296. *Homolytic Aromatic Substitution. Part XI.* The Phenylation of Toluene, Ethylbenzene, and* iso*Propylbenzene.*

By D. H. Hey, B. W. Pengilly, and Gareth H. Williams.

Partial rate factors are determined for the phenylation of ethylbenzene and *iso*propylbenzene by an analysis of the products formed in the competitive phenylation of mixtures of them with (*a*) nitrobenzene and (*b*) pyridine. The proportions of the isomers formed in the nuclear phenylation, and the relative amounts of the products derived from nuclear and side-chain attack, are determined by infrared spectroscopy. The partial rate factors for ethylbenzene are similar to those for toluene, and those for *iso*propylbenzene are similar to those for *tert.*-butylbenzene, the determination of which has been reported previously. The existence of a steric effect which inhibits substitution *ortho* to an *iso*propyl group is thus revealed. A reinvestigation of the by-products of the phenylation of toluene shows the presence of a little dibenzyl, resulting from attack in the side-chain, and necessitates a small modification of the partial rate factors previously reported for the phenylation of toluene. The theoretical significance of these results is discussed.

The analysis of the products obtained in the reactions of benzoyl peroxide with *tert.*-butylbenzene and with toluene, and the determination of the partial rate factors for the phenylation of these compounds, was reported in Parts VII and VIII of this series.[1] In addition, the possibility of attack on the side-chains of alkylbenzenes was briefly discussed. The absence of α-hydrogen atoms in the side-chain of *tert.*-butylbenzene, and their low reactivity in the side-chain of toluene, results in very little attack on the side-chain of toluene and none on that of *tert.*-butylbenzene when benzoyl peroxide is allowed to

---

* Part X, *J.*, 1955, 3963.

[1] (*a*) Cadogan, Hey, and Williams, *J.*, 1954, 3352; (*b*) Hey, Pengilly, and Williams, *J.*, 1955, 6.

decompose in solutions in these solvents. The side-chain of ethylbenzene and of *iso*propylbenzene, on the other hand, is known to be much more susceptible to free-radical attack than that of toluene. This attack takes the form of the abstraction of an α-hydrogen atom, and the subsequent dimerisation of the radicals so formed. These radicals are, like the benzyl radical, considerably stabilised by resonance, and their consequently low reactivity is demonstrated by their inability to effect substitution at aromatic nuclei. They are, apparently, sufficiently stable to exist in solution in concentrations high enough to enable dimerisation to take place. This property of radicals analogous to benzyl is well known and, indeed, the production of 2 : 3-dimethyl-2 : 3-diphenylbutane (dicumyl) from *iso*propylbenzene has long been regarded as a test for the incidence of homolytic mechanisms.[2]

Thus it is apparent that a complete account of the phenylation of these two hydrocarbons requires a knowledge of the reactivity of the side-chains compared with that of the nuclei, as well as the specification of the reactivities of the nuclear positions in terms of partial rate factors. Measurements are therefore reported in the present communication of the relative amounts of the products derived from side-chain and nuclear attack, the ratios of the amounts of the products derived from substitution at the various nuclear positions, and the reactivities of the compounds towards nuclear attack compared with standard compounds, nitrobenzene and pyridine. In this manner, complete specifications of the reactivity of ethylbenzene and *iso*propylbenzene towards attack by phenyl radicals become possible and comparisons can be made among the members of the series of alkylbenzenes in order to discover the effects of various alkyl groups on homolytic reactivity.

The first of the above determinations, namely, that of the relative amounts of side-chain and nuclear attack, is of significance only if the side-chain and nuclear reactions are of the same kinetic order, for, if they are not, the amount of side-chain attack must depend on the concentration of benzoyl peroxide. The non-dependence of the relative amounts of side-chain and nuclear attack on the concentration of benzoyl peroxide is demonstrated for the case of *iso*propylbenzene, where the same result was obtained from solutions of different concentration. It is also demonstrated (see below) that the radical which attacks the side-chain is phenyl, and thus the nuclear and side-chain reactions with, for example, *iso*propylbenzene, can be represented by schemes (1) and (2) respectively.

$$C_6H_5{\cdot}CHMe_2 + Ph{\cdot} \longrightarrow Ph{\cdot}C_6H_4{\cdot}CHMe_2 + H{\cdot} \quad . \; . \; . \; . \; . \quad (1)$$

$$\left.\begin{array}{r}C_6H_5{\cdot}CHMe_2 + Ph{\cdot} \longrightarrow C_6H_5{\cdot}CMe_2{\cdot} + PhH \\ 2C_6H_5{\cdot}CMe_2{\cdot} \longrightarrow C_6H_5{\cdot}CMe_2{\cdot}CMe_2{\cdot}C_6H_5\end{array}\right\} \quad . \; . \; . \; . \; . \quad (2)$$

The application of the " steady-state " treatment to scheme (2) reveals that it obeys the same kinetic law as that which governs scheme (1), namely, that the rate of formation of the products is proportional to the concentrations of *iso*propylbenzene and the phenyl radical.

In addition to the products of nuclear and side-chain attack, some acetophenone is formed in the reactions, presumably by oxidation of ethylbenzene and *iso*propylbenzene. The oxidising agent in this side-reaction is not benzoyl peroxide, because almost all the peroxide used is accounted for by the amounts of the products formed from nuclear and side-chain attack. The oxidising agent is therefore probably oxygen, since the reactions were not conducted in an inert atmosphere. The aerial oxidation of ethylbenzene has been discussed by Emerson, Heyd, Lucas, Cook, Lyness, and Stevenson,[3] who suggested that 1-phenylethyl hydroperoxide $C_6H_5{\cdot}CH(O{\cdot}OH){\cdot}CH_3$ was first formed, and that this decomposed thermally into two free radicals (1-phenylethoxy and hydroxyl), either of which, by subsequent reaction with more ethylbenzene, could lead to the formation of acetophenone. The formation of acetophenone by the atmospheric oxidation of *iso*propylbenzene has been noted on a number of occasions (see, for example, Pines, Kvetinskas, and Ipatieff[4]), and is believed to proceed in an analogous manner.

In a recent report by Rondestvedt and Blanchard[5] of the phenylation of toluene,

---

[2] Kharasch, McBay, and Urry, *J. Org. Chem.*, 1945, **10**, 401.

[3] Emerson, Heyd, Lucas, Cook, Lyness, and Stevenson, *J. Amer. Chem. Soc.*, 1948, **70**, 3764.

[4] Pines, Kvetinskas, and Ipatieff, *J. Amer. Chem. Soc.*, 1955, **77**, 343.

