from tables[46] and atomic polarization was neglected.[8] The data are summarized in Table VIII.

Acknowledgments. The authors are indebted to Professor R. C. Taylor for the Raman spectrum, to Dr. M. A. Da Rooge and Mr. C. L. Neumann for the dipole moment measurements, and to Professor B. Rickborn for helpful comments.

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(46) A. I. Vogel, W. T. Cresswell, G. J. Jeffery, and J. Leicester, *Chem. Ind.* (London), 358 (1950).

Boron Fluoride Catalyzed Alkylation. II.[1]
Tertiary Butylation at Low Temperatures

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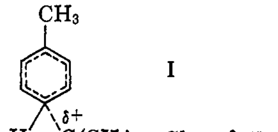
Contribution from the Institute of Physical and Chemical Research, Tokyo, Japan. *Received November 16, 1965*

Abstract: It is found that Friedel–Crafts *t*-butylation caused by decomposition of the alkylbenzene–*t*-butyl chloride–boron fluoride 1:1:1 oriented π complexes at low temperatures shows high substrate selectivity. The isomer distribution of *t*-butyltoluene formed is 100% *para* isomer. Hence the electrophile in this aromatic substitution is not a *t*-butyl cation or an incipient *t*-butyl cation but a polar donor–acceptor complex $^{\delta+}C(CH_3)_3$, the electrophilic character of which is very weak.

Olah, *et al.*,[2] found that Friedel–Crafts *t*-butylation of toluene and benzene with *t*-butyl bromide and isobutylene under nonisomerizing conditions at room temperature shows intermediate substrate selectivity ($k_{\text{toluene}}/k_{\text{benzene}}$ = 13–16) and that the isomer distribution of *t*-butyltoluene formed is 5.7–7% *meta* and 94.3–93% *para* isomers.

Allen, *et al.*,[3] suggested that all *t*-butylations of toluene can be obtained by alkylations producing isomeric mixtures containing 7% *m*- and 93% *p-t*-butyltoluene, 67% *m*- and 33% *p-t*-butyltoluene, or an intermediate distribution; the first isomer distribution is the substitution distribution and the second the thermodynamically controlled subsequent or concurrent isomer distribution caused by predominant intermolecular migration of the *t*-butyl group.

In a recent publication[1] we reported that when a small amount of toluene was dissolved in polarized *t*-butyl chloride–boron fluoride complex and the absorption spectrum of the solution was measured at −95°, strong absorption characteristic of a toluene–*t*-butyl chloride–boron fluoride 1:1:1 complex was observed around 260 and 361 mμ. When the solution was diluted with liquid isopropyl chloride at low temperatures, the strong absorption disappeared and the fine structure of the benzenoid band of toluene was observed. The 1:1:1 complex is a dissociable π complex, but its absorption band closely resembles those of benzenium ions.[4] The thermodynamic isotope effect showed that the complex system contains $^{-}Cl\cdots{}^{\delta-}BF_3$ but not BF_3Cl^-. Hence the complex seems to be an oriented π complex such as structure I but not an unlocalized π complex. When a small portion of the boron fluoride was withdrawn from the solution that dissolved the oriented π complex, the peaks became faint and the fine structure of the benzenoid band of *t*-butyltoluene appeared, overlapped with the above peaks. When boron fluoride was withdrawn completely, the peaks disappeared and only the fine structure of the benzenoid band of *t*-butyltoluene remained. Hence *t*-butylation can proceed at low temperatures by decomposition of the oriented π complex. In the present work the relative reactivity and isomer distribution in this Friedel–Crafts *t*-butylation are investigated.



I

Results

The dissociation pressure of the toluene–*t*-butyl chloride–boron fluoride 1:1:1 oriented π complex, which melts at −122°, is approximately 760 mm at −95°. The vapor is composed mostly of boron fluoride. The vapor was withdrawn through a leak into an evacuated reservoir, while the liquid complex was kept in a constant temperature bath at −95° (melting point of toluene) until the amount of boron fluoride introduced in the reservoir became nearly equal to that of the boron fluoride contained in the complex. Ammonia was added to the liquid in order to quench the trace of boron fluoride. This caused the white solid boron fluoride–ammonia complex to deposit. After the liquid was allowed to warm to room temperature, the separated liquid was analyzed by gas–liquid partition chromatography and found to be composed of *t*-butyl chloride, toluene, and *t*-butyltoluene in an amount which was only about 3% of that of toluene, as shown in Table I. By complete withdrawal of boron fluoride, the oriented π complex dissociated mostly into toluene, yielding only a small amount of *t*-butyltoluene.

