Homolytic Aromatic Substitution. Part VII. Partial Rate Factors for the Phenylation of* tert.-*Butylbenzene and* p-*Di-*tert.-*butylbenzene.*

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The proportions of the three isomeric *tert.*-butyldiphenyls formed in the phenylation of *tert.*-butylbenzene are determined by infra-red spectrometry. In addition, competitive experiments are carried out on the action of phenyl radicals derived from benzoyl peroxide on mixtures of *tert.*-butylbenzene and of *p*-di-*tert.*-butylbenzene with nitrobenzene. From these results the partial rate factors for the phenylation of *tert.*-butylbenzene and of *p*-di-*tert.*-butylbenzene are calculated. *tert.*-Butylbenzene provides the first example of over-all deactivation encountered in homolytic substitution and this is attributed to a marked steric effect on the *ortho*-positions. Homolytic substitution, while insensitive to the polar character of nuclear substituents, is nevertheless sensitive, as is electrophilic substitution, to steric influences. Synthetic work leading to the preparation of the three isomeric *tert.*-butyldiphenyls is also reported.

THE partial rate factors for homolytic phenylation of nitrobenzene, the halogenobenzenes, and diphenyl have been reported in Parts I—V (Hey, Nechvatal, and Robinson, *J.*, 1951, 2892; Augood, Hey, and Williams, *J.*, 1952, 2094; 1953, 44; Augood, Cadogan, Hey, and Williams, *J.*, 1953, 3412; Cadogan, Hey, and Williams, *J.*, 1954, 794), and these and other results have been discussed by Hey and Williams (*Discuss. Faraday Soc.*, 1953, **14**, 216). In the present communication the survey of homolytic aromatic substitution is extended by the determination of partial rate factors for the phenylation of *tert.*-butylbenzene and *p*-di-*tert.*-butylbenzene with benzoyl peroxide. The phenylation of toluene, ethylbenzene, and *iso*propylbenzene will be reported in later papers.

Phenylation of the alkylbenzenes is complicated by the possibility of attack in the side chain (Augood, Hey, Nechvatal, Robinson, and Williams, *Research*, 1951, **4**, 386; Dannley and Zarensky, Amer. Chem. Soc. Abs., 124th Meeting, 1953, 36.0). In the reactions reported in this paper, however, no products derived from attack on the side chain by free radicals were isolated. This is not unexpected, because Kooyman (*Discuss. Faraday Soc.*, 1951, **10**, 163), in a comparison of the reactivities of the alkylbenzenes towards free trichloromethyl radicals based on the retardation of the addition of carbon tetrachloride to hexadecene, has shown that little or no retardation occurs with compounds such as benzene and *tert.*-butylbenzene, which do not contain α-methylenic hydrogen atoms. Gregg and Mayo (*Discuss. Faraday Soc.*, 1947, **2**, 328) came to similar conclusions after a study of the inhibition of the polymerisation of styrene by alkylbenzenes. The kinetics of the decomposition of benzoyl peroxide in *tert.*-butylbenzene have been investitated (Bartlett and Nozaki, *J. Amer. Chem. Soc.*, 1946, **68**, 1686; Hartmann, Sellers, and Turnbull, *ibid.*, 1947, **69**, 2416), but no attempt was made, in either case, to isolate any products of the reaction. The arylation of *p*-di-*tert.*-butylbenzene has not previously been studied.

The overall effect of the *tert.*-butyl group was measured by means of competitive experiments with nitrobenzene, which were conducted under conditions which reduced the importance of any possible side reactions such as the removal of the products by further phenylation. This was achieved by the use of a large excess of an equimolar mixture of the competing solvents compared with the source of the phenyl radicals. Under these conditions 90% of the benzoyl peroxide was accounted for in the experiments with *tert.*-butylbenzene and 77% in those with *p*-di-*tert.*-butylbenzene (see Experimental section). The hitherto unknown 2 : 5-di-*tert.*-butyldiphenyl was isolated from the products of the phenylation of the mixture of nitrobenzene and *p*-di-*tert.*-butylbenzene, thus showing that phenylation at a position *ortho* to the bulky *tert.*-butyl group does occur. The ratios of the isomerides produced in the phenylation of *tert.*-butylbenzene were measured by infra-

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red spectroscopy, after synthetic work had been completed to obtain the three isomeric *tert.*-butyldiphenyls, two of which had not previously been described. 2-, 3-, and 4-*tert.*-Butyldiphenyl were obtained as the results of the decomposition in benzene of *o*- and *m*-*tert.*-butylbenzoyl peroxides and *p*-*tert.*-butyl-*N*-nitrosoacetanilide respectively.

