

Reaction of Boron Triflate with Polyfluoroolefins. Synthesis of Polyfluorinated Allyl Trifluoromethanesulfonates†

Viacheslav A. Petrov

DuPont Central Research and Development, Experimental Station, P.O. Box 80328,
Wilmington, Delaware 19880-0328

Received December 1, 1997

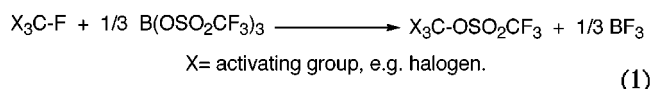
Terminal *F*-olefins (*F* designates perfluorinated molecules) react with boron triflate (**1**) to form corresponding allyl triflates $R_fCF=CFCF_2OSO_2CF_3$ in moderate yield. The reaction of *F*-pentene-2 is much slower, resulting in insertion of CF_3SO_2O into the CF_3 group of fluorolefin. Mono- and dihydrofluoroolefins were found to be more reactive toward **1**. Both *F*-cyclobutene and *F*-cyclopentene were converted into corresponding cyclic allyl triflates by reaction with **1**, but *F*-cyclohexene was found to be resistant to the action of boron triflate. In contrast to terminal fluorolefins, both 5H-, 6H-*F*-*n*-decene-5 and 1H,1H-*F*-isobutene react with **1** without rearrangement, producing corresponding allyl triflates in 47 and 63% yields, respectively.

Polyfluorinated allyl fluorosulfates $R_fCF=CFCF_2OSO_2F$ have recently become important intermediates in the synthesis of "functionalized" polyfluorinated olefins, since the fluorosulfate group is an excellent leaving group and can be replaced by variety of nucleophiles such as Br^- , I^- , R_fO^- , and F^- .^{1–3} The Lewis acid-catalyzed insertion of sulfur trioxide into allylic C–F bonds of fluorolefins is the most general route to compounds of the general formula $R_fCF=CFCF_2OSO_2F$,^{1–5} and it has been the subject of several review articles.^{6–8}

As was demonstrated earlier $B(OSO_2CF_3)_3$ (**1**) is a strong Lewis acid. A solution of 30 mol % of boron triflate in CF_3SO_2OH was reported to have a H_0 value of ca. –20.5.⁹ It is much more active than the corresponding aluminum and gallium triflates.¹⁰ Boron triflate by itself or as a solution in triflic acid was used for the generation of stable hydrocarbon cations¹¹ and was found to be an effective catalyst for a number of electrophilic reactions of hydrocarbons.^{12–14}

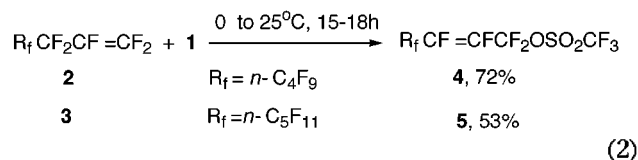
Recently we demonstrated that **1** is an effective reagent for the introduction of a CF_3SO_2O group into polyfluorinated compounds containing activated C–F bonds.¹⁵ The

reaction is stoichiometric with the formation of boron trifluoride as byproduct.



This paper presents the results of the reactions of boron triflate with polyfluorinated olefins of different structures, along with some data on the reactivity of the product triflates toward nucleophiles.

Perfluorinated olefins containing a terminal double bond, such as *F*-heptene-1 (**2**) and *F*-octene-1 (**3**), readily react with **1** to produce the corresponding allyl triflates **4** and **5** in 53–72% yield. The reaction with boron triflate



is accompanied by rearrangement and results in the formation of allyl triflates containing the CF_3SO_2O group connected to the terminal carbon. Similar behavior was previously observed in the reaction of terminal perfluoroolefins with sulfur trioxide in the presence of boron oxide,² although the corresponding fluorosulfates are always formed in a mixture with the corresponding β -sulfones, apparently because rates of insertion and cycloaddition reaction are comparable. Similar to the corresponding allyl fluorosulfates, prepared by the reaction of SO_3 with fluorolefins and catalyzed by Lewis acids, triflates **4** and **5** exist predominantly as trans isomers (>95%). Small amounts of cis isomer were detected by ¹⁹F NMR in both products but were not characterized further. Parameters of the ¹⁹F NMR spectrum of compound **5** are in excellent agreement with those reported for allyl fluorosulfate $C_5F_{11}CF=CFCF_2OSO_2F$.⁵ Predominant formation of trans isomer is consistent with the reported data on the isomerization of terminal polyfluoroolefins by another strong Lewis acid, antimony pentafluoride, reported to proceed with exclusive formation of trans isomers of Δ -2 fluoroolefins.¹⁶

† Contribution no. 7678.