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(1) Part I: R. Nakane, A. Natsubori, and O. Kurihara, *J. Am. Chem. Soc.*, **87**, 3597 (1965).

(2) G. A. Olah, S. H. Flood, and M. E. Moffatt, *ibid.*, **86**, 1060 (1964); G. A. Olah and N. A. Overchuck, *ibid.*, **87**, 5786 (1965).

(3) R. H. Allen and L. D. Yates, *ibid.*, **83**, 2799 (1961).

(4) G. Dallinga, E. L. Mackor, and A. A. Verrijn Stuart, *Mol. Phys.*, **1**, 123 (1958).

Table I. *t*-Butylation Caused by Decomposition of the Toluene–*t*-Butyl Chloride–Boron Fluoride 1:1:1 Oriented π Complex at −95°

Mole ratio of reactant			Product				
			Mole ratio		Isomer distribution in *t*-butylmethylbenzene, %		
Toluene	*t*-Butyl chloride	Boron fluoride	*t*-Butylmethylbenzene	Toluene	*o*	*m*	*p*
1	1	1	0.03	1	...	≪0.1	100
1	2	2	0.35	1	...	≪0.1	100
1	100	150	>100	1	...	≪0.1	100

Table II. Competitive *t*-Butylation of *o*-Xylene and Toluene at −95°

Mole ratio of reactant				Mole ratio of product		Isomer distribution in *t*-butylated alkylbenzenes					
						Isomeric *t*-butylmethylbenzene, %			Isomeric *t*-butyldimethylbenzene, %		
Toluene	*o*-Xylene	*t*-Butylchloride	Boron fluoride	*t*-Butylmethylbenzene	*t*-Butyldimethylbenzene	*o*	*m*	*p*	1,2,3	1,2,4	$\frac{k_{o\text{-xylene}}}{k_{\text{toluene}}}$
1	0.05	2.06	2.06	1	0.47	...	≪0.1	100	...	100	9.4
1	0.05	2.05	2.04	1	0.45	...	≪0.1	100	...	100	9.0
1	0.10	2.22	2.14	1	0.98	...	≪0.1	100	...	100	9.8
1	0.10	2.21	2.22	1	0.94	...	≪0.1	100	...	100	9.4
1	0.20	2.41	2.42	1	1.73	...	≪0.1	100	...	100	8.7
1	0.20	2.42	2.42	1	1.84	...	≪0.1	100	...	100	9.2

When boron fluoride was withdrawn by evacuation from the oriented π complex dissolved in the polarized *t*-butyl chloride–boron fluoride complex, considerable *t*-butylation was found together with the reversible dissociation. The oriented π complex is re-formed immediately from dissociated toluene and the polarized complex, and further decomposition of the oriented π complex to *t*-butyltoluene will proceed. However, after a certain amount of boron fluoride gas was withdrawn, the solution solidified. For example, when about one-tenth of the boron fluoride was withdrawn from a solution composed of toluene, *t*-butyl chloride, and boron fluoride in a ratio of 1:2:2, a small part of the *t*-butyl chloride began to deposit. In the solid phase, dissociated toluene may be surrounded with solid *t*-butyl chloride and protected against the attack of the polarized complex. Re-formation of the oriented π complex may occur only in the liquid phase. When the relative amount of toluene in the reactant solution is large, full *t*-butylation may not proceed while the system remains in the liquid state. Hence the amount of *t*-butyltoluene relative to toluene in the products becomes larger as the amount of toluene relative to the polarized complex in the reactant solution decreases, as shown in Table I.

In the decomposition process only *p*-*t*-butyltoluene was formed. Neither *m*-*t*-butyltoluene nor *o*-*t*-butyltoluene was formed, nor were di- or higher *t*-butylated products obtained. Thus the *t*-butylation caused by the decomposition of the oriented π complex at low temperatures is an electrophilic substitution producing 100% *p*-*t*-butyltoluene.