In an attempt to prepare 2-*tert.*-butyldiphenyl it was observed that *o*-*tert.*-butyl-*N*-nitrosoacetanilide, on decomposition in benzene, gave (*a*) *tert.*-butylbenzene, (*b*) *o*-*tert.*-butylacetanilide, (*c*) diphenyl, and (*d*) an ester or mixture of esters believed to be the isomeric *tert.*-butylphenyl acetates. An intermediate in the preparation of 3-*tert.*-butyldiphenyl was *m*-*tert.*-butylbenzoic acid, which Crawford and Stewart (*J.*, 1952, 4443) obtained by deamination of 2-bromo-4-*tert.*-butylaniline to *m*-bromo-*tert.*-butylbenzene (b. p. 100°/40 mm.; 70%) followed by carboxylation of the Grignard reagent. In our hands the deamination step yielded *tert.*-butylbenzene (b. p. 100°/40 mm.; 48·5%), and *m*-bromo-*tert.*-butylbenzene (b. p. 108—110°/16 mm.; 37%), indicating that removal of a bromine atom from a position *ortho* to the diazonium group had taken place. It may be noted that, in the preparation of *o*-*tert.*-butylbenzoic acid, the deamination of 3-bromo-4-*tert.*-butylaniline revealed no such anomaly. *m*-*tert.*-Butylbenzoic acid was also prepared by a new route, by means of the von Richter reaction with alcoholic potassium cyanide and *tert.*-butyl-*p*-nitrobenzene, but the yield was too low to make the method of synthetic value.

Experimental methods and results

Determination of the Extent of Side-chain Attack in tert.-*Butylbenzene.*—The possible products of attack by phenyl or benzoyloxy-radicals on the side chain of *tert.*-butylbenzene were considered to be those derived from (*a*) abstraction of a β-hydrogen atom by the radical to give benzene and/or benzoic acid, together with the product derived from dimerisation of the fragment so produced, that is, 2 : 5-dimethyl-2 : 5-diphenylhexane, and (*b*) substitution of a β-hydrogen atom by a phenyl or benzoyloxy-radical to give 2-methyl-2 : 3-diphenylpropane or 2 : 2-dimethylphenethyl benzoate. The former product has the same molecular formula as the products of nuclear phenylation and its presence cannot, therefore, be detected by microanalysis for carbon and hydrogen.

Benzoyl peroxide (8 g.) was allowed to decompose in *tert.*-butylbenzene (150 ml.) in a thermostat at 80° for 72 hr. The fraction likely to contain the products of phenylation was isolated by the standard procedure described in Part II (*loc. cit.*). No benzene was isolated. The yield of phenylated product was 3·718 g. (b. p. 60—100°/0·1 mm.; n_D^{17} 1·5750) (Found: C, 91·3; H, 8·6. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%). This fraction, therefore, contained no dimer (Calc. for $C_{20}H_{26}$: C, 90·2; H, 9·8%). Quantitative infra-red analysis, as described below, of this and similar fractions obtained from other experiments, proved the absence of 2-methyl-2 : 3-diphenylpropane which, if it had been formed, would have been isolated with the products of nuclear phenylation. After removal of this fraction the high-boiling resin (1·2 g.) was purified by distillation and chromatographed on alumina (2 × 25 cm.) with benzene–light petroleum as eluant. This afforded irresolvable gums which were thought to be mixtures of the many possible *tert.*-butylterphenyls (Found: C, 91·3; H, 7·7. Calc. for $C_{22}H_{22}$: C, 92·3; H, 7·7%). Benzoic acid (3·40 g.; m. p. and mixed m. p. 118°) and diphenyl-4-carboxylic acid (0·2 g.; m. p. and mixed m. p. 224—225°) were also isolated. Thus, 86% of the benzoyl peroxide was accounted for and no products of side-chain attack were isolated or detected.

Direct Determination of $^{PhBu^t}_{PhNO_2}K$.—Benzoyl peroxide (6 g.) was added during 20 min. to an equimolar mixture (200 ml.) of *tert.*-butylbenzene and nitrobenzene maintained at 80° in a thermostat. The decomposition was considered to be complete after 72 hr. The mixture of diphenyls was isolated quantitatively and analysed by estimation of the nitro-compound by reduction with titanous chloride. The standard procedure described in Part II (*loc. cit.*) was employed. In the final distillation, fore-runs, *i.e.*, mixed fractions containing the last traces of nitrobenzene and the first traces of *tert.*-butyldiphenyls, were collected separately from the *tert.*-butyldiphenyl–nitrodiphenyl fraction, so that the latter should not be contaminated with the last traces of nitrobenzene. The fore-runs were analysed for nitrobenzene with titanous chloride, and a correction in terms of *tert.*-butyldiphenyl, found by difference, was applied to the composition of the *tert.*-butyldiphenyl–nitrodiphenyl fraction. In order to estimate the nitrobenzene content of the fore-runs, a slight modification of the procedure outlined in Part II became necessary in order to overcome loss of nitrobenzene by volatilisation during the estimation.

Carbon dioxide was passed through the mixture of buffer (30 ml.) and acetone (10 ml.; "AnalaR") for 15 min. The solution to be analysed was made up with acetone saturated with carbon dioxide, and 20 ml. were pipetted into the buffer–acetone mixture. Carbon dioxide was passed through the mixture for a further 10 min., the titanous chloride was then added, and the estimation completed as described for the nitrodiphenyls (Part II, *loc. cit.*).* A fraction taken immediately before the fore-run proved to consist entirely of nitrobenzene, showing that neither the fore-run nor the product fraction contained residual *tert.*-butylbenzene. It can be assumed that the fore-runs contained no nitrodiphenyls, since these were found not to distil until a temperature 60° above that at which the fore-runs were collected had been reached. The high-boiling residue left after completion of the distillation was of negligible weight. The results of these experiments (1—3) are given in Table 1. The weight of benzoic acid recorded is composed

TABLE 1.