[5] Rondestvedt and Blanchard, *ibid.*, p. 1769.

ethylbenzene, and *iso*propylbenzene, the presence of dibenyl and of a small amount of an unidentified substance believed to be diphenyl (or diphenylmethane) in the product of the reaction of benzoyl peroxide with toluene, is reported. This is now confirmed by a re-investigation of the by-products of this reaction.

EXPERIMENTAL METHODS AND RESULTS

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 and Baker), nitrobenzene, and pyridine were purified according to the procedures described in Part II,[6] and nitromethane according to that described in Part IV.[7] Ethylbenzene and *iso*propylbenzene (B.D.H.) were washed with concentrated sulphuric acid until the washings were colourless, then with aqueous sodium hydrogen carbonate, and with water, and dried ($MgSO_4$); the pure hydrocarbons were obtained after distillation from sodium through a 6-foot, helix-packed column (b. p.s 136°/760 mm. and 152°/760 mm. respectively). Specimens of 2-ethyl-, 3-ethyl-, and 2-*iso*propyl-diphenyl were kindly supplied by Drs. I. A. Goodman and P. H. Wise of the National Advisory Committee for Aeronautics at the Lewis Flight Propulsion Laboratory, Cleveland, Ohio, U.S.A. 4-Ethyldiphenyl was prepared from 4-acetyldiphenyl, which was prepared by Ferriss and Turner's method[8] from acetyl chloride and diphenyl. The 4-acetyldiphenyl (2·6 g.) was reduced by Huang-Minlon's modification[9] of the Wolff–Kishner method; it was heated with potassium hydroxide (2·5 g.), hydrazine hydrate (1·8 ml.), and ethylene glycol (18 ml.) on a metal-bath at 230°, and water and hydrazine hydrate were distilled off until the temperature of the liquid reached 190°. The mixture was maintained under reflux for 2 hr., then allowed to cool. It was extracted with ether and the extracts were dried (Na_2SO_4). Evaporation of the ethereal extract and distillation yielded colourless, crystals, b. p. 74°/10 mm. (1·85 g.). These crystallised from aqueous methanol yielding 4-ethyldiphenyl, m. p. 35° (Mowry, Renoll, and Huber[10] reported m. p. 34—35°). 4-*iso*Propyldiphenyl was prepared by heating *p*-*iso*propylbenzoic acid (Eastman-Kodak) under reflux with thionyl chloride, and the acid chloride so formed was distilled; it had b. p. 138°/22 mm. This was used to prepare di-*p*-*iso*propylbenzoyl peroxide by Hey and Walker's method.[11] The peroxide [m. p. 89° after crystallisation from methanol (Cooper[12] reports m. p. 98°); 6 g.] was allowed to decompose in benzene (500 ml.) at 80°, and the product was worked up by the standard procedure (Part II[6]). Distillation yielded 4-*iso*propyldiphenyl, b. p. 134°/3 mm.; this oil was further purified by fractional freezing, to give pure 4-*iso*propyldiphenyl (2·9 g.), m. p. 11° (Found: C, 91·6; H, 8·4. Calc. for $C_{15}H_{16}$: C, 91·8; H, 8·2%). Rondestvedt and Blanchard[5] reported b. p. 110—112°/1 mm., n_D^{20} 1·5831 for 4-*iso*propyldiphenyl.

3-Nitrodiphenyl[13] was reduced catalytically in benzene solution with hydrogen at 1 atm. in the presence of Raney nickel. The amine was obtained as the hydrochloride (93%). 3-Iododiphenyl was prepared from 3-aminodiphenyl hydrochloride by diazotisation with sodium nitrite and reaction of the diazonium salt solution with potassium iodide. It was obtained as a pale yellow solid, m. p. 25°, b. p. 146°/1·5 mm., in 57% yield. Cadogan, Hey, and Williams[1a] reported m. p. 26·5°.

3-*iso*Propyldiphenyl was prepared from 3-*iso*propenyldiphenyl, which was prepared by Mowry, Dazzi, Renoll, and Shortridge's method[14] by adding 3-iododiphenyl (22·4 g.) in dry ether (46 ml.) slowly to magnesium turnings (1·94 g.) and ether (46 ml.) in a flask equipped with a stirrer and a double-surface condenser. Initiation of the reaction proved difficult, but was effected by a trace of ethylmagnesium bromide. When addition of the 3-iododiphenyl was complete, the mixture was boiled under reflux for 1 hr. A mixture of dry (K_2SO_4) acetone (7 ml.) and ether (35 ml.) was then added at such a rate as to maintain gentle boiling. The mixture was allowed to boil under reflux overnight. Saturated aqueous ammonium chloride (50 ml.) was then added with stirring, and when hydrolysis was complete, the aqueous layer was extracted several times with ether, and the extracts were combined with the main ethereal layer.

---

[6] Augood, Hey, and Williams, *J.*, 1952, 2094.
[7] Augood, Cadogan, Hey, and Williams, *J.*, 1953, 3412.
[8] Ferriss and Turner, *J.*, 1920, 1140.
[9] Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.
[10] Mowry, Renoll, and Huber, *ibid.*, p. 1105.
[11] Hey and Walker, *J.*, 1948, 2213.
[12] Cooper, *J.*, 1951, 3106.
[13] Elks, Haworth, and Hey, *J.*, 1940, 1284.
[14] Mowry, Dazzi, Renoll, and Shortridge, *J. Amer. Chem. Soc.*, 1948, **70**, 1916.

Evaporation of the ether yielded impure 2-(3-diphenylyl)propan-2-ol (18·5 g.). The crude alcohol was boiled under reflux with acetic anhydride (19·5 ml.) for 3 hr. After removal of the acetic acid and the excess of anhydride by fractional distillation under reduced pressure, the product was carefully fractionated. The first fraction (b. p. 135—150°/14 mm.) consisted of diphenyl, and the second (b. p. 160—177°/14 mm.) of crude 3-*iso*propenyldiphenyl. This was redistilled, yielding 3-*iso*propenyldiphenyl, b. p. 167—170°/14 mm. (3·8 g.) (Mowry, Dazzi, Renoll, and Shortridge[14] reported b. p. 160—161°/12 mm.). 3-*iso*Propenyldiphenyl (3·8 g.) in glacial acetic acid (30 ml.) was hydrogenated catalytically with Adams catalyst (0·1 g.) and the theoretical quantity of hydrogen at room temperature and atmospheric pressure. The product was distilled three times, yielding 3-*iso*propyldiphenyl, b. p. 80°/ 0·1 mm., n_D^{20} 1·5765 (3·5 g.) (Found: C, 91·4; H, 8·4. Calc. for $C_{15}H_{16}$: C, 91·8; H, 8·2%) (Rondestvedt and Blanchard[5] reported b. p. 110—115°/1·3 mm., n_D^{20} 1·5807).

