91. *Homolytic Aromatic Substitution. Part XXVII.* The Reactions of Toluene with some* para-*Substituted Diaroyl Peroxides.*

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The extent of reaction at the side-chain of toluene with the free radicals formed by the decomposition of some *para*-substituted diaroyl peroxides has been investigated. These results have been used in conjunction with the results of competitive experiments to obtain the relative rates of arylation of toluene with various aryl radicals. Both the relative rates, and the variations in the extent of side-chain attack, are discussed, and are shown to be consistent with current views concerning polar influences on the reactivity of free radicals.

ALKYLBENZENES have been shown to react with the free radicals formed by the decomposition of benzoyl peroxide in two ways: (*a*) by substitution in the aromatic nucleus to give biaryls and esters of benzoic acid, and (*b*) by α-hydrogen abstraction from the side-chain to give resonance-stabilised benzyl-type radicals, which subsequently dimerise.[1,2] The rates of both these processes should be affected by the polar characteristics of the free radicals which bring them about, and hence the presence of polarising substituents in the nuclei of the diaroyl peroxides might be expected to alter (i) the relative rate of arylation of alkylbenzenes and (ii) the proportion of side-chain to nuclear reaction. The first of these predictions has already been tested, by using nitrobenzene and chlorobenzene as substrates.[3-5] Both these compounds contain substituents which are deactivating towards electrophilic reagents, and the relative rates of their arylation were decreased by the presence of substituents which rendered the radicals electrophilic, and were increased by the presence of substituents which rendered the radicals nucleophilic. It may be predicted that the opposite tendencies will be observed in the arylation of alkylbenzenes, the nuclei of which are activated towards electrophilic substitution. The results of a test of this prediction, with toluene as substrate, are now reported. The nature of polar influences on the reaction at the side-chain may well be different from the corresponding influences on the nuclear reaction, and these can be determined by measuring the proportion of side-chain attack on alkylbenzenes which occurs when radicals of various polar characteristics are used. Measurements of this kind with some *para*-substituted diaroyl peroxides and toluene are also now reported.

EXPERIMENTAL

Nitrobenzene was purified as described in Part II,[6] and toluene as described in Part VIII.[7] *p*-Nitro- and *p*-methoxy-benzoyl peroxide were prepared as described in Part XIX,[4] *p*-methylbenzoyl peroxide as described in Part XXIV,[5] and *p*-chlorobenzoyl peroxide as described in Part XIV.[8] 2,4′-Dimethylbiphenyl was prepared as a colourless oil, b. p. 108°/0·7 mm., 67°/0·05 mm., n_D^{20} 1·5850, by Gomberg and Pernert's method[9]; a higher-boiling solid fraction was also obtained (see below). 3,4′-Dimethylbiphenyl, m. p. 14°, n_D^{20} 1·5970, was prepared by Hey and Jackson's method.[10] 4,4′-Dimethylbiphenyl, m. p. 121°, was prepared by Kharasch and Fields' method;[11] this compound was also obtained from the higher-boiling solid fraction

* Part XXVI, *J.*, 1961, 3116.

[1] Rondestvedt and Blanchard, *J. Amer. Chem. Soc.*, 1955, **77**, 1769.
[2] Hey, Pengilly, and Williams, *J.*, 1956, 1463.
[3] Cadogan, Hey, and Williams, *J.*, 1955, 1425.
[4] Hambling, Hey, and Williams, *J.*, 1960, 3782.
[5] Hambling, Hey, Orman, and Williams, *J.*, 1961, 3108.
[6] Augod, Hey, and Williams, *J.*, 1952, 2094.
[7] Hey, Pengilly, and Williams, *J.*, 1955, 6.
[8] Chang, Hey, and Williams, *J.*, 1958, 1885.
[9] Gomberg and Pernert, *J. Amer. Chem. Soc.*, 1926, **48**, 1372.
[10] Hey and Jackson, *J.*, 1934, 645.
[11] Kharasch and Fields, *J. Amer. Chem. Soc.*, 1941, **63**, 2318.

which was collected, as described above, during the preparation of 2,4′-dimethylbiphenyl. Crystallisation of this crude material from ethanol gave 4,4′-dimethylbiphenyl as a white crystalline solid, m. p. 121°, not depressed on the addition of the compound prepared by Kharasch and Fields' method.

