

## Friedel-Crafts Isopropylation in Nonpolar Solvents

RYOHEI NAKANE,\* OSAMU KURIHARA, AND AKIKO TAKEMATSU

*The Institute of Physical and Chemical Research, Saitama, Japan*

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Competitive boron trifluoride catalyzed isopropylations of benzene and toluene with isopropyl fluoride in nonpolar organic solvents were carried out at  $-23$ ,  $0$ , and  $25^\circ$ . The relative rates of toluene to benzene were always smaller than 1. The isopropylations were accelerated by a trace of water. The isopropylations of benzene- $d_6$  and toluene- $d_8$  at  $25^\circ$  showed small secondary inverse kinetic isotope effects. These results suggest that an alkylation catalyst is a hydrate of boron trifluoride, that an electrophile in isopropylation is an isopropyl carbonium ion or its ion pair, that the rate-determining transition state formed in the substitution of toluene closely resembles the oriented  $\pi$  complex, and that the difference in rates between benzene and toluene is due primarily to the difference in the entropies of activation, which can be negative, when the difference in the activation energies between both aromatics is very small.

Boron trifluoride catalyzed ethylation carried out in nonpolar organic solvent shows an anomalous substrate selectivity. Benzene is more reactive than toluene.<sup>1</sup> The ethylation with ethyl- $2$ - $^{14}\text{C}$  fluoride indicates that an electrophile is an ethyl carbonium ion or its ion pair.<sup>2</sup> In order to investigate further the question of the anomalous reactivity and selectivity found in the aromatic substitutions involving strong electrophiles, boron trifluoride catalyzed isopropylations of benzene and toluene with isopropyl fluoride have been carried out in nonpolar organic solvents.

## Results

**Competitive Isopropylation.**—Competitive isopropylations of benzene and toluene with isopropyl fluoride, using boron trifluoride as catalyst, were carried out at  $25^\circ$  in *n*-hexane, cyclohexane, and nitromethane solutions. The mole ratio of *n*-hexane or cyclohexane, combined aromatics, and isopropyl fluoride to boron trifluoride was 1000:100:10:1. The mole ratio of nitromethane, combined aromatics, and isopropyl fluoride to boron trifluoride was 30:10:1:1. In all cases less than 10% of combined aromatics were isopropylated. The data are summarized in Table I.

TABLE I  
COMPETITIVE BORON TRIFLUORIDE CATALYZED  
ISOPROPYLATION OF BENZENE AND TOLUENE  
WITH ISOPROPYL FLUORIDE AT  $25^\circ$

Solvent	$k_T/k_B$	Isopropyltoluene, %		
		Ortho	Meta	Para
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	0.69	45.6	21.0	33.4
C <sub>6</sub> H <sub>12</sub>	0.70	45.1	21.5	33.4
CH <sub>3</sub> NO <sub>2</sub>	2.18	43.2	22.3	34.5

The amount of di- or higher isopropylate did not exceed 5% of that of monoisopropylate.

The isopropylation is a fast reaction. According to Olah's method,<sup>3</sup> the relative rate was determined by changing the concentration in competitive experiments in *n*-hexane solution from the ratio 1:1 to 3:1 and to 0.3:1 at  $25^\circ$ . The results as shown in Table II indicate that the relative rate remains almost constant if a first-order dependence in aromatics is accepted.

The relative rates of toluene to benzene in *n*-hexane

TABLE II  
CONCENTRATION VARIATION IN COMPETITIVE BORON  
TRIFLUORIDE CATALYZED ISOPROPYLATION OF  
BENZENE AND TOLUENE WITH ISOPROPYL FLUORIDE  
IN *n*-HEXANE SOLUTION AT  $25^\circ$

Toluene:benzene ratio	Obsd relative rates	$k_T/k_B$
2.94:1	2.17	0.74
2.04:1	1.35	0.66
1.02:1	0.69	0.69
0.514:1	0.36	0.70
0.307:1	0.20	0.66

solution were determined also at  $-23$  and  $0^\circ$ . The obtained value was always  $0.69 \pm 0.03$  in the temperature range from  $-23$  to  $25^\circ$ .

