

from CuO at 750 °C). The system was closed off and the sample was heated to 600 °C. The total pressure in the reaction system began to drop at 550 °C and remained at 0.85 Torr at 600 °C when the heat was cut off. Residual O₂ (about one-third of the pressure) was removed by CuO at 600 °C. A glass capillary at the temperature of liquid N₂ reduced the pressure to $\sim 10^{-3}$ Torr. The Ar was adsorbed on charcoal at liquid N₂ temperature, isolated from the combustion system, and cleaned on Ti sponge, on Ti foil, and in two additional steps on Ti–Pd getters. The Ar was then admitted to the mass spectrometer. The amount of Ar was determined by calibrating the instrument with known

air pipets to give $(1.14 \pm 0.1) \times 10^{-4}$ cm³ at standard temperature and pressure (STP) obtained from the 1.3 mg of 1–I-G. The procedure was repeated by heating a finger without sample. The total procedural blank was 1.0×10^{-6} cm³ (STP), or 0.9% of the Ar from the sample. Thus 1 g of 1–I-G would have provided 8.8×10^{-2} cm³ (STP) of Ar, or 0.016% of the weight of the sample was Ar.

Registry No. 1, 95841-28-4; 9, 83136-19-0; 10, 83136-20-3; 11, 83136-21-4; 12, 95799-47-6; 13, 95799-48-7; 14, 95799-49-8; Cs₂CO₃, 534-17-8; D₂O, 7789-20-0; freon 114, 76-14-2; argon, 7440-37-1.

Boron, Aluminum, and Gallium Tris(trifluoromethanesulfonate) (Triflate): Effective New Friedel–Crafts Catalysts¹

George A. Olah,* Omar Farooq, S. Morteza F. Farnia, and Judith A. Olah

Contribution from the Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661. Received August 12, 1987

Abstract: Boron, aluminum, and gallium tris(trifluoromethanesulfonate) (triflate) were prepared from the corresponding chlorides (bromides) and triflic acid. The group IIIA triflates were isolated in pure form and fully characterized (elemental analysis, molecular weight, and NMR and IR spectroscopy). Boron tris(triflate) is a monomeric, relatively volatile compound [mp 43–45 °C, bp 68–73 °C (0.5 Torr)], whereas aluminum and gallium triflate are associated, high-melting associated solids. Boron, aluminum, and gallium tris(triflate) are efficient new Friedel–Crafts catalysts as shown in alkylation, isomerization, and acylation reactions. Alkylation of benzene and toluene with methyl, ethyl, isopropyl, and *tert*-butyl halides (fluoride, chloride, and bromide) were carried out with boron, aluminum, and gallium tris(triflate) as catalyst in CH₂Cl₂ and CH₃NO₂ solvent at room temperature. Substrate (k_T/k_B) and positional selectivity (isomer distribution) were determined by GLC. Boron triflate shows the highest catalytic activity followed by gallium and aluminum triflate as reflected by overall yields in the alkylation reactions and tendency of accompanying isomerization, causing substantially increased meta substitution and disproportionation.

In the course of more than 100 years of Friedel–Crafts chemistry,² two catalysts achieved preeminence. Anhydrous aluminum trichloride was introduced by Friedel and Crafts themselves and maintained its wide use ever since despite some unfavorable properties such as being a subliming solid (limiting its use to solution chemistry) and only limited solubility in apolar or hydrocarbon solvents. Boron trifluoride became a significant catalyst since the 1920s following fundamental studies by Meerwein, Nieuwland, and others.^{2,3} Because it is a low-boiling gas (bp –101 °C), some of its more convenient complexes, albeit reduced in reactivity, are frequently used, such as ether complexes. Although a significant number of other Lewis acid halide (and pseudohalide) catalysts are also used, none of them achieved similar wide application. Since the 1960s, some superacid catalysts such as antimony pentafluoride gained significance.⁴

The most widely used Lewis acids in Friedel–Crafts chemistry are halides of different metals.² Other derivatives are more seldom used. Following the discovery of trifluoromethanesulfonic (triflic) acid by Haszeldine and Kidd⁵ in 1954, there has been a rapid

growth in the chemistry of triflic acid and its metal derivatives.⁶ Many metal triflates have been successfully used in various types of chemical transformations. The triflates of group IIIA elements remained, however, less studied.

Boron tris(triflate) was first prepared by Engelbrecht and Tschager⁷ in trifluoromethanesulfonic (triflic) acid solution in the form of its conjugate Brønsted–Lewis superacid, 2CF₃SO₃H–B(OSO₂CF₃)₃. The catalytic activity of this superacid was subsequently explored by Olah, Laali, and Farooq.⁸ Boron tris(triflate) was obtained free of protic acids only in our recent work and was used in the preparation of stable carbocations.⁸ It was, however, till now not studied concerning its Friedel–Crafts catalytic activity. Reports on the study of the triflates of aluminum and gallium are even more scanty. Although Cheradame et al. reported^{9a} the preparation of aluminum tris(triflate) from triethylaluminum and triflic acid, no details were given, nor was the compound characterized or its catalytic activity studied, except in some olefin polymerizations.^{9a,b}

We report now that in our continued study of Friedel–Crafts chemistry boron, aluminum, and gallium tris(trifluoromethanesulfonate) (triflate) were found to be convenient and effective new Friedel–Crafts catalysts.¹⁰ We report their preparation, char-

(1) Friedel–Crafts Chemistry. 11. Part 10, see: Olah, G. A.; Donovan, D. J.; Lin, H. C. *J. Am. Chem. Soc.* 1976, 98, 2661.

