

The isomeric chlorotoluenes and chloroethylbenzenes were not separated sufficiently well even on capillary columns, although it was possible to separate well the *o*-isomers from the combined *meta* + *para* isomers. In these cases the isomers were analyzed by infrared spectroscopy.

Analyses were carried out by the standard baseline technique, with suitable corrections made for the interference of any isomer on the others by use of an electronic computer.

It was found advantageous for the infrared analyses to separate the combined chlorotoluene or chloroethylbenzene fractions by preparative scale gas chromatography, thus eliminating

solvent and other aromatic interferences. The following analytical wave lengths were used for the analyses ( $\mu$ ): *o*-chlorotoluene, 13.40; *m*-chlorotoluene, 12.96; *p*-chlorotoluene, 12.42; *o*-chloroethylbenzene, 13.37; *m*-chloroethylbenzene, 12.90; *p*-chloroethylbenzene, 12.18.

**Acknowledgment.**—Drs. D. S. Erley and L. B. Westover, Chemical Physics Research Laboratory, The Dow Chemical Co., Midland, Mich., are thanked for the infrared and mass spectroscopic analyses.

[CONTRIBUTION NO. 84 FROM THE EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LTD., SARNIA, ONTARIO, CAN.]

## Aromatic Substitution. XVIII.<sup>1</sup> Friedel–Crafts *t*-Butylation of Benzene and Methylbenzenes with *t*-Butyl Bromide and Isobutylene

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RECEIVED SEPTEMBER 28, 1962

Friedel–Crafts *t*-butylation of benzene and methylbenzene with *t*-butyl bromide and isobutylene was investigated in nitromethane solution with various acidic halide and proton acid catalysts. Relative rates and isomer distributions were determined by gas–liquid chromatography. *t*-Butylation of toluene and benzene under nonisomerizing conditions shows intermediate substrate selectivity ( $k_{\text{toluene}}:k_{\text{benzene}} = 14\text{--}16$ ). The isomer distribution of the *t*-butyltoluenes formed was found to be 5.7–7% *m*- and 94.3–93% *p*-isomer. No *t*-butylation *ortho* to a methyl group was observed in homogeneous butylations of methylbenzenes in nitromethane solution with either *t*-butyl bromide or isobutylene. *t*-Butylation of *m*-xylene gave only 5-*t*-butyl-1,3-dimethylbenzene, with a reaction rate only one-twentieth of that of the butylation of *o*-xylene. A small secondary isotope effect was observed in the *t*-butylation of benzene-*d*<sub>6</sub>. The mechanism of the reactions is discussed.

### Introduction

Orientations in Friedel–Crafts alkylations have frequently been considered to be anomalous,<sup>2–4</sup> and it has been difficult to explain directive effects in alkylation of aromatics. Temperature, solvent, nature, and amount of catalyst seemed to have a large effect on the orientation of the products formed.

To explain the relatively high proportions of *m*-isomers in Friedel–Crafts alkylation of toluene and other alkylbenzenes under nonisomerizing conditions, Brown suggested that this is a consequence of a high reactivity and resulting low selectivity aromatic electrophilic substitution reactions.<sup>3</sup>

Brown reported low selectivity in the *t*-butylation of toluene and benzene in aluminum and gallium bromide catalyzed reactions with *t*-butyl bromide in excess aromatics as solvent.<sup>5</sup> The relative reactivity of toluene and benzene was found  $k_T:k_B = 1.61$ , whereas the isomer distribution of *t*-butyltoluenes was reported as 32.1% *m*- and 67.9% *p*-isomer, with no *o*-*t*-butyltoluene formed.

In view of Schlatter's data,<sup>6</sup> which indicated in a number of *t*-butylations of toluene with isobutylene or *t*-butyl alcohol the isomer distribution as 7% *m*- and 93% *p*-isomer, the values for the *t*-C<sub>4</sub>H<sub>9</sub>Br butylation were acknowledged as being due to partial isomerization.<sup>5,7,8</sup> Schlatter's lowest *m*-isomer containing isomer distribution with *t*-butyl chloride butylation was 15% *m*- and 85% *p*-isomer. No consideration was given to the possible effect of intermolecular isomerization (disproportionation) on the observed relative reactivity values.

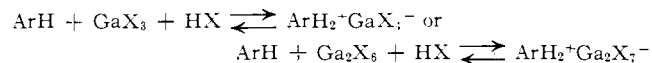
Allen and Yats<sup>9</sup> recently reviewed the present status of concurrent alkylation and isomerization of alkyl-

benzenes with alkyl halides, olefins, and alcohols. They concluded, on the basis of Schlatter's results, that all *t*-butylations of toluene could have been obtained by alkylations producing isomeric mixtures containing 7% *m*- and 93% *p*-*t*-butyltoluene and subsequent or concurrent isomerization of the mixtures. However, they carried out no butylations of their own to substantiate this suggestion and no rate data were available to allow conclusions relating the effect of disproportionation to relative rates.

