# 596. *Homolytic Aromatic Substitution. Part XXIV.* The* p-*Methylphenylation of Nitrobenzene and Chlorobenzene.*

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

IN Part XIX,[1] determinations were reported of the relative rates of arylation of nitrobenzene and chlorobenzene, with the electrophilic *p*-nitrophenyl and *p*-methoxyphenyl radicals, and of the proportions in which the *ortho*-, *meta*-, and *para*-isomers were formed in the *p*-nitrophenylation of nitrobenzene. These results, together with those reported in earlier papers in this series, were shown to be consistent with the hypothesis that a measure of electrophilic character is conferred on the radicals by virtue of the electron-attracting properties of the substituents present therein. It is, therefore, of interest to investigate the polar properties of radicals containing electron-repelling substituents, since these should, on the basis of the above-mentioned hypothesis, exhibit a measure of nucleophilic character, and the rates of attack by them on individual positions in aromatic nuclei,

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* Part XXIII, *J.*, 1961, 565.

[1] Hambling, Hey, and Williams, *J.*, 1960, 3782.

when compared with the corresponding rates of attack by phenyl radicals, should exhibit changes in the opposite sense from those observed with electrophilic radicals. The present investigation is directed to the observation of such changes in the arylation of nitrobenzene and chlorobenzene with *p*-methylphenyl radicals. The relative rates of attack by these radicals on nitrobenzene and chlorobenzene, and the distribution of the isomeric biaryls formed in the *p*-methylphenylation of nitrobenzene, have therefore been measured. The results are shown to be consistent with the assumption of slight nucleophilic character by the *p*-methylphenyl radical.

## EXPERIMENTAL

*Reagents.*—Solids were recrystallised to constant m. p. Benzene, chlorobenzene, and nitrobenzene were purified as described in Part II,[2] and *NN*-dimethylformamide as described in Part XIX.[1] *p*-Toluoyl peroxide was prepared by Swain, Stockmayer, and Clarke's method [3] and had m. p. 136° (decomp.).

4-Methyl-2′-nitrobiphenyl (m. p. 37°) was prepared by the reaction of diazotised *p*-toluidine with a stirred mixture of nitrobenzene and aqueous sodium hydroxide, Hey, Nechvatal, and Robinson's method [4] being used. The product was purified by chromatography on alumina and crystallisation from light petroleum (b. p. 60—80°). 4-Methyl-4′-nitrobiphenyl (m. p. 140°) was prepared by the nitration of 4-methylbiphenyl (Grieve and Hey's method [5]). 4-Methylbiphenyl (m. p. 49°) was prepared by Gomberg and Pernert's method.[6]

A specimen of 4-methyl-3′-nitrobiphenyl, originally prepared by the Hey, Nechvatal, and Robinson method,[4] was recrystallised from light petroleum (b. p. 60—80°) to m. p. 76·5°

*Determination of* ${}_{\mathrm{PhH}}^{\mathrm{Ph\cdot NO_2}}K$ *for* p-*Methylphenylation.*—In experiments 1—4, *p*-toluoyl peroxide (6 g.) was allowed to decompose in a mixture of benzene (107·3 ml.) and nitrobenzene (92·3 ml.) in a thermostat at 80° for 72 hr. The mixed biaryls formed were isolated by a modification of the procedure described in Part XVIII,[7] each mixture being divided into two portions (A and B) before the final distillation. The modification of this procedure, which was introduced in order to prevent losses of the relatively volatile 4-methylbiphenyl, was that the bulk of the residual nitrobenzene solvent was distilled at a relatively high pressure (b. p. 140°/105 mm.). Before the final distillation the remaining nitrobenzene was removed at room temperature by maintaining the contents of the distillation flask at a pressure of 0·01 mm. for 12 hr., after which the flask was warmed to 35° to give the fore-run. The fore-runs were analysed by estimation of their content of nitro-group, and corrections in terms of methylbiphenyl were applied to the yield and composition of the biaryl fractions. Fractions taken immediately before the fore-runs were shown to consist entirely of nitrobenzene, showing that neither the fore-runs nor the biaryl fractions were contaminated with benzene, and that the whole of the 4-methylbiphenyl formed was contained in the fore-runs and the biaryl fractions. The absence of methylnitrobiphenyls from the fore-runs is inferred, since these compounds did not begin to distil until a temperature of 45° above that at which the fore-runs were collected had been reached. The biaryl fractions, the fore-runs, and the final fraction of the solvent were analysed volumetrically for nitro-groups by titration with titanous sulphate as described in Part XVIII.[7] The results of experiments 1—4 are given in Table 1.

