22. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part III.*[1] *Partial Rate Factors for the Acid-catalysed Bromination of* tert.*-Butylbenzene by Hypobromous Acid.*

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The products of acid-catalysed reaction of *tert.*-butylbenzene with hypobromous acid in 50% aqueous dioxan have been determined, by isotopic dilution, as *o*-bromo-*tert.*-butylbenzene, 37·7%; *m*-, 7·2%; *p*-, 53·2%; bromobenzene, 1·9%. Negligible side-chain substitution accompanies the reaction, the kinetic form of which is $-d[BrOH]/dt = k[ArH][BrOH][H^+]$, with $k = 435$ l.^{2} mole^{-2} min.$^{-1}$ at 25°, 12 times greater than for benzene. These results show that, in a comparison of *tert.*-butylbenzene with toluene, the *para*-position is less reactive, and the *meta*-position is about equally reactive. Significant electrophilic displacement of the *tert.*-butyl group by bromine occurs during the reaction. The results are discussed with particular reference to the hyperconjugative power of alkyl groups, and to the effect of steric hindrance in determining the reactivity of the *ortho*-position. Some nitro-derivatives of the bromo-*tert.*-butylbenzenes are described.

IN Part II,[1] partial rate factors for the acid-catalysed bromination of toluene by hypobromous acid were discussed. It was suggested that there is less steric hindrance to the entry of Br^+ than of NO_2^+ *ortho* to an alkyl group. A consequence of this would be that the bromination of *tert.*-butylbenzene under these conditions would give a substantial proportion of *o*-bromo-*tert.*-butylbenzene, whereas it is known that neither molecular bromination [2] nor nitration [3] gives much *ortho*-derivative.

The present paper describes the use of the technique of isotopic dilution for determination of the proportions of the products formed in the bromination of *tert.*-butylbenzene, with hypobromous acid as a source of electrophilic halogen, under the conditions that were used in the earlier investigation. The reagent has been shown to be the same positively charged halogenating species, either Br^+ or $BrOH_2^+$.

EXPERIMENTAL

Materials and Methods.—These have mostly been described in Part II.[1] *tert.*-Butylbenzene, obtained by careful fractionation of a commercial specimen, had b. p. 54°/10 mm. *p*-Bromo-*tert.*-butylbenzene was prepared (*a*) by using Derbyshire and Waters's method,[4] in which case the crude bromo-*tert.*-butylbenzene mixture had f. p. 2·7°, or (*b*) by following Cohen and Dakin's procedure [5] for the bromination of benzene with pyridine as catalyst, in which case the crude bromo-*tert.*-butylbenzene, b. p. 100—102°/12 mm., had f. p. 8·6°. Fractional freezing, followed by crystallisation from ethanol at low temperature, gave material of f. p. 15·7°. *m*-Bromo-*tert.*-butylbenzene was prepared by Crawford and Stewart's method.[6] In our hands,[7] the intermediate 1-acetamido-2-bromo-4-*tert.*-butylbenzene had m. p. 158° after recrystallisation from benzene or from ethanol. The final product had b. p. 95—97°/10 mm., n_D^{25} 1·5335 (Found: C, 56·6; H, 6·3. Calc. for $C_{10}H_{13}Br$: C, 56·3; H, 6·1%).

o-Bromo-*tert.*-butylbenzene, also prepared as described by Crawford and Stewart,[6] had b. p. 102°/14 mm., n_D^{25} 1·5410. Bromobenzene, obtained by fractionation of a commercial specimen, had b. p. 157°/758 mm.

Nitration of o-*Bromo*-tert.*-butylbenzene.*—*o*-Bromo-*tert.*-butylbenzene was heated at 80° with

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[1] Part II, de la Mare and Harvey, *J.*, 1956, 36.

[2] Robertson, de la Mare, and Swedlund, *J.*, 1953, 782.

