Homolytic Aromatic Substitution. Part VIII.* Partial Rate Factors for the Phenylation of Toluene.

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Partial rate factors are determined for the phenylation of toluene by an analysis of the products formed in the competitive phenylation of mixtures of toluene and nitrobenzene, and of toluene and pyridine. The proportions of the isomers formed in the phenylation of toluene are determined by infrared spectroscopy. It is shown that at higher concentrations of benzoyl peroxide toluene undergoes some substitution at the side chain with the formation of diphenylmethane. The partial rate factors for toluene show an overall activation of the molecule when compared with benzene. The sequence of activation shows the order $o > p > m$, the activity at the *meta*-position being little different from that of any position in benzene.

THE determination of the partial rate factors for the phenylation of a monosubstituted benzene, PhR, has been reported for R = NO_2, F, Cl, Br, I, Ph, and Bu^t (Parts I—V and VII ; *J.*, 1951, 2892 ; 1952, 2094 ; 1953, 44, 3412 ; 1954, 794, 3352). In Part VII attention was drawn to the special difficulties which are encountered in attempts to determine the partial rate factors for the phenylation of alkylbenzenes because of the possibility of substitution in or hydrogen abstraction from the side chain by the free phenyl radical. These difficulties are absent in *tert.*-butylbenzene, but in the phenylation of toluene by means of benzoyl peroxide such side-reactions could lead to the formation of diphenylmethane by substitution, and of dibenzyl by hydrogen abstraction and subsequent

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dimerisation. In the early qualitative work on the reaction between benzoyl peroxide and toluene, however, there is no mention of the occurrence of either of these hydrocarbons (Gelissen and Hermans, *Ber.*, 1925, **58**, 476), but recently Dannley and Zaremsky have reported (124th Meeting of the American Chemical Society, September, 1953) the presence of diphenylmethane in the product from the reaction between benzoyl peroxide and toluene. In a subsequent paper (Dannley, Gregg, Phelps, and Coleman, *J. Amer. Chem. Soc.*, 1954, **76**, 445) on the phenylation of the halogenobenzenes it was observed that these workers used concentrations of benzoyl peroxide considerably higher than those used in our own work. A repetition of our method, using concentrations similar to those reported by Dannley and his co-workers, showed with the aid of infra-red spectroscopy that some diphenylmethane was in fact formed. When, however, the reaction was conducted under the conditions of concentration normally used by us in the determination of partial rate factors, it was confirmed that diphenylmethane was absent from the product, both by the use of infra-red analysis and by the application of other physical and chemical methods. It appears, therefore, that the facility of side-chain attack is dependent upon the concentration of the attacking free radicals and that by the use of radicals in high dilution it should be possible to determine the partial rate factors for the phenylation of toluene without the intrusion of complications arising from side-chain attack. On the other hand, with hydrocarbons containing more than one alkyl group, other than *tert.*-butyl, it is apparent that hydrogen abstraction from the side-chain takes place more readily because 4 : 4′-dimethyldibenzyl and 3 : 5 : 3′ : 5′-tetramethyldibenzyl have been isolated from the products of the reaction of benzoyl peroxide with *p*-xylene and mesitylene respectively (Augood, Hey, Nechvatal, Robinson, and Williams, *Research*, 1951, **4**, 386).

The apparent dependence of diphenylmethane formation on the concentration of benzoyl peroxide has some far-reaching consequences. If the nuclear and side-chain phenylation processes are simultaneous reactions of the same order, then the composition of the mixed product should be independent of the concentration of the reagents. The formation of diphenylmethane must therefore be a reaction of a higher order than the nuclear phenylation reaction, with respect to phenyl radicals, since its rate of formation increases the more rapidly with an increase in the concentration of free phenyl radicals. The mechanistic consequences of this observation will be elaborated in a later publication.

