383. *Homolytic Aromatic Substitution. Part XIV.* Ratio of Isomerides Formed in the Arylation of Nitrobenzene with* p-*Chlorophenyl and* p-*Bromophenyl Radicals.*

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Measurements are reported of the ratios of isomers obtained in the arylation of nitrobenzene with *p*-chlorophenyl and *p*-bromophenyl radicals. The measurements for *p*-chlorophenylation were made by the infrared spectrographic method, and those for *p*-bromophenylation by the infrared and the isotope-dilution methods. The agreement between the results obtained by the two methods is satisfactory. In order to confirm earlier results, and for comparison, the ratio of isomers obtained in the phenylation of nitrobenzene was measured by the ultraviolet-spectrophotometric method. The results show that the slightly electrophilic nature of the halogen-substituted radical gives rise to a small increase in the proportion of the *meta*-substituted isomer when it reacts with nitrobenzene.

In Part IX [1] competitive experiments on the arylation of chlorobenzene and nitrobenzene with *p*-chlorophenyl radicals were described, whereby the relative rates of *p*-chlorophenylation of nitrobenzene $({}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K)$ and chlorobenzene $({}^{\mathrm{PhCl}}_{\mathrm{PhH}}K)$ were measured. From these results it was apparent that both relative rate ratios were significantly lower than the corresponding quantities for phenylation of these compounds, and in explanation it was suggested that, as a result of the inductive $(-I)$ effect of the chlorine atom, the probability of localisation of the unpaired electron at the *para*-position of the radical is reduced. The *p*-chlorophenyl radical was therefore considered to assume some measure of electrophilic character, and since both nitrobenzene and chlorobenzene are deactivated towards electrophilic substitution, it is to be expected that a decrease should be observed in the relative rates of arylation of these compounds as more electrophilic radicals are used. Changes, due to the presence of substituent groups in the radicals, in the ratios of isomers formed in the arylation of various compounds have been reported by DeTar and Kazimi,[2] Dannley and Sternfeld,[3] and Simamura and Migita.[4] These changes are consistent with the above hypothesis. In order further to establish its validity a systematic study of the arylation of a number of selected compounds with substituted radicals containing substituents of various polar characteristics, was undertaken, the results being reported in this and subsequent papers.

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* Part XIII, preceding paper.

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

[2] DeTar and Kazimi, *J. Amer. Chem. Soc.*, 1955, **77**, 3842.

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

[4] Simamura and Migita, *Bull. Chem. Soc. Japan*, 1954, **27**, 228.

In this paper, measurements of the ratios of isomers produced in the *p*-chlorophenylation and *p*-bromophenylation of nitrobenzene at 80° are reported. The mixtures of chloronitrodiphenyls were analysed by infrared spectroscopy, and mixtures of bromonitrodiphenyls by both infrared spectroscopy and the isotope-dilution method. The agreement between the results obtained by the two methods is good, and is a measure of the accuracy of the determinations. Theoretical interpretation of these results involves their comparison with the ratio of isomers formed in the phenylation of nitrobenzene. This ratio has been measured for the reaction at 80° by Hey, Nechvatal, and Robinson (Part I) [5], by the infrared method. The two mixtures analysed by these workers had the following compositions: *ortho* 59·5 ± 4 and 59·5 ± 4, *meta* 8·5 ± 2 and 11·5 ± 2, *para* 32 ± 4 and 29 ± 4%. However, it is apparent from the infrared absorption spectra of 2-, 3-, and 4-nitrodiphenyl that some overlapping of the absorption bands of the three isomers occurs, and therefore that the accuracy of the infrared method is somewhat diminished in this system. The ratio of isomers for this reaction at 125° has been measured by Hey, Stirling, and Williams (Part VI),[6] who showed that good results could be obtained by ultraviolet spectrophotometry. Owing to the difference in temperature, however, these measurements are not suitable for comparison with the measurements presently reported, and hence it was considered desirable to repeat the determination of the ratio of isomers obtained in the phenylation of nitrobenzene at 80°, using the ultraviolet method for the analysis. This desirability becomes of greater significance in view of the small differences, only just outside the experimental error of the determinations, which are expected between the isomer ratios displayed by the unsubstituted and substituted phenyl radicals. The results are summarised in Table 1. The results for *p*-bromophenylation may be compared with those of Hey, Nechvatal, and Robinson [5] who found, as a result of a volumetric analysis, that such reactions gave rise to about 12% of the *meta*-isomer.