[3] (*a*) Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **169**, 291; (*b*) Nelson and Brown, *J. Amer. Chem. Soc.*, 1951, **73**, 5605.

[4] Derbyshire and Waters, *J.*, 1950, 564.

[5] Cohen and Dakin, *J.*, 1899, **75**, 894.

[6] Crawford and Stewart, *J.*, 1952, 4443; cf. Cadogan, Hey, and Williams, *J.*, 1954, 3352.

[7] Cf. Gelzer, *Ber.*, 1888, **21**, 2944.

1½ equivs. of 98% nitric acid in a mixture of sulphuric acid (35% v/v) and glacial acetic acid. The product was poured into water, and the solid material was filtered off and chromatographed in benzene on alumina. Early fractions containing unchanged starting material and material of low m. p. were rejected. The main product, obtained in 50% yield, was recrystallised from pentane, giving *1-bromo-2-*tert.*-butyl-4-nitrobenzene*, m. p. 118° (Found: C, 46·7; H, 5·0; N, 5·3; Br, 31·3. $C_{10}H_{12}O_2NBr$ requires C, 46·5; H, 4·7; N, 5·4; Br, 31·0%). The position of the nitro-group was proved in the following way. The nitro-compound (7·5 g.) was heated with 30% nitric acid in 3 sealed tubes for 50 hr. at 160°. From the product there was recovered, in about 3% yield, 2-bromo-5-nitrobenzoic acid, m. p. and mixed m. p. 181° (authentic specimen obtained by nitration of *p*-bromobenzoic acid [8]) (Found, for the material obtained by oxidation: C, 34·5; H, 2·2; N, 5·9; Br, 33·5. Calc. for $C_7H_4O_4NBr$: C, 34·2; H, 1·6; N, 5·7; Br, 32·5%). Model experiments showed that 2-bromo-4-nitro-1-*tert.*-butylbenzene,[9] m. p. 94°, could be similarly oxidised, though in equally poor yield, to 2-bromo-4-nitrobenzoic acid, m. p. 166°.

Nitration of m-*Bromo-*tert.*-butylbenzene.*—*m*-Bromo-*tert.*-butylbenzene was heated at *ca.* 80° with 2 equivs. of 98% nitric acid dissolved in a mixture of sulphuric acid (50% v/v) and glacial acetic acid. The mixture was poured into water, and *1-bromo-5-*tert.*-butyl-2(?) : 4-dinitrobenzene* filtered off and recrystallised from pentane (30% yield; m. p. 92°) (Found: C, 40·6; H, 3·6; N, 9·9; Br, 25·8. $C_{10}H_{11}O_4N_2Br$ requires C, 39·6; H, 3·6; N, 9·2; Br, 26·4%).

Nitration of p-*Bromo-*tert.*-butylbenzene.*—*p*-Bromo-*tert.*-butylbenzene (5 g.) was heated for 6 hr. at *ca.* 80° with 98% nitric acid (15 ml.) in glacial acetic acid containing 15% (v/v) of sulphuric acid. The mixture was left for 24 hr. and then poured into ice and excess of sodium hydroxide solution. The organic material was recovered by extraction with ether, which was then removed by distillation. The remaining yellow oil was chromatographed on alumina, pentane being used as solvent. The earliest fractions contained much unchanged material and were rejected. The later fractions contained material of m. p. increasing from 111° to 118°. This was recrystallised four times from pentane, and gave a small quantity of slightly impure *p*-bromonitrobenzene, m. p. 124°, not depressed on admixture with authentic *p*-bromonitrobenzene, m. p. 127° (Found: C, 35·7; H, 2·1. Calc. for $C_6H_4O_2NBr$: C, 35·6; H, 2·0%).

Kinetics of Bromination.—The following is an example of a typical kinetic run. From a solution of *tert.*-butylbenzene (0·00564M), hypobromous acid (0·0028M), and perchloric acid (0·0221M), all in 50% dioxan, aliquot parts (25 ml.) were removed at intervals for titration with 0·00113N-sodium thiosulphate, starch being used as indicator. A blank, with *tert.*-butylbenzene omitted, was run side by side with this measurement.