Decomposition of Diaroyl Peroxides.—Except where otherwise stated, the various diaroyl peroxides (6 g.) were allowed to decompose in the pure solvent or solvent mixture (200 ml.) in a thermostat-bath at 80° for 72 hr. The resulting mixtures were worked up as described in Part II [6] in order to isolate from them the binuclear reaction products (biaryls and bibenzyl). Deviations from this general procedure are detailed below as appropriate.

Determination of the Extent of Side-chain Attack in the Arylation of Toluene.—Experiments 1 and 2 were carried out with *p*-chloro- and *p*-methoxy-benzoyl peroxide. Experiments 3 and 4 were carried out with *p*-methylbenzoyl peroxide and the quantities of the products obtained in these two experiments were in close agreement. In experiment 1, the composition of the binuclear fraction was estimated by microanalysis for chlorine, and in experiment 2 by microanalysis for methoxy-group. Two methods were used for the analysis of the binuclear fraction obtained in experiments 3 and 4 as follows:

(i) A weighed portion was added to an equal volume of light petroleum (b. p. 40—60°), and the mixtures were cooled to −60°, the bibenzyl crystallising. The mixture was then quickly filtered through a pre-cooled, weighed sintered-glass Hirsch funnel. The filtrate was cooled again to −60° and the process repeated until no further crystallisation occurred. The precipitated bibenzyl was washed with light petroleum at −80°, dried, and weighed (m. p. 48°).

TABLE 1.

Infrared analysis of dimethylbiphenyl–bibenzyl mixtures.

	Composition (%)			
		Dimethylbiphenyls		
Mixture	Bibenzyl	2,4′-	3,4′-	4,4′-
3	43·6	37·9	11·4	7·1
4	40·4	40·7	11·9	7·0
Mean (3 & 4)	42·0	39·3	11·6	7·1
S1 (Found)	40·3	38·1	13·8	7·7
S1 (Calc.)	42·0	39·3	11·6	7·1

(ii) The infrared spectrographic method, involving complete analysis of the four-component mixture of isomeric dimethylbiphenyls and bibenzyl, was applicable in this instance, although certain attendant difficulties reduced the accuracy of the results, particularly those concerning the relative proportions of the three isomeric dimethylbiphenyls. Nevertheless, the result obtained for the proportion of bibenzyl in the mixture is in fairly close agreement with that obtained by method (i). The procedure described in Part XIV [8] was used for the analysis, the solvent being *NN*-dimethylformamide.[4] Examination of the spectra of the pure compounds revealed characteristic absorption bands suitable for use in the analysis as follows: 2,4′-dimethylbiphenyl 766·4 cm.$^{-1}$, 3,4′-dimethylbiphenyl 787·4 cm.$^{-1}$, 4,4′-dimethylbiphenyl 810 cm.$^{-1}$. The first of these was partly coincident with a broad band due to bibenzyl at 761 cm.$^{-1}$ and the accuracy of this analysis was therefore reduced. The amount of bibenzyl in the mixtures was obtained by difference. In order to check the accuracy of the analysis a synthetic mixture (S1), of known composition, was made up and analysed. The results are given in Table 1.

TABLE 2.

Side-chain attack in the arylation of toluene.

Experiment	1	2	3 & 4 (mean)	Ref. 13
Peroxide	*p*-Chlorobenzoyl	*p*-Methoxybenzoyl	*p*-Methylbenzoyl	*p*-Nitrobenzoyl
Binuclear fraction (g.)	1·306	1·959	2·241	1·775
Bibenzyl in binuclear fraction (%)	10·0	45·0	42·0	0·0
Total aroic acid (free and by hydrolysis of esters) (g.)	3·80	3·42	1·51	3·71
Residue (g.)	0·607	1·803	1·659	0·007

The ultraviolet spectrographic method (cf. Part V [12]) was used to confirm this analysis for bibenzyl content. In the range 230—290 mμ, bibenzyl is transparent to ultraviolet radiation, while all three isomeric dimethylbiphenyls have strong, overlapping absorption bands. The method could not, therefore, be used for the complete quantitative analysis of the quaternary mixture. However, the composition derived from infrared analysis (Table 1) satisfied the equations derived as described in Part V [12] from the measured optical densities (and hence the extinction coefficients) of the pure compounds and experimental mixtures at a series of wavelengths in the ultraviolet region. These results are therefore consistent with the ultraviolet, as well as the infrared, spectra.