(1) Krespan, C. G.; England, D. *J. Am. Chem. Soc.* **1981**, *103*, 5598.

(2) Cherstkov, V. F.; Sterlin, S. R.; German, L. S.; Knunyants, I. L. *Izv. AN SSSR. Ser. Khim.* **1982**, 2791; *Chem. Abstr.* **1983**, *98*, 143032.

(3) Cherstkov, V. F.; Sterlin, S. R.; German, L. S.; Knunyants, I. L. *Izv. AN SSSR. Ser. Khim.* **1983**, 1872.

(4) Krespan, C. G.; Dixon, D. A. *J. Org. Chem.* **1986**, *51*, 4460.

(5) Cherstkov, V. F.; Sterlin, S. R.; German, L. S.; Knunyants, I. L. *Izv. AN SSSR. Ser. Khim.* **1985**, 1864; *Chem. Abstr.* **1986**, *105*, 42306.

(6) Zyk, N. V.; Beloglazkina, E. K.; Zefirov, N. S. *Zh. Org. Khim.* **1995**, *31*, 1283.

(7) Krespan, C. G.; Petrov, V. A. *Chem. Rev.* **1996**, *96*, 3269.

(8) Petrov, V. A.; Bardin, V. V. Reactions of Electrophiles with Polyfluorinated Olefins. In *Top. Curr. Chem.* **1997**, *192*, 39.

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

(10) Olah, G. A.; Farooq, O.; Farnia, S. M. F.; Olah, J. *J. Am. Chem. Soc.* **1988**, *110*, 2560.

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

(12) Olah, G. A.; Farooq, O.; Farnia, S. M. F.; Wu, A. *J. Org. Chem.* **1990**, *55*, 1516.

(13) Farooq, O.; Farnia, S. M. F.; Stephenson, M.; Olah, G. A. *J. Org. Chem.* **1988**, *53*, 2840.

(14) Olah, G. A.; Farooq, O. *J. Org. Chem.* **1986**, *51*, 5410.

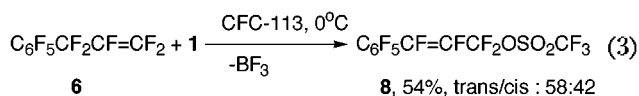
(15) Petrov, V. A. *J. Fluorine Chem.* **1995**, *73*, 17.

Table 1. Reaction of 1 with Polyfluorinated Compounds

entry	compd	ratio substr/1 ^a	time (h)	convn of substr (%)	product (yield, %)	comments
1	2	2.3	16	75	4 , 72	trans:cis 96:4
2	3	4	18	70	5 , 53	trans:cis 97:3
3	6	2.6	3		8 , 54	trans:cis 58:42
4	CFC-113	4.0	30		7 , 7a , 55	ratio 7:7a = 4:1
5	10	3	24	45	11 , 35	trans:cis 97:3
6	12	2.6	15	70	14 , 50	trans:cis 93:7
7	13	3.0	16	75	15 , 57	trans:cis 98:2
8	16	3.5	15	60	17 , 30	
9	18 ^{b,c}	3.0	8	60	19 , 47 ^c	
10	20	3.0	72	0		
11	21	4.1	15	70	22 , 57	
12	23	2.2	16	65	25 , 25a , 47	25:25a:26 = 83:7.5:9.5
13	24	3.0	18		30 , 63	

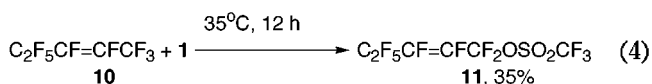
^a Reaction was carried out at 25 °C. ^b Yield is calculated on the basis of ¹⁹F NMR data. ^c Reaction was carried out in 75 mL Houke cylinder at 0 °C.