2 : 3-Dimethyl-2 : 3-diphenylbutane (tetramethyldibenzyl, dicumyl) was prepared from *iso*propylbenzene and acetyl peroxide (Kharasch, McBay, and Urry [2]). An ethereal solution of acetyl peroxide was prepared by Gambarjan's method.[15] Ice (35 g.) was added slowly to a stirred mixture of acetic anhydride (18 g.), ether (100 ml.), and sodium peroxide (10 g.) at −15°. When the temperature reached 0° the mixture was kept at this temperature for 2 hr. and the ethereal layer decanted off. Calcium chloride was added to the ethereal layer and the mixture set aside overnight at 0°. After filtration, the ether was removed from the filtrate by gentle suction at room temperature, while a little *iso*propylbenzene was added to ensure that no crystalline acetyl peroxide was deposited. The resulting solution was added dropwise to well-stirred *iso*propylbenzene (250 ml.) on a steam-bath. After the addition was complete the excess of *iso*propylbenzene, together with the acetic acid formed, was removed by distillation, and the residue distilled under reduced pressure. The fraction of b. p. 125—128°/0·7 mm. consisted of crude 2 : 3-dimethyl-2 : 3-diphenylbutane (2 g.), which crystallised from methanol in needles, m. p. 118° (Kharasch, McBay, and Urry[2] reported m. p. 115°).

2 : 3-Diphenylbutane, in both its racemic and its *meso*-form, was prepared by a similar reaction with ethylbenzene and acetyl peroxide at 100°. The product was distilled at 0·5 mm., and racemic and *meso*-2 : 3-diphenylbutane were separated by treatment of the mixture with methanol, in which the *meso*-form is almost insoluble. The methanolic solution of racemic 2 : 3-diphenylbutane was distilled, and the fraction of b. p. 114—118°/2 mm. was twice redistilled, yielding racemic 2 : 3-diphenylbutane as a colourless oil (b. p. 116°/2 mm., n_D^{23} 1·5495). Kharasch, McBay, and Urry[2] reported b. p. 106°/2 mm., n_D^{20} 1·5517, for this form. The *meso*-2 : 3-diphenylbutane was purified by crystallisation (m. p. 128°) from nitromethane (Kharasch, McBay, and Urry[2] reported m. p. 123—125°).

Determination of the Extent of Side-chain Attack and the Ratio of the Isomeric Ethyldiphenyls formed in the Phenylation of Ethylbenzene.—Benzoyl peroxide (6 g.) was allowed to decompose in ethylbenzene (214 ml.) in a thermostat at 80° for 80 hr. When the reaction was complete free benzoic acid was removed by extraction with saturated sodium hydrogen carbonate solution. The mixture was then worked up by the standard procedure described in Part II.[6] In Expt. 3, carbon tetrachloride (60 ml.) was added to the mixture after reaction, and the lowest-boiling fraction (b. p. 78—80°) from the first distillation, containing carbon tetrachloride and any benzene formed in the reaction, was collected separately. This fraction was treated with a mixture of concentrated sulphuric acid (10 ml.) and fuming nitric acid (10 ml.), dropwise with shaking at room temperature. When addition was complete the mixture was refluxed for ½ hr. and poured on ice (25 g.). The crystalline product formed was filtered off, washed with water, and dried. Crystallisation from aqueous ethanol gave *m*-dinitrobenzene (0·87 g.), m. p. and mixed m. p. 90°. This is equivalent to 0·40 g. of benzene. The diaryl fraction from Expt. 2 was carefully distilled under reduced pressure into two fractions. The second fraction, b. p. 70—100°/0·2 mm., consisted of a mixture of diaryls. The first fraction, b. p. 20—60°/0·3 mm. (1·5 g.), which was shown by infrared analysis not to contain any ethyldiphenyls or 2 : 3-diphenylbutane, was identified as acetophenone (semicarbazone, m. p. and mixed m. p. 201—202°). The diaryl fractions from expts. 1 and 3 were treated with sodium hydrogen sulphite solution to remove any acetophenone present.

In each reaction a high-boiling residue was left after separation of the diaryl fraction by distillation. This residue was assumed to consist of ethylterphenyls and products arising from the phenylation of, and abstraction of hydrogen from, 2 : 3-diphenylbutane. The results of these reactions are summarised in Table 1.

[15] Gambarjan, *Ber.*, 1909, **42**, 4003.

TABLE 1. *Products obtained in the phenylation of ethylbenzene.*

Experiment	1	2	3
Diaryl fraction (b. p. 70—100°/0·2 mm.) (g.)	2·373	2·419	2·385
Residue (b. p. >120°/0·3 mm.) (g.)	1·485	1·538	1·670
Free Ph·CO$_2$H (g.)	1·53	1·35	1·43
Ph·CO$_2$H from hydrolysis of esters (g.)	0·57	0·55	0·49
Total Ph·CO$_2$H (g.)	2·10	1·90	1·92
Benzoyl peroxide accounted for (neglecting residues) (%)	79	76	75·5

meso-2 : 3-Diphenylbutane was separated from the other compounds present in the diaryl fraction (racemic 2 : 3-diphenylbutane and 2-, 3-, and 4-ethyldiphenyl) by fractional crystallisation from nitromethane, in which *meso*-2 : 3-diphenylbutane is only sparingly soluble. Its identity was confirmed by its m. p. and mixed m. p. (128°). The weights of *meso*-2 : 3-diphenylbutane obtained from experiments 1, 2, and 3 were 0·532, 0·545 and 0·536 g. respectively.

Spectrographic analysis of the diaryl fractions after treatment with nitromethane was carried out with a Grubb-Parsons single-beam instrument fitted with an automatic pen-recorder. Nitromethane was used as solvent, since it has no bands in the range 11—15 mμ, where the characteristic bands of the ethyldiphenyls occur. The spectra were recorded by using 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. Calibration spectra were recorded for 2-, 3-, and 4-ethyldiphenyl and for *meso*- and racemic 2 : 3-diphenylbutane, and measurements on the spectra of mixtures for analysis made at the following characteristic absorption maxima: 2-ethyldiphenyl, 747 cm.$^{-1}$; 3-ethyldiphenyl, 806 cm.$^{-1}$; 4-ethyldiphenyl, 842 cm.$^{-1}$. These measurements enabled the concentrations of these isomerides to be calculated. The concentration of racemic 2 : 3-diphenylbutane was then obtained by difference. The accuracy of the determinations was tested by preparing mixtures of the three ethyldiphenyls and racemic 2 : 3-diphenylbutane in known concentration in nitromethane. These were analysed by the infrared method and the results obtained are given in Table 2.