(2) For reviews see: (a) *Friedel–Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley: New York, 1963–64; Vol. I–IV. (b) Olah, G. A. *Friedel–Crafts Chemistry*; Wiley-Interscience: New York, 1973.

(3) (a) Bowlus, H.; Nieuwland, J. *J. Am. Chem. Soc.* 1931, 53, 3835. (b) Meerwein, H.; Pannwitz, W. *J. Prakt. Chem.* 1934, 141, 123. (c) Booth, H. S.; Martin, D. R. *Boron Trifluoride and Its Derivatives*; Wiley: New York, 1949. (d) Topchiev, A. V.; Zavgorodnii, S. V.; Paushkin, Y. M. *Boron Trifluoride and Its Compounds as Catalysts in Organic Chemistry*, (Engl. Ed.); Pergamon: New York, 1959.

(4) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley-Interscience: New York, 1985.

(5) Hazeldine, R. N.; Kidd, J. M. *J. Chem. Soc.* 1954, 4228.

(6) (a) For a review, see: Howells, R. D.; McCown, J. C. *Chem. Rev.* 1977, 77, 69. (b) Emde, H.; Domsch, D.; Feger, H.; Frick, U.; Göyz, A.; Hergott, H. H.; Hofmann, K.; Kober, W.; Krägeloh, K.; Oesterle, T.; Steppan, W.; West, W.; Simchen, G. *Synthesis* 1982, 1. (c) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Ibid.* 1982, 85. (d) Stang, P. J.; White, M. R. *Aldrichimica Acta* 1983, 15.

(7) Engelbrecht, A.; Tschager, E. *Z. Anorg. Allg. Chem.* 1977, 433, 19.

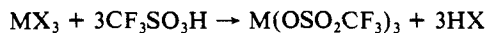
(8) Olah, G. A.; Laali, K.; Farooq, O. *J. Org. Chem.* 1984, 49, 4591.

(9) (a) Collomb, J.; Gandini, A.; Cheradame, H. *Makromol. Chem., Rapid Commun.* 1980, 1, 489. (b) Collomb, J.; Morin, B.; Gandini, A.; Cheradame, H. *Eur. Polym. J.* 1980, 16, 1135.

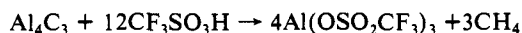
acterization, spectroscopic study, and application in Friedel-Crafts alkylations and acylations.

Results and Discussion

Preparation and Characterization of Boron, Aluminum, and Gallium Tris(triflate). Boron, aluminum, and gallium tris(triflate) are conveniently prepared by reacting the corresponding trichlorides (tribromides) with triflic acid. Reactions with boron



halides are fast and can be carried out in SO_2ClF or 1,1,2-trichlorotrifluoroethane (Freon-113) solution at -78°C . Reactions with other halides are usually slower and are carried out to reflux from room temperature in Freon-113. Aluminum triflate can also be prepared from aluminum carbide and triflic acid, methane being the byproduct. Boron and aluminum triflates can also be obtained



by reacting boron and aluminum trialkyls or the corresponding mixed alkyl chlorides (bromides) with triflic acid, but the reactions with boron alkyls are more sluggish to go to completion and mixed boron alkyl triflates tend to form.

Any complexed hydrogen halide was removed in vacuum after repeated washing with dry Freon-113. Boron triflate was subsequently distilled at reduced pressure. Aluminum and gallium triflate are obtained as high-melting solids. All three triflates were obtained in pure form and gave satisfactory elemental analysis (see the Experimental Section). Absence of any residual halide or complexed hydrogen halide was ascertained by alkaline hydrolysis of the triflates followed by titration with silver nitrate.

Boron tris(triflate) is a relatively volatile colorless compound [bp $68-73^\circ\text{C}$ (0.5 Torr), mp $43-45^\circ\text{C}$] differing significantly from aluminum and gallium tris(triflate), which are high-melting powdery solids. Whereas $\text{B}(\text{OSO}_2\text{CF}_3)_3$ distills without decomposition in vacuum at atmospheric pressure, heating above 100°C results in thermal decomposition, giving COF_2 , SO_2 , BF_3 , $\text{CF}_3\text{SO}_3\text{CF}_3$,¹¹ and a yet unidentified boron compound, most probably a fluorinated boroxane. Boron tris(triflate) is extremely hygroscopic and must be strictly kept away from moisture. It is readily soluble in such solvents as methylene chloride, 1,1,2-trichlorotrifluoroethane (Freon-113), SO_2 , SO_2ClF , etc. Aluminum tris(triflate) in contrast is only sparingly soluble in SO_2 and SO_2ClF . Gallium tris(triflate) is practically insoluble in these solvents. All the studied triflates, including aluminum and gallium tris(triflate), are soluble in strongly coordinating solvents such as ether, acetone, acetonitrile, nitromethane, or diglyme. Boron triflate is well soluble in nitromethane, but aluminum and gallium triflate have relatively poor solubility in this solvent.

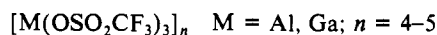
We have investigated the spectroscopic properties of the prepared group IIIA triflates. The IR spectra exhibit characteristic absorptions for the triflate groups. Whereas for boron tris(triflate) the IR absorption bands (CCl_4) are at 1400, 1205, 1140, and 950 cm^{-1} , aluminum and gallium triflate exhibit characteristic absorptions (KBr) at 1270-1250, 1180, 1035, and 770 cm^{-1} and 1260, 1170, 1040, and 760 cm^{-1} , respectively.