When boron trifluoride gas was quickly introduced into the *n*-hexane solution with a trace of water, in which the aromatics and isopropyl fluoride were dissolved, the solution showed a Tyndall effect, indicating a formation of polymer.<sup>2</sup> When boron trifluoride was slowly introduced into the *n*-hexane solution containing the trace of water, the clear solution was obtained. The polymer was not formed, but the isopropylation of aromatics proceeded. As the quantity of water contained in the solution increased, the yields of isopropylated products obtained per unit time became larger. The trace of water may accelerate the isopropylation. Water is a cocatalyst. However, the relative rates of toluene were independent of the quantity of water contained in the solution within experimental error.

As observed previously,<sup>2</sup> no transalkylation between *p*-cymene and benzene takes place when a boron trifluoride catalyzed ethylation with ethyl fluoride in *n*-hexane solution is carried out in a glass flask, because the produced hydrogen fluoride is immediately captured by the wall of the flask and thus preventing a protonated complex to form in the solution.

These results indicate that the competitive method to determine the relative rates and the kinetic isotope effects can be taken into consideration for the boron trifluoride catalyzed isopropylation with isopropyl fluoride in nonpolar organic solvents.

**Kinetic Isotope Effect.**—In order to determine the kinetic isotope effect upon the boron trifluoride catalyzed isopropylation, Olah's method<sup>3</sup> was used. Competitive isopropylations of benzene-toluene, benzene- $d_6$ -toluene, and benzene-toluene- $d_8$  mixtures with isopropyl fluoride were carried out in *n*-hexane, cyclohexane, and nitromethane solutions. Gas chromatog-

(1) R. Nakane, O. Kurihara, and A. Natsubori, *J. Amer. Chem. Soc.*, **91**, 4528 (1969).

(2) A. Natsubori and R. Nakane, *J. Org. Chem.*, **35**, 3372 (1970).

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

raphy was used to analyze the products. The relative rate ratios are shown in Table III. The small secondary

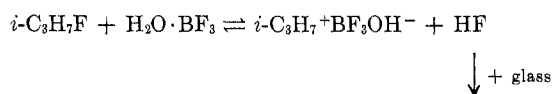
TABLE III  
KINETIC ISOTOPE EFFECT FOR BORON TRIFLUORIDE  
CATALYZED ISOPROPYLATION WITH ISOPROPYL  
FLUORIDE AT 25°

Solvent	$k_T/k_B$	$k_T/k_{B-d_6}$	$k_{T-d_3}/k_B$	$k_D/k_H$	
				Benzene	Toluene
$n\text{-C}_6\text{H}_{14}$	0.69	0.64	0.83	1.08	1.20
$\text{C}_6\text{H}_{12}$	0.70	0.65	0.80	1.08	1.14
$\text{CH}_3\text{NO}_2$	2.18	2.17	2.32	1.00	1.07

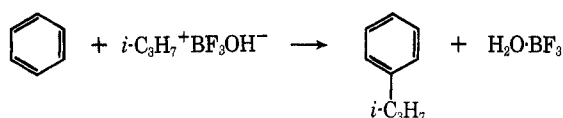
inverse kinetic isotope effects as found in the nitration with nitronium tetrafluoroborate<sup>4</sup> were observed both in nonpolar and in basic organic solvents.

### Discussion

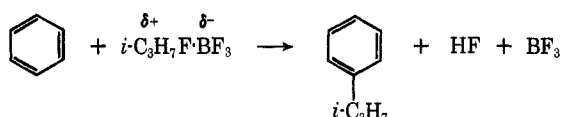
**Electrophile in Isopropylation.**—The boron trifluoride catalyzed isopropylation with isopropyl fluoride carried out in nonpolar organic solvents are accelerated by a trace of water. This indicates that an alkylation catalyst in nonpolar organic solvents is not boron trifluoride itself but a hydrate of boron trifluoride which is a strong proton-acid catalyst. When the hydrate of boron trifluoride reacts with isopropyl fluoride, an ion pair of isopropyl carbonium ion and hydrogen fluoride which reacts with the wall of the glass flask is produced.<sup>2</sup>



In nonpolar organic solvents the polarized complex,  $i\text{-C}_3\text{H}_7\text{F} \cdot \text{BF}_3$ , dissociates into its original components which are the neutral molecules. The boron trifluoride catalyzed ethylation with ethyl- $2\text{-}^{14}\text{C}$  fluoride carried out in  $n$ -hexane solution indicates that the main electrophile is the ethyl carbonium ion or its ion pair.<sup>2</sup> These facts suggest that the isopropyl carbonium ion or its ion pair is the main electrophile in isopropylation carried out in nonpolar organic solvents.