The reaction of *F*-3-phenylpropene-1 (**6**) with **1** is exothermic, readily occurring upon the addition of the olefin to a solution of **1** in CFC-113 at 0 °C.¹⁷ This process is accompanied by rearrangement, producing triflate **8**, this time with almost equal amount of trans and cis isomers. The observed ratio of trans and cis isomers of



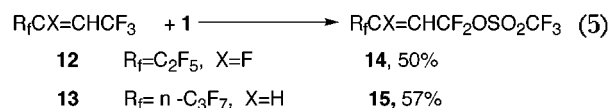
8 is close to that reported for the isomerization of **6** by SbF₅ (1:1).¹⁶ The formation of equal amounts of trans and cis isomers of *F*-1-phenylpropene-1 in this reaction was originally ascribed to the formation of two isomers of *F*-1-phenylallyl carbocation as independent intermediates. However, as was demonstrated recently by NMR spectroscopy, this cation exists as only one isomer even at low temperature.¹⁸

Perfluoroolefins containing an internal double bond are much less reactive toward **1**. For instance, the reaction between **1** and *F*-pentene-2 (**10**) is slow at ambient temperature and requires a longer reaction time or higher temperature to give triflate **11**. The latter was not isolated, but characterized by ¹⁹F NMR spectroscopy, after the excess starting material had been removed. The

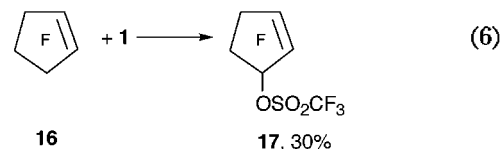


¹⁹F NMR spectrum of **11** is in good agreement with the proposed structure and with data reported for the corresponding fluorosulfate.⁵ The replacement by hydrogen of vinylic fluorine substituents in the olefin molecule significantly increases the reactivity. Both 2-*H*-*F*-pentene-2 (**12**) and 2,3-*H*-*F*-hexene-2 (**13**) rapidly react with **1** to give corresponding triflates **14** and **15** in moderate yield (see Table 1, entries 6 and 7). On the other hand, perfluoroalkyl ethylenes are too active, and several attempts to prepare an allyl triflate by reaction of C₄F₉-

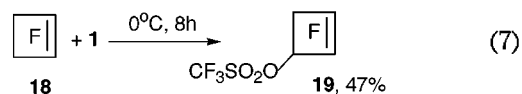
CH=CH₂ with **1**, even at -20 °C, using CFC-113 as a solvent, resulted in formation of oligomeric materials and tar. Similar behavior of this olefin in superacidic media was observed earlier.¹⁹



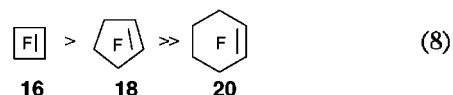
F-Cyclopentene (**16**) has reactivity similar to that of **10** and slowly reacts with **1** at ambient temperature forming cyclic triflate **17**. *F*-Cyclobutene (**18**) is more



active and rapidly reacts with boron triflate already at 0 °C, producing cyclobutene **19** along with some (CF₃-SO₂)₂O. Compound **19** was not isolated but was characterized by IR and NMR spectroscopy in mixture (see Table 2). The data of both methods are in good agreement with the proposed structure (similar data reported by Smart²⁰ for 3-fluorosulfonyl-*F*-cyclobutene-1).



At the same time, the absence of expected allyl triflate in reaction of *F*-cyclohexene (**20**) with **1** (even after 72 h at 25 °C) is an evidence of a much lower reactivity for this cycloolefin. This is also consistent with reported data



on the reactivity of **16** and **18** in reaction with fluoroethylenes. *F*-Cyclobutene is known to react with tetrafluoroethylene in the presence of SbF₅ catalyst,²¹ while *F*-cyclopentene does not interact with fluoroethylenes under similar conditions,²² as was reported recently,²³ the

(16) Belen'kii, G. G.; Savicheva, G. I.; Lur'e, E. P.; German, L. S. *Izv. AN SSSR. Ser. Khim.* **1978**, 1640; *Chem. Abstr.* **1978**, 89, 162986.

(17) As was previously shown¹⁵ CFC-113 slowly interacts with **1** at ambient temperature, producing ClCF₂CCl₂OSO₂CF₃ (**7**). In this study it was found that the reaction produces a substantial amount (up to 25%) of isomeric triflate CCl₃CF₂OSO₂CF₃ (**7a**). This material was not isolated but characterized by NMR spectroscopy in mixture with **7** (see Table 2).