Boron, aluminum, and gallium tris(triflate) were also characterized through their ^{11}B , ^{13}C , ^{19}F , ^{27}Al , ^{69}Ga , and ^{71}Ga nuclear magnetic resonance spectra. The ^{11}B NMR spectrum of $\text{B}(\text{OSO}_2\text{CF}_3)_3$ in SO_2ClF shows a single, broad (198 Hz) absorption at $\delta(^{11}\text{B}) -1.11$. The ^{19}F NMR spectrum shows a singlet absorption at $\delta(^{19}\text{F}) -78.6$ and the ^{13}C NMR spectrum exhibits the expected quartet absorption for CF_3 at $\delta(^{13}\text{C}) 118$ ($J_{\text{C-F}} = 319.5\text{ Hz}$).

Both aluminum and gallium triflate have poor or no solubility in most of the common solvents. Aluminum triflate was found to be slightly soluble in SO_2 and SO_2ClF , sufficient to observe

its ^{27}Al NMR spectrum [$\delta(^{27}\text{Al}) -121.0$, $W_{1/2} = 416\text{ Hz}$, SO_2ClF] but not the ^{13}C NMR spectrum at -25°C . The extremely poor solubility of gallium triflate did not allow any NMR study in these solvents. However, both aluminum and gallium tris(triflate) are well soluble in coordinating solvents such as diglyme, acetonitrile, acetone, etc., in which their NMR spectra could be recorded. In diglyme for $\text{Al}(\text{OSO}_2\text{CF}_3)_3$ $\delta(^{27}\text{Al}) -108.5$ (221 Hz), $\delta(^{13}\text{C}) 119.5$ ($J_{\text{C-F}} 319.8\text{ Hz}$) and for $\text{Ga}(\text{OSO}_2\text{CF}_3)_3$ in acetonitrile $\delta(^{71}\text{Ga}) -328$ (200 Hz), $\delta(^{69}\text{Ga}) -329$ (225 Hz) and $\delta(^{13}\text{C}) 119.6$ ($J_{\text{C-F}} = 316.6\text{ Hz}$) was observed.

The physical properties (such as melting point, boiling point, and solubility) of both aluminum and gallium triflate are very different from those of boron tris(triflate), indicating different states of association. Consequently molecular weight determinations were carried out for all three triflates. In high-dilute methylene chloride solution in which both aluminum and gallium triflates are somewhat soluble, molecular weights of 1831 and 2370 were obtained for aluminum and gallium triflate, respectively. These values suggest that they are oligomeric (associated) containing from four to five metal tris(triflate) units. On the other hand, boron triflate gave a molecular weight of 454 in the same solvent, in accord with its monomeric nature.



Study of Catalyzed Reactions. Alkylation. The catalytic activity of boron, aluminum, and gallium tris(triflate) in Friedel-Crafts alkylation and acylation reactions was studied. In the context of the present study probing catalytic activity of the new Lewis acid catalysts, reactions with typical alkyl or acyl halides are reported. All reactions were carried out at room temperature ($\sim 25^\circ\text{C}$).

Alkylation of aromatics was investigated on the most representative case of benzene and toluene. In connection with alkylation studies of toluene, related isomerization of alkyltoluenes was also studied.

Boron, aluminum, and gallium tris(triflate) catalyzed alkylations were studied both in weakly coordinating methylene chloride and strongly coordinating nitromethane solvents. Boron triflate could be used as a homogeneous catalyst in both solvents whereas aluminum and gallium triflate because of their limited solubility were limited to nitromethane or studied as heterogeneous systems.

Methylation, ethylation, isopropylation, and *tert*-butylation of benzene and toluene with the corresponding alkyl fluorides, chlorides, or bromides were carried out. The mole ratio of aromatic/alkyl halides/catalyst was usually 12:2:1. Reactions were generally carried out at 25°C for 30 min. In experiments carried out to determine isomer distribution, no attempt was made to optimize yields. Data are summarized in Table I. In preparative-scale experiments, isolated yields of methylation of 15-41%, ethylation 21-53%, isopropylation 29-60%, and *tert*-butylation 30-78% were obtained. In the boron triflate catalyzed methylation and ethylation, 3-8% dialkylated products were identified. In the case of isopropylation and *tert*-butylation, 3-6% dialkylated products were also formed. While gallium triflate catalyzed isopropylation and *tert*-butylation gave 1-2% dialkylated product, aluminum triflate gave no apparent dialkylation. Under competitive reaction conditions, substrate selectivities (based on relative rates of alkylation of toluene and benzene) $k_{\text{T}}/k_{\text{B}}$ were found to be generally low (0.7-4), except for *tert*-butylation in CH_3NO_2 solution where $k_{\text{T}}/k_{\text{B}}$ values of 20-23 were observed. As alkylation reactions are to a significant degree (vide infra) affected by isomerization and disproportionation, yields and particularly relative reactivities cannot be considered in a quantitative way. Dialkylation is also much dependent on reaction condition and reagent mole ratios, as customary in Friedel-Crafts reactions. Isomer distributions of the alkylation of toluene are as usual affected by the solvent. Data with the studied catalyst systems in CH_2Cl_2 and CH_3NO_2 solution are summarized in Table I, including the results of some time-dependence studies.

Friedel-Crafts alkylation of aromatics with primary halides (such as methyl or ethyl halides) is considered to involve displacement by the aromatic ring of the α -carbon atom of the alkyl

(10) Olah, G. A. U.S. Pat. 4721 559, 1988.

(11) Similar decomposition of $\text{B}(\text{O}_3\text{SCF}_3)_3\text{-CF}_3\text{SO}_3\text{H}$ systems with higher concentration of $\text{B}(\text{O}_3\text{SCF}_3)_3$ was previously observed; see ref 7.