Expt. No.	1	2	3
Diaryl fraction (g.)	3·389	3·444	3·302
$Ph{\cdot}C_6H_4{\cdot}NO_2$ (%)	84·00	83·63	86·79
Fore-run (g.)	1·333	0·814	1·852
$Ph{\cdot}NO_2$ in fore-run (%)	88·73	92·96	88·13
But^t-diphenyls in fore-run (g.)	0·150	0·058	0·220
Corr. wt. of diaryl fraction (g.)	3·539	3·502	3·522
$Ph{\cdot}C_6H_4{\cdot}NO_2$ corr. (%)	80·41	82·23	81·38
${}^{PhBu^t}_{PhNO_2}K$	0·230	0·205	0·217
$Ph{\cdot}CO_2H$ (g.)	3·300	3·195	3·293
$(Ph{\cdot}CO_2)_2$ accounted for (%)	90·4	88·3	90·2

Hence ${}^{PhBu^t}_{PhNO_2}K = 0·217$.

of that obtained from the saponification (0·12 mole per mole of benzoyl peroxide) and that formed in the free state (0·94 mole per mole of benzoyl peroxide).

Direct Determination of ${}^{p\text{-}But^t_2C_6H_4}_{PhNO_2}K$.—Experiments 4, 5, 6, and 7 were carried out with benzoyl peroxide (6 g.) in an equimolar mixture (200 g.) of nitrobenzene and *p*-di-*tert.*-butylbenzene. The reactions were allowed to proceed in a thermostat at 80° for 72 hr. The isolation and analysis of the mixed diphenyls were carried out by the standard procedure (Part II, *loc. cit.*). The fore-runs were analysed for nitrodiphenyl and the necessary correction applied to the composition of the di-*tert.*-butyldiphenyl–nitrodiphenyl fraction. A fraction taken immediately before the fore-run proved to consist entirely of *p*-di-*tert.*-butylbenzene. Again it can be assumed that the fore-runs contained no nitrobenzene or 2 : 5-di-*tert.*-butyldiphenyl. The high-boiling resin left after the distillation was of negligible weight. The results are given in Table 2. The amount of benzoyl peroxide accounted for is lower than in previous cases

TABLE 2.

Expt. No.	4	5	6	7
Diaryl fraction (g.)	2·635	1·805	2·550	2·657
$Ph{\cdot}C_6H_4{\cdot}NO_2$ (%)	82·09	79·73	82·43	81·93
Fore-run (g.)	0·422	0·245	0·868	0·588
$Ph{\cdot}C_6H_4{\cdot}NO_2$ in fore-run (%)	27·56	7·23	6·12	21·28
$Ph{\cdot}C_6H_4{\cdot}NO_2$ in fore-run (g.)	0·116	0·018	0·053	0·125
Corr. wt. of diaryl fraction (g.)	2·751	1·823	2·603	2·782
$Ph{\cdot}C_6H_4{\cdot}NO_2$ corr. (%)	82·85	79·98	82·79	82·74
${}^{p\text{-}But^t_2C_6H_4}_{PhNO_2}K$	0·155	0·166	0·156	0·156
$Ph{\cdot}CO_2H$ (g.)	2·930	—	3·100	3·050
$(Ph{\cdot}CO_2)_2$ accounted for (%)	76·0	—	77·0	77·0

Hence ${}^{p\text{-}But^t_2C_6H_4}_{PhNO_2}K = 0·158$.

(Parts II, III, and IV) because benzoic acid is lost in the distillation of the unchanged *p*-di-*tert.*-butylbenzene in the first stage of the working-up process. The weight of the diaryl fraction in experiment 5 is low because some of the homogeneous reaction mixture was accidentally lost on removal of the reaction flask from the thermostat. This will not alter the value of ${}^{p\text{-}But^t_2C_6H_4}_{PhNO_2}K$, which depends on the relative amounts of diaryls present and not on the total amount.

* This modification was also used in the estimation of nitrobenzene in the fore-runs obtained from experiments with nitrobenzene–bromobenzene and nitrobenzene–iodobenzene mixtures (Part IV, *loc. cit.*) but was not described therein.

Determination of the Ratio of Isomerides formed in the Phenylation of tert.*-Butylbenzene.*—Benzoyl peroxide was allowed to decompose in *tert.*-butylbenzene at 80° in a thermostat. The standard procedure described in Part II (*loc. cit.*) was used for the isolation of the *tert.*-butyldiphenyl fraction from the products of experiments 8, 9, and 10. The details of these experiments are given in Table 3.

TABLE 3.

Expt. no.	$(Ph\cdot CO_2)_2$ (g.)	PhBu^t (ml.)	Bu$^t\cdot C_6H_4\cdot Ph$ [mole/mole of $(Ph\cdot CO_2)_2$]	n_D^{17}	Found (%) C	H
8	8·00	130	0·53	1·5750	91·3	8·6
9	4·00	90	0·53	1·5750	91·4	8·4
10	4·00	90	0·52	1·5750	91·3	8·7