Allen<sup>9</sup> concluded from his observations, that in the alkylations of toluene the particular catalysts and alkylating agents used influence the extent of isomerization that accompanies the alkylation. He found in the cases he studied that the ratio of *p*- to *m*-substitution was constant within experimental error. In the case of *t*-butylation steric hindrance prevents the formation of *o*-isomer.

### Results and Discussion

Brown's *t*-butylation work was carried out using only an excess of aromatic as solvent. Under these conditions formation of  $\sigma$ -complexes (preferentially with the more basic alkylation products) is to be expected



The formation of these complexes also promotes secondary isomerization. In the case of *t*-butyltoluenes secondary or concurrent isomerization involving predominantly intermolecular migration of the *t*-butyl group was suggested.<sup>9</sup> Therefore, if isomerization takes place, not only is the isomer distribution affected, but the relative toluene–benzene butylation rates may also be affected. Disproportionation could easily lower the relative rate, as *t*-butyltoluenes are more basic and consequently more sensitive to intermolecular isomerization than *t*-butylbenzene.

To prove this point we carried out an investigation of the effect of Lewis acid halide catalysts on the isomeric *t*-butyltoluenes (neat and also in nitromethane and benzene solution). Details of this investigation

(1) Part XVII: *J. Am. Chem. Soc.*, **86**, 1055 (1964).  
 (2) C. C. Price, "Organic Reactions," Vol. 11, John Wiley and Sons, Inc., New York, N. Y., 1948; C. C. Price, *Chem. Rev.*, **29**, 37 (1941).  
 (3) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).  
 (4) A. W. Francis, *Chem. Rev.*, **43**, 257 (1948).  
 (5) H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 6255 (1956); H. C. Brown and H. Jungk, *ibid.*, **78**, 2182 (1956).  
 (6) M. J. Schlatter and R. D. Clark, *ibid.*, **75**, 261 (1953).  
 (7) K. L. Nelson, *J. Org. Chem.*, **21**, 145 (1956).  
 (8) R. H. Allen and L. D. Yats, *J. Am. Chem. Soc.*, **83**, 2799 (1961).

(9) R. H. Allen, *ibid.*, **82**, 4856 (1960).

are being reported elsewhere.<sup>10</sup> With aluminum chloride rapid isomerization takes place. *o*-*t*-Butyltoluene was found to isomerize much more rapidly than the *p*-isomer and both isomerize more rapidly than the *m*-isomer. As a result of isomerizations the amount of *m*-isomer substantially increases in the reaction mixtures. The equilibrium composition is 64% *m*- and 36% *p*-*t*-butyltoluene. If the isomerization is carried out in benzene, considerable intermolecular transalkylations (disproportionation) is observed. These data clearly indicate the difficulties in using rate data obtained from *t*-butylation systems when only excess aromatics as solvent. Consequently, the calculation of partial rate and selectivity factors from these data without proving the absence of thermodynamically controlled isomerization must be questioned.

Competitive rate determinations of the alkylation of benzene and alkylbenzene with olefins in the presence of  $\text{BF}_3 \cdot \text{H}_3\text{PO}_4$  catalyst, carried out by Volkov and Zavgorodnii<sup>11</sup> at temperatures ranging from 30 to 80°, must for the same reasons be treated with reservation. Claims that alkylbenzenes (*e.g.*, toluene, xylenes, etc.) are alkylated generally more slowly than benzene must be based not on kinetics, but are the result of concurrent or consecutive substantial intermolecular isomerization (disproportionation). The evidence for nonisomerization under such conditions is in our opinion quite insufficient.

No rate data were reported in either Schlatter's or Allen's work. It was therefore felt that a reinvestigation of the *t*-butylation of benzene and toluene and an extension of the work to butylation of xylenes and trimethylbenzenes should be undertaken if reaction conditions enabling one to avoid substantial isomerization could be found.

We first carried out competitive *t*-butylation of toluene and benzene with *t*-butyl bromide and isobutylene in nitromethane solution, using a number of catalysts.

The data obtained are summarized in Tables I and II (for the mole ratio of catalyst:aromatic:alkylating agent used, see Experimental part).