Table I. Alkylation of Toluene with Alkyl Halides at 25 °C

RX	catalyst	solvent	reactn time, min	% yield	% isomer distribution		
					ortho	meta	para
methyl fluoride	B(OTf) ₃	CH ₂ Cl ₂	1	18	41	24	35
			5	23	52	18	30
			10	30	47	28	25
			30	30	47	26	27
methyl chloride	B(OTf) ₃	CH ₂ Cl ₂	1	2	46	22	32
			5	5	44	28	28
			10	7	39	36	25
			30	10	28	48	23
ethyl fluoride	B(OTf) ₃	CH ₂ Cl ₂	1	23	17	70	13
			5	28	15	67	18
			15	24	27	46	27
			30	32	28	45	27
ethyl chloride	B(OTf) ₃	CH ₂ Cl ₂	1	15	3	97	
			2	22	3	97	
			30	31	3	97	tr
			60	25	4	83	13
			150	20	7	64	29
ethyl bromide	B(OTf) ₃	CH ₂ Cl ₂	10	15		100	
			45	25		100	
			60	18		100	
	Ga(OTf) ₃	CH ₂ Cl ₂	60	16	tr		
			240	28	44	15	43
			480	45	41	15	44
isopropyl chloride	B(OTf) ₃	CH ₂ Cl ₂	1260	30	11	33	36
			5	25		83	17
			15	23		80	20
			30	17		77	23
			5	10	47	24	29
			15	18	53	21	26
	Ga(OTf) ₃	CH ₂ Cl ₂	60	27	58	21	21
			5	27	44	20	36
			60	28	53	53	47
			5	10	44	22	34
			30	23	44	23	33
			90	30	44	23	33
Al(OTf) ₃	CH ₂ Cl ₂	5	32	43	21	36	
		90	34	39	22	39	
		30	low	44	23	33	
		90	low	44	22	33	
		120	low	45	22	33	
		5	42		60	40	
<i>tert</i> -butyl fluoride	B(OTf) ₃	CH ₂ Cl ₂	10	44		54	46
			15	38		37	63
			25	46		4	96
			5	30		79	21
<i>tert</i> -butyl chloride	B(OTf) ₃	CH ₂ Cl ₂	30	36		75	25
			1	30		45	55
			2	33		42	58
			5	23		70	30
			30	16		70	30
			5	31		73	27
	Ga(OTf) ₃	CH ₂ Cl ₂	30	29		68	32
			120	29		66	34
			15	15		7	93
			60	34		7	93
			90	54		7	93
			5	71		18	82
Al(OTf) ₃	CH ₂ Cl ₂	10	69		27	73	
		30	60		29	71	
		120	47		50	50	
		5	low		4	96	
		15	5		8	92	
		60	26		7	93	
		CH ₃ NO ₂	90	43		7	93

halide-catalyst complex.¹² With increasing branching of the alkyl groups (isopropyl and *tert*-butyl halides), evidence favors a change toward a carbocationic mechanism.¹² Orientations in aromatic Friedel-Crafts alkylations were frequently considered to be

anomalous.^{13,14} Temperature, nature, and amount of catalysts and most importantly solvents were found to have a large effect on the orientation of products formed.¹⁵

(12) (a) Smoot, C. R.; Brown, H. C. *J. Am. Chem. Soc.* **1956**, *78*, 6249. (b) Jungk, H.; Smoot, C. R.; Brown, H. C. *J. Am. Chem. Soc.* **1956**, *78*, 2185. (c) Smoot, C. R.; Brown, H. C. *J. Am. Chem. Soc.* **1956**, *78*, 6245. (d) Olah, G. A.; Flood, S. H.; Moffatt, M. E. *J. Am. Chem. Soc.* **1964**, *86*, 1060.

(13) (a) Price, C. C. *Organic Reactions*; Wiley: New York, 1946; Vol. III. (b) Price, C. C. *Chem. Rev.* **1941**, *29*, 37.

(14) Francis, A. W. *Chem. Rev.* **1948**, *43*, 257.

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

Table II. Equilibrium Composition of Isomeric Alkyltoluenes [R(CH₃)C₆H₄]¹⁸

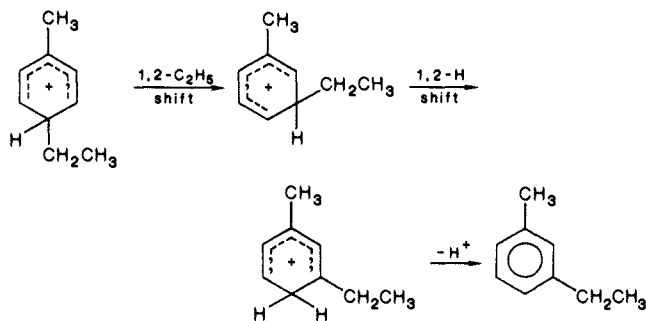
R	% ortho	% meta	% para
CH ₃	18	58	24
C ₂ H ₅	9	65	26
<i>i</i> -C ₃ H ₇	1.5	69.5	29
<i>t</i> -C ₄ H ₉		64	36

Lewis acid catalyzed Friedel-Crafts alkylation of alkylbenzenes, such as toluene, was found generally to lead to the formation of increased amounts of *m*-dialkylbenzene isomers.¹⁶ Brown et al.¹⁶ suggested that the relative high proportions of meta isomers are a consequence of the high reactivity and therefore low selectivity aromatic alkylation reactions in accordance with their "selectivity principle". It was reasoned, however,¹⁷ that anomalous isomer distributions to a substantial degree arise from consecutive or concurrent isomerization to the more stable meta isomer or related intermediate arenium ion complexes.