The composition of the three mixtures of isomeric *tert.*-butyldiphenyls, which had identical physical properties, was determined by an infra-red spectrographic method, using a Grubb-Parsons single-beam instrument with rock-salt optics and equipped with an automatic pen recorder. Examination of the spectra of 3-*tert.*-butyldiphenyl as a capillary film, and of 2- and 4-*tert.*-butyldiphenyl as crystalline powders in Nujol mulls between rock-salt plates, revealed that intense absorption bands occurred in the region 12—13 μ. The frequencies of these " key " bands were almost identical with those of the key bands exhibited by all other 2-, 3-, and 4-substituted diphenyls so far investigated by us (Parts III and IV, *loc. cit.*). The frequencies were: 2-*tert.*-butyldiphenyl 755, 779 cm.$^{-1}$; 3-*tert.*-butyldiphenyl 763, 803 cm.$^{-1}$; 4-*tert.*-butyldiphenyl 770, 842 cm.$^{-1}$. Calibration spectra of solutions in nitromethane of the pure isomerides were recorded in the frequency range 700—850 cm.$^{-1}$. The spectra of the three experimental mixtures 8, 9, and 10 in nitromethane, and the background spectrum of the solvent were then recorded. The same rock-salt cell of thickness 130 μ was used in each case. The determination is most accurate when the absorption at the key wave-length is about 60%. The concentrations of the solutions employed (g./5 ml.), which absorbed radiation to this extent at the key wave-lengths, were: 3-*tert.*-butyldiphenyl, 0·8320; 4-, 0·2923; and the experimental mixtures about 0·89. The compositions of the mixtures, calculated by the method outlined below, are given in Table 4.

TABLE 4. *Analysis of products obtained in the phenylation of* tert.*-butylbenzene.*

Expt. no.	Composition (%) 2-	3-	4-	Expt. no.	Composition (%) 2-	3-	4-
8	23	50	27	10	25	48	27
9	24	50	26	Mean	24	49	27

Calculation of the Ratio of Isomerides.—The method was based on that described in Part V (*loc. cit.*), which involved solution of equations of the type

$$\text{(at a given wave-length)}\quad \varepsilon_{\text{mixture}} = x\varepsilon_2 + y\varepsilon_3 + z\varepsilon_4 \quad . \quad . \quad . \quad . \quad (1)$$

where x, y, and z are the fractions of the 2-, 3-, and 4-isomeride present in the mixture, and the ε terms, in this case, are not absolute values of the extinction coefficients (as in Part V) but involve a constant (cell thickness). The magnitudes of these extinction coefficients were obtained from the spectra of the standard solutions of the pure isomerides and the experimental mixtures. Measurements were made at the frequencies of the key bands of the 3- and the 4-isomeride (803, 842 cm.$^{-1}$). The key band of the 2-isomeride was not employed because it was too close to an intense band common to each isomeride, as in previous cases. It was observed that ε_2 was negligible at 803 and 842 cm.$^{-1}$ and hence could be neglected. Such transparency of a benzene derivative to infra-red radiation at the frequencies of the key absorption bands of its isomeric forms is not uncommon (Thompson, Torkington, and Whiffen, *Trans. Faraday Soc.*, 1945, **41**, 200).

The accuracy of the analysis was determined by two methods, both of which involve the analysis of artificial mixtures of known composition. Insufficient 2-*tert.*-butyldiphenyl was available for inclusion in these, so that synthetic mixtures, containing known weights of an experimental mixture with known amounts of 3- and 4-isomerides added, were made up in nitromethane. Presupposing that the experimental mixture included in this synthetic mixture had been correctly analysed, the composition of the synthetic mixture was known. An estimate of its composition was made from its spectrum by the standard method. Comparison of this " found " value with the known value for the composition then gave an estimate of the

reliability of the method. A further check was imposed by application of the principle of additivity of optical densities. In this way, the extinction coefficient, $\varepsilon_{mixt.}$, of any of the synthetic mixtures at any wave-length, can be predicted by substituting for y, z, ε_3 and ε_4 in equation 1, ε_2 being zero. Comparison of this predicted value for $\varepsilon_{mixt.}$, with that actually observed is a measure of the accuracy of the determination. The results of the accuracy determinations are given in Table 5. That the compositions of the mixtures and their optical densities can be predicted to within a few per cent., coupled with the observation that the spectra of the experimental mixtures contained absorption bands peculiar to the three isomerides only, is taken to be proof that the experimental mixtures isolated by our methods contained no extraneous products, and that the mean value for the composition of the mixtures presented in Table 4 is reliable to within a few per cent.

TABLE 5. *Infra-red analysis of synthetic mixtures of* tert.*-butyldiphenyls.*

Solution		Composition (%) 2-	3-	4-	$\varepsilon_{mixt.}$ 803 cm.$^{-1}$	842 cm.$^{-1}$
S_1 containing Expt. no. 8	Found	4·0	65·2	30·8	0·5217	0·5781
	Known	7·0	61·6	31·4	0·4854	0·5895
S_2 containing Expt. no. 9	Found	19·2	52·0	28·8	0·4128	0·5342
	Known	18·6	52·4	29·0	0·4160	0·5384
S_3	Found	0	70·6	29·6	0·5540	0·5592
	Known	0	70·1	29·9	0·5600	0·5560
S_4 containing Expt. no. 10	Found	18·5	53·1	28·3	0·4116	0·5265
	Known	20·8	50·8	28·4	0·4035	0·5269
S_5 containing Expt. no. 8	Found	15·0	45·3	39·7	0·3650	0·7401
	Known	14·7	45·3	40·0	0·3645	0·7299

Preparation of Reagents.—Unless otherwise stated, the light petroleum used had b. p. 60—80° and all solids were recrystallised to constant m. p.

