Chemistry in Superacids. 6.[1a] Perfluoroalkanesulfonic Acid-Boron Perfluoroalkanesulfonates: New Superacid Systems for Generation of Carbocations and Catalysts for Electrophilic Transformations of Hydrocarbons[1b]

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Boron trihalides (BX_3, X = Cl, Br) react with excess perfluoroalkanesulfonic acids to give conjugate superacids of the type $R_FSO_2OH_2^+[B(OSO_2R_F)_4]^-$ (R_F = CF_3, C_4F_9, and $C_{10}F_{21}$). The systems were characterized by spectroscopy and their chemical (catalytic) properties were studied. The parent of the series $CF_3SO_3H_2^+[B(OSO_2CF_3)_4]^-$ (1) (first reported by Engelbrecht and Tschager) was found to O-protonate ketones and to generate stable *tert*-alkyl- and methyl-substituted benzylic cations at low temperature in SO_2ClF. Stable ions are similarly generated in $B(OSO_2CF_3)_3/SO_2ClF$. The catalytic activity of the conjugate superacid 1 has been demonstrated in trans-bromination/transalkylation of aromatics as well as in isomerization of *n*-butane, *n*-hexane, and trimethylenenorborane to adamantane under mild conditions.

Continued interest in superacids and their chemistry has made the development of new systems highly desirable.[2a]

Many of the known superacids are also strongly oxidizing systems, i.e., $HF-SbF_5$, FSO_3H-SbF_5, etc. Others such as $HF-TaF_5$, $HF-NbF_5$, and $HF-BF_3$ which have weaker or nonoxidizing nature have lower acidity.[2b]

Trifluoromethanesulfonic (triflic) acid is similar in acidity to fluorosulfuric acid (H_0 = ca. −14.1) and is only weakly oxidizing. Our earlier studies showed that mixtures of CF_3SO_2OH with certain Lewis acids greatly enhanced acidity. For example, $CF_3SO_2OH-SbF_5$ was used for the isomerization of alkanes,[2] and $CF_3SO_2OH-NbF_5$ and $CF_3SO_2OH-TaF_5$ were found to be improved Friedel-Crafts catalysts.[3]

A sharp increase in H_0 value of 100% H_2SO_4 upon addition of $HB(OSO_3H)_4$ was reported by Gillespie and coworkers, measured cryoscopically, and by UV indicator studies.[4] Engelbrecht and Tschager first reported the preparation of boron tris(fluorosulfate) and the more stable boron tris(triflate) and their conjugate superacids.[5] Solutions of CF_3SO_3H containing 30 mol % of boron tris(triflate) were reported to have H_0 values of ca. −20.5.[5] The acid systems were, however, not further characterized and no structural (spectroscopic) study reported, nor was the chemical (catalytic) activity of the systems examined.

Interested in the development and chemistry of new superacid systems, we have extended the preparation of superacids derived from boron trihalides and perfluoroalkanesulfonic acids and characterized them by spectroscopic data. The ability of the systems was also studied in generation of carbocations, protonation of weak bases, and catalysts in typical acid-catalyzed transformations of hydrocarbons and their derivatives.

Results and Discussion

The ^{11}B NMR spectrum of $B(OTf)_3$ prepared by the reaction of BCl_3 or BBr_3 with CF_3SO_3H showed a single broad absorption (198 Hz) at $\delta_{^{11}B}$ −1.11 and the IR spectrum confirmed the presence of B–O streching at 1380 cm^{-1} and of triflate absorptions at 1200, 1140, 1380, and 950 cm^{-1}. Addition of 2 molar equiv of triflic acid to $B(OTf)_3$ gave the conjugate acid $CF_3SO_2OH_2^+[B(OTf)_4]^-$ (1). 1