(18) Galakhov, M. V.; Petrov, V. A.; Chepick, S. D.; Belen'kii, G. G.; Bakhmutov, V. I.; German, L. S. *Izv. AN SSSR Ser. Khim.* **1989**, 1773.

(19) Petrov, V. A. *J. Org. Chem.* **1995**, 60, 3423.

(20) Smart, B. E. *J. Org. Chem.* **1976**, 41, 2353.

(21) Belen'kii, G. G.; Lur'e, E. P.; German, L. S. *Izv. AN SSSR. Ser. Khim.* **1976**, 2365.

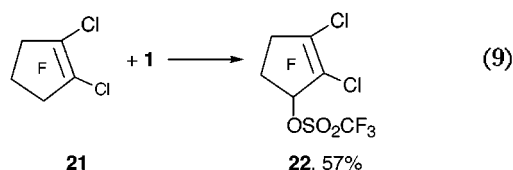
Table 2. Properties of New Compounds

compd	bp, °C (mm Hg)	¹ H NMR, δ, ppm (<i>J</i> , Hz)	¹⁹ F NMR (CFCl ₃), ppm	IR (cm ⁻¹)	Anal. or MS, found (calcd)
4	71–72 (50)		–63.31 (2F, dm, 25); –72.54 (3F, t, 6); –79.95 (3F, t, 11); –117.51 (2F, m); –123.31 (2F, m); –125.44 (2F, m); –151.40 (1F, dm, 141); –154.31 (1F, dm, 141)	1451	C, 20.21 (20.01); F, 64.39 (63.31)
5	68–70 (25)		–67.21 (2F, dm, 26); –72.25 (3F, t, 6); –79.72 (3F, tt, 9, 3); –117.01 (2F, m); –121.07 (2F, m); –122.03 (2F, m); –125.00 (2F, m); –151.20 (1F, dm, 145); –154.18 (1F, dm, 145)	1458 (SO ₂)	C, 20.25 (20.39); F, 64.85 (64.51)
7, 7a 8^b	125–127 ^a 48 (0.1)		–73.06 (2F, t, 10); –78.61 (3F, q, 10) trans: –67.72 (2F, dm); –73.89 (3F, t); –133.50 (1F, dm); –135.61 (2F, m); –145.12 (1F, m); –158.80 (1F, dm); –159.10 (2F, m) cis: –69.20 (2F, m); –74.09 (3F, t); –11.88 (1F, m); –133.50 (1F, dm); –136.30 (2F, m); –143.35 (1F, m); –144.83 (1F, dm) –159.10 (2F, m)	1731 ^a (C=C); 1450 (SO ₂)	<i>m/e</i> 427.9408 (427.9377)
11			–68.72 (2F, dm, 26, 11, 5.5); –73.91 (3F, t, 5.5); –84.79 (3F, m); –122.06 (2F, dd, 26, 11); –154.14 (1F, dm, 143); –156.33 (1F, dm, 143)	1715 (C=C, w); 1450 (SO ₂)	
14	55–57 (130)	6.20 (dt, 28, 9)	–57.76 (2F, dm, 16); –73.38 (3F, d, 5); –82.74 (3F, d, 5); –108.78 (1F, m); –121.96 (2F, d, 11)	1723 (C=C); 1449 (SO ₂)	C, 19.61 (19.90); F, 57.87 (57.71)
15	85–86 (130)	6.56 (m)	–64.99 (2F, dm, 6); –74.06 (3F, t, 7); –80.43 (3F, t, 8); –115.22 (2F, m); –127.47 (2F, s)	1723 (C=C); 1446 (SO ₂)	<i>m/e</i> 244.9987 (245.0013, C ₆ H ₂ F ₉ , [M – CF ₃ SO ₃] ⁺)
17	116–118		–73.86 (3F, d, 10); –114.01 (1F, dm, 251); –117.90 (1F, dm, 251); –120.00 (1F, dm, 237); –126.41 (1F, dm, 237); –146.25 (1F, q, 16); –146.50 (1F, q, 20)	1723 (C=C, w); 1453 (SO ₂)	C, 21.11 (21.06); F, 55.82 (55.53)
19			–74.11 (3F, d, 9); –114.20 (1F, dm, 191); –117.49 (1F, dm, 191); –124.13 (1F, m); –125.13 (1F, m); –125.18 (1F, m)	1792 (C=C); 1443 (SO ₂)	
22	108–108.6 (100)		–73.73 (3F, dd, 11, 6); –109.56 (1F, dd, 253, 4); –113.55 (1F, m); –114.30 (1F, dd, 253, 5); –118.92 (1F, d, 239); –126.00 (1F, dt, 239, 3)	1634 (C=C); 1448 (SO ₂)	C, 19.39 (19.22); Cl, 19.42 (18.91)
25	49 (0.03)	25 , 6.60 (m); 25a , 5.82 (1H, dd, 27, 10); 5.95 (1H, q, 10)	–73.44 (3F, d, 6); –80.05 (3F, t, 10); –80.19 (3F, t, 9); –113.38 (2F, q, 10); –121.04 (2F, m); –121.33 (1F, m); –123.33 (2F, m); –123.88 (2F, m); –124.99 (2F, m)	1447 (SO ₂)	C, 21.96 (22.24); F, 63.44 (63.95)
26^c		6.58 (m)	–73.98 (3F, d, 7); –74.09 (3F, d, 7); –80.74 (6F, m); –124.25 (2F, dm, 293); –124.93 (2F, dm, 293); –121.21 (2F, m); –12.36 (2F, m); –121.78 (1F, m); –121.94 (1F, m) ^c	1448 (SO ₂)	C, 19.44 (19.70); F, 57.94 (57.71)
27	98–100 (145)	7.21 (1H, q, 3); 7.45 (1H, d, 5)	–82.73 (3F, t, 8); –83.18 (3F, tt, 9, 3); –115.68 (2F, q, 8); –123.58 (2F, q); –125.59 (2F, m); –127.61 (2F, m); –129.56 (2F, s)	1739 (C=O); 1649 (C=C)	C, 27.13 (27.17); F, 68.51 (68.76)
30	110–112	6.69 (1H, s); 6.72 (1H, s)	–63.10 (2F, m, 6); –63.23 (3F, t, 6); –72.83 (3F, t, 6)	1666 (C=C, w); 1448 (SO ₂)	C, 20.44 (20.42); F, 63.44 (63.95)