Benzoyl peroxide (May & Baker) and nitrobenzene were purified according to the procedure described in Part II (*loc. cit.*), and nitromethane according to that described in Part IV (*loc. cit.*). *tert.*-Butylbenzene was prepared by the method of Kharasch and Brown (*J. Amer. Chem. Soc.*, 1939, **61**, 2142); the crude product was washed with concentrated sulphuric acid until the washings were colourless, then with aqueous sodium hydrogen carbonate, and with water, and dried ($CaCl_2$); pure *tert.*-butylbenzene was obtained after distillation from sodium through a 4-foot helix-packed column (b. p. 169°/760 mm., n_D^{20} 1·4927).

p-Di-*tert.*-butylbenzene was prepared by the Friedel–Crafts reaction from *tert.*-butyl chloride and *tert.*-butylbenzene. Freshly prepared *tert.*-butyl chloride (400 g.) was added dropwise during 3 hr. to a stirred mixture of anhydrous aluminium chloride (16 g.) and *tert.*-butylbenzene (800 ml.) at room temperature. Solid separated after 1½ hr. and stirring became difficult after the addition was complete, but was continued for ½ hr. The pale yellow semi-solid mass was homogenised by warming and poured slowly into vigorously agitated water, to give colourless needles (m. p. 73—76°), which were collected. After being pressed and washed with cold methanol (150 ml.), the product recrystallised from methanol in colourless needles (550 g.), m. p. 76—77°.

tert.-*Butyl*-o- *and* -p-*nitrobenzene*.—Nitration of *tert.*-butylbenzene (Brown and Nelson, *ibid.*, 1951, **73**, 5605) gave a mixture of isomeric *tert.*-butylnitrobenzenes in 96% yield. This was rectified by means of a 7-foot helix-packed column, and gave *tert.*-butyl-*o*-nitrobenzene (b. p. 128°/20 mm., n_D^{20} 1·5175; 14%), *tert.*-butyl-*p*-nitrobenzene (b. p. 152°/24 mm., n_D^{20} 1·5334, supercooled; 62%), and an intermediate fraction (b. p. 128—150°/20 mm.; 12%), which was discarded.

4-tert.-*Butyldiphenyl*.—Reduction of *tert.*-butyl-*p*-nitrobenzene by granulated tin and hydrochloric acid gave crude *p-tert.*-butylaniline (87%), which was converted into the acetyl derivative and recrystallised from benzene–light petroleum to constant m. p. (174°; colourless plates). The anilide (7·1 g.) so obtained was stirred with acetic acid (30 ml.), acetic anhydride (25 (ml.), fused potassium acetate (5 g.), and phosphoric oxide (0·5 g.) at 0°, while nitrosyl chloride (3 g.) in acetic anhydride (15 g.) was added dropwise during 20 min. After a further 90 min. at 8°, the pale yellow solution was poured slowly into agitated iced water containing sufficient sodium hydrogen carbonate to neutralise the acetic acid. The yellow solid which separated was collected on a cooled filter and washed with iced water (100 ml.). The product (7·9 g.), m. p. 57·5° (decomp.), was dried at 0° in an evacuated desiccator containing potassium hydroxide and phosphoric oxide. *p-tert.*-Butyl-*N*-nitrosoacetanilide (7·9 g.) was dissolved at room temperature in dry benzene (400 ml.; "AnalaR") containing a suspension of anhydrous

sodium sulphate (15 g.) and sodium hydrogen carbonate (15 g.). Decomposition immediately commenced, as indicated by rapid evolution of gas and darkening. The red solution was stirred for 24 hr. and then boiled under reflux for a further 2 hr. Removal of benzene from the filtered solution left a dark red oil, which on distillation *in vacuo* gave a yellow solid (3·5 g.; b. p. 100°/0·15 mm., m. p. 49°). The product was purified by shaking its solution in benzene with successive portions (15 ml.) of concentrated sulphuric acid until both layers were colourless. The benzene solution was freed from acid, and evaporation of the solvent gave a white crystalline solid which, on recrystallisation from ethanol, gave 4-tert.-*butyldiphenyl* in colourless plates, m. p. 52·2° (corr.) (Found: C, 91·1; H, 8·7. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%).

