112. *Homolytic Aromatic Substitution. Part XXIII.* A Redetermination of the Relative Rate of Phenylation of Nitrobenzene.*

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With the aid of improved experimental techniques the relative rate of phenylation of nitrobenzene has been redetermined. The value for ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$ reported in 1952 as 4·0 was regarded as a *maximum* value. The redetermined value is 2·94. The wide use of nitrobenzene as a standard substrate in the competitive method for measuring the relative rates of arylation reactions has necessitated a revaluation of a number of relative rates and partial rate factors. The corrections, which amount to small reductions in the absolute values, do not invalidate any of the theoretical deductions made on the basis of the earlier figures.

The determination of the relative rate of phenylation of nitrobenzene, by means of competitive experiments in which benzoyl peroxide was allowed to decompose in a large excess of an equimolar mixture of benzene and nitrobenzene, was reported in Part II.[1] The value obtained for the relative rate, ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$, was 4·0. This result was, however, accepted as a *maximum* value, since the results of a number of experimental determinations revealed that the measurement of the relative rate was uniquely subject to an error due to loss of the rather volatile biphenyl in the nitrobenzene fraction during the removal of solvents by distillation. At that time, it was not possible completely to eliminate or correct for this error, and the value obtained for ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$ was therefore accepted with these reservations, as the possible error was not considered to be serious and the order of magnitude of the result was undoubtedly correct. More recently, however, it has become clear that a more accurate knowledge of this relative rate is desirable, partly because nitrobenzene has been used as a sub-standard for the determination of the relative rates of phenylation of a large number of other compounds and partly for purposes of comparison with the relative rates of arylation of nitrobenzene and other substances with aryl radicals other than phenyl. A more accurate determination of ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$ was therefore called for and, as a result of the development of more refined analytical techniques (particularly that of gas–liquid chromatography), this has become possible. The results of this redetermination are now reported, and their implications discussed.

EXPERIMENTAL

Benzoyl peroxide, benzene, and nitrobenzene were purified as described in Part II.[1]

Determination of ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$.—In experiments 1—4 benzoyl peroxide (6 g.) was allowed to decompose in an equimolar mixture (200 ml.) of benzene and nitrobenzene at 80° (thermostat) for 72 hr. The products of these reactions were isolated by the following procedure, which differs appreciably from that described in Part II.[1]

(i) The reaction mixture was extracted with saturated aqueous sodium hydrogen carbonate (5 × 50 ml.) to remove free benzoic acid, and then washed with water (2 × 25 ml.). The combined aqueous extracts were washed with ether (3 × 30 ml.), and the ethereal washings added to the reaction mixture, which was then dried ($MgSO_4$). Benzoic acid (m. p. 122°) was obtained from the alkaline extracts by acidification with hydrochloric acid and extraction with ether (4 × 30 ml.). The ethereal extracts were dried ($MgSO_4$) and the ether removed by evaporation.

(ii) Benzene was removed from the reaction mixture after treatment as described above, by slow distillation through a 40 cm. helix-packed column. The bulk of the nitrobenzene was then removed by fractional distillation under reduced pressure (b. p. 140°/105 mm.). The distillate was redistilled through the column under the same conditions, and the final fraction

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* Part XXII, preceding paper.

[1] Augood, Hey, and Williams, *J.*, 1952, 2094.

(~3 ml.) combined with the residue from the first distillation (~15 ml.). The distillate was again redistilled, and the final fraction (~5 ml.) retained as a pre-forerun. The column and still-head were washed with ether, the washings were combined with the residue, and the ether was removed by evaporation.