Benzene and *p*-xylene were not dissolved in the polarized complex at low temperatures. When a small amount of *o*-xylene or 1,2,3-trimethylbenzene was dissolved in the polarized complex, a yellow liquid was obtained as in other oriented π-complex systems. When boron fluoride was withdrawn by evacuation, the yellow liquid became colorless, and *t*-butylated alkylbenzenes were obtained. *m*-Xylene and mesitylene formed the oriented π complexes but were not *t*-butylated at low temperatures.[1]

The polarized complex seems not to form stable π complexes with benzene or *p*-xylene but does with *o*-xylene or 1,2,3-trimethylbenzene at low temperatures. In previous work[1] we concluded that the π complexes isolated at low temperatures are oriented π complexes, because their absorption spectra resemble closely those of benzenium ions.[4] A specific orientation in the π complex is suggested also by the result that the polarized complex forms a π complex with toluene, *o*-xylene, or *m*-xylene but not with *p*-xylene. Usually, in order to determine substrate selectivity, the relative reactivity of alkylbenzenes over benzene was observed by Ingold's method of competitive substitution.[5] For the investigation of the mechanism of *t*-butylation caused by decomposition of the oriented π complex at low temperatures, competitive *t*-butylation between *o*-xylene and toluene and between 1,2,3-trimethylbenzene and toluene was carried out.

A mixture of toluene and *o*-xylene was dissolved at −95° in the polarized complex, the amount of which was twice the amount of combined aromatic substrate. A yellow solution, in which both toluene–*t*-butyl chloride–boron fluoride and *o*-xylene-*t*-butyl chloride–boron fluoride 1:1:1 oriented π complexes were dissolved, was obtained. When about one-twentieth of boron fluoride in the yellow solution was withdrawn by evacuation, ammonia was added to the solution. Both the oriented π complexes and the polarized complex were quenched simultaneously. By this procedure, more than a few per cent of toluene and perhaps 12% of *o*-xylene were not *t*-butylated, but, when boron fluoride was completely withdrawn by evacuation, about 25% of toluene and a large part of *o*-xylene were *t*-butylated. The relative concentrations of toluene and *o*-xylene were changed from a 1:0.05 to 1:0.2 ratio. When the relative concentration was in a 1:0.3 ratio, *t*-butylation did not occur, for a small part of *o*-xylene deposited. Changing the rate of withdrawal of boron fluoride had almost no effect on the relative rates observed. The mole ratios of *t*-butylated

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(5) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **83**, 4571 (1961), and subsequent papers.

