

The semicarbazone was transformed into the ketone, b.p. 156° at 3 mm., n_D^{20} 1.5748.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.66; H, 7.62. Found: C, 85.39; H, 7.29.

Each of the ketones was established to be of high purity by vapor phase chromatographic examination.

Rates of Benzoylation.—The rates of benzoylation were measured by the technique previously utilized for determining the rates of benzoylation of benzene and toluene.⁷ The reactions were run in duplicate. The rate constants reported in Table I are averages of these duplicate measurements with an average deviation no greater than $\pm 2\%$.

Relative Rates of Acetylation.—A solution of acetyl chloride-aluminum chloride complex in ethylene dichloride with excess acetyl chloride was added quickly to a vigorously stirred solution containing an excess of toluene and the second hydrocarbon. It was established that the temperature did not increase by more than 0.5°. An inert internal standard, 1,2,4-trichlorobenzene, was added to facilitate the determination of the actual concentrations of the products.

After 4 to 6 minutes, the reaction mixture was quenched in an ice-sodium hydroxide mixture. The organic layer was washed twice with water. The greater portion of the solvent was removed by distillation and the product concentrations determined by vapor phase chromatographic examination. The extent of reaction ranged from 80 to 90%. The relative rates were determined using the formula

$$\frac{k_A}{k_T} = \frac{\log A/A_0}{\log T/T_0}$$

The experimental results are summarized in Table VII. **Isomer Distributions.**—The composition of the products was determined utilizing a polyadipate substrate (Rubber Corporation of America polymeric BGA). In the acetylation products of isopropylbenzene and *t*-butylbenzene only two major peaks were observed, corresponding to the *meta* and *para* acetylation products. In the case of ethylbenzene, a minor peak at the position anticipated for the *ortho* isomer was observed. This peak was estimated from the area to be 0.3%, but no great precision is claimed for this analysis.

The major peaks ascribed to the *meta* and *para* isomers were isolated and identified as these isomers by infrared ex-

TABLE IX
RETENTION TIMES OF ALKYLACETO-^{a,b} AND -BENZO-
PHENONES^{a,c}

Compound	Temp., °C.	Retention time, min.			Separation, min.	
		<i>o</i> -	<i>m</i> -	<i>p</i> -	<i>o</i> - <i>m</i>	<i>m</i> - <i>p</i>
Methylacetophenone	165	8.0	10.4	11.7	2.4	1.3
Ethylacetophenone	175	7.1	10.1	12.1	3.0	2.0
Isopropylaceto- phenone	185		8.9	11.2		2.3
<i>t</i> -Butylacetophenone	195		8.1	11.0		2.9
Methylacetophenone	185	4.9	6.0	6.6	1.1	0.6
Ethylacetophenone	185	6.3	7.9	9.2	1.6	1.3
Isopropylaceto- phenone	185		8.9	11.2		2.3
<i>t</i> -Butylacetophenone	185		10.5	13.9		3.4
Methylbenzophenone	247	9.4	11.9	13.9	2.5	2.0
Ethylbenzophenone	247	10.9	15.4	19.4	4.5	4.5
Isopropylbenzo- phenone	247	10.9	16.2	22.0	5.8	5.3
<i>t</i> -Butylbenzophenone	247		17.0	24.8		7.4

^a Column: 2 m. RCA polymeric BGA on Celite. ^b Flow rate 125 cc. of helium per min. ^c Flow rate 350 cc. of helium per min.

amination. The characteristic absorption bands for *ortho* disubstituted benzenes (13–13.5 μ) were definitely absent in all the spectra.

The comparative examination of the infrared spectra of *m*- and *p*-alkyl-acetophenones exhibits an interesting shift of the absorption bands toward shorter wave lengths with increasing size of the alkyl groups (Table VIII).

Retention times of all the alkylacetophenones and benzophenones are summarized in Table IX. The retention times exhibit a consistent regularity and the separations improve with increasing size of the alkyl substituent.

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[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Relative Rates and Isomer Distributions in the Halogenation of *t*-Butylbenzene and Some of Its Derivatives. Partial Rate Factors for Non-catalytic Bromination and Chlorination in Acetic Acid¹⁻³

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The non-catalytic bromination of *t*-butylbenzene in 85% acetic acid at 25° yields 1.20% *o*-, 1.47% *m*- and 97.3% *p*-bromo-*t*-butylbenzene. Under these conditions the relative rate of bromination of benzene to *t*-butylbenzene is 1.00/138. These data provide the partial rate factors o_i 4.7, m_i 6.1 and p_i 806. Greater than 99% 2- and 3-bromo-4-*t*-butyltoluene are formed in the bromination of *p*-*t*-butyltoluene. The isomer distribution for the non-catalytic chlorination of *t*-butylbenzene in 99.9% acetic acid at 25° is 21.5% *o*-, 2.29% *m*- and 76.2% *p*-chloro-*t*-butylbenzene. Under these conditions the relative rate of chlorination of benzene to *t*-butylbenzene is 1.00/87.7. The partial rate factors for this reaction are o_i 56.6, m_i 6.02 and p_i 401. The chlorination of *p*-di-*t*-butylbenzene produces 28.6% *p*-chloro-*t*-butylbenzene and 71.4% 2-chloro-1,4-di-*t*-butylbenzene. The chlorination of *p*-*t*-butyltoluene yields 5.0% *p*-chlorotoluene and 95% 2- and 3-chloro-4-*t*-butyltoluene. The observed relative rates of chlorination of these *p*-alkyl-*t*-butylbenzenes, after correction for the chloro-de-*t*-butylation side-reaction, are in good agreement with the relative rates calculated on the basis of the partial rate factors.