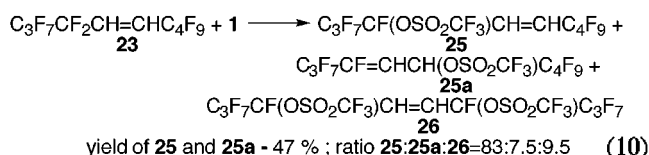
^a Mixture of isomers, ratio **7:7a** 75:25. ^b Mixture of isomers. ^c Mixture of diastereomers.

reaction requires the more active catalyst—aluminum chlorofluoride.

1,2-Dichloro-*F*-cyclopentene (**21**) has reactivity similar to that of 2,3-dichloro-*F*-butene-2¹⁵ and readily reacts with **1** to form allyl triflate **22**, isolated in moderate yield.



Both 5H,6H-*F*-*n*-decene-5 (**23**) and 1H,1-H-*F*-isobutene-1 (**24**) exhibit quite interesting reactivity toward **1**. For instance, the interaction of olefin **23** with **1** results in formation of triflate **25** along with small amounts of isomeric **25a** and bis-triflate **26**. The structures of **25**

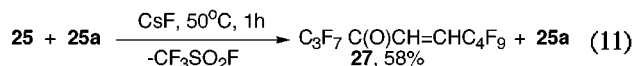


(22) Belen'kii, G. G.; German L. S. *Chem. Rev., Sec. B*, Vol'pin, M. E., Ed.; Soviet Scientific Reviews, Harwood Academic Publishers: New York, 1984; p 183.

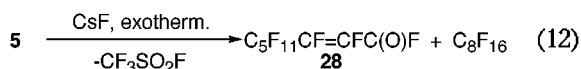
and **25a** were supported by their rather complex ¹H and

(23) Krespan, C. G.; Dixon, D. A. *J. Fluorine Chem* **1996**, *77*, 117.