Previous studies using metal halide catalysts showed that alkylations in excess aromatic hydrocarbons or in weakly basic solvents generally result in isomerizing conditions.^{16,18} In contrast, nucleophilic and coordinating solvents such as nitromethane tend to decrease isomerization.

Boron tris(triflate) catalyzed methylation of benzene and toluene with methyl fluoride and chloride is relatively slow in methylene chloride and does not proceed in nitromethane solution. The boron triflate catalyzed methylation with methyl fluoride and chloride gave after 1 min 22–24% meta isomer, which increased with time, reaching in 1 h about 58%, corresponding to the thermodynamic equilibrium of isomeric xylenes (Table II). The boron triflate catalyzed ethylation with ethyl chloride and bromide is also relatively slow, but with ethyl fluoride the reaction proceeds well. In the boron triflate catalyzed ethylation with ethyl chloride or bromide in CH₂Cl₂ solution, the isomer distribution shows very high or exclusive meta isomer formation and only after more prolonged reaction times changes the isomer distribution in the former, approaching the equilibrium isomer distribution of 65% meta. Gallium triflate catalyzed ethylation with ethyl bromide showed substantially lower (15–33%) meta isomer content whereas aluminum triflate was found to give no detectable amount of ethyltoluenes. Generally, no ethylation was observed in nitromethane solution.

The observation of predominant or exclusive formation of meta isomer can be explained only by intramolecular isomerization within the arenium ion intermediates of the ethylation reaction to the most stable 1,3-substituted isomeric ion. It should be



pointed out that the isomeric ethyltoluenium ion equilibrium is 100% of the corresponding ion, contrasting the discussed equilibrium composition of neutral ethyltoluenes. When HF or HCl is the byproduct of the reactions (in alkylation with C₂H₅F or C₂H₅Cl), they form very strong conjugate acid with B(OOSO₂-

Table III. B(OSO₂CF₃)₃-Catalyzed Isomerization of Ethyltoluenes in CH₂Cl₂ at 25 °C

	reaction time min	% isomer distribution		
		ortho	meta	para
ortho	0	100		
	1	88	9	3
	5	55	35	10
	10	33	37	30
	25	23	40	37
	60	15	42	43
meta	120	11	56	33
	0		100	
	5	3	97	
	30	4	68	28
	120	7	55	38
	para	0		
1		11	18	71
5		12	21	67
10		13	24	63
30		12	32	56
60		11	36	54
120		11	58	21

CF₃)₃, and this will start to cause isomerization of the meta isomer. Indeed meta, as well as ortho and para, ethyltoluenes were found to be readily isomerized by boron tris(triflate) in methylene chloride solution to give eventually the thermodynamic ethyltoluene composition (Table III).

The gallium tris(triflate) catalyzed ethylation with ethyl bromide in methylene chloride solution is also slow. After 1 h of reaction time, only traces of ethylated products were observed, but in 4 h a 28% yield was obtained, which increased to 45% in 8 h. The isomer distribution of 44% ortho, 13% meta, and 43% para isomer (4 h) or 42% ortho, 17% meta, and 44% para (after 8 h) changes upon prolonged reaction (~50 h) to 11% ortho, 33% meta, and 36% para. These data also indicate isomerization leading to increasing amount of the meta isomer.

Isopropylation of toluene/benzene mixtures was similarly carried out under comparable reaction conditions. Data (Table I) show that the boron tris(triflate) catalyzed reaction in methylene chloride after 5 min gives no ortho isomer, whereas the meta isomer was 83% and para 17%. In nitromethane solution the isomer distribution is different: 47% ortho, 24% meta, and 29% para cymene. The data indicate substantially increased isomerization in the less coordinating methylene chloride solvent. Gallium triflate causes less isomerization in CH₂Cl₂, and aluminum triflate gives similar isomer distributions in both solvents.

Boron tris(triflate) catalyzed *tert*-butylation with *tert*-butyl fluoride and chloride in methylene chloride solution gives initially 60–79% meta and 40–21% para isomers. Interestingly, in the boron triflate catalyzed alkylation with *tert*-butyl fluoride in CH₂Cl₂, the meta isomer content rapidly decreases, and after 25 min only 4% is left. This is explained by fast *trans tert*-butylation of excess toluene giving predominant para substitution (the kinetic product). More prolonged reaction times result again in building up the meta isomer due to thermodynamically directed isomerization. In nitromethane solution with short reaction time (1–2 min), 42–45% meta and 55–58% para substitution is observed. Gallium triflate catalyzed *tert*-butylation in methylene chloride gave comparable results, but in nitromethane solution only 7% meta and 93% para substitution was obtained. Aluminum triflate in nitromethane gave similar results, but even in methylene chloride the amount of meta isomer initially was only 18% and increased with time to 50%. The *k_T/k_B* selectivity data corresponding to high meta substitution are low (0.7–2), indicative of disproportionation, but in the case of low meta substitution increases to 25, characteristic of the predominantly kinetic reaction. The data show extensive intermolecular isomerization (*trans tert*-butylation) in the case of the stronger catalysts (boron and gallium triflate), which diminishes in the more coordinating nitromethane solvent. In separate studies, the boron tris(triflate) catalyzed isomerization of *o*- and *p*-*tert*-butyltoluenes in methylene chloride solution was found to give rapidly the thermodynamic equilibrium (Table IV).