That the electrophilic substitution reactions of toluene are correlated by the proposed simple

(1) Directive Effects in Aromatic Substitution. XL.
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(3) Based upon a thesis submitted by Leon M. Stock in partial fulfillment for the degree Doctor of Philosophy.

(4) Monsanto Chemical Co. Fellow, 1957–1958.

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linear relationship⁶⁻⁸ has been adequately confirmed.⁹ It has been suggested that the substitution reactions of other monosubstituted benzenes obey a similar relationship.^{6,7} Unfortunately, the number of quantitative experimental observations for compounds other than toluene is quite limited.

(6) H. C. Brown and K. L. Nelson, *THIS JOURNAL*, **75**, 6292 (1953).

(7) H. C. Brown and C. W. McGary, *ibid.*, **77**, 2300 (1955).

(8) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

(9) L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

Data were available, however, for the nitration, acid-catalyzed bromination, desilylation and deuteration reactions of *t*-butylbenzene.¹⁰ This compound therefore was selected for further study. The mercuration¹¹ and Friedel-Crafts acylation¹² results have been presented. In addition, it was desirable to have available the partial rate factors for the "selective" non-catalytic halogenation reactions.

Rate studies in the non-catalytic bromination of *t*-butylbenzene were first undertaken by de la Mare and Robertson.¹³ They observed that the relative rate of bromination of *t*-butylbenzene to toluene was 23/100 in 85% acetic acid at 24°. This result was confirmed in a later study.¹⁴ In addition, the reaction was shown to yield 92% *p*-bromo-*t*-butylbenzene by isotopic dilution techniques.¹⁴ The bromination of *t*-butylbenzene and toluene also has been studied in 85% acetic acid with sodium acetate catalyst.¹⁵ The observed relative rate was 18/100. A competitive examination of the relative rate in 92% acetic acid with iodine catalyst¹⁶ indicated the relative rate, *t*-butylbenzene to benzene, to be 115. Andrews and Keefer have investigated the zinc chloride-catalyzed bromination in acetic acid. A relative rate of approximately 130 was observed for *t*-butylbenzene compared to benzene.¹⁷

The chlorination reactions have received considerably less attention. The relative rate *t*-butylbenzene to toluene was determined to be 32/100 by examination of the time required for a 10% reaction in 99% acetic acid.¹⁸ More recently, Lerer and co-workers have examined the products of the electrophilic catalyzed chlorination of *t*-butylbenzene.¹⁸ These authors point out that their observations were most probably the result of selective dichlorination and isomerization of the monochloro-*t*-butylbenzenes initially produced.

Since no comprehensive examination of the halogenation was available, a detailed study of the rates and isomer distributions realized in these reactions was undertaken. It was desirable to avoid the problems associated with the catalytic reactions and to obtain data that were directly comparable with the information previously available for toluene.^{19,20} Accordingly, the selective non-catalytic reaction in acetic acid at 25.0° was selected for study.

Results

In order to avoid the kinetic difficulties associated with the bromination reaction^{19,21} the relative rates were established by the determination of the tenth-life of the reaction under standardized

conditions. Since *t*-butylbenzene and *p*-*t*-butyltoluene were soluble in 85% acetic acid, these compounds were compared to toluene in that solvent. Unfortunately, *p*-di-*t*-butylbenzene was not sufficiently soluble to permit its examination under the selected conditions. The experimental observations are reported in Table I.

TABLE I

TIME REQUIRED FOR 10% REACTION IN THE BROMINATION OF AROMATIC HYDROCARBONS IN 85% ACETIC ACID AT 25°

Compound	Concentration, <i>M</i>		<i>t</i> _{10%} min.
	[ArH]	[Br ₂]	
Benzene ^a	0.450	0.0425	77,000
Toluene ^a	.450	.0425	127
Toluene ^a	.200	.0200	409
<i>t</i> -Butylbenzene	.200	.0200	1,820
<i>p</i> - <i>t</i> -Butyltoluene	.200	.0200	156

^a Reference 19. The data there reported support the conclusion that the relative reactivities are not altered by a change in the solvent from 100% acetic to 85% aqueous acetic, or by moderate changes in the initial concentrations of the reactants.

The derived relative rate data are compared with the appropriate literature values in Table II.

TABLE II

RELATIVE RATES OF BROMINATION IN ACETIC ACID SOLVENTS

Compound	This study	Literature		
		Ref. 13, 14 ^a	Ref. 16 ^b	Ref. 17 ^c
Benzene	1.00		1.00	1.00
Toluene	605	(605)		148
<i>t</i> -Butylbenzene	138	139	115	129
<i>p</i> - <i>t</i> -Butyltoluene	1580			
<i>p</i> -Di- <i>t</i> -butylbenzene				90
3,5-Dimethyl- <i>t</i> -butylbenzene ^d		2.46 × 10 ⁸		
1,3,5-Tri- <i>t</i> -butylbenzene				7.7

^a In 85% acetic acid at 25°, toluene taken as 605. ^b In 92% acetic acid with iodine catalyst. ^c In acetic acid with zinc chloride catalyst, *k*₂ values compared. ^d Relative rate for mesitylene under these conditions, 1.89 × 10⁸, ref. 19.