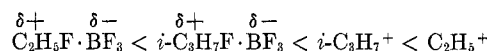


In basic organic solvents the hydrate of boron trifluoride cannot ionize isopropyl fluoride, for a basic organic solvent is a suitable proton acceptor. The polarized complex is stable in basic organic solvents. The boron trifluoride catalyzed ethylation with ethyl- $2\text{-}^{14}\text{C}$  fluoride carried out in nitromethane solution indicates that the main electrophile is the polarized complex.<sup>2</sup> These facts suggest that the polarized complex is the main electrophile in the isopropylation carried out in basic organic solvents.



(4) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Amer. Chem. Soc.*, **83**, 4571 (1961).

The relative rates of toluene to benzene,  $k_T/k_B$ , obtained in nonpolar organic solvents are smaller than 1 both in the ethylation<sup>1</sup> and in the isopropylation, but the latter is a little larger than the former. On the other hand, the relative rates of toluene to benzene obtained in basic organic solvents are larger than 1 both in the ethylation<sup>1</sup> and in the isopropylation, but the latter is smaller than the former. The electrophilic character of electrophiles decreases as follows.



**Anomalous  $m_f^{\text{Me}}$  Values.**—The  $o_f^{\text{Me}}$  and  $p_f^{\text{Me}}$  values of the boron trifluoride catalyzed isopropylation with isopropyl fluoride in nonpolar organic solvents have values closer to 1, but the  $m_f^{\text{Me}}$  values are smaller than 1 as shown in Table IV. The anomalous  $m_f^{\text{Me}}$  values are sometimes found when highly electrophilic substituting agents are used.<sup>3-6</sup> The partial rate factors in the aromatic substitutions showing the anomalous  $m_f^{\text{Me}}$  values are summarized in Table IV. To these substitutions Brown's selectivity relationship<sup>7</sup> cannot be applied. The lower relative reactivity of toluene found in nonpolar organic solvents cannot be interpreted in terms of the relative electronic properties of the aromatics alone. It also cannot be interpreted in terms of a solvent cage effect,<sup>8</sup> because if a diffusion of an aromatic molecule in the solvents determines the rate, the relative rates of toluene to benzene obtained in the ethylation should be equal to those obtained in the isopropylation and a heavy isotope molecule should react slower than a light one, but they do not do so.

**Oriented  $\pi$  Complex.**—The small secondary inverse kinetic isotope effects were observed in the boron trifluoride catalyzed competitive isopropylation of toluene-benzene, toluene-benzene- $d_6$ , and toluene- $d_3$ -benzene with isopropyl fluoride. As suggested by Olah,<sup>3-5</sup> it appears that the rate-determining transition state involving strong electrophiles resembles the  $\pi$  complex.

Due to inductive and hyperconjugative effects of the methyl group, the regions of the ortho and para positions in toluene have a higher electron density than the ones of the meta positions. That this effect is further increased by polarization through a strong acceptor results in a formation of the oriented  $\pi$  complex. When alkylbenzene is dissolved in a liquid polarized alkyl fluoride-boron trifluoride complex at low temperatures, a termolecular oriented  $\pi$  complex<sup>9-11</sup> which shows two strong peaks of absorption bands near 270 and 370  $m\mu$  is formed. The intensity of these peaks is much higher than those of the benzenoid band of alkylbenzene. This fact can possibly be explained by assuming that the quinoid type resonance structures as pictured below make a substantial contribution to the ground state but are the predominant contribution to the excited

(5) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1688 (1962).

(6) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *ibid.*, **86**, 1039 (1964).

(7) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953); H. C. Brown and C. W. McGray, *ibid.*, **77**, 2300 (1955); H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

(8) D. E. Pearson, C. V. Breder, and J. C. Craig, *ibid.*, **86**, 5054 (1964).

