

*Homolytic Aromatic Substitution. Part IX.\* Competitive Experiments on the Arylation of Chlorobenzene and Nitrobenzene with p-Chlorophenyl Radicals.*

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Competitive experiments have been carried out on the action of *p*-chlorophenyl radicals derived from *p*-chlorobenzoyl peroxide on mixtures of nitrobenzene with chlorobenzene and benzene. The relative rate ratios derived therefrom are lower than the corresponding ratios previously obtained with phenyl radicals. This is considered to be due to the electrophilic character which is conferred on the *p*-chlorophenyl radical by the inductive effect of the chlorine atom.

IN Parts I—VIII (*J.*, 195, 2892; 1952, 2094; 1953, 44, 3412; 1954, 794, 2747, 3353; 1955, 6) the determination of the effects of substituent atoms or groups on the course of the homolytic phenylation of a number of aromatic compounds was reported. The method employed was the measurement of partial rate factors, which express the rate of substitution at the positions concerned relative to the rate of substitution at one position in unsubstituted benzene, for the various nuclear positions at which phenylation is possible. The present communication is concerned with the effect of a substituent, chlorine, in the attacking radical, on the nuclear substitution. Di-(*p*-chlorobenzoyl) peroxide was used

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as the source of *p*-chlorophenyl radicals. This substance has been used for the arylation of pyridine, 2- and 4-*p*-chlorophenylpyridine being produced, by Hey and Walker (*J* 1948 2213). This and many other examples of aromatic arylation reactions with

the final distillation. This difficulty does not arise in the present determination, when *p*-chlorophenyl radicals are used in place of phenyl radicals, since 4-chlorodiphenyl is considerably less volatile than diphenyl, and the necessary separation is therefore easily accomplished. A correction for the slight loss of 4-chlorodiphenyl which occurs in this way is made possible by the analysis of foreruns.

Expts. 3 and 4 were carried out with di-(*p*-chlorobenzoyl) peroxide (8 g.), which was allowed to decompose for 72 hr. in a thermost at 80° in an equimolar mixture (200 ml.) of nitrobenzene and benzene. The isolation and analysis of the diaryl fraction were carried out by the standard procedure. Fore-runs were taken, and the necessary corrections to the composition of the diaryl fractions were made. Fractions taken immediately before the fore-runs proved to consist entirely of nitrobenzene. Once again, the small amount (0.2 g.) of high-boiling material left after the distillation was of negligible influence. The results are given in Table 2.

TABLE 2.

	Expt. no. 3	4
Diaryl fraction (g.) (b. p. 55—130°/0.1 mm.)	3.543	3.705
Nitrodiaryls (%)	72.97	71.24
Fore-run (g.) (b. p. 41—55°/0.1 mm.)	4.286	3.501
Chlorine in fore-run (%)	1.69	1.30
Chlorodiphenyls in fore-run (g.)	0.364	0.234
Corr. wt. of diaryl fractions (g.)	3.907	3.939
Nitrodiaryls, corr. (%)	66.18	67.01
$\frac{\text{PhNO}_2}{\text{PhH}}K$	1.50	1.55
<i>p</i> -Cl·C <sub>6</sub> H <sub>4</sub> ·CO <sub>2</sub> H (g.)	3.70	3.71
( <i>p</i> -Cl·C <sub>6</sub> H <sub>4</sub> ·CO <sub>2</sub> ) <sub>2</sub> accounted for (%)	82.0	82.5

Hence,  $\frac{\text{PhNO}_2}{\text{PhH}}K = 1.53$

*Preparation of Reagents.*—Benzene, chlorobenzene, and nitrobenzene were purified according

very much greater extent than chlorobenzene. The experimental observations are in accord with this requirement. Polar effects of a similar nature have been observed by Kooyman, van Helden, and Bickel (*Proc. k. ned. Akad. Wetenschap.*, 1953, *B*, **56**, 75) on the rate of removal of hydrogen atoms from the methyl group of substituted toluenes by the strongly electronegative radicals  $\text{Br}\cdot$  and  $(\text{CH}_2\text{CO})_2\text{N}\cdot$ , and by van Helden and Kooyman (*Rec. Trav. chim.*, 1954, **73**, 269) on the atomic chlorination of substituted toluenes and some aliphatic compounds.

These conclusions, if correct, therefore adumbrate the concept of a whole series of free radical reagents of varying electrophilic or nucleophilic character, since the presence of an electron-repelling group in a phenyl radical should confer a measure of nucleophilic character on the radical. The phenyl radical itself is regarded as unique in being the only reagent for aromatic substitution so far investigated in which polar influences are absent, since there is no reason to postulate any polarisation of this radical. The polar influences of the directing groups do not therefore play a part in determining the course of reaction, which is governed only by the factors discussed in previous papers of this series, and by Hey and Williams (*Discuss. Faraday Soc.*, 1953, **14**, 216).

In addition to the alteration of relative rates of substitution, the assumption of electrophilic or nucleophilic character on the part of the substituting radical would be expected to give rise to the formation of different proportions of the *ortho*-, *meta*-, and *para*-isomerides from those which are formed in the phenylation reaction. Such an effect has been reported by Dannley and Sternfeld (*loc. cit.*) in the *p*-chlorophenylation of benzotrichloride, and interpreted by these workers in a manner similar to that which we have outlined. Further work on these lines with *p*-chlorophenyl and other substituted radicals is now in progress.

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