(iii) The residue from (ii) was refluxed with 2N-aqueous sodium hydroxide solution (100 ml.) for 24 hr. in order to hydrolyse the esters present. The resulting dark mixture was filtered through toughened paper and then extracted as follows: (*a*) The mixture was extracted with benzene (3 × 30 ml.) and the extracts were combined (portion X). (*b*) The aqueous layer was washed with benzene (30 ml.; portion Y). (*c*) Portion X was washed with 2N-sodium hydroxide (2 × 25 ml.). (*d*) The combined aqueous washings were shaken with the benzene portion Y. (*e*) All the benzene extracts were combined and washed with 3N-hydrochloric acid (25 ml. portions) until the washings were colourless, in order to remove any basic material formed by reduction of nitrobenzene. The benzene solution was then washed with water (2 × 25 ml.) and dried (Na_2SO_4). (*f*) The aqueous extracts obtained in stages (*a*)—(*d*) were combined, warmed, acidified with hydrochloric acid, and neutralised with an excess of solid sodium hydrogen carbonate. The mixture was boiled, cooled in ice, and filtered to remove silicic acid formed as sodium silicate by solution of the glass of the flask in sodium hydroxide during the hydrolysis stage. The residue was digested with sodium hydrogen carbonate solution (100 ml.) and filtered. The combined filtrates were extracted with ether (3 × 30 ml.) to remove phenols formed by the hydrolysis of the esters. The aqueous layer was acidified with hydrochloric acid, and the precipitated benzoic acid removed by extraction with ether (4 × 30 ml.). The resulting ethereal solution was dried ($MgSO_4$) and the ether removed by evaporation, giving benzoic acid (m. p. 122° after crystallisation).

(iv) The dried benzene solution obtained in (iii*e*) was reduced in volume by distillation through the helix-packed column, the last traces of benzene (~15 ml.) being removed at 150 mm. A mixture of anhydrous ether and dry " AnalaR " acetone was used to wash the column and accessories, and these washings were used for the transfer of the residue in the next stage.

(v) The residue (~18 ml.) was divided into two portions (A and B), which were quantitatively transferred, with acetone wash-liquid, to small, weighed distilling flasks (~15 ml. capacity). The wash-liquid was removed by careful distillation at atmospheric pressure. The pressure was then reduced to 0·01 mm. and the bath-temperature raised gradually to 55° during 36 hr. During this period the forerun (b. p. 17—35°/0·01 mm.) was collected in a cooled, weighed receiver. The bath-temperature was then slowly raised to 250° and the biaryl fraction (b. p. 40—115°/0·01 mm.) collected in a second cooled, weighed receiver.

Analysis of products. The eight biaryl fractions were analysed for nitrobiphenyls by titration with titanous sulphate as described in Part XVIII,[2] and the foreruns and pre-foreruns for nitrobenzene by the same method. Tests with appropriate synthetic mixtures of known composition showed that both nitrobenzene and nitrobiaryls could be estimated to $\pm 1\%$.

These analytical results were confirmed by analysis of the foreruns, pre-foreruns, and biaryl fractions by gas–liquid chromatography. The instrument used was a Perkin–Elmer model 116 vapour fractometer. The stationary phase was Apiezon " L " grease supported on Celite, and contained in a 1 m. column, and the carrier gas was nitrogen. The pre-foreruns were found to consist entirely of nitrobenzene, so that all the biaryls formed were contained in the foreruns and biaryl fractions. The foreruns consisted largely of nitrobenzene, but contained a little biphenyl, the amount of which could be estimated from the chromatograms. The compositions of the foreruns, as determined titrimetrically and chromatographically, were in close agreement ($\pm 1\%$).

Chromatography of synthetic mixtures of 2-, 3-, and 4-nitrobiphenyl showed that complete separation of the peaks corresponding to the 3- and 4-isomers could not be effected, and conditions were therefore chosen such that these two isomers emerged together and were shown on the chromatogram as a single peak. The biaryl fractions were then chromatographed under these conditions (column temperature 330°; detector block temperature 202°; detector voltage 6 v; carrier gas flow rate 10 ml. $min.^{-1}$; gas pressure 0·25 kg. $cm.^{-2}$). The composition of these mixtures of biphenyl and 2-, 3-, and 4-nitrobiphenyl could not be obtained directly by measurement of the areas of the peaks corresponding to these components since, as the detector unit of the instrument is a catharometer, these areas depend, not only on the amounts

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[2] Hey, Moulden, and Williams, *J.*, 1960, 3769.

of the various components present, but also on the thermal conductivities of their vapours. Calibration was therefore necessary, and was effected as follows.