*Determination of* ${}_{\mathrm{PhCl}}^{\mathrm{Ph\cdot NO_2}}K$ *for* p-*Methylphenylation.*—In experiments 5 and 6, *p*-toluoyl peroxide (6 g.) was allowed to decompose in a mixture of chlorobenzene (99·3 ml.) and nitrobenzene (100·7 ml.) in a thermostat at 80° for 72 hr. The reactions were conducted, and the products isolated and analysed, as described in Part XIX [1] for the determination of this relative rate for arylation with other aryl radicals. Fore-runs were collected and analysed, and corrections in terms of chloromethylbiphenyls were applied to the weight and composition of the biaryl fractions. Fractions taken immediately before the fore-runs were shown to consist entirely of nitrobenzene. The absence of methylnitrobiphenyls from the fore-runs is assumed, since

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[2] Augood, Hey, and Williams, *J.*, 1952, 2094.
[3] Swain, Stockmayer, and Clarke, *J. Amer. Chem. Soc.*, 1950, **72**, 5432.
[4] Hey, Nechvatal, and Robinson, *J.*, 1951, 2892.
[5] Grieve and Hey, *J.*, 1932, 1888.
[6] Gomberg and Pernert, *J. Amer. Chem. Soc.*, 1926, **48**, 1372.
[7] Hey, Moulden, and Williams, *J.*, 1960, 3769.

these compounds did not begin to distil until a temperature 45° above that at which the fore-runs were collected had been reached. The results are given in Table 2.

TABLE 1.

| | Expt. 1 | | Expt. 2 | | Expt. 3 | | Expt. 4 | |
|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | A | B |
| Biaryl fraction (b. p. 38—130°/0·015 mm.) (g.) | 1·588 | 1·516 | 1·686 | 1·395 | 1·698 | 1·306 | 1·468 | 1·555 |
| Nitrobiaryls in biaryl fraction (%) | 82·6 | 82·9 | 82·9 | 82·2 | 82·6 | 82·9 | 82·9 | 82·2 |
| Fore-run (b. p. 17—35°/0·01 mm.) (g.) | 1·153 | 1·478 | 0·820 | 1·229 | 1·314 | 1·277 | 1·003 | 0·962 |
| 4-Methylbiphenyl in fore-run (g.) | 0·013 | 0·021 | 0·011 | 0·010 | 0·054 | 0·060 | 0·029 | 0·042 |
| Corr. wt. of biaryl fraction (g.) | 1·601 | 1·537 | 1·697 | 1·405 | 1·752 | 1·366 | 1·497 | 1·597 |
| Nitrobiaryls, corr. (%) | 82·0 | 81·8 | 82·4 | 81·7 | 80·0 | 79·5 | 81·3 | 80·0 |
| ${}^{\text{Ph·NO}_2}_{\text{PhH}}K$ for *p*-methylphenylation | 3·58 | 3·55 | 3·70 | 3·52 | 3·12 | 2·96 | 3·43 | 3·12 |
| Residue (g.) | 0·199 | | 0·210 | | 0·200 | | 0·202 | |
| Free *p*-toluic acid (g.) | 2·80 | | 2·76 | | 2·70 | | 2·64 | |
| *p*-Toluic acid from hydrolysis of esters (g.) | 0·34 | | 0·35 | | 0·34 | | 0·35 | |
| ($p$-$CH_3$·$C_6H_4$·CO·O)$_2$ accounted for (%) | 87·6 | | 86·1 | | 80·7 | | 79·6 | |

Hence ${}^{\text{Ph·NO}_2}_{\text{PhH}}K$ for *p*-methylphenylation = 3·4.

TABLE 2.

| | Expt. 5 | Expt. 6 |
|---|---|---|
| Biaryl fraction (b. p. 40—128°/0·01 mm.) (g.) | 3·291 | 3·371 |
| Nitrobiaryls in biaryl fraction (%) | 73·6 | 73·5 |
| Fore-run (b. p. 25—40°/0·01 mm.) (g.) | 2·020 | 1·105 |
| Chloromethylbiphenyls in fore-run (g.) | 0·068 | 0·047 |
| Corr. wt. of biaryl fraction (g.) | 3·359 | 3·418 |
| Nitrobiaryls, corr. (%) | 72·1 | 72·5 |
| ${}^{\text{Ph·NO}_2}_{\text{PhCl}}K$ for *p*-methylphenylation | 2·48 | 2·52 |
| Free *p*-toluic acid (g.) | 2·60 | 2·65 |
| *p*-Toluic acid from hydrolysis of esters (g.) | 0·31 | 0·29 |
| Residue (g.) | 0·270 | 0·329 |
| ($p$-$CH_3$·$C_6H_4$·CO·O)$_2$ accounted for (%) | 85·0 | 86·5 |

Hence ${}^{\text{Ph·NO}_2}_{\text{PhCl}}K$ for *p*-methylphenylation = 2·5.