TABLE I

COMPETITIVE *t*-BUTYLATION OF TOLUENE AND BENZENE WITH *t*-BUTYL BROMIDE IN NITROMETHANE SOLUTION AT 25°

Catalyst	$k_{\text{toluene}}:k_{\text{benzene}}$	<i>t</i> -Butyltoluene, %		
		<i>ortho</i>	<i>meta</i>	<i>para</i>
$\text{AlCl}_3$	1.90	46.4	53.6	
$\text{FeCl}_3$	1.17	64.8	35.2	
$\text{SnCl}_4$	16.6	7.0	93.0	
$\text{ZnI}_2$	14.5	6.9	93.1	
$\text{AgClO}_4$	15.3	5.7	94.3	
$\text{AgBF}_4$	1.86	50.3	49.7	

TABLE II

*t*-BUTYLATION OF TOLUENE AND BENZENE WITH ISOBUTYLENE IN NITROMETHANE SOLUTION AT 25°

Catalyst	$k_{\text{toluene}}:k_{\text{benzene}}$	<i>t</i> -Butyltoluene, %		
		<i>ortho</i>	<i>meta</i>	<i>para</i>
$\text{AlCl}_3$	15.2	6.0	94.0	
$\text{FeCl}_3$	15.3	5.7	94.3	
$\text{H}_2\text{SO}_4$	16.3	5.6	94.4	

As seen from the data of Table I *t*-butylation of toluene with *t*-butyl bromide gives large amounts of *m*-isomer with aluminum chloride, ferric chloride, and anhydrous silver tetrafluoroborate as catalysts. The conjugate acids of these catalysts (formed by proton elimination from the aromatics) must therefore be

sufficiently strong acids even in nitromethane solution to effect isomerization. When the catalyst concentration was lowered to the minimum amount capable of producing detectable amounts of alkylates (0.005 mole), the  $\text{FeCl}_3$  catalyzed butylation gave only 7% of *m*-isomer instead of the 64.8% obtained with 0.05 mole of catalyst (under reactions conditions described in the Experimental part), and the relative rate of  $k_{\text{toluene}}:k_{\text{benzene}}$  was 12. The relative toluene:benzene reactivity ratio was found to be 1.17, 1.86, and 1.90, respectively, in the cases where high *m*-isomer content indicated isomerization conditions.

As observed previously,<sup>12</sup> one of the ways to overcome in certain cases the ability of acid catalysts, such as aluminum, gallium, iron, etc., halides, to form  $\sigma$ -complexes (and consequently separate layers) with aromatics in the presence of hydrogen halides (or other cocatalyst), is to use a solvent sufficiently basic to complex the acid preferentially, thus rendering it less active for aromatic ring protonation. Nitromethane was found among others to be a suitable solvent for this purpose. No isomerization of isomeric cymenes, ethyltoluenes, or xylenes with aluminum chloride catalyst in nitromethane solution at 25° is observed during 15 min. of reaction time. No transalkylation of added benzene takes place in the same reaction media.

However the treatment of *p*-*t*-butyltoluene in nitromethane solution with  $\text{AlCl}_3 \cdot \text{CH}_3\text{NO}_2$  catalysts at 25° results in substantial isomerization (ultimately reaching the thermodynamic equilibrium). Treatment of *p*-*t*-butyltoluene in the presence of benzene in nitromethane solution at 25° with  $\text{AlCl}_3 \cdot \text{CH}_3\text{NO}_2$  catalyst under the general conditions of alkylations reported in this work resulted in about 30% transalkylation with formation of *t*-butylbenzene. At the same time about 10% *m*-*t*-butyltoluene was also formed, indicating that isomerization of *t*-butyltoluene is not entirely an intermolecular process. With *m*-*t*-butyltoluene under identical conditions, transalkylation was less than 1%, with only traces of *p*-*t*-butyltoluene found. Thus the reaction of the *m*-isomer is much slower than that of the *p*-isomer.

Isomerization of *o*-*t*-butyltoluene results in a very fast *ortho*-*para* (*meta*) conversion, followed by a slower isomerization of the *p*-*t*-butyltoluene formed to the equilibrium *meta*-*para* mixture.<sup>10</sup> Thus under acid conditions even if some *o*-*t*-butyltoluene were primarily formed despite strong steric hindrance, for which there is presently no evidence, it probably would be immediately isomerized to the *para* (and *meta*) isomers.

Whereas ferric chloride behaves similarly to aluminum chloride, stannic chloride in nitromethane solution causes no detectable isomerization (either inter- or intramolecular) of *t*-butyltoluenes.

Because isomerization of *t*-butylbenzenes involves predominantly intermolecular butyl migration, relative reactivity ratios cannot be considered significant if they were obtained under nonkinetic reaction conditions. (Isomerizations must be considered thermodynamically and not kinetically controlled.) The toluene:benzene reactivity ratios in alkylations showing low *m*-isomer ratios (5.7-7%) and consequently little or no isomerizations, were found between 14.5 and 16.6 in the case of butylation with *t*-butyl bromide and between 15.2 and 16.3 in butylations with isobutylene.

Whereas  $\text{AlCl}_3$  and  $\text{FeCl}_3$  cause substantial isomerization in alkylations with *t*-butyl bromide, they do not when isobutylene is used as an alkylating agent. This observation indicates that the presence of an equimolar

(10) G. A. Olah and M. W. Meyer, to be published.

(11) R. N. Volkov and S. V. Zavgorodnii, *Proc. Acad. Sci. U.S.S.R.*, **133**, 889 (1960).