TABLE 2. *Analysis of mixtures of ethyldiphenyls and racemic* 2 : 3-*diphenylbutane.*

	Solution S1		Solution S2	
	Known composition (%)	Composition found (%)	Known composition (%)	Composition found (%)
2-Ethyldiphenyl	41	41	23	21
3- „	10	12	30	33
4- „	6	7	17	17
Racemic 2 : 3-diphenylbutane	43	40	30	29

The analyses of the products from reactions 1, 2, and 3 are reported in Table 3. Dannley and Zaremsky[16] have reported the formation of 50% of 2-, 25% of 3-, and 25% of 4-ethyldiphenyl in the phenylation of ethylbenzene with benzoyl peroxide.

The results on the composition of the products, calculated from the data contained in Table 3, together with the weights of *meso*-2 : 3-diphenylbutane, are given in Table 4.

TABLE 3. *Spectrographic analyses of product of phenylation of ethylbenzene.*

	Composition (% by weight)			
Expt.	2-Ethyldiphenyl	3-Ethyldiphenyl	4-Ethyldiphenyl	Racemic 2 : 3-diphenylbutane
1	37·8	18·8	13·5	29·9
2	37·5	19·8	13·4	29·3
3	36·6	19·7	14·0	29·7

TABLE 4. *Composition of the product of reaction of ethylbenzene with benzoyl peroxide.*

	Nuclear attack	Side-chain attack	Composition of products of nuclear attack (% by wt.)		
Expt.	(% by wt.)	(% by wt.)	2-Ethyldiphenyl	3-Ethyldiphenyl	4-Ethyldiphenyl
1	44	56	54	27	19
2	46	54	53	28	19
3	46	54	52	28	20
Mean	45	55	53	28	19

Determination of the Extent of Side-chain Attack and the Ratio of Isomeric iso*Propyldiphenyls formed in the Phenylation of* iso*Propylbenzene.*—In expt. 4, benzoyl peroxide (6 g.) was allowed to decompose in *iso*propylbenzene (226 ml.) in a thermostat at 80° for 72 hr. In expts. 5 and 6, benzoyl peroxide (10 g.) and *iso*propylbenzene (150 ml.) were used. Mixture 7 was the neutral fraction of the product of expt. 14 (see below), one of the pyridine–*iso*propylbenzene competitive reactions. After the reactions were complete the mixtures were worked up by the standard procedure, except that in expt. 4 free benzoic acid was removed as described for the reactions with ethylbenzene, and benzene was estimated as described for the reaction with ethylbenzene and found to be 1·2 g. The determination of acetophenone was also carried out on this mixture, and 1·25 g. were isolated and identified as the semicarbazone (m. p. and mixed m. p. 201—202°). Since the diaryl fractions were solid, they clearly contained material other than the *iso*propyldiphenyls, as these are all liquids. Careful treatment of these fractions with nitromethane was therefore employed in order to separate them into 2 : 3-dimethyl-2 : 3-diphenylbutane (dicumyl) (m. p. and mixed m. p. 119°) and liquid fractions the analyses of which corresponded closely with that calculated for *iso*propyldiphenyl (Found : C, 91·6; H, 8·4. Calc. for $C_{15}H_{16}$: C, 91·8; H, 8·2%), and which was found by spectrographic analysis to contain only a small amount of 2 : 3-dimethyl-2 : 3-diphenylbutane. The results of these reactions are summarized in Table 5.

TABLE 5. *Products obtained in the phenylation of* iso*propylbenzene.*

Experiments :	4	5	6	7
Diaryl fraction (b. p. 60—120°/0·1 mm.) (g.)	3·303	4·650	4·666	1·657
Residue (b. p. >120°/0·1 mm.) (g.)	1·631	2·366	2·217	—
Dimethyldiphenylbutane removed from diaryl fraction (g.)	1·801	2·538	2·195	0·807
Free Ph·CO_2H (g.)	1·55	—	—	—
Ph·CO_2H from hydrolysis of esters (g.)	0·28	—	—	—
Total Ph·CO_2H (g.)	1·83	3·40	3·38	—
Benzoyl peroxide accounted for (neglecting residue) (%)	75	72·5	69	—

The spectrographic analysis of the diaryl fractions after treatment with nitromethane was carried out by the method used for the reactions with ethylbenzene. Calibration spectra were recorded for 2-, 3-, and 4-*iso*propyldiphenyl and for 2 : 3-dimethyl-2 : 3-diphenylbutane, and measurements on the mixtures for analysis were made at the following frequencies : 2-*iso*propyldiphenyl, 751 cm.$^{-1}$; 3-*iso*propyldiphenyl, 803 cm.$^{-1}$; 4-*iso*propyldiphenyl, 841 cm.$^{-1}$. The concentration of 2 : 3-dimethyl-2 : 3-diphenylbutane was obtained by difference. The accuracy of the determinations was tested by the analysis of known mixtures of the three *iso*propyldiphenyls and 2 : 3-dimethyl-2 : 3-diphenylbutane. These results are given in Table 6.

TABLE 6. *Analysis of mixtures of* iso*propyldiphenyls and* 2 : 3-*dimethyl*-2 : 3-*diphenylbutane.*

	Solution S3		Solution S4	
	Known composition (%)	Composition found (%)	Known composition (%)	Composition found (%)
2-*iso*Propyldiphenyl	28	25	39	41
3- „	40	39	30	30
4- „	22	24	16	18
2 : 3-Dimethyl-2 : 3-diphenylbutane	10	12	15	11

TABLE 7. *Spectrographic analysis of product of phenylation of* iso*propylbenzene.*

	Composition (% by weight)			
Experiment	2-*iso*Propyldiphenyl	3-*iso*Propyldiphenyl	4-*iso*Propyldiphenyl	2 : 3-Dimethyl-2 : 3-diphenylbutane
4	25·8	33·0	22·4	18·8
5	27·0	37·6	23·7	11·7
6	25·1	36·3	21·8	16·8
7	26·4	33·8	22·6	17·2

The analyses of the products from reactions 4, 5, 6, and 7 are reported in Table 7. Dannley and Zaremsky [16] have reported the formation of 10% of 2-, 60% of 3-, and 30% of 4-*iso*propyldiphenyl, and Rondestvedt and Blanchard [5] 29%, 50%, and 21% respectively, in the phenylation of *iso*propylbenzene.

The results of the composition of the products calculated from the data contained in Table 7, together with the weights of 2 : 3-dimethyl-2 : 3-diphenylbutane removed in treatment with nitromethane (Table 5), are given in Table 8.

---

[16] Dannley and Zaremsky, *J. Amer. Chem. Soc.*, 1955, **77**, 1588.

