750. *Homolytic Aromatic Substitution. Part XVIII.*[1] *Some Reactions with* ortho-*Substituted Phenyl Radicals.*

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Relative rates of arylation of chlorobenzene, nitrobenzene, and toluene with *o*-nitro- and *o*-bromo-phenyl radicals have been measured by means of competitive experiments. The proportions in which substitution by these radicals takes place at the *ortho*-, *meta*-, and *para*-positions of nitrobenzene have also been determined. The corresponding partial rate factors have been derived and discussed in terms of the polarity of the attacking radical and the steric influence of its substituent. The anomalous formation of bibenzyl in the reaction between *o*-nitrobenzoyl peroxide and toluene is reported and tentative explanations for this finding are advanced.

Recent determinations [2] of the reactivity of the nuclear positions of benzene derivatives towards substitution by *para*-substituted aryl radicals have led to the conclusion that, compared with the phenyl radical, the substituted radicals possess a measure of polar character. This has been confirmed by the observation of changes, attributable to the presence of substituents in the attacking radical, in the distribution of isomers formed in the arylation of various compounds.[3-5] The study of the reactivity of aromatic compounds towards arylation has now been extended to include radicals which contain *ortho*-substituents.

Many reactions have been carried out, mainly for preparative purposes, in which *ortho*-substituted aryl radicals have been allowed to react with aromatic compounds, and anomalous products have been obtained in several instances. Gomberg and Pernert [6] obtained *m*-bromotoluene from reactions of diazotised 2-bromo-4- and 4-bromo-2-methylaniline with benzene. Hey and Walker [7] isolated methyl benzoate in addition to the isomeric 2-methoxycarbonylphenylpyridines from the reaction between 2-methoxycarbonylbenzoyl peroxide and pyridine, and more recently Cadogan, Hey, and Williams [8] found t-butylbenzene and biphenyl in the products of the reaction of 2-t-butyl-*N*-nitrosoacetanilide and benzene. The expected product, 2-t-butylbiphenyl, was not isolated. In the present work, *o*-nitro- and *o*-bromo-phenyl radicals were studied. The isomeric *p*-nitro- and *p*-bromo-phenyl radicals, while retaining their essential radical characteristics, have been shown to possess electrophilic properties.[2, 9] Hey and Walker [7] allowed *o*-nitrobenzoyl peroxide to decompose in benzene and noted no anomalous behaviour. This finding is now confirmed, and the expected products, namely, 2-nitrobiphenyl and *o*-nitrobenzoic acid, are shown to account for some 86% of the starting material. The decomposition of *o*-bromobenzoyl peroxide in aromatic solvents has not been previously investigated, and the reaction in benzene is now shown to give the expected products.

The determination of relative rates of arylation of nitrobenzene, chlorobenzene, and toluene $\left({}^{\text{PhX}}_{\text{PhH}}K\right)$ with *o*-bromo- and *o*-nitro-phenyl radicals, by means of an improved version of the competitive technique devised by Augood, Hey, and Williams,[10] is now reported. The mixtures of biaryls, obtained by allowing a small quantity of a diaroyl peroxide (0·025 mole) to react with a large excess of an equimolar mixture of nitrobenzene and the

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[1] Part XVII, *J.*, 1959, 1871.
[2] Chang, Hey, and Williams, *J.*, 1958, 4403.
[3] DeTar and Kazimi, *J. Amer. Chem. Soc.*, 1955, **77**, 3842.
[4] Dannley and Sternfeld, *J. Amer. Chem. Soc.*, 1954, **76**, 4543.
[5] Chang, Hey, and Williams, *J.*, 1958, 2600.
[6] Gomberg and Pernert, *J. Amer. Chem. Soc.*, 1926, **48**, 1372.
[7] Hey and Walker, *J.*, 1948, 2213.
[8] Cadogan, Hey, and Williams, *J.*, 1954, 3352.
[9] Hambling, Hey, and Williams, unpublished work.
[10] Augood, Hey, and Williams, *J.*, 1952, 2094.

competing solvent (2 moles), were analysed volumetrically by reduction of the nitrobiaryls with titanous sulphate by the methods described in Parts II [10] and VII.[8] Titanous chloride had been employed in previous work, but it was found that titanous sulphate is superior in that its solutions in dilute sulphuric acid are less susceptible to aerial oxidation than are solutions of the chloride. The relative rates of *o*-bromo- and *o*-nitro-phenylation of nitrobenzene $\left({}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K\right)$ were determined directly. Combination of these values with the rates of *o*-bromophenylation and *o*-nitrophenylation of chlorobenzene relative to nitrobenzene $\left({}^{\mathrm{PhCl}}_{\mathrm{PhNO_2}}K\right)$ gave relative rates of arylation of chlorobenzene $\left({}^{\mathrm{PhCl}}_{\mathrm{PhH}}K\right)$. The relative rate of *o*-bromophenylation of toluene was determined similarly. The biaryl fractions obtained from reactions with toluene contained bibenzyl, arising from reaction at the side chain, in addition to bromomethyl- and bromonitro-biphenyls, and their composition was determined by analyses for bromine and for nitro-compounds. This method could not be applied to the mixtures obtained by *o*-nitrophenylation of toluene–nitrobenzene mixtures. The relative rate of *o*-nitrophenylation of toluene was therefore determined without the use of this experiment. Instead, its rate of reaction relative to chlorobenzene $\left({}^{\mathrm{PhMe}}_{\mathrm{PhCl}}K\right)$ was measured, and by taking this value in conjunction with the relative reactivity of chlorobenzene $\left({}^{\mathrm{PhCl}}_{\mathrm{PhH}}K\right)$ for *o*-nitrophenylation, the desired relative rate was calculated.

The results of all these experiments indicate that, apart from the polar character of the attacking radical, a second factor, which is probably steric in origin, is instrumental in modifying the relative reactivites of these compounds when these radicals are used. In order to investigate the nature of this other factor, a more detailed knowledge of reactivity was obtained by measurement of the ratios of the isomeric products of some *o*-bromo- and *o*-nitro-phenylations. This enabled the partial rate factors to be calculated for these reactions. Nitrobenzene was chosen as the substrate, since comparison could be made with its known partial rate factors for arylation with the isomeric *para*-substituted phenyl radicals. Infrared and ultraviolet spectrography were used for analysis of the mixtures of isomers. The composition of the mixture of 2-bromo-*x*′-nitrobiphenyls, which results from *o*-bromophenylation of nitrobenzene, was determined by the standard infrared method described in Part III.[11] This method, and the ultraviolet method described in Part V,[12] were inapplicable for the analysis of the mixture of the isomeric 2,*x*′-dinitrobiphenyls, resulting from *o*-nitrophenylation of nitrobenzene, because of the marked similarity of the ultraviolet and infrared spectra of the individual components of this mixture. Dewar and Urch's graphical ultraviolet method [13] was applied successfully to this mixture after its 2,3′-dinitrobiphenyl content had been determined by an infrared method.