The apparent high reactivity of *p*-*t*-butyltoluene led us to examine this reaction in some detail. It was demonstrated spectroscopically that the hydrocarbon was free of the highly reactive *meta* isomer. Whether the reaction time was measured from 0 to 10% or from 5 to 15% reaction, at the selected concentrations, it had only a minor influence on the tenth-life measurement. In addition, several check experiments revealed that side-chain substitution was not more than 2%. Since bromo-de-*t*-butylation (see below) does not occur under the conditions of this experiment, the observed tenth-life measurement apparently is real.

The necessary relative rate data for the chlorination reaction were obtained by measurement of the second-order rate constants for chlorination in 99.9% acetic acid. The kinetics observed for each compound were clearly second-order to 80% reaction. The rate constant for *p*-di-*t*-butylbenzene appeared to vary slightly with the initial concentration. Accordingly, the observed rate constants were averaged to obtain the mean value. The kinetic results are summarized in Table III.

The isomer distribution for the halogenation reactions was determined in reactions carried out

(10) These results are summarized in the following publication: L. M. Stock and H. C. Brown, *THIS JOURNAL*, **81**, 5621 (1959).

(11) H. C. Brown and M. Dubeck, *ibid.*, **81**, 5608 (1959).

(12) H. C. Brown and G. Marino, *ibid.*, **81**, 5611 (1959).

(13) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943).

(14) P. W. Robertson, P. B. D. de la Mare and B. F. Swedlund, *ibid.*, 782 (1953).

(15) E. Berliner and F. Berliner, *THIS JOURNAL*, **71**, 1195 (1949).

(16) E. Berliner and F. J. Bondhus, *ibid.*, **70**, 854 (1948).

(17) L. J. Andrews and R. M. Keefer, *ibid.*, **78**, 4549 (1956).

(18) M. Lerer, C. Fabre and G. Hugel, *Bull. soc. chim.*, [5] 173 (1957).

(19) H. C. Brown and L. M. Stock, *THIS JOURNAL*, **79**, 1421 (1957).

(20) H. C. Brown and L. M. Stock, *ibid.*, **79**, 5175 (1957).

(21) S. F. Mason, *J. Chem. Soc.*, 4329 (1958).

TABLE III

OBSERVED SPECIFIC SECOND-ORDER RATE CONSTANTS AND RELATIVE RATES FOR THE CHLORINATION OF ALKYL-BENZENES IN ACETIC ACID AT 25°

Compound	Concentration		$k_2 \times 10^4$, l. mole ⁻¹ sec. ⁻¹	Relative rate ^b	Relative rate ^c
	[ArH] ^M	[Cl ₂]			
Benzene ^d			0.0154	1.00	1.00
Toluene ^d			5.30	344	344
<i>t</i> -Butylbenzene	0.206	0.0343	1.34 ± 0.04		
	.200	.0339	1.36 ± .03	87.7	87.7
<i>p</i> -Di- <i>t</i> -butyl- benzene	.158	.0312	4.30 ± .10		
	.190	.0327	4.15 ± .07		
	.097	.0272	4.89 ± .02		
	.100	.0291	5.16 ± .02	300	215
<i>p</i> - <i>t</i> -Butyltoluene	.159	.0321	23.6 ± .3		
	.194	.0348	22.0 ± .2	1480	1410

^a The rate constant is not corrected for the cleavage reaction. ^b The relative rate is not corrected for the cleavage reaction and is the result of the mean observed specific rate constants. ^c The relative rate is corrected for the cleavage reaction. ^d Ref. 20.

under the conditions of the kinetic experiments. In each case, the product halo-*t*-butylbenzenes were analyzed by infrared spectroscopy. The results of the individual determinations and the mean values are summarized in Table IV.

TABLE IV

ISOMER DISTRIBUTION IN THE HALOGENATION OF *t*-BUTYLBENZENE

Reaction	Halo- <i>t</i> -butylbenzene, %		
	<i>o</i> -	<i>m</i> -	<i>p</i> -
Bromination ^a			
Detmn. A		1.40	98.60
Detmn. B		1.24	98.80
Detmn. C	1.06	1.29	97.65
Detmn. D	1.34	1.64	97.02
Mean ^b	1.20 ± 0.14	1.47 ± 0.18	97.3 ± 0.3
Chlorination ^c			
Detmn. A	23.3		74.4
Detmn. B	20.6	2.14	76.8
		2.34	
Detmn. C	20.6	2.43	77.0
		2.24	
Mean	21.5 ± 1.2	2.29 ± 0.1	76.2 ± 1.1

^a In 85% acetic acid at 25°. ^b Based on detmn. C and D; based on all experiments the normalized isomer distribution is: *o*- 1.20, *m*- 1.38 and *p*- 97.4. ^c In 99.9% acetic acid at 25°.