(16) (a) Serijan, K. T.; Hipsher, H. F.; Gibbons, L. C. *J. Am. Chem. Soc.* **1949**, *71*, 873. (b) Simmons, J. H. Hart, H. *Ibid.* **1947**, *69*, 979. (c) Condon, F. E. *Ibid.* **1949**, *71*, 3544. (d) Brown, H. C.; Nelson, K. L. *Ibid.* **1953**, *75*, 6292. (e) Brown, H. C.; Smoot, C. R. *Ibid.* **1956**, *78*, 6255. (f) Choi, S. U.; Brown, H. C. *Ibid.* **1959**, *81*, 3315. (g) McCaulay, D. A.; Lien, A. P. *Ibid.* **1952**, *74*, 6246.

(17) (a) McCaulay, D. A.; Lien, A. P. *J. Am. Chem. Soc.* **1951**, *73*, 2013. (b) Brown, H. C.; Brady, J. D. *Ibid.* **1952**, *74*, 3570.

(18) Allen, R. H.; Yats, L. D. *J. Am. Chem. Soc.* **1961**, *83*, 2799.

Table IV. B(OSO₂CF₃)₃-Catalyzed Isomerization of *tert*-Butyltoluenes in CH₂Cl₂ at 25 °C

	reaction time, min	% isomer distribution		
		ortho	meta	para
ortho	0	100		
	1	<0.5	66	34
	60		70	30
para	0			100
	1		69	31
	5		69	31
	15		70	30
	60		72	28

On the basis of the studied alkylations and isomerizations, the relative reactivity of the catalysts was found to be B(OSO₂CF₃)₃ > Ga(OSO₂CF₃)₃ > Al(OSO₂CF₃)₃.

In comparison with widely used boron trifluoride, which does not catalyze alkylation with primary or secondary alkyl chlorides or bromides, but only fluorides, boron tris(triflate) is more active and effects these reactions. This indicates that B(OSO₂CF₃)₃ is a stronger Lewis acid catalyst in alkylations than BF₃.

It should be pointed out that due to limited solubilities of the catalysts in methylene chloride only the boron tris(triflate) catalyzed reactions are homogeneous. Gallium triflate is only partially soluble, whereas aluminum triflate gives substantially heterogeneous systems.

Acylation. Friedel–Crafts acylations studied were acetylation and benzylation of benzene and toluene with acetyl chloride and benzoyl chloride, respectively, under competitive reaction conditions. Data are summarized in Table V.

Acetylation and benzylation of toluene, in the presence of benzene, gave predominant para substitution (para isomer, 90%). The meta isomer is generally 2–7% in acetylation and except for the boron triflate catalyzed reactions only 1–2% in benzylation. Boron tris(triflate) catalyzed benzylation of toluene in methylene chloride gives 6–10% meta, 17–18% ortho, and 72–90% para isomer. The k_T/k_B selectivities in boron triflate catalyzed acetylation are 31–73 whereas in benzylation 78–120. With gallium and aluminum triflate catalysts substrate selectivities substantially increase. The data are in accord with the previously discussed relative acidity strength of the catalysts and the corresponding change in electrophilic activity of their complexes with acetyl

halides. The acetylation reactions seem to be not affected by any significant isomerization as indicated by isomer distributions and related reactivity (k_T/k_B) data (Table V).

Conclusions

Boron, aluminum, and gallium tris(triflate) were found to be effective new Friedel–Crafts catalysts in alkylation and isomerization reactions. Due to their favorable properties such as considerable decreased volatility as compared to boron trifluoride and aluminum trichloride, as well as good catalytic activity, they promise to become widely used. We are continuing our studies into the scope and applications in various Friedel–Crafts reactions, including applications as supported solid catalysts in heterogeneous gas-phase reactions where BF₃ and AlCl₃ generally are not applicable. Boron triflate due to its high activity, good solubility, but more limited thermal stability is the preferred catalyst in solution under mild conditions, whereas aluminum and gallium triflates are applicable as solid or support Friedel–Crafts catalyst.

Experimental Section

Boron trichloride was obtained from Matheson. Sublimed aluminum trichloride was purchased from Fluka. Aluminum and boron tribromide and triiodide, gallium trihalides, and aluminum carbide were from Alfa. Boron tribromide was twice distilled, followed by distillation from aluminum metal in an all-glass distillation apparatus, until it was colorless. Other commercial metal trihalides were used as received. Trifluoromethanesulfonic (triflic) acid (3 M) was freshly distilled under dry nitrogen prior to use. Ethyl bromide, isopropyl chloride, *tert*-butyl chloride, benzene, toluene, and isomeric alkyltoluenes all were of highest commercial purity or in the latter case were available from our previous studies and used as such. 1,1,2-Trichlorotrifluoroethane (Freon-113), methylene chloride, and nitromethane were purified and dried over phosphorus pentoxide under reflux.

¹¹B, ²⁷Al, ⁷¹Ga, and ⁶⁹Ga NMR spectra were recorded on a Varian Associates FT-80 spectrometer equipped with a variable-temperature probe with BF₃·Et₂O, AlCl₃·CH₃CN, and GaCl₃·CH₃CN as external references. ¹³C and ¹⁹F NMR spectra were obtained on a Varian XL-200 spectrometer with Me₄Si and CCl₄ as external references.

Infrared spectra were recorded on a Perkin-Elmer Model 7500 FTIR spectrometer. GC product analyses were carried out on a Varian Model 3700 gas chromatograph equipped with a 50-m OV-101 glass capillary column and a Varian Model 3300 gas chromatograph equipped with a 50-m Carbowax fused silica gel column. Elemental analyses and molecular weight determinations were carried out by Galbraith Laboratories, Knoxville, TN.