Table III. Reactivity and Selectivity in Electrophilic Substitutions

Reaction	Substituting agent	Catalyst	Solvent	Temp, °C	$\frac{k_{o\text{-xylene}}}{k_{\text{toluene}}}$	$\frac{k_{1,2,3\text{-trimethylbenzene}}}{k_{\text{toluene}}}$	Isomer distribution in substituted toluene, %			Partial rate factors at 25°, m_f^{Me}	Ref
							o	*m*	*p*		
Methylation	MeBr	$GaBr_3$	ArH	25			55.7	9.9	34.4	1.70^a	*c*
Ethylation	EtBr	$GaBr_3$	ArH	25			38.4	21.0	40.6	1.56^a	*c*
Isopropylation	*i*-PrBr	$GaBr_3$	ArH	25			26.2	26.6	47.2	1.47^a	*c*
	i-PrBr	$AlCl_3$	$MeNO_2$	25	1.1	2.12	46.7	14.7	38.6	0.90^a	*d*
	C_3H_6	$AlCl_3$	$MeNO_2$	25	0.89	2.04	46.1	15.1	38.8	0.88^a	*d*
t-Butylation	*t*-BuBr	$GaBr_3$	ArH	25			...	32.1	67.9	1.56^a	*c*
	t-BuBr	$AlCl_3$	$MeNO_2$	25			...	46.4	53.6	2.6^a	*e*
	t-BuBr	$FeCl_3$	$MeNO_2$	25			...	64.8	35.2	2.3^a	*e*
	t-BuBr	$SnCl_4$	$MeNO_2$	25	2.7	10.2	...	5.9	94.1	2.3^a	*e*
	t-BuBr	ZnI_2	$MeNO_2$	25			...	6.9	93.1	3.0^a	*e*
	t-BuBr	$AgClO_4$	$MeNO_2$	25			...	5.7	94.3	2.6^a	*e*
	t-BuBr	$AgBF_4$	$MeNO_2$	25			...	50.3	49.7	2.8^a	*e*
	i-C_4H_8	$AlCl_3$	$MeNO_2$	25	3.1	7.2	...	6.0	94.0	2.7^a	*e*
	i-C_4H_8	$FeCl_3$	$MeNO_2$	25			...	5.7	94.3	2.6^a	*e*
	i-C_4H_8	H_2SO_4	$MeNO_2$	25			...	5.6	94.4	2.7^a	*e*
	t-BuCl	BF_3	*t*-BuCl·BF_3	−95	9.3	40	...	$\ll 0.1$	100	4^b	*f*
Benzylation	$PhCH_2Br$	$GaBr_3$	ArH	25			41.1	19.4	39.5	2.3^a	*g*
	$PhCH_2Cl$	$AlCl_3$	$MeNO_2$	25	1.3		43.5	4.5	52.0	0.43^a	*h*
Acetylation	MeCOCl	$AlCl_3$	$C_2H_4Cl_2$	25			1.17	1.25	97.6	4.8^a	*i*
	MeCOCl	$SbCl_5$	$PhNO_2$	25	5.7		0.6	1.8	97.6	6.1^a	*j*
	MeCOF	SbF_5	$MeNO_2$	25	10.1		1.4	0.9	97.7	5.2^a	*j*
Benzoylation	PhCOCl	$AlCl_3$	$PhNO_2$	25			7.2	1.1	91.7	5.0^a	*k*
	PhCOCl	$AlCl_3$	$C_2H_4Cl_2$	25			9.3	1.45	89.3	4.9^a	*l*
Nitration	HNO_3		HOAc + H_2O	45			56.5	3.5	40.0	2.5^a	*m*
	HNO_3	H_2SO_4	HOAc + $C_4H_8SO_2$	25	0.56		56.3	2.6	41.0	1.25^a	*n*
	HNO_3	H_2SO_4	$MeNO_2$	25			61.7	1.9	36.4	1.3^a	*o*
	NO_2BF_4		$C_4H_8SO_2$	25	1.1		65.4	2.8	31.8	0.14^a	*p*
Chlorination	Cl_2	$AlCl_3$	$MeNO_2$	25	3.8		63.2	2.0	34.8	0.93^a	*q*
	Cl_2	$FeCl_3$	$MeNO_2$	25	2.8		67.8	2.3	29.9	1.10^a	*q*
	Cl_2	$FeCl_3$	ArH	25	4.2		63.0	2.2	34.8	0.98^a	*q*
	Cl_2	...	HOAc–H_2O	25	6.1		59.8	0.5	39.7	5.0^a	*r*
Bromination	Br_2	$FeCl_3$	$MeNO_2$	25	1.0		64.6	1.8	33.6	0.12^a	*s*
	Br_2	...	HOAc–H_2O	25	8.8		32.9	0.3	66.8	5.5^a	*t*

[a] Calculated from rate ratio of toluene to benzene and *meta* isomer ratio in substituted toluene. [b] Calculated by eq 1. [c] See ref 7. [d] See ref 14. [e] See ref 2. [f] Present report. [g] H. C. Brown and B. A. Bolto, *J. Am. Chem. Soc.*, **81**, 3320 (1959). [h] G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1688 (1962). [i] See ref 9. [j] See ref 8. [k] See ref 10. [l] See ref 11. [m] H. Cohn, E. D. Hughes, M. H. Johnes, and M. G. Peeling, *Nature*, **169**, 291 (1952). [n] G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **83**, 4571 (1961). [o] L. M. Stock, *J. Org. Chem.*, **26**, 4120 (1961). [p] G. A. Olah, S. J. Kuhn, S. H. Flood, and J. C. Evans, *J. Am. Chem. Soc.*, **84**, 3687 (1962). [q] G. A. Olah, S. J. Kuhn, and B. A. Hardie, *ibid.*, **86**, 1055 (1964). [r] See ref 12. [s] G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *J. Am. Chem. Soc.*, **86**, 1039 (1964). [t] See ref 12 and 13.