Reaction			Reaction			Blank			Blank		
Time (min.)	Titre (ml.)	10^2k_1 (min.$^{-1}$)	Time (min.)	Titre (ml.)	10^2k_1 (min.$^{-1}$)	Time (min.)	Titre (ml.)	10^2k_1 (min.$^{-1}$)	Time (min.)	Titre (ml.)	10^2k_1 (min.$^{-1}$)
0	12·40	—	12·20	7·00	4·69	0	13·41	—	13·00	13·14	0·16
3·12	10·43	5·48	15·38	6·16	4·55	3·80	13·33	0·15	16·57	13·08	0·16
6·03	9·05	5·22	18·25	5·57	4·38	8·82	13·22	0·16	20·33	13·02	0·15
9·13	7·90	4·94									

The following results show the effect of varying the initial concentrations of reactants. The second-order rate-coefficients, k_2, are initial values, corrected for the decomposition of the blank.

(i) *tert.*-Butylbenzene, *ca.* 0·008M; $HClO_4$, 0·014M.

BrOH (M)	0·0018	0·0020	0·0025
k_2 (l. mole^{-1} min.$^{-1}$) ...	6·07	6·20	6·25

(ii) $HClO_4$, 0·016-M; BrOH, *ca.* 0·0020M.

tert.-Butylbenzene (M)	0·0038	0·0054	0·0077	0·0090
k_2 (l. mole^{-1} min.$^{-1}$) ...	6·86	6·92	6·99	6·98

(iii) *tert.*-Butylbenzene, 0·0060—0·0090M; BrOH, *ca.* 0·0020M.

$HClO_4$ (M)	0·0034	0·0065	0·0097	0·0113	0·0129	0·014	0·016	0·0172	0·0221
k_2 (l. mole^{-1} min.$^{-1}$) ...	1·41	2·85	4·01	4·97	5·65	6·20	6·92	7·56	10·1
k_2/H$^+$ (l.^{2} mole^{-2} min.$^{-1}$)	415	438	413	440	438	443	433	440	457

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[8] Holleman and De Bruyn, *Rec. Trav. chim.*, 1901, **20**, 210.

[9] Shoesmith and Mackie, *J.*, 1928, 2336.

These results show that the kinetic form is in accordance with the equation $-d[BrOH]/dt = k[ArH][BrOH][H^+]$; the mean value of k is 435 l.^{2} mole^{-2} min.$^{-1}$.

Proportions of Products formed in the Bromination of tert.-*Butylbenzene*.—(i) p-*Bromo*-tert.-*butylbenzene*. Labelled *p*-bromo-*tert*.-butylbenzene was prepared as in method (*a*), $NH_4{}^{82}Br$ first having been shaken with the bromine used in the reaction. The product after recrystallisation from ethanol at low temperatures had f. p. 15·7°.

To a solution (10 l.) of hypobromous acid and perchloric acid (0·05M) in 50% dioxan was added *tert*.-butylbenzene (19·18 g.). After 20 min. the decrease in titre of a 25 ml. portion, corrected for the small blank decomposition determined in a parallel experiment, was 5·20 ml. of 0·0795N-sodium thiosulphate. The reaction was stopped by adding formic acid. To 9770 ml. of the reaction mixture, which from the decrease in titre should contain 17·25 g. of mixed bromo-*tert*.-butylbenzenes, was added labelled *p*-bromo-*tert*.-butylbenzene (2·37 g.). The mixture was then extracted with ether; the ether extract was washed with water and fractionally distilled. There were recovered 15 g. (70%) of bromo-*tert*.-butylbenzene, which after fractional freezing and recrystallisation from ethanol had f. p. 15·7°; a solution in ethanol (0·0498M) had an activity of 251 counts/min.; at the same time, a solution (0·00881M) of the original labelled *p*-bromo-*tert*.-butylbenzene had a count of 217 counts/min., whence 9·19 g. (53·3 ± 1·4%) of *p*-bromo-*tert*.-butylbenzene were produced.