(12) G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffatt, and N. A. Overchuck, *J. Am. Chem. Soc.*, **86**, 1046 (1964).

amount of halide (which from a catalytic point of view can be considered as cocatalyst) is able to initiate substantial isomerization, whereas in the olefin alkylation system the minor amount of water added as cocatalyst is unable in the solvent used to initiate similar isomerization.

The isomer distributions and relative rates (obtained from competitive experiments) were determined by gas-liquid chromatography. Details of the analytical determination and the alkylation conditions are described in the Experimental part. With a homogeneous alkylation system (in which no separate alkylate layer was formed) and a constant large excess of aromatics, very little di- or higher alkylation was observed in any of the systems investigated (less than 5% of monoalkylates). Based on data obtained from mixtures of known compositions, the analytical method used was reliable to  $\pm 5$  relative per cent.

As is to be seen from the data of Table I the choice of catalyst (and solvent) is essential in determining isomer distributions and relative rates. Using only an excess of aromatics as solvent caused both intra- and intermolecular isomerization (disproportionation). Table III summarizes the isomer distribution of *t*-butyltoluenes found in butylations with a number of different catalysts under heterogeneous reaction conditions, using excess toluene as solvent (diluent).

TABLE III

*t*-BUTYLATION OF TOLUENE WITH *t*-BUTYL BROMIDE AT 25°  
(HETEROGENEOUS REACTION CONDITIONS, EXCESS TOLUENE AS SOLVENT)

Catalyst	Reacn. time, min.	<i>t</i> -Butyltoluene, %	
		<i>meta</i>	<i>para</i>
AlCl <sub>3</sub>	5	64.4	35.6
FeCl <sub>3</sub>	5	64.6	35.4
TiCl <sub>4</sub>	15	5.7	94.3
SnCl <sub>4</sub>	15	3.8	96.2
ZrCl <sub>4</sub>	15	7.9	92.1
BCl <sub>3</sub> (with <i>t</i> -C <sub>4</sub> H <sub>9</sub> F)	15	16.4	83.6
AgBF <sub>4</sub>	15	62.8	38.2
	10	50.4	49.6
	5	30.7	69.3
AgClO <sub>4</sub>	5	5.6	94.4
AgPF <sub>6</sub>	10	37.4	63.6
AgSbF <sub>6</sub>	5	66.2	33.8
I <sub>2</sub>	18 hr	5.5	94.5

Use of a basic solvent like nitromethane instead of excess of the aromatic hydrocarbons should however result in weaker electrophilic conditions and therefore a higher degree of selectivity. It is therefore regretful that it seems to be impossible to carry out Friedel-Crafts *t*-butylation of benzene and alkylbenzenes in the presence of strong acid catalyst using only excess of the aromatics as solvent, under nonisomerizing conditions.

Whereas strong Lewis acids like aluminum and ferric chloride caused substantial isomerization (based on the high amount of *m*-isomers formed and disproportionation observed), weaker acid catalysts gave isomer ratios comparable with those obtained in alkylations in homogeneous nitromethane solution. When anhydrous silver salts are used as metathetic cation-forming agents, in the beginning the reaction media are acid-free; however, the corresponding conjugate acids are formed from the proton elimination step of the alkylations as the reactions proceed. AgClO<sub>4</sub> gave no isomerization, whereas AgBF<sub>4</sub> and AgSbF<sub>6</sub> caused substantial isomerization. The absence of *o*-isomer, as in the case of the homogeneous butylations in nitromethane solutions, can be attributed to steric effects.

Competitive *t*-butylation of benzene and xylenes, as well as the trimethylbenzenes, was also carried out both with *t*-butyl bromide and isobutylene in nitromethane solution at 25°, using SnCl<sub>4</sub> and AlCl<sub>3</sub>·CH<sub>3</sub>NO<sub>2</sub> as catalyst (for details of ratio of reagents used see Experimental part). The data obtained are summarized in Tables IV and V.

TABLE IV

COMPETITIVE SnCl<sub>4</sub> CATALYZED *t*-BUTYLATION OF BENZENE AND METHYLBENZENES WITH *t*-BUTYL BROMIDE IN NITROMETHANE SOLUTION AT 25°

Aromatic	<i>k</i> <sub>Ar</sub> : <i>k</i> <sub>benzene</sub>	<i>t</i> -Butylalkylbenzenes, %	
Benzene	1.00		
Toluene	16.6	1,3- <sup>a</sup>	6.4 1,4- 93.6
<i>o</i> -Xylene	44.3	1,2,4-	100
<i>m</i> -Xylene	2.54	1,3,5-	100
<i>p</i> -Xylene		No <i>t</i> -butylation obsd. in competition	
Mesitylene		with benzene	
1,2,4-Trimethylbenzene			
1,2,3-Trimethylbenzene	170	1,2,3,5-	100

<sup>a</sup> Position of *t*-butyl group italicized.