It has been shown that, in the arylation of toluene, reaction at the side chain results in abstraction of a hydrogen atom, with the consequent formation of bibenzyl. The extent of this side reaction has been shown by Hey, Pengilly, and Williams [14,15] and by Hambling, Hey, and Williams [9] to reflect the polarity of the attacking radical. For example, the reaction with the slightly nucleophilic *p*-tolyl radical yields bibenzyl to the extent of 42% of the binuclear products, while the reaction with the electrophilic *p*-nitrophenyl radical gives no bibenzyl. This was interpreted on the basis that nuclear substitution in toluene should be favoured by electrophilic radicals, while side-chain attack should be favoured by nucleophilic radicals.[15] The reaction of *o*-nitrophenyl radicals with toluene is now reported

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[11] Augood, Hey, and Williams, *J.*, 1953, 44.
[12] Cadogan, Hey, and Williams, *J.*, 1954, 794.
[13] Dewar and Urch, *J.*, 1957, 345.
[14] Hey, Pengilly, and Williams, unpublished work.
[15] Augood and Williams, *Chem. Rev.*, 1957, **57**, 171.

to give bibenzyl (32·8%). Although the explanation of this apparent anomaly in the concept of polarised radicals is at present not completely clear, alternative possible interpretations of it are suggested below.

EXPERIMENTAL

Reagents.—Benzene, chlorobenzene, nitrobenzene, and toluene were purified as described in Parts II [10] and VIII.[16] *o*-Nitrobenzoyl peroxide (m. p. 147°) and *o*-bromobenzoyl peroxide (m. p. 107°) were preapred by Hey and Walker's method [7] from *o*-nitro- and *o*-bromo-benzoyl chloride respectively. 2-Bromo-2′-nitrobiphenyl was prepared by means of the Gomberg reaction of *o*-nitroaniline (100 g.) with bromobenzene (1250 ml.). The portion of the biaryl mixture having b. p. 100—125°/0·1 mm. was fractionally crystallised from ethanol to give 2-bromo-2′-nitrobiphenyl (6·3 g.; m. p. 71·5—72°). 2-Bromo-3′-nitrobiphenyl (m. p. 74—76°; b. p. 120—130°/0·1 mm.) was prepared in 12% yield in similar manner from *m*-nitroaniline. 2-Bromo-4′-nitrobiphenyl (m. p. 82—83°) was prepared by Scarborough and Waters's method.[17] 2,2′-Dinitrobiphenyl (m. p. 125°) was prepared by the method of Atkinson, Morgan, Warren, and Manning.[18] 2,3′-Dinitrobiphenyl was prepared by nitration of 3-nitrobiphenyl (15 g.), prepared as described in Part II,[10] with nitric acid at 35° by the method of DeTar and Kazimi.[3] Fractional crystallisation from methanol of the mixture of dinitrobiphenyls gave the more soluble 2,3′-dinitrobiphenyl (4·8 g.), m. p. 118·5—119°. 2,4′-Dinitrobiphenyl, prepared by Hambling, Hey, and Williams,[9] was recrystallised from ethanol to m. p. 93°.

Decomposition of o-*Nitrobenzoyl Peroxide in Benzene.*—*o*-Nitrobenzoyl peroxide (30 g.) in benzene (700 ml.) was boiled under reflux for 48 hr. Sodium hydrogen carbonate extracts of the reaction mixture gave *o*-nitrobenzoic acid (15·87 g.) m. p. 144°, which after crystallisation from ethanol had m. p. and mixed m. p. 148°. The benzene was distilled from the mixture after extraction, and the residue boiled under reflux with aqueous 2N-sodium hydroxide (100 ml.) for 16 hr. The resulting mixture was extracted with hot benzene, and the extracts were washed with water. Distillation gave a fraction, b. p. 90—105°/0·1 mm. (13·8 g.), and left a residue (0·27 g.), b. p. >165°/0·1 mm. The distillate, 2-nitrobiphenyl, was a yellow solid, m. p. 29—34°, which on crystallisation from ethanol gave needles, m. p. 36°.

Decomposition of o-*Bromobenzoyl Peroxide in Benzene.*—*o*-Bromobenzoyl peroxide (15·0 g.) in benzene (500 ml.) was boiled under reflux for 48 hr. The mixture, after treatment as described above, gave *o*-bromobenzoic acid (4·80 g.), m. p. 150°. Distillation of the benzene solution gave a fraction (5·94 g.), b. p. 63—110°/0·01 mm., and left a residue (1·58 g.), b. p. >140°/0·1 mm. The distillate, which was a colourless liquid, was redistilled to give 2-bromobiphenyl (5·32 g.), b. p. 78—95°/0·01 mm., n_D^{20} 1·6262, and its identity was confirmed by means of its infrared absorption spectrum.

Competitive Experiments.—*Isolation of the biaryls.* The mixtures of biaryls were isolated from the reaction mixture by the following method, which is similar to, but not identical with, that described in Part II.[10] (i) The free acids were extracted with saturated aqueous sodium hydrogen carbonate. (ii) The bulk of the residual solvents was distilled off slowly. (iii) The residue was boiled under reflux with 2N-aqueous sodium hydroxide (100 ml.) for 15 hr. The mixture, while still hot, was extracted with benzene and the extracts were washed with hot water. Acids were extracted from the combined alkaline solution and water-washings as described in Part VIII.[16] The benzene extracts were washed with hydrochloric acid (*d* 1·18) to remove any products of the reduction of nitrobenzene, and then washed with water. (iv) The benzene solution was distilled, and the residue adsorbed on an alumina column. Elution with benzene (150 ml.) and ether (100 ml.) gave a solution containing the residual nitrobenzene, the biaryls, and some high-boiling material. (v) Most of the remaining nitrobenzene was slowly distilled from the eluate, which had been reduced in volume by distillation, through a 9 cm. fractionating column, leaving a mixture of biaryls and the last traces of nitrobenzene. The nitrobenzene distillate was redistilled and a residual 0·5 ml. was combined with the biaryls. (vi) The mixture of biaryls, final traces of nitrobenzene, and some of the high-boiling material was distilled at a pressure of 0·1 mm. No fractions were taken. The greatest

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[16] Hey, Pengilly, and Williams, *J.*, 1955, 6.

[17] Scarborough and Waters, *J.*, 1927, 91.