(9) R. Nakane, A. Natsubori, and O. Kurihara, *ibid.*, **87**, 3597 (1965).

(10) R. Nakane, T. Ōyama, and A. Natsubori, *J. Org. Chem.*, **33**, 275 (1968).

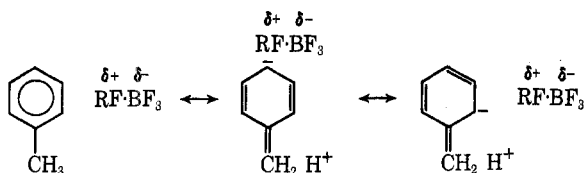
(11) T. Ōyama and R. Nakane, *ibid.*, **34**, 949 (1969).

TABLE IV  
 PARTIAL RATE FACTORS OF AROMATIC SUBSTITUTIONS WITH STRONG ELECTROPHILES AT 25°

Substituting agent	Catalyst	Solvent	$k_T/k_B$	Isomer ratio, %			Partial rate factors			Ref
				Ortho	Meta	Para	$o_f^{Me}$	$m_f^{Me}$	$p_f^{Me}$	
C <sub>2</sub> H <sub>5</sub> F	BF <sub>3</sub>	<i>n</i> -C <sub>8</sub> H <sub>14</sub>	0.56	45.3	29.2	25.5	0.76	0.49	0.86	<i>a</i>
C <sub>2</sub> H <sub>5</sub> F	BF <sub>3</sub>	C <sub>6</sub> H <sub>12</sub>	0.57	45.5	29.2	25.3	0.78	0.50	0.87	<i>a</i>
C <sub>2</sub> H <sub>5</sub> F	BF <sub>3</sub>	CCl <sub>4</sub>	0.70	46.0	29.7	24.3	0.97	0.62	1.02	<i>a</i>
C <sub>2</sub> H <sub>5</sub> I	AlBr <sub>3</sub>	<i>n</i> -C <sub>8</sub> H <sub>14</sub>	0.63	44.8	10.9	44.3	0.85	0.20	1.67	<i>a</i>
<i>i</i> -C <sub>3</sub> H <sub>7</sub> F	BF <sub>3</sub>	<i>n</i> -C <sub>8</sub> H <sub>14</sub>	0.70	45.6	21.0	33.4	0.96	0.44	1.40	<i>b</i>
<i>i</i> -C <sub>3</sub> H <sub>7</sub> F	BF <sub>3</sub>	C <sub>6</sub> H <sub>12</sub>	0.70	45.1	21.5	33.4	0.95	0.45	1.40	<i>b</i>
<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br	GaCl <sub>3</sub>	CH <sub>3</sub> NO <sub>2</sub>	1.68	46.9	17.4	38.6	2.84	0.90	4.20	<i>c</i>
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	AlCl <sub>3</sub>	CH <sub>3</sub> NO <sub>2</sub>	3.20	43.5	4.5	52.0	4.20	0.43	10.0	<i>d</i>
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	AlBr <sub>3</sub>	CH <sub>3</sub> NO <sub>2</sub>	2.62	42.5	5.5	52.0	3.34	0.43	8.17	<i>e</i>
Br <sub>2</sub>	FeCl <sub>3</sub>	CH <sub>3</sub> NO <sub>2</sub>	3.6	68.7	1.8	29.5	7.42	0.19	6.37	<i>f</i>
Br <sub>2</sub>	AlBr <sub>3</sub>	CH <sub>3</sub> NO <sub>2</sub>	15.5	60.5	0.2	39.3	28.2	0.09	36.5	<i>e</i>
NO <sub>2</sub> BF <sub>4</sub>		C <sub>4</sub> H <sub>8</sub> SO <sub>2</sub>	1.67	65.4	2.8	31.8	3.27	0.14	3.19	<i>g</i>

<sup>a</sup> See ref 1. <sup>b</sup> Present report. <sup>c</sup> See ref 3. <sup>d</sup> See ref 5. <sup>e</sup> T. Oyama and R. Nakane, unpublished. <sup>f</sup> See ref 6. <sup>g</sup> See ref 4.