It is well known that the *t*-butyl group undergoes facile migration under the influence of electrophilic catalysts. Low yields and unexpected cleavage products have often been reported for the halogenation of aromatic compounds containing *t*-butyl substituents.²²⁻²⁹ Therefore, it appeared desirable to examine the product distribution in the halogenation of *p*-alkyl-*t*-butylbenzenes. In each case the reaction products were subjected to vapor phase chromatographic analysis. Under the mild

(22) W. Quist and N. Hohnberg, *C. A.*, **27**, 5726 (1933).(23) D. I. Legge, *THIS JOURNAL*, **69**, 2086 (1947).(24) E. P. Taylor and G. E. Watts, *J. Chem. Soc.*, 1123 (1952).(25) J. Thiec, *Ann. chim.*, (Paris), [12] **9**, 51 (1954).(26) P. D. Bartlett, M. Roha and R. M. Stiles, *THIS JOURNAL*, **76**, 2349 (1954).(27) M. Lerer, C. Fabre and G. Hugel, *Bull. soc. chim.*, [5] 1238 (1956).(28) F. Bell, *J. Chem. Soc.*, 120 (1958).(29) P. B. D. de la Mare, J. T. Harvey, M. Hassan and S. Varma, *ibid.*, 2756 (1958).

conditions employed in this study, *p*-*t*-butyltoluene did not undergo bromode-*t*-butylation. However, chlorode-*t*-butylation readily occurred with both *p*-*t*-butyltoluene and *p*-di-*t*-butylbenzene. The results are presented in Table V.

TABLE V

PRODUCT DISTRIBUTION IN THE HALOGENATIONS OF *p*-ALKYL-*t*-BUTYLBENZENES IN ACETIC ACID SOLVENTS AT 25°

Reaction	Product distribution, mole %	
	Substitution	Cleavage
Bromination of <i>p</i> - <i>t</i> -butyltoluene ^a		
Detmn. A	99.2	0.8
Detmn. B	100	.0
Mean	99.6	.4
Chlorination of <i>p</i> - <i>t</i> -butyltoluene ^b		
Detmn. A	95.1	4.9
Detmn. B	94.9	5.1
Mean	95.0	5.0
Chlorination of <i>p</i> -di- <i>t</i> -butylbenzene ^{c,d}		
Detmn. A	73.4	26.6
Detmn. B	69.4	30.6
Mean	71.4	28.6

^a In 85% acetic acid, substitution products: 2- and 3-bromo-4-*t*-butylbenzene; cleavage product: *p*-bromotoluene. ^b In 99.9% acetic acid, substitution products: 2- and 3-chloro-4-*t*-butyltoluene; cleavage product: *p*-chlorotoluene. ^c In 99.9% acetic acid, substitution product: 2-chloro-1,4-di-*t*-butylbenzene; cleavage product: *p*-chloro-*t*-butylbenzene. ^d Approximately 1% 2,5-dichloro-1,4-di-*t*-butylbenzene was formed concurrently.

Careful examination of the chromatograms indicated that the reaction products were free of significant concentrations of other compounds. It was established that *t*-butylbenzene was present only in trace quantities. On this basis, it was assumed (see Discussion) that the chlorode-*t*-butylation products resulted by a second-order kinetic process. The observed rate constants are then the sum of the constants for nuclear substitution and chlorode-*t*-butylation. Knowledge of the product ratios, Table V, permitted the evaluation of the rate constants for each of these reactions. The true rate constant for substitution in *p*-di-*t*-butylbenzene is 3.31×10^{-4} l. mole⁻¹ sec.⁻¹ and the rate constant for cleavage, 1.32×10^{-4} l. mole⁻¹ sec.⁻¹. Statistical correction for the presence of two substituents provided the rate constant per *t*-butyl group, 0.66×10^{-4} l. mole⁻¹ sec.⁻¹. A similar examination of the data for *p*-*t*-butyltoluene indicated the rate constants for nuclear substitution, 21.7×10^{-4} l. mole⁻¹ sec.⁻¹, and chlorode-*t*-butylation, 1.1×10^{-4} l. mole⁻¹ sec.⁻¹.

Discussion

The relative rate, *t*-butylbenzene to benzene, and the isomer distribution for the bromination reaction provide the partial rate factors σ_f 4.67, m_f 6.09 and p_f 806. There is a minor discrepancy between our value for p_f and that derived from the data of Robertson, de la Mare and Swedlund,¹⁴ 760. The variation arises from the different analytical results for the *para* isomer, 97.4 and 92%, respectively. This discrepancy, 6%, is minor with respect to the actual value for p_f . Conversely, an error of this magnitude in the analytical result for the *para* isomer has a significant influence on the *ortho* and

meta partial rate factors. Unfortunately, the reaction product was not analyzed for these isomers in the earlier study.¹⁴

Several methods for the independent evaluation of m_i are available. Since the extent of substitution *ortho* to the *t*-butyl group in *p*-*t*-butyltoluene is small, the relative rate of bromination depends largely on o_i^{Me} and $m_i^{\text{t-Bu}}$. On this basis, the relative rate is approximated

$$\frac{k_{p-t\text{-butyltoluene}}}{k_B} = \frac{2o_i^{\text{Me}}m_i^{\text{t-Bu}}}{6} = 1580 \quad (1)$$

The value for o_i^{Me} , 600, is known with some confidence.¹⁹

Solution of the equation 1 provides $m_i^{\text{t-Bu}}$ 7.9. This partial rate factor indicates 1.91% *meta* isomer in the bromination of *t*-butylbenzene. A more refined calculation, in which the reaction at the sites *ortho* to the *t*-butyl group is considered, predicts 1.88% *meta* substitution.

The *meta* partial rate factor also has been estimated through the comparison of the rate of bromination of *p*-*t*-butylanisole relative to the *p*-methyl derivative,³⁰ 1.18. On the basis of the m_i value for the methyl group, 5.5, determined in our earlier study,¹⁹ $m_i^{\text{t-Bu}}$ is estimated as 6.5. This value predicts 1.57% *m*-bromo-*t*-butylbenzene. These estimates for $m_i^{\text{t-Bu}}$ and % *meta* isomer suggest that the observed spectroscopic value, 1.47%, may be slightly low. However, the general agreement between these different approaches indicates that the error cannot be large.