Preparation of m-*tert.*-*Butylbenzoic Acid.*—(i) *By the von Richter reaction* (cf. *Chem. Reviews*, 1951, **49**, 382). *tert.*-Butyl-*p*-nitrobenzene (14 g., 1 mol.) was heated for 3 hr. at 140° with crystalline potassium cyanide (60 g., 12 mol.) and ethylene glycol (250 ml., 90%). The resulting dark brown mixture was poured into water and basified with aqueous sodium hydroxide. The red emulsion which had formed was dispersed by ether-extraction, and the aqueous layer was acidified and steam-distilled. The distillate (4 l.) was extracted with ether (three times). Evaporation of the solvent gave a white solid (m. p. 124—126°), which on recrystallisation from 5% acetic acid gave *m-tert.*-butylbenzoic acid (0·7 g.), m. p. 128° (corr.). A mixed m. p. with a sample prepared by method (ii) below was 127° (Found: C, 74·1; H, 7·9. Calc. for $C_{11}H_{14}O_2$: C, 74·2; H, 7·9%). (ii) *By the method of Crawford and Stewart* (*loc. cit.*). *m*-Bromo-*tert.*-butylbenzene was prepared by the bromination of *p-tert.*-butylacetanilide by bromine in acetic acid followed by hydrolysis of the 2-bromo-4-*tert.*-butylacetanilide, m. p. 138°, to the amine. 2-Bromo-4-*tert.*-butylaniline hydrochloride (140 g.) was diazotised at 0° and 50% hypophosphorous acid (780 ml.) added dropwise to the stirred ice-cold solution. The mixture was kept at 0° for 24 hr., and the red oil which had separated was extracted with ether. The ether extracts were washed with 4N-potassium hydroxide solution (four times) and with water, and dried ($CaCl_2$). Distillation of the residue after removal of ether gave fractions: (i) b. p. 100°/40 mm., 70—82°/16 mm., 34·2 g., n_D^{20} 1·4940, (ii) b. p. 82—108°/16 mm., 1·2 g., n_D^{20} 1·5133, and (iii) b. p. 108—110°/16 mm., 41·7 g., n_D^{20} 1·5341. Fraction (i) contained no bromine and had n_D^{20} similar to that of *tert.*-butylbenzene (1·4927). It was converted into the *p*-sulphonamide which crystallised from ethanol in colourless needles, m. p. 137·5°, both alone and admixed with *p-tert.*-butylbenzenesulphonamide (Found: C, 56·1; H, 6·8. Calc. for $C_{10}H_{15}O_2NS$: C, 56·3; H, 7·1%). Fraction (iii) was converted into the Grignard reagent, carboxylation of which gave *m-tert.*-butylbenzoic acid (70%), which after recrystallisation from light petroleum had m. p. 127°. This reaction therefore gave *tert.*-butylbenzene (48·5%) in addition to the expected 3-bromo-*tert.*-butylbenzene (37%). Crawford and Stewart (*loc. cit.*) reported the isolation of only 3-bromo-*tert.*-butylbenzene, b. p. 100°/40 mm., in 70% yield.

m-tert.-*Butylbenzoyl Peroxide.*—*m-tert.*-Butylbenzoyl chloride, prepared from the acid (21·4 g.), was added dropwise during 3 hr. to a well-stirred ice-cold 10% solution of sodium hydroxide (40 ml.) and hydrogen peroxide (16 ml.; 100-vol.). The diacyl peroxide, which separated as a white powder, was collected and dried. The filtrate contained some unchanged acid chloride which, on addition of sodium hydroxide (5 g.) followed by vigorous shaking, was converted into more peroxide. The total product crystallised from methanol in colourless plates, m. p. 80° (13·6 g.), and was shown by analysis (acidified potassium iodide/thiosulphate titration) to be *m-tert.*-butylbenzoyl peroxide (98·1% pure).

3-tert.-*Butyldiphenyl.*—A solution of the peroxide (9·9 g.) in benzene (400 ml.; "AnalaR," dried over sodium) was boiled under reflux for 3 days. The volume of the pale yellow solution was reduced, and the residual oil was boiled under reflux with 2N-sodium hydroxide (200 ml.) for 8 hr. The organic layer was extracted with benzene (4 times), and the combined extracts were washed with water (twice) and dried ($CaCl_2$). The solvent was removed and the residue was distilled and redistilled *in vacuo*, to give a colourless oil (3·8 g.), b. p. 105°/0·4 mm., n_D^{20} 1·5680 (Found: C, 91·2; H, 8·8. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%).

Decomposition of o-tert.-*Butyl*-N-*nitrosoacetanilide in Benzene.*—*o-tert.*-Butylnitrobenzene (70 g.) was reduced in boiling ethanol solution by iron dust (70 g.) and hydrochloric acid (8 ml.; *d* 1·16) to *o-tert.*-butylaniline (b. p. 64°/0·1 mm.; 80%). Its acetyl derivative, m. p. 163° (from benzene–light petroleum), was converted into *o-tert.*-butyl-*N*-nitrosoacetanilide [m. p. 62° (decomp.); 90%] by the method described above for the *p*-isomeride. The nitroso-compound (8 g.) was allowed to decompose in benzene under conditions similar to those employed for the decomposition of the *p*-isomeride. Removal of the solvent and distillation of the residue gave a yellow oil (1·6 g.), b. p. 52—65°/0·1 mm., and *o-tert.*-butylacetanilide as a yellow solid (0·6 g.), b. p. 70°/0·1 mm., m. p. and mixed m. p. 160°. The yellow oil was dissolved in benzene (20 ml.)