state. The quinoidal resonance structures should be written as

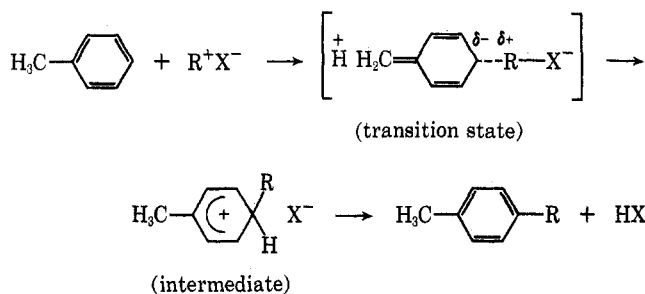


In the termolecular oriented  $\pi$  complex, therefore, the 1:1 addition complex which is the acceptor would be substantially oriented in the regions of ortho and para positions in terms of inductive and hyperconjugative effects of the methyl group, although the hybridization of the ortho or para carbon atom is still  $sp^2$  but not  $sp^3$ . The ortho and para oriented  $\pi$  complexes are probably more stable than the meta oriented one, in which the acceptor is oriented in the region of the meta position in terms of inductive effect of the methyl group alone. The termolecular oriented  $\pi$  complex offers an attractive model concerning the formation of rate-determining transition states in aromatic substitution involving strong electrophiles.

**Transition States.**—When boron trifluoride is withdrawn from the termolecular oriented  $\pi$  complex at low temperatures, one part of the complex decomposes into the alkylated products.<sup>9</sup> The formation of a  $\sigma$  complex determines the rate of alkylation carried out at low temperatures. The alkylation at room temperature probably proceeds by a similar reaction mechanism as at low temperatures.

In all aromatic substitutions both substrate and positional selectivities seem to be determined by a free energy required to form the intermediate  $\sigma$  complex.<sup>1</sup> The termolecular oriented  $\pi$  complex is not isolated at room temperature, but the existence of the low-energy  $\pi$  complex does not affect the rate. The activation energy is the energy difference between the initial state and the transition state for the formation of the  $\sigma$  complex. It is well known that the transition state for the formation of a  $\sigma$  complex contains more  $\pi$  character with increasing reactivity of the electrophiles. The small secondary kinetic isotope effects observed indicate that the early transition state which closely resembles the  $\pi$  complex occurs. The rate-determining transition state formed in the substitution of toluene involving a strong electrophile would resemble the oriented  $\pi$  complex, in which the electrophile is oriented

near some definite aromatic carbon atom and a partially formed carbon-carbon bond is contained. The oriented  $\pi$  complex type transition states of toluene would be composed of the separate transition states corresponding to the ortho, meta, and para positions among which the meta position represents the highest energy barrier, because the ortho and para oriented  $\pi$  complexes of toluene are more stable than its meta oriented  $\pi$  complex in terms of resonance effects. The complex cation passes over the lower energy barrier leading to the  $\sigma$  complex. The strong electrophiles can distinguish the difference between the ortho or para and the meta sites in toluene. Thus, the low substrate but high positional selectivity is found in the aromatic substitutions involving strong electrophiles. The ortho and the para oriented  $\pi$  complex type transition states of toluene would be quinoid in structure.



The formation of the rate-determining transition state in the substitution of benzene would similarly be of the oriented  $\pi$  complex type.

**Entropy Factor.**—The differences in rates between benzene and toluene have been believed to arise primarily from the differences in the enthalpies of activation, with similar values of the entropies of activation,  $\Delta S^\ddagger$ , obtained for both aromatics.<sup>12</sup> However, when the boron trifluoride catalyzed isopropylations in *n*-hexane solution were carried out in the temperature range from  $-23$  to  $25^\circ$ , the difference in the enthalpies of activation between toluene and benzene could not be found within experimental error, but the difference between both entropies of activation,  $\Delta\Delta S^\ddagger$ , was calculated to be  $-0.7 \text{ cal mol}^{-1} \text{ deg}^{-1}$ .