TABLE V

COMPETITIVE AlCl<sub>3</sub>·CH<sub>3</sub>NO<sub>2</sub> CATALYZED *t*-BUTYLATION OF BENZENE AND METHYLBENZENES WITH ISOBUTYLENE IN NITROMETHANE SOLUTION AT 25°

Aromatic	<i>k</i> <sub>Ar</sub> : <i>k</i> <sub>benzene</sub>	<i>t</i> -Butylalkylbenzenes, %	
Benzene	1.00		
Toluene	15.2	1,3- <sup>a</sup>	7.8 1,4- 92.2
<i>o</i> -Xylene	47.8	1,2,4-	100
<i>m</i> -Xylene	3.82	1,3,5-	100
<i>p</i> -Xylene		No <i>t</i> -butylation obsd. in competition	
Mesitylene		with benzene	
1,2,4-Trimethylbenzene			
1,2,3-Trimethylbenzene	110	1,2,3,5-	100

<sup>a</sup> Position of *t*-butyl group italicized.

The isomer distributions and relative rates (obtained from competitive experiments) were determined by gas-liquid chromatography. Using homogeneous alkylation systems (in which no separate complex layer was formed) and a constant large (10:1) excess of aromatics over the alkylating agent, little di- and no higher *t*-butylations were observed (no more in any case than 5% on monoalkylates). Carrying out the alkylations at 25° in nitromethane solution with the aromatic: reagent:catalyst ratios described in the Experimental part during the average 15-min. reaction time yielded over-all about 30% monoalkylate. The rest of the material balance, as established from quantitative gas chromatographic separation on a preparative scale gas chromatograph and also from mass spectroscopic analysis of the reaction mixture, was accounted for in the form of unreacted starting aromatic hydrocarbons and alkylating agent, with a minor amount (as previously stated) of dialkylate. It was possible to account for more than 98% of the over-all material balance. On the basis of data obtained analyzing mixtures of known composition, the used gas chromatographic analytical method was reliable to  $\pm 3\%$ .

To establish that relative rate data were obtained in real competitive experiments, the concentration of benzene-toluene mixtures was varied from 1:9 to 9:1 (molar ratio). The experimental data (as summarized in Tables VI and VII) gave good agreement if first-order dependence on aromatics is accepted. Thus it was established that the observed relative rates are real and represent direct competition of the substrates (toluene-benzene).

The relative reactivity of toluene over benzene in our *t*-butylations shows substantial deviation from

TABLE VI  
CONCENTRATION VARIATION OF TOLUENE AND BENZENE IN  
COMPETITIVE *t*-BUTYLATION WITH *t*-BUTYL BROMIDE + SnCl<sub>4</sub> IN  
NITROMETHANE SOLUTION AT 25°

Ratio		Obsd. rel. rate	$k_T:k_B$
toluene:benzene			
1	9	1.86	16.7
1	4	3.98	15.9
1	2	8.2	16.4
1	1	16.6	16.6
2	1	31.8	15.9
4	1	66.8	16.7
9	1	128.7	14.3

TABLE VII  
CONCENTRATION VARIATION OF TOLUENE AND BENZENE IN  
COMPETITIVE *t*-BUTYLATION WITH ISOBUTYLENE + AlCl<sub>3</sub>·CH<sub>3</sub>NO<sub>2</sub>  
IN NITROMETHANE SOLUTION AT 25°

Ratio		Obsd. rel. rate	$k_T:k_B$
toluene:benzene			
1	9	1.24	11.2
1	4	3.20	12.8
1	2	6.95	13.9
1	1	15.2	15.2
2	1	25.0	12.5
4	1	51.2	12.8
9	1	119.7	13.3

previously reported data indicating low substrate selectivity of the order of 2. The present data show  $k_{\text{toluene}}:k_{\text{benzene}} = \sim 15$ . The evidence presented in this work demonstrates that *t*-butylations giving intermediate substrate selectivity in homogeneous butylations in nitromethane were carried out under substantially nonisomerizing conditions. The corresponding isomer distributions are about 93 *p*- and 7% *m*-*t*-butyltoluene. Previously reported low selectivity butylations, giving high proportions of *m*-isomer, must inevitably be considered as at least partially thermodynamically and not kinetically controlled. Inter- and intramolecular isomerizations (disproportionation) influence both substrate and positional selectivity values.

Our present data fit the selectivity correlation better than those reported previously. However, as pointed out previously,<sup>12</sup> our own investigations have not provided general evidence for the linear correlation between positional and substrate selectivities in all electrophilic aromatic substitutions and in particular in those involving strong electrophiles.