A mixture of 2-, 3-, and 4-nitrobiphenyl was prepared which contained these compounds in as nearly as possible the proportions in which they are formed by the phenylation of nitrobenzene with benzoyl peroxide [3,4] (2-nitrobiphenyl 58%, 3-nitrobiphenyl 10%, 4-nitrobiphenyl, 32%). Weighed portions of this homogeneous mixture were added to weighed amounts of biphenyl to give a range of mixtures which simulated the biaryl fractions and contained from 10 to 17% of biphenyl. These mixtures were chromatographed, and a graph drawn of the areas of the biphenyl peaks expressed as percentages of the sum of the areas of all the peaks against the known percentages of biphenyl in the mixture. This graph, which was a straight line, enabled the composition of the unknown mixtures (biaryl fractions) to be obtained from the peak areas in their chromatograms by interpolation. Very small peaks corresponding to nitrobenzene were observed in the chromatograms of all the biaryl fractions, and from their areas it was calculated that the amount of nitrobenzene present in these mixtures was not more than 0·2%. The results obtained in experiments 1—4 are summarised in Table 1.

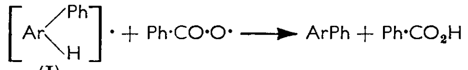
TABLE 1.

Expts.	1		2		3		4	
Portions	A	B	A	B	A	B	A	B
Biaryl fraction (g.)	1·770	1·650	1·493	1·770	1·748	1·492	1·685	1·725
Nitrobiphenyls (%) in biaryl fractions:								
(*a*) by titration	84·04	87·00	86·70	85·19	85·43	87·24	85·22	85·81
(*b*) by chromatography	84·95	86·60	87·65	85·03	86·80	87·07	85·00	86·25
Forerun (g.)	2·866	4·572	2·879	3·957	5·619	4·934	4·710	5·957
Nitrobenzene (%) in forerun (mean of determinations by titration and chromatography)	96·49	95·85	95·32	96·96	97·21	96·07	97·83	97·31
Biphenyl (g.) in forerun	0·101	0·190	0·135	0·120	0·157	0·194	0·102	0·160
Corr. wt. of biaryl fractions (g.)	1·871	1·840	1·628	1·890	1·905	1·686	1·787	1·885
Nitrobiphenyls (corr. %):								
(*a*) by titration	79·6	78·0	79·6	79·8	78·4	77·2	80·4	78·5
(*b*) by chromatography	80·4	76·7	80·4	79·5	79·7	77·0	80·2	78·9
(*c*) mean	80·0	77·9	80·0	79·7	79·1	77·1	80·3	78·7
${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$	3·10	2·73	3·10	3·04	2·94	2·61	3·15	2·86
Residue (g.)	0·120	0·139	0·139	0·161	0·135	0·102	0·143	0·148
Free benzoic acid (g.)	2·940		2·921		2·961		2·904	
Benzoic acid from hydrolysis of esters (g.)	0·416		0·469		0·448		0·440	
Benzoyl peroxide accounted for (%) (excluding residue)	95·4		93·8		95·0		94·9	

Hence ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K = 2{\cdot}94$.