TABLE 8. *Composition of the product of reaction of* iso*propylbenzene with benzoyl peroxide.*

Experiment	Nuclear attack (% by wt.)	Side-chain attack (% by wt.)	Composition of products of nuclear attack (% by wt.)		
			2-*iso*Propyl-diphenyl	3-*iso*Propyl diphenyl	4-*iso*Propyl diphenyl
4	37	63	31·8	40·7	27·5
5	40	60	30·5	42·5	27·0
6	38·5	61·5	30·2	43·6	26·4
7	42	58·5	31·8	40·8	27·4
Mean	39·5	60·5	31	42	27

In view of the excellent agreement between the results of expts. 4—7, and the satisfactory results obtained in the analyses of synthetic mixtures (Table 6), the present results are considered to be more accurate than those of the earlier workers. A similar assessment may be applied to the results obtained with ethylbenzene (Tables 2 and 4).

Determination of ${}^{\mathrm{PhEt}}_{\mathrm{PhNO_2}}K$.—Benzoyl peroxide (6 g.) was allowed to decompose in an equimolar mixture (200 ml.) of ethylbenzene and nitrobenzene in a thermostat at 80° for 72 hr. The mixture was then worked up by the procedure described in Part VIII [1b] for competitive experiments with mixtures of nitrobenzene and toluene. As in those experiments, three fractions—the pre-forerun, the forerun, and the diaryl fraction—were retained from the final distillation. All three fractions were analysed for the nitro-group by titration with titanous chloride and, as a check, for nitrogen by the micro-Dumas method. The pre-forerun (~3 g., b. p. 96°/20 mm.) consisted of pure nitrobenzene, thus showing that no ethyldiphenyls had been lost in the distillation. The forerun (b. p. 30—80°/0·1 mm) consisted of nitrobenzene together with some of the ethyldiphenyls. It may be safely assumed that the forerun contained no nitrodiphenyls, since these were found not to distil until a temperature 40° above that at which the forerun was collected had been reached. The diaryl fraction (b. p. 80—130°/0·1 mm.) consisted of ethyldiphenyls, nitrodiphenyls, and *meso-* and racemic 2 : 3-diphenylbutane. The residue in the flask after distillation amounted to less than 10% of the diaryl fraction and consisted mainly of tar not removed on the alumina column. The results of these competitive experiments are summarised in Table 9.

TABLE 9.

Experiment :	8	9
Diaryl fraction (g.)	1·783	1·805
$\mathrm{Ph{\cdot}C_6H_4{\cdot}NO_2}$ in diaryl fraction (%)	70·9	73·7
Forerun (g.)	2·537	2·147
N in foreruns (%)	9·95	9·60
Hydrocarbons in forerun (g.)	0·312	0·338
$\mathrm{Ph{\cdot}C_6H_4{\cdot}NO_2}$ (g.) in diaryl fraction	1·264	1·331
Corr. wt. of diaryl fraction (g.)	2·095	2·143
Total hydrocarbons (g.)	0·831	0·812
$\mathrm{Ph{\cdot}C_6H_4{\cdot}C_2H_5}$ (g.)	0·374	0·365
Free $\mathrm{Ph{\cdot}CO_2H}$ (g.)	2·82	2·80
$\mathrm{Ph{\cdot}CO_2H}$ from hydrolysis of esters (g.)	0·50	0·50
Benzoyl peroxide accounted for (%)	84	82
${}^{\mathrm{PhEt}}_{\mathrm{PhNO_2}}K$	0·32	0·30

Hence ${}^{\mathrm{PhEt}}_{\mathrm{PhNO_2}}K = 0{\cdot}31$

The sum of the weights of 2-, 3-, and 4-ethyldiphenyl formed was obtained from the total weight of hydrocarbon by correcting for side-chain attack, using the data given in Table 4.

Determination of ${}^{\mathrm{Ph}iso\mathrm{Pr}}_{\mathrm{PhNO_2}}K$.—In expts. 10 and 11, benzoyl peroxide (6 g.) was allowed to decompose in an equimolar mixture (200 ml.) of *iso*propylbenzene and nitrobenzene in a thermostat at 80° for 72 hr. The mixtures were then worked up and analysed by the procedure described above for the determination of ${}^{\mathrm{PhEt}}_{\mathrm{PhNO_2}}K$. The results of these experiments are summarised in Table 10.

The sum of the weights of 2-, 3-, and 4-*iso*propyldiphenyl formed was obtained from the total weight of hydrocarbon by correcting for side-chain attack from the data given in Table 8.

Determination of ${}^{\mathrm{PhEt}}_{\mathrm{PyH}}K$ *and* ${}^{\mathrm{Ph}iso\mathrm{Pr}}_{\mathrm{PyH}}K$.—In expts. 12 and 13, benzoyl peroxide (6 g.) was allowed to decompose in an equimolar mixture (200 ml.) of ethylbenzene and pyridine. In expts. 14 and 15, the same weight of benzoyl peroxide was allowed to decompose in an equimolar mixture (200 ml.) of *iso*propylbenzene and pyridine. The products were worked up and separated into neutral and basic fractions as described in Part VIII.[1b] The results of these experiments are summarised in Tables 11 and 12.

TABLE 10.

Experiment :	10	11
Diaryl fraction (g.)	2·537	2·153
$\mathrm{Ph{\cdot}C_6H_4{\cdot}NO_2}$ in diaryl fraction (%)	66·5	71·7
Forerun (g.)	0·547	0·81
N in forerun (%)	9·75	8·05
Hydrocarbons in forerun (g.)	0·079	0·237
Corr. wt. of diaryl fraction (g.)	2·616	2·390
$\mathrm{Ph{\cdot}C_6H_4{\cdot}NO_2}$ in diaryl fraction (g.)	1·689	1·543
Total hydrocarbons (g.)	0·927	0·847
$\mathrm{Ph{\cdot}C_6H_4{\cdot}Pr^i}$ (g.)	0·366	0·335
$\mathrm{Ph{\cdot}CO_2H}$ (g.)	3·3	3·4
Benzoyl peroxide accounted for (%)	86	85
${}^{\mathrm{Ph}iso\mathrm{Pr}}_{\mathrm{PhNO_2}}K$	0·215	0·220

Hence ${}^{\mathrm{Ph}iso\mathrm{Pr}}_{\mathrm{PhNO_2}}K = 0{\cdot}217$

TABLE 11.