The influence of the methyl group on the nuclear phenylation of toluene at 80° has now been determined by means of competitive experiments with nitrobenzene, a large excess of an equimolar mixture of the competing solvents being used compared with the benzoyl peroxide used as the source of the phenyl radicals. Under these conditions more than 80% of the benzoyl peroxide was accounted for and the rate ratio ${}^{\text{PhMe}}_{\text{PhNO}_2}K$ was derived from an analysis of the mixture of substituted diphenyls by means of titrations with titanous chloride as used in Part II (*loc. cit.*). Nitrobenzene was used as the competing solvent because its comparatively high reactivity minimises the formation of resins. In cases where the two competing solvents are of low reactivity (*e.g.*, toluene and pyridine) the diaryls formed are considerably more reactive than the original solvents and the percentage of resins formed in such reactions therefore increases. The ratios of the isomeric methyldiphenyls formed in the phenylation of toluene have also been measured by means of infra-red spectroscopy, the spectra for each of the three pure isomerides having been first established.

Competitive experiments have also been carried out with the phenylation of mixtures of toluene and pyridine. In this instance this method is not entirely satisfactory on account of the formation of compounds of higher molecular weight, but the results obtained give general support to those derived from the competitive experiments between toluene and nitrobenzene, as indicated below.

EXPERIMENTAL METHODS AND RESULTS

Reagents.—Nitrobenzene was purified as described in Part II (*loc. cit.*). Toluene (B.D.H.) was washed with concentrated sulphuric acid until the washings were colourless, then with water, and finally dried ($MgSO_4$). It was then refluxed over sodium and distilled twice through a 6-ft. helix-packed column. Benzoyl peroxide was purified to constant m. p. 104·8° as described in Part II. Diphenylmethane was purified to constant m. p. 26° by fractional freezing. 4-Methyldiphenyl, m. p. 48°, was prepared by the method of Gomberg and Pernert (*J. Amer. Chem. Soc.*, 1926, **48**, 1372) and similar methods, starting from *m*-toluidine and *o*-toluidine respectively, were used for the preparation of 3- (b. p. 141°/14 mm.) and 2-methyldiphenyl (b. p. 138°/23 mm.) respectively. The yellow colour was removed from the last two hydrocarbons by shaking them with four portions of concentrated sulphuric acid and then with water before they were dried and distilled.