$$BX_3 + 3CF_3SO_3H \rightarrow B(OSO_2CF_3)_3 + 3HX$$

X = Cl, Br

could similarly be prepared from BBr_3 and triflic acid at 0 °C. The ^{11}B NMR spectrum of 1 showed a shielded single absorption, much sharper than that of boron tris(triflate) (53 Hz), centered at $\delta_{^{11}B}$ −3.55. The ^{19}F NMR spectrum showed a single absorption of $\delta_{^{19}F}$ −78.8 shielded by 1.5 ppm as compared to the fluorine singlet absorption of neat triflic acid ($\delta_{^{19}F}$ −77.2). The ^{13}C NMR spectrum exhibited the expected quartet absorption for CF_3 at $\delta_{^{13}C}$ 118 (J_{C-F} = 320 Hz).

The absence of residual halogen attached to boron or any associated HX was confirmed by titration of boron tris(triflate) and 1 with $AgNO_3$ after alkaline hydrolysis. Boron tris(triflate) could also be prepared from silver triflate and BBr_3 in heptane solution by mixing at room temperature. However, the removal of silver bromide byproduct is difficult.

$$BX_3 + 3CF_3SO_3Ag \rightarrow B(OSO_2CF_3)_3 + 3AgX$$

Analogous to the reaction of $PhBCl_2$ with 2 molar equiv of acetic acid or TFA which is known to give $PhB(OCOCH_3)_2$ or $PhB(OCOCF_3)_2$ and benzene,[6] TfOH reacted with $PhBCl_2$ to form benzene and $B(OTf)_2Cl$; $\delta_{^{11}B}$ −3.34 (470 Hz), with the CF_3 quartet absorption at $\delta_{^{13}C}$ 117.4 (J_{C-F} = 318 Hz). Reaction of $PhBCl_2$ with 3 molar equiv of TfOH gave benzene (ca. 80%), which was isolated and identified by IR and GLC, together with boron tris(triflate). Easy to handle $PhBCl_2$ can, therefore, be used as an alternative route to boron tris(triflate).

$$C_6H_5BCl_2 + 3CF_3SO_3H \rightarrow B(OSO_2CF_3)_3 + C_6H_6 + 2HCl$$

Turning our attention to the behavior of the longer chain perfluorinated alkane-sulfonic acids, we found that both $C_4F_9SO_3H$ and $C_{10}F_{21}SO_3H$ react with BBr_3 (3:1 molar

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Table I. NMR Spectroscopic Data for Boron Tris(triflate) and Its Conjugate Superacids 1-3

compound[a]	$\delta^{11}B$	$\delta^{19}F$	$\delta^{13}C$[b]
$B(OSO_2CF_3)_3$	-1.11 (198 Hz)	-78.6	118
1	-3.55 (53 Hz)	-78.8	118
2	-3.94 (50 Hz)	-81.33 -81.37 -81.42	c
3	-3.88 (95 Hz)	-80.14 -82.1	c

[a] In SO_2ClF at -35 °C. [b] J_{C-F} = 318-320 Hz. [c] Not obtained.

ratio) in dry heptane solvent to form the corresponding boron tris(perfluoroalkanesulfonates). It was also possible

$$BBr_3 + 3C_nF_{2n+1}SO_3H \rightarrow B(OSO_2C_nF_{2n+1})_3 + 3HBr$$
$$n = 4, 10$$

to prepare them from the sodium salts of the acids and BBr_3. Addition of 2 molar equiv of perfluorobutanesulfonic acid to $B(OSO_2C_4F_9)_3$ generated the superacid $C_4F_9SO_2OH_2^+B(OSO_2C_4F_9)_4^-$ (**2**). The ^{11}B NMR spectrum of **2** in SO_2ClF showed a sharp singlet absorption at $\delta_{^{11}B}$ -3.94, and the ^{19}F NMR spectrum recorded in the same solvent showed three not entirely resolved absorptions for the perfluorobutyl ligands at $\delta_{^{19}F}$ -81.33, -81.37, -81.42. Due to very limited solubility, a ^{13}C spectrum could not be recorded.