DISCUSSION

Stoicheiometry.—The rate-determining stage of the process of replacement of hydrogen attached to an aromatic nucleus by a phenyl radical has been shown (cf. Part XVII [5]) to be the addition of the phenyl radical to the nucleus of the substrate molecule to give an arylcyclohexadienyl radical, or " σ-complex " (I). This process is thought to be followed by the removal of a hydrogen atom from (I) by another radical or other oxidising agent, leaving the biaryl product. It has been considered that the most likely oxidising agent is the benzoyloxy-radical, which may be present, together with the σ-complex, in a " solvent-cage." [6] The oxidation process is then represented as follows:



$$\left[\mathrm{Ar}\begin{smallmatrix}\mathrm{Ph}\\ \mathrm{H}\end{smallmatrix}\right]\cdot + \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} \longrightarrow \mathrm{ArPh} + \mathrm{Ph{\cdot}CO_2H}$$

(I)

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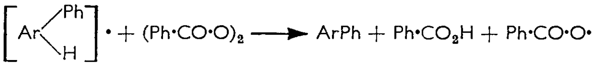
[3] Hey, Nechvatal, and Robinson, *J.*, 1951, 2892.

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

[5] Chang, Hey, and Williams, *J.*, 1959, 1871.

[6] Huisgen and Sorge, *Annalen*, 1950, **566**, 162; Waters, *Ann. Reports*, 1952, **49**, 110.

In addition, Foster and Williams (unpublished observations) have shown that benzoyl peroxide molecules also contribute appreciably to the oxidation process, and the stoicheiometry of this reaction is represented by the equation:



$$\left[\mathrm{Ar}\langle^{\mathrm{Ph}}_{\mathrm{H}}\right]\cdot + (\mathrm{Ph{\cdot}CO{\cdot}O})_2 \longrightarrow \mathrm{ArPh} + \mathrm{Ph{\cdot}CO_2H} + \mathrm{Ph{\cdot}CO{\cdot}O}\cdot$$

The benzoyloxy-radicals formed in such a process may react further by decarboxylation to give phenyl radicals, with arylcyclohexadienyl radicals as suggested above, or with molecules of the substrate to give, ultimately, phenolic esters. The formation of these esters (benzoyloxylation) is a reaction of homolytic aromatic substitution which always accompanies arylation when aroyl peroxides and related substances are used as radical sources. With benzene and its simple derivatives it is generally a minor contribution to the total reaction, and probably proceeds by a mechanism involving, as its first stage, the formation of σ-complexes similar to (I), which then become oxidised by analogous means.

If the foregoing is a correct representation of the total reaction, it follows that the molar yield of benzoic acid should be equal to the sum of the molar yields of all the products of substitution. If, however, other reactions of the various σ-complexes, which do not involve benzoyloxy-radicals or benzoyl peroxide, occur, then the yield of benzoic acid should be less than the sum of the yields of the substitution products. Such processes, in which two arylcyclohexadienyl radicals interact to give either a biaryl and a dihydrobiaryl, or a tetrahydroquaterphenyl derivative, have been shown to take place when benzoyl peroxide is allowed to decompose in very dilute solution in benzene under a nitrogen atmosphere.[7] The relevant data for the reactions at present under consideration are given in Table 2. If the small residues formed are considered to be substitution products, the results show that the balance of the yields of the two groups of products is in excellent agreement with the mechanism involving oxidation by benzoyloxy-radicals and benzoyl peroxide only. If these residues are omitted from the calculation, the yield of benzoic acid exceeds the combined yield of the substitution products. In either event, the results afford no evidence for dimerisation or disproportionation involving two arylcyclohexadienyl radicals, and it may therefore be concluded that such processes do not contribute appreciably to this reaction when it is carried out under the conditions described in the foregoing experimental section.

TABLE 2.

Expt.	1	2	3	4
Free acid (mole)	0·0241	0·0239	0·0243	0·0238
Acid from esters (mole)	0·0034	0·0038	0·0037	0·0036
Nitrobiaryls (mole)	0·0147	0·0141	0·0141	0·0147
Biphenyl (mole)	0·0051	0·0046	0·0051	0·0049
Residue (mole, calc. on $M = 300$)	0·0009	0·0010	0·0008	0·0010
Total substitution products (mole)	0·0241	0·0235	0·0237	0·0242
Ratio of molar yields (free acid/substitution products)	1·000	1·017	1·025	0·9835
Peroxide accounted for (%) (including residue)	97·1	95·8	96·6	96·8

Mean ratio of molar yields = 1·006.