Direct Determination of $^{\mathrm{PhMe}}_{\mathrm{PhNO_2}}K$.—Benzoyl peroxide (6 g.) was allowed to decompose in an equimolar mixture (200 ml.) of toluene and nitrobenzene in a thermostat at 80° for 72 hr. The toluene was distilled off at atmospheric pressure through a 25-cm. helix-packed column, the jacket of which was electrically heated to the b. p. of the distilling solvent. As much nitrobenzene as possible was distilled off under reduced pressure (b. p. 136°/95 mm.) and the nitrobenzene distillate was redistilled at the same pressure, the final 5 ml. being added to the main product. This was done in order to ensure that no methyldiphenyls were lost in the nitrobenzene distillate. Since benzoic acid was found to be appreciably volatile in nitrobenzene but not in toluene, the nitrobenzene distillate was extracted with 2N-aqueous sodium hydroxide (100 ml.), which was subsequently employed to hydrolyse the main product. After hydrolysis for 12 hr. at 100°, the main product was extracted while hot with benzene (4 × 30 ml.), and the combined benzene extracts were well washed with sodium hydroxide solution (100 ml.) followed by water (50 ml.) and finally dried ($CaCl_2$; 24 hr.). The combined aqueous extracts, containing sodium benzoate and substituted sodium phenoxides, were acidified while hot with concentrated hydrochloric acid, neutralised with solid sodium hydrogen carbonate, and filtered. The filtrate, after extraction with ether (2 × 30 ml.) to remove phenols, was reacidified with concentrated hydrochloric acid and extracted quantitatively with methylene chloride (4 × 30 ml.). The aqueous layer was then discarded and the methylene chloride solution, after being dried ($CaCl_2$), was evaporated at room temperature, the residual benzoic acid being dried over concentrated sulphuric acid and then weighed (m. p. 119—120°). The benzene solution, containing the main product, was passed through a 15-cm. alumina column to remove tar, and the column was eluted first with benzene (100 ml.) and finally with a mixture of benzene (20 ml.) and ether (10 ml.). Under these conditions only tar is retained on the column, and the diaryls pass through without loss. Solvents were removed by distillation through the 25-cm. column mentioned above, and the residue was quantitatively transferred, by using benzene as wash-liquid, to a small fractionation apparatus which was equipped with a 10-cm. helix-packed column with electrically heated jacket (see Part II, *loc. cit.*). After removal of the wash-benzene at atmospheric pressure the bulk of the residual nitrobenzene was carefully distilled off (b. p. 142°/115 mm.). The nitrobenzene distillate was redistilled under the same conditions, the final fraction (3 ml.) remaining in the flask being retained (the pre-forerun). The main product (5 ml.) remaining in the flask was transferred to the small distillation apparatus (capacity 10 ml.) described in Part II, and the benzene used in the transference was carefully removed at atmospheric pressure. The pressure was then lowered to 0·1 mm. and two fractions were collected. The first fraction, termed the fore-run (b. p. 30—80°/0·1 mm.), consisted of nitrobenzene with some of the methyldiphenyls. It may be safely assumed that the fore-runs contained no nitrodiphenyls, since these were found not to distil until a temperature 43° above that at which the fore-runs were collected had been reached. The second fraction (b. p. 80—130°/0·1 mm.) was composed of methyl- and nitro-diphenyls. The residue in the flask amounted to less than 10% of the diaryl fraction and consisted mainly of tar not removed on the alumina column. Weighed portions of the pre-forerun, fore-run, and run were made up to the required strength with acetone and subsequently analysed for nitro-group by the titanous chloride method. The standard procedure described in Part II was employed. The pre-forerun was found to consist of pure nitrobenzene, thus showing that no methyldiphenyls had been lost in the distillation. The fore-runs were also analysed for nitrogen by the micro-Dumas method. After extraction of the runs with concentrated hydrochloric acid, they were analysed for nitrogen by the micro-Dumas method and the basic material from runs (1) and (2) amounted to 27 mg. and 31 mg. respectively. The results of these competitive reactions are summarised in Table 1. The comparatively small loss of benzoyl peroxide not accounted for is due in part to the polyaryl resin in which phenyl radicals are incorporated and in part to the fact that no attempt was made to isolate the benzene which is known also to be formed in a side-reaction.

Determination of Ratio of Isomerides formed in the Phenylation of Toluene.—Benzoyl peroxide was allowed to decompose in toluene at 80° in a thermostat. In experiments (3) and (4) 6 g.

of benzoyl peroxide and 200 ml. of toluene were used, in experiment (5) 15 g. and 500 ml., and in experiment (6) 26·7 g. and 93·5 ml. respectively. The mixtures of methyldiphenyls were isolated by the standard procedure described in Part II [Product from (3): Found, C, 92·6; H, 7·2. Product from (4): Found, C, 92·9; H, 7·3. Product from (6): Found, C, 92·5; H, 7·3. Calc. for $C_{13}H_{12}$: C, 92·8; H, 7·2%]. Each of the four products was chromatographed on alumina before distillation and in every case a resin was collected, having b. p. 130—170°/0·1 mm., which was presumed to consist substantially of higher phenylation products (Found: C, 91·4; H, 8·4%; *M*, 238). In reaction (6) a white solid (0·1 g.) separated from the original reaction mixture, which was identified as diphenyl-4-carboxylic acid, m. p. 215° and mixed m. p. 219—220°; this probably arises from phenylation of benzoic acid. The results of these reactions are summarised in Table 2.

TABLE 1.