Experiment :	12	13
Phenylpyridines (g.)	0·603	0·529
Neutral diaryl fraction (g.)	1·771	1·557
Basic residue (g.)	0·145	0·129
Non-basic residue (g.)	0·968	0·916
N in non-basic residue (%)	0·82	0·76
Phenylpyridines (corr.) (g.)	0·789	0·694
Neutral diaryl fraction (corr.) (g.)	2·372	2·133
$\mathrm{Ph{\cdot}C_6H_4{\cdot}C_2H_5}$ in neutral fraction (g.)	1·068	0·960
$\mathrm{Ph{\cdot}CO_2H}$ (g.)	2·85	2·75
Benzoyl peroxide accounted for (%)	94·5	88
${}^{\mathrm{PhEt}}_{\mathrm{PyH}}K$	1·16	1·19

Hence ${}^{\mathrm{PhEt}}_{\mathrm{PyH}}K = 1{\cdot}175$

TABLE 12.

Experiment :	14	15
Phenylpyridines (g.)	0·595	0·620
Neutral diaryl fraction (g.)	1·657	1·604
Basic residue (g.)	0·162	0·167
Non-basic residue (g.)	0·667	0·576
N in non-basic residue (%)	0·97	0·51
Phenylpyridines (corr.) (g.)	0·776	0·765
Neutral diaryl fraction (corr.) (g.)	2·078	1·999
$\mathrm{Ph{\cdot}C_6H_4{\cdot}Pr^i}$ in neutral fraction (g.)	0·821	0·790
$\mathrm{Ph{\cdot}CO_2H}$ (g.)	2·9	2·8
Benzoyl peroxide accounted for (%)	89	85
${}^{\mathrm{Ph}iso\mathrm{Pr}}_{\mathrm{PyH}}K$	0·84	0·82

Hence ${}^{\mathrm{Ph}iso\mathrm{Pr}}_{\mathrm{PyH}}K = 0{\cdot}83$

The weights of ethyl- and *iso*propyl-diphenyls formed were obtained from the total weights of hydrocarbon by correcting for side-chain attack, using the data given in Tables 4 and 8.

By-products in the Phenylation of Toluene.—Benzoyl peroxide (50 g.) was allowed to decompose in toluene (500 ml.) in a thermostat at 80° for 72 hr. and the diaryl fraction of the product isolated by the standard procedure. The diaryl fraction was treated with an equal volume of light petroleum (b. p. 40—60°) and cooled to −80°. The solid which separated was removed by filtration and washed with cooled light petroleum. The solid (1·25 g.) was identified as dibenzyl (m. p. and mixed m. p. 51°). This comprised 13% of the weight of the diaryl fraction. Since, in the determination of the ratio of isomerides reported in Part VIII[1b] the amount of 2-methyldiphenyl in the diaryl fraction was obtained by difference, this figure should be corrected for the dibenzyl formed as indicated above. The corrected values show 13% of side-chain attack and 87% of nuclear attack, and the product of nuclear attack contains 66·5% of 2-, 19·2% of 3-, and 14·3% of 4-methyldiphenyl. The altered ratio of isomerides leads to a change in the relative rate of phenylation and of the partial rate factor for the *ortho*-position, although those for the *meta*- and the *para*-position remain unaltered. The corrected partial rate factors are : F_o, 3·5;

F_m, 1·0; and F_p, 1·4. The general conclusions drawn concerning these partial rate factors are unaltered by this amendment.

Consideration of the spectroscopic evidence reported in Part VIII[1b] for the presence of diphenylmethane in the product of this reaction led to attempts to isolate diphenylmethane from the diaryl fraction of the product of the reaction described above, and also from mixtures made up to contain 2-, 3-, and 4-methyldiphenyl and diphenylmethane. Physical methods, such as distillation, chromatography, and fractional freezing failed to effect the desired separation of the synthetic mixtures. Oxidation with chromic acid, followed by attempted isolation of benzophenone as its 2 : 4-dinitrophenylhydrazone, also proved unsatisfactory. The only method which could be used successfully with the synthetic mixtures was that employed by Yost and Hauser,[17] which involves the metallation of diphenylmethane with potassamide and treatment of the resulting diphenylmethylpotassium with solid carbon dioxide. Diphenylacetic acid was precipitated by addition of hydrochloric acid, and crystallised from light petroleum. From a synthetic mixture containing 20% of diphenylmethane, 15% was recovered as diphenylacetic acid in this way. A sample of the diaryl fraction of the product of the reaction of benzoyl peroxide with toluene, however, gave no diphenylacetic acid when subjected to this procedure, and it therefore seems that the presence of diphenylmethane in it is unlikely. The infrared absorption at 13·5 mμ which was assigned to diphenylmethane is therefore probably due to the presence of a little diphenyl, which absorbs at 13·49 mμ in nitromethane solution. Diphenyl was previously reported by De Tar[18] and by Hey, Nechvatal, and Robinson[19] to be formed in the reaction of benzoyl peroxide with nitrobenzene at high concentrations of the peroxide. It therefore seems not unlikely that diphenyl is also formed from high concentrations of benzoyl peroxide in toluene. The spectrum of a synthetic mixture containing 2-, 3-, and 4-methyldiphenyl together with about 5% of diphenyl, showed that the observed absorption could be accounted for by the presence of about this amount of diphenyl. However, all attempts to isolate diphenyl from the reaction product have failed. If the observed absorption at 13·5 mμ is in fact due to diphenyl, the dependence of its formation on the concentration of benzoyl peroxide is easily understood, since there is clearly a greater probability of the collision of two phenyl radicals under conditions of high concentration, especially since the present solvent, toluene, is relatively unreactive towards phenyl radicals.

DISCUSSION

Reactivity of the Side-chain.—The proportions of side-chain and nuclear attack by phenyl radicals in the four alkylbenzenes so far investigated are as follows :

	Product of side-chain attack (% by wt.)	Product of nuclear attack (% by wt.)
Toluene	13	87
Ethylbenzene	55	45
*iso*Propylbenzene	60·5	39·5
tert.-Butylbenzene	0	100

The absence of attack on the side-chain of *tert.*-butylbenzene indicates that the reactivity of the β-hydrogen atoms of the side-chain is very low. This is not unexpected, since the radicals to which reactions of this type should give rise enjoy no stabilisation by resonance, and their stability, compared with that of the radicals resulting from attack in the α-position, must be very low. The reactivity of the α-hydrogen atoms is, however, seen to increase with increasing methylation of the α-position, notwithstanding their decreased number which results from successive replacement of them by methyl groups. This, again, must be due to the enhanced stability conferred on the radicals resulting from abstraction of hydrogen from the α-positions by the presence of adjacent methyl groups. This enhanced stability may arise from the hyperconjugation of the methyl groups.

The experiments described above also throw some light on the mechanism of the reaction of hydrogen-abstraction. Consideration of the results makes it possible to identify the attacking radical which is responsible for the abstraction of hydrogen as the phenyl radical and not the benzoyloxy-radical, since, with both ethylbenzene and *iso*propylbenzene, the amount of benzoic acid formed is grossly insufficient to account for the number of

---

[17] Yost and Hauser, *J. Amer. Chem. Soc.*, 1947, **69**, 2325.