o-xylene to *t*-butylated toluene obtained are shown in Table II. The relative rate ratio remained almost unchanged on the assumption that the rates of *t*-butylation are first order with respect to the aromatic concentrations and that a practically constant excess of the aromatics was maintained. Thus, by the method of competitive alkylation, the average value of relative rate ratio of *t*-butylation between *o*-xylene and toluene at −95° was found to be $k_{o\text{-xylene}}/k_{\text{toluene}} = 9.3$.

In the toluene–1,2,3-trimethylbenzene system, the average value of relative rate ratio at −95° was found to be $k_{1,2,3\text{-trimethylbenzene}}/k_{\text{toluene}} = 40$.

Discussion

The product distribution for 1,2,3-trimethylbenzene and *o*-xylene and the rate ratio may be analyzed by applying the additivity principle[6] as follows.

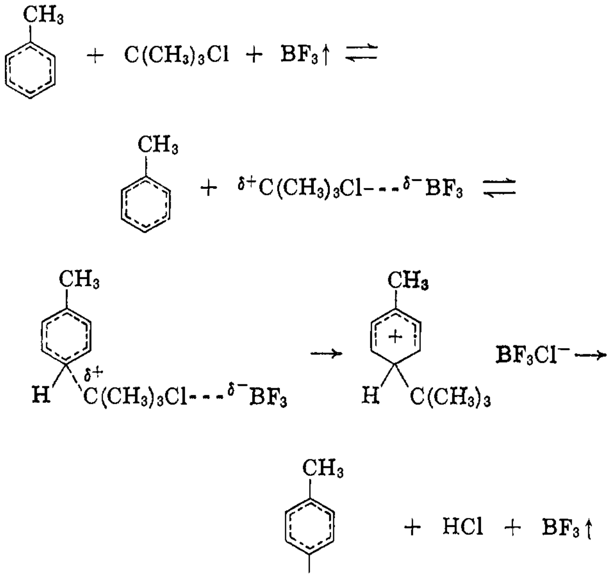
$$\frac{k_{1,2,3\text{-trimethylbenzene}}}{k_{o\text{-xylene}}} = \frac{(m_f^{\text{Me}})^2 p_f^{\text{Me}}}{2m_f^{\text{Me}} p_f^{\text{Me}}} = \frac{m_f^{\text{Me}}}{2} \qquad (1)$$

Thus, $m_f^{\text{Me}} = 9$ at −95°. This is equivalent to an m_f^{Me} value of about 4 at 25°. The relative rate ratios of *o*-xylene to toluene and of 1,2,3-trimethylbenzene to toluene, isomer distributions in substituted toluene, and partial rate factors of electrophilic substitutions are summarized in Table III. With regard to both the relative reactivity and isomer distribution, *t*-butylation at low temperatures is different from conventional Friedel–Crafts *t*-butylation at room temperature;[2,7] it rather resembles Friedel–Crafts acetylation[8,9] and benzoylation[10,11] or noncatalyzed chlorination[12] and bromination.[12,13]

Olah, *et al.*,[8,14] suggested that when the attacking agent is weakly electrophilic as with acylium ion in acylation, the formation of the π complex becomes reversible and is followed by a transition state corresponding to a σ complex which determines both substrate and positional selectivity. In this case a high substrate and positional selectivity is obtained. *t*-Butylation at room temperature shows intermediate substrate and positional selectivity, because *t*-butyl cation is more electrophilic than acetyl cation but less electrophilic than methyl or isopropyl cations.[2,15]