The concentration of *o*-bromo-*t*-butylbenzene as determined spectroscopically is also quite small. In this case, the procedures for independent estimation provide quite variable results. The calculated values for o_i vary from 20, based on m_i 6.1 and the observed rate for *p*-*t*-butyltoluene, to less than 1.0 in the polysubstituted compounds reported in Table II. This variation is possibly the result of the large steric requirements of this group. It has been suggested previously that for reactions with large steric requirements substitution between two groups would not be in agreement with the prediction based on substitution *ortho* to a single substituent.^{17,20,31,32}

On the basis of this discussion, the *meta* and *para* partial rate factors appear to be free of significant experimental error. The value for o_i , although lacking independent confirmation, will be adopted with reservation. Fortunately, the latter value is not critical for the purposes of this study.

The partial rate factors for the chlorination reaction calculated from the relative rate and isomer distribution are o_i 56.6, m_i 6.0 and p_i 401. There is a minor discrepancy between our value for the relative rate of chlorination of *t*-butylbenzene and benzene and that reported in 1943.¹³ The difference could conceivably arise from the different techniques employed in each study.

The isomer distribution for the non-catalytic chlorination reaction has not been reported previously. For the ferric chloride-catalyzed chlori-

(30) In 99.9% acetic acid by measurement of the time required for 10 and 20% reaction; unpublished observations of L. M. Stock.

(31) H. C. Brown and C. W. McGary, *THIS JOURNAL*, **77**, 2310 (1955).

(32) L. J. Andrews and R. M. Keefer, *ibid.*, **78**, 5623 (1956).

nation in *t*-butylbenzene solvent, Lerer and his associates report the composition of the monochloro-*t*-butylbenzene fraction to be 39% *o*-, 23% *m*- and 38% *p*-. For the same reaction in carbon tetrachloride, they observed 59% *o*- and 41% *p*- isomer. Since, under the conditions of the experiment, considerable di- and trisubstitution products were obtained, the authors suggest that the monochloro fraction is not a reliable measure of the composition of the initial substitution products.¹⁸

Under the non-catalytic conditions employed in this study, 21.5% *o*- and 76.2% *p*-chloro-*t*-butylbenzene were obtained. Since significant concentrations of these isomers were formed, the spectroscopic procedure provided an accurate method of analysis. Thus, the partial rate factors derived from these experimental observations are adopted with confidence.

The *meta* isomer, however, represented a much smaller portion of the product and its analysis is less exact. To assess the precision of the observed value, the rates and product distributions in the chlorination of *p*-*t*-butyltoluene and *p*-di-*t*-butylbenzene were examined. The rate constants for nuclear substitution were employed to calculate the relative rates of chlorination (Table III). Each relative rate is the result of four experimental measurements and as such is subject to error. However, we have employed these data for evaluation of m_i for the chlorination reaction.

In the chlorination of *p*-*t*-butyltoluene, substitution presumably occurs in both the 2- and 3-positions. Hence, the approximation utilized for the bromination reaction 1 is not applicable and the complete expression must be employed (2)

$$\frac{k_{p-t\text{-butyltoluene}}}{k_B} = \frac{2o_i^{\text{Me}}m_i^{\text{t-Bu}} + 2o_i^{\text{t-Bu}}m_i^{\text{Me}}}{6} = 1410 \quad (2)$$

The utilization of this equation requires the values for o_i^{Me} , m_i^{Me} and $o_i^{\text{t-Bu}}$. The partial rate factors for substitution in toluene have been evaluated with precision²⁰ and the m_i value subsequently confirmed.³³ On the basis of $o_i^{\text{t-Bu}}$, 56.6, the expression 2 is solved to yield $m_i^{\text{t-Bu}}$ 6.3. The value predicts 2.39% *m*-isomer. The rate expression for *p*-di-*t*-butylbenzene (3) depends only on $o_i^{\text{t-Bu}}$ and $m_i^{\text{t-Bu}}$.

$$\frac{k_{p\text{-di-}t\text{-butylbenzene}}}{k_B} = \frac{4o_i^{\text{t-Bu}}m_i^{\text{t-Bu}}}{6} = 215 \quad (3)$$

Its solution indicates m_i 5.8, 2.20% *m*-chloro-*t*-butylbenzene. Finally, these two equations (2, 3) were coupled with the expression for substitution in *t*-butylbenzene (4).

$$\frac{k_{t\text{-butylbenzene}}}{k_B} = \frac{2o_i^{\text{t-Bu}} + 2m_i^{\text{t-Bu}} + p_i^{\text{t-Bu}}}{6} = 87.7 \quad (4)$$

Solutions of this set of simultaneous equations (2, 3, 4) provides $o_i^{\text{t-Bu}}$ 50.0, $m_i^{\text{t-Bu}}$ 6.4 and $p_i^{\text{t-Bu}}$ 413. These various procedures all provide values for $m_i^{\text{t-Bu}}$ well within the limits of experimental error and serve to confirm the spectroscopic value, 2.29%. Moreover, the latter solution provides partial rate factors which are in excellent agreement with those based on the spectroscopic pro-

(33) P. B. D. de la Mare and M. Hassan, *J. Chem. Soc.*, 1519 (1958).

cedure. The partial rate factors for the halogenation of toluene and *t*-butylbenzene are summarized in Table VI.