Table V. Acylation of Toluene and Benzene

RCOCl	catalyst	solvent	reaction time, min	% yield	k_T/k_B	% isomer distribution			
						ortho	meta	para	
acetyl chloride	B(OTf) ₃	CH ₂ Cl ₂	2	63	31	1	7	92	
			5	61	30	1	7	92	
			30	62	37	1	6	93	
		CH ₃ NO ₂	15	43	71	2.5	2.5	95	
			30	50	73	2.5	2.5	95	
			45	low	167	3	1	96	
	Al(OTf) ₃	CH ₂ Cl	720	low	170	5	1	94	
			15	2	157	3.5	1.5	95	
			90	11	156	1	2	97	
	Ga(OTf) ₃	CH ₂ Cl ₂	1440	21	132	2	2	96	
			15	28	104	3	2	95	
			60	56	75	3	2	95	
		CH ₃ NO ₂	180	65	67	2	2	96	
			700	72	66	2	3	95	
			2	55	78	18	10	72	
benzoyl chloride	B(OTf) ₃	CH ₂ Cl ₂	5	64	78	17	8	75	
			30	53	78	17	6	77	
			720	trace	119	8	1	91	
		Al(OTf) ₃	CH ₂ Cl ₂	60	67	120	8	1	91
				15		172	9		91
				45		252	10		90
	Ga(OTf) ₃	CH ₂ Cl ₂	45	28	247	8	2	90	
			300	44	170	10	1	89	
			720	63	177	11	1	88	
		CH ₃ NO ₂	30		131	7	1	92	
			60		134	7	1	92	
			700	69	95	7	1	92	

Preparation of Boron Tris(triflate). To 15 mL of SO_2ClF or 100 mL of Freon-113 placed into a 250-mL Schlenk flask cooled to -30°C was added 9 mL (0.103 mol) of BCl_3 . To the stirred solution cooled to -78°C was added dropwise 26.4 mL (0.30 mol) of $\text{CF}_3\text{SO}_3\text{H}$ over a period of 1 h. The temperature was maintained at -78°C for 4–6 h and then slowly was allowed to warm up to room temperature within 4–6 h. At the end of this period, evolution of HCl ceased, and a clear colorless solution was obtained. Removal of the solvent in vacuum gave boron tris(triflate) as a white solid. Distillation at reduced pressure [68–73 $^\circ\text{C}$ (0.5 Torr)] gave pure boron tris(triflate) as a highly viscous compound, which subsequently solidifies (mp 43–45 $^\circ\text{C}$). Preparations from BBr_3 were similarly carried out at 0°C . The prepared boron tris(triflate) gave satisfactory elemental analysis. $\text{B}(\text{O}_3\text{SCF}_3)_3$ MW calcd 458, found 454. Calcd: C, 7.8; S, 21.00; B, 2.36; F, 37.33. Found: C, 7.75; S, 21.07; B, 2.10; F, 37.20.

Preparation of Aluminum and Gallium Tris(triflate). Preparation of aluminum and gallium tris(triflate) from the corresponding trihalides and triflic acid were carried out according to the previously described procedure except that the reactions were run under mild reflux in Freon-113 solution for 10–12 h. At the end of this period, no further evolution of HX was observed. Removal of solvent under vacuum gave the triflates as white powders. The triflates were then washed several times with dry Freon-113 under dry nitrogen. Preparation of aluminum tris(triflate) from triethylaluminum was similarly carried out but at low temperature (-78°C).

Preparation of Aluminum Triflate from Aluminum Carbide. A 100-mL stainless-steel autoclave equipped with a magnetic stirrer was charged with 1 g (7.0 mmol) of Al_4C_3 and 7.35 mL (83.4 mmol) of $\text{CF}_3\text{SO}_3\text{H}$ diluted in 15 mL of Freon-113. The autoclave was then sealed and heated to 180–200 $^\circ\text{C}$ for 10–12 h. After depressurizing, the product was extracted several times with SO_2 or SO_2ClF . Removal of solvent gave aluminum tris(triflate) as a white powder.

Both aluminum and gallium tris(triflate) gave satisfactory elemental analyses. $\text{Al}(\text{OSO}_2\text{CF}_3)_3$ calcd: C, 7.99; S, 20.28; Al, 5.60; F, 35.32. Found: C, 7.48; S, 20.06; Al, 5.50; F, 35.20. $\text{Ga}(\text{OSO}_2\text{CF}_3)_3$ calcd: C, 6.97; S, 18.61; Ga, 13.40; F, 33.08. Found: C, 6.81; S, 18.40; Ga, 13.00; F, 33.16.

General Method for Alkylation and Acylation of Toluene and Benzene with $\text{M}(\text{OSO}_2\text{CF}_3)_3$ Catalysts. To a solution or suspension of $\text{M}(\text{OSO}_2\text{CF}_3)_3$ (5.5 mmol) in 25 mL of dichloromethane or nitromethane

were added toluene (11.0 mmol) and benzene (55 mmol) under a dry nitrogen or argon atmosphere. The reaction flask was then placed in a constant-temperature bath at 25°C . The corresponding alkyl or acyl halide (11 mmol) in the same solvent was added with vigorous stirring, and the reaction was allowed to proceed. The progress of the reaction was monitored by taking periodically samples and after usual workup (ice- NaHCO_3 quench and extraction with dichloromethane or nitromethane) by analyzing them by GC and GC-MS.

Preparative-scale experiments were similarly carried out with 10-fold amounts of the reagents. After usual workup, products were isolated by distillation (crystallization).