At low temperatures, *t*-butylation shows higher reagent selectivity, which is characteristic of Friedel–Crafts acylation, than at room temperature. At low temperatures *t*-butyl chloride forms a polarized complex with boron fluoride but is not ionized to a more reactive *t*-butyl cation.[16] When alkylbenzenes are dissolved in the polarized complex, the oriented π complexes which contain a polar donor–acceptor complex $^{\delta+}\text{C(CH}_3)_3\text{Cl}\cdots{}^{\delta-}\text{BF}_3$, but not a *t*-butyl cation, are formed. By decomposition of this oriented π complex, *t*-butylation proceeds. Hence the electrophile in *t*-butylation at low temperatures seems to be not the *t*-butyl cation or an incipient *t*-butyl cation but the polar donor–acceptor complex which is very weakly electrophilic as is acylium ion.[17] The oriented π complex is transformed into the σ complex. The σ-complex formation is the rate-determining step. In this case the *t*-butyl group will be bound first at the *para* position, because, only in *para* and *ortho* positions, the intermediate σ complex is conjugatively stablilized as suggested by Olah, *et al.*,[14] and the formation of *ortho* σ complex is prevented by steric hindrance.

Allen[18] suggested that the isomerization of *t*-butyltoluene under acidic conditions proceeds not by an intramolecular 1,2 shift but by an intermolecular migration. In *t*-butylation at low temperatures too the intramolecular migration of the *t*-butyl group within the σ complex will not occur. When the polarized complex coexists, it will attack immediately a free toluene molecule dissociated from the oriented π complex. Hence there will not be much chance that the electronically deficient *t*-butyl group of the σ complex will attack the free toluene molecule and intermolecular migration of the *t*-butyl group will occur.



(2)

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(6) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 40, 135 (1963).

(7) H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 6255 (1956).

(8) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *ibid.*, **86**, 2203 (1964).

(9) H. C. Brown, G. Marino, and L. M. Stock, *ibid.*, **81**, 3310 (1959); H. C. Brown and G. Marino, *ibid.*, **81**, 5611 (1959).

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(11) H. C. Brown and G. Marino, *J. Am. Chem. Soc.*, **81**, 3308 (1959).

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

(13) H. C. Brown and L. M. Stock, *ibid.*, **79**, 1421 (1957).

(14) G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffatt, and N. A. Overchuck, *ibid.*, **86**, 1046 (1964).

(15) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953).

(16) R. Nakane, O. Kurihara, and A. Natsubori, *J. Phys. Chem.*, **68**, 2876 (1964); R. Nakane and T. Oyama, *ibid.*, **70**, 1146 (1966).

(17) When boron fluoride gas is introduced into methylbenzenes in which alkyl fluorides are dissolved, alkyl cations are formed. Thus, at room temperature alkylated methylbenzenes are obtained and at low temperatures σ complexes are isolated: G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **80**, 6541 (1958).

When boron fluoride gas is introduced at room temperature into *m*-xylene, in which *t*-butyl chloride is dissolved, 1,3-dimethyl-5-*t*-butylbenzene is obtained. However, in a similar procedure at −45°, 1,3-dimethyl-5-*t*-butylbenzene is not produced and any intermediate complex is not isolated. Hence *t*-butyl cation is formed at room temperature but will not be formed at temperatures lower than −45°.

The polarized *t*-butyl chloride–boron fluoride complex exists at −95°, but dissociates at higher temperatures. It forms the oriented π complexes with methylbenzenes at −95°. The thermodynamic isotope effect shows[1] that the structure of the oriented π complexes is $\text{Ar}\cdots{}^{\delta+}\text{RCl}\cdots{}^{\delta-}\text{BF}_3$. By withdrawal of boron fluoride from the oriented π complexes, toluene, *o*-xylene, and 1,2,3-trimethylbenzene are *t*-butylated, but *m*-xylene and mesitylene are not, because of steric hindrance.

These observed results suggest that the mechanism of boron fluoride catalyzed alkylation with alkyl chloride at low temperatures is different from that at room temperature. Details will be reported later.

(18) R. H. Allen, *J. Am. Chem. Soc.*, **82**, 4856 (1960).

The hydrogen chloride formed by proton elimination from aromatics dissolves in the solution, but it cannot form a complex with boron fluoride.[19] A free proton is not formed and aromatic ring protonation does not occur. Thus under the present conditions, thermodynamically controlled isomerization does not occur even though *t*-butylation proceeds *via* the σ complex and only the *para* isomer is produced.