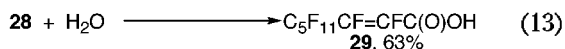
^{19}F NMR spectra and by the reaction of this mixture with dry CsF , leading to vinyl ketone **27**. The latter originated from nucleophilic attack of F^- on the sulfur atom of $\text{CF}_3\text{-SO}_2$ group (according to GC and NMR data compound **25a** was unreactive under reaction conditions). This type



of process leading to formation of unsaturated acyl fluorides $\text{R}_f\text{CF}=\text{CFC}(\text{O})\text{F}$ is well documented for reaction of *F*-allyl fluorosulfates and CsF at elevated temperature ($50\text{--}80^\circ\text{C}$).³ To obtain comparative data on the reactivity of *F*-allyl triflates, the reaction of compound **5** with dry CsF was carried out. Triflate **5** seems to be more reactive toward CsF , since after completion of the exothermic reaction the conversion of **5** was greater than 95% (GC). However, along with expected acyl fluoride **28**, the crude reaction mixture contained a significant amount (25%) of the isomeric *F*-octenes. The formation

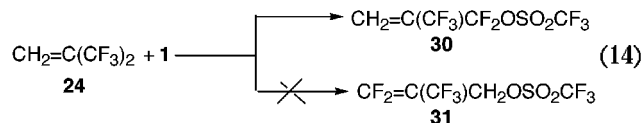


of *F*-octenes in this reaction indicates that nucleophilic attack by fluoride ion on the sulfur atom of the triflate group competes with replacement of this group by nucleophilic attack on allylic carbon of **5**. Compound **28** was not isolated but was converted into acid **29**.



It is noteworthy that the formation of isomer **25** as the major product in the reaction of olefin **23** and **1** is in sharp contrast with the result of electrophilic condensation of **23** with tetrafluoroethylene.²³ This reaction is catalyzed by aluminum chlorofluoride and proceeds with migration of the C=C bond and predominant (97%) formation of olefin, $\text{C}_3\text{F}_7\text{CF}=\text{CHCH}(\text{C}_2\text{F}_5)\text{C}_4\text{F}_9$.

Compound **24** in reaction with **1** behaves similarly. Reaction proceeds under mild conditions, producing exclusively compound **30** instead of triflate **31** (**31** is expected to form, based on the reported orientation in condensation reactions of corresponding hydropolyfluoroolefins^{4,8,19,24}). The structure assigned to **30** is based

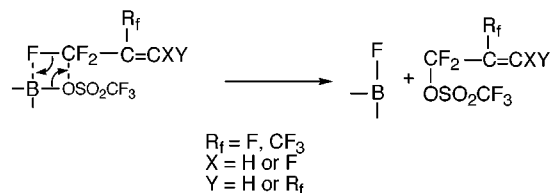


on data of NMR spectroscopy. ^1H NMR contained two separate, although poorly resolved signals (6.69 and 6.72 ppm) in a 1:1 ratio, whereas the ^{19}F NMR exhibited three signals at -63.05 , -63.21 , and -72.83 ppm (2:3:3) with the multiplicities in agreement with the proposed structure.

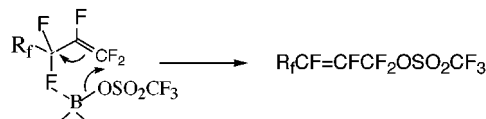
On the basis of the experimental data available, it can be concluded that boron triflate belongs to the group of strong Lewis acids with acidity comparable to or slightly lower than that of SbF_5 .

The mechanism of the reaction of $\text{B}(\text{OSO}_2\text{CF}_3)_3$ with polyfluorinated materials containing activated C–F bonds

Scheme 1



Scheme 2



strongly depends on the nature of the substrate. For example, the reaction between **1** and polyfluoroolefins capable of generating stable allyl cations such as *F*-propene or $\text{CCl}_2=\text{CClCF}_3$ ^{8,24} likely proceeds through the mechanism involving free allylic carbocation. On the other hand, interaction of **1** with less reactive substrates such as olefins **23** and **24** giving compounds **25** and **30** may be an indication of a different mechanism not involving a free carbocation. A concerted process involving a cyclic four-membered ring transition state (Scheme 1) would account for the mechanism of these reactions, since no evidence for the formation of allylic carbocations derived from internal *F*-olefin in condensed phase was reported so far.^{8,25}

Furthermore, the replacement of fluorine by the triflate group in the reaction of terminal fluorolefins most likely proceeds via a six-membered ring cyclic transition state.