Experiment:	1	2
Diaryl fraction (g.)	1·7918	2·1344
$Ph{\cdot}C_6H_4{\cdot}NO_2$ (%)	89·8	84·5
Total $Ph{\cdot}C_6H_4{\cdot}NO_2$ (g.)	1·6091	1·8044
Fore-run (g.)	3·8760	3·5976
N in fore-run by $TiCl_3$ (%)	10·0	10·2
N in fore-run by micro-Dumas (%)	10·2	10·4
N in run by $TiCl_3$ (%)	5·95	6·3

Experiment:	1	2
N in run by micro-Dumas (%)	5·75	6·1
$Me{\cdot}C_6H_4{\cdot}Ph$ in fore-run (%)	12·7	10·7
$Me{\cdot}C_6H_4{\cdot}Ph$ in fore-run (g.)	0·4942	0·3833
Total $Me{\cdot}C_6H_4{\cdot}Ph$ (g.)	0·6769	0·7133
${}^{\text{PhMe}}_{\text{PhNO}_2}K$	0·498	0·468
$Ph{\cdot}CO_2H$ (g.)	3·3	3·4
$(Ph{\cdot}CO_2)_2$ accounted for (%)	81·5	84·5

Hence ${}^{\text{PhMe}}_{\text{PhNO}_2}K = 0{\cdot}48$.

TABLE 2.

Experiment	Diaryl fraction (g.)	Resin (g.)	Free $Ph{\cdot}CO_2H$ (g.)	$Ph{\cdot}CO_2H$ after hydrolysis (g.)	Peroxide accounted for (%)
3	2·144	1·945	Not extracted	1·4	80
4	2·069	2·188	,,	1·4	84
5	6·1	5·17	3·3	0·55	72
6	6·5	5·7	7·0	1·6	60

The spectrographic analysis of the products of these reactions was carried out on a Grubb-Parsons single-beam instrument fitted with an automatic pen recorder. Nitromethane was used as solvent, since it had no pronounced bands in the range 11—15 mμ where the characteristic methyldiphenyl bands exist. The spectrum was recorded through a 130-mμ rock-salt cell with a speed of wave-length scanning and slit opening such that the energy of transmission recorded for the pure solvent was nearly constant over the required range. Owing to the low percentage of the *meta-* and *para*-isomerides found in the mixtures, very concentrated solutions had to be used in order to attain a sufficiently high degree of accuracy. For this purpose grade " A " 1-ml. volumetric flasks were used containing from 0·35 to 0·5 g. of mixture per ml. The calibration spectra of the pure 3- and 4-methyldiphenyl were taken with 0·05 g. in 1 ml. and that of the 2-methyldiphenyl with about 0·25 g. in 1 ml. The accuracy of the method was tested on two artificial mixtures (A) and (B) of known composition and the results are given in Table 3. The analyses of the products from reactions 3, 4, and 5 are reported in Table 4. Dannley and Zaremsky (*loc. cit.*) have reported *ortho-* 65%, *meta-* 19%, and *para*-substitution 16% for the phenylation of toluene.

TABLE 3. *Analysis of mixtures of methyldiphenyls.*

	Known composition (%)			Composition found (%)		
Solution	2-	3-	4-	2-	3-	4-
A	50	24	26	46	26	28
B	41	34	25	37	36	27

TABLE 4. *Analysis of product obtained in phenylation of toluene.*

	Composition (%)		
Solution	2-	3-	4-
3	70·6	17·0	12·4
4	70·1	17·0	12·9
5	71·8	16·1	12·0
Mean	70·8	16·7	12·4

In addition to the spectra of the three pure methyldiphenyls an examination of the spectrum of diphenylmethane showed a very intense band which was not quite coincident with a band common to the three methyldiphenyls, whereas elsewhere in the relevant region diphenylmethane absorbed only very weakly. At the high concentrations of the mixtures used in the determination of the isomer ratios the peak characteristic of diphenylmethane would be swamped, but examination of more dilute solutions (0·1 g. in 1 ml.) of the products from reactions 3, 4, and 5 showed no trace of the presence of diphenylmethane. Addition of diphenylmethane to the mixtures could be detected in the spectrum down to a concentration of 4%. In mixture 6 at a concentration of 0·1 g. in 1 ml., the diphenylmethane band was very pronounced and a comparison with similar mixtures made up with known quantities of added diphenylmethane showed that mixture 6 contained approximately 15% of diphenylmethane.