The results of all these experiments are summarised in Table 2, which also contains results previously obtained for the corresponding reaction with *p*-nitrophenyl radicals.[13] These results were used in conjunction with those of competitive experiments in the calculation of the relative rate of arylation of toluene by the various radicals. The large residue formed in the reactions with *p*-methoxy- and *p*-methyl-benzoyl peroxide render these results rather less significant than the others in the series.

TABLE 3.

Experiment:	5	6
Binuclear fraction (b. p. 45—195°/0·1 mm.) (g.)	2·002	2·079
Dinitrobiphenyls in binuclear fraction (%)	30·1	31·2
Fore-run (b. p. 25—40°/0·1 mm.) (g.)	4·343	1·465
Methylnitrobiphenyls in fore-run (%)	0·00	0·80
,, ,, (g.)	0·000	0·012
Corr. wt. of binuclear fraction (g.)	2·002	2·091
Dinitrobiphenyls corr. (%)	30·1	30·8
${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ for *p*-nitrophenylation	0·376	0·384
Free *p*-nitrobenzoic acid (g.)	2·98	3·06
p-Nitrobenzoic acid from hydrolysis of esters (g.)	0·40	0·42
Residue (g.)	0·137	0·091
$(p\text{-}NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}O)_2$ accounted for (%)	82·0	84·0

Hence, ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ for *p*-nitrophenylation = 0·38.

Determination of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ *for* p-*Nitrophenylation.*—In experiments 5 and 6, *p*-nitrobenzoyl peroxide was allowed to decompose in an equimolar mixture of nitrobenzene and toluene. The binuclear fractions were isolated as described above, except that the chromatography stage was omitted since the product was unusually clean. The binuclear fractions were analysed for nitro-groups by titration with titanous chloride. Fore-runs were collected immediately before the binuclear fractions in the final distillation. These were also analysed for nitro-groups, and their content of methylnitrobiphenyls thus obtained by difference. A correction in these terms could then be applied to the weight and composition of the binuclear fractions. Fractions taken immediately before the fore-runs in the final distillation were shown by analysis to consist only of nitrobenzene. The absence of dinitrobiphenyls from the fore-runs is assumed, since these did not distil until a temperature considerably above that at which the fore-runs were collected had been reached. No correction for side-chain attack is required in this case. The results are given in Table 3.

Determination of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ *for* p-*Chlorophenylation.*—In experiments 7 and 8 *p*-chlorobenzoyl peroxide was allowed to decompose in an equimolar mixture of nitrobenzene and toluene. The reactions were carried out and the binuclear fractions isolated and analysed for nitro-groups by the standard procedure described above. The result of experiment 1 was used to apply corrections to the weight and composition of the binuclear fraction to allow for its bibenzyl content. The results are given in Table 4.

Determination of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ *for* p-*Methoxyphenylation.*—In experiments 9 and 10, *p*-methoxybenzoyl peroxide was allowed to decompose in an equimolar mixture of nitrobenzene and toluene. The experiments were carried out and the results calculated exactly as described above for the corresponding experiments with *p*-chlorobenzoyl peroxide. The result of experiment 2 was used in applying the bibenzyl corrections. The results are given in Table 5.

Determination of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ *for* p-*Methylphenylation.*—In experiments 11 and 12 *p*-toluoyl peroxide was allowed to decompose in an equimolar mixture of nitrobenzene and toluene.

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

[13] Pengilly, Ph.D. Thesis, University of London, 1955.

The experiments were carried out by the standard procedure except that, owing to the relatively greater volatility of the dimethylbiphenyls, the removal of nitrobenzene at 40 mm. in the penultimate distillation was carried out very carefully, through a 6" helix-packed column. The mean of the results obtained by infrared analysis in experiments 3 and 4 was used in applying the bibenzyl corrections. The results are given in Table 6.

TABLE 4.