A similar mechanism was proposed earlier for Lewis acid-catalyzed isomerization of fluorolefins containing a terminal double bond¹⁶ and also for in those catalyzed by the SbF_5 reaction of Δ -1*F*-alkenes with SO_3 .^{2,5}

Experimental Section

^{19}F and ^1H NMR spectra were recorded on QE-300 (General Electric, 200 MHz) or Bruker DRX-400 instruments (400.5524 and 376.8485 MHz, respectively) using CFCl_3 as internal standard and *d*-chloroform or *d*-acetone as lock solvent. IR spectra were recorded on a Perkin-Elmer 1600 FT spectrometer in a liquid film. Triflic acid (3M) and boron trichloride (Aldrich) were commercially available and were used without further purification. Boron triflate (**1**) was prepared by a slightly modified literature method,¹⁰ stored in a refrigerator, and for the most of the reaction was used without purification; however, for the reaction with **10**, distilled material was used. Compound **28**⁵ was identified by NMR spectroscopy and $\text{CF}_3\text{-SO}_2\text{F}$ by comparison with an authentic sample.

Preparation of Boron Triflate (1). BCl_3 (80 g, 0.7 mol, 20% excess) was transferred into a dry three-necked flask equipped with a dry ice condenser, thermometer, and additional funnel, and 225 g (1.5 mol) of $\text{CF}_3\text{SO}_3\text{H}$ was added dropwise over a period of 2 h at $10\text{--}15^\circ\text{C}$. The HCl evolved was scrubbed by a solution of KOH . After addition was completed the viscous reaction mixture was stirred at 25°C for 2 h, and excess BCl_3 and dissolved HCl were removed using a vacuum line. The solid reaction product (230 g) was transferred into another glass vessel inside the drybox and was stored in a refrigerator.

General Procedure for Reaction of 1 with Polyfluorinated Compounds. Boron triflate (0.01 mol) was loaded into the reaction flask inside a drybox, and olefin (0.03–0.035 mol) was slowly added (*caution: in the beginning reaction may be*

(24) Petrov, V. A.; Belen'kii, G. G.; German, L. S. *Izv. AN SSSR. Ser. Khim.* **1982**, 1591.

(25) Bakhmutov, V. I.; Galakhov, M. V. *Usp. Khim.* **1988**, 57, 1467.

exothermic) at 0 °C. The reaction mixture was allowed to warm to 25 °C (1 h) and stirred at this temperature for 16–24 h. Boron trifluoride, evolving in the course of the reaction, was scrubbed with a solution of KOH. The reaction mixture was quenched with ice water (*caution: reaction of boron triflate with water is highly exothermic*), and the organic (lower) layer was separated, dried over P₂O₅, and distilled. The reaction conditions and isolated yields are given in Table 1. Compounds **10** and **18** were not isolated but characterized by IR and ¹⁹F NMR spectroscopy (see Table 2) after the excess of starting olefin has been removed.

Reaction of Compounds 5 with CsF. To 12 g of freshly dried CsF (2 h at 100 °C, in a vacuum) was added 10 g of **5** slowly (5 min) at 25 °C. A slightly exothermic reaction was observed, and the reaction temperature rose to 38 °C. After completion of the reaction (40 min) GC analysis showed 95% conversion of **5** and according to NMR spectroscopy the reaction mixture at this point contained **28** and a mixture of isomeric internal *F*-octenes in a ratio of 75:25, along with a

small amount of **5** and CF₃SO₂F. Then 30 mL of water was added to the reaction mixture, and it was stirred for 10 min. The white solid was filtered and distilled to give 4.4 g (63%) of **29**, bp 87–89/5 mmHg, mp 54–55 °C (lit.⁵ bp 93–95/7 mmHg, mp 54–55 °C).

Reaction of 25 and CsF. A mixture of 7.3 g of **25**, **25a**, and 2 g of dry CsF was kept at 50 °C for 1.5 h. The reaction mixture was diluted with water, and the organic layer was separated, dried over MgSO₄, and analyzed by GC and NMR. The crude product (4 g) contained ketone **27** and unchanged triflate **25a**, along with some CF₃SO₂F. An analytically pure sample of **27** was isolated by distillation, bp 98–99 °C/145 mmHg. IR, NMR, and MS data are given in Table 2.

Acknowledgment. The author thanks Dr. Carl Krespan for stimulating discussion and R. Smith, Jr., for technical assistance.

JO972166X