(ii) o-*Bromo*-tert.-*butylbenzene*. The reaction mixture contained 0·0166N-perchloric acid, 0·00991M-*tert*.-butylbenzene, and 0·00345M-^{82}BrOH. After 20 min., the fall in the titre of a 25 ml. sample, corrected for blank decomposition, was 5·95 ml. of 0·0176N-sodium thiosulphate. The reaction was stopped with formic acid. To 1830 ml. of solution, which should have contained 0·815 g. of mixed bromo-*tert*.-butylbenzenes, were added 10·15 g. of inactive *o*-bromo-*tert*.-butylbenzene. The crude bromo-*tert*.-butylbenzene mixture was recovered as before (7·6 g.), and nitrated as described above for *o*-bromo-*tert*.-butylbenzene. The crude derivative (6 g.) was chromatographed and recrytallised from pentane to constant m. p. and specific activity. To the final product (1 g.) was added 0·1 g. of the crude product obtained by nitrating a mixture of *p*- and *m*-bromo-*tert*.-butylbenzene under similar conditions, in order to ensure removal, by dilution, of any trace of active isomeric nitro-compounds. Recrystallisation to m. p. 118° gave material unchanged in specific activity (152 counts/min.; 0·0332M). The original hypobromous acid was counted as lithium bromide; 432 counts/min. (0·00268M) at the time relevant for comparison. Hence 0·308 g. (37·7 ± 0·5%) of *o*-bromo-*tert*.-butylbenzene had been produced in the reaction.

(iii) m-*Bromo*-tert.-*butylbenzenc*. The general procedure was as for the *o*-isomer. The reaction mixture contained 0·843 g. of active bromo-*tert*.-butylbenzenes, to which were added 11·45 g. of inactive *m*-bromo-*tert*.-butylbenzene. The recovered material was counted as bromo-*tert*.-butyldinitrobenzene, m. p. 92°, specific activity (unchanged by recrystallisation), 151 counts/min. (0·0330M), compared with 1423 counts/min. (0·00164M) for lithium bromide derived from the original hypobromous acid. Thus 0·0606 g. (7·2 ± 0·1%) of *m*-bromo-*tert*.-butylbenzene was produced in the reaction.

(iv) *Bromobenzene*. To a reaction mixture which should, from the fall in titre, have contained 1·36 g. of mixed active bromo-*tert*.-butylbenzenes, and other brominated products, were added 12·74 g. of bromobenzene. This was recovered by extraction and fractionation as before, giving 6·5 g. of b. p. 157°/760 mm. The specific activity was determined, and the material was fractionated twice with addition each time of 2 g. of the inactive mixture of bromo-*tert*.-butylbenzenes, f. p. 8·6°, obtained by method (*b*) above, to act as a hold-back carrier. The activity fell from 486 (0·0953M) to 183 and 182 counts/min. The product was then nitrated for 2—3 hr. at *ca*. 80° with 1 equiv. of 98% nitric acid in glacial acetic acid containing 15% v/v of sulphuric acid. The crude product was recovered and chromatographed on alumina, with ethanol as solvent. The final product had activity 193 counts/min. (0·0953M). The original hypobromous acid, counted as lithium bromide, had activity 232 counts/min. (0·000176M). Hence the reaction mixture contained 0·0197 g. (1·9 ± 0·03 mol. %) of bromobenzene.