[18] Atkinson, Morgan, Warren, and Manning, *J. Amer. Chem. Soc.*, 1945, **67**, 1513.

source of error in the working-up procedure comes from the final separation of the high-boiling resin and the biaryls. To provide a check on this separation and hence to minimise such errors, the distillate, consisting of nitrobenzene, biaryls, and resin, was homogenised by warming and divided into two parts (A and B). Each part was then fractionally distilled as described in Part II,[10] giving the " forerun," consisting of nitrobenzene and traces of the lowest-boiling biaryl, and the biaryl fraction.

Determination of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ *for* o-*Nitrophenylation.*—Experiments 1 and 2 were carried out with *o*-nitrobenzoyl peroxide (8·63 g.) in an equimolar mixture of benzene and nitrobenzene (200 ml., peroxide : solvent molar ratio = 0·025 : 2). The reactions were allowed to proceed in a thermostat at 80° for 72 hr. The biaryl fraction, b. p. 87—140°/0·01 mm., was isolated as described above and was analysed volumetrically by reduction with titanous sulphate. The forerun, b. p. 35—80°/0·1 mm., which contained nitrobenzene and 2-nitrobiphenyl, was analysed similarly. The absence of dinitrobiphenyls in this fraction can be assumed, since they did not begin to distil until a temperature of 120° had been reached. A small quantity of material, b. p. $>170°$/0·01 mm., remained after the distillation. The results are given in Table 1.

TABLE 1.

	Experiment 1		Experiment 2	
	A	B	A	B
Forerun (g.)	1·484	0·966	1·296	0·612
Nitrogen in forerun (%)	11·32	11·32	11·39	11·32
2-Nitrobiphenyl in forerun (g.)	0·024	0·015	0·000	0·010
Biaryl fraction (g.)	2·407	1·986	1·819	2·627
Nitrogen in biaryl fraction (%)	8·11	8·12	8·11	8·10
Total 2-nitrobiphenyl (g.)	1·851	1·518	1·381	2·010
Dinitrobiphenyls (g.)	0·580	0·483	0·438	0·627
${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$	0·255	0·259	0·259	0·254
Total wt. of biaryls (g.)	4·432		4·456	
o-Nitrobenzoic acid (g.): free	4·31		4·23	
from esters	0·51		0·50	
Residue (g.)	0·256		0·169	
o-Nitrobenzoyl peroxide accounted for (%)	96·7		95·8	

Hence ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ (mean) = 0·26

Determination of ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ *for* o-*Bromophenylation.*—Experiments 3 and 4 were carried out by the same procedure with *o*-bromobenzoyl peroxide (10·40 g.) and an equimolar mixture of benzene and nitrobenzene (200 ml., peroxide : solvent molar ratio = 0·025 : 2). Foreruns containing nitrobenzene and 2-bromobiphenyl were taken at b. p. 35—50°/0·1 mm., and analysed for nitrogen. The absence of bromonitrobiphenyls in this fraction is inferred from

TABLE 2.

	Experiment 3		Experiment 4	
	A	B	A	B
Forerun (g.)	0·651	0·363	0·319	0·256
Nitrogen in forerun (%)	10·81	10·51	10·55	10·21
2-Bromobiphenyl in forerun (g.)	0·033	0·028	0·024	0·027
Biaryl fraction (g.)	2·624	1·744	2·168	1·839
Nitrogen in biaryl fraction (%)	2·43	2·50	2·49	2·52
Total 2-bromobiphenyl (g.)	1·392	0·907	1·121	0·947
Bromonitrobiphenyls (g.)	1·265	0·865	1·071	0·919
${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$	0·761	0·799	0·801	0·814
Total wt. of biaryls (g.)	4·429		4·058	
o-Bromobenzoic acid (g.): free	4·33		4·35	
from esters	0·51		0·46	
Residue (g.)	0·739		0·536	
o-Bromobenzoyl peroxide accounted for (%)	79·0		77·1	

Hence ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K = 0·79$

their higher b. p. The biaryl fraction distilled at 60—122°/0·01 mm., and a residue (b. p. >137°/0·01 mm.) was left after the distillation. The results are given in Table 2.

Determination of ${}_{\mathrm{PhNO_2}}^{\mathrm{PhCl}}K$ *for* o-*Nitrophenylation.*—Experiments 5 and 6 were carried out with *o*-nitrobenzoyl peroxide (8·00 g.) in an equimolar mixture of nitrobenzene and chlorobenzene (200 ml., molar ratio peroxide : solvent = 0·022 : 2). From the mixtures were obtained a forerun (b. p. 35—60°/0·1 mm.) containing nitrobenzene and 2-chloro-2′-nitrobiphenyl, and the biaryl fraction (b. p. 80—140°/0·01 mm.). The absence of dinitrobiphenyls in the forerun is inferred from their b. p., which is some 60° higher than the highest temperature reached in the distillation of the forerun. A small residue (b. p. >160°/0·01 mm.) was left after the distillation. The results are given in Table 3.

Determination of ${}_{\mathrm{PhNO_2}}^{\mathrm{PhCl}}K$ *for* o-*Bromophenylation.*—*o*-Bromobenzoyl peroxide (9·76 g.) was allowed to decompose in an equimolar mixture of nitrobenzene and chlorobenzene in a similar manner (molar ratio peroxide : solvent = 0·025 : 2). The biaryls in expts. 7 and 8 were isolated by the standard method and distilled at 81—140°/0·01 mm. The forerun (b. p. 35—60°/0·1 mm.) contained nitrobenzene and traces of bromochlorobiphenyls. The absence of bromonitrobiphenyls is inferred from their higher b. p. Residues (b. p. >155°/0·01 mm.) were left after the distillation. The results are given in Table 4.

TABLE 3.

	Experiment 5		Experiment 6	
	A	B	A	B
Forerun (g.)	1·482	0·727	1·230	0·596
Nitrogen in forerun (%)	11·40	11·38	11·39	11·30
Chloronitrobiphenyl in forerun (g.)	0·000	0·000	0·000	0·010
Biaryl fraction (g.)	2·949	1·473	3·016	1·593
Nitrogen in biaryl fraction (g.)	7·39	7·28	7·41	7·35
Total chloronitrobiphenyls (g.)	2·201	1·129	2·241	1·211
Dinitrobiphenyls (g.)	0·748	0·344	0·775	0·392
${}_{\mathrm{PhNO_2}}^{\mathrm{PhCl}}K$	3·07	3·43	3·02	3·23
Total wt. of biaryls (g.)	4·422		4·619	
o-Nitrobenzoic acid (g.): free	3·27		3·64	
from esters	0·62		0·70	
Residue (g.)	0·164		0·198	
o-Nitrobenzoyl peroxide accounted for (%)	87·5		94·9	

Hence ${}_{\mathrm{PhNO_2}}^{\mathrm{PhCl}}K$ (mean) = 3·19

TABLE 4.