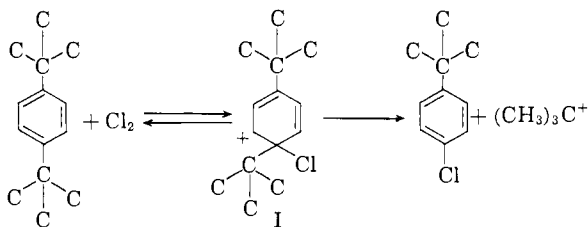
TABLE VI

Reaction	Toluene ^a				<i>t</i> -Butylbenzene			
	<i>o</i> -Me	<i>m</i> -Me	<i>p</i> -Me	<i>S</i> _I	<i>o</i> - <i>t</i> -Bu	<i>m</i> - <i>t</i> -Bu	<i>p</i> - <i>t</i> -Bu	log $\frac{\rho_{t-Bu}}{m_1}$
Chlorination	617	4.95	870	2.219	56.6	6.0	401	1.824
Bromination	600	5.5	2420	2.648	4.7	6.1	806	2.121

^a Reference 19 and 20.

In the course of this investigation it was necessary to examine the products obtained in the chlorination and bromination of *p*-*t*-butyltoluene and *p*-di-*t*-butylbenzene. Lerer and his associates had previously examined the displacement of the *t*-butyl group from the aromatic nucleus under the influence of ferric chloride.²⁷ It was observed that disproportionation and isomerization readily occurred in the presence of the electrophilic catalyst. In order to account for their observations, it was suggested that the products of the catalytic chlorination arose by direct chlorode-*t*-butylation and also from subsequent chlorination of the disproportionation products.²⁷ Robertson had previously suggested that the *t*-butyl substituent could be removed from the aromatic nucleus as an ion in bromode-*t*-butylation reactions.³⁴

In order to separate the second-order rate constants observed for the chlorination of *p*-*t*-butyltoluene and *p*-di-*t*-butylbenzene into their substitution and chlorode-*t*-butylation components, it was necessary to establish that the disproportionation path was not important under the non-catalytic conditions. The rates of chlorination of the *p*-di-*t*-butylbenzene is more rapid than that of *t*-butylbenzene by a factor of 3.4. This fact requires that significant concentrations of *t*-butylbenzene be formed in the course of the reaction in order that the chlorode-*t*-butylation products arise from a disproportionation product. The virtual absence of this hydrocarbon in the products of the reaction indicates it was not the precursor to *p*-chloro-*t*-butylbenzene. The results are most simply viewed as the removal of the *t*-butyl group from the σ -complex I.



This interpretation allows the evaluation of the rate constants for both substitution and chlorode-*t*-butylation from the observed second-order rate constants and the product distributions.³⁵

De la Mare and his associates have found that the chlorode-*t*-butylation reaction occurs with *t*-butyl-

(34) P. W. Robertson, *Sci. Prog.*, **43**, 418 (1955).

(35) Both processes are second order; the observed rate constant is the sum of the constants for each process. The ratio of the constants is given by the product ratio. The two equations are solved to provide the specific second-order constants for each path.

benzene in acetic acid to yield 0.13% chlorobenzene.²⁹ The rate constant calculated for this process on the basis of the rate of chlorination of *t*-butylbenzene is 0.0018×10^{-4} l. mole⁻¹ sec.⁻¹. The rate constants for chlorode-*t*-butylation of *p*-di-*t*-butylbenzene and *p*-*t*-butyltoluene are 0.66 and 1.1×10^{-4} l. mole⁻¹ sec.⁻¹, respectively. These values provide the relative rates (partial rate factors) for chlorode-*t*-butylation: H 1.00, *p*-*t*-Bu 380 and *p*-Me 610. Thus, chlorode-*t*-butylation appears to be a selective aromatic substitution reaction with the *p*-Me group being considerably more activating than the *p*-*t*-Bu group.

Experimental Part

Materials.—The aromatic hydrocarbons employed were commercial materials further purified by fractionation or crystallization to greater than 99.5 mole %. Purities were established by analysis of the cooling curves.³⁶ Commercial *p*-*t*-butyltoluene was observed to contain approximately 5% of the *meta* isomer. This material was removed by selective mercuration. The solid arylmercuric acetate was removed from the residual hydrocarbon and fractionated to yield a pure sample of *p*-*t*-butyltoluene, b.p. 91° at 23 mm., n_D^{20} 1.4920, f.p. -53.18°, 99.6 mole %. The *p*-di-*t*-butylbenzene employed for kinetic measurements exhibited m.p. 78.5–79.6°. The compounds utilized for infrared and vapor phase chromatographic standards were obtained by the following procedures:

p-Bromo-*t*-butylbenzene was prepared by the direct bromination of *t*-butylbenzene in 85% acetic acid. The reaction required two weeks at room temperature. The reaction was quenched in water, the organic materials extracted into benzene and the solvent distilled off. The residue then was fractionated at reduced pressure. The bromo-*t*-butylbenzene fraction was then crystallized from ethanol to isolate the *para* isomer. This material was then fractionated, b.p. 228–229° at 740 mm., n_D^{20} 1.5334. The compound was shown to be free of *o*- and *m*-bromo-*t*-butylbenzene by examination of the infrared spectra of the pure liquid in 0.026-mm. cells. The *o*- and *m*-isomers were available from a previous study.³⁷ *o*-Chloro-*t*-butylbenzene was obtained in 29% yield (based on *t*-butylbenzene) by the method described by Lerer and Fabre.³⁸ It exhibited the physical properties, b.p. 98° at 25 mm., n_D^{20} 1.5194. The absence of *m*- and *p*-chloro-*t*-butylbenzene was established by the infrared spectra.