In a preliminary experiment, the crude bromobenzene was not, before nitration, distilled from a hold-back carrier, and the calculation suggested that 2·5 mol. % of bromobenzene had been produced. This result is too high, in our view, because the following reaction occurs to a significant extent:

$$p\text{-Bu}^t\cdot C_6H_4{}^{82}Br + NO_2^+ \longrightarrow p\text{-}O_2N\cdot C_6H_4{}^{82}Br + tert.\text{-}Bu^+$$

Contamination of the diluted bromobenzene with only a very small proportion of undiluted *p*-bromo-*tert.*-butylbenzene, followed by the above reaction, would give *p*-bromonitrobenzene of activity spuriously high for a direct dilution-analysis for bromobenzene.

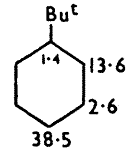
DISCUSSION

The independently determined molecular proportions of products of bromination of *tert.*-butylbenzene, estimated by isotope dilution, add up to 100·1%, *i.e.*, they account, within experimental error, for all the hypobromous acid consumed in the reaction. The following rounded values have been used in the following discussion :

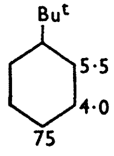
o-bromo-*tert.*-butylbenzene, 37·7% ; *m*- 7·2% ; *p*- 53·2% ; bromobenzene, 1·9%.

Each of these figures is, on grounds of statistical fluctuations in the counting rate, subject to a probable error as indicated in the experimental section.

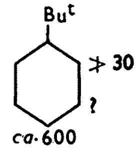
The kinetic form of the reaction makes it clear that the reagent is, as in the similar work on toluene, a positively charged brominating species, either Br^+ or $BrOH_2^+$. Combination of the relative rates of reaction of benzene and *tert.*-butylbenzene with these isomeric proportions gives the values, shown on the annexed formulæ, for the partial rate factors in the bromination, by this reagent, of *tert.*-butylbenzene. For comparison, are given values for nitration,[3] and, incompletely, for bromination by molecular bromine.[2] The similarity in general pattern between bromination and nitration by positive entities, noted in Part II for toluene, is here repeated, and the contrast between bromination by positive and by molecular bromine is almost equally marked. The reactions of the two positive reagents are almost equally selective, steric hindrance being neglected, as is indicated by the approximate equality of the ½*m* : *p* ratios.



Br^+ or $BrOH_2^+$



NO_2^+



Br_2 *

* These values, and the corresponding values given in Part II for toluene, are a composite of the isomeric proportions established for molecular bromination[2] and the rate measurements for iodine-catalysed bromination established by Berliner and Bondhus.[10] They may later need revision, when rate and product measurements have been made under similar conditions.

Steric Hindrance.—The conclusion, developed in Part II, that there is greater hindrance to the entry of NO_2^+ than of Br^+ *ortho* to an alkyl group, because of the sideways overlap between the entering nitro-group and the *ortho*-substituent, is amply confirmed by the present investigation, and should be contrasted [1] with the situation existing for molecular bromination.[11] In the case of toluene, the ½*o* : *p* ratio is 1·29 for bromination by positive bromine, but in nitration is only 0·72. It is fair to ascribe such a difference, in first approximation, to steric hindrance, since differential inductive effects, which may be important in determining the absolute value for each separate reaction, are likely not to be very different when the reactions of two positively charged reagents, such as Br^+ and NO_2^+, are compared for the same aromatic compound. The free-energy difference between bromination and nitration of toluene, to be ascribed to steric hindrance on these assumptions, is 0·31 kcal./mole from the above ratios.

For *tert.*-butylbenzene, the corresponding rate ratios are 0·37 and 0·07 respectively, and the free-energy difference corresponding to these figures is 0·87 kcal./mole. Since, in

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[10] Berliner and Bondhus, *J. Amer. Chem. Soc.*, 1948, **70**, 854.
[11] Holleman, *Chem. Rev.*, 1925, **1**, 187.

aromatic substitutions, it is usually found that changes in rate, and hence in free energy, represent very largely changes in energy of activation, the above differences may be taken as representing fairly closely the differences in energy of activation resulting from steric hindrance in these reactions. It is obviously reasonable that the value for the methyl group should be considerably less than that for the *tert.*-butyl group.