TABLE 1. *Ratios of isomers obtained in the arylation of nitrobenzene* (80°).

	Composition of diaryl (%)		
Radical	2-	3-	4-
C_6H_5	62·5	9·8	27·7
p-$Cl{\cdot}C_6H_4$	59·0	13·8	27·2
p-$Br{\cdot}C_6H_4$ *	57·7	13·2	29·1

* Mean of results obtained by infrared and isotope-dilution methods.

The influence of the electrophilic or nucleophilic character of the radicals is made apparent most clearly by the amount of substitution at the *meta*-position, since electrophilic radicals should give rise to an increased, and nucleophilic radicals a decreased amount of *meta*-substitution when they react with a compound such as nitrobenzene containing a directing group which is deactivating, and *meta*-directing towards electrophilic substitution. It may be seen from Table 1, therefore, that *p*-chlorophenyl and *p*-bromophenyl radicals are both slightly electrophilic, since both give rise to a small increase in the amount of *meta*-substitution. The differences are small, but in view of the special precautions taken to confirm the values obtained for phenylation and *p*-bromophenylation, the effects they illustrate are accepted as real, at least in a qualitative sense. These results, together with others reported in subsequent papers, will be further discussed in a later paper.

EXPERIMENTAL

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

[5] Hey, Nechvatal, and Robinson, *J.*, 1951, 2892.

[6] Hey, Stirling, and Williams, *J.*, 1954, 2747.

Benzoyl peroxide (May and Baker) and nitrobenzene were purified according to the procedures described in Part II,[7] and nitromethane according to that described in Part IV.[8]

p-Bromobenzoyl peroxide (m. p. 142°) and *p*-chlorobenzoyl peroxide (m. p. 138°) were prepared by Hey and Walker's method.[9] 2-Nitrodiphenyl (m. p. 35—36°) and 4-nitrodiphenyl (m. p. 114°) were prepared by Bell, Kenyon, and Robinson's method.[10] 2-Nitrodiphenyl was further purified by repeated fractional distillation *in vacuo*. 3-Nitrodiphenyl was prepared by Hey and Walker's method [9] (m. p. 61°) and by Elks, Haworth, and Hey's method [11] (m. p. 60°).

4-*Chloro-2′-nitrodiphenyl* was prepared by direct chlorination of 2-nitrodiphenyl. Dry chlorine was passed into a mixture of 2-nitrodiphenyl (10 g.) and stannic iodide (0·5 g.) at 40° until the gain in weight was 2 g. The rate of flow of chlorine, and the temperature at which the reaction was carried out, were found to be critical, and consequently the rate of flow of chlorine was controlled by a simple flow-meter adjusted to about 0·5 ml. per second. The product, after repeated crystallisation from methanol, and chromatography on alumina with chloroform as eluent, was obtained as yellow prisms, m. p. 61° (1·9 g.) (Found: Cl, 14·7. $C_{12}H_8O_2NCl$ requires Cl, 15·2%).

4-Chloro-3′-nitrodiphenyl (m. p. 89°) was prepared by Blakey and Scarborough's method [12] by chlorination of 3-nitrodiphenyl at 80° in the presence of ferric chloride. 4-Chloro-4′-nitrodiphenyl (m. p. 158°) was prepared by Le Fèvre and Turner's method,[13] chlorination of 4-nitrodiphenyl at a temperature just above its m. p. in the presence of a little stannic iodide.