$B(OSO_2C_{10}F_{21})_3$ itself has only limited solubility in SO_2 or SO_2ClF and showed a very broad signal in the ^{11}B NMR. Removal of SO_2 under dry nitrogen followed by the addition of 2 molar equiv of triflic acid gave the acid $CF_3SO_2OH_2^+[B(OSO_2C_{10}F_{21})_3(OSO_2CF_3)]^-$ (**3**) as a fuming semisolid which had slightly better solubility in SO_2ClF and gave a single absorption at $\delta_{^{11}B}$ -3.88 in the boron spectrum and two absorptions in the ^{19}F spectrum, one for the CF_3 and the other broader unresolved one for the $C_{10}F_{21}$ groups at $\delta_{^{19}F}$ -80.14 and -82.1, respectively. Once again, a ^{13}C spectrum could not be recorded due to insufficient solubility. The obtained NMR data are shown Table I.

It should be pointed out that the perfluoroalkanesulfonic acid/boron perfluoroalkanesulfonates studied in the present work have limited thermal stability and slowly decompose above +70 °C. They also darken even on standing at room temperature. Their lifetime can, however, be increased by storing in the dark under argon (or nitrogen). The thermal instability of **1** was previously noted by Engelbrecht[5] with the products of decomposition being $CF_3SO_2OCF_3$, SO_2, COF_2, and BF_3.

Generation of Carbocations. The observations that **1** dissolves readily in SO_2ClF and does not precipitate out of solution even at -75 °C encouraged us to examine its use to generate carbocations under stable ion conditions. As model reaction, we studied the ionization of alkyl halides and protonation of ketones, both of which are well-known processes in superacids.[7] *tert*-Butyl- and *tert*-pentyl chloride were ionized to their corresponding stable tertiary cations, the formation of which was confirmed by ^1H and ^{13}C NMR. Similarly, adamantyl bromide gave the corresponding bridgehead cation, the ^{13}C NMR spectrum of which was identical with that obtained in magic acid.[7] Attempts to ionize isopropyl chloride to isopropyl cation were unsuccessful. However, the isopropyl cation is also unstable even in magic acid as it is quenched by the fluorosulfate ion. When acetophenone is protonated in CF_3SO_3H, the $C{=}OH^+$ proton signal is exchanging rapidly with the acid. The ^1H NMR spectrum of acetophenone protonated in **1** shows the $C{=}OH^+$ proton as a separate distinct signal up to -30 °C, indicating the increased acidity. The ^{13}C NMR spectrum of acetophenone protonated in **1** showed the $C{=}OH^+$ signal at $\delta_{^{13}C}$ 218.34. Similarly, cyclopropylmethyl ketone is protonated in **1** and gives a distinct $=OH^+$ signal at -30 °C; the ^{13}C NMR spectrum of protonated cyclopropyl methyl ketone exhibited the $C{=}OH^+$ signal at $\delta_{^{13}C}$ 238.19. Attempts to generate stable cations in **2** were, however, unsuccessful indicating decreased acidity.

The potential of $B(OTf)_3$ as a Lewis acid to generate carbocations was also examined. Whereas *tert*-butyl chloride was ionized with $B(OTf)_3$ in SO_2ClF solution to give the corresponding *tert*-butyl cation ($\delta_{^{13}C}$ 333.46), attempts to ionize isopropyl chloride to Me_2CH^+ were unsuccessful. Only the corresponding donor–acceptor complex was observed. Adamantyl fluoride, chloride, and bromide were all ionized to give the bridgehead cation in SO_2ClF ($\delta_{^{13}C^+}$ 300.8). Similarly, pentamethylbenzyl chloride gave the pentamethylbenzyl cation ($\delta_{^{13}C^+}$ 186.8), the spectrum of which was identical with that of the ion generated in SbF_5/SO_2ClF solution ($\delta_{^{13}C^+}$ 187.3).