Hyperconjugation.—Comparison of partial rate factors for *para*- and *meta*-substitution in toluene and *tert.*-butylbenzene provide further material relevant to the conjugative effects of alkyl groups in the transition states of these reactions. In the present experiments, the rates of *meta*-substitution fall in the order expected, on the basis of the inductive effects of the substituents, namely, $Bu^t : Me : H = 2{\cdot}6 : 2{\cdot}5 : 1$. The same sequence of reactivities has been observed in other aromatic substitutions in which the *meta*-position is activated by alkyl groups, as, for example, in the iodination by I^+ of *p*-alkylphenols and of *p*-alkylanilines.[12] The differences between the *meta*-activating power of *tert.*-butyl and methyl substituents was larger in these cases than in that studied in the present work; the present comparison is in some ways more direct, since the aromatic ring is not also activated by other powerfully *op*-directing substituents.

The rates of *p*-bromination, in the present series of experiments, fall clearly in the order, $Me > Bu^t$, required if hyperconjugative electron release were the dominant electronic requirement of the system. The rate sequence, $H = 1$, $Me = 59$, $Bu^t = 38{\cdot}5$, represents differences in free energy of activation, associated with change in structure of the reactant, similar in magnitude to those observed in other examples in which hyperconjugation is considered to be important, *e.g.*, in the alcoholysis in ethanol of the *p*-alkyldiphenylmethyl chlorides,[13] $H = 1$, $Me = 23{\cdot}4$, $Bu^t = 18{\cdot}6$.

Not many aromatic substitutions involving positive ions have been examined sufficiently closely to enable one to be sure whether the *p*-methyl group is superior in activating power to the *p-tert.*-butyl group. In mercuration [14] the differences are apparently rather small, though definitely in the order required for the dominance of hyperconjugation. In nitration, it has been reported [2] that the inductive effect predominates. It is clear, however, that in aromatic substitution, as in many other reactions, alkyl groups are very closely spaced in their power of electron release, and inductive effects combine with hyperconjugative effects to give sequences which differ quantitatively and even qualitatively according to the conditions of reaction. Thus [13] the rate ratio $Me : Bu^t$ for the alcoholysis of the *p*-alkyldiphenylmethyl chlorides is $23{\cdot}4 : 18{\cdot}6$; for hydrolysis of the same compounds in 50% acetone, the ratio is $21{\cdot}4 : 10{\cdot}9$. Again, in the alkaline hydrolysis of *p*-alkylbenzoates,[15] the inductive order was observed in 56% acetone, but the hyperconjugation order was observed in 85% ethanol.

Displacement of the tert.*-Butyl Group.*—The small proportion of bromobenzene (1·9 moles %) detected in the products of bromination is, in the authors' opinion, significant. Care was taken, by careful fractionation, to show that benzene was absent from the starting material, though even the crude commercial *tert.*-butylbenzene was shown, by infrared examination, to contain only insignificant amounts of benzene.* The recovered *p*-nitrobromobenzene was very carefully recrystallised to constant specific activity, and was then scavenged with inactive carrier to hold back any traces of active contaminants; this procedure hardly affected the specific activity.

There are no cases previously recorded, so far as we are aware, in which a *tert.*-butyl group has been displaced from *tert.*-butylbenzene by an electrophilic reagent. In molecules in which substitution is rather more hindered, however, displacement of the *tert.*-butyl

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* With a rate ratio for *tert.*-butylbenzene : benzene of 12 : 1, it would require the presence of nearly 10% of benzene to give 1·0% of bromobenzene in the product.

[12] Berliner and Berliner, *J. Amer. Chem. Soc.*, 1954, **76**, 6179; Berliner, Berliner, and Nelidow, *ibid.*, p. 507.

[13] Hughes, Ingold, and Taher, *J.*, 1940, 945.