Experiment:	7	8
Binuclear fraction (b. p. 45—130°/0·1 mm.) (g.)	1·623	1·872
Chloronitrobiphenyls in binuclear fraction (%)	57·1	59·9
Fore-run (b. p. 25—45°/0·1 mm.) (g.)	2·405	4·021
Chloromethylbiphenyls + bibenzyl in fore-run (g.)	0·106	0·137
Chloronitrobiphenyls (g.)	0·927	1·121
Total chloromethylbiphenyls + bibenzyl (g.)	0·802	0·890
Bibenzyl correction (%)	10·0	10·0
Chloromethylbiphenyls (g.)	0·722	0·801
${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ for *p*-chlorophenylation	1·11	1·21
Free *p*-chlorobenzoic acid (g.)	3·27	3·30
p-Chlorobenzoic acid from hydrolysis of esters (g.)	0·71	0·73
Residue (g.)	0·110	0·081
(p-$ClC_6H_4{\cdot}CO{\cdot}O)_2$ accounted for (%)	89·2	90·4

Hence, ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ for *p*-chlorophenylation = 1·16.

TABLE 5.

Experiment:	9	10
Binuclear fraction (b. p. 40—120°/0·1 mm.) (g.)	0·917	0·959
Methoxynitrobiphenyls in binuclear fraction (%)	65·6	62·0
Fore-run (b. p. 25—40°/0·1 mm.) (g.)	0·930	0·906
Methoxymethylbiphenyls + bibenzyl in fore-run (g.)	0·140	0·118
Methoxynitrobiphenyls (g.)	0·600	0·595
Total methoxymethylbiphenyls + bibenzyl (g.)	0·457	0·482
Bibenzyl correction (%)	45·0	45·0
Methoxymethylbiphenyls (g.)	0·251	0·265
${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ for *p*-methoxyphenylation	2·07	1·94
Free *p*-methoxybenzoic acid (g.)	4·23	4·35
p-Methoxybenzoic acid from hydrolysis of esters (g.)	0·43	0·49
Residue (g.)	0·143	0·093
(p-$CH_3O{\cdot}C_6H_4{\cdot}CO{\cdot}O)_2$ accounted for (%)	95·0	96·0

Hence, ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ for *p*-methoxyphenylation = 2·00.

TABLE 6.

Experiment:	11	12
Binuclear fraction (b. p. 40—128°/0·1 mm.) (g.)	2·126	2·078
Methylnitrobiphenyls in binuclear fraction (%)	80·0	82·9
Fore-run (b. p. 25—40°/0·1 mm.) (g.)	0·912	3·907
Dimethylbiphenyls + bibenzyl in fore-run (g.)	0·042	0·195
Methylnitrobiphenyls (g.)	1·700	1·723
Total dimethylbiphenyls + bibenzyl (g.)	0·468	0·550
Bibenzyl correction (%)	42·0	42·0
Dimethylbiphenyls (g.)	0·271	0·319
${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ for *p*-methylphenylation	5·36	4·61
Free *p*-toluic acid (g.)	3·14	3·16
p-Toluic acid from hydrolysis of esters (g.)	0·26	0·32
Residue (g.)	0·265	0·263
(p-$CH_3C_6H_4{\cdot}CO{\cdot}O)_2$ accounted for (%)	85·0	85·3

Hence, ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ for *p*-methylphenylation = 4·98.

Reaction of Diazotised p-*Anisidine with Isopropylbenzene in the Presence of Alkali*.—This reaction, previously reported by Pengilly,[13] has been repeated, with gas–liquid chromatography for the analysis of the product. *p*-Anisidine (31 g.) in a mixture of hydrochloric acid (*d* 1·18; 80 ml.) and water (40 ml.) was diazotised at 5° with aqueous sodium nitrite (17·5 g. in 50 ml.). Isopropylbenzene (400 ml.) was added, followed by 40% aqueous sodium hydroxide dropwise during 3 hr. until the mixture was just alkaline, while the vigorously stirred mixture was kept at 5°. This temperature was maintained for a further 3 hr. and then allowed to rise to room temperature. After the mixture had been stirred for a further 48 hr. the organic layer was separated and dried ($CaCl_2$), and the excess of isopropylbenzene removed by distillation. The residual oil was distilled at 80—130°/0·1 mm. and then passed through an alumina column, which was eluted with benzene (100 ml.). After being washed with dilute hydrochloric acid and with water, the dried ($CaCl_2$) eluate was distilled to remove benzene, and the residual oil collected at 130—185°/14 mm. Submission of the distillate to gas–liquid chromatography showed that 2,3-dimethyl-2,3-diphenylbutane could not have been present at a concentration greater than 1%.