	Experiment 7		Experiment 8	
	A	B	A	B
Forerun (g.)	0·744	0·282	0·202	0·330
Nitrogen in forerun (%)	11·34	11·15	11·33	11·26
Bromochlorobiphenyls in forerun (g.)	0·003	0·006	0·002	0·004
Biaryl fraction (g.)	3·153	1·264	1·977	2·987
Nitrogen in biaryl fraction (%)	2·55	2·53	2·27	2·32
Bromochlorobiphenyls (g.)	1·561	0·636	1·089	1·616
Bromonitrobiphenyls (g.)	1·595	0·634	0·890	1·375
${}_{\mathrm{PhNO_2}}^{\mathrm{PhCl}}K$	1·02	1·04	1·27	1·22
Total wt. of biaryls (g.)	4·426		4·970	
o-Bromobenzoic acid (g.): free	3·93		3·87	
from esters	0·42		—	
Residue (g.)	0·936		0·958	
o-Bromobenzoyl peroxide accounted for (%)	77·3		78·5	

Hence ${}_{\mathrm{PhNO_2}}^{\mathrm{PhCl}}K$ (mean) = 1·14

Determination of ${}^{\mathrm{PhMe}}_{\mathrm{PhNO_2}}K$ *for* o-*Bromophenylation.*—In experiments 9 and 10 *o*-bromobenzoyl peroxide (9·60 g.) was allowed to decompose in an equimolar mixture of nitrobenzene and toluene (200 ml., molar peroxide : solvent ratio = 0·025 : 2). The mixtures were treated in the usual way. Owing to the presence of bibenzyl in the products, the forerun was distilled at a lower temperature range (b. p. 35—44°/0·1 mm.) and contained nitrobenzene and a small quantity of bibenzyl. This fraction was analysed for nitrogen by reduction of the nitro-compounds with titanous sulphate. The " biaryl " fraction (b. p. 50—125°/0·01 mm.), which contained the remaining bibenzyl and the biaryl products, was analysed for nitrogen and for bromine by the micro-Carius method. The absence of biaryl products in the forerun is inferred from their higher b. p. Unidentified material (b. p. >150°/0·01 mm.) remained after the final distillation. A smaller quantity of peroxide (6·00 g.) was used in experiment 11, and the reaction mixture was not divided before the final ditillation. The results are given in Table 5.

Reaction of o-*Nitrobenzoyl Peroxide with Toluene.*—*Qualitative.* The purpose of this experiment was to determine whether bibenzyl was formed. *o*-Nitrobenzoyl peroxide (15·0 g.) in toluene (300 ml.) was heated on a boiling-water bath for 48 hr. The binuclear products were isolated as described above and distilled at 30—130°/0·1 mm., to give a yellow oil (16·9 g.). This was redistilled, and the fraction (5·92 g.), b. p. 30—110°/0·1 mm., was dissolved in dry benzene and shaken under hydrogen with Raney nickel. The filtered benzene solution was extracted with hydrochloric acid (*d* 1·18), washed with water, and dried (Na_2SO_4). The residue obtained on evaporation of the benzene solution was adsorbed on alumina and eluted with light petroleum (150 ml.; b. p. 40—60°) to give bibenzyl (0·8 g.), which on crystallisation from methanol had m. p. and mixed m. p. 51—52°.

TABLE 5.

	Experiment 9		Experiment 10		Experiment 11
	A	B	A	B	
Forerun (g.)	1·899	0·497	1·679	0·836	1·916
Nitrogen in forerun (%)	11·16	10·83	11·37	11·31	11·40
Bibenzyl in forerun (g.)	0·038	0·024	0·003	0·006	0·000
" Biaryl " fraction (g.)	1·585	0·878	1·559	0·825	1·610
Nitrogen in " biaryl " fraction (%)	1·59	1·56	1·66	1·64	1·66
Bromine in " biaryl " fraction (%)	29·4	29·5	28·00	28·75	29·3
Bromonitrobiphenyls (g.)	0·500	0·272	0·513	0·268	0·530
Bromomethylbiphenyls (g.)	0·996	0·559	0·893	0·495	0·987
Total bibenzyl (g.)	0·127	0·071	0·156	0·068	0·093
${}^{\mathrm{PhMe}}_{\mathrm{PhNO_2}}K$	2·24	2·32	1·96	2·07	2·09
Total wt. of binuclear product (g.)	2·525		2·393		1·610
o-Bromobenzoic acid (g.): free	5·17		5·18		3·16
from esters	0·71		0·68		0·53
Residue (g.)	0·488		—		0·214
o-Bromobenzoyl peroxide accounted for (%)	80·0		78·7		81·1

Hence ${}^{\mathrm{PhMe}}_{\mathrm{PhNO_2}}K$ (mean) = 2·14

Quantitative. In experiments 12 and 13, *o*-nitrobenzoyl peroxide (6·00 g.) was allowed to decompose in toluene (200 ml.) at 80°. The method of isolation of bibenzyl and the biaryls was that used in the competitive experiments, except tht the reaction mixtures were not divided in the final stage. Both the forerun (b. p. 35—60°/0·1 mm.), which contained bibenzyl and nitrobenzene, and the " biaryl " fraction, containing bibenzyl and the isomeric methyl-2′-nitrobiphenyls, were analysed for nitrogen by reduction of the nitro-compounds with titanous sulphate. Before the final distillation the mixture was kept at room temperature at 0·1 mm. to remove any residual toluene. The absence of methylnitrobiphenyls in the forerun is inferred from their higher b. p. Residues (b. p. >150°/0·1 mm.) were left after the final distillation. Table 6 records the results. Nitrobenzene was not isolated quantitatively.

Determination of ${}^{\mathrm{PhMe}}_{\mathrm{PhCl}}K$ *for* o-*Nitrophenylation.*—In experiment 14, *o*-nitrobenzoyl peroxide (8·00 g.) was allowed to decompose in an equimolar mixture of toluene and chlorobenzene

TABLE 6.

	Experiment 12	Experiment 13
Forerun (g.)	0·681	0·498
Nitrogen in forerun (%)	7·16	7·19
Bibenzyl in forerun (g.)	0·253	0·184
Nitrobenzene in forerun (g.)	0·428	0·314
" Biaryl " fraction (g.)	1·287	1·317
Nitrogen in " biaryl " fraction (%)	5·27	5·05
Methylnitrobiphenyls (g.)	1·031	1·012
Total wt. bibenzyl (g.)	0·509	0·489
o-Nitrobenzoic acid (g.): free	2·95	2·92
from esters	1·25	1·30
Residue (g.)	0·116	0·155
o-Nitrobenzoyl peroxide accounted for (%)	93·2	90·9
Bibenzyl in binuclear product (% by weight of total binuclear products)	33·04	32·62
	Mean = 32·8%	

(200 ml., molar ratio peroxide : solvent = 0·022 : 2) at 80°. The " biaryl " fraction (b. p. 50—122°/0·01 mm.), which contained bibenzyl in addition to the biaryls, was isolated by the standard method and was analysed for nitrogen and for chlorine. The forerun (b. p. 35—50°/0·1 mm.), which contained bibenzyl, nitrobenzene, and traces of chlorobenzene, was not analysed, since its composition is not relevant to the calculation of the rate ratio. The residue had b. p. >140°/0·01 mm. The results are recorded in Table 7.