Experimental Section

The toluene used was Matheson Coleman and Bell spectral reagent. *o*-Xylene was obtained from Wako Pure Chemical Industries. Their average purity was more than 99% by gas–liquid chromatography analysis. 1,2,3-Trimethylbenzene was obtained from Tokyo Kasei Co. It contained about 5% of 1,2,4-trimethylbenzene, which is not *t*-butylated.[2] These methylbenzenes were used without further purification. Boron fluoride was obtained from the Harshaw Chemical Co. This was purified by low-temperature fractional distillation. *t*-Butyl chloride was obtained from the Tokyo Kasei Co. This was also purified by fractional distillation.

The apparatus used for *t*-butylation is shown in Figure 1. Glass flask A (20 ml) with universal joint B was connected to the vacuum line. It was charged with known amounts of purified *t*-butyl chloride and aromatics, which were frozen with liquid nitrogen. The universal joint and stopcocks were Kel-F greased. The entire apparatus was evacuated. After stopcocks 1, 2, and 4 were closed, stopcock 5 was opened and boron fluoride (molar amount fixed at 0.05) was introduced from gas reservoir C into the flask. Then stopcocks 3 and 5 were closed, and the flask was immersed in a low-temperature bath at the melting point of toluene (−95°). The contents of the flask melted. The liquid-oriented π complex was formed while the vapor pressure remained at approximately 1 atm. When stopcock 4 was opened, the vapor, which was composed mostly with boron fluoride, was introduced through leak E into evacuated vessel F. The average withdrawal rate[20] of boron fluoride was about 0.01 mole/min. When the pressure in vessel F increased and reached a certain value, stopcock 4 was closed and stopcocks 1 and 2 were opened to evacuate the vessel again. By repeating this procedure, if necessary, boron fluoride was withdrawn from the flask. Lastly, after stopcocks 1, 2, and 4 were closed and content of the flask was again frozen with liquid nitrogen, stopcocks 3 and 6 were opened. Ammonia was introduced from gas reservoir D into the flask. When the flask was allowed to warm gradually, the melted complexes reacted with ammonia, and white solid boron fluoride–ammonia complex deposited immediately in the flask. The production of this complex occurred freely even below −95°. After the flask was allowed to warm to room temperature, the organic liquid in it was separated and analyzed directly by gas–liquid chromatography. The analysis was carried out with a Hitachi Perkin-Elmer programmed temperature gas chromatograph, Model F 6 D, by the use of Golay column HB-2000 (L, 45 m i.d., 0.25 mm) coated with polypropylene glycol (UCON oil 50-HB-2000 Poly) and a hydrogen flame ionization detector. The column temperature was 120° with dry nitrogen gas flow rate at approximately 1.1 ml/min atm. The accuracy of measurement was checked by analysis of the products prepared by Friedel–Crafts *t*-butylation of aromatics with *t*-butyl bromide under heterogeneous reaction conditions at room temperature according to the method of Olah, *et al.*[2]

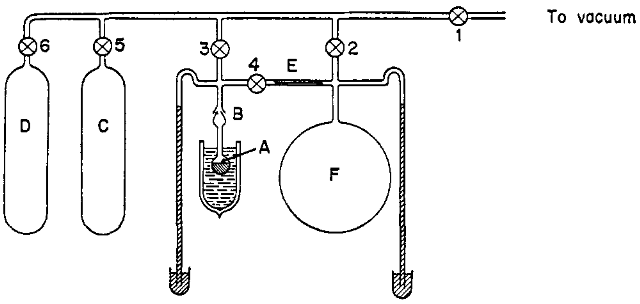

Figure 1. Reactor and accessories.

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[19] H. S. Booth and D. R. Martin, *J. Am. Chem. Soc.*, **64**, 2198 (1942).

[20] The polarized complex is solid at −95° and shows a dissociation pressure of approximately 700 mm. When boron fluoride is withdrawn from the polarized complex solution in which the oriented π complex is dissolved, a part of the polarized complex decomposes directly into boron fluoride gas and *t*-butyl chloride, while another part is consumed to re-form the oriented π complex. Consequently, the withdrawal rate of boron fluoride is not identical with the rate of *t*-butylation.