*t*-Butylation of di- and trimethylbenzenes also show intermediate substrate selectivity (as compared with benzene). The isomer distributions are characterized by the fact that no *o*-substitution relative to a methyl group is possible. *o*-Xylene gives exclusively 4-*t*-butyl-1,2-dimethylbenzene; *m*-xylene produces only 5-*t*-butyl-1,3-dimethylbenzene, but with a relative rate of only one-twentieth of that of the butylation of *o*-xylene. These data are in good agreement with the observed 5-6% *m*-*t*-butyltoluene isomer formation in the *t*-butylation of toluene, thus giving a *meta*:*para* ratio of about 1/20 and providing strong evidence for direct, kinetically controlled alkylation in the *m*-position *meta* to methyl groups.

*p*-Xylene, mesitylene, and 1,2,4-trimethylbenzene (pseudocumene) were not *t*-butylated in competitive *t*-butylation with benzene in nitromethane solution, since no positions other than those *ortho* to methyl group are available.

**Kinetic Isotope Effect.**—The kinetic isotope effect in the *t*-butylation of benzene-*d*<sub>6</sub> was determined by the previously used competitive method, using *t*-C<sub>4</sub>H<sub>9</sub>Br + AgClO<sub>4</sub> as an alkylating agent in nitro-

methane solution at 25°. Direct competition of benzene and benzene-*d*<sub>6</sub> (analyzed by mass spectroscopy) and competitive butylation of toluene-benzene and toluene-benzene-*d*<sub>6</sub> (analyzed by gas-liquid chromatography) were used. Both methods give a small secondary kinetic isotope effect.

$$k_{\text{benzene}}:k_{\text{benzene-d}_6} = 1.16 \quad k_H:k_D = 1.16 \pm 0.05$$

$$k_{\text{toluene}}:k_{\text{benzene}} = 15.3$$

$$k_{\text{toluene}}:k_{\text{benzene-d}_6} = 18.5 \quad k_H:k_D = 1.21 \pm 0.06$$

The *t*-C<sub>4</sub>H<sub>9</sub>Br + AgClO<sub>4</sub> alkylation system in nitromethane caused only slight hydrogen-deuterium exchange according to mass spectroscopic analysis. Therefore the method could be used for the determination of the kinetic isotope effect. Corrections were applied for di-*t*-butylated products. The effects causing a small secondary isotope effect, similar to those observed in previous benzylations<sup>13</sup> and isopropylation,<sup>11</sup> have been discussed and need not be repeated.

### Conclusions

The observed relative reactivities of methylbenzenes and benzene cannot be simply related to the stabilities of complexes corresponding to strictly  $\pi$ - or  $\sigma$ -complex natures although they show substantially closer resemblance to  $\pi$ - than  $\sigma$ -complex stabilities. The *t*-butylations of benzene and toluene show higher substrate selectivity than those of the corresponding isopropylation discussed previously.<sup>12</sup> Consequently, the alkylating agent in the present *t*-butylations must be a weaker electrophile than that of the isopropylation systems.

The trimethyl carbonium ion or its precursor is a weaker electrophile than the dimethyl carbonium ion or its precursor (the electron deficiency of the carbon atom is decreased by hyperconjugation with one more methyl group). This can explain why *t*-butylation shows higher substrate selectivity than isopropylation. At the same time considerable steric hindrance, interfering with the formation of *o*-*t*-butyl derivatives, makes it more difficult to evaluate positional selectivity. The same steric factors also make it impossible to evaluate substrate reactivities in cases where no positions other than those *ortho* to a methyl group are available (as in the case of *p*-xylene, mesitylene, pseudocumene).

As to the mechanism of the *t*-butylation reactions, it is suggested somewhat similarly to that of isopropylation<sup>12</sup> that it involves two transition states: one (T<sub>1</sub>) of an oriented  $\pi$ -complex nature which is involved in the substrate rate-determining step and a subsequent second one (T<sub>2</sub>) corresponding to a  $\sigma$ -complex which is involved in determining the positional selectivity.

As discussed previously T<sub>2</sub> should be different in energy for the *m*- and *p*-positions. The relative rate data indicate that T<sub>1</sub> must be higher than T<sub>2</sub> (otherwise the formation of T<sub>1</sub> should become reversible). If T<sub>2</sub> should be also involved in the substrate rate-determining step, much higher substrate rates would be expected for the methylbenzenes, as compared with benzene. However, the energy difference between T<sub>1</sub> and T<sub>2</sub> is probably smaller than in the case of reactions involving stronger electrophiles, which could explain the higher substrate selectivity.