Relative Rates and Partial Rate Factors for Phenylation.—In previous papers in this series the determination was reported of the relative rates of phenylation of a number of benzene derivatives. Most of these determinations were conducted by means of competitive experiments in which nitrobenzene was used as the standard competing solvent.

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[7] De Tar and Long, *J. Amer. Chem. Soc.*, 1958, **80**, 4742.

Thus, the relative rate determined, for a solvent PhX, was ${}^{\mathrm{PhX}}_{\mathrm{Ph\cdot NO_2}}K$, and the rate of phenylation relative to benzene, ${}^{\mathrm{PhX}}_{\mathrm{PhH}}K$, was obtained from this ratio by multiplication by the relative rate of phenylation of nitrobenzene, since

$$ {}^{\mathrm{PhX}}_{\mathrm{PhH}}K = {}^{\mathrm{PhX}}_{\mathrm{Ph\cdot NO_2}}K \times {}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K $$

These determinations were not, in general, subject to the errors discussed above in connection with the determination of ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$, since all the biaryls $X\cdot C_6H_4\cdot C_6H_5$ are considerably less volatile than biphenyl, and hence were not lost during the distillation of the solvents. In most cases, this was made clear by the analysis of foreruns and pre-foreruns. Nevertheless, the derived relative rates ${}^{\mathrm{PhX}}_{\mathrm{PhH}}K$ previously reported must now be corrected, by using the new value of 2·94 for ${}^{\mathrm{Ph\cdot NO_2}}_{\mathrm{PhH}}K$ in their calculation, since the value of 4·0 was previously used. Partial rate factors (F_o, F_m, and F_p) obtained by combination of these relative rates with the ratios of the isomeric biaryls formed in the phenylation of the compounds PhX must also be corrected. The new values of these quantities are given in Table 3.

TABLE 3. *Relative rates and partial rate factors for phenylation of benzene derivatives* (80°).

Compound (ArH)	F_o	F_m	F_p	${}^{\mathrm{ArH}}_{\mathrm{PhH}}K$
$Ph\cdot NO_2$ [1,4]	5·5	0·86	4·9	2·94
PhF [8]	1·7	0·95	0·86	1·03
PhCl [1,9,10]	1·6	1·0	1·2	1·06
PhBr [8]	1·9	1·3	1·3	1·29
PhI [8]	2·0	1·3	1·3	1·32
PhMe [11]	2·5	0·71	1·0	1·23
PhEt [11]	1·4	0·76	1·0	0·90
$PhPr^i$ [11]	0·60	0·81	1·0	0·64
$PhBu^t$ [12]	0·46	0·94	1·0	0·64
Ph_2 [13]	2·1	1·0	2·5	2·94
p-$C_6H_4Cl_2$ [9]	—	—	—	1·98
1,3,5-$C_6H_3Cl_3$ [9]	—	—	—	3·68
p-$C_6H_4Bu^t_2$ [12]	—	—	—	0·47

The corrections in all the above cases take the form of a small reduction in the absolute values of these quantities, although their order of magnitude and relationship to one another, and hence the conclusions drawn from them in previous papers in this series, remain unaltered. Moreover, the alterations are not sufficiently great to affect the validity of qualitative arguments [2,14] based on comparisons of partial rate factors for phenylation with those for arylation with substituted aryl radicals.

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[8] Augood, Cadogan, Hey, and Williams, *J.*, 1953, 3412.
[9] Augood, Hey, and Williams, *J.*, 1953, 44.
[10] Chang, Hey, and Williams, *J.*, 1958, 2600.
[11] Hey, Pengilly, and Williams, *J.*, 1956, 1463.
[12] Cadogan, Hey, and Williams, *J.*, 1954, 3352.
[13] Cadogan, Hey, and Williams, *J.*, 1954, 794.
[14] Hambling, Hey, and Williams, *J.*, 1960, 3782.