For the preparation of 4-bromo-2′-nitrodiphenyl, Le Fèvre and Turner's method [13] was first used, but it was found that the yield was poor, and the isolation of the product troublesome. The following modified procedure was, however, found to be satisfactory. 2-Nitrodiphenyl was first carefully purified by repeated fractional distillation *in vacuo* and repeated crystallisation from ethanol. Traces of 4-nitrodiphenyl, with which the 2-isomer is usually contaminated, were thus removed. In this way, isolation of the final product was greatly facilitated, since contamination with bromo-derivatives of 4-nitrodiphenyl was avoided. A mixture of this purified 2-nitrodiphenyl (9 g.), bromine (3·2 ml.), ferric chloride (0·4 g.), and water (10 ml.) was stirred overnight at room temperature. The mixture was then stirred with an excess of 5% sodium carbonate solution and extracted with ether. The ethereal extract was washed with 5% aqueous sodium carbonate and, after being dried (K_2CO_3), the ether was removed by evaporation. The residue was crystallised repeatedly from ethanol, and final purification by chromatography yielded 4-bromo-2′-nitrodiphenyl as yellow plates, m. p. 66° (3·2 g.). This represents a yield of 25%, and is a considerable improvement on Hey, Nechvatal, and Robinson's method,[5] which gave only 10%. Le Fèvre and Turner [13] recorded neither yield nor m. p., but Schultz, Schmidt, and Strasser [14] recorded m. p. 65°.

4-Bromo-3′-nitrodiphenyl (m. p. 94°) was obtained by bromination of 3-nitrodiphenyl as described by Blakey and Scarborough,[12] and 4-bromo-4′-nitrodiphenyl (m. p. 176°) similarly by Le Fèvre and Turner's method.[13]

The preparation of ^{82}Br-labelled 4-bromo-4′-nitrodiphenyl and 4-bromo-2′-nitrodiphenyl, which were required for the isotope-dilution analyses, was carried out by using radioactive ^{82}Br supplied by the United Kingdom Atomic Energy Research Establishment, Harwell.

4-[^{82}Br]*Bromo-4′-nitrodiphenyl*.—Pure 4-nitrodiphenyl (2 g.), acetic acid (4·6 ml.), and radioactive bromine (1 ml.) were heated together for 4 hr. on a water-bath. The mixture was then cooled, and filtered, and the residue washed with a little acetic acid. After crystallisation from glacial acetic acid (3 times) the pure compound was obtained as pale yellow needles, m. p. 176° (1·9 g.).

4-[^{82}Br]*Bromo-2′-nitrodiphenyl*.—Pure 2-nitrodiphenyl (5·6 g.), water (6 ml.), ferric chloride (0·2 g.), and active bromine (2 ml.) were stirred overnight at room temperature. The product was isolated by the procedure previously described for the preparation of the inactive material, giving bright yellow needles, m. p. 65° (2 g.).

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[7] Augood, Hey, and Williams, *J.*, 1952, 2094.
[8] Augood, Cadogan, Hey, and Williams, *J.*, 1953, 3412.
[9] Hey and Walker, *J.*, 1948, 2216.
[10] Bell, Kenyon, and Robinson, *J.*, 1926, 1243.
[11] Elks, Haworth, and Hey, *J.*, 1940, 1285.
[12] Blakey and Scarborough, *J.*, 1927, 3003.
[13] Le Fèvre and Turner, *J.*, 1928, 253.
[14] Schultz, Schmidt, and Strasser, *Annalen*, 1881, **207**, 351.

Reaction of p-*Chlorobenzoyl Peroxide with Nitrobenzene.*—In experiments 1 and 2, *p*-chlorobenzoyl peroxide (6 g.) was allowed to decompose in nitrobenzene (200 ml.) in a thermostat at 80° for 72 hr. The diaryl fraction containing the isomeric 4-chloronitrodiphenyls was obtained as a pale yellow solid (b. p. 55—130°/0·1 mm.) from the dark brown reaction mixture by standard methods (cf. Part II [7]). The yields of diaryls from these two experiments were 3·725 and 3·667 g. respectively. No high-boiling resins were formed, and the diaryl fractions were shown by spectrographic analysis to contain no extraneous material.