Catalyzed Reactions. Transalkylation and transbromination reactions have been studied extensively under Friedel–Crafts conditions.[8] These typical acid-catalyzed transformations have found renewed interest in recent years with solid and liquid superacid systems.[9-11] In the present study, to probe the catalytic activity of the studied novel superacids, as a model reaction we examined the potential of **1** in transbromination of bromoarenes and transethylation of diethylbenzene. Using an acid:substrate molar ratio of 1:10, 89% yield of bromotoluene isomers was obtained in **1** as compared to a 5.5% yield in neat triflic acid. Similarly, a 50% yield of isomeric ethyltoluenes was obtained in **1** as compared to 5% in triflic acid. No attempts was made to optimize yields. Instead, the present study merely emphasized comparison of yields obtained under identical conditions by overnight stirring of the reaction mixtures at room temperature.

The isomer distribution in the obtained bromotoluenes was 42% ortho, 44% meta, and 14% para, which reflects closely the equilibrium isomer distribution of bromotoluenes under the isomerizing conditions.

In transbromination reactions 2-bromo-*m*-xylene itself also undergoes isomerization, giving in the recovered bromxylenes an isomer distribution of 27.4% 2-bromo, 69.1% 4-bromo, and 3.5% 5-bromo-*m*-xylene. The observed isomer distribution closely resembles that observed in the transbromination of *m*-xylene with bromomesitylene, giving 23% 2-bromo, 70.1% 4-bromo, and 6.9% 5-bromo-*m*-xylene.[9]

The isomer distribution of the obtained ethyltoluenes was 7.6% ortho, 55.6% meta, and 36.8% para. This isomer distribution resembles the distribution obtained in the gas-phase alkylation of toluene with ethyl chloride over Nafion-H, i.e., 4.1% ortho, 62.1% meta, and 33.8% para,[12] and again is indicative of close to equilibrium isomer distribution.

For the isomerization of straight-chain alkanes to their branched isomers, it is of particular interest to find cata-

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lysts effective at modest temperatures. In the present study we found that *n*-butane isomerized in a flow reactor over superacid system 1 immobilized on graphite in a flow system even at room temperature to give isobutane in 7.5% yield. Cracking products, i.e., methane, ethane, and propane, were formed only in trace amounts. Much higher conversions were obtained by increasing contact time in autoclave experiments by reacting *n*-butane with 1 (acid:alkane = 1.18) under a small pressure of argon (200 psi). GC analysis of the gas phase after 24 h indicated a 40% isomerization to isobutane, together with methane (2.7%), ethane (6%), and propane (4%), but only a trace of isopentane. After 24 h at room temperature, a 57% (mol %) isomerization to isobutane was obtained. Isopentane remained a trace and no higher hydrocarbons could be detected. When the pressure vessel was opened and the organic layer was extracted with ether after quenching of the acid, GC of the organic layer showed only traces of higher boiling organic material and no polymeric residue was found. In a control experiment using neat triflic acid after 24 h only 1.5% isobutane was obtained.

The isomerization of *n*-hexane over 1 (acid:alkane = 1:2) was also studied in similar experiments. GC analysis of the products after 2-h reaction at room temperature showed that ca. 65% of *n*-hexane had reacted to form 2-methylpentane, 2,3-dimethylbutane (a total of 24%), 2,2-dimethylbutane (34%), and 3-methylpentane (6%). The total amount of cracking products (viz. C_1, C_2, C_3, *i*-C_4, and *n*-C_4) stayed below 2%. After 4 h only 16% of *n*-C_6 remained unreacted and the cracking products slowly increased (ca. 21%). In a control experiment using neat triflic acid as catalyst (acid:alkane = 1:2), it was found that after 2-h reaction at room temperature only 5% of *n*-C_6 reacted, forming more cracking products than branched C_6 hydrocarbons.