The entropy of activation is related to the freedom of atomic motions as a first rough approximation. In the displacement processes the entropies of activation

are usually negative, because the freedom of atomic motions becomes lower in the transition state. A more negative value of the entropy of activation indicates a stronger bond in the transition state between the atoms forming a new bond.<sup>12</sup> In the oriented  $\pi$  complex an interaction between the central carbon atom of the acceptor and the aromatic carbon atom becomes stronger as either the basicity of aromatics or the electron deficiency of acceptor becomes larger, causing the oriented  $\pi$  complex to become more stable.<sup>9</sup> At low temperatures, the existence of the oriented  $\pi$  complex of toluene can be demonstrated, but the oriented  $\pi$  complex of benzene could not be found.<sup>13</sup> The interaction between two carbon atoms is stronger in the oriented  $\pi$  complex of toluene than in that of benzene. It may be expected, therefore, that the partially formed carbon-carbon bond would be slightly stronger in the oriented  $\pi$  complex type transition state of toluene than in that of benzene. The more negative value of the entropy of activation would be obtained for the reaction of toluene, when the electrophile is very powerful.

When the enthalpy factor is very small, the entropy factor cannot be neglected. The difference in the enthalpies of activation between the meta oriented  $\pi$  complex type transition state of toluene and the oriented  $\pi$  complex type transition state of benzene would be very small. In that case, the entropy factor would be more predominant than the enthalpy factor. Consequently, the  $m_i^{\text{Me}}$  values obtained in the kinetically controlled substitution involving very strong electrophiles become smaller than 1.

$$\ln m_i^{\text{Me}} = \ln \frac{k_{m-\text{Me}}}{k_{\text{H}}} = -\frac{\Delta\Delta F^\ddagger}{RT} = -\frac{(\Delta\Delta H^\ddagger - T\Delta\Delta S^\ddagger)}{RT}$$

$$\Delta\Delta H^\ddagger < 0, \Delta\Delta S^\ddagger < 0$$

$$|\Delta\Delta H^\ddagger| < |T\Delta\Delta S^\ddagger|$$

$$\Delta\Delta F^\ddagger > 0$$

$$\therefore m_i^{\text{Me}} < 1$$

The  $o_f^{\text{Me}}$  and  $p_f^{\text{Me}}$  values obtained in the kinetically controlled substitution are larger than the  $m_i^{\text{Me}}$  values, because the enthalpy of activation for ortho or para oriented  $\pi$  complex type transition state is lower than the meta oriented  $\pi$  complex type transition state. When the enthalpy factors are able to almost compensate the entropy factors, the ortho and para partial rate factors,  $o_f^{\text{Me}}$  and  $p_f^{\text{Me}}$ , have values closer to 1. When the  $o_f^{\text{Me}}$  and  $p_f^{\text{Me}}$  values are nearly equal to 1 and the  $m_i^{\text{Me}}$  value is smaller than 1, the relative rates of toluene to benzene,  $k_{\text{T}}/k_{\text{B}}$ , are smaller than 1.

After the intermediate  $\sigma$  complex is formed, and before it is deprotonated, intramolecular isomerization could proceed. The increase of the amount of the meta isomer by intramolecular isomerization results in an increase of apparent  $m_i^{\text{Me}}$  value and in a decrease of apparent  $o_f^{\text{Me}}$  and  $p_f^{\text{Me}}$  values.

(13) R. Nakane and A. Natsubori, *J. Amer. Chem. Soc.*, **88**, 3011 (1966).

## Experimental Section

**Material.**—Benzene, toluene, isopropyl fluoride, boron trifluoride, *n*-hexane, cyclohexane, and nitromethane were prepared and purified by the previously described methods.<sup>9</sup> Benzene-*d*<sub>6</sub> was obtained from Syowa Denko Co. (Tokyo, Japan). Toluene-*d*<sub>8</sub> was obtained from Merck Sharp and Dohme of Canada Limited (Montreal, Canada). We used them without further purification.