and washed with sulphuric acid as in the case of the *p*-isomeride. Evaporation of the solvent afforded diphenyl in colourless plates, m. p. and mixed m. p. 68°. The decomposition was repeated with the nitroso-compound (35 g.) in benzene (400 ml.), giving *o-tert.*-butylacetanilide (3 g.) and a pale yellow liquid (15 g.), b. p. 100—128°/16 mm., n_D^{20} 1·5120. Careful fractionation of the latter gave *tert.*-butylbenzene (2·93 g.), b. p. 61—62°/15 mm., n_D^{20} 1·4930, proved by conversion into the *p*-sulphonamido-derivative, m. p. and mixed m. p. 137·5°, and a liquid (A) (10 g.), b. p. 115—125°/15 mm., n_D^{20} 1·5170 (Found: C, 78·4; H, 8·0%), which contained oxygen and could not be further fractionated. A portion (2 g.) was boiled under reflux with 3N-sodium hydroxide (100 ml.) for 5 hr. The organic layer was extracted with benzene, and evaporation of the solvent gave diphenyl, m. p. and mixed m. p. 68—69°. The basic portion was acidified and extracted with benzene (four times) and washed with water (twice), and the solvent was removed. The residual oil, which was not solid at 0°, was phenolic and was converted into the corresponding aryloxyacetic acid. The crude acid (m. p. 100—109°) was recrystallised to constant m. p. (114°) from benzene–light petroleum (Found: C, 68·8; H, 7·3. Calc. for $C_{12}H_{16}O_3$: C, 69·2; H, 7·7%). The analysis corresponds to that of a *tert.*-butylphenoxyacetic acid. The *o*- and *p*-isomerides have been previously described and have m. p.s 145—146° and 86° respectively. It appears likely that the phenolic product of the hydrolysis was a mixture of isomeric *tert.*-butylphenols, the *m*-isomeride preponderating. These phenols were formed as the result of hydrolysis of esters formed during the original decomposition. Although no acetic acid was isolated it is considered that the esters were the *tert.*-butylphenyl acetates, and a mixture consisting of 15% of diphenyl and 85% of *tert.*-butylphenyl acetate has the same percentage composition as that found for liquid (A).

2-tert.-*Butyldiphenyl.*—*o-tert.*-Butylbenzoic acid, prepared by Crawford and Stewart's method (*loc. cit.*), was converted into the acid chloride by the action of thionyl chloride. *o-tert.*-Butylbenzoyl peroxide was not formed under the conditions employed for the formation of the *m*-isomeride but the following modification was successful: Powdered sodium peroxide (2 g.) was added carefully to water (4 ml.) stirred vigorously in a cooling-bath. The acid chloride (5 g.) was added during 1 hr., followed by sodium peroxide (1·5 g.), and the stirring was continued for 2 hr. The yellow oil which separated was extracted with light petroleum and the combined extracts were washed with 2N-sodium hydroxide (twice), then water (once), and dried ($CaCl_2$). The solvent was removed by evaporation at room temperature and the residual oil was triturated with methanol until it solidified. The pale yellow solid (0·9 g.; m. p. 47—51°) was recrystallised with difficulty from methanol. It had m. p. 59° and liberated iodine from acid potassium iodide solution. The peroxide (0·3 g.) was decomposed in benzene (100 ml.; "AnalaR," sodium-dried) by boiling under reflux for 72 hr. Most of the benzene (90 ml.) was removed by distillation through a 12" helix-packed column, which was afterwards washed with ether (15 ml.), the washings being combined with the residue. The ether was removed from the distillation flask by evaporation at room temperature and the yellow residue was boiled under reflux with 2N-sodium hydroxide (50 ml.) for 4 hr. The remainder of the working-up procedure was identical with that used in the preparation of 3-*tert.*-butyldiphenyl described above. The product (90 mg.) was a low-melting solid which contained oxygen, probably resulting from the presence of ester. The entire product was dissolved in light petroleum (b. p. 40—60°; 10 ml.) and chromatographed on an alumina column (6" × ¼"). Elution with light petroleum (b. p. 40—60°) gave 2-tert.-*butyldiphenyl* as a colourless crystalline solid (60 mg.), m. p. 31—34° (Found: C, 91·8; H, 8·0. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%). Its infra-red spectrum was recorded and it had bands at 735, 755, and 779 cm.$^{-1}$, which are characteristic of a 2-substituted diphenyl, and at 1200 and 901 cm.$^{-1}$, which are characteristic of a *tert.*-butyl group.

2 : 5-*Di*-tert.-*butyldiphenyl.*—The combined diaryl fractions from experiments 4, 5, 6, and 7, after portions had been analysed for nitrodiphenyl content, were reduced in ethanol (60 ml.) by granulated tin and hydrochloric acid. Unchanged tin was removed by filtration and some ethanol (25 ml.) removed from the filtrate by evaporation. At this point a colourless oil separated which solidified on cooling. The crystals (0·5 g.) were removed from the surface of the mixture by hand, and recrystallisation from methanol gave 2 : 5-*di*-tert.-*butyldiphenyl* in colourless needles, m. p. 94·2° (Found: C, 90·2; H, 9·8. $C_{20}H_{26}$ requires C, 90·2; H, 9·8%). The infra-red spectrum of this compound as a crystalline powder in a Nujol mull was recorded. It had bands at 1200, 822·5, 761·5 cm.$^{-1}$, indicative of a 2 : 5-disubstituted diphenyl containing at least one *tert.*-butyl group.

Note: The preparation of 3-iododiphenyl as a colourless oil (b. p. 114·5°/0·3 mm.) was reported in Part IV (*loc. cit.*). This has now solidified (m. p. 26·5°) and its m. p. is unchanged on recrystallisation from light petroleum (b. p. 40—60°).

Discussion.