[18] DeTar, *ibid.*, 1950, **72**, 1028.

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

benzoyloxy-radicals which must react in this way to give the observed amounts of the products derived from side-chain attack. On the other hand, benzene, resulting from hydrogen-abstraction by phenyl radicals, has been shown to occur in the products of reactions with ethylbenzene and *iso*propylbenzene. The work herein described shows that with benzoyl peroxide 60·5% of the product from *iso*propylbenzene consists of 2 : 3-dimethyl-2 : 3-diphenylbutane, while the remainder consists of products arising from nuclear substitution. Neither in this reaction nor in the preceding reaction with ethylbenzene could any evidence be obtained of substitution in the side-chain.

The results now reported are in complete agreement with a number of observations reported from other laboratories. For example, in 1939 Cuthbertson, Gee, and Rideal[20] discovered that the use of toluene as a solvent reduced the rate constant and degree of polymerisation of vinyl acetate, and they deduced that toluene was participating in the transfer mechanism. Other workers[21, 22] have shown that little or no retardation occurs with compounds which do not contain α-methylenic hydrogen atoms, and thus it appears that polymer radicals derived from the vinyl acetate must attack the methyl group of toluene. Jaquiss and Szwarc[23] studied the pyrolysis of benzyl benzoate in the presence of toluene at 700° and inferred that the following reactions must occur:

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}CH_2Ph} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} + \mathrm{Ph{\cdot}CH_2{\cdot}} \quad (1)$$

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} \longrightarrow \mathrm{Ph{\cdot}} + \mathrm{CO_2} \quad (2)$$

$$\mathrm{Ph{\cdot}CH_3} + \mathrm{Ph{\cdot}} \longrightarrow \mathrm{Ph{\cdot}CH_2{\cdot}} + \mathrm{PhH} \quad (3)$$

$$\mathrm{2Ph{\cdot}CH_2{\cdot}} \longrightarrow \mathrm{Ph{\cdot}CH_2{\cdot}CH_2Ph} \quad (4)$$

They obtained a yield of dibenzyl greater than could be explained by reaction (1) alone, and thus postulated the occurrence of reaction (3). More recently McBay, Tucker, and Milligan[24] have allowed acetyl peroxide and several dialkyl peroxydicarbonates to undergo decomposition in toluene, and claim that a quantitative yield of dibenzyl is obtained when the ratio of toluene to radical source is large.

Kharasch, McBay, and Urry[2] have shown that methyl radicals derived from acetyl peroxide readily attack the alkyl group of ethylbenzene, abstracting hydrogen and yielding *meso-* and racemic 2 : 3-diphenylbutane in approximately equal quantities. Dannley and Zaremsky[16] have recently reported that the decomposition of benzoyl peroxide in ethylbenzene gave a product of which 65% by weight consisted of *meso-* and racemic 2 : 3-diphenylbutane, while the remainder was a mixture of the three isomeric ethyldiphenyls. With *iso*propylbenzene Kharasch, McBay, and Urry[2] claimed an almost quantitative yield of 2 : 3-dimethyl-2 : 3-diphenylbutane in the reaction with acetyl peroxide. In the decomposition of benzoyl peroxide in *iso*propylbenzene, Dannley and Zaremsky[16] reported that the product contained 31% of 2 : 3-dimethyl-2 : 3-diphenylbutane, whilst Rondestvedt and Blanchard[5] reported a yield of 59% of this hydrocarbon. Dannley and Zaremsky's figure would appear to be low, since it is clearly out of accord with the results of other workers (cf. Table 13). In addition, Rondesvedt and Blanchard obtained a similar ratio of nuclear to side-chain attack when they employed *N*-nitrosoacetanilide and 3 : 3-dimethyl-1-phenyltriazen as sources of phenyl radicals. This further supports the view that phenyl radicals alone abstract hydrogen from the side-chain of the alkylbenzene when benzoyl peroxide is used as the source of radicals.

Gregg and Mayo[21] have studied the inhibition of the polymerisation of styrene by various alkylbenzenes and noted that molecules containing α-hydrogen atoms appreciably reduced the molecular weight of the polymer. They suggested that such molecules transferred hydrogen atoms to the growing polymer radical, giving a substituted benzyl radical which did not participate further in the chain process. The transfer constants *C* for this process, which are proportional to the relative reactivities of the inhibitors, were measured and their values at 60° are shown in Table 13.

[20] Cuthbertson, Gee, and Rideal, *Proc. Roy. Soc.*, 1939, *A*, **170**, 300.
[21] Gregg and Mayo, *Discuss. Faraday Soc.*, 1947, **2**, 328.
[22] Kooyman, *ibid.*, 1951, **10**, 163.
[23] Jaquiss and Szwarc, *Nature*, 1952, **170**, 312.
[24] McBay, Tucker, and Milligan, *J. Org. Chem.*, 1954, **19**, 1003.

TABLE 13.

Compound	$C \times 10^5$ *	$K_r \times 10^2$ †	% Side-chain attack by Ph
Benzene	0·18	0·03	—
tert.-Butylbenzene	0·6	0·1	0
Toluene	1·25	0·42	13
Ethylbenzene	6·7	1·28	55
*iso*Propylbenzene	8·2	1·75	60·5

* Gregg and Mayo.[21] † Kooyman.[22]

Kooyman[22] has examined the reactivity of alkylbenzenes towards trichloromethyl radicals by a similar method. He measured the efficiency of various hydrocarbons as retarders in the free-radical addition of carbon tetrachloride to cet-1-ene. The values for various retarders of the quantity K_r, which is proportional to the reactivity of the retarder, are also shown in Table 13. The general agreement between the three sets of figures recorded in Table 13, which arise out of three separate and independent investigations directed towards entirely different objectives, is very satisfactory.

Russell and Brown[25] have recently measured the relative reactivity of the side-chains of toluene, *iso*propylbenzene, and *tert.*-butylbenzene towards photochemical chlorination, and have pointed out the close analogy between their results and those of Gregg and Mayo,[21] and of Kooyman.[22]

Ratios of Isomerides.—In Table 14 the relative amounts of the 2-, 3-, and 4-isomerides resulting from the phenylation of toluene, ethylbenzene, *iso*propylbenzene, and *tert.*-butylbenzene are compared with the relative amounts of the *ortho-*, *meta-*, and *para-*isomerides resulting from the nitration of these hydrocarbons (cf. Ingold[26]). The isomer ratios for the nitration of *iso*propylbenzene were measured by Brown and Bonner,[27] and those for the phenylation of *tert.*-butylbenzene by Cadogan, Hey, and Williams.[1a]

TABLE 14.