TABLE 7.

	Experiment 14	
	A	B
" Biaryl " fraction (g.)	1·056	1·214
Nitrogen in " biaryl " fraction (%)	5·74	5·77
Chlorine in " biaryl " fraction (%)	6·14	6·14
Chloronitrobiphenyls (g.)	0·426	0·490
Methylnitrobiphenyls (g.)	0·533	0·618
${}^{\mathrm{PhMe}}_{\mathrm{PhCl}}K$	1·37	1·38
o-Nitrobenzoic acid (g.): free	3·74	
from esters	1·37	
Residue (g.)	0·267	
o-Nitrobenzoyl peroxide accounted for (%)	83·3	

Hence ${}^{\mathrm{PhMe}}_{\mathrm{PhCl}}K$ (mean) = 1·38

Determination of the Ratio of Isomers formed in the o-*Bromophenylation of Nitrobenzene.*—*o*-Bromobenzoyl peroxide (8·00 g.) was allowed to decompose in nitrobenzene (165 ml., molar ratio peroxide : solvent = 0·025 : 2) at 80°. The biaryls were isolated by the standard procedure described above, with the following modifications. (*a*) Stage (i) was omitted. (*b*) The difference in the b. p.'s of nitrobenzene and the biaryls (60° at 0·1 mm.) allowed a clean separation by distillation, and so no forerun was taken. Nitrobenzene was slowly evaporated from the mixture at 0·1 mm., mostly at room temperature, and for the final traces by keeping the distillation flask at 80°. Similarly, a clean separation of the biaryls and high-boiling material was possible and so the reaction mixtures were not divided before the final distillation.

In expts. 15 and 16, the mixtures of isomeric 2-bromo-*x*′-nitrobiphenyls were distilled as pale yellow semi-solids (3·209 g. and 3·726 g., respectively) at 96—141°/0·01 mm., leaving residues (b. p. >190°/0·01 mm.) of 0·81 g. and 0·80 g. respectively.

Infrared analysis. The composition of the mixtures of 2-bromo-*x*′-nitrobiphenyls was determined by means of the infrared spectrographic method described in Part III.[11] In nitromethane solution 2-bromo-2′-nitrobiphenyl absorbs at 790 cm.$^{-1}$, and 2-bromo-3′-nitrobiphenyl absorbs at 742 and 813 cm.$^{-1}$. These bands were used for the analysis. The absorption bands of 2-bromo-4′-nitrobiphenyl lie too close to other absorption bands of its isomers to be of any analytical value, and the amount of this isomer in the mixture was therefore obtained by difference. The accuracy of the method was checked by the analysis of artificial mixtures (S1 and S2) of the three pure isomers. The results are recorded in Table 8.

TABLE 8. *Infrared analysis of mixtures of 2-bromo-x′-nitrobiphenyls.*

	Composition (%), found			Composition (%), known		
Mixture	2,2′-	2,3′-	2,4′-	2,2′-	2,3′-	2,4′-
S1	41·2	20·6	38·2	41·7	19·9	38·4
S2	54·0	18·9	27·1	54·2	18·9	26·9
15	35·5	25·6	38·9			
16	35·1	25·0	39·9			
Mean 15 & 16	35·3	25·3	39·4			

Determination of the Ratios of Isomers formed in the o-*Nitrophenylation of Nitrobenzene.*—o-Nitrobenzoyl peroxide (8·00 g.) was allowed to decompose in nitrobenzene (206 ml., molar ratio peroxide : solvent = 0·024 : 2) at 80°. The biaryls were isolated by the method described for the isolation of the 2-bromo-x'-nitrobiphenyls. In expts. 17 and 18, the biaryls were obtained as yellow solids (4·410 g. and 3·741 g., respectively) at b. p. 118—160°/0·01 mm. (A portion of the homogeneous solution of the biaryls was lost in expt. 18.) Small quantities of residue (0·159 g. and 0·134 g., respectively, b. p. >210°/0·01 mm.) were left after the final distillation.

Analysis of the isomer mixtures. The simple infrared method is not suitable for the analysis of the mixture of isomeric 2,x'-dinitrobiphenyls. The spectrum of 2,2′-dinitrobiphenyl is identical with that of 2,4′-dinitrobiphenyl in the 910—700 cm.$^{-1}$ region except for a band at 855 cm.$^{-1}$. However, 2,3′-dinitrobiphenyl absorbs at 853 cm.$^{-1}$, and so renders the band at 855 cm.$^{-1}$ useless for analytical purposes. The ultraviolet spectra of the three isomers are very similar in the 220—310 mμ region. At no wavelength does one isomer absorb more strongly than the others, and the ultraviolet method of analysis described in Part V [12] is therefore also unsuitable.

Dewar and Urch's method [13] for the analysis of a binary mixture from its ultraviolet spectrum, with slight modification, was applied to the analysis of the mixtures of dinitrobiphenyls. The exact procedure was as follows. If standard solutions of the pure components (1, 2, and 3) have concentration c_1, c_2, and c_3 g./l., and at wavelength λ have optical densities o_1, o_2, and o_3, respectively, and if the concentrations of the three isomers in a solution of a mixture of unknown composition are x, y, and z g./l. and at wavelength λ, the solution has optical density R, then, provided Beer's law is obeyed

$$R = x \,.\, o_1/c_1 + y \,.\, o_2/c_2 + z \,.\, o_3/c_3 \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

Therefore

$$R/o_1 - (y/c_2)(o_2/o_1) = x/c_1 + (z/c_3)(o_3/o_1) \quad . \; . \; . \; . \; . \; . \quad (2)$$

The graph of $[R/o_1 - (y/c_2)(o_2/o_1)]$ against o_3/o_1 will therefore be a straight line of slope z/c_3 and have an intercept on the ordinate of x/c_1. Dewar and Urch used this method with success to analyse a mixture of two components (*i.e.*, $y = 0$), and they suggested that the method could be extended to include mixtures of three components by plotting graphs using various arbitrary values of y until a straight line was obtained. This method was attempted for an artificial mixture of the isomers, but it was realised that it would have been an extremely laborious, if not impossible task, to estimate the value of y accurately by trial and error. The value of y (in this case the concentration of 2,3′-dinitrobiphenyl) was determined by an infrared method, and this value was used in conjunction with the graphical method to determine the concentrations of the other two isomers in the mixture. A possible source of error is the determination of the best straight line through the various points. However, a second equation, analogous to equation (2), can be derived from equation (1), *i.e.*,

$$R/o_3 - (y/c_2)(o_2/o_3) = z/c_3 + (x/c_1)(o_1/o_3) \quad . \; . \; . \; . \; . \; . \quad (3)$$

A graph of $[R/o_3 - (y/c_2)(o_2/o_3)]$ against o_1/o_3 will also be a straight line of slope x/c_1 and having an intercept on the ordinate equal to z/c_3. Thus a check on the graphical errors is provided by the agreement between the results obtained by use of equations (2) and (3).