Reaction of p-*Bromobenzoyl Peroxide with Nitrobenzene.*—Experiments 3 and 4 were conducted with 6 g., and experiments 5 and 6 with 9 g., of *p*-bromobenzoyl peroxide in nitrobenzene (200 ml.). The diaryl fractions were isolated as above (b. p. 55—135°/0·1 mm.), and shown by spectrography to contain no extraneous material. No high-boiling resins were formed. The yields of diaryl were 3·075, 2·984, 4·764, and 4·465 g. respectively. The products of experiments 3 and 4 were analysed spectrographically, and those of experiments 5 and 6 by the isotope-dilution method.

Reaction of Benzoyl Peroxide with Nitrobenzene.—In experiments 7 and 8, benzoyl peroxide (3 g.) was allowed to decompose in nitrobenzene (100 ml.) at 80° for 72 hr. The mixtures of diaryls were obtained as yellow oils (b. p. 90—125°/0·2 mm.). The yields were 1·947 and 1·987 g. respectively, only a small amount of high-boiling resinous material being obtained. The diaryl fractions were shown by spectrographic analysis to contain no extraneous material.

Analysis of Mixtures of Isomers by the Infrared Method.—The instrument used was a Grubb-Parsons single-beam spectrometer fitted with an automatic pen-recorder. Nitromethane was used as solvent, since it has only one intense absorption band in the region 700—900 cm.$^{-1}$, in which the characteristic bands of the relevant diaryls fall, and this band does not coincide with any of the characteristic diaryl bands. Calibration spectra were recorded for the isomeric 4-chloronitrodiphenyls and 4-bromonitrodiphenyls, and measurements on the spectra of mixtures for analysis made at the following characteristic absorption maxima: 4-chloro-2′-nitrodiphenyl, 788 cm.$^{-1}$; 4-chloro-3′-nitrodiphenyl, 811 cm.$^{-1}$; 4-bromo-2′-nitrodiphenyl, 784 cm.$^{-1}$; and 4-bromo-3′-nitrodiphenyl, 774 cm.$^{-1}$. These measurements enabled the composition of mixtures of isomers to be calculated by the method described by Augood, Hey, and Williams,[15] the amounts of 4-chloro-4′-nitrodiphenyl and 4-bromo-4′-nitrodiphenyl being obtained by difference. The accuracy of the determinations was tested by the preparation and analysis of synthetic mixtures of known composition of the two sets of isomers. The results obtained are given in Table 2.

TABLE 2. *Analyses of mixtures of known composition.*

Mixture	Method	X in p-X·C$_6$H$_4$·C$_6$H$_4$·NO$_2$	Composition of p-X·C$_6$H$_4$·C$_6$H$_4$·NO$_2$ Known (%)			Found (%)		
			4 : 2′-	4 : 3′-	4 : 4′-	4 : 2′-	4 : 3′-	4 : 4′-
S$_1$	Infrared	Cl	45·8	24·9	29·3	43·2	26·0	30·8
S$_2$	,,	Br	59·5	30·0	10·5	59·4	29·7	10·9
S$_3$	,,	Br	59·1	29·7	11·2	59·9	30·5	9·6
S$_4$	Isotope diln.	Br	29·3	9·8	60·9	29·5	10·3	60·2

The reliability of the method of analysis is demonstrated by these results. The analyses of the products of *p*-chlorophenylation and *p*-bromophenylation of nitrobenzene (experiments 1—6) are given in Table 3.