Direct Determination of ${}^{\mathrm{PhMe}}_{\mathrm{PyH}}K$.—Experiments (7) and (8) were performed with an equimolar mixture of benzene and pyridine, using conditions already described. After hydrolysis the mixture was separated by extraction with aqueous hydrochloric acid (7N) and separated into neutral and basic portions. These were worked up separately and the weights of methyldiphenyls and of phenylpyridines were obtained. A high-boiling residue was obtained from the neutral portion and from its nitrogen content (1·4%) it is regarded as a 4 : 1 mixture of methylterphenyls and diphenylpyridines. A correction was made for this in the calculation of ${}^{\mathrm{PhMe}}_{\mathrm{PyH}}K$. The occurrence of diphenylpyridines in the residue obtained from the neutral portion of the product, thus demonstrating the feeble basicity of such compounds, had been observed in previous work (Part II). The results are recorded in Table 5.

TABLE 5.

Experiment :	7	8
Phenylpyridines (g.)	0·922	0·884
Methyldiphenyls (g.)	1·350	1·201
Benzoic acid (g.)	2·9	3·1
Residue (g.)	1·170	1·278
${}^{\mathrm{PhMe}}_{\mathrm{PyH}}K$	1·68	1·69
$(\mathrm{Ph{\cdot}CO{\cdot}O})_2$ accounted for (%)	87	88·5

This result gives a value of 1·75 for ${}^{\mathrm{PhMe}}_{\mathrm{PhH}}K$ (*i.e.*, ${}^{\mathrm{PhMe}}_{\mathrm{PyH}}K \times {}^{\mathrm{PyH}}_{\mathrm{PhH}}K = 1{\cdot}685 \times 1{\cdot}04$), but as a result of the relatively large amount of residue formed in these reactions this method for the determination of the rate ratio cannot, in this case, be considered to be very satisfactory. The results, however, do support, within the limits of the method, the rate ratio for toluene obtained by using nitrobenzene as the second solvent.

It is of interest that Professor R. Huisgen (personal communication) found a value of 1·9 for ${}^{\mathrm{PhMe}}_{\mathrm{PyH}}K$, using nitrosoacetanilide as a source of phenyl radicals, while Dr. R. L. Dannley (personal communication), using benzoyl peroxide, found a value of 1·4.

DISCUSSION

The rate of phenylation of toluene with reference to that of benzene as unit is given by ${}^{\mathrm{PhMe}}_{\mathrm{PhNO_2}}K \times {}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$, *i.e.*, 0·48 × 4·0 (cf. Part II) = 1·9. Use of this value and the mean values obtained by spectrographic analyses for the ratio of isomerides formed in the phenylation of toluene gives the following partial rate factors for this reaction :

$$F_o = 4{\cdot}1\,;\; F_m = 1{\cdot}0\,;\; F_p = 1{\cdot}4.$$

The high degree of activation of the *ortho*-position is noteworthy, whereas the introduction of the methyl group into benzene has no significant effect on the phenylation at the *meta*-position. Unlike *tert.*-butylbenzene (cf. Part VII, *loc. cit.*) the overall effect in toluene is one of mild activation with the notable absence of any steric influence. Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 900) calculated the atom localisation energies for free-radical substitution in toluene, and predicted that the observed sequence of activation should be *o*-, *p*- > *m*. This is now shown to be in agreement with experiment.

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