DISCUSSION

The Incidence of Side-chain Attack.—The results available concerning the percentage of the binuclear fraction, which consists of the products of side-chain attack for the reactions of various alkylbenzenes with a series of diaroyl peroxides, are summarised in Table 7, in which results previously reported for reactions with ethylbenzene and isopropylbenzene, and with benzoyl peroxide are included for comparison.

It is obvious from these results that the incidence of side-chain attack is strongly influenced by the polarity of the attacking radicals, and that, apart from the apparently anomalous results obtained with *p*-methoxybenzoyl peroxide, which are discussed below, the susceptibility of the side-chains to attack increases with the nucleophilic character of the radicals. Since, in the alkylbenzenes, the direction of polarisation is such that the side-chain suffers a deficit, and the nucleus a surplus, of electron-density, it is to be expected that nucleophilic radicals should be directed preferentially to the side-chain, and electrophilic radicals to the nucleus. With the above-mentioned exception, these predicted tendencies have in fact been observed.

The dipole moments of the compounds C_6H_5R (where R is the same substituent as is present in the peroxides) are included in Table 7 as an approximate index of the polar characteristics of the radicals derived from the peroxides. It is to be noted that no simple quantitative relation exists between these dipole moments and the incidence of side-chain attack although, qualitatively, the peroxides fall into the predicted sequence.

TABLE 7.

Attack upon alkylbenzene side-chain (moles %).

Peroxide (p-RC_6H_4·CO·O$)_2$	$PhCH_3$	PhC_2H_5	$PhCH(CH_3)_2$	Dipole moment[14] of C_6H_5R
p-Nitrobenzoyl	0[13]	0[13]	0[13]	−3·98
p-Chlorobenzoyl	11·0	—	37·5[13]	−1·55
p-Bromobenzoyl	—	—	49·9[13]	−1·55
p-Methoxybenzoyl	47·1	—	87·9[13]	−1·23
Benzoyl	12·1[2]	51·4[2]	55·5[2]	0
p-Methylbenzoyl	42·0	—	—	+0·4

The reason for this lack of quantitative agreement is probably that both aryl- and aroyloxy-radicals are capable of abstracting hydrogen from the side-chains. The relative contributions of these two reagents are, at present, indeterminate (since both reagents lead to the same binuclear products) and, moreover, may vary from peroxide to peroxide. Foster and Williams[15] have shown that both types of radical contribute in reactions with benzoyl peroxide. Since it is hardly to be expected that the polar influences exerted by substituent groups affect the polar characteristics of aryl and aroyloxy-radicals in which they are present in ways which are quantitatively similar, the observed lack of a simple quantitative relation between dipole moment and product distribution is not surprising. Moreover, the assumption that dipole moments can be used as indices of polar character of the aryl and aroyloxy-radicals itself involves an approximation, since the influence of the substituents on the polarisability of the radicals is neglected. In view of these factors, no more than qualitative agreement can be expected.

[14] Waters, "Physical Aspects of Organic Chemistry," 4th edn., Routledge and Kegan Paul, Ltd., London, 1950, p. 88.

[15] Foster and Williams, unpublished work.

The foregoing considerations suggested a possible explanation of the anomalous results obtained with *p*-methoxybenzoyl peroxide.[13] It was considered probable, in view of the relatively large amounts of *p*-methoxybenzoic acid formed in reactions with this peroxide, that the contribution of *p*-methoxybenzoyloxy-radicals to hydrogen-abstraction at the side-chain is, in this case, unusually large. The postulate that it is the *p*-methoxybenzoyloxy-radicals which are responsible for the high incidence of side-chain attack was supported by the failure to isolate any product of such attack in the reaction of *p*-methoxybenzene-diazoic acid with isopropylbenzene, since in this reaction aroyloxy-radicals are not present as intermediates in the formation of aryl radicals. This result has been confirmed in the present work. The enhanced reactivity of the *p*-methoxybenzoyloxy-radical in the side-chain reaction probably arises from the development of nucleophilic character in this radical (although the *p*-methoxyphenyl radical is slightly electrophilic [4]) and must therefore be directly consequent on the presence of a carbonyloxy-group in the former radical. It was thought that, in the presence of this strongly electron-attracting group in the *para*-position, the large conjugative polarisability conferred upon the radical by the methoxy-group ($+E$ effect) allows the movement of electron-density in the direction of the carbonyloxy-group. This process must obviously confer additional nucleophilic character on the *p*-methoxybenzoyloxy-radical, while in the *p*-methoxyphenyl radical, which does not contain an electron-attracting group in the *para*-position, the $-I$ effect of the methoxy-group is the dominant polar influence.