The *meta* isomer was prepared from *p*-nitro-*t*-butylbenzene by reduction,³⁹ acetylation,⁴⁰ chlorination and deamination.⁴¹ The yield based on the nitro compounds was 54.5%. The compound exhibited the physical properties, b.p. 105.8–106° at 25 mm., n_D^{20} 1.5126, f.p. -27.3°, minimum purity 98.7%.⁴²

p-Chloro-*t*-butylbenzene was prepared by the alkylation of chlorobenzene.³⁸ The infrared spectra of the fractionated reaction product indicated an impurity, presumably the *meta* isomer. Recrystallization from acetone removed the contaminant, f.p. 22.5°, n_D^{20} 1.5106, purity 98.9%.

2-Chloro-1,4-di-*t*-butylbenzene was obtained by the chlorination of the hydrocarbon. In a 1-l. three-neck flask equipped with a gas introduction tube, reflux condenser and magnetic stirrer were placed 56.0 g. of *p*-di-*t*-butylbenzene in 900 ml. of glacial acetic acid. Chlorine (0.2 mole), trapped as the liquid, was allowed to vaporize rapidly into the

(36) K. L. Nelson, *Anal. Chem.*, **29**, 512 (1957).

(37) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *THIS JOURNAL*, **79**, 1897 (1957).

(38) M. Lerer and C. Fabre, *Bull. soc. chim.*, [5], 198 (1956).

(39) S. A. Mahood and P. V. L. Schaffner, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 160.

(40) J. R. Johnson and L. T. Sandborn, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 111.

(41) N. Kornblum, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 294.

(42) Certain derivatives of *t*-butylbenzene provide cooling curves which are difficult to interpret. These materials appear to have low heats of fusion. Consequently, the infrared spectra have been examined as the principal criteria of purity.

solution. The chlorine addition required approximately 1 hour. The reaction was protected from light and allowed to stir for an additional 18 hours. The residual chlorine was destroyed with aqueous bisulfite. The organic materials were extracted into carbon disulfide. The extracts were washed with aqueous bicarbonate, water and then dried over calcium sulfate. The solvent was distilled off and the column washed down with ethanol. A part of the *p*-di-*t*-butylbenzene (3.0 g.) was recovered as a solid from the ethanol solution. The residue was fractionated to remove *p*-chloro-*t*-butylbenzene and the remaining *p*-di-*t*-butylbenzene. A fraction, 17.0 g., b.p. 158–164° at 45 mm., was subjected to rectification which provided a liquid, b.p. 160–161° at 45 mm., n_D^{20} 1.5165. The liquid crystallized after exposure to the atmosphere to provide a solid, m.p. 33–34°.

Anal. Calcd. for $C_{14}H_{21}Cl$: C, 74.81; H, 9.42; Cl, 15.77. Found: C, 74.97; H, 9.20; Cl, 15.61.

In a preliminary experiment wherein the mole ratio of chlorine to aromatic was 2:1, the material which formed after the addition of ethanol was a dichloro-di-*t*-butylbenzene, m.p. 118.5–119.3°. The infrared spectrum of this material in the 5–6 μ region is consistent with a structural assignment as 2,5-dichloro-1,4-di-*t*-butylbenzene.

Anal. Calcd. for $C_{14}H_{20}Cl_2$: C, 64.88; H, 7.78; Cl, 27.36. Found: C, 65.09; H, 7.75; Cl, 27.22.

The 2-halo-4-*t*-butyltoluenes were prepared by the mercuriation of *p*-*t*-butyltoluene. In a 2-l. round-bottom flask were placed 450 g. of *p*-*t*-butyltoluene and 195 g. (0.58 mole) of mercuric acetate in 1 l. of acetic acid. The solution was refluxed for three hours. After cooling, the solution was poured into ice and the solid arylmercuric acetate recovered and recrystallized from acetic acid. The recrystallized material was divided into two portions and treated with potassium chloride or bromide in acetic acid. The precipitated arylmercuric halides were filtered and air-dried. The solids were subjected to halogen replacement by the slow addition of bromine or chlorine to a cooled chloroform slurry until the slurry discolored with excess halogen. The slurry then was filtered and the filtrate dried over calcium sulfate. The solutions were fractionated to yield 2-chloro-4-*t*-butyltoluene, 10.5 g., b.p. 123° at 26 mm., n_D^{20} 1.5142, and 2-bromo-4-*t*-butyltoluene, 14.5 g., b.p. 138° at 25 mm., n_D^{20} 1.5348. An additional 155 g. of arylmercuric bromide was recovered from the crystallization solvent indicating a material balance of 88%.

Kinetic Measurements.—The kinetic methods for bromination¹⁹ and chlorination²⁰ have been described previously. The procedure was modified only in the case of the bromination of *p*-*t*-butyltoluene which was not sufficiently soluble in 85% acetic acid to provide a 0.40 *M* solution. Therefore, a somewhat less concentrated solution was prepared and the bromine solution appropriately adjusted to achieve the desired concentrations. A representative set of data is provided for the bromination and chlorination of *p*-*t*-butyltoluene in Table VII and VIII, respectively.