There is continued interest in the preparation of adamantane, improving Schleyer's method of acid-catalyzed rearrangement of *endo*-trimethylenenorbornane, which is known to occur through a multistep carbocationic rearrangement process. With sulfuric acid or related protic acids no adamantane could be obtained.[13] On the other hand, with superacidic $AlCl_3$–HCl, 20–30% yield of adamantane is obtained, a 30% yield was reported with the HF–BF_3 acid system, and HF–SbF_5 gave a 47% yield.[13,14]

We have found in the present study that superacid system 1 is a highly efficient catalyst for this rearrangement. When to *endo*-(or *exo*-)trimethylenenorbornane 0.5 molar equivalent of 1 was added in Freon-113 solvent at 0 °C and the mixture stirred overnight under dry nitrogen, a 62% yield of adamantane was obtained. The remaining products were *exo*-trimethylenenorbornane (23%), *endo*-trimethylenenorbornane (0.5%), together with a $C_{10}H_{16}$ (M = 136 by GC–MS) side product. Formation of protoadamantane as a possible byproduct is excluded since the retention time of a reference sample of protoadamantane, synthesized according to the literature in three steps from adamantan-1-ol,[15,16] did not agree with the yet unidentified side product. It was indeed possible to continue the isomerization reaction by adding fresh catalyst to the reaction mixture after workup. The yield of adamantane increased to 85% after a further 8-h reaction at room temperature in Freon solvent, and adamantanol (10%) was also detected (confirmed by coinjection with an authentic sample and by GC–MS). In a control experiment, when adamantane itself was treated with the superacid 1 in Freon-113 solvent under the conditions of isomerization reaction, adamantanol (25%) was the only product formed after quenching of the reaction mixture and ether extraction.

In further experiments when the acid:alkane molar ratio was lowered to 1:4 the yield of adamantane slightly decreased (55%), whereas by increasing the molar ratio to 1:1 the yield increased to 68%, and no *exo*-trimethylenenorborane remained. However, the side products increased to 30% of the reaction mixture.

We believe the higher yield of adamantane obtained in 1 as compared to HF–SbF_5, which is a stronger superacid, is due to its lower oxidizing ability preventing oxidative side-product formation which is usually observed in HF–SbF_5.

Conclusions

The conjugate superacids obtained from boron trihalides and perfluoroalkanesulfonic acids are useful in the preparation of stable carbocations and as catalysts in a variety of acid-catalyzed reactions giving little side products. Their limited thermal stability, however, substantially limits the useful temperature range in which these acids can be used.

Experimental Section

Boron tribromide was twice distilled, followed by distillation from aluminum metal, in all-glass distillation aparatus, until it was colorless. It was then stored in the dark in a drybox.

Trifluoromethanesulfonic (triflic) acid (3 M) was freshly distilled under dry nitrogen prior to use. Phenylboron dichloride (Alfa, 95%) was used without further purification.

Boron trichloride (Matheson) and silver triflate (Aldrich) were of highest available purity and used as received.

tert-Butyl chloride, isopropyl chloride, adamantyl halides, alkanes, and trimethylenenorbornane, as well as ketones used for protonation studies, were all high purity (>99%) commercial samples.

^{11}B and ^{13}C NMR spectra were recorded on a Varian Associates FT-80 spectrometer equipped with a variable-temperature probe, using external $BF_3{\cdot}Et_2O$ and Me_4Si as references, respectively; ^{19}F spectra were obtained on a Varian XL-200 spectrometer at −35 °C in SO_2ClF solvent. Chemical shifts are relative to $CFCl_3$ (negative upfield). ^1H NMR spectra were recorded on Varian Associates EM360L and Varian XL-200 spectrometry.

Infrared spectra were recorded on a Perkin-Elmer Model 297 instrument.

GLC analyses were performed on a Varian Model 3700 gas chromatograph equipped with a capillary column [silicone OV 101 (methyl)] and an on-line automatic integrator as well as on a Perkin-Elmer Model 900 chromatograph with a 150 ft × 0.1 in. capillary column packed with *m*-bis(*m*-phenoxyphenoxy)benzene and Apiezon L.