**Competitive Isopropylation.**—A constant temperature bath at 25.0° and low constant temperature baths at melting points of ice (0°) and carbon tetrachloride (−22.9°) were used. An apparatus made of glass was used. When competitive isopropylation of benzene and toluene were carried out in *n*-hexane or cyclohexane solution, benzene ( $1 \times 10^{-2}$  mol), toluene ( $1 \times 10^{-2}$  mol), and *n*-hexane ( $2 \times 10^{-1}$  mol) or cyclohexane ( $2 \times 10^{-1}$  mol) were first charged in the flask, in which silica gel was contained. A greaseless vacuum valve 1 (Fisher and Porter Co., Warminster, Pa.) was joined to the flask. After valve 1 was connected to the vacuum line, the flask was immersed in liquid nitrogen and evacuated. Valve 1 was closed and the flask was separated from vacuum line. Valve 1 was connected to one neck of the two-necked reaction flask. The greaseless vacuum valve 2 was joined to another neck of the reaction flask. The reaction flask was evacuated through valve 2 and placed in the constant temperature bath. After valve 2 was closed, valve 1 was opened. The solution melted in the flask was introduced through valve 1 into the reaction flask with the silica gel remaining in the flask. Magnetic stirring was started. After valve 1 was closed, gaseous isopropyl fluoride ( $2 \times 10^{-3}$  mol) and then boron trifluoride ( $2 \times 10^{-4}$  mol), both contained in the gas reservoirs, were slowly introduced through valve 2 in the reaction flask and dissolved; a clear solution was obtained. However, a complete removal of traces of water was impossible in the operation mentioned above. After the reaction which continued for 5 min, the solution was quenched in water. The organic layer was separated, dried over calcium chloride, and analyzed by gas chromatography. When the competitive isopropylation was carried out in the nitromethane solution, benzene ( $3 \times 10^{-2}$  mol), toluene ( $3 \times 10^{-2}$  mol), and nitromethane ( $1.8 \times 10^{-1}$  mol) were charged in the flask. Then isopropyl fluoride ( $6 \times 10^{-3}$  mol) and boron trifluoride ( $6 \times 10^{-3}$  mol) were introduced in the solution. After 10 min, the solution was quenched in water. The organic layer was washed with 5% NaOH solution and then with water. The organic layer was separated, extracted with ether, dried, and analyzed by gas chromatography.

**Determination of Kinetic Isotope Effect.**—Toluene ( $1 \times 10^{-2}$  mol) or benzene ( $1 \times 10^{-2}$  mol), benzene-*d*<sub>6</sub> ( $1 \times 10^{-2}$  mol) or toluene-*d*<sub>8</sub> ( $1 \times 10^{-2}$  mol), and *n*-hexane ( $2 \times 10^{-1}$  mol) or cyclohexane ( $2 \times 10^{-1}$  mol) were charged in the glass flask. The isopropyl fluoride ( $2 \times 10^{-3}$  mol) and boron trifluoride ( $2 \times 10^{-4}$  mol) were introduced in the solution. After 5 min, the solution was quenched in water. The organic layer was separated, dried, and analyzed by gas chromatography. In order to observe the kinetic isotopic effect in nitromethane solution, toluene ( $3 \times 10^{-2}$  mol) or benzene ( $3 \times 10^{-2}$  mol), benzene-*d*<sub>6</sub> ( $3 \times 10^{-2}$  mol) or toluene-*d*<sub>8</sub> ( $3 \times 10^{-2}$  mol), nitromethane ( $1.8 \times 10^{-1}$  mol), isopropyl fluoride ( $6 \times 10^{-3}$  mol), and boron trifluoride ( $6 \times 10^{-3}$  mol) were charged in the flask.

**Gas Chromatographic Analysis.**—Analyses were carried out with a Hitachi gas chromatograph Model K-53 using a hydrogen flame ionization detector. Goley column (length 90 m, i.d. 0.25 mm) coated with MBMA [*m*-bis(*m*-phenoxyphenoxy)benzene and Apiezon L] was used. The column temperature was 100° with dry nitrogen gas flow rate at approximately 1.3 ml/min (atm). The accuracy of measurements concerning ortho, meta, and para isomers of isopropyltoluene was checked against the analytical data of the standard samples of isomers obtained from Tokyo Kagaku Seiki Co.

**Registry No.**—Boron trifluoride, 7637-07-2; benzene, 71-43-2; toluene, 108-88-3; isopropyl fluoride, 420-26-8.