Isomer Distribution in Bromination of *t*-Butylbenzene.—In a 1-l. round-bottom flask were placed 37.98 g. (0.282 mole) of *t*-butylbenzene in 550 ml. of 85% acetic acid, and 10.70 g. (0.073 mole) of bromine. The system was closed and the reaction allowed to proceed in the dark for 17 days. An analyzed aliquot of the solution indicated 2.89 g. of bromine remained in the reaction mixture. This residual halogen was destroyed with 3% aqueous borohydride. The solution then was transferred to a continuous liquid-liquid extractor, water added and the system extracted with carbon disulfide for 20 hours. The solvent and excess *t*-butylbenzene were removed from the product by fractionation. The residual materials were then fractionated through a Podbielniak semi-micro distilling column with tetraglyme added as a chaser. The fraction, 66–142° at 25 mm. (7.07 g.), was collected and retained for analysis. This fraction was collected almost exclusively at 118°. However, in order to ensure that no losses of bromo-*t*-butylbenzenes occurred, a trace of *t*-butylbenzene and tetraglyme were also included. This material then was analyzed in dilute carbon disulfide solution (0.10 *M*) for the *para* isomer, while the *ortho* and *meta* concentrations were determined in more concentrated solution (0.5 *M*). The following wave lengths were employed: *o*-13.35 μ , *m*-12.85 μ and *p*-12.21 μ . In each case the analysis was carried out employing known mixtures of the standard bromo compounds in the same concentration

TABLE VII

RATE DATA FOR THE REACTION OF CHLORINE WITH *p*-*t*-BUTYLTOLUENE IN ACETIC ACID AT 25.0°

Time, sec. $\times 10^{-2}$	<i>p</i> - <i>t</i> -Butyltoluene, <i>M</i> (<i>a</i> - <i>x</i>)	Chlorine, <i>M</i> (<i>b</i> - <i>x</i>)	Rate constant $k_2 \times 10^4$, l. mole ⁻¹ sec. ⁻¹
0	0.1587	0.0321	
2.72	.1556	.0290	24.2
9.79	.1491	.0225	23.7
15.8	.1449	.0183	23.7
21.8	.1416	.0150	23.5
34.4	.1369	.0103	22.8

TABLE VIII

RATE DATA FOR THE REACTION OF BROMINE WITH *p*-*t*-BUTYLTOLUENE IN 85% ACETIC ACID AT 25.0°^a

Time, min.	Bromine, <i>M</i>	Reaction, %
0	0.0196	0.00
108	.0183	6.78
154	.0177	9.99
184	.0174	11.3

^a Initial concentration *p*-*t*-butyltoluene, 0.1974 *M*, 10% reaction time evaluated graphically to be 159 min. This value is corrected to 154 min. for 0.200 *M* aromatic and 0.0200 *M* bromine by a third-order rate expression.

range as that of the unknown mixture. The results of the spectroscopic analyses are presented in Table IV. The yield in the experiment based on bromine was 81.3%. A second experiment⁴³ performed in identical manner provided an excellent check on the results of the first experiment. The yield based on bromine was 89.2%.

Isomer Distribution in Chlorination of *t*-Butylbenzene.—Procedures were quite similar to those described above. The only significant difference was that the products were not subjected to further fractionation after the removal of the greater portion of *t*-butylbenzene. In this case the *ortho* and *para* isomers were analyzed in dilute solution (0.10 *M*), while the *meta* isomer was established in the more concentrated solution (0.5 *M*). The wave lengths employed for analysis were *o*-13.3 μ , *m*-12.8 μ and *p*-12.15 μ . The results also are reported in Table IV. The yields in two experiments were 82 and 88% based on a determination of the chlorine available initially.

Product Distribution in the Chlorination of *p*-Di-*t*-butylbenzene.—Under the conditions of the kinetic experiments the reaction was allowed to proceed to completion. The product solution in acetic acid was poured into water and extracted with three 50-ml. portions of carbon disulfide. The extracts were combined and dried. The solvent was removed and the resultant solid phase taken up in a minimum volume of warm ether. The ether solution then was analyzed by gas-liquid partition chromatography employing a Perkin-Elmer Vapor Fractometer model 154B at 190° with 50 ml. of helium per minute. Silicone oil on Celite was utilized as the stationary phases. The method was standardized employing known mixtures of *p*-chloro-*t*-butylbenzene and 2-chloro-1,4-di-*t*-butylbenzene with *p*-di-*t*-butylbenzene also present. Excellent agreement between known and found weight per cent. values was obtained by utilization of the planimeter determined areas and the expression of Eastman.⁴⁴ In this manner the weight per cent. of the two chloro compounds was established. These values were utilized to compute the mole per cent. concentrations. The analyses of the products of the chlorination of *p*-*t*-butyltoluene and the bromination of *p*-*t*-butyltoluene were carried out in a similar manner. The results are reported in Table V.

Acknowledgment.—We are indebted to Miss Margee Haley for the infrared spectra and to Mrs. C. S. Yeh for the microanalyses.

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(43) The experiments outlined here are reported in Table IV as detmn. C and D. The results of preliminary analyses in which only the *meta* to *para* ratio was examined are reported as detmn. A and B.

(44) R. H. Eastman, *THIS JOURNAL*, **79**, 4243 (1957).