Isomeric alkanes were analyzed on a Hewlett Packard 5730A gas chromatograph with a 12A Poropak QS column.

Potassium Perfluorobutanesulfonate and Perfluorobutanesulfonic Acid. The salt was prepared according to a procedure described in the literature for the preparation of $KOSO_2CF_3$ from CF_3SO_2F.[17] $KOSO_3C_4F_9$ was mixed and heated with concentrated H_2SO_4 and the regenerated $C_4F_9SO_3H$ was isolated by vacuum distillation from H_2SO_4.

Perfluorodecanesulfonic Acid. The potassium salt of the acid (Produits Chimique Ugine Kuhlman, France) was mixed with concentrated H_2SO_4 and heated to 80–90 °C for several hours, followed by continued overnight stirring at room temperature. After filteration, the solid was refluxed over $SOCl_2$ for several hours, filtered, and washed several times with CH_2Cl_2, and the

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solvent was removed to give the sulfonic acid as a white hydroscopic powder in ca. 80% yield.

Preparation of $B(OSO_2R_F)_3$ and Derived Conjugate Superacids. (a) From BCl_3. In a well-dried three-necked flask equipped with magnetic stirrer bar, a pressure-equalizing dropping funnel, and dry nitrogen inlet and outlet cooled to −75 °C was added a premeasured amount of liquid BCl_3 (usually 2 mL). Triflic acid (3 equiv) placed in the dropping funnel was added dropwise with efficient magnetic stirring, whereby HCl slowly evolved. The temperature was gradually raised until completion of reaction. The reaction mixture was then evacuated to give $B(OTf)_3$ as a white solid which was purified by crystallization from SO_2ClF followed by drying under vacuum. $B(OTf)_3$ is air-sensitive and liquiefies immediately on exposure to air, thus it must be handled and kept in an efficient drybox. It is also light-sensitive and should be kept in the dark.

The conjugate superacid 1 was prepared by addition of 2 molar equiv of CF_3SO_3H to $B(OTf)_3$ under dry nitrogen. 1 can also be prepared directly from BCl_3 by the addition of 5 molar equiv of CF_3SO_3H. The resulting colorless fuming superacid must be thoroughly evacuated in vacuum to remove HCl.

Following the literature procedure,[5] triflic acid was placed in a glass reactor with an outlet and cooled to −75 °C. BCl_3 was liquified in a cold measuring cylinder and was transferred directly into the frozen acid under dry nitrogen. The temperature was allowed to rise slowly with magnetic stirring, whereby HCl slowly evolved. The reaction mixture was then evacuated and the white solid purified as before, prior to spectroscopic studies.

(b) From BBr_3. To BBr_3 (1 equiv) placed in a three-necked flask was dropwise added triflic acid (3 equiv) from a pressure-equalizing dropping funnel with efficient magnetic stirring, under dry nitrogen at 0 °C. A white precipitate was initially formed with evolution of HBr, which on competion of the addition of triflic acid slowly dissolved to form a viscous almost colorless liquid. The reaction mixture was then thoroughly evacuated in vacuum at room temperature to remove HBr.

$B(OSO_2C_4F_9)_3$ and $B(OSO_2C_{10}F_{21})_3$ were similarly prepared by the addition of their corresponding acids (3 equiv) or sodium salts to BBr_3 (1 equiv) in dry heptane solvent.

(c) From Silver Triflate. (Under argon in dry heptane as solvent to BBr_3 was added exactly 3 equiv of AgOTf. The heterogeneous mixture was stirred for 48 h at room temperature, before removal of solvent under vacuum.

(d) From $PhBCl_2$. To phenylboron dichloride (2 g) placed in a three-necked flask was dropwise added, with efficient magnetic stirring at room temperature, the required amount of triflic acid (2 or 3 molar equiv) via a pressure-equalizing dropping funnel. After the evolution of HCl ceased, the reaction mixture was pumped and benzene byproduct was collected in a cold trap (at −75 °C).