*Determination of the Ratio of Isomerides formed in the* p-*Methylphenylation of Nitrobenzene*.—In experiments 7 and 8, *p*-toluoyl peroxide (6 g.) was allowed to decompose in nitrobenzene (200 ml.) in a thermostat at 80° for 72 hr. The standard procedure (Part II [2]) 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 3.

TABLE 3.

| | Expt. 7 | Expt. 8 |
|---|---|---|
| Biaryl fraction (b. p. <128°/0·01 mm.) (g.) | 3·543 | 3·536 |
| Free *p*-toluic acid (g.) | 2·63 | 2·61 |
| *p*-Toluic acid from hydrolysis of esters (g.) | 0·41 | 0·34 |
| Residue (g.) | 0·394 | 0·294 |
| *p*-Toluoyl peroxide accounted for (%) | 92·5 | 91·0 |

TABLE 4. *Analysis of mixtures of* 4-*methylnitrobiphenyls*.

| | Composition (%) | | |
|---|---|---|---|
| Mixture | 4,2′- | 4,3′- | 4,4′- |
| 7 | 59·3 | 11·9 | 28·8 |
| 8 | 59·7 | 12·0 | 28·3 |
| Mean | 59·5 | 11·9 | 28·6 |
| S (Found) | 69·1 | 2·4 | 28·5 |
| S (Known) | 67·7 | 2·9 | 29·4 |

The mixtures of isomeric methylnitrobiphenyls were analysed by the infrared spectrographic method described in Part XIX.[1] The characteristic absorption bands used for the analysis were as follows: 4-methyl-2′-nitrobiphenyl, 787 cm.$^{-1}$; 4-methyl-3′-nitrobiphenyl, 744 cm.$^{-1}$. The amount of 4-methyl-4′-nitrobiphenyl present in the mixtures was obtained by difference. In order to check the accuracy of the analyses, a synthetic mixture (S) of known composition was made up and analysed. The results of these analyses are given in Table 4.

## DISCUSSION

The relative rate of *p*-methylphenylation of nitrobenzene has been determined directly, while that of chlorobenzene may be calculated from the measured value of ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhCl}}K$, since ${}^{\mathrm{Ph\cdot Cl}}_{\mathrm{PhH}}K = {}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K / {}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhCl}}K$. These results are given in Table 5, in which the relative rates of phenylation of nitrobenzene and chlorobenzene are included for comparison.

It is immediately obvious from these results that both aromatic compounds, which contain electron-attracting directing groups, are relatively more reactive towards *p*-methylphenyl than towards phenyl radicals. This is consistent with the hypothesis, outlined earlier, that the electron-repelling methyl group confers a measure of nucleophilic character on the *p*-methylphenyl radical. This conclusion is also consistent with the values of the partial rate factors for *p*-methylphenylation of nitrobenzene, which may be calculated from the relative rate and isomer distribution for this reaction. These values are given in Table 6, together with the corresponding values for phenylation for comparison.

TABLE 5.

| | ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$ | ${}^{\mathrm{PhCl}}_{\mathrm{PhH}}K$ |
|---|---|---|
| *p*-Methylphenylation ......... | 3·4 | 1·4 |
| Phenylation [8] ..................... | 2·9 | 1·1 |

TABLE 6. *Partial rate factors for arylation of nitrobenzene.*

| | $F_o$ | $F_m$ | $F_p$ |
|---|---|---|---|
| *p*-Methylphenylation .............. | 6·1 | 1·2 | 5·8 |
| Phenylation .......................... | 5·5 | 0·86 | 4·9 |

It may be noted that, although the polar influences involved are too weak to affect the isomer distribution to any appreciable extent (the differences are actually within the estimated experimental error of ±2%), all the partial rate factors for *p*-methylphenylation are higher than those for phenylation, as would be expected on the basis of the above interpretation of the properties of substituted aryl radicals.

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[8] Hey, Orman, and Williams, *J.*, 1961, 565.