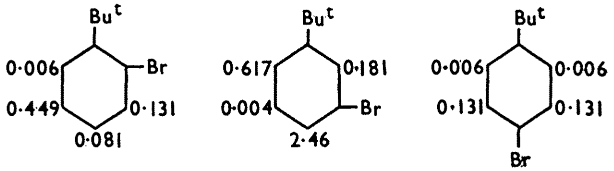
[14] Brown and McGary, *J. Amer. Chem. Soc.*, 1955, **77**, 2310.

[15] Berliner, Beckett, Blommers, and Newman, *ibid.*, 1952, **74**, 4940.

group has been observed. Thus it has been recorded [16] that the bromination, in carbon tetrachloride with iron as catalyst, of 1 : 3 : 5-tri-*tert.*-butylbenzene gives a 71% yield of 1-bromo-3 : 5-di-*tert.*-butylbenzene. It is interesting that nitration of the same compound gives, in 55% yield, 1 : 3 : 5-tri-*tert.*-butyl-2-nitrobenzene; apparently attack by bromine is, in that system, more favourable than attack by the nitronium ion for removal of the *tert.*-butyl group. Similar results had earlier been obtained for bromination [17] and nitration [18] of other polyalkylbenzenes.

The absolute rate of displacement of a *tert.*-butyl group from *tert.*-butylbenzene is rather faster than that of displacement of a proton from benzene. The inductive electron-release by the *tert.*-butyl group to the carbon atom to which it is attached must, of course, be considerable, so it would be consistent to believe that the displacement of a proton is in fact rather more difficult that displacement of a *tert.*-butyl group from a similarly activated position.

*Nitration of the Bromo-*tert.*-butylbenzenes.*—The partial rate factors recorded for the nitration of *tert.*-butylbenzene [3a] and of bromobenzene [19] allow estimates to be made for the relative reactivities of the various positions in the bromo-*tert.*-butylbenzenes, additivity being assumed for the effects of the substituents on the free energies of activation for substitution at the various positions.[20] They are as indicated in the annexed formulæ.



Rel. total rate (PhH = 1) 0·11 0·54 0·046

The results which we have recorded are, as far as they go, in agreement with these predictions. Thus we have isolated the 4-nitro-derivative on nitration of 1-bromo-2-*tert.*-butylbenzene, the 5-position of which should be the most reactive. *m*-Bromo-*tert.*-butylbenzene should be more reactive than its *o*-isomer, and this accords with our observation that a dinitro-derivative, which we consider is 1-bromo-5-*tert.*-butyl-2 : 4-dinitrobenzene, is obtained easily from this compound. *p*-Bromo-*tert.*-butylbenzene should be less reactive than either of its isomers; and this accords with our observations. We have, indeed, isolated nearly pure *p*-bromonitrobenzene in poor yield from the nitration of *p*-bromo-*tert.*-butylbenzene, together with much unchanged starting material, and this confirms the deduction made above on the basis of isotopic dilution experiments, that significant nitro-de-*tert.*-butylation occurs with this compound.

Some analyses were made in part by Mr. A. V. Winter of this Department, and some others by the analytical laboratories, Department of Chemistry, Imperial College of Science and Technology. We are indebted to Mr. T. J. Collins for the preparation of several of the intermediates, and to Mr. H. Smith for the preparation of authentic 2-bromo-5-nitrobenzoic acid. We greatly appreciate the continued interest of Professor E. D. Hughes, F.R.S., and Professor C. K. Ingold, F.R.S.

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[16] Bartlett, Roha, and Stiles, *J. Amer. Chem. Soc.*, 1954, **76**, 2349.
[17] Hennion and Anderson, *ibid.*, 1946, **68**, 424.
[18] Battegay and Kappeler, *Bull. Soc. chim., France*, 1924, **35**, 989.
[19] Roberts, Sanford, Sixma, Cerfontain, and Zagt, *J. Amer. Chem. Soc.*, 1954, **76**, 4525.
[20] Bradfield and Jones, *Trans. Faraday Soc.*, 1941, **37**, 726.