General Method of Isomerization of Isomeric Alkyltoluenes. To a well-stirred solution of $\text{B}(\text{OSO}_2\text{CF}_3)_3$ (3.0 mmol) in 25 mL of dichloromethane was added the corresponding isomeric alkyltoluene (6.0 mmol) under dry nitrogen or argon atmosphere. The reaction flask was then placed in a constant-temperature bath at 25°C . Samples taken periodically, after usual workup (as described above), were analyzed by gas chromatography.

Acknowledgment. Support of our work by the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

Registry No. BCl_3 , 10294-34-5; BBr_3 , 10294-33-4; AlEt_3 , 97-93-8; AlCl_3 , 7446-70-0; AlBr_3 , 7727-15-3; AlI_3 , 7784-23-8; GaCl_3 , 13450-90-3; GaBr_3 , 13450-88-9; GaI_3 , 13450-91-4; Al_4C_3 , 1299-86-1; $\text{CF}_3\text{SO}_3\text{H}$, 1493-13-6; $\text{B}(\text{OTf})_3$, 64371-01-3; $\text{Al}(\text{OTf})_3$, 75562-37-7; $\text{Ga}(\text{OTf})_3$, 74974-60-0; methyl fluoride, 593-53-3; methyl chloride, 74-87-3; ethyl fluoride, 353-36-6; ethyl chloride, 75-00-3; ethyl bromide, 74-96-4; isopropyl chloride, 75-29-6; *tert*-butyl fluoride, 353-61-7; *tert*-butyl chloride, 507-20-0; acetyl chloride, 75-36-5; benzoyl chloride, 98-88-4; toluene, 108-88-3; benzene, 71-43-2; *o*-acetyltoluene, 577-16-2; *m*-acetyltoluene, 585-74-0; *p*-acetyltoluene, 122-00-9; *o*-benzoyltoluene, 131-58-8; *m*-benzoyltoluene, 643-65-2; *p*-benzoyltoluene, 134-84-9; *o*-methyltoluene, 95-47-6; *m*-methyltoluene, 108-38-3; *p*-methyltoluene, 106-42-3; *o*-ethyltoluene, 611-14-3; *m*-ethyltoluene, 620-14-4; *p*-ethyltoluene, 622-96-8; *o*-isopropyltoluene, 527-84-4; *m*-isopropyltoluene, 535-77-3; *p*-isopropyltoluene, 99-87-6; *m*-*tert*-butyltoluene, 1075-38-3; *p*-*tert*-butyltoluene, 98-51-1; *o*-*tert*-butyltoluene, 1078-92-6.

Rearrangement of Suitably Constituted Aryl, Alkyl, or Vinyl Radicals by Acyl or Cyano Group Migration¹

Athelstan L. J. Beckwith,* Dennis M. O'Shea,² and Steven W. Westwood*

Contribution from the Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601, Australia. Received August 20, 1987

Abstract: Treatment of *o*-bromobenzyl acetoacetate (**14**) with tributyltin hydride affords the rearranged product **20** by a mechanism involving 1,4-acetyl migration in the aryl radical **15** via a cyclic intermediate **16**. Similarly, 1,4-cyano migration in the radical **22** derived from **21** affords rearranged product **24**. However, radicals, e.g., **26**, derived from cyclic keto esters give products formed both by 1,4-acyl migration and by H-atom transfer followed by 1,2-acyl migration. 1,2-Acy migration in species containing a radical center exocyclic to a β -keto ester ring, e.g., **35** \rightarrow **36**, provides a synthetically useful route to cyclic γ -keto esters. Examples of 1,4 or 1,5 migration of acyl or cyano groups to alkyl or vinyl radicals are given.

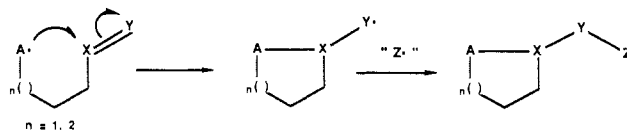
Early experimental investigations³ of radical ring closures were designed mainly to reveal new insights into the factors affecting the intimate mechanism of homolytic addition processes. Not only did they afford a solid basis of kinetic data and related mechanistic

(1) For a preliminary account of this work, see: Beckwith, A. L. J.; O'Shea, D. M.; Gerba, S.; Westwood, S. W. *J. Chem. Soc., Chem. Commun.* **1987**, 666.

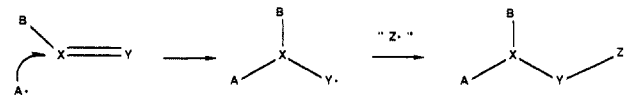
(2) Present address: Department of Chemistry, Imperial College, South Kensington, London SW7 2AY, U.K.

(3) (a) Walling, C.; Cooley, J. H.; Ponaras, A. A.; Racah, E. *J. Am. Chem. Soc.* **1966**, *88*, 5361. (b) Kochi, J. K.; Krusic, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 3940. (c) Lamb, R. C.; Ayers, R. W.; Toney, M. K. *J. Am. Chem. Soc.* **1963**, *85*, 3483. (d) Walling, C.; Pearson, M. S. *J. Am. Chem. Soc.* **1964**, *86*, 2262. (e) Julia, M.; Descoins, C.; Baillarge, M.; Jacquet, B.; Uguen, D.; Groeger, F. A. *Tetrahedron* **1975**, *31*, 1737. (f) Struble, D. L.; Beckwith, A. L. J.; Gream, G. E. *Tetrahedron Lett.* **1968**, 3701.

Scheme I



Scheme II



information,⁴ but they led to the recognition that intramolecular radical additions can often be carried out with highly predictable