		PhMe	PhEt	$\mathrm{PhPr^i}$	$\mathrm{PhBu^t}$
Nitration	*ortho* (%)	57	55	30	11·8
	meta (%)	3	0	7·7	8·7
	para (%)	40	45	62·3	79·5
Phenylation	2- (%)	66·5	53	31	24
	3- (%)	19·2	28	42	49
	4- (%)	14·3	19	27	27

It is of interest that in both reactions the characteristic patterns of electrophilic and homolytic substitution, respectively, are shown by toluene and ethylbenzene, while in both reactions the proportion of the *ortho*(2)-isomer is drastically reduced when substitution is effected in the nuclei of *iso*propylbenzene and *tert.*-butylbenzene. This reduction has been attributed to the steric effect of the *iso*propyl and *tert.*-butyl groups, which inhibits substitution at the adjacent positions (Ingold;[26] Cadogan, Hey, and Williams[1a]).

Partial Rate Factors.—The rate of nuclear phenylation of ethylbenzene, relative to that of benzene as unity, is given by ${}^{\mathrm{PhEt}}_{\mathrm{PhNO_2}}K \times {}^{\mathrm{PhNO_2}}_{\mathrm{PhH}}K$, *i.e.*, 0·31 × 4·0 (cf. Part II[6]) = 1·24. In the same manner, the rate of nuclear phenylation of *iso*propylbenzene, relative to that of benzene as unity, is calculated to be 0·87. The competitive experiments with mixtures of pyridine with ethylbenzene and with *iso*propylbenzene lead to values of ${}^{\mathrm{PhEt}}_{\mathrm{PhH}}K$ and ${}^{\mathrm{Ph}iso\mathrm{Pr}}_{\mathrm{PhH}}K$ of 1·22 and 0·86 respectively [*e.g.*, ${}^{\mathrm{PhEt}}_{\mathrm{PhH}}K = {}^{\mathrm{PhEt}}_{\mathrm{PyH}}K \times {}^{\mathrm{PyH}}_{\mathrm{PhH}}K = 1{\cdot}175 \times 1{\cdot}04$ (cf. Part II[6])], thus confirming the values obtained by means of competitive experiments with nitrobenzene. These relative rates indicate that the behaviour of ethylbenzene is akin to that of toluene, the overall effect being one of mild activation. *iso*Propylbenzene, on the other hand, behaves like *tert.*-butylbenzene, the steric effect producing an overall deactivation of the nucleus. Partial rate factors for the phenylation of ethylbenzene and *iso*propylbenzene are calculated from the relative rates together with the mean values

---

[25] Russell and Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 4578.

[26] Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 1953, p. 258.

[27] Brown and Bonner, *J. Amer. Chem. Soc.*, 1954, **76**, 605.

obtained by spectrographic analysis for the ratio of isomerides resulting from nuclear phenylation. These factors, together with those obtained for toluene and *tert.*-butylbenzene (Part VII [1a]) are given in Table 15.

TABLE 15. *Partial rate factors for phenylation.*

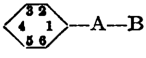
	F_o	F_m	F_p
Toluene	3·5	1·0	1·4
Ethylbenzene	1·97	1·04	1·41
*iso*Propylbenzene	0·81	1·1	1·41
tert.-Butylbenzene	0·63	1·28	1·41

The effects of the various alkyl groups on nuclear homolytic substitution are best assessed by consideration of the values of F_p, since these must be free from any complication arising from steric effects. This leads to the conclusion that, steric effects excepted, all of the alkyl groups influence the course of substitution in the same way and to the same extent, and that the degree of activation occasioned by them is, to a first approximation, independent of the alkyl group. The theoretical implication of this result is either (*a*) that the β-methyl groups are too remote from the aromatic nucleus for their influence to be significant, especially since no conjugation exists between them and the nucleus, or (*b*) that they exert a slight activating effect which is exactly compensated by the removal of the α-hydrogen atoms which their presence necessarily entails. These α-hydrogen atoms influence the nucleus by hyperconjugation, and their removal therefore results in some loss of activation. It is not easy to make a decision between these two possibilities, but on balance (*b*) seems the more likely explanation, partly on account of the inherent improbability of the complete lack of any effect required by (*a*), and partly because the activation of toluene relative to benzene suggests that the hyperconjugation of the α-hydrogen atoms in toluene is a real phenomenon.

Calculations by Wheland [28] of atom localisation energies for substitution in toluene are available for comparison with these experiments. Wheland calculated them for free-radical substitution in toluene and, by substitution of these in the Arrhenius equation, the following partial rate factors are obtained:

$$F_o = 1{\cdot}48 \qquad F_m = 0{\cdot}93 \qquad F_p = 1{\cdot}51$$

The agreement with experiment is good, especially since the predicted values depend exponentially on a small energy difference. Although no atom localisation energies have been derived for the remaining members of the series of alkylbenzenes, certain predictions can be made by consideration of the electronegativities of the alkyl substituents. Wheland considered the generalised structure:



and took into account only the π-electrons. In the secular equations the electronegativities of the various atoms were represented by dimensionless parameters δ_B, δ_A, δ_1, δ_2 - - - -. For toluene, if δ_A, δ_1, and δ_2 are put equal to —0·3, —0·1, and —0·01 respectively, and all the other quantities δ are considered to be zero, the equations give rise to atom localisation energies which give the above values for the partial rate factors for homolytic substitution and also give reasonable values for the partial rate factors for electrophilic substitution. Passing along the series of alkylbenzenes, there is a considerable change in the electronegativities of the substituents, and this gives rise to considerably altered partial rate factors for heterolytic substitution. In order to take account of this change the values —2·0 and —0·5 were used for the parameters δ_A and δ_1 in Wheland's equations for toluene. The increased steric effect was accommodated by the introduction of an increment of energy $E_0(= 0{\cdot}02$ kcal. mole$^{-1})$ which was added to the atom localisation energy for the *ortho*-position. The values were chosen so as to give a reasonable approximation to the experimental partial rate factors for the nitration of *iso*propylbenzene. When they were used in Wheland's equations for homolytic substitution the following partial rate factors were

---

[28] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

derived which correspond closely with the experimentally determined figures for *iso*-propylbenzene :

$$F_o = 0{\cdot}49 \qquad F_m = 0{\cdot}9 \qquad F_p = 1{\cdot}51$$

These values are in accord with the experimental result that free-radical substitution in the *meta*- and the *para*-position of alkylbenzenes is largely independent of the nature of the alkyl group.

Thanks are accorded to the Department of Scientific and Industrial Research for the award of a Maintenance Grant to B. W. P.

KING'S COLLEGE (UNIVERSITY OF LONDON),
STRAND, LONDON, W.C.2.

[*Received, November 4th,* 1955.]