Transalkylation/Transbromination Reactions. The reactions were all carried out at room temperature with the exclusion of moisture, generally by reacting overnight with good mixing.

To 2-bromo-*m*-xylene (1.16 g, 6.28 mmol) or diethylbenzene (0.81 g, 6 mmol) dissolved in toluene (60 mmol) was added 1 mmol of 1 with efficient mixing. After being reacted for 18 h at room temperature, the reaction mixture was quenched in ice/bicarbonate, extracted in ether, and dried ($MgSO_4$) prior to GLC analysis.

The identification of products was by GLC retention times and comparison with authentic samples. For transbromination reactions the yield is based on the ratio (by GLC) of the product formed by bromine transfer to the unreacted bromine donor substrate. Similarly, for transethylation reactions the yield is based on the ratio of the isomeric ethyltoluenes to unreacted diethylbenzene.

Isomerization of *n*-Butane. The immobilized catalyst was prepared in the drybox by dropwise addition of the superacid 1 (2 g) to dry graphite (7 g). The catalyst was placed inside a 3-in. Teflon chamber. The Teflon chamber was then inserted into a brass reaction chamber and was placed directly in the gas flow system at higher pressures (30 psi).

For static pressure autoclave experiments, the acid (14.0 g, 18.4 mmol) and a Teflon-coated magnetic stirrer bar was placed in the reactor under nitrogen. The autoclave was cooled in dry ice/acetone, *n*-butane (1.5 mol, 15.5 mmol) was added, and the autoclave was sealed, pressurized with argon (200 psi), and stirred at room temperature. GC samples were taken through the autoclave gas sampling valve at intervals.

After 48 h the autoclave was opened, the acid was carefully quenched in ice/bicarbonate, and the organic layer was extracted in ether, separated, and dried ($MgSO_4$), and was subjected to GC analysis.

Isomerization of *n*-Hexane. Following the procedure described above, the autoclave was charged with the catalyst (6 g) and was initially cooled to −75 °C before the addition of *n*-hexane (3 mL). It was then sealed, pressurized with argon, and allowed to warm up to room temperature. Gas samples were withdrawn and analyzed by GC at intervals.

Isomerization of *exo*-(or *endo*-)Trimethylenenorbornane to Adamantane. In a typical run to trimethylenenorbornane (1.4 g, 0.3 mmol) dissolved in 30 mL of dry Freon-113 was added dropwise the superacid 1 (2 g, 0.5 equiv) with efficient magnetic stirring at 0 °C under dry nitrogen. The reaction was allowed to continue at 0 °C for 1 h followed by overnight mixing at room temperature, after which it was quenched by pouring slowly into ice–bicarbonate, extracted with CH_2Cl_2, separated, dried ($MgSO_4$) and was subjected to GC analysis.

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Registry No. BCl_3, 10294-34-5; BBr_3, 10294-33-4; $B(OTf)_3$, 64371-01-3; $B(OSO_2C_4F_9)_3$, 92525-60-5; $B(OSO_2C_{10}F_{21})_3$, 92525-61-6; $PhBCl_2$, 873-51-8; $CF_3SO_2OH_2^+[B(OSO_2CF_3)_4]^-$, 92525-63-8; $C_4F_9SO_2OH_2^+[B(OSO_2C_4F_9)_4]^-$, 92525-65-0; $C_{10}F_{21}SO_2OH_2^+[B(OSO_2C_{10}F_{21})_4]^-$, 92525-67-2; triflic acid, 1493-13-6; perfluorobutanesulfonic acid, 375-73-5; perfluorodecanesulfonic acid, 335-77-3; silver triflate, 2923-28-6; 2-bromo-*m*-xylene, 576-22-7; diethylbenzene, 25340-17-4; *n*-butane, 106-97-8; *n*-hexane, 110-54-3; *exo*-trimethylenenorbornane, 2825-83-4; *endo*-trimethylenenorbornane, 2825-82-3.