Data indicating substantial steric hindrance also suggest that the alkylating agent is the polarized donor-acceptor complex of the alkyl halide and catalyst (or olefin-catalyst-cocatalyst) which is then displaced by the aromatic substrate. No free trimethyl carbon-

(13) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **84**, 1688 (1962).

ium ion as alkylating agent can be demonstrated either from relative rate and isomer distribution data (the steric hindrance with  $(\text{CH}_3)_3\text{C}^+$  should be smaller) or spectroscopic investigations of the alkylating systems (ultraviolet, infrared, and nuclear magnetic resonance investigations, to be reported separately). In nitromethane (or related polar solvents) ionization of alkyl halides by Lewis acids is not favored, because of the competing donor effect of the solvent, "deactivating" the catalyst. However, an equilibrium containing small amounts (subspectroscopic) of the carbonium ion cannot be ruled out and this could contribute to the alkylation. The carbonium ion should be present in the form of a solvated ion pair and not a "free" ion, thus still showing substantial bulkiness.

A comparison of the isopropylation and *t*-butylation of benzene and alkylbenzenes with previously investigated nitration, bromination, and chlorination of the same systems allows one to point out certain similarities.

Nitration, bromination, and isopropylation show similar low substrate selectivities (with otherwise predominant *ortho*-*para* directing effects) and obviously are due to strong electrophiles. Chlorination and *t*-butylation, on the other hand, show higher substrate selectivity, indicating that in these cases the substitutions are effected by somewhat weaker electrophilic reagents. Our knowledge concerning the electrophilic nature of the corresponding positive ions (which are of course only the limiting cases and not necessarily reached in the substitution reactions, where strong ion-pair interactions and solvations exclude the presence of "free" ions) is in accordance with these observations, the decreasing order of electrophilic character being  $(\text{CH}_3)_2\text{CH}^+ \sim \text{NO}_2^+ > \text{Br}^+ > \text{Cl}^+ \sim (\text{CH}_3)_3\text{C}^+$ .

### Experimental

Benzene, methylbenzenes, and *t*-butyl bromide used were commercially available products of highest purity. If necessary, they were redistilled on a Podbielniak column or purified by preparative scale gas chromatography (using a Wilkens Model Aerograph Autoprep A-700 instrument). Average purity was 99.5%, as analyzed by gas-liquid chromatography. Isobutylene (Matheson Chemical Co.) was used without further purification. We are grateful for samples of *o*-*t*-butyltoluene and 5-*t*-butyl-1,3-dimethylbenzene from Drs. B. S. Friedman (Sinclair Research Inc., Harvey, Ill.) and D. A. McCaulay (American Oil Co., Whiting, Ind.). Reference isomeric *m*- and *p*-*t*-butyltoluenes were obtained from the National Bureau of Standards, Washington, D. C. Other isomeric *t*-butyl-di- and trimethylbenzenes, as well as di-*t*-butylmethylbenzenes, were prepared by known methods in this laboratory. The purity of all standard isomers used was checked by gas-liquid chromatography and infrared spectroscopy. The nitromethane used was purified as described previously<sup>11</sup> by the use of the method of Winstein and Smith. Anhydrous acidic halide catalysts were commercial products purified with standard methods (sublimation, azeotropic distillation, treatment with thionyl halides) or halides prepared by known methods in this laboratory.

Commercial "anhydrous" silver perchlorate was dehydrated in a manner similar to that described recently by Radell, Connelly, and Raymond<sup>15</sup> by azeotropic distillation with benzene.

Anhydrous silver tetrafluoroborate,<sup>16</sup> hexafluoroantimonate,<sup>15</sup> hexafluoroarsenate,<sup>17</sup> and hexafluorophosphate<sup>17</sup> were prepared as described.

Benzene-*d*<sub>6</sub> was purchased from Ciba Ltd., Basel, Switzerland.

**Competitive *t*-Butylation of Benzene and Methylbenzenes with *t*-Butyl Bromide in Nitromethane Solution.**—To a solution of 0.05 mole of catalyst in 50 g. of nitromethane were added 0.25 mole each of toluene and benzene, in a 3-necked reaction flask equipped with a thermometer, reflux condenser (connected through a drying tube to a hydrogen halide absorber), and dropping funnel. The reaction flask was then placed in a constant temperature bath and kept at  $25 \pm 0.5^\circ$ . While vigorously stirred (magnetic stirrer), 0.05 mole (7 g.) of *t*-butyl bromide in 30 g. of nitromethane was added dropwise. The addition took approximately

10 min. and the reaction was then allowed to proceed for another 5 min. Thereafter the solution was washed with water, three times with 200-ml. portions of 5% NaOH (to remove nitromethane), and again with water. The organic layer was separated, dried over  $\text{CaCl}_2$ , and analyzed by gas-liquid chromatography.

The data obtained are summarized in Table I.

**Competitive *t*-Butylation of Toluene and Benzene with Isobutylene in Nitromethane Solution.**—To a solution of 0.02 mole of catalyst in 50 g. of nitromethane were added 0.10 mole each of toluene and benzene. One drop of water was added as cocatalyst to avoid discrepancies owing to minor amounts of moisture present in the system. The reaction flask fitted with thermometer, reflux condenser, and gas inlet tube was then placed in a constant temperature bath and kept at  $25 \pm 0.05^\circ$ ; isobutylene gas was introduced with a constant rate (75 ml./min.) for 15 min. with stirring. The solution was then washed with water, 5% NaOH solution, and again with water. The organic layer was separated, dried, and analyzed by gas-liquid chromatography.

