyl, 839 cm.$^{-1}$. The amounts of 4-chloro-4′-nitrodiphenyl, 4-bromo-4′-nitrodiphenyl, and 2-chlorodiphenyl present in mixtures containing them were obtained by difference. In order to check the accuracy of the analyses, synthetic mixtures of chloro-4′-nitrodiphenyls, bromo-4′-nitrodiphenyls, and chlorodiphenyls of known composition were made up and analysed spectroscopically. The compositions found by analysis are compared with the known compositions in Table 3.

The results obtained in the analysis of the mixtures of isomers obtained in experiments 1—6 are given in Tables 2 and 4.

TABLE 3. *Analysis of synthetic mixtures.*

	Known compositions (%)			Compositions found from spectra (%)		
Mixture	2-	3-	4-	2-	3-	4-
S_1 (Chloro-4′-nitrodiphenyls)	54·2	24·1	21·7	55·3	24·8	19·9
S_2 (Bromo-4′-nitrodiphenyls)	48·0	26·1	25·9	50·1	27·2	22·7
S_3 (Bromo-4′-nitrodiphenyls	55·9	28·5	15·6	58·1	28·9	13·0
S_4 (Chlorodiphenyls)	54·7	30·0	15·3	55·0	29·1	15·9

TABLE 4. *Analysis of mixtures of isomeric halogeno-4′-nitrodiphenyls obtained in the* p-*nitrophenylation of chloro- and bromo-benzene* (PhX).

		Composition of halogeno-4′-nitrodiphenyls (%)		
Experiments	X in PhX	2 : 4′-	3 : 4′-	4 : 4′-
3	Cl	60·2	24·3	15·5
4	Cl	59·1	24·0	16·9
Mean	—	59·6	24·2	16·2
5	Br	60·0	25·5	14·5
6	Br	61·0	24·7	14·3
Mean	—	60·5	25·1	14·4

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