Analysis of Mixtures of Isomers by the Ultraviolet Method.—The determination of the ratios of isomers present in the mixture of isomeric nitrodiphenyls formed in experiments 7 and 8 was carried out by ultraviolet spectrophotometry with the aid of a Unicam "S.P. 500" quartz spectrophotometer, the method of calculation described by Cadogan, Hey, and Williams [16] being used. The calibration curves for the pure isomers were those obtained by Hey, Stirling, and Williams.[6] Spectra were taken by reading the extinction coefficient at intervals of 2 mμ in the range 230—320 mμ. Measurements on the spectra were made at six pairs of wavelengths, and the ratio of isomers calculated from each pair. The results are given in Table 4. The accuracy of the determinations was checked by using the mean composition of the mixture, as

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

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

determined, in conjunction with the known calibration spectra of the pure isomers to calculate the extinction coefficient of the mixture at each wavelength at which this had been measured. Comparison of these values with the observed extinction coefficients showed completely satisfactory accuracy; the standard deviation from the mean error (−0·75%) for the determination of the composition of the mixture of nitrodiphenyls was ±1·24%. The method of analysis was therefore considered satisfactory.

TABLE 3. *Analysis of products of* p-*halogenophenylation of nitrobenzene.*

Exp. no.	Method	X in p-X·C_6H_4·C_6H_4·NO_2	Composition of p-X·C_6H_4·C_6H_4·NO_2 (%) 4 : 2′-	4 : 3′-	4 : 4′-
1	Infrared	Cl	58·3	14·0	27·7
2	,,	Cl	59·6	13·5	26·9
Mean	,,	Cl	59·0	13·8	27·2
3	,,	Br	57·9	13·6	28·5
4	,,	Br	59·7	13·3	27·0
Mean	,,	Br	58·8	13·5	27·7
5	Isotope diln.	Br	57·1	12·9	30·0
6	,,	Br	56·2	12·8	31·0
Mean	,,	Br	56·6	12·9	30·5

TABLE 4. *Analysis of products obtained in the phenylation of nitrobenzene.*

Wavelength pair	Composition (%) 2-	3-	4-	Wavelength pair	Composition (%) 2-	3-	4-
	Experiment 7				Experiment 8		
258, 306	61·7	10·7	27·6	258, 306	62·2	10·0	27·8
266, 300	61·9	10·6	27·5	266, 300	62·8	9·9	27·3
254, 310	62·0	10·3	27·7	254, 310	62·7	9·8	27·5
250, 294	62·6	9·1	28·3	250, 294	64·9	8·0	27·1
262, 302	61·8	10·5	27·7	262, 302	62·5	10·2	27·3
246, 290	61·5	10·1	28·4	246, 290	63·4	8·8	27·8
				Mean (expts. 7 & 8)	62·5	9·8	27·7

Analysis of Mixtures of Isomers by the Isotope-dilution Method.—The mixtures of isomeric 4-bromonitrodiphenyls from experiments 5 and 6 were analysed by the isotope-dilution method. Mixtures of inactive materials were first used in order to develop a method of isolation of pure samples of at least two of the isomers. It was possible to isolate 4-bromo-2′- and -4′-nitrodiphenyl by fractional crystallisation. The following procedure was therefore adopted for the analysis. Two portions (0·4—0·8 g.) of the mixture of isomers obtained from each of experiments 5 and 6 were diluted, one with labelled 4-bromo-4′-nitrodiphenyl (10—25 mg.; portion A) and the other with labelled 4-bromo-2′-nitrodiphenyl (10—25 mg.; portion B). Mixture A was dissolved in hot ethanol and crystallised. The 4-bromo-4′-nitrodiphenyl which separated was purified by crystallisation 9 times from ethanol, and its specific activity measured. The m. p. (176°) and specific activity were checked before and after the last crystallisation: the difference was negligible. Portion B was dissolved in hot ethanol and the solution cooled. The 4-bromo-4′-nitrodiphenyl which separated was discarded. On evaporation and cooling of the mother-liquor, 4-bromo-2′-nitrodiphenyl was obtained, which was purified by recrystallisation (11 times) from light petroleum to constant m. p. (65°) and specific activity.

In this way the mixtures were analysed for 4-bromo-2′- and 4′-nitrodiphenyl, the proportion of the third isomer, 4-bromo-3′-nitrodiphenyl, being obtained by difference. In order to check the accuracy of the determinations, a synthetic mixture of known composition was analysed, with the results given in Table 2.

The results obtained for the analysis of the experimental mixtures are given in Table 3.

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