The concentration of 2,3′-dinitrobiphenyl in the mixtures was determined as follows. The relation between the apparent extinction coefficient of a ternary mixture ($k_{\text{mixt.}}$) and the apparent extinction coefficients of its components (k_1, k_2, and k_3) is given by

$$k_{\text{mixt.}} = k_1x + k_2y + k_3z$$

where x, y, and z are the *fractions* of each component in the mixture. Thus, if $k_2 \gg k_1$ and k_3, a graph of $k_{\text{mixt.}}$ against y is a straight line of slope k_2. 2,3′-Dinitrobiphenyl absorbs infrared radiation in the 910—700 cm.$^{-1}$ region at 814 and 776 cm.$^{-1}$. Absorption by the other isomers at these frequencies is very small. Mixtures of the three isomers with varying proportions of 2,3′-dinitrobiphenyl were dissolved in nitromethane, and the values of $k_{\text{mixt.}}$ at these frequencies determined. A linear relation was found to exist between the values of $k_{\text{mixt.}}$ and the concentration of 2,3′-dinitrobiphenyl. The value of $k_{\text{mixt.}}$ was then measured for the mixtures to be analysed and the corresponding concentrations of 2,3′-dinitrobiphenyl were determined from the graph. The analytical method was shown to be satisfactory by the analysis of an artificial mixture (S_3) of the pure isomers. The results are given in Table 9.

TABLE 9. *Determination of* 2,3′*-dinitrobiphenyl.*

Mixture		S3	17	18
2,3′-Dinitrobiphenyl (%)	Found	51·1	18·1	18·5
	Known	50·9	—	—

The proportions of 2,2′- and 2,4′-dinitrobiphenyl were determined by the ultraviolet spectrometric method described above. Analysis of mixture S_3 showed the method to be valid. Standard solutions of the pure isomers and of mixtures S_3, 17, and 18 were made in ethanol (concentration ~ 3×10^{-5} mole/l.) and their optical densities measured at 5 mμ intervals through the 220—310 mμ region. The results of the analysis are recorded in Table 10.

Since this method gives the concentration of each component in the mixture directly, that is, none of the concentrations is obtained by difference as, for example, in the method used for the analysis of the 2-bromo-x'-nitrobiphenyl mixture, the sum of the "percentages" of each isomer in Table 10 is not 100. If the proportion of each isomer is expressed as a true percentage, the mean composition of 17 and 18 becomes 2,2′- 55·2%, 2,3′- 18·0%, 2,4′-dinitrobiphenyl 26·8%.

TABLE 10. *Analysis of the dinitrobiphenyl mixtures.*

	Composition (%)					
	Found			Known		
Mixture	2,2′-	2,3′-	2,4′-	2,2′-	2,3′-	2,4′-
S_3	19·7	51·1	26·3	19·2	50·9	29·9
17	58·8	18·1	28·6	—	—	—
18	53·8	18·5	26·3	—	—	—

DISCUSSION

Relative rates of arylation with *o*-nitro- and *o*-bromo-phenyl radicals, calculated from the results of the competitive experiments described above, are compared in Table 11 with the relative rates of phenylation and arylation with the corresponding *para*-substituted radicals.

TABLE 11.

Radical	${}^{\text{PhNO}_2}_{\text{PhH}}K$	${}^{\text{PhCl}}_{\text{PhH}}K$	${}^{\text{PhMe}}_{\text{PhH}}K$
o-$NO_2\cdot C_6H_4\cdot$	0·26	0·83	1·16
p-$NO_2\cdot C_6H_4\cdot$ [9]	0·94	1·3	2·50
o-$Br\cdot C_6H_4\cdot$	0·79	0·90	1·69
p-$Br\cdot C_6H_4\cdot$ [2]	1·76	—	—
$C_6H_5\cdot$	4·0 [10]	1·44 [10]	1·68 [19]

The relative rates of *o*-bromo- and *o*-nitro-phenylation of nitrobenzene are significantly lower than the corresponding rate of phenylation, and are consistent with the theory of polarised radicals in that the changes in their values are in accord with the known properties of nitrobenzene towards electrophilic reagents. A similar variation occurs in the relative

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[19] Hey, Pengilly, and Williams, *J.*, 1956, 1463.

rates of arylation of chlorobenzene, but in this case the differences are much smaller. The values of ${}^{\mathrm{PhCl}}_{\mathrm{PhH}}K$ are all derived values, and so contain greater errors than the values of rate ratios, such as ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$, which are measured directly. The differences in ${}^{\mathrm{PhCl}}_{\mathrm{PhH}}K$ are therefore of doubtful significance. However, all the relative rates of arylation with *ortho*-substituted aryl radicals are lower than the relative rates of arylation with the corresponding *para*-substituted radicals. It is to be expected that substituents *ortho* to the radical centre should have a stronger polarising influence than substituents in the *para*-position, since the magnitude of the inductive effect is known to depend on the distance of the polarising field from the site of the reaction. Thus, for example, it is not unexpected that nitrobenzene is less reactive towards *o*-nitrophenyl radicals than towards *p*-nitrophenyl radicals, since the former should be the more powerfully electrophilic. This reasoning does not, however, explain the decreased reactivity of toluene towards *o*-nitrophenyl radicals compared with its reactivity towards *p*-nitrophenyl radicals, since toluene would be expected to display a greater reactivity in *o*-nitrophenylation than in *p*-nitrophenylation.

It is therefore considered probable that steric factors influence the reactivity of aromatic compounds towards arylation with *ortho*-substituted phenyl radicals. The *ortho*-positions of certain aromatic compounds have been found to show a much diminished reactivity in phenylation when they are adjacent to bulky substituents (*e.g.*, t-butylbenzene[8] and benzotrichloride[4,20]). In the cases of nitrobenzene,[2] chlorobenzene,[2] and toluene,[19] however, there appears to be very little hindrance to the attachment of a phenyl radical at the *ortho*-positions and, in fact, these are the most reactive positions in the molecule. Nevertheless, as the effective size of the attacking radical increases, as must be the case with *ortho*-substituted phenyl radicals, hindrance to the attachment of the radical at the *ortho*-positions of these compounds might well become significant and may lead to a reduction of the total reactivity of the molecule. The reduced reactivities of nitrobenzene and chlorobenzene for *o*-nitro- and *o*-bromo-phenylation (compared with their reactivites for *p*-nitro- and *p*-bromo-phenylation) may therefore be due to such a steric effect as well as to an enhancement of the polar character of the radical. For substitution in toluene, these two influences oppose each other, and the reduced reactivity of toluene to *o*-nitrophenylation may be explicable in terms of the preponderance of the steric effect. For *o*-bromophenylation it appears that the steric and the polar factor are about equal in magnitude, and their combination causes the reactivity of toluene to be about the same as its reactivity in phenylation.