TABLE 8.

Thermodynamically corrected acid dissociation constants.

Acid	Benzoic	*o*-Anisic	*m*-Anisic	*p*-Anisic
10^5K_a	6·27	8·06	8·17	3·38

This reinforcement of the polar influences of these two groups when orientated *para* to one another is also illustrated by the dissociation constants of the anisic acids,[16] which are given in Table 8. The acid-weakening effect of the *para*-methoxy-group is due to the influence of its electromeric polarisability, as discussed above. *m*-Anisic acid, on the other hand, is a stronger acid than benzoic acid, since only inductive effects are capable of exerting a marked influence on the *meta*-position and groups situated thereat.

Relative Rates of Nuclear Arylation.—The various values of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ reported in this paper, and derived values of the relative rates of arylation of toluene, ${}^{\mathrm{PhCH_3}}_{\mathrm{PhH}}K$, are given in Table 9, in which the corresponding figures for phenylation are included for comparison. The values of ${}^{\mathrm{PhCH_3}}_{\mathrm{PhH}}K$ were obtained from those of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ by the use of the relationship:

$${}^{\mathrm{PhCH_3}}_{\mathrm{PhH}}K = {}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K / {}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K.$$

The values of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ used were those reported in previous papers in this series.[3-5,17] The figures given for ${}^{\mathrm{PhCH_3}}_{\mathrm{PhH}}K$ in Table 9, being derived values, are probably somewhat less reliable than those for ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$, which are the results of direct determination. The value of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$ for *p*-methylphenylation may be a slight overestimate, since the well-known volatility of methyl derivatives of biphenyl may have resulted in the loss of a small portion of the dimethylbiphenyls by co-distillation with nitrobenzene (the less volatile solvent in these experiments), although, as described in the Experimental section, precautions were taken to avoid this source of error as far as possible. The value for ${}^{\mathrm{PhCH_3}}_{\mathrm{PhH}}K$ given in Table 9 should therefore be regarded as a *minimum* value.

The observed increase in the values of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$, and the consequent decrease in ${}^{\mathrm{PhCH_3}}_{\mathrm{PhH}}K$, as the attacking radicals become less electrophilic and more nucleophilic in character, is entirely consistent with the theory of the reactivity of polarised radicals outlined above, since the methyl group activates aromatic nuclei towards attack by electrophilic, and deactivates them towards attack by nucleophilic, reagents. The only

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[16] Dippy, *Chem. Rev.*, 1939, **25**, 151.

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

figure which appears to be slightly out of sequence is that for ${}^{\mathrm{PhCH_3}}_{\mathrm{PhH}}K$ for *p*-methoxyphenylation, but the discrepancy is small and appears only in the derived relative rate. We therefore accept the position of the *p*-methoxyphenyl radical in the series as indicated by the value of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$, and we consider this radical to be very slightly electrophilic in character. This interpretation is consistent with the direction and magnitude of the dipole moment of anisole, as well as with results previously reported [4] for other homolytic substitutions with this radical.

TABLE 9.

Relative rates of arylation of toluene.

	${}^{\mathrm{PhNO_2}}_{\mathrm{PhCH_3}}K$	${}^{\mathrm{PhCH_3}}_{\mathrm{PhH}}K$
p-Nitrophenylation	0·38	2·50
p-Chlorophenylation	1·16	1·32
p-Methoxyphenylation	2·00	1·46
Phenylation	2·40	1·23
p-Methylphenylation	4·98	0·68

Ratios of isomers formed in the arylation of toluene with a series of substituted aryl radicals have not been investigated in detail, since the expected differences in isomer composition are very small and would almost certainly not be greater than the experimental error inherent in their determinations. The differences in isomer distribution reported in Part XIX [4] for the arylation of nitrobenzene, which is extensively polarised, while greater than the experimental error, were only of the order of 5% in the proportion of each isomer. Considerably smaller differences would be expected for toluene, in which the polarisation (in the opposite direction) is much less pronounced.

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