The data obtained are summarized in Table II.

**Concentration Variation of Toluene and Benzene in Competitive *t*-Butylations.**—The concentration variations were carried out in the same manner as the competitive studies varying only the relative amounts of toluene and benzene. The data obtained are summarized in Tables III and IV.

***t*-Butylation of Toluene with *t*-Butyl Bromide under Heterogeneous Reaction Conditions, Excess Toluene as Diluent.**—*t*-Butylations of toluene with *t*-butyl bromide were carried out by mixing the catalyst (0.05 mole) and toluene (0.5 mole) and then adding 0.05 mole of *t*-butyl bromide to the stirred reaction mixtures at  $25^\circ$ . The reaction mixtures were allowed to react generally for 5 to 15 min. in cases where the reactions appeared to occur readily as evidenced by liberation of hydrogen halide (see Table V) and were thereafter quenched with water. Mixtures with less reactive catalysts (like  $\text{I}_2$ ), where no product formation was observed, were allowed to react for longer periods of time (up to several hours) in order to obtain 10–15% alkylation, suitable in amount for analysis. The solutions were then washed, dried, and analyzed by gas-liquid chromatography, as in previous experiments. The data obtained are summarized in Table V.

**Determination of Kinetic Isotope Effect.** (a) *t*-Butylation of  $\text{C}_6\text{D}_6$  +  $\text{C}_6\text{H}_6$ .—Benzene-*d*<sub>6</sub> (0.1 mole) and benzene (0.1 mole) were dissolved together with 0.02 mole of  $\text{AgClO}_4$  in 30 g. of nitromethane. To this stirred solution, kept at  $25 \pm 0.5^\circ$ , 0.02 mole of *t*-butyl bromide dissolved in 5 g. of nitromethane was added and the reaction carried out as in previous experiments. The reaction mixture was washed twice with 50-ml. of water; the organic layer was dried over  $\text{CaCl}_2$  and analyzed by mass spectroscopy.

TABLE VIII

RETENTION TIMES OF *t*-BUTYLBENZENE AND *t*-BUTYL-METHYLBENZENES AT  $150^\circ$

	Time, min.
<i>t</i> -Butylbenzene	10.5
<i>o</i> - <i>t</i> -Butyltoluene	23
<i>m</i> - <i>t</i> -Butyltoluene	16
<i>p</i> - <i>t</i> -Butyltoluene	17
1,2-( $\text{CH}_3$ ) <sub>2</sub> -4- <i>t</i> -Butylbenzene	29
1,3-( $\text{CH}_3$ ) <sub>2</sub> -5- <i>t</i> -Butylbenzene	24
1,4-( $\text{CH}_3$ ) <sub>2</sub> -3- <i>t</i> -Butylbenzene	31
1,2,3-( $\text{CH}_3$ ) <sub>3</sub> -5- <i>t</i> -Butylbenzene	49

(b) *t*-Butylation of  $\text{CH}_3\text{C}_6\text{H}_5$  +  $\text{C}_6\text{H}_6$  and  $\text{CH}_3\text{C}_6\text{H}_5$  +  $\text{C}_6\text{D}_6$ .—Toluene (0.1 mole) and 0.1 mole of benzene-*d*<sub>6</sub> together with 0.02 mole of anhydrous  $\text{AgClO}_4$  were dissolved in 30 g. of nitromethane. To the stirred solutions, kept at  $25 \pm 0.5^\circ$ , 0.02 mole of *t*-butyl bromide dissolved in 5 g. of nitromethane was added dropwise. The reactions were then carried out as in previous experiments. The mixtures were washed twice with 50 ml. of water, dried over  $\text{CaCl}_2$ , and analyzed by gas-liquid chromatography.

**Gas-Liquid Chromatographic Analyses.**—The analyses of all *t*-butylations were carried out by gas-liquid chromatography on a Perkin-Elmer Model 154-C vapor fractometer equipped with a thermistor thermal conductivity cell detector. The 4-m. by 0.25 in. stainless steel column was packed with polypropylene glycol (UCON LB 550-X) on diatomaceous earth (30% w./w.). The column temperature was generally  $150^\circ$  with dry hydrogen carrier gas flow rate at approximately 60 ml. per minute. Peak areas were obtained by the use of electronic printing integrator. Characteristic retention times of *t*-butylbenzene and *t*-butylmethylbenzenes on a column are given in Table VIII.

Relative response data were obtained by running known quantities of *t*-butylbenzene and *t*-butyltoluenes in benzene in the approximate amounts in which they appeared in the experimental samples, according to Messner, Rosie, and Argabright.<sup>18</sup>

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