Partial Rate Factors for Phenylation.—(i) tert.-*Butylbenzene.* The relative rate of substitution in *tert.*-butylbenzene ${}^{\mathrm{PhBu^t}}_{\mathrm{PhH}}K$ may be calculated from ${}^{\mathrm{PhBu^t}}_{\mathrm{PhNO_2}}K$ and ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$, the determination of which was reported in Part II (*loc. cit.*). In this way ${}^{\mathrm{PhBu^t}}_{\mathrm{PhH}}K$ is found to be 0·87. By using this value and the mean values obtained in the spectrographic analysis for the ratio of isomerides (Table 4), the following values are obtained for the partial rate factors :

$$F_o = 0{\cdot}63 \quad F_m = 1{\cdot}28 \quad F_p = 1{\cdot}41$$

Thus, the *o*-position is deactivated, while the *m*- and the *p*-positions are activated slightly, the overall effect being deactivation. This is the first example of deactivation in homolytic phenylation of aromatic nuclei encountered by us. The simplest interpretation is that the large *tert.*-butyl group exerts a selective steric repression of *o*-substitution, and since substitution by phenyl radicals takes place mainly at the *o*-position (Parts I—V, *loc. cit*; Hey, Pengilly, and Williams, unpublished results) in all cases so far studied, this repression results in a slight overall deactivation of the molecule. A similar steric inhibition of *o*-substitution has been observed in the heterolytic nitration of *tert.*-butylbenzene (Brown and Nelson, *loc. cit.*; Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **169**, 29). It should be noted that the *amounts* of the isomerides formed in the phenylation reaction vary in the order $m > p > o$, while in the nitration reaction the order is $p > o > m$, which is a further indication that the electronic requirements for homolytic and heterolytic aromatic substitution reactions are different. The formation of a large amount of polyphenylated *tert.*-butylbenzene during the phenylation of *tert.*-butylbenzene is consistent with the low value determined for ${}^{\mathrm{PhBu^t}}_{\mathrm{PhH}}K$, because the *tert.*-butyldiphenyls first produced by monophenylation are much more reactive than the substrate molecule (Cadogan, Hey, and Williams, Part V). It appears that the decomposition of benzoyl peroxide in dilute solutions in " fast " solvents, such as nitrobenzene, 1 : 3 : 5-trichlorobenzene, and diphenyl, produces negligible amounts of polyphenylation products, whereas decomposition in less reactive solvents, such as the monohalogenobenzenes, benzene, and *tert.*-butylbenzene, affords an appreciable amount of polyphenylation. Decomposition of benzoyl peroxide in a mixture of a " fast " and a " slow " solvent, as in the determination of ${}^{\mathrm{PhBu^t}}_{\mathrm{PhNO_2}}K$, results in a negligible amount of residue.

(ii) p-*Di*-tert.-*butylbenzene.* The rate of phenylation relative to benzene of *p*-di-*tert.*-butylbenzene is obtained from the value of ${}^{p\text{-}\mathrm{But_2C_6H_4}}_{\mathrm{PhNO_2}}K$ by multiplication by 4, since ${}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$ is equal to 4 (Part II). Thus, ${}^{p\text{-}\mathrm{But_2C_6H_4}}_{\mathrm{PhH}}K = 0{\cdot}63$. It follows that the partial rate factor for phenylation in any position in *p*-di-*tert.*-butylbenzene is 0·93. The introduction of a *tert.*-butyl group into the *p*-position of *tert.*-butylbenzene therefore produces further deactivation of the molecule but increases the partial rate factor of the *o*-position. A decrease in overall activation is to be expected because the number of positions available for substitution has been decreased, and each of the four positions is now *ortho* with respect to a *tert.*-butyl group. The increase in the value of the partial rate factor at the *o*-position, on the other hand, indicates that the intrinsic effect of the *tert.*-butyl group is possibly one of slight activation, as observed for all other groups so far investigated, although the fact that all four positions are also *meta*- to a *tert.*-butyl group, and are therefore slightly activated, may be a contributory factor.

The results of these experiments, together with those previously reported, show that, whereas homolytic substitution reactions are very much less sensitive to polar influences than are heterolytic reactions, they are nevertheless susceptible in the normal manner to steric effects.

Decomposition of o-tert.-*Butyl*-N-*nitrosoacetanilide in Benzene.*—This decomposition took an anomalous course, the expected product, 2-*tert.*-butyldiphenyl, not being isolated. The main products were *tert.*-butylbenzene, *o-tert.*-butylacetanilide, diphenyl, and the isomeric *tert.*-butylphenyl acetates. The results of this non-quantitative experiment suggest that the formation of *tert.*-butylbenzene is due to the preferred abstraction by an *o-tert.*-butylphenyl radical of a hydrogen atom from the solvent, and the phenyl radical so

formed then attacks the solvent to give diphenyl. The quantities of diphenyl and *tert.*-butylbenzene formed are approximately equivalent. Examples of the abstraction of an " aromatic " hydrogen atom in place of the normal nuclear arylation have been reported by Haworth and Hey (*J.*, 1940, 364). The formation of the isomeric *tert.*-butylphenyl acetates is considered unlikely to be due to attack of free acetoxy-radicals on *tert.*-butylbenzene, because benzene was present in large excess and no phenyl acetate was detected. The process is probably intermolecular. *o-tert.*-Butylacetanilide results from denitrosation, a similar example with 2-acetamido-*N*-nitrosodiphenyl having been reported in Part V. The absence of 2-*tert.*-butyldiphenyl must be attributed to the existence of a large energy barrier, possibly due to steric effects, with the result that all the processes mentioned above become energetically favoured.

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