The proportions of isomeric biaryls formed in the *o*-bromophenylation of nitrobenzene (cf. Table 12) clearly demonstrate the existence of steric hindrance, arising from the increased size of the radical, to reaction at the *ortho*-position. For *o*-nitrophenylation, on the other hand, the isomer proportions do not indicate the incidence of an analogous steric effect. These considerations may be subjected to further discussion in terms of the partial rate factors for arylation, assembled in Table 13.

TABLE 12. *Ratios of isomers formed in the arylation of nitrobenzene* (%).

Radical	2,2′-	2,3′-	2,4′-
o-$NO_2 \cdot C_6H_4 \cdot$	55	18	27
p-$NO_2 \cdot C_6H_4 \cdot$ [9]	58	15	27
o-$Br \cdot C_6H_4 \cdot$	35	25	40
p-$BrC_6H_4 \cdot$ [21]	58	13	29
$C_6H_5 \cdot$ [21]	62	10	28

In order to rationalise these partial rate factors it is necessary to distinguish between steric and polar effects. Changes in the size of the attacking radical will have their greatest influence on the reactivity of the *ortho*-positions of the substrate molecules. The

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[20] Hey, Saunders, and Williams, unpublished work.

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

TABLE 13. *Partial rate factors for arylation of nitrobenzene.*

Radical	F_o	F_m	F_p	F_o/F_m	F_p/F_m
o-Br·C_6H_4·...............	0·83	0·59	1·90	1·41	3·22
p-Br·C_6H_4· [2]	3·1	0·7	2·9	4·43	4·14
o-NO_2·C_6H_4·	0·43	0·14	0·42	3·07	3·00
p-NO_2·C_6H_4· [9]	1·64	0·43	1·56	3·81	3·63
C_6H_5· [2, 10, 21]	7·5	1·2	6·6	6·25	5·50

reactivity of the *para*-positions should be least affected. It is therefore possible to consider the effect of changes in the polar characteristics of the radical by reference to the partial rate factors for substitution at the *para*-position, and the influence of the effective size of the radical by reference to the partial rate factors for substitution at the *ortho*-positions. If it can be assumed that the movement of a substituent from the *para*- to the *ortho*-position of the phenyl radical causes an enhancement of its polar influence, the partial rate factor for substitution at the *para*-position of nitrobenzene should decrease as the transition is made from the phenyl to the *p*-bromophenyl and then to the *o*-bromophenyl radical. This decrease, in fact, occurs. The almost insignificant decrease in the partial rate factor for substitution at the *meta*-position for this transition, and the decrease in the ratio of the partial rate factors for substitution in the *para*- to the *meta*-position (F_p/F_m), which shows that the decrease in F_m is not so marked as in F_p, suggests that the reactivity of the *meta*-position in nitrobenzene is little affected by changes in the polar character of the attacking radical. Exactly the same trend is observed for nitrophenylation.

The reactivity of the *ortho*-positions of nitrobenzene is seen to be approximately equal to that of the *para*-position in both phenylation and *p*-bromophenylation. For *o*-bromophenylation the reactivity of the *ortho*- is much less than that of the *para*-position. Furthermore, the F_o/F_m ratio for *p*-bromophenylation is more than three times as great as for *o*-bromophenylation. This indicates a definite hindrance to substitution at the *ortho*-position of nitrobenzene arising from the increased effective size of the *o*-bromophenyl radical. On the other hand, this situation does not arise for the reaction with *o*-nitrophenyl radicals. The reactivities of the *ortho*- and *para*-positions are the same, but are lower than their reactivity towards *p*-nitrophenyl radicals. This decreased reactivity can therefore be ascribed to the more pronounced electrophilic character of the *o*-nitrophenyl radical. It is suggested that the absence of a steric effect in this reaction is the result of the rotation of the nitro-groups, attached to both the radical and the substrate molecule, out of the plane of their respective nuclei as the transition state leading to *ortho*-substitution is formed. If such a rotation may be assumed, steric hindrance to substitution may be circumvented and the steric requirements of the reactions at the *ortho*-positions of nitrobenzene with both *o*- and *p*-nitrophenyl radicals would be similar.

The reaction between diaroyl peroxides and toluene, leading to the formation of bibenzyl, can proceed by two mechanisms. Both the aryl and the aroyloxy-radical can, in theory, abstract hydrogen atoms from the side chain to give benzyl radicals which then dimerise. For the reaction with benzoyl peroxide, it was considered that the phenyl radical alone was responsible for this reaction,[19] but more recent work has indicated that the benzoyloxy-radical also takes part in it.[22] No products of side-chain attack have been isolated from the reaction of toluene,[9,14] ethylbenzene,[14] and isopropylbenzene [14] with *p*-nitrobenzoyl peroxide. Augood and Williams [15] have commented on the relation between the polarity of the attacking radical, assumed to be the free aryl radical, and the extent of the reaction at the side chain, by pointing out that a higher incidence of nuclear attack is to be expected to result from reactions with the more strongly electrophilic radicals. Similar reasoning can be applied to attack by aroyloxy-radicals. The finding now reported that bibenzyl is produced from toluene and *o*-nitrobenzoyl peroxide is, however, anomalous if considered solely in these terms. The isolation of nitrobenzene from this

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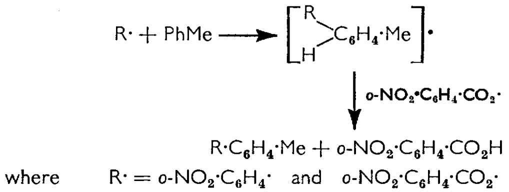
[22] Foster and Williams, unpublished observation.

reaction indicates that the *o*-nitrophenyl radical is at least partially responsible for the abstraction, although the extent to which the *o*-nitrobenzoyloxy-radical participates is uncertain. *o*-Nitrobenzoic acid was isolated from the reaction mixture in excess of the quantity expected from substitution alone:



$$R\cdot + PhMe \longrightarrow \left[\begin{matrix}R\\H\end{matrix}{>}C_6H_4\cdot Me\right]\cdot \xrightarrow{o\text{-}NO_2\cdot C_6H_4\cdot CO_2\cdot} R\cdot C_6H_4\cdot Me + o\text{-}NO_2\cdot C_6H_4\cdot CO_2H$$

where $R\cdot = o\text{-}NO_2\cdot C_6H_4\cdot$ and $o\text{-}NO_2\cdot C_6H_4\cdot CO_2\cdot$

Thus the anomalous conclusion is reached that, in reactions with nitrobenzene, radicals derived from *o*-nitrobenzoyl peroxide appear to more strongly electrophilic than those derived from *p*-nitrobenzoyl peroxide, while in reactions with the toluene side chain, they appear to be more strongly nucleophilic than radicals derived from *p*-nitrobenzoyl peroxide, and even more strongly nucleophilic than those derived from benzoyl peroxide. This is illustrated in Table 14. Several possible explanations of this anomaly may be advanced.

TABLE 14. *Side-chain attack in reactions with toluene.*

Radical source	$(p\text{-}NO_2\cdot C_6H_4\cdot CO_2)_2$ [9, 14]	$(C_6H_5\cdot CO_2)_2$ [19]	$(o\text{-}NO_2\cdot C_6H_4\cdot CO_2)_2$
Bibenzyl (moles/mole peroxide)	0·0	0·03	0·11

It is clear that for reactions between *p*-nitrophenyl (or *p*-nitrobenzoyloxy-) radicals and toluene, the activation energy for reaction at the side chain is greater than that for reaction with the nucleus. In reactions with *o*-nitrophenyl (or *o*-nitrobenzoyloxy-) radicals, it follows that some factor causes either a decrease in the activation energy for reaction at the side chain, or an increase in the activation energy for the reaction with the nucleus, in order that both reactions may take place. If the *o*-nitrophenyl radical and the toluene molecule can undergo some form of association through their substituents, possibly in the nature of a very weak hydrogen bond between the hydrogen atoms of the toluene side-chain and the oxygen atoms of the nitro-group attached to the radical, the configuration of the resulting complex may be favourable for the reaction at the side-chain. Hydrogen bonds of the type –C–H • • • • O– are considered to be very weak, but their formation has been invoked to account for the high acid dissociation constant of *o*-toluic acid compared with that of its *meta*- and *para*-isomers.[23] If such an association occurs, it is clear that it will also occur in reactions with *p*-nitrophenyl radicals, but in this case the reactive positions in the radical and the methyl group are separated by a greater distance and would not be expected to interact. A similar argument may be applied to the *o*-nitrobenzoyloxy-radical.

The reaction of aromatic nuclei with *ortho*-substituted aryl radicals may also be subject to the following additional steric influence of the *ortho*-substituent. If some interaction occurs between any *ortho*-substituents present in the radical and the π-electrons of the nucleus of the substrate molecule during the formation of the transition state, the absolute rate of reaction of the radical with *all* the nuclear positions may be decreased independently of the polar characteristics of the radical. Such an interaction would be much smaller in the case of the *para*-substituted radical, whose only *ortho*-substituents are hydrogen atoms. There would therefore exist an additional energy barrier to substitution by *o*-nitrophenyl radicals, which is not present in reaction with *p*-nitrophenyl radicals. If such a retardation of substitution by *ortho*-substituted radicals occurs at all, it should occur in reactions with all aromatic nuclei and, it may be assumed, as a first approximation, to a similar extent. It is therefore incapable of observation by measurement of partial rate factors, since these

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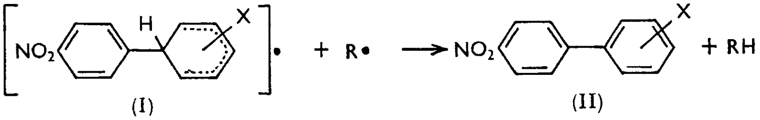
[23] Dippy, Evans, Gordon, Lewis, and Watson, *J.*, 1937, 1421.

relate the reactivity of the various nuclear positions of the aromatic compound to that of any one nuclear position in benzene. When the reactivity of an aromatic compound towards substitution by *ortho*-substituted phenyl radicals is compared with its reactivity towards arylation with *para*-substituted phenyl radicals by means of partial rate factors, there is no need to consider this additional energy barrier, since for reactions with any aryl radical, the reactivity of any position of the benzene nucleus with that radical is taken as the standard and is given the value of unity. However, if, as in the reactions with toluene, another reaction distinct from nuclear arylation can also take place, it may be necessary to consider this additional energy barrier when, for example, the behaviour of the substrate towards *o*-nitrophenyl radicals is compared with its behaviour towards the isomeric *p*-nitrophenyl radicals. This additional energy barrier to the nuclear reaction should render the activation energies of the reactions at the nucleus and at the side-chain more nearly equal, and may provide an explanation of the observed anomaly.

A third possible explanation of this anomaly is based on the postulate that the removal of a hydrogen atom from an arylcyclohexadienyl radical [*e.g.*, (I) for *p*-nitrophenylation], which is the σ-complex intermediate in the arylation reaction, may be facilitated if this



radical contains a nitro- or other conjugating substituent. Such a decrease in the activation energy of this process might be associated with the participation of the nitro-group in resonance forms involving the two aryl nuclei in the biaryl (II), and is consistent with the non-formation of high-boiling resins in arylation reactions in which nitro-groups are present in either the radical or the substrate. Thus in these circumstances, the above hydrogen-abstraction reaction is favoured relative to the dimerisation of the radical (I) which would lead to higher-boiling products. If it is now assumed that in arylation of toluene, benzyl radicals are capable of fulfilling the function of the radical R• in the hydrogen-abstraction reaction, the amount of bibenzyl formed by dimerisation of benzyl radicals should vary inversely with the facility of this process, whereby benzyl radicals are consumed and are therefore rendered unavailable for dimerisation. This may well be at least part of the explanation of the non-formation of bibenzyl in the *p*-nitrophenylation of toluene.

However, in the *o*-nitrophenylation reaction the two nuclei of the *x*′-methyl-2-nitrobiphenyls are probably not coplanar, and hence any resonance stabilisation of these compounds would be expected to be substantially reduced, and the hydrogen-abstraction rendered less easy. Thus fewer benzyl radicals should be consumed in this process and hence more bibenzyl might be expected to be formed by their dimerisation.

Although the extent to which bibenzyl is formed in the reaction of *o*-bromobenzoyl peroxide with toluene has not been investigated directly, it is clear from Table 7, in which the results of competitive reactions of this peroxide with mixtures of nitrobenzene and toluene are summarised, that some bibenzyl is probably formed in the reaction with toluene alone. Some of the influences discussed above with reference to *o*-nitrophenyl and *o*-nitrobenzoyloxy-radicals may, therefore, also apply to *o*-bromophenyl and *o*-